

Phase diagram of electron-doped Mn perovskites

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Abstract

We study the competition between ferromagnetic double exchange and antiferromagnetic superexchange present in Mn perovskites. The model represents each Mn^{4+} ion by a spin $\frac{1}{2}$, on which an electron can be added to produce Mn^{3+} . We include a hopping energy t , a strong intratomic interaction exchange J (in the limit $J/t \rightarrow \infty$), and an interatomic antiferromagnetic interaction K between the local spins. Using the renormalized perturbation expansion and a mean-field approximation we calculate the free energy from which the stability of the antiferromagnetic, canted, ferromagnetic and 'pseudo-spin-glass' phases can be determined. The phase diagram can be drawn in terms of temperature and doping x , for each value of K/t . We discuss the presence of new 'pseudo-spin-glass' phases. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Magnetically ordered materials

The discovery of 'colossal' magnetoresistance (CMR) in LaSrMnO_3 type compounds [1] together with its many unusual properties have attracted considerable attention. The phase diagram, as a function of Sr concentration, temperature, magnetic field, or magnitude of the superexchange interaction is not quite clear yet for the different compounds. The metallic phase can be reached by hole doping of the parent compound LaMnO_3 , substituting La for divalent alkalies, Pb, or by stoichiometry changes. A large variety of phases have been observed including ferromagnetic, antiferromagnetic, canted, charged ordered, spin glass, etc. [2].

Much less is known about the electron-doped compounds where doping does not seem to produce metallization like for instance $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$, or $\text{CaMnO}_{3-\delta}$ [3] where the doping introduces electrons in background lattice of Mn $3d^3$ ions. We focus attention on these type of systems.

From the theoretical point of view, de Gennes [4] proposed a canted phase to resolve the competition be-

tween the ferromagnetic double interaction introduced by the presence of itinerant holes and the superexchange interaction. Recently, several contribution to this problem have been reported [5–7].

Here we extend our work on this subject [8] to calculate the temperature vs. concentration phase diagram of electron-doped compounds. To this end we modify the original Hamiltonian containing the double-exchange interaction in the following way: (i) we include the superexchange interaction (K) originated by the t_{2g}^3 electrons, (ii) we consider two interpenetrating simple cubic sublattices (I and II) with local quantization direction on each one to describe the canted phase, and (iii) we take the dependence on the angle of the hopping constant t_{ij} in a classical approximation: $t_{ij} = t \cos(\theta)$, where θ is half the angle between localized spin directions in I and II sublattices. The model Hamiltonian reads

$$H = c \sum_{i,\sigma} n_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - J \sum_i S_{zi} \sigma_{zi} + K \sum_{\langle i,j \rangle} S_{zi} S_{zj} + \sum_{\langle i,j \rangle, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} \quad (1)$$

Where $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$, and $c_{i\sigma}^\dagger, c_{i\sigma}$ creates and destroys an itinerant electron with spin σ at site i , respectively. S_{zi} and

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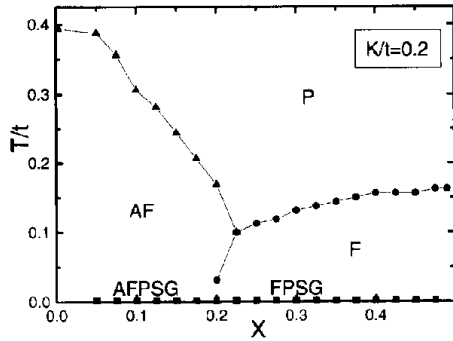


Fig. 1. Phase diagram T/t vs. x , with a $K/t = 0.2$. Transitions into the P phase are second order. All other transitions are first order.

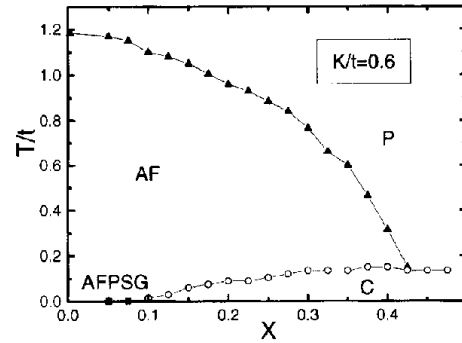


Fig. 2. Phase diagram T/t vs. x , with a $K/t = 0.6$.

