Progress in Physics of Applied Materials 1 (2021) 39 – 43

Semnan University

Progress in Physics of Applied Materials

journal homepage: https://ppam.semnan.ac.ir/

Study of Landau theory and universal curve on $La_{0.6-x}Gd_xSr_{0.4}MnO_3$ (x= 0 - 0.1) manganite

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ARTICLE INFO

Article history:
Received: 11 July 2021
Revised: 27 July 2021
Accepted: 31 July 2021

Keywords:
Manganite
Landau theory
Universal curve
Magneto-caloric effect
Second-order phase transition.

ABSTRACT

In this study, the magnetocaloric effect and magnetic properties of $La_{0.6-x}Gd_xSr_{0.4}MnO_3$ (*x= 0-0.1*) samples (with the R-3c space group crystalize in rhombohedral structure) synthesized by the Sol-gel method is presented here. The aim of the study is the investigation of the Landau theory and universal curve approach applied to the magnetic entropy change of $La_{0.6-x}Gd_xSr_{0.4}MnO_3$ (*x= 0-0.1*) compounds. A universal curve is an important tool that allows us to compare the performance quality of different materials during measurements, regardless of their nature, processing, or experimental settings. Thermodynamic models were used to calculate the MCE. Theoretical and experimental data $-\Delta S_M(T)$ are well-matched in the compounds. The study of the universal curve and Landau theory showed that the nature of the transition is the second-order ferromagnetic (FM) -paramagnetic (PM) magnetic phase transition. From an application point of view, theoretical research confirmed that compounds containing Gd in the La site can be used for magnetic refrigeration technology.

1. Introduction

In recent years, magnetic refrigeration, which is cooled by the magnetocaloric effect (MCE) of magnetic materials, has become increasingly popular due to its significant energy efficiency, environmental friendliness, and chemical stability advantages over traditional refrigeration. Has become popular [1-2]. MCE is characterized by different entropy changes due to external magnetic fields. La-based manganites with the formula $La_{1-x}A_xMnO_3$ (A represents divalent alkaline earth cations such as Ca^{2+}, Sr^{2+}, Ba^{2+}, etc.) have attracted the attention of researchers because they can be used in refrigeration applications at room temperature. [3]. Their unique physical properties, such as high chemical stability, low cost, simple synthesis, the ability to adjust their magnetic transition temperatures close to room temperature by substitution, and remarkable MCE, make them a good choice for magnetic refrigeration [4].

The double exchange (DE) and super-exchange (SE) interaction model has been used to explain the magnetic mechanism of manganites [3]. The variation of Mn-O bond length and Mn-O-Mn bond angle, which are controlled by the average ionic radius of A or Mn site ions and the carrier density of Mn3+/Mn4+ ratio, affects the strength of DE and SE interactions [5].

In previous researches, we used the thermodynamics equation to calculate the magnetic entropy change using $La_{0.6-x}Gd_xSr_{0.4}MnO_3$ experimental data and various methods to determine the critical exponents near TC [6, 7]. The following are the main experimental results of MCE for $La_{0.6-x}Gd_xSr_{0.4}MnO_3$ compounds: - The samples showed a second-order PM-FM phase transition around the blind temperature. By substituting Gd, TC decreases near room temperature, and entropy change increases, meaning that La0.6-xGdxSr0.4MnO3 compounds can be used as magnetic refrigeration. - The values of critical exponents were not belonging to any of the common classical models which could be explained with the induced lattice disordering and magnetic disordering, as a result of Gd substitution.

However, to optimize and improve magnetic refrigeration materials, accurate thermodynamic equations are needed, especially to determine the nature of the order transfer. Significant progress has been made in interpreting the magnetocaloric properties of the material in this scenario. The universal curve enables the researcher to estimate the MCE response of materials that are not easily accessible locally and whose preparation is extremely expensive. In some previous studies in manganites, the Landau theory

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DOI: 10.22075/PPAM.2021.23933.1010

and universal curve have been employed in investigations to better understand phase transition and MCE around the TC [8-10].

The first goal of this study is to use Landau theory and universal curves to determine the nature of the transition. The next objective is to use the Landau method to investigate MCE by scaling experimental magnetization curves.

