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A SHARP DECREASE OF RESISTIVITY IN $La_{0.7}Ca_{0.3}Mn_{0.96}Cu_{0.04}O_3$: EVIDENCE FOR Cu ASSISTED COHERENT TUNNELING OF SPIN POLARONS

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Nearly a 50% decrease of resistivity $\rho(T,x)$ due to just 4% Cu doping on the Mn site of $La_{2/3}Ca_{1/3}Mn_{1-x}Cu_xO_3$ is observed. Attributing the observed phenomenon to the decrease of the spin-polaron energy $E_\sigma(x)$ below $T_C(x)$, all data are found to be well fitted by the nonthermal coherent tunneling expression $\rho(T,x)=\rho_0 e^{-\gamma M^2(T,x)}$ assuming Eq.(2) for the magnetization in the ferromagnetic state. The best fits through all the data points suggest $M_0(x)\simeq\sqrt{1-x}M_0(0)$, $M_R(x)\simeq\sqrt{x}M_0(0)$, and $E_\sigma(x)\simeq E_\sigma(0)(1-x)^4$ for explicit x dependence of the Cu induced modifications of the Mn spins dominated zero-temperature spontaneous magnetization, residual paramagnetic contribution, and spin-polaron tunneling energy, respectively, with $E_\sigma(0)=0.12\,\mathrm{eV}$.

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As is well known, [1] the ground state of $La_{2/3}Ca_{1/3}MnO_3$ exhibiting colossal magnetoresistance is ferromagnetic (FM) and the paramagnetic-ferromagnetic transition is accompanied by a sharp drop in resistivity below T_C. Such a correlation is considered as a basic element for the so-called magnetically induced electron localization scenario [2-4] in which the changes of observable resistivity at low temperatures are related to the corresponding changes of the local magnetization, and a coherent nonthermal tunneling charge carrier transport mechanism dominates other diffusion processes.

The effects of elemental substitution on the properties of $La_{2/3}Ca_{1/3}MnO_3$ have been widely studied in an attempt to further shed some light on the underlying transport mechanisms in this interesting material [5-14]. In particular, substitution of the rare-earth atoms (like Y or Gd) on the La site leads to the lowering of the ferromagnetic (and "metal-insulator") transition temperature T_C due mostly to the cation size mismatch. [5, 11-14]. At the same time, the reduction of T_C and a rather substantial drop of resistivity in the FM region due to Mn ions replacement with metals (like Co or Ni) are ascribed to a weakening of the Zener double-exchange interaction between two unlike ions [1,13]. In other words, metal-ion doping was found [13] to decrease the polaron tunneling energy barrier thus facilitating the carriers transfer in the FM region.

In this Letter we present a comparative study of resistivity measurements on two manganite samples from the $La_{2/3}Ca_{1/3}Mn_{1-x}Cu_xO_3$ family for $x=0$ and $x=0.04$ and for a wide temperature interval (from 20 to 300 K). As we shall see, this very small amount of impurity leads to a marked (factor of two) drop in resistivity value, hardly understandable along the conventional scattering theories. The data are in fact well fitted by a nonthermal spin tunneling expression for the resistivity assuming a magnetization $M(T,x)$ dependent charge carrier correlation length $L(M)$.

The samples examined in this study were prepared by the standard solid-state reaction from stoichiometric amounts of La_2O_3, $CaCO_3$, MnO_2, and CuO powders. The necessary heat treatment was performed in air, in alumina crucibles at 1300° C for 2 days to preserve the right phase stoichiometry. Powder X-ray diffraction patterns are characteristic of perovskites. No appreciable changes in the diffraction patterns induced by Cu doping have been observed (suggesting thus that no structural changes have occured after replacement of Mn by Cu). Energy Dispersive X-ray microanalyses confirm the presence of copper on the manganese crystallographic sites.

The electrical resistivity $\rho(T,x)$ was measured using the conventional four-probe method. To avoid Joule and Peltier effects, a dc current $I = 1\,\mathrm{mA}$ was injected (as a one second pulse) successively on both sides of the sample. The voltage drop V across the sample was measured with high accuracy by a $KT256\,\mathrm{nVm}$. Fig.1 presents the temperature dependence of the resistivity $\rho(T,x)$ for two $La_{2/3}Ca_{1/3}Mn_{1-x}Cu_xO_3$ samples, with $x = 0$ and $x = 0.04$, respectively. Notice a rather sharp (nearly a 50%) drop of resistivity (both near the peak and on its low temperature side) for the doped sample along with a small reduction of the transition (peak) temperature $T_C(x)$ reaching $T_C(0) = 265\,\mathrm{K}$ and $T_C(0.04) = 250\,\mathrm{K}$, respectively. A kink-like behavior in the resistivity of the Cu-free sample seen just below $T_C(0)$ is most likely due to a slight oxygen non-stoichiometry induced grain boundary (GB) scattering [12]. It completely disappears upon doping, suggesting [14] a healing role of copper in reducing the GB resistivity (see below).

