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# Modeling specific heat and entropy change in La(Fe-Mn-Si)<sub>13</sub>-H compounds

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## Abstract

In this paper we model the magnetocaloric effect of LaFe<sub>x</sub>Mn<sub>y</sub>Si<sub>z</sub>-H<sub>1.65</sub> compound ( $x + y + z = 13$ ), a system showing a transition temperature finely tunable around room temperature by Mn substitution. The thermodynamic model takes into account the coupling between magnetism and specific volume as introduced by Bean and Rodbell. We find a good qualitative agreement between experimental and modeled entropy change  $-\Delta s(H, T)$ . The main result is that the magnetoelastic coupling drives the phase transition of the system, changing it from second to first order by varying a model parameter  $\eta$ . It is also responsible for a decrease of  $-\Delta s$  at the transition, due to a small lattice contribution to the entropy counteracting the effect of the magnetic one. The role of Mn is reflected exclusively in a decrease of the strength of the exchange interaction, while the value of the coefficient  $\beta$ , responsible for the coupling between volume and exchange energy, is independent on the Mn content and appears to be an intrinsic property of the La(Fe-Si)<sub>13</sub> structure.

**Keywords:** magnetocaloric effect, entropy change, mean field theory, magnetoelastic coupling

**PACS:** 75.30.Kz, 75.30.Sg, 75.50.Bb

## 1. Introduction

Two classes of magnetic materials are currently the most promising candidates for room-temperature magnetic cooling applications: the La(Fe-Si)<sub>13</sub> based [1, 2] and the MnFe(*X*-P) based with *X* = As, Ge, Si [3, 4]. Both systems display magnetic transition of the first order type between ferro- (FM) and paramagnetic (PM) phases with an enhanced magnetocaloric effect (MCE). In hydrogenated LaFe<sub>x</sub>Mn<sub>y</sub>Si<sub>z</sub>-H (with  $x + y + z = 13$ ) the transition temperature can be finely tuned by Mn substitution [1]. The material shows, with Mn increasing from  $y = 0.06$  to  $y = 0.46$ , a transition temperature changing from 339 K to 270 K, an entropy change (at 1.5 T field) which goes from 18.7 J kg<sup>-1</sup> K<sup>-1</sup> to 10.2 J kg<sup>-1</sup> K<sup>-1</sup>, and a temperature hysteresis going from 1.5 K to zero [5, 6]. The specific heat measured by Peltier calorimetry in magnetic field is shown in Figure 1. Modeling the measured behavior of these systems is of primary importance for the further optimization of the material.

In this paper we consider a thermodynamic model which takes into account magnetoelastic effects by introducing an explicit dependence of the exchange interaction on the specific volume, as proposed by Bean and Rodbell [7]. The model is based on the fact that the exchange interaction may depends on the distance between magnetic atoms and a volume change is reflected by an overall change in the interatomic distances. Bean and Rodbell [7] described this

effect by introducing a Curie temperature depending on the lattice specific volume  $\Omega = (v - v_0)/v_0$  ( $v, v_0$  being the deformed and equilibrium lattice volumes, respectively) as  $T_c = T_0(1 + \beta\Omega)$ , with  $\beta$  being a dimensionless coefficient describing the magnetoelastic coupling and  $T_0$  the Curie temperature at  $\beta = 0$ . The model is developed by considering localized magnetic moments and treating the exchange interaction as in mean field theory and is able to display both first and second order transitions depending on the strength of  $\beta$ .

The use of the Bean and Rodbell model to describe La(Fe-Mn-Si)<sub>13</sub> is motivated by the fact that the compound shows, at the transition temperature, a volume shrink of about 1% upon heating without changes in the cubic crystal symmetry of the elementary cell [8]. The FM ordered phase is associated with a larger volume of the crystal cell while the PM disordered state with a smaller volume. The Bean and Rodbell mechanism is then a good candidate to describe the phenomenology of La(Fe-Mn-Si)<sub>13</sub>. One of the issues concerning the application of the Bean and Rodbell model, is how the lattice contribution affects the entropy change at the transition temperature. Both Bean and Rodbell [7] in their original work on MnAs and more recently Jia et. al [9] on La(FeSi)<sub>13</sub> have argued that a lattice shrink should always correspond to a decrease of the lattice entropy. This means that at the FM-PM transition the magnetic and lattice entropies behave differently: the first one is increasing, while the second one is decreasing, with the balance in favor of the first. Interestingly, recent experiments on the phonon spectrum of La(Fe-Mn-Si)<sub>13</sub> compounds below and above the transi-

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tion temperature, have reached a different conclusion [10]. Experiments shows a lattice entropy that appears to be slightly larger in the PM state, then acting cooperatively with the magnetic contribution. These different facts poses several interesting questions on the nature of the transition and on the ferromagnetic state of  $\text{La}(\text{Fe}-\text{Mn}-\text{Si})_{13}$ [11]. One may wonder if, in the context of ferromagnetism, the sum a positive contribution from the lattice plus a positive contribution from the spins is compatible with the measured entropy change.

