Positive magnetoresistance and orbital ordering in La$_{1-x}$Sr$_x$MnO$_3$

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We report on detailed transport measurements of single crystalline La$_{1-x}$Sr$_x$MnO$_3$ ($x \lesssim 0.2$). We have found a giant positive magnetoresistance in the compositions range between $0.1 \lesssim x \lesssim 0.125$ and give an explanation in terms of orbital ordering due to the interplay between superexchange interactions and Jahn-Teller distortions.

In the last years an overwhelming interest in the manganite perovskites La$_{1-x}$A$_x$MnO$_3$ arose primarily due to the observation of a colossal negative magnetoresistance (CMR) close to $x = 0.3$. These CMR effects at the ferromagnetic (FM) phase transition were explained within extended double-exchange (DE) models. Since then it became clear that this compounds reveal many intersting and puzzling phenomena which can not be accounted for by double exchange alone. It was Millis et al. who first related dynamic Jahn-Teller (JT) distortions to the CMR effect. In a recent paper we have presented a detailed phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ at low Sr concentrations. In the concentration regime $0.1 \lesssim x \lesssim 0.15$ we detected a ferromagnetic (FM) and insulating (I) ground state which is followed by a canted antiferromagnetic (CA) or mixed phase at elevated temperatures. This insulating FM-phase results from superexchange (SE) interactions in a charge-ordered (CO) phase which probably also reveals orbital order.

In this paper we will present detailed transport measurements on La$_{1-x}$Sr$_x$MnO$_3$ single crystals. It will be shown that the double degeneracy of the $e_g$ orbitals and their ordering in real space must be considered in order to understand the ferromagnetic and insulating ground state in this doping regime. Recently theoretical models considered the orbital degrees of freedom, but have mainly focused on the properties of the LaMnO$_3$ and La$_{0.5}$Sr$_{0.5}$MnO$_3$ compounds. Although Ahn and Millis discussed the interplay of orbital and charge ordering for La$_{0.875}$Sr$_{0.125}$MnO$_3$ they did not considered the effect of this types of ordering on the magnetic properties. Using a mean field approximation Macezono et al. have obtained an overall phase diagram of doped manganites based on the interplay of SE- and DE-interactions.

Here we provide strong experimental evidence that the competition between JT-, SE- and DE-interactions is responsible for the rich variety of magnetic and structural phase transitions in the low doping phase diagram ($x \lesssim 0.2$). At the phase boundary of the insulating FM ground state, a strong (colossal) positive MR appears. We will show that the close coupling of structural and magnetic phase transitions and especially the magnetic field induced structural transitions can only be explained assuming orbital order in the $O^\prime$-phase.

Single crystals of La$_{1-x}$Sr$_x$MnO$_3$, with concentrations $0.1 \lesssim x \lesssim 0.2$ were grown by a floating zone method with radiation heating in air atmosphere. X-ray diffraction of crushed single crystals revealed high-quality single-phase materials. X-ray topography indicated twinning of the crystals. Transport measurements in the temperature range 1.5-300 K were performed with the standard four-probe method in fields up to 14 T.

The relevant part of the phase diagram around $x = 0.125$ is reproduced in Fig. 1. Close to this concentration a rather unusual sequence of phase transitions has been detected. At room temperature La$_{0.875}$Sr$_{0.125}$MnO$_3$ is orthorhombic. A long range JT distortion (and hence orbital order) appears at $T_{OO\cdot}=265$ K, both orthorhombic phases beeing insulating. At $T_{CA}=180$ K a CA structure is established where the resistivity is reduced almost by a factor of 10. It is this regime which has been treated as a FM and metallic phase during the last years. This however was not based on experimental results but only due to the fact that $d\rho/dT > 0$ in a limited temperature range and that a transition which is followed by a canted spin structure at lower temperatures nicely fits into de Gennes phase diagram. We have shown that this phase reveals a canted structure. Of course, we also can not exclude a mixed phase in this regime, but it is definitely not metallic. The decrease in the resistivity probably indicates an increase of the charge transfer matrix elements due to the increasing importance of the DE mechanism combined with the freezing out of spin-disorder. Finally at $T_{OO\cdot}=150$ K and $T_{CA}=140$ K a structural phase transition is immediately followed by the onset of FM order. The O$'$-phase reveals charge order in an almost pseudocubic lattice and the ground state is a FM insulator.

