Doping dependence of the exchange energies in bilayer manganites: Role of orbital degrees of freedom

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Recently, an intriguing doping dependence of the exchange energies in the bilayer manganites La$_{2-x}$Sr$_{x+2}$Mn$_2$O$_7$ has been observed in the neutron scattering experiments. The intra-layer exchange only weakly changed with doping while the inter-layer one drastically decreased. Here we propose a theory which accounts for these experimental findings. We argue, that the observed striking doping dependence of the exchange energies can be attributed to the evaluation of the orbital level splitting with doping. The latter is handled by the interplay between Jahn-Teller effect (supporting an axial orbital) and the orbital anisotropy of the electronic band in the bilayer structure (promoting an in-plane orbital), which is monitored by the Coulomb repulsion. The presented theory, while being a mean-field type, describes well the experimental data and also gives the estimates of the several interesting energy scales involved in the problem.

PACS numbers: 75.30.Ds, 75.10.Lp, 75.30.Vn

The three-dimensional (3D) cubic manganites R$_{1-x}$B$_x$MnO$_3$ (where R is trivalent rare-earth and B is divalent alkaline ion, respectively) as well as the two-dimensional (2D) bilayer ones La$_{2-x}$Sr$_{x+2}$Mn$_2$O$_7$ have attracted recent interest not only due to the discovery of colossal magnetoresistance (CMR) in these compounds but also because of their rich and rather unusual physical properties. At different doping concentration the manganese oxides exhibit a wide diversity of the ground states, and the small changes of some external parameters of the system such as doping, chemical pressure, temperature or magnetic field can result in a drastic modification of the physical properties as well as cause the transition from one to another ground state.

In fact, in very recent spin-wave measurements on the bilayer manganites La$_{2-x}$Sr$_{x+2}$Mn$_2$O$_7$ (in the doping range $x = 0.3 - 0.5$) strongly anisotropic doping dependence of the inter-layer (within the bilayer) ($J_\|)$ and of the intra-layer ($J_\perp$) exchange couplings has been revealed. At $x = 0.3$ both exchange constants are ferromagnetic (FM) and of the same order $J_\perp=5$ meV, and $J_\| = 4$ meV. With further doping ($x > 0.3$), $J_\|$ changes very slightly while inter-layer exchange rapidly decreases, by a factor of four at $x = 0.4$, and changes sign at $x \sim 0.45$.

Within the double-exchange (DE) picture FM coupling between the nearest-neighbour (NN) $t_{2g}$ core spins is mediated by the hopping of $e_g$-electrons ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbital states) and scales as a kinetic energy of these electrons on a given bond. Since only $d_{3z^2-r^2}$ (axial) orbital has a finite inter-layer transfer amplitude ($z$-axes is set perpendicular to a bilayer), the inter-layer exchange is only mediated by this orbital. While the intra-layer one is mainly determined by the $d_{x^2-y^2}$ (in-plane) orbital state, that has a highest intra-plane transfer amplitude. Therefore, above discussed decrease of the inter-layer exchange constant with doping can be ascribed to the change of the nature of occupied orbital state from mainly $d_{3z^2-r^2}$ character, at low doping $x < 0.3$, to mostly $d_{x^2-y^2}$ one at higher doping $x > 0.3$. This qualitative picture is also consistent with the recent x-ray magnetic Compton-profile measurements. The results of this experiment have shown that upon doping (for $0.35 < x < 0.45$) the electrons are mainly withdrawn from $d_{3z^2-r^2}$ orbital state and the occupancy of $d_{x^2-y^2}$ state remains practically the same. However, we point out, that the observed doping dependence of the exchange constants and of the orbital occupancy, being interrelated, can not be understood within a rigid band picture that assumes a constant value of orbital level splitting. Interpretation of the experimental findings within this picture would imply that only $d_{3z^2-r^2}$ band crosses the Fermi level and is emptied out upon doping, while the $d_{x^2-y^2}$ band lies below and shows a constant filling. From the other hand, if $d_{x^2-y^2}$ band does not cross Fermi surface, then it is no longer active to generate the intra-layer ferromagnetic DE interaction leading to $J_\| < J_\perp$, in contrast to experimental findings $J_\| > J_\perp$.

