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Landau mean-field analysis and estimation of the spontaneous magnetization from magnetic entropy change

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Abstract

We investigated the critical exponents for the compounds $La_{1-x}\Box_x MnO_3$ (x = 0.1; 0.2 and 0.3) prepared by the sol-gel method. Our samples show a second-order transition inferred from the positive slope, in accordance with the Banerjee Criterion. Using the slope of different models on the T_C , the relative slope (RS) was traced. From this perspective, the best models for the three samples prove to be the mean field and the tricritical mean field models. This model is characterized by critical exponents β , γ and δ which are determined by many methods such as MAP, KF method and critical isotherm analysis.

The theoritical methods and experimental results were in good agreement for the three compounds. The universality class has been shown. After detremining the spontaneous magnetization for x = 0.2 from $(-\Delta S_M)$ vs. M², we detected a good agreement with those obtained from the classical extrapolation of Arrott curves (μ_0 H/M vs. M²). Furthermore, based on the magnetocaloric effect (MCE), Landau's theory is valid for the compound x = 0.2.

Keywords: Landau, Spontaneous magnetization, Magnetic refrigeration, Mean field model, Tricritical mean field, Heisenberg model, Ising model.

I. Introduction

In the past few years, perovskite-type $A_{1-x}B_xMnO_3$ has attracted the attention and aroused the interest of multiple scientist for its metallic nature, large bandwidth, and magnetic phase transition around the room temperature **[1]**. The magnetocaloric effect which

discovered by the German physicist Warburg Win 1881 in the iron **[2]**, was found in many perovskites and observed around the Curie temperature. Nowadays, the magnetic refrigeration is presented as the competing technique for conventional systems.

Several studies have been performed in the field of perovskite type ABO₃ and very significant finding have revealed the great potential of materials for spin-polarized or spintronic electronics [3-5]. Among the most studied materials, we mention manganesebased perovskite oxides, whose chemical formula is LnMnO₃, where Ln is a trivalent rareearth. The substitution of lanthanum by divalent earth cations triggers the variation of their crystallographic, magnetic and electrical properties [6]. Furthermore, the preparation method plays a crucial role in the variation of the physical property of manganite. For instance, the decrease of Curie temperature is related not only to the change of the Mn-O-Mn bond-angle but also to the Mn-O distance and induces a transition from the paramagnetic to the ferromagnetic phase transition [7]. Other phenomena such as frustration can be stated. Indeed, frustration is present in both magnetism and other areas, namely non-magnetic ceramics [8], water ice [9, 10], liquid crystals [11] and even superconductors [12]. However, magnetism seems to be an interesting field of investigation based on a large number of techniques. In the field of magnetism, frustration can yield several applications as highlighted by Ballou and Lacroix [9]. In fact, some frustrated systems, such as the $Gd_2Ti_2O_7$ compound [13], can have a tremendous magnetocaloric effect. Various models including that of Hamed, Landau and Monte carlo have been set foward to simulate the experimental and theoretical results [14-16].

Within this framework, it is worthnoting that the discovery of a magnetocaloric effect is defined by the heating or cooling of certain magnetic materials under the application or removal of an external magnetic field **[17]**. Recently, the discovery of colossal magnetoresistance (CMR) in manganese-based oxides, such as Ln_{1-x}A_xMnO₃ (Ln = rare earth, A = Ba, Ca, Sr ...) has gained considerable interest. Actually, it has been thoroughly explored in a totally new field, namely spin electronics, for both theory (magnetic and electrical structural transitions) and its interpretation, such as the double exchange (DE)**[18]**, super exchange (SE) **[19]**, electron-phonon coupling **[20]**, Griffiths phase **[21]** (GP). A basic question, which arises related to the FM/PM transition, centers around the class of universality depending on the dimensionality of the space and the parameter of order. The study of critical behavior with the DE model has been characterized for the first time in the mean field theory **[22]**. However, recent theoretical studies based on the

DE model have predicted that the FM-PM transition in manganites should belong to the Heisenberg universality class at a 3D dimension **[23-26]**. On the other side, the experimental estimates for critical exponents are still controversial, including those of the Heisenberg model with short-range interactions, values of mean field theory, and those which cannot be classified in any other universality class.

