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# Role of spin polarized tunneling in magnetoresistance and low temperature minimum of polycrystalline $La_{1-x}K_xMnO_3$ ($x$ = 0·05, 0·1, 0·15) prepared by pyrophoric method

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**Abstract.** **The low temperature resistivity and magnetoresistance of bulk samples of $La_{1-x}K_xMnO_3$ has been investigated between 10 K and 300 K with and without the magnetic field ($H$ = 0·8 T). All the samples show metal–insulator transitions with Curie temperature ($T_C$) ranging between 260 K and 309 K. At temperature below 60 K, the K-doped manganites exhibit a shallow minimum, which disappears under an applied field of 0·8 T. This field dependent minimum in resistivity, observed in K-doped lanthanum manganites is explained in the light of intergrain tunneling of the charge carriers between anti-ferromagnetically coupled grains of the polycrystalline samples. The field variation of magnetoresistance below $T_C$ follows a phenomenological model which considers spin polarized tunneling at the grain boundaries. The intergranular contribution to the magnetoresistance is separated out from that due to spin polarized tunneling part at the grain boundaries. The temperature dependence of intrinsic contribution to the magnetoresistance follows the prediction of the double exchange model for all values of field at $T < T_C$.**

**Keywords.** **Manganites; magnetoresistance; low temperature resistivity; spin polarized tunneling.**

## 1. Introduction

The discovery of colossal magnetoresistance (CMR) in the doped manganese perovskites has gained much attention recently (von Helmolt *et al* 1993; Ju *et al* 1994; Righi *et al* 1997). The existence of the dopant in $La_{1-x}A_xMnO_3$ compounds (where A is the divalent/monovalent atom) leads to the formation of both $Mn^{3+}$ and $Mn^{4+}$ ions in the system. This mixed valency then generates the strong ferromagnetic interactions which can be explained by double-exchange (DE) mechanism (Zener 1951) depending on the doping concentration ($x$) and the colossal magnetoresistance (CMR) property is induced in this system.

Recently, monovalent-doped (e.g. Ag, Na, K etc) lanthanum manganites are studied with the aim to achieve high magnetic ordering temperature near room temperature. In the present communication, we report our results on the influence of K-doping on the temperature dependence of the electrical resistivity and magnetoresistance of polycrystalline $La_{1-x}K_xMnO_3$ compounds. All the samples show metal–insulator transitions and field-dependent minima below 60 K in the temperature dependent resistivity curve. The results are analysed in light of recent models.

## 2. Results and discussion

The polycrystalline $La_{1-x}K_xMnO_3$ ($x$ = 0·05, 0·1, 0·15) are prepared by pyrophoric method. XRD patterns of all the $La_{1-x}K_xMnO_3$ samples confirm the single phasic nature of the samples and the average crystallite size, estimated from XRD data varies between 10 and 13 nm (table 1). The temperature dependence of the a.c. susceptibility of all the samples show sharp magnetic transition from ferromagnetic to paramagnetic state and $T_C$ obtained shows substantial increase from 260 K ($x$ = 0·05) to 309 K ($x$ = 0·15).

Resistivity and magneto-resistance of the prepared pellets is measured between 10 and 300 K using d.c. four-probe method in a cryo-refrigerator placed between the pole pieces of an electromagnet (maximum field, 0·8 T). A distinct metal–insulator transition for all the K doped manganites of the present series is clearly evident from figure 1. The increase in metal–insulator transition temperature ($T_{MI}$) along with the decrease in resistivity with K content in lanthanum manganites indicates that the ferromagnetic metallic state becomes dominant with K substitution (table 1).

