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Regular article

Large recalescence-like event at the first cooling across the magnetic transition of $(Mn,Fe)_2(P,Si)$ magnetocaloric materials

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ABSTRACT

An unconventional phenomena is observed at the first-order magnetic transitions in $(Mn,Fe)_2(P,Si)$ materials. Here, we show that the first crossing of the transition upon cooling is associated with an abnormal temperature increase. While differential scanning calorimetry can detect this recalescence-like event, purposely-designed probes were employed to quantify it. Recalescence at a magnetic transition is extremely rare. But in $(Mn,Fe)_2(P,Si)$, it is even more remarkable by its amplitude, with the temperature rising up to +4.0 K. In $(Mn,Fe)_2(P,Si)$, this phenomenon is associated with irreversible burst-like evolution of the microstructure (increase in defect concentration and micro-cracking) and of the crystal structure.

First-order magnetic transitions (FOMTs) separating two phases with a large difference in net magnetization are attracting great interest for their potential applications and rich physics. The most studied materials families include FeRh, MnAs, $Gd_5(Si,Ge)_4$, $La(Fe,Si)_{13}$, MnFe(P,Si), MnCoGe, Heusler alloys, Laves phases [1–4], their giant magnetocaloric effect is an hot topic as it is at the heart of new heat pumping technologies particularly energy efficient and environmentally friendly. The FOMTs in these materials present some unusual phenomena such as hysteresis, aging, metastability and irreversibility. Some of them also exhibit a very peculiar magneto-thermal history dependence, with the transition of the as-prepared sample occurring at a significantly lower temperature during the first cooling than for subsequent thermal cycles. This phenomenon sometime referred to as "virgin effect" (VE) has been observed in MnAs [5], MnCoGe [6], $(Mn,Fe)_2(P,X)$ materials with $X =$ As, Ge, Si or B [7–12].

Despite numerous investigations, the VE mechanism in MnFe(P,X) is not fully understood yet. The first studies suggested different origins: an anisotropic change in cell parameters [8], an interchange of the atomic positions [10], an additional contribution to the hysteresis originating from the coupling between magnetization and strains [13], or an irreversible magneto-structural transition [7]. More recently, it was pointed out that the microstructure and its evolution may play a role due to (micro-)cracking and an increase in defect concentration (e.g. linear defects like dislocations) [12]. In the hexagonal MnFe(P,Si) system though the crystal symmetry remains unmodified, large discontinuities in the lattice parameters a and c occur at the FOMT. In randomly oriented polycrystalline MnFe(P,Si), an anisotropic internal stress can develop at the contact surface between crystallites with different orientations. It may lead to intergranular cracking during the VE, as seen by optical and SEM microscopy [12]. Further studies by x-ray powder diffraction, differential scanning calorimetry (DSC) and Hall probe imaging, highlighted that dislocation rearrangement can be responsible for the VE, and a difference in dislocation mobility may explain the differences in VE amplitude between different samples [14,15]. On the other hand, detailed neutron studies gave additional insights. In MnFe(P,Si), an irreversible structural transformation was found at the VE, with atoms in the as-prepared sample showing a larger spread around their equilibrium crystallographic position than after cycling [16]. In MnFe(P,Ge), development of strains and suppression of an incommensurate antiferromagnetic ordering were found to accompany the VE [17]. It is clear that the virgin effect in MnFe(P,X) materials is a multifaceted problem. There is still no consensus on the various questions: about the underlying mechanisms of the VE (why?), as well as about the thermodynamic stability of the different phases involved and the kinetic of the transformations between them (how?).

Polycrystalline $Mn_{1.23}Fe_{0.72}P_{0.48}Si_{0.52}$ and $MnFe_{0.95}P_{0.62}Si_{0.34}B_{0.04}$ were prepared by ball-milling and solid state sintering as previously reported [12]. Differential scanning calorimetry (DSC) experiments were carried out with TA instruments DSC 2500 (Figs. 1 and 2), DSC Q2000 (Fig. 3) and using Tzero Aluminium pans. Additional DSC experiments (not shown) were performed using a Netzsch DSC200F3 calorimeter. Two specific probes were developed to obtain quantitative estimates

