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Landau model evaluation of the magnetic entropy change in magnetocaloric materials

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ABSTRACT

The field exponent for the magnetic entropy change $n = dln(|\Delta S|)/dln(H)$ in a magnetic field was evaluated using the Landau model to provide a classification for the nature of the ferromagnetic-to-paramagnetic transitions at the Curie temperature T_C in magnetocaloric materials. The magnetic phase transition can be classified as a first-order magnetic transition (FOMT), a second-order magnetic transition (SOMT) or a critical point (CP) at the border between the first and second order transitions. The value of n is mapped as a function of the reduced temperature and the reduced magnetic field for the FOMT, SOMT and CP. The influence of the magnetic field on the transition temperature was found to be relatively weak for the SOMT and corresponds to a power law for the CP and FOMT.

1. Introduction

Magnetocaloric materials provide promising candidate materials for efficient magnetic cooling, magnetic heat pumping and magnetic energy conversion near room temperature [1–3]. Materials that show a magnetic phase transition with latent heat generally show a giant magnetocaloric effect in the vicinity of the magnetic transition temperature. When a magnetic field is applied (or removed) the magnetocaloric effect (MCE) manifests itself in the form of a temperature change under adiabatic conditions or a magnetic entropy change at constant temperature. The optimal materials properties combine a maximum adiabatic temperature change ΔT_{ad} and a maximum magnetic entropy change $|\Delta S_m|$ with a low hysteresis as a function of temperature and magnetic field. As a large MCE, which is strongest for a discontinuous first-order magnetic transition (FOMT) with latent heat, is often in conflict with a low hysteresis, which is mainly observed for a continuous second-order magnetic transitions (SOMT) without latent heat, a good compromise is often found near the cross-over point where the latent heat vanishes. The most common experimental methods to evaluate the proximity to this cross-over are calorimetric measurements of the latent heat, Arrott plots from magnetisation measurements as a function of field and temperature and X-ray diffraction measurements as a function of temperature to evaluate whether the lattice parameters evolve continuous or discontinuous across the magnetic transition [4,5].

Recently, the field exponent for the magnetic entropy change n was proposed [4,6,7] as an alternative method to reliably distinguish first-order and second-order magnetic transitions in magnetocaloric materials. The field exponent is defined as:

$$n = \frac{dln(|\Delta S|)}{dln(H)} \tag{1}$$

where the entropy change $\Delta S = S(H) - S(0)$ is induced by the applied magnetic field $\mu_0 H$. The predicted behaviour for both transitions was evaluated from experimental data and calculations with the Bean and Rodbell model [8–10]. Recently, Moreno and co-workers [11] have reported that a combination of the Bean-Rodbell model with the Kolmogorov-Johnson-Mehl-Avrami nucleation and growth theory can be used to accurately describe the field-induced transition in magnetocaloric alloys with a FOMT.

Here we will apply the Landau model to expand these predictions and provide a detailed model analysis of the influence of the magnetic field on the entropy change and the transition temperature for the first-order and second-order magnetic transitions, as well as the critical point (CP) at the transition between the FOMT and the SOMT. For the FOMT we explicitly distinguish the cases for the reversible transition without hysteresis and the irreversible transition with hysteresis, relevant for

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cases with a high and a low nucleation rate of the forming phase in the transition.

The Landau model that assumes that the transition from an unordered to an ordered phase can be described by an expansion of an order parameter [12,13]. In the case of a paramagnetic-to-ferromagnetic transition in magnetocaloric materials the (mean-field) order parameter is the average spin alignment characterised by the magnetisation. For magnetocaloric materials the Landau model has been widely applied to characterise the experimental data for a wide range of systems [14–20] and the related Arrott plots [21] are often used to define the nature of the magnetic transition [22]. In order to generalise the mean-field description of the Landau model, several studies have investigated the critical scaling behaviour to describe the magnetic phase transition in magnetocaloric materials [23–27]. In a magnetic material the magnetic order generally experiences an interaction with the elastic properties of the material via the magneto-elastic coupling. This magneto-elastic coupling will result in a renormalisation of the Landau parameters [28]. Here it is assumed that the Landau parameters correspond to effective values, where this renormalisation has been included.

2. Landau model

To evaluate the magnetic phase transition in magnetocaloric materials we start from the Landau model [12,13,17] to describe the change in Gibbs free energy (per unit of volume) ΔG from the unordered paramagnetic state to the magnetically ordered state by a Taylor expansion in terms of the order parameter in the form of the magnetisation M:

$$\Delta G = \frac{\alpha}{2}M^2 + \frac{\beta}{4}M^4 + \frac{\gamma}{6}M^6 - \mu_0 HM \tag{2}$$

where $\mu_0 H$is the applied magnetic field. In the vicinity of the magnetic transition with a characteristic temperature T_0 one can assume $\alpha = \alpha_0(T - T_0)$, where $\alpha_0 > 0$, β and $\gamma \geqslant 0$ are constants. Depending on the value of β one now finds three different types for the ferromagnetic transition: (i) a first-order phase transition (FOMT) for $\beta < 0$, (ii) a second-order phase transition (SOMT) for $\beta > 0$ and (iii) a critical point (CP) for $\beta = 0$. For a SOMT the Taylor expansion can be limited to the first two terms ($\gamma = 0$).

A minimisation of ΔG to the order parameter M results in the equation of state:

$$\alpha M + \beta M^3 + \gamma M^5 = \mu_0 H \tag{3}$$

Combining Eqs. (1) and (2) one finds that the magnetic entropy corresponds to:

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_H = -\frac{1}{2}\alpha_0 M^2 \tag{4}$$

Note that the corresponding specific heat change is $\Delta C = T\left(\frac{\partial \Delta S}{\partial T}\right)_H = -T\left(\frac{\partial^2 \Delta G}{\partial T^2}\right)_H$. In the absence of an applied magnetic field ($H = 0$) the magnetic phase transition takes place at $T_C = T_0$ for the SOMT and the CP ($\beta \geqslant 0$), while for the FOMT ($\beta < 0$) a lowest energy state with $\Delta G \leqslant 0$ and a finite order parameter M is obtained for $T_C > T_0$.

For the FOMT it depends on the kinetics of the phase transition whether the transition is defined by (*i*) the global minimum in ΔG, resulting in a *reversible* transition, or by (*ii*) one of the local minima (depending to the history), resulting in an *irreversible* transition with a finite thermal and field hysteresis. The occurrence of a (quasi-)reversible or irreversible transition is largely defined by the details of the nucleation process. For a reversible FOMT with a sufficiently effective nucleation process the transition takes place at $T_C^* = T_0 + \frac{3\beta^2}{16\alpha_0\gamma}$. Without nucleation the transition takes place when the local minimum becomes unstable at a transition temperature for heating T_C^+ and for cooling T_C^- where $T_C^- < T_C^* < T_C^+$. For an increasing magnetic field the thermal hysteresis $\Delta T_C(H) = T_C^+(H) - T_C^-(H)$ reduces until it disappears when $T_C^+(H) = T_C^-(H)$ at a critical field H_{cr} [17]. Above this critical field no thermal hysteresis is observed.

3. Landau model in in dimensionless parameters

The change in Gibbs free energy of Eq. (2) can be rewritten in terms of the following unitless parameters:

$t = \frac{T - T_0}{T_0}$; $m = \frac{M}{M_0}$; $g = \frac{\Delta G}{\Delta G_0}$; $s = \frac{\Delta S}{\alpha_0 M_0}$; $h = \frac{\mu_0 H}{\mu_0 H_0} = \frac{M_0}{\Delta G_0}\mu_0 H$; $\delta = \beta\frac{M_0^4}{\Delta G_0}$; $\chi = \gamma\frac{M_0^6}{\Delta G_0}$ where t is the reduced temperature, m the reduced magnetisation, g the reduced change in Gibbs free energy, h the reduced applied magnetic field and δ and χ the criticality parameters. The normalisation parameters $\Delta G_0 = \alpha_0 T_0 M_0^2$ and $\mu_0 H_0 = \alpha_0 T_0 M_0$ are directly related to M_0. The reduced entropy change corresponds to $s = -(\partial g/\partial t)_h = -\frac{1}{2}m^2$ and the reduced specific heat to $c = (1+t)(\partial s/\partial t)_h = -(1+t)\left(\partial^2 g/\partial t^2\right)_h$. In dimensionless parameters the change in Gibbs free energy now corresponds to:

$$g = \frac{1}{2}tm^2 + \frac{1}{4}\delta m^4 + \frac{1}{6}\chi m^6 - hm \tag{5}$$

with an equation of state ($dg/dm = 0$) that corresponds to: $m(t + \delta m^2 + \chi m^4) = h$. The field exponent of the reduced entropy change corresponds to $n = dln(|\Delta s|)/dln(h)$, where the reduced entropy change is given by $\Delta s = s(h) - s(0)$.