The corresponding $Mn^{4+}/Mn^{3+}$ ratio, obtained from the valency calculation (table 1) is seen to increase with $x$, thus favouring the ferromagnetic DE interaction. In the low temperature regime below $T_{MI}$ (50 K < $T$ < $T_{MI}$), temperature dependence of resistivity can be expressed by considering the electron–electron interaction, electron–magnon scattering and electron–phonon interaction, viz.

$$\rho = \rho_0 + \rho_2 T^2 + \rho_{4\cdot5} T^{4\cdot5}, \tag{1}$$

where the terms $\rho_0$, $\rho_2$ and $\rho_{4\cdot5}$ have their usual meanings (Urushibara *et al* 1995). Figure 2 shows a good fit of this equation with experimental data for $H$ = 0 T. Similar

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good fits are also obtained for resistivity data under magnetic field. Lowering of $\rho_0$ value (table 2) on application of magnetic field suggests that such imperfections are magnetically coupled. In the high temperature insulating regime above $T_{MI}$ ($T_{MI} < T < 300$ K), electrical conduction is generally governed by adiabatic small polaron hopping (Emin and Holstein 1969) where the electrical resistivity is given by,

$$\rho = BT\exp\left(\frac{E_a}{K_B T}\right), \quad (2)$$

where $E_a$ is the activation energy and $B$ the resistivity coefficient.

**Table 1.** Some important estimated parameters of the $La_{1-x}K_xMnO_3$.

| Sample $x$ | Crystal size (nm) | $T_{MI}$ (K) | $T_C$ (K) | $Mn^{+4}/Mn^{+3}$ (%) |
|---|---|---|---|---|
| 0·05 | 10·70 | 239·8 | 260·45 | 11·11 |
| 0·10 | 12·43 | 261·9 | 287·43 | 25·00 |
| 0·15 | 13·27 | 275·8 | 309·76 | 42·86 |

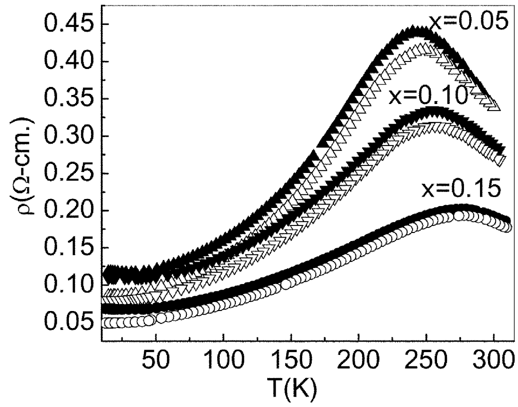


**Figure 1.** Electrical resistivity of polycrystalline $La_{1-x}K_x MnO_3$ pellets from 10–300 K. Filled symbols correspond to field $H = 0$ T, open symbols to $H = 0{\cdot}8$T.

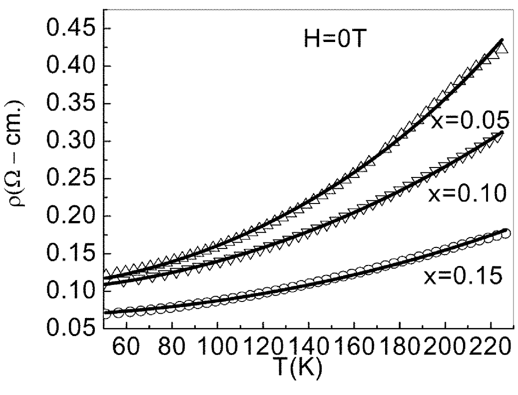


**Figure 2.** The best fit to experimental data for $La_{1-x}K_xMnO_3$ pellets in the ferromagnetic region ($50\text{ K} < T < T_{MI}$) for $H = 0$ T.

A typical fit of the experimental data with (2) is shown in figure 3. The polaron activation energy, $E_a$, is seen to be decreasing systematically with increasing $x$ (table 2).

In the low temperature region below 60 K, a minimum appears in resistivity curve for all the samples. The temperature at which the minimum occurs is substantially influenced under the applied magnetic field. Helmen and Abeles (1976) and Rozenberg *et al* (2000) argued that this low temperature minimum in manganites originates from the antiferromagnetic tunneling of the charge carriers across the grain boundaries. The field dependent tunneling resistivity is expressed as a function of temperature and field ($15\text{ K} < T < 50$ K) as

$$\rho(T, H) = \frac{\rho_0 + \rho_1 T^{3/2}}{1 + \varepsilon\langle\cos\theta_{ij}\rangle}, \quad (3)$$

where $\rho_0$ and $\rho_1$ are field independent parameters and $\langle\cos\theta_{ij}\rangle$ the spin correlation function. The spin correlation function is defined as

$$\langle\cos\theta_{ij}\rangle = -L(|J_S|/k_B T) \quad (\text{for } H = 0), \quad (4)$$

where $L(x) = [\coth(x) - 1/x]$ is the Langevin function and $J_S$ represents anti-ferromagnetic exchange between the grains. For $H \neq 0$, a simplified analytical expression for spin correlation functions of the classical Heisenberg model for ultra small systems of spins, interacting via isotropic, nearest-neighbour ($n$–$n$) exchange can be obtained as

$$\langle\cos\theta_{ij}\rangle = 1/4 - [1/3 + \exp(-3J_S/K_B T)], \quad (5)$$

where $g\mu_B H/J_S = 3/2$.