In this paper, the critical exponent and the Curie temperature for the compounds are determined resting on a modified Arrot plot **[27]**, Kouvel–Fisher methods **[28]** and critical isotherm. Subsquently, spontaneous magnetization (M_{spont}) was estimated and then compared to that estimated from the classical extrapolation of the Arrott curves (μ_0 H/M vs. M²) and from the magnetic entropy change ((- ΔS_M) vs. M²) for *x* = 0.2. Landau mean-field analysis was carried out to specify the magnetic entropy change (- ΔS_M) near the Curie temperature.

II. <u>Experimental details</u>

The series of La_{1-x} \square_x MnO₃ (x = 0.1; 0.2 and 0.3) were prepared by sol-gel method using the lanthanum nitrate, manganese nitrate, citric acid and glycol ethylene. The steps of this method were reported in reference **[29]**. The samples cristallize in the rhombohedral space group with R3c with the existance of the secondary phase Mn₃O₄ for x = 0.3. A Vibrating Sample Magnetometer (VSM) in Physics Department-I3N, University of Aveiro (Portugal) was invested for the magnetic measurements (magnetization versus applied magnetic field in a temperature range near T_c). To extract the critical exponent of the samples accurately, isothermal magnetization data as a function of magnetic field were analyzed in the range of 0–2 T, in the vicinity of the PM to FM phase transition. These isothermals are adjusted by a demagnetization factor D that has been estimated by a standard procedure from low-field DC magnetization measurement at low temperatures ($\mu_0 H = \mu_0 H_{app}$ -DM).

III. <u>Results and discussion</u>

Fig.1 presents the variation of M vs μ_0 H for different temperatures, in steps of 3 K for x = 0.1 and 4 K for x = 0.2 and 0.3. These curves depict that the state is FM for T < T_C, and is PM for T > T_C. A positive slope (**fig.2**) portrays that the second- order PM-FM transition can be estimated for these compounds according to the Banerjee criterion [**30**].

Based on 4 models (**mean filed model** β = 0.5 and γ = 1, **tricritcal mean field model** β = 0.25 and γ = 1, **Heisenberg model** β = 0.365 and γ = 1.336 and **Ising model** β = 0.325 and γ = 1.24) **[31-33]**, the variation of M^{1/ β} vs (μ_0 H/M)^{1/ γ} was traced in **Fig.2**. Changer

fig.2a. en fig2 et fig.2.b. en fig.3 et ainsi de suite

In order to determine the best model, the variation of the relative slope (RS) was traced versus temperature in **Fig.3**. (RS) was calculated by dividing the slope of the curve in each temperature by its slope in T_c, (S(T)/S(T_c)). The curve closet to the horizontal line (RS = 1) corresponds to the most applicable model. We noticed that the mean field is the best model for x = 0.1 and the tricritical model for x = 0.2 and 0.3. Afterwards, we traced M_s (T) and $1/\chi$ (T) (MAP) (**Fig.4**) and the variation of ((M_s)/ (dM_s/dT)) and (($1/\chi$)/ d($1/\chi$ /dT)) (KF) **Fig.5**, in order to detremine the value of β , γ and T_c. The values of these three unknown parameters were determined by the fitting of M_s (T) and $1/\chi$ as indicated in the following relation:

$$\begin{split} &M_{S}(T) = M_{0}(\text{-}(T\text{-}T_{C})/T_{C})^{\beta}, T < T_{C} \text{ (1)} \\ &\chi_{0}^{-1}(T) = \left(\frac{h_{0}}{M_{0}}\right) ((T - T_{C})/T_{C})^{\gamma}, T > T_{C} \text{ (2)} \end{split}$$

And $((M_S)/(dM_S/dT))$ and $((1/\chi)/d(1/\chi/dT))$ by the following relation:

$$M_s/dM_s/dT$$
)=((T-T_c)/ β),Tc (3)

$$\chi_0^{-1}/d\chi_0^{-1}/dT) = ((T - T_C)/\gamma), T > T_C$$
 (4)

Based on the variation of M_s (T) and $1/\chi$ (T) illustrated on Fig.3.a, we report that the values of β , γ and T_c for the two samples are:

For x = 0.

