# Electron-doped manganese perovskites: The magnetic polaron state

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Using the Lanczos method in linear chains we study the ground state of the double exchange model including an antiferromagnetic superexchange in the low concentration limit. We find that this ground state is always inhomogeneous, containing ferromagnetic polarons. The extension of the polaron spin distortion, the dispersion relation and its trapping by impurities, are studied for different values of the superexchange interaction and magnetic field. We also find repulsive polaron-polaron interaction. [S0163-1829(98)51846-2]

The discovery of ''colossal'' magnetoresistance (CMR) (Ref. 1) together with its many unusual properties has received considerable attention lately.

Experiments have revealed very rich phase diagram interpreted in terms of magnetic ferro, antiferro, canted, polaronic, and nonsaturated phases. Charge ordered phases also have been found.[2] The phase diagram, as a function of concentration $x$, 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 $LaMnO_3$, by substituting La for divalent alkalies, Pb, or by stoichiometry changes. Very recently, neutron-scattering experiments have been interpreted in terms of polaronic droplets.[3] Much less is known about the electron doped compounds where doping does not seem to produce metallization.

From the theoretical point of view, the pioneering work of de Gennes[4] proposed a canted phase to resolve the competition between the ferromagnetic double interaction introduced by the presence of itinerant holes and the superexchange interaction. Recently, several contributions to this problem have been reported. Arovas and Guinea[5] studied this problem using a Schwinger boson formalism to obtain a phase diagram showing several homogeneous phases and pointing out that phase separation replaces the canted phase in a large region. Indeed phase separation appears in several numerical treatments of the problem.[6] In other analytical treatments, more adequate to treat local instabilities, nonsaturated local magnetization states have appeared at zero temperature.[7] Kagan *et al.*[8] have studied the stability of the canted phases against the formation of large ferromagnetic ''droplets'' containing several particles and they conclude that the formation of droplets is favored in the ground state. The variety of results obtained from the different approaches points to the need of clarifying the picture and testing the results. To this end it is important to understand the interaction between charge and spin before introducing lattice effects. As is it shown in Ref. 9, at low temperatures, the optical responses of $La_{0.7}Ca_{0.3}MnO_3$ indicate that the coherent and incoherent bands have strong correlations with the spin degrees of freedom.

In this work we find the low-energy quasiparticles and characterize their structure and dispersion relation in the low-concentration limit. These quasiparticles correspond to the electron followed by a ferromagnetic local distortion (ferromagnetic polaron) in the antiferromagnetic (AF) background. The dispersion relation is dominated by $k \rightarrow k+\pi$ scattering due to the presence of AF order. In order to make a connection with transport properties, we also study the tendency to localization of these polarons in the presence of impurities and magnetic field.

To render evident the nature of the ground state, we resort to the Lanczos method. The Hamiltonian is simplified to a single orbital per site, no lattice effects are considered, and we have to reduce to one-dimensional chains. Based on the results of Ref. 6 for one to three dimensions we expect that reduction to one dimension does not modify the picture of the nature of the ground state. Our results provide a simple picture that, we presume, can be put to the test of the dilute limit of electron doped systems. In these systems, the limitations of the model Hamiltonian may not be as stringent as in the hole doped systems for the following reasons: the lattice structure is more symmetric so Jahn Teller distortions should play a less important role, the large in-site Coulomb repulsion inhibits double occupation so that it may be possible to describe the physics by the use of a single effective orbital, and finally the antiferromagnetic structure of two interpenetrating lattices can be properly described in one dimension.

In order to describe the manganites we consider two degrees of freedom: localized spins that represent the $t_{2g}$ electrons at the Mn sites, and itinerant electrons that hop from $e_{2g}$ Mn orbitals to nearest-neighbor $e_{2g}$ orbitals. The model Hamiltonian includes exchange ($J$) energies, an antiferromagnetic interaction between localized spins ($K$) and a hopping term of strength $t$ which we will use as energy unit hereafter. It reads

$$H = -J_h \sum_i \mathbf{S}_i \cdot \sigma_i + K \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \tag{1}$$

$$+ \sum_{\langle i,j \rangle, \sigma} t_{ij} (c^+_{i\sigma} \cdot c_{j\sigma} + \text{H.c.}), \tag{2}$$

where $n_{i,\sigma} = c^+_{i\sigma} c_{i\sigma}$, and $c^+_{i\sigma}, c_{i\sigma}$ creates and destroys an itinerant electron with spin $\sigma$ at site $i$, respectively. $\mathbf{S}_i$ and $\sigma_i$ are the localized and itinerant spin 1/2 operators at site $i$, respectively. In what follows we take large values of $J_h$ which prevents double occupation and makes the on-site Coulomb interaction $U$ irrelevant. This model has been studied nu-

