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Onur Nane[(a)], Hasan Ağıl[(b)], Berdan Özkurt[(c)], Bekir Özçelik[(a)]*, Ali Gencer[(b)]

[(a)] ***Department of Physics, Faculty of Sciences and Letters, Cukurova University 01330 Adana,Turkey***
[(b)] ***Department of Physics, Faculty of Sciences, Ankara University,Turkey***
[(c)] ***Department Electronic and Computer Education,*** **Tarsus** ***Technical Education Faculty, Mersin University, İçel, Turkey***

e-mail: ozcelik@cu.edu.tr

Abstract:Low field magnetic and magnetocaloric properties of the compound $LaMn_{1.9}Fe_{0.1}Si_2$ have been investigated. Using the M-H data measured at various temperatures, we have derived the magnetic entropy change $|\Delta S|$ as a function of temperature and magnetic field, by using the Maxwell relation. The temperature dependence of the Landau coefficient has been derived by fitting the magnetization, using the Landau expansion of magnetic free energy and Arrott plots. The results show that $LaMn_{1.9}Fe_{0.1}Si_2$ is ferromagnetically ordered around room temperature (285 K) and the nature of the phase transition at this temperature is found to be second order.

1.Introduction

The magnetic properties and structures of the ternary rare-earth compounds RT_2X_2, where R is the rare earth metal, T is the transition metal and X is Si or Ge, with tetragonal $ThCr_2Si_2$-type structure (space group I4/mmm) have recently been studied extensively [1-6]. In early studies, the $LaMn_2Si_2$ compound was considered as a simple ferromagnet with a Curie temperature Tc=305 K [1,2]. Based on the neutron diffraction and Mössbauer studies, it was reported that $LaMn_2Si_2$ has a canted ferromagnetic structure (F_{mc}) at temperatures $T<Tc$ and in-plane antiferromagnetic structure at $T>Tc$ up to T_N=470 K [3,4]. In addition to the canted ferromagnetic structure, the conical magnetic arrangement (F_{mi}) was observed around $T_h \approx 45$ K. In the last decade, the magnetic properties of the $R(1)_{1-x}R(2)_xMn_2X_2$ systems were extensively studied [7-11]. The substitution of Fe or Co for Mn on $LaMn_{2-x}T_xSi_2$ systems results in a decrease of the value of d^a_{Mn-Mn} due to the size effects. This substitution should induce the transition from ferromagnetic to antiferromagnetic alignment in adjacent Mn layers [6]. The X-ray diffraction patterns showed that $LaMn_{2-x}Fe_xSi_2$ compounds are single phase and the lattice parameters *a, c* and unit cell volume *V* of $LaMn_{1.9}Fe_{0.1}Si_2$ were found to be 4.1088 Å, 10.6034 Å and 179 $Å^3$, respectively [5]. The nature of the magnetic coupling in these compounds within and between the Mn layers is closely related to the in-plane Mn-Mn spacing d^a_{Mn-Mn}. Roughly, if d^a_{Mn-Mn} >2.87 Å, the intra-layer in-plane coupling is antiferromagnetic and interlayer coupling is ferromagnetic (F_{mi} or F_{mc}). If 2.84Å< d^a_{Mn-Mn} <2.87Å, both the intra-layer in-plane coupling and the interlayer coupling are antiferromagnetic (AF_{mi} or AF_{mc}). In the case when d^a_{Mn-Mn} <2.84 Å, there is no intra-layer in-plane spin component, and the interlayer coupling remains antiferromagnetic (AF_{il}) [5].

Since the discovery of the giant magnetocaloric effect (MCE) in $Gd_5Si_2Ge_2$ ($\Delta S = 18.5 J/kg-K$ under 5 T field at Tc=276 K) [12], the number of studies in magnetocaloric materials that can be used around

room temperature has increased considerably. The MCE is defined as the heating or cooling (i.e. the temperature change) of a magnetic material due to the application of a magnetic field. This effect has been called adiabatic demagnetization for years, though this phenomenon is just one practical application of the MCE in magnetic materials [13,14]. The magnetocaloric effect was discovered in 1881, during an experiment performed on iron [15]. The origin of the MCE was explained independently by Debye [16] and Giauque [17]. Nowadays, there is a great deal of interest in using the MCE as an alternative technology for refrigeration, from room temperature to the temperatures of hydrogen and helium liquefaction (~4.2-20 K). An ideal magnetic refrigerant should work over a wide range of temperatures (e.g 220-330 K). The magnetic refrigeration offers the prospect of an energy-efficient and environmentally friendly alternative to the common vapor-cycle refrigeration technology in use today [18,19].

