PHYSICAL REVIEW B **90**, 104422 (2014)

# Scaling and universality in magnetocaloric materials

Anders Smith, Kaspar K. Nielsen, and Christian R. H. Bahl
*Department for Energy Conversion and Storage, Technical University of Denmark, Risø Campus, Frederiksborgvej 399, DK-4000 Roskilde, Denmark*

(Received 30 April 2014; revised manuscript received 7 August 2014; published 24 September 2014)

The magnetocaloric effect of a magnetic material is characterized by two quantities, the isothermal entropy change and the adiabatic temperature change, both of which are functions of temperature and applied magnetic field. We discuss the scaling properties of these quantities close to a second-order phase transition within the context of the theory of critical phenomena. Sufficiently close to the critical temperature of a second-order material, the scaling of the isothermal entropy change will be determined by the critical exponents and will be the same as that of the singular part of the entropy itself. However, this is only true in the critical region near $T_c$ and for small fields; for finite fields, scaling with constant exponents, in general, break down, even at $T_c$. The field dependence can then be described by field-dependent scaling exponents. We show that the scaling exponents at finite fields are not universal, showing significant variation for models in the same universality class. As regards the adiabatic temperature change, it is not determined exclusively by the singular part of the free energy and its derivatives. We show that the field dependence of the adiabatic temperature change at the critical temperature depends on the nonsingular part of the specific heat. The field dependence can still be fitted to a power-law expression but with nonuniversal exponents, as we show explicitly both within mean-field theory and using the so-called Arrott-Noakes equation of state. Within the framework of the Bean-Rodbell model, we briefly consider the scaling properties of the magnetocaloric effect in first-order materials. Finally, we discuss the implications of our findings for a widely used phenomenological scaling procedure for magnetocaloric quantities.

DOI: 10.1103/PhysRevB.90.104422 PACS number(s): 75.30.Sg, 64.60.F−, 75.40.Cx

## I. INTRODUCTION

The magnetocaloric effect in magnetic systems with second- or first-order transitions near room temperature has attracted significant interest in recent years due to its potential use in refrigeration devices and heat pumps [1]. The two most important characteristics of a magnetocaloric material (loosely defined as a magnetic material with a sizable magnetocaloric effect) are the isothermal entropy change and the adiabatic temperature change, although several other materials properties also play a crucial role for the actual applicability of a given material in a high-performing device [2]. The temperature and field dependence of the magnetocaloric quantities not only influence the performance of the material in a device but are also of scientific significance in themselves. Indeed, the use of the magnetocaloric effect to gain insight into the intrinsic magnetic properties of a ferromagnetic material close to its transition temperature goes back to the very discovery of the effect [3]. Thus Weiss and coworkers showed how the adiabatic temperature change may be used to determine the intrinsic magnetization of a ferromagnetic material just below the critical temperature [4–6]; due to domain effects this magnetization is not observable directly in zero applied field. With the development of the theory of critical phenomena and critical scaling exponents, several authors in the late 1960's and early 1970's investigated the adiabatic temperature change close to second-order phase transitions and discussed the field dependence of it within this context [7,8]. Recently, the question of the scaling behavior of both the isothermal entropy change and the adiabatic temperature change has been discussed in a series of papers by V. Franco and coworkers, see, e.g., Refs. [9,10]. The theory of critical phenomena has also been invoked to justify a phenomenological scaling procedure widely used in the magnetic refrigeration community [11]. However, much of the recent work in this direction has been based on an application of scaling theory outside its obvious range of applicability. The object of the present work is to reconsider these questions using, as far as possible, exact relations for the magnetocaloric quantities and investigating the validity of the scaling hypotheses in selected model systems.

The plan of the paper is as follows. First, we briefly review the standard scaling theory of second-order transitions and discuss the extent to which it is applicable to magnetocaloric quantities. Then we consider in detail the isothermal entropy change and the adiabatic temperature change. We show that in the critical region the scaling of the isothermal entropy change for low fields is the same as that of the singular part of the entropy, while the adiabatic temperature change in general is nonuniversal, even in the critical region. By explicitly evaluating the isothermal entropy change for different second-order materials within the Bean-Rodbell model, we show that the field dependence of the entropy change is not universal for finite fields. We also consider the field dependence of the adiabatic temperature change both within the Bean-Rodbell model and for materials obeying the Arrott-Noakes equation of state; we show that the field dependence is determined by the relative size of the background specific heat and the magnetic specific heat, making the field dependence nonuniversal also in this case. We then go on to consider first-order materials as described by the Bean-Rodbell model and discuss to which extent scaling exponents for the magnetocaloric quantities can meaningfully be applied in this case. Finally, we briefly review the experimental evidence both for second-order and first-order transitions and discuss the implications for the interpretation of the phenomenological scaling procedures.

## II. CRITICAL SCALING THEORY

It is useful briefly to review the main assumptions of the scaling theory of second-order phase transitions. These can be formulated in slightly different ways; here we follow that of Stanley [12]. In zero field and at the critical temperature $T_c$ separating the two phases of a material undergoing a second-order phase transition, the free energy (per volume), $F(T,H)$, will be a nonanalytic function of temperature $T$, i.e., not all of its derivatives will exist; $H$ is the applied field. The basic scaling hypothesis is that the singular part of the free energy, $F_{\text{sing}}(T,H)$, close to the critical point is a generalized homogeneous function. This means that there exist two scaling exponents $a_H$ and $a_T$ such that for arbitrary positive $\lambda$ the following equation is obeyed:

$$F_{\text{sing}}(\lambda^{a_T}t,\lambda^{a_H}H)=\lambda F_{\text{sing}}(t,H), \tag{1}$$

where $t=(T-T_c)/T_c$ is the reduced temperature. It should be kept in mind that this scaling *a priori* only holds asymptotically close to $T_c$ and that the scaling only applies to the *singular* part of the free energy. The full free energy is the sum of the singular part and a nonsingular (analytic) background:

$$F(T,H)=F_{\text{sing}}((T-T_c)/T_c,H)+F_{\text{n.s.}}(T). \tag{2}$$

A generalized homogeneous function must either be zero or tend to infinity when both of its arguments are 0, as can be seen from the definition, Eq. (1). Since the free energy must remain finite at the critical point, $F_{\text{sing}}(0,0)=0$. This makes the decomposition of the free energy into a singular and a nonsingular (regular) part unique. In writing the nonsingular part as a function of temperature only, we have made the usual assumption that the magnetization contains no regular part [13]. It immediately follows that both the entropy, $S=-(\partial F/\partial T)_H$, and the specific heat, $C_H=T(\partial S/\partial T)_H$, can be written as the sum of a singular, field-dependent term and a field-independent regular term:

$$S(T,H)=S_{\text{sing}}((T-T_c)/T_c,H)+S_{\text{n.s.}}(T), \tag{3}$$

and

$$C_H(T,H)=C_{H,\text{sing}}((T-T_c)/T_c,H)+C_{\text{n.s.}}(T). \tag{4}$$

The explicit scaling form of, e.g., the singular part of the entropy follows from differentiation of Eq. (1):

$$S_{\text{sing}}(\lambda^{a_T}t,\lambda^{a_H}H)=\lambda^{1-a_T}S_{\text{sing}}(t,H). \tag{5}$$

It is straightforward to make the connection between the scaling exponents $a_H$ and $a_T$ and the usual critical exponents $\alpha,\beta,\gamma,\delta$ and $\Delta$ (see Table I). For reference, we note that the above assumption for the free energy implies that the magnetization can be written as

$$M(t,H)=H^{1/\delta}f_M(tH^{-1/\Delta}), \tag{6}$$

where $f_M$ is a scaling function and $\delta^{-1}=(1-a_H)/a_H$, $\Delta^{-1}=a_T/a_H$. The singular part of the entropy is

$$\begin{aligned}S_{\text{sing}}(t,H)&=H^{1-\Delta^{-1}+\delta^{-1}}f_S(tH^{-1/\Delta})\\&=H^{(1-\alpha)/\Delta}f_S(tH^{-1/\Delta}).\end{aligned} \tag{7}$$

Here, $f_S$ is another scaling function. In the last equality we have used the Griffiths equality [12] in the form $\alpha+\Delta(1+\delta^{-1})=2$ to introduce $\alpha$, the exponent characterizing the temperature dependence of the singular part of the zero-field specific heat. We have $C_{\text{sing}}(t,H)=H^{-\alpha/\Delta}f_C(tH^{-1/\Delta})$ with yet another scaling function $f_C$.

In much work on critical phenomena, it is usual to ignore the nonsingular part of the free energy and other thermodynamic properties since it is only the singular part which determines the critical exponents [14]. However, for quantities that depend on the values of, e.g., the full entropy or heat capacity, the nonsingular part will of course play a crucial role. In particular, this is true of the adiabatic temperature change which, as we discuss below, depends on the full entropy curves (or, equivalently, the total specific heat) of the material. This may seem like an obvious remark but it has in fact been overlooked in previous work on the scaling of magnetocaloric quantities. Using only the singular scaling form of the entropy or the specific heat will lead to wrong predictions of the scaling of the adiabatic temperature change.

The scaling relations above are only valid in the so-called critical region. The width of this region on the temperature axis is not known *a priori* and depends on the specifics of the sample, e.g., the amount of impurities and the crystallinity. A further difficulty is the uncertainty in the determination of $T_c$ which will influence the parameter fits, as discussed by Kadanoff *et al.* in their classic review [15]. For single-crystal gadolinium they quote a value of the critical region of $|t|<5\times10^{-2}$, which corresponds to about 15 K on either side of the critical temperature. As one goes further away from the critical temperature, the simple power laws are modified by additional terms, the so-called corrections to scaling. However, even inside the critical region the scaling relations are only valid for small applied fields. This is most obviously seen for the exponent $\delta$ governing the dependence of the magnetization on field at $T=T_c$: $M\sim H^{\delta}$. This cannot hold for arbitrarily large fields since $M$ must eventually saturate. The formal scaling relation can only be retained at the expense of introducing an effective $\delta$, which is field dependent. Since the critical exponents are not mutually independent, this also introduces a field dependence of the other exponents. To allow field-dependent critical exponents would of course be to go against the very spirit of critical scaling theory since *any* functional relation $M(H)$ can be rewritten as $M(H)\sim H^{\delta(H)}$. Thus we have to distinguish carefully between the field-independent critical exponents valid close to $T_c$ for small applied fields, and scaling exponents valid for finite fields, which—as the argument above shows—necessarily become field dependent at some point. As one is often interested in the magnetocaloric quantities in quite large fields (of the order of 1–10 T) for

TABLE I. The definition of the usual critical exponents and their connection to the scaling exponents $a_H$ and $a_T$; $\chi$ is the susceptibility.

| Exponent | Definition | Connection to $a_H$ and $a_T$ |
|---|---|---|
| $\alpha$ | $C_{\text{sing}}\sim\|t\|^{-\alpha}\ (H=0)$ | $2-a_T^{-1}$ |
| $\beta$ | $M\sim\|t\|^{\beta}\ (t<0,H=0)$ | $(1-a_H)/a_T$ |
| $\gamma$ | $\chi\sim\|t\|^{-\gamma}\ (H=0)$ | $(2a_H-1)/a_T$ |
| $\delta$ | $M\sim H^{\delta}$ | $a_H/(1-a_H)$ |
| $\Delta$ | $\beta\delta$ | $a_H/a_T$ |

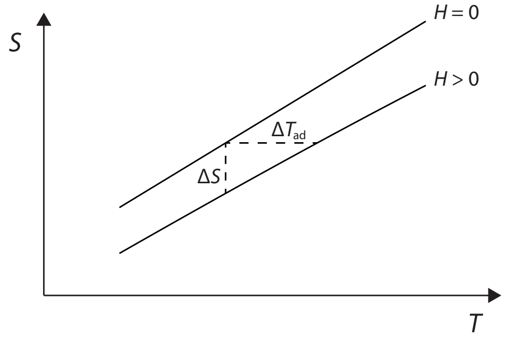

FIG. 1. The isothermal entropy change $\Delta S(T,H)$ and the adiabatic temperature change $\Delta T_{\text{ad}}$ are defined from the difference between two different thermodynamical states.

applications, this distinction between critical exponents and scaling exponents in fact becomes practically relevant, as we shall see below.