3.1. Second-order magnetic transition

For a SOMT ($\beta > 0$) the used normalisation constants are $M_0 = \left(\frac{\alpha_0 T_0}{\beta}\right)^{1/2}$ and $\Delta G_0 = \frac{\alpha_0^2 T_0^2}{\beta}$ with$\mu_0 H_0 = \left(\frac{\alpha_0^3 T_0^3}{\beta}\right)^{1/2}$. This gives $\delta = 1$ and with $\chi = 0$ ($\gamma = 0$) this results in:

$$g = \frac{1}{2}tm^2 + \frac{1}{4}m^4 - hm \tag{6}$$

with an equation of state ($dg/dm = 0$) that corresponds to: $m(t + m^2) = h$. In zero applied magnetic field ($h = 0$) only one real solution $m = 0$ is found for $t > 0$, while two real solutions $m \neq 0$ are found for $t < 0$. In an applied magnetic field ($h \neq 0$) one finds: (*i*) one real solution for $t \geqslant 0$, (*ii*) two real solutions for $t < 0$ and $|h| < h_{cr}(t) = 2\left(\frac{-t}{3}\right)^{3/2}$ and (*iii*) one real solution for $t < 0$ and $|h| > h_{cr}(t) = 2\left(\frac{-t}{3}\right)^{3/2}$. This critical field $h_{cr}(t)$ can also be translated in a critical temperature: $t_{cr}(h) = -3\left(\frac{|h|}{2}\right)^{2/3} < 0$.

In Fig. 1 the reduced magnetisation m, the reduced entropy change s and the reduced specific heat c are shown for a SOMT ($\beta > 0$) as a function of the reduced temperature t for increasing values of the reduced applied magnetic field h. In zero field ($h = 0$)one finds $m = \pm\sqrt{(-t)}$, $g = -\frac{1}{4}t^2$, $s = \frac{1}{2}t$, $c = \frac{1}{2}(1+t)$ for $t < 0$ and $m = g = s = c = 0$ for $t > 0$. The reduced specific heat reaches a maximum of $c = \frac{1}{2}$ at $t = 0$.

3.2. Critical point for the magnetic transition

For a CP ($\beta = 0$) the used normalisation constants are $M_0 = \left(\frac{\alpha_0 T_0}{\gamma}\right)^{1/4}$ and $\Delta G_0 = \left(\frac{\alpha_0^3 T_0^3}{\gamma}\right)^{1/2}$ with$\mu_0 H_0 = \left(\frac{\alpha_0^5 T_0^5}{\gamma}\right)^{1/4}$. This gives $\chi = 1$ and with $\delta = 0$ this results in:

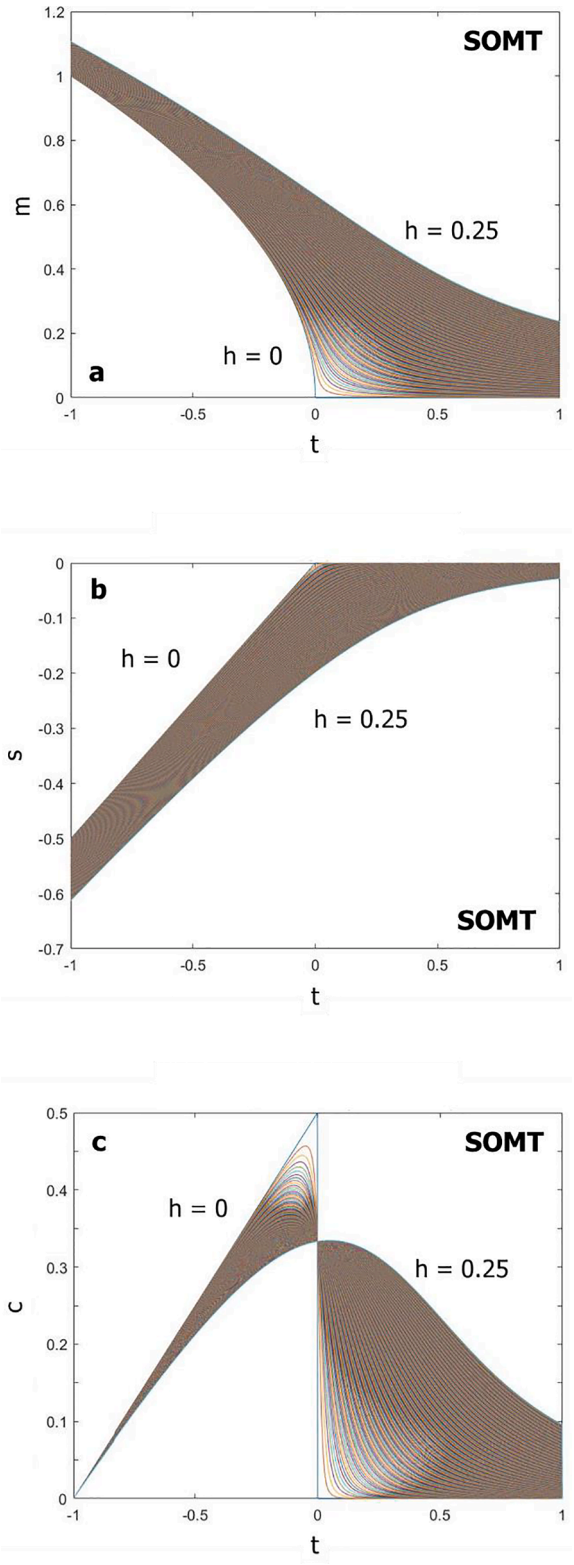


Fig. 1. (a) Reduced magnetisation m, (b) reduced entropy s and (c) reduced specific heat c for a SOMT ($\beta > 0$) as a function of the reduced temperature t in reduced magnetic fields ranging from $h = 0$ to 0.25 in steps of 0.001.

$$g = \frac{1}{2}tm^2 + \frac{1}{6}m^6 - hm \tag{7}$$

with an equation of state ($dg/dm = 0$) that corresponds to: $m(t + m^4) = h$. In zero applied magnetic field ($h = 0$) only one real solution $m = 0$ is found for $t > 0$, while two real (unique) solutions $m \neq 0$ are found for $t < 0$. In an applied magnetic field ($h \neq 0$) one finds: (*i*) one real solution for $t > 0$, (*ii*) two real solutions for $t < 0$ and $|h| < h_{cr}(t) = 4\left(\frac{-t}{5}\right)^{5/4}$ and (*iii*) one real solution for $t < 0$ and $|h| > h_{cr}(t) = 4\left(\frac{-t}{5}\right)^{5/4}$. This critical field $h_{cr}(t)$ can also be translated in a critical temperature: $t_{cr}(h) = -5\left(\frac{|h|}{4}\right)^{4/5} < 0$.

In Fig. 2 the reduced magnetisation m, the reduced entropy change s and the reduced specific heat c are shown for the CP ($\beta = 0$) as a function of the reduced temperature t for increasing values of the reduced applied magnetic field h. In zero field ($h = 0$) one finds $m = \pm\sqrt[4]{(-t)}$, $g = -\frac{1}{3}(-t)^{3/2}$, $s = -\frac{1}{2}(-t)^{1/2}$, $c = \frac{1}{4}(1 + t)(-t)^{-1/2}$ for $t < 0$ and $m = g = s = c = 0$ for $t > 0$. The reduced specific heat diverges ($c \to \infty$) at $t = 0$.

