I. INTRODUCTION

Doped transition metal compounds exhibit a number of very interesting and fascinating phenomena, including high material temperature superconductivity in cuprates and pnictides and colossal magnetoresistance in manganites. The hole-doped perovskite manganites are well known for their complexity, originating from the competing tendencies in their rich phase diagrams with a variety of spin, charge and orbital orders. Several phases are energetically close to each other and small changes of electronic parameters or electron concentration result in phase transitions. Hole doping, realized e.g. in La$_{1-y}$(Ca,Sr)$_y$MnO$_3$ for increasing $y$, triggers then a transition from an antiferromagnetic (AF) to a ferromagnetic (FM) phase by the double-exchange (DE) mechanism that became a crucial idea to explain the onset of the metallic FM phase and electronic transport.

The DE model is one of the most widespread models of ferromagnetism. It describes the kinetic energy of electronic charge carriers coupled by Hund’s exchange and the strength of AF superexchange. It describes the magnetic transition from nonmagnetic (N) to ferromagnetic (FM) phase by the double-exchange (DE) mechanism that became a crucial idea to explain the onset of the metallic FM phase and electronic transport.

We introduce a microscopic model for electron doped manganites that explains the mechanism of the observed transition from G-type antiferromagnetic (G-AF) to C-type antiferromagnetic (C-AF) order under increasing doping by double exchange mechanism. The model unravels the crucial role played by $e_g$ orbital degrees of freedom and explains the observed metal-to-insulator transition by a dimensional crossover at the magnetic phase transition. The specific heat and the spin canting angle found for the G-AF phase agree with the experimental findings. As a surprising outcome of the theory we find that spin canting is suppressed in the C-AF phase, in agreement with the experiment, due to the Fermi surface topology.

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Usually, however, accurate studies of the DE model were hindered by the presence of strong intraorbital Coulomb interaction $U$ in a lattice distorted by strong cooperative Jahn-Teller effect. A qualitatively different situation arises in an ideal cubic perovskite SrMnO$_3$, with $e_g$ bands being completely empty. Here the only interaction is AF superexchange between $S = 3/2$ spins at Mn$^{4+}$ ions. They are generated by $t_{2g}$ charge excitations and stabilize the isotropic three-dimensional (3D) G-type AF (G-AF) phase. Weakly doped SrMnO$_3$ represents an ideal situation for the DE model as the $e_g$ electrons hardly interact with each other at low doping $x$ and strong on-site Coulomb interactions between them may be neglected. In this case the DE model can be almost exactly solved under a single approximation, i.e., neglecting weak quantum fluctuations of large $S = 3/2$ spins.

Early studies of electron doped Ca$_{1-x}$Ce$_x$MnO$_3$ systems gave a magnetic transition to the C-AF phase. The magnetic order in doped CaMnO$_3$ was analyzed within the density-functional theory calculations that give instead a transition from the G-AF to A-AF phase. Recently single crystals of Sr$_{1-x}$La$_x$MnO$_3$ and Sr$_{1-x/2}$Ce$_{x/2}$MnO$_3$ were synthesized and investigated showing that the transition to the C-AF phase occurs in both systems, in agreement with the prediction by Maezono et al. and the magnetic phase diagram is remarkably universal as a function of doping $x$.

In electron doped manganites chemical doping of Sr$^{2+}$ with La$^{3+}$ (Ce$^{4+}$) ions generates $e_g$ electronic carriers at Mn$^{3+}$ ions. Following the standard picture of de Gennes one expects spin canting on AF bonds. Until recently only one exception from this rule was reported — spin canting is absent in the A-AF phase when electrons occupy $x^2-y^2$ orbitals and the hopping along AF bonds between the FM $ab$ planes is blocked. In this context the recent experimental result of no canting in the C-AF phase is puzzling and requires theoretical explanation, as hopping on the AF bonds in $ab$ planes is there finite for electrons within $3z^2-r^2$ orbitals, and spin canting is expected.
Hole doped La$_1-y$Sr$_y$MnO$_3$ manganites with large $e_g$ electron density remain insulating up to $y \simeq 0.17$ as the metallic behavior is hindered here by formation of orbital polaronic$^{23,24}$. This is in sharp contrast with the electron doped systems with the G-AF metallic phase found in Sr$_{1-x}$La$_x$MnO$_3$ by Sakai et al$^{22}$ already at a very low electron doping $x = 0.01$. Surprisingly, when doping increases further to $x \simeq 0.04$ this 3D weakly metallic phase changes to an insulating phase with quasi one-dimensional (1D) orbital order of partly occupied $3z^2-r^2$ orbitals, accompanied by tetragonal lattice distortion and the C-AF spin order.

