

# Determination of adiabatic temperature change in MnFe(P,Ge) compounds with pulse-field method

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## Abstract

Fast magnetic measurements performed by means of a 20 T pulse-field magnet provide a good approach for directly monitoring the magnetocaloric effect of the MnFe(P,Ge) compounds. Based on the comparison of magnetization curves obtained either in an adiabatic or isothermal process, we propose that the method introduced by Levitin *et al* is applicable to determine the adiabatic temperature change for an equivalent field change in first-order magnetic transition materials. More strikingly, experimental results confirm that the first-order nature of the transition in MnFe(P,Ge) alloys is not a limiting factor to the operation frequency of a magnetic refrigerator.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

An external magnetic field can strongly affect the magnetic order of a material, and also its temperature if phonon and magnetic excitations are well coupled via spin–lattice coupling [1]. Neglecting the minor contribution of electronic entropy change, the magnetic entropy change ( $\Delta S_m$ ) must be compensated by an equal but opposite change in the entropy associated with the lattice vibrations under adiabatic conditions [2]. The resulting change in temperature of the material ( $\Delta T_{ad}$ ) is known as the magnetocaloric effect (MCE). Direct techniques to evaluate the MCE are based on the measurement of temperature change in a sample while varying the magnetic field under adiabatic conditions. Indirect evaluations can be performed by using magnetization and heat-capacity measurements, using the fundamental Maxwell relations. Nowadays, most studies devoted to

room-temperature applications of magnetic refrigeration are focused on materials showing a giant MCE associated with a first-order magneto-structural transition (FOMT) [3–7]. A common feature of the compounds showing a FOMT is that the large MCE observed in these materials is often accompanied by a large thermal hysteresis ( $\Delta T_{hys}$ ). However, a large  $\Delta T_{hys}$  could make them unsuitable for applications because a commercial competitive refrigerator is expected to operate at rather high thermal cycling frequencies. To date, most of the prototypical magnetic regenerators employing second-order magnetic phase transition (SOMPT) refrigerants can operate at a frequency in the range 1–5 Hz [8, 9]. In this paper, a pulse-field magnet was used to simulate the operation of MnFe(P,Ge) compounds, which typically show a FOMT behaviour [10, 11], at frequencies that can rise up to 25 Hz. By comparing the difference between isothermal and adiabatic magnetization curves, the MCE of MnFe(P,Ge) compounds was directly observed and the field dependence of  $\Delta T_{ad}$  was also calculated.

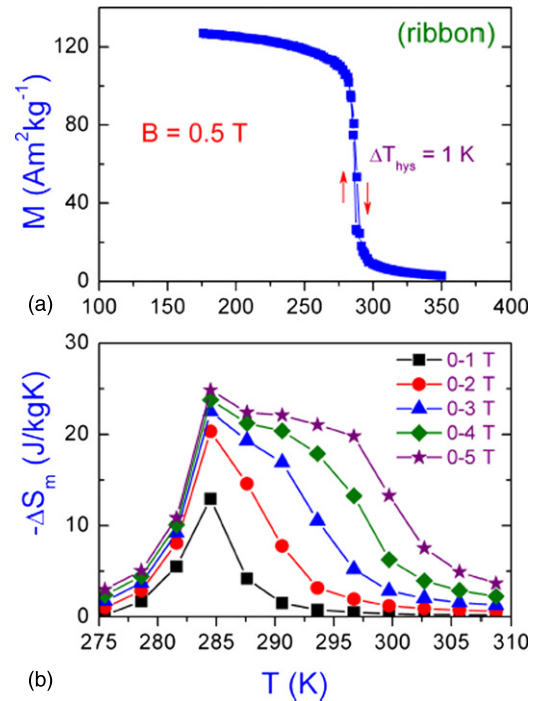
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## 2. Experimental procedure

