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NEGATIVE MAGNETORESISTANCE IN A MIXED-VALENCE $La_{0.6}Y_{0.1}Ca_{0.3}MnO_3$: EVIDENCE FOR CHARGE LOCALIZATION GOVERNED BY THE CURIE–WEISS LAW

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Colossal negative magnetoresistance $\Delta\rho$ observed in $La_{0.6}Y_{0.1}Ca_{0.3}MnO_3$ at $B = 1\,T$ shows an unusual, nearly perfect symmetry (around the peak temperature $T_0 = 160\,K$) suggestive of Curie-Weiss dominated transport mechanism in this material both above and below the field-dependent Curie temperature $T_C \equiv T_0$. Attributing this symmetry to strong magnetic fluctuations below T_C (which are triggered by the Y substitution and cause a "bootstrap" destruction of the ferromagnetic phase), the data are interpreted in terms of the nonthermal spin hopping and magnetization M dependent charge carrier localization scenario leading to $\Delta\rho = -\rho_s\left(1 - e^{-\gamma M^2}\right)$ with $M(T,B) = CB/|T - T_C(B)|^{\nu}$. The separate fits through all the data points above and below T_C yield $C^+ \simeq 2C^-$ and $\nu_+ \simeq \nu_- \simeq 1$, in agreement with the predictions of the Landau mean-field theory.

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Since recently, interest in the mixed-valence manganite perovskites $R_{1-x}Ca_xMnO_3$ (where R=La,Y,Nd,Pr) has been renewed due to the large negative magnetoresistive (MR) effects observed near the ferromagnetic (FM) ordering of Mn spins [1–12]. In the doping range $0.2 < x < 0.5$, these compounds are known to undergo a double phase transition from paramagnetic-insulating to ferromagnetic-metallic state near the Curie temperature T_C. Above $x = 0.5$, the specific heat and susceptibility measurements reveal [3,6,8,9] an extra antiferromagnetic (AFM) canted-like transition at T_{AFM} lying below T_C. At the same time, substitution on the La site was found to modify the phase diagram through cation size effects leading toward either charge-ordered or AFM instability [1–3, 6, 9]. On the other hand, Babushkina et al. [1,2] have found that a composition $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ with $y = 0.75$ undergoes a metal-insulator transition even upon a mere isotopic substitution of oxygen. This conclusion has been further corroborated by Balagurov et al. [3] who determined magnetic structure of this compound (using a method of neutron diffraction) and found that substitution of ^{16}O by ^{18}O leads to the modification of electronic state which correlates both with the observed alteration of the magnetic structure and charge ordering process.

At the same time [6, 9], Y substitution is responsible for two major modifications of the parent manganite $La_{0.7}Ca_{0.3}MnO_3$: (i) it lowers the FM Curie temperature T_C, and (ii) weakens the system's robustness against strong AFM fluctuations (which are developed

locally within the ordered FM matrix) by shifting T_C closer to T_{AFM}. The latter is considered [4, 10, −13] the most probable reason for strong magnetic localization of spin polarized carriers which in turn results in hopping dominated charge carrier transport mechanism below T_C. Above T_C, the resistivity presumably follows a thermally activated Mott-like variable-range hopping law $\rho \propto \exp(T_0/T)^z$ with $1/4 \leq z \leq 1$.

In this Letter we present some typical results for magnetoresistivity (MR) measurements on a manganite sample $La_{0.6}Y_{0.1}Ca_{0.3}MnO_3$ at $B = 1\,T$ field for a wide temperature interval (ranging from 20 K to 300 K) and compare them with the available theoretical explanations. As we shall see, the data are best described in terms of the nonthermal (rather than Mott-like thermally activated) spin hopping scenario with magnetization-dependent charge carrier localization length $L(M)$ both above and below T_C. The interpretation is essentially based on the assumption of rather strong magnetic fluctuations in this material far beyond the Curie point T_C which were found [5] to dominate its magneto-thermopower behavior as well.

