



# MAGNETIC PROPERTIES AND CRITICAL BEHAVIOR IN $\text{La}_{0.66}\text{Ca}_{0.33}\text{Mn}_{(1-x)}\text{Fe}_x\text{Mn}^{3+}\text{O}_3$ -system: A MONTE CARLO APPROACH

F. F. Jurado-Lasso, N. Jurado-Lasso and J. F. Jurado

Grupo Propiedades Térmicas Dieléctricas de Compositos, Dep. de Ciencias Básicas Universidad Nacional de Colombia,  
Sede Palmira, ColombiaE-Mail: [ifjurado@unal.edu.co](mailto:ifjurado@unal.edu.co)

## ABSTRACT

Standard Metropolis Monte Carlo (S-MMC) simulations allowed us to calculate magnetization as a function of temperature and magnetic field, for the  $\text{La}_{0.66}\text{Ca}_{0.33}\text{Mn}_{(1-x)}\text{Fe}_x\text{Mn}^{3+}\text{O}_3$  ( $x=0, 5, 10, 20$  and  $30\%$ ) (LCMF $_x$ ) compound. The respective critical exponents for  $M(T)$ ,  $H/M(H)$  and  $M(H, T=T_c)$  close to the critical temperature, were calculated using the Arrott plot (AP). The values of the critical exponents evinced a type of magnetic universality present in this type of material. The results of the simulation leads us to believe that there is a correlation between the displacement of the magnetic transition temperature (ferromagnetic-paramagnetic), which is characterized by the Curie temperature and an increased percentage of iron present in material. On the other hand, the model determines a value of the critical temperature and this is correlated to the number of Monte Carlo Steps (MCS). For a number of MCS of the order of  $10^2$ , the system tends to relax with the transition temperature which depends on the percentage of iron. By comparing the  $T_c$  values determined based on the two methodologies  $M(T)$  and AP, we can see that, the greater percentage of iron in the material, the more distance between the two trends. Based on these results, it is possible to infer that the increased percentage of Fe increases the presence of effects in the material that lead to an increased variation of the magnetic anisotropy.

**Keywords:** monte carlo simulation, manganites, arrott plot, critical exponent.

## INTRODUCTION

The interest of the science community is geared towards significantly increasing the use of magnetic refrigeration technology, harnessing the magnetocaloric effect (MCE). The advantages of this technology with respect to conventional refrigeration (compression-evaporation) lies in reducing pollution levels, easy manufacture, and miniaturization, among others. Materials that present MCE are characterized by involving second order phase transitions. For example, in some special cases of ferromagnetic-paramagnetic (FM-PM) type transitions, a correlation has been found between these and the presence of a first ordered phase transition (structural). This correlation can lead to the optimization of the capacity of magnetic refrigeration.

There have been many reports of families of compounds that represent MCE, among which we highlight those known as "Heusler alloys". For example,  $\text{MnAs}$  [1],  $\text{MnFeP}_{1-x}\text{As}_x$  [2],  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  [3],  $\text{MnNiGe:Fe}$  [4], among others.

Most cases report the substitution of localized ions in lattice sites, which leads to a change in the number of immediate neighbors that present interaction between magnetic ions: for the particular case of  $\text{Mn-Mn}$  type interactions, we assume that these are directly responsible for the magnetic and structural stability of the material. It has been established that these bonds are directly responsible for the more localized magnetism, as a consequence of the configuration of the orbitals  $d$  of the  $\text{Mn}$  ion [5] ions, whereas for alloys that do not involve  $\text{Mn}$  ions, it is highly probable that there may be mechanisms in which the electrons can be more itinerant [5, 6].

For the perovskites-type family of compounds (manganite) with the formula  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{Ln}$  =rare

earth metal and  $\text{A}$  = divalent element), the physical properties are mainly governed by the strong competition between the double-exchange (DE) ferromagnetic interaction, super-exchange antiferromagnetic interaction, and spin-phonon coupling [7-9]. These interactions are determined mainly by intrinsic parameters such as: ionic radius, disorder, stoichiometry, doping level, among other extrinsic factors such as: pressure and temperature among others [10, 11].

In the semanganites,  $\text{Mn}$  ions play a preponderant role in the DE phenomenon represented by factor  $\text{Mn}^{3+}/\text{Mn}^{4+}$  that correlates the magnetic properties with the itinerant and/or localized electrons. The reports reveal that the research is geared towards the effect of the substitution of the  $\text{Mn}$  ion by transition elements that can coexist with multiple valence, such as:  $\text{Cr}$ ,  $\text{Co}$ ,  $\text{Fe}$ , among others [12, 13]. Given the closeness of the ionic radii of  $\text{Mn}^{3+}$  and  $\text{Fe}^{3+}$ , there has been an intensification of research into manganite-ferrite type compounds  $\text{AMn}_{1-y}\text{Fe}_y\text{O}_3$  [14-16]. Most of these seek to find concluding explanations on the incidents of the effect of the substitution of the  $\text{Fe}/\text{Mn}$  ion on the crystalline order, magnetic properties, and electric charge transport, among others [17, 18]. Advances are being made in the search for new families of compounds of the  $\text{Ln}_{1-x}\text{A}_x\text{Mn}_{1-y}\text{Fe}_y\text{MnO}_3$  type, and results have shown that they are very sensitive to the preparation method [19, 20]. In the simulation field for these materials, a recent report shows the effect of iron on the critical temperature in the compound  $\text{LaCaMnFeO}_3$  [21]. In order to adjust the results, they had to introduce a factor so that the values of  $T_c$  coincided with the experimental reports.