To shed some new light on this issue, we have compared the experimental data concerning the series of Mn substituted  $\text{La}(\text{Fe}-\text{Mn}-\text{Si})_{13}-\text{H}_{1.65}$  samples with the model, taking explicitly into account the lattice contribution to the entropy, which can be either positive or negative [12]. We have determined the model parameters by comparison with the experiments. Indeed, the entropy change has a number of peculiar features that the model is able to describe up to a certain level of detail and we have used them to derive the model parameters. The latter are then needed to discuss the physics behind the behavior of the hydrogenated  $\text{La}(\text{Fe}-\text{Mn}-\text{Si})_{13}$  compounds at the transition.

We find a good qualitative agreement between experimental and modeled entropy change  $-\Delta s(H, T)$ . The main result is that the magnetoelastic coupling drives the phase transition of the system, changing it from second to first order by varying a model parameter  $\eta$ . It is also responsible for a decrease of  $-\Delta s$  at the transition, due to a small lattice contribution to the entropy counteracting the effect of the magnetic one. The role of Mn is reflected exclusively in a decrease of the strength of the exchange interaction, while the value of the coefficient  $\beta$ , responsible for the coupling between volume and exchange energy, is independent on the Mn content and appears to be an intrinsic property of the  $\text{La}(\text{Fe}-\text{Si})_{13}$  structure.

## 2. Thermodynamic theory

The thermodynamic model is developed by defining a non equilibrium Landau free energy depending on the temperature and on extensive variables such as the magnetization  $M$  and the specific volume  $v$  of the system. The Landau free energy of a ferromagnet is expressed as the sum of the ferromagnetic energy  $f_M$  and of the energy associated to the non magnetic degrees-of-freedom  $f_S$ :

$$f_L = f_M + f_S \quad (1)$$

The magnetic contribution can be estimated in terms of the Weiss molecular field theory of ferromagnetism and it is expressed as:

$$f_M = -\frac{1}{2}W(\Omega)\mu_0 M^2 - Ts_M \quad (2)$$

The coupling between magnetic and structural degrees of freedom is encompassed in the molecular field coefficient

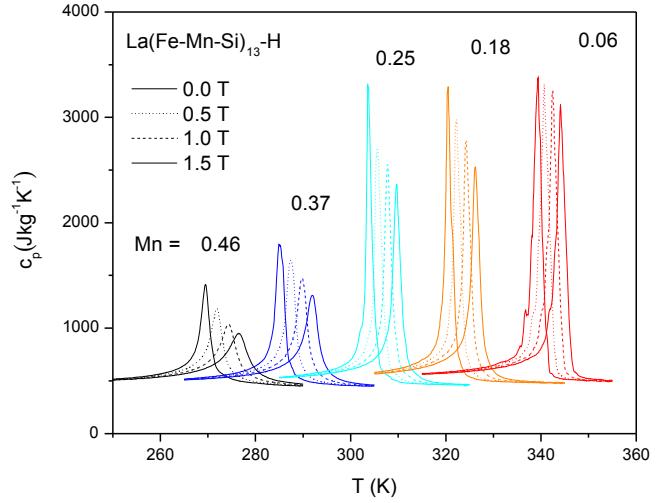


Figure 1: Specific heat capacity of hydrogenated  $\text{La}(\text{Fe}-\text{Mn}-\text{Si})_{13}$  with different Mn content. Measurements upon heating at different magnetic fields.

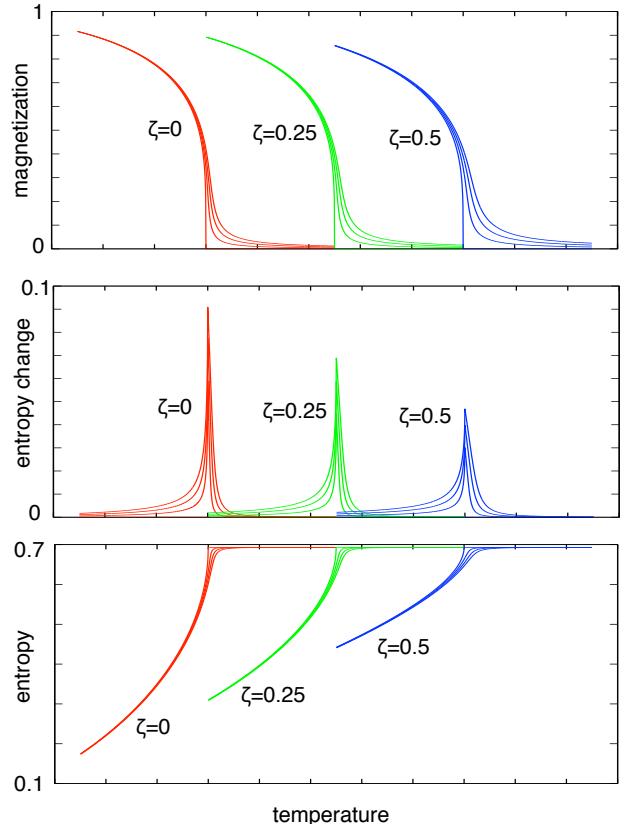


Figure 2: Model results at various fields  $h$  ranging from 0 to 0.003 in steps of 0.001. Top: normalized magnetization  $m(h, t)$ . Center: magnetic field induced entropy change  $-\Delta s = \hat{s}(h = 0, t) - \hat{s}(h, t)$ . Bottom: normalized entropy  $\hat{s}(h, t)$ . The curves are displaced along the temperature axis for clarity.

