One-Center Charge Transfer Transitions in Manganites

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In frames of a rather conventional cluster approach, which combines the crystal field and the ligand field models we have considered different charge transfer (CT) states and O 2p-Mn 3d CT transitions in MnO$_6$ octahedra. The many-electron dipole transition matrix elements were calculated using the Racah algebra for the cubic point group. Simple ”local” approximation allowed to calculate the relative intensity for all dipole-allowed $\pi - \pi$ and $\sigma - \sigma$ CT transitions. We present a self-consistent description of the CT bands in insulating stoichiometric LaMn$_{3+}$O$_6$ compound with the only Mn$^{3+}$ valent state and idealized octahedral MnO$_6$ centers which allows to substantially correct the current interpretation of the optical spectra. Our analysis shows the multi-band structure of the CT optical response with the weak low-energy edge at 1.7 eV, associated with forbidden $t_{1g}(\pi) - e_g$ transition and a series of the weak and strong dipole-allowed high-energy transitions starting from 2.5 and 4.5 eV, respectively, and extending up to nearly 11 eV. The most intensive features are associated with two strong composite bands near 4.6 $\div$ 4.7 eV and 8 $\div$ 9 eV, respectively, resulting from the superposition of the dipole-allowed $\sigma - \sigma$ and $\pi - \pi$ CT transitions. These predictions are in good agreement with experimental spectra. The experimental data point to a strong overscreening of the crystal field parameter $D_q$ in the CT states of MnO$_6$ centers.

I. INTRODUCTION

The discovery of the colossal magnetoresistance in doped manganites like La$_{1-x}$Sr$_x$MnO$_3$ have generated a flurry of the ideas, models and scenarios of this puzzling phenomena, many of which are being developed up to date, although the situation remains controversial. There are many thermodynamic and local microscopic quantities that cannot be explained by the conventional double-exchange model with the predominantly Mn 3d location as different valent states of octahedral MnO$_6$ centers. Namely these slightly distorted octahedra are believed to be the basic units both for crystalline and electronic structure in manganites.

As for an examination of the energy spectrum and electronic structure one should emphasize an importance of different optical methods because these provide valuable information concerning the dielectric function. The nature of the low-energy optical electron-hole excitations in the insulating transition metal (3d-) oxides represents one of the most important challenging issues for these strongly correlated systems. It is now believed that the most intensive low-energy electronic excitations in insulating 3d-oxides correspond to the transfer of electrons from oxygen anion to 3d metal cation, hence these materials are charge transfer (CT) insulators. However, the more detailed assignment of these excitations remains open. All these are especially interesting because they could play a central role in multiband Hubbard models used to describe both the insulating state and the unconventional states developed under electron or hole doping.

It is now generally accepted that the ground state of the MnO$_6$ centers in LaMnO$_3$ corresponds to the orbital doublet $^5E_g$ term of the high-spin $t_{2g}^2e_g^1$ configuration. The optical conductivity spectrum of LaMnO$_3$ exhibits two broad peaks centered around 2.0 and 5.0 eV. However, it has remained unclear just what the nature of the intensive low-energy optical electron-hole excitation peaked near 2.0 eV as well as more intensive excitations with higher energy peaked near 5.0 eV. Some authors assign these both features to the dipole-allowed CT transitions like $t_{2g}^3e_g^1 - t_{2g}^3e_g^1 L$ and $t_{2g}^3e_g^1 - t_{2g}^3e_g^1 L$ (L denoting a ligand hole), respectively. However, others assign the low-energy peak to the ”intra-atomic” $^5E_g - ^5E_g'$ transition, or doubly-forbidden (parity and orbital quasimomentum) d-d-like crystal-field transition between two $^5E_g$-sublevels separated by a splitting due to low-symmetry crystalline field. Both interpretations being particularly qualitative suffer from many shortcomings and give rise to many questions concerning the details of the charge transfer states or expected weak intensity for the d-d transitions.

Unfortunately, the main body of the optical data for manganites is obtained from reflectivity measurements, that often implies a parasitic contribution due to a deterioration of the sample surface, and can give rise to some ambiguities due to problems with Kramers-Kröning transformation. The more straightforward optical transmission spectra of the LaMnO$_3$ films revealed a fine structure of the low-energy 2 eV band with two features near 1.7 and 2.4 eV, respectively, which were assigned in contrast with the preceding interpretations to the Mn$^{3+}$ d-d crystal-field transition $^5E_g - ^3T_{1g}$, split by the JT effect. Such an ambiguity leaves the question of the nature of the main optical transitions in LaMnO$_3$ far from being resolved. The band structure calculations, including the LDA+U, fail to clear up the situation because of these cannot reproduce the important effects of intra-atomic correlations forming the term structure both of ground and excited CT states. In this connection a rather conventional quantum-chemical cluster approach,
which combines the crystal field and the ligand field models with real opportunity to include all correlation effects, seems more relevant.

Below, in frames of such an approach we consider different CT states and O 2p-Mn 3d CT transitions in MnO$_6$ octahedra. As we suppose, they define the main part of the optical response both for undoped LaMnO$_3$ and different doped manganites.

