Field Dependence of the Magnetocaloric Effect in MnFe(P,Si) Materials

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The field dependence of the magnetocaloric effect (MCE) in $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$ is studied in terms of the entropy change (ΔS) and the temperature change (ΔT) for applied magnetic fields up to 5 and 14 T, respectively. The magnetic fields required to saturate the MCE in this system are ∼1.7 and 4–5 T for ΔS and ΔT, respectively. The MCE field dependence is compared with the two approaches of the literature: 1) latent heat model and 2) the power law evolution predicted from the universal analysis of the MCE. It turns out that both of these methods are unsuitable to describe the MCE field evolution in MnFe(P,Si) materials.

Index Terms—**Magnetic materials, magnetic properties, magnetocaloric effect (MCE).**

I. Introduction

RECENTLY, materials undergoing a first-order magnetic transition (FOMT) near room temperature have attracted much attention due to the possibility to use their large magnetocaloric effect (MCE) for magnetic refrigeration [1]. Among the various candidates as magnetic refrigerant, the MnFe(P,X) (X = As, Ge, Si, and B) family turns out to be very promising as it presents a large field-induced entropy change (ΔS) and temperature change (ΔT). Until now, most of the MCE studies on this material system were focused on the intermediate magnetic field range ($B \leq 2$ T), as it is most relevant for applications [2]–[5]. However, extending the field range of the MCE derivation is important from both fundamental and an applied point of view. On one hand, it allows one to address the field dependence of the MCE quantities and the possible influence of a critical end point. On the other hand, high-field ΔS or ΔT data are advantageous for the optimization of the MCE at the intermediate field. At the first glance, for the materials undergoing a FOMT, ΔS and ΔT are expected to saturate above a specific magnetic field (hereafter noted as $B^*_{\Delta S}$ and $B^*_{\Delta T}$, respectively). The values of B^* are: 1) strongly dependent on the material considered, as shown in Table I for several giant-MCE materials and 2) sometime located at high magnetic fields, especially $B^*_{\Delta T}$. In practice, it is advantageous to bring the saturation field as close as possible to the field used for applications, as it would correspond to a situation where the MCE of the FOMT is optimally used, while the negative side-effects of the FOMT (hysteresis, fatigue, and so on) can be kept to their minimum. Understanding the field dependence of ΔS and ΔT and quantifying B^* in MnFe(P,X) materials are thus required for further optimizations.

However, it is not possible to simply extrapolate ΔS and ΔT from the intermediate field data to high fields, as the MCE field dependence remains an open topic in the literature, with two main approaches. The first one is based on a schematic description of the entropy versus temperature lines at the FOMT. More precisely, it describes the field evolution of the entropy jump of the phase transformation ($\Delta S_{tr} = L/T_C$) by the use of the Clausius–Clapeyron relationship. In this latent heat model, two field regimes are distinguished, and ΔS or ΔT should increase linearly until it reaches a saturation $\Delta S = L/T_C$ at $B^*_{\Delta S}$ or $\Delta T = L/c_b$ at $B^*_{\Delta T}$, where T_C is the Curie temperature, L is the latent heat, and c_b is the heat capacity outside the FOMT [14]. Several authors have further developed this approach by implementing other parameters, such as the width of the transition, the hysteresis, or the relationship between ΔS and ΔT [15]–[18]. Another method originates from the so-called universal analysis of the MCE, which predicts for materials with a second-order transition a power law evolution $\Delta S \propto B^n$ and $\Delta T \propto B^m$ (with n and m, both composed of critical exponents), in a way similar to the mean-field model for which $n = 2/3$ [19], [20]. Since then, many studies tried to extend this power-law approach to the FOMT materials. It has, for instance, been reported that the field dependence of $\Delta S \propto B^n$ is valid for inverse giant-MCE [21]. However, this possibility remains controversial [22].

TABLE I
Saturation Magnetic Field for Selected Giant-MCE Materials

Material	$B^*_{\Delta S}$ (T)	$B^*_{\Delta T}$ (T)	Reference
$Gd_5Si_2Ge_2$	3	7.5	[6]
$LaFe_{11.4}Si_{1.6}$	0.5	3	[7]
$Mn_{1.25}Fe_{0.7}$(P,Si)	2	--	[8], this work
FeRh	0.5	1.5	[9,10]
MnAs	1	> 5	[11]
$Ni_{43}Mn_{37.9}In_{12.1}Co_7$	8	> 8	[12]
$Ni_{49.5}Mn_{25.4}Ga_{25.1}$	1	--	[13]

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In this paper, we present the adiabatic temperature change measured in magnetic fields up to 14 T for one prototypical MnFe(P,Si) material. In addition, the field dependence of ΔS has been revisited. The results are compared with the two approaches of the literature to check whether these models can be used to describe the field dependence of the MCE in this system.