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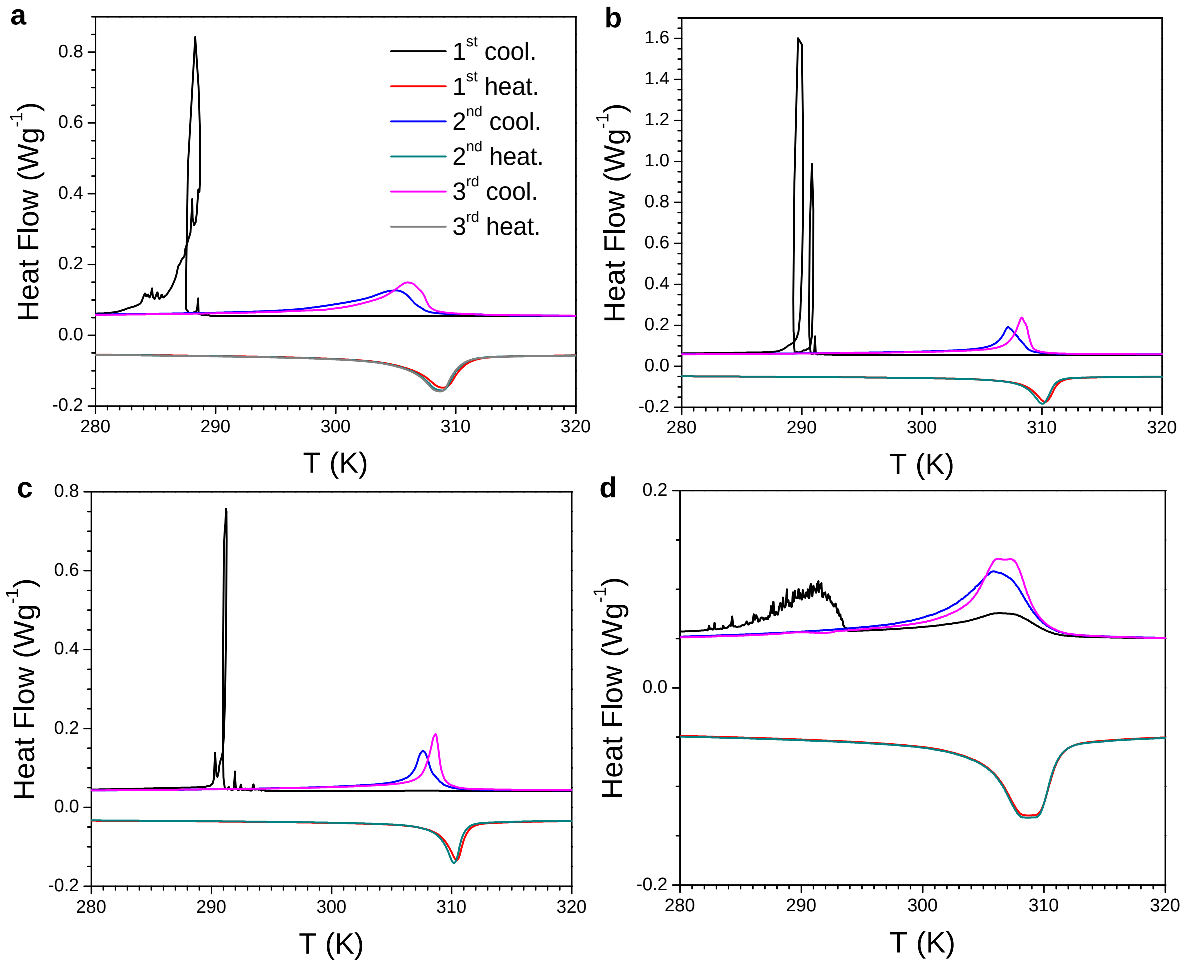

Fig. 1. Heat flow upon successive cooling and heating (at 5 K min^{-1}) across the first-order magnetic transition of $Mn_{1.23}Fe_{0.72}P_{0.48}Si_{0.52}$ in different shapes: (a) large bulk piece (mass = 110.1 mg), (b) an intermediate size bulk piece (35.5 mg), (c) crushed powder having particle size >75 μm, and (d) powder having particle size <30 μm.