3.3. First-order magnetic transition

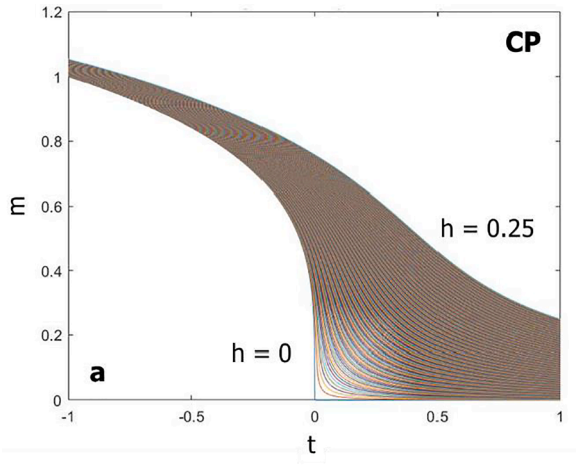
For a FOMT ($\beta < 0$) the used normalisation constants are $M_0 = \left(\frac{\alpha_0 T_0}{\gamma}\right)^{1/4}$ and $\Delta G_0 = \left(\frac{\alpha_0^3 T_0^3}{\gamma}\right)^{1/2}$ with $\mu_0 H_0 = \left(\frac{\alpha_0^5 T_0^5}{\gamma}\right)^{1/4}$. This gives $\chi = 1$ and with $\delta < 0$ as free parameter this results in:

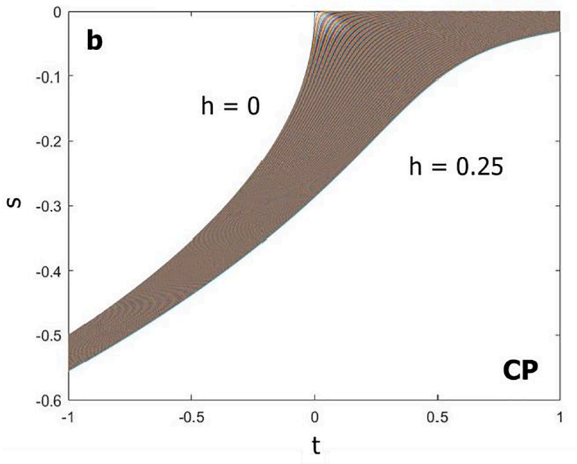
$$g = \frac{1}{2}tm^2 + \frac{1}{4}\delta m^4 + \frac{1}{6}m^6 - hm \tag{8}$$

with an equation of state ($dg/dm = 0$) that corresponds to: $m(t + \delta m^2 + m^4) = h$. In zero applied magnetic field ($h = 0$) only one real solution $m = 0$ is found for $t > \delta^2/4$, while two real solutions with $m^2 = -\delta/2 + \sqrt{(\delta/2)^2 - t}$ are found for $t < \delta^2/4$. In an applied magnetic field ($h \neq 0$) one finds either (*i*) one real solution for high temperature and/or high fields and (*ii*) two real solutions for low temperatures and low fields. For all fields only one solution is obtained for $t > 9\delta^2/20$. In the following first the reversible FOMT and then the irreversible FOMT will be discussed.

3.3.1. Reversible first-order magnetic transition

In Fig. 3 the reduced magnetisation m, the reduced entropy change s and the reduced specific heat c are shown for the reversible FOMT ($\beta < 0$) as a function of the reduced temperature t for increasing values of the reduced applied magnetic field h. In the reversible FOMT the system is defined by the global minimum in g. In zero field ($h = 0$) the reversible FOMT (where $g \leqslant 0$ for $m \neq 0$) takes place at: $t_c^*(h = 0) = \frac{3}{16}\delta^2$. The corresponding steps in magnetisation and entropy are from $m = 0$ to $m_c^* = \sqrt{-\frac{3\delta}{4}}$ and from $s = 0$ to $s_c^* = \frac{3}{8}\delta$, respectively. The reduced specific heat diverges ($c \to \infty$) at $t = t_c^*$. The jump in the entropy can be related to the low-temperature value by $\frac{\Delta s}{s_0} = \left(\frac{\Delta m}{m_0}\right)^2 = \left(\frac{m_c^*}{m(t=-1)}\right)^2 = \frac{3}{2}\left(\frac{-\delta}{-\delta+\sqrt{\delta^2+4}}\right)$, where for $|\delta| \ll 2$ the ratio is $\frac{\Delta s}{s_0} \approx -\frac{3}{4}\delta$ and for $|\delta| \gg 2$ the ratio is $\frac{\Delta s}{s_0} \approx \frac{3}{4}$. In an applied magnetic field the transition temperature shifts to higher temperatures $t_c^*(h \neq 0) > t_c^*(h = 0)$ and the steps in the reduced magnetisation and the reduced entropy decrease with h until they disappear at a critical field h_{cr}.





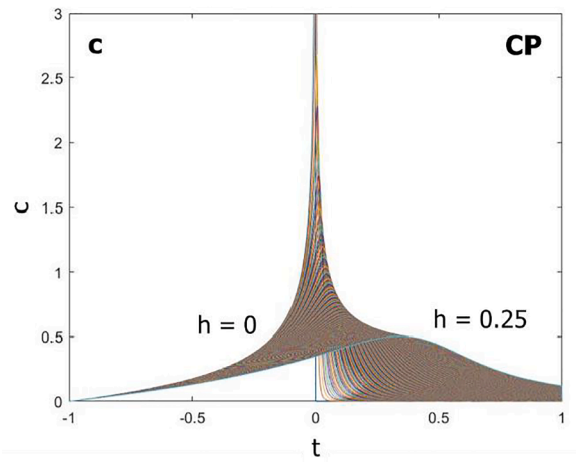
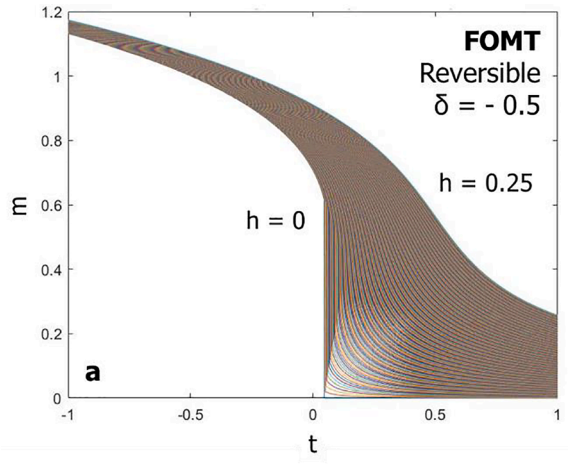
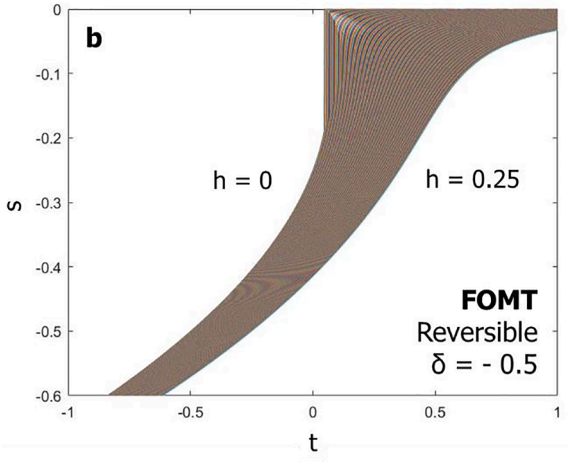


Fig. 2. (a) Reduced magnetisation m, (b) reduced entropy s and (c) reduced specific heat c for a CP ($\beta = 0$) as a function of the reduced temperature t in reduced magnetic fields ranging from $h = 0$ to 0.25 in steps of 0.001.





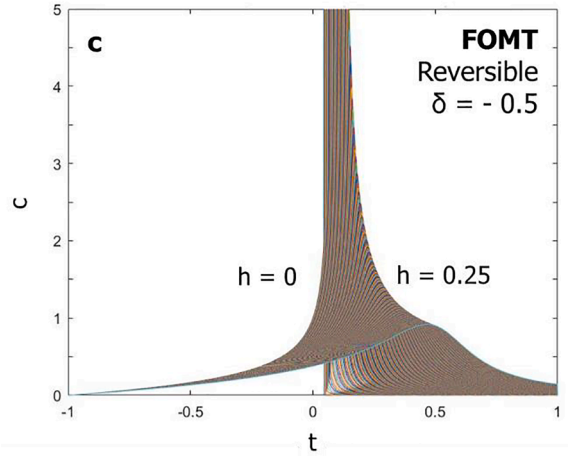


Fig. 3. (a) Reduced magnetisation m, (b) reduced entropy s and (c) reduced specific heat c for the reversible FOMT ($\beta < 0$) with $\delta = -1/2$ as a function of the reduced temperature t in reduced magnetic fields ranging from $h = 0$ to 0.25 in steps of 0.001.