In this paper we investigate the DE model for doped $e_g$ electrons, extended here by the coupling to the tetragonal lattice distortion which occurs in the C-AF phase. We derive the exact electronic structure, show a remarkable difference between the Fermi surface topology in the above magnetic phases, and demonstrate that it explains the absence of spin canting in the C-AF phase. The calculated values of the specific heat coefficient $\gamma$ and the critical doping $x_c$ for the G-AF/C-AF phase transition are in quantitative agreement with experiment.

The paper is organized as follows. In Sec. II we introduce the microscopic model and specify its parameters. The model is solved in Sec. III where we analyze the remarkable difference between the electronic structure found in two magnetic phases. This leads to the magnetic transition which occurs under increasing doping as we show in Sec. IV. The paper is summarized in Sec. V.

II. THE DOUBLE EXCHANGE MODEL

We consider the DE model for degenerate $e_g$ electrons$^{22}$ extended by the coupling to the lattice,

\[
\mathcal{H} = - \sum_{ij, \alpha \beta, \sigma} t^{ij}_{\alpha \beta} c_{i \alpha \sigma}^\dagger c_{j \beta \sigma} - 2JH \sum_i \bar{S}_i \cdot \bar{s}_i + J \sum_{\langle ij \rangle} \bar{S}_i \cdot \bar{S}_j - gu \sum_i (n_{iz} - n_{ix}) + \frac{1}{2} N K u^2. \tag{1}
\]

Here the $c_{i \alpha \sigma}^\dagger$ operator creates an electron with spin $\sigma = \uparrow, \downarrow$ in orbital $\alpha = x, y, z$ at site $i$, and $n_{i \alpha \sigma} \equiv \sum_{\gamma} \gamma_{i \alpha \sigma} c_{i \alpha \gamma}^\dagger c_{i \alpha \sigma}$ is the electron density in orbital state $\alpha$ at site $i$, and $N$ is the number of sites. Two $e_g$ orbitals are labeled as

\[
z \equiv (3z^2 - r^2)/\sqrt{6}, \quad x \equiv (x^2 - y^2)/\sqrt{2}, \tag{2}
\]

and correspond to two components of the pseudospin $\tau = 1/2$. The hopping elements between a pair of nearest neighbors $(ij)$ along the axis $\gamma = a, b, c$ are:

\[
t^{a/b}_{\alpha \beta} = t \left( \begin{array}{c} \pm 1 \\ \pm \sqrt{3} \\ 3 \end{array} \right), \quad t^{c}_{\alpha \beta} = t \left( \begin{array}{c} 1 \\ 0 \\ 0 \end{array} \right), \tag{3}
\]

where $t$ in an effective $(dd\sigma)$ hopping element between two $3z^2-r^2$ orbitals along the $c$ cubic axis. Following the estimates of $t$ performed within the polaronic picture$^{21}$ and using the optical spectroscopy for LaMnO$_3$$^{22}$ we fix the effective $(dd\sigma)$ hopping element at $t = 0.4$ eV.

Hund’s exchange between $e_g$ and $t_{2g}$ electrons at Mn$^{4+}$ ions $J_H \simeq 0.74$ eV is here the largest parameter. It aligns the spin of an $e_g$ electron $\bar{S}_i$ with the localized $t_{2g}$ spin $\bar{S}_i$ at site $i$. In this way the electronic structure depends crucially on the magnetic order of localized $t_{2g}$ spins $\{\bar{S}_i\}$ that interact by the nearest neighbor AF superexchange $J > 0$. It follows from virtual charge excitations $d^{\dagger}_i d_j^\pm = d^{\dagger}_i d^{\pm}_j$ along nearest-neighbor bonds $(ij)$ in the presence of strong on-site Coulomb interaction $U$ between $t_{2g}$ electrons$^{19}$.

The tetragonal distortion $u$ is finite only in the C-AF phase. Here we define it as proportional to a difference between two lattice constants $a$ and $c$ along the respective axis, $u \equiv 2(c - a)/(c + a)$. Increasing lattice distortion ($u > 0$) causes increasing $e_g$ orbital splitting $4\varepsilon_E$ determined by the Jahn-Teller energy, $E_T = g^2/2K \simeq 0.2$ eV$^{17,20}$. Furthermore, using the experimental data of Ref. 22, we arrived at a semiempirical relation $u \simeq 3x/20$.