## III. SCALING OF THE ISOTHERMAL ENTROPY CHANGE

The isothermal entropy change of a magnetocaloric material between initial field $H_i$ and final field $H_f$ is by definition $\Delta S(T;H_f,H_i) = S(T,H_f) - S(T,H_i)$. In general, $\Delta S$ is a function of both $H_f$ and $H_i$ and not just their difference $H_f - H_i$. However, in the rest of this paper we shall assume that the entropy change is measured with respect to an initial field equal to zero and write

$$\Delta S(T,H) = S(T,H) - S(T,0). \tag{8}$$

This is shown graphically in Fig. 1. Since the nonsingular part of the entropy is only a function of $T$ it immediately follows that the isothermal entropy change is uniquely determined by the singular part of the entropy. Going back to the scaling form of the singular part of the entropy, Eq. (5), it is apparent that

$$\begin{aligned} &S_{\text{sing}}(\lambda^{a_T}t,\lambda^{a_H}H) - S_{\text{sing}}(\lambda^{a_T}t,0)\\ &\quad = \lambda^{1-a_T}(S_{\text{sing}}(t,H) - S_{\text{sing}}(t,0)), \end{aligned} \tag{9}$$

i.e., the scaling of $\Delta S(t,H)$ is the same as that of $S_{\text{sing}}$. We can then write

$$\Delta S(t,H) = H^{(1-\alpha)/\Delta}\tilde{f}_S(tH^{-1/\Delta}), \tag{10}$$

where $\tilde{f}_S$ is a new scaling function. This result has previously been derived by V. Franco and coworkers using the scaling of the magnetization, Eq. (6), in combination with the Maxwell relation $\Delta S = \mu_0\int_0^H(\partial M/\partial T)_H dH$ ($\mu_0$ is the vacuum permeability) [11,16]. As usual, the scaling form (10) implies that if curves of isothermal entropy change for different fields are plotted as $\Delta S(t,H)H^{-(1-\alpha)/\Delta}$ versus $tH^{-1/\Delta}$, they will all collapse onto the same curve. However, the scaling function of two different materials will not in general be identical even if their critical exponents agree, cf. Sec. V below.

At $T = T_c$, the scaling relation predicts that the field dependence of $\Delta S$ is a simple power law:

$$\Delta S(t=0,H) = \text{const.} \times H^{(1-\alpha)/\Delta}. \tag{11}$$

Away from $T_c$, one can also try to fit power-law expressions to $\Delta S$. The theoretical justification of this becomes progressively smaller, as one allows the fitting exponents to depend on temperature and even field. Even so, sometimes a "local" exponent $n$ is defined as [17]

$$n(t,H) = \frac{\partial \ln|\Delta S(t,H)|}{\partial \ln H}. \tag{12}$$

This is simply rewriting $\Delta S(t,H) = a(t)H^{n(t,H)}$, which, of course, can be done for arbitrary field and temperature dependence of $\Delta S$; as indicated, $n$ depends on both $t$ and $H$. If we use the scaling form of $\Delta S$, Eq. (10), we get [11]

$$n(t,H) = \frac{1-\alpha}{\Delta} - \frac{1}{\Delta}\frac{d\ln\tilde{f}_S(x)}{d\ln x}\bigg|_{x=tH^{-1/\Delta}}. \tag{13}$$

As long as we are in the critical region, $n$ for different fields will collapse on a single curve when plotted as a function of $x = tH^{-1/\Delta}$. At $T_c$ we have already noted that $n = (1-\alpha)/\Delta$ as the second term in Eq. (13) vanishes. Since $d\ln\tilde{f}_S/d\ln x = x\tilde{f}_S'/f_S$, it follows that the second term also vanishes if $\tilde{f}_S'(x) = 0$ (as long as $\tilde{f}_S(x) \neq 0$). Thus, if the peak temperature, $T_{\text{peak}}(H)$, of $\Delta S(T,H)$ (i.e., the temperature for which $-\Delta S$ is a maximum) is different from $T_c$, the second term in Eq. (13) also vanishes, making $n$ attain the value $(1-\alpha)/\Delta$ here also [18]. Again, this is only true in the critical region and for low fields. One may ask whether $n$ at finite fields is uniquely determined by the critical exponents of the model. Below, we calculate $n$ both in the Bean-Rodbell and the Arrott-Noakes models and discuss its behavior as a function of temperature and field. We show explicitly that $n$ is not universal by evaluating it for different Bean-Rodbell models, which are all in the same universality class, i.e., have the same critical exponents. To calculate $n$ numerically it is convenient to use the Maxwell relation in the form $\partial\Delta S/\partial H = \mu_0(\partial M/\partial T)_H$ to get

$$n(t,H) = \frac{\mu_0 H}{T_c\Delta S(t,H)}\left(\frac{\partial M}{\partial t}\right)_H. \tag{14}$$

Experimentally, the resolution in field is usually not sufficient to calculate the local exponent $n$ directly. Instead, a common way of obtaining an exponent is to measure $\Delta S$ in a number of fields $H_1 < H_2 < \cdots < H_k$ and then simply fit a power law $aH^b$ to the data set $\{(H_i,\Delta S_i), i = 1,\ldots,k\}$, either at a given, constant temperature or for the peak temperature. Since all curves by definition meet in (0,0), such a fit will in fact mostly be determined by the high-field data. This means that the behavior of the exponent $b$ determined in this way will be similar to that of the local exponent $n(t,H)$.

## IV. SCALING OF THE ADIABATIC TEMPERATURE CHANGE

The adiabatic temperature change is defined as the change in temperature upon an adiabatic (isentropic) application of a magnetic field. As above, we only consider temperature changes from zero field to $H$. In that case, the defining equation is

$$S(T,0) = S(T + \Delta T_{\text{ad}}(T,H),H). \tag{15}$$

Now, if we unthinkingly identify the scaling form of the singular part of the entropy, $S_{\text{sing}}(t,H) = H^{(1-\alpha)/\Delta}f_S(tH^{-1/\Delta})$, with the entire entropy in the above equation, it is immediately apparent that the result is nonphysical. Indeed, since [according to Eq. (5)] the singular part of the entropy is zero for $T = T_c$ and $H = 0$, Eq. (15) would become

$$0 = f_S\left(\frac{\Delta T_{\rm ad}}{T_c}H^{-1/\Delta}\right) \tag{16}$$

at $T = T_c$. Since $S_{\rm sing}$ is a nondecreasing function of temperature, so is $f_S$ as a function of its argument. From the fact that $f_S(0) = 0$ we have $f_S(x) \geqslant 0$ for $x > 0$. But then a solution of Eq. (16), i.e., the existence of some $x^* > 0$ for which $f_S(x^*) = 0$, implies that $f_S$ is identically zero on the interval $[0,x^*]$ and there is no unique solution for $\Delta T_{\rm ad}$.

Previous studies have taken the following equation for the adiabatic temperature change as their starting point [7,10]:

$$\Delta T_{\rm ad}(T,H) = -T\int_0^H \frac{1}{C_H(T,H')}\frac{\partial S(T,H')}{\partial H'}dH', \tag{17}$$

where, by the Maxwell relation, $(\partial S/\partial H)_T = \mu_0(\partial M/\partial T)_H$. However, it has to be remembered that this is in fact an approximate expression, derived by expanding Eq. (15) to first order in $\Delta T_{\rm ad}/T_c$ [2,19]. And when the relation is derived from the definition of the adiabatic temperature change, it is apparent that $C_H(T,H)$ cannot be identified with $C_{\rm sing}$ whose scaling is known from critical theory. Rather, $C_H$ is the full specific heat, $C_H(T,H) = C_{\rm sing}(T,H) + C_{\rm n.s.}(T)$. Even when we are sufficiently close to the critical temperature for scaling theory to apply, we only get the field and temperature dependence of $C_{\rm sing}$, not its absolute magnitude. And the magnitude and temperature dependence of $C_{\rm n.s.}$ is of course completely undetermined by critical theory. This means that Eq. (17) becomes of limited use to discuss the scaling behavior of $\Delta T_{\rm ad}$ directly. In particular, wrong conclusions will be drawn if the scaling form of the singular heat capacity is simply substituted into the equation, as some authors do [10]. It should be noted that below $T_c$ the integral in Eq. (17) is in general well-behaved and convergent even when using only the singular part of $C$. However, in that case one is calculating a quantity that is not related to the true adiabatic temperature change; indeed, for $T + \Delta T_{\rm ad} > T_c$, the adiabatic temperature change diverges in mean-field theory if determined using the magnetic entropy curves only (see Fig. 2), even though the approximate expression, Eq. (17), is still finite. The divergence is related to the fact that above $T_c$ the magnetic entropy in zero field actually becomes constant in the mean-field theory. In more realistic models, e.g., the Heisenberg model, this is no longer true. However, the magnetic entropy is still bounded by $\ln(2J + 1)$ per site, where $J$ is the size of the spin (when we neglect spin-lattice interactions), and will not dominate the total entropy except at extremely low temperatures. So in this case too, the nonsingular entropy cannot be ignored.

The present starting point will be the definition of the adiabatic temperature change, Eq. (15), together with the decomposition of the entropy into a singular and a nonsingular part. Furthermore, we make the reasonable assumption that the entropy alternatively can be written as a sum of magnetic, lattice and electronic terms, where it is solely the magnetic part (calculated from considering the magnetic spin system only) that depends on field. Often the lattice entropy is approximated with that of a Debye model and the electronic entropy with that of the Sommerfeld model [20], but for the present we only need the fact that the lattice and electronic terms are independent of field. The magnetic entropy differs only by a field-independent term from the singular entropy (which, it will be remembered, is 0 at $T_c$). By using the fact that $\Delta S(T,H) = S_{\rm sing}(T,H) - S_{\rm sing}(T,0) = S_{\rm mag}(T,H) - S_{\rm mag}(T,0)$, we can rewrite Eq. (15) as

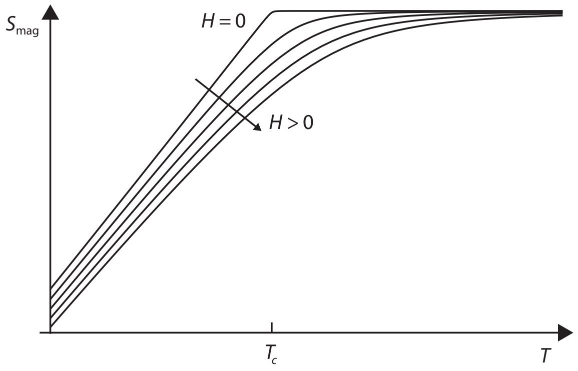

FIG. 2. The magnetic entropy in a mean-field model; the zero-field magnetic entropy is independent of temperature above $T_c$. The arrow indicates the direction of increasing $H$. For $T \geqslant T_c$, there is no finite solution for the adiabatic temperature change using only the magnetic entropy.

$$S_0(T + \Delta T_{\rm ad}) - S_0(T) = -\Delta S(T + \Delta T_{\rm ad},H) - (S_{\rm mag}(T + \Delta T_{\rm ad},0) - S_{\rm mag}(T,0)). \tag{18}$$

Here, $S_0$ is the entropy associated with the lattice and electronic degrees of freedom. We note that the last term on the right-hand side is determined only by the zero-field properties of the spin system; in the critical region, the temperature dependence (but not the amplitude) of this term is determined from the critical scaling of the zero-field specific heat. The scaling properties of $\Delta S$ (but not its absolute amplitude) can be derived from the critical exponents as shown above. The left-hand side of the equation is a nonsingular function of temperature only.

To proceed, we note that the nonsingular entropy is a slowly varying function of temperature (with a scale typically given by a Debye temperature). Thus we can write $S_0(T + \Delta T_{\rm ad}) - S_0(T) \simeq \Delta T_{\rm ad}(\partial S_0/\partial T) = \Delta T_{\rm ad}C_0(T)/T$. We then get the following implicit equation for $\Delta T_{\rm ad}$:

$$\frac{C_0(T)}{T}\Delta T_{\rm ad} = -\Delta S(T + \Delta T_{\rm ad},H) - [S_{\rm mag}(T + \Delta T_{\rm ad},0) - S_{\rm mag}(T,0)]. \tag{19}$$

The last term can be rewritten as a temperature integral, giving

$$\frac{C_0(T)}{T}\Delta T_{\rm ad} = -\Delta S(T + \Delta T_{\rm ad},H) - \int_T^{T+\Delta T_{\rm ad}} \frac{C_{\rm mag}(T',0)}{T'}dT'. \tag{20}$$

This reformulation of the defining equation for the adiabatic temperature change shows that it can be determined straightforwardly (if implicitly) from magnetic measurements (giving $\Delta S$) and zero-field heat capacity measurements in the temperature region of interest. In particular, low-temperature determination of the zero-field specific heat is not necessary. This form of the equation turns out to be useful to discuss the scaling properties of the adiabatic temperature change.

The implicit equation for $\Delta T_{\mathrm{ad}}$, Eq. (20), is sufficiently general to be valid for both second-order materials and for those first-order materials for which a split of the entropy into purely magnetic and lattice/electronic contributions makes sense. We discuss first-order materials below and focus here on second-order materials.

Since $\Delta T_{\mathrm{ad}}/T$ is typically of the order of at most a few percent for most fields of interest, it may be thought that Eq. (20) can straightforwardly be expanded to first-order in $\Delta T_{\mathrm{ad}}/T$. However, to do so we must inquire into the scale that characterizes the temperature dependence of the isothermal entropy change. The negative of the entropy change peaks at a temperature close to $T_c$ and falls off with a full width-half maximum ($\mathrm{FWHM}_{\Delta S}$), which from Eq. (10) is proportional to $H^{1/\Delta}$ in the critical region. On the other hand, the zero-order solution of the equation, $-T\Delta S(T,H)/C_o(T)$ scales as $H^{(1-\alpha)/\Delta}$, which for $\alpha > 0$ goes to zero slower than $\mathrm{FWHM}_{\Delta S}$ as $H$ goes to zero. However, to expand $-\Delta S(T+\Delta T_{\mathrm{ad}},H) \simeq -\Delta S(T,H) - \Delta T_{\mathrm{ad}}(C_{\mathrm{mag}}(T,H) - C_{\mathrm{mag}}(T,0))/T$ requires that $\Delta T_{\mathrm{ad}} \ll \mathrm{FWHM}_{\Delta S}$. This evidently becomes an increasingly bad approximation for $H \to 0$ when $\alpha > 0$. Even for $\alpha = 0$, the accuracy of the approximation does not increase as $H \to 0$, and the specific range of validity of the expansion will be determined by the size of the nonsingular specific heat. For large $H$, the approximation, being a first-order expansion, also becomes increasingly poor.