$$\begin{cases} \beta = 0.44 \pm 0.03 \text{ with } T_{C} = 214 \pm 1.10 \\ \gamma = 1.01 \pm 0.18 \text{ with } T_{C} = 215 \pm 2.30 \end{cases}$$

For x = 0.2

$$\begin{cases} \beta = 0.23 \pm 0.005 \text{ with } T_C = 298.36 \pm 0.12 \\ \gamma = 0.89 \pm 0.46 \text{ with } T_C = 298.07 \pm 4.19 \end{cases}$$

For x = 0.3
$$\left\{ \begin{cases} \beta = 0.22 \pm 0.06 \text{ with } T_{C} = 295 \pm 0.54 \\ \gamma = 1.13 \pm 0.53 \text{ with } T_{C} = 294 \pm 3.43 \end{cases} \right\}$$

By examining the variation of ((M_s)/ (dM_s/dT)) and ((1/ χ)/ d(1/ χ /dT)) on **Fig.3-b**, the values of β , γ and T_c for our compound are:

For x = 0.1

$$\begin{cases} \beta = 0.42 \pm 0.03 \text{ with } T_{C} = 214 \pm 1.86 \\ \gamma = 0.95 \pm 0.13 \text{ with } T_{C} = 215 \pm 1.97 \end{cases}$$
For x = 0.2

$$\begin{cases} \beta = 0.22 \pm 0.02 \text{ with } T_{C} = 298 \pm 3.22 \\ \gamma = 0.83 \pm 0.017 \text{ with } T_{C} = 298 \pm 1.66 \end{cases}$$
For x = 0.3

$$\begin{cases} \beta = 0.21 \pm 0.02 \text{ with } T_{C} = 297 \pm 6.99 \\ \gamma = 1.21 \pm 0.13 \text{ with } T_{C} = 294 \pm 0.95 \end{cases}$$

 β , γ and T_c were given from the intercept of T axes with M_s and 1/ χ curves. The values of β and γ obtained by both methods MAP and KF for *x* = 0.1; *x* = 0.2 and *x* = 0.3 prove to be

very close (see Table 1).

Another parameter δ related to β and γ can be detremined by the experimental or theoretical results. This parameter is δ is given by the following relations:

$$\delta = 1 + \frac{\gamma}{\beta}$$
 (5)

And to M (T) by:

$M=D^*H^{1/\delta}$ when $T=T_C$ (6)

Applying the logarithm, the equ (6) becomes:

$Ln(M)=Ln(D)+(1/\delta)Ln(H)$ (7)

As a result, **Fig.6** exhibits the variation of Ln(M) vs Ln (μ_0 H) for T = T_C for the 3 compounds. The slope of linarly fitted curve is the value of δ and equal to 3.75; 6.95 and 5.27 for x = 0.1; 0.2 and 0.3 respectively. Based on equ (7) and referring to the values of β and γ determined by the modified arrot plot method, the value of δ is 3.29; 5.33 and 6.23 for x = 0.1; 0.2 and 0.3 respectively. Relying on KF method, the values are equal to 3.26; 5.52 and 6 for x = 0.1; 0.2 and 0.3 respectively. The difference between the experimental and theoretical can be accounted for in terms of experiments errors **[34]**.

Therfore, we deduce that the obtained values go in good accordance with those given by the theoretical models: mean field and Tricritcal mean field models.

Eventually, we traced the variation of $\frac{M}{|\epsilon|^{\beta}}$ vs $\frac{\mu_0 H}{|\epsilon|^{(\beta+\gamma)}}$ using the critical exponent β and γ in order to check to scaling behaviour. The choice of β and γ whether by MAP or KF yielded values close to the values of two models.

Fig.7 presents $\frac{M}{|\epsilon|^{\beta}}$ versus $\frac{\mu_0 H}{|\epsilon|^{(\beta+\gamma)}}$ for our compounds. The curves were plotted for temperatures below and above T_C. The inside graph stands for the same data but on a loglog scale for the three samples.

It can be clearly detected in **Fig.7** that the scale behaviour is well verified for all samples, i.e., all points were regrouped on two curves, one for $T < T_c$ and the other for $T > T_c$.

Therefore, the values of the critical exponent and the Curie temperature are in good agreement.