In this paper, we have investigated the low field magnetic and magnetocaloric properties of $LaMn_{1.9}Fe_{0.1}Si_2$ with the expectation that this will exhibit MCE. The Curie temperature is measured as 285 K which is very close to the room temperature range consistent with the values reported by other workers [5,6]. If high Curie temperature and magnetic behavior in the low field are considered the $LaMn_{1.9}Fe_{0.1}Si_2$ compound appears to show the MCE with second order phase transition, thus being an appropriate candidate for magnetic refrigerators.

2.Experimental procedure

The preparation method of the compound was given in detail elsewhere [5]. The magnetic properties were measured by a Closed Cycle Vibrating Sample Magnetometer (Model-7304, Lake Shore).

3.Results and Discussion

The zero field cooled (ZFC) magnetization of $LaMn_{1.9}Fe_{0.1}Si_2$ with respect to temperature is given in Fig.1, for different applied magnetic fields. As can be seen, the magnetization increases rapidly from room temperature up to 270 K, then goes to slightly so-called saturation values for the individual field values. On the other hand, the decrease around 90 K for the field value of 200 Oe is probably due to a reorientation of a sub-lattice magnetization, and the conical ferromagnetic structure (F_{mi}) together with canted ferromagnetic structure (F_{mc}) known to establish below 50 K which is in agreement with the ac susceptibility results [5].

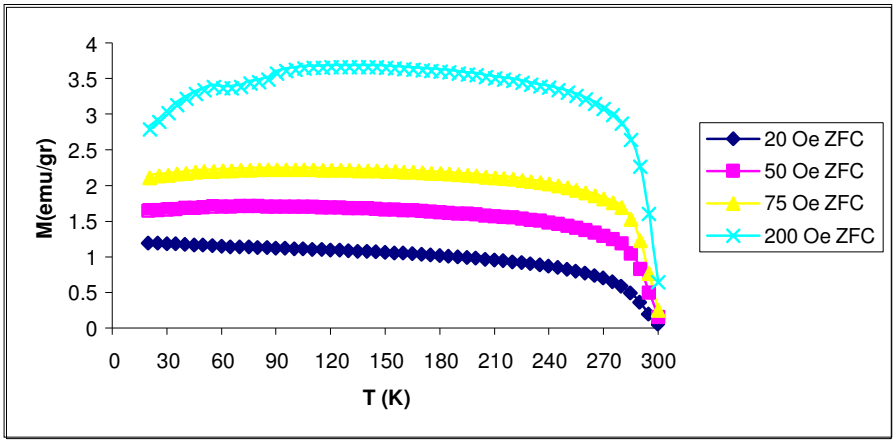

Fig.1. Temperature dependence of magnetization of the $LaMn_{1.9}Fe_{0.1}Si_2$ compound, measured for different field values.

We have shown the zero field cooled (ZFC) and field cooled (FC) magnetization results, measured in a field of 200 Oe, in Fig.2. It is seen that there is a large difference between the FC and ZFC results. In the FC measurement, the sample undergoes a phase change (from an antiferromagnetic to a ferromagnetic

regime) during the cooling process with an external magnetic field. This gives a preferred orientation of the ferromagnetic components. On the other hand, in the ZFC process a preferred orientation is not formed and so the magnetization for ZFC becomes smaller than the FC case. The decreasing behavior around 90 K at the ZFC magnetization is not observed in the FC magnetization measurements. This is probably due to pinning of the canted ferromagnetic phase by conical ferromagnetic phase, and means the canted ferromagnetic phase is suppressed by the external magnetic field during FC process.

