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Magnetoresistance and magnetic susceptibility of phase-separated La–Pr–Ca manganites

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Abstract

Electrical resistivity, magnetoresistance and magnetic susceptibility were measured for ceramic $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ samples ($y = 0.75$ and 1) with different content of ^{18}O isotope. All samples were paramagnetic insulators in the high-temperature range. Some of them became ferromagnetic (FM) metals at temperatures below 60–80 K. The high-temperature behaviour of the resistivity, magnetoresistance and magnetic susceptibility was practically identical for all samples in spite of the significant difference in their low-temperature properties. In particular, the magnetoresistance was proportional to the magnetic field squared and decreased approximately as $1/T^5$ in a wide magnetic field and temperature range. The results were interpreted based on the concept of an inhomogeneous state with pronounced FM correlations in the paramagnetic phase.

1. Introduction

The mechanisms determining the transport and magnetic properties of manganites in the paramagnetic region are of fundamental importance for the nature of the colossal magnetoresistance (CMR) effect [1]. It is well established that the tendency to phase separation is an intrinsic feature of manganites. Usually the phase separation manifests itself most clearly in magnetically ordered phases and in the vicinity of phase transitions. However, there are a lot of indications that even in the paramagnetic region, the state of the system is strongly inhomogeneous and is characterized by appreciable local ferromagnetic (FM) correlations [2–4]. Such correlations should affect both transport and magnetic properties of manganites at

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elevated temperatures. Unfortunately, the paramagnetic phase received much less attention from researchers than the magnetically ordered states. In this paper, we focus on the study of $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ in the paramagnetic phase.

The magnetoresistance and magnetic susceptibility of $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ manganites at $0.5 \leqslant y \leqslant 1$ were measured. In this concentration range of Pr, the $^{16}O \rightarrow ^{18}O$ isotope substitution results in considerable changes in the characteristics of the system under study [5, 6]. This was used to diversify the properties of samples without changing their chemical composition. The experiment was performed in the high-temperature range (80 K $< T <$ 300 K) in magnetic fields H up to 4 T, where our samples had no FM order and were characterized by a non-metallic behaviour of conductivity $\sigma(T)$. Even in the non-metallic phase, the magnetoresistance MR $= (\sigma(H) - \sigma(0))/\sigma(0)$ of manganites is rather high, attaining a value of 100%. In a wide range of parameters, it increases as the square of magnetic field, MR $= a(T)H^2$. For all samples, the factor $a(T)$ is strongly temperature dependent, $a(T) \sim 1/T^5$. The magnetic susceptibility $\chi(T)$ is relatively high and nearly obeys the Curie–Weiss law.

It has been shown that the observed effects can be interpreted assuming the existence of an inhomogeneous state with the pronounced FM correlations in the paramagnetic phase. The data on resistivity were analysed based on a simple model of the electron transport in phase-separated manganites. Taking into account the spin-dependent electron tunnelling between the FM correlated regions provides a natural explanation of the strong temperature dependence of magnetoresistance. The same model of the paramagnetic state allows us to describe the magnitude and temperature dependence of the magnetic susceptibility.

2. Samples

We used $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ ceramic samples with $y = 0.75$ and 1 and with different ^{18}O content. The details of their preparation and properties can be found in [5, 6]. The samples had the form of rectangular bars 7 mm long and the cross-section size 1 × 1 mm^2. For the present study we choose five samples with different low-temperature behaviour of the electrical resistivity $\rho(T)$. Their characteristic features are listed below.

(i) $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ with ^{16}O, exhibiting the metal–insulator transition at $T_{MI} =$ 87 K;
(ii) $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ with 30% ^{18}O and $T_{MI} = 58$ K;
(iii) $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ with complete substitution of ^{16}O by ^{18}O;
(iv) $Pr_{0.7}Ca_{0.3}MnO_3$ with ^{16}O;
(v) $Pr_{0.7}Ca_{0.3}MnO_3$ with ^{18}O.

