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Abstract

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Analytical Parametrization for Magnetization of Gadolinium based on Scaling Hypothesis

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Gadolinium, which has a Curie temperature of 293 K, has been served as the reference material for the room-temperature magnetic energy conversion. Using the scaling hypothesis and universality class of phase transition, we propose an analytical parametrization of Gd magnetization ($M(T, H)$) for fields up to 5 T and temperatures between 250 and 340 K. The key step is to fit the single-variable scaling function, beyond the leading divergent term, that well describes the entire two-variable $M(T, H)$ near the Curie temperature. Constraints of the scaling function are derived and are used to construct the parametrization form. A stable fitting algorithm based on separating the length scale is introduced. The final expression is analytical, well defined at Curie temperature, and is validated by comparing to experiments including the magnetization and the specific heat. The proposed parametrization turns the knowledge of scaling hypothesis into an efficient and accurate scheme that quantitatively describes the material near the second-order transition. This advantage can become significant when considering realistic applications.

I. INTRODUCTION

Magnetic refrigeration is considered to be one of the promising and environmentally friendly alternatives to the existing vapour-compression technology [1, 2]. It uses the magnetocaloric mechanism where the temperature can be controlled by varying the applied magnetic field, and this effect is particularly pronounced when the material is close to the magnetic phase transition. Gadolinium (Gd) is typically served as the reference magnetocaloric material for room-temperature magnetic energy conversion [3–8]. Gd is considered to be a simple Heisenberg ferromagnet [9–11] with a second-order paramagnetic–ferromagnetic phase at the Curie temperature $T_c = 293$ K [11, 12]. The first step to consider any applications involving magnetocaloric effect is to have a faithful representation for the material equation of states – the magnetization as a function of temperature and field $M(T, H)$. For Gd, Mean Field (MF) theory has been used as the primary tool to generate $M(T, H)$ which is usually sufficient for a reasonable estimation [5, 8, 13]. However, MF theory by construction cannot fully capture the spatial fluctuations which become important near the critical point. For this reason it is very difficult to fine-tune MF theory to better match the experiments. From a more practical aspect, MF equation is implicit and takes iterations to get M at a given field and temperature. If the field or temperature itself also has to be determined iteratively (e.g. demagnetization effect), using MF can become time consuming; an explicit $M(T, H)$ is practically useful.

Close to the second-order phase transition, the equation of states near the critical point exhibits a phenomenon of “data collapse” [14–16]. For the magnetic phase transition the two-variable equation of states $M(T, H)$ can be completely described by a single-variable *scaling* function $F(x)$ when properly scaling M, H by the reduced temperature $t = \frac{T-T_c}{T_c}$ to some *critical exponents* [17]. This observation can be efficiently described by the static scaling hypothesis [18, 19] and eventually derived from the renormalization group (RG) theory [20, 21]. Ideally critical exponents depend only on the universality class, but in reality their values should be strictly determined from measurements and are material specific [9]. Typically the scaling function is analyzed up to the leading divergent order [14–16, 22], which is sufficient to derive the relationships among various critical exponents (scaling laws) [23, 24]. In this work, we propose to parametrize the entire scaling function $F(x)$; by doing so we are able to construct an analytical expression of Gd magnetization $M(T, H)$ for $H \lesssim 5$ T (Tesla) and T ranging from 250 K to 340 K; the total specific heat $C_v(T, H)$ can be reasonably described over the same range of (T, H) once the zero-field $C_v(T, H = 0)$ is given. In this application, the usefulness of the scaling hypothesis is to isolate the singular behavior so that an efficient and accurate evaluation (i.e., an analytical expression) of $M(T, H)$ can be constructed. A crucial step is to derive the required analytical properties of the scaling functions from general considerations so only legitimate functions are included in the first place. Fitting a multi-parameter function is tricky and a stable procedure resembling numerical RG [25, 26] that separates the length scale will be introduced. The resulting equation of states and its derivatives are analytical, explicit, and well defined at T_c . Our results will be compared with the magnetization, entropy, and specific heat measured by Dan’kov et.al. reported in Ref. [11].

The paper is organized as follows. In Section II we review the MF theory and show its intrinsic inadequacy. We then propose to fit the scaling function to better capture the behavior near the phase transition. By some general consideration we derive conditions that the scaling function has to satisfy, based on which the analytical form of the parametrized function is constructed. In Section III we describe the procedure on how the scaling functions are determined from magnetization measurements. In Section IV magnetic entropy, adiabatic temperature change, and specific heat are computed and compared to experiments. Comments on the universal scaling method [27, 28], which are very relevant to the problem of interest, will also be given. A brief conclusion is given in Section V. In Appendix we explore the flexibility of the parametrization. Given that the parametrization form is not unique, we provide another two sets of fitting results to illustrate this degree of freedom.

II. MAGNETIZATION PARAMETRIZATION

A. Reference: mean field theory

We begin our discussion by briefly summarizing MF theory which will be used as a baseline reference. Denoting \bar{M} to be the magnetic moment per Gd ion, MF theory gives an implicit equation $\bar{M} = f(T, H, \bar{M})$ from which we can get \bar{M} at a given temperature T and field H . To simplify the notation, the field H is understood as $\mu_0 H$ in mks unit and will be measured in Tesla throughout the paper (i.e., flux density B and field strength H are the same). With this notation the MF equation reads [29, 30]

$$\bar{M}(T, H) = Jg\mu_B \cdot B_J \left(\frac{Jg\mu_B \cdot (H + \bar{\lambda}\bar{M})}{k_B T} \right) \equiv M_0 B_J \left(\frac{\bar{M}_0}{M_0} \frac{H + \bar{\lambda}\bar{M}}{k_B T} \right) \quad (1)$$

$$\text{with } \bar{\lambda} = \frac{3k_B T_c}{J(J+1)(g\mu_B)^2}.$$

μ_B is the Bohr magneton, k_B is the Boltzmann constant, J is the total angular momentum, and g is the g-factor. For Gd the angular momentum comes from 7 unpaired 4f-electron spins so $J = \frac{7}{2}$ and $g = 2$ [13]. $B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$ is the Brillouin function. Eq. (1) indicates that the maximum moment of Gd is $\bar{M}_0 = Jg\mu_B \approx 7\mu_B$. There are no fitting parameters in Eq. (1): T_c is obtained experimentally and J, g are intrinsic properties of the Gd ion. To compute the magnetic entropy we will need $\partial_T \bar{M}(H, T)$ [see Eq. (8)]:

$$\left[\frac{\partial \bar{M}}{\partial T} \right]_H = \frac{\left[\frac{-H + \bar{\lambda}\bar{M}}{T} \right] \frac{dB_J(x)}{dx} \Big|_{x=\frac{M_0(H + \bar{\lambda}\bar{M})}{k_B T}}}{\frac{k_B T}{M_0^2} - \bar{\lambda} \frac{dB_J(x)}{dx} \Big|_{x=\frac{M_0(H + \bar{\lambda}\bar{M})}{k_B T}}}. \quad (2)$$

Notice $\bar{M}(H, T)$ is the solution of MF Eq. (1) and has to be solved iteratively. The magnetization M is given $M = n_{\text{Gd}} \bar{M}$ with n_{Gd} the number density of Gd. Given the Gd saturation moment $\bar{M}_0 = 7\mu_B$, the saturation magnetization is $n_{\text{Gd}} \bar{M}_0 \approx 1950 \frac{\text{emu}}{\text{cm}^3}$ [using Gd specific volume of $19.9 \frac{\text{cm}^3}{\text{mol}}$] which also corresponds to $247 \frac{\text{emu}}{\text{g}}$ [using Gd density of $7.9 \frac{\text{g}}{\text{cm}^3}$].

B. Scaling hypothesis and inadequacy of MF theory

Near the 2nd-order transition, several material properties (e.g., magnetization, specific heat, etc.) exhibit the power-law divergence $\sim T - T_c^{\eta_1}$ and H^{η_2} . Critical exponents of different quantities are not independent and their relationships, referred to as scaling laws, can be derived from the static scaling hypothesis [17]. For magnetic systems, the scaling hypothesis implies that the singular part of magnetic free energy \tilde{G} near T_c can be expressed as [14, 15]

$$\tilde{G}(T, H) = -t^{\beta+\beta\delta} G \left(\frac{H}{t^{\beta\delta}} \right). \quad (3)$$

Derivatives of the free energy give the magnetization

$$M(T, H) = -\frac{\partial \tilde{G}}{\partial H} = t^{\beta} G' \left(\frac{H}{t^{\beta\delta}} \right), \quad (4)$$

and the magnetic contribution of the specific heat

$$C_{v,\text{mag}}(T, H) = -T \frac{\partial^2 \tilde{G}}{\partial T^2}. \quad (5)$$

Here $t = \frac{T - T_c}{T_c}$ is the dimensionless reduced temperature. $G(x)$ is referred to as the scaling function. β, δ are two critical exponents whose values depend on the universality class. Our best fitting gives $\beta = 0.368$ and $\delta = 4.22$, consistent with values of 3D Heisenberg universality class (see Table 12.1 of Ref. [22]).

