

Electron-phonon interactions in manganites: effect on the electronic transport and magnetization

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Mixed-valent manganese oxides with perovskite structure offer a certain degree of chemical flexibility that allows making systematic studies of the relationship between the electric and magnetic properties with the crystalline structure. Here we present magnetic measurements in $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$ that demonstrate that the adiabatic approximation breaks down at low x , due to the strong coupling of the electronic and the lattice degrees of freedom.

Keywords: electron-phonon interaction; colossal magnetoresistance (CMR); Double exchange (DE).

Interacción electrón-fonón en manganitas: efecto en el transporte eléctrico y en la magnetización.

Los óxidos de manganeso con valencia mixta y estructura de perovskita poseen un cierto grado de flexibilidad química que permite hacer estudios sistemáticos entre las propiedades eléctricas y magnéticas, con la estructura cristalina. En este trabajo presentamos medidas magnéticas en la serie $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$ donde se demuestra que la aproximación adiabática falla para pequeñas x , debido al fuerte acoplamiento de los grados de libertad electrónicos y de la red.

Palabras clave: interacción electrón-fonón; magnetorresistencia colosal (CMR); Doble intercambio (DE).

1. INTRODUCTION

The unusual richness of the magnetic/electronic phase diagram of manganites ($\text{R}_{1-x}\text{A}_x\text{MnO}_3$; R=Lanthanide, A=alkaline earth) constitute an ideal bench to test solid-state physics models and theories. Many of these models rely on the validity of the adiabatic approximation, that stands that electrons and ions can be treated separately and hence conventional one-electron band theory should be applicable with a small perturbation from the lattice. However, that is not the case in many of the most interesting manganites, and a strong electron-phonon interaction has been invoked as the reason for most of the peculiar properties of these systems(1). However, and in spite of the enormous interest raised by these materials in the last few years, a quantitative analysis of the effect of the coupling to the lattice over the magnetic and transport properties of a particular material is lacking.

In this work, we present experimental results of magnetization (versus temperature and field) in $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$ that demonstrate that the adiabatic approximation breaks down at low x , due to the strong coupling of the electronic and the lattice degrees of freedom.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Metallicity and ferromagnetism is linked in manganites through de Gennes Double Exchange (DE) model (2). In this model, a real charge transfer occurs between two Mn atoms across the Mn-O-Mn (180°) bridge, which in first order perturbation theory gives a magnetic exchange energy, J , proportional to $\cos\phi$. This approximation reproduces

satisfactorily the evolution of T_C with x in the rhombohedral part of the phase diagram presented in Fig. 1, but completely overestimates the value of T_C in the orthorhombic phases.

$\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$ samples were synthesized by a conventional solid-state reaction in air. Differential Scanning Calorimetry (DSC) and SQUID magnetometry were used to determine the structural and magnetic transitions respectively.

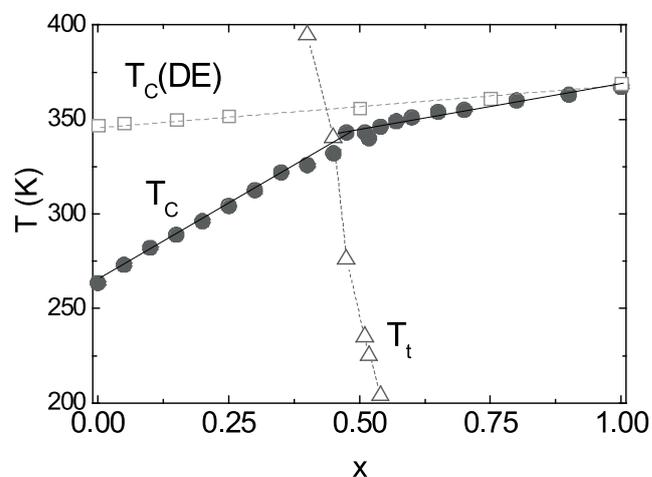


Figure 1: (solid circles): evolution of T_C with x across the series $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$ determined experimentally. (open triangles): $\text{Pnma} \leftrightarrow \text{R-3c}$ structural transition temperature determined experimentally. (open squares): evolution of T_C with x calculated from a free-electron de Gennes DE model.

The presence of Mn^{3+} ions with a degenerate electronic state introduces the possibility of lattice distortion (Jahn-Teller, JT) that reduces the electronic energy at the expenses of an elastic term. In the rhombohedral phases this distortion is forbidden by symmetry considerations (all distances and angles must be equal). However, symmetry considerations are more relaxed in the orthorhombic structure, and the JT stabilization energy (through the formation of a vibron) competes with the delocalised, itinerant electronic phase in which purely electronic DE model works well.

To prove that point we have measured the low field ZFC-FC magnetization curves of the $x=0.5$ sample, which undergoes a structural transition in the FM metallic region (Fig. 2). The splitting in the ZFC-FC curves and the lower magnetization in the orthorhombic part with respect to the high temperature rhombohedral phase is a clear indication of an inhomogeneous magnetic system.