II. Experimental Details

A $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$ sample has been prepared by solid-state reaction [4]. Elemental starting materials were ball milled during 10 h, and then pressed into tablets and sealed in quartz ampoules under 200 mbar of Ar. The heat treatment is performed at 1100 °C during 40 h and ends by water quenching to room temperature. The samples were cycled five times across the FOMT prior to the measurements. Magnetization measurements have been carried out in a Quantum Design magnetometer equipped with a reciprocating sample option. Differential scanning calorimetry (DSC) in zero magnetic field was performed in a commercial TA Q2000. The in-field DSC data for indirect ΔS and ΔT or for the direct ΔS_{cyclic} were performed in a homemade equipment resembling the setup used in [5]. The thermal and field ramps were 1.5 Kmin^{-1} and 0.4 Tmin^{-1}, respectively. Direct ΔT_{cyclic} measurements for an external field change of 1.1 T were carried out as in [4]. The high-field MCE measurements have been carried out in a Bitter magnet, at the International Laboratory of High Fields and Low Temperatures in Wroclaw, Poland. The field ramp is 12 Tmin^{-1}, and the field homogeneity is of the order 10^{-3} T. The probe is similar to the one reported in [12]. The bulk sample (a pellet of 13 mm diameter and a mass of 2.34 g) was placed with the long axis oriented along the magnetic field. A relaxation curve has been measured, and the time constant (~800 s) is significantly larger than the duration of the field ramp. Calculation of the MCE for the indirect methods is done according to the usual process: 1) use of the Maxwell equation for magnetization data [either $M_B(T)$ or $M_T(B)$] and 2) construction of the entropy lines $S_B(T)$ and then differences for calorimetric ΔS and ΔT [1].

III. Results and Discussion

To allow the comparison with the previous MCE study in this system, a full set of MCE characterization at $B = 1$ T for the $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$ sample has been carried out prior the high field measurements. From the DSC measurements in zero magnetic field, T_C upon heating is at 311 K. The thermal hysteresis of $\delta T_{\text{hyst}} = 1.1$ K fulfills our standard criterion to ensure the cyclic character of the MCE. The full-width at half-maximum of the heat capacity peak is 3 K in zero magnetic field. Hereafter, a transition width $\delta T_{\text{tr}} = 2\text{FWHM} = 6$ K will be considered. By integrating the DSC peak over δT_{tr} and by using a linear background, the latent heat is 5.8 Jkg^{-1}. Fig. 1 shows the magnetization as a function of the temperature in magnetic fields from 0.05 to 2 T. The evolution of the transition temperature with respect to the field is $dT_C/dB = 3.5(2)$ KT^{-1}. The magnetization jump ΔM at the transition observed at $B = 0.5$ T is ~65 $\text{Am}^2\text{kg}^{-1}$.

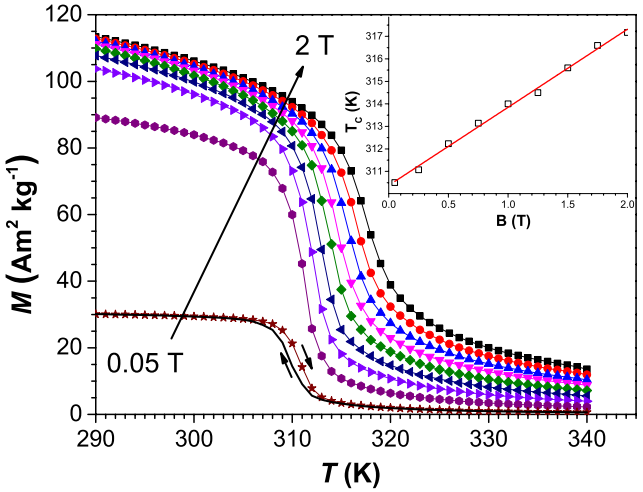

Fig. 1. Magnetization of $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$ as a function of the temperature (upon heating, except for $B = 0.05$ T) in various magnetic fields (0.05 T and then from 0.25 to 2 T in 0.25 T increments). Inset: field dependence of the transition temperature.