Because we shall rely mainly on the measured magnetization, we introduce the magnetic scaling function $F(x) = G'(x)$ based on which Eq. (4) becomes

$$\frac{M(T, H)}{t^{\beta}} = F \left(\frac{H}{t^{\beta\delta}} \right) = \begin{cases} F^+(H/t^{\beta\delta}) & T > T_c, \\ F^-(H/t^{\beta\delta}) & T < T_c. \end{cases} \quad (6)$$

Notice that $F(x)$ and $G(x)$ are both single-variable functions so the integration constant K in $\int F(x)dx \equiv \tilde{F}(x) + K = G(x)$ has no dependence on either H or T . Eq. (6) implies that the two-variable equation of states $M(T, H)$ is completely encoded in the single-variable $F(x)$; this data collapse of Gd magnetization is shown in 1(a) and (b) where the experimental $M(T, H)$ is taken from Ref. [11]. The same data collapse applies to MF $M(T, H)$ [i.e., solutions of Eq. (1)] with exponents $\beta_{\text{MF}} = 0.5$ and $\delta_{\text{MF}} = 3$ [see 1(b)]. Because of the wrong critical exponents, MF theory can never completely match the experiments. Actually MF theory by construction does not properly account for the spatial fluctuations that become increasingly crucial when approaching the phase transition [14, 15]. To better describe the measured equation of states, the natural strategy is to use the correct critical exponents in the first place and fit the material-specific scaling function.

Our approach is to fit $F(x)$ because $M(T, H)$ is usually accessible and accurately measured from experiments. Once $F(x)$ is known, the magnetization, entropy, and specific heat near the transition can be computed accordingly. We point out there are constraints on $F(x)$ so that equations of states and its derivatives are well defined near the critical point, and a proper parametrization of the scaling function is very essential in fitting $F(x)$ for the following two reasons. First, we need $F(x)$ for $x \in [0, \infty)$ which requires extrapolation of measurements. $F(x)$ diverges at $x \rightarrow \infty$, and the wrong asymptotic behavior will lead to a divergent $M(T, H)$. Moreover, any experimental uncertainty of magnetization will be magnified by $t^{-\beta}$ so that the experimental $F(x)$ becomes less reliable at large x . In the next two sections we derive general constraints based on which the parametrization form $F(x)$ is determined.

C. Magnetic entropy change

Starting from $M(T, H) = t^\beta F\left(\frac{H}{t^{\beta\delta}}\right)$, its partial derivatives are

$$\frac{\partial M}{\partial H} = \frac{t^\beta}{t^{\beta\delta+1}} F'\left(\frac{H}{t^{\beta\delta}}\right), \quad (7a)$$

$$\begin{aligned} \frac{\partial M}{\partial T} &= \frac{1}{T - T_c} \left[\beta M(T, H) - \beta \delta \cdot H \frac{\partial M}{\partial H} \right] \\ &= \frac{1}{T - T_c} \left[(\beta + \beta \delta) M(T, H) - \beta \delta \frac{\partial(MH)}{\partial H} \right]. \end{aligned} \quad (7b)$$

In Eq. (7b) the integration by part $H \frac{\partial M}{\partial H} = \frac{\partial(MH)}{\partial H} - M$ is used. Eq. (7) holds for both $T > T_c$ and $T < T_c$. Using Eq. (7b) one can compute the isothermal magnetic entropy change using $\Delta S_{\text{mag}} = \int dH \frac{\partial S}{\partial H} = \int dH \frac{\partial M(H, T)}{\partial T}$ ($\frac{\partial S}{\partial H} = \frac{\partial M}{\partial T}$ from Maxwell relation):

$$\begin{aligned} \Delta S_{\text{mag}}(T, H) &= \int_0^H dH \frac{\partial M}{\partial T} = \frac{1}{T - T_c} \left[(\beta + \beta \delta) \int_0^H dHM(T, H) - (\beta \delta) \cdot H \cdot M(T, H) \right] \\ &= \frac{t^{\beta+\beta\delta}}{T - T_c} \left[(\beta + \beta \delta) \int_0^{\bar{x}} dx' F(x') - (\beta \delta) \cdot \bar{x} \cdot F(\bar{x}) \right] \\ &= \text{sgn}(t) \frac{t^{\beta+\beta\delta-1}}{T_c} \left[(\beta + \beta \delta) \int_0^{\bar{x}} dx' F(x') - (\beta \delta) \cdot \bar{x} \cdot F(\bar{x}) \right] \end{aligned} \quad (8)$$

where $\bar{x} = \frac{H}{t^{\beta\delta}}$. Same result can be obtained from the free energy $\Delta S_{\text{mag}}(T, H) = -\frac{\partial \tilde{G}(T, H)}{\partial T} \Big|_{H=0}^{H=H}$. The last expression of Eq. (8) shows there would be a jump in ΔS_{mag} across T_c if $F^+(0) = F^-(0)$. Given that this is not observed, $F^+(0)$ has to be different from $F^-(0)$. Eq. (8) also indicates that for a given H and t we only need to know the $F(x)$ from $x = 0$ to $x = \frac{H}{t^{\beta\delta}}$. In this sense, the scaling function $F(x)$ at small x controls the system far away from the transition (large t) whereas its asymptotic property determines the system close to the critical point (small t).

To facilitate later discussion we consider an x -offset power-law scaling function $F(x) = (x + d)^{-\alpha_1}$. Substituting $F(x)$ and $\int dx F(x) = \frac{(x+d)^{1-\alpha_1}}{1-\alpha_1}$ into Eq. (8) gives

$$\begin{aligned} \Delta S_{\text{mag}}(T, H) &\rightarrow \Delta \tilde{S}_{\text{mag}}^{\text{pl}}(H, T; d, \alpha_1) \\ &= \left\{ \frac{1}{T_c} |t|^{\beta(1+\alpha_1\delta)-1} H^{1-\alpha_1} \left[\frac{\beta + \beta \delta}{1 - \alpha_1} \left(1 + \frac{d \cdot |t|^{\beta\delta}}{H}\right)^{1-\alpha_1} - \beta \delta \left(1 + \frac{d \cdot |t|^{\beta\delta}}{H}\right)^{-\alpha_1} \right] \right. \\ &\quad \left. - \frac{1}{T_c} \frac{\beta + \beta \delta}{1 - \alpha_1} d^{1-\alpha_1} \cdot |t|^{\beta\delta+\beta-1} \right\} \text{sgn}(t). \end{aligned} \quad (9)$$

$\Delta \tilde{S}_{\text{mag}}^{\text{pl}}(T, H; d, \alpha_1)$ is an analytical function of T, H parametrized by an x -offset d and an exponent $-\alpha_1$. The superscript ‘pl’ indicates the power-law form of $F(x)$. The H -independent term vanishes as $t \rightarrow 0$ because $\beta \delta + \beta - 1 \approx 0.92 > 0$. Eq. (9)

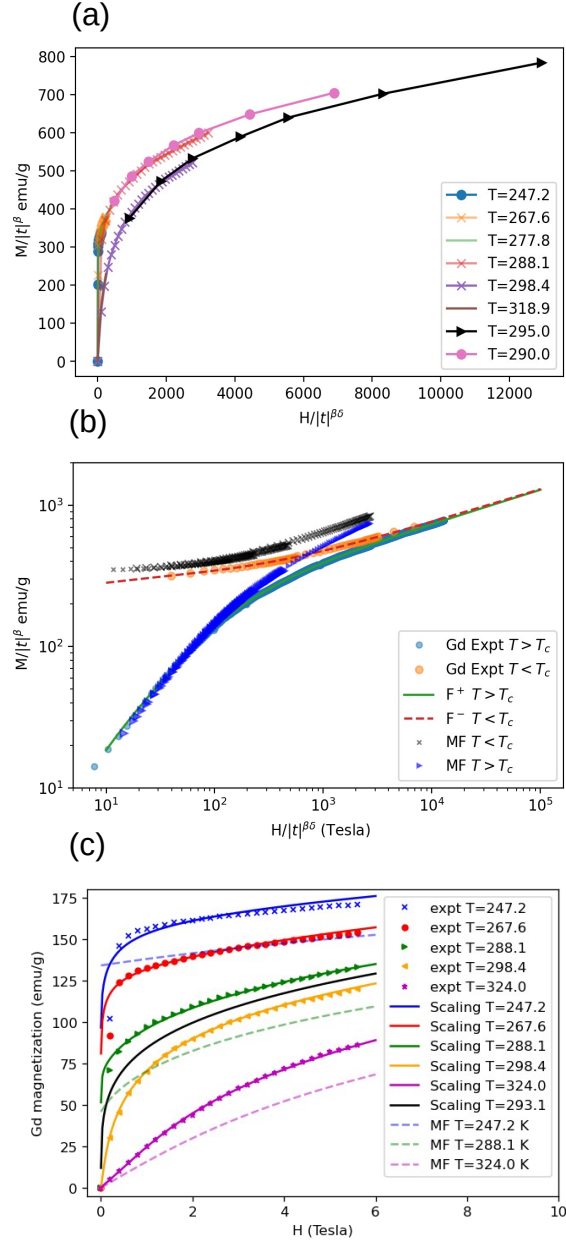


FIG. 1: (a) Measured $M(H, T)$ plotted in the reduced state variables $\frac{M}{|t|^\beta}$ and $\frac{H}{|t|^{\beta\delta}}$; the data are collapsed to two curves $F^\pm(x)$. (b) F^\pm from experiments [same as (a)] and from fitted scaling functions [Eq. (14) and Eq. (15)]. Notice that the fitted curves extends well beyond the experimental data. For MF, $\beta_{MF} = 0.5$ and $\delta_{MF} = 3$ are used. (c) $M(H, T)$ from experiments (symbols), fitted scaling functions Eq. (14) (solid), and MF approximation (dashed). The MF generally underestimates the magnetization. Experimental data are taken from Ref. [11].