Samples (iii)–(v) remained insulating down to the lowest temperatures. The value of T_{MI} was determined at the point of the maximum temperature derivative of $\rho(T)$ below the resistivity peak.

3. Experimental results

The temperature dependence of resistivity $\rho(T)$ at zero magnetic field is shown in figure 1 for the five samples listed above. The dc resistivity measurements were performed by the conventional four-probe method for $T = 4.2$–300 K. The obtained results agree well with

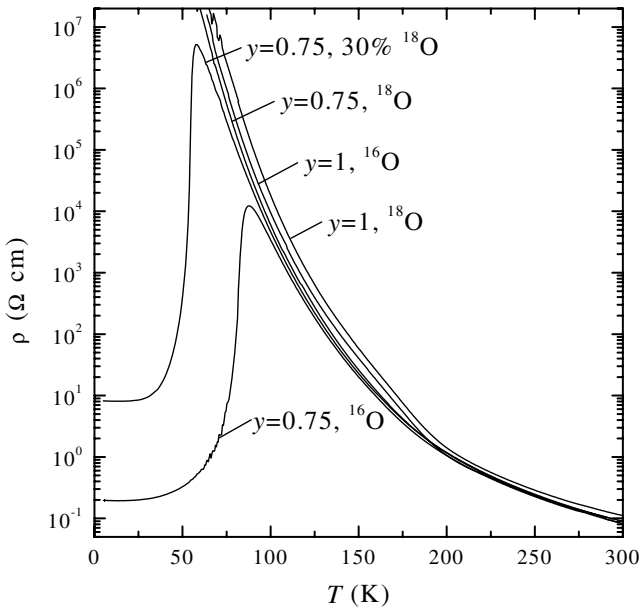

Figure 1. The temperature dependence of the electrical resistivity ρ at zero applied magnetic field for the five samples under study.

the published data for similar samples [5]. Note that in the high-temperature range the $\rho(T)$ curves for all samples are very much alike and can be fitted by the thermoactivation law

$$\rho(T) = \rho_0 T^{\gamma} \exp\left(\frac{E_g}{k_B T}\right). \tag{1}$$

The activation energy E_g is practically independent of the choice of exponent γ within the experimental error. Relationship (1) is in agreement with the results of the other authors obtained for the samples of the same type [7, 8]. Such a relationship follows from the theoretical analysis of the transport properties of the non-metallic phase-separated manganites [9].

The analysis of the low-frequency ac magnetic susceptibility $\chi(T)$ suggests the existence of the inhomogeneous state even in the paramagnetic phase of the La–Pr–Ca manganites [5, 10]. For the samples under study the $1/\chi(T)$ curves are shown in figure 2. In the high-temperature range $1/\chi(T)$ curves for all samples are rather similar, whereas the neutron experiments [6] reveal appreciable differences in their structure. Indeed, according to [6], at $y = 0.75$, the homogeneous antiferromagnetic (AFM) state is observed for the samples with ^{18}O in contrast to those with ^{16}O, in which the macroscopic phase separation into FM and AFM regions takes place. The function $\chi(T)$ can be approximated by the Curie–Weiss type law $\chi = C/(T - \theta)$ with a positive value of θ slightly increasing with temperature. The positive θ and high values of the magnetic susceptibility as compared to typical antiferromagnets are the signature of significant FM correlations, which seem give a dominant contribution to χ.

