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Investigation of critical behavior in $La_{1-x}Ce_xMn_2Si_2$ (x=0.35 and 0.45) by using the dependence of magnetic entropy change

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Abstract

The critical exponents of $La_{1-x}Ce_xMn_2Si_2$ (x=0.35 and 0.45) compounds are studied in the vicinity of Curie temperature (T_C) which is a second order phase transition. The magnetic field dependence of the magnetic entropy change is brought out and implemented to deduce the critical exponents. The critical exponents are estimated by various techniques such as the Modified Arrott plot and critical isotherm technique. The obtained values of critical exponents for both compounds have been satisfied with the scaling theory. The results have showed that the critical values and universal curve depends on the strength of secondary magnetic phase existing in the compound, which is antiferromagnetic phase in our case.

Keywords: *Intermetallics, magnetic properties, magnetocaloric effect, critical phenomena.*

$La_{1-x}Ce_xMn_2Si_2$ (x=0.35 ve 0.45) kritik davranışının manyetik entropi değişim bağlılığına göre araştırılması

Özet

$La_{1-x}Ce_xMn_2Si_2$ (x=0.35 ve 0.45) bileşiklerinin, kritik üstelleri ikinci derece bir faz geçişi olan, Curie sıcaklığı (T_C) civarında incelenmiştir. Manyetik entropi değişiminin, manyetik alana bağımlılığı ortaya konulmuş ve kritik üstelleri bulmak için uygulanmıştır. Kritik üsteller, Modifiye Arrott çizimi ve kritik izoterm tekniği gibi çeşitli yöntemlerle tahmin edilmiştir. Elde edilen kritik üsteller, ölçekleme teorisi uygun oldukları belirlenmiştir. Sonuçlar, kritik değerin ve evrensel eğrinin; bu çalışmada

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antiferromanyetik faz olan, bileşikte oluşan ikinci manyetik fazın şiddetine bağlı olduğunu göstermiştir.

Anahtar kelimeler: *Intermetalik, manyetik özellikler, manyetokalorik etki, kritik olay.*

1. Introduction

It is a fact that energy consumption and the world energy demand of countries is continuously increasing. Refrigeration is one of area where energy is intensely used, thereby demand of environmental-friendly refrigeration techniques is also increasing. Simultaneously, alternative ways of energy efficient technologies are receiving more attention. As a consequence of this situation, materials displaying large caloric effects such as magnetocaloric, barocaloric, electrocaloric and elastocaloric are also receiving more attention, which are the response of material to external change of magnetic field, pressure, electric field, and force, respectively [1, 2].

Among these caloric effects, the most studied one is the magnetocaloric effect [1-2]. Large MCE reported in various systems, such as $Gd_5Si_2Ge_2$, RCo_2, MnAs, MnAsSb, $LaFe_{11.4}Si_{1.6}$, MnFePGe, Heusler alloys, and some manganites [2 -15], generally shows first-order ferromagnetic to paramagnetic phase transition. However, these alloys have large thermal and magnetic field hysteresis on variation in magnetization with temperature and magnetic field, respectively. Another category of materials that exhibit substantial magnetocaloric effect (MCE) are those that undergo antiferromagnetic-ferromagnetic (AF-FM) transitions and are found in a variety of intermetallic alloys and compounds [16]. In many cases, these transitions are free of thermal hysteresis—a property that makes such systems particularly attractive as magnetic refrigerants [16].

In addition, it is reported that the knowledge of magnetic field dependence of magnetic entropy change ($-\Delta S_M$) of a magnetic refrigerant material is important, since understanding the field dependence can provide further knowledge to improve the performance of refrigerant materials [17]. Investigation of MCE is not only providing practical application knowledge it may also provide understanding the properties of the material. In particular, the details of the magnetic phase transition and critical behavior can be obtained by studying the MCE of the material [17, 18]. Magnetocaloric effect is one of the issues observed in the ternary intermetallic compounds of the RT_2X_2 series (R = rare earth, T =transition metal, X = Si or Ge). These compounds have attracted considerable attention because of the rich variety of interesting phenomena, including superconductivity, magnetism-magnetocaloric effect, mixed valence, heavy fermions, and Kondo behavior [16, 19 - 23]. Most of the study in RMn_2Si_2 structure concentrated on properties at low temperatures and moderate temperatures. However, the magnetic properties around Curie temperature (T_C) may also provide additional information about the magnetic structure with the critical behavior analysis by using the dependence of magnetic entropy change. To further understand the nature of magnetic transition $La_{1-x}Ce_xMn_2Si_2$ system, in this paper, the critical properties of $La_{1-x}Ce_xMn_2Si_2$ (x=0.35 and 0.45) compounds around the Curie temperature have been investigated by using the field dependence of magnetic entropy change method. In addition, to the best of our knowledge there exists a few works on the critical exponents analysis on $ThCr_2Si_2$ type ternary intermetallic compounds [24-27].