 

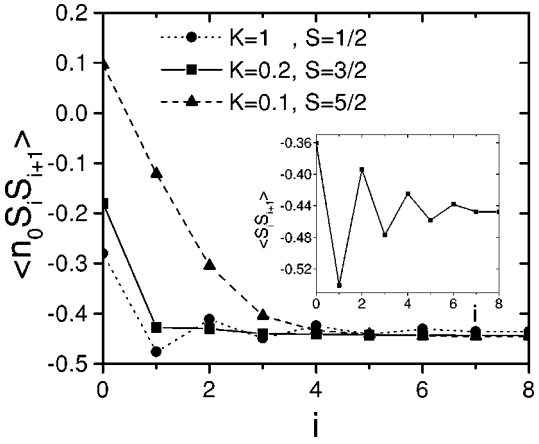


FIG. 1. We show the correlation function $\langle n_0 S_j S_{j+1}\rangle$ for a 16-site chain, with $J_h=10$ and different values of $K$. The total $S$ value of the ground state is indicated in the figure for each value of $K$. One can observe that the total $S$ and the extension of the magnetic distortion increase as $K$ decreases. The oscillatory behavior found at $K=1$ is a consequence of the weakening of the antiferromagnetic links around the charge. The inset shows $\langle S_j S_{j+1}\rangle$ for a 16-site Heisenberg chain where the link at site zero is a factor of 2 smaller than the rest.

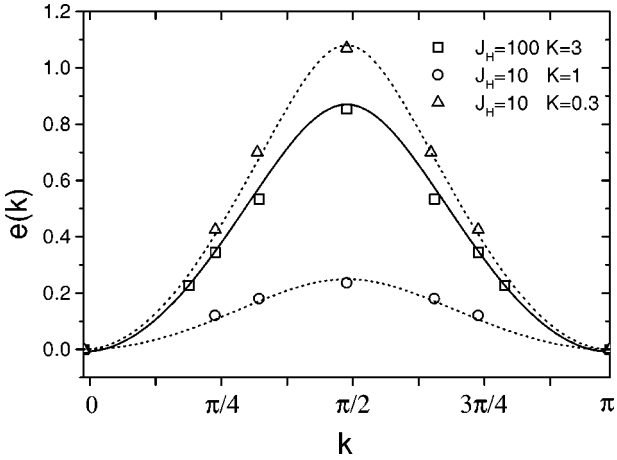


FIG. 2. Dispersion relation scaled to the thermodynamic limit for different sets of parameters. In full line we show a fit with the expression discussed in the text for the limit $J_H \gg K > t$ with $\Delta = 1.4 \approx K/2$. In dotted line fit with $\Delta=1$ and $t=0.75$ for $K=1$, and $\Delta=0.6$ and $t=0.23$ for $K=0.3$.

merically for finite concentration in Ref. 10, and in the absence of AF coupling ($K=0$) in Ref. 6. In this paper we focus on the dilute limit.

We first investigate the homogeneity of the solutions for different values of the antiferromagnetic interaction $K$ (in units of $t$). To this end, we calculate the ground state with one electron added for chains of different sizes up to $N=20$. With the aim of looking for spin distortions around the charge, we calculate a correlation function which makes such a situation evident: $\langle n_i S_j S_{j+1}\rangle$. Because of translational symmetry the results depend only on $|i-j|$. The results are shown in Fig. 1 where we plot $N\langle n_0 S_j S_{j+1}\rangle$ vs $j$, where $N$ is the number of sites. As it can be seen in Fig. 1, for large $j$, this correlation function takes a value very close to the one obtained from the Bethe ansatz solution for the Heisenberg chain, $\langle S_j S_{j+1}\rangle \cong 0.443$. The extension and the magnitude of the spin distortion around the particle increases as $K$ decreases. The oscillations observed in the curve corresponding to $K=1$ are also observed for larger values of $K$. They are a consequence of the weakening of the antiferromagnetic links around the charge position which produce a sort of local spin dimerization. To prove this point, we show in the inset the nearest-neighbors spin-spin correlation functions for a Heisenberg chain of the same size where the link at site zero is a factor of 2 smaller than the rest.