The magnetoresistance was measured in the temperature range 80–273 K at magnetic field up to 4 T. The current and the applied magnetic field were directed parallel to the long side of the sample. For all the studied samples, the conductivity increased with the applied magnetic field H. The relative change in the conductivity obeyed the universal quadratic law $\mathrm{MR} = a(T)H^2$ in almost the whole temperature and magnetic field range under study. Appreciable deviations from the quadratic law arise at lower temperatures near the metal–insulator transition. As an

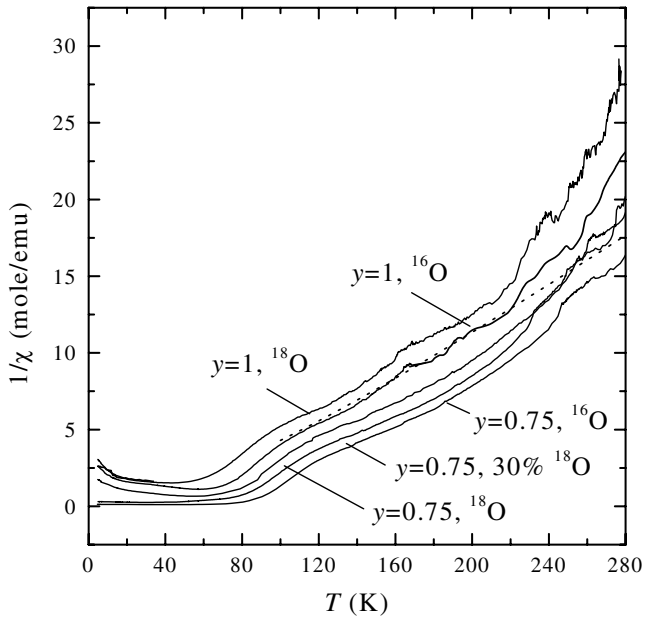

Figure 2. The temperature dependence of the inverse magnetic susceptibility $1/\chi$. Experimental data—solid curves; calculations—dashed curve. The calculations were performed at $p = 5\%$, $S = 2$, $g = 2$, $N_{ef} = 130$ and material density 6.2 g cm^{-3}.

illustration, in the inset to figure 3, we present the MR(H) dependence for the $Pr_{0.7}Ca_{0.3}MnO_3$ sample with ^{16}O within the temperature range $T = 80$–273 K. The temperature dependence of the factor a is shown in figure 3. For all the samples $a(T)$ is a fast-decreasing function, which behaves approximately as $1/T^5$.

4. Discussion

Thus, in the high-temperature region the temperature dependences of resistivity, magnetic susceptibility and magnetoresistance for all samples are very much alike both qualitatively and quantitatively (see figures 1–3). This suggests that the mechanisms determining the transport and magnetic characteristics of the studied materials in the non-metallic phase are rather similar. As mentioned above, the data on the magnetic susceptibility indicate the possible existence of the strong FM correlations in the paramagnetic state in our samples. This possibility does not contradict the current theoretical analysis of the ground state structure of manganites [1–4]. Another signature of the FM correlated domains is a relatively high and strongly temperature-dependent magnetoresistance. Indeed, the electrical resistance is of activation type (1) and it is natural to suggest that the magnetoresistance of non-metallic manganites is caused by the change in the effective activation energy $E_g(H)$ with the magnetic field. Then, we have

$$MR = \exp[-(E_g(H) - E_g)/k_B T] - 1. \tag{2}$$

According to the common concepts concerning the band structure of the magnetically ordered materials (in the framework of the s–d or Kondo lattice model), the magnetoresistance can be represented as a quadratic function of the magnetic moment M. This was confirmed in different experiments (see [1] and references therein) and agrees with our results for the low-field range where $M = \chi H$. At MR $\ll 1$, following simple dimensionality considerations,