$W(\Omega)$  appearing in Eq. (2), depending on the specific volume  $\Omega = (v - v_0)/v_0$  as  $W = W_0(1 + \beta\Omega)$ .  $\beta$  is a dimensionless parameter describing the rate of change of the molecular field coefficient with the reduced volume. This idea has been originally introduced by Bean and Rodbell [7] and further developed to describe magnetocaloric materials [13, 14, 15, 16, 12]. The expression for the magnetic entropy  $s_M$  is obtained assuming the magnetic moments to be localized at atomic sites. In particular, the magnetic moment along the direction of the magnetic field is  $\mu(m_J) = -g_L\mu_B m_J$ , where  $g_L$  is the Landé  $g$ -factor,  $\mu_B$  is the Bohr magneton and  $m_J$  can assume  $2J+1$  discrete values between  $-J$  and  $J$ .  $J$  is the total angular momentum quantum number due to the contribution of the orbital and spin momentum of the electrons. The power expansion of the magnetic entropy around  $m = 0$  is

$$s_M(m) = nk_B [\ln(2J+1) - \frac{1}{2a_J} \left( m^2 + \frac{b_J}{2} m^4 + \mathcal{O}(m^6) \right)] \quad (3)$$

where  $m = M/M_0$  ( $-1 \leq m \leq 1$ ) is the reduced magnetization,  $M_0 = n\mu(m_J = -J)$  is the saturation magnetization ( $n$  being the number of magnetic moments per unit mass).  $k_B$  is the Boltzmann constant and the coefficients  $a_J$ ,  $b_J$  are given by  $a_J = (J+1)/(3J)$  and  $b_J = (3/10)[(J+1)^2 + J^2]/(J+1)^2$ .

The structural part of the free energy,  $f_S$ , gives rise to an entropy contribution that is mainly due to the atomic vibrations, i.e. to the phonons, and to the fluctuations of electrons around the Fermi energy level. Phenomenologically it can be expanded around the temperature  $T_0$  as

$$f_S(\Omega, T) = f_S(0, T_0) + \frac{v_0}{\kappa_T} \frac{\Omega^2}{2} - \left[ \frac{\alpha_p v_0}{\kappa_T} \Omega + s_0 \right] (T - T_0) - b_v \frac{1}{2} (T - T_0)^2 \quad (4)$$

where  $\kappa_T$  is the isothermal compressibility,  $\alpha_p$  is the thermal expansion coefficient and  $b_v$  is the entropy coefficient at constant volume. From Eq. (4) it is possible to derive the following linear equations of state, describing the structural behavior alone:

$$\Omega = -\kappa_T p + \alpha_p(T - T_0) \quad (5)$$

$$s - s_0 = -v_0 \alpha_p p + b_p(T - T_0) \quad (6)$$

where  $b_p$  is the entropy coefficient at constant pressure related to  $b_v$  by the relation

$$b_v = b_p - \frac{\alpha_p^2 v_0}{\kappa_T} \quad (7)$$

Both the entropy coefficients  $b_v$  and  $b_p$  are related to the specific heat  $c$  by the relation  $b = c/T_0$ .

We introduce now the normalized magnetic field  $h = H/H_0$ , where  $H_0 = WM_0$ , and the normalized temperature  $t = T/T_0$ , where  $T_0 = a_J\mu_0 H_0 M_0 / (nk_B)$  is the Curie temperature at  $\beta = 0$ . By evaluating the derivative  $\partial f_L/\partial m = h$ , we determine the equation of state to be solved in order to obtain the behavior of the magnetization  $m$  at various  $t$  and  $h$ :

$$h = -[1 + \zeta(1-t)]m - \frac{1}{3}\eta m^3 + ta_J \mathcal{B}^{-1}(m) \quad (8)$$

where  $\mathcal{B}^{-1}(m)$  is the inverse Brillouin function and  $\eta$ ,  $\zeta$  are two dimensionless parameters introduced to describe the magnetostructural coupling. They are expressed as:

$$\eta = \frac{3}{2} \frac{\beta^2 \kappa_T n k_B}{a_J v_0} T_0 \quad (9)$$

$$\zeta = \alpha_p \beta T_0 \quad (10)$$

In particular Bean and Rodbell [7] demonstrated that the magnetic transition may transform from the second to the first order type depending on the value of the parameter  $\eta$ . In particular, the transition between PM and FM states is of the second order for  $\eta < \eta_c$  while becomes of the first order for  $\eta > \eta_c$ , with  $\eta_c = 3b_J$ . When the transition is of the first order the entropy jump occurring at the phase transition may include a structural contribution. The latter is regulated by the parameter  $\zeta$  [12, 14].