II. ELECTRONIC STRUCTURE OF MANGANESE IONS AND MANGANESE-OXYGEN OCTAHEDRAL CENTERS IN MANGANITES

Five manganese Mn 3d and eighteen oxygen O 2p atomic orbitals in octahedral MnO$_6$ complex with the point symmetry group $O_h$ form both hybrid Mn 3d-O 2p bonding and antibonding $e_g$ and $t_{2g}$ molecular orbitals (MO), and non-bonding $a_{1g} (\sigma)$, $t_{1g} (\pi)$, $t_{1u} (\sigma)$, $t_{2u} (\pi)$ ones. $t_{1u} (\sigma)$ and $t_{1u} (\pi)$ with the same symmetry are hybridized due to the oxygen-oxygen O 2p$\sigma$ - O 2p$\pi$ transfer. The relative energy position of different non-bonding oxygen orbitals is of primary importance for the spectroscopy of the oxygen-manganese charge transfer. This is firstly determined by the bare energy separation $\Delta \epsilon_{2p,\pi} = \epsilon_{2p,\pi} - \epsilon_{2p,\sigma}$ between O 2p$\pi$ and O 2p$\sigma$ electrons. Since the O 2p$\sigma$ orbital points towards the two neighboring positive 3d ions, an electron in this orbital has its energy lowered by the Madelung potential as compared with the O 2p$\pi$ orbitals, which are perpendicular to the respective 3d-O-3d axes. Thus, Coulomb arguments favor the positive sign of the $\pi - \sigma$ separation $\epsilon_{\pi} - \epsilon_{\sigma}$ which numerical value can be easily estimated in frames of the well-known point charge model and appears to be of the order of 1.0 eV. In a first approximation, all the $\gamma (\pi)$ states $t_{1g} (\pi)$, $t_{1u} (\pi)$, $t_{2u} (\pi)$ have the same energy. However, the O 2p$\pi$-O 2p$\pi$ transfer yields the energy correction to its bare energies with the largest in value and positive in sign for the $t_{1g} (\pi)$ state. The energy of $t_{1u} (\pi)$ state drops due to hybridization with cation 4p$\sigma$($u$) state. In other words, the $t_{1g} (\pi)$ state is believed to be the highest in energy non-bonding oxygen state. For illustration, in Fig.1 we show the energy spectrum of the 3d-2p manifold in octahedral complexes like MnO$_6$ with the relative energy position of the levels according to the $X_\gamma$-method calculations for the FeO$^{2-}_6$ octahedral complex in a lattice environment typical for perovskites like LaFeO$_3$, LaMnO$_3$.

The conventional electronic structure of octahedral MnO$_6$ complexes is associated with the configuration of the completely filled O 2p shells and partly filled Mn 3d shells. The typical high-spin ground state configuration and crystalline term for Mn$^{3+}$ in octahedral crystal field or for the octahedral MnO$_6$ complex is $t_{2g} e_g^2$ and $\Delta E_g$, respectively. Namely this orbital doublet results in a vibronic coupling and Jahn-Teller (JT) effect for the MnO$^{2-}_6$ complexes, and cooperative JT ordering in LaMnO$_3$. In the framework of crystal field model the $\Delta E_g$ term originates from the (3d$^4$ 5$^D$) term of free Mn$^{3+}$ ion. Under the low-energy crystal field d-d transitions for the high-spin Mn$^{3+}$ ions one should note a single spin-allowed and parity-forbidden $\Delta E_g - \Delta E_g$ transition at energy varying from about 2.0 to 2.5 eV depending on the crystalline matrix. So, this is likely to be near 2.5 eV for the Mn$^{3+}$ impurity in perovskite YAlO$_3$. The transition is magneto-optically active, and could manifest itself in the Faraday and Kerr effects. A detection of the spin- and parity-forbidden $\Delta E_g - \Delta E_g$ transition with, probably, lower energy could be rather important in the Mn$^{3+}$ assignment.

The unconventional electronic configuration of octahedral MnO$_6$ complexes is associated with a charge transfer state with one hole in O 2p shells. The excited CT configuration $\gamma_{2p}^1 3d^{n+1}$ arises from the transition of an electron from the MO predominantly anionic in nature (the $t_{2g}$ hole 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 $\gamma_{2p}$, and the cation 3d$^1 (t_{2g}^{1+} e_g^{1+})$ shell, respectively. It should be emphasized that the oxygen hole having occupied the non-bonding $\gamma_{2p}$ orbital interact ferromagnetically with 3d$^1 (t_{2g}^{1+} e_g^{1+})$ shell. This rather strong ferromagnetic coupling results in Hund rule for the CT configurations, and provides the high-spin ground states. The maximal value of the total spin for the Hund-
like CT state in MnO$_6^{3-}$ center equals $S = 3$, that uncovers some perspectives to unconventional magnetic signatures of these states.

It should be noted that the presence of the oxygen hole moving around 3d-ion in the CT state can, in common, provide a strong screening both of the 3d crystal field and intra-atomic electron-electron repulsion with the renormalization of the appropriate correlation Racah parameters $A, B, C$ and crystal field splitting $D_q$. It should be noted that unlike the "monopole" parameter $A$ the "multipole" ones $B$ and $C$ usually manifest relatively weak response to crystalline environment. Nevertheless, all these effects can strongly complicate the calculation of the energy structure for the respective 3d$^{n+1}$ configuration. This configuration in the case of CT states in MnO$_6^{3-}$ center nominally corresponds to Mn$^{2+}$ ion. In are spin- and parity-forbidden, therefore these are extremely weak (oscillator strength $\sim 10^{-7}$) and hardly observable in the optical absorption spectra. However, it has been recently shown (see Ref. [13] and references therein) that the dipole- and spin-forbidden d-d excitations can be examined excellently by spin-polarized electron energy loss spectroscopy (EELS). Fromme et al. [13] have measured with high accuracy ($\lesssim 0.02$ eV) the excitation energies for almost all quartet $^4T$ terms of Mn$^{2+}$ ions in MnO: $^4T_{1g}(^6G)$ (2.13), $^4T_{2g}(^6G)$ (2.4), $^4A_{1g}, ^4E_g(4^4G)$ (2.82), $^4T_{2g}(^4D)$ (3.31), $^4E_g(4^4D)$ (3.82), $^4T_{1g}(^4P)$ (4.57), $^4A_{2g}(4^4F)$ (5.08), $^4T_{1g}(^4F)$ (5.38 eV). The energy of $^4T_{2g}(^4F)$ term is expected to be near 6.0 eV. Simple textbook three-parameter $(B, C, D_q)$ crystal field theory [14] provides a self-consistent description of these data given the crystal field parameter $D_q = 0.15$ eV (see Fig.2). Rigorously speaking, we should conclude $D_q = \pm 0.15$ eV because the energies of all quartet and sextet terms for the half-filled 3d$^5$ configuration depend only on modulus $|D_q|$. Parameter $D_q$ defines not only the value of the cubic crystal field splitting $\Delta = 10D_q = E(e_g) - E(t_{2g})$, but its sign. In other words, measuring only the energy of quartet terms for Mn$^{2+}$ (or Fe$^{3+}$) we cannot separate two opposite cases: $E(e_g) > E(t_{2g})$ and $E(e_g) < E(t_{2g})$. However, this puzzling effect concerns only the energy rather than wave functions for the $^4T_g$ terms which strongly depend on the sign of $D_q$. Given $D_q > 0$ the lowest $^4T_{1g}$ term is of dominant $t_{2g}^2e_{g}^1$ configuration, while for $D_q < 0$ this is of dominant $t_{2g}^1e_{g}^2$ configuration. Below we shall see that the latter effect would result in very strong difference in the lineshape of the CT bands for $D_q > 0$ and $D_q < 0$ given the same energy spectrum of the CT states.