2. Experimental

Different samples of $La_{0.6-x}Gd_xSr_{0.4}MnO_3$ (x = 0 - 0.1) were synthesized by the nitrate-complex auto-ignition method. The experimental information was published in our previous study [6].

Using a quantum design magnetic properties measurement system (MPMS), the isothermal magnetization versus applied field near the Curie temperature was measured.

3. Results and Discussion

A phenomenological version of the universal curve for $\Delta S_M (T)$ has recently been presented as a way for comparing the properties of several materials and extrapolating to fields and/or temperatures outside the experimental range [11]. Also, for determining the order of PM-FM phase transition based on the scaling of the magnetic entropy change [12], Franco et al. also suggested more precise methods for constructing a universal curve based on the magnetic entropy change [13]. These approaches can be used to calculate the type of phase transition for a wide range of ferromagnetic materials. Following the scaling process, all the entropy change curves at different applied magnetic fields collapse into a phenomenological universal curve. The main hypothesis is based on this reality that, if there is a universal curve, the corresponding points of the $\Delta S_M (T)$ curves measured at different applied fields, should fall on the same universal curve [14]. The master curve is also demonstrated by normalizing all the ΔS_M curves with the peaks associated with the entropy change:

$$\Delta S^{/}(T, H_{Max}) = \frac{\Delta S(T, H_{Max})}{\Delta S_M^{pk}(T, H_{Max})} \tag{1}$$

Rescaling the temperature axis is possible by defining a new variable [15]:

$$\theta = \begin{cases} \frac{-(T-T_C)}{T_{r1}-T_C} & T \le T_C \\ \frac{(T-T_C)}{T_{r2}-T_C} & T \rangle T_C \end{cases} \tag{2}$$

Where T_{r1} and T_{r2} are the temperatures of the reference points. In the present study, their values are selected $\frac{1}{2}$ ΔS_M^{PK}. As shown in Fig.1, the θ depends on $\Delta S_M (T)$ for different samples with various applied magnetic fields. The curve confirms the predictable behavior of a master plot. As it is seen, all the curves have collapsed onto a single universal curve, regardless of the magnetic field that is involved in the second-order transition. The universal curve has shown that the phase transition in our compounds was second-order, which matches with the results of Arrott plots in the previous report. The average curve, depicted as a solid curve in Fig. 1, is derived from universal scaling and provides a smoother representation of the curve. Once the temperature axis is again changed from reduced to unnormalized, this average curve emerges extrapolation to lower (higher) temperatures is possible for high field data. At the same time, a better description of the peak is possible for low field curves. The inverse transformation to the experimental temperature and magnetic entropy change axes could be achieved by combining all of these data in the average universal curve described above, generating predictions about the curve's behavior.

To further the theoretical study of MCE, the Landau theory is employed to study the type of magnetic phase transition, the effect of Gd substitution on the Curie temperature, and the magnetic entropy change value of compounds [16]. The temperature dependence and magnitude of the ΔS_M value are controlled by the magneto-elastic coupling and electron conduction energy in the Landau theory, which plays an essential role in the MCE properties [17]. According to the Landau theory of phase transition, free energy is a function of magnetization and temperature. Also, in the vicinity of the transition temperature T_C, Gibbs free energy of a ferromagnetic system can be expanded as follows [18]:

$$G(M,T) = G_0 + \frac{1}{2}\alpha(T)M^2 + \frac{1}{4}\beta(T)M^4 + \ldots\ldots - \mu_0 HM \tag{3}$$

Where "α" and "β" are Landau coefficients, respectively. Assuming the equilibrium condition of Gibbs energy is when $\left(\frac{\partial G}{\partial M}\right) = 0$, the following equation can be obtained in the vicinity of T_C [17, 19]:

$$\mu_0 H = \alpha(T)M + \beta(T)M^3 \tag{4}$$

These coefficients can be determined by fitting the experimental isothermal magnetization measurements with a polynomial function. Fig 2. a and b exhibit the temperature dependence on the $\alpha (T)$ and $\beta (T)$ coefficients, respectively.

