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Magnetic Study Above Curie Temperature in $La_{0.4}Re_{0.1}Ca_{0.5}MnO_3$ (Re=La, Eu, Gd and Dy) Polycrystalline Manganites

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Abstract: *We have studied in this work the magnetic interactions above the Curie point T_c in $La_{0.4}Re_{0.1}Ca_{0.5}MnO_3$ (Re= La, Eu, Gd and Dy) polycrystalline manganites. The magnetic field dependence of magnetization M(H) curves above T_c shows strong evidence of the phase separated nature of our compounds. For Re=La, the presence of ferromagnetic interactions was detected in the temperature range 220-270K. For other rare earth substituted samples, M (H) curves indicate the persistence of charge ordered antiferromagnetic domains within the paramagnetic phase. The temperature dependence of the inverse of paramagnetic susceptibility reveals that all elaborated samples do not follow the Curie-Weiss law above T_c. The deviation from linearity increases with increasing the magnetic moment of substituent. In the case of Re=Eu, Gd and Dy, we have detected the presence of both ferromagnetic and charge ordered antiferromagnetic clusters in the paramagnetic phase, which confirms that the charge ordering characterizing the parent compound did not collapse by substitution.*

Keywords: *Perovskite manganites; Magnetic properties; Phase separation; Charge ordering.*

1. INTRODUCTION

In the last years, manganites having the general formula $Re_{1-x}Ae_xMnO_3$, where Re is a rare earth (La, Pr, Nd…) and Ae is an alkaline earth (Ca, Sr, Ba…) seems to attract the interest of researchers because of their several applications as well as the diversity of their fascinating electrical and magnetic responses. These compounds possess great technological applications especially based on colossal magnetoresistance [1, 2] and magnetocaloric effect [3]. Thus, they can be used for spintronics applications or even magnetic refrigeration. In addition, these compounds possess several interesting physical properties like charge ordering (CO), orbital ordering, magnetic and metamagnetic transitions, phase separation [4, 5]. In all the previous works performed on manganites, detailed structural and physical investigations were carried out in order to elucidate the parameters controlling the physical behavior of these compounds. It was found that magnetic interactions mostly originate from double exchange and super exchange mechanisms between manganese ions. In addition, several parameters seem to control the behavior of these compounds like elaboration conditions, the average ionic radius in A-site $\langle r_A \rangle$, the cationic disorder in A-site (cationic mismatch) σ^2 given by $\sigma^2 = \sum_i (y_i r_i^2 - \langle r_A \rangle^2)$ [6], the amount of Mn^{4+} ions, A-site or B-site doping, oxygen deficiency…

Half doped $La_{0.5}Ca_{0.5}MnO_3$ is one of most important compounds due to its special magnetic behavior: when cooled, this compound undergoes first paramagnetic (PM) to ferromagnetic (FM) transition at T_C=220K and this transition is followed by another one from FM to charge-ordered antiferromagnetic (CO-AFM) state at T_{CO}=150K [5, 7]. Phase separation phenomenon characterizes $La_{0.5}Ca_{0.5}MnO_3$ compound. In fact, below T_{CO}, the structure was found to be as an AFM matrix in which some FM domains were trapped [8]. In a previous work, we have studied the effect of lanthanum substitution by rare earth elements on the structural, magnetic and magnetocaloric properties of $La_{0.4}Re_{0.1}Ca_{0.5}MnO_3$ (Re= La, Eu, Gd and Dy) [5]. We found that T_C decreases with decreasing $\langle r_A \rangle$ and increasing σ^2. We have suggested that the CO state is not completely suppressed by rare earth substitution of lanthanum. In this work, we tried to study the magnetic behavior of the compounds $La_{0.4}Re_{0.1}Ca_{0.5}MnO_3$ (Re= La, Eu, Gd and Dy) above T_C in order to verify the validity of our suggestion and to check the contribution of each rare earth element to the magnetic interactions in the PM phase.

2. EXPERIMENTAL TECHNIQUES

$La_{0.4}Re_{0.1}Ca_{0.5}MnO_3$ (Re= La, Eu, Gd and Dy) samples were elaborated using traditional solid state method at high temperature. The elaboration conditions were previously detailed [5]. X-ray powder diffraction was used to check phase purity. Crystallographic study was done using standard Rietveld refinement technique. Magnetization measurements in the temperature range 10-300K and in the magnetic field range 0-5T were performed using a vibrating sample magnetometer.

