Landau-type parametrization of the equation of state of a ferromagnet

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An approximate equation of state is proposed for ferromagnets, with a particular reference to magnetic refrigerants such as gadolinium. The equation applies for $T \lesssim T_C$ and an arbitrary magnetic field and is based on Landau's theory of second-order phase transitions, with Bloch's 3/2 power law built in one of Landau's coefficients. The displacement of the maximum in the specific heat under an applied magnetic field is demonstrated to be nonmonotonic: the maximum shifts toward lower temperatures in a weak field but toward higher temperatures in a strong field.

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I. INTRODUCTION

Finding a single equation of state to describe the thermodynamic properties of ferromagnets in a broad range of temperatures and magnetic fields is a problem that has defied generations of solid-state physicists. After the initial success of Weiss's molecular-field theory[1] a century ago, the progress toward this goal has been slow. Satisfactorily accurate expressions have been obtained only for some special cases: the low temperatures,[2–4] the vicinity of the Curie point,[5] and the paramagnetic region. The interest in equations of state for magnetic materials has been rekindled in recent years in connection with the rapid development of magnetic cooling.[6,7] We shall therefore undertake an attempt at constructing a wide-range equation of state for ferromagnets, with a particular emphasis on the archetypal magnetic refrigerant—gadolinium.

As a framework for our phenomenological approach, we take the known theory of second-order phase transitions of Landau,[8] hereafter referred to as Landau's theory (LT). The applicability of this rather old theory to ferromagnets is still a matter of great confusion. Thus, Belov[9] came to a conclusion—entirely based on experiment—that LT well describes ferromagnetic 3*d* metals and alloys. Unfortunately, Belov's statement was largely unheeded at the time when the newer scaling theories were coming into fashion. The attitude to LT has changed over the past decades; now its applicability to, e.g., ferroelectrics is regarded as firmly established.[10,11] Many of the arguments put forward by Ginzburg and co-workers[10,11] equally apply to ferromagnets.

The paper is structured as follows. Before turning to constructing the equation of state, a brief revision of the main facts about LT is given in Sec. II. Special attention is paid to those issues that supposedly give cause for regarding LT as inaccurate. LT is often mixed up with its simplest version, limited to an immediate neighborhood of the Curie point. Sometimes LT is confused with mean-field theories in general and has to bear the responsibility for their drawbacks. In an attempt to measure the feature that LT (upon being appropriately extended) can describe, but other mean-field theories cannot, a quantity termed as "characteristic quotient" (Q) is introduced. Thereafter, in Sec. III, we proceed to constructing the magnetic equation of state, and in Sec. IV, the caloric equation of state.

Toward the end of the paper, we shall discuss an interesting and unexpected phenomenon—the nonmonotonic displacement of the heat-capacity peak under an applied magnetic field. This effect is proper to ferromagnets in general. The interest in the subject is not purely academic because it is closely related to another hotly debated issue—the exact location of the maximum of the magnetocaloric ΔT effect with respect to the Curie point.[12]

II. LANDAU'S THEORY AT FINITE σ

A. Essential points in brief

The theory in its general form was first stated by Landau in 1937.[8] Here, we shall follow the 1947 version by Ginzburg,[13] which is specific to ferromagnets. Its starting point is a thermodynamic potential written as an expansion in even powers of magnetization M,

$$\Phi(M,H,T) = \Phi_0 + \tfrac{1}{2}AM^2 + \tfrac{1}{4}BM^4 + \tfrac{1}{6}CM^6 + \cdots - MH. \tag{1}$$

The coefficients of this expansion, $\Phi_0, A, B, C, \ldots$, may depend on temperature (as well as on further external thermodynamic parameters such as pressure) but not on the magnetic field H. For simplicity, the system is assumed isotropic. At thermal equilibrium, Φ must be a minimum with respect to M,

$$\frac{\partial \Phi}{\partial M} = AM + BM^3 + CM^5 + \cdots - H = 0. \tag{2}$$