Finally, one should emphasize that both the energy and wave functions for $^6A_{1g}, ^4A_{1g}, ^4A_{2g}, ^4E_g$ terms do not depend on the crystal field parameter $D_q$ at all.

### III. CHARGE TRANSFER TRANSITIONS IN MnO$_6^{3-}$ CENTERS

A set of the intensive and broad absorption bands in parent manganites is usually assigned to the anion-cation O 2p-Mn 3d 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$_6^{3-}$ centers. The intra-center CT transitions could be associated with the small CT Frenkel exciton and represent the oxygen hole moving around 3d$^{n+1}$-cation. The inter-center CT transitions form a set of small CT excitons, which in terms of chemical notions represent somewhat like the disproportionation quanta

$$MnO_6^{3-} + MnO_6^{2-} \rightarrow MnO_6^{10-} + MnO_6^{0-}$$ (1)

resulting in a formation of the bounded electron MnO$_6^{10-}$ ($e$-) and hole MnO$_6^{0-}$ ($h^-$) small radius centers. A minimal energy of such an exciton or the disproportionation threshold usually proves to be lower than appro-

![Energy level diagram](image.png)

**FIG. 2:** The energy-level Tanabe-Sugano diagram for the high-spin terms of 3d$^5$ configuration in octahedral (or cubic) crystal field.
priate purely ionic quantity which value equals to the electrostatic correlation energy \( U_{\text{d}} \approx 10 \text{ eV} \). The estimates made in Ref.\[8\] yield for this energy in \( \text{LaMnO}_3 \): \( \Delta E \approx 3.7 \text{ eV} \).

A. Intra-center charge transfer transitions in \( \text{MnO}_6^{\text{2-}} \) centers

The conventional classification scheme of the CT transitions in the octahedral \( \text{MnO}_6^{\text{2-}} \) centers (intra-center CT transitions) incorporates the electric-dipole allowed transitions \( \gamma_u \rightarrow 3d_{t_2g}, 3d_{e_g} \) from the odd oxygen \( \gamma_u = t_{1u}(\pi), t_{2u}(\pi), t_{1u}(\sigma) \) orbitals to the even manganese \( 3d_{t_2g} \) and \( 3d_{e_g} \) orbitals, respectively. These one-electron transitions generate a manifold of the many-electron ones \( 5E_g \rightarrow 5T_u \) (\( T_u \) may be equal both to \( T_{1u} \), and \( T_{2u} \)) which may additionally differ by the crystalline term of the respective \( 3d^{n+1} \) configuration:

\[
(t_{3g}^4 \ A_{2g}^4 \ e_{g}^1 \ e_{g}^1) \ E_g \rightarrow \left( (t_{3g}^4 \ A_{2g}^4 \ e_{g}^2 \ e_{g}^2) \Gamma_{1g} \right) \ (\gamma_u) \ \left( 5T_u \right), \tag{2}
\]

\[
(t_{3g}^4 \ A_{2g}^3 \ e_{g}^1 \ e_{g}^1) \ E_g \rightarrow \left( (t_{3g}^4 \ A_{2g}^4 \ e_{g}^2 \ e_{g}^2) \right) \left( 2S+1 \Gamma_{1g} \right) \ (\gamma_u) \ \left( 5T_u \right), \tag{3}
\]

for \( \gamma_u \rightarrow 3d_{t_2g} \) and \( \gamma_u \rightarrow 3d_{e_g} \) transitions, respectively. Here, we already took into account the Pauli principle and the "triangle rules" for spin momenta and orbital "quasi-momenta" like \( \Gamma \). Proceeding with this analysis we can obtain full selection rules for the many-electron CT transitions:

1. Each \( \gamma_u \rightarrow 3d_{t_2g} \) transition generates two doublets of many-electron CT transitions \( 5E_g \rightarrow 5T_{1,2u} \), differing by the term of the \( t_{2g}^1 e_{g}^1 \) configuration: \( 4T_{1g} \) and \( 4T_{2g} \), respectively.

2. Each \( \gamma_u \rightarrow 3d_{e_g} \) transition generates 5 many-electron CT transitions \( 5E_g \rightarrow 5T_{1,2u} \), differing by the term of the \( t_{2g}^3 e_{g}^5 \) configuration: \( 4A_{1g}, 4A_{2g}, 6A_{1g}, 4E_g \), respectively (in the case of \( 4E_g \) term each one-electron transition generates the \( 3T_{1,2u} \) doublet). The \( \Gamma_{1g} \) quasimomentum is determined by the triangle rule: \( \Gamma_{1g} = A_{2g} \otimes \Gamma_{1g} \).

Additionally, we should take into account the configurational interaction. Indeed, the terms with the same symmetry for different configurations interact and mix with each other. In our case, for the \( 3d^5 \) configuration we have 3 terms \( 4T_{1g} \) and 3 terms \( 4T_{2g} \) which present both in the \( t_{2g}^3 e_{g}^5 \) and \( t_{2g}^1 e_{g}^1, t_{2g}^2 e_{g}^2 \) configurations (see Fig.2).

