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2011 J. Phys.: Conf. Ser. 303 012067

(http://iopscience.iop.org/1742-6596/303/1/012067)

Journal of Physics: Conference Series **303** (2011) 012067 doi:10.1088/1742-6596/303/1/012067

Low-field magnetic properties of $La_{1-x}Sr_xMn_{1-y}Fe_yO_3$

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Abstract. Low-field (B = 10 G – 1 kG) magnetic properties are investigated in ceramic samples of $La_{1-x}Sr_xMn_{1-y}Fe_yO_3$ (LSMFO) with x = 0.3 and y = 0.15, 0.20 and 0.25. A substantial decrease of the ferromagnetic (FM) Curie temperature, T_C, with increasing y is observed, which is connected to breaking of the FM double-exchange interactions by doping with Fe. Strong magnetic irreversibility at B = 10 G gives evidence for a frustrated magnetic state of LSMFO. The asymptotic Curie-Weiss behaviour of the magnetic susceptibility, χ (T), observed well above T_C, yields the values of the effective Bohr magneton per magnetic ion, exceeding considerably those of single ions. Critical behaviour of χ (T) ~ $(T/T_C - 1)^{-\gamma}$ is influenced at y = 0.15 and 0.20 by a percolative ($\gamma \approx 1.8$) and non-percolative or Heisenberg ($\gamma \approx 1.4$) spin systems. At y = 0.25 the percolative contribution to χ (T) is not observed. The low-field magnetic properties above can be explained by the phase separation effect or generation of nanosize FM particles in the paramagnetic host matrix of LSMFO.

1. Introduction

$La_{1-x}Sr_xMn_{1-y}Fe_yO_3$, briefly LSMFO, belongs to a family of mixed-valence ($Mn^{3+/4+}$) manganite perovskites, exhibiting the colossal magnetoresistance effect (CMR) [1]. The mixed valence of Mn is realized by the hole doping, including substitution of a divalent element for La^{3+} or formation of cation vacancies. Rich magnetic phase diagram and interesting transport properties of such compounds are connected basically to competition between the ferromagnetic (FM) Mn^{3+} – Mn^{4+} double-exchange (DE) and the antiferromagnetic (AF) Mn^{3+} – Mn^{3+} superexchange interactions [1]. In addition, the properties of manganites and related CMR compounds are determined by interplay between orderings of the spin, the charge and the orbital degrees of freedom, as well as by a phase separation or generation of the nanosize hole-rich FM particles in the paramagnetic (PM) or AF host matrix [1, 2].

Doping with Fe influences strongly the magnetic and the transport properties of manganite perovskites, including LSMFO [3, 4]. In $La_{1-x}Ca_xMn_{1-y}Fe_yO_3$ such influence is connected to additional microscopic disorder, induced by Fe [5, 6]. Another possible reason may be connected to suppression of the FM properties of a material by doping with Fe, because a direct replacement of Mn^{3+} by Fe^{3+} takes place in manganites and Fe^{3+} does not support the DE interactions in the Fe^{3+} – Mn^{4+} pairs [3, 4].

In this paper is investigated influence of Fe on the low-field magnetic properties of LSMFO.

2. Results and discussion

LSMFO samples with x = 0.3 and y = 0.15, 0.20 and 0.25 (marked below as # 15, # 20 and # 25) were obtained with the conventional solid-state reaction method [1]. According to the x-ray diffraction data all samples had a rhombohedrally distorted structure (space group R-3c) with lattice parameters a = 5.508(4), 5.513(2) and 5.513(4) Å and c = 13.365(6), 13.360(4) and 13.376(7) Å for # 15, # 20 and # 25, respectively. The size of the grains in ceramic LSMFO samples were of few micrometers, and the homogeneous and stoichiometric distribution of the elements over the volume of samples and in separate grains was observed with the microprobe and scanning-tunneling microscopy analyses. Magnetization M (T) was measured with an RF-SQUID magnetometer after cooling the sample from the room temperature down to 5 K in zero magnetic field (M_{ZFC} or zero-field cooled) or in fields of B = 10 G, 0.5 kG and 1 kG (M_{FC} or field-cooled). Temperature dependence of the thermoremanent magnetization (TRM) was measured after cooling the sample from 300 K down to 3 K in the field of 10 G and then reducing the field to zero.