3. RESULTS AND DISCUSSION

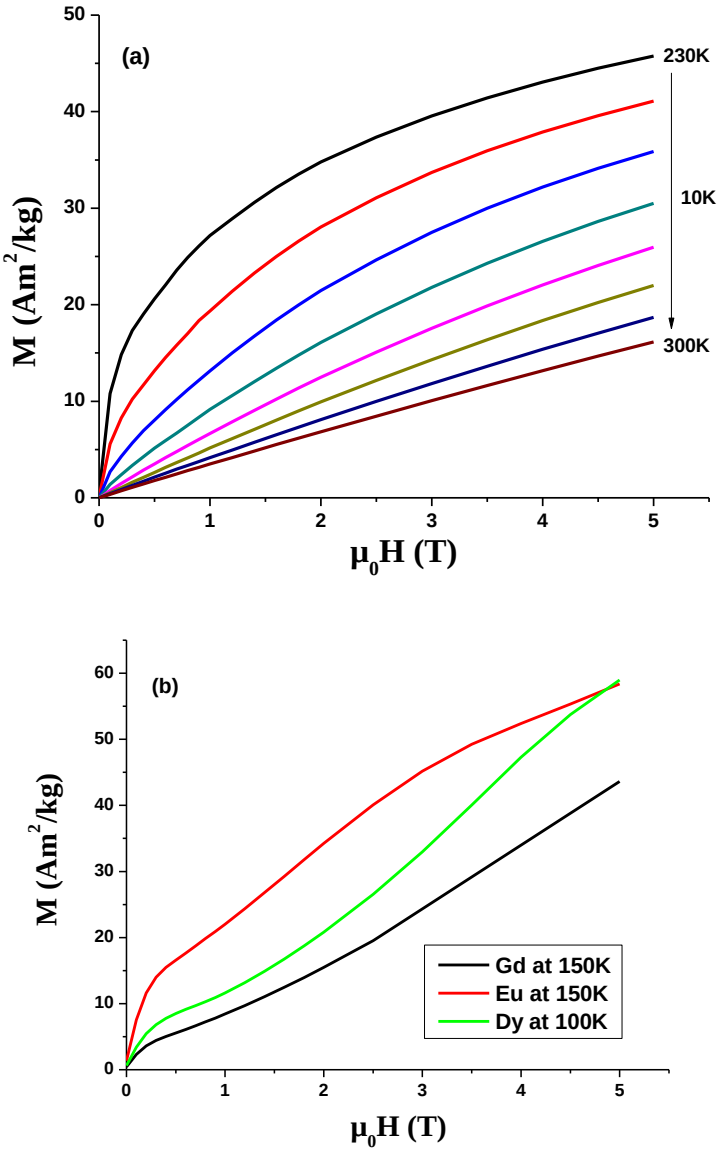


Fig1. *Magnetic applied field dependence of magnetization recorded above Curie temperature for $La_{0.4}Re_{0.1}Ca_{0.5}MnO_3$ samples (a) Re= La and (b) Re= Eu, Gd and Dy.*

X-ray powder diffraction patterns for all our samples showed that the samples were pure and single phase. Rietveld refinement indicated that all our compounds crystallize in the orthorhombic structure and belong to *Pnma* space group. Temperature dependence of magnetization for all our samples showed that the Curie temperature T_C is 220K, 130K, 100K and 70K for Re=La, Eu, Gd and Dy, respectively [5]. We have also noticed that the PM-FM transition for all our samples is a broad one. In order to study the applied magnetic field effect on the magnetic behavior in the PM phase, we have plotted in Fig.1 the magnetic field dependence of magnetization above T_C for all our compounds. It is very clear that all our samples are not completely PM above T_C. For Re=La, the M(H) curves show the typical behavior of FM state above T_C, which indicates the presence of some FM clusters in the

PM phase. According to Fig.1(a), the compound $La_{0.5}Ca_{0.5}MnO_3$ becomes completely PM only above 270K. Similar behavior of M(H) curves has been reported for thin films of $Nd_{0.5}Sr_{0.5}MnO_{3-\delta}$ [9]. Such behavior was explained by the presence of magnetic particles having different sizes which indicates that these particles did not evolve to the PM phase at the same time with increasing temperature. This fact can explain the wide PM-FM transition observed for this compound. Generally, the $La_{1-x}Ca_xMnO_3$ family is characterized by phase coexistence and by the presence of some FM clusters above T_C [10].