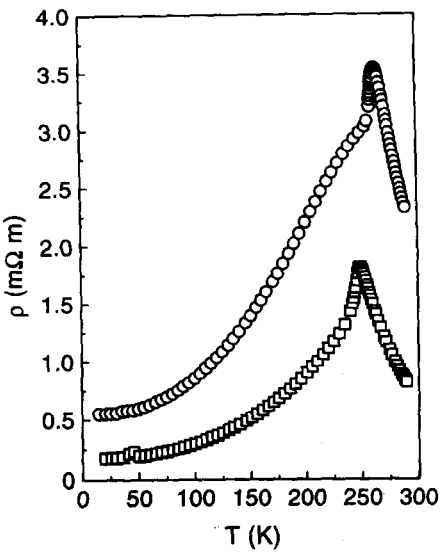

Fig.1. Temperature behavior of the observed resistivity $\rho(T,x)$ in $La_{2/3}Ca_{1/3}Mn_{1-x}Cu_xO_3$ for $x = 0$ (circles) and $x = 0.04$ (squares)

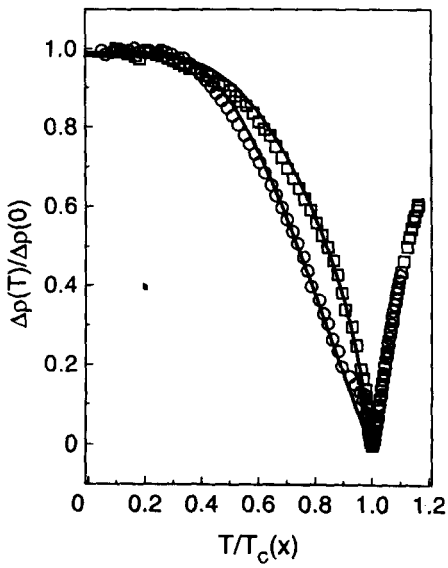

Fig.2. The temperature dependence of the normalized resistivity $\Delta\rho(T,x)/\Delta\rho(0,x)$ in $La_{2/3}Ca_{1/3}Mn_{1-x}Cu_xO_3$ for $x = 0$ (circles) and $x = 0.04$ (squares) as a function of the reduced temperature $T/T_C(x)$. The solid lines through all the data points are the best fits according to Eqs.(1) and (2)

Since no tangible structural changes have been observed upon copper doping, the Jahn – Teller mechanism can be safely ruled out and the most reasonable cause for the resistivity drop in the doped material is the reduction of the spin-polaron tunneling energy

E_σ which within the localization scenario [2 – 4] is tantamount to an increase of the charge carrier correlation length $L \simeq \hbar/\sqrt{2mE_\sigma}$ (here m is an effective polaron mass). In the FM region (below $T_C(x)$), the tunneling based resistivity reads [2, 3] $\rho[M(T,x)] = \rho_s e^{2R/L(M)}$ where $\rho_s^{-1} = e^2R^2\nu_{ph}N_m$ with R being the tunneling distance (and $2R$ being a size of a small spin polaron), ν_{ph} the phonon frequency, and N_m the density of available states. In turn, the correlation length $L(M)$ depends on the temperature and concentration of copper x through the corresponding dependencies of the magnetization $M(T,x)$. Assuming, along the main lines of conventional mean-field approximation scheme [3] that $L(M) = L_0/(1 - M^2/M_L^2)$ (with M_L being a fraction of the saturated magnetization $M(0)$), we arrive at the following expression for the tunneling dominated resistivity

$$\rho(T,x) = \rho_0 e^{-\gamma M^2(T,x)}, \tag{1}$$

with $\rho_0 = \rho_s e^{2R/L_0}$ and $\gamma = 2R/L_0M_L^2$.

To account for the observed behavior of the resistivity, we identify T_C with the doping-dependent Curie temperature $T_C(x)$, and consider that the temperature and x dependence of the magnetization is the sum of a classical Curie – Weiss contribution and a residual term, namely