TABLE II
Maximum of the MCE for $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$ From Various Methods

$\lvert\Delta S\rvert$ ($\text{Jkg}^{-1}\text{K}^{-1}$)	$\lvert\Delta T\rvert$ (K)	ΔB (T)	Method
11.5	-	1	Maxwell equation on $M_B(T)$
11.4	-	1	Maxwell equation on $M_T(B)$
11.0	1.9	0.95	In-field DSC (*vs* T)
9.8	-	0.95	Direct ΔS in DSC (*vs* B) with ZFC
8.9	-	0.95	Direct ΔS_{cyclic} in DSC (*vs* B)
-	1.7	1.1	Direct ΔT_{cyclic} measurements
-	1.5	1	Direct ΔT_{cyclic} probe up to 14 T

As the MCE derivation can be prone to artifacts in the case of FOMT, the entropy change ΔS and the temperature change ΔT of this sample have been cross-checked by several direct and indirect methods: Maxwell method is applied on $M_B(T)$ and $M_T(B)$ magnetization data, indirect ΔS and ΔT from the in-field DSC calorimetry, and direct ΔS_{cyclic} and ΔT_{cyclic} setups. The results are summarized in Table II. ΔS and ΔT derived from the various methods are in good agreement. In particular, the small thermal hysteresis results only in a limited difference between the ΔS and ΔT maxima derived from the indirect methods, and the cyclic quantities ΔS_{cyclic} and ΔT_{cyclic}. Compared with the previous combined ΔS and ΔT_{cyclic} study [4], the present sample shows higher ΔS but a lower ΔT_{cyclic}, in such a way that the overall MCE remains comparable.

The field evolution of the entropy change $\Delta S(B)$ derived from $M_T(B)$ magnetization data measured up to 5 T at T_C (311 K) and $T > T_C$ (313 K) is presented in Fig. 2(a) and compared with the latent heat model. The S shape of the $\Delta S(B)$ curve at $T > T_C$ has the typical character of a FOMT. To check the validity of the power law method in this material, $\Delta S(B)$ was subsequently processed following the approach from [21]. The local coefficient $n(T, B)$ in $\Delta S \propto B^n$

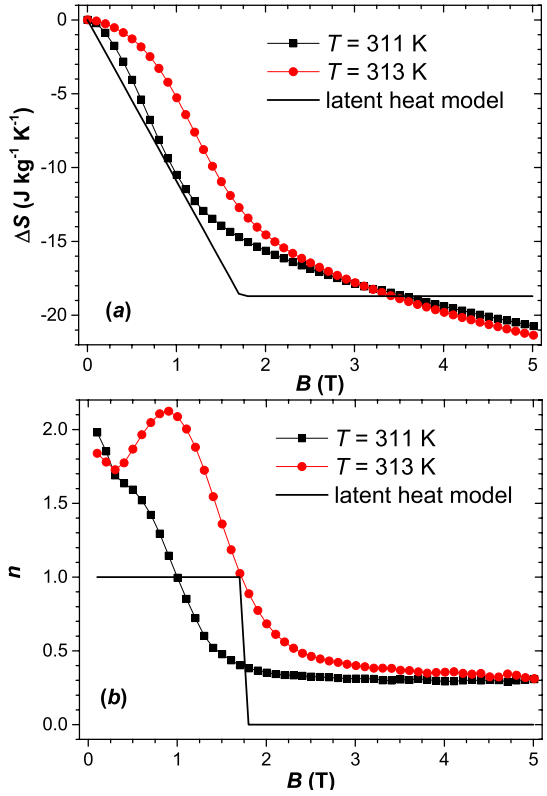

Fig. 2. Entropy change of $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$. (a) $\Delta S(B)$ derived from $M_T(B)$ data. (b) Local $n(T, B)$ exponent.