The aim of the present work is to propose a mechanism that can explain the experimental findings. The paper is organized as follows: First we briefly discuss the structural aspects of the compound relevant for our study. Next we give the basic physical ideas and set up the minimal model Hamiltonian to provide a microscopic description. We then present our results on the doping evaluation of the orbital occupancies and the exchange energies, and finally, compare the theoretical findings with that of the experiments.

The compound La$_{2-x}$Sr$_{x+2}$Mn$_2$O$_7$ consists of bilayer slices of MnO$_6$ octahedra, separated by insulating (La,Sr)$_2$O$_2$ layers that serve to decouple the bilayers both electronically and magnetically. Therefore, as a first ap-
proximation the system can be treated as composed of independent bilayers. One electron placed in the doubly degenerate $e_g$ level, makes the Mn$^{3+}$O$_6$-2 complex Jahn-Teller (JT) active. The experimental analysis of the crystal strutter has revealed, that JT distortion results in the elongation of MnO$_6$ octahedra along $z$-axis. Five bonds (four equatorial and one apical with shared oxygen ion) are essentially identical. The elongation of octahedra occurs mainly because the apical bond with unshared oxygen atom is longer than the other five bonds. These type of JT distortion promotes the axially directed $d_{3z^2-r^2}$ orbital by lowering its on-site energy. The dimensionless parameter describing the static Jahn-Teller distortion can be defined as $\delta_{\text{JT}} = (\langle d_{\text{apic(equat)}}^\alpha \rangle - \langle d_{\text{Mn-O}}^\alpha \rangle) / \langle d_{\text{Mn-O}}^\alpha \rangle$, where $\langle d_{\text{Mn-O}}^\alpha \rangle$ is an averaged apical (equatorial) Mn-O length. The relative distortion $\delta_{\text{JT}}$ also gives the scale of JT induced orbital level splitting.

The physical picture we shall be based on is as follows: Both the orbital occupancy and exchange energies strongly depend on the orbital level splitting. The latter consist of the two parts: JT induced gap and correlation induced one. The JT distortion is largest at low doping and monotonically relaxes upon doping ($\delta_{\text{JT}} \sim 0.036$, 0.020, and 0.0 for $x = 0.3$, 0.4, and 0.5, respectively). Therefore, at low doping the axial orbital, promoted by the JT distortion is predominantly occupied. The matrix element of the inter-orbital Coulomb energy does not depend on the character of predominantly occupied orbital state. Therefore, on-site repulsion further supports already preferred orbital state and by enhancing the orbital polarization reduces the Coulomb energy. At low doping, the physics is mainly determined locally and kinetic energy term is less important. However, upon increasing the carriers number the JT induced gap decreases while the kinetic energy starts to play more dominant role. In the bilayer system, the latter promotes the in-plane orbital state, that has the highest intra-layer transfer amplitude and by forming the wider band can lower the kinetic energy of the system. Therefore, one would expect that at some doping $x = x_c$ the possible energy gain due to the kinetic energy will overcome the crystal-field splitting of the orbital levels. Therefore, for $x > x_c$, it becomes energetically more favorable to lower the energy of the in-plane orbital and hence, correlation induced splitting will change the sign. As will be shown below, the doping dependence of the orbital level splitting, resulted from the discussed interplay, gives the consistent description of the experimental findings.