In the vicinity of the Curie temperature, a prominent variation in the magnetization curves has been observed, including observation of a significant magnetic entropy change due to the ferromagnetic–paramagnetic phase at the transition temperature. As the temperature increases, the sign of the coefficient $\alpha (T)$ changes from negative to positive, corresponding to T_C. after passing the zero point. The coefficient $\beta (T)$ of these compounds shows a positive signal in all temperature ranges, which indicates the second-order of FM-PM phase transition in the samples. These results agree with the analysis of the Arrott plots reported in previous work [6]. The change in magnetic entropy can be expressed by differentiating Gibbs free energy from temperature as follows. [20]:

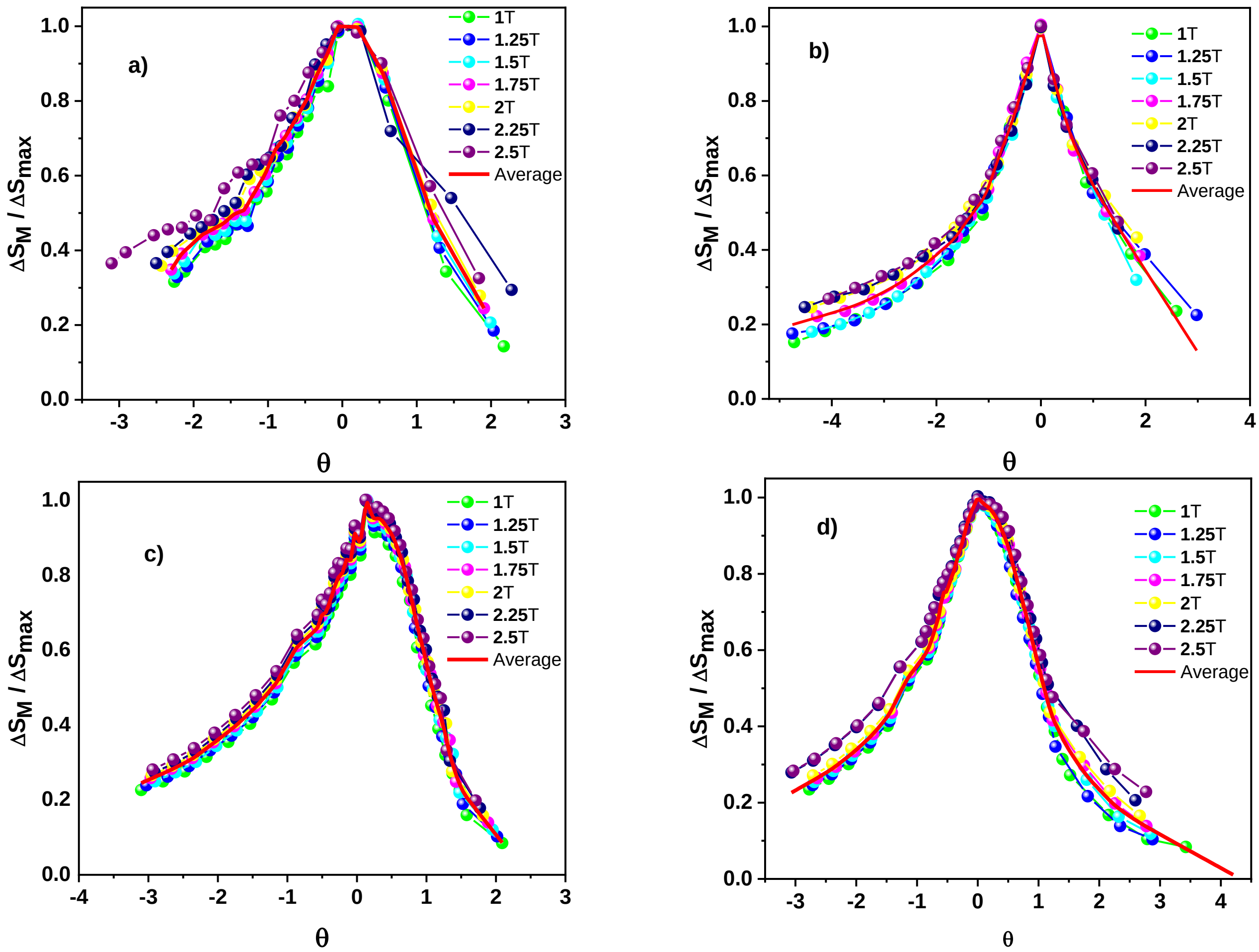

Fig. 1. Universal behavior of the scaled entropy change curves of the samples *x=0* (a), *x= 0.0125* (b), *x= 0.05* (c) and *x= 0.1* (d)