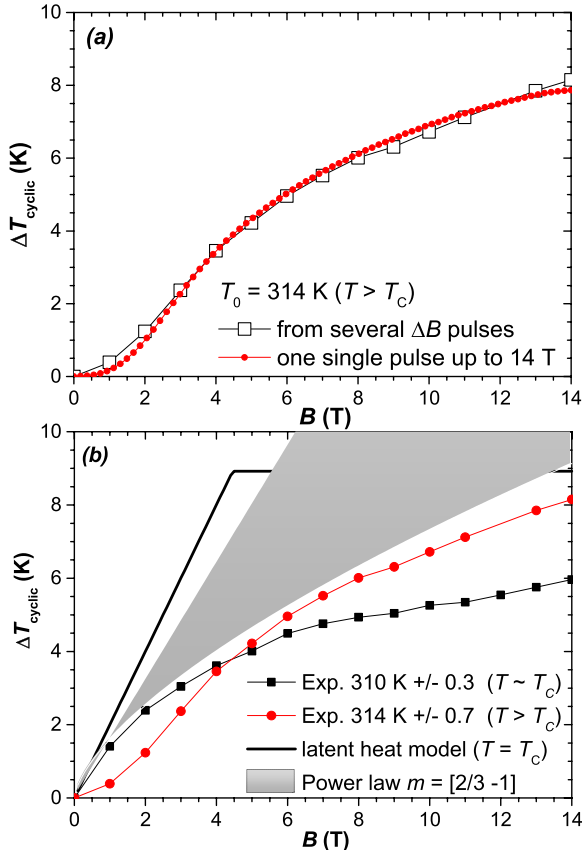

Fig. 3. Temperature change of $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$. (a) $\Delta T_{\text{cyclic}}(B)$ measured using the Bitter magnet probe up to 14 T. (b) Comparison between experimental $\Delta T_{\text{cyclic}}(B)$ and ΔT calculated by the latent heat model and the power law approach.

is shown in Fig. 2(b). The pronounced field dependence of n demonstrates that a power law cannot be used to describe $\Delta S(B)$ in this material. In contrast, it seems that the latent heat model using the parameters given above reproduces reasonably well saturation field $B^*_{\Delta S} = \delta T_{\text{tr}}/(dT_C/dB) \approx 1.7$ T at T_C. The entropy change given by the latent heat model below $B^*_{\Delta S}$, $\Delta S = [\Delta S_{\text{tr}} \Delta B(dT_C/dB)]/\delta T_{\text{tr}}$, is a good estimate of the experimental ΔS in 1 T. However, looking more closely into the simulated $\Delta S(B)$ curve, one easily sees the limitation of such a model. It fails in reproducing the rounding in the wings of the transition. In addition, it simply considers the MCE at the phase transformation, but neglects the MCE within the ferromagnetic and paramagnetic phases, which are not negligible at high fields, as shown in Fig. 2(a), by the evolution of $\Delta S(B)$ above 3 T.

To probe the field dependence of the temperature change in the vicinity of T_C, ΔT as a function of magnetic field $\Delta T(B)$ has been recorded up to 14 T [Fig. 3(a)]. The measurements have been performed in two different ways. The first approach consists in applying a series of field changes of $0 \rightarrow B \rightarrow 0$ with B from 1 to 14 T in 1 T increment, at a constant initial temperature (at $B = 0$). The resulting ΔT_{cyclic} values correspond to an average between the two field branches (field increase and field decrease) $\Delta T_{\text{cyclic}} = [\Delta T_{\text{ad}}(+\Delta B) - \Delta T_{\text{ad}}(-\Delta B)]/2$. The second method is a point-by-point analysis of a single field change $0 \rightarrow 14$ T. Comparing the two approaches, the second method appears more suitable, as the field increments are given by the measurement frequency. It clearly shows the S shape of $\Delta T_{\text{cyclic}}(B)$ expected for an FOMT at $T > T_C$. However, the results from the second approach are more prone to time delays between the sample and the temperature sensor. Therefore, although the results from the two methods are consistent with each other, the first method based on several ΔB field changes is preferred.