III. ELECTRONIC STRUCTURE

Following de Gennes$^{25}$ we determined the electronic structure for the G-AF phase by considering spin canting by angle $\theta$ caused by electron doping. Hund’s exchange at each site favors aligned $\uparrow\uparrow$ or $\downarrow\downarrow$ spins in momentum space, i.e.,

\[
\varepsilon_{k}^{\pm} = -\sqrt{(t \sin \theta_{\pm}^k + J_H S)^2 + (t \cos \theta_{\pm}^k)^2}, \tag{5}
\]

where

\[
\theta_{\pm}^k = \sum_{\lambda} \cos k_{\lambda} \pm \left\{ \sum_{\lambda} \cos^2 k_{\lambda} - \cos k_x \cos k_y - \cos k_z \cos k_z \cos k_x \right\}^{1/2}, \tag{6}
\]

and the summations in Eq. 6 are over three cubic directions in momentum space, i.e., $\lambda = x, y, z$. The remaining $e_g$ bands correspond to excited states of $e_g$ electrons with spins antiparallel to those of localized $t_{2g}$ electrons.
— they are given by $\pm \varepsilon_k^\pm$ and separated from the lower bands by a large gap of $2J_H S$ at $\pm \theta = 0$.

In the undoped G-AF phase of SrMnO$_3$ spin canting is absent ($\theta = 0$) and the electronic structure consists of four Slater bands $\pm \varepsilon_k^\pm$, see Fig. 1. Both $e_g$ orbitals are equivalent here and equally contribute to each electronic band. The lowest energy is obtained along the $\Gamma - X$ and equivalent directions in the Brillouin zone and here electrons are doped. By considering the electron energy close to these lines one finds that the Fermi surface in the regime of low electron doping, shown in the inset in Fig. 1 consists of narrow cylinders along equivalent main directions in the reciprocal space.

The canting angle in the G-AF phase is given by

$$\sin \theta \simeq \frac{iJ_H S}{\sqrt{(3t)^2 + (J_H S)^2}} \frac{x}{12J^2S^2},$$

and increases linearly with $x$ in the low doping regime. Using an empirical formula for the Néel temperature of a Heisenberg antiferromagnet, we obtained $J = 3.79$ meV for SrMnO$_3$ from the experimental $T_N \simeq 230 \text{ K}$. For the parameters of Fig. 1 one finds from Eq. (7) that the canting angle is rather small, $\sin \theta \simeq 2.7x$, and quite close to the experimental value, $\theta_{\text{exp}} \simeq 2x$.22

The electronic structure $\{\varepsilon_k\}$ for the C-AF phase is quite distinct from the one in the G-AF phase and was determined numerically. It depends on doping $x$ as the tetragonal lattice distortion increases with it. We have verified that this dependence is weak for the realistic parameters, i.e., with $q \simeq 3.0 \text{ eV}$ and $K \simeq 20 \text{ eV}$. A representative result is shown in Fig. 2 for $x = 0.05$. As the FM order along the $c$ axis breaks the cubic symmetry, the orbitals decouple from each other in the electronic structure and form two independent subsets of bands. This is best visible along the $\Gamma - Z$ directions where one band has a large dispersion close to $4t$, and the other one is dispersionless (Fig. 2). In addition, the former band has also a very weak dispersion along two (equivalent) $\Gamma - X$ and $\Gamma - Y$ directions, with two minima at the $X$ and $Y$ points that arise due to the weak mixing between $z$ and $x$ orbitals by hopping in $ab$ planes, but this hopping is almost fully quenched due to the AF order.

Surprisingly, we found no spin canting in the C-AF phase. Here the spins form an ideal staggered AF structure in the $ab$ planes, while they are aligned in FM chains along the $c$ axis. The reason of this behavior is the electronic structure with the lowest energy at the $X$ and $Y$ points and the Fermi surface consisting of two pockets that are centered around these two equivalent points at low doping, see the inset in Fig. 2. For this Fermi surface topology no kinetic energy can be gained by spin canting, since the resulting nearest-neighbor hopping between $z$ orbitals in $ab$ planes, $\frac{1}{4}t \sin (\cos k_x + \cos k_y)$, vanishes at the $X$ and $Y$ points. Thus, the observed suppression of spin canting in the C-AF phase follows from the abrupt change of the Fermi surface topology at the magnetic transition.

The consequences of flavor separated band structure in the C-AF phase are remarkable. First of all, electrons doped in SrMnO$_3$ have pure $z$ orbital character. Second, this implies that they can propagate only along the $c$ axis where localized spins are FM, but their motion is blocked in the $ab$ planes by the AF order, in agreement with DE. Altogether this leads to a dimensional reduction of electronic transport to 1D chains along the $c$ axis.