To investigate more in detail the various contributions to the entropy, we the derivative of Eq. (1) with respect to  $T$  obtaining:

$$s = s_M(m) + s_W(m) + s_S(p, T) \quad (11)$$

where  $s_M(m)$  is the magnetic entropy of Eq. (3),  $s_S(p, T)$  is the structural lattice entropy of Eq. (6) and

$$s_W(m) = \frac{n k_B}{2a_J} \zeta m^2 \quad (12)$$

is the magnetoelastic entropy, a term of structural lattice origin induced by the ferromagnetic exchange interaction through the magnetoelastic coupling. The magnetic entropy  $s_M(m)$  has a maximum at  $m = 0$  and it decreases to zero for  $|m| = 1$ . The magnetoelastic entropy depends upon the value of the parameter  $\zeta$  and it is proportional to  $m^2$ . To analyze the competition between  $s_M$  and  $s_W$ , the two terms depending on  $m$ , we introduce the normalized magnetoelastic entropy,  $\hat{s}(m) = (s_M(m) + s_W(m))/(nk_B)$ . The maximum difference is between the entropy at  $m = 0$  and  $|m| = 1$ ,  $\Delta\hat{s}_{max} = \hat{s}(0) - \hat{s}(1)$ , and it is given by  $\Delta\hat{s}_{max} = \ln(2J+1) - \frac{1}{2a_J}\zeta$ . By using the power expansion of  $s_M$  from Eq. (3) we obtain the following expression for  $\hat{s}$ :

$$\hat{s} = \ln(2J+1) - \frac{1}{2a_J} \left[ (1 - \zeta) m^2 + \frac{b_J}{2} m^4 + \mathcal{O}(m^6) \right]. \quad (13)$$

Eq. (13) clearly shows that the total magnetoelastic entropy may be increased or decreased depending on the sign

of  $\zeta$ . The physics encompassed in the model ensures that for  $\zeta > 0$  the lattice entropy contribution counteracts the magnetic entropy one, thus reducing the entropy change at the transition. Moreover, when  $\eta > \eta_c$  the transition is first order and there is a discontinuous jump of the magnetization  $m$ . Consequently, at the transition temperature between the low temperature phase (LT) and the high temperature phase (HT) the entropy  $\hat{s}$  increases also discontinuously with a jump that must satisfy the thermodynamic condition  $\Delta\hat{s} = \hat{s}_{\text{HT}} - \hat{s}_{\text{LT}} > 0$ . Figure 2 shows the reduced magnetization  $m(h, t)$ , the normalized entropy  $\hat{s}(h, t)$  and the entropy change  $-\Delta\hat{s} = \hat{s}(h = 0, t) - \hat{s}(h, t)$  computed by solving Eq. (8) for  $\eta = 1$  and  $\zeta = 0, 0.25, 0.5$ .

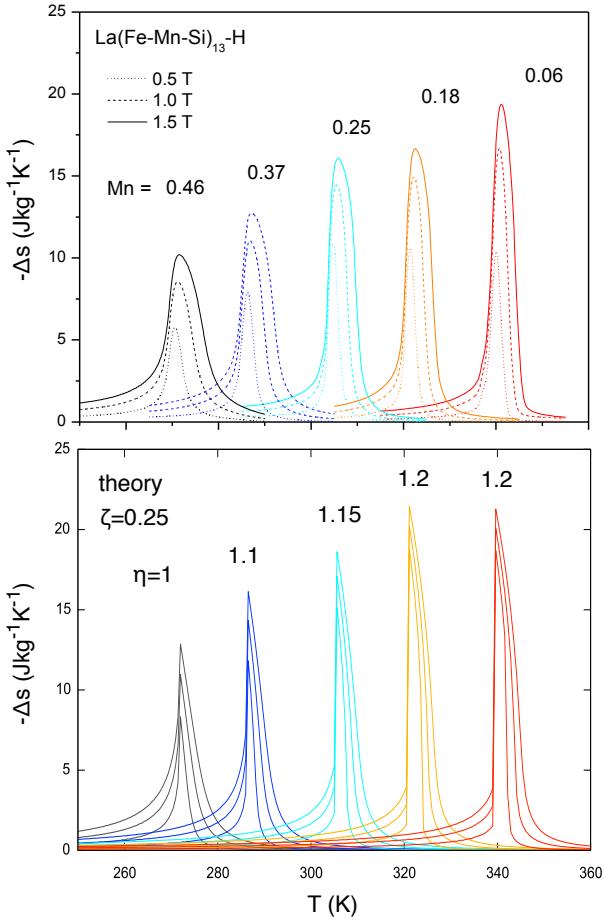


Figure 3: Magnetic field induced entropy change  $-\Delta s(H, T)$  in hydrogenated  $\text{La}(\text{Fe}-\text{Mn}-\text{Si})_{13}$  samples with different Mn content. Top: experimental curves obtained by Peltier calorimetry after Ref. [5]. Bottom: model results derived for the same  $h$  values set in Figure 2.