will be used to constraint the asymptotic behavior. We also consider an exponential-decay scaling function $F(x) = e^{-x/x_0}$: with $\int dx F(x) = -x_0 e^{-x/x_0}$ Eq. (8) gives

$$\begin{aligned} \Delta S_{\text{mag}}(T, H) &\rightarrow \Delta \tilde{S}_{\text{mag}}^{\text{exp}}(H, T; x_0) \\ &= \text{sgn}(t) \frac{t^{\beta+\beta\delta-1}}{T_c} \left[-[\beta(1+\delta)x_0 + (\beta\delta) \cdot \bar{x}] e^{-\bar{x}/x_0} + \beta(1+\delta)x_0 \right]_{\bar{x}=Ht^{-\beta\delta}} \end{aligned} \quad (10)$$

The superscript ‘exp’ indicates the exponential-decay scaling function. x_0 is referred to as the characteristic length or the

correlation length beyond which the function value is small. The exponential-decay function does not affect the asymptotic behavior and will be used to capture the features for $x \lesssim x_0$.

D. Asymptotic behavior

The magnetic scaling function $F(x)$ has to satisfy certain constraints to be able to describe some general behavior of the equation of states. First, a finite $M(T = T_c, H)$ requires a well defined $t^\beta F(\frac{H}{t^{\beta\delta}})$ at $t = 0$; this demands that $F(x)$ has to diverge exactly as $x^{1/\delta} \approx x^{0.237}$. Second, a finite $\Delta S_{\text{mag}}(T = T_c, H)$ in Eq. (9) requires a non-negative exponent of $t^{\beta(1+\alpha_1\delta)-1}$: $\beta(1 + \alpha_1\delta) - 1 \geq 0$. The equality defines an exponent $\frac{1-\beta}{\beta\delta} \approx 0.407$ and a power law of $x^{-\frac{1-\beta}{\beta\delta}}$ is *required* to generate a non-zero $\Delta S_{\text{mag}}(T = T_c, H)$. Taking $t = 0$ in Eq. (9) the magnetic entropy change at T_c is

$$\Delta S_{\text{mag}}(T_c, H) = \text{sgn}(t) \frac{\tilde{B}}{T_c} \times \underbrace{\frac{\beta\delta}{\beta\delta + \beta - 1}}_{\approx 1.686} \times H^{\frac{\beta\delta + \beta - 1}{\beta\delta}}. \quad (11)$$

$\frac{\beta\delta + \beta - 1}{\beta\delta} \approx 0.59$ and \tilde{B} is the proportional constant. Similarly by taking the partial temperature derivative to Eq. (9) at $t = 0$, one obtains that the $x^{-\alpha_1}$ with $\alpha_1 = \frac{2-\beta}{\beta\delta} \approx 1.051$ is the power-law term that contributes to the non-zero $\frac{\partial(\Delta S_{\text{mag}})}{\partial T}$ at T_c ; this term will be used in Appendix. $\Delta S_{\text{mag}}(T_c, H)$ being continuous implies the coefficient of this term in F^\pm should have the same amplitude but opposite sign due to $\text{sgn}(t)$ in Eq. (8). Finally we take $\alpha_1 = -1/\delta$ in Eq. (9) and examine its t dependence. The divergent term t^{-1} vanishes because of the vanishing coefficient $\frac{\beta + \beta\delta}{1 + 1/\delta} - \beta\delta = 0$, meaning the divergent $x^{1/\delta}$ term in F does not contribute to ΔS_{mag} at *all* temperatures. To consider the next order we use $(1 + \frac{dt^{\beta\delta}}{H})^{1/\delta} \approx 1 + \frac{1}{\delta} \frac{dt^{\beta\delta}}{H}$, the leading power in small t is given by

$$t^{\beta + \beta\delta - 1} \left(\frac{H}{t^{\beta\delta}} \right)^{1 + 1/\delta} \cdot \frac{1}{\delta} \frac{dt^{\beta\delta}}{H} \sim t^{\beta\delta - 1}. \quad (12)$$

This term vanishes at $t = 0$ and therefore the $(x + c)^{1/\delta}$ is allowed.

Putting everything together, a legitimate parametrization of scaling function is

$$F(x) \approx \tilde{A}(x + c_0)^{1/\delta} + \tilde{B}(x + c_1)^{-\frac{1-\beta}{\beta\delta}} + \text{terms decay faster than } x^{-\frac{1-\beta}{\beta\delta}}. \quad (13)$$

The coefficient \tilde{A} has the positive value for F^\pm ; the coefficient \tilde{B} is positive/negative for F^-/F^+ with the same amplitude. The sign of \tilde{B} is determined by the fact that the magnetic entropy is smaller in a higher field. The x -offsets c_0, c_1 are positive so $F(0)$ is well defined. The remaining terms have to be regular at $x = 0$ and decay faster than $x^{-\frac{1-\beta}{\beta\delta}}$ asymptotically. Both x -shifted power-law functions and exponential decay functions satisfy these criteria.

III. PROCEDURE TO CONSTRUCT SCALING FUNCTIONS

A. Expression for the parameterized scaling function

Based on Eq. (13) the scaling function $F^\pm(x)$ is parametrized as:

$$F(x) = \begin{cases} F^-(x) = a_1 x^{1/\delta} + a_2 (x + a_3)^{-\frac{1-\beta}{\beta\delta}} & T < T_c \\ F^+(x) = f^{(0)}(x; b_1^{(0)}, b_2^{(0)}) + \sum_{i=1}^3 f^{(i)}(x; b_1^{(i)}, b_2^{(i)}) & T > T_c, \end{cases} \quad (14)$$

with $f^{(0)}(x; b_1^{(0)}, b_2^{(0)}) = a_1 (x + b_1^{(0)})^{1/\delta} - a_2 (x + b_2^{(0)})^{-\frac{1-\beta}{\beta\delta}}$,

$$f^{(i)}(x; b_1^{(i)}, b_2^{(i)}) = b_1^{(i)} e^{-x/b_2^{(i)}} \quad (i > 0).$$

In Eq. (14) a_1, a_2, a_3 , and $b_1^{(0)}, b_2^{(0)}, b_1^{(1)}, b_2^{(1)}, b_1^{(2)}, b_2^{(2)}, b_1^{(3)}, b_2^{(3)}$ [$b_j^{(n)}$ ($n=0,1,2,3$ and $j=1,2$)] are 11 parameters to be determined from experiments. The parametrization of Eq. (14) keeps the power-law terms required to describe the finite magnetization and

entropy. For both F^\pm , the divergent $x^{1/\delta}$ term is needed for a finite magnetization; $(x+c)^{-\frac{1-\beta}{\beta\delta}}$ is needed for a finite ΔS_{mag} while the x -offset c accounts for a well defined $F^\pm(0)$. For F^- , using three parameters (two amplitudes a_1, a_2 and one x -offset a_3) appears sufficient. For F^+ , the amplitudes of $x^{1/\delta}$ and $x^{-\frac{1-\beta}{\beta\delta}}$ are fixed to be a_1 and $-a_2$ respectively because of the continuity of $M(T, H)$ and ΔS_{mag} across T_c . Three exponential-decay terms of correlation lengths $b_2^{(1)}, b_2^{(2)}$ and $b_2^{(3)}$ are introduced to account for finite- x behavior. The rationale is that the power-law terms enforce the correct asymptotics whereas exponential-decay terms capture the medium- x to small- x features. One of our best fits is

$$[a_1, a_2, a_3] = [84.57, 710.50, 47.03], \quad (15a)$$

$$[b_1^{(0)}, b_2^{(0)}] = [5.00, 27.63], \quad (15b)$$

$$[b_1^{(1)}, b_2^{(1)}] = [-25.46, 351.34], \quad (15c)$$

$$[b_1^{(2)}, b_2^{(2)}] = [71.59, 20.46], \quad (15d)$$

$$[b_1^{(3)}, b_2^{(3)}] = [14.34, 3.72]. \quad (15e)$$

The fitting procedure will be described shortly.

We emphasize that $F(x)$ in Eq. (14) is constructed for the *entire* non-negative x and can therefore describe the behavior approaching T_c that requires an accurate $x \rightarrow \infty$ behavior. In 1(c) we explicitly show well-behaved $M(T = 293.1\text{K}, H)$; to compute this curve requires $F(x)$ well beyond those provided by experiments. The scaling hypothesis becomes less accurate away from the critical point so Eq. (14) is a good approximation only for small t . This can be seen in 1(c) where the difference of magnetization between experiments and Eq. (14) increases slightly (visible only in linear scale) when the temperature is away from T_c . For Gd of $T_c = 293\text{K}$, the scaling works well for the temperature span of 263 K - 323 K, corresponding to $t \lesssim 0.1$.