The minimal model Hamiltonian which describes above discussed scenario consists of the two contributions $H = H_{\text{el}} + H_{\text{sp}}$, where $H_{\text{el}}$ and $H_{\text{sp}}$ describe charge and spin degrees of freedom, respectively. We retain only the preferred spin component of the fermionic operators, in the fully polarized (semi-metallic) FM case and also assume that all the other degrees of freedom are integrated out to give effective model parameters relevant to the low energy physics. The electronic part of the Hamiltonian can be written as:

$$H_{\text{el}} = -\sum_{i,j,\alpha,\beta} t_{ij}^{\alpha\beta} \left[ d_{i\alpha}^\dagger d_{j\beta} + d_{i\alpha} d_{j\beta}^\dagger \right] - \sum_{i,\alpha,\beta} U_{i\alpha\beta}^{\alpha\beta} \left[ d_{i\alpha}^\dagger d_{i\beta} + \text{H.c.} \right] + \sum_i \left[ (-1)^i \Delta_{\text{JT}} - \mu \right] \left[ n_{i\alpha} + \bar{n}_{i\alpha} \right] + \sum_i U_{\text{eff}} \left[ n_{i1} n_{i2} + \bar{n}_{i1} \bar{n}_{i2} \right]$$

The first and the second term of Eq.(1) describe an intra- and inter-layer electron hopping between the two $e_g$ orbitals of the NN Mn-ions, respectively. Index $i$ numbers the unit cell composed by two Mn sites, $d_{i\alpha}$ and $\bar{d}_{i\alpha}$ are the electron annihilation operators on these two sites. The orbitals $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ correspond to $\alpha (\beta) = 1$ and 2, respectively. Intra- and inter-layer transfer matrix elements are given by

$$t_{i\alpha}^{\alpha\beta} = \begin{cases} t \left( \begin{array}{c} 1/4 \\ \sqrt{3}/4 \\ 3/4 \end{array} \right), & \text{if } \alpha = \beta, \\ t \left( \begin{array}{c} 0 \\ 0 \\ 0 \end{array} \right), & \text{if } \alpha \neq \beta, \end{cases}$$

The electron density operator on a given orbital state is denoted by $n_{i\alpha}$, $\mu$ is chemical potential, $\Delta_{\text{JT}} = g \delta_{\text{JT}}$ is JT induced orbital level splitting, $g$ is properly normalized coupling constant of electrons with JT active phonon modes, and $\delta_{\text{JT}}$ is a measure of JT distortion discussed above. In the present paper we do not attempt to calculate JT distortion by minimizing the total energy of the system (including lattice elastic energy) and model the dimensionless parameter $\delta_{\text{JT}}$ by the following doping dependence $\delta_{\text{JT}} = 0.17(0.5-x)$, that reasonably reproduces the experimental data.

The last term in Eq.(1) represents an effective, relevant for the low energy physics, on-site inter-orbital Coulomb repulsion between electrons. We assume that $U_{\text{eff}}$ has been already renormalized due to the many-body effects and properly screened in the metallic state. Therefore, one expects that $U_{\text{eff}}$ is much smaller than the bare ionic value of Hubbard $U$. We treat this term within the mean-filed (MF) approximation by introducing the MF parameter describing the anisotropy of the orbital occupancy $\delta n = \langle n_{i1} \rangle - \langle n_{i2} \rangle$. This introduces additional splitting of local orbital levels due to the electron-electron interaction. Therefore the total splitting of orbital levels will be determined by both JT effect and electron-electron repulsion with following value:

$$2\Delta = 2\Delta_{\text{JT}} + U_{\text{eff}} \delta n.$$ We emphasize, that the nonzero value of MF parameter $\delta n$ does not imply any symmetry breaking long range orbital order and the symmetry of Hamiltonian remains tetragonal. Even in the non-interacting case and absence of any JT distortion one finds $\delta n \neq 0$. The band structure with tetragonal symmetry brakes the local cubic symmetry and promotes planar $d_{x^2-y^2}$ orbital with wider band leading to $\delta n < 0$. In the orbital pseudo-spin language the ground state can be represented by nonzero value of the axial component of the orbital pseudo-spin $\langle \sigma_z^i \rangle = \langle (n_{i1} - n_{i2})/2 \rangle \neq 0$ due to the nonzero pseudo-magnetic field produced by the 2D
structure of the system, and with no order in the pseudo-spin basal plane \((\tau^{(g)}) = 0\).

