Magnetic polarons in $Ca_{1-x}Y_xMnO_3$

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Experimental evidence show that in the magnetoresistive manganite $Ca_{1-x}Y_xMnO_3$, ferromagnetic (FM) polarons arises in an antiferromagnetic (AF) background, as a result of the doping with Yttrium. This hypothesis is supported in this work by classical Monte Carlo (MC) calculations performed on a model where FM Double Exchange (DE) and AF Superexchange (SE) compete.

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In this work we try to explain experimental results on magnetoresistive $Ca_{1-x}Y_xMnO_3$ doped manganites, that point towards the existence of magnetic polarons. The pure sample ($x=0$) presents G-type AF ordering with a transition temperature $T_N=123K$, and insulator characteristics. In this sample, all the Mn ions have valence $4+$, where the localized $t_{2g}$ spins have a spin $S=3/2$. As Yttrium ions are added, itinerants $e_g$ electrons with spin $s=1/2$ are introduced and there is a mixed valence state of $Mn^{3+}$ and $Mn^{3+}$ in the proportion $(1-x)$ and $x$, respectively. The magnetic moment raised and the resistivity drops sharply as $x$ is increased up to $x \leq 0.15$. A thermally activated polaronic behaviour for the conductivity was fitted between room temperature and 100K. The experimental results were interpreted in terms of FM polarons, produced by the alignment of neighboring $t_{2g}$ spins by the $e_g$ electrons and immersed in the AF background. In this work we compare the experimental magnetic measurements with the properties predicted by MC calculations on a model where FM-DE and AF-SE interactions compete.

Ceramic polycrystalline samples of $Ca_{1-x}Y_xMnO_3$ were prepared by solid state reaction methods. Room temperature x-rays diffractograms show that all the samples crystallize in an orthorhombic $Pnma$ cell. The dc-magnetization, $M$, was measured with a SQUID magnetometer between 5K and 300K for $H \leq 50kOe$.

We measured $M$ vs. $H$ at different temperatures for the samples $x=0, 0.03, 0.05$ and $0.1$ and we found a linear dependence at high fields: $M=M_0 + \chi H$. In Fig. 1(a) we show $M_0$ vs. $T$. The behavior resembles that of a ferromagnet with a characteristic ordering temperature $T_{m_0}$, almost constant for all the samples. For $x=0$, a small $M_0 \sim 0.03\mu_B/f.u.$ reflects a weak ferromagnetic Dzialoshynskii-Moriya interaction. In Fig. 2(a) we plot $M_0$ vs. $T$ at $5K$. The curve has an S shape starting with a slope of $1\mu_B$ per $Mn^{3+}$ ion and reaching a slope $M_0/x \sim T\mu_B$ at $x=0.07$. Notice that full FM alignment ($3\mu_B$/Mn site) is not reached.

FIG. 2. (a) $M_0$ and (b) $\chi$, as function of doping $x$, measured at 5K (squares), and calculated (circles).

In Fig. 1(b), we show $\chi(T)$ vs. $T$. The general behavior above $T_{m_0}$ has been studied in Ref. 1, for $x=0, 0.05, 0.07$ and $0.1$. The most peculiar feature observed is a deviation from the Curie-Weiss law, presenting a negative curvature in $\chi^{-1}(T)$. This temperature dependence was described in terms of two contributions:

$$\chi(T) = (1-x)\chi_{AF}(T) + x \chi_{FM}(T), \quad (1)$$

where $\chi_{AF}(T)$ is the susceptibility of the AF background and $\chi_{FM}(T)$ reflects the strong FM-DE correlations that results in polaron formation in the PM
phase. For \( x=0 \), a maximum in \( \chi(T) \) is present at \( T_N \). For \( x=0.1 \) the behavior is qualitatively similar: a maximum is observed around \( T_{mo} \), although with a much larger value. Below \( T_{mo} \), \( \chi(T) \) decreases rapidly and reaches \( \sim 0.6\chi(T_{mo}) \) at \( T=5K \). For the intermediate concentration, \( x=0.05 \), a peak at \( T_{mo} \) is only a relative maximum: \( \chi(T) \) increases again below \( T\sim70K \) and \( \chi_{AF}(5K) \sim 1.2\chi(T_{mo}) \). For the low doped \( x=0.03 \) sample no peak is observed at \( T_{mo} \) and \( \chi(T) \) continues to increase below \( T_{mo} \) up to \( T\sim60K \), where a broad maximum is present. The large values of \( \chi(T_{mo}) \) take into account the progressive polaron formation, indicated by the proportionality \( \chi(T_{mo}) \propto x \), given by Eq.\,(1), where \( \chi_{AF}(T_{mo}) < \chi_{FM}(T_{mo}) \). In Fig. 2(b), \( x=5K \) vs. \( x \) The simplest picture for the behavior of \( M(H,T) \) below \( T_{mo} \), is to associate \( \chi(T) \) with the AF background and assume that \( M_0(T) \) corresponds to the FM order of polarons. However, the measured \( \chi(T) \) is in all cases much larger than the Ca\( MnO_3 \) susceptibility. Thus, this simple model seems not appropriate to describe the experiments in the ordered region. In order to obtain a better description of the magnetization behavior, we have performed a calculation of \( M \) vs. \( H \) using the numerical classical MC technique.