of the recalescence. A first probe records simultaneously the temperature and a magnetic signal in quasi-adiabatic conditions. A thermoresistor of negligible mass is glued on a large piece of sample (2.2120 g). Two Hall sensors are mounted in equatorial and longitudinal positions near the sample. The sample is fixed to the sampler holder by nylon wires. The sample and its holder are placed in a sample chamber under vacuum (~10^{-2} mbar). The sample chamber fits into the bore of a dipole electromagnet. Resistance and Hall voltages are measured using Keithley 2400 sourcemeters. The uncertainty on the temperature

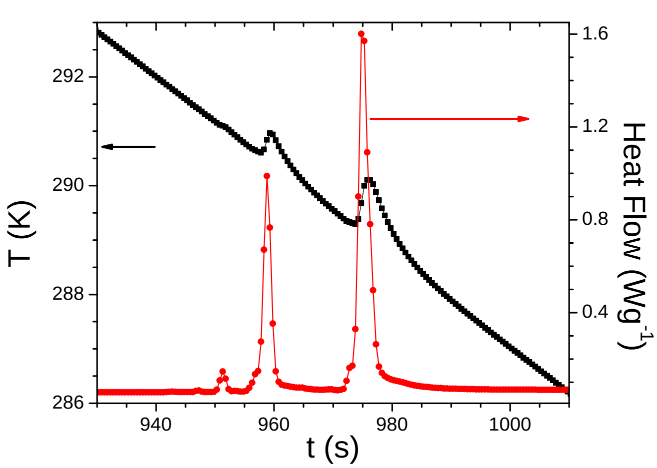

Fig. 2. Time dependence of the sample pan temperature and heat flow during the first cooling of an as-prepared $Mn_{1.23}Fe_{0.72}P_{0.48}Si_{0.52}$ sample (intermediate size bulk piece, 35.5 mg, Fig. 1(b)).

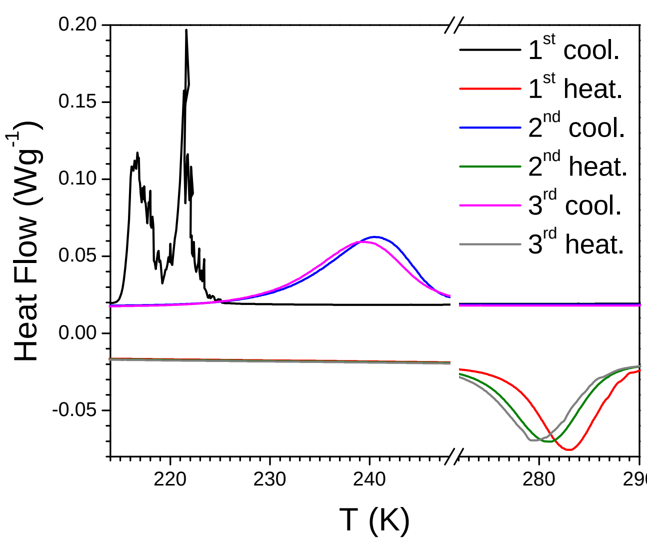

Fig. 3. Heat flow upon successive cooling and heating (measured at 2 $Kmin^{-1}$) across the first-order magnetic transition of $MnFe_{0.95}P_{0.62}Si_{0.34}B_{0.04}$ (bulk piece of 108.0 mg).

change is about 5.6%. A second probe aims to measure the heat released during the recalescence by measurements in quasi-isothermal conditions. For that purpose the approach proposed by A. Kamantsev et al. to perform magnetocaloric measurements was used [18]. It consists in fixing the sample of limited mass (0.2310 g) to a bulk piece of W (10.4505 g) used as heat sink. The amount of heat transferred by the sample to the bulk piece can be estimated: $\Delta Q = (m_W/m_S)\cdot c_W\cdot\Delta T_W$, where m_W, c_W and ΔT_W are the mass, the specific heat and apparent temperature change of the tungsten bulk piece, respectively, and m_S the sample mass. The instrumental uncertainty on the corresponding entropy change is estimated around 12%.