The resulted MF Hamiltonian is bilinear and can be diagonalized by two subsequent canonical transformations. First step is to introduce the bonding and anti-bonding states as \(a(b)_{\alpha(\beta)k} = [d_{\alpha(\beta)k} + \bar{d}_{\alpha(\beta)k}]/\sqrt{2}\) and decouple the MF Hamiltonian in two parts each consisting of the two orbitals. The next transformation \(A(B)_{1k} = \bar{u}_{1k}a_{\alpha(\beta)k} + \bar{v}_{1k}b_{\alpha(\beta)k}\) diagonalizes the two-band Hamiltonian bringing it into the form:

\[
H = \sum_{k\alpha} \left[ \epsilon_{\alpha k} A_{\alpha k} A_{\alpha k}^\dagger + \epsilon_{\alpha k} B_{\alpha k} B_{\alpha k}^\dagger \right].
\]

The coherence factors and eigen-frequencies are given by

\[
u[(\epsilon^{12})k] = \left\{ \frac{1}{\sqrt{2}} \left[ \epsilon^{11} - \epsilon^{22} \right]^{\alpha(\beta)}k \right\}
\]

\[
\epsilon^{a(b)} \epsilon^{1(2)k} = \frac{\epsilon^{11}_{\alpha k} + \epsilon^{22}_{\alpha k}}{2} \pm \sqrt{\left( \frac{\epsilon^{11}_{\alpha k} - \epsilon^{22}_{\alpha k}}{4} \right)^2 + \left( \epsilon^{12}_{\alpha k} \right)^2},
\]

with the following notations \(\epsilon_{\alpha k}^{11} = -t_{\gamma k} \pm t - \mu + \Delta, \epsilon_{\alpha k}^{22} = -3t_{\gamma k} - \mu - \Delta, \epsilon_{\alpha k}^{12} = -\sqrt{3}\gamma_{\alpha k}\), and \(\gamma_{\alpha k} = \{\cos k_x \pm \cos k_y\}/2\).

The above introduced MF parameter \(\delta n\) and chemical potential \(\mu\) for a given doping can be obtained from the system of self-consistent equations which in terms of the obtained eigen-states of MF Hamiltonian reads as:

\[
n = \frac{1}{2N} \sum_{k} \{ n(\epsilon_{1k}) + n(\epsilon_{2k}) + [b \to a] \}
\]

\[
\delta n = \frac{1}{2N} \sum_{k} \{ [(1 - 2\tilde{v}_{\alpha k}^2)][n(\epsilon_{1k}) - n(\epsilon_{2k})] + [b \to a] \}
\]

where \(n(\epsilon)\) is the Fermi distribution function.

Let us now discuss the spin degrees of freedom of the system. In the DE exchange limit (Hund’s coupling \(J_H \gg W\) carriers band-width) the spin subsystem in the two orbital model can be also mapped to an effective NN Heisenberg model \(H = -\sum_{i,\delta = 1} J_{\parallel} S_i S_{i+\delta_{\parallel}} - \sum_{i,\delta, j, l} J_{\perp} S_i S_{i+\delta_{\perp}} + \text{effective intra-layer } J_{\parallel}\) and inter-layer \(J_{\perp}\) FM exchange couplings defined as \(J_{\parallel} = J_{\parallel}^{DE} - J, J_{\perp} = J_{\perp}^{DE} - J,\) and \(J\) is the antiferromagnetic superexchange constant between the \(t_{2g}\) spins. Ferromagnetic intra- and inter-layer DE energies are given by

\[
J_{\parallel}^{DE} = \sum_{\alpha, \beta} \left\{ \epsilon_{\parallel}^{\alpha(\beta)} \frac{\langle d_{\alpha, a}^{\dagger} d_{\beta, a} \rangle}{2S^2} \right\}, \quad J_{\perp}^{DE} = \sum_{\alpha, \beta} \left\{ \epsilon_{\perp}^{\alpha(\beta)} \frac{\langle d_{\alpha, a}^{\dagger} d_{\beta, \beta} \rangle}{2S^2} \right\}.
\]

With the above formulated scheme we proceed as follows. First, we solve the MF equations \((4)\) to determine, the orbital level splitting \(\Delta\) and chemical potential \(\mu\) for a given doping. Then, expressing the Eq. \((5)\) for the exchange constants in terms of the eigen-states of the MF Hamiltonian we end up with the intra- and inter-layer exchange energies for a given doping. Model parameters are fixed in a way to reproduce the experimental results.