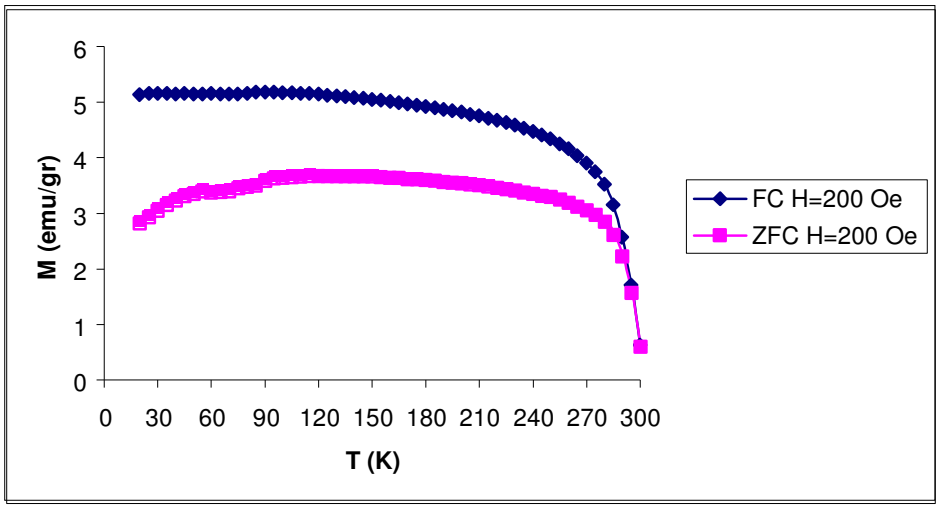

Fig.2. Temperature dependence of magnetization of the $LaMn_{1.9}Fe_{0.1}Si_2$ compound, measured for *H*=200 Oe

For the temperature value of 40 K, the hysteresis loop of $LaMn_{1.9}Fe_{0.1}Si_2$ is given in Fig.3. The variations in the magnetization curves exhibit typical ferromagnetic behavior. The coercivity field and saturation magnetization are measured to be about 540 Oe and 29 emu/g, respectively.

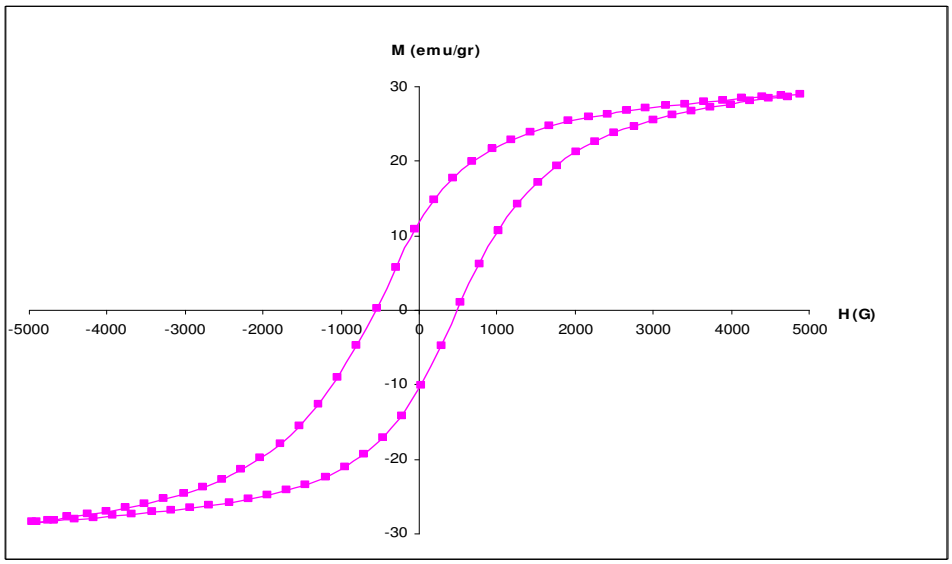

Fig.3. Hysteresis loops of the $LaMn_{1.9}Fe_{0.1}Si_2$ compound, for *T*=40 K

From the *M-H* data, the magnetic entropy change associated with the magnetocaloric effect can be calculated from the thermodynamic Maxwell relation:

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \tag{1}$$

or integrating over the magnetic field

$$\Delta S = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \tag{2}$$

which gives the magnetic entropy change, ΔS. The integral in eq.2 may be computed numerically, and $|\Delta S|$ can be approximated as

$$|\Delta S| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H \tag{3}$$

where, M_i and M_{i+1} are the experimental values of the magnetization at the temperatures of T_i and T_{i+1}, respectively, under an applied magnetic field H_i. Fig. 4 shows the magnetization isotherms for $LaMn_{1.9}Fe_{0.1}Si_2$, which were measured around its transition temperature from canted antiferromagnetic state to canted ferromagnetic state. The magnetization behavior is similar to that of typical ferromagnetic materials. It is observed that the magnetization increases rapidly with magnetic field and then almost saturates in a small magnetic field indicating a canted ferromagnetic state. The magnetizations around room temperature (above *Tc*) are much lower than those at lower temperatures (below *Tc*) and increase almost linearly with magnetic field.