Only for $\alpha \leqslant 0$ and not too large fields can we then use the first-order expression for $-\Delta S$. The integral involving the specific heat in Eq. (20) can be approximated as $(1/T)\int_T^{T+\Delta T_{\mathrm{ad}}} C_{\mathrm{mag}}(T')dT'$. This results in the following equation for $\Delta T_{\mathrm{ad}}$:

$$\Delta T_{\mathrm{ad}} = \frac{-T}{C_{\mathrm{mag}}(T,H)+C_0(T)}\Delta S(T,H) + \frac{1}{C_{\mathrm{mag}}(T,H)+C_0(T)}\left(\Delta T_{\mathrm{ad}} C_{\mathrm{mag}}(T,0) - \int_T^{T+\Delta T_{\mathrm{ad}}} C_{\mathrm{mag}}(T',0)dT'\right). \tag{21}$$

If $\Delta T_{\mathrm{ad}}$ is sufficiently small that both $T$ and $T+\Delta T_{\mathrm{ad}}$ are within the critical region, we can use the general scaling form of the zero-field magnetic specific heat, $C_{\mathrm{mag}}(T,0) = A(|T-T_c|/T_c)^{-\alpha} + K$, where $A$ and $K$ are (undetermined) constants (which can be different above and below $T_c$). At $T = T_c$, we then get

$$\left(1 + \frac{1}{C_{\mathrm{mag}}(T_c,H)+C_0(T_c)}\frac{AT_c^{\alpha}}{1-\alpha}\Delta T_{\mathrm{ad}}^{-\alpha}\right)\Delta T_{\mathrm{ad}} = -\frac{T_c}{C_{\mathrm{mag}}(T_c,H)+C_0(T_c)}\Delta S(T_c,H). \tag{22}$$

The scaling behavior of $\Delta T_{\mathrm{ad}}$ will depend on the relative magnitudes of $C_{\mathrm{mag}}(T_c,H)$, $C_0(T_c)$ and $A$, i.e., on the relative magnitude of the magnetic specific heat at the finite field $H$, the nonsingular specific heat, and the zero-field magnetic specific heat. Some limiting cases can be discerned.

(1) Let us first consider the case $C_0(T_c) + C_{\mathrm{mag}}(T_c,H) \gg A$. Then the second term on the left-hand side of Eq. (22) can be ignored and we get the well-known approximate expression for the adiabatic temperature change at $T_c$: $\Delta T_{\mathrm{ad}} = -T_c\Delta S(T_c,H)/(C_{\mathrm{mag}}(T_c,H) + C_0(T_c))$ [2]. The relative size of $C_0$ and $C_{\mathrm{mag}}$, as well as the field dependence of the latter, will determine the $H$ dependence of the adiabatic temperature change. In the limit that $C_{\mathrm{mag}}(T_c,H) \ll C_0(T_c,0)$, we simply have that $\Delta T_{\mathrm{ad}}$ scales identically to $\Delta S$, i.e., with a scaling exponent of $(1-\alpha)/\Delta$. In the opposite limit, we get $\Delta T = -\mathrm{const.} \times \Delta S/C_{\mathrm{mag}}(T_c,H)$ giving a scaling exponent of $1/\Delta$. The latter result has been derived by Franco *et al.* [10] who claim that the scaling of $\Delta T_{\mathrm{ad}}$ is determined by universal exponents. However, it is only by neglecting the nonsingular contribution to the specific heat that this can be derived. Experimentally, the two terms, $C_{\mathrm{mag}}(T,H)$ and $C_0(T)$, are in fact of the same order of magnitude for many (if not all) second-order materials with a critical temperature at noncryogenic temperatures, including gadolinium [21], nickel [22], and the manganites [23]. This fact makes the field dependence nonuniversal and intermediate between the two limits above.

(2) The other limiting case is $C_0(T_c) + C_{\mathrm{mag}}(T_c,H) \ll A$. Then the second term on the right-hand side of Eq. (22) dominates, as long as $H$ is not very small, and we get a scaling exponent for the adiabatic temperature change between $1/\Delta$ [for $C_{\mathrm{mag}}(T_c,H) \ll C_0(T_c,0)$] and $1/[\Delta(1-\alpha)]$ [for $C_{\mathrm{mag}}(T_c,H) \gg C_0(T_c,0)$]. Experimentally, the condition $C_0(T_c) + C_{\mathrm{mag}}(T_c,H) \ll A$ does not seem to hold except for materials with $T_c$ close to the absolute zero.

To sum up, even at $T = T_c$, there is no exact critical scaling for the adiabatic temperature change. The effective scaling exponent for the field dependence of $\Delta T_{\mathrm{ad}}$ will for small fields be between $1/\Delta$ and $(1-\alpha)/\Delta$, depending on the ratio of the magnetic to the nonsingular specific heat. It may be remarked that since $\alpha$ usually is close to 0, the two extreme values of the exponent can be challenging to distinguish experimentally. As is the case for the isothermal entropy change, the exponent will be field dependent due to the effects of saturation. Below, we investigate the field dependence of the scaling exponents in two model systems.

TABLE II. Parameters used for calculations in the Bean-Rodbell model. For $\eta \leqslant 1$, the critical temperature $T_c$ of the model is equal to $T_0$.

| | | |
|---|---|---|
| spin density | $n_0$ | $3.03 \times 10^{28}$ m$^{-3}$ |
| magnitude of spin | $J$ | 7/2 |
| $g$ factor | $g$ | 2 |
| critical temperature ($\eta = 0$) | $T_0$ | 293 K |
| compressibility | $\kappa$ | $1/(37.9 \times 10^9)$ Pa$^{-1}$ |
| density | $\rho$ | 7900 kg/m$^3$ |
| atomic weight | $M_A$ | 0.157 kg/mol |
| Debye temperature | $\Theta_D$ | 169 K |
| Sommerfeld constant | $\gamma_e$ | 548.5 J/(K$^2$ m$^3$) |

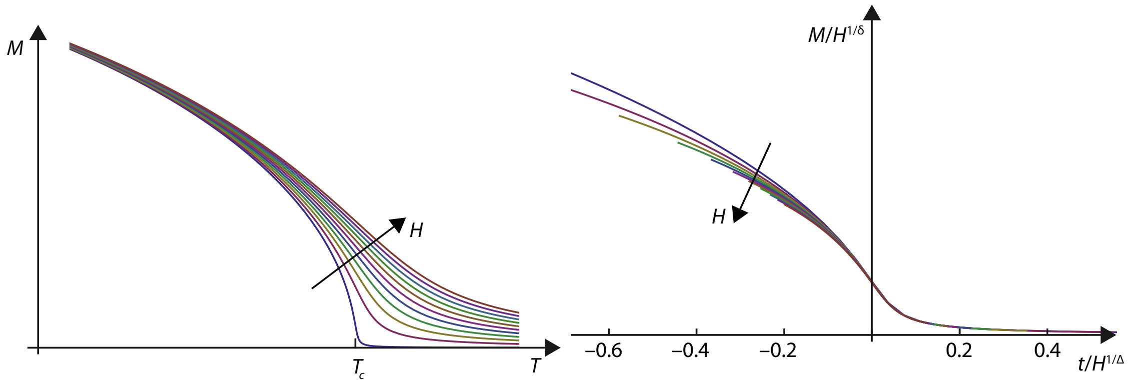

FIG. 3. (Color online) (Left) Magnetization curves for different field values $H$ in a standard mean-field model ($\eta = 0$); $H$ increases in the direction of the arrow. The field range, $\mu_0 H = 0.01$–$2.0$ T, is such that the variation in scaling exponent for $M$ at $T_c$ is negligible. (Right) Rescaled magnetization curves. Close to $T_c$ (and above), the curves collapse to a single curve with scaling exponents $\delta = 3$ and $\Delta = 3/2$, as predicted by scaling theory. However, as the temperature is lowered, the data collapse becomes increasingly imperfect. This is due to the fact that all magnetization curves approach saturation for $T \to 0$.

## V. SCALING IN THE MEAN-FIELD AND BEAN-RODBELL MODELS

First, we consider the mean-field theory. It is well known that this theory in fact does not give a good description of the critical properties close to a second-order phase transition, and that, in particular, it predicts the wrong critical exponents [14]. However, away from the critical point, mean-field theory in many cases gives a reasonable agreement with experiment, and, for this reason, it has been used extensively to calculate magnetocaloric properties [24]. A particular advantage of the mean-field model in the present context is that the total magnetic entropy can be calculated directly from the magnetization. We will also consider the Bean-Rodbell model, which is a generalization of the mean-field model including a coupling of the exchange constant to the spin-spin distance, see Appendix A. A parameter $\eta \geqslant 0$, which depends on the size of this coupling, determines whether the Bean-Rodbell model describes a first-order or a second-order phase transition; for $\eta < 1$, the transition is of second order, with the same critical exponents as the ordinary mean-field model (which corresponds to $\eta = 0$).

The magnetization is calculated by numerically minimizing the free energy, and then the magnetization is used to calculate the magnetic entropy. The nonsingular part of the entropy is calculated using the Debye and Sommerfeld models (see Appendix B). For concreteness, we use the parameters listed in Table II for our calculations. The parameters are those appropriate to a gadoliniumlike material.

Within the mean-field model, the critical exponents are $\alpha = 0$, $\delta = 3$, and $\Delta = 3/2$. In Fig. 3, we show the resulting scaling behavior of the magnetization. It is evident that it is only close to the critical temperature that the magnetization curves collapse to a single curve upon rescaling.

### A. The isothermal entropy change

With the above values of the critical exponents, the critical scaling of the isothermal entropy change in Eq. (10) becomes

$$\Delta S(t,H) = H^{2/3} \tilde{f}_S(t H^{-2/3}). \tag{23}$$

Thus, at the critical temperature, mean-field theory predicts that the magnitude of the isothermal entropy change scales as $H^{2/3}$ [25]. However, it should be noted that this scaling is only

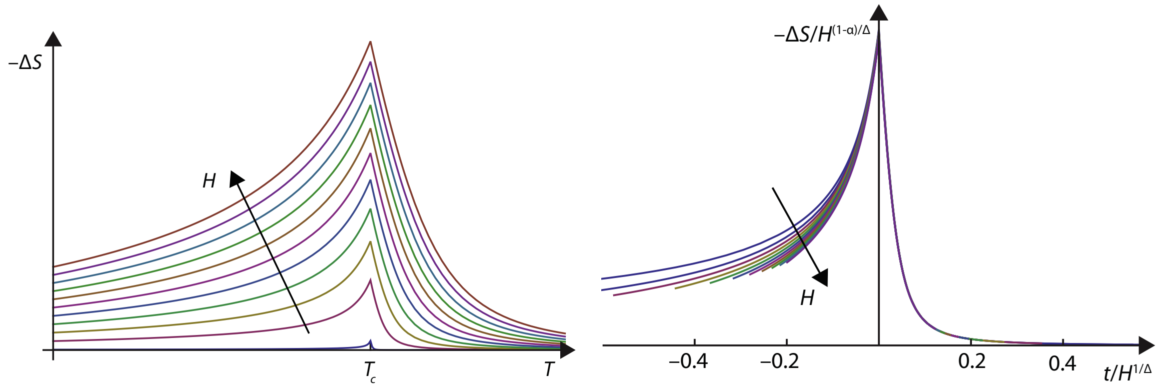

FIG. 4. (Color online) (Left) The isothermal entropy change for different field values $H$ in a standard mean-field model ($\eta = 0$); $H$ increases in the direction of the arrow. The field range is the same as in Fig. 3. (Right) The isothermal entropy change rescaled according to Eq. (10). Close to $T_c$ (and above) the curves collapse to a single curve with the scaling exponents predicted by scaling theory. However, as in the case of the magnetization, the data collapse becomes increasingly imperfect as the temperature is lowered.

