Double Exchange via Degenerate Orbitals

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We consider the double exchange for systems in which doped electrons occupy degenerate orbitals, treating the realistic situation with double degenerate e_g orbitals. We show that the orbital degeneracy leads in general to the formation of anisotropic magnetic structures and that, in particular, depending on the doping concentration, the layered magnetic structures of the A-type and the chainlike structures of the C-type are stabilized. The phase diagram that we obtain provides an explanation for the experimentally observed magnetic structures of some overdoped (electron-doped) manganites of the type $\mathrm{Nd}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3$, $\mathrm{Pr}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3$, and $\mathrm{Sm}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$, with $x > 0.5$. [S0031-9007(98)08277-5]

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The double-exchange (DE) model [1–3] is one of the main models of ferromagnetism in metallic systems. The interest in this model was renewed recently in connection with the active study of the manganites with colossal magnetoresistance (CMR) [4]. Although it is not yet clear whether DE alone can explain the CMR in manganites [5], and there are some problems with the model itself (e.g., the tendency to phase separation [6–9]), the double-exchange mechanism is a necessary ingredient for the theoretical understanding of the CMR effect [5,10] and remains the main explanation at least of the presence of the ferromagnetic state in doped manganites of the type $\mathrm{La}_{1-x}M_x\mathrm{MnO}_3$ ($M = \mathrm{Ca}, \mathrm{Sr}$).

Most experimental data in the study of the CMR materials are obtained for the hole-doped manganites ($x < 0.5$) as it is usually in this doping range that CMR is observed. Recently, however, interesting data appeared on the properties of overdoped (or electron-doped) manganites ($x > 0.5$). Theoretically, in a conventional DE model one expects qualitatively similar behavior for small x and for $x \sim 1$. Experimentally, however, there exists a very strong asymmetry. The behavior of doped manganites for $x < 0.5$ and $x > 0.5$ is drastically different. In particular, a very stable insulating stripe phase is observed for $x > 0.5$ with the period determined by doping [11], whereas for $x < 0.5$, depending on the exact composition, either the metallic ferromagnetic state is realized [4] or a charged-ordered state with a doubled unit cell [12], which, however, can be easily transformed into a ferromagnetic metal by a magnetic field [13]. Recently, Maignan *et al.* [14,15] succeeded in obtaining the state similar in some respects to the one predicted by the DE model in the electron-doped region. In $\mathrm{Ca}_{1-y}\mathrm{Sm}_y\mathrm{MnO}_3$ they observe metalliclike behavior with unsaturated ferromagnetism for $y = 7\%–12\%$ with indications that the state is not really ferromagnetic but has a more complicated, possibly canted, magnetic order.

Other recent data [16–19] show that the system $\mathrm{Nd}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3$ is ferromagnetic for $0.25 < x < 0.5$, A-type antiferromagnetic ordered for $0.5 < x < 0.6$ and that C-type antiferromagnetic order is realized for $0.6 < x < 0.8$. In $\mathrm{Pr}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3$ the A-type magnetic structure exists for $0.5 < x < 0.7$. All these results show again that the behavior of the hole-doped and electron-doped manganites is indeed very different.

There is an important factor which is overlooked until now when one tries to apply the DE picture to these transition metal oxides. The e_g levels, or bands, in which the charge carriers move are orbitally degenerate. The first attempt to take this into account is the recent work of Gor'kov and Kresin [20], who aimed to explain, starting from a band picture, the properties of undoped and lightly doped LaMnO_3. They show, in particular, that one can indeed rationalize in this way some properties of $\mathrm{La}_{1-x}M_x\mathrm{MnO}_3$ for small x. They neglect, however, the strong Coulomb interactions that make undoped LaMnO_3 a Mott-Hubbard insulator, making their approach in this regime somewhat questionable.

In undoped LaMnO_3 the localized e_g electrons are orbitally ordered, lifting the orbital degeneracy. Thus for the doped system we can in a first approximation ignore the orbital degeneracy and apply the conventional DE model. If we, however, proceed from the opposite direction and consider, e.g., adding electrons to the insulating CaMnO_3, containing Mn^{4+} (t_{2g}^3) ions with localized moments in the t_{2g} levels, one dopes these electrons into the empty e_g levels, which are orbitally degenerate. Thus we have now a problem of *double-exchange via degenerate orbitals*. As we show below, this orbital degeneracy drastically modifies the picture of the DE and results in the formation of anisotropic magnetic structures. Our theoretical results have much in common with the behavior of manganites in this doping range as found in experiments [14–19].