Moreover, Fisher et al. **[35]** carried out an analysis of the renormalization group of systems with an exchange interaction of the form J (r) = $1 / r^{d+\sigma}$ (d is the dimension of the system and σ is the scope of the system interaction). If σ is less than 3/2, the mean-field exponents hold, while the Heisenberg exponents hold for σ greater than 2. For the

intermediate range, i.e., for J (r) ~ $r^{-3-\sigma}$ with $3/2 \le \sigma \le 2$, the exponents belong to a different universality class depending on σ [36].

Numerous researchers elaborated the effect of the universality class like Gharsallah et .al [37] who argued that the average grain size plays an important role. Others illustrated the existence of boundary between the first (x < 0.4) and the second-order (x > 0.4). For instance for the compound $La_{1-x}Ca_xMnO_3$ when x = 0.4, the dominant model is tricritical mean field ($\beta = 0.25$, $\gamma = 1.03$, and $\delta = 5$) [38]. A first-order transition in La_{2/3}Ca_{1/3}MnO₃ and across over continuous phase transition on either side of phase diagram indicate that Ca-doped manganites are distinct from other manganites [39]. In the case of electrondoped manganite $La_{0.9}Te_{0.1}MnO_3$ [40], the nature of the magnetic transition is completely different from that of hole-doped manganites. However, the composition of La_{0.9}Te_{0.1}MnO₃ might be close to a tri-critical point in the La _{1-x}Te_xMnO₃ phase diagram [40]. Baaziz et .al [41] emphasized on the effect of the annealing temperature for the compound $La_{0.67}Sr_{0.33}MnO_3$ when T = 600 °C, 800 °C and 1000 °C. The mean field is the best model. However, for T = 1200 °C the best model is the 3D Heisenberg. This can be explained by the fact that the mean field is long-range while 3D Heisenberg is short-range. This implies that the size reduction tends to create in the system a transition phase from a long-range to a short-range order.

Otherwise, several methods allow us to determine spontaneous magnetization, the meanfield theory is one of these methods. This theory is expressed by the following relation [42-45]:

$$S(\sigma) = NK_{B}\left[Ln(2J+1) - Ln\left[\frac{\sin\left[\frac{2J+1}{2J}B_{J}^{-1}(\sigma)\right]}{\sin\left[\frac{1}{2J}B_{J}^{-1}(\sigma)\right]}\right] + B_{J}^{-1}(\sigma)\sigma\right] (8)$$

where $\sigma = \frac{M}{gm_{\mu}B_{J}N'}$, M is the magnetization, N is the number of spins, J is the spin value and k_{B} is the Boltzmann constant respectively and B_{J} is the Brillouin function given by the following expression **[46]**:

$$B_{J}(\sigma) = \frac{2J+1}{2J} \operatorname{coth}\left(\frac{2J+1}{2J}\sigma\right) - \frac{1}{2J} \operatorname{coth}\left(\frac{\sigma}{2J}\right) (9)$$

When M is very small, the equ (9) becomes:

$$-S(\sigma) = \frac{3}{2J+1} NK_B \sigma^2 + O(\sigma^2)$$

Or when $T < T_c$, we realize that the state is FM. Then, the spontaneous magnetization is different from zero. The equ (8) becomes in first order:

$$-\Delta S(\sigma) = \frac{3}{2J+1} NK_{B}(\sigma^{2} + \sigma_{spon}^{4})$$
 (10)
As $\sigma = \frac{M}{gm_{\mu}B_{I}N'}$, the equ (10) becomes in first order:

$$-\Delta S (M) = \frac{3}{2_{N\mu_B^2}g^2 J (J+1)} (M^2 + M_{spont}^4)$$
(11)

Fig.8 displays the variation of $(-\Delta S_M)$ versus T for different $\mu_0 H$, determined from the Maxwell relation **[30]**:

$$\Delta S_{M}\left(\frac{T_{1}+T_{2}}{2}\right) = \left(\frac{1}{T_{2}-T_{1}}\right) \left(\int_{0}^{\mu_{0}H} M(T_{2},\mu_{0}H) \mu_{0} dH - \left(\int_{0}^{\mu_{0}H} M(T_{1},\mu_{0}H) \mu_{0} dH \right) (12)$$

Fig.9 illustrates $(-\Delta S_M)$ vs. M^2 curves when $(T < T_C)$ for the compound $La_{0.8}\square_{0.2}MnO_3$. The slope of a linear fit for this curve corresponds to the spontaneous magnetization. The inset figure depict the variation of the spontaneous magnetization M_{spont} as a function of temperature obtained from the curves $\mu_0 H/M$ vs M^2 and from- ΔS_M vs M^2 . So, we note that the M_{spont} decreases when the temperature increases. These two curves are aligned, which confirms the validity of this method.