Polycrystalline samples of MnFe(P,Ge) with equal Curie temperature ( $T_C$ ) were prepared by two different techniques. A ribbon of nominal composition  $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.75}\text{Ge}_{0.25}$  was prepared by melt-spinning at  $40 \text{ m s}^{-1}$  surface speed of the Cu wheel. A bulk sample of  $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.78}\text{Ge}_{0.22}$  was synthesized by high-energy ball milling and solid state reaction [12]. Powder x-ray diffraction (XRD) on the samples was performed at room temperature in a Philips PW-1700 diffractometer with Cu  $K\alpha$  radiation. Electron probe micro analysis (EPMA) was made on the bulk sample in order to obtain further information about the homogeneity and the stoichiometry. Specific-heat measurements on a bulk sample were done with the so-called hybrid method known as a modification of the traditional semi-adiabatic method, in an Oxford Instruments MagLab Exa system [13]. The isothermal magnetic measurements were carried out in a commercial SQUID magnetometer (Quantum Design MPMS 5XL). The  $\Delta S_m$  is derived from the isothermal magnetization data collected at discrete equidistant temperatures by using the Maxwell relation [1]. Fast and accurate measurements of the magnetization were performed with a pulse-field magnet in fields up to 20 T [14]. At a field-sweep rate of about  $3 \times 10^2 \text{ T s}^{-1}$ , which corresponds to a refrigerator frequency of about 25 Hz of a permanent-magnet rotary refrigerator [8], the magnetization process of the sample is close to being adiabatic. To avoid any effects from eddy currents that might influence the accuracy of the pulse-field measurements, both ribbon and bulk samples were crushed into powder with a particle diameter of about  $50 \mu\text{m}$ . As the typical response time of a thermocouple is of the same order as the pulse duration, a thermocouple fixed into the sample space, in the close vicinity of the sample position, was used to measure the starting temperature ( $T_{\text{start}}$ ) and a possible change in sample temperature after the pulse.

## 3. Results and discussion

The EPMA and XRD analysis confirm that the main phase of the bulk sample, crystallized in the hexagonal  $\text{Fe}_2\text{P}$ -type structure (space group  $P\bar{6}2m$ ), is homogeneous. Also, a small amount ( $\sim 4 \text{ vol}\%$ ) of secondary phase  $\text{Mn}_2\text{O}_3$  is detected [15]. Refinement of the XRD pattern for the ribbon indicates that all reflections can be indexed on the basis of a single-phase  $\text{Fe}_2\text{P}$ -type structure with no minor impurity phase being present [12]. In figure 1(a), the temperature dependence of the magnetization given for the ribbon sample shows a sharp magnetic transition. The value of the ordering temperature ( $T_C$ ) is about 288 K and the  $\Delta T_{\text{hys}}$  between the magnetic transitions observed on heating and cooling processes is only 1 K. The  $\Delta S_m$  results as a function of temperature are presented in figure 1(b). Under a magnetic-field change of 2 T, which is comparable to the maximum field change from a permanent magnet used in a refrigerant device, the  $\Delta S_m$  value recorded for the ribbon sample is  $-20.3 \text{ J kg}^{-1} \text{ K}^{-1}$ . For a higher magnetic field change, the maximum magnetic entropy change hardly increases. However, the relative cooling power [16] is considerably enhanced. This phenomenon is observed

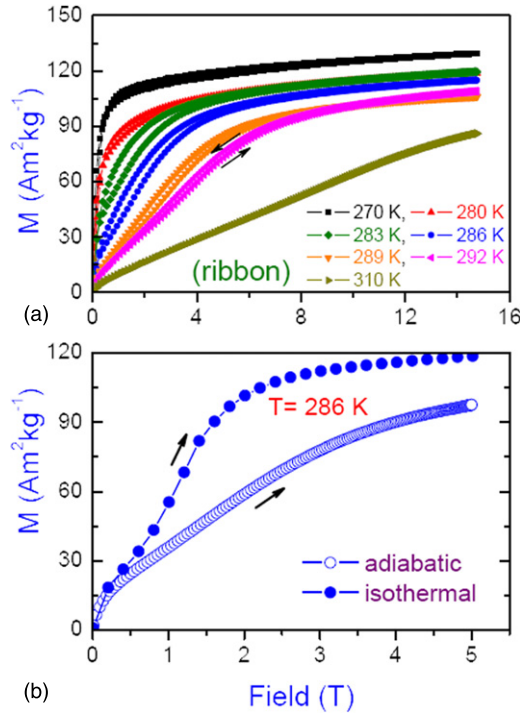


**Figure 1.** Temperature dependence of the magnetization of the ribbon sample (see text) measured in magnetic field of 0.5 T (a). Isothermal magnetic entropy changes ( $-\Delta S_m$ ) for different field changes calculated for the same sample (b).

for most of the magnetocaloric materials undergoing a FOMT [3–7, 17, 18]. Recently, it was found that it is possible to tune the  $\Delta T_{\text{hys}}$  of MnFe(P,Ge) compounds by processing [12]. In the melt-spun ribbon of composition  $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.75}\text{Ge}_{0.25}$  we meet conditions that result in a large MCE in combination with a very small observed  $\Delta T_{\text{hys}}$ .