σ_{zi} are the localized and itinerant z-component spin operators at site i , respectively. ε is the site diagonal energy, U represents the intra-atomic electronic repulsion and we take ($U \rightarrow \infty$) to forbid double occupancy, and J is the magnitude of the intratomic exchange coupling which we assume to be large as compared to t .

To obtain the kinetic energy of the itinerant electrons, we take $S_{zi}S_{zj}$ in mean-field and we use Green's functions formalism and we calculate $\langle\langle c_{i\sigma}; c_{i\sigma}^\dagger \rangle\rangle$ following Ref. [8]. To this purpose we consider a Bethe lattice with two interpenetrating sublattices (I and II) and we use the renormalized perturbation expansion (RPE) [9] to obtain $G_x = v_x/\omega - (k+1)t^2(\cos^2(\theta)g_x + \sin^2(\theta)g - \alpha)$, where $(k+1)$ is the number of nearest neighbors, $v_x = (1 + \alpha m)/2$ is the probability that a site has parallel (antiparallel) $\alpha = + (-)$ localized spin to the quantization axes in each sublattice with a given magnetization m , and $g_x = v_x/(\omega - kt^2(\cos^2(\theta)g_x + \sin^2(\theta)g - \alpha))$. Solving these equations we calculated the density of states per site as $\rho(m, \theta, \omega) = (\text{Im}(G_+) + \text{Im}(G_-))/\pi$. For $\theta \leq \pi/4$ and arbitrary value of m , we have a single band structure similar to the ferromagnetic case [8]. For $\theta > \pi/4$, we have a central band and two lateral bands with the possibility of a gap for large values of m . The gap structure is a consequence of the fact that the spin ordering induces alternation in the hopping values, so that the electron dynamics is similar to that of a dimerized system.

We calculate the free energy as $F = E_{\text{kin}}(m, \theta, x) + E_K(m, \theta, K) - TS(m)$, where $E_{\text{kin}}(m, \theta, x) = \int_{-\infty}^{\varepsilon_F} \rho(m, \theta, \omega) \omega d\omega$ is the kinetic energy with the Fermi energy ε_F given by the doping $x = \int_{-\infty}^{\varepsilon_F} \rho(m, \theta, \omega) \omega d\omega$, $E_K(m, \theta, K) = Km^2 \cos(2\theta)$ is the superexchange energy in mean-field approximation, and finally $S(m) = \ln(2) - v_+ \ln(2v_+) - v_- \ln(2v_-)$ is the main contribution (localized spins) to the total entropy. For given values of x, K, t , and the temperature T , the minimum of F gives m and θ , which characterize the different phases. According to the (m, θ) values, at zero temperature we define: (a) fer-

romagnetic (F) phase ($m = 1, \theta = 0$), (b) antiferromagnetic (AF) ($m = 1, \theta = \pi/2$), (c) paramagnetic (P) ($m = 0$), (d) canted (C) ($m = 1, \theta < \pi/2$), (e) ferromagnetic pseudo-spin glass (FPSG) ($m < 1, \theta = \pi/2$), (f) antiferromagnetic pseudo-spin glass (AFPSG) ($m < 1, \theta = \pi/2$). Henceforth, we take $k = 5$ (simple cubic Bethe lattice) and $t = 1$. Figs. 1 and 2 show the phase diagrams for two values of K . At zero temperature we see that the competition between double exchange (DE) and superexchange (SE) is resolved differently for large or small values of K .

The temperature dependence of m and θ is also particular with first- and second-order transitions between the different ordered phases.

Figs. 1 and 2 show that, as expected, superexchange favors the AF and C phases against the F state. The new results that we find most interesting are the presence of the pseudo-spin glass (PGS) phases. For large K , electron doping produces small distortions from the AF phase so that the pseudo spin glass phases almost disappear, while for values of K such that SE competes in magnitude with DE, the PSG are present at most of the doping range.

We interpret these results as a failure of the homogeneous phases to describe the ground state. Indeed, the PSG correspond to inhomogeneous phases in which the doped electrons form self-trapped states with reduced sublattice magnetization. Although there are many interesting results, and conclusions we can draw from them, we believe that our main conclusion is contained in the effect of the self-trapped electrons discussed above.

Electron-doped systems, where our results apply have not been studied experimentally as thoroughly as the metallic ones. We hope to stimulate investigations in this area.

R.A. is supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). B.A. is partially supported by CONICET.

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