DSC experiments performed on as prepared $Mn_{1.23}Fe_{0.72}P_{0.48}Si_{0.52}$ samples are presented in Fig. 1. The heat flow is recorded as a function of the temperature during the first cooling from 373 K to 200 K, subsequent heating from 200 K to 373 K, and then the cooling/heating cycles are repeated. During the 3rd cycle, the transition temperatures are ~310.2 K upon heating and ~308.3 K upon cooling, thus marking a limited thermal hysteresis of ~2 K. A limited spread in transition temperatures can be observed between samples of different shapes. It may originate from experimental artefacts (different thermal transfer and relaxation time), as well as from an effect of sample shape on the drift in transition temperatures upon cycling (at longer term than the VE) already observed in Ref. [12]. Integrating the heat flow peak provides us an estimate of the latent heat ~6.1 Jg^{-1} and the corresponding transition entropy $\Delta S_{tr} = L/T_{tr} \approx 19.7$ Jkg^{-1} K^{-1}. When looking at the first cooling, heat peaks and spikes mark the occurrence of the FOMT in as-prepared sample at 290 K. The temperature difference between the 1st cooling and the 3rd cooling reveals a VE of about 18 K. While the sample was stored during a long period of time (several weeks) at temperatures between VE and Curie temperatures, the VE is still fully observed. This suggests that the supercooling in the as-prepared sample is poorly dependent on the rate of cooling and corresponds to a long lifetime metastable state.

Transition temperatures, hysteresis, latent heat and VE are in line with the values expected for manganese-rich and silicon-rich $(Mn,Fe)_2(P,Si)$ [12,14,15,19]. The shape of the DSC curves during the first cooling is however more surprising. First, one can notice heat flow spikes, well-illustrated in Fig. 1 (d), small successive burst of heat flow <0.05 Wg^{-1} in amplitude. Such burst-like heat flows were observed in several materials families presenting FOMTs [20,21] and at the VE of MnFe(P,*X*) materials [15]. These heat avalanches are often attributed to a complex energy landscape in materials with first-order magnetic transitions, in particular with the nucleation and growth of a new phase with a different structure/lattice parameters at the expense of another [22]. This burst phenomenon is an autocatalytic process of rapid successive formation of the new phase occurring in a small temperature/time window triggered by large elastic stresses set up ahead of the nucleation site. Here, while these heat flux avalanches are clearly observed at the VE, they are no longer noticeable during the following cycles. Additional DSC experiments were performed at slower rates (down to 8 mKs^{-1}), but heat flux avalanches could not be detected in cycled samples. One should recall that the FOMT in $(Mn,Fe)_2(P,Si)$ is not a pure magnetic process but also involves a solid-solid transformation between two phases with large differences in lattice parameters. Therefore, the general principles of nucleation/growth theory apply, which implies that the concentration in nucleation sites will influence the rate of transformation. Suitable nucleation sites are non-equilibrium defects such as vacancies, dislocations, grain boundaries, stacking faults, inclusions and free surfaces. The irreversible changes in the microstructure at the VE (micro-cracking and increase in defects concentration [12]) lead to a multiplication in nucleation sites, making heat flux avalanches undistinguishable in cycled samples. It is interesting to note that pulverizing the sample into particles with dimension close to the grain size also leads to a decrease in amplitude and an increase in number of heat flux avalanches.

In Fig. 1(a) to (c), we can observe a quite unusual phenomenon with the opening of a loop in the heat flow versus temperature signal. When sample temperature and heat flow are shown as a function of time, Fig. 2, the origin of this loop becomes more apparent. The temperature-time dependence corresponds to the average cooling rate of the experiment (-5 $Kmin^{-1}$) with in addition 3 sudden temperature rises (up to $+1.0$ K). The heat flux bursts marking the transition are accompanied by a recalescence-like event, i.e. a sudden increase of the sample temperature during the cooling. This recalescence is clearly observed in the two DSC measurements on bulk samples (Fig. 1a and b) and on large particles (Fig. 1c). However, it is no longer observed when the sample is pulverized into particles as small as or smaller than the grain size (Fig. 1d).