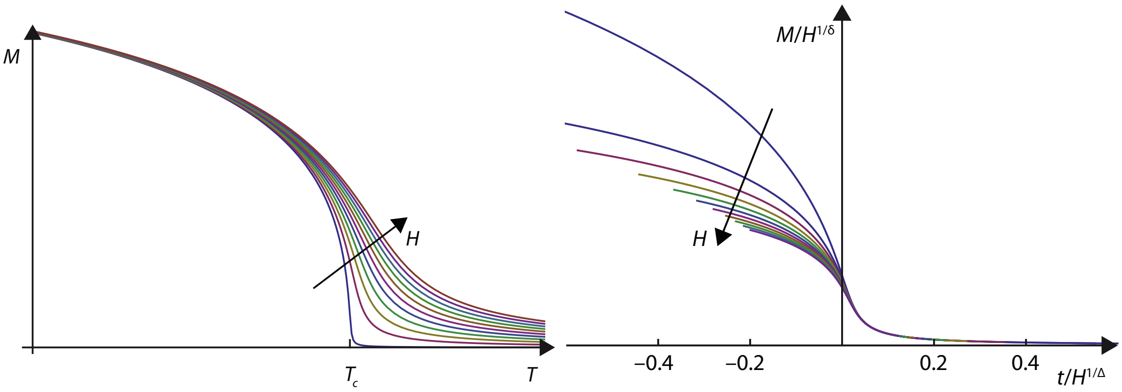

FIG. 5. (Color online) (Left) Magnetization curves for different field values $H$ in a Bean-Rodbell model with $\eta = 0.8$; $H$ increases in the direction of the arrow. The field range is the same as in Figs. 3 and 4. (Right) Rescaled magnetization curves. The scaling exponents for $\eta > 0$ are much more sensitive to $H$ than for $\eta = 0$. In this case even at $T = T_c$ there is not a collapse to a single curve since the low-field and high-field curves scale differently.

strictly valid for small fields. If we numerically calculate the field dependence of $\Delta S$ at $T_c$ and fit the results to a power law, the exponent will depend on the field. For example, for a field of $\mu_0 H = 1$ T, the scaling exponent is changed to 0.66, 1% lower than the low-field, universal value (using parameters appropriate to gadolinium). Although this is probably at the limit of possible experimental validation, it certainly demonstrates that studies claiming to see a deviation from the mean-field exponents of this order of magnitude should carefully state the fitting intervals. As the field is increased, the field dependence of $\Delta S$ at $T_c$ deviates increasingly from the $2/3$ scaling law as the field increases. This can be easily understood once we recall that no matter how large the field is, $-\Delta S(T_c, H)$ is always bounded by $k_B \ln(2J+1)$ per site (or, for a monatomic compound, $k_B \ln(2J+1) N_A/m_A$ per mass, where $k_B$ is Boltzmann's constant and $m_A$ the atomic weight). Thus, if one attempts to fit a power law $aH^b$ to $\Delta S(T_c, H)$, $b$ will decrease monotonously from its low field value of $2/3$ to 0 for (unrealistically) high fields. It should be emphasized that this is not a shortcoming of the mean-field model but rather a strength, showing that it captures the correct limiting values of the entropy (or, equivalently, the saturation of the magnetization). As expected, the local scaling exponent $n(T_c, H)$ shows the same behavior but with a slightly more pronounced field dependence. Thus, in contrast to some statements in the literature [9], the scaling exponent in the mean-field theory depends on the field, even at $T_c$.

In Fig. 4, the scaling behavior of the isothermal entropy change is shown. As is the case for the magnetization, it is only close to $T_c$ that the scaling law applies.

All Bean-Rodbell models share the same critical behavior as that of the standard mean-field model, with a critical scaling of $\Delta S$ given by Eq. (23) at low fields. This can be shown directly by expansion of the free energy given in Eq. (A4) around the critical point. Outside the critical field region this is no longer true. Although the field dependence of the scaling exponent of $\Delta S$ at $T = T_c$ is quite weak for the standard mean-field model, for Bean-Rodbell-like second-order materials having $0 < \eta < 1$ the exponents for finite fields change quickly away from the low field value of $2/3$. In Figs. 5 and 6, we show the scaling behavior of the magnetization and entropy change for $\eta = 0.8$. Even though the field range in the plots is such that scaling is approximately observed at $T = T_C$ in the $\eta = 0$ case, this is far from true here. Indeed, for $\eta > 0$, the exponents depend strongly on $\eta$ even for quite low fields, see Fig. 7. As the magnitude of the spin-lattice interaction increases, i.e.,

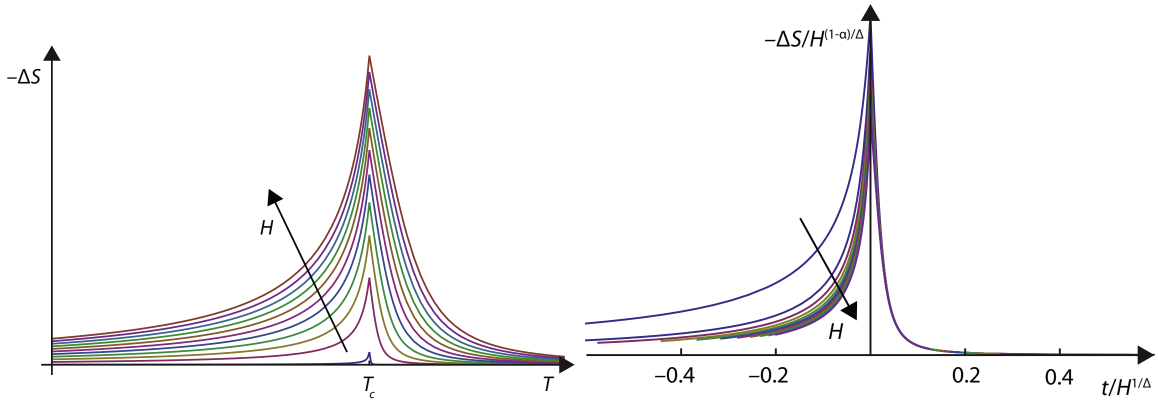

FIG. 6. (Color online) (Left) The isothermal entropy change for different field values $H$ in a Bean-Rodbell model with $\eta = 0.8$; $H$ increases in the direction of the arrow. The field range is the same as in Fig. 5. (Right) The isothermal entropy change rescaled according to Eq. (10). It is seen that the field range is too wide to have a collapse to a single curve at $T = T_c$.

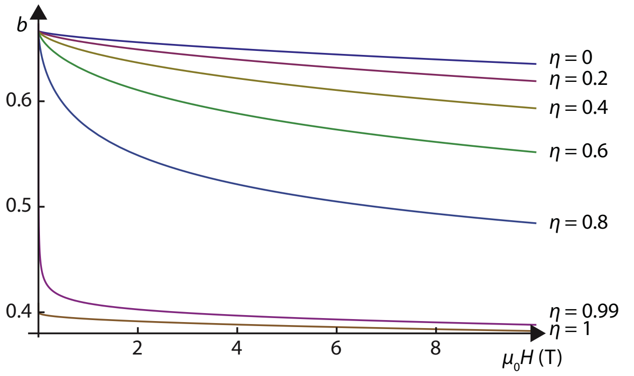

FIG. 7. (Color online) Scaling exponent $b$ for the isothermal entropy change at $T = T_c$ as a function of applied field for different second-order materials described by a Bean-Rodbell model. Note how the scaling exponents for $\eta < 1$ only for low fields approach the exponent $2/3$ derived from scaling theory. For $\eta = 1$, the critical point is tricritical with a low-field scaling exponent of $2/5$. For each $\eta$ and $H$, the exponent was calculated by fitting $\Delta S$ evaluated in 10 field values spaced evenly from 0 to $H$ to a power law.

for growing $\eta$, the deviation of the scaling exponents from their critical values increases rapidly at finite $H$, in agreement with the fact that the size of the critical field region decreases. This is the case even though all systems with $\eta < 1$ belong to the same universality class (in the sense that they have the same critical exponents as the standard mean-field theory). For example, at $\mu_0 H = 1$ T, one can have scaling exponents ranging from 0.66 ($\eta = 0$) to 0.40 ($\eta \to 1^-$), all for model materials with a second-order phase transition. This clearly demonstrates the nonuniversality of the scaling exponent of $\Delta S$ at finite fields, even at $T = T_c$. In Fig. 8, we show the corresponding behavior of the local scaling exponent $n$, evaluated using Eq. (14). Since the derivative of $M$ is only evaluated at finite fields, it is numerically well behaved. The trend of the local scaling exponent is clearly the same as that of the fitted scaling exponent, although $n$ shows a slightly more pronounced field dependence.

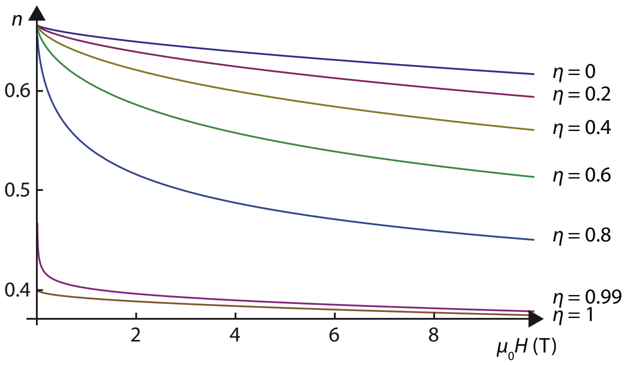

FIG. 8. (Color online) Local scaling exponent $n$ [cf. Eq. (12)] for the isothermal entropy change at $T = T_c$ as a function of applied field for different second-order materials described by a Bean-Rodbell model. Note how the scaling exponents for $\eta < 1$ only for low fields approach the exponent $2/3$ derived from scaling theory. For $\eta = 1$, the critical point is tricritical with a low-field scaling exponent of $2/5$. The behavior of $n$ is similar to that of the scaling exponent $b$ derived from a $\Delta S$ versus $H$ fit.

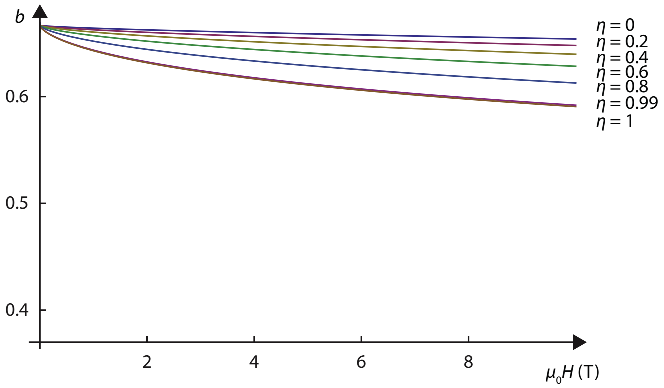

FIG. 9. (Color online) Scaling exponent $b$ for the adiabatic temperature change at $T = T_c$ as a function of applied field for different second-order materials described by a Bean-Rodbell model. Only for low fields do the exponents approach the exponent $2/3$ derived from scaling theory. However, the field dependence of the exponents is weaker than for the isothermal entropy change. The reason that the scaling exponent of $\eta = 1$ is close to $2/3$ is discussed in the text. For each $\eta$ and $H$, the exponent was calculated by fitting $\Delta S$ evaluated in ten field values spaced evenly from 0 to $H$ to a power law. The scale on the $y$ axis is the same as in Fig. 7.

The point $\eta = 1$ separates the line of second-order and first-order transitions, i.e., it is a tricritical point. In this case, the fourth-order term in the expansion of the free energy in powers of $M$ is zero at the critical point; the transition is still continuous but with critical exponents that differ from the standard mean-field exponents. In particular, we have $\alpha = 1/2$, $\beta = 1/4$, $\delta = 5$, and therefore $\Delta = 5/4$ [26]. This makes the scaling exponent of $\Delta S$ equal to 2/5, as is also evident from Figs. 7 and 8. It is seen that the field dependence of the exponent is much weaker for $\eta = 1$. This partly reflects the fact that the scaling exponent is smaller to start out with, making the approach to saturation slower. All models with $\eta < 1$ have a scaling exponent of $2/3$ at low fields. However, as $\eta$ approaches 1, the exponent even at small finite fields quickly approaches that of $\eta = 1$.

### B. The adiabatic temperature change

We calculate the adiabatic temperature change by solving Eq. (18) numerically, as the nonmagnetic entropy can be evaluated directly in the present model. Since $\alpha = 0$ in the Bean-Rodbell model for $\eta < 1$, the adiabatic temperature change is for small fields expected to scale as the isothermal entropy change, i.e., with an exponent of $2/3$. This is borne out by the numerical results shown in Fig. 9. Compared to the isothermal entropy change, the field dependence of the exponents is weaker.