This work presents results and discussion of the simulation of the magnetic thermal response close to the transition phase (ferromagnetic-paramagnetic)



of  $La_{0.66}Ca_{0.33}Mn_{(1-x)}^{4+}Fe_xMn^{3+}O_3$  (LCMFx)( $x=0,5,10,20$  and 30%) compound. The methodology is developed using the Standard Metropolis Monte Carlo (S-MMC) simulations for a 3D classical Hamiltonian-Heisenberg. The critical exponents for  $M(T)$ ,  $H/M(T)$  and  $M(H, T=T_c)$  are calculated following the Arrott plot (AP) method.

### THE MODEL

In ideal conditions the compound  $La_{2/3}Ca_{1/3}MnO_3$  crystallizes into a simple cubic structure and a presence of three types of magnetic ions has been identified:  $Mn^{4+}_{3d}(s=3/2)$ ,  $Mn^{3+}_{eg}$  and  $Mn^{3+}_{eg'}$  ( $s=2$ ). Spin interaction is conceived via double exchange with the respective bonds  $M^{3+}_{eg'}-O-Mn^{3+}_{eg}$ ,  $M^{3+}_{eg}-O-Mn^{4+}_{d3}$  and  $M^{3+}_{eg'}-O-Mn^{4+}_{d3}$  [22, 23]. For the distribution of  $Mn$  ions throughout the volume, the option proposed by Hotta *et al.* [24, 25] is well accepted. Under the conditions described above, the magnetic response in the model is usually calculated based on the 3D classic Hamiltonian-Heisenberg [26–29].

$$H = -\sum_{\langle i,j \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j - K_a \sum_i (\vec{S}_i \cdot \vec{a})^2 - \sum_i \vec{S}_i \cdot \vec{h} \quad (1)$$

For the first term, the sum extends to the closest neighbors with constant interaction  $J_{ij}$  between the sites  $i$  and  $j$ . It is established that the most relevant interactions are those which occur between three types of ions:  $Mn^{4+}_{3d}$ ,  $Mn^{3+}_{eg}$  and  $Mn^{3+}_{eg'}$ .

**Table-1.** Exchange parameters  $J_{ij}$  used in the model.

Bond	$J_{ij}$ (meV)
$Mn^{4+} - Mn^{3+}_{eg}$	7.6
$Mn^{4+} - Mn^{3+}_{eg'}$	3.8
$Mn^{3+} - Mn^{3+}_{eg'}$	4.65
$Mn^{3+}_{eg} - Fe^{3+}$	-4.95
$Mn^{3+}_{eg'} - Fe^{3+}$	-1.95

The second term involves crystalline anisotropy along the easy axis ( $K_a = 1.24844$  meV). The third term refers to the Zeeman Interaction. The proposal considers the substitution of the manganese ion for iron in the following compound  $La_{0.66}Ca_{0.33}Mn_{(1-x)}^{4+}Fe_xMn^{3+}O_3$  ( $x=0, 5, 10, 20$  and 30 %). Despite the complex electronic configuration of iron, the substitution of a high-spin ion is more likely  $Fe^{3+}(t^3_{2g}e^2_g; s=5/2)$ , justified by the fact that there is greater favorability with respect to a low-spin iron.

**Table-2.** Model parameters for the number  $Mn^{4+}$  atoms per unit cell.

x(%)	$Fe^{3+}$	$Mn^{4+}$	$Mn^{3+}$
0	0	33	66
5	90	28	66
10	225	23	66
20	450	13	66
30	1350	3	66

### SIMULATION

For a three-dimensional simple cubic lattice, the periodic boundary conditions are determined only for nearest neighbor interactions. The transverse direction has been taken as plane  $xy$ , whereas the direction perpendicular to the film is axis  $z$ . The volume of the sample considered was  $V = (30)^2 5 (u.c.)^3$  (unit cells), for a total of  $N=4500$  atoms. In this way, we multiply all the exchange constants listed in the Table-1. Of this total of atoms, only 33% correspond to  $Mn^{4+}$ , with the presence of iron, this total varies (see Table-2). A simulation was carried out of the cooling process in the temperature range with the extremes slightly distanced from the critical temperature. A configuration of fixed spins aligned along the  $j$  axis is assigned, as a starting point. Magnetization per site is calculated based on expression.

$$\vec{m} = \frac{1}{N} \sum_i \vec{S}_i \quad (2)$$

The average thermal equilibrium is established based on the critical temperature value reported for this material in the absence of iron. For simulation model, it was identified that critical temperature value correlates with the number of Monte Carlo Steps (MCS). For a number of MCS of the order of  $10^2$ , the system tends to relax with a transition temperature that depends on the %Fe content. The acceptance or rejection of a change of a spin of an assigned site is governed by the transition probability  $W = \min(1, \exp[-\Delta H/KT])$ . The critical temperature value was assessed from the position of the maximum of the specific heat curves (not shown here).