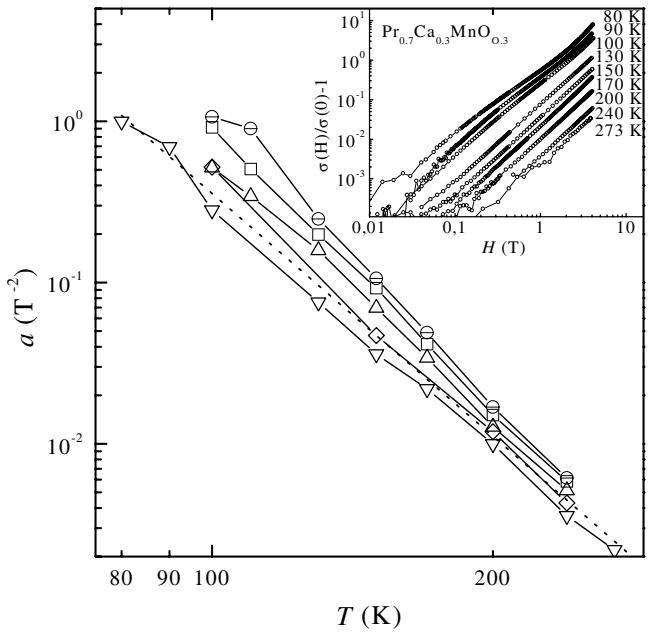

Figure 3. The temperature dependence of the factor a in the expression MR $= a(T)H^2$ for different samples. Experimental data—symbols (⊖—^{16}O, $y = 0.75$; □—30% ^{18}O, $y = 0.75$; △—^{18}O, $y = 0.75$; ◇—^{16}O, $y = 1$; ▽—^{18}O, $y = 1$); calculations according to formula (8)—dashed line. The calculations were performed at $S = 2$, $g = 2$, $Z = 6$, $N_{ef} = 130$, $J/k_B = 15$ K, $H_a = 0.5$ T and $\cos\beta = 1$. The field dependence of the magnetoresistance at different temperatures for the $Pr_{0.7}Ca_{0.3}MnO_3$ sample with ^{16}O is shown in the inset.

we can rewrite (2) as

$$MR = \frac{\chi^2 H^2}{M_s^2}\frac{\Delta E_g}{k_B T}, \qquad \Delta E_g = \frac{E_g(M^2) - E_g}{(M/M_s)^2}, \tag{3}$$

where M_s is the saturation magnetization. Substituting into (3) the measured values of MR and χ and assuming for estimates that $4\pi M_s = 1$ T we obtain, for example, $\Delta E_g \sim 0.1$ eV for $Pr_{0.7}Ca_{0.3}Mn^{16}O_3$ at $T = 150$ K. This value of ΔE_g far exceeds the characteristic energy per magnetic atom for any magnetic ordering. This estimate for ΔE_g is typical for manganites in the non-metallic state for the temperature range under study [1]. Even such a rough estimate shows that the mechanism of the magnetoresistance is related to correlated regions of rather large size. This is a manifestation of some general physics. If the system consists of non-correlated magnetic atoms, the energy of the interaction of an atom with the magnetic field $\mu_B SgH$ (where μ_B is the Bohr magneton, g is the Lande factor and S is the atomic spin) is small compared to $k_B T$ for T of the order of 100 K and higher. Thus, in the absence of correlations, the applied magnetic field could not cause significant changes in the state of the system and its transport properties.

We can describe the high-temperature magnetoresistance based on a rather simple model of the electron transport in the system with strong FM correlations. These FM correlated regions should have a higher conductivity than a non-FM host according to the double-exchange model [11]. When these regions do not overlap, the dominant contribution to the conductivity is due to the tunnelling of charge carriers between them. The tunnelling probability depends on the mutual orientations of the electron spin and the magnetic moments of the FM correlated

regions. Simple estimates show that the electron spin direction remains virtually unchanged for tunnelling over several lattice constants if the magnetic field is of the order of or lower than 1 T. Hence, the electron leaving a correlated region enters another one with the same spin and the tunnelling probability depends only on the mutual orientation of the magnetic moments of the corresponding regions. Aligning of these magnetic moments in the applied field gives rise to the increase in the tunnelling probability and consequently to the observed resistance lowering in growing magnetic field.