We start with the model that is realistic, for example, for $\mathrm{Ca}_{1-y}R_y\mathrm{MnO}_3$ (R is a rare earth, y is small). For $y = 0$ this system is a Mott insulator with localized t_{2g}- electrons (the localized spin $\mathbf{S}$) with antiferromagnetic exchange interaction $J\mathbf{S}_i \cdot \mathbf{S}_j$, where i and j are nearest neighbors, leading to a G-type (simple two-sublattice) antiferromagnetic ground state. Doped electrons enter the doubly degenerate e_g- levels. The strong on-site Hund's rule exchange tends to align the spins of the t_{2g} and e_g electrons parallel. The effective Hamiltonian describing the low energy properties for this system is thus

$$H = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - J_H \sum_{i,\alpha,\sigma,\sigma'} \mathbf{S}_i \cdot c^{\dagger}_{i\alpha\sigma} \vec{\sigma}_{\sigma\sigma'} c_{i\alpha\sigma'} - \sum_{\langle ij \rangle,\sigma} t_{ij}^{\alpha\beta} c^{\dagger}_{i\alpha\sigma} c_{j\beta\sigma} \,. \tag{1}$$

The first and the second terms are explained above, and the last term describes the hopping of e_g- electrons. These electrons are labeled by the site index i, spin σ, and orbital index $\alpha(\beta) = 1, 2$, corresponding, e.g., to the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals. The presence of the orbital degeneracy, together with the very particular relations between the hopping matrix elements $t_{ij}^{\alpha\beta}$ [21,22] makes this problem, and its outcome, very different from the usual DE case.

Our approach follows the standard route [3] of treating the spin subsystem quasiclassically and assuming a homogeneous ground state. Furthermore, we assume that the intra-atomic Hund's rule exchange interaction J_H is strong, so that only states with the maximal possible spin at each site are realized and that the intersite exchange interaction J is smaller than the electron hopping integral t. Both are certainly good assumptions for the manganites.

In a first step we have to determine the spectrum of the e_g- electrons ignoring their interaction with the localized spins. This spectrum is given by the solution of the matrix equation

$$\| t_{\alpha\beta} - \epsilon \delta_{\alpha\beta} \| = 0 \,, \tag{2}$$

where

$$\begin{aligned} t_{11} &= -2t_{xy}(\cos k_x + \cos k_y) \,, \\ t_{12} = t_{21} &= -\frac{2}{\sqrt{3}}\, t_{xy}(\cos k_x - \cos k_y) \,, \\ t_{22} &= -\frac{2}{3}\, t_{xy}(\cos k_x + \cos k_y) - \frac{8}{3}\, t_z \cos k_z \,. \end{aligned} \tag{3}$$

Here t_{11} is the dispersion due to an overlap between $d_{x^2-y^2}$ orbitals on neighboring sites, t_{12}—between a $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbital and t_{22} between two $d_{3z^2-r^2}$ orbitals. In writing Eq. (3) we have taken into account the ratios of different hopping integrals [21,22], which are determined by the symmetry of the e_g wave functions, and introduced the notation t_{xy} and t_z, to be defined later. In the absence of magnetic order, $t_{xy} = t_z = t$. The solutions $\epsilon_{\pm}(\mathbf{k})$ of Eq. (2) are

$$\begin{aligned} \epsilon_{\pm}(\mathbf{k}) = &-\frac{4t_{xy}}{3}(\cos k_x + \cos k_y) - \frac{4t_z}{3}\cos k_z \\ &\pm \left(\left[\frac{2t_{xy}}{3}(\cos k_x + \cos k_y) - \frac{4t_z}{3}\cos k_z \right]^2 \right. \\ &\left. + \frac{4t_{xy}^2}{3}(\cos k_x - \cos k_y)^2 \right)^{1/2} . \end{aligned} \tag{4}$$

These bands agree with those obtained in Ref. [20].

We now take into account the interaction of the e_g- electrons with a magnetic background. We assume that the underlying magnetic structure is characterized by two sublattices, with a possible canting, so that the angle between neighboring spins in the xy plane is θ_{xy} and in the z direction is θ_z. This rather general assumption covers the G-type antiferromagnets (two-sublattice structure, $\theta_{xy} = \theta_z = \pi$), A-type one (ferromagnetic planes coupled antiferromagnetically, $\theta_{xy} = 0$, $\theta_z = \pi$), and C-type structures (antiferromagnetically coupled ferromagnetic chains, $\theta_{xy} = \pi$, $\theta_z = 0$). For angles different from these, we get a canted spin structure which originates from a simple antiferromagnetic one (G-, A-, or C-type). Following [3] we then have the effective hopping matrix elements $t_{xy} = t\cos(\theta_{xy}/2)$ and $t_z = t\cos(\theta_z/2)$. This clarifies the notation introduced in Eq. (3). As in the quasiclassical treatment of the nondegenerate DE model, the energy spectrum (4) is renormalized by the magnetic order and, because of the orbital-dependent hopping matrix elements in a degenerate system, this results, in general, in an anisotropic magnetic structure.