### NUMERICAL RESULTS AND DISCUSSION

Figure-1a) shows the dependence of the magnetization on the temperature in the absence of an external magnetic field for different percentages of  $Fe$ . The increased ion content shifts the critical temperature towards the lower temperature region following the trend shown in Figure-1b). The magnetic order in the LCMFx compound is affected by the presence and increase of iron ions. The presence of these ions modifies the distance between the ions  $Mn/Fe-O$ . This effect has also been reported for the following compound types  $PrLaCaMnFeO_3$  [31, 32]. In reference [18, 33, 34], it can be inferred that the  $Fe$  ion does not significantly affect the

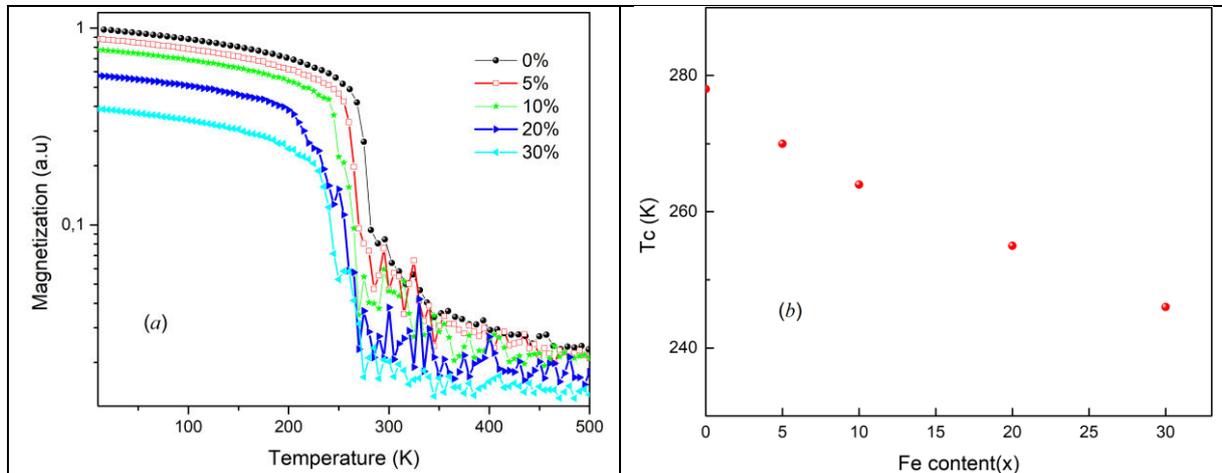


double exchange mechanism, but it is a fact that it is part of the  $Mn^{3+}-O_2-Mn^{4+}$  chains.

### CRITICAL BEHAVIOR STUDY

The magnetic response of the LCMFx compound to an external magnetic field, for temperatures close to the

phase transition (ferromagnetic-paramagnetic) was studied based on isotherms  $M(H)$  vs  $H/M$ , following the Arrott plot (AP) method (Figures 2a, 3a, 4a, 5a and 6a). The methodology followed is shown in the inset of each figure. Spontaneous magnetization  $M_s(T,0)$  for LCMFx was obtained through  $M^2$  linearity vs.



**Figure-1.** (a) Temperature dependence of the magnetization. (b) Fe content ( $x$ ) dependent  $T_c$  of the LCMFx ( $x = 0, 5, 10, 20, 30$  %) compounds.

**Table-3.** Summary of data calculated at compound LCMFx.

$x$ (%)	$T_c$ (K)	$T_c$ (K)*	$\beta$	$\gamma$	$\delta$	Ref.
0	278	255	0.414	0.772	7.57	This work
5	270	243	0.431	0.779	6.07	This work
10	264	223	0.420	0.958	5.32	This work
20	255	185	0.493	0.954	4.59	This work
30	246	156	0.414	1.025	4.36	This work
Mean Field Theory			0.5	1	3	[30]
3D Ising model			0.325	1.24	4.82	[30]
3D-Heisenber			0.365	1.336	4.80	[30]

### Arrott's Plot

$H/M$  extrapolated towards the ordinate, whilst  $H/M$  is determined based on the interception with the abscissa. Figures 2b, 3b, 4b, 5b and 6b show the trend of  $M_s^2$  and  $H/M$  with the temperature for LCMFx. By comparing the values of  $T_c$  determined based on  $M(T)$  and Arrott plot (see Figure-7f), it is possible to see that there is dispersion in the two trends and this becomes more considerable when the percentage of iron increases. This may be associated to an increase of effects that cause great variations in the entropy. This trend can also be seen in other families of compounds [35]. The critical behavior close to the transition phase of compounds LCMFx was characterized through the critical exponents:  $\beta, \gamma$ , and  $\delta$ . Associated to spontaneous magnetization  $M_s(T)$ ,

reciprocal susceptibility of ( $\chi_0(T)$ ) and isotherm  $M(H)$  for  $T=T_c$ , In accordance with the staggering hypothesis, these magnetic magnitudes can be written as [36, 37];

