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- 1 Correlation between deformation and total entropy change at the first-order magnetic
- 2 transition of Fe₂P-based magnetocaloric materials
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- 9 Highlights:
- latent heat or transition entropy are key parameters in giant magnetocaloric materials
- a general scaling of Δ S_{tr} with Δ(c/a) is observed in Fe₂P-related materials family
- deformation has a crucial role even in volume preserving FOMTs
- 13 Abstract:
- While there is a growing consensus that lattice is an important source of entropy change at
- structural or elastic first-order magnetic transitions (FOMT) with finite volume change, the case
- of volume preserving transitions ($\Delta V = 0$) remains more controversial. Here, the evolution of the
- total transition entropy change within the Fe₂P family is presented as a function of the
- discontinuity on the ratio of the cell parameters. A striking correlation between ΔS_{tr} and $\Delta (c/a)$ is
- observed. This relationship is a first step towards a systematization of the FOMT properties in
- 20 the Fe₂P materials system. It also demonstrates that deformation can play a leading role in
- volume preserving FOMT.
 - **Keywords:**

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- 23 Latent heat; First-order Magnetic Transition; Magnetism; Magnetocaloric effect;
- 24 Thermomagnetic materials

Magnetic transitions often involve simultaneous changes in the electronic (S_{el}), lattice (S_{latt}), and magnetic (S_{mag}) properties. The expression $S = S_{latt} + S_{el} + S_{mag}$ is commonly employed to express how these degrees of freedoms and their entropy are expected to sum up. By extension, at first-order magnetic transition (FOMT) with transition temperature (T_{tr}), the transition entropy $\Delta S_{tr} = L/T_{tr}$ related to the latent heat (L) is expected to originate from one or several of these contributions. Unfortunately, estimating individually each term is challenging. On top of that, the above summation relies on a strong and disputable assumption that the degrees of freedom are independent, *i.e.* there is no cooperativity between them.

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Understanding the driving mechanisms for the latent heat of giant magnetocaloric materials is of outmost importance for applications, as the optimization primarily consists in triggering a large latent heat for an external magnetic field change as small as possible. Following the discovery of a giant magnetocaloric effect with magneto-structural FOMT in Gd₅Si₂Ge₂, a structural entropy change representing about half of the magnetocaloric effect was proposed as primary reason for overcoming the performances of elemental Gd [1,2]. This led to a general scaling that the larger the relative volume change $\Delta V/V$, the stronger the lattice contribution and therefore the higher the magnetocaloric effect [3]. This approach may however be confusing as it considers the isothermal entropy change induced by a magnetic field change (referred to as ΔS), whose relationship with the transition entropy discontinuity in zero field (referred to as ΔS_{tr}) is indirect. In addition, an accurate determination of ΔS can be challenging at FOMT due to the spike artefact. A $\Delta V/V$ scaling of the magnetocaloric effect appears also applicable to isotropic magneto-elastic FOMT such as in La(Fe,Si)₁₃. For this system, after some early controversies on whether the lattice entropy change counteracts the magnetic one [4], direct insights using inelastic resonant x-ray scattering techniques have led to a consensus that the lattice entropy change adds up to the magnetic contribution and may be responsible for nearly half the isothermal entropy change [5-8]. However, ΔV or $\Delta V/V$ is not a convenient parameter for characterizing magneto-elastic anisotropic FOMT as in hexagonal Fe₂P compounds where the contraction on the a axis is compensated by an expansion along the c axis leading to nearly negligible volume changes.