2. Experimental

Experimental details of this study were explained in Ref. [19], such as polycrystalline samples $La_{1-x}Ce_xMn_2Si_2$ (x=0.35 and 0.45) synthesized by arc melting the elements in a water-cooled Cu hearth under purified argon gas. Magnetization measurements were carried out in the temperature range 5-350 K and from 0 T up to 7 T with a physical property measurement system (PPMS) (Quantum Design).

According to the scaling hypothesis, a continuous phase transition at near the critical temperature T_C, shows a power law dependence of spontaneous magnetization $Ms(T)$ and an inverse initial susceptibility $\chi_0(T)$ on the reduced temperature with a set of interdependent critical exponents β, γ and δ etc [28]. Generally, the critical exponents are not defined for the first-order transition because the magnetic field can shift the transition, leading to a field-dependent phase boundary $T_C(\mu_0 H)$ [29]. The mathematical definitions of the exponents from magnetization measurements can be described as [28, 30, 31].

- Below T_C, the temperature dependence of the spontaneous magnetization $Ms(T) = \lim_{H\to 0}(H)$ is governed by β exponent through the relation:

$$M_s(T) = M_0(-\varepsilon)^{\beta}, \varepsilon < 0,\ T < T_C \tag{1}$$

- Above T_C, the initial susceptibility $\chi_0^{-1}(T) = \lim_{H\to 0}(H/M)$ given by

$$\chi_0^{-1}(T) = \left(\frac{h_0}{M_0}\right)\varepsilon^{\gamma}, \varepsilon > 0,\ T > T_C \tag{2}$$

- At T_C, M and H are related by the following equation:

$$M = D\mu_0 H^{\delta^{-1}}, \varepsilon = 0,\ T = T_C \tag{3}$$

where M_0, h_0/M_0 and D are the critical amplitudes and M_s, χ_0^{-1}, $\varepsilon = (T-T_C)/T_C$ are spontaneous magnetization, initial susceptibility and the reduced temperature, respectively.

3. Results and discussions

RT_2X_2 compounds form mainly in the $ThCr_2Si_2$ structure (space group I4/mmm), with the layered nature of this crystal structure leading to strong dependence of the magnetic interactions on the interplanar and intraplanar interatomic distances [20-23]. RMn_2X_2 compounds with X = Si or Ge have attracted special attention, due to the interesting interplay between the magnetism of the layers of 3d and 4f atoms, the strong dependence of the magnitude of the Mn moment and the magnetic state of the Mn sublattice on the Mn–Mn interatomic distances [21]. The high sensitivity of exchange parameters to the intralayer Mn-Mn spacing governed by the lattice parameter a leads to complex and very interesting magnetic phase diagrams of these compounds, which is very well explained in Ref. [23] and references therein.

The thermomagnetization curves of the $La_{1-x}Ce_xMn_2Si_2$ (x=0.35 and 0.45) were published in a previous study [19]. Briefly, the x=0.35 compound shows ferromagnetic properties below Curie temperature (T_C) = 294 K, while decreasing temperature, till 200 K where the magnetization decreases with further cooling. Below 200 K this compound showed antiferromagnetic properties. The magnetic structure of these systems depends on Mn-Mn intralayer distance [16, 20, 21]. Similarly, x=0.45 compound shows ferromagnetic properties below T_C =285 K. But the T_N of x=0.45 is observed around at 254 K [19]. In the parent compound $LaMn_2Si_2$, the Mn moments within the (0 0 1) plane order antiferromagnetically below T_N = 470 K [23] down to T_C. Therefore, one can imagine a similar for x=0.35 and x=0.45 above the T_C. Thereby, we have a dominant ferromagnetic component amid the two antiferromagnetic components.