Even though the scaling exponent of $\Delta S$ is 4/5 for $\eta = 1$, the corresponding scaling exponent of the adiabatic temperature change is still close to $2/3$. This is related to the breakdown of the first-order expression for $\Delta T_{\mathrm{ad}}$ discussed above. This can be understood as follows. In the Bean-Rodbell model, as is true for other mean-field models, the zero-field magnetic specific

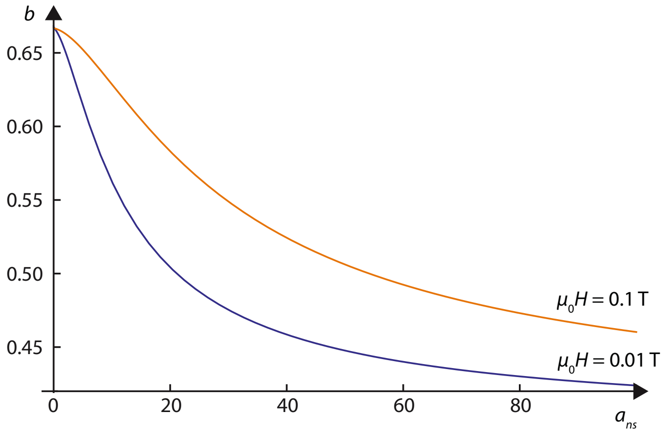

FIG. 10. (Color online) Scaling exponent $b$ for the isothermal entropy change at $T = T_c$ in the Bean-Rodbell model with $\eta = 1$ (tricritical state). The exponent is plotted as a function of the magnitude of the nonsingular specific heat, which is varied by multiplying the nonsingular specific heat derived from the Debye and Sommerfeld models with a factor $a_{ns}$. Only for $a_{ns} \gg 1$, i.e., large nonsingular specific heat, does the scaling exponent begin to differ markedly from 2/3. Two different fields are shown, $\mu_0 H = 0.01$ and 0.1 T. In the low-field case, the exponent approaches the scaling value $1/\Delta = 2/5$ as $a_{ns} \to \infty$.

heat is identically zero for $T > T_c$. This means that for $T \geqslant T_c$ the equation for the adiabatic temperature change becomes

$$\frac{C_0(T)}{T}\Delta T_{\text{ad}} = -\Delta S(T + \Delta T_{\text{ad}}, H); \qquad (24)$$

in addition, $\alpha = 0$ in this temperature range. Focusing, in particular, on $T = T_c$ and considering $C_0(T_c)$ as a parameter, we see that $\Delta T_{\text{ad}}$ diverges as $C_0(T_c) \to 0$. This means that for small $C_0$, $T_c + \Delta T_{\text{ad}}$ will lie far beyond the critical region, beyond the validity of the scaling form and the first-order expansion of $\Delta S$. Instead, the high-temperature "Curie-Weiss" form of $\Delta S$ can be used, $\Delta S = -C_{\text{C-W}} H^2/(T - T_c)^2$, where $C_{\text{C-W}}$ is a constant (this can be derived by using $M = C_{\text{C-W}} H/(T - T_c)$ together with the Maxwell relation). Then Eq. (24) becomes

$$\Delta T_{\text{ad}}^3 = \frac{T_c C_{\text{C-W}}}{C_0(T_c)} H^2, \qquad (25)$$

i.e., a scaling exponent of 2/3. Only in the limit of $C_0(T)$ becoming very large do we recover the scaling exponent $1/\Delta = 2/5$, see Fig. 10.

## VI. THE ARROTT-NOAKES EQUATION OF STATE

Going beyond the mean-field model, one can consider the so-called Arrott-Noakes equation of state [27]. This is an empirical equation of state originally put forward as a convenient way to fit the magnetization data of nickel close to its Curie point. By construction the equation exhibits perfect critical scaling behavior for all values of $H$, $M$, and $T$. The equation in itself is of no deep theoretical significance but should be considered as a succinct way of encapsulating the temperature and field dependence of the magnetization close to $T_c$, essentially being a first-order expansion around that point [28]. In particular, it can not be expected to hold for high fields [29], and for $T \to 0$ the Arrott-Noakes equation predicts a dependence of $M$ on $H$, which is not negligibly small as it should be [30]. Therefore the results of using the Arrott-Noakes equation for large reduced temperatures or high fields should be treated with caution.

TABLE III. Parameters for nickel used in the present paper in the Arrott-Noakes equation of state.

| | |
|---|---|
| $\gamma$ | 1.31 |
| $\beta$ | 0.395 |
| $T_c$ | 626.94 K |
| $T_1$ | 0.309 K |
| $M_1$ | $39.5 \times 10^3$ A/m |

The Arrott-Noakes equation of state is defined for arbitrary scaling exponents $\beta$ and $\gamma$ as follows [27]:

$$\left(\frac{4\pi H}{M}\right)^{1/\gamma} = \frac{T - T_c}{T_1} + \left(\frac{M}{M_1}\right)^{1/\beta}, \qquad (26)$$

where $\beta$ and $\gamma$ as well as the parameters $T_1$ and $M_1$ in principle are determined experimentally (the factor of $4\pi$ appears when using SI units). The magnetization derived from Eq. (26) obeys the scaling relation, Eq. (6), for *all* $T$ and $H$. Therefore the same is true of the isothermal entropy change. Indeed, the scaling exponent for $\Delta S(T_c, H)$ is completely independent of $H$ which, as we argued above, is an unphysical result. In effect, using the Arrott-Noakes equation one has assumed that the critical region extends throughout the entire temperature axis and that there are no corrections to scaling. Of course, this makes the equation of state of limited relevance when one wants to discuss the scaling or lack of scaling far from $T_c$ or for high fields.

For concreteness, we use the parameters for nickel given by Arrott and Noakes in their original paper in the calculations below [27]. However, the value of $\alpha = -0.08$ derived from their choice of $\gamma$ and $\beta$ deviates slightly from the commonly accepted value of $\alpha = -0.1$ deduced directly from specific heat measurements [22]. To make the equation of state consistent with the singular specific heat used below, we adjust $\beta$ by hand (from the Arrott-Noakes value of 0.3854 to 0.395) to make $\alpha = -0.1$. This does not change the conclusions markedly. The parameters used are listed in Table III.

### A. The isothermal entropy change

We calculate the isothermal entropy change numerically using the following expression:

$$\Delta S(T,H) = -\mu_0 \frac{\gamma}{4\pi T_1} \int_{M_0(T)}^{M(T,H)} M \left[\frac{T - T_c}{T_1} + \left(\frac{M}{M_1}\right)^{1/\beta}\right]^{\gamma - 1} dM, \qquad (27)$$

where $M_0(T)$ is the zero-field (saturation) magnetization at the given temperature (see Appendix C). Both $M_0(T)$ and the upper integration limit $M(T,H)$ are obtained from a numerical solution of the Arrott-Noakes equation.

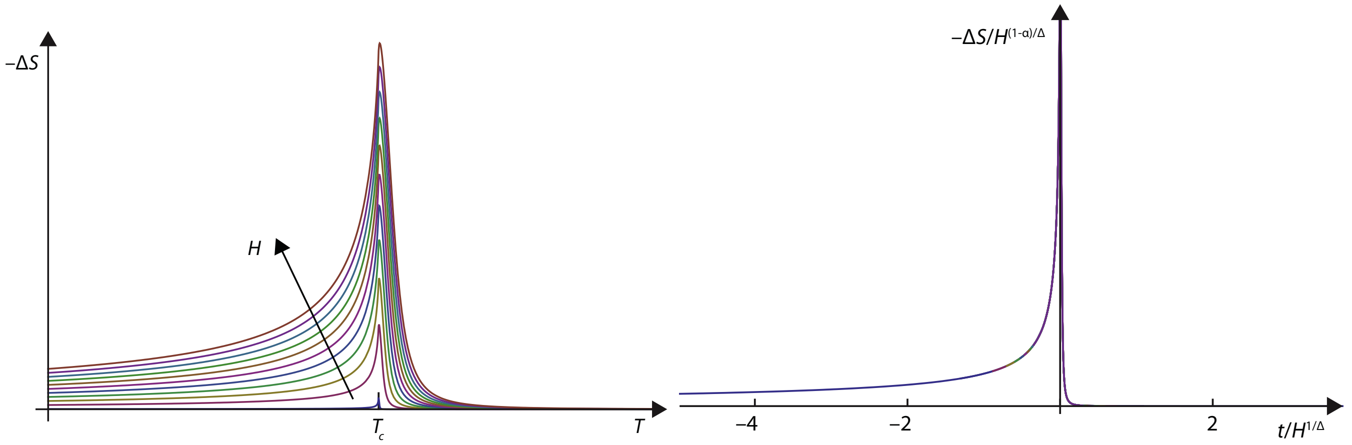

FIG. 11. (Color online) (Left) The isothermal entropy change for different field values $H = 0.01$–$2$ T in the Arrott-Noakes model; $H$ increases in the direction of the arrow. (Right) The isothermal entropy change rescaled according to Eq. (10). Over the entire temperature range the curves collapse to a single curve with the scaling exponents predicted by scaling theory. This is an artefact of the perfect scaling assumed in the Arrott-Noakes equation of state.

In Fig. 11, we plot the isothermal entropy change for a range of fields. Since the magnetization obeys perfect scaling in the Arrott-Noakes equation, it is not surprising that $\Delta S$ does as well.

In contrast to the mean-field case, the maximum of $-\Delta S$ is attained at a (field dependent) temperature above $T_c$. It should also be noted that the derivative of $\Delta S$ with respect to temperature is discontinuous at $T = T_c$. The local exponent $n(t,H)$ can be evaluated for the Arrott-Noakes equation using the following expression:

$$n(t,H) = -\frac{\mu_0 H M(t,H)}{\Delta S(t,H)} \times \frac{1}{\frac{1}{\gamma}T_c t + \left(\frac{1}{\beta}+\frac{1}{\gamma}\right)T_1\left(M(t,H)/M_1\right)^{1/\beta}}. \tag{28}$$

The Arrott-Noakes equation is defined for arbitrary $\beta$ and $\gamma$. In particular, one can consider the Arrott-Noakes equation with the mean-field values $\beta = 1/2$ and $\gamma = 1$. However, this does not make the scaling behavior identical to that of the mean-field theory which, as noted above, does not exhibit perfect scaling for all field and temperature values. This also means that the local scaling exponents for the Arrott-Noakes "mean-field" theory cannot be taken as representative of the behavior of the mean-field theory at finite fields. In Fig. 12, we compare the local scaling exponent derived from two different mean-field models ($\eta = 0$ and $\eta = 0.8$) and that of the Arrott-Noakes equation with the same critical exponents; the value of $T_1$, which determines how fast $n$ approaches its limiting values, has been adjusted such that the scale of variation on the $t$ axis is comparable to the two mean-field models. In the mean-field models, the curves do not meet at $T_c$ (although the deviation is not very large for $\eta = 0$); such behavior is by construction excluded in the Arrott-Noakes case.

### B. The adiabatic temperature change

Even though the isothermal entropy change derived from the Arrott-Noakes equation of state exhibits perfect scaling for all $T$ and $H$ with a universal exponent, this is not true of the adiabatic temperature change due to the influence of the nonsingular heat capacity. To investigate the field dependence of the adiabatic temperature change, we use a similar form of the nonsingular specific heat as above, with a Debye temperature of 390 K and a Sommerfeld constant (per mass) of $9.84 \times 10^{-2}$ J/K$^2$ kg appropriate for Ni [20]. The zero-field magnetic specific heat we take as [22]

$$C_{\text{mag}}(t,0) = \begin{cases} A'(-t)^{-\alpha} + K' & \text{for} \quad T < T_c, \\ At^{-\alpha} + K & \text{for} \quad T > T_c, \end{cases} \tag{29}$$

where the values of the four constants are $A = 27.4$ J/kg K, $A' = 24.1$ J/kg K, $K = 230$ J/kg K, and $K' = 267$ J/kg K. We then solve Eq. (20) numerically.

With the parameters used for nickel, $C_{\text{mag}}$ is about 20% of $C_0$ at $T_c$. This means that the scaling of the adiabatic temperature change will be almost the same as that of the isothermal entropy change. Indeed, numerically one finds an exponent for $\Delta T_{\text{ad}}$ at $T_c$ of 0.655 at low fields, and only varying about 1% between 0 and 10 T. This is very close to the scaling exponent of the entropy change, $(1-\alpha)/\Delta = 0.645$, and significantly different from $1/\Delta = 0.587$ (since we are using the full expression, Eq. (20), the exponent can lie slightly outside the interval $[1/\Delta,(1-\alpha)/\Delta]$). If one varies the relative magnitude of the singular and the nonsingular specific heat in the model, the scaling exponent $1/\Delta$ is only approached in the limit where the singular term dominates, in accordance with the general discussion in Sec. IV above.

## VII. FIRST-ORDER TRANSITIONS

We will only briefly consider first-order transitions here. Close to a first-order transition there will in general not be critical scaling in the classical sense due to the relative unimportance of fluctuations. For example, a Bean-Rodbell type transition (with $\eta > 1$) takes place from a ferromagnetic state far below its nominal critical temperature to a high-temperature state far into the paramagnetic regime. From a scaling point of view, the fact that both the magnetization and the entropy change from being discontinuous at $T_c$ to