This is, in an implicit form, a magnetic equation of state—a relation between M, H, and T. In terms of the so-called reduced magnetization and temperature,

$$\sigma = \frac{M}{M_0}, \quad \tau = \frac{T}{T_C}, \tag{3}$$

where M_0 is the saturation magnetization and T_C is the Curie temperature; Eq. (2) is conveniently rewritten as

$$H = a\sigma + b\sigma^3 + c\sigma^5 + \cdots. \tag{4}$$

The coefficients on the right-hand side of Eq. (4), which are regarded as functions of reduced temperature, are expanded in a Taylor series about the Curie point, i.e., about $\tau = 1$,

$$a(\tau) = a(1) + a'(1)(\tau - 1) + \tfrac{1}{2}a''(1)(\tau - 1)^2 + \cdots,$$

$$b(\tau) = b(1) + b'(1)(\tau - 1) + \cdots,$$

$$c(\tau) = c(1) + \cdots. \tag{5}$$

In principle, the first two coefficients would have sufficed for a study of the asymptotic behavior *near* the Curie point, i.e., when $\tau \to 1$, $H \to 0$, and σ is infinitesimal. Here, however, we have kept an extra coefficient c because we intend to investigate the case of finite $1-\tau$ and σ. In doing so, we follow the idea put forward by Ginzburg in his 1947 paper,[13] even though he himself thought such an extension to the theory would be of little value. We certainly do not share his pessimistic view on this matter.

An important special case in the theory of ferromagnetic transformation is that of vanishing applied magnetic field, $H=0$, when there is a sharp distinction between the paramagnetic ($\sigma=0$) and the spontaneously magnetized ($\sigma \neq 0$) states, so that a changeover from one to the other is necessarily a phase transition. Like Landau and Ginzburg, we shall limit ourselves to the more interesting case when this is a second-order phase transition.

The simplest possibility to realize such a transition is by demanding a change of sign of the first coefficient in Eq. (4): $a(1)=0$, while $a'(1)>0$ and $b(1)>0$. In the ferromagnetic phase ($\sigma \neq 0, H=0$), one can divide Eq. (4) by σ, carry the coefficient $a \approx a'(1)(\tau-1)$ over to the left-hand side of the equation and then proceed to solving it for τ. Thus, one arrives at

$$\tau = 1 - \frac{b(1)}{a'(1)}\sigma^2 - \left\{ \frac{c(1)}{a'(1)} - \frac{b(1)b'(1)}{[a'(1)]^2} + \frac{a''(1)}{2a'(1)}\left[\frac{b(1)}{a'(1)}\right]^2 \right\}\sigma^4 - \cdots. \tag{6}$$

This presentation of τ as an expansion in even powers of σ, with coefficients independent of τ (any remaining dependence on τ can be eliminated by iterations), is obviously unique. We find it instructive to consider the dependence $\tau(\sigma)$ rather than the more usual $\sigma(\tau)$ for the following reason: Let Q be the ratio of the coefficients of σ^4 and σ^2 in expansion (6),

$$Q = \frac{\text{factor of } \sigma^4}{\text{factor of } \sigma^2} = \frac{c(1)}{b(1)} - \frac{b'(1)}{a'(1)} + \frac{a''(1)b(1)}{2[a'(1)]^2}. \tag{7}$$

