High field measurement of the magnetocaloric effect in MnFe(P,Si) materials.

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I. INTRODUCTION

Recently, materials undergoing a first-order magnetic transition (FOMT) near room temperature have attracted much attentions due to the possibility to use their large magnetocaloric effect (MCE) for magnetic refrigeration [1]. Among them, the MnFe(P,*X*) (*X* = As, Ge, Si, B) family turns out to be one of the most promising due to the large isothermal entropy change ΔS, adiabatic temperature change ΔT_{ad}, a tunable Curie temperature (T_C) and the practical advantages. Till now, most of the MCE studies on MnFe(P,X) focused on the intermediate magnetic field range ($B \leq 2$T) as it is the most relevant field for applications [2]. However, extending the field range of the MCE derivation is important from both fundamental and practical points of view. On one hand, it allows one to address the field dependence of the MCE quantities, the possible influence of the critical point, etc; On the other hand, high field ΔS or ΔT_{ad} data are useful for the optimization of the MCE at intermediate field. Indeed, at first glance, one can consider for FOMT that the ΔS or ΔT_{ad} will saturate above a given field value ($B^*(\Delta S)$ or $B^*(\Delta T)$). The point is that in Giant-MCE materials, it might be advantageous to bring these B^* (often at high field) as close as possible to the field used in application. Understanding the field dependence of ΔS, ΔT_{ad} and quantifying the B^* in MnFe(P,X) is required for further optimizations.

Unfortunately, it is not possible to simply extrapolate the high field ΔS and ΔT_{ad} from intermediate field data. In the literature, the field dependence of the Giant-MCE is still a controversial topic, with mostly two approaches. *(i)* The first is based on schematic description of the entropy *vs* temperature lines at the FOMT. In this case, two field regimes are distinguished, the ΔS or ΔT_{ad} should increase linearly until it reaches a saturation $\Delta S = L/T_C$ at $B^*(\Delta S)$, or $\Delta T_{ad} = L/c_b$ at $B^*(\Delta T)$, where L is the latent heat and c_b the heat capacity outside the FOMT [3]. (ii) The second originates from the so-called "Universal analysis of the MCE", and predicts a power law evolution of $\Delta S \propto H^n$ the for materials based on a second order transition [4,5]. Recently, many works have tried to extend this power law approach to FOMT materials or to the field dependence of ΔT_{ad}. However, there is no consensus.

In this work, we present the adiabatic temperature change (direct and cyclic) measured for various magnetic fields up to 14 T for one prototypical MnFe(P,Si) material.

II. RESULTS

In order to fulfill the prerequisites for the high field ΔT probe (mass ~ 2 g, T_C ~ 300 K, limited hysteresis) [6], a new batch of Mn-rich MnFe(P,Si) material has been prepared. Prior to the high field measurements, a full set of MCE characterization at B = 1 T has been carried out. The ΔS and ΔT have been measured by both direct and indirect methods based on: Maxwell method applied on $M_B(T)$ and $M_T(B)$ magnetic data, ΔS and ΔT_{ad} from in-field DSC calorimetry, direct ΔS_{cyclic}, and ΔT_{cyclic} setups. The MCE derived from the various methods is in good agreement. Large cyclic ΔS of ~11 $Jkg^{-1}K^{-1}$ and ΔT_{ad} of ~ 1.6 K for a field change of 1 T are observed at the T_C of 310 K. These MCE values are usual for this range of composition and will allow comparison with other MnFe(P,X) materials.

The direct measurements have been performed in cyclic mode (several field application/removal) in a Bitter magnet allowing field changes at a rate of 14 T/min thus ensuring quasi-adiabatic conditions while being slow enough to not be influenced by any kinetic aspects of the FOMT or eddy currents. The cyclic adiabatic temperature change (ΔT_{cyclic}) measured up to a magnetic field of 14 T are presented in Figure 1 for $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$ material at two temperatures, at $T_0 = T_C = 310$ K and $T_0 = 314$ K, and compared to the latent heat model (i), presented in section I. The main results can be summarized as follows. At $T_0 > T_C$, the ΔT_{cyclic} vs B curve clearly shows a signature of the FOMT. At $T_0 = T_C$, the ΔT calculated from the model are clearly overestimated. One of the main reason is probably that the width of the FOMT and its evolution in magnetic field is not taken into account. On the other hand, the model well reproduces the change of regime at $B^*(\Delta T) \sim 5$ T. Since $B^*(\Delta S) = 1.2$ T (from indirect ΔS data), this $B^*(\Delta T)$ boundary lies at much higher magnetic field than that for the $\Delta S(B)$ evolution. The continuous increase of ΔT_{cyclic} at $B > B^*$ shows that the MCE outside the FOMT is not negligible. The field evolution of ΔT_{cyclic} can not be scaled by a power law with n~2/3.

It is thus shown that the field evolution of the ΔT_{cyclic} in MnFe(P,Si) materials can not be described by the methods proposed in the literature. The reasons will be discussed. The relatively high compared to the magnetic field used for applications indicates that further improvements of the properties of these materials are possible by driving the MCE associated with the FOMT to lower magnetic fields. In this sense, the present data bring support to the scenario proposed in the studies of boron substituted MnFe(P,Si) materials [7], in particular for the explanation of their large ΔT_{cyclic}.

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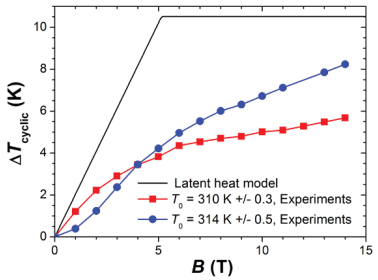

Figure 1. Field dependence of the cyclic adiabatic temperature change ΔT_{cyclic} at $T_0 = T_C = 310$ K (squares) and $T_0 = 314$ K (circles) for $Mn_{1.22}Fe_{0.73}P_{0.47}Si_{0.53}$, compared to the schematic model at T_C.