Amaral et al. **[47]** set forward a theoretical model taking into consideration the magnetoelastic contribution and the interaction between electrons to simulate magnetic entropy in the case of manganites. This model rests on the Landau theory applied to phase transitions. The basic idea of this model is based on the hypothesis that the free energy (G) can be developed as a function of the power of the parameter of order. The free energy in a ferromagnetic system around the transition temperature T_c is provided as follows:

G (M,T) = C₀ + $\frac{1}{2}$ A (T)M² + $\frac{1}{4}$ B (T)M⁴ + $\frac{1}{6}$ C (T)M⁶ - μ_0 HM (13)

Where the coefficients A, B and C are temperature-dependent parameters usually known as Landau coefficients. According to the equilibrium condition $\frac{\partial G}{\partial M} = 0$, we obtain the equation (15), which provides the total magnetization in the vicinity of the Curie temperature:

 $H = A (T) M + B (T) M^{3} + C (T) M^{5} (14)$

Fig.10 exhibits the variation of A (T), B (T) and C (T) values for $La_{0.8}\square_{0.2}MnO_3$, determined from μ_0H /Mversus the magnetization M².

Therfore, the corresponding magnetic entropy displayed in **Fig.11** obtained by the differentiation of the free energy with respect to temperature, can be expressed by the following relation:

- S(T,H) =
$$\left(\frac{\partial G}{\partial T}\right)_{\mu_0 H} = \frac{1}{2}A'(T)M^2 + \frac{1}{4}B'(T)M^4 + \frac{1}{6}C'(T)M^6$$
 (15)

Where A'(T), B'(T) and C'(T) are the derivatives of the Landau coefficients with respect to the temperature.

IV. <u>Conclusion</u>

At this stage of analysis, we assert that we studied the critical exponents for the compounds $La_{1-x}\Box_xMnO_3$ (x = 0.1; 0.2 and 0.3). Our samples present a second-order transition by the positive slop, which confirms the Banerjee Criterion. The curves of relative slope show that the best models for the samples are the mean field as well as the tricritical mean field models. These models are caracterized by critical exponents which are determined by several methods such as modified MAP, KF method and critical isotherm analysis. A good agreement between these methods for the three compounds is recorded. Furthermore, the tracing of $(-\Delta S_M)$ vs. M^2 for x = 0.2 provides a spontaneous magnetization M_{spont} , which is similar to that determined by the Arrott curves.

Based on the Landau's theory for x = 0.2, we developed a correlation that was used to calculate magnetic entropy at different temperatures and under 2 T magnetic field. These simulated values were found to be in good agreement with the experimental results. The study also demonstrated that this La_{0.8} $\Box_{0.2}$ MnO₃ system exhibits a universal behaviour.

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Figure captions:

Figure.1: the variation of M vs μ_0 H for different temperatures, in steps of 3 K for x = 0.1 and 4 K for x 0.1; 0.2 and 0.3.

Figure.2: Modified Arrott plots (MAP) with mean field model, tri-critical mean field model, 3D Heisenberg model and 3D Ising model.

Figure.3: Relative slope (RS) vs. Temperature.

Figure.4: Variation of M_s (T) and $1/\chi$ (T). Solid lines are symbol's fit curves.

Figure.5: Variation of $((M_S)/(dM_S/dT))$ and $((1/\chi)/d(1/\chi/dT))$ (KF). Solid lines are symbol's fit curves.

Figure.6: M vs. μ_0 H; the inset curves M vs. μ_0 H on log-log scale at T = T_C

Figure.7: Scaling plots $\frac{M}{|\epsilon|^{\beta}}$ versus $\frac{\mu_0 H}{|\epsilon|^{(\beta+\gamma)}}$, the inset exhibits the same curve on log–log scale.