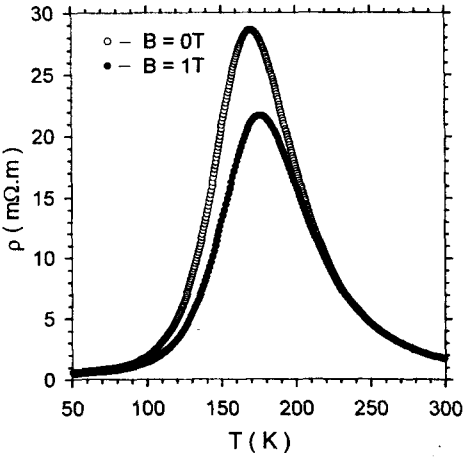

Fig.1. Temperature behavior of the observed resistivity $\rho(T, B)$ in $La_{0.6}Y_{0.1}Ca_{0.3}MnO_3$ at zero and $B = 1T$ fields

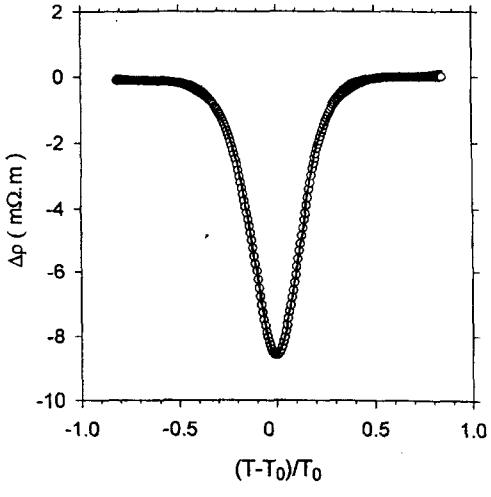

Fig.2. The dependence of the observed MR $\Delta\rho(T, B) = \rho(T, B) - \rho(T, 0)$ in $La_{0.6}Y_{0.1}Ca_{0.3}MnO_3$ at $B = 1T$ as a function of $(T - T_0)/T_0$ with $T_0 = 160\,K$ being the temperature where the MR reaches its minimum. The solid line through all the data points is the best fit according to Eq.(3)

The polycrystalline $La_{0.6}Y_{0.1}Ca_{0.3}MnO_3$ samples used in our measurements were prepared from stoichiometric amounts of La_2O_3, Y_2O_3, $CaCO_3$, and MnO_2 powders. The mixture was heated in air at 800° C for 12 hours to achieve the decarbonation and then pressed at room temperature to obtain parallelipedic pellets. An annealing and sintering from 1350° C to 800 C was made slowly (during 2 days) to preserve the right phase stoichiometry. A small bar ($10mm \times 4mm^2$) was cut from one pellet. The electrical resistivity $\rho(T, B)$ was measured using the conventional four-probe method. To avoid Joule and Peltier effects, a dc current $I = 1mA$ 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 nanovoltmeter. The magnetic field B of 1 T was applied

normally to the current. Fig.1 presents the temperature dependence of the resistivity $\rho(T,B)$ for a $La_{0.6}Y_{0.1}Ca_{0.3}MnO_3$ sample at zero and $B = 1\,T$ fields. The corresponding MR $\Delta\rho(T,B) = \rho(T,B) - \rho(T,0)$ is shown in Fig.2 as a function of reduced temperature $(T - T_0)/T_0$ with $T_0 = 160\,K$ being the temperature where the negative MR exhibits a minimum. Notice the nearly perfect symmetry of the MR with respect to left ($T < T_0$) and right ($T > T_0$) wings thus suggesting a "universal" magnetotransport mechanism above and below T_0. Before discussing a probable scenario for the observed MR temperature behavior, let us briefly review the current theoretical models. Several [10 - 13] unification approaches have been suggested. In essence, all of them are based on a magnetic localization concept which relates the observable MR at any temperature and/or applied magnetic field to the local magnetization. In particular, one of the most advanced models of this kind [10] ascribes the metal-insulator (M-I) like transition to a modification of the spin-dependent potential $J_H\mathbf{s}\cdot\mathbf{S}$ associated with the onset of magnetic order at T_C (here $J_H \simeq 1eV$ is the on-site Hund's-rule exchange coupling of an e_g electron with $s = 1/2$ to the localized Mn t_{2g} ion core with $S = 3/2$). Specifically, the hopping based conductivity reads