$$M(T,x) = M_R(x) + M_0(x)\tanh\left\{\sqrt{[T_C(x)/T]^2 - 1}\right\}. \tag{2}$$

Specifically, $M_R(x)$ is interpreted as a copper induced residual paramagnetic contribution while $M_0(x)$ accounts for the deviation of the FM aligned Mn magnetic moments of the undoped material in the presence of copper atoms. In fact, save for the $M_R(x)$ term, Eq.(2) is an analytical (approximate) solution of the well-known Curie – Weiss mean-field equation on spontaneous magnetization, viz. $M(T,x)/M(0,x) = \tanh\{[M(T,x)/M(0,x)]\,(T_C(x)/T)\}$. Among the possible reasons for the observed sharp decline of resistivity in the Cu-doped sample is also the electronic nature of its grain boundary (GB). Indeed, since Cu(d^9) has a substantially larger ionic radius than Mn ion, it may actually improve the GB conduction (through releasing the local strain), eventually reducing the overall resistivity [14]. In order to exclude any of such extrinsic effects (related to GB scattering), we consider the normalized resistivity $\Delta\rho(T,x)/\Delta\rho(0,x)$ with $\Delta\rho(T,x) = \rho(T,x) - \rho(T_C(x),x)$ and $\rho(0,x)$ being the resistivity taken at the lowest available temperature. Fig.2 depicts the above-defined normalized resistivity versus the reduced temperature $T/T_C(x)$ for the two samples. First of all, notice that the $x = 0$ and $x = 0.04$ data merge both at low temperatures and above $T_C(x)$. The latter suggests the absence of the GB related effects in the normalized resistivity. At the same time, starting from $T_C(x)$ and below the Cu-doped (squares) and Cu-free (circles) samples follow different routes. In particular, approaching $T_C(x)$ from low temperatures, a (most likely) oxygen non-stoichiometry driven [12] crossover from undoped to doped transport mechanism is clearly seen near $T/T_C(x) \simeq 0.9$. On the other hand, a lack of the data merger below $T_C(x)$ suggests the presence of some magnetic structure related scattering mechanism, probably due to Cu spins induced modifications (domains) in the FM structure of the undoped sample. The solid lines are the best fits through all the data points according to Eqs.(1) and (2), yielding $M_0(0)/M_L = 1.41\sqrt{L_0/2R}$, $M_R(0) = 0$, $M_0(0.04) = 0.98M_0(0)$, and $M_R(0.04) = 0.06M_0(0)$ for the model parameters. Recalling that in our present study the copper content is $x = 0.04$, the above estimates can be cast (with a rather good accuracy) into the following explicit x dependencies of the residual

$M_R(x) \simeq \sqrt{x}M_0(0)$ and spontaneous $M_0(x) \simeq \sqrt{1-x}M_0(0)$ magnetizations, giving rise to an exponential (rather than power) x dependence of the observed resistivity $\rho(T,x)$ (see Eqs.(1) and (2)). Furthermore, assuming (as usual [2]) $2R/L_0 \simeq 1$ for the (undoped) tunneling distance to correlation length ratio and using the found value of the residual resistivity $\rho(T_C(0),0) = \rho_0 \simeq 3.5\,\mathrm{m\Omega m}$, the density of states [2] $N_m \simeq 9 \cdot 10^{26}\,\mathrm{m^{-3}eV^{-1}}$ and the phonon frequency $\nu_{ph} \simeq 2 \cdot 10^{13}\mathrm{s}^{-1}$ (estimated from Raman shift for optical Mn–O modes), we obtain $R \simeq 5$ Å for an estimate of the tunneling distance (corresponding to $2R \simeq 10$ Å for a spin-polaron's size) which in turn results in $L_0 \simeq 10$ Å(using a free electron approximation for a polaron's mass m) and $E_\sigma(0) \simeq 0.12\,\mathrm{eV}$ for a zero-temperature copper-free carrier charge correlation length and the spin-polaron tunneling energy, respectively, both in good agreement with reported [1–5, 9, 13] estimates of these parameters in other systems. Based on the above estimates, we can roughly estimate the copper induced variation of the correlation length $L(x)$ and the corresponding spin polaron tunneling energy $E_\sigma(x)$. Indeed, according to the earlier introduced definitions, $L[M(T_C(x))] = L_0/(1 - M_R^2(x)/M_L^2) \simeq L_0/(1-2x)$ and $E_\sigma(x) \propto L^{-2}(x)$ which lead to $L(x) \simeq L(0)/(1-x)^2$ and $E_\sigma(x) \simeq E_\sigma(0)(1-x)^4$ for small enough x. These explicit x dependencies (along with the composition variation of the transition temperature $T_C(x) \simeq T_C(0)(1-x)$) remarkably correlate with the recently observed [13, 14] transition-element (T) induced changes in $La_{2/3}Ca_{1/3}Mn_{1-x}T_xO_3$.

In summary, a rather substantial drop in resistivity $\rho(T,x)$ in a lightly Cu doped manganite $La_{2/3}Ca_{1/3}Mn_{1-x}Cu_xO_3$ sample is reported. Along with lowering the Curie point $T_C(x)$, the copper substitution is argued to add a small paramagnetic contribution $M_R(x)$ to the Mn spins dominated spontaneous magnetization M of the undoped material leading to a small decrease of the spin-polaron tunneling energy $E_\sigma(x)$. However, due to the tunneling dominated carrier transport process, this small amount of impurity is sufficient for the drastical changes in resistivity absolute value across the whole temperature range. The temperature and x dependencies of the observed resistivity was found to be rather well fitted by a nonthermal coherent tunneling of spin polarons with a heuristic expression for the magnetization $M(T,x)$ in the ferromagnetic state (as an approximate analytic solution to the mean-field Curie – Weiss equation), resulting in the exponential (rather than linear) doping dependence of $\rho(T,x)$.

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