However as $K$ decreases, it is difficult to find an adequate approximation to describe the large polaronic distortion. In order to obtain the effective mass of these polarons, we investigate the dispersion relation for charge excitations. To this end we calculate the lowest energy state for different values of the momentum $k=2\pi n/N$ within the subspace where the total spin is that of the ground state. In Fig. 2 we show the dispersion relation scaled to the thermodynamic limit for $K=3$, $J_h=100$; $K=1$, $J_h=10$; and $K=0.3$, $J_h=10$.

We start analyzing the dynamics in the regime where $(J_h \gg K \gg t)$. In that case, the charge moves as a spin one ($\mathbf{\Sigma}$). The effective hopping resulting from the projection of the hopping term onto the reduced $S=1$ Hilbert space is $tP_{ij}(\mathbf{\Sigma}_i \mathbf{S}_j + 1/2)$, where $P_{ij}$ is the permutation operator between sites $i$ and $j$. We can picture the movement of the particle, in this limit, as going from a state $\downarrow\uparrow\downarrow\Uparrow\downarrow\uparrow\downarrow$ to an intermediate state $\downarrow\uparrow\downarrow\uparrow 0\uparrow\downarrow$, and finally to $\downarrow\uparrow\downarrow\uparrow\downarrow\Uparrow\downarrow$, where $\Uparrow(0)$ represents the $S_z=+1(0)$ components of the spin $S=1$. Thus, in order to move, the charge has to hop to the nearest neighbor, via a spin-flip process, through states that differ in energy by $\Delta \approx K/2$. It can be easily verified that the effective hopping of this process is equal to $t_{ef}=t/\sqrt{2}$. The dispersion relation given by this dynamics is: $\Delta/2 \pm \sqrt{(\Delta/2)^2 + 4t_{ef}^2 \cos^2(k)}$. The expression corresponding to the lower band is plotted with full line in Fig. 2 and compared with the numerical result for $K=3$ and $J_h=100$. This expression is valid in general for a particle moving in an antiferromagnetic background where scattering between $k$ and $k+\pi$ states dominates the dynamics of the particle (dotted lines in Fig. 2).

In the case where $K \gg J_h \gg t$ the spin distortion can be neglected and the particle propagates in an antiferromagnetic lattice. The Hund interaction alternates the site energy of the propagating particle so that the difference between the two sublattices is given by $\Delta = J_h(\langle \sigma_j S_{j+1}\rangle - \langle \sigma_j S_j\rangle) \cong J_h(\langle S_j S_{j+1}\rangle - \langle \sigma_j S_j\rangle)$ where we approximate $\langle \sigma_j S_j\rangle \approx 1/4$ its value at the triplet state, and $\langle \sigma_j S_{j+1}\rangle \approx \langle S_j S_{j+1}\rangle = \ln 2 - 1/4$, the Bethe ansatz value. Using these values we find $\Delta = 0.19 J_h$. In this case $t_{ef}$ is equal to $t$.

When $J_h \gg t \gtrsim K$, the magnetic distortion around the charge is large and the effective hopping is dominated by the overlap between the magnetic distortions about the nearest-neighbors sites. This last effect dominates the polaron effective mass. Therefore, the mass of polarons increases when $K$ decreases, as obtained in Fig. 2, where $t_{ef}$ decreases from 0.75 for $K=1$ to 0.23 for $K=0.3$, in agreement with the above results showing that the spin distortion around the charge increases in magnitude and extension when $K$ de-

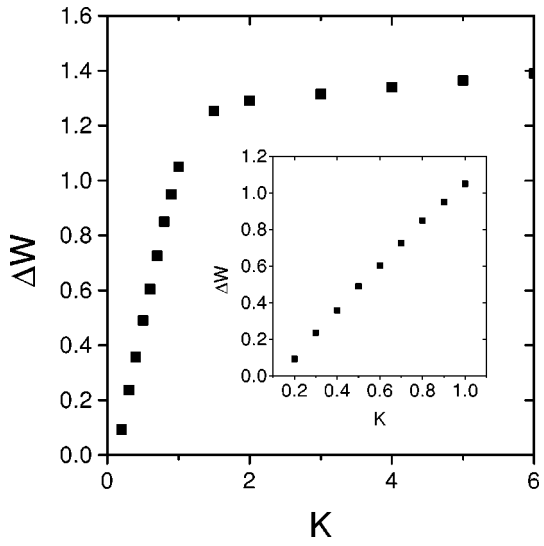


FIG. 3. Effective bandwidth as a function of $K$. The change of regime as $K$ increases through $t$ is evident.