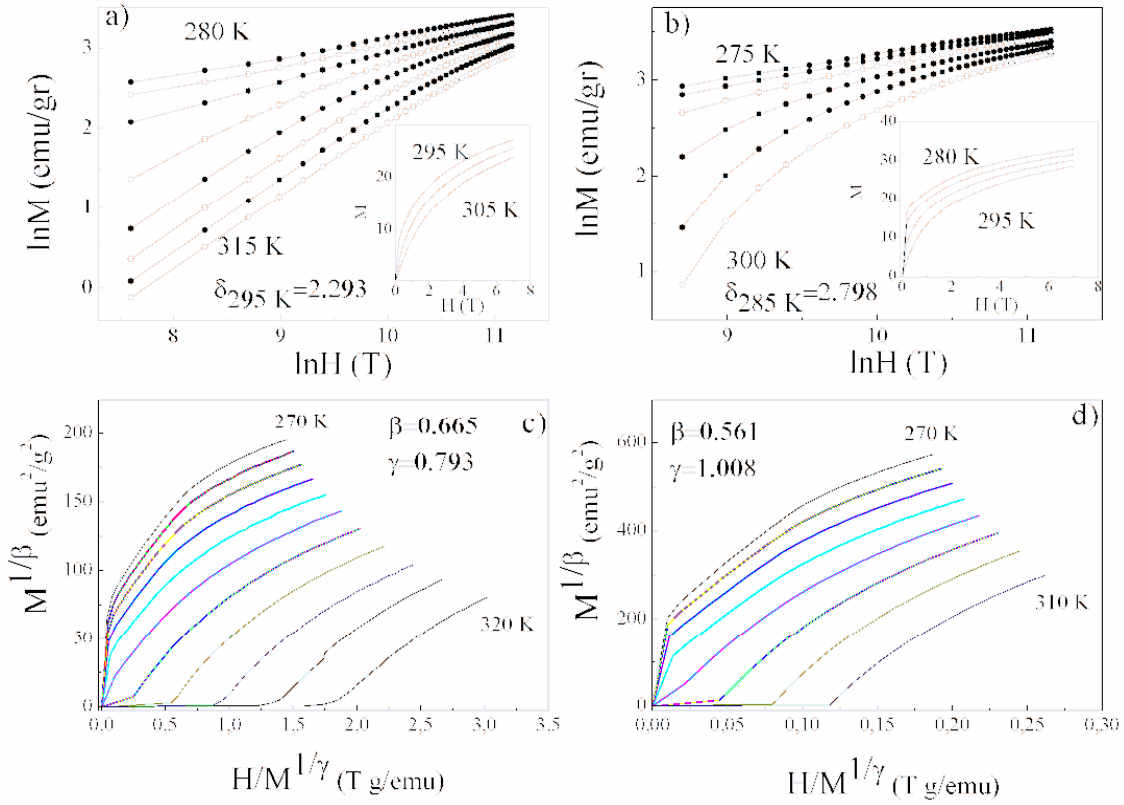

Figure 1. The critical isotherm analysis at T_C for the x = 0.35 (a) and x=0.45 (b) compounds in ln-ln scale. Inset shows the data close to Curie temperature. The modified Arrott plot of the x = 0.35 (c) and x=0.45 (d).

To analyze the nature of the magnetic phase transition around T_C in detail, we carried out a critical exponents study on the compounds. In this context, we have used the field dependence of ΔS_M to investigate the critical behavior. According to the scaling hypothesis [32], a second-order magnetic phase transition near T_C is characterized by a set of critical exponents β (the spontaneous magnetization), γ (the initial susceptibility), and δ (the initial isotherm). To investigate the magnetic property, the M(H) curves represented as ln-ln form in Fig. 1(a) and (b), the Arrott plots presented around the Curie temperature are shown in Fig. 1(c) and (d), respectively. In an Arrott plot, a negative slope represents a first order phase transition meanwhile a positive slope represents second order transition [33]. It is clear that, the positive slopes in Figs. 1(c) and (d) refer to 2nd order transition for both compounds. However, the curves are all

nonlinear and show downward curvature even at high the magnetic field region. According to the mean field theory, the critical exponents have value 0.5 for β and 1.0 for γ [33]. However, the nonlinearity refers that the conditions for mean field theory will not be not satisfied. Therefore, the mean-field theory cannot be used to describe the critical behavior.