B. Scale-separated fitting procedure

The fitting procedure is now described in detail. Eq. (14) has 11 parameters to determine. The first fitting step is to plot the measured $M(T, H)$ in the reduced state variables $\frac{M}{t^\beta}$ and $\frac{H}{t^{\beta\delta}}$; $\beta = 0.368$ and $\delta = 4.22$ are used. Two ‘‘data collapse’’ curves shown in 1(a) represent the experimental scaling functions $F_{\text{expt}}^\pm(x)$ which are available only for a *finite* range of x and are the targets Eq. (14) aims to match. Using $F_{\text{expt}}^-(x)$, three parameters a_1, a_2, a_3 of F^- are determined; the fitted values are given in Eq. (15a). Formally we write

$$[a_1, a_2, a_3] = \text{argmin} \|F^-(x) - F_{\text{expt}}^-(x)\| \quad (16)$$

Here $\|h(x; p)\| \sim \sum_i h(x_i; p)^2$ where x_i are experimentally available points.

With a_1, a_2, a_3 determined from Eq. (16), F^+ has eight parameters to fix. To proceed we ask what makes $F_{\text{expt}}^+(x) \approx F^+(x) = \sum_{i=0}^3 f^{(i)}(x; b_1^{(i)}, b_2^{(i)})$ [Eq. (14)] a valid approximation. The crucial feature of this expansion is that $f^{(0)}, f^{(1)}, f^{(2)}, f^{(3)}$ have very different characteristic lengths: $f^{(0)}$ is composed of power-law terms and thus has a diverging characteristic length, $f^{(1)}, f^{(2)}$ and $f^{(3)}$ are exponential decay terms with characteristic lengths $b_2^{(1)} \gg b_2^{(2)} \gg b_2^{(3)}$. With the distinct length separation, $f^{(0)}(x)$ has to match the target $F_{\text{expt}}^+(x)$ for $x \gg b_2^{(1)}$ because in this regime $f^{(0)}(x)$ is the only significant term. Once $f^{(0)}(x)$ is fixed this way, the discrepancy between F_{expt}^+ and $f^{(0)}(x)$ resides only on $x \lesssim b_2^{(1)}$ and has to be compensated by $f^{(1)}(x)$ because $f^{(0)}(x)$ already accounts for large x behavior whereas $f^{(2)}(x \sim b_2^{(1)}) \sim 0$. For the same reason $f^{(2)}(x)$ has to compensate the difference between $F_{\text{expt}}^+(x)$ and $\sum_{i=0}^1 f^{(i)}(x)$ around $x \lesssim b_2^{(2)}$. This procedure can go on in principle.

Formally we define the residual of order n as

$$dF^{(n)}(x; \{b_k^{(i)}\}) \equiv F_{\text{expt}}^+(x) - \sum_{i=0}^n f^{(i)}(x; b_1^{(i)}, b_2^{(i)}), \quad (17)$$

so $dF^{(n)}$ ($n \geq 0$) has $2(n+1)$ parameters composed of $(b_1^{(i)}, b_2^{(i)})$ with $i = 0$ to n . Eight parameters $b_k^{(i)}$'s are determined by *sequentially* minimizing the residual:

$$[b_1^{(0)}, b_2^{(0)}] = \text{argmin} \|dF^{(0)}(x)\|, \quad (18a)$$

$$\rightarrow [b_1^{(1)}, b_2^{(1)}] = \text{argmin} \|dF^{(1)}(x)\|, \quad (18b)$$

$$\rightarrow [b_1^{(2)}, b_2^{(2)}] = \text{argmin} \|dF^{(2)}(x)\|, \quad (18c)$$

$$\rightarrow [b_1^{(3)}, b_2^{(3)}] = \text{argmin} \|dF^{(3)}(x)\|, \quad (18d)$$

In Eq. (18a), $dF^{(0)}(x)$ only depends on $(b_1^{(0)}, b_2^{(0)})$. In Eq. (18b), the $b_k^{(0)}$'s dependence in $dF^{(1)}(x)$ is fixed by Eq. (18a) and the minimization is over $(b_1^{(1)}, b_2^{(1)})$ only. Similarly in Eq. (18c), $b_k^{(0)}$'s and $b_k^{(1)}$'s are fixed from previous two calculations and the minimization is over $(b_1^{(2)}, b_2^{(2)})$ only. Same procedure is applied $(b_1^{(3)}, b_2^{(3)})$. The results are given in Eqs. (15b) to (15e).

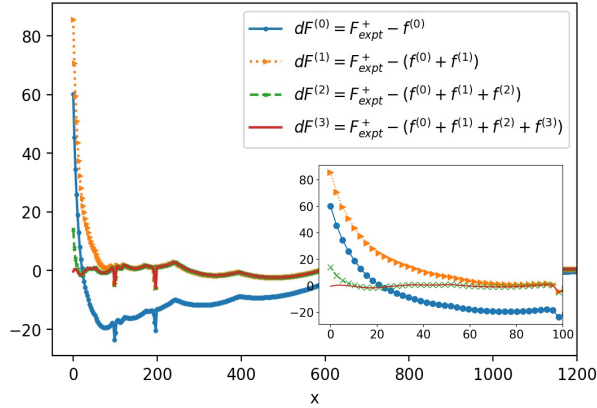


FIG. 2: Residual $dF^{(n)}(x)$ defined Eq. (17). Power-law terms describe the correct asymptotics so $dF^{(0)}(x)$ (blue dots) becomes small when x is larger than $x_1 \sim 1000$. The sequential procedure reduces the fitting error in descending length scale: $|dF^{(1)}(x)|$ is small for $x \gtrsim 100$; $|dF^{(2)}(x)|$ is small for $x \gtrsim 5$; $|dF^{(3)}(x)|$ is small for all x . The inset highlights the behavior for $x < 100$.

2 illustrates how the residual $dF^{(n)}(x)$ decreases upon increasing n in this fitting procedure. Because power-law terms describe the correct asymptotics, $dF^{(0)}(x)$ is expected to become small for x larger than a certain length. This can be seen in the blue dots of 2 which decays to small values around $x_1 = 1000$. $f^{(1)}$ is introduced to compensate $dF^{(0)}(x)$ over the scale of x_1 ; and the optimization procedure of Eq. (18b) gives an expected correlation length $b_2^{(1)} \approx 350$. $f^{(2)}$ is then introduced to compensate $dF^{(1)}(x)$ for a smaller length scale around 10. This procedure can go on but it will need a very high resolution of $F(x \sim 0)$; this may not be available and is usually not necessary. In our example using three exponential functions is sufficient.

Three general remarks are pointed out. First, the set of parameter values given in Eq. (15) is by no means unique. There are many sets of parameters that give almost indistinguishable $F(x)$ and thus $M(T, H)$, and the goal is to find one of them. Even the form of Eq. (14) can be altered, but we find that the exponential function is the most convenient choice. In the Appendix we provide the fitting results using two more parametrization forms. Second, the eleven parameters in Eq. (14) cannot be optimized simultaneously; doing so does not give any meaningful answer due to the highly non-linear nature. The proposed fitting procedure groups the parameters by the phase and the length scale and sequentially deals with parameters of one phase and one scale at a time. It resembles the numerical RG formalism that deals with one energy scale at a time [25, 26]; the final answer is the combination of the results at all scales. From a numerical perspective, dividing a large multi-parameter minimization problem into multiple sub-problems of fewer parameters makes the algorithm stable and efficient. We use python package `curve_fit` for numerical fitting. Lastly, we notice that with the proper critical exponents β_{MF} , δ_{MF} [see crosses in 1(b)] one can apply the same parametrization scheme to the MF equation of states [solutions of Eq. (1)] to obtain an explicit $M_{MF}(T, H)$.

IV. COMPARISON WITH EXPERIMENTS

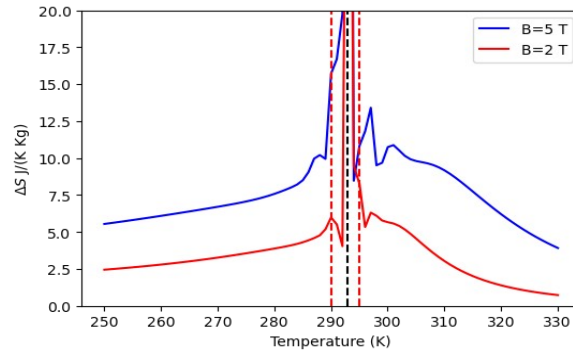
A. Magnetic entropy

With the parameters in Eq. (14) fixed, we compute the change of magnetic entropy upon increasing field $\Delta S_{\text{mag}}(T, H)$. This quantity involves partial derivatives of $M(T, H)$ and presents a more stringent test (compared to $M(T, H)$ itself) of the parametrization scheme. With Eq. (14), an analytical expression is granted:

$$\Delta S_{\text{mag}}(T, H) = \begin{cases} a_2 \Delta \tilde{S}_{\text{mag}}^{\text{pl}}(T, H; a_3, \frac{1-\beta}{\beta\delta}), & T < T_c \\ -a_2 \Delta \tilde{S}_{\text{mag}}^{\text{pl}}(T, H; b_2^{(0)}, \frac{1-\beta}{\beta\delta}) + \sum_{i=1}^3 b_1^{(i)} \Delta \tilde{S}_{\text{mag}}^{\text{exp}}(T, H; b_2^{(i)}) & T > T_c. \end{cases} \quad (19)$$

(a)

(b)



(c)

FIG. 3: (a) Change of magnetic entropy $-\Delta S_{\text{mag}}(T)$ when increasing field from 0 to $H = 5$ and 2 T. (b) Same plot as (a) but using the interpolated scaling function $F(x)$ for $M(T, H)$. The results around T_c are totally unreliable because the asymptotic behavior of $F(x)$ is not captured. (c) Adiabatic temperature increase $\Delta T^{\text{ad}}(T)$ when increasing the field from 0 to $H = 5$ and 2 T. The vertical dash line indicates the Curie temperature and experimental data are taken from Ref. [11].