3.3.2. *Irreversible first-order magnetic transition*

In Fig. 4 the reduced magnetisation m, the reduced entropy change s and the reduced specific heat c are shown for the irreversible FOMT ($\beta < 0$) for heating and cooling as a function of the reduced temperature t for increasing values of reduced applied magnetic field h. In the irreversible FOMT the system is defined by one of the local minima in g. The selected minimum depends on the temperature and field history, which generally results in thermal and field hysteresis in the vicinity of the magnetic transition. In zero field ($h = 0$) the irreversible FOMT takes place at

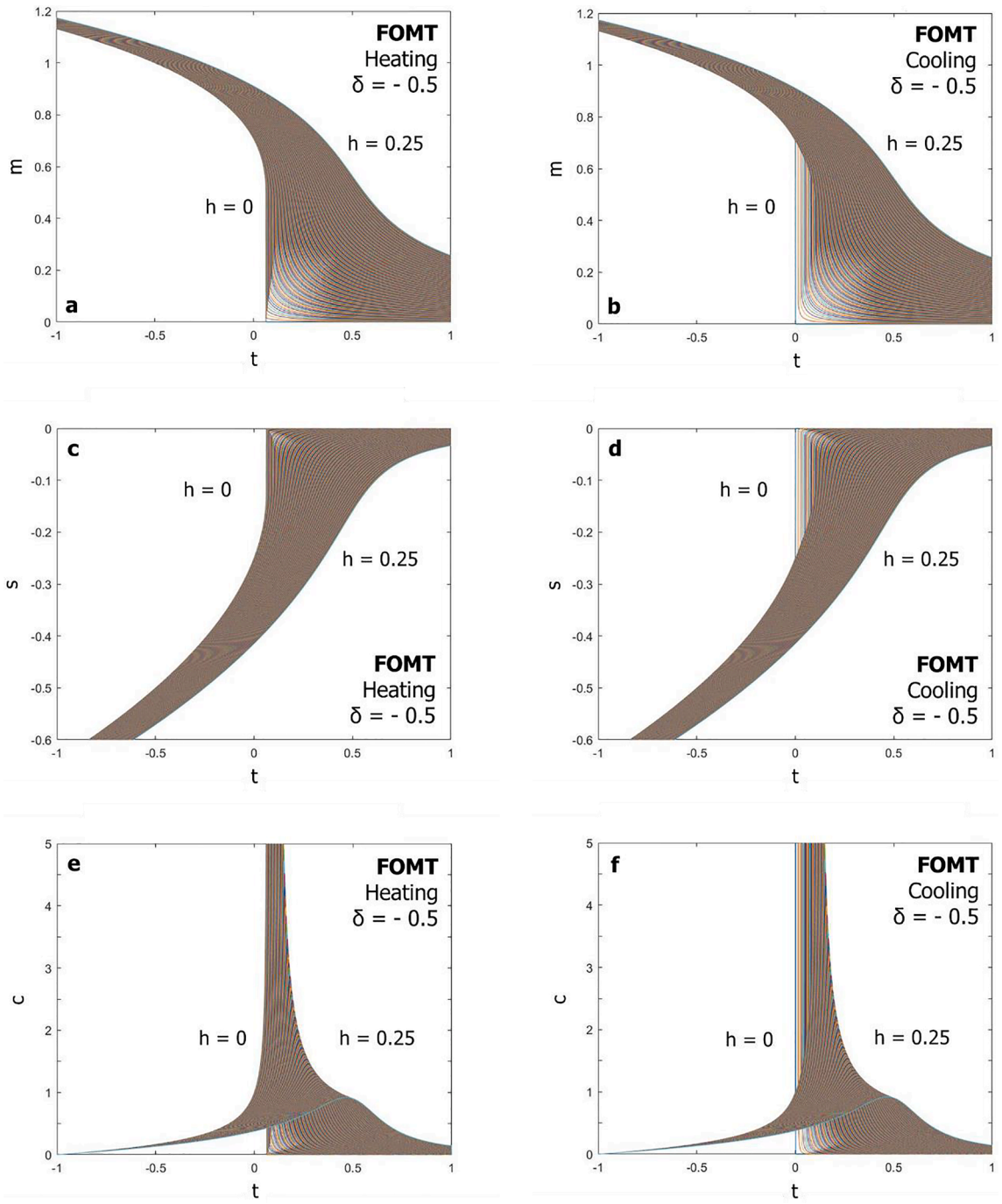


Fig. 4. (a,b) Reduced magnetisation m, (c,d) reduced entropy s and (e,f) reduced specific heat c in the irreversible FOMT ($\beta < 0$) as a function of the reduced temperature t for heating and cooling in reduced magnetic fields ranging from $h = 0$ to 0.25 in steps of 0.001.

$t_c^+(h=0) = \frac{\delta^2}{4}$ for heating and at $t_c^-(h=0) = 0$ for cooling. At these transition temperatures for heating and cooling steps in magnetisation and entropy are found. The reduced specific heat diverges ($c \to \infty$) at $t = t_c^{\pm}$. In an applied magnetic field the transition temperature shifts to higher temperatures $t_c^{\pm}(h \neq 0) > t_c^{\pm}(h=0)$ and the steps in the reduced magnetisation and the reduced entropy decrease with h until they disappear at a critical field h_{rev}.

4. Field exponent for the entropy change

The field exponent of the reduced entropy change corresponds to $n = dln(|\Delta s|)/dln(h)$, where the reduced entropy change is given by $\Delta s = s(h) - s(0)$. As proposed [4], this field exponent can be used to classify the nature of the magnetic order. Here we will analyse the field exponent for the entropy change in the Landau model as a function of temperature and magnetic field for the SOMT, CP and the FOMT. Before we present the detailed model predictions it is illustrative to review three special cases for the SOMT, CP and FOMT: (i) $t \gg 0$, (ii) $t \ll 0$ and (iii) $t = 0$.

In the high-temperature limit ($t \gg 0$) the reduced Gibbs free energy can be approximated by $g \approx \frac{1}{2} tm^2 - hm$ with an equation of state that can be expressed as $tm \approx h$. The reduced susceptibility $\frac{m}{h} \approx \frac{1}{t}$ is consistent with the Curie-Weiss law for the paramagnetic state $\chi = \frac{M}{H} = \frac{C}{T - \theta_{CW}}$ [29], where $T_0 \approx \theta_{CW}$ and $C \approx \frac{\mu_0}{\alpha_0}$. As in the high temperature limit $m \propto h$, the

reduced entropy change scales as $s \propto h^2$, which results in $n \approx 2$ for the SOMT, CP and FOMT.

In the low temperature limit ($t \ll 0$) the order parameter is well developed with $|m| = m_0 \gg 0$ and the system is positioned in the global minimum, which can be described by a parabolic approximation: $g \approx g_0 + \frac{1}{2}a_2(m - m_0)^2 - hm$. Parameter $a_2 = \left(\partial^2 g/\partial m^2\right)(m = m_0)$ corresponds to $a_2 = 2$ for the SOMT, $a_2 = 4$ for the CP and $a_2 = \delta^2 + 4 + \frac{1}{4}\delta\sqrt{\delta^2 + 4}$ for the FOMT at $t = -1$. Minimisation gives $m \approx m_0 + \frac{h}{a_2}$ for the order parameter, resulting in $\Delta s = s(h) - s(0) \approx -\frac{1}{2}\left(m_0 + \frac{h}{a_2}\right)^2 + \frac{1}{2}m_0^2 \approx -\frac{m_0 h}{a_2} \propto h$ for the reduced entropy change and $n \approx 1$ for the field exponent of the reduced entropy change for the SOMT, CP and FOMT.

At the critical temperature $t = 0$ ($T = T_0$) the first term in the reduced Gibbs free energy vanishes. This significantly reduces the equation of state with: (1) $m^3 = h$ for the SOMT, (2) $m^5 = h$ for the CP and (3) $m^3\left(\delta + m^2\right) = h$ for the FOMT. For the SOMT $m = h^{1/3}$ gives a reduced entropy change that scales as $\Delta s \propto h^{2/3}$, which results in $n = 2/3$. For the CP $m = h^{1/5}$ gives a reduced entropy change that scales as $\Delta s \propto h^{2/5}$, leading to $n = 2/5$. For the FOMT the critical temperature t_c is finite and positive with a step in the reduced magnetisation Δm at the transition. This effectively means that $t = 0$ corresponds to the low temperature limit for the FOMT with $n \approx 1$.

In Fig. 5 the field exponent of the entropy change n is presented for the SOMT (a) as a function of t for different values of h and (b) as a colour map as a function of t and h. The high-temperature limit $n(t \gg 0) \approx 2$ and the low-temperature limit $n(t \ll 0) \approx 1$ are clearly illustrated. At $t = 0$ the minimum value for the exponent $n(t = 0) = 2/3$ is obtained (independent of h), which forms a characteristic feature for the SOMT. The field exponent is restricted by the high-temperature value as an upper limit: $n \leqslant 2$.