To further clarify the nature of the magnetic transition, we attempted to use various techniques to investigate the critical behavior of our compounds. Generally, the common method to deduce the critical exponents always depends on the fitting values obtained from the Arrott plot according to Arrott–Noakes equation of state. In this technique one needs to apply some different theoretical models to first build some Arrott plots and afterwards pick the best one for fitting data, in light of the obscure fitting information toward the beginning. Nonetheless, initial choice of the critical exponents influences the last esteem value the critical exponents. In this manner, it is hard to settle on of the critical exponents [34]. Many authors used the field dependence of magnetic entropy in literature [34 - 36]. In this approach, first, the Widom scaling relates the critical exponents β, γ, and δ to each other with: $\delta = 1 + \gamma/\beta$ [37]. Meanwhile, according to the scaling hypothesis, at T_C the exponent δ is associated with the critical magnetization isotherm by $M_{TC} = DH^{1/\delta}$, where D is the critical amplitude [30 - 32,38]. In this context, Fig. 1(a) and (b) shows the magnetic isotherms M(H) curves around T_C for x=0.35 and 0.45 compounds in ln-ln scale, which should be a straight line with a slope 1/δ, where inset shows normal scale. A linear behavior can be observed under high field region close to T_C in ln-ln scale. From the linear fit of the straight line, the obtained values of δ are 2.293 and 2.798 for x=0.35 and 0.45, respectively.

Furthermore, for a magnetic system with a 2nd order phase transition, a universal relation of the field dependence of magnetic entropy is proposed as $\left|\Delta S_M^{pk}\right|$ vs H^n, where n=2/3 [39]. In addition, a new relation proposed which agrees with experimental result and confirmed the existence of the universal curve [39]:

$$n = 1 + [\frac{\beta-1}{\beta+\gamma}] \quad (4)$$

thereby one can calculate critical exponents of β and γ if n is known value at T_C. In order to obtain the value of n, we first calculated ΔS_M as in Ref. [11] and shown as a function of magnetic field change (H) in Fig. 2 (a) and (b). By this manner, we calculated the n value for x=0.35 and 0.45 compounds, as 0.78 and 0.72, respectively. In addition, we illustrated the variation of n with respect to temperature by using the formula

$$n = \frac{dln|\Delta S_M|}{dlnH} \quad (5)$$

in Figs. 2 (c) and (d), for x=0.35 and 0.45 compounds, respectively. In generally, the value of n is approximately to 2 for the temperature well below T_C and ~1 for temperature well above T_C [39]. In the case of the temperature corresponding to the maximum entropy change based on mean field model, it has been predicted close to 2/3 [40]. Both compounds show similar behavior, n decreases gradually with increasing temperature and show a minimum at around T_C, then increases gradually with further increasing temperature. As one can see the values of the x=0.35 is more in line with

proposed earlier [39]. As stated previously, according to the thermomagnetization data [19], the ferromagnetic region of x=0.35 compound is between 294 K – 200 K, meanwhile, for x=0.45 compound is 290 – 254 K. The rapid increase of n at 267.5 K of x=0.45 compound should be related with antiferromagnetic magnetic structure around 255 K. We guess that the anomaly below 275 K is the sign of antiferromagnetic ordering this antiferromagnetic structure, which should be further investigated.