creases. In Fig. 3, we calculate the bandwidth for several values of $K$. One can distinguish clearly two regimes: $K \ll t$ and $K \gg t$; the first corresponds to a large magnetic distortion and the second corresponds to a smaller one according to Fig. 1.

In order to test how robust is the polaronic description of the results, we pin the polaron to a site by lowering in $\epsilon_0$ the diagonal energy at site zero. This may be relevant to the real materials since the doping process necessarily introduces some disorder. Since we are treating a linear chain, this always localizes the particle, but the localization length should be very different for different effective masses, so that a small $\epsilon_0$ localizes much more the polaron for low values of $K$ than for larger ones. This is shown in Fig. 4 where we plot $\langle n_i \rangle$ around site zero for different values of $K$. For comparison we also show in full line the exponential fit of the different curves showing the change in localization length.

In Fig. 5, we show the change in the values of $\langle n_i \rangle$ for different magnetic fields. It can be seen that the localization

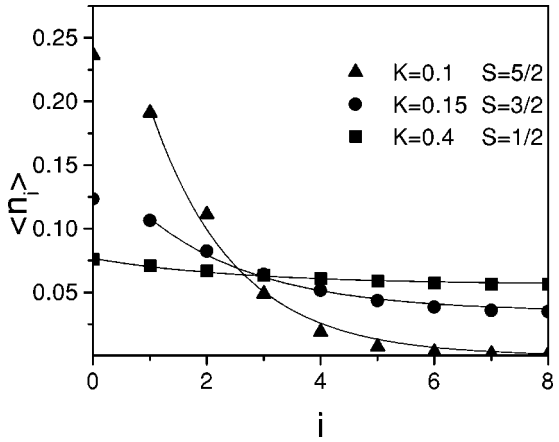


FIG. 4. Charge localization. We show $\langle n_i \rangle$ as a function of position in a 16-site chain where the energy at site zero is lowered from the rest by 0.05 units of $t$. Full lines are exponential fits to the curves. The short localization length of the lower $K$ curves indicate effective bandwidths of the order of the energy change.

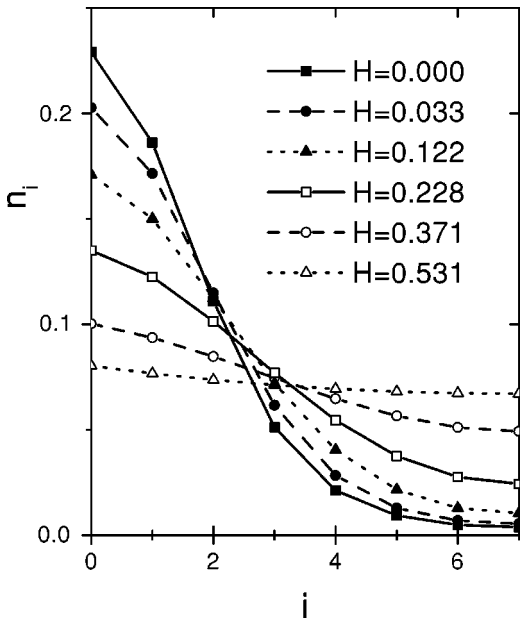


FIG. 5. Effect of magnetic field on charge localization. We show $\langle n_i \rangle$ for different values of an external magnetic field for the same chain as in Fig. 4.

of the polaron decreases with magnetic field as a consequence of increased effective hopping between nearest neighbors, a fact that may be important for the transport properties of these systems since it implies a negative magnetoresistive behavior for conductivity due to hopping between localized states.[11]

Finally, in Fig. 6 we present some of the results for the two particles' ground states. The charge-charge correlation function, normalized to the noncorrelated ($J_h = 0$) case, clearly shows repulsion between the particles. This long-range repulsion increases with the magnetic distortion indicating its magnetic origin.