$\Delta S_{\text{mag}}^{\text{pl}}$ and $\Delta S_{\text{mag}}^{\text{exp}}$ are respectively given in Eq. (9) and in Eq. (10). 3(a) gives the $-\Delta S_{\text{mag}}(T, H)$ at $H = 5$ and 2T. The overall agreement between experiment and Eq. (19) is good. In particular how the entropy decays away from T_c is quantitatively captured. One small but obvious discrepancy is that the calculated maximum $\Delta S_{\text{mag}}(T)$ occurs at a temperature slightly higher than T_c . As a reference we provide the MF results which also agree with the experiments reasonably well, but the results from Eq. (19) are apparently better over the entire temperature range.

To illustrate the importance of the correct asymptotic $F(x)$, in 3(b) we show the same $-\Delta S_{\text{mag}}(T, H)$ at $H = 5$ and 2T, but with $F(x)$ fitted (cubic spline) from the experimental data [dots of 1(b)]. The values away from T_c are reasonable but those around T_c

are unphysically oscillatory and divergent. We have tried a few fitting schemes, with the number of parameters ranging from 20 to a few hundreds, such as polynomials, linear interpolation, and cubic spline; the latter two almost use all measured $M(T, H)$. In all these cases the resulting $M(T, H)$ are fine but the magnetic entropy change, which involves the derivatives of $M(T, H)$, are totally unreliable around T_c .

With Eq. (19) we compute the adiabatic temperature change upon applying field, which is the most relevant quantity for the magnetic energy conversion. To compute this quantity one needs the total entropy that includes spin (magnetization), lattice, and electron degree of freedom [13]:

$$\begin{aligned} S_{\text{tot}}(T, H) &= \int_0^T dT \frac{\partial S_{\text{tot}}}{\partial T} + \int_0^H dH \frac{\partial S_{\text{tot}}}{\partial H} \\ &\approx \int_0^T dT \frac{C(T, H=0)}{T} + \underbrace{\int_0^H dH \frac{\partial M(H, T)}{\partial T}}_{=\Delta S_{\text{mag}}(T, H)} \end{aligned} \quad (20)$$

Eq. (20) assumes that the lattice and electron entropy depend only on the temperature not field so that $\frac{\partial S_{\text{tot}}}{\partial H} \approx \frac{\partial S_{\text{mag}}}{\partial H}$. $C(T, H=0)$ denotes the zero-field specific heat and is obtained from fitting the data reported in Ref. [12]. Once $S_{\text{tot}}(T, H)$ is known, the adiabatic temperature change $\Delta T^{\text{ad}}(T, H)$ upon applying the field from 0 to H is obtained by

$$S_{\text{tot}}(T, 0) = S_{\text{tot}}(T + \Delta T^{\text{ad}}(T, H), H). \quad (21)$$

3(c) shows the adiabatic temperature change $\Delta T^{\text{ad}}(T)$ upon increasing the field from 0 to $H = 5$ and 2 T. The agreement between experiments and calculations is again very satisfactory. The calculated maximum temperature change occurs at $T = T_c$ and its value is very close to the experiment ($\lesssim 5\%$ difference); how $\Delta T^{\text{ad}}(T, H)$ decays when T is away from T_c over the entire temperature range is also well reproduced. The MF result is also reasonable in terms of the correct peak structure at T_c , but MF theory generally underestimates (overestimates) the adiabatic temperature change for $T > T_c$ ($T < T_c$). The overall good agreement to experiments validates that the analytical expression Eq. (14) can be used as an accurate and efficient representation for Gd magnetization close to T_c .

B. Magnetic specific heat

Now we examine the properties involving both integration and derivative of the magnetic scaling function $F(x)$ – the specific heat from magnetization. With $F(x)$ in Eq. (14) we need $\int dx(x+a)^b = \frac{1}{1+b}(x+a)^{b+1} + K$ and $\int dx e^{-x/b} = -be^{-x/b} + K$; the corresponding free-energy scaling function $G(x)$ in Eq. (3) is

$$\begin{aligned} G(x) &= \begin{cases} G^-(x) = \frac{a_1}{1+1/\delta} x^{1/\delta+1} + \frac{a_2}{1-\frac{1-\beta}{\beta\delta}} (x+a_3)^{1-\frac{1-\beta}{\beta\delta}} + K_- & T < T_c \\ G^+(x) = g^{(0)}(x; b_1^{(0)}, b_2^{(0)}) + \sum_{i=1}^3 g^{(i)}(x; b_1^{(i)}, b_2^{(i)}) + K_+ & T > T_c \end{cases}, \\ \text{with } g^{(0)}(x; b_1^{(0)}, b_2^{(0)}) &= \frac{a_1}{1+1/\delta} (x+b_1^{(0)})^{1/\delta+1} - \frac{a_2}{1-\frac{1-\beta}{\beta\delta}} (x+b_2^{(0)})^{1-\frac{1-\beta}{\beta\delta}}, \\ g^{(i)}(x; b_1^{(i)}, b_2^{(i)}) &= -b_1^{(i)} b_2^{(i)} e^{-x/b_2^{(i)}} \quad (i > 0). \end{aligned} \quad (22)$$

With Eq. (3) and (22) we can compute the singular part of the specific heat defined in Eq. (5). The complete analytical expression is complicated but straightforward, and we simply note

$$\begin{aligned} -T \frac{\partial^2 \tilde{G}}{\partial T^2} &= \frac{T}{T_c^2} \left[(\beta + \beta\delta)(\beta + \beta\delta - 1) t^{\beta+\beta\delta-2} G\left(\frac{H}{t\beta\delta}\right) \right. \\ &\quad - H(\beta\delta)(2\beta + \beta\delta - 1) t^{\beta-2} F\left(\frac{H}{t\beta\delta}\right) \\ &\quad \left. + H^2(\beta\delta)^2 t^{\beta-\beta\delta-2} F'\left(\frac{H}{t\beta\delta}\right) \right]. \end{aligned} \quad (23)$$

The singular behavior at $t \rightarrow 0$ ($T \rightarrow T_c$) is from $t^{\beta+\beta\delta-2}$, and $\beta + \beta\delta - 2 \approx -0.079$ gives a weak power-law divergence. The integration constants K_{\pm} only appear in the first line of Eq. (23) and provide a field independent contribution

$$K_{\pm}(\beta + \beta\delta)(\beta + \beta\delta - 1) \frac{T}{T_c^2} t^{\beta+\beta\delta-2} \quad (24)$$

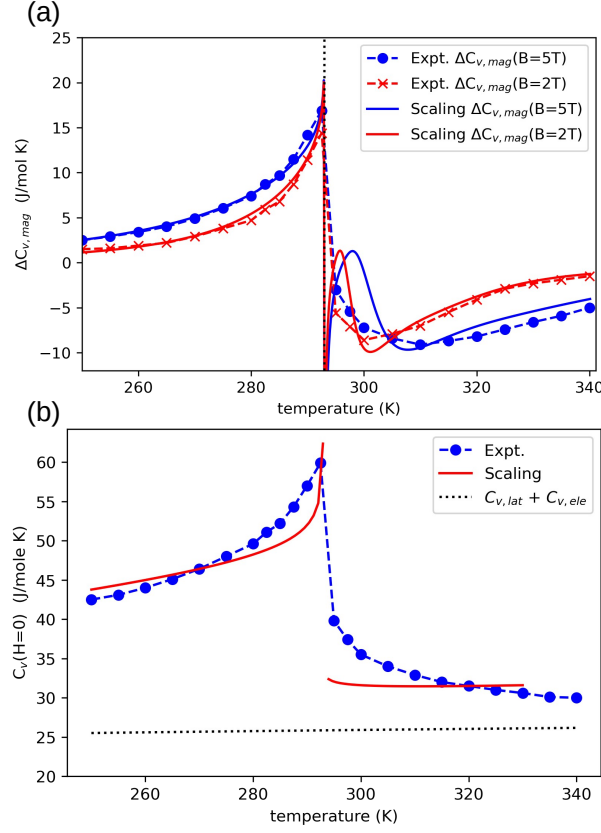


FIG. 4: (a) The change of specific heat $\Delta C_{v,mag}(T, H)$ for $H=5$ and 2 T. The agreement between fitting and experiment is reasonably good for $T < T_c$ and $T \gg T_c$. Around $T \gtrsim T_c$ the agreement is only qualitative in the sense of the correct order of magnitude and a non-monotonic “basin-shaped” behavior. (b) The $C_v(H=0)$ including all magnetic, lattice, and electron contributions. The combined contribution from lattice and electron is plotted in dotted curve for reference. The experimental data are taken from Fig.7 of Ref. [11].

to $C_{v,mag}$. Our unit convention in M is such that G (and thus \tilde{G}) has the dimension Joule/kg and C_v Joule/(kg K); multiplying the Gd atomic mass ≈ 0.157 kg/mol gives the quantities per mole.