$$\sigma = \sigma_m \exp\left(-\frac{2R}{L} - \frac{W_{ij}}{k_B T}\right), \tag{1}$$

where

$$\sigma_m = e^2 R^2 \nu_{ph} N(E_m). \tag{2}$$

Here R is the hopping distance (typically [10], of the order of 1.5 unit cells), L the charge carrier localization length (typically [12], $L \simeq 2R$), ν_{ph} the phonon frequency, $N(E_m)$ the density of available states at the magnetic energy $E_m \simeq J_H$, and W_{ij} the effective barrier between the hopping sites i and j. There are two possibilities to introduce an explicit magnetization dependence into the above model: either by modifying the hopping barrier $W_{ij} \to W_{ij} - \alpha\mathbf{M}_i\cdot\mathbf{M}_j$ or by assuming a magnetization-dependent localization length $L(M)$. The first scenario (suggested by Viret et al. [10]) results in a thermally activated behavior of MR over the whole temperature range. Indeed, since a sphere of radius R contains $(4/3)\pi R^3/v$ sites where $v = 5.7\times10^{-29}\,m^3$ is the lattice volume per manganise ion, the smallest value of W_{ij} is therefore $[(4/3)\pi R^3 N(E_m)]^{-1}$. Minimizing the hopping rate, one finds that the resistivity should vary as $\ln(\rho/\rho_0) = [T_0\{1 - (M/M_s)^2\}/T]^{1/4}$. This scenario was used by Wagner et al. [12] to interpret their MR data on low-conductive $Nd_{0.52}Sr_{0.48}MnO_3$ films. Assuming the molecular-field result for the magnetization, they found that their data scale with the Brillouin function $\mathcal{B}$ in the ferromagnetic state and follow a $\mathcal{B}^2$ dependence in the paramagnetic state. Unfortunately, all attempts to fit our MR data with the above thermally activated hopping formula have failed. In our case the observed MR seems to follow a steeper temperature behavior exhibiting a remarkable symmetry around T_0. Instead, we were able to successfully fit our data for the whole temperature interval with

$$\Delta\rho(T,B) = -A[1 - e^{-\beta(T)}], \tag{3}$$

where

$$\beta(T) = \beta_0\left[\frac{T_0}{T - T_0}\right]^{2\nu}, \tag{4}$$

and A, β_0 and ν are temperature-independent parameters. The separate fits for our MR data above and below $T_0 = 160\,K$ produce $A = 0.873 \pm 0.001\,\Omega\,cm$, $\beta_0^+ = 0.015 \pm 0.001$,

$\beta_0^- = 0.004 \pm 0.001$, $\nu^+ = 1.16 \pm 0.01$, and $\nu^- = 1.12 \pm 0.01$, in agreement with the observed symmetry. This suggests us to interpret our findings in terms of a nonthermal localization scenario [4, 5, 13], which emphasizes the role of a nonmagnetic disorder and assumes a magnetization dependence of the localization length $L(M)$ (rather than hopping barrier W_{ij}) which diverges at the M-I phase transition. Within this scenario, the Curie point T_C is defined through the Curie–Weiss susceptibility $\chi = C/(T_C - T)$ as $\chi^{-1}(T_C, B) = 0$, while the M-I transition temperature $T_{\rm MI}$ is such that $M(T_{\rm MI}, B) = M_0$ (with M_0 being a fraction of the saturated magnetization M_s). In terms of the spontaneous magnetization M, it means that for $M < M_0$ the system is in a highly resistive (insulator-like) phase, while for $M > M_0$ the system is in a low resistive (metallic-like) state. Adopting this scenario (with $W_{ij}/k_BT \ll 2R/L$, see Eq.(1)), we can write $\rho(T, B) = \rho_0(T) + \rho_m \exp[2R/L(M)]$ for the field-induced resistivity in our sample. Here, $\rho_0(T)$ is a field-independent background resistivity, $\rho_m = 1/\sigma_m$, and the localization length $L(M)$ depends on the field and temperature through the corresponding dependencies of the magnetization $M(T, B)$. Assuming after Sheng et al. [13] that $L(M) = L_0/(1 - M^2/M_0^2)$, we arrive at the following simple expression for the MR