It is worth noting that for  $\zeta < 1$  the transition is from LT-FM ( $m \neq 0$ ) to HT-PM ( $m = 0$ ) (see Figure 2, top panel) and the magnetic entropy change is positive, i.e.  $\Delta s_M > 0$ . For what concerns  $s_W$ , we can distinguish two different cases depending on the sign of  $\zeta$ . For  $\zeta < 0$ , from Eq. (12) we have  $\Delta s_W > 0$  and there is an enhancement of the total entropy change with respect to the magnetic contribution alone, i.e.  $\Delta\hat{s} > \Delta s_M$ . On the opposite,

$\Delta s_W < 0$  for  $0 < \zeta < 1$  and there is a reduction of the total entropy change  $\Delta\hat{s} < \Delta s_M$ . For  $\zeta > 1$  a novel feature appears: the magnetic entropy change is negative  $\Delta s_M < 0$  but the magnetoelastic entropy change is positive and large enough ( $\Delta s_W > |\Delta s_M|$ ) to invert the transition, i.e. from LT-PM ( $m = 0$ ) to HT-FM ( $m \neq 0$ ) [12].

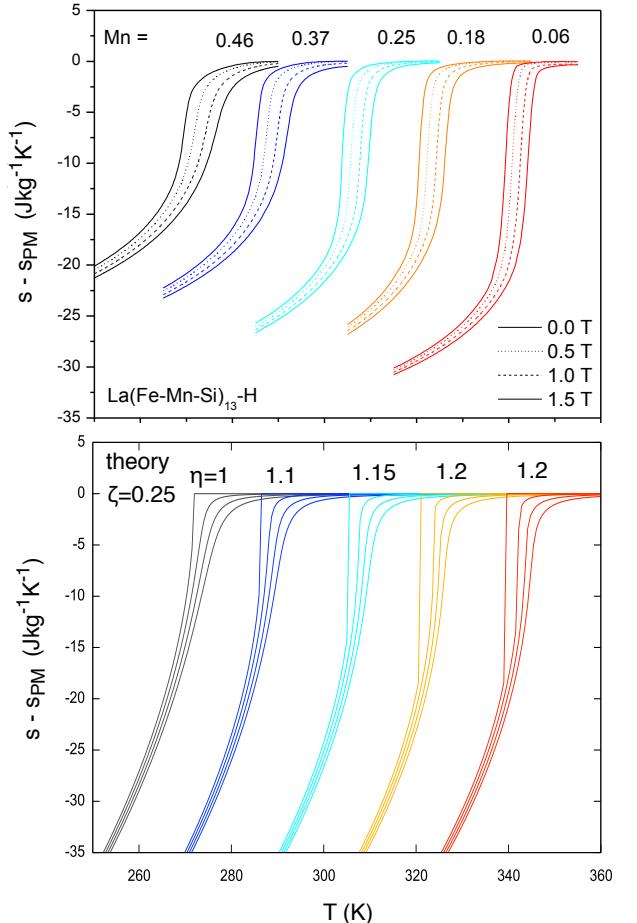


Figure 4: Entropy change  $s(H, T) - s_{\text{PM}}(T)$  in hydrogenated  $\text{La}(\text{Fe}-\text{Mn}-\text{Si})_{13}$  compounds with different Mn content. Top: experimental curves obtained by Peltier calorimetry after Ref. [5]. Bottom: model results obtained with the same  $h$  field values set in Figure 2.

### 3. Comparison with experiments

To compare the model with experimental data we have fixed  $J = S = 1/2$ . The remaining free parameters to determine are then  $\eta$ ,  $\zeta$ ,  $T_0$  and  $n$ . The value of  $T_0$  has been set to fit the transition temperature measured for the  $\text{La}(\text{Fe}-\text{Mn}-\text{Si})_{13}\text{-H}_{1.65}$  samples under investigation (see Table 1). The values of the remaining parameters,  $\eta$ ,  $\zeta$  and  $n$ , have been set by looking at the shape of the entropy change  $-\Delta s$  (see Figure 3, bottom panel); numerical calculations show that the parameter  $\eta$  mainly affects the shapes of the curve  $-\Delta s$  (see Figure 3, bottom panel); the parameter  $\zeta$  changes the ratio between the height and width of the  $-\Delta s$  peak (see Figure 2, central panel); the