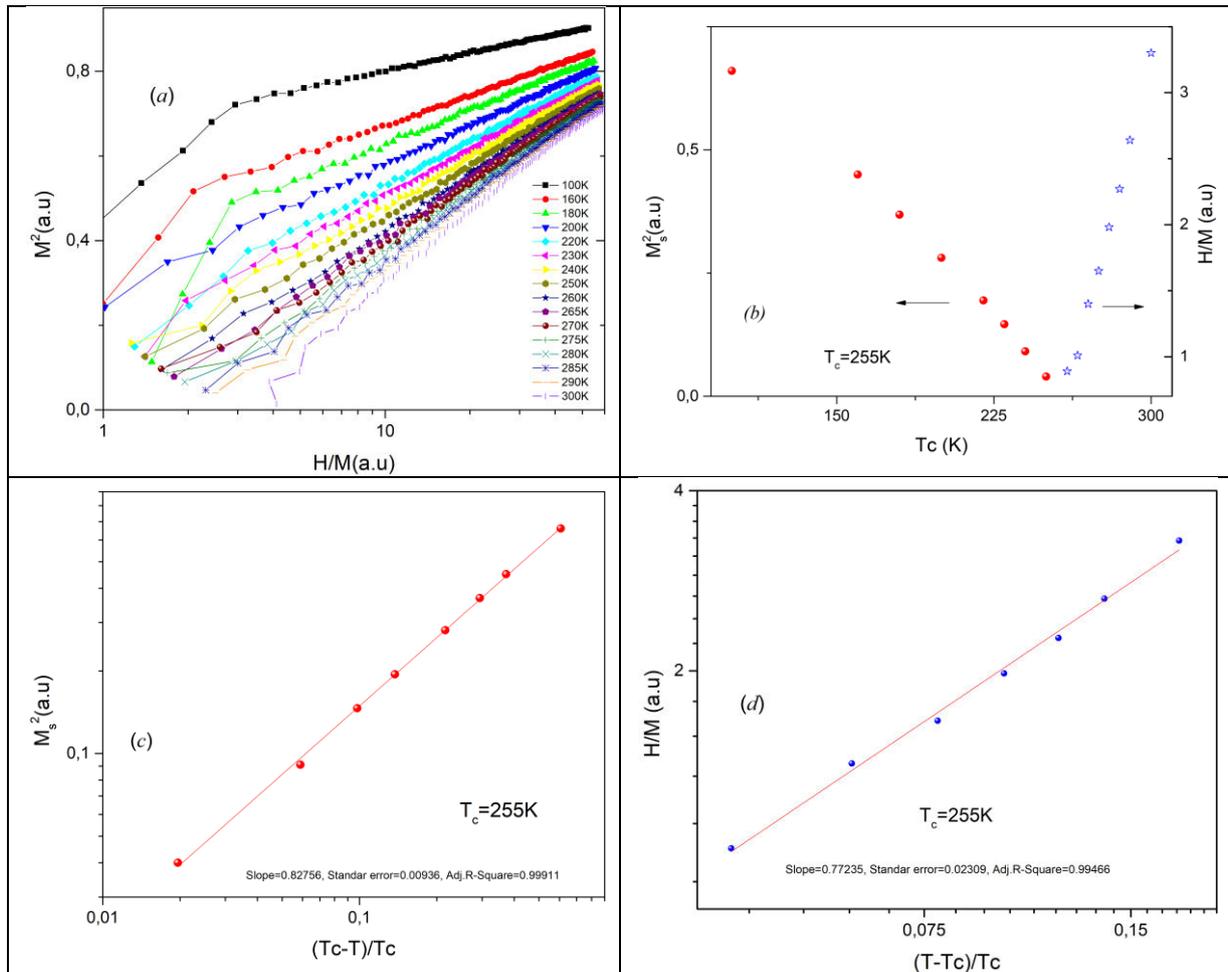
$$\begin{aligned}
 M_s(T) &= M_0(-\varepsilon)^\beta \quad \varepsilon < 0 \\
 \chi^{-1}(T) &= \frac{h_0}{M_0}(\varepsilon)^\gamma \quad \varepsilon > 0 \\
 M(T) &= D(H)^\frac{1}{\delta} \quad T = T_c
 \end{aligned}
 \tag{3}$$

Where  $\varepsilon = \frac{T-T_c}{T_c}$  is the reduced temperature. The constants  $M_0, h_0/M_0$  and  $D$  are critical amplitudes. Figures (2c-2d, 3c-3d, 4c-4d, 5c-5d and 6c-6d) show the linear trend of  $M^2$  and  $H/M$  with the reduced temperature,