In figure 2(a) we show the hysteresis magnetization curves [14] of the ribbon sample measured in the 20 T pulse-field magnet in fields up to 15 T at different  $T_{\text{start}}$  of 270, 280, 283, 286, 289, 292 and 310 K. In the vicinity of the magnetic transition, we observe a quite small magnetization hysteresis and the field-induced transition is not very pronounced. Note that the MCE causes the sample to be heated up with increasing applied field. This heat amount is then totally compensated when the field decreases from 15 T to zero field. By reading a thermocouple, it was confirmed that the sample temperature does not change after the field pulse. Therefore, the influence of eddy currents on the accuracy of the pulse-field measurements is negligible. To monitor the sample temperature during the pulse, we exploit the fact that magnetization becomes lower with increasing temperature. Figure 2(b) shows isothermal (filled symbol) and adiabatic (open symbol) magnetization curves, which are measured in the vicinity of  $T_C$  in increasing fields up to 5 T, of the ribbon sample. Both curves start with the sample temperature at 286 K. It is evident that the magnitude of magnetization in the adiabatic process is lower than that in the isothermal process because of the MCE.

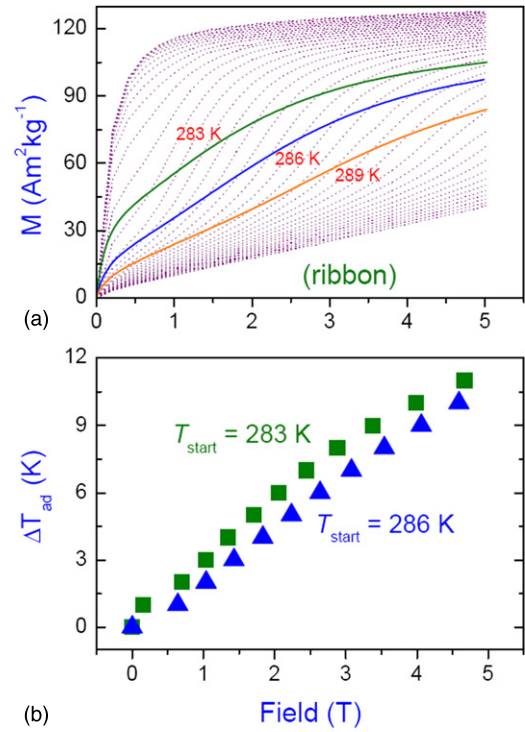
Without any direct measurements of the sample temperature, Levitin introduced an elegant method that can be used to determine the MCE of a material exhibiting a SOMPT



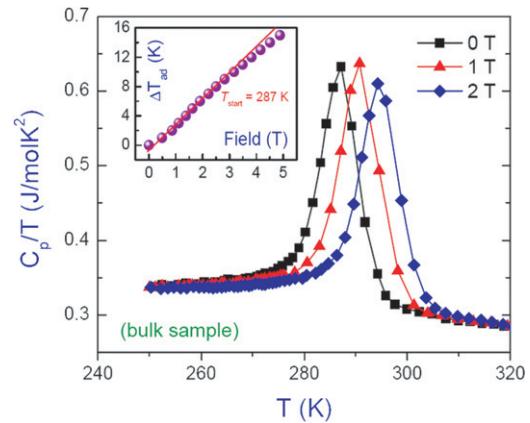
**Figure 2.** Magnetization loops of the ribbon sample measured in a 20 T pulse-field magnet at different starting temperatures ( $T_{\text{start}}$ ) in fields up to 15 T (a). Adiabatic and isothermal magnetization curves measured on the same sample in the vicinity of  $T_c$  in increasing fields up to 5 T (b). (Colour online.)

behaviour by comparing magnetization curves obtained under isothermal and adiabatic conditions [19]. The field dependence of the sample temperature during its adiabatic magnetization process will be constructed via the crossing points of the adiabatic curve with the set of isothermal curves. Here, we propose that this method is also applicable for determining the  $\Delta T_{\text{ad}}$  of a first-order transition material. This can be seen in figure 3(a) for several adiabatic magnetization curves (solid lines) measured at different  $T_{\text{start}}$  around  $T_c$  of the ribbon sample. Also shown in figure 3(a) is a set of isothermal  $M(H)$  curves of the same sample (dotted lines) measured from 273 to 310 K with the temperature step between the adjacent curves  $\Delta T = 1 \text{ K}$ . An estimate of the adiabatic temperature variation can be made by evaluating the crossing points of the adiabatic curve with the set of isothermal curves, resulting in the curves of  $\Delta T_{\text{ad}}(B = 0-5 \text{ T})$  as depicted in figure 3(b) for two different values of  $T_{\text{start}}$  of 283 K and 286 K. Below a critical field  $B_{\text{crit}} = 2.5 \text{ T}$ , we can see an almost linear field dependence of sample-temperature change. The small deviations near zero field are attributed to the formation of magnetic domains [18]. Above  $B_{\text{crit}}$ , however, this linearity is no longer observed [17]. In practice, the largest  $\Delta T_{\text{ad}}$  during the field sweep of a ribbon sample is observed for  $T_{\text{start}} = 283 \text{ K}$  when the magnetization of the sample is going through the transition from the ferromagnetic to the paramagnetic state. At this temperature, the sample-temperature change is estimated to be approximately  $3 \text{ K T}^{-1}$  with the external field varying from  $B = 0$  to  $B = 2 \text{ T}$ .