To have a comparison not involving integration constants K_{\pm} , we compute the change of specific heat due to the applied field:

$$\Delta C_{v,mag}(T, H) = C_{v,mag}(T, H=0) - C_{v,mag}(T, H). \quad (25)$$

A direct comparison to experiments is shown in 4(a) for $H = 5$ and 2 T. The electron and phonon contributions to the specific heat are assumed to be field independent so one can use Eq. (5) that only accounts for the magnetic contribution. The overall coincidence is fine in terms of the amplitudes. The agreement between fitting and experiment is reasonably good for $T < T_c$ and $T \gg T_c$. Around $T \gtrsim T_c$ the agreement is not very satisfactory, and the discrepancy can be traced to the fact that the $\partial_T \Delta S_{mag}$ around T_c [see 3(a)] is not ideal. However the scaling-based model does capture the non-monotonic “basin-shaped” behavior for $T > T_c$.

For completeness we compute the total zero-field specific heat $C_v(T, H=0) = C_{v,ele}(T) + C_{v,lat}(T) + C_{v,mag}(T, H=0)$. The electron contribution is $C_{v,ele}(T) = \gamma_e T$ with $\gamma_e = 4.48$ mJ/mol K² [11, 31]; the lattice contribution is

$$C_{v,lat}(T) = 9Nk_B \left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2} \quad (26)$$

with $T_D = 168$ K the Debye temperature, N the number of Gd ions and k_B the Boltzmann constant. For the temperature range of interest, $T > T_D$ and the lattice contribution is close to $3Nk_B \approx 25$ Joule/(K mol). For magnetic part we need to determine K_{\pm} which requires at least two C_v measurements: one above and one below T_c . We use C_v measured at $T = 270$ and 330 K based on which

$$\begin{aligned} K_- &\approx 1200.18 \text{ Joule}/(\text{mol K}^2), \\ K_+ &\approx -642.23 \text{ Joule}/(\text{mol K}^2). \end{aligned} \quad (27)$$

The scaling-based and the experimental C_v 's are shown in 4(b). The agreement is qualitatively fine but may not be sufficient for quantitative simulations. We point out that as both $C_{v,\text{ele}}(H=0)$ and $C_{v,\text{lat}}(H=0)$ are monotonically increasing in T [dotted curve in 4(b)], the scaling-based $C_{v,\text{mag}}(H=0)$ does generate a jump (the power-law divergence is so weak and looks like a jump) at T_c and a negative $\partial C_v/\partial T$ when $T \gtrsim T_c$.

C. Practical consideration

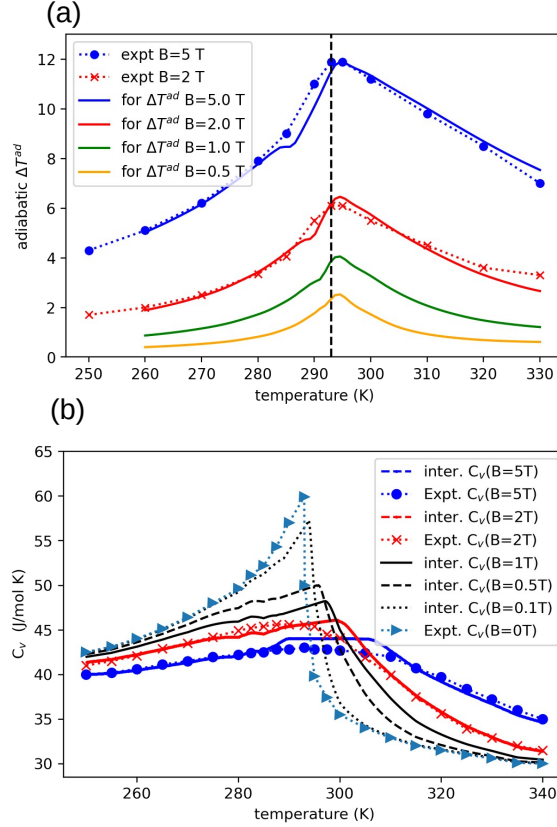


FIG. 5: (a) ΔT^{ad} using the parameters that best fit the magnetic entropy change [Table I, set 1 with parentheses]. (b) The total interpolated specific heat $\Delta C_v(T, H)$ from Eq. (29) for $H = 5, 2, 1, 0.5,$ and 0.1 T. Experiments are taken from Ref. [11] are provided as the reference.

In practice, what we need are good and efficient approximations for the measured $M(T, H)$, $\Delta T^{\text{ad}}(T, H)$ and $C_v(T, H)$. This can be better achieved if we are allowed to use slightly different parameter values (but keep the same parametrization form) for different measurements. Note that by doing so the thermodynamic relations are not exactly satisfied.

As an illustration, we use the second parametrization form given in Eq. (A1). The fitted values that best match the measured magnetization and the magnetic entropy change are provided in I. The resulting ΔT^{ad} 's for $H = 5, 2, 1, 0.5$ T are given in 5(a) [see also 6], and a good agreement to experiments (for $H = 5$ and 2T) is seen. To get the specific heat $C_v(T, H)$ is more involved. We use the measured zero-field specific heat $C_{v,\text{exp}}(T)$ as the *given* reference to get

$$C_v(T, H) = C_{v,\text{exp}}(T) - \Delta C_{v,\text{mag}}(T, H). \quad (28)$$

$\Delta C_{v,\text{mag}}(T, H)$ is obtained using the same parameters that best fit the magnetic entropy change. At a non-zero H , $C_v(T, H)$ is smooth across T_c . However, both $C_{v,\text{exp}}(T)$ and $\Delta C_{v,\text{mag}}(T, H)$ display sharp jumps across T_c which makes the fitting very sensitive to any numerical uncertainty. In other words, one needs to add two sharp functions, each has its own uncertainty, to produce a smooth function. We propose the interpolation scheme:

$$C_{v,\text{inter}}(T, H) = \begin{cases} C_v(T, H) & T < T_a \text{ or } T > T_b \\ C_v(T_a, H) + \frac{C_v(T_b, H) - C_v(T_a, H)}{T_b - T_a} (T - T_a) & T_a \leq T \leq T_b. \end{cases} \quad (29)$$

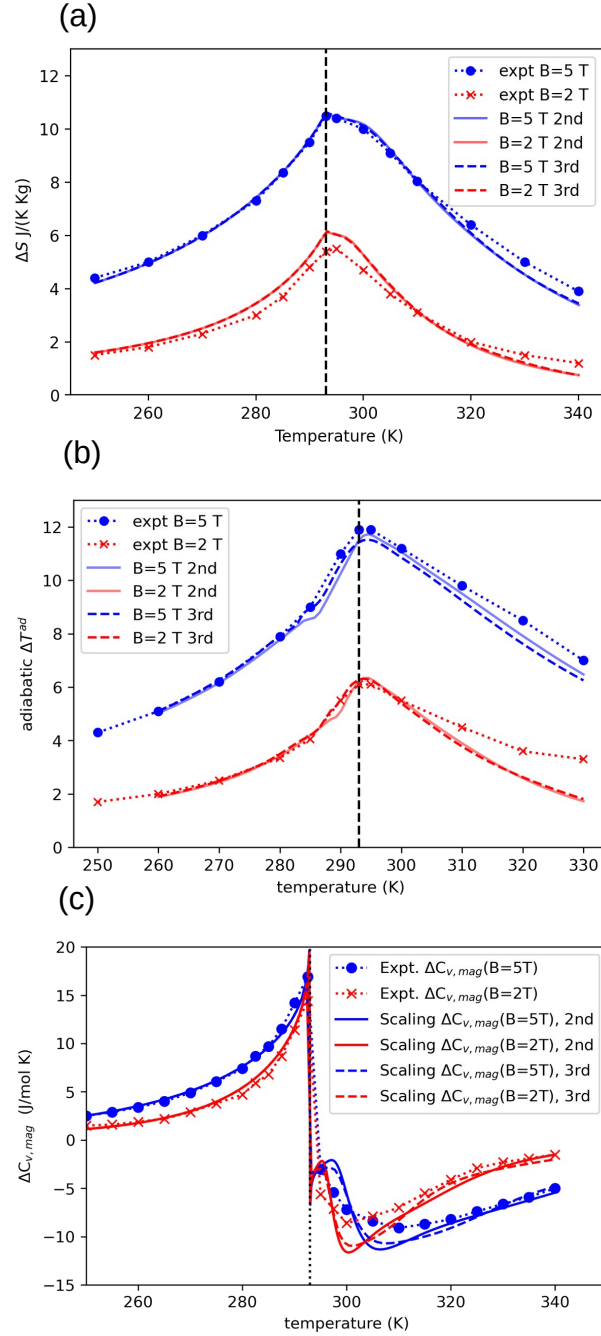


FIG. 6: The fitting results for $H=5$ and 2 T from Eq. (A1) (solid curves) and Eq. (A2) (dashed curves). $T < T_c$ results are identical. For Eq. (A1), results using two sets of parameters in Table I are very close so only those using set 1 are shown. (a) The magnetic entropy change. (b) The adiabatic temperature change. (c) The change of specific heat $\Delta C_{v,mag}(T, H)$. Experiments taken from Ref. [11] are provided as the reference.