To confirm that the temperature rise detected in this first series of DSC experiments does not originate from an experimental artefact, complementary DSC measurements were performed, first, by using the same $Mn_{1.23}Fe_{0.72}P_{0.48}Si_{0.52}$ sample but a different type of DSC. While the transition, VE and the heat flux avalanches were observed, the opening of a loop could not be detected (results not shown). Second, using a similar type of DSC as initial experiments (but a different model), measurements were carried out on a sample showing a VE at temperature much lower than room temperature. Fig. 3 shows DSC results for an as-prepared piece of $MnFe_{0.95}P_{0.62}Si_{0.34}B_{0.04}$. The initial transition upon cooling is centered around 220 K. During subsequent cycles the transition temperatures are 241 K and 283 K upon cooling and heating, respectively. $MnFe_{0.95}P_{0.62}Si_{0.34}B_{0.04}$ presents large hysteresis (~42 K), latent heat (~13.8 Jg^{-1}) and VE (~21 K). We can observe the opening of a loop in the heat flow curve during the first cooling denoting a recalescence of about $+0.6$ K at 222 K. It is surprising that this unconventional temperature rise upon cooling was not reported during former DSC studies [15] and that its detection depends on the type of DSC. We believe that its detection by DSC (Fig. 1-3) is linked to the use of the so-called Tzero® technology. By providing independent sample and reference temperatures, this technique considers sample and reference calorimeters as thermally independent [23]. In addition to smaller baseline and higher sensitivity, this DSC technique is known to also strongly affect resolution and peak shape of first-order transitions, for instance it allowed detecting a temperature rise during the solidification of indium [23,24]. The temperature rise during cooling through the VE of $(Mn,Fe)_2(P,Si)$ materials is most likely an intrinsic phenomenon not detected till now due to inadequate resolution. Though useful to detect recalescence, DSC experiments can however not be used to quantify its amplitude due to thermal dilution between sample and pan, as well as large heat leaks.

Fig. 4 shows quasi-adiabatic and quasi-isothermal characterizations of the temperature rise upon cooling in as-prepared $Mn_{1.23}Fe_{0.72}P_{0.48}Si_{0.52}$. During the quasi-adiabatic measurements, Fig. 4 (a), a magnetic signal is recorded (in 0.1 T) during the cooling of a bulk piece of $Mn_{1.23}Fe_{0.72}P_{0.48}Si_{0.52}$. The temperature increase happens simultaneously with the appearance of the magnetic order. In these quasi-adiabatic conditions (the recalescence appears almost instantaneous compared to the underlying cooling rate), the temperature rise occurs at 284 K and reaches up to $+4.0 \pm 0.3$ K. Thus, the recalescence-like event is observed over a broad range of cooling rates from -5 $Kmin^{-1}$ (DSC) to -0.5 $Kmin^{-1}$ (adiabatic probe). In quasi-isothermal conditions, Fig. 4(b), the temperature increase of the assembly heat sink plus sample is about $+0.4$ K (an order of magnitude smaller than in adiabatic conditions). We can estimate it corresponds to a release of heat of $\Delta Q \approx 2.7$ Jg^{-1}. In terms of entropy, this translates into $\Delta S_{recalescence} = \Delta Q/T \approx 9 \pm 1$ Jkg^{-1} K^{-1}. Clearly, this recalescence-like event is an intense phenomenon amounting to approximately 50% of the entropy change of the transition itself ($\Delta S_{tr} \approx 19.7$ Jkg^{-1} K^{-1}).

Burst-like temperature rise upon cooling can occur at phase change transitions, in particular liquid to solid transformations. Upon cooling, if the liquid lacks nucleation sites, it may be kept in liquid form, supercooled below its standard solidification temperature. When the supercooled liquid suddenly cystallizes forming a solid, it releases heat

