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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 :**

- 10 - latent heat or transition entropy are key parameters in giant magnetocaloric materials
11 - a general scaling of ΔS_{tr} with $\Delta(c/a)$ is observed in Fe₂P-related materials family
12 - deformation has a crucial role even in volume preserving FOMTs

13 **Abstract:**

14 While there is a growing consensus that lattice is an important source of entropy change at
15 structural or elastic first-order magnetic transitions (FOMT) with finite volume change, the case
16 of volume preserving transitions ($\Delta V = 0$) remains more controversial. Here, the evolution of the
17 total transition entropy change within the Fe₂P family is presented as a function of the
18 discontinuity on the ratio of the cell parameters. A striking correlation between ΔS_{tr} and $\Delta(c/a)$ is
19 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
21 volume preserving FOMT.

22 **Keywords:**

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

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

33 Understanding the driving mechanisms for the latent heat of giant magnetocaloric materials is
34 of outmost importance for applications, as the optimization primarily consists in triggering a large
35 latent heat for an external magnetic field change as small as possible. Following the discovery
36 of a giant magnetocaloric effect with magneto-structural FOMT in $Gd_5Si_2Ge_2$, a structural entropy
37 change representing about half of the magnetocaloric effect was proposed as primary reason
38 for overcoming the performances of elemental Gd [1,2]. This led to a general scaling that the
39 larger the relative volume change $\Delta V/V$, the stronger the lattice contribution and therefore the
40 higher the magnetocaloric effect [3]. This approach may however be confusing as it considers
41 the isothermal entropy change induced by a magnetic field change (referred to as ΔS), whose
42 relationship with the transition entropy discontinuity in zero field (referred to as ΔS_{tr}) is indirect.
43 In addition, an accurate determination of ΔS can be challenging at FOMT due to the spike
44 artefact. A $\Delta V/V$ scaling of the magnetocaloric effect appears also applicable to isotropic
45 magneto-elastic FOMT such as in $La(Fe,Si)_{13}$. For this system, after some early controversies
46 on whether the lattice entropy change counteracts the magnetic one [4], direct insights using
47 inelastic resonant x-ray scattering techniques have led to a consensus that the lattice entropy
48 change adds up to the magnetic contribution and may be responsible for nearly half the
49 isothermal entropy change [5-8]. However, ΔV or $\Delta V/V$ is not a convenient parameter for
50 characterizing magneto-elastic anisotropic FOMT as in hexagonal Fe_2P compounds where the
51 contraction on the a axis is compensated by an expansion along the c axis leading to nearly
52 negligible volume changes.

53 In view of the strong interest in Fe_2P compounds [9-28], insights into the mechanism of their
54 FOMT are highly desirable. Fe_2P -based compounds can exhibit ferromagnetic transitions with