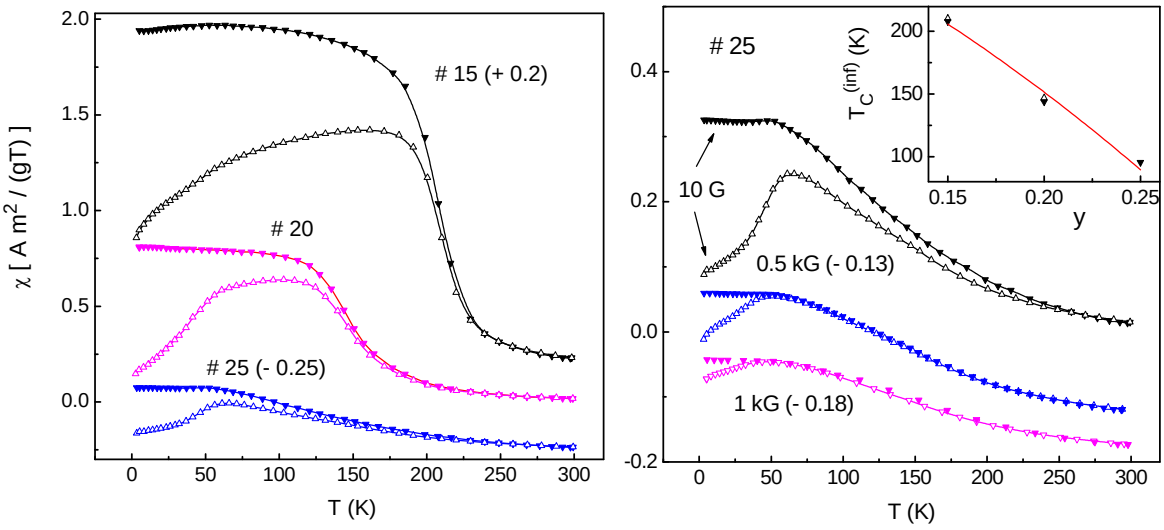

Figure 1. Temperature dependences of χ_{ZFC} (Δ) and χ_{FC} (▼) in LSMFO samples at B = 10 G (left panel) and in # 25 in various magnetic fields (right panel). Some of the plots are shifted along the vertical axis by the values given in parenthesis. Inset: The dependence of $T_C^{(inf)}$ on y, obtained in the ZFC (Δ) and FC (▼) regimes. The solid line is the fit with equation (1).

In the left panel of figure 1 one can see that both χ_{ZFC} (T) and χ_{FC} (T) (where $\chi \equiv M / B$) exhibit at B = 10 G a FM transition at a Curie temperature, T_C, defined initially by inflection of the corresponding curves ($T_C^{(inf)}$). In # 25 the transition is broaden, whereas the values of χ (T) are decreased substantially. It should be mentioned also a strong decay of $T_C^{(inf)}$ with y, as evident from the inset to the right panel of figure 1. In manganite perovskites analysis of T_C can be done with the Varma model [7], predicting the expression

$$kT_C \approx 0.05\, W\, c\, (1 - c), \qquad (1)$$

where W is the width of the electron band and c is the concentration of the holes or Mn^{4+} [7]. Because Fe^{3+} substitutes directly Mn^{3+} and do not support the DE interactions (see section 1), in LSMFO one can put $c \approx c_0 - y$, where $c_0 \sim x$ and deviations from x may be due to the cation vacancies [1]. The

values of W = 2.6 ± 0.1 eV and c_0 = 0.31 ± 0.01 are obtained by fitting the dependence of $T_C^{(in)}$ (y) with equation (1) (the solid line in the inset to the right panel of figure 1). Hence, c_0 deviates from x = 0.3 only negligibly, whereas W coincides within the error with the value of $W \approx 2.5$ eV in $La_{1-x}Sr_xMnO_3$ [7]. Therefore, the decay of T_C with y in LSMFO is determined by breaking of the DE interaction by Fe^{3+}, whereas the disorder induced by doping with Fe plays a negligible role.

Another important feature of figure 1 is the magnetic irreversibility or deviation of χ_{ZFC} (T) from χ_{FC} (T). The magnetic irreversibility is damped strongly with increasing field in # 25 (right panel of figure 1) and disappears completely in # 15 and 20 already at B = 1 kG (not shown).