$$-S_T(T,H) = \left(\frac{\partial G}{\partial T}\right)_H = \frac{1}{2}\alpha'(T,H)M^2 + \frac{1}{4}\beta'(T)M^4 \qquad (5)$$

Where $\alpha'\ (T)$ and $\beta'\ (T)$ are temperature derivatives from the expansion coefficient. Using the relation (5), the theoretical variation of the magnetic entropy change $-\Delta S_M$ as a function of temperature was calculated for all the specimens.

$$-\Delta S_T(T,H) = S_T(T,0) - S_T(T,H) = \frac{1}{2}\alpha'(T)(M^2 - M_0^2) + \frac{1}{4}\beta'(T)(M^4 - M_0^4) \qquad (6)$$

Figure 3 shows the temperature dependence of the magnetic entropy change curve under an applied magnetic field of 2.5 T for all samples. Considering this point, it is observable that the calculated results from theoretical experiments are in good agreement with the empirical data, except for a slight difference at the maximum of the magnetic entropy change near the Curie temperature.

The experimental results are in agreement with the Landau theory results, as shown in the pictures. For all samples, a difference between theoretical and experimental curves occurs below T_C. Kamilov et al. propose that electronic entropy causes a slight divergence from accurate MCE [20] and that indirect measurement is another possible explanation of the inconsistencies. As a result, the electron's magnetic entropy change value could be the explanation for this variation.

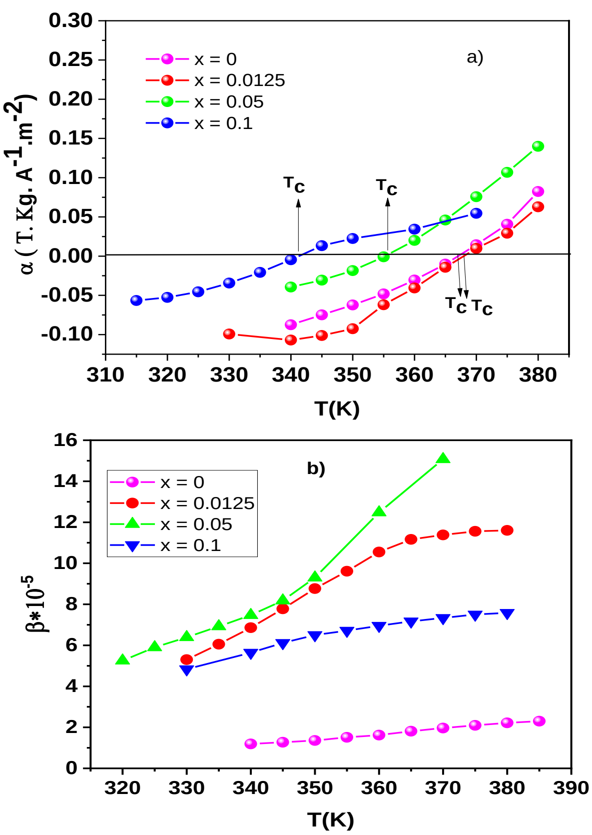

Fig. 2. a) Temperature dependence on **α** coefficient b) ß coefficient for the samples