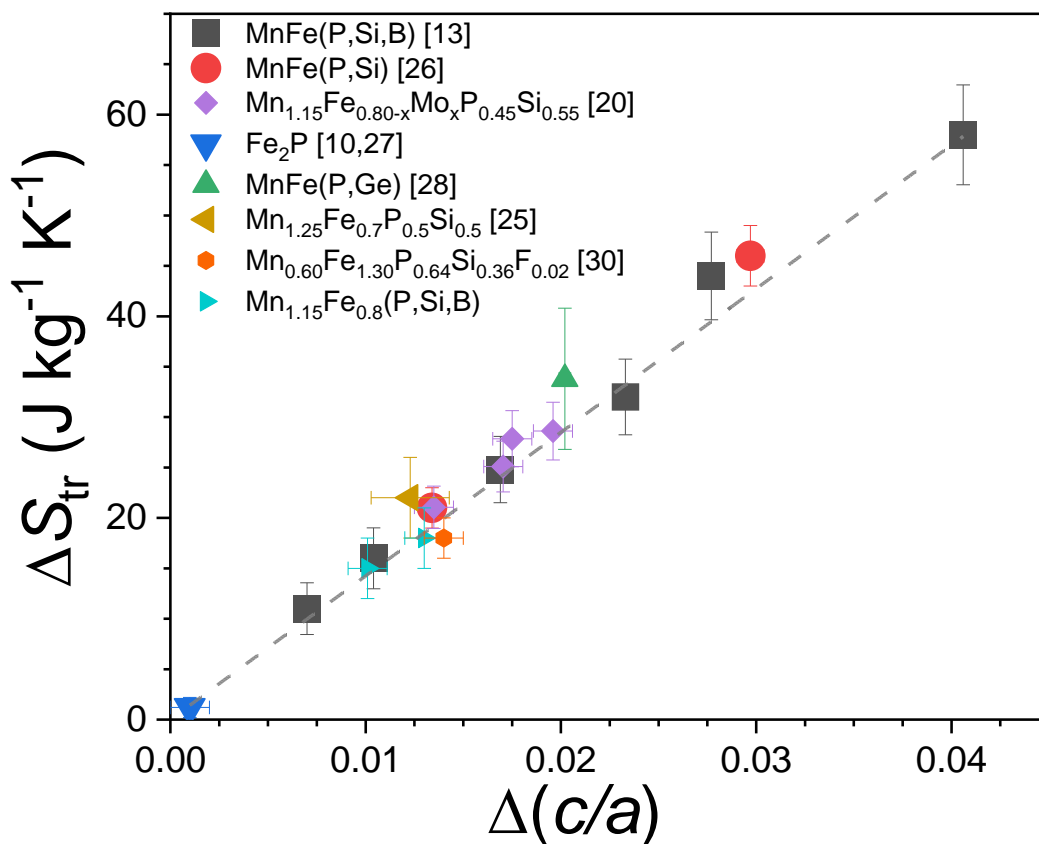
55 extreme behaviors. Depending on chemical compositions, it is possible to achieve: *i*) second-
56 order transitions (typically $\text{Mn}_{2-x}\text{Fe}_x\text{P}_{0.5}\text{Si}_{0.5}$ with $x < 0.7$) [9]; *ii*) FOMT with particularly small
57 hysteresis and latent heat (case of the Fe_2P binary parent) [10,11]; *iii*) FOMT with small
58 hysteresis but significant latent heat (best compositions for magnetocaloric or thermomagnetic
59 applications, e.g. $\text{MnFe}_{0.95}\text{P}_{0.585}\text{Si}_{0.34}\text{B}_{0.075}$) [12]; and *iv*) up to giant hysteresis and giant latent
60 heat as in $\text{MnFe}_{0.95}\text{P}_{2/3}\text{Si}_{1/3}$ [13]. In all these materials the volume discontinuity is either limited
61 ($\Delta V/V < 0.2\%$) or down to virtually zero. For the Fe_2P -based family, no consensus has ever
62 emerged about the dominant(s) contribution(s) to ΔS_{tr} and even the most recent reports still led
63 to puzzling results. First, there is a one order of magnitude difference on the integrated magnetic
64 entropy between Fe_2P and $\text{MnFe}_{0.95}\text{P}_{0.585}\text{Si}_{0.34}\text{B}_{0.075}$ [11,16]. This is hardly understandable in
65 view of their comparable saturation magnetizations (M_{sat} approximately 2.9 and 4.0 $\mu_B/\text{f.u.}$,
66 respectively). Second, in contrast to early theoretical studies pointing out that the latent heat has
67 mostly a magnetic origin [17], recent phonon calculations and inelastic scattering experiments
68 suggest that nearly all the transition entropy (ΔS_{tr}) has a structural origin [18,19]. Finally, former
69 attempts at scaling the FOMT in Fe_2P -based materials (either via L , hysteresis or even ΔS) failed
70 to encompass the broad variety of properties observed in this system. Dung *et al.* pointed out
71 that isothermal entropy changes (ΔS) are correlated with $|\Delta a/a|$ and $|\Delta c/c|$ in a couple of
72 $(\text{Mn,Fe})_2(\text{P,Si})$ samples [25]. In $\text{MnFe}(\text{P,Si,B})$ compounds, Maschek *et al.* found that the thermal
73 hysteresis varies like $\Delta(c/a)$, but no specific correlation could be established for ΔS [22]. In
74 $(\text{Mn,Fe})_2(\text{P,Si})$ compounds, You *et al.* reported a linear relation between hysteresis and c/a (after
75 a given threshold), while they pointed an absence of correlation between L and (c/a) [29]. Miao
76 *et al.* claimed the existence of a striking relationship between thermal hysteresis and elastic
77 strain energy for a large panel of Fe_2P compounds [20]. It must be emphasized, however, that
78 all these previous observations carry some ambiguities. First, even though ΔS is correlated with
79 ΔS_{tr} , it also involves other parameters such as the sensitivity of the transition to the magnetic
80 field $T_{tr}(B)$ or even extrinsic ones like the transition width. Second, thermal hysteresis can also
81 not be regarded as an intrinsic quantity for a FOMT. Indeed hysteresis is known to be impacted
82 by external features like the microstructure and is even not a necessity for FOMTs, as materials
83 with nearly negligible hysteresis but sizable latent heat can be observed like in
84 $(\text{Mn,V,Fe})_2(\text{P,Si,B})$ [23]. Actually, ΔS_{tr} (or $L = T_{tr}\Delta S_{tr}$) are more genuine intrinsic quantities, directly
85 connected to the Ehrenfest definition of first-order transitions.