For the \( t_{2g}^3 e_{g}^5 \) configuration there are two interacting \( 4E_g \) terms.

Hence, beginning from 3 \( t_{1u}(\pi), t_{2u}(\pi), t_{2u}(\pi) \) non-bonding purely oxygen orbitals as initial states for one-electron CT we come to 60 (!) many-electron dipole-allowed CT transitions \( 5E_g \rightarrow 5T_{1,2u}: 24 \) transitions \( t_{1u}(\pi), t_{2u}(\pi) - t_{2g} (\pi - \pi \text{ channel}), 16 \) transitions \( t_{1u}(\pi), t_{2u}(\pi) - e_g (\pi - \sigma \text{ channel}), 12 \) transitions \( t_{1u}(\sigma) - t_{2g} (\sigma - \pi \text{ channel}), \text{ and } 8 \) transitions \( t_{1u}(\sigma) - e_g (\sigma - \sigma \text{ channel}) \), respectively. Thus, the real situation with the multi-band structure of the dipole-allowed O 2p - Mn 3d CT transitions in \( \text{MnO}_6^{\text{2-}} \) centers requires the crucial revision of the oversimplified approaches based on the concept of the only O 2p - Mn 3d CT transition 

B. Dipole transition matrix elements

Making use of the Racah algebra, the method of the irreducible tensorial operators \[1-5\] both for spins and quasimomenta we obtain after some cumbersome calculations the following expressions for the dipole transition matrix elements between the ground \( (t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) \ E_g \) and excited CT states in \( \text{MnO}_6^{\text{2-}} \) octahedra:

\[
\gamma_u \rightarrow t_{2g} \text{ transfer}
\]

\[
\left\langle (t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) E_g \mu|d_q|((t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) \Gamma_{1g} \gamma_u)^5 T_{u\mu} \right\rangle = \]

\[
(\text{2.3)} \left\langle (t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) E_g |d_q|((t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) \Gamma_{1g} \gamma_u)^5 T_{u\mu} \right\rangle ,\tag{4}
\]

where for the many-electron submatrix element

\[
(\text{5.4)}) \left\langle (t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) E_g |d_q|((t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) \Gamma_{1g} \gamma_u)^5 T_{u\mu} \right\rangle = \]

\[
(\text{5.5)}) \left\langle (t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) E_g |d_q|((t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) \Gamma_{1g} \gamma_u)^5 T_{u\mu} \right\rangle = \]

\[
\gamma_u \rightarrow e_g \text{ transfer}
\]

\[
\left\langle (t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) E_g \mu|d_q|((t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) \Gamma_{1g} \gamma_u)^5 T_{u\mu} \right\rangle = \]

\[
(\text{5.6)}) \left\langle (t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) E_g |d_q|((t_{2g}^4 \ A_{2g}^1 \ e_{g}^1) \Gamma_{1g} \gamma_u)^5 T_{u\mu} \right\rangle ,\tag{5}
\]
\[-1\mu \langle E_g \ T_{1u} \ T_u \mid \begin{bmatrix} T_{2u} \ T_{2g} \end{bmatrix}^\dagger \rangle \ast \langle (t_{2g}^3 \ A_{2g}; e_{g}^1)^5 E_g \mid \hat{d} \rangle \langle (t_{2g}^3 \ A_{2g}; e_{g}^2, 2S_{1} + 1 \Gamma_{1})_{2S_{1} + 1 \Gamma_{1}}; \gamma_u \rangle^\dagger T_u \rangle \],

where for the many-electron submatrix element

\[
\langle (t_{2g}^3 \ A_{2g}; e_{g}^1)^5 E_g \mid \hat{d} \rangle \langle (t_{2g}^3 \ A_{2g}; e_{g}^2, 2S_{1} + 1 \Gamma_{1})_{2S_{1} + 1 \Gamma_{1}}; \gamma_u \rangle^\dagger T_u \rangle = \n
\n
\n
(6)

Here, the expressions [4] - [7] represent the Wigner-Eckart theorem for many-electron transition matrix elements with \( \langle \ldots \rangle \) being the Wigner coefficient for the cubic point group. In [8], the conventional notations are used for spin 6j- and orbital 6\( \Gamma \) symbols \( \{ \ldots \} \); \( |S| = 2S + 1 \), \( [\Gamma] \) is the dimensionality of the corresponding irreducible representation of the cubic point group; \( j(\Gamma) \) the so-called quasimomentum number;

\[ \langle \gamma_u \mid \hat{d} \rangle \langle \gamma_g \rangle \]

It should be noted that the above calculation of the dipole matrix elements implies the same character of the one-electron \( t_{2g}, e_{g} \) orbital for the ground state \( t_{2g}^3, e_{g}^1 \) and excited \( t_{2g}^3, e_{g}^2, t_{2g}^2, e_{g}^1 \) CT configurations, particularly with the invariable values of the appropriate covalency parameters.

The one-electron dipole moment submatrix elements can be rather simply evaluated in frames of the so-called “local” approximation, in which the calculation of the matrix of the dipole moment implies the full neglect all many-center integrals:

\[ \langle \phi_k, (R_1 - r) | \hat{d} | \phi_k, (R_2 - r) \rangle = eR_1 \delta_{R_1, R_2} \delta_{k_1, k_2}, \]

where \( R_1, R_2 \) label sites, \( k_1, k_2 \) atomic functions, respectively. Then

\[ \langle t_{2u}(\pi) \mid \hat{d} \rangle \langle e_g \rangle = 0; \langle t_{2u}(\pi) \mid \hat{d} \rangle \langle t_{2g} \rangle = -i \sqrt{3/2} \lambda_{\pi} d; \]

\[ \langle t_{1u}(\sigma) \mid \hat{d} \rangle \langle t_{2g} \rangle = 0; \langle t_{1u}(\sigma) \mid \hat{d} \rangle \langle e_g \rangle = -2 \sqrt{3/3} \lambda_{\sigma} d; \]

\[ \langle t_{1u}(\pi) \mid \hat{d} \rangle \langle e_g \rangle = 0; \langle t_{1u}(\pi) \mid \hat{d} \rangle \langle t_{2g} \rangle = \sqrt{3/2} \lambda_{\pi} d. \]