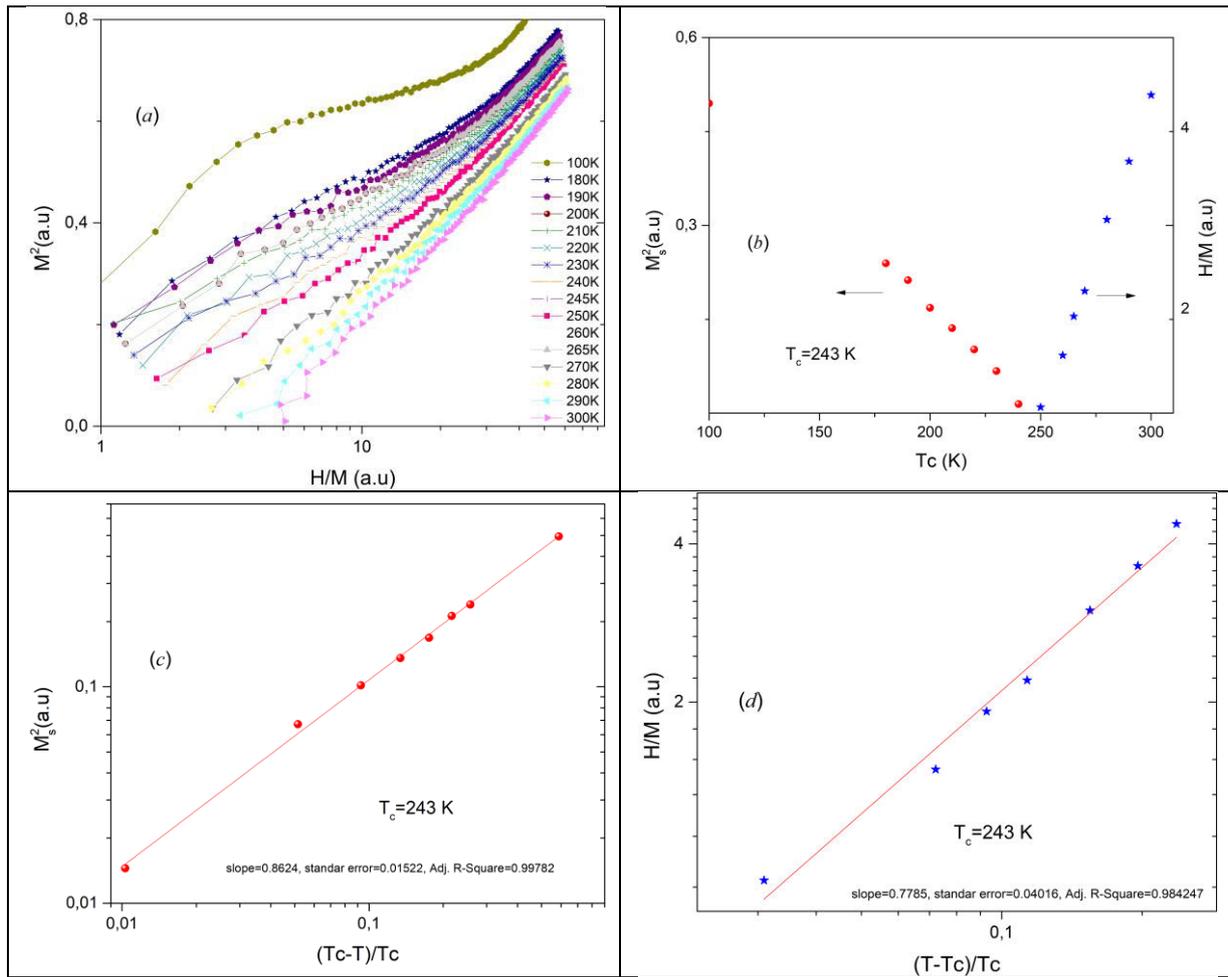


respectively. The insets in the figures show the respective adjustment values for critical exponents (see Table-3). The positive slope in the entire range of the calculation implies

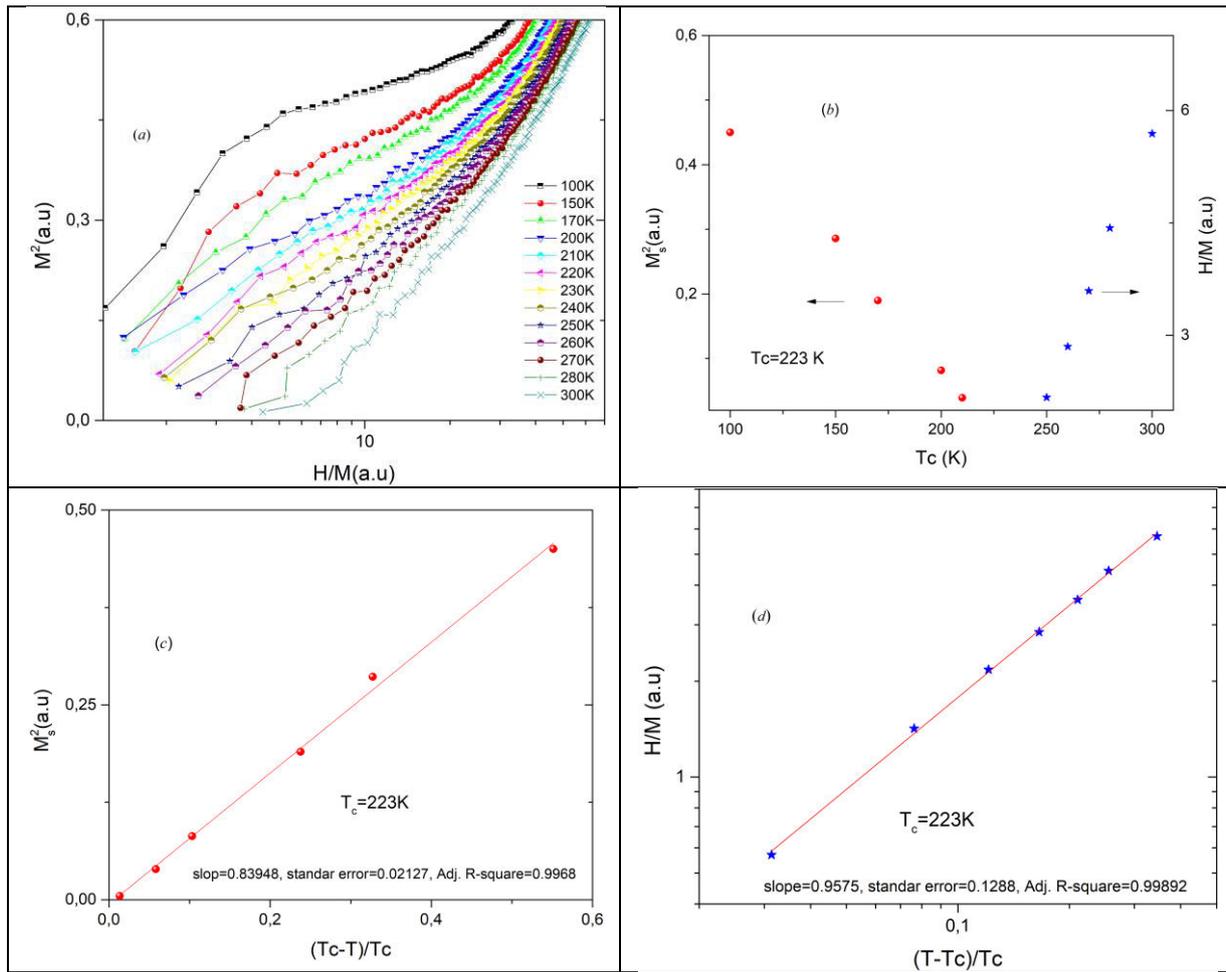
that the transition here is a second-order transition, according to the Banerjee [38] criteria.