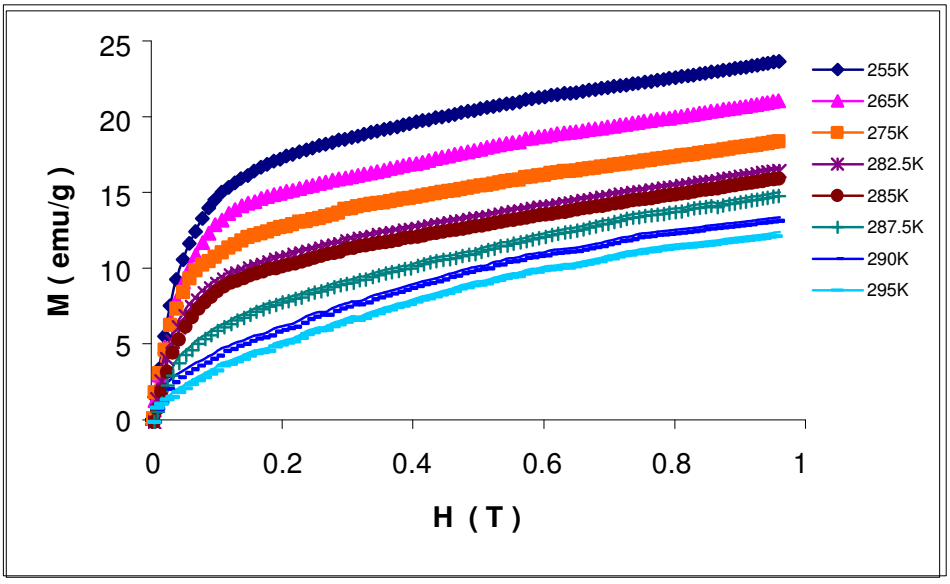

Fig.4. Magnetization isotherm of the $LaMn_{1.9}Fe_{0.1}Si_2$ compound as a function of magnetic field

The magnetic entropy change calculated using eq. 3 as a function of temperature is illustrated in Fig.5. It can be seen that the magnetic entropy change (ΔS) exhibits a single peak around 286 K which is somewhat above *Tc*. It is predominantly negative (positive MCE) and the magnitude increases with applied field. Furthermore, the temperatures of the entropy peaks stay almost constant with increasing field within experimental accuracy. The peak values of $|\Delta S|$, for the fields of 0.2 and 0.9 T are about 0.2 J/kg-K and 0.53 J/kg-K, respectively. The small values of magnetic entropy in $LaMn_{1.9}Fe_{0.1}Si_2$ are probably due to the small value of saturation magnetization and the nature of the complex phase transition. This is in agreement with the results given in literature that the materials having second order magnetic phase transitions exhibit very small magnetocaloric effects [20-22].

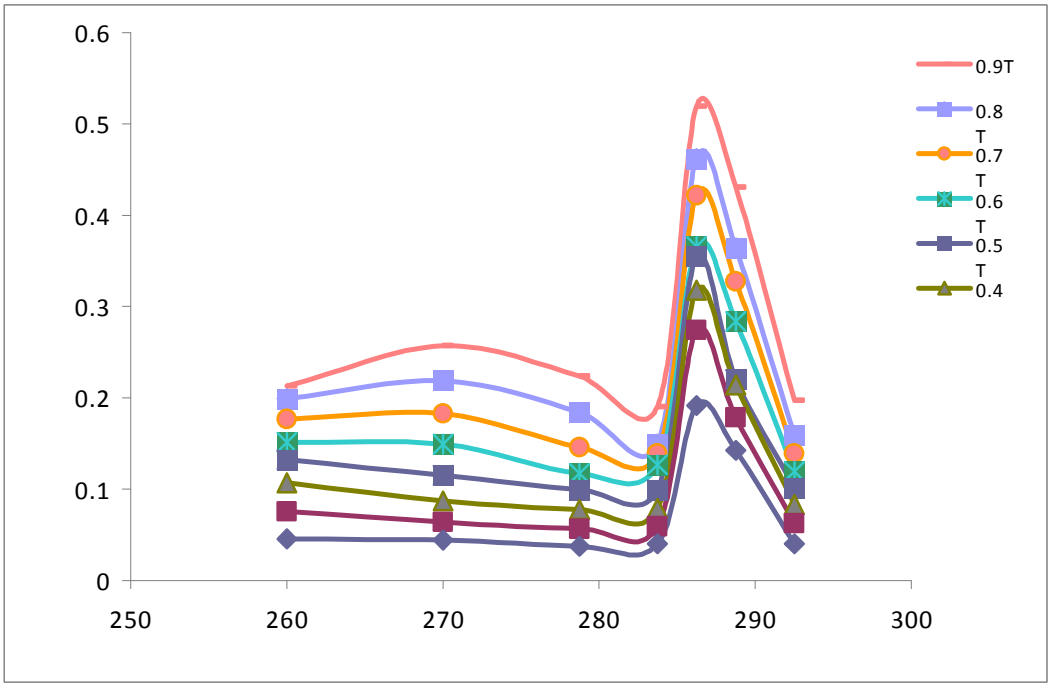

Fig.5. Magnetic entropy change versus temperature at various magnetic fields, the lines are drawn by simply connecting the data points.