coefficient  $nk_B$  changes the amplitude of  $-\Delta s$ . The result of the balance of the three effects is not trivial and the choice of the values of the parameters leaves some arbitrariness. As a result we have found a good agreement with experiments by choosing the same coefficient  $nk_B = 170 \text{ J kg}^{-1} \text{ K}^{-1}$  for all the samples. The changes in the shape of the curves obtained by lowering the Mn content are well described by slight changes in the value of  $\eta$  and a positive  $\zeta$  is needed to fit the whole set of curves. The value is approximately the same for all the series and it is  $\zeta = 0.25$ . The comparison between the experimental  $-\Delta s$  and the theoretical one evaluated with the above  $\eta$ ,  $\zeta$  and  $nk_B$  values is shown in Figure 3. To compare the experimental entropy with the theoretical expected one we have subtracted from the experimental  $s(H, T)$  a contribution  $s_{PM}(T)$ , depending only on  $T$ , representing the lattice contribution in the HT-PM phase. This term is evaluated as  $s_{PM}(T) = \int c_{PM}/T dT$ , where  $c_{PM}$  is the constant value of the specific heat evaluated above the transition. The experimental  $s(H, T) - s_{PM}(T)$  curves are shown in Figure 4, top panel, and the results from theory are displayed below. The comparison shows that the model is able to reproduce the entropy change at the transition.

Fe	Mn	Si	$T_0$ (K)	$\mu_0 H_0$ (T)	$\eta$
11.22	0.46	1.32	272	405	1.0
11.33	0.37	1.30	286	426	1.1
11.47	0.25	1.28	305	455	1.15
11.60	0.18	1.22	320.5	478	1.2
11.76	0.06	1.18	339	505	1.2

Table 1: Parameters  $T_0$ ,  $\mu_0 H_0$  and  $\eta$  used to model the entropy change behaviour of  $\text{La}(\text{Fe}_x\text{Mn}_y\text{Si}_z)_{13}\text{-H}_{1.65}$  samples with compositions  $x$  (Fe),  $y$  (Mn),  $z$  (Si) shown in the first, second and third columns, respectively.

The values found for  $\eta$  are approximately linear with  $T_0$ , in agreement with Eq. (9). By making a linear fit of the  $\eta$  values reported in Table 1 versus the corresponding  $T_0$  values we find a linear coefficient of  $3.7 \times 10^{-3} \text{ K}^{-1}$ . The latter can be used to determine the value of  $\beta$  through Eq. (9). By taking a literature value for the compressibility  $\kappa_T = 8.6 \times 10^{-12} \text{ Pa}^{-1}$  [17] we find  $\beta \simeq 15$  for all the samples, independently of the Mn content. This value appears reasonable in comparison with other estimates made on different magnetocaloric materials [12]. At the same time Eq. (10) gives another relation linking this time  $\beta$  and  $\zeta$ . We have therefore an alternative independent route to check the feasibility of the chosen value of  $\zeta$ , i.e.  $\zeta \simeq 0.25$ . If in Eq. (10) we substitute  $\alpha_p \simeq 5 \times 10^{-5} \text{ K}^{-1}$ , the typical value of the thermal expansion coefficient for iron alloys (that in the model should be an expansion due to the lattice only) we end up with  $\zeta$  values ranging between 0.20 and 0.25, depending on the transition temper-

ature. Since we do not have a very precise method to fit with accuracy  $\zeta$  from the experimental data, the fact that the value fixed at the beginning, i.e.  $\zeta \simeq 0.25$ , is within the calculated range is quite satisfactory. This result provides global coherency of the whole modeling approach.

#### 4. Discussion

The physical picture of the phase transitions occurring in  $\text{La}(\text{Fe}-\text{Mn}-\text{Si})_{13}\text{-H}_{1.65}$  compounds emerging from the comparison between the model and the experiments can be summarized as follows. The phase transition is driven by magnetoelastic effects. The latter are at the same time responsible for the transformation of the phase transition from second to first order ( $\eta \geq 1$ ) and for a decrease of the entropy change  $-\Delta s$  at the transition ( $\zeta > 0$ ). The variation of Mn content in the compounds results exclusively in a change of the transition temperature  $T_0$ , i.e. in a change of the strength of the exchange interaction  $W \propto T_0$  (see Sec. 2). On the opposite, the magnetoelastic coefficient  $\beta$ , linking  $W$  to the specific volume  $\Omega$ , is basically independent on the variation in Mn content. This fact may be explained by noting that it is the particular arrangement of the magnetic atoms in the  $\text{La}(\text{Fe}-\text{Si})_{13}$  unit cell to be responsible for the magnetoelastic effects, so for the  $\beta$  value. The partial substitution of Fe atoms with Mn does not change too much the arrangement of the atoms, but it weakens the effective FM interaction between them.

Moreover, our results show that in magnetocaloric materials in which the transition is from a LT magnetically ordered to a HT magnetically disordered state ( $\zeta < 1$ ), the origin of the entropy change at the transition shall be searched in the spin contribution, since lattice entropy plays only a minor counteracting role. Another important point to mention is that the performed modeling led us to consider magnetoelastic effects with both  $\beta > 0$  and  $\zeta > 0$ . This is a confirmation of the results obtained by Jia et al. [9], foreseeing a lattice entropy decrease at the FM-PM magnetic transition accompanied by lattice shrink. The result recently obtained by Gruner et al. [10] may be due to the fact that the experimental technique used by the authors to access the phonon density of states may display a sensitivity on magnetic fluctuations. Therefore, the results they have obtained may represent the sum of both magnetic and structural contributions to the entropy and not the lattice contribution alone.