This characteristic quotient determines how far below the Curie point Landau's asymptotic relation, $|\sigma| \propto (1-\tau)^{1/2}$, still holds. It is obviously required that

$$|\sigma| \ll Q^{-1/2} \tag{8}$$

or

$$|\tau - 1| \ll \frac{b(1)}{a'(1)}\frac{1}{Q}. \tag{9}$$

Being truly phenomenological, LT does not commit itself to any specific value of Q. This often leads to a misunderstanding. The theory is undeservedly blamed for contradicting experiment, referring typically to the interval $0.3 \lesssim \sigma \lesssim 0.8$. The misplaced expectation that Landau's asymptotic relation, $|\sigma| \propto (1-\tau)^{1/2}$, should be observable at such magnetizations is usually inferred from the molecular-field theory, which severely underestimates the characteristic quotient Q (see Sec. II B). In reality, Q is always greater than unity and the asymptotic regime sets in at much smaller magnetizations. This was confirmed by more careful measurements on Gd.[14]

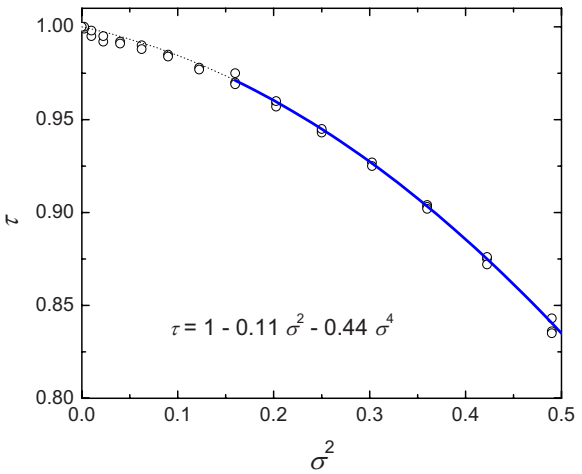

FIG. 1. (Color online) Reduced temperature vs square of reduced magnetization in the spin-1/2 Heisenberg model on the fcc lattice. The open circles are numerical data from Table III of Ref. 16 (Padé approximants); the line represents Eq. (12). The line thickness reflects the degree of confidence expressed in Ref. 16—the thin line in the top-left corner is drawn through poorly converged data points.

B. How large is the characteristic quotient Q?

Since LT gives no answer to this question, it has to be sought elsewhere. The promptest response comes from the molecular-field theory (for simplicity, restricted here to spin=1/2).[15] Its magnetic equation of state,

$$\sigma = \tanh\frac{\sigma}{\tau}, \tag{10}$$

is readily rewritten as

$$\tau = \frac{2\sigma}{\ln\dfrac{1+\sigma}{1-\sigma}} = 1 - \tfrac{1}{3}\sigma^2 - \tfrac{4}{45}\sigma^4 - \cdots, \tag{11}$$

whence by definition (7), $Q=4/15 \approx 0.27$. This is a grossly underestimated value, as will soon become clear. The molecular-field theory appears far too inaccurate near the Curie point.

In a more refined approach, one has to be more specific, so we choose the spin-$\frac{1}{2}$ Heisenberg model on the face-centered cubic (fcc) lattice. The corresponding dependence $\tau(\sigma)$ was numerically computed by Baker *et al.*[16] by using the Padé approximants to the high-temperature series. The data points from Table III of Ref. 16 (open circles in Fig. 1) are fitted to an expression similar to Eq. (6),

TABLE I. Values of parameters used in conjunction with Eqs. (15)–(20) to generate the curves shown in Figs. 2–5. The values of Q in the last column were obtained from Eq. (22).

Metal	Fixed parameters		Adjustable parameters			Derived
	M_0 (emu/g)	T_C (K)	p	κ	a_0 (MOe)	Q
Gd	266	293	1.5	0.35	0.9	1.9
Ni	58	631	0.28	0.47	1.85	1.3
Fe	222	1044	0.25	0.18	3.3	4.6
Co	164	1390	0.25	0.43	3.7	1.5

$$\tau = 1 - 0.11\sigma^2 - 0.44\sigma^4. \tag{12}$$

The agreement in Fig. 1 is better where the Padé approximants were particularly well converged (according to the authors' opinion). This portion of the fit is shown in bold. We observe a noticeable curvature in the τ vs σ^2 dependence (Fig. 1), which means that the term in σ^4 is indispensable for $0.3 \lesssim |\sigma| \lesssim 0.7$. The linear regime is limited to much smaller magnetizations, $|\sigma| < 0.1$.