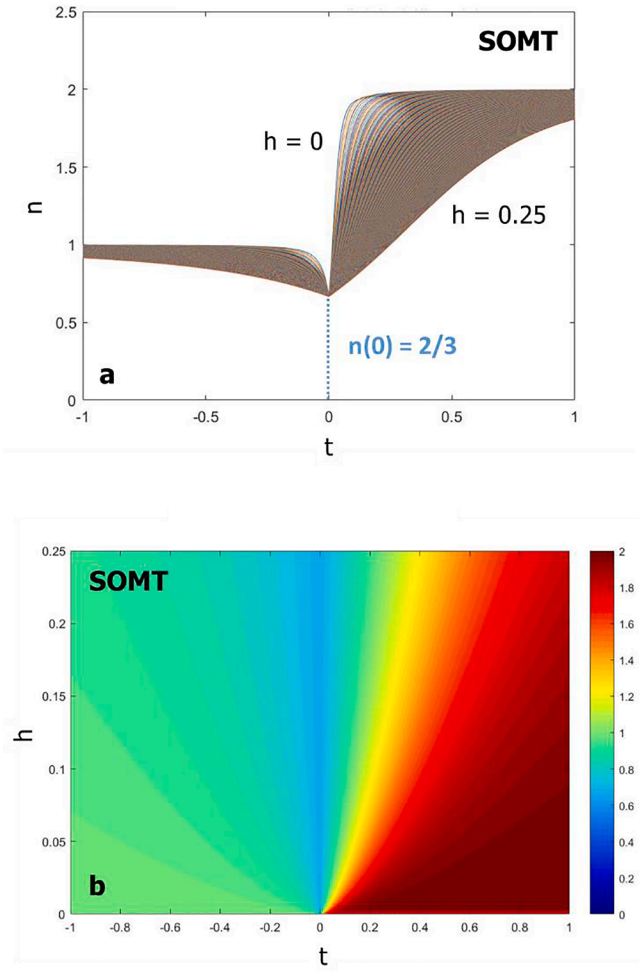


Fig. 5. Field exponent of the entropy change $n = dln(|\Delta s|)/dln(h)$ for the SOMT (a) as a function of the reduced temperature t for different reduced magnetic fields $h = 0$ to 0.25 in steps of 0.001 (b) as a colour map as a function of t and h.

In Fig. 6 the field exponent of the entropy change n is presented for the CP (a) as a function of t for different values of h and (b) as a colour map as a function of t and h. The high-temperature limit $n(t \gg 0) \approx 2$ and the low-temperature limit $n(t \ll 0) \approx 1$ are clearly illustrated. At $t = 0$ the minimum value for the exponent $n(t = 0) = 2/5$ is obtained (independent of h), which forms a characteristic feature for the CP. The field exponent is restricted by the high-temperature value as an upper limit: $n \leqslant 2$.

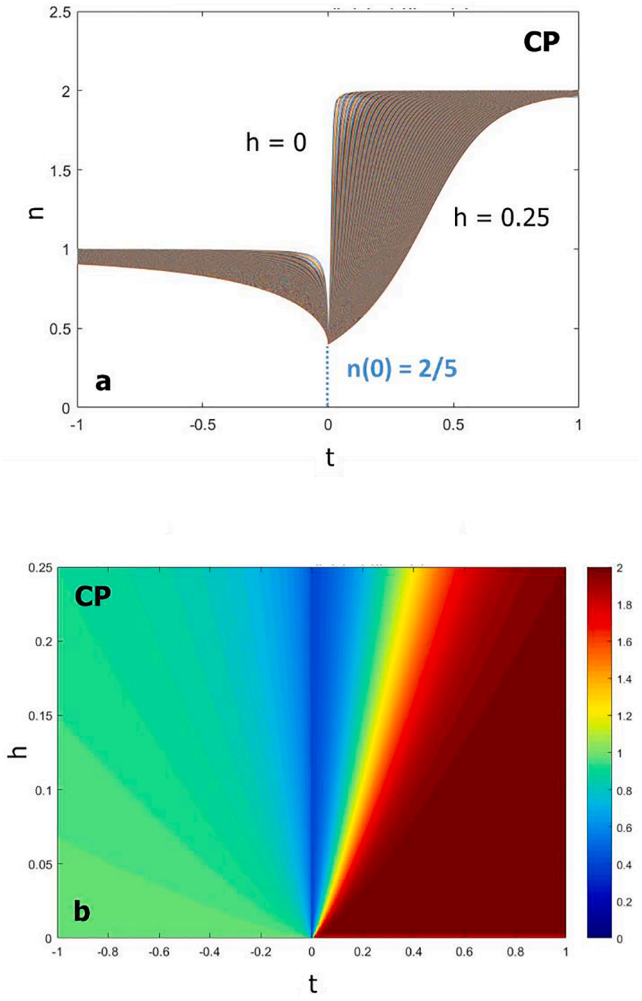


Fig. 6. Field exponent of the entropy change $n = dln(|\Delta s|)/dln(h)$ for the CP (a) as a function of the reduced temperature t for different reduced magnetic fields $h = 0$ to 0.25 in steps of 0.001 (b) as a colour map as a function of t and h.

The field exponent of the entropy change n is presented for the reversible FOMT in Fig. 7 and for the irreversible FOMT in Fig. 8, plotted (a) as a function of t for different values of h and (b) as a colour map as a function of t and h. The high-temperature limit $n(t \gg 0) \approx 2$ and the low-temperature limit $n(t \ll 0) \approx 1$ are again clearly illustrated. At $t = t_c$ both the minimum value of $n = 0$ and the maximum value $n \to \infty$ for the exponent are obtained (caused by the step in s), which forms a characteristic feature for the FOMT.

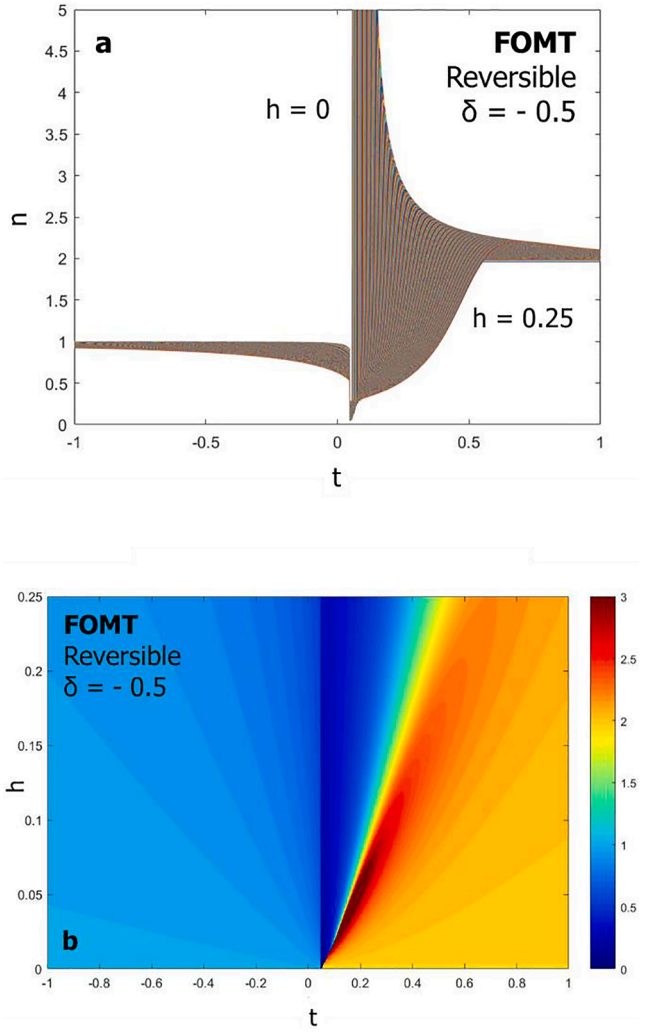


Fig. 7. Field exponent of the entropy change $n = dln(|\Delta s|)/dln(h)$ for the reversible FOMT with $\delta = -1/2$ (a) as a function of the reduced temperature t for different reduced magnetic fields $h = 0$ to 0.25 in steps of 0.001 (b) as a colour map as a function of t and h.

5. Critical temperature in a magnetic field

It is informative to evaluate how the critical temperature of the magnetic order is affected by the applied magnetic field in the SOMT, CP and FOMT. This however also directly poses questions on how the critical temperature should be defined. When there is a finite step in the magnetisation and the entropy (FOMT in low fields), when the specific heat diverges (CP in zero field) and when the specific heat shows a finite step in the specific heat (SOMT in zero field) there is no ambiguity. In finite magnetic fields all thermodynamic quantities generally show a more gradual change across the transition.