In view of the strong interest in Fe₂P compounds [9-28], insights into the mechanism of their FOMT are highly desirable. Fe₂P-based compounds can exhibit ferromagnetic transitions with

extreme behaviors. Depending on chemical compositions, it is possible to achieve: i) secondorder transitions (typically $Mn_{2-x}Fe_xP_{0.5}Si_{0.5}$ with x < 0.7) [9]; ii) FOMT with particularly small hysteresis and latent heat (case of the Fe₂P binary parent) [10,11]; iii) FOMT with small hysteresis but significant latent heat (best compositions for magnetocaloric or thermomagnetic applications, e.g. MnFe_{0.95}P_{0.585}Si_{0.34}B_{0.075}) [12]; and iv) up to giant hysteresis and giant latent heat as in MnFe_{0.95}P_{2/3}Si_{1/3} [13]. In all these materials the volume discontinuity is either limited $(\Delta V/V < 0.2 \%)$ or down to virtually zero. For the Fe₂P-based family, no consensus has ever emerged about the dominant(s) contribution(s) to ΔS_{tr} and even the most recent reports still led to puzzling results. First, there is a one order of magnitude difference on the integrated magnetic entropy between Fe₂P and MnFe_{0.95}P_{0.585}Si_{0.34}B_{0.075} [11,16]. This is hardly understandable in view of their comparable saturation magnetizations (M_{sat} approximately 2.9 and 4.0 μ_B/f.u., respectively). Second, in contrast to early theoretical studies pointing out that the latent heat has mostly a magnetic origin [17], recent phonon calculations and inelastic scattering experiments suggest that nearly all the transition entropy (ΔS_{tr}) has a structural origin [18,19]. Finally, former attempts at scaling the FOMT in Fe₂P-based materials (either via L, hysteresis or even ΔS) failed to encompass the broad variety of properties observed in this system. Dung et al. pointed out that isothermal entropy changes (ΔS) are correlated with $|\Delta a/a|$ and $|\Delta c/c|$ in a couple of (Mn,Fe)₂(P,Si) samples [25]. In MnFe(P,Si,B) compounds, Maschek et al. found that the thermal hysteresis varies like $\Delta(c/a)$, but no specific correlation could be established for ΔS [22]. In (Mn,Fe)₂(P,Si) compounds, You et al. reported a linear relation between hysteresis and c/a (after a given threshold), while they pointed an absence of correlation between L and (c/a) [29]. Miao et al. claimed the existence of a striking relationship between thermal hysteresis and elastic strain energy for a large panel of Fe₂P compounds [20]. It must be emphasized, however, that all these previous observations carry some ambiguities. First, even though ΔS is correlated with ΔS_{tr} , it also involves other parameters such as the sensitivity of the transition to the magnetic field $T_{tr}(B)$ or even extrinsic ones like the transition width. Second, thermal hysteresis can also not be regarded as an intrinsic quantity for a FOMT. Indeed hysteresis is known to be impacted by external features like the microstructure and is even not a necessity for FOMTs, as materials with nearly negligible hysteresis but sizable latent heat can be observed like in $(Mn,V,Fe)_2(P,Si,B)$ [23]. Actually, ΔS_{tr} (or $L=T_{tr}\Delta S_{tr}$) are more genuine intrinsic quantities, directly connected to the Erhenfest definition of first-order transitions.

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Seeking to bring back together the diversity in FOMTs observed in Fe₂P materials, **Figure 1** presents the transition entropy ΔS_{tr} as a function of the elastic deformation quantified as the discontinuity in the cell parameters ratio $\Delta(c/a)$. The MnFeP_{0.66-x}Si_{0.34}B_x series is particularly important as it covers a wide ΔS_{tr} range while keeping chemical substitutions limited [13]. Results for Fe₂P, MnFe(P,Si) and MnFe(P,Ge) were included depending upon availability of ΔS_{tr} and temperature dependent structural data. The criteria used to determine $\Delta(c/a)$ and ΔS_{tr} as well as the list of the eighteen considered samples are presented in Supplementary Materials.