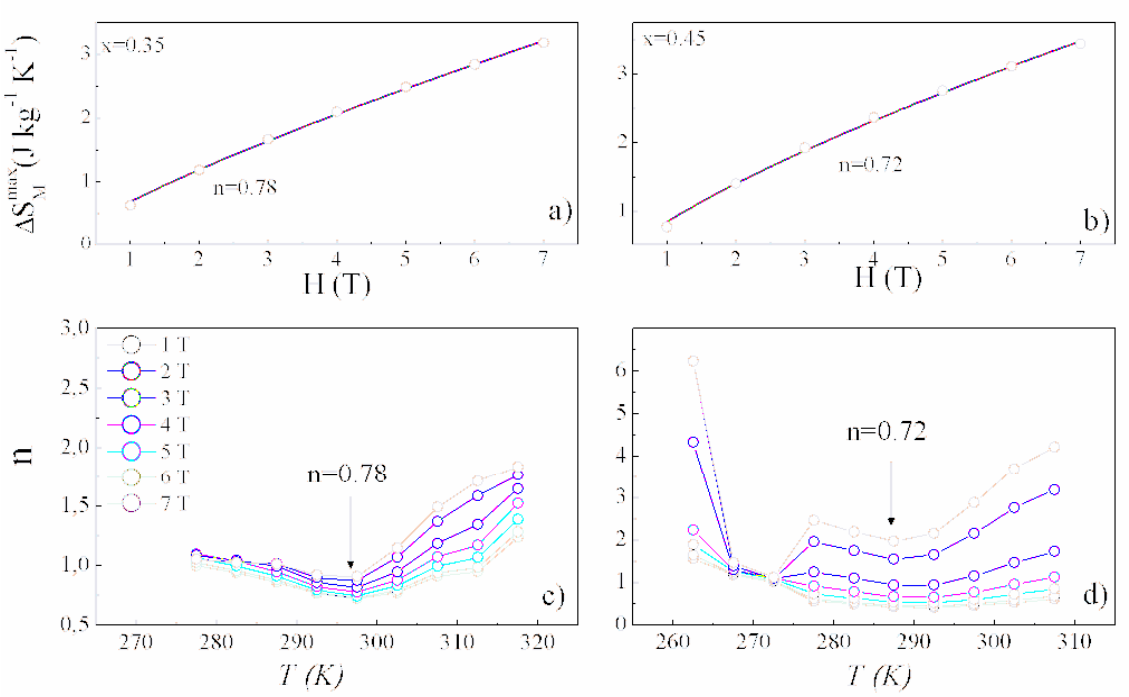

Figure 2. The maximal entropy changes vs. H (circles) and the solid line is the fitting curve for x=0.35 (a) and x=0.45 compounds (b). Temperature dependence of the exponent characterizing the field dependence of n for x=0.35 (c) and x=0.45 compounds (d).

Moreover, one can obtain β and γ by using the obtained values of n and δ with Eq. (4). For the x = 0.35 compound, we calculated β and γ as 0.665 and 0.793. For the x=0.45 compound, we calculated β and γ as 0.561 and 1.008. The value of the critical exponents β and γ for the x = 0.45 compound is close to that obtained from the mean field theory, which indicates a long-range magnetic interaction. However, the derived values of the critical exponents of the x = 0.35 compound are slightly lower. The modified Arrott plots are shown in Fig. 1(c) and (d) with the obtained β and γ.

The obtained critical exponents (β, γ, δ, and T_C) can be also verified by the prediction of the scaling theory in the critical region. According to the scaling theory, the magnetic equation of state can be written as [31, 32]:

$$M(H,\varepsilon) = \varepsilon^{\beta} f_{\pm}\left(H/\varepsilon^{\beta+\gamma}\right) \quad (6)$$

where $\varepsilon=(T-T_C)/T_C$, f_+ and f_- are regular functions for $T>T_C$ and $T<T_C$, respectively. $M\varepsilon^{-\beta}$ vs $H\varepsilon^{-(\beta+\gamma)}$ yields two universal curves: one for temperatures above T_C and the other for temperatures below T_C. Thus we can verify the reliability by comparing the obtained

results with the scaling hypothesis. As shown in Fig. 3(a), all the experimental data fall on two curves which is in agreement with the scaling theory for x=0.35 compound, therefore field dependence of S_M are reasonably accurate. However, for the x=0.45 compound, it falls on below T_C, data above T_C almost fall on one branch (Fig. 3(b)). It is proposed that non-collapsing character could be due to the existence of a second magnetic phase, even its transition temperature well above the experimental range [39]. We know that both samples have a intra antiferromagnetic structure above T_C, therefore the non-collapsing behavior of the x = 0.45 compound might be due to strength of antiferromagnetic structure. In other words, the x=0.45 compound behaves as if double phase magnetic system meanwhile x=0.35 compound behaves as if mono phase magnetic system. Since the values of the x=0.45 compound is more close to the mean field theory, then we can conclude that the behavior of x=0.45 compound is more in line with the observed thermomagnetization curves [19] than the x=0.35 compound. In addition, as shown in Fig. 2 (c) and (d), the values for n of x=0.45 compound is higher than previously stated in Ref. [39], which might be due to significance of the second magnetic phase (intra layer antiferromagnetic in this case).