The $\Delta T(B)$ profile for $T > T_C$ in Fig. 3(b) clearly exhibits the influence of the FOMT, in a way similar to the shape of $\Delta S(B)$ at $T > T_C$. At $T = T_C$, the saturationlike shape of $\Delta T(B)$ turns out to be less pronounced than for $\Delta S(B)$, but one can still observe a rounding centered ~4–5 T. On one hand, if one uses a power law dependence $\Delta T \propto B^m$ with m from 2/3 to 1, as proposed in [22] and considering $\Delta T(\Delta B = 1 \text{ T}) = 1.6$ K, the range of simulated $\Delta T(B)$ does not match the experimental ΔT data. The use of $m \approx 0.5$ would improve the description of the field dependence of ΔT, but will not perfectly render it. On the other hand, the latent heat model from [17] parameterized with the same terms as for the ΔS in Fig. 2 corresponds to $\Delta T = \Delta B(dT_C/dB)[1 - \delta T_{\text{tr}}/(L/c_b + \delta T_{\text{tr}})]$ in the field-dependent region and to $\Delta T = L/c_b$ after saturation. In both the regimes, for $B \geq 2$ T, the ΔT values are overestimated by the model. This might arise from various reasons. In particular, considering field independent transition width, magnetization jump, heat capacity background, and latent heat lead systematically to an overestimation of the MCE. This effect of the field dependence of the parameters will be more salient for the simulation of ΔT than

for ΔS, as larger magnetic fields are required to reach the saturationlike behavior. Nevertheless, the saturation magnetic field for ΔT calculated by the latent heat model $\Delta B^*_{\Delta T} = L/\{c_b(dT_C/dB)[1 - \delta T_{\rm tr}/(L/c_b + \delta T_{\rm tr})]\} \approx 4.4$ T seems to be a reasonable estimate for the rounding of $\Delta T(\Delta B)$ around 4–5 T.

Therefore, neither of the methods proposed in the literature are suitable to describe the field evolution of the MCE in manganese-rich MnFe(P,Si) materials. For the power law approach $\Delta S \propto B^n$ or $\Delta T \propto B^m$, the main issue is actually that this approach was initially proposed for the second-order transitions [19], and its extension to an FOMT remains prone to controversy. Our data suggest that it cannot be applied to MnFe(P,Si) as a distinction between two the regimes is required: 1) the latent heat of the FOMT and 2) purely magnetic regime reflecting the MCE intrinsic to the paramagnetic state. The latent heat model provides a reasonable estimate of ΔS and ΔT at intermediate fields and, in particular, for $B = 1$ T. However, it neglects the MCE not related to the phase transformation or the field dependence of the various variables, so that it becomes improper at large magnetic fields.

Compared with other giant-MCE materials, the saturation fields $B^*_{\Delta S} \approx 1.7$ T and $\Delta B^*_{\Delta T} \approx 4$–5 T of $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$ are in the midrange values. The saturation fields remain significantly larger than the top-performance MCE material at 1 T, which is FeRh. It indicates that Mn-rich materials can be further optimized by driving the MCE to lower magnetic field. In this respect, it is interesting to consider the MCE predicted by the latent heat model for boron-substituted materials at intermediate magnetic fields. Using $dT_C/dB = 4.3$ KT^{-1}, $L = 3.8$ Jkg^{-1}, and $\delta T_{\rm tr} = 5$ K, which are typical of MnFe(P,Si,B) materials [5], the latent heat model is predicting $B^*_{\Delta S} \approx 1.1$ T, $\Delta S(1\ {\rm T}) \approx 11$ Jkg^{-1} K^{-1}, $B^*_{\Delta T} \approx 2.6$ T and $\Delta T(1\ {\rm T}) \approx 2.5$ K. Therefore, the decrease in L and the corresponding increase in dT_C/dB in boron material, compared with Mn-rich MnFe(P,Si), are driving $B^*_{\Delta S}$ and $B^*_{\Delta T}$ to lower magnetic fields, while keeping $\Delta S(1\ {\rm T})$ unmodified and increasing $\Delta T(1\ {\rm T})$. However, it appears that this strategy, decrease of L to increase in dT_C/dB, cannot be pursued further, as it will bring $B^*_{\Delta S}$ below 1 T, which will result in a decrease in $\Delta S(1\ {\rm T})$. Future attempts to optimize the MCE at intermediate field in the MnFe(P,X) system should focus on increasing ΔM (the link between L and dT_C/dB) and decreasing $\delta T_{\rm tr}$.

IV. Conclusion

This paper highlights the difficulty to describe the field dependence of the MCE in materials based on a FOMT. It turns out that none of the approaches available in the literature are suitable to describe the $\Delta S(B)$ and $\Delta T(B)$ field dependence in Mn-rich MnFe(P,Si) materials. The saturation magnetic fields for ΔS and ΔT are significantly larger than 1 T in $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$, so that there is still room for optimization in this system.

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