There are two additional parameters T_a and T_b . $T_a (< T_c)$ is determined by the largest possible $T (< T_c)$ satisfying $\partial_T C_v(T_a, H) = 0$; $T_b (> T_c)$ is determined by the largest $T (> T_c)$ satisfying $\partial_T C_v(T_b, H) = 0$ (one can increase T_b slightly based on $T_b - T_c$ to better fit the experiments; the results are not shown here). It is based on the following two observations: (i) the fitted $\Delta C_{v,mag}(T, H)$ away from T_c ($T - T_c \gg T_c$) is reliable; (ii) $C_v(T, H)$ has a single peak around T_c for a given H . The resulting $C_{v,inter}(T, H)$'s for $H = 5, 2, 1, 0.5, 0.1$ T are given in 5(b). Notice that $C_{v,inter}(T, H)$ does not require the measured $C_v(T, H \neq 0)$. A very reasonable agreement to experiments is seen. We have checked that the results are very insensitive to the all three parametrization forms parametrization [Eq. (14), Eq. (A1), and Eq. (A2)] (not shown).

Finally let us comment on the Universal Scaling Method (USM) developed by Franco et.al. [27, 28]. USM introduces two additional temperatures (besides T_c) and finds that the *ratio* of ΔS as a function of rescaled temperature is collapsed to a single universal curve for the same universality class of 2nd order transition. This collapse is a consequence of scaling hypothesis [27]. USM does not explicitly address how to fit the equation of states. If the critical exponents are not known, some empirical equation of states, such as Arrott–Noakes equation [32], can be used to extract the universal curve from experimental data. As USM utilizes a universal function that depends only on the universality class, it is very valuable for early material characterization when the complete information is not available. Our proposed scheme, also based on scaling hypothesis, provides a recipe for constructing the scaling functions that are *different* for materials of the *same* universality class. With sufficient measurements, our scheme is more straightforward in obtaining the equation of states including both magnetization and specific heat.

parameter	set 1 (for ΔT^{ad})	set 2 (for ΔT^{ad})
$[b_1^{(0)}, b_2^{(0)}, b_3^{(0)}]$	[15.69, 513.11 ($\times 0.5$), 2.07]	[16.37, 212.97, 1.81]
$[b_1^{(1)}, b_2^{(1)}]$	[-19.45 ($\times 0.8$), 390.72]	[-16.82, 405.25]
$[b_1^{(2)}, b_2^{(2)}]$	[67.18, 21.91]	[99.89, 19.69]
$[b_1^{(3)}, b_2^{(3)}]$	[-101.11, 1.91]	[-28.82, 1.06]
$[b_1^{(4)}, b_2^{(4)}]$	[46.13, $1.56 \cdot 10^{-2}$]	[59.32, 0.20]

TABLE I: Two sets of fitted parameters for Eq. (A1). The corresponding observables and their comparisons with experiments are given in Fig. 6. For set 1, the multiplication factors for $b_2^{(0)}$ and $b_1^{(1)}$ (in parentheses) are applied to get the best fit of magnetic entropy change; the resulting ΔT^{ad} 's are shown in Fig. 5(a).

V. CONCLUSION AND DISCUSSION

To conclude, using scaling hypothesis we propose an efficient fitting scheme for the magnetization $M(T, H)$, the adiabatic temperature change $\Delta T^{\text{ad}}(T, H)$, and specific heat $C_v(T, H)$ of Gd for temperatures between 250 and 340 K and magnetic fields $\lesssim 5$ T. The essence of our scheme is to fit the single-variable scaling function $F(x)$ [Eq. (6)] that well describes the entire two-variable equation of states $M(H, T)$ near the Curie temperature of 293 K for Gd. The continuity of magnetization and entropy change across the critical temperature imposes the constraints on the asymptotic behavior of $F(x)$ which are most conveniently expressed in power law: the only allowed divergent term is $x^{1/\delta}$ and all other terms have to decay faster than $x^{-\frac{1-\beta}{\beta\delta}}$. The parametrized scaling function contains the power-law and exponential-decay functions. The parameters are grouped by the phase and the length scale, and are determined by a scale-separated fitting procedure that only has to deal with one phase and one length scale at a time. The resulting analytical expression of $M(T, H)$ has a well defined value at $T = T_c^\pm$ and can be used to compute any thermodynamic related quantities. We validate our scaling based parametrization by comparing to experiments: the equations of state that involve $F(x)$ and its derivatives, i.e., the magnetization $M(T, H)$, the magnetic entropy change ΔS_{mag} and the adiabatic temperature change ΔT^{ad} , match the experiments well. The improvements over mean-field results are obvious. The specific heat, which involves an integration of $F(x)$, also qualitatively agrees with the experiments. Given the zero-field specific heat $C_v(T, H = 0)$, a reasonable $C_v(T, H)$ can be generated from our scheme. Because the proposed parametrization is based on the scaling hypothesis, it can apply to materials close to 2nd-order phase transition and thus suggests a scheme to specify a material near the second-order transition: the critical exponents, the critical temperature, and a few material specific parameters are sufficient to give a fast and accurate evaluation of the material equation of states via (6) and (14). Our work extends the scaling hypothesis analysis, which typically focuses on the leading divergence, to the entire scaling function and finds its usefulness in a few-parameter analytical parametrization for the equations of states. We believe the parametrization scheme, supplemented with the robust RG-like fitting procedure, can be practically valuable when realistic applications are considered.

Acknowledgement

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Appendix A: Other parametrization forms

In this Appendix we aim to illustrate the degrees of freedom in parametrizing the scaling function. There are two aspects of arbitrariness. First, the parametrization form used in Eq. (14) is not unique; the general considerations given in IID only impose constraints on the leading exponents. Second, given a fixed parametrization form there can be still many solutions that well fit the experiments, and the job is simply to find one of them. It is the second aspect that proposed sequential fitting becomes essential. To cover both aspects, we will use two slightly different parametrizations and provide results from two sets of fitted parameters. Finally by mildly violating the thermodynamic relations we provide the fitting results specific to $M(T, H)$, $\Delta T^{\text{ad}}(T, H)$ and $C_v(T, H)$ which could be relevant for practical applications.

1. Second parametrization form

We explore an alternate parametrization form of the magnetic scaling function:

$$F(x) = \begin{cases} F^-(x) = a_1 x^{1/\delta} + a_2 (x + a_3)^{-\frac{1-\beta}{\beta\delta}} & T < T_c \\ \tilde{F}^+(x) = \tilde{f}^{(0)}(x; b_1^{(0)}, b_2^{(0)}, b_3^{(0)}) + \sum_{i=1}^4 f^{(i)}(x; b_1^{(i)}, b_2^{(i)}) & T > T_c \end{cases}, \quad (\text{A1})$$

with $\tilde{f}^{(0)}(x; b_1^{(0)}, b_2^{(0)}) = a_1 x^{1/\delta} - a_2 (x + b_1^{(0)})^{-\frac{1-\beta}{\beta\delta}} + b_2^{(0)} (x + b_3^{(0)})^{-\frac{2-\beta}{\beta\delta}}$,

$$f^{(i)}(x; b_1^{(i)}, b_2^{(i)}) = b_1^{(i)} e^{-x/b_2^{(i)}} \quad (i > 0).$$

Compared with Eq. (14), only the paramagnetic scaling function F^+ is modified. Following the same fitting procedure described in III B, we get the same $[a_1, a_2, a_3] = [84.57, 710.50, 47.03]$ and

In principle any power-law terms that comply with the constraints given in IID are legitimate, and we state our criterion of choosing the exponents. In Eq. (14), we choose the minimum number of power-law terms required to have the correct $F^+(x \rightarrow \infty) \sim x^{1/\delta}$ and $F^+(x = 0) = 0$; in Eq. (A1) the power-law with the exponent $-\frac{2-\beta}{\beta\delta}$ is kept because it contributes to the non-zero $\frac{\partial(\Delta S_{\text{mag}})}{\partial T}$ at T_c [see IID]. Since an exponential-decay term only accounts for the behavior below its correlation length, the number of terms is determined upon minimizing $\|F - F_{\text{expt}}\|$. As shown in I, the fitted correlation length is indeed decaying for both sets, (i.e., $b_2^{(1)} > b_2^{(2)} > b_2^{(3)} > b_2^{(4)}$) consistent with the scale-separate fitting scheme.

The results using Eq. (A1) (parameters given in I) are shown in 6. Results from two parametrization forms Eq. (14), Eq. (A1) are very similar. Compared with experiments, results using Eq. (A1) appears to be slightly better in the $T \gtrsim T_c$ regime for magnetic entropy change ΔS , but its overall adiabatic temperature change ΔT^{ad} is worse. Overall Eq. (14) is a better for $H \lesssim 2.5$ T whereas Eq. (A1) for $H \gtrsim 2.5$ T. One bears in mind that this conclusion is based on all measurements; one cannot really tell which parametrization form is better using $M(T, H)$ alone.