The value $Q=4$, which was deduced from a well-converged high-temperature expansion,[16] should be regarded as a fairly accurate estimate of the characteristic quotient of the spin-$\frac{1}{2}$ Heisenberg model. (This value refers to the fcc lattice; similar although not as well-converged results were obtained for the other two cubic lattices.[16]) Fitting experimental data also produces values of Q greater than one (see Table I). (This is, of course, not to suggest that the Heisenberg model is directly applicable to the ferromagnetic $3d$ metals.) Therefore, the validity of the asymptotic relation $\tau = 1 - \text{const}\ \sigma^2$ is limited to $|\sigma| < 0.1$ or $|1-\tau| < 10^{-3}$. This was experimentally observed in Gd (see Fig. 6 of Ref. 14).

Obtaining data very close to the Curie point in experiment and/or numerical calculations is usually more difficult. Thus, the thin part of the fit in Fig. 1 is drawn through the points regarded as less reliable by Baker *et al.*[16] The bold portion of the curve can be alternatively fitted to a simpler formula, $\tau = 1 - \text{const}\ \sigma^{1/\beta}$ or $\sigma \propto |1-\tau|^{\beta}$, with $\beta \approx 1/3$. This single-exponent expression can be sometimes useful provided one keeps in mind that it is an approximate relation, which is not valid for very small σ. We shall refer to this relation in a qualitative discussion of the shape of the heat-capacity peak in Sec. IV B.

That experimental data are conventionally fitted to expressions with adjustable exponents rather than to Landau's expansion (6) or (12) does not amount to a disagreement between the experiment and LT[11] provided the latter is used in conjunction with an appropriate Q. As a matter of fact, no instances of disagreement between the two are known to exist. The real problem is the use of the molecular-field Q, which is an order of magnitude too small.

Incidentally, treating the spin-1/2 Heisenberg model in a more sophisticated random-phase approximation brings little improvement in this respect. From Eq. (33.11) in Tyablikov's book,[17] one derives

$$Q = \frac{C}{3}\left(1 - \frac{C}{5}\frac{Z+1}{Z}\right), \tag{13}$$

where Z is the coordination number and C is the constant defined by Eq. (33.13) of Ref. 17. For the fcc lattice ($Z=12$, $C=1.345$), Eq. (13) yields $Q=0.32$. Practically the same value is obtained for the other cubic lattices. This is far short of the target value, $Q=4$, and is only a minor improvement on the molecular-field result, $Q=0.27$. Whatever the drawbacks of the various approximate solutions to the Heisenberg model in three dimensions may be, a realistically high characteristic quotient Q is a prerequisite of any successful phenomenological equation of state.

C. Limitations of Landau's theory: Critical fluctuations

LT should not apply in the so-called fluctuation region,[18] when the applied field is weak and at the same time the temperature is very close to the critical point (i.e., when fluctuations of the order parameter are not small in comparison to its mean value). The width of the critical interval is known to be extremely small in the case of superconductors.[19] For ferroelectrics, this region is also rather narrow,[19] and it is believed that all phenomena observed so far are fully accounted for by LT.[10] However, ferromagnets are generally thought to be strongly affected by fluctuations in a broad range of temperatures around the Curie point. Let us briefly reexamine the grounds for such a belief.