For other rare earth substituted specimens (Fig.1.b), it is obvious that these compounds are not completely PM above their Curie temperatures. In fact, M(H) curves display a different magnetic behavior compared to the pristine compound. For low field values (below 1T), magnetization quickly increases then saturates, which is a characteristic feature of FM phase. With further increase of applied magnetic field, we can notice a great enhancement of magnetization. Such behavior is the signature of a field-induced metamagnetic transition due to the presence of some AFM clusters. The increase of magnetization by the applied field is attributed to the conversion of AFM clusters to FM ones due to the collapsing of the CO state. The question rises about the origin of these AFM clusters. The answer lies in the magnetic properties of the pristine compound. In fact, $La_{0.5}Ca_{0.5}MnO_3$ is characterized by CO-AFM state below 150K. Thus, lanthanum substitution by Re= Eu, Gd and Dy will decrease T_C due to the weakening of double exchange FM interactions, but the CO-AFM state is not suppressed by substitution. In the case of $La_{0.4}Nd_{0.1}Ca_{0.5}MnO_3$, authors have found that CO did not collapse and that T_{CO}=230K [11]. Stabilization of CO state was also observed in $La_{0.4}Sm_{0.1}Ca_{0.5}MnO_3$ [2]. Therefore, this fact indicates that our substituted compounds are phase separated above T_C with the presence of both FM and AFM clusters. Phase separation phenomenon mainly originates from the competition between double exchange and super exchange mechanisms inside the structure.

To confirm such observation, we have tried to plot theoretical and experimental evolution of the inverse of PM susceptibility as a function of temperature for all our samples. In the PM phase, magnetization is related to magnetic applied field by:

$$M=\chi.H \quad (1)$$

So, we can write:

$$\mu_0 H/M = \mu_0/\chi \quad (2)$$

In the PM phase, the Curie-Weiss law is given by:

$$\chi= C_P / (T-\theta_P) \quad (3)$$

Relations (2) and (3) indicate that the inverse of the PM susceptibility should exhibit a linear dependence of temperature in PM phase. Thus, if we can evaluate the values of C_P and θ_P, we can find the theoretical shape of $\chi^{-1}(T)$. We know that θ_P is very close to T_C. Besides, the values of C_P can be determined using the following relation:

$$C_P = \frac{\mu_0}{3k}\mu_{eff}^2 \quad (4)$$

where k is the Boltzmann constant and μ_{eff} is the effective moment which can be calculated considering all the magnetic species inside the structure. For our samples, μ_{eff} values are given by the relation:

$$\mu_{eff}^2 = \left\{0.1g_{Re}^2 J_{Re}(J_{Re}+1)+0.5g_{3+}^2 S_{3+}(S_{3+}+1)+0.5g_{4+}^2 S_{4+}(S_{4+}+1)\right\}\mu_B^2 \quad (5)$$

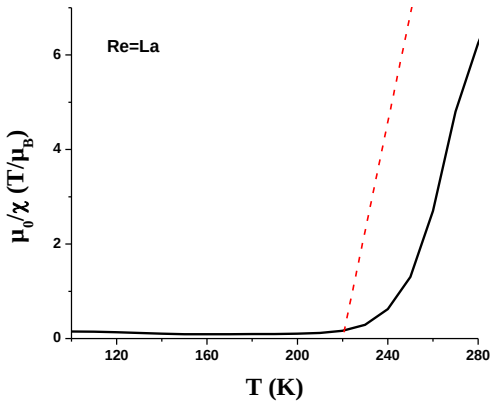
where μ_B is the Bohr magneton, g is the Landé factor, J is the total magnetic moment and S is spin magnetic moment. Re, 3+ and 4+ are associated to rare earth substituent, Mn^{3+} and Mn^{4+} respectively. Landé factor g is evaluated considering the following relation:

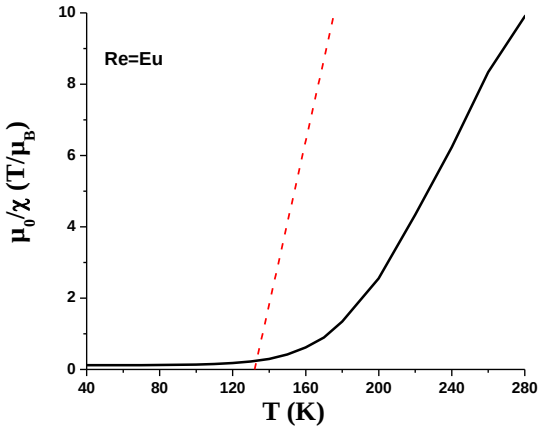
$$g = \frac{3}{2}+\frac{S(S+1)-L(L+1)}{2J(J+1)} \quad (6)$$

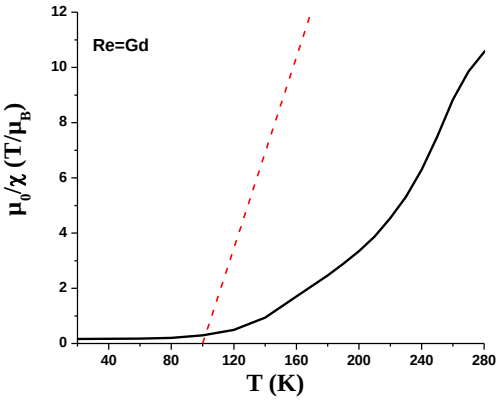
Table1. *Electronic configuration and theoretical magnetic moment values for all the cations inside our samples.*