In Fig. \((6)\) the calculated doping dependence of intra- and inter-layer exchange couplings is presented together with the experimental data from Refs. \((2,3,9)\) (see also Ref. \((11)\)). The best fit to the data has been achieved for \(t = 0.18\ eV, U_{\text{eff}} = 0.7\ eV, \gamma = 0.5\ eV,\) and \(2S J = 11\ meV\) (see also discussion below). The hopping integral sets the overall energy scale. The value of electron-phonon coupling strength fixes the doping at which \(J_{\parallel} = J_{\perp}\) and system shows the isotropic behavior. The interaction term \(U_{\text{eff}}\) determines the steepness of the drop of inter-plane exchange constant and the AFM superexchange \(J\) shifts rigidly the whole picture relative to the \(Y\) axis of Fig. 1. Therefore, despite the number of independent parameters all of them can be unambiguously extracted from the fitting.

As it is seen from Fig. \((1)\) the intra-layer exchange is practically unaffected by doping while the inter-layer one is dramatically reduced. When inequality \(J_{\parallel}^{DE} < J\) becomes valid, the antiferromagnetic super exchange prevails ferromagnetic DE signaling the instability of the FM ground state of the bilayer. In fact, neutron diffraction study on \(x = 0.5\) sample revealed the A-type AFM ordering \((6)\).

As it follows, the above discussed doping dependence of the exchange constants is in one to one correspondence with the doping dependence of the orbital occupancy. The latter is shown in Fig. \((2)\) calculated for the same values of the model parameters. The experimental data from Ref. \((11)\) is also presented on the same plot. The in-plane \(d_{3z^2-r^2}\) orbital (dashed line in Fig. \((2)\) is predominantly occupied and shows weak doping dependence in almost whole presented range of the hole concentration. While axially directed \(d_{3z^2-r^2}\) orbital (solid line in Fig. \((2)\) is emptied-out linearly with doping, i.e. all the doped hole in this doping range resides on \(d_{3z^2-r^2}\) orbital.
The above discussed evaluation of the orbital occupancy upon doping can be understood as follows. In the doping range \( x < x_c \), \( x_c \approx 0.26 \) being the hole concentration at which both orbitals are equally occupied [see Fig. 2] the JT distortion is large and stabilizes the axially directed orbital. With doping JT induced gap weakens and at \( x = x_c \) the kinetic energy term supporting the in-plane orbital state takes over. Therefore, \( \delta n \) changes sign at \( x = x_c \) and the \( d_{3x^2-r^2} \) orbital starts to be predominantly populated. For \( x > x_c \) correlation induced splitting \( 2\Delta_{\text{cor}} = U\delta n \) is negative and supports in-plane orbital. With farther doping, the orbital anisotropy \( \delta n \) increases, leading to increase of correlation induced splitting. Therefore, the axial band is pushed up relative to the in-plane band upon doping, while the chemical potential is practically pinned. Therefore, all the doped holes go to the upper \( d_{3x^2-r^2} \) band and its occupancy linearly decrease upon doping, while the population of lower \( d_{x^2-y^2} \) band is only weakly changed.

This doping dependence of the band structure is explicitly shown in Fig. 3, where the bonding \( d_{x^2-y^2} \) and \( d_{3x^2-r^2} \) bands are presented for hole concentration \( x = 0.3 \) (dashed line) and \( x = 0.4 \) (solid line).