$\rho(T)$ data for all the samples are fitted to (3) with corresponding $\langle\cos\theta_{ij}\rangle$ value for both with and without field. An excellent fit is obtained for all the samples. Figure 4 shows a typical example for sample with $x = 0{\cdot}05$. The best fitted parameters ($\rho_0$, $\rho_1$, $\varepsilon$ and $J_S$) are given in table 3.

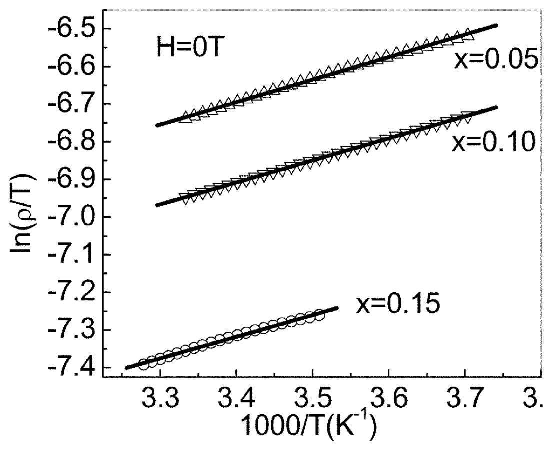


**Figure 3.** Fit to the resistivity data of $La_{1-x}K_xMnO_3$ samples according to adiabatic small polaron hopping in the paramagnetic region $T_{MI} < T < 300$ K for $H = 0$ T.

**Table 2.** Best-fit parameters corresponding to models at $T < T_{MI}$ and at $T > T_{MI}$.

| $H$ (Tesla) | $\rho_0$ (Ω-cm) | $\rho_2$ (Ω-cm $K^{-2}$) | $\rho_{4\cdot5}$ (Ω-cm $K^{-4\cdot5}$) | $B$ (Ω-cm $K^{-1}$) | $E_a$ (meV) |
|---|---|---|---|---|---|
| $x$ = 0·05 | | | | | |
| 0 | 0·102 | $5{\cdot}747 \times 10^{-6}$ | $1{\cdot}085 \times 10^{-12}$ | $161{\cdot}62 \times 10^{-6}$ | 51·48 |
| 0·8 | 0·0815 | $5{\cdot}457 \times 10^{-6}$ | $1{\cdot}261 \times 10^{-12}$ | $159{\cdot}45 \times 10^{-6}$ | 51·06 |
| $x$ = 0·10 | | | | | |
| 0 | 0·0986 | $4{\cdot}106 \times 10^{-6}$ | $0{\cdot}1446 \times 10^{-12}$ | $136{\cdot}6 \times 10^{-6}$ | 50·35 |
| 0·8 | 0·0746 | $4{\cdot}228 \times 10^{-6}$ | $0{\cdot}0604 \times 10^{-12}$ | $131{\cdot}4 \times 10^{-6}$ | 49·78 |
| $x$ = 0·15 | | | | | |
| 0 | 0·066 | $2{\cdot}16 \times 10^{-6}$ | $0{\cdot}122 \times 10^{-12}$ | $94{\cdot}24 \times 10^{-6}$ | 49·38 |
| 0·8 | 0·049 | $2{\cdot}27 \times 10^{-6}$ | $0{\cdot}113 \times 10^{-12}$ | $90{\cdot}68 \times 10^{-6}$ | 49·30 |

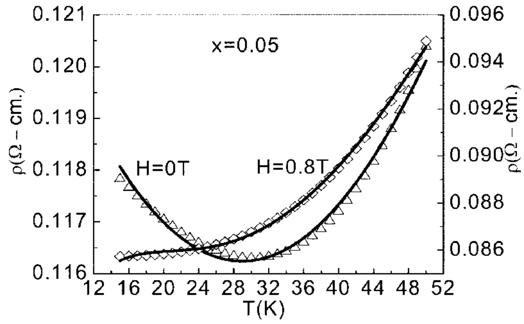


**Figure 4.** Electrical resistivity for $x$ = 0·05 sample for $H$ = 0 and 0·8 T showing the minimum. Solid lines are calculated using (3). Points are the experimental data.