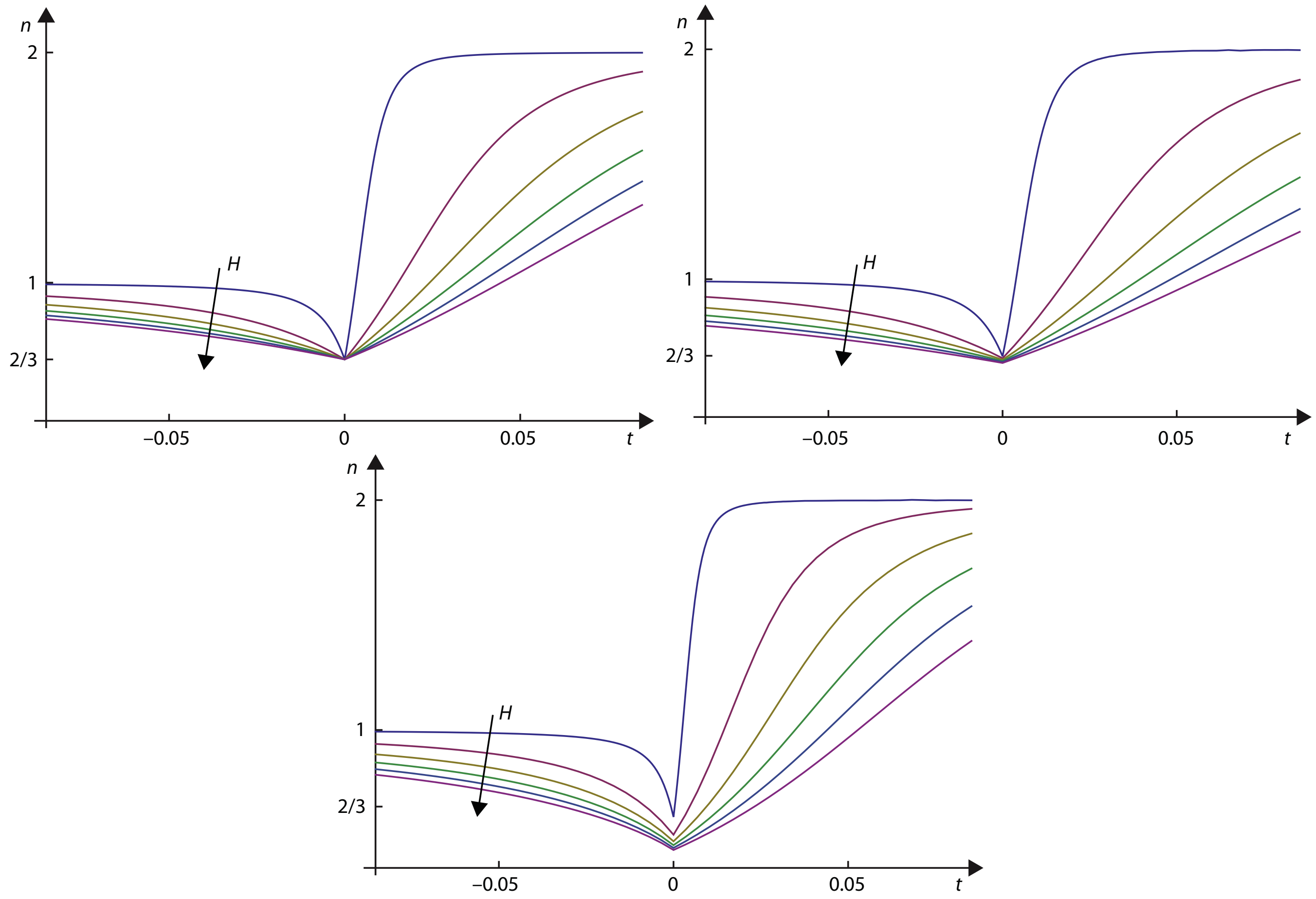

FIG. 12. (Color online) (Top left) The local scaling exponent derived from the Arrott-Noakes equation of state with mean-field exponents $\beta = 1/2$ and $\gamma = 1$; the field range is 0.1–5 T. (Top right) The local scaling exponent derived from the mean-field model ($\eta = 0$) for the same field range. (Bottom) The local scaling exponent for a Bean-Rodbell model with $\eta = 0.8$ and the same field range.

being continuous as the applied field increases, means that they cannot be rescaled to a single curve. Even so, the general expression, Eq. (19), is of course still applicable as long as nonequilibrium effects connected with hysteresis are unimportant and the decomposition of the entropy is meaningful.

The general behavior of the magnetocaloric quantities can be understood quantitatively from an examination of the full entropy curves for $H = 0$ and $H > 0$, respectively. Figure 13 shows the quantitative behavior of the entropy. For $H = 0$, there is a discontinuity in $S(T,H)$ for $T = T_c$. The magnitude is given by $L$, the latent heat associated with the phase transition. The main effect of applying a finite field is to move the discontinuity towards higher temperatures (we assume that the field is still low enough that the discontinuity does not disappear). This means that the shape of the $\Delta S$ curve will be more or less rectangular, peaking at $T_c$ and having a width which increases as a function of applied field. The maximum adiabatic temperature change will be given by the width of the $\Delta S$ curve, as shown graphically in the figure; above $T_c$ the adiabatic temperature change rapidly decreases as a function of temperature with a slope of $-1$ [31], giving rise to a characteristic asymmetric, triangular curve form. As a consequence $\Delta S$ considered as a function of field at $T_c$ (and above) will be a constant plus a field dependent term, i.e. it will not depend on field as a power law. The field dependence of $\Delta T_{\rm ad}$ will be the same as that of $dT^*/dH$ [where $T^*(H)$ is the temperature for which $\Delta S(T,H)$ is discontinuous], which for strongly first-order materials experimentally seems to be close to linear in $H$ near $T_c$ [32].

These remarks can be made more precise by calculating the field dependence of the magnetocaloric quantities within the Bean-Rodbell model with $\eta > 1$. This model has been used several times previously to describe magnetocaloric materials with a first-order transition [33–35]. In Figs. 14 and 15, we show $\Delta S$ and $\Delta T_{\rm ad}$ for a weakly first-order ($\eta = 1.1$) and a strongly first-order ($\eta = 1.75$) material. In the first case, the entropy curves do not exhibit the plateau like behavior seen in the $\eta = 1.75$ case. This is due to the fact that the entropy curves become continuous at a much lower field for $\eta = 1.1$. As $\eta$ becomes larger, the plateau becomes more pronounced, and the corresponding curves for the adiabatic temperature change become increasingly asymmetric around $T_c$. Both for $\Delta S$ and $\Delta T_{\rm ad}$, the position of the peak is practically unchanged as a function of $H$, and the curves mainly broaden on the high temperature side as the field is increased.

In Fig. 16, the isothermal entropy change at $T_c$ (which itself is a function of $\eta$) is plotted as a function of field for different values of $\eta$. It is apparent that the curves extrapolate to a finite intersection of the axis, with a value which increases as the transition becomes more strongly first-order, i.e., $\eta$ increases.

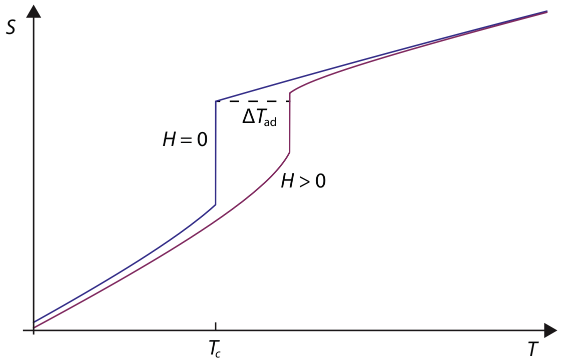

FIG. 13. (Color online) Representative entropy curves for a material with a first-order transition at $T_c$. The main effect of the applied field is to move the discontinuity towards higher temperatures. The isothermal entropy change, which is found by subtracting the two curves from each other, will exhibit two discontinuities as a function of temperature. The maximum adiabatic temperature change is given by the distance between the two discontinuities as shown. For sufficiently high fields, the $H > 0$ curve becomes continuous and $\Delta S$ will only have one discontinuity. The curves are calculated from the Bean-Rodbell model with $\eta = 1.75$.

The corresponding adiabatic temperature change of course extrapolates to 0 for $H \to 0$. If it is fitted to a power law, the exponent depends on both field and $\eta$. For the field range considered in here, the exponent changes from close to 2/3 for $\eta$ close to 1 to almost linear for $\eta = 2$.

Thus, for the first-order models considered here, the maximum isothermal entropy change does not scale with the field as a power law, while the maximum adiabatic temperature change scales with a field (and $\eta$) dependent exponent, which, in general, is larger than 2/3.

## VIII. PHENOMENOLOGICAL SCALING APPROACHES

In several papers, Franco and coworkers have proposed a phenomenological scaling approach to the understanding of the magnetocaloric quantities [9,10]. It is based on the claim that in different fields, "states" that have the same value of $\Delta S/\Delta S_{\mathrm{peak}}$ are equivalent and should fall on the same point on a "universal" curve [9]. The scaling is carried out on a set of $\Delta S(T,H_i)$ curves, measured in different fields $H_i$. Each curve is rescaled such that the peak corresponds to the value 1, and then the temperature axis is shifted and rescaled to make all curves pass through the points $(0,1)$, $(-1,h)$ and $(1,h)$, where $h$ is a number between 0 and 1, which, in principle, can be chosen arbitrarily. The procedure can be described as plotting $\Delta S(\theta,H_i)/\Delta S(0,H_i)$, where the new temperature variable $\theta$ is defined as

$$\theta = \begin{cases} \frac{T-T_{\mathrm{peak}}(H)}{T_{\mathrm{peak}}(H)-T_{r1}(H)} & \text{if} \quad T \leqslant T_{\mathrm{peak}}(H) \\ \frac{T-T_{\mathrm{peak}}(H)}{T_{r2}(H)-T_{\mathrm{peak}}(H)} & \text{if} \quad T > T_{\mathrm{peak}}(H) \end{cases}, \tag{30}$$

where $T_{r,i}(H)$ is defined as the temperature at which $\Delta S$ has fallen to a fraction $r$ of its peak value [with $T_{r1}(H) < T_{\mathrm{peak}}(H) < T_{r2}(H)$] [16,36]. Using a single $T_r$ both above and below the peak temperature has also been considered [9].

This is certainly a succinct way of summarizing a collection of experimental curves. The approach has been used for a number of different materials, including Gd [10], $(\mathrm{Er}_{1-x}\mathrm{Dy}_x)\mathrm{Al}_2$ [37], FeMoCuB amorphous alloys [38], hitperm- and nanoperm-type alloys [39,40], and Fe-B-Cr-based amorphous alloys [41], and in many cases the rescaled curves for an individual material do collapse onto a single curve.

From a theoretical point of view, it is somewhat misleading to talk of "states" being associated with the magnetocaloric quantities (which are defined as the difference between two *different* states). Apart from this, it may be asked whether scaling theory lends support to the phenomenological approach. It is notable that many of the results are obtained on alloys which can have considerable impurity content and which certainly are not single crystal. However, any impurity content tends to smear out the sharpness of the phase transition and makes the observation of scaling very difficult. Even in relatively pure samples of, e.g., gadolinium or nickel, scaling of the susceptibility is only observed at a reduced temperature of

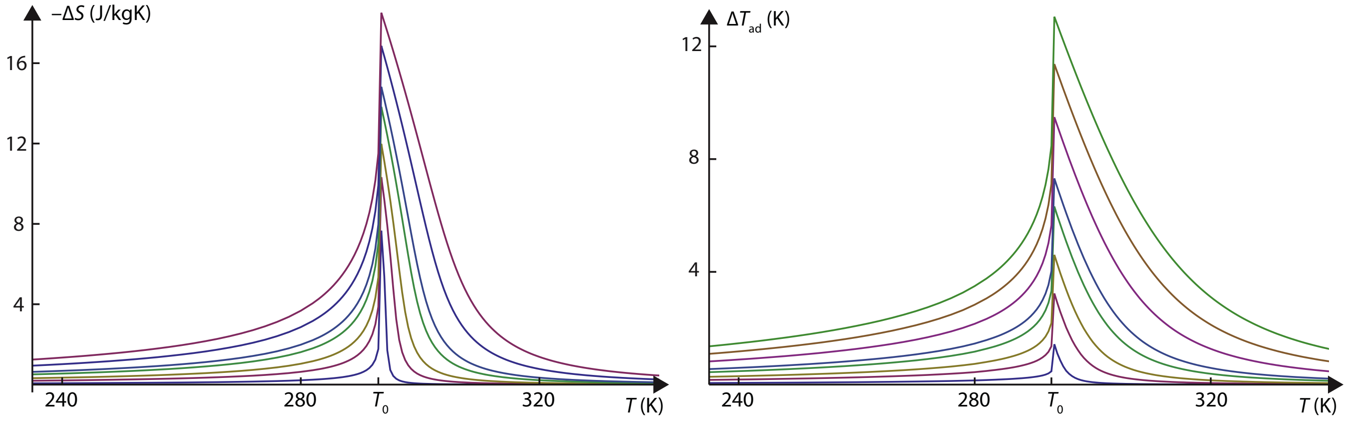

FIG. 14. (Color online) The isothermal entropy change (left) and the adiabatic temperature change (right) as calculated within the Bean-Rodbell model with $\eta = 1.1$. This corresponds to a weakly first-order material, only for very low fields will the entropy curves be discontinuous; for the entire field range 0.1–2 T considered here, the entropy curves are continuous. This means that $\Delta S$ will only exhibit one discontinuity as a function of temperature. In addition, $T_c$ will be close to $T_0$, the transition temperature in the absence of spin-lattice interaction. The entropy curves do not exhibit a pronounced plateau but the adiabatic temperature change is still asymmetric with respect to $T = T_c$.