When we dope the system with electrons, these go into states with minimal energy, in our case into the Γ point $\mathbf{k} = 0$. Let us first assume that all doped charges go into the state with lowest energy, which is strictly speaking only the case for very small doping, and neglect for the moment the effects due to a finite filling of the bands. At the Γ point the energies are $\epsilon_{\pm}(0) = -\frac{4}{3}(2t_{xy} + t_z) \pm \frac{4}{3}|t_{xy} - t_z|$. We can now write down the total energy per site of our system containing y electrons ($y = 1 - x$ for conventional notation for, e.g., $\mathrm{La}_{1-x}\mathrm{A}_x\mathrm{MnO}_3$),

$$\begin{aligned} E &= \frac{J}{2}(\cos\theta_z + 2\cos\theta_{xy}) + y\epsilon_{\min}(0) \\ &= -\frac{3J}{2} + 2J\cos^2(\theta_{xy}/2) + J\cos^2(\theta_z/2) \\ &\quad - \frac{4}{3}\, yt[2\cos(\theta_{xy}/2) + \cos(\theta_z/2) \\ &\quad + |\cos(\theta_{xy}/2) - \cos(\theta_z/2)|] \,. \end{aligned} \tag{5}$$

There exist two possible situations. If $\cos(\theta_{xy}/2) > \cos(\theta_z/2)$, then the magnetic structure is A-type-like; in this case the minimization of the energy with respect to the angles θ_{xy} and θ_z gives

$$\cos(\theta_{xy}/2) = \frac{t}{J}\, y, \qquad \cos(\theta_z/2) = 0\,, \tag{6}$$

and the energy of the corresponding state amounts to

$$E^{(1)} = -\frac{3}{2}\, J - \frac{2t^2}{J}\, y^2. \tag{7}$$

Physically this state corresponds to an xy plane with a canted structure, with the spins in neighboring planes being antiparallel. If $\cos(\theta_{xy}/2) < \cos(\theta_z/2)$, then the magnetic structure is C-type-like and one finds for θ_{xy} and θ_z

$$\cos(\theta_{xy}/2) = \frac{t}{3J}\, y, \qquad \cos(\theta_z/2) = \frac{4t}{3J}\, y\,. \tag{8}$$

The energy of this state $E^{(2)}$ is exactly equal to that of the A-type state $E^{(1)}$. In this situation we have a canted structure in all three directions with the correlations in the z direction being "more ferromagnetic." Thus in the lowest order in J approximation the two solutions (6) and (8) are degenerate.

One can easily show that in this approximation (filling of only the $\mathbf{k} = 0$ point and ignoring the Fermi energy for finite concentration) we would have degenerate solutions up to a concentration $y_c = \frac{3J}{4t}$ beyond which the A type solution becomes more favorable. It is also worthwhile to note that this solution never evolves into a ferromagnetic one: for $y > J/t$ the canting angle θ_{xy} in Eq. (6) is zero and the basal plane becomes ferromagnetic, but the moments of the neighboring planes will be opposite to it; i.e., we obtain pure A-type antiferromagnetism. In contrast to that, the C-type-like solution (8) would give with increasing y first the state with completely ferromagnetic chains but with neighboring chains at a certain angle to those and, finally, at $y = 3J/t$, also the angle $\theta_{xy} = 0$ and we would get an isotropic ferromagnetic state. However, the A-type solution has lower energy in this region; thus we would never reach the ferromagnetic state in this approximation, contrary to experiment.

The stability of the A phase is easy to explain: in this state the d electrons occupy predominantly the orbitals of $d_{x^2-y^2}$ character and their delocalization requires the spins in the xy plane to be parallel, while spin correlations in the z direction may remain antiferromagnetic. However, this all is true only at the Γ point ($\mathbf{k} = 0$). With increasing electron doping the higher lying states will be filled which will modify the picture.

We therefore perform the same calculation as above, but taking into account that at larger doping concentrations the e_g bands gradually fill up. In order to do so, we fix the doping concentration y as well as the ratio t/J and numerically evaluate the values of θ_{xy} and θ_z which minimize the total energy, taking into account that for every pair of angles the bands given in Eq. (4) are filled up to the Fermi energy.