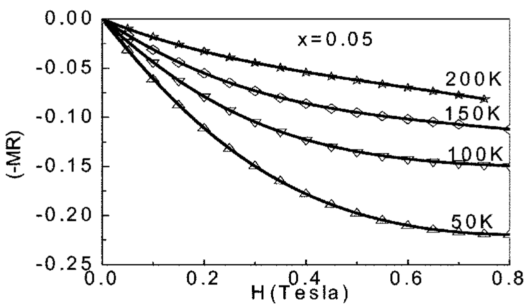


**Figure 5.** Points are the measured MR data for $x$ = 0·05 sample. Lines are the curves fitted using (7).

The field dependence of the magneto-resistance, defined as

$$\mathrm{MR} = [\rho(\mathrm{H}) - \rho(0)]/\rho(0),$$

is shown in figure 5 at different temperatures for $T << T_C$. A sharp decrease in resistance at low field, followed by a nearly linear decrease at higher field, is observed for all the samples. Taking into account the MR reported in single-crystalline manganites, Hwang *et al* (1996) proposed the crucial role of spin polarized tunneling at the polycrystalline grain boundaries as the possible origin of the low field–low temperature MR in polycrystalline manganites. According to which the magnetoresistance in polycrystalline pellets comprises of contributions from two sources, the intrinsic

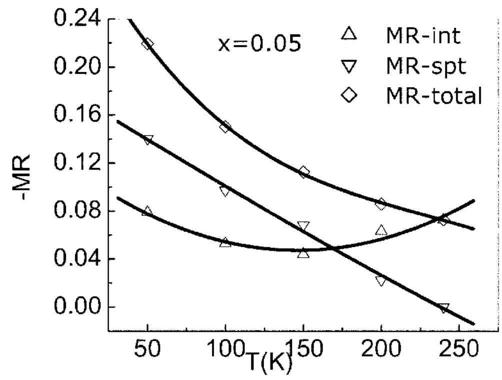


**Figure 6.** Typical contributions of the spin polarized part and the intrinsic part to the total MR for $x$ = 0·05.

part originating from double-exchange interaction between two neighbouring Mn ions, and that due to intergranular spin polarized tunneling. Magnetoresistance due to spin polarized tunneling contributes to a sharp drop in resistance at low fields and is dominant at low temperatures ($T << T_C$), whereas the intrinsic part is more pronounced near $T_C$. The observed low field decrease in resistance is supposed to be due to the progressive alignment of the magnetic domains associated with the grains by the movement of the domain walls across the grain boundaries. Raychaudhuri *et al* (1998, 1999) proposed a simple phenomenological model based on the idea of gradual slippage of domain walls across the grain boundaries pinning centres in an applied magnetic field. The total resistance, $R(H)$, is taken as the sum of a field independent part, $R_0$, arising from nonmagnetic defects and phonon scattering, a field dependent part due to spin polarized tunneling, $R_{spt}(H)$ and a part, $R_{int}(H)$, originating from the reduction of spin fluctuation, viz. $R(H) = R_0 + R_{spt}(H) + R_{int}(H)$.

Assuming the contribution of the field dependent components as:

$$R_{spt}(H) = R_{spt}(H=0)\left[1 - \int_0^H f(k)\mathrm{d}k\right], \tag{6}$$

and

$$R_{int}(H) = -aH - bH^3,$$

**Table 3.** Best-fit parameters obtained from intergranular tunneling model.

| $H$ (Tesla) | $\rho_0$ ($\Omega$ cm) | $\rho_1 \times 10^5$ ($\Omega$ cm $K^{-3/2}$) | $\varepsilon$ | $J_S/K_B$ (K) |
|---|---|---|---|---|
| $x = 0.05$ | | | | |
| 0 | 0.0731 | 6.00 | 0.4175 | 95.61 |
| 0.8 | 0.0388 | 8.00 | 6.15 | 18.41 |
| $x = 0.10$ | | | | |
| 0 | 0.0805 | 4.00 | 0.3012 | 99.78 |
| 0.8 | 0.0551 | 5.00 | 3.455 | 16.98 |
| $x = 0.15$ | | | | |
| 0 | 0.0434 | 3.00 | 0.3968 | 103.07 |
| 0.8 | 0.0219 | 4.00 | 6.2358 | 18.82 |