Let us now discuss the model parameters used to reproduce the experimental data. The value of the hopping integral \( t = 0.18 \) eV is in the range estimated for manganese oxides \( t \approx 0.1 \sim 0.3 \) eV. We also point out, that some of the authors estimated hopping integral to be higher \( t \sim 0.7 \text{eV} \). Moderate value of the effective inter-orbital Coulomb repulsion \( U_{\text{eff}} = 0.7 \text{eV} \) is sufficient to give reasonable fit to the data, which justifies the MF treatment adopted here. The AFM superexchange energy of \( t_{2g} \) spins remarkably coincides with one \( (2SJ = 10 \text{meV}) \) estimated from the spin-wave data of \( \text{Nd}_0.45\text{Sr}_{0.55}\text{MnO}_3 \). Another important parameter is the JT splitting of the orbital states, that is difficult to directly detected experimentally. For \( x = 0.3 \), with the above estimate of the electron-phonon coupling constant \( (g = 0.5 \text{eV}) \) one obtained the JT splitting \( 2\Delta_{\text{JT}} \approx 0.035 \text{eV} \). Hence, in the doping range considered here, the JT binding energy is much smaller than the carriers band-width. This explains why the polaronic effects, not considered in the present paper, can be ignored.

The authors would like to thank T. Chatterji, N. M. Plakida, V. Yu. Yushankhai and M. E. Zhitomirsky for useful discussions. G. J. acknowledges support from a Bourse Post-Doctoral du ministère de l'Éducation nationale, de la recherche et de la technologie and N. B. P. acknowledges support from the Visitor Program of MPI-PKS, Dresden. The partial support by INTAS program, Grant No. 97-11066, is also acknowledged.

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1 For a review, see, for example, E. Dagotto, T. Hotta and A. Moreo, Phys. Rep. 344, 1 (2001); E.L. Nagaev, ibid. 346, 387 (2001).

2 K. Hirota, S. Ishihara, H. Fujioka, M. Kubota, H. Yoshizawa, Y. Morimoto, Y. Endoh, and S. Maekawa, Phys. Rev. B 65, 064414 (2002).

3 T.G.Perring, D.T. Adroja, G. Chaboussant, G. Aepli, T. Kimura, and Y. Tokura, Phys. Rev. Lett. 87, 217201 (2001).

4 A. Koizumi, S. Miyaki, Y. Kakutani, H. Koizumi, N. Hiroaka, K. Makoshi, and N. Sakai, K. Hirota, and Y. Muraoka, Phys. Rev. Lett. 86, 5589 (2001).

5 M. Kubota, H. Fujioka, K. Hirota, K. Ohoyama, Y. Morimoto, H. Yoshizawa, and Y. Endoh, J. Phys. Soc. Jpn. 69, 1606 (2000).

6 In the fully polarized ferromagnetic phase the role of...
intra-orbital Coulomb repulsion is insignificant and can be dropped out.

7 Since we only consider the effect of orbital degree's of freedom on the exchange energies, the interaction term between the spin and charge degrees of freedom is dropped out from the model Hamiltonian.

8 For a detailed discussion on this issue see K. H. Ahn and A. J. Millis, Phys. Rev. 61, 13545 (2000); I. Solovyev, N. Hamada, and K. Terakura, ibid. 53, 7158 (1996).

9 G. Jackeli, N. B. Perkins and N. M. Plakida, Phys. Rev. B 62, 372 (2000); 64, 092403 (2001).

10 T. Chatterji, L. P. Regnault, P. Thalmeier, R. Suryanarayanan, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B 60, R6965 (1999).

11 The slight discrepancy between the values of the intra-layer exchange reported by the various experimental groups is probably due to the fact, that the different momentum regions of the spin–wave spectra have been used by those groups to extract $J_\parallel$. The inter-layer exchange can be more accurately determined, since it sets the momentum independent splitting of bonding and anti-bonding spin-wave spectra.

12 K. I. Kugel and D. I. Khomskii, Sov. Phys. Usp. 25, 231 (1982). Slightly different estimate $t = 0.2 - 0.5 (eV)$ has been reported in Ref.1.

13 See, for example, Y.-R. Chen and P. B. Allen, Phys. Rev. B 64, 204401 (2001).

14 The strength of electron-phonon coupling estimated here is close to the lower boundary of the estimation given by A. J. Millis, Phys. Rev. B 53, 8434 (1996) and agrees with that reported by M. O. Dzero, L. P. Gor’kov, and V. Z. Kresin, Solid State Comm., 112, 707 (1999).