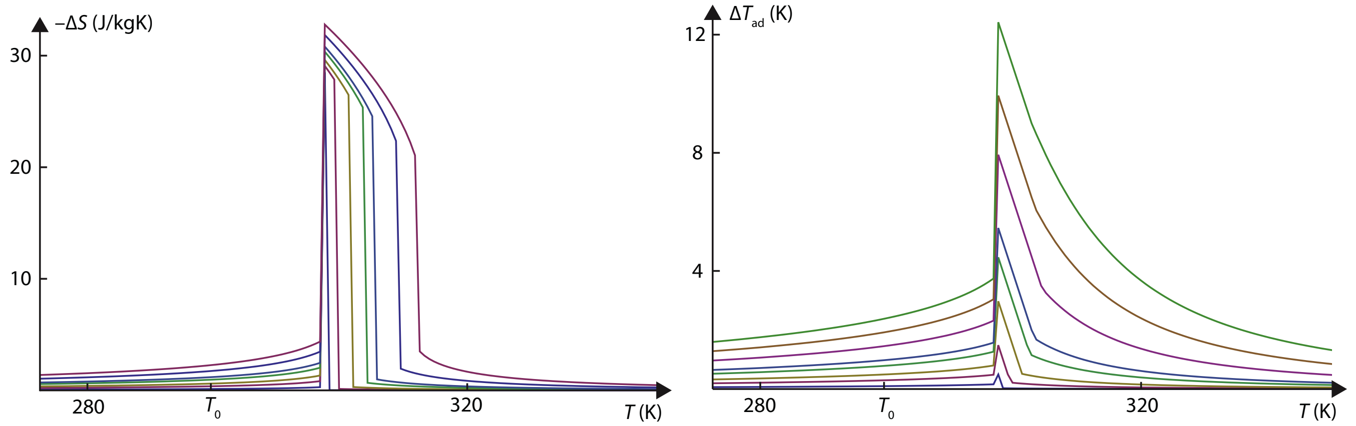

FIG. 15. (Color online) The isothermal entropy change (left) and the adiabatic temperature change (right) as calculated within the Bean-Rodbell model with $\eta = 1.75$. This corresponds to a strongly first-order material, and the entropy curves are discontinuous for the entire field range 0.1–2 T. This gives rise to two discontinuities in the $\Delta S$ curve, resulting in a characteristic plateaulike behavior. Note also the significant shift in critical temperature with respect to $T_0$.

about 2–5 $\times$ $10^{-2}$, as noted above, while extracting a single power law or logarithm from the zero-field specific heat often requires $|t| \lesssim 10^{-2}$ [15]. The latter corresponds to an interval of about 3 K at either side of $T_c$ for a transition temperature near room temperature. On the other hand, the $\Delta S$ curves of many of the materials considered have significantly larger widths (easily 20–50 K on either side of $T_c$) in the usual range of experimental fields (1–10 T). This corresponds to reduced temperatures of perhaps 0.1 or higher. Since a value of the order of 0.5 is usually chosen for $h$ in the phenomenological approach, even the interval $-1 < \theta < 1$ goes far beyond the experimentally observed critical region. This means that critical scaling cannot be invoked as the reason for the collapse of the curves. Closest to $T_c$ ($\theta = 0$), where the scaling hypothesis is expected to apply (at least in a limited field range), the constrained nature of the rescaling where all phenomenologically scaled curves pass through the same three points $(-1,h)$, $(0,1)$, $(1,h)$ means in any case that, as Franco and coworkers acknowledge themselves, "the deviation from collapse cannot be very large, as the curves coincide by construction" [42].

It is of interest to note that mean-field theories can show different degrees of collapse for $\theta < -1$. In Figs. 17 and 18, we show the phenomenological scaling for both $\eta = 0$ and $\eta = 0.8$ for a field range of 0.01–2 T. In both cases, an almost perfect collapse is seen for $-1 < \theta < 1$. As mentioned, this is due to the highly constrained nature of the scaling procedure in this interval. Nevertheless, it is remarkable since the case of $\eta = 0.8$ is very far from exhibiting universal scaling (cf. the discussion above). On the low-temperature side, the collapse for $\eta = 0$ becomes increasingly imperfect (this seems to be due to the effects of saturation) while $\eta = 0.8$ shows almost perfect scaling here also. Thus different mean-field models can show different degrees of collapse, and the model most closely showing critical scaling close to $T_c$ is the one which deviates most from the phenomenological scaling behavior at low temperatures.

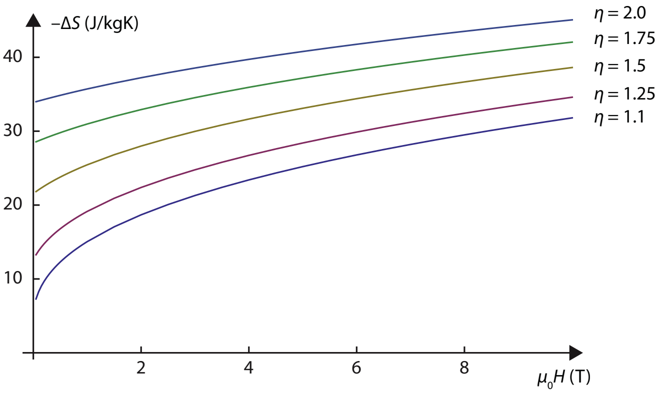

FIG. 16. (Color online) The isothermal entropy change at $T_c$ for different first-order Bean-Rodbell models. The extrapolated intersection with the $y$ axis increases as $\eta$ increases, and the field dependence of $\Delta S$ becomes more and more unlike a power law.

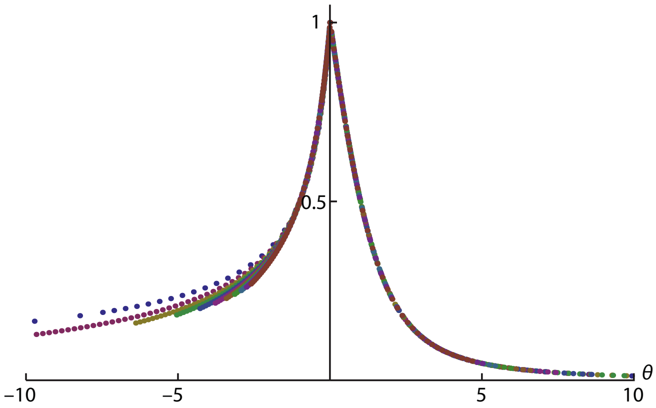

FIG. 17. (Color online) Phenomenological scaling of the isothermal entropy change $\Delta S$ in the standard mean-field model ($\eta = 0$); the field range is 0.01–2 T, and $h = 0.5$. The collapse to a single curve becomes increasingly imperfect as the temperature becomes lower ($\theta < -1$).

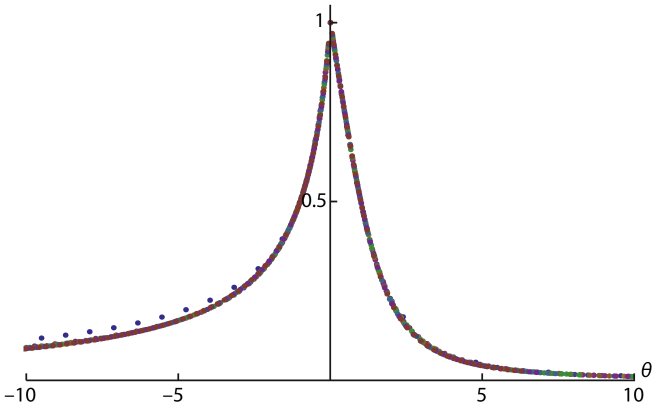

FIG. 18. (Color online) Phenomenological scaling of the isothermal entropy change $\Delta S$ in the Bean-Rodbell model ($\eta = 0.8$); the field range is 0.01–2 T, and $h = 0.5$. For this field range, $\Delta S$ does not scale with a single exponent at $T = T_c$. Even so, a nearly perfect collapse to a single curve is seen for all $\theta$.

### A. First-order materials

The question of how to distinguish experimentally between a first-order and a second-order transitions from measurements of the magnetocaloric quantities has been discussed extensively in the literature. From a fundamental point of view, the identification of a transition as first-order requires measurement of a finite latent heat associated with it. This can be achieved using sophisticated calorimetry [43,44]. The Banerjee criterion is often used to deduce the order of the transition based only on magnetic measurements [45]; however, this presupposes the validity of a Landau expansion of the free energy. On the other hand, it would be useful to have an experimental criterion based on the isothermal entropy change calculated from magnetization curves which is still the most common way in the literature to measure the magnetocaloric effect. It has been proposed that a useful criterion is whether the $\Delta S$ curves, calculated from magnetization measurements, exhibit the phenomenological scaling collapse to a single curve [46]. This means that second-order materials should exhibit the collapse, while first-order materials should not. Since the curves are constrained close to $T_c$, the authors state: "Within the range $-1 < \theta < 0$ the collapse is real in second-order transitions and only apparent in first-order transitions. Therefore the effect of the order of the transition is decisive only below $\theta = -1$, in this phenomenological approach." However, far from $T_c$ scaling is in general not obeyed, and we have seen above that the collapse for some second-order models becomes increasingly imperfect at low temperatures ($\theta < -1$). So a lack of collapse here does not necessarily mean than the transition is first-order. On the other hand, experimentally some first-order materials are seen to exhibit collapse of their full $\Delta S$ curves [2].

This question can be investigated theoretically within the context of the Bean-Rodbell model for $\eta > 1$. Since the $\Delta S$ curves are discontinuous at $T = T_c$, it is, in general, not possible to find a reference temperature $T_{r1}(H) < T_c$ for which $\Delta S(T_{r1},H) = h\Delta S(T_c,H)$. However, the curves can be scaled using only a single reference temperature $T_{r2}(H)$. When the discontinuity above $T_c$ is large, $T_{r2}(H)$ will fall on the discontinuity; then the rescaling breaks down and the rescaled curves no longer all pass through $(1,h)$. Large discontinuities will of course also be visible in the $\Delta S$ curves themselves. However, small discontinuities will tend to smear out experimentally, and the interesting question becomes whether weakly first-order materials can be identified by their phenomenological scaling behavior.

In Fig. 19, we show the rescaled $\Delta S$ curves for a weakly first-order material ($\eta = 1.1$) and a strongly first-order material ($\eta = 1.7$). We see that the weakly first-order material exhibits scaling behavior which in practical terms is indistinguishable from that of a second-order material. The fact that both second-order and first-order models can show the presence or absence of this scaling behavior seems to preclude using the experimental fact of phenomenological collapse to draw strong conclusions about the order of the phase transition or the underlying microscopics.

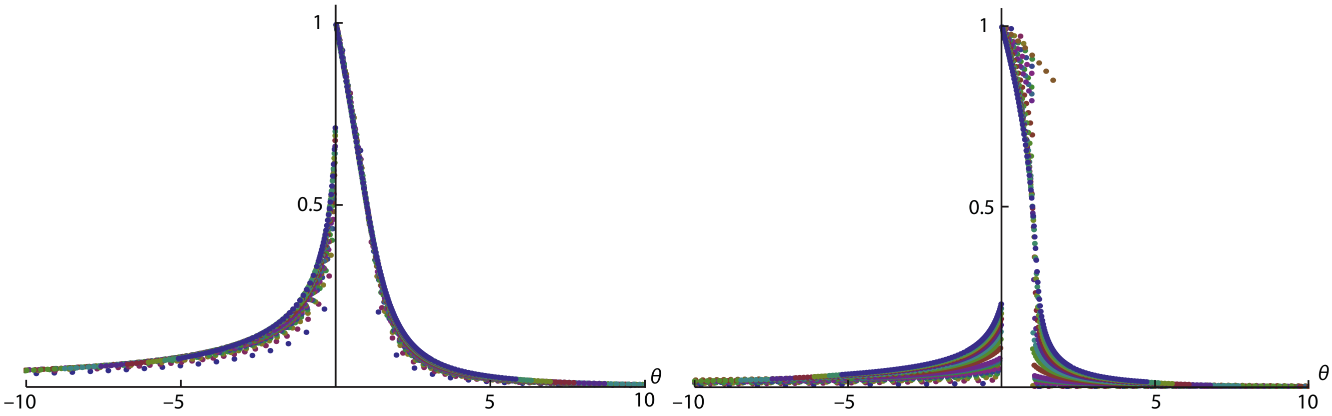

FIG. 19. (Color online) (Left) Phenomenological scaling of the isothermal entropy change $\Delta S$ in a weakly first-order mean-field model ($\eta = 1.1$); the field range is 0.1–5 T, and $h = 0.5$. Only a single reference temperature $T_{r2}(H)$ is used. Even though the model is first-order, there is an approximate collapse to a single curve. (Right) Phenomenological scaling of the isothermal entropy change $\Delta S$ in a strongly first-order mean-field model ($\eta = 1.75$); the field range is 0.1–5 T, and $h = 0.5$. Only a single reference temperature $T_{r1}(H)$ is used. The breakdown of the scaling procedure is obvious.

## IX. DISCUSSION AND CONCLUSION

In this paper, we have investigated the scaling of the magnetocaloric quantities within the context of the theory of critical phenomena. We have shown that a universal scaling exponent $(1-\alpha)/\Delta$ characterizes the isothermal entropy change only close to $T_c$ and for a limited field range. By explicitly calculating the scaling exponents for $\Delta S$ in a range of second-order Bean-Rodbell models all sharing the same critical exponents, we demonstrate that at finite fields, the exponents not only become field dependent but also exhibit a marked dependence on additional model parameters, making them nonuniversal. This is true over a large interval in fields, including those of practical interest, i.e., of the order of 1–10 T.

For the adiabatic temperature change, we have shown that, in general, there is no universal scaling exponent associated with the adiabatic temperature change since it is determined by both the singular and the nonsingular parts of the entropy. This means that the field dependence of the adiabatic temperature change will depend on the ratio between the singular and the nonsingular specific heat. However, when the two are of comparable size, as is the case in many materials, the exponent characterizing the field dependence of $\Delta T_{\mathrm{ad}}$ for $T = T_c$ will be intermediate between $(1-\alpha)/\Delta$ and $1/\Delta$. Since $\alpha$ typically is small, of the order of $-0.1$, experimental validation of this requires careful measurements corrected for demagnetization and domain effects.