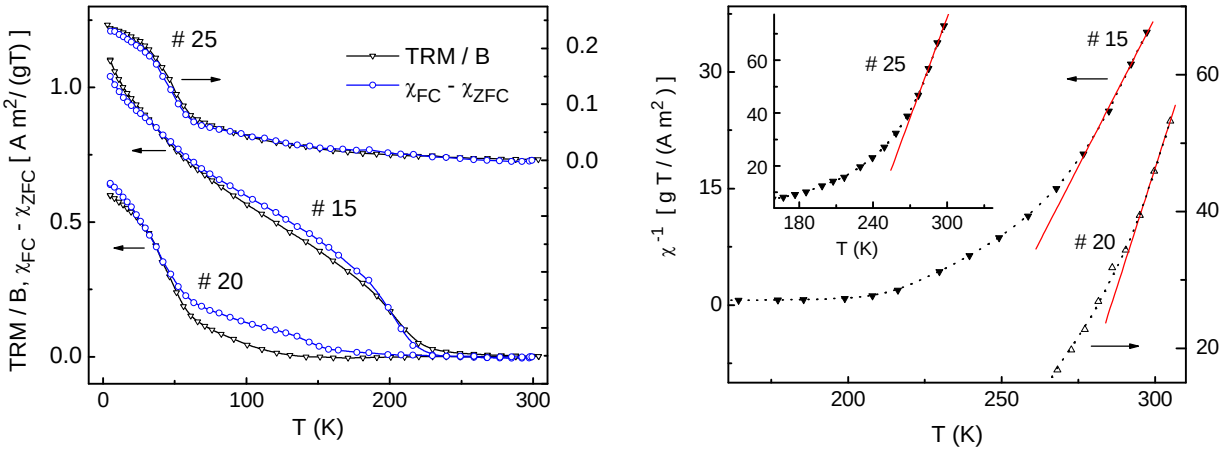

Figure 2. Temperature dependences of TRM / B (∇) and $\chi_{FC} - \chi_{ZFC}$ (O) (left panel) and the plots of χ^{-1} versus T in the ZFC (Δ) and FC (▼) regimes (right panel) for the LSMFO samples. The solid lines are linear fits and the dotted lines are to guide the eye.

Additional features of the magnetic irreversibility in LSMFO are displayed in the left panel of figure 2, where the plots of the TRM / B versus T are compared with the difference of χ_{FC} (T) − χ_{ZFC} (T). One can see a reasonable coincidence of these plots for # 25 and clear divergence for # 15 and # 20. The irreversible magnetic behavior in figure 1 and in the left panel of figure 2 indicates a frustrated magnetic state of LSMFO. Such behavior is pertinent to spin-glass (SG) or cluster-glass (CG) phases, which set in below the onset of freezing of the magnetic moments in conditions of competing interactions between the moments [8]. In the SG phase the expression TRM (T) = M_{FC} (T) − M_{ZFC} (T) reflects a symmetry of the energy distribution of potential barriers in the presence or absence of the external magnetic field [9]. In the CG phase this symmetry may be broken due to the anisotropy, associated with the shape and orientation of the magnetic clusters, leading to violation of the expression above [9].

The irreversibility disappears well above T_C and an asymptotic Curie-Weiss behavior is observed (the right panel of figure 2), given by the law χ (T) = C / (T − θ), where $C = p_{eff}^2 \mu_B^2 N / (3k)$ is the Curie constant, p_{eff} is the effective Bohr magneton (μ_B) number per magnetic ion, N is the concentration of the magnetic ions and θ is the Weiss temperature. The values of $p_{eff}^2 \approx 240 - 280$, 280 – 300 and 140 – 180 for # 15, # 20 and # 25, respectively, are obtained with the linear fit of the plots of χ^{-1} versus T (the solid lines in the right panel of figure 2), if N is taken equal to the concentration $N_0 = 1.42 \times 10^{22}$ cm^{-3} of magnetic ions in LSMFO. Hence, p_{eff}^2 exceeds considerably the

corresponding values of $p_{eff}^{\ 2}$ = 24, 15 and 35 for Mn^{3+}, Mn^{4+} and Fe^{3+} single ions, respectively. This implies the phase separation with the onset already above the room temperature and well above T_C.