The field dependence of the magnetoresistance ($\Delta\rho/\rho(0)=\rho(H)−\rho(0)/\rho(0)$) for $x = 0.1$ and $x = 0.125$.
is shown in Fig. 2 for various temperatures. For tempera-
tures $T > T_{O'O''}$ we find negative MR effects. However we would like to point out that here the negative MR
appears at the transition from a paramagnetic (PM) ins-
ulator into a CA or mixed phase. Small negative MR ef-
effects again appear for $T < T_{C} = 105$ K. However, between $T_{O'O''}$ and $T_{C}$ large or even colossal positive MR ef-
effects appear, due to the fact that the FM ground state is
indeed more insulating than the CA phase. A closer in-
spection of Fig. 2 reveals that two subsequent jumps ap-
ppear as a function of increasing field. Both jumps induce
higher resistivity states and correspond to those ones ob-
erved in the magnetization curves (see Fig. 3 in [1]).
The first jump is due to a field induced structural phase
transition from the JT-distorted $O'$- to the pseudocubic
$O'$-orthorhombic phase and obviously is accompanied
by a real space charge ordering of the Mn$^{3+}$ and Mn$^{4+}$
ions [1]. At the subsequent second jump the sample under-
goes a transition into a FM state with the mag-
netoresistance showing a saturated behavior at higher
fields. For $x = 0.125$ these jumps are not clearly sepa-
rated, a fact that has also been observed in the magneti-
cization curves. In contradiction to the $x = 0.1$ compound,
the magnetoresistance of the $x = 0.125$ sample decreases
with increasing field below the field induced transition to
the charge ordered FM state. Finally for the $x = 0.15$
 sample (not shown) only negative CMR effects have been
observed in agreement with previous published results
[2]. It is remarkable that in the temperature range be-
tween $T_{C_{A}}$ and $T_{C}$ the magnetoresistance at a given field
changes sign and becomes positive.

To show these large positive MR effects, the tempera-
ture dependence of the magnetoresistance for various
fields and doping levels is plotted in Fig 3. For $x = 0.1$
two pronounced peaks yielding an increase in resistivity
up to +400% when the magnetic field is raised to 5 T
are clearly visible. These peaks corresponds to the tran-
sitions into the $O'$ and FM-state respectively. Around
$T_{C_{A}}$ the typical negative MR effect can be seen. The
same features are also present for $x = 0.125$, though
the two positive enhancements at $T_{O'O''}$ and $T_{C}$ obvi-
ously merge resulting into a single peak. The positive MR
is maximal for $x = 0.1$, becomes significant smaller for
$x = 0.125$ and finally disappears for $x \geq 0.15$. Sum-
marizing the magnetoresistance measurements indicate
a large positive MR at the transitions $O'$/CA$\rightarrow O'/CA$
and $O''$/CA$\rightarrow O''$/FM, while negative MR effects ap-
ppear close to the $O'$/PM$\rightarrow O'/CA$ and O/PM$\rightarrow O$/FM
phase boundaries (see Fig. 1). The negative MR ob-
viously result from the onset of spin order below $T_{C_{A}}$
(i.e. $T_{C}$ for $x > 0.15$) and can be explained within a
double-exchange picture as proposed by [2]. The elec-
tronic properties in the $O''$-phase are more complicated
and can not be explained taking only double-exchange
interactions in account.

Finally in Fig. 4 we show a H-T-phase diagram for
$La_{0.9}Sr_{0.1}MnO_{3}$. We choose this concentration as for this
sample the sequence of two strongly coupled phase tran-
sitions ($O'\rightarrow O''$, CA$\rightarrow$FM) can be easily documented
(see e.g. Figs. 2 and 3). The insulating region of positive
MR is embedded in insulating phases which reveal nega-
tive MR effects. Both transition temperatures ($T_{O'O''}$,
$T_{C}$) are shifted to higher temperatures as the external
field is increased. At the two closely related phase bound-
aries $T_{O'O''}$ and $T_{C}$ three degrees of freedom, namely
the spins ($Mn^{3+}/Mn^{4+}$), the spins and the orbitals
undergo an ordering process. The structural phase tran-
sition $T_{O'O''}$ indicates charge ordering [1] and most
probably also orbital ordering.

We start our discussion summarizing the most im-
portant experimental results presented here. It is obvi-
ous that the transition from the canted-AFM and JT-
distorted $O'$-phase to the pseudocubic charge-ordered
$O'$/PM is intimately coupled to a transition into an in-
sulating FM state. The positive CMR effect observed in
the vicinity of the commensurate doping value $x = 0.125$
counts for a very different picture as it can be given by
the interplay of JT-distortion and DE-interactions alone.

It is well know that the double degeneracy of the $e_{g}$
levels of 3d ions in an octahedral environment is lifted
by an JT-distortion of the lattice [13], accompanied by
an ordering of the orbitals in real space. The possibil-
ity of orbital ordering in transition-metal ions due to
exchange interactions different than that resulting from
JT-distortions was first pointed out by Roth [14] and has
been extensively studied by Kugel and Khomskii [15].
It has been shown that two transitions take place, one
into an orbitally ordered state and a second into a spin-
ordered state, both driven by SE-mechanisms. This SE
differs from the ordinary one due to the fact that each
electron has four degrees of freedom, two orbital states
($d_{xz}$, $d_{xy}$) and two spin states (spin-up, spin-down).
The presence of intra-atomic exchange in case of orbital
degeneracy produce ferromagnetism below the orbital-
ordering phase transition [16]. It is important to notice
that above the orbital-ordering transition temperature
the effective spin-spin interaction is AFM, which is mod-
ified by the appearance of the orbital ordered state and
finally goes over into a FM coupling. A modern view of
this problem has been recently considered by Held and
Vollhardt [17].