Here, \( \lambda_{\sigma}, \lambda_{\pi} \) are effective covalency parameters for \( e_{g}, t_{2g} \) electrons, respectively, \( d = eR_0 \) is an elementary dipole moment for the cation-anion bond length \( R_0 \). We see, that the “local” approximation results in an additional selection rule: it forbids the \( \sigma \rightarrow \pi \), and \( \pi \rightarrow \sigma \) transitions, \( t_{1u}(\sigma) \rightarrow t_{2g}, \) and \( t_{1u}(\pi) \rightarrow e_{g}, \) respectively, though these are dipole-allowed. In other words, in frames of this approximation only \( \sigma \)-type \( (t_{1u}(\sigma) \rightarrow e_{g}) \) or \( \pi \)-type \( (t_{1u}(\pi) \rightarrow t_{2g}) \) CT transitions are allowed. It should be emphasized that the “local” approximation, if non-zero, provides the leading contribution to transition matrix elements with corrections being of the first order in the cation-anion overlap integral. Interestingly, that the one-electron dipole moment submatrix elements for both \( \pi \rightarrow \pi \) transitions in Eq. (6) have the same absolute value. Hereafter, we make use of the terminology of “strong” and “weak” transitions for the dipole-allowed CT transitions going on the \( \sigma \rightarrow \sigma, \pi \rightarrow \pi, \) and \( \pi \rightarrow \sigma, \sigma \rightarrow \pi \) channels, respectively. Thus, for \( MoO_6^3- \) center we predict a series of 32 strong many-electron dipole-allowed CT transitions \( 5E_g \rightarrow 5T_{1u} \) \( (24 \) for \( \pi \rightarrow \pi \), and \( 8 \) for \( \sigma \rightarrow \sigma \) channel) and 28 weak dipole-allowed CT transitions \( (\pi \rightarrow \sigma \) and \( \sigma \rightarrow \pi \) cross-channels).
for the $\pi - \pi$ and $\sigma - \sigma$ channel, respectively. For the $\pi - \pi$ channel we have
\[
I(4T_{1g}; 5T_u) : I(4T_{2g}; 5T_u) = \frac{1}{2} : \frac{1}{2} \tag{12}
\]
irrespective of the type of the transferred oxygen $\pi$ electron, $t_{2u}$, or $t_{1u}$. Here, each intensity represents the sum for two doublets, $5T_{1u}$ and $5T_{2u}$. Interestingly, the relative intensity for these two components is $3 : 1$ and $1 : 3$ for the $4T_{1g}$ and $4T_{2g}$ "intermediate" terms, respectively. It should be noted that absolutely the same relations are fulfilled for the weak dipole-allowed CT transitions in the $\sigma - \pi$ channel.

For the strong $\sigma - \sigma$, and weak $\pi - \pi$ channels we have the more nontrivial relation:
\[
I(6A_{1g}; 5T_u) : I(4A_{1g}; 5T_u) : I(4E_g; 5T_u) : I(4A_{2g}; 5T_u) = \frac{8}{15} : \frac{2}{15} : \frac{1}{9} : \frac{2}{9}, \tag{13}
\]
where the third transition is doublet with the equal intensity of both components. It should be reminded that all these numerical data are obtained for CT transitions to "pure" $t_{2g}^2 e_g^0$ and $t_{2g}^0 e_g^2$ configurations. The configuration interaction effect results in a redistribution of the respective intensities in between all interacting terms with the same symmetry.

IV. CHARGE TRANSFER TRANSITIONS IN PARENT LaMnO$_3$

Now we can apply the model theory to the undoped stoichiometric manganite LaMnO$_3$. For our analysis to be more quantitative we make two rather obvious model approximations. First of all, one assumes that for MnO$_6^{2-}$ centers in LaMnO$_3$ as usually for cation-anion octahedra in 3d-oxides the non-bonding $t_{1g}(\pi)$ oxygen orbital has the highest energy and forms the first electron removal oxygen state. Moreover, to be definite we assume that the energy spectrum of the non-bonding oxygen states for Mn$^{3+}$O$_6^{2-}$ centers in LaMnO$_3$ coincides with that calculated in Ref.1 for Fe$^{3+}$O$_6^{2-}$ in LaFeO$_3$ with the same crystalline environment, in other words, we have (in eV):
\[
\Delta(t_{1g}(\pi) - t_{2u}(\pi)) \approx 0.8; \quad \Delta(t_{1g}(\pi) - t_{1u}(\pi)) \approx 1.8; \quad \Delta(t_{1g}(\pi) - t_{1u}(\pi)) \approx 3.0.
\]
This is believed to be a rather reasonable choice of the energy parameters, because the purely oxygen states mainly depend only on crystalline environment. Secondly, we choose for the Racah parameters $B$ and $C$ the numerical values typical for Mn$^{2+}$ in oxides, 0.12 and 0.41 eV, respectively (see above). The crystal-field parameter $Dq$ may be varied, however, we decide in favor of only two model considerations with the same absolute value but the different sign of $|Dq| = 0.15$ eV ("conventional" $Dq > 0$ and "unconventional" $Dq < 0$ sign). Let us mention that this value, irrespective of the sign, provides a reasonable explanation of the Mn$^{2+}$ spectra in MnO$_2$ (see above). Moreover, the photoemission data are believed to confirm the relevance of this value for crystal field splitting parameter in LaMnO$_3$.

Hereafter, this set of parameters is used for the model theoretical simulation of the overall CT band in LaMnO$_3$. Firstly, we argue that the lowest in energy spectral feature observed in LaMnO$_3$ near 1.7 eV is believed to be associated with the onset of the series of the dipole-forbidden CT transitions $t_{1g}(\pi) \rightarrow e_g$, rather than with any d-d crystal field transition. The energy of this transition was picked out to be a starting point to assign all other CT transitions.