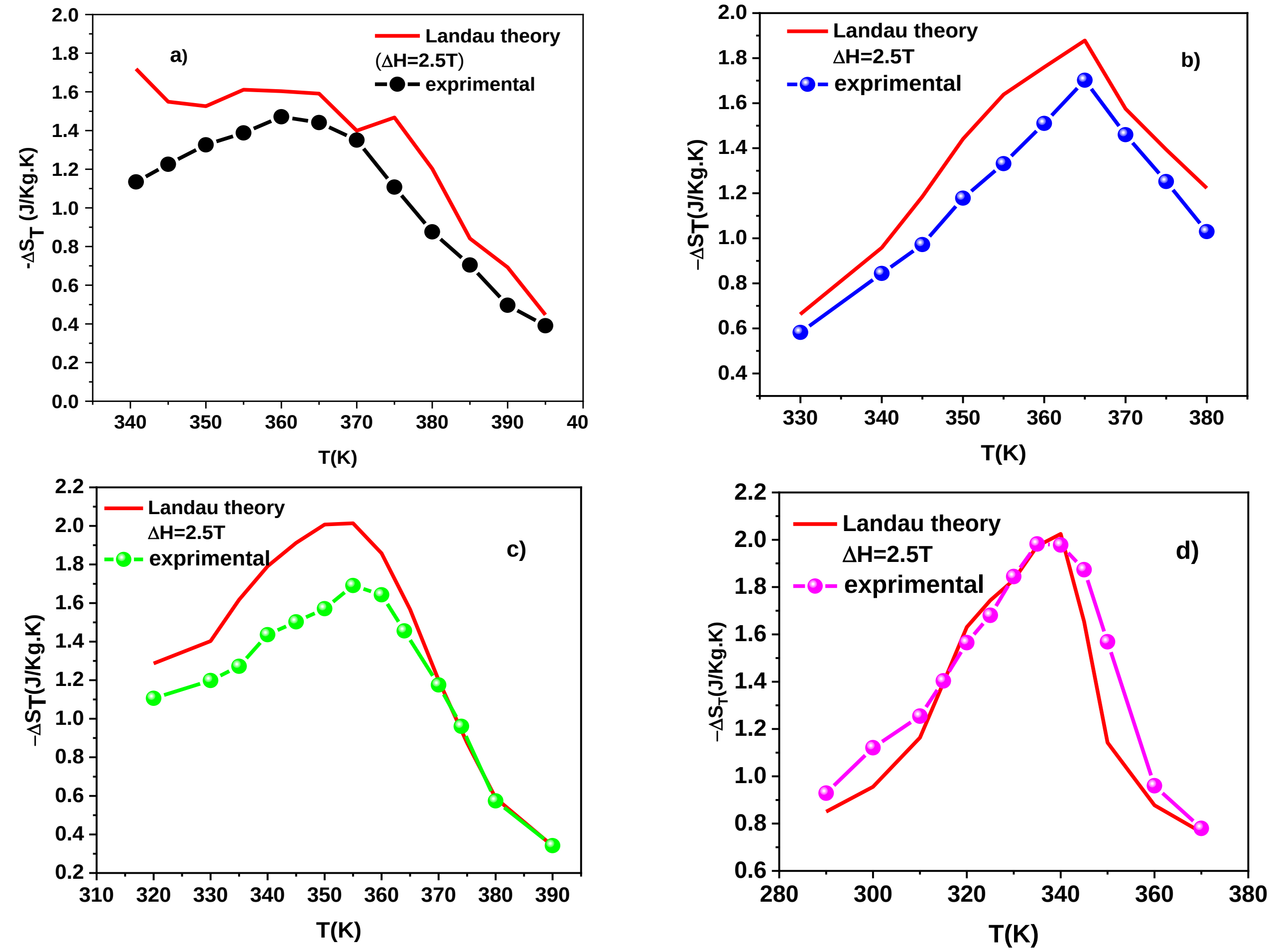

Fig. 3. Temperature dependence of the magnetic entropy change derived from magnetic measurements estimated by the Landau theory at the applied magnetic fields for samples *x=0* (a), *x= 0.0125* (b), *x= 0.05* (c) and *x= 0.1* (d)

4. Conclusion

In conclusion, we have mainly studied the application of Landau theory and the universal curve to identify the nature of the transition and to determine the change in magnetic entropy of manganite. The universal curve for materials with second-order phase transitions can be used to characterize magnetic entropy variation. It is possible to extrude experimental results $-\Delta S_M$ in various magnetic fields and temperatures. In addition, the results can be used by engineers to build a magnetic refrigerator. The experimental and theoretical changes of magnetic entropy (Landau theory) corresponded well.

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