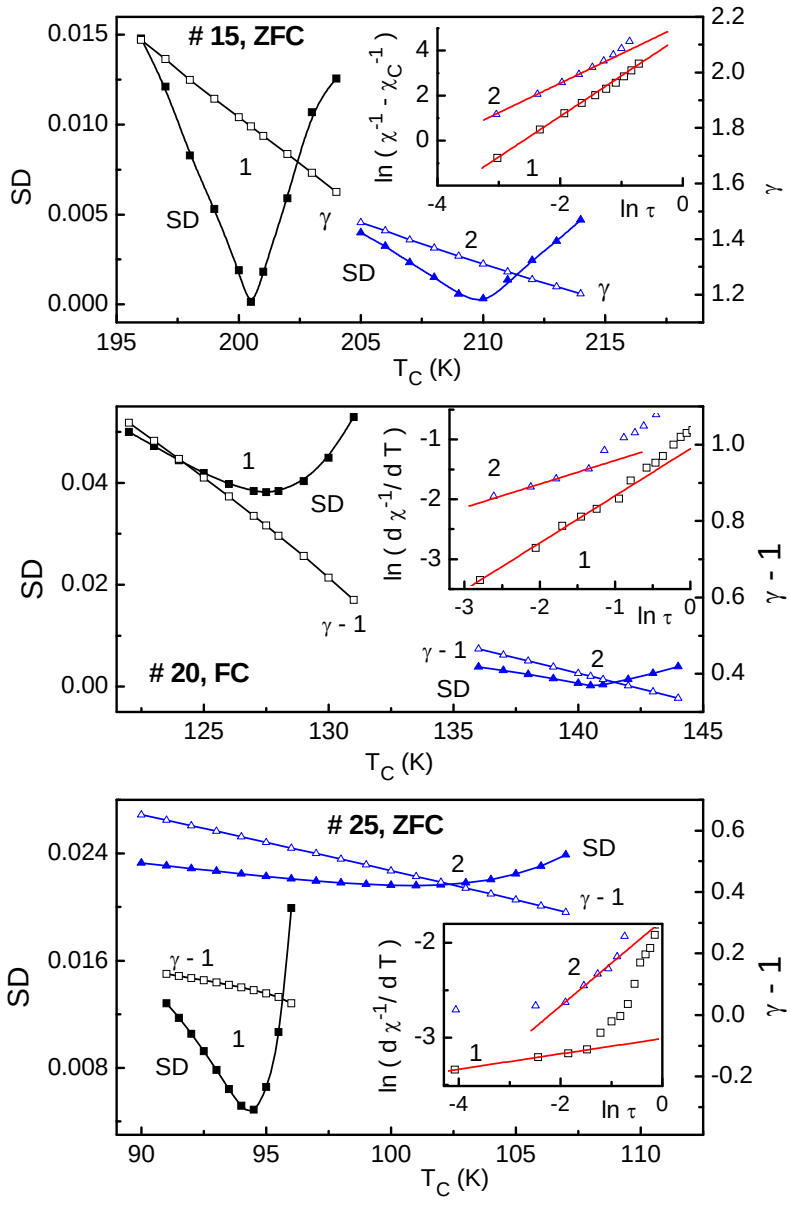

Figure 3. The dependences of SD and γ (top panel) or γ – 1 (middle and bottom panels) on T_C in the intervals Δ T_1 (1) and Δ T_2 (2) in the investigated LSMFO samples. Insets: the plots of ln ($\chi^{-1} - \chi_C^{-1}$) (in arbitrary units) vs. τ (top panel) and the plots of ln (d χ^{-1} / d T) (in arbitrary units) vs. τ (middle and bottom panels) in the intervals Δ T_1 (1) and Δ T_2 (2) for the LSMFO samples. The lines are linear fits.

The deviation from the Curie-Weiss dependence with lowering the temperature in the right panel of figure 2 is attributable to the critical behaviour of $\chi\ (T) \sim (T / T_C - 1)^{-\gamma}$ at $T \to T_C$, where γ is the critical exponent, depending on the nature and dimensionality of a spin system [10]. The behavior of $\chi\ (T)$ is analyzed here using the critical law above, presented in the two following forms,

$$\chi^{-1} - \chi_C^{-1} \sim \tau^{\gamma} \quad \text{and} \quad \mathrm{d}\,\chi^{-1} / \mathrm{d}\,T \sim \tau^{\gamma - 1}, \tag{2}$$

where $\tau = T / T_C - 1$ and $\chi_C^{-1}\ (T) \equiv \chi^{-1}\ (T_C)$. Such procedure is performed by interpolation of $\chi\ (T)$ and variation of T_C by a step of 0.5 – 1 K, to obtain the minimum standard deviation (SD) of the plots of ln $(\chi^{-1} - \chi_C^{-1})$ versus τ and ln $(\mathrm{d}\,\chi^{-1} / \mathrm{d}\,T)$ versus τ. This yields the pairs of T_C and γ or T_C and $\gamma - 1$, applying the first or the second of equations (2), respectively, and the optimum temperature interval, ΔT, corresponding to the minimum of the SD vs. T_C plots.