Finally, a more detailed study of the magnetocaloric properties was carried out on our bulk sample which reveals



**Figure 3.** Experimental data used to obtain the field dependence of the adiabatic temperature change ( $\Delta T_{\text{ad}}$ ) of the ribbon sample by comparing the isothermal curves (dotted lines) and adiabatic curves (solid lines) measured in increasing fields up to 5 T (a). The field dependence of  $\Delta T_{\text{ad}}$ , as constructed for the same sample from the crossing points of the adiabatic curves with the set of isothermal curves, for  $T_{\text{start}} = 283 \text{ K}$  and  $286 \text{ K}$ , respectively (b).



**Figure 4.** Temperature dependence of the heat capacity measured with increasing temperature in different applied fields for a bulk sample. Inset: field dependences of  $\Delta T_{\text{ad}}$ , as calculated from the crossing points of the adiabatic pulse-field curve measured at  $T_{\text{start}} = 287 \text{ K}$  with the set of isothermal curves measured on the same bulk sample.

about 4 K thermal hysteresis. The FOMT gives rise to a large  $\Delta S_m$  of  $-20 \text{ J kg}^{-1} \text{ K}^{-1}$  calculated for a field change  $\Delta B = 0-2 \text{ T}$ . By comparing the isothermal and adiabatic magnetization curves and doing the above-mentioned analysis, we obtained an almost linear dependence of the  $\Delta T_{\text{ad}}$  on the magnetic-field change (figure 4, inset). The maximum  $\Delta T_{\text{ad}}$  recorded for the bulk sample at  $T_{\text{start}} = 287 \text{ K}$  is about

$2.9 \text{ K T}^{-1}$ . The heat capacity ( $C_p$ ) of the sample measured in different external fields with temperature increasing from 250 to 320 K is shown in figure 4. In zero field the peak position corresponding to the transition is about 287 K. When applying magnetic fields of 1 T and 2 T, the peak is linearly shifted to higher temperatures, which are about 291 K and 295 K, respectively, with a shift of  $4 \text{ K T}^{-1}$ . From a numerical integration of  $C_p/T$  we derived  $S(T)$  curves for the bulk sample, and from these we can directly derive values for  $\Delta S_m$  and  $\Delta T_{ad}$  being the vertical and horizontal distance between the curves in the various fields, respectively. However, we found values that were about 30% lower than the magnetically determined values. From the agreement between the two pulse-field results for  $\Delta T_{ad}$  observed in the ribbon sample and the bulk sample, we conclude that these lower values cannot be attributed to differences in properties between the two materials although these are slightly different in composition. Obviously, because of the well-known difficulties in measuring heat capacities around first-order transitions, the observed results do not cover all the latent heat of the transition [16, 20]. It is noted that the values of adiabatic temperature change ( $\Delta T_{ad} \sim 3 \text{ K T}^{-1}$ ) obtained for both the ribbon and the bulk sample are in agreement with that obtained from direct measurements for  $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.47}\text{As}_{0.53}$  [21], a compound exhibits similar structural and magnetocaloric properties in comparison with the  $\text{MnFe}(\text{P},\text{Ge})$  alloys presented in this paper, and in the same order of magnitude with those found in other magnetic refrigerants such as  $\text{Gd}$ ,  $\text{Gd}_5(\text{Ge},\text{Si})_4$  and  $\text{La}(\text{Fe},\text{Si})\text{H}$  [1].

#### 4. Conclusion

In conclusion, a large low-field MCE was observed near room temperature in both a bulk sample and a melt-spun sample. The pulse-field technique is emphasized to be a very good tool for determining the adiabatic temperature change and for simulating the operation of  $\text{MnFe}(\text{P},\text{Ge})$  alloys at rather high cycle frequencies. When accompanied with small thermal hysteresis, the first-order nature of the transition appears not to be a limiting factor to the speed of the transition, and puts, therefore, no upper limit on the working frequency of MCE-based refrigerators.

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