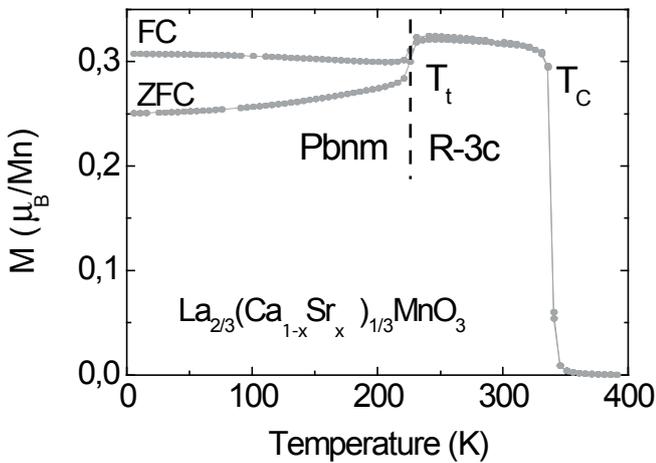


Figure 2: Temperature dependence of the ZFC-FC magnetization curves of $x=0.5$ measured at 100 Oe.

On the other hand, Mira et al.(3)(4) demonstrated that character of the magnetic phase transition changes from first to second order when going from $x=0$ to $x=1$. In figure 3 we show the H/M vs M^2 plots for some representative compositions of the series. There is a change in the slope of the isotherms, which following the Landau criterion (5) indicates a change in the order of the phase transition. So, we have delimited the change in the order of the magnetic phase transition to occur between $x=0.05$ and $x=0.1$. This invalidates the argument of the relationship between the nature of the phase transition with the structural symmetry and calls for a new interpretation.

Decreasing the x in the orthorhombic structure, increases ϕ , and hence increases the frequency of vibration of the oxygen optical mode that traps a carrier at a single site. In fact, Goodenough (6) proposed that a transition from itinerant (like in $x=1$) to polaronic behaviour can be realized as the time for an electron to tunnel between two Mn increases with respect to the period of an oxygen lattice vibration. Therefore, when x is reduced towards $La_{2/3}Ca_{1/3}MnO_3$ the vibration frequency of the oxygen mode increases, coupling more effectively to the electrons and making the Bohr-Oppenheimer approximation invalid.

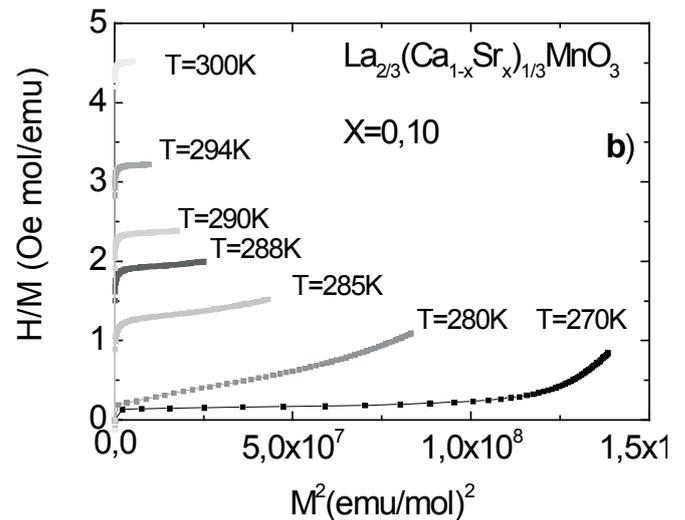
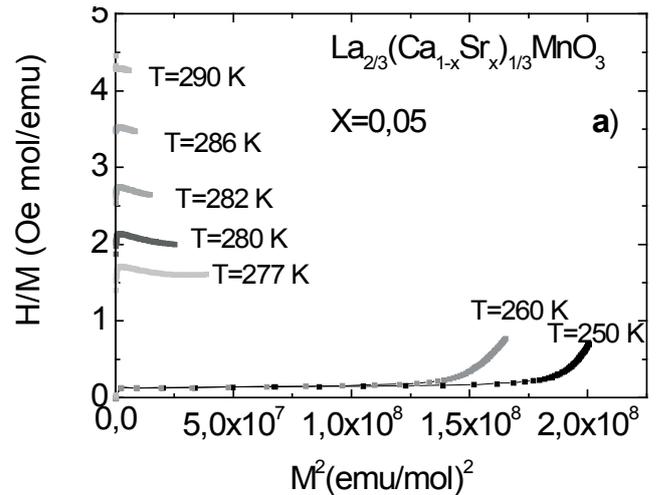


Figure 3 : a) $La_{2/3}(Ca_{0.95}Sr_{0.05})_{1/3}MnO_3$ shows a negative slope for temperatures above the Curie temperature, indicating the first order character of the transition. b) $La_{2/3}(Ca_{0.95}Sr_{0.10})_{1/3}MnO_3$ shows a positive slope in all the points, and hence the transition is conventional second order.

3. CONCLUSIONS

In summary, we have demonstrated that the adiabatic approximation breaks down in the orthorhombic side of the phase diagram of FM-metallic manganites. Due to the continuous increase in the frequency of the oxygen-lattice vibration that traps a carrier at a single site, a vibronic state is stabilized at low x , competing with an itinerant electronic phase (de Gennes). This effect must be taken into account to develop a realistic model that predicts the effects of the lattice vibrations on the magnetic and transport properties of these materials.

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