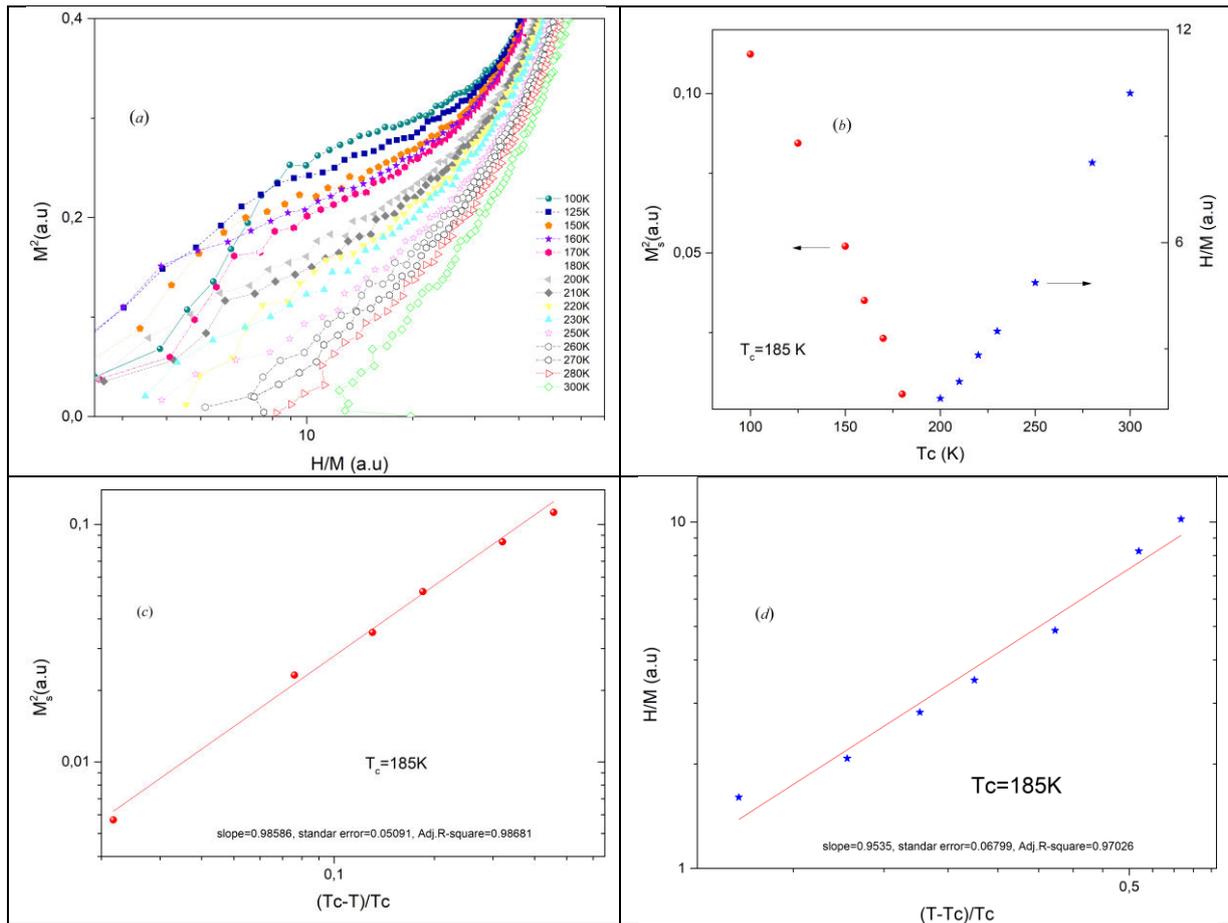
**Figure-2.** (a) Arrott's plot ( $M^2$  versus  $H/M$ ) for the  $LCMF_x(x = 0\%)$  compound. (b) Temperature dependence of the spontaneous magnetization  $M_s$  and reciprocal of susceptibility, respectability. (c,d) Reduced temperature dependence of the spontaneous magnetization  $M_s$  and reciprocal of susceptibility  $H/M$ . Straight solid lines denote the fitted linear dependence. The inset shows the fitting data.