Let us represent the conductivity in the form $\sigma(H) = \sigma_0\langle\Sigma(H)\rangle$, where $\Sigma(H)$ is a 'spin' contribution to the electron tunnelling probability and angular brackets denote averaging over the sample volume. Under such a definition, we can write MR $= (\langle\Sigma(H)\rangle/\langle\Sigma(0)\rangle) - 1$. For a particular case of this model, the value of σ_0 was calculated in [9].

Let us consider N identical non-overlapping regions (droplets) with a preferred orientation of atomic magnetic moments within each of them. Denote the effective magnetic moment of the droplet as $M_{ef} = \mu_B g N_{ef} S$, where N_{ef} is the effective number of magnetic atoms in the droplet ($SN_{ef} \gg 1$). Neglecting the magnetic interaction between the droplets, we can write the droplet free energy in the form [12]

$$U(H) = U(0) - M_{ef}(H\cos\theta + H_a\cos^2\psi), \tag{4}$$

where θ is the angle between applied magnetic field $\boldsymbol{H}$ and the direction of $\boldsymbol{M}_{ef}$, H_a is the anisotropy field and ψ is the angle between the easy axis and the direction of the droplet magnetic moment (for simplicity, we assume the anisotropy to be uniaxial). In metallic manganites, the usual magnetic anisotropy related to the crystal lattice is rather small [13]. Then, H_a seems to be mainly determined by the shape effect [14]. For an ellipsoid, we have $H_a = \pi m_{ef}(1\text{–}3\tilde{N})$, where m_{ef} is the magnetic moment of the droplet per unit volume and $\tilde{N}$ is the corresponding demagnetizing factor. Even at relatively low eccentricity, the value of H_a is of the order of 1 T at the characteristic values of the involved parameters ($S = 2$, $g = 2$ and crystal lattice constant $d = 4$–5 Å).

Let $\boldsymbol{H}$ be parallel to the z axis and the easy axis be directed in the (x, z) plane at an angle β to the $\boldsymbol{H}$ vector. Then we have

$$\cos\psi = \sin\theta\sin\beta\cos\varphi + \cos\theta\cos\beta,$$

where φ is the angle between the x axis and the projection of the $\boldsymbol{M}_{ef}$ vector onto (x, y) plane. In the classical limit, each orientation of $\boldsymbol{M}_{ef}$ corresponds to the tunnelling probability

$$P(H, \theta, \varphi) = A(H)\exp[M_{ef}(H\cos\theta + H_a\cos^2\psi(\theta, \varphi))/k_BT], \tag{5}$$

where $A(H)$ is the normalization factor.

The electron eigenstates are the states with the conserving spin projection $s = \pm 1/2$ onto the direction of the effective magnetic field in an FM correlated region. Let us assume that the electron interacts with Z magnetic atoms in the droplet, $Z < N_{ef}$, and Z is supposed to be of the order of the number of nearest neighbours of a magnetic atom in the crystal lattice. The energy of this interaction is $E_s = -JSZs$, where J is the exchange integral. Supposing that JSZ is of the order of the Curie temperature, we readily find that E_s is much larger than the interaction energy of the electron spin with the magnetic field if $H \ll 100$ T. In this case, the effective field direction coincides with that of $\boldsymbol{M}_{ef}$. Then, the probability for the electron to have spin projection s equals

$$P_s = \frac{\exp(-E_s/k_BT)}{2\cosh(E_s/k_BT)}. \tag{6}$$

When an electron is transferred from one droplet to another, its spin turns out to be in the effective field directed at an angle ν with the respect to the effective field within the first

droplet. Hence,

$$\cos\nu = \cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\varphi_1 - \varphi_2),$$

where subscripts 1 and 2 are numbers of droplets. The work needed to transfer the electron from the first to the second droplet is equal to $\Delta E_s = E_s(1-\cos\nu)$. The respective probability of the interdroplet transition is proportional to $\exp(-\Delta E_s/k_BT)$. After averaging over all droplets with a due account of the normalizing factors, we can write the expression for $\langle\Sigma(H)\rangle$ in the form