The fact that polarons repel each other points to a picture of the electron doped systems similar to that proposed originally by de Gennes[4] of ''self-trapped electrons.'' Further dis-

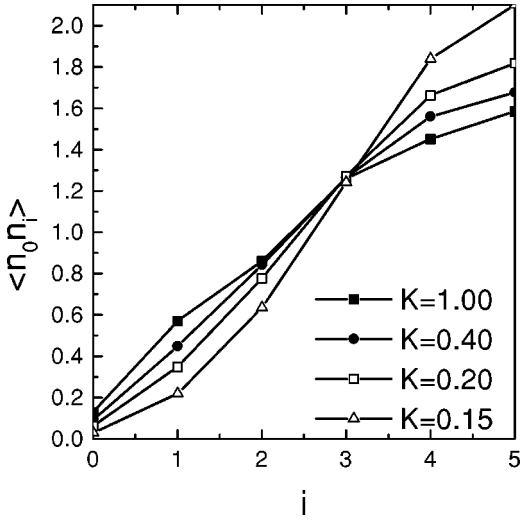


FIG. 6. Charge-charge correlation function for two particles in a ten-site chain for $J_h = 10$, and different values of $K$. Values are normalized to the uncorrelated values.

cussion on the nondiluted limit will be postponed for a later publication where newer results will be shown.

In summary, we have investigated the possibility of a nonuniform ground state in a model Hamiltonian using the Lanczos technique. The model describes chains of localized spins coupled antiferromagnetically on which electrons are added. These electrons suffer a strong ferromagnetic interaction with the local spins and can hop from site to site. Assuming the model adequately describes the physics of electron doped manganites, the results presented here point to a picture of these systems where heavy one-electron polarons dominate the magnetic and transport properties. Their masses depend strongly on the relation between the hopping energy and the AF superexchange interaction. Clearly, the doping itself will localize the polarons so that transport will result from hopping between pinned sites. Negative magnetoresistance should appear as a consequence of the decrease of the pinning energy with magnetic field.[11] Adding two particles to the chains we find long-range repulsion between them. This long-range repulsion could give rise to charge ordering.

Finally, we would like to point out that the order of oxygen vacancies in $CaMnO_{3-\delta}$ makes real the possibility of one-dimensional electron paths in these materials.[12] Furthermore, similar physics can occur in other one-dimensional systems like Ni-O chains contained in doped $Y_2BaNiO_5$. In fact the proposed Hamiltonians coincide in the limit of very large values of $J_h$.[13] We hope that our results will stimulate more experimental and theoretical investigations on the electron doped manganites.

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[1] R. von Helmholt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).

[2] A. P. Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1997), and references therein.

[3] M. Hennion *et al.*, cond-mat/9806272 (unpublished).

[4] P. G. de Gennes, Phys. Rev. **118**, 141 (1960).

[5] D. P. Arovas and F. Guinea, cond-mat/9711145 (unpublished).

[6] E. Dagotto *et al.*, Phys. Rev. B **58**, 6414 (1998); cond-mat/9709029 (unpublished); J. Riera, K. Hallberg, and E. Dagotto, Phys. Rev. Lett. **79**, 713 (1997); S. Yunoki *et al.*, *ibid.* **80**, 845 (1998).

[7] D. I. Golosov *et al.*, J. Appl. Phys. **83**, 7360 (1998); Phys. Rev. B **58**, 8617 (1998); H. Aliaga, R. Allub, and B. Alascio, cond-mat/9804248 (unpublished).

[8] M. Yu. Kagan *et al.*, cond-mat/9804213 (unpublished).

[9] K. H. Kim, J. H. Jung, and T. W. Noh, Phys. Rev. Lett. **81**, 1517 (1998).

[10] S. Yunoki, and A. Moreo, Phys. Rev. B **58**, 6403 (1998).

[11] R. Allub and B. Alascio, in *Proceedings of the International Workshop on Current Problems in Condensed Matter Physics*, Cocoyoc, Mexico, edited by J. L. Moran-Lopez (Plenum, New York, 1998).

[12] J. Briatico *et al.*, Phys. Rev. B **53**, 14 020 (1996).

[13] C. D. Batista, A. A. Aligia, and J. Eroles, Europhys. Lett. **43**, 71 (1998).