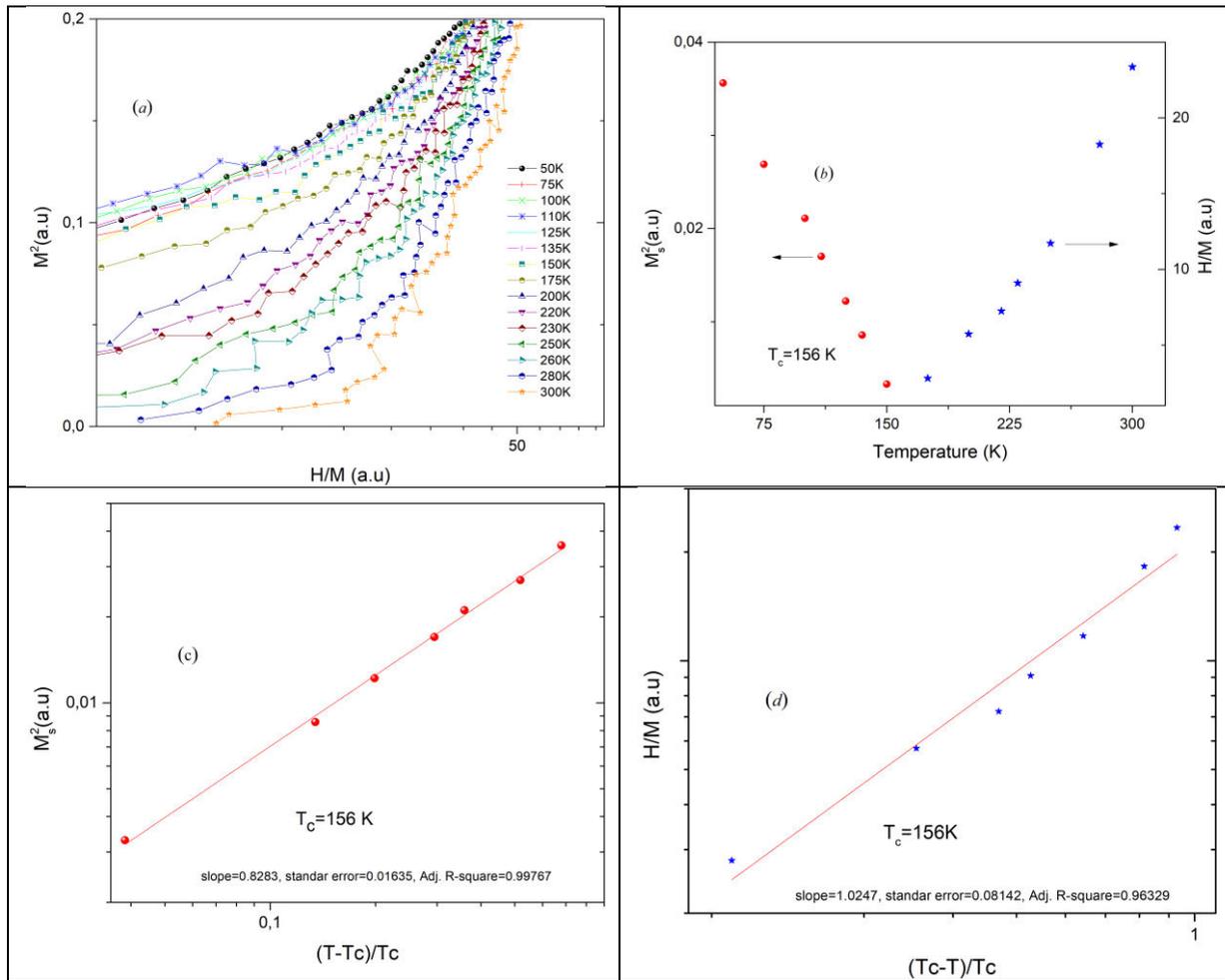
**Figure-3.** (a) Arrott's plot ( $M^2$  versus  $H/M$ ) for the  $LCMF_x$  ( $x = 5\%$ ) compound. (b) Temperature dependence of the spontaneous magnetization  $M_s$  and reciprocal of susceptibility, respectively. (c, d) Reduced temperature dependence of the spontaneous magnetization  $M_s$  and reciprocal of susceptibility  $H/M$ . Straight solid lines denote the fitted linear dependence. The inset shows the fitting data.



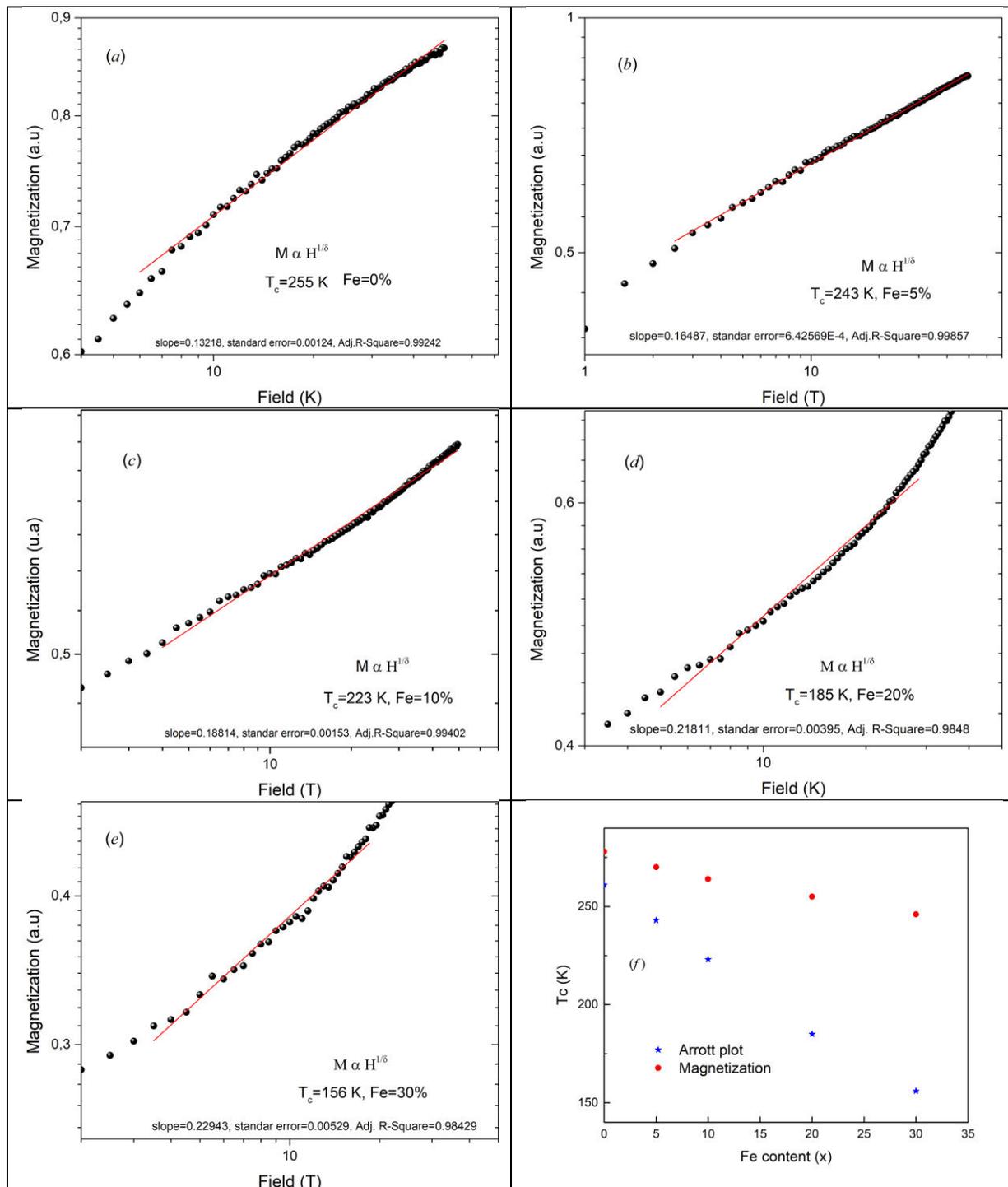
**Figure-4.** (a) Arrott's plot ( $M^2$  versus  $H/M$ ) for the  $LCMF_x$  ( $x = 10\%$ ) compound. (b) Temperature dependence of the spontaneous magnetization  $M_s$  and reciprocal of susceptibility, respectively. (c, d) Reduced temperature dependence of the spontaneous magnetization  $M_s$  and reciprocal of susceptibility  $H/M$ . Straight solid lines denote the fitted linear dependence. The inset shows the fitting.