We consider the following Hamiltonian:

\[
\mathcal{H} = - \sum_{(ij)\sigma} t_{ij} \left( c_{i\sigma}^\dagger c_{j\sigma} + h.c. \right) - J_H \sum_i s_i \cdot S_i + g\mu_B H \sum_i S_{z,i} + K \sum_{(ij)} s_i \cdot S_j,
\]

where \( c_{i\sigma}^\dagger \) is the operator creating an itinerant electron of spin \( \sigma \) at site \( i \), and \( s_i = \sum_\alpha \sigma_{i\alpha} s_{i\alpha} \) gives the spin projection of the electron. Due to the strong Hund coupling (\( J_H \to \infty \)) between itinerants \( c_\sigma \) electrons and the localized \( t_{2g} \) spins, only parallel spin projections were taken into account. In this way, the hopping of itinerant electrons depends on the orientation of the localized \( t_{2g} \) spins, according to the DE expression in one dimension: 

\[
t_{ij} = t \cos(\theta_{ij}/2),
\]

where \( \theta_{ij} \) is the relative angle between localized spins \( S_i \) and \( S_j \), \( t \) is the hopping parameter. The third term, represents Zeeman coupling between magnetic field \( H \) and \( S_{z,i} \), the \( z \) component of localized spin \( S_i \). The AF-SE interaction between localized neighboring spins \( S_i \) and \( S_j \) is represented by the last term in Eq.\,(2).

Numerical calculations were performed in one dimension, using the MC algorithm for a 48 sites chain with open boundary conditions. The localized spins were classical with modulus \( 1 \), and later renormalized to \( (3+x)\mu_B \) in order to compare with experiments. Local changes in \( t_{2g} \) spins were made in conjunction with exact diagonalization of the itinerant electron system. The resulting electronic energy levels were then filled by the available number of electrons in the canonical ensemble. We take the hopping parameter \( t=0.1eV \) as the reference energy, and the temperature \( T=0.005t\sim6K \). Mermin-Wagner's theorem precludes magnetic ordering at finite temperatures in 1D systems. However, we estimated a value for \( K \) from the ordering temperature \( T_{mo} \) that would arise from a classical Heisenberg model for a system with \( z=2 \) neighbors. For \( T_{mo}=100K \), we derive \( KS^2/t=0.05 \).

![FIG. 3. Magnetization \( M \) vs. \( H \), for \( x=0 \)(squares), 1/48(circles)... ,5/48(plus signs), obtained by MC calculations. Characteristics error bars are displayed for few points.](image)
of 1µB, and for x >0.03, increases up to 7µB/polaron. In the present model, we find a linear dependence in the curve $M_0$ vs $x$. The size of each polaron is fixed by the ratio $K/D$. The distribution of the itinerant charge, shows that each polaron extends over 5 to 6 sites. The differential susceptibility $\chi$ is a measurement of the the canting of the AF background and the enlargement of polarons with $H$. In Fig. 2(b) we show the calculated $\chi$ vs. $x$, that shows an almost constant behaviour. Since for $x=0.1$, about half of the sites take part in the polaron phase, we conclude that the response of polarons to $H$ is of the same order to that of the canting of the AF background.

We found a remarkable agreement between experimental and numerical values of $M_0$ and $\chi$. The numerical simulations suggest that linear regime $M$ vs. $H$, is not fully reached at $H=50kOe$, thus experiments at higher fields are suggested in order to make a better comparison with numerical prediction, specially in the low doped regime, where some discrepancies are observed.

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1 H. Aliaga et al., cond-mat/0010295, (submitted to PRB).
2 D. Vega et al. J. Solid State Chem., 156, 458 (2001).
3 H. Aliaga et al. JMMM, 226-230, 791, (2001).
4 H. Aliaga, unpublished.