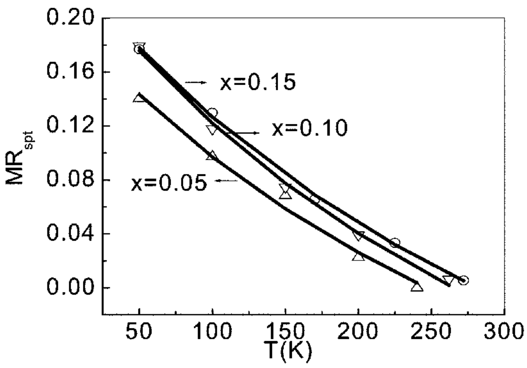


**Figure 7.** Temperature variation of spin polarized part of MR.

total MR was then derived as

$$\mathrm{MR} = -A\int_0^H f(k)\mathrm{d}k - JH - KH^3. \quad (7)$$

The first term in (7) is the contribution from spin polarized tunneling and the other two terms represent the intrinsic contribution from Zener double exchange. $J$ and $K$ are some constants. The field dependence of $R_{\mathrm{int}}(H)$ is calculated from the MR behaviour of single crystal manganites. The distribution of the pinning strength, $k$, at which the domain boundaries are pinned to the grain boundary pinning centre, $f(k)$, was mapped as a weighted average of a Gaussian and skewed Gaussian distribution, viz.

$$f(k) = A\exp(-Bk^2) + Ck^2\exp(-Dk^2), \quad (8)$$

where $A$, $B$, $C$ and $D$ are constants.

In order to fit the above expression to our data, (7) is differentiated with respect to $H$ to get,

$$d(\mathrm{MR})/\mathrm{d}H = A\exp(-BH^2) + CH^2\exp(-DH^2) - J - 3KH^2. \quad (9)$$

The measured data were then differentiated and fitted to (9). Fairly good agreement between the experimental and calculated values is obtained for all the $La_{1-x}K_xMnO_3$ samples. A typical example is shown in figure 5 for $La_{1-x}K_x MnO_3$ ($x = 0.05$).

Using the best-fit parameters, as described above, the contributions from intrinsic and spin polarized part are calculated at various temperatures and are shown in figure 6. As expected, $\mathrm{MR_{spt}}$ (0.8 T) steadily decreases with increase in temperature and its contribution becomes marginal at around 230 K. On the other hand, the intrinsic component shows the expected double exchange behaviour, viz. slow increase with increase in temperature and finally accounts for the observed total magneto resistance near $T_C$. According to Hwang *et al* (1996), the functional expression of the type, $a + b/(c + T)$, which is a characteristic of spin polarized tunneling in granular ferromagnetic systems, also fits well (figure 7) with the values of $\mathrm{MR_{spt}}$ ($H = 0.8$ T) extracted using the present model.

## 3. Conclusions

The electrical resistivity and magnetoresistance of polycrystalline $La_{1-x}K_xMnO_3$ pellets have been studied from 10–300 K. All the K-doped samples show sharp metal–insulator transition and the system becomes conducting with K-doping. The Curie temperature, $T_C$, is enhanced from 260–309 K. The electrical transport is governed by small polaron hopping in paramagnetic region whereas various scattering processes govern the resistivity in ferromagnetic region. The field dependent minima in resistivity below 60 K are explained by the tunneling of charge carriers between antiferromagnetically coupled grains. Field dependence of magnetoresistance at temperatures below $T_C$ is also described well by a phenomenological model based on spin polarized tunneling at the grain boundaries. The contributions in MR from the intrinsic part due to DE mechanism, as well as, the part originating from intergranular spin polarized tunneling are also estimated.

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