Two popular methods to define the transition temperature in field are: (*i*) the maximum rate of change in the magnetisation versus temperature $\left|\left(\frac{dm}{dt}\right)_h\right| \propto \left|\left(\frac{dM}{dT}\right)_H\right|$ and (*ii*) the maximum in the specific heat $c \propto \Delta C$. Recalling that $s = -\frac{1}{2}m^2$ and $c = (1+t)\left(\frac{ds}{dt}\right)_h$ it is obvious that for a gradual transition these methods probe something slightly different. Here we will define the transition temperature as the maximum rate of change in the magnetisation versus temperature $\left|\left(\frac{dm}{dt}\right)_h\right|$.

In Fig. 9 the reduced critical transition temperature t_c is shown as a function of the magnetic field h for the SOMT, the CP and the reversible and irreversible FOMT. For the SOMT no significant field dependence of t_c is observed, while the CP and FOMT show a continuous increase as the magnetically ordered state is stabilised by the magnetic field. For the reversible FOMT the critical temperature is finite in zero field $t_c^*(h = 0) = \frac{3}{16}\delta^2$, while for the irreversible FOMT the critical temperature depends on the history and corresponds to $t_c^+(h = 0) = \frac{\delta^2}{4}$ for heating and to $t_c^-(h = 0) = 0$ for cooling. For increasing magnetic fields the heating and cooling transitions approach each other until they coincide at a critical field h_{rev}. As the temperature above which a single reversible solution is found corresponds to $t_{rev} = \frac{9}{20}\delta^2$ with $m^2 = -\frac{3}{10}\delta$ the reversible field should scale as $h_{rev} \propto \frac{6}{25}\sqrt{\frac{3}{10}}(-\delta)^{5/2}$.

The field dependence of the critical temperature in Fig. 9 can be approximated by a power law dependence : $t_c(h) = t_c(0) + ch^z$. For the reversible FOMT ($\delta = -0.5$) a fit to the data provides $t_c(0) = 0.0367(3)$, $c = 1.333(1)$ and $z = 0.759(1)$. The fit value of $t_c(0)$ is close to the exact solution of $t_c(0) = \frac{3}{16}\delta^2$. For the CP a fit with $t_c(0) = 0$ results in $c = 1.1948(4)$ and $z = 0.8021(2)$. For the SOMT no significant shift in the critical temperature is observed. The field exponent for the critical temperature z is found to be close to a linear behaviour for both the FOMT and the CP. In low fields ($h < h_{rev}$) the results for the FOMT may depend strongly on the presence of irreversible behaviour and need to be treated with caution. Considering the equation of state it is clear that for the SOMT and CP, independent of field, only one solution is found for $t > 0$. As a result, the maximum in $|dm/dt|$ for the CP in finite magnetic field reflects a cross-over point rather than a true phase transition.

Approximate solutions for the field scaling can be obtained by comparing the high-temperature (paramagnetic) solution with $m \approx \frac{h}{t}$ and the solution near $t_c(0) = 0$. For the SOMT at $t \approx 0$ a field scaling of $m \approx h^{1/3}$ is found. Comparing the reduced Gibbs free energy of both approximate solutions results in a critical temperature of $t_c(h) \approx \frac{2}{3}h^{2/3}$. For the CP at $t \approx 0$ a field scaling of $m \approx h^{1/5}$ is found, resulting in $t_c(h) \approx \frac{3}{5}h^{4/5}$. The approximated field scaling of the critical temperature is in reasonable agreement with the fitted data for the CP, while for the SOMT it is weaker than approximated.

In zero field the reversible FOMT takes place at $t_c(0) = \frac{3}{16}\delta^2$ with a step in the magnetisation of $\Delta m = \sqrt{-\frac{3\delta}{4}}$ and a step in the entropy of $\Delta s = \frac{3}{8}\delta$. Assuming that for low field values Δm is independent of the magnetic field, the equation of state results in $\Delta t_c(h) = t_c(h) - t_c(0) = \frac{h}{\Delta m} \propto h$. This initial linear field dependence ($z = 1$) of the critical temperature for the FOMT corresponds to $\frac{dt_c}{dh} = \frac{1}{\Delta m} = -\frac{1}{2}\frac{\Delta m}{\Delta s}$ and is in agreement with the Calusius-Claperon relation $\frac{1}{\mu_0}\frac{dT_C}{dH} = -\frac{\Delta M}{\Delta S}$. Beyond the initial low-field approximation the filed exponent gradually decreases as indicated by the fitted field exponent of $z = 0.76$ obtained for $\delta = -0.5$ in the range up to $h = 0.25$.

6. Estimate of the scaling parameters

In order to relate the presented data in reduced units to experimental data it is useful to estimate the scaling parameters. The scaling parameter for the order parameter M_0 can be estimated from the low-temperature saturation magnetisation $M(0)$ and the corresponding average internal magnetic field $\mu_0 M(0)$. The saturation magnetisation corresponds to $M(0) = Z\mu/V_0$, where μ is the magnetic moment per formula unit, Z the number of formula units per unit cell and V_0 the unit cell volume. For the SOMT and the CP saturation magnetisation equals the scaling parameter($M(0) = M_0$), while for the FOMT we find $\frac{M(0)}{M_0} = \left(\frac{-\delta+(\delta^2+4)^{1/2}}{2}\right)^{1/2}$ with $\frac{M(0)}{M_0} \approx 1 - \frac{\delta}{4}$ for $-\delta \ll 1$. In the best MCE materials the internal magnetic field $\mu_0 M(0)$ ranges from 1 to 2.5 T. For $Mn_{1.25}Fe_{0.70}P_{0.5}Si_{0.5}$ the total moment per formula unit amounts to 4 μ_B

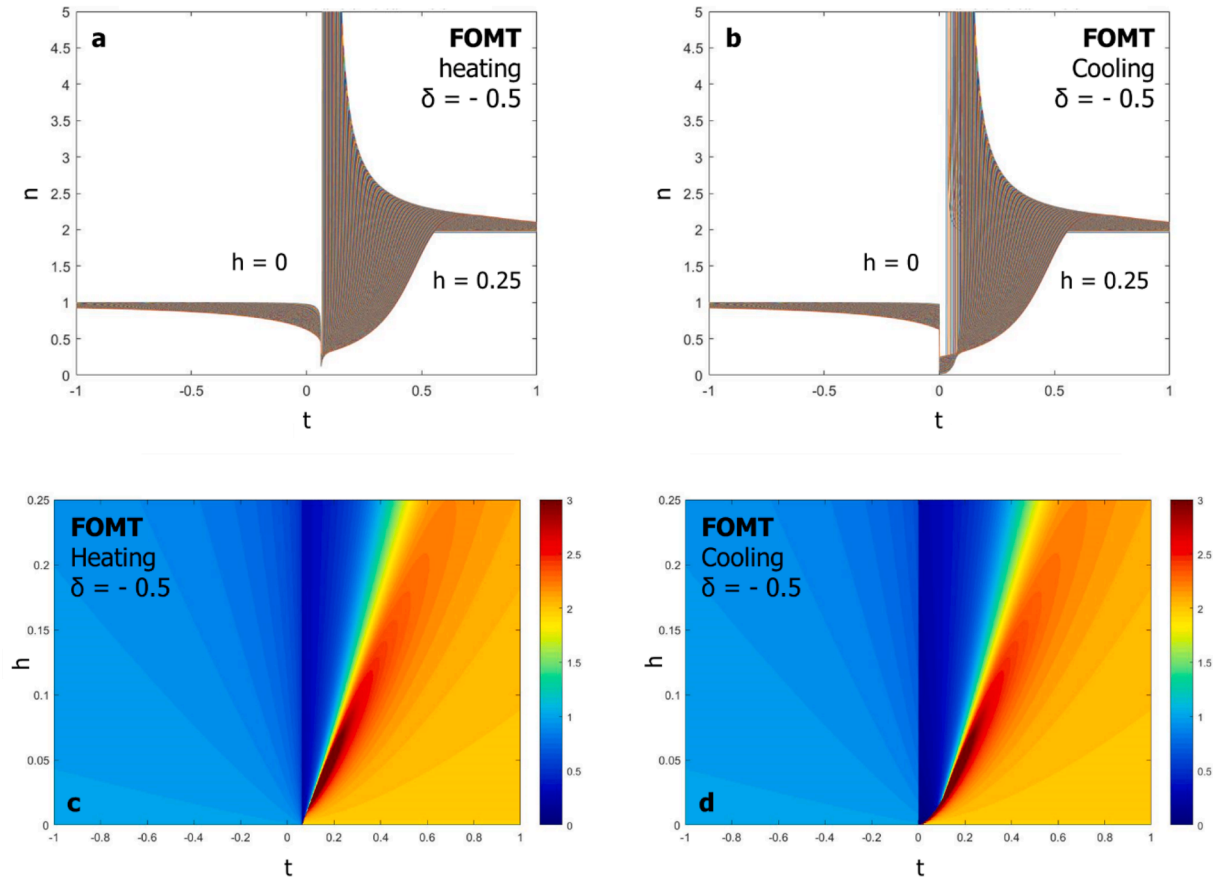


Fig. 8. Field exponent of the entropy change $n = dln(|\Delta s|)/dln(h)$ for the irreversible FOMT (a,b) for heating and cooling as a function of the reduced temperature t for different reduced magnetic fields $h = 0$ to 0.25 in steps of 0.001 (c,d) for heating and cooling as a colour map as a function of t and h.