Ion	La^{3+}	Eu^{3+}	Gd^{3+}	Dy^{3+}	Mn^{3+}	Mn^{4+}
Configuration	[Xe]	[Xe] $4f^6$	[Xe] $4f^7$	[Xe] $4f^9$	$3d^4$	$3d^3$
$g\sqrt{j(j+1)}$	0	0	7.94	10.63	4.9	3.87

where L is the orbital magnetic moment. In table 1, we have gathered the electronic configuration as well as the theoretical magnetic moments of rare earth and manganese ions. From the values of table 1, it is easy to evaluate the theoretical values of μ_{eff} and C_P. The results were summarized in table 2. From these results, we can plot the theoretical $\chi^{-1}(T)$ curve for each sample (Fig.2). It is evident that the Curie-Weiss law is not respected in the PM phase for all our samples. For Re=La, there is no big difference between the theoretical and experimental results (compared to the other samples). One can notice for this sample that experimental line possesses a lower slope compared to theoretical one. This indicates that the experimental effective moment is higher than the theoretical value, which is attributed to the presence of FM interactions above T_C. This result is in perfect agreement with M(H) curves (Fig.1(a)). For manganites, the deviation from linearity in the PM phase can be ascribed to several factors like the difference between grains size, the mismatch effect, Griffiths phase [12]…In our case, it seems that phase separation phenomenon is responsible for such deviation.







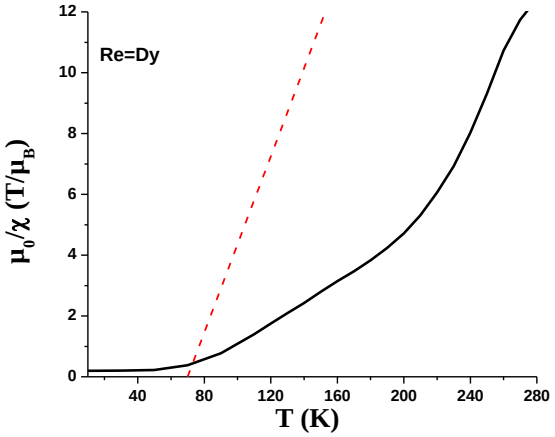


Fig2. *Experimental (continuous line) and theoretical (dashed line) temperature dependence of $\mu_0 H/M$ for $La_{0.4}Re_{0.1}Ca_{0.5}MnO_3$ (Re= La, Eu, Gd and Dy) samples.*

Table2. *Theoretical effective moment and Curie constant values for La0.4Re0.1Ca0.5MnO3 (Re= La, Eu, Gd and Dy) samples.*

Re	La	Eu	Gd	Dy
μ_{eff} (μ_B)	4.416	4.416	5.079	5.549
C_P/μ_0 (μ_B.KT^{-1})	4.367	4.367	5.780	6.897

For other rare earth elements, it is clear that there is no match at all between theoretical and experimental results, which indicates that the Curie-Weiss law is not suitable to describe the magnetic behavior of these samples above T_C. The failure of this law can be attributed to the phase-segregated nature of these samples. This result supports the observations taken from M(H) curves for these specimens (Fig.1(b)). Moreover, one can observe that the deviation from the Curie-Weiss law increases with increasing substituent magnetic moment. This fact indicates that magnetic properties are highly influenced by the nature of rare earth dopant. Theoretically, we thought that europium-based sample would evolve like the pristine compound because Eu^{3+} ions are theoretically devoid of magnetic moment (table 1). However, experiments have shown that these ions possess magnetic moment (~3.5μ_B) because J can take both maximum and minimum values because these two states have close energy values. These observations confirm that the substituent moment plays a crucial role in the evolution of the magnetic properties of $La_{0.5}Ca_{0.5}MnO_3$. We can suppose that rare earth elements interact antiferromagnetically with manganese ions, which induces a weakening of double exchange FM interactions in favor of super exchange AFM ones. Thus, substitution did not collapse the CO state characterizing the parent compound.

4. CONCLUSION

We have studied the PM-FM transition for $La_{0.4}Re_{0.1}Ca_{0.5}MnO_3$ (Re= La, Eu, Gd and Dy) samples. The M(H) curves recorded above the Curie point indicate that all our samples are phase separated above T_C. For the parent compound, we have detected the presence of some FM clusters above T_C. For other rare earth substituted samples, we have noticed the presence of both FM and AFM clusters in the PM phase, which implies that substitution did not suppress the CO state characterizing the parent compound. These observations are confirmed by the fact that the Curie-Weiss law cannot describe the magnetic behavior above T_C. The deviation from this law is more important with the increase of rare earth magnetic moment, which gives an idea about the important role of substituent's nature in the magnetic interaction.

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