Weak dipole-allowed $\pi - \sigma$ CT transitions $t_{2u}(\pi) - e_g$ and $t_{1u}(\pi) - e_g$ form more intensive CT bands starting at higher than the preceding series energies, near 2.5 and 3.5 eV, respectively, in accordance with the magnitude of the $t_{1g}(\pi) - t_{2u}(\pi)$ and $t_{1g}(\pi) - t_{1u}(\pi)$ separations. Actually, the $t_{1u}(\pi) - e_g$ transition has to be more intensive because the $t_{1u}(\pi)$ state is partly hybridized with $t_{1u}(\sigma)$, hence this transition borrows a portion of intensity from the strong dipole-allowed $t_{1u}(\sigma) - e_g$ CT transition.

The latter $\sigma - \sigma$ transition as we see from Eq.(13) forms intensive broad CT band starting from the main $5E_g - 4A_{1g}; 5T_{1u}$ peak at $\approx 4.7$ eV and ranging to the $5E_g - 4A_{2g}; 5T_{2u}$ peak at $\approx 10.2$ eV with interstitial peaks at $\approx 8.0$ eV being the result of the superposition of two transitions $5E_g - 4A_{1g}; 5T_{1u}$ and $5E_g - 4E_g; 5T_{1u}$, and at $\approx 8.8$ eV due to another $5E_g - 4E_g; 5T_{1u}$ transition, respectively. Thus, the overall width of the CT bands with final $t_{2g}^2 e_g^2$ configuration occupies a spectral range from 1.7 up to $\sim 10$ eV.

As it is seen from Eq.(12) strong dipole-allowed $\pi - \pi$ CT transitions $t_{2u}(\pi), t_{1u}(\pi) - t_{2g}$ form two manifolds of equally intensive CT bands shifted with respect each other by the $t_{2u}(\pi) - t_{1u}(\pi)$ separation ($\approx 1.0$ eV). In turn, each manifold consists of two triplets of weakly split and equally intensive CT bands associated with $5E_g - 4T_{1g}, 5T_u$ and $5E_g - 4T_{2g}, 5T_u$ transitions, respectively. In accordance with the assignment of crystal-field transitions in LaMnO$_3$ (see Fig.2) we should expect the low-energy edge of the dipole-allowed $\pi - \pi$ CT band starting at $\approx 4.5$ eV ($1.7 + 2.0 + (t_{1g}(\pi) - t_{2u}(\pi))$ separation). Taking account of strong configuration interaction we should expect the high-energy edge of this band associated with the highest in energy $4T_{2g}$ term of the 3d$^5$ configuration to be situated near $\approx 9.9$ eV. In between, in accordance with our scheme of energy levels we predict peaks at 5.2; 5.5; 6.2 ($\times 2$); 7.2; ($\times 2$); 7.9; 8.2; 8.3; 8.9 eV. The weak dipole-allowed $\sigma - \pi$ transitions occupy the high-energy spectral range from 6.7 to 11.1 eV.

Overall, our analysis shows the multi-band structure of the CT optical response in LaMnO$_3$ with the weak low-energy edge at 1.7 eV, associated with forbidden $t_{1g}(\pi) -$
$e_g$ transition and a series of strong bands in the range $4.6 \div 10.2$ eV beginning from composite peak at $\sim 4.5 \div 4.7$ eV and closing by composite peak at $8 \div 10$ eV both resulting from the superposition of strong dipole-allowed $\pi - \pi$ and $\sigma - \sigma$ CT transitions.

Above we addressed the model energies of the CT transitions. In frames of our model approach the relative intensities for different dipole-allowed CT transitions are governed by the relative magnitude of different one-electron dipole submatrix elements. We have performed the theoretical simulation of the overall O 2p-Mn 3d CT optical band in LaMnO$_3$ generated by dipole-allowed CT transitions in MnO$_6^{2-}$ octahedra given simple physically reasonable assumptions concerning the one-electron submatrix elements. We have assumed: i) the equal integral intensities for the $\sigma - \sigma$ and $\pi - \pi$ channels: $I_{\sigma \sigma} = I_{\pi \pi}$, that corresponds $\lambda_{\sigma}^2 = 6\lambda_{\pi}^2$; and ii) the equal integral intensities $I_{\sigma \sigma} = I_{\pi \pi} = 0.1I_{\sigma \sigma}$ for all weak dipole-allowed transitions $t_{2u}(\pi) - e_g$, $t_{1u}(\pi) - e_g$, and $t_{1u}(\sigma) - t_{2g}$. The former assumption agrees with the well-known semi-empirical rule that simply states: $\lambda_{\sigma} \sim 2\lambda_{\pi}$. Indeed, the theoretical calculations and experimental data for 3d$^5$ configuration in FeO$_6^{9-}$ octahedra yield: $\lambda_{\pi}^2 \approx 3.5\lambda_{\pi}^2$ and $\lambda_{\pi}^2 \approx 2(5 \div 6.0)\lambda_{\pi}^2$, respectively. The latter assumption concerns the outgoing beyond the "local" approximation and seems to be more speculative. Probably, this yields an overestimation for $t_{2u}(\pi) - e_g$ transition, but underestimation for $t_{1u}(\pi) - e_g$ and $t_{1u}(\sigma) - t_{2g}$ transitions, which intensity can be enhanced due to $t_{1u}(\pi) - t_{1u}(\sigma)$ hybridization. The more detailed quantitative description of the weak dipole-allowed CT transitions needs the substantial expansion of our model approach and further theoretical studies.

The calculated model contributions of the dipole-allowed CT transitions to the imaginary part of dielectric function are presented in Figs.3a,b for conventional $Dq > 0$ (Fig.3a) and unconventional $Dq < 0$ (Fig.3b) sign for the crystal field parameter. The top panels in both cases show the partial contributions of different dipole-allowed transitions modeled by rather narrow Lorentzians with linewidth $\Gamma = 0.5$ eV to clearly reveal the multiplet structure. The lower panels present the overall contribution to the imaginary part of dielectric function of the dipole-allowed CT transitions. Here, the Lorentzian linewidth is assumed to be $\Gamma = 1.0$ eV for all contributions to maximally reproduce the experimental situation. All the spectra are presented in the same relative units.