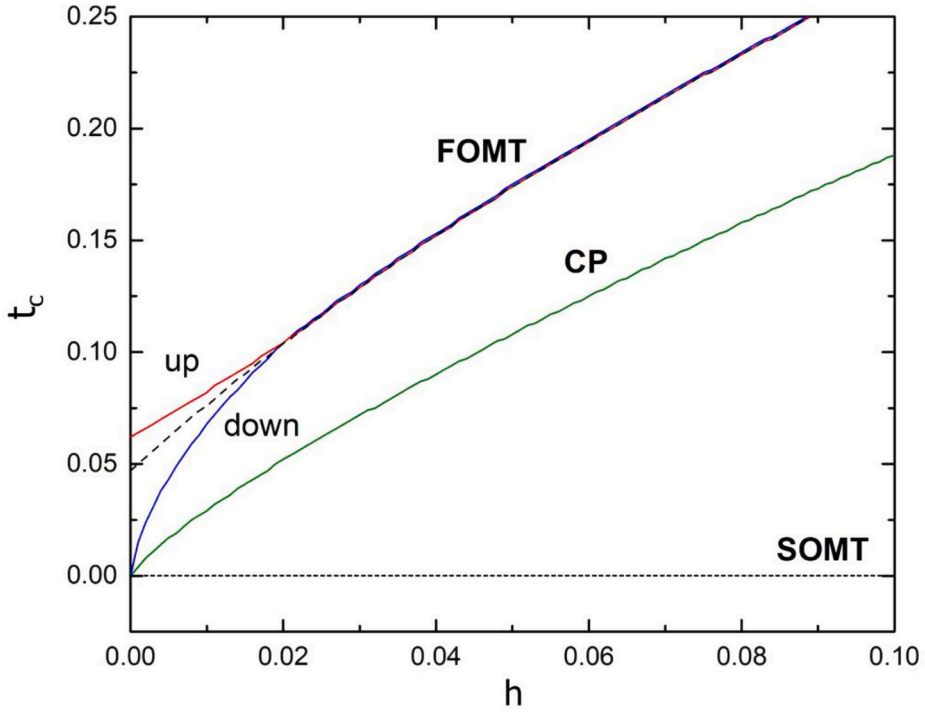


Fig. 9. Reduced transition temperature t_c as a function of the reduced magnetic field h for the SOMT, the CP and the FOMT with $\delta = -1/2$. For the reversible FOMT the transition is indicated by the dotted line. For the irreversible FOMT the red line corresponds to the transition for heating (up) and the blue curve to the transition for cooling (down). The curves for heating and cooling coincide above a critical field h_{rev}.

[30], which with a unit-cell volume of 110 Å^3 ($Z = 3$) results in $\mu_0 M(0) = 1.27$ T. The scaling parameter for the applied magnetic field corresponds to $\mu_0 H_0 = \frac{\Delta G_0}{M_0} = \alpha_0 T_0 M_0$, where $T_0 \approx T_C$ is about 300 K for near-room temperature MCE materials. Parameter α_0 can be estimated from the susceptibility in the paramagnetic state $\chi \approx \frac{C}{T-T_0}$, where $C \approx \frac{\mu_0}{\alpha_0}$. For $Mn_{1.25}Fe_{0.70}P_{0.5}Si_{0.5}$ the Curie constant amounts to $C \approx$ 1.1 K [30], resulting in $\mu_0 H_0 = \left(\frac{T_0}{C}\right)\mu_0 M_0 \approx$ 300 T for a transition temperature near room temperature. In the calculations the maximum field then corresponds to 75 T ($h = 0.25$) with a step size of 0.3 T ($\Delta h = 0.001$). The temperature range extends up to $2T_0 \approx 600$ K ($t = 1$) with a step size of 0.3 K ($\Delta t = 0.001$).

7. Discussion

Consistent with the calculations with the Bean and Rodbell model [4], our model calculations show that a FOMT can be distinguished from the SOMT and the CP when $n > 2$ for the magnetic field exponent for the entropy change. The high value of $n > 2$ in the vicinity of the FOMT reflects the presence of a step anomaly in the entropy. For the continuous transformations in the SOMT and the CP the value of the magnetic field exponent is restricted to $n \leqslant 2$ for all temperatures and magnetic fields, even when the specific heat diverges in the case of the CP in zero magnetic field.

Besides the differences in the maximum value of n for the SOMT, CP and FOMT the calculations with the Landau model indicate that there are also characteristic differences in the minimum value of n for these transitions: (*i*) $n = 2/3$ for the SOMT, (*ii*) $n = 2/5$ for the CP and (*iii*) $n = 0$ for the FOMT. This difference in the minimum value of n provides an additional method to establish the nature of the transition. The minimum values for n are consistent with the predictions from critical scaling [26] and qualitatively agree with the calculations for the Bean and Rodbell model [4], which indicate that for the minimum value the following sequence is observed $n_{min}^{FOMT}(\eta > 1) < n_{min}^{CP}(\eta = 1) < n_{min}^{SOMT}(\eta < 1)$, where η is the control parameter that defines the nature of the transition. However, the minimum value of n for the FOMT was found to be finite for the Bean and Rodbell model, while in the current Landau model calculations it reaches zero.

8. Conclusions

Recently, the field exponent for the magnetic entropy change $n = dln(|\Delta S|)/dln(H)$ was proposed as an alternative method to reliably distinguish first-order (FOMT) and second-order (SOMT) magnetic transitions in magnetocaloric materials. The predicted behaviour for both transitions was evaluated from experimental data and calculations with the Bean and Rodbell model. Here we used the Landau model to expand these predictions and provide a detailed model analysis of the influence of the magnetic field on the entropy change and the transition temperature for the first-order and second-order magnetic transitions, as well as the critical point (CP) at the transition between the FOMT and the SOMT. For the FOMT we explicitly distinguish the cases for the reversible transition without hysteresis and the irreversible transition with hysteresis, relevant for cases with a high and a low nucleation rate of the forming phase in the transition. In order to generalise the discussion, the model is formulated in reduced dimensionless parameters. The main conclusions are:

1. In agreement with the predictions from the Bean and Rodbell model the current Landau model calculations show that the FOMT can be distinguished from the SOMT and the CP by the maximum value of n. For the FOMT we find a maximum value of $n_{max} > 2$ in the vicinity of the transition, while for the SOMT and the CP we find a maximum value of $n_{max} = 2$ in the high-temperature limit.
2. Besides the maximum value of n, also its minimum value can be used to establish the nature of the transition. The SOMT shows a minimum value of $n_{min} = 2/3$, while for the CP $n_{min} = 2/5$ and for the FOMT $n_{min} = 0$ is found in the vicinity of the transition.
3. The transition temperature is found to be relatively insensitive to the magnetic field in the SOMT, while for the (reversible) FOMT and the CP a power law dependence for the field shift in the critical temperature is found with $\Delta T_C(H) \propto H^z$. The field dependence for the shift in the transition temperature is close to linear with a field exponent of $z = 0.76$ for the reversible FOMT ($\delta = -0.5$) and of $z = 0.80$ for the CP.