2. Third parametrization form

A third parametrization form is considered:

$$F(x) = \begin{cases} F^-(x) = a_1 x^{1/\delta} + a_2 (x + a_3)^{-\frac{1-\beta}{\beta\delta}} & T < T_c \\ \bar{F}^+(x) = \bar{f}^{(0)}(x; b^{(0)}) + \sum_{i=1}^4 f^{(i)}(x; b_1^{(i)}, b_2^{(i)}) & T > T_c \end{cases}, \quad (\text{A2})$$

with $\bar{f}^{(0)}(x; b^{(0)}) = a_1 x^{1/\delta} - a_2 \cdot x^{-\frac{1-\beta}{\beta\delta}} (1 - e^{-x/b^{(0)}})$,

$$f^{(i)}(x; b_1^{(i)}, b_2^{(i)}) = b_1^{(i)} e^{-x/b_2^{(i)}} \quad (i > 0).$$

This form also complies with all required properties stated in IID. This parametrization has less number of fitting parameters but it also loses the analytical expressions for the specific heat due to the product of exponential and power-law. The fitting gives the same $[a_1, a_2, a_3]$ and

$$[b^{(0)}; b_1^{(1)}, b_2^{(1)}] = [9.46(\times 0.8); -12.27, 400.54], \quad (\text{A3a})$$

$$[b_1^{(2)}, b_2^{(2)}] = [102.30, 33.79], \quad (\text{A3b})$$

$$[b_1^{(3)}, b_2^{(3)}] = [-134.84, 3.92], \quad (\text{A3c})$$

$$[b_1^{(4)}, b_2^{(4)}] = [14.92, 0.97]. \quad (\text{A3d})$$

$b^{(0)} = 9.46 \times 0.8$ is the value for best ΔT^{ad} .

To compute the magnetic entropy change, we consider $F(x) = x^{-\alpha_1} e^{-x/x_0}$; substituting $F(x)$ and $\int dx F(x) = \frac{x^{1-\alpha_1}}{1-\alpha_1} \cdot {}_1F_1(1-\alpha_1, 2-\alpha_1, \frac{x}{x_0})$ (here ${}_1F_1(a, b, x)$ is the confluent hypergeometric function) into Eq. (8) gives

$$\begin{aligned} \Delta S_{\text{mag}}(T, H) &\rightarrow \Delta \tilde{S}_{\text{mag}}^{\text{pl-exp}}(H, T; x_0, \alpha_1) \\ &= \frac{t^{\beta+\beta\delta-1}}{T_c} \left[(\beta + \beta\delta) \frac{x^{1-\alpha_1}}{1-\alpha_1} \cdot {}_1F_1(1-\alpha_1, 2-\alpha_1, \frac{x}{x_0}) - (\beta\delta) \cdot x^{1-\alpha_1} e^{-x/x_0} \right] \Bigg|_{x=\frac{H}{|\beta\delta}}. \end{aligned} \quad (\text{A4})$$

For $T > T_c$ the magnetic entropy change according to Eq. (A2) is

$$\Delta S_{\text{mag}}(T, H) = -a_2 \Delta \tilde{S}_{\text{mag}}^{\text{pl}}(T, H; 0, \frac{1-\beta}{\beta\delta}) + a_2 \Delta \tilde{S}_{\text{mag}}^{\text{pl-exp}}(H, T; b^{(0)}, \frac{1-\beta}{\beta\delta}) + \sum_{i=1}^4 b_1^{(i)} \Delta \tilde{S}_{\text{mag}}^{\text{exp}}(T, H; b_2^{(i)}). \quad (\text{A5})$$

There appears no simple analytical expression for $C_{v,\text{mag}}$. However, since Eq. (A5) can be evaluated efficiently, one can compute $C_{v,\text{mag}} \approx T \frac{\partial S_{\text{mag}}(T, H)}{\partial T}$ using the finite difference. The results are also shown in 6. The overall behavior is very close to those using Eq. (A1).

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- [1] A. Kitanovski, J. Tušek, U. Tomc, U. Plaznik, M. Ožbolt, and A. Poredoš, *Magnetocaloric Energy Conversion: From Theory to Applications* (Springer International Publishing, 2015).
- [2] S. Tassou, J. Lewis, Y. Ge, A. Hadaway, and I. Chaer, *Applied Thermal Engineering* **30**, 263 (2010), ISSN 1359-4311.
- [3] G. V. Brown, *Journal of Applied Physics* **47** (1976).
- [4] W. A. Steyert, *Journal of Applied Physics* **49**, 1216 (1978).
- [5] T. F. Petersen, K. Engelbrecht, C. R. H. Bahl, B. Elmegaard, N. Pryds, and A. Smith, *Journal of Physics D: Applied Physics* **41**, 105002 (2008), URL <https://doi.org/10.1088/0022-3727/41/10/105002>.
- [6] K. Gschneidner and V. Pecharsky, *International Journal of Refrigeration* **31**, 945 (2008), ISSN 0140-7007, URL <https://www.sciencedirect.com/science/article/pii/S0140700708000236>.
- [7] Z. Zheng, H. Yu, X. Zhong, D. Zeng, and Z. Liu, *International Journal of Refrigeration* **32**, 78 (2009), ISSN 0140-7007, URL <https://www.sciencedirect.com/science/article/pii/S0140700708001217>.
- [8] J. Tušek, A. Kitanovski, and A. Poredoš, *International Journal of Refrigeration* **36**, 1456 (2013).
- [9] M. Campostrini, M. Hasenbusch, A. Pelissetto, P. Rossi, and E. Vicari, *Phys. Rev. B* **65**, 144520 (2002).
- [10] C. S. Arnold and D. P. Pappas, *Phys. Rev. Lett.* **85**, 5202 (2000), URL <https://link.aps.org/doi/10.1103/PhysRevLett.85.5202>.
- [11] S. Y. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, *Phys. Rev. B* **57**, 3478 (1998), URL <https://link.aps.org/doi/10.1103/PhysRevB.57.3478>.
- [12] M. Griffel, R. E. Skochdopole, and F. H. Spedding, *Phys. Rev.* **93**, 657 (1954), URL <https://link.aps.org/doi/10.1103/PhysRev.93.657>.
- [13] T. Hashimoto, T. Numasawa, M. Shino, and T. Okada, *Cryogenics* **21**, 647 (1981), ISSN 0011-2275, URL <http://www.sciencedirect.com/science/article/pii/001122758190254X>.
- [14] N. D. Goldenfeld, *Lectures On Phase Transitions And The Renormalization Group*, *Frontiers in physics* (Westview Press, 1992), ISBN 9780201554090.
- [15] K. Huang, *Statistical Mechanics* (John Wiley & Sons, 2nd edition, 1991).
- [16] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, 1995).
- [17] B. Widom, *The Journal of Chemical Physics* **43**, 3898 (1965).
- [18] L. P. Kadanoff, *Physics Physique Fizika* **2**, 263 (1966).
- [19] 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).
- [20] K. G. Wilson, *Phys. Rev. B* **4**, 3174 (1971).
- [21] M. E. Fisher, *Rev. Mod. Phys.* **70**, 653 (1998), URL <https://link.aps.org/doi/10.1103/RevModPhys.70.653>.
- [22] P. R.K. and B. P.D. (2011), third ed. ed.
- [23] G. S. Rushbrooke, *The Journal of Chemical Physics* **39**, 842 (1963), URL <https://doi.org/10.1063/1.1734338>.
- [24] J. W. Essam and M. E. Fisher, *The Journal of Chemical Physics* **38**, 802 (1963), URL <https://doi.org/10.1063/1.1733766>.
- [25] H. R. Krishna-murthy, J. W. Wilkins, and K. G. Wilson, *Phys. Rev. B* **21**, 1003 (1980), URL <https://link.aps.org/doi/10.1103/PhysRevB.21.1003>.
- [26] R. Bulla, T. A. Costi, and T. Pruschke, *Rev. Mod. Phys.* **80**, 395 (2008), URL <https://link.aps.org/doi/10.1103/RevModPhys.80.395>.
- [27] V. Franco, A. Conde, J. Romero-Enrique, and J. Blázquez, *J. Phys.: Condens. Matter* **20** (2008).
- [28] C. Bonilla, F. Bartolomé, L. García, M. Parra-Borderías, J. Herrero-Albillos, and V. Franco, *Journal of Applied Physics* **107** (2010).

- [29] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College Publishing, 1976).
- [30] G. Grosso and G. P. Parravicini, *Solid State Physics* (Academic Press, 2000).
- [31] R. W. Hill, S. J. Collocott, K. A. Gschneidner, and F. A. Schmidt, *Journal of Physics F: Metal Physics* **17**, 1867 (1987), URL <https://doi.org/10.1088/0305-4608/17/9/013>.
- [32] A. Arrott and J. E. Noakes, *Phys. Rev. Lett.* **19**, 786 (1967), URL <https://link.aps.org/doi/10.1103/PhysRevLett.19.786>.