For undoped LaMnO$_3$ the magnetic properties can be
well explained taking only the predominant JT-distortion
of the MnO$_6$ octahedra into account. The double degen-
eracy of the $e_{g}$ orbitals is lifted by a long range coopera-
tive Jahn-Teller distortion resulting in an ordering of the
d$_{z^{2}}$ orbitals as has been argued by Solovey et al. [18]
and has recently been confirmed experimentaly by Murakami
et al. [19]. As a result of this JT driven orbital ordering
the A-type AFM state is established below $T_{N}$.

Upon doping with holes the long-range JT-distortion
become suppressed and concomitantly double-exchange
interactions have to be taken into account. At room temperature the lattice is distorted as in LaMnO₃ (O′-phase) due to the JT effect removing the double degeneracy of the e₉ levels. Since mobile holes are present, the double exchange mechanism plays a fundamental role. The magnetic structure observed in undoped LaMnO₃ is modified by the appearance of three-dimensional ferromagnetic DE-interactions, competing with the JT driven A-type AFM yielding a canted AFM state (or mixed phase). Thus canted antiferromagnetism is established below T_C,A = 150 K, accompanied by a drop in the resistivity, since a gain in kinetic energy of the carriers due to DE-interactions can be achieved. Further lowering of the temperature favours SE-interactions between Mn⁢³⁺ ions in a manner discussed above, yielding the ordering of orbitals and subsequently the evolution of ferromagnetism. At T_O′O′, the SE-interactions become dominant, suppress the JT-distortion and enforces the structural transition into the pseudocubic O′′-phase, followed by the onset of ferromagnetism at T_C. At the same time an insulating behavior appears due to charge and orbital ordering, which decreases the hole mobility and explains the positive jumps in the MR curves. The transition to the orbital ordered FM state, is stabilized by the application of an external magnetic field as can be seen in Fig. 1 and Fig. 2. We remind that by application of an external magnetic field jumps in the magnetization curves has been observed, leading the sample to higher magnetization states. This field induced transitions can not be ascribed to magnetocrystalline anisotropy since no dependence was found for different orientations of the crystal axes in respect to the applied external field. The possibility of magnetic field induced transitions due to the interplay of the JT-effect and SE-interactions has been first pointed out by Kugel and Khomskii. It was shown that when orbital ordering is enforced by the SE mechanism such transitions are possible. On the other hand if orbital ordering is established due to electron-lattice interactions (JT-effects) as it is believed to be in LaMnO₃, then such transitions may not appear.

At the moment only predictions about how the orbitals are ordered in the low temperature state can be made, but an alternation of occupied d₂₋ₓ and dₓ₋₂y orbitals on neighbouring Mn³⁺ sites appear most probably to us (Fig. 5). This would cause a displacement of the O²⁻ ions due to secondary electrostatic interactions, yielding alternating long and short Mn-O bonds. Together with the real space ordering of the Mn³⁺/Mn⁴⁺ ions this would result in additional superstructure reflections in the diffraction patterns. Finally for doping levels higher than x ⩾ 0.175 the double exchange mechanism becomes dominant and a metallic ferromagnetic state is established. The orbital liquid picture recently proposed by Ishihara et al. may be appropriate to describe the physics in the metallic phase.

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FIGURE CAPTIONS:

Fig. 1: Phase diagram of La₁₋ₓSrₓMnO₃ at low doping concentrations. The shaded area represents an orbitally and charge ordered insulating ferromagnet.

Fig. 2: Isothermal magnetoresistance curves for the x = 0.1 and x = 0.125 samples.

Fig. 3: Temperature dependence of the MR for x = 0.1 and x = 0.125 at various applied magnetic fields.

Fig. 4: H-T-phase diagram for x = 0.1. The shaded area corresponds to the region of positive MR. A strong negative MR appears close to the OO′-phase boundary.

Fig. 5: Orbital ordering in La₀.₈⁷⁵Sr₀.₁₂₅MnO₃ which is in accord with the charge order proposed by Yamada et al. [11].
$\text{La}_{0.875} \text{Sr}_{0.125} \text{MnO}_3$

- $\text{Mn}^{3+}$
- $d_{z^2}$ orbital
- $\text{Mn}^{3+}$
- $d_{x^2-y^2}$ orbital
- $\text{Mn}^{4+}$