Some final comments on the physical robustness of the overall model can be argued by looking in more detail another interesting aspect, concerning the choice of the  $nk_B$  coefficient we have made. In the fit with the experimental data (see Sec. 3)  $nk_B$  has been treated as a free parameter. However, the density of spins (i.e. of magnetic moments)  $n$  in a given compound can be calculated knowing the saturation magnetization  $M_0$ . Indeed,  $M_0 = n g_L \mu_B J$  and  $n$  can be expressed as  $n = (N_A/P_M) N_m N_s$ , where  $N_A$  is the Avogadro's number,  $P_M$  is the molecular weight of the system under consideration,  $N_m$  represents the number of

magnetic ions per formula unit and  $N_s$  is the number of spins per magnetic ion. In particular, for the  $\text{La}(\text{Fe-Si})_{13}$  system, since  $J = 1/2$ ,  $g_L = 2$  and iron atoms are the only magnetic ions of the compound, knowing the ground state spontaneous magnetization  $M_0 = 165 \text{ A m}^2 \text{ kg}^{-1}$  for  $N_m = 11.5$  [18], we get a number spins  $N_s \simeq 2.08$ , corresponding to an atomic magnetic moment of  $2.08 \mu_B$  per Fe atom. We have then considered the  $\text{La}(\text{Fe-Mn-Si})_{13-\text{H}_{1.65}}$  compounds: since the Fe content varies between 11.22 and 11.76 (Table 1) we can safely assume that the same  $N_s$  evaluated for  $\text{La}(\text{Fe-Si})_{13}$  [18]. Taking the  $N_m$  values from Table 1, we get a mass density of spins  $n/N_A = 28.8 \text{ mol kg}^{-1}$ . This value can be compared with the corresponding one as obtained from the model ( $nk_B = 170 \text{ J kg}^{-1} \text{ K}^{-1}$ ). The result is that from the entropy fit the value,  $n/N_A \simeq 20.5 \text{ mol kg}^{-1}$ , is only 70% of the one derived from the saturation magnetization. This fact should probably be ascribed to the limitations of the mean field theory to describe the details of the magnetic entropy  $s_M$  of the system.

Indeed, it is well known that the sharp peaks experimentally observed in the specific heat of magnetic compounds are insufficiently reproduced by mean field theory. This difficulty is related to the presence of spin correlations both below and above the Curie point, producing a similar effect. Below the Curie point the long range spin correlations lower the spin entropy as obtained from the individual localized moments estimate of mean field theory. Thus, in the FM state the experimental  $c_p$  is lower than the MFT estimate. On the other hand, in the  $m = 0$  disordered PM state, above the Curie point, short range correlations are still present and they are able to lower the magnetic entropy below the maximum value  $nk_B \ln(2J + 1)$ . This is the reason why in the PM state the experimental  $c_p$  is higher than the MFT one.

The presence of magnetoelastic coupling does not change too much this picture. As an example, Figure 6 shows the normalized specific heat  $\hat{c} = t d\hat{s}/dt$  computed through our MFT model. The specific heat displays a peak at the transition temperature which is smoothed out by the magnetic field. This phenomenology corresponds qualitatively to what is observed in the experiments on hydrogenated  $\text{La}(\text{Fe-Mn-Si})_{13}$  shown in Figure 1, but for what concerns quantitative comparison the model still suffers from the defects of MFT just described. The overestimation of the magnetic entropy due to MFT causes the density of magnetic moments  $n$ , resulting from the fit with experiments, to be lower of  $\simeq 30\%$  than the experimental value, as pointed out previously. This fact can be interpreted as an indirect effect of the existence of spin correlations close to the Curie point.

The whole above discussion clarifies that a detailed theoretical description of the entropy change measured in magnetocaloric materials should rely on an improvement of the evaluation of the magnetic entropy. Various approaches to achieve this aim have been proposed in the literature. It is worth mention here, as an example, the use of

Monte Carlo simulations to evaluate the energy dependent density of states of systems including spin fluctuations. Magnetic entropy is then derived from the density of state through common thermodynamic relations. In particular, Tamura et al. [19] have recently applied this approach to the Ising ferromagnet, deriving the density of state by means of the fast Wang-Landau sampling algorithm [20]. The resulting model allows to better capture the peculiar shape of the specific heat peak observed at the first order phase transition of the  $\text{La}(\text{Fe-Mn-Si})_{13-\text{H}_{1.65}}$  compounds and it is promising for the eventual inclusion of magnetoelastic effects. Future work shall be dedicated to the understanding of which approach may have the advantage of being physically sound and computationally feasible.