**Figure-5.** (a) Arrott's plot ( $M^2$  versus  $H/M$ ) for the  $LCMF_x(x = 20\%)$  compound. (b) Temperature dependence of the spontaneous magnetization  $M_s$  and reciprocal of susceptibility, respectively. (c, d) Reduced temperature dependence of the spontaneous magnetization  $M_s$  and reciprocal of susceptibility  $H/M$ . Straight solid lines denote the fitted linear dependence. The inset shows the fitting data.



**Figure-6.** (a) Arrott's plot ( $M^2$  versus  $H/M$ ) for the  $LCMF_x(x = 30\%)$  compound. (b) Temperature dependence of the spontaneous magnetization  $M_s$  and reciprocal of susceptibility, respectively. (c, d) Reduced temperature dependence of the spontaneous magnetization  $M_s$  and reciprocal of susceptibility  $H/M$ . Straight solid lines denote the fitted linear dependence. The inset shows the fitting data.



**Figure-7.** Variation of magnetization  $M$  as a function of applied field at  $T=T_c$  for LCMFx compounds for: (a) $x=0$ , (b) $x=5$ , (c)  $x=10$ , (d) $x=20$  and (e) $x=30$ %. Straight solid lines denote the fitted linear dependence. The inset shows the fitting data. (f) Fe content ( $x$ ) dependent  $T_c$  to the two formalism; magnetization and y Arrott's plot for LCMFx compounds.

On the other hand, the nonlinear curves (downward curvature even at a high field) indicate that the magnetic response of the compounds distances itself a little from the ideal average field model ( $\beta=0.5$  and  $\gamma=1.0$ ). This trend is usually associated with the presence magnetic anisotropy effects [39-41], as well as the presence of order/disorder effects in the material.

However, despite the lack of linearity in the trend, it is possible to infer the presence of a short-range magnetic order in the compounds. Based on the  $\log(M(H))$  isotherm vs.  $\log H a$  respective critical temperature for each content value for  $Fe$  (Figure-7), it is possible to determine the critical exponent  $\delta$ . The corresponding value was calculated with a good level of refinement (see Table-3).



The non-linearity in the trend with regards field-dependent magnetization applied for a greater percentage of iron corroborated the increased presence of the effects of magneto crystalline anisotropy that give rise to great entropy variations. By comparing the values of the critical exponents calculated here, with those reported in the references for other materials and models (see Table-3), it is possible to see that the magnetic order of these compounds adjust to the kind of universality surrounding magnetic responses to thermal-magnetic effects.

## CONCLUSIONS

The results obtained by Monte Carlo simulation using the Standard Metropolis Monte Carlo (SMMC) simulations for LCMFx compounds, where the only ions replaced are the *Fe* by *Mn*<sup>4+</sup>, showed correlation between the displacement of the magnetic transition temperature (ferromagnetic -paramagnetic) that is characterized by the Curie temperature, and the increased levels of *Fe* present in the material. The model is optimized for MCS of the order of 10<sup>2</sup> and the system tends to relax with a transition temperature that depends on the *Fe* content. The critical behavior close to the second-order transition, showed universal behavior, evinced by the critical exponents of: spontaneous magnetization *M<sub>s</sub>(T)*, reciprocal magnetic susceptibility *H/M(H)*, and isotherm *M(H, T = T<sub>c</sub>)*. The difference of *T<sub>c</sub>* with the *Fe* content for procedures *M(T)* and Arrott plot, can be indicative of great entropy variations in the compound whose effect can be used in magnetic refrigeration.

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