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

93 A striking correlation is observed between the transition entropy ΔS_{tr} and the deformation $\Delta(c/a)$.
94 We emphasize, however, that this correlation does not imply a predominant lattice component
95 in the entropy change; it neither addresses the respective weights of the magnetic, lattice or
96 electronic contributions within the net ΔS_{tr} value. First of all, one must keep in mind that the
97 experimental determinations of ΔS_{tr} can only yield a global quantity incorporating all the degrees
98 of freedom. Second, we stress that even when using additional experimental data, the aim at
99 separating the various contributions in ΔS_{tr} is basically impossible owing to the intrication
100 between degrees of freedom that characterizes FOMTs. Recently, it has been proposed that the
101 elastic deformation energy could be expressed as $\Delta U_{elastic}/V_{mol} \approx (c_{11}+c_{12})\epsilon_1^2+2c_{13}\epsilon_1\epsilon_3+(c_{33}\epsilon_3^2)/2$
102 where ϵ_{ij} denotes the strains and c_{ij} the elastic constants [20]. Considering the theoretical elastic
103 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}
104 [13], the above equation leads to a $\Delta S_{elastic} = \Delta U_{elastic}/T_{tr}$ estimated in the range 8 – 18 J kg⁻¹ K⁻¹,
105 which would be compatible with the experimental $\Delta S_{tr} = 16$ J kg⁻¹ K⁻¹. Nevertheless, the above
106 equation involves squared strains, whereas ΔS_{tr} appears to linearly scale with $\Delta(c/a)$. Even
107 though large uncertainties make it difficult to distinguish the two possibilities, a ΔS_{tr} - $\Delta(c/a)$
108 scaling was found to be the most reliable.

109 The main result of Figure 1 is that the deformation appears as the source of the *total* transition
110 entropy change ΔS_{tr} . But no complementary information about the various contributions to this
111 overall result is accessible. Let us also specify that the correlation appears so far limited to Fe₂P
112 materials. Considering iso-structural FOMTs in other hexagonal materials, (Sc,Ti)Fe₂ ($\Delta(c/a) \approx$
113 0.004 and $\Delta S_{tr} \approx 7$ J kg⁻¹ K⁻¹ [31]) would be close to fit in, but (Hf,Ta)Fe₂ ($\Delta(c/a) \approx 0.014$ and ΔS_{tr}
114 ≈ 4 J kg⁻¹ K⁻¹ [32]) strongly departs from the trend. This might reflect that each materials family
115 has its own underlying FOMT mechanism, leading to distinct ΔS_{tr} -deformation relations.

116 To conclude, the scaling shown in Fig. 1 is a first step towards a systematization of the FOMT
 117 properties in the Fe_2P materials family. From an applicative viewpoint, this correlation between
 118 ΔS_{tr} and $\Delta(c/a)$ also illustrates the challenges met when optimizing Fe_2P -related magnetocaloric
 119 materials. In order to reach large isothermal entropy changes, one needs sizable ΔS_{tr} , but the
 120 latter necessarily goes along with sizable deformations having negative consequences such as
 121 hysteresis or mechanical embrittlement. Besides tailoring the microstructure, fine tuning of ΔS_{tr}
 122 is therefore a crucial issue to target magnetocaloric materials compatible with applications.



123

124 **Figure 1:** Transition entropy of the FOMT as a function of deformation $\Delta(c/a)$ of the lattice
 125 parameters for Fe_2P -based materials. The dashed line marks out the linear regression with
 126 intercept fixed at 0 ($R^2 = 98.7\%$).

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