CRediT authorship contribution statement

N.H. van Dijk: Conceptualization, Formal analysis, Methodology, Software, Visualization, Writing - oroginal draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] O. Gutfleisch, M.A. Willard, E. Brück, C.H. Chen, S.G. Sankar, J.P. Liu, Magnetic materials and devices for the 21st century: Stronger, lighter, and more energy efficient, Adv. Mater. 23 (2011) 821–842, https://doi.org/10.1002/adma.201002180.
[2] E. Brück, 2008, Magnetocaloric refrigeration at ambient temperature, in Handbook of Magnetic Materials, Vol. 17, edited by K.H.J. Buschow, Elsevier, Amsterdam 235.
[3] X. Moya, S. Kar-Narayan, N.D. Mathur, Caloric materials near ferroic phase transitions, Nature Mater. 13 (2014) 439–450, https://doi.org/10.1038/nmat3951.
[4] J.Y. Law, V. Franco, L.M. Moreno-Ramírez, A. Conde, D.Y. Karpenkov, I. Radulov, K.P. Skokov, O. Gutfleisch, A quantitative criterion for determining the order of magnetic phase transitions using the magnetocaloric effect, Nature Comm. 9 (2018) 2680, https://doi.org/10.1038/s41467-018-05111-w.
[5] M.F.J. Boeije, M. Maschek, X.F. Miao, N.V. Thang, N.H. van Dijk, E. Brück, Mixed magnetism in magnetocaloric materials with first-order and second-order magnetoelastic transitions, J. Phys. D: Appl. Phys. 50 (2017), 174002, https://doi.org/10.1088/1361-6463/aa5db9.
[6] L.M. Moreno-Ramírez, C. Romero-Muñiz, J.Y. Law, V. Franco, A. Conde, I. A. Radulov, F. Maccari, K.P. Skokov, O. Gutfleisch, The role of Ni in modifying the order of the phase transition of La(Fe, Ni, Si_j)13, Acta Mater. 160 (2018) 137–146, https://doi.org/10.1016/j.actamat.2018.08.054.
[7] L.M. Moreno-Ramírez, C. Romero-Muñiz, J.Y. Law, V. Franco, A. Conde, I. A. Radulov, F. Maccari, K.P. Skokov, O. Gutfleisch, Tunable first order transition in La(Fe, Cr, Si_j)13 compounds: Retaining magnetocaloric response despite a magnetic moment reduction, Acta Mater. 175 (2019) 406–414, https://doi.org/10.1016/j.actamat.2019.06.022.
[8] C. Bean, D. Rodbell, Magnetic disorder as a first-order phase transformation, Phys. Rev. 126 (1962) 104–115, https://doi.org/10.1103/PhysRev.126.104.
[9] M. Piazzi, C. Bennati, C. Curcio, M. Kuepferling, V. Basso, Modeling specific heat and entropy change in La(Fe-Mn-Si)$_{13}$-H compounds, J. Magn. Magn. Mater. 400 (2016) 349–355, https://doi.org/10.1016/j.jmmm.2015.07.055.
[10] D.Y. Karpenkov, A.Y. Karpenkov, K.P. Skokov, I.A. Radulov, M. Zheleznyi, T. Faske, O. Gutfleisch, Pressure dependence of magnetic properties in La(Fe, Si_j)13: Multistimulus responsiveness of caloric effects by modeling and experiment, Phys. Rev. Appl. 13 (2020), 034014, https://doi.org/10.1103/PhysRevApplied.13.034014.
[11] L.M. Moreno-Ramirez, J.S. Blázquez, I.A. Radulov, K.P. Skokov, O. Gutfleisch, V. Franco, A. Conde, Combined Kinetic and Bean-Rodbell approach for describing field-induced transitions in LaFe11.6Si1.4 alloys, J. Phys. D, Accepted manuscript, https://doi.org/10.1088/1361-6463/abd583.
[12] L.D. Landau, 1937, On the theory of phase transitions. I., Zh. Eksp. Teor. Fiz. 7 19–32.
[13] D.I. Uzinov, Introduction to the theory of critical phenomena: Mean field, Fluctuations and Renormalization, World Scientific, Singapore, 2010.

[14] B. Teng, M. Tu, Y. Chen, J. Tang, A phenomenological description of the first-order transition in the $Gd_5(Si_xGe_{1-x})_4$ ($0.24 < x < 0.5$) alloys, J. Phys.: Condens. Matter 14 (2002) 6501–6507, https://doi.org/10.1088/0953-8984/14/25/317.
[15] V.S. Amaral, J.S. Amaral, Magnetoelastic coupling influence on the magnetocaloric effect in ferromagnetic materials, J. Magn. Magn. Mater. 272–276 (2004) 2104–2105, https://doi.org/10.1016/j.jmmm.2003.12.870.
[16] X.B. Liu, D.H. Ryan, Z. Altounian, The order of magnetic phase transition in $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ compounds, J. Magn. Magn. Mater. 270 (2004) 305–311, https://doi.org/10.1016/j.jmmm.2003.08.028.
[17] A.M.G. Carvalho, A.A. Coelho, S. Gama, F.C.G. Gandra, P.J. von Ranke, N.A. de Oliveira, Investigation of the first-order metamagnetic transitions and the colossal magnetocaloric effect using a Landau expansion applied to MnAs compound, Eur. Phys. J. B 68 (2009) 67-72; 78 (2010) 137. https://doi.org/10.1140/epjb/e2009-00083-9; https://doi.org/10.1140/epjb/e2010-00296-9.
[18] J.S. Amaral, V.S. Amaral, On estimating the magnetocaloric effect from magnetization measurements, J. Magn. Magn. Mater. 322 (2010) 1552–1557, https://doi.org/10.1016/j.jmmm.2009.06.013.
[19] B. Li, H. Meng, W. Ren, Z. Zhang, Intrinsic magnetocaloric effect at a first-order magnetic transition, EPL 97 (2012) 57002, https://doi.org/10.1209/0295-5075/97/57002.
[20] N.G. Bebenin, R.I. Zainullina, V.V. Ustinov, Magnetocaloric effect in inhomogeneous ferromagnets, J. Appl. Phys. 113 (2013), 073907, https://doi.org/10.1063/1.4792306.
[21] A. Arrott, Criterion for ferromagnetism from observations of magnetic isotherms, Phys. Rev. 108 (1957) 1394–1396, https://doi.org/10.1103/PhysRev.108.1394.
[22] S.K. Banerjee, On a generalised approach to first and second order magnetic phase transitions, Phys. Lett. 12 (1964) 16–17, https://doi.org/10.1016/0031-9163(64)91158-8.
[23] V. Franco, J.S. Blázquez, A. Conde, Field dependence of the magnetocaloric effect in materials with a second order phase transition: A master curve for the magnetic entropy change, Appl. Phys. Lett. 89 (2006), 222512, https://doi.org/10.1063/1.2399361.
[24] R. Venkatesh, M. Pattabiraman, K. Sethupathi, G. Rangarajan, S. Angappane, J.-G. Park, Tricritical point and magnetocaloric effect of $Nd_{1-x}Sr_xMnO_3$, J. Appl. Phys. 103 (2008) 07B319, https://doi.org/10.1063/1.2832412.
[25] P. Shamba, J.L. Wang, J.C. Debnath, S.J. Kennedy, R. Zeng, M.F.M. Din, F. Hong, Z. X. Cheng, A.J. Studer, S.X. Dou, The magnetocaloric effect and critical behaviour of the $Mn_{0.94}Ti_{0.06}CoGe$ alloy, J. Phys. Condens. Matter 25 (2013), 056001, https://doi.org/10.1088/0953-8984/25/5/056001.
[26] V. Franco, J.Y. Law, A. Conde, V. Brabander, D.Y. Karpenkov, I. Radulov, K. Skokov, O. Gutfleisch, Predicting the tricritical point composition of a series of LaFeSi magnetocaloric alloys via universal scaling, J. Phys. D: Appl. Phys. 50 (2017), 414004, https://doi.org/10.1088/1361-6463/aa8792.
[27] O. Hassayouna M.R. Laouyennea M. Baazaouia E.K. Hlilb M. Oumezzinea Kh. Farahc, Critical phenomena in the double-exchange ferromagnet La0.8Na0.2Mn1-xNixO3 around the critical temperature, Current Appl. Phys. 19 2019 1305 1313 10.1016/j.cap.2019.08.015.
[28] A. Planes, E. Obradó, A. Gonzàlez-Comas, L. Mañosa, Premartensitic Transition Driven by Magnetoelastic Interaction in bcc Ferromagnetic Ni_2MnGa, Phys. Rev. Lett. 79 (1997) 3926–3929, https://doi.org/10.1103/PhysRevLett.79.3926.
[29] J.M.D. Coey, Magnetism and magnetic materials, Cambridge University Press, Cambridge, 2009.
[30] N.H. Dung, L. Zhang, Z.Q. Ou, L. Zhao, L. van Eijck, A.M. Mulders, M. Avdeev, E. Suard, N.H. van Dijk, E. Brück, High/low-moment phase transition in hexagonal Mn-Fe-P-Si compounds, Phys. Rev. B 86 (2012), 045134, https://doi.org/10.1103/PhysRevB.86.045134.