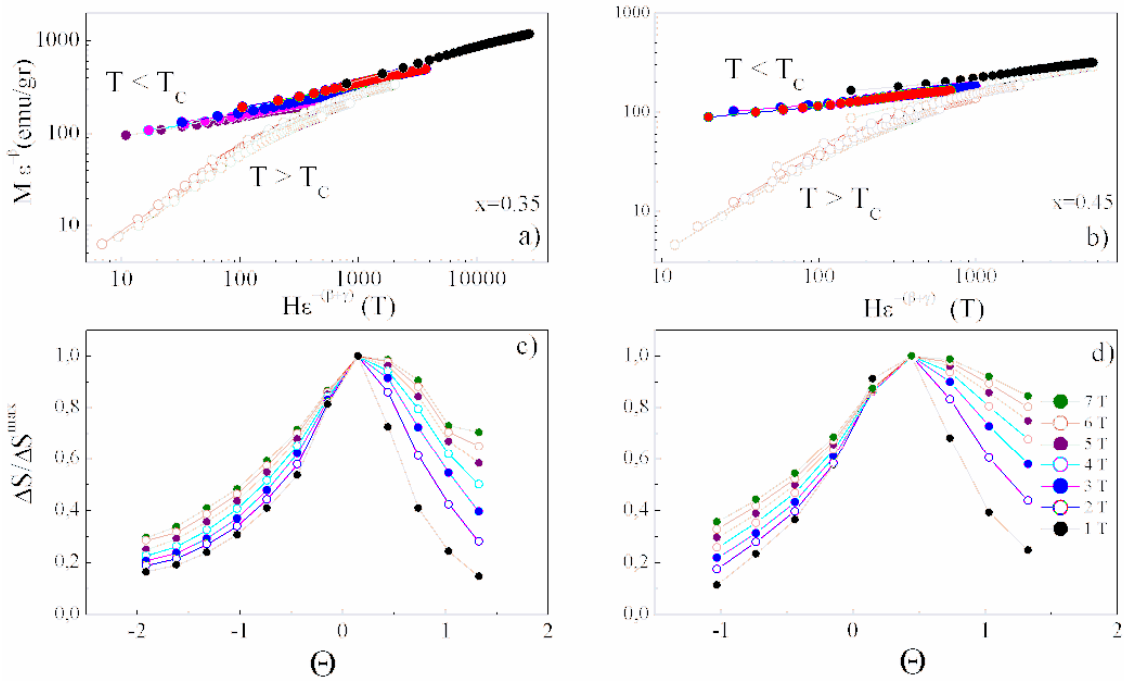

Figure 3. (a) logarithmic scaling plot of $M\varepsilon^{-\beta}$ vs $H\varepsilon^{-(\beta+\gamma)}$ in the critical region for x=0.35 compound all experimental data fall on either of the two branches of the universal curve, (b) x=0.45 compound all experimental data do not fall on above T_C. Rescaled curves of x=0.35 (c) and x=0.45 (d) compounds for a maximum applied field of 7 T.

Recently Franco and co-workers proposed that the $\Delta S_M(T)$ curves measured with different maximum applied fields should collapse on to a single master curve for alloys with second order phase transition [41]. To the best our knowledge the master curve of ΔS_M for $ThCr_2Si_2$ system is absent. Here, we have attempted to make a master curve for the x=0.35 and 0.45 systems. A phenomenological universal curve for $|\Delta S_M|$ has been proposed to extrapolate magnetocaloric properties with different applied fields and temperatures. The construction can be achieved by using normalized entropy change ($\Delta S_M = \Delta S_M^{max}$) and rescaling the temperature axis as [42]:

$$\theta = \frac{|T-T_C|}{T_r-T_C} \quad (7)$$

where θ is the rescaled temperature, T_C is the Curie temperature, T_r is the reference temperature corresponding to 0.75 ΔS_M^{max} . It should be noted that a factor (0.75 in this case) close to 1 would enhance the effect of experimental noise in the resulting master curve [43]. The rescaled magnetic entropy change curves of the present alloys are shown in Figs. 3(c) and (d). All the curves collapse into a single curve in temperature regions near to ordering temperature (θ=0) further validating our treatment of data according to second order phase transition in these compounds [43]. However, as we move away from the ordering temperature where is observed, breakdown can be observed in the curve which is acceptable as scaling laws need not hold far away from Curie temperature (T_C). As proposed in Ref. [39], this might be due to the sample consisting of different magnetic phases. The universal curve (Fig. 3(c-d)) and scaling theory (Fig. 3(a-b)) shows similar result for x=0.35 and 0.45 compounds with a small deviation for x=0.45 compound which might be related with the strength of the antiferromagnetic structure. Namely, that difference might be due to different significance of intralayer antiferromagnetic character in two compounds. Thereby, the non-collapsing character of the magnetocaloric curves might be helpful for detecting the existence of second magnetic phase [39].

In neutron diffraction studies on $La_{0.65}Nd_{0.35}Mn_2Si_2$ [21, 44], $La_{0.6}Pr_{0.4}Mn_2Si_2$ [45], $LaMn_2Si_2$ [46] authors reported several magnetic moments values (μ_{ab}) at different temperatures given in Table 1. The magnetic structure of these compounds explained in Ref. [23, 21, 46]. Above the Curie temperature samples have antiferromagnetic structure called AFl (magnetic structure is characterized by antiferromagnetic (001) Mn layers). Below Curie temperature samples have ferromagnetic structure called Fmc (ferromagnetic interplane coupling of Mn planes unison with in-plane antiferromagnetic coupling), down to T_N. Below T_N in-plane antiferromagnetic coupling was observed. In. Ref. [46], it was stated that there exists the dominant antiferromagnetic Mn-Mn intralayer couplings observed in $LaMn_2Si_2$.Since the magnetic structure around Curie temperature is governed by Mn-Mn planes, one may expect similar magnetic moments values as listed above. However, the results are not exactly the same, which shows the below T_C antiferromagnetic – ferromagnetic and above T_C antiferromagnetic strength of each sample differs due to the different in-plane Mn moments. The different behavior of the studied alloys in this research is also might due to this strength difference for each sample.

Table 1. μ_{ab} values of several compounds in $La_{1-x}R_xMn_2Si_2$ system.

	$La_{0.65}Nd_{0.35}Mn_2Si_2$ [44]		$La_{0.65}Nd_{0.35}Mn_2Si_2$ [21]		$La_{0.6}Pr_{0.4}Mn_2Si_2$ [44]		$LaMn_2Si_2$ [45]
	287 K (F)	350 K (AF)	267 K (F)	312 K (AF)	260 (K) (F)	350 K (AF)	315 K (AF)
μ_{ab} (μ_B)	1.29	0.75	1.26	1.10	1.44	≈1.2	1.20

4. Conclusions

In conclusion, in order to further analyze the magnetic structure of the $La_{1-x}Ce_xMn_2Si_2$ (x=0.35 and 0.45), we have studied the field dependence of ΔS_M and critical behavior with the aid of previously published neutron diffraction data. According to the analyze, the strength of antiferromagnetic structure may affect the behavior of the magnetic structure even if it exists as secondary phase. Namely, the field and temperature dependent magnetization behavior of x= 0.35 compound (weaker antiferromagnetic sample in this study) follows the scaling theory and universal curve in Fig. 3(a-c). For x=0.35 compound, all data points fall onto the two district branches which indicates the obtained critical exponents are reasonably accurate. However, for the x = 0.45 compound, data fall almost fall for $T > T_C$. Thereby we deduced that the small deviation from collapsing behavior of the x = 0.45 compound is due to the inherent of the multiphase system. The master curve of both samples implies that actually both samples are multiphase system, however the varying strength of antiferromagnetic phase, leads to different critical behavior. In other words, the difference between the critical exponents of both compounds is related with the strength of the antiferromagnetic state around T_C. This result is supported with previous results of neutron diffraction results.

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