Although the main aim of the manuscript is to describe entropy change at the transition, the model is also able to give some insight about the hysteresis. Even if hysteresis is related to extrinsic effects, such as defects, acting as pinning centers for the structural domain transformation that should be described by appropriate models [2], the present MFT model, can at least provide the information about the extension of the metastability region. This latter corresponds to the region in which the solution of Eq. shows two coexisting FM and PM solutions. These appear for  $\eta > 1$  (at  $S = 1/2$ ). The inset of Fig. shows the magnetization versus temperature upon heating and cooling obtained by taking the local metastable solutions, depending on the temperature history, instead of the equilibrium solution. In the model the temperature hysteresis  $\Delta T_{hyst} = T_h - T_c$  depends on the eta value. From the previous discussion one expects that the MFT model provides an upper limit of the measured material hysteresis. As an example we reported in Fig. the experimental  $\Delta T_{hyst}$  data from [cite] corresponding to different Mn content versus each transition temperature  $T_h$  together with the model predictions. The theoretical curve is obtained by changing  $\eta$  from 1 to 1.25. In the graph for the sake of comparison with experiments, we have used the linear relation between eta and  $T_0$  (Eq.) with the proportionality constant  $3.7 \times 10^{-3} \text{ K}^{-1}$  found before. One can observe that the measured hysteresis is always lower or equal to the model curve.

## 5. Conclusions

In this paper we have applied a thermodynamic model describing magnetism and comprising the magnetoelastic coupling between magnetic exchange interactions and crystal lattice to explain the behavior of the specific heat  $c_p(H, T)$  and entropy change  $-\Delta s(H, T)$  experimentally measured in a series of  $\text{LaFe}_x\text{Mn}_y\text{Si}_z\text{-H}_{1.65}$  samples ( $x + y + z = 13$ ) having different Mn content.

The model is able to describe the change in the transition type from second order (high Mn content) to first order (low Mn) by varying the MFT exchange interaction coefficient. The detailed description of the shape of the entropy change allowed us to obtain the values of the free

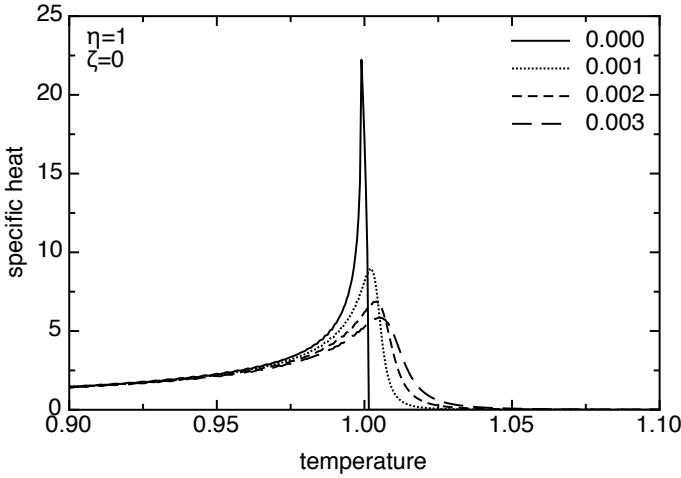


Figure 5: Normalized specific heat  $\hat{c} = t \partial \hat{s} / \partial t$  computed through the model. Values of the normalized magnetic field  $h$  are shown in the legend.

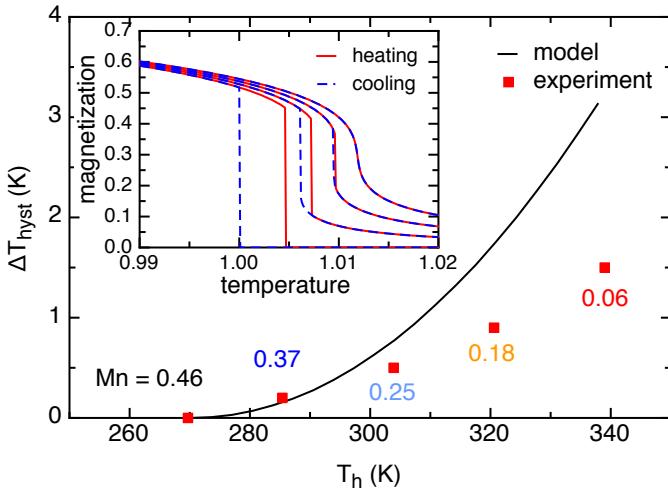


Figure 6: Temperature hysteresis versus transition temperature. Line  $\Delta T_{hys}$  has derived from the metastability region of the model. Points: experimental data from Ref. Inset magnetization

parameters of the model. In particular we have found a positive magnetoelastic coefficient  $\beta = 15$ , describing the coupling between the exchange energy and lattice volume, independent on the Mn content. This value implies also that the lattice entropy has a small action in the FM-PM phase transition, counteracting the magnetic entropy increase. This result is in agreement with the conclusions previously evidenced by Ref. [9].

While the MFT model is accurate enough to describe the shape of the entropy change  $-\Delta s(H, T)$ , it is too simple to allow a satisfactory description of the main features shown by the specific heat  $c_p(H, T)$ . Thus, it appears evident that a detailed interpretation of the thermodynamic behavior of magnetocaloric materials close to the phase transitions deeply rely on the improvement of the underlying theoretical treatment of the magnetic entropy.

## 6. Acknowledgement

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