As it was mentioned above, the energy spectrum of CT states in MnO$_6^{2-}$ octahedra does not depend on the sign

FIG. 3: Theoretical simulation of the overall O 2p-Mn 3d CT band in LaMnO$_3$ with conventional $Dq > 0$ (a) and unconventional $Dq < 0$ (b) sign for the crystal field parameter. The top panels shows the partial contributions of different dipole-allowed transitions. The lower panels present the overall contribution of the dipole-allowed CT transitions to the imaginary part of dielectric function. Experimental spectrum for La$_{1-x}$Sr$_x$MnO$_3$ given $x \approx 0$ from the paper by Okimoto et al. is shown in insert (see text for details).
of the crystal-field parameter $Dq$. However, the intensities of certain CT transitions appear to be extremely sensitive to the sign of $Dq$, or in other words, to the relative energy position of $e_g$ and $t_{2g}$ orbitals. First of all, this concerns the $\pi - \pi$ and $\sigma - \pi$ channels which manifest anomalously strong dependence on the $Dq$ sign with clearly seen spectral weight transfer from the composite band centered around $\sim 5$ eV given $Dq > 0$ (Fig.3a) to the composite band centered around $\sim 9$ eV given $Dq < 0$ (Fig.3b). From the other hand, the $\sigma < \sim \tau$ to the composite band centered around $\sim 5$ eV given $Dq > 0$. 

From the other hand, the $\sigma - \sigma$ and $\pi - \pi$ channels which define the low-energy part of the overall CT band show no change with the $Dq$ sign inversion. Thus, the high-energy part of the overall CT band provides a very sensitive tool to examine the screening effects for crystal field in the 3d$^5$ configuration with the oxygen hole surrounding.

The theoretical findings are in reasonable quantitative agreement with experimental spectra available. Indeed, a rather broad spectral structure with distinctly revealed peaks near 5 eV and 8 ÷ 9 eV is observed in the $e_g$ spectra for undoped LaMnO$_3$ (see inserts in Fig.3), although only the band peaked near 5 eV was assigned earlier to the O 2p-Mn 3d charge transfer. The high-energy peak at 8 ÷ 9 eV was assigned by Okimoto et al. to O 2p-La 5d interband transition; albeit this was argued rather on the quantitative considerations than either calculations. However, Arima and Tokura in their optical study of different perovskite-type RMO$_3$ (R=La, Y, M=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu) have shown that similar band is commonly observed for all both LaMoO$_3$ and YMoO$_3$ compounds. In other words, it seems more natural to ascribe this band rather to the high-energy edge of the O 2p-Mn 3d CT transitions, than the O 2p-Mn 3d CT transitions. We present a self-consistent model allows to associate this effect with the localization of the doped holes in the upper purely charge transfer optical response. In a sense, the fundamental O 2p - Mn 3d CT transition, whereas the band at $\sim 5$ eV is associated with the fundamental O 2p - Mn 3d CT transition, whereas the band at $\sim 2$ eV is rather associated with the presence of Mn$^{4+}$ and/or O$^-$ self-trapped holes in probably non-stoichiometric LaMnO$_3$ compound. Broad band peaked near 9 eV is assigned to O 2p - La 5d CT transition. However, their assignment is based on the numerical results obtained in frames of the semi-empirical shell model with the full neglect of the orbital degeneracy, many-electron intra-atomic correlations, and crystal field effects both for manganese and oxygen electrons. On the other hand, namely these effects are shown here to be responsible for multi-band structure of the CT optical response. In a sense, the fundamental O 2p - Mn 3d CT energy evaluated in Ref.18 to be 5.6 eV represents a mean value of the respective CT energies.

V. CONCLUSIONS

In frames of a rather conventional quantum-chemical cluster approach, which combines the crystal field and the ligand field models we have examined different CT states and O 2p-Mn 3d CT transitions in MnO$^{2-}_{6}$ octahedra. The many-electron dipole transition matrix elements were calculated using the Racah algebra for the cubic point group. Simple ”local” approximation allowed to calculate the relative intensity for all dipole-allowed $\pi - \pi$ and $\sigma - \sigma$ CT transitions. We present a self-consistent description of the CT bands in insulating stoichiometric LaMnO$_3$. Our analysis shows the multi-band structure of the CT optical response with the weak low-energy edge at 1.7 eV, associated with forbidden $t_{1g}(\pi) - e_g$ tran-
sition and a series of the high-energy weak and strong dipole-allowed high-energy transitions starting from 2.5 and 4.5 eV, respectively, and extending up to nearly 11 eV. The most intensive features are associated with two strong composite bands near 4.6±4.7 eV and 8±9 eV, respectively, resulting from the superposition of the dipole-allowed $\sigma - \sigma$ and $\pi - \pi$ CT transitions. These theoretical findings are in quantitative agreement with experimental spectra available. We examined the effects of the sign of the crystal field parameter $Dq$ and showed that the $\pi - \pi$ and $\sigma - \sigma$ channels contrary to $\sigma - \sigma$ and $\pi - \sigma$ ones manifest anomalously strong dependence on the $Dq$ sign with clearly seen spectral weight transfer from the composite band centered around $\sim 5$ eV given $Dq > 0$ to the composite band centered around $\sim 9$ eV given $Dq < 0$. Thus, the high-energy part of the overall CT band provides a very sensitive tool to examine the screening effects for the crystal field in the 3d$^5$ configuration with the oxygen hole surrounding. The experimental data point to a strong overscreening of the crystal-field parameter $Dq$ in the CT states of MnO$_9$ centers. In addition, we would like emphasize the specific role of the intra-atomic correlation effects. It seems, the actual spectral picture of the CT optical response is determined on equal footing both by the intra-atomic d-d electron-electron repulsion and single electron effects. We believe that these and many other semi-quantitative conclusions drawn from our model will stimulate the further theoretical and experimental studies of the CT states and transitions both in LaMnO$_3$ and another 3d oxides. We did not consider the inter-center CT transitions. Its role in optical response remains so far unclear, however, appropriate intensities seem to be small because these are proportional to small inter-center d-d transfer integrals squared.