A qualitatively different character of the electronic structure in both AF phases is visible in the orbital-resolved density of states (DOS) $N_z(\omega)$ and $N_x(\omega)$ in the spin majorities bands, see Fig. 3. In the G-AF phase both orbital DOSs are the same and have low bandwidth of $\sim 0.5 \text{ eV}$ due to the AF order in all three cubic directions [Fig. 3(a)]. At the lower band edge one finds a character-
FIG. 3: (Color online) Densities of states for $e_g$ electrons, $N_z(\omega)$ and $N_x(\omega)$, in the spin majority bands as obtained for: (a) the G-AF phase ($N_z(\omega)$ and $N_x(\omega)$ are here degenerate) with a singularity arising from the AF order at $\omega = -1.11$ eV, and (b) the C-AF phase; here the density of $z$, $N_z(\omega)$, and $x$, $N_x(\omega)$, electron states is shown by solid (red) and dashed (blue) line. Parameters: $t = 0.4$ eV, $J_H = 0.74$ eV; for C-AF phase in addition $g = 3$ eV and $x = 0.05$.

FIG. 4: (Color online) Total energies of the G-AF ($E_{GAF}$) and C-AF ($E_{CAF}$) phase as obtained for increasing electron doping $x$. Parameters: $t = 0.4$ eV, $J_H = 0.74$ eV, $g = 3$ eV, $K = 20$ eV, and $J = 3.79$ meV. Inset shows the phase diagram in the $(t, x_c)$ plane obtained for: $g = 0$ (circles, dashed line), and $g = 3$ eV (diamonds, solid line).

IV. MAGNETIC PHASE TRANSITION

Now we show that the DE triggers the magnetic transition in an electron doped system by comparing the total energies in both magnetic phases. In the undoped system in an electron doped system by comparing the total and a pseudometallic subband gives a characteristic 1D DOS $N_G$ the majority spin bands in the AF phase in addition $g = 3$ eV and $x = 0.05$.

A large gap between the spin majority and spin minority states in the AF phase generates a van Hove singularity at the upper edge of the DOSs. Due to the AF order in the $C$-AF phase, the orbital flavors separate in the ($C$-AF) phase, while only a small fraction of $t$ contributes to the kinetic energy in the isotropic $3D$ G-AF phase. Therefore, the total energy of the C-AF phase decreases faster with increasing doping $x$, see Fig. 4 and finally this phase becomes more stable than the G-AF one for $x > x_c$, as observed in the experiment. We note that small spin canting in the G-AF phase has almost no effect on the phase boundary as the gain in the kinetic energy is almost cancelled by the loss of the superexchange energy.

The crucial role played by the DE mechanism is visible in the phase diagram of electron doped manganites shown in the inset of Fig. 4. For increasing hopping $t$ both phases have increased kinetic energy gains, but a larger energy gain is found in the C-AF phase. As a result, the critical concentration $x_c$ is lowered when $t$ increases, but one finds that $x_c$ lies still in a relatively narrow window of doping $0.03 < x_c < 0.04$ in a broad range of realistic values of $t \in (0.3, 0.6)$ eV.

The magnetic transition is first order and occurs at a somewhat lower doping $x_c$ when the tetragonal distortion
which stabilizes the C-AF phase is considered, see the inset of Fig. 1. However, this energy gain is rather small compared with the kinetic energy difference between the two magnetic phases, so we conclude that the tetragonal distortion has only a weak stabilizing effect for the 1D $\sqrt{3}z^2 - r^2$ structure in the C-AF phase, while the transition itself follows from the DE interaction. We remark that this scenario does not apply to La$_3$Ca$_{1-x}$MnO$_3$ nanoparticles where phase separation into AF and FM domains takes place.\(^{16}\)

V. SUMMARY

Summarizing, we have introduced the microscopic model that explains the mechanism of the magnetic transition in electron doped manganites from canted G-AF to collinear C-AF phase at low doping $x \approx 0.04$. We demonstrated that the DE supported by the cooperative Jahn-Teller effect leads then to dimensional reduction from an isotropic 3D G-AF phase to a quasi-1D order of partly occupied $3z^2 - r^2$ orbitals in the C-AF phase. This prediction of the theory can be verified by future angle resolved photoemission experiments as the shape of the Fermi surface in the G-AF and C-AF phases is radically different.

The presented theory explains as well the absence of spin canting in the C-AF phase by the Fermi surface topology. This is a subtle effect as electron doping occurs here near the $X$ and $Y$ points in the Brillouin zone, and the kinetic energy cannot be gained in spin canted structure.

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