Figure.8: Experimental magnetic entropy changes for x = 0.2 and isothermal ((- ΔS_M) vs. M²) curves.

Figure.9: Variation of the spontaneous magnetization deduced from the extrapolation of the isothermal ($(-\Delta S_M)$ vs. M²) curves and from the Arrott plots (M² vs. μ_0 H/M).

Fig.10: Variation of A, B, C as a function of temperature for the compound $La_{0.8}\Box_{0.2}MnO_3$ at 2 T.

Figure.11: Variation of magnetic entropy changes versus temperature for the compound $La_{0.8}\square_{0.2}MnO_3$ at 2 T.



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Figure.1



















Figure.3





Figure.4







Figure.5





Figure.6





Figure.7



Figure.8



Figure.9



Fig.10



Fig.11

Table Captions:

Table.1: Comparison of critical exponents of $La_{1-x} \Box_x MnO_3$ (x = 0.1; 0.2 and 0.3) with other reports and various theoretical models.

	Methods	β	γ	δ	Ref
		T _C	T _C		
Mean- field	Theory	0.5	1	3	[31]
model					
Tricritical	Theory	0.25	1	5	[31]
mean field					
3D-Ising	Theory	0.325	1.24	4.82	[32]
model					
3D-	Theory	0.365	1.336	4.8	[33]
Heisenberg					
model					
<i>x</i> = 0.1	MAP	0.44 ± 0.033	1.01 ± 0.18	M (T _C)	This work
		214 <u>+</u> 1.10	215 <u>+</u> 2.30	$\delta = 3.75$	
				$Ln(M(T_C))$	
	KF	0.42 <u>+</u> 0.33	0.95 ± 0.13	δ = 3.29	
		214 ± 0.13	215 <u>+</u> 1.97		
<i>x</i> = 0.2	МАР	0.23 <u>+</u> 0.005	0.89 <u>+</u> 0.46	M (T _C)	•
		298 ± 0.12	298.07 <u>+</u> 4.19	δ = 6.95	
				$Ln(M(T_C))$	
	KF	0.22 ± 0.02	0.83 ± 0.017	δ = 5.33	
		298 <u>+</u> 3.22	298 <u>+</u> 1.66		

		Journal Pre-	proofs	
<i>x</i> = 0.3	МАР	0.22 ± 0.06	1.13 <u>+</u> 0.53	M (T _c)
		295 <u>+</u> 0.54	294 <u>+</u> 3.43	δ = 5.27
				$Ln(M(T_c)$
				δ = 6.23
	KF	0.21 ± 0.02	1.21 ± 0.13	
		297 <u>+</u> 6.88	294 ± 0.95	
				X

Credit Author Statement

- C. Henchiri: Writing original draft, Formal analysis.
- T. Mnasri: Writing review & editing.
- A. Benali: Writing review & editing.
- E. Dhahri: Supervision.
- M. A. Valente: Data curation.

Declaration of Interest Statement

We investigated the critical exponents for the compounds $La_{1-x}\Box_x MnO_3$ (x = 0.1; 0.2 and 0.3) prepared by the sol-gel method. After detremining the spontaneous magnetization for x = 0.2 from (- ΔS_M) vs. M².

In this study, we show that:

- La_{1-x}□_xMnO₃ (x = 0.1, 0.2 and 0.3) compound was elaborated using the sol-gel method.
- Structural properties of $La_{1-x}\Box_x MnO_3$ (x = 0.1, 0.2 and 0.3) manganite were studied.
- We investigated the critical exponents for the compounds La_{1-x}□_xMnO₃ (x = 0.1; 0.2 and 0.3).
- We detremining the spontaneous magnetization for x = 0.2 from $(-\Delta S_M)$ vs. M².

Graphical abstract



<u>Highlights</u>

- The La_{1-x}□_xMnO₃ (x = 0.1, 0.2 and 0.3) compounds was successfully prepared by sol-gel method.
- The variation of (M) vs. (T) reveals a ferromagnetic to paramagnetic phase transition around T_c .
- we investigated the critical exponents for the compounds La_{1-x}□_xMnO₃ (x = 0.1; 0.2 and 0.3)