The magnetic free energy generally can be expressed in powers of magnetization, neglecting higher order terms as:

$$F(M,T) = \frac{1}{2}c_1(T)M^2 + \frac{1}{4}c_3(T)M^4 - MH \tag{4}$$

where c_1 and c_3 are known as Landau coefficients. The sign of the $c_3(T)$ for the M^4 term allows us to identify the characteristic of the magnetic phase transition. The first order phase transition is expected in the case $c_3(T) < 0$ and second order phase transition in the case $c_3(T) > 0$ [20,23,24].
From the condition of equilibrium $\partial F(M,T)/\partial M = 0$, one can obtain around *Tc*:

$$H = c_1(T)M + c_3(T)M^3 \quad (5)$$

Eq. 5 can be arranged into the form

$$\frac{H}{M} = c_1(T) + c_3(T)M^2 \quad (6)$$

Using eq. 6, one can plot M^2 versus H/M in the critical region which is known as the Arrott plot. The slope of the curves points out whether the nature of the magnetic transition is of first- or second order. It is possible to deduce that if all curves have positive slopes, the magnetic transition is second order. On the other hand, if the curves have negative slopes at some point or inflection points, then the magnetic transition is first order. We have plotted the Arrott plots of $LaMn_{1.9}Fe_{0.1}Si_2$ compound in fig. 6. The Arrott curves have positive slope and no inflection points, in agreement with a positive $c_3(T)$ around the transition temperature, which is indicative of a second order magnetic phase transition. We have calculated the value of $c_3(T)$ approximately as $3x10^{-4}$ $T.gr^3/emu^3$ at 285 K, which is somewhat smaller than the value mentioned in the literature [20,23,24].We attribute this to our limited experimental condition in which the maximum applied magnetic field is 1 Tesla, and the small value of saturation magnetization is inconsistent with the nature of the magnetic transition.

In conclusion, we have used a known technique [13] to determine MCE. To best of our knowledge, this kind of experiment is the first to be applied to the $LaMn_{1.9}Fe_{0.1}Si_2$ compound which deserves a further investigation in terms of potential applications in refrigerators.

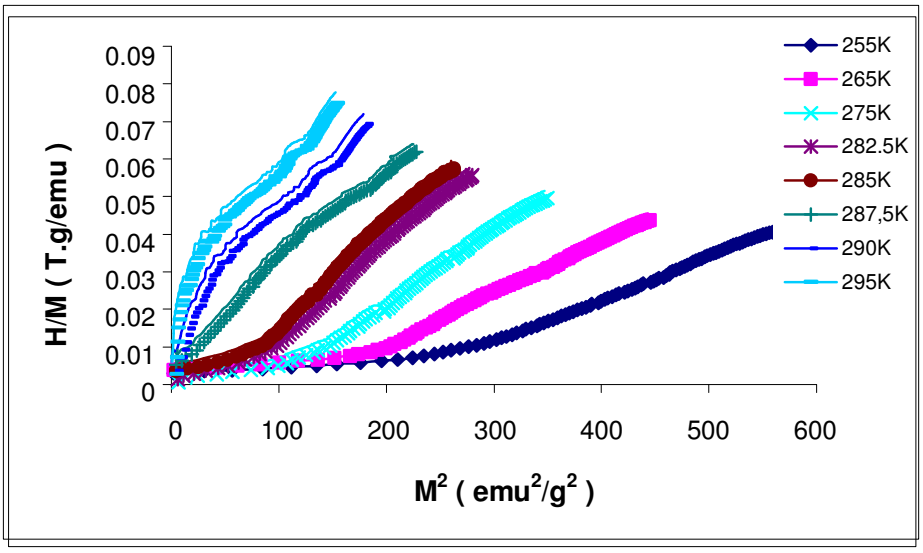

Fig.6. Arrott plots of the $LaMn_{1.9}Fe_{0.1}Si_2$ compound at different temperatures

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