For first-order materials, the field dependence of $\Delta S$ is offset by a constant term corresponding to the latent heat associated with the transition. The adiabatic temperature change can still be fitted to a power law dependence on field for $T = T_c$; for the Bean-Rodbell model, the exponent can vary from close to 2/3 for weakly first-order materials to 1 for strongly first-order materials, with a limited dependence on field.

Finally, we have discussed the phenomenological scaling procedure for magnetocaloric measurements proposed by Franco *et al.* and argued that it can not be theoretically justified by an appeal to scaling theory. Furthermore, we have shown within the context of the Bean-Rodbell model that there is no one-to-one connection between the behavior of the phenomenological scaling procedure and the order of the phase transition. This seems to make the phenomenological scaling procedure of limited value for probing the order of the phase transition of a given material.

## ACKNOWLEDGMENTS

This work was in part financed by the ENOVHEAT project, which is funded by the Danish Council for Strategic Research (Contract No. 12-132673) within the Programme Commission on Sustainable Energy and Environment.

## APPENDIX A: THE BEAN-RODBELL MODEL

For reference, we briefly summarize the expressions for the free energy, the magnetization and the magnetic entropy in the Bean-Rodbell model. The Bean-Rodbell model is basically a mean-field model in which the exchange constant $\lambda$ is assumed to depend on the spin-spin distance as $\lambda = \lambda_0(1+\beta\frac{V-V_0}{V_0})$, where $V_0$ is the volume of the lattice in the absence of exchange interactions and $\beta$ is a parameter. This leads to a spin-lattice coupling which, if sufficiently strong, makes the phase transition between the magnetic and nonmagnetic phase first-order. The magnetic entropy per unit volume has the same form as in the standard mean-field model:

$$S_{\mathrm{mag}} = k_B\frac{N}{V}\left[\ln\frac{\sinh\left(\frac{2J+1}{2J}x\right)}{\sinh\left(\frac{1}{2J}x\right)} - xB_J(x)\right], \tag{A1}$$

where $N/V$ is the number density of spins and each spin has a magnitude of $J$. The Brillouin function $B_J(x)$ is

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right), \tag{A2}$$

and $x = \gamma_{\mathrm{el}}(H+\lambda M)J/(k_BT)$, where $\gamma_{\mathrm{el}}$ is the electron $g$ factor.

The free energy as a function of temperature, field, and pressure is

$$F(T,H,p;M,V) = -TS_{\mathrm{mag}} - \mu_0MH - \frac{1}{2}\lambda\mu_0M^2 + \frac{1}{2\kappa}\frac{(V-V_0)^2}{V_0^2} + p\frac{V-V_0}{V_0}, \tag{A3}$$

where $M$ and $V$ has to be determined from the condition that $F$ should be a minimum; $\kappa$ is the isothermal compressibility. The minimization with respect to $V$ is straightforward and we get (putting the pressure $p = 0$):

$$F(H,T;M) = -k_BT\frac{N}{V_0}\ln\frac{\sinh\left(\frac{2J+1}{2J}x'\right)}{\sinh\left(\frac{1}{2J}x'\right)} + \frac{1}{2}\lambda_0\mu_0M^2 + \frac{3}{8}\lambda_0^2\beta^2\kappa\mu_0^2M^4 \tag{A4}$$

with $x' = \gamma_{\mathrm{el}}J[H+\lambda_0(1+\frac{1}{2}\lambda_0\beta^2\kappa M^2)M]/(k_BT)$. To get the equilibrium magnetization as a function of field and temperature, we have to do a (numerical) minimization of $F$ with respect to $M$. This magnetization can then be inserted into Eq. (A1) to get the magnetic entropy.

It turns out that the phase transition is continuous if $\eta \leqslant 1$ where the Bean-Rodbell parameter $\eta$ is

$$\eta = 40\frac{N}{V}\kappa(k_BT_0)\beta^2\frac{[J(J+1)]^2}{(2J+1)^4-1}. \tag{A5}$$

Here, $T_0$ is the transition temperature for $\beta = 0$. For $0 < \eta \leqslant 1$, the transition is second-order but with scaling exponents which for finite fields depend on $\eta$, as discussed in the text above.

## APPENDIX B: THE NONMAGNETIC CONTRIBUTIONS TO THE ENTROPY

We assume that the pure lattice contribution to the entropy takes the Debye form:

$$S_{\mathrm{Debye}}(T) = -3\frac{N_{\mathrm{atom}}}{V}k_B(\ln(1-e^{-\Theta_D/T}) - 4D(\Theta_D/T)), \tag{B1}$$

where $\Theta_D$ is the Debye temperature and $D(\tau)$ is the Debye function

$$D(\tau) = \frac{1}{\tau^3}\int_0^\tau \frac{x^3}{e^x - 1}dx. \tag{B2}$$

For the entropy associated with the conduction electrons, we assume a Sommerfeld model where

$$S_{\mathrm{el}} = \gamma_e T, \tag{B3}$$

where $\gamma_e$ is a constant which can be calculated in a free electron model or be deduced experimentally from low temperature measurements of the specific heat.

## APPENDIX C: THE ISOTHERMAL ENTROPY CHANGE IN THE ARROTT-NOAKES EQUATION OF STATE

To calculate the isothermal entropy change for a material obeying the Arrott-Noakes equation of state, Eq. (26), we use the Maxwell relation in the form

$$\Delta S(T,H) = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T}\right)_{H'} dH'. \tag{C1}$$

From the Arrott-Noakes equation, we get

$$\begin{aligned}\left(\frac{\partial M}{\partial T}\right) &= \left(\frac{\partial T}{\partial M}\right)^{-1}\\ &= -M\left[\frac{1}{\gamma}(T - T_c) + \left(\frac{1}{\beta} + \frac{1}{\gamma}\right)T_1\left(\frac{M}{M_1}\right)^{1/\beta}\right]^{-1}.\end{aligned} \tag{C2}$$

Inserting into Eq. (C1) and changing the integration variable from $H$ to $M$ gives the final result [47]:

$$\begin{aligned}\Delta S(T,H) = -\mu_0 \frac{\gamma}{4\pi T_1}\int_{M_0(T)}^{M(T,H)} M'\\ \times\left[\frac{T - T_c}{T_1} + \left(\frac{M'}{M_1}\right)^{1/\beta}\right]^{\gamma - 1} dM',\end{aligned} \tag{C3}$$

where $M_0(T)$ is the zero field (saturation) magnetization at the given temperature and the upper integration limit $M(T,H)$ is obtained from a numerical solution of the Arrott-Noakes equation. This expression for $\Delta S$ as an integral over $M$ avoids the numerically troublesome derivative of the magnetization in the vicinity of $T_c$.

---

[1] K. A. Gschneidner, Jr. and V. K. Pecharsky, Int. J. Refrig. **31**, 945 (2008).

[2] A. Smith, C. R. H. Bahl, R. Bjørk, K. Engelbrecht, K. K. Nielsen, and N. Pryds, Adv. Energy Mater. **2**, 1288 (2012).

[3] A. Smith, Eur. Phys. J. H **38**, 507 (2013).

[4] P. Weiss and A. Piccard, J. Phys., 5th series **7**, 103 (1917).

[5] P. Weiss and R. Forrer, Comptes Rendus **178**, 1448 (1924).

[6] P. Weiss and R. Forrer, Annales de Physique (Paris), 10th series **5**, 153 (1926).

[7] J. Mathon and E. Wohlfarth, J. Phys. C **2**, 1647 (1969).

[8] J. E. Noakes and A. S. Arrott, AIP Conf. Proc. **10**, 899 (1973).

[9] V. Franco and A. Conde, Int. J. Refrig. **33**, 465 (2010).

[10] V. Franco, A. Conde, J. M. Romero-Enrique, Y. I. Spichkin, V. I. Zverev, and A. M. Tishin, J. Appl. Phys. **106**, 103911 (2009).

[11] V. Franco, A. Conde, J. M. Romero-Enrique, and J. S. Blázquez, J. Phys.: Condens. Matter **20**, 285207 (2008).

[12] H. Stanley, Rev. Mod. Phys. **71**, S358 (1999).

[13] A. Hankey and H. Stanley, Phys. Rev. B **6**, 3515 (1972).

[14] J. J. Binney, N. J. Dowrick, A. J. Fisher, and M. E. J. Newman, *The Theory of Critical Phenomena* (Oxford University Press, Oxford, 1992).

[15] L. P. Kadanoff, W. Götze, D. Hamblen, R. Hecht, E. A. S. Lewis, V. V. Palciauskas, M. Rayl, J. Swift, D. Aspnes, and J. Kane, Rev. Mod. Phys. **39**, 395 (1967).

[16] V. Franco, J. S. Blázquez, and A. Conde, Appl. Phys. Lett. **89**, 222512 (2006).

[17] T. D. Shen, R. B. Schwarz, J. Y. Coulter, and J. D. Thompson, J. Appl. Phys. **91**, 5240 (2002).

[18] V. Franco, A. Conde, M. D. Kuz'min, and J. M. Romero-Enrique, J. Appl. Phys. **105**, 07A917 (2009).

[19] A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Applications* (Institute of Physics Publishing, Bristol and Philadelphia, 2003).

[20] R. Pawel and E. Stansbury, J. Phys. Chem. Solids **26**, 757 (1965).

[21] S. Y. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **57**, 3478 (1998).

[22] D. Connelly, J. Loomis, and D. Mapother, Phys. Rev. B **3**, 924 (1971).

[23] H. Yang, H. Huang, P. Ho, W. Huang, C. Huang, S. Mollah, S. Liu, and J. Lin, Physica B **329**, 801 (2003).

[24] J. S. Amaral, S. Das, and V. S. Amaral, in *Thermodynamics - Systems in Equilibrium and Non-Equilibrium*, edited by J. C. Moreno-Piraján (InTech, Rijeka, Croatia, 2011), Chap. 8.

[25] H. Oesterreicher and F. T. Parker, J. Appl. Phys. **55**, 4334 (1984).

[26] L. Landau and E. Lifshitz, *Statistical Physics, Part 1*, 3rd ed. (Pergamon Press, Oxford, 1988).

[27] A. Arrott and J. E. Noakes, Phys. Rev. Lett. **19**, 786 (1967).

[28] A. Aharoni, J. Magn. Magn. Mater. **58**, 297 (1986).

[29] A. Aharoni, J. Appl. Phys. **56**, 3479 (1984).

[30] T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

[31] K. K. Nielsen, C. R. H. Bahl, and A. Smith, Phys. Rev. B **81**, 054423 (2010).

[32] L. Caron, Z. Q. Ou, T. T. Nguyen, D. T. Cam Thanh, O. Tegus, and E. Brück, J. Magn. Magn. Mater. **321**, 3559 (2009).

[33] O. Tegus, G. X. Lin, W. Dagula, B. Fuquan, L. Zhang, E. Brück, F. R. de Boer, and K. H. J. Buschow, J. Magn. Magn. Mater. **290-291**, 658 (2005).

[34] E. Z. Valiev, J. Exp. Theor. Phys. **108**, 279 (2009).

[35] J. H. Belo, J. S. Amaral, A. M. Pereira, V. S. Amaral, and J. P. Araujo, Appl. Phys. Lett. **100**, 242407 (2012).

[36] Q. Y. Dong, H. W. Zhang, J. R. Sun, B. G. Shen, and V. Franco, J. Appl. Phys. **103**, 116101 (2008).
[37] V. Franco, A. Conde, V. K. Pecharsky, and K. A. Gschneidner, Jr., Europhys. Lett. **79**, 47009 (2007).
[38] V. Franco, C. Conde, J. S. Blázquez, A. Conde, P. Švec, D. Janičkovič, and L. F. Kiss, J. Appl. Phys. **101**, 093903 (2007).
[39] V. Franco, C. F. Conde, J. Blázquez, M. Millán, and A. Conde, J. Appl. Phys. **102**, 013908 (2007).
[40] V. Franco, J. S. Blázquez, and A. Conde, J. Appl. Phys. **103**, 07B316 (2008).
[41] J. Y. Law, V. Franco, and R. V. Ramanujan, Appl. Phys. Lett. **98**, 192503 (2011).
[42] C. M. Bonilla, J. Herrero-Albillos, F. Bartolomé, L. M. García, M. Parra-Borderías, and V. Franco, Phys. Rev. B **81**, 224424 (2010).
[43] K. Morrison, J. Lyubina, K. Sandeman, L. Cohen, A. Caplin, J. Moore, and O. Gutfleisch, Phil. Mag. **92**, 292 (2012).
[44] V. Basso, C. P. Sasso, and M. Küpferling, Rev. Sci. Instrum. **81**, 113904 (2010).
[45] B. Banerjee, Phys. Lett. **12**, 16 (1964).
[46] C. M. Bonilla, F. Bartolomé, L. M. García, M. Parra-Borderías, J. Herrero-Albillos, and V. Franco, J. Appl. Phys. **107**, 09E131 (2010).
[47] V. Franco, R. Caballero-Flores, A. Conde, Q. Y. Dong, and H. W. Zhang, J. Magn. Magn. Mater. **321**, 1115 (2009).