A striking correlation is observed between the transition entropy ΔS_{tr} and the deformation $\Delta(c/a)$. We emphasize, however, that this correlation does not imply a predominant lattice component in the entropy change; it neither addresses the respective weights of the magnetic, lattice or electronic contributions within the net ΔS_{tr} value. First of all, one must keep in mind that the experimental determinations of ΔS_{tr} can only yield a global quantity incorporating all the degrees of freedom. Second, we stress that even when using additional experimental data, the aim at separating the various contributions in ΔS_{tr} is basically impossible owing to the intrication between degrees of freedom that characterizes FOMTs. Recently, it has been proposed that the elastic deformation energy could be expressed as $\Delta U_{\text{elastic}}/V_{\text{mol}} \approx (c_{11}+c_{12})\epsilon_1^2+2c_{13}\epsilon_1\epsilon_3+(c_{33}\epsilon_3^2)/2$ where ε_{ij} denotes the strains and c_{ij} the elastic constants [20]. Considering the theoretical elastic constants for MnFeSi_{0.33}P_{0.58}B_{0.08} [21] and the experimental strains for MnFe_{0.95}P_{0.595}Si_{0.33}B_{0.075} [13], the above equation leads to a $\Delta S_{\text{elastic}} = \Delta U_{\text{elastic}}/T_{\text{tr}}$ estimated in the range 8 – 18 J kg⁻¹ K⁻¹, which would be compatible with the experimental $\Delta S_{tr} = 16 \text{ J kg}^{-1} \text{ K}^{-1}$. Nevertheless, the above equation involves squared strains, whereas ΔS_{tr} appears to linearly scale with $\Delta(c/a)$. Even though large uncertainties make it difficult to distinguish the two possibilities, a ΔS_{tr} - $\Delta (c/a)$ scaling was found to be the most reliable.

The main result of Figure 1 is that the deformation appears as the source of the *total* transition entropy change ΔS_{tr} . But no complementary information about the various contributions to this overall result is accessible. Let us also specify that the correlation appears so far limited to Fe₂P materials. Considering iso-structural FOMTs in other hexagonal materials, (Sc,Ti)Fe₂ (Δ (c/a) ≈ 0.004 and ΔS_{tr} ≈ 7 J kg⁻¹ K⁻¹ [31]) would be close to fit in, but (Hf,Ta)Fe₂ (Δ (c/a) ≈ 0.014 and ΔS_{tr} ≈ 4 J kg⁻¹ K⁻¹ [32]) strongly departs from the trend. This might reflect that each materials family has its own underlying FOMT mechanism, leading to distinct ΔS_{tr} -deformation relations.

To conclude, the scaling shown in Fig. 1 is a first step towards a systematization of the FOMT properties in the Fe₂P materials family. From an applicative viewpoint, this correlation between ΔS_{tr} and $\Delta (c/a)$ also illustrates the challenges met when optimizing Fe₂P-related magnetocaloric materials. In order to reach large isothermal entropy changes, one needs sizable ΔS_{tr} , but the latter necessarily goes along with sizable deformations having negative consequences such as hysteresis or mechanical embrittlement. Besides tailoring the microstructure, fine tuning of ΔS_{tr} is therefore a crucial issue to target magnetocaloric materials compatible with applications.

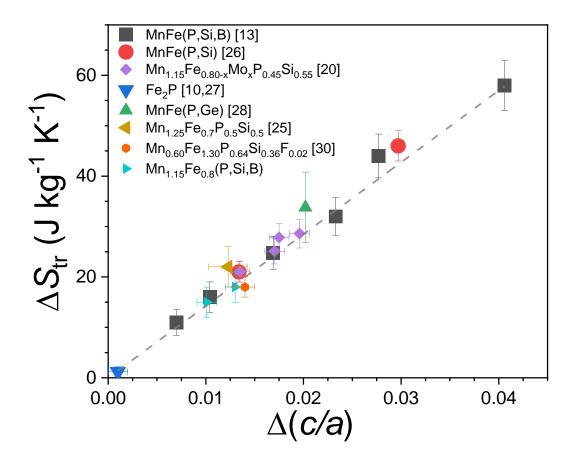


Figure 1: Transition entropy of the FOMT as a function of deformation $\Delta(c/a)$ of the lattice parameters for Fe₂P-based materials. The dashed line marks out the linear regression with intercept fixed at 0 ($R^2 = 98.7\%$).

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