We find that at very low doping concentrations the A-type solution given by Eq. (6) and the C-type solution given by Eq. (8) are indeed the magnetic structures of lowest energy, in accordance with our analytical treatment. We find, however, that in this region the A-type solution is always slightly lower in energy than the C-type solution; i.e., the degeneracy of these two states is lifted. This has a simple physical reason. In the A-type structure the dispersion of the bands is strictly two dimensional (2D), so that the density of states (DOS) at the band edge is nonzero. For the C-type solution of Eq. (8), the bands have a highly anisotropic but already three-dimensional character, leading typically to a vanishing DOS at the band edge. Therefore the A-type magnetic structure is stabilized as it has a larger DOS at the band edge. At a somewhat higher doping level, however, the quasi-one-dimensional peak in the DOS close to the band edge starts to play a role and can cause the transition to a C-type state.

The full phase diagram resulting from our calculations is presented in Fig. 1. At very low electron doping we find that the A phase (with canting) is stable for all values of t/J. Increasing the doping, the system first enters the C phase and, depending on the value of t/J, reenters the A phase before becoming ferromagnetic at large electron doping. This sequence of phases is determined by the form of the DOS of these structures. Our phase diagram has certain features in common with that of Maezono *et al.* [23], although our approach is quite different.

We now compare our results with experimental data on electron-doped manganites. For example, for $t/J \approx 4$, we find a stable ferromagnetic phase up to $x \approx 0.5$ (our $y = 1 - x$) and the A phase up to $x \approx 0.6$, and for larger hole doping we find the C-type phase to be stable, in agreement with observations in $\mathrm{Nd}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3$ [16,17]. The A-type state also strongly resembles the one observed

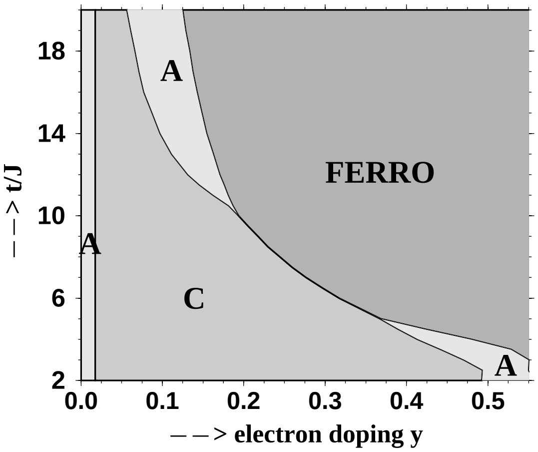

FIG. 1. Phase diagram of the double-exchange model with degenerate e_g bands. Depending on the electron doping concentration and the ratio of the e_g bandwidth and the t_{2g} superexchange one finds A-type, C-type, or ferromagnetic magnetic order.

in $Pr_{1-x}Sr_xMnO_3$ [18,19]. Moreover, there are indications that the unsaturated ferromagnetic and (semi-)metallic state observed for $Ca_{1-y}R_yMnO_3$ in Refs. [14,15] also has C-type magnetic correlations [24]. This is consistent with the fact that our C-type solution can have canting in all three directions and consequently has a net magnetic moment, whereas the A-type solution has no net moment.

Our calculations show that in the C-type phase the electronic band is nearly one dimensional. In this case any disorder renders the 1D system insulating. This provides a possible explanation for the observation that the C-type phase is insulating for electron doping above $y = 0.15$ [17]. According to the same argument, the 2D bands of A-type phase and the 3D dispersion in ferromagnetic phase makes these magnetic structures less susceptible to disorder so that they are more likely to show metallic behavior, as observed in experiment.

We note also that there exist other physical factors that may stabilize a particular state and that can therefore modify details of the phase diagram of Fig. 1. In the A-type solution, for instance, predominantly the $x^2 - y^2$ orbitals are occupied, giving rise to a lattice distortion—in this case a compression of the MnO_6 octahedra along the z direction. One can show, however, that due to the anharmonicity the Jahn-Teller distortion always leads to a local *elongation* [25]. If strong enough, this tendency would favor a structure in which the $3z^2 - r^2$ orbitals are occupied, in this case lowering the energy of C-type structures.

As already mentioned in the introduction, there are some subtle points in the conventional treatment of the DE model, as adapted above. All these complications (quantum nature of the spins, possible existence of inhomogeneous states) can be present also in the degenerate case. For large doping, one should also consider the interaction between e_g electrons themselves. Nevertheless, we believe that the main consequences of the degeneracy of electronic states responsible for the double exchange, e.g., in overdoped manganites, are correctly captured in our treatment.

We conclude that the double exchange via degenerate orbitals has very interesting special features that are very different from the conventional, nondegenerate, situation. In particular, we have shown that the double exchange via e_g states naturally leads to formation of anisotropic magnetic structures, layered or chainlike, in otherwise cubic compounds. We have presented the phase diagram for this model. Our treatment has a general applicability because orbital degeneracy is experimentally found in many real systems. In particular, it can serve as a basis for an explanation of magnetic and transport properties of overdoped (electron-doped) manganites.

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