$$\langle\Sigma(H)\rangle = \int_0^{2\pi} \mathrm{d}\varphi_1 \int_0^{2\pi} \mathrm{d}\varphi_2 \int_0^{\pi} \sin\theta_1\,\mathrm{d}\theta_1 \int_0^{\pi} \sin\theta_2\,\mathrm{d}\theta_2\, P(\theta_1,\varphi_1)P(\theta_2,\varphi_2) \times \sum_{s=\pm 1/2} P_s(\theta_1)\exp(-\Delta E_s/k_BT). \tag{7}$$

In the high-temperature limit, using (5)–(7) we get

$$MR = \frac{2}{225}(\cos^2\beta - 1/3)\frac{\mu_B^3 S^5 N_{ef}^3 Z^2}{(k_BT)^5} g^3 J^2 H_a H^2. \tag{8}$$

This expression is formally valid if k_BT is much larger than the characteristic energies E_s, that is, the Zeeman energy $\mu_B g S N_{ef} H$ and the energy of the magnetic anisotropy $\mu_B g S N_{ef} H_a$. However, the numerical calculations demonstrate that (8) remains valid even if k_BT is of the order of or slightly lower than these energies.

Magnetoresistance (8) depends explicitly on the angle β between the easy axis and the applied magnetic field. If the anisotropy is dominated by the shape effect, it is reasonable to assume that the long axes of the droplets have the preferable orientation along the applied field. Note, in addition, that the measuring current was directed along the applied magnetic field. In this case, a relatively large contribution to the conductivity is due to the droplets oriented along the magnetic field. This effect reduces the influence of the possible droplet misorientation. Therefore, in the further estimates we assume that $\cos\beta \approx 1$.

The discussed model correctly reproduces the experimentally observed dependence of the magnetoresistance on the magnetic field and temperature, MR $\sim H^2/T^5$. Let us take for numerical estimates $S = 2$, $g = 2$, $Z = 6$, $H_a = 0.5$ T and $J/k_B = 15$ K. Then, formula (8) provides the quantitative agreement with the experiment if $N_{ef} \sim 10^2$. The corresponding dependence MR(T) calculated at $N_{ef} = 130$ is shown by the dashed line in figure 3.

Following a conventional approach and making use of (5) we can calculate the magnetic susceptibility $\chi(T)$. The appropriate expression has a form

$$\chi(T) = A(0)\frac{(\mu_B g S N_{eff})^2 n}{k_BT}\int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi}\exp\left[\frac{\mu_B g S N_{eff}}{k_BT}H_a\cos^2\psi(\theta,\varphi)\right]\cos^2\theta\sin\theta\,\mathrm{d}\theta, \tag{9}$$

where n is the droplet density. For the simple cubic lattice of Mn ions, n can be related to the concentration p of FM correlated phase by an evident formula $n = p/N_{eff}d^3$. At high temperatures, $\chi(T) \propto 1/T$ since we neglect here the magnetic interaction between droplets.

At the aforementioned values of the parameters and the concentration p of the order of 5–10%, we find the correct value of $\chi(T)$ within the order of magnitude at the same $N_{ef} \sim 10^2$. The calculated $\chi(T)$ curve is shown by the dashed line in figure 2.

Thus, figures 2 and 3 demonstrate that the proposed model provides a reasonable description of the experimental data. The characteristic size of FM correlated regions turns out to be about five lattice constants. This size is corresponds to the picture of the small-scale phase separation of the ferron type [3, 4] and agrees well with the small-angle neutron scattering data [15].

5. Conclusion

The experimental data and their analysis in the framework of a simple model of electron transport provide a clear indication of the possible existence of the inhomogeneous state with strong FM correlations even in the paramagnetic phase of manganites. However, the presented picture does not reveal the actual mechanisms underlying the formation of the inhomogeneous state and needs further refinement.

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