Some examples of the analysis described above are exhibited in figure 3. For all LSMFO samples in both ZFC and FC regimes at $B = 10$ G were found two different intervals, ΔT_1 and ΔT_2, where the formal dependence of SD (T_C) exhibited a distinct minimum, corresponding to $T_C^{(1)}$ and $T_C^{(2)}$ with $T_C^{(1)} < T_C^{(2)}$, and to different values of γ_1 and γ_2. Both $T_C^{(j)}$, $j = 1$ and 2, exhibit a decrease with y alike $T_C^{(\mathrm{inf})}$. The values of γ_1 and γ_2 in # 15 and # 20 are concentrated closely around the values of $\gamma_p = 1.80$ and $\gamma_H = 1.39$, respectively, which characterize a percolative spin system [11] and non-percolative (Heisenberg) spin system [10], respectively. In # 25 γ_2 is close to γ_H, as well, whereas γ_1 is found to lie near the mean-field value, $\gamma_{mf} = 1$ [10], implying the absence of the percolation behavior.

Therefore, in # 15 and # 20 the complex critical behavior of $\chi\ (T)$ reflects coexistence of two different spin systems. The first one is connected to generation of large and strongly correlated FM clusters, attributable to the phase separation and percolation by joining of nanosize FM particles into critical clusters when T is decreased [2]. The second system demonstrates the features, pertinent to an assembly of smaller and weakly correlated magnetic units and can be associated with the material, which do not enter the percolative critical clusters. Such units can exist because the volume fraction, η, of the second (FM) phase, has been estimated to be only ~ 0.29 [12] to achieve eventually the percolative FM transition at $T_C^{(1)} < T_C^{(2)}$.

In # 25 influence of the percolative spin system on the critical behavior of $\chi\ (T)$ is not observed. At this point it is important to note that in # 25 the FM properties are pronounced much weaker than in # 15 and # 20, but the irreversibility is enhanced (figure 1). In addition, the good coincidence of the plots of TRM/B versus T and $\chi_{FC}\ (T) - \chi_{ZFC}\ (T)$ is consistent with absence of large percolative clusters in # 25, whereas divergence of the corresponding plots for # 15 and # 20 is in line with presence of such clusters (the left panel of figure 2). Hence, it is possible to attribute ferromagnetism of LSMFO presumably to the first (percolative) spin system, whereas frustration and magnetic irreversibility to the second (non-percolative) system.

It is worth mentioning that influence of the percolative and non-percolative (Heisenberg) processes on the critical behavior of $\chi(T)$ has been observed in thin films of $La_{1-x}Ca_xMnO_3$ [13], as well as in bulk $La_{1-x}Ca_xMn_{1-y}Fe_yO_3$ [5] and $La_{1-x}Ba_xMnO_3$ [14], which reflects universality of the phase separation effect in manganite perovskites and related CMR compounds [2]. Similar to the aforementioned papers [5, 13, 14], one can estimate the following parameters, addressed to the onset of the percolation critical behavior in LSMFO: $\eta \approx 0.16$ and 0.11, the mean radius of FM particles $r \approx$ 3.4 nm and 3.8 nm and the mean magnetic moment $\mu/\mu_B \approx 0.9\times10^4$ and 1.1×10^4 in # 15 and # 20, respectively. All these data are quite typical of the nanosize hole-rich FM clusters in manganite perovskites and other CMR materials, obtained with macroscopic (magnetization) [5, 13 ,14], as well as with various microscopic [15 – 17] methods.

3. Conclusions

Investigations of the low-field magnetic properties of LSMFO give evidence for coexistence of the FM and irreversible magnetic properties. Strong decay of T_C with y is explained by damping of the DE interactions by doping with Fe. Asymptotic Curie-Weiss behavior well above T_C yields the values of p_{eff}, incompatible with those of single magnetic ions. The complex critical behavior of χ (T) demonstrates existence of the percolative and non-percolative or Heisenberg spin systems. The observed low-field magnetic properties of LSMFO are explained by the phase separation, pertinent to the manganite perovskites and leading to generation of nanosize FM clusters in the PM host matrix.

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