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APPENDIX A: NUMERICAL VALUES FOR $6_\sigma$- AND $6_\pi$-COEFFICIENTS THAT ONE NEEDS TO CALCULATE THE DIPOLE TRANSITION MATRIX ELEMENTS

$$\begin{align*}
&\left\{\frac{3}{2} 1 \frac{5}{2} \right\} = -\frac{1}{\sqrt{15}}; \left\{\frac{3}{2} 1 \frac{3}{2} \right\} = \frac{1}{2\sqrt{10}}; \left\{\frac{3}{2} 0 \frac{3}{2} \right\} = \frac{1}{2\sqrt{2}}; \\
&\left\{A_2 E E \right\} = \left\{A_2 E A_1 \right\} = \left\{A_2 E A_2 \right\} = -\frac{1}{\sqrt{2}}; \left\{A_2 E E \right\} = -\frac{1}{2}.
\end{align*}$$

$$\begin{align*}
&-\left\{T_1 T_1 E \right\} = \left\{T_1 T_1 E \right\} = \left\{T_2 A_2 T_1 \right\} = -\left\{T_2 A_2 T_1 \right\} = -\left\{T_2 A_2 T_1 \right\} = \frac{1}{\sqrt{6}}; \\
&\left\{T_2 T_1 T_2 \right\} = \left\{T_1 T_1 T_2 \right\} = \left\{T_2 T_1 T_1 \right\} = \left\{T_1 T_1 T_2 \right\} = \frac{1}{6}; \\
&\left\{T_1 T_1 E \right\} = \left\{T_1 T_1 E \right\} = \left\{T_1 T_1 E \right\} = \left\{T_1 T_1 T_2 \right\}; \\
&-\left\{T_1 T_1 T_2 \right\} = -\left\{T_2 T_1 T_2 \right\} = -\left\{T_2 T_1 T_2 \right\} = \frac{1}{2\sqrt{3}}.
\end{align*}$$
1. A.S. Moskvin, I.L. Avvakumov, cond-mat/0108355 (submitted to Physica B).
2. T. Arima, Y. Tokura, J. Phys. Soc. Jap. 64, 2488 (1995).
3. Y. Okimoto, T. Katsufui, T. Ishikawa, A. Urushibara, T. Arima, and Y. Tokura, Phys. Rev. Lett. 75, 109 (1995);
   Y. Okimoto, T. Katsufui, T. Ishikawa, T. Arima, and Y. Tokura, Phys. Rev. B 55, 4206 (1997).
4. J.H. Jung, K.H. Kim, T.W. Noh et al., Phys. Rev. Lett. 75, 109 (1995);
   Y. Okimoto, T. Katsufui, T. Ishikawa, T. Arima, and Y. Tokura, Phys. Rev. B 55, 4206 (1997).
5. Koshi Takenaka, Kenji Iida, Yuko Sawaki et al., J. Phys. Soc. Jap. 68, 1828 (1999).
6. J.F. Lawler, J.G. Lunney, and J.M.D. Coey. J. Appl. Phys. Lett. 65, 3017 (1994).
7. I.B. Bersuker, Electronic structure and properties of transition metal compounds (introduction to the theory), New York, Wiley, 1996.
8. B.E. Douglas, C.A. Hollingsworth, Symmetry in Bonding and Spectra, Orlando, Acad. Press, 1985.
9. C.N.R. Rao, B. Raveau, Transition Metal Oxides, VCH, 1995.
10. F.J. Kahn, P.S. Pershan, J.P. Remeika, Phys. Rev. 186, 891 (1969).
11. A.I. Liechtenstein, A.S. Moskvin, V.A. Gubanov, Fizika Tverdago Tela 24, 3596 (1982) (in Russian).
12. Gen Matsumoto, J. Phys. Soc. Jap. 29, 615 (1970).
13. B. Fromme, U. Brunokowski, and E. Kisker, Phys. Rev. B 58, 9783 (1998).
14. L.E. Orgel, J. Chem. Phys. 23, 1004 (1955); G.W. Pratt, Phys. Rev. 116, 281 (1959).
15. J. van Elp, R.H. Potze, H. Eskes, R. Berger, and G.A. Sawatzky, Phys. Rev. B 44, 1530 (1991).
16. S. Sugano, Y. Tanabe, H. Kamimura, Multiplets of Transition Metals in Crystals. N.Y.:Acad. Press., 1971; T. Inui,
   Y. Tanabe, Y. Onodera, Group Theory and its Application in Physics, Springer-Verlag, Berlin-Heidelberg, 1990.
17. A.S. Davydov, Theory of Molecular Excitons, McGraw-Hill, New York, 1962.
18. N.N. Kovaleva, J.L. Gavartin, A.L. Shluger et al., cond-mat/0108207.
19. D. A. Varshalovich, A. N. Moskalev, V. K. Khersonskii. Quantum Theory of Angular Momentum (World Scientific,
   Singapore, 1988).
20. We make use of the Racah algebra for cubic point group in the form developed by Lithuanian school (see e.g.
   I.V. Batarunas, I.B. Levinson, Tr. AN Lit.SSR, ser. B, 2(22), Vilnius, 1960, s.15). For a rather complete summary of this approach, see e.g.
   A.S. Moskvin, I.G. Bostrem, Metod Neprivodimykh Tenzornykh Operatorov Tochechnykh Grup (Method of Irreducible Tensorial Operators for
   Point Groups), Uralskiy Universitet, Ekaterinburg, 1998, 106 s (in Russian).
21. J.H. Park, C.T. Chen, S.W. Cheong et al., Phys. Rev. Lett. 76, 4215 (1996).
22. P. Freund, J. Owen, B.F. Hann, J. Phys. C: Solid St. Phys. 6, 2139 (1973).