$$\Delta\rho(T, B) = -\rho_s \left[1 - e^{-\gamma M^2(T,B)}\right], \tag{5}$$

where $\gamma = 2R/L_0M_0^2$ and $\rho_s = \rho(T, 0) - \rho_0(T)$ is the temperature-independent residual resistivity [12]. To account for the observed symmetry of the MR around T_0, we identify T_0 with the Curie temperature $T_C(B)$ at the finite magnetic field B, and assume that the field and temperature dependence of the magnetization is governed by the same Curie–Weiss like law $M(T, B) = \chi^{\pm}(T, B)B$ with $\chi^{\pm}(T, B) = C^{\pm}/|T - T_C|^{\nu\pm}$ above (+) and below (−) T_C, respectively. Given the above definitions, we obtain $|T_C(B) - T_{MI}|^{\nu-} = C^-B/M_0$ for the difference between the two critical temperatures which implies that within the Curie–Weiss scenario, $T_{MI} \equiv T_C(0)$. Thus, in agreement with the Landau theory of the second order phase transitions (see, e.g., Landau and Lifshitz [14], Chapter V), below $T_C(B)$ the Curie–Weiss law exists in the form of the "generalized susceptibility" $\chi^-(T, B) \propto 1/B$ leading to a nonzero value of the spontaneous magnetization M even at zero magnetic field. Finally, by comparing Eq.(5) with the above-used fitting formula (see Eq.(3)), we arrive at the following relations between the fitting and model parameters, viz., $A = \rho_s$, $\beta_0^- = (2R/L_0)[1 - T_C(0)/T_C(B)]^{2\nu-}$, and $C^+/C^- = T_0^{\phi}\sqrt{\beta_0^+/\beta_0^-}$ with $\phi = \nu_+ - \nu_-$, and $T_0 = T_C(B)$. Taking into account the zero-field Curie temperature for this material [5] $\nu_{\pm}$ we obtain $2R/L_0 \simeq 1$ for the hopping distance to localization length ratio and $C^+/C^- = 1.98 \pm 0.01$ for the ratio of Curie constants above and below T_C, in accord with the mean-field theory predictions [14]. Furthermore, using the former ratio and the found value of the residual resistivity $\rho_s \simeq 0.873\Omega\,\text{cm}$ we get an estimate for the hopping distance R provided the density of states $N(E_m)$ and the phonon frequency ν_{ph} are known. Assuming [10] $N(E_m) \simeq 9 \cdot 10^{26}\text{m}^{-3}\cdot\text{eV}^{-1}$ and $\nu_{ph} \simeq 2 \cdot 10^{13}\text{s}^{-1}$ (estimated from Raman shift for optical Mn–O modes [12]) for these two parameters, we arrive at a reasonable value of $R \simeq 5.5$Å which in turn results in $L_0 \simeq 11$Å for a zero-temperature zero-field carrier charge localization length, in good agreement with the other reported [4–6, 10, 12] estimates of this parameter.

In conclusion, we would like to comment on the plausibility of our interpretation which is essentially based on the Curie–Weiss behavior of magnetization. Clearly, the possibility to use the Curie–Weiss law (which is usually limited to the critical region around T_C)

throughout the whole region (ranging from the paramagnetic to the ferromagnetic state) suggests the presence of strong fluctuations both above and below T_C. To account for a possible source of these fluctuations, we turn to the magnetic structure of our sample. As we mentioned in the introductory part, along with lowering the Curie point, Y substitution brings about another important effect. Namely, it drives the magnetic structure closer to a canted AFM phase (which occurs [9] at $T_{AFM} < T_C$) thus triggering the development of local AFM fluctuations within the parent FM matrix. In turn, these fluctuations cause a trapping of spin polarized carriers in a locally FM environment leading to hopping dominated transport of charge carriers between thus formed spin polarons, for the whole temperature interval. Besides, according to Jaime et al. [6] polaronic distortions in the PM phase of these manganites should inevitably persist in the FM phase (below T_c) as well, where there remain significant indications of spin scattering due to the collapse of large polarons in the FM state which reduces the effective exchange coupling via the double exchange mechanism, causing a "bootstrap" destruction of FM and triggering the concomitant M-I transition.

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