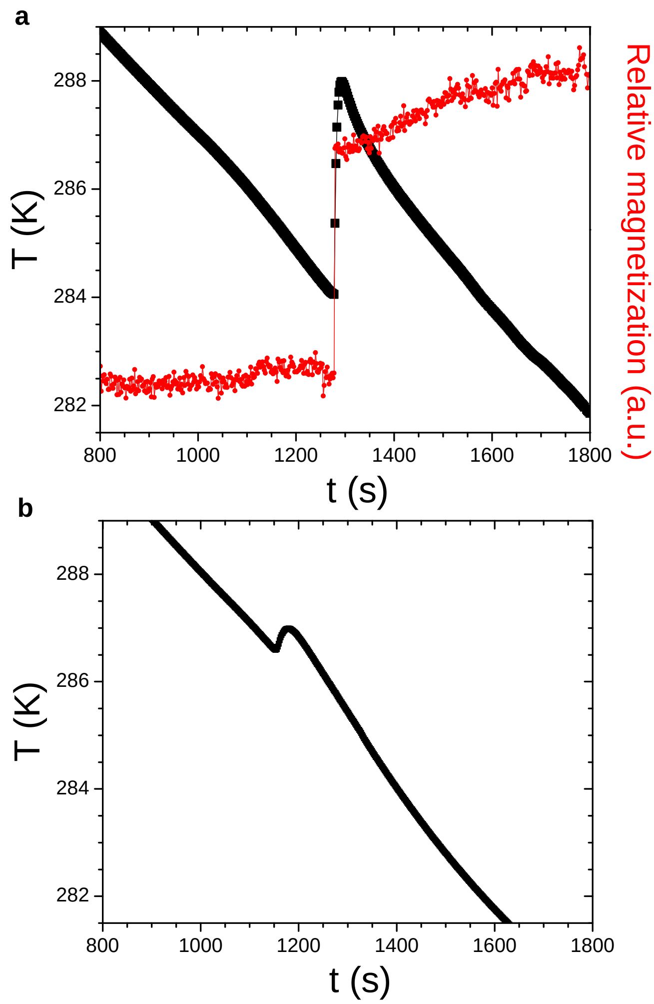

Fig. 4. Quasi-adiabatic (a) and quasi-isothermal (b) thermal measurements during the first cooling of as-prepared $Mn_{1.23}Fe_{0.72}P_{0.48}Si_{0.52}$.

through a burst-like increase in temperature. This recalescence phenomenon can occur during the solidification of metals. The temperature rise at the VE of $(Mn,Fe)_2(P,Si)$ presents great similitudes with such a recalescence event and clearly demonstrates that, below the usual Curie temperature, the as-prepared state should be seen as a supercooled state.

Remarkably, recalescence phenomena seldom happen around magnetic transitions. In high purity Dy and Er rare-earth metals, some unusual thermal effects were observed [25,26]. It was suggested that magnetoelastic strains play an important role in the superheating or supercooling at these FOMTs. More recently, multiple temperature increases upon cooling were observed across the FOMT of $Hf_{0.82}Ta_{0.18}Fe_2$ and interpreted as the result of a quenched disorder broadening of the FOMT [27]. However, the recalesence in $(Mn,Fe)_2(P,Si)$ presents significant differences with these -only two- former examples at magnetic transitions. First, the temperature increase (~ 4.0 K) is much more intense in $(Mn,Fe)_2(P,Si)$, more than one order of magnitude larger than in rare-earth metals (~ 0.15 K in Er) or in $Hf_{0.82}Ta_{0.18}Fe_2$ (~ 0.34 K). Second, the recalescence is only observed at the first cooling across the FOMT of as-prepared $(Mn,Fe)_2(P,Si)$. We thus believe that the mechanisms involved in the giant recalescence event of $(Mn,Fe)_2(P,Si)$ are notably different from these two former examples. They most probably encompass the release of magnetoelastic strains through micro-cracking [12] and a rearrangement of the spread in atomic positions [16]. The recalescence thus appears irreversible when thermal cycles are performed around the FOMT, as it requires healing the cracks by sintering or creating sufficient thermal diffusion to regenerate the spread in atomic positions. As a sufficient grain boundaries mobility usually requires to reach approximately 0.5 of the melting temperature (T_{melt} ~ 1423 K, incongruent melting), the VE and recalescence can be observed in cycled materials only after re-annealing at ~850 K or more.

In conclusion, an unusual temperature increase is detected at the FOMT of $(Mn,Fe)_2(P,Si)$ materials during the first cooling of as-prepared samples. Quantitative estimates of the temperature rise (up to +4.0 K) and heat involved (~50% of the latent heat) are gained by measurements using purposely-built probes. The amplitude of this effect is particularly large in comparison to the very few similar examples around magnetic transitions. This recalescence-like event clearly demonstrates that the lower transition temperature of the as-prepared sample than observed in subsequent thermal cycles, the virgin effect, should be seen as a supercooling phenomenon. The FOMT in the as-prepared sample proceeds upon cooling via single or multiple step temperature increases. The recalescence appears to be closely linked to the microstructure and its evolution upon cycling, as it is irreversible, and disappears when the sample is pulverized into particles close to the grain size. The most probable driving force for this recalescence is a burst-like overcoming of the stresses surrounding the nucleation sites of the ferromagnetic phase. More generally, this study shows that FOMTs in giant magnetocaloric materials are accompanied by spurious thermal effects, highlighting the need for deeper understanding of the thermodynamic stability of the different phases and the kinetics of the transformations.

Declarations of interest

None.

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