The main argument in favor of the fluctuations' being important has been Ginzburg's criterion.[19] According to Ginzburg's own estimates, the right-hand side of his inequality (5b) for Ni is ~ 0.1.[19] That is, LT should apply to nickel only if $|\tau - 1| \gg 0.1$. However, in the paragraph following immediately after the inequality (5b), Ginzburg mentioned the omission "for convenience" of a prefactor $1/32\pi^2$. Unfortunately, this "truncated" form of Ginzburg's inequality was later included in the textbook.[18] Having allowed for the small prefactor would have yielded a very different result: $|\tau - 1| \gg 3 \times 10^{-4}$. The latter places practically no limitation on the use of LT for gadolinium since the purity of the best samples is only $\sim 1 \times 10^{-3}$.[20]

The second important argument against LT is the nonfulfillment of its prediction for spontaneous magnetization, $\sigma \propto (1-\tau)^{1/2}$, where $\tau < 1$. What is observed looks more like $\sigma \propto (1-\tau)^{1/3}$. On closer inspection, σ appears to follow no power law at all. As pointed out earlier by Ginzburg and

co-workers,[10,11] such a behavior is not attributable to critical fluctuations and is not indicative of any failure of LT. It is merely a sign of proximity to the tricritical point—b is small, c is non-negligible, and Q is large.

In conclusion, no deviations from LT near T_C have yet been reliably documented for ferromagnets. On the contrary, careful measurements on Gd very close to the Curie point have found Landau's asymptotic behavior, $\sigma \propto (1-\tau)^{1/2}$, $\tau < 1$, and $\chi \propto (\tau-1)^{-1}$, $\tau > 1$.[14] Apparently, critical fluctuations are confined to a much narrower interval around T_C than previously thought. In this work, they are disregarded altogether.

III. MAGNETIC EQUATION OF STATE

A. Main statements

In Sec. II, we have learned that LT provides a valid framework for constructing equations of state of ferromagnets. The simplest version of the theory, with Eq. (4) truncated after the term in σ^3, is valid for small σ, strictly speaking, infinitesimal. The interval of validity can be widened by including in Eq. (4) the term in σ^5, as proposed by Ginzburg.[13] Now, we set ourselves a goal—to work out an approximate equation of state that would apply in all situations of practical importance, i.e., for $|\sigma| \lesssim 1$, $0 < \tau \lesssim 1$, and arbitrary H. This excludes temperatures significantly exceeding the Curie point. In Sec. III, we shall concentrate on the magnetic equation of state [Eq. (4)]. The caloric equation of state will be dealt with in Sec. IV.

We postulate that the magnetic equation of state of a ferromagnet can be presented as Eq. (4), (i) which has been truncated after the term in σ^5, (ii) where the coefficients b and c are independent of τ, and (iii) the coefficient a depends on τ in such a way that Bloch's 3/2 power law is fulfilled at low temperatures,

$$a(\tau) = a_0 \frac{\tau^3 - 1}{1 + p\tau^{3/2}}. \tag{14}$$

Here, a_0 and p are parameters.[21]

Taking into consideration the above three points, as well as the normalization condition whereby $\sigma = 1$ at $\tau = 0$ and $H = 0$, we rewrite Eq. (4) as follows:

$$H = a_0 \sigma \left[\frac{\tau^3 - 1}{1 + p\tau^{3/2}} + \kappa\sigma^2 + (1-\kappa)\sigma^4 \right], \tag{15}$$

where $\kappa = b/a_0$. Alternatively, the equation of state can be solved for τ,

$$\tau = (\sqrt{1 - 2u + p^2u^2} - pu)^{2/3}, \tag{16}$$

where

$$u = \frac{1}{2}\left[\kappa\sigma^2 + (1-\kappa)\sigma^4 - \frac{H}{a_0\sigma} \right]. \tag{17}$$

The two forms of the equation of state complement each other: while Eq. (15) can be used for fitting experimental magnetization curves (σ vs H at fixed τ), Eqs. (16) and (17) are suitable for fitting temperature dependences of magnetization at a fixed magnetic field. Both purposes would be better served with a closed expression for $\sigma(\tau, H)$. This is not obtainable, however, because Eq. (15) is a fifth-degree polynomial in σ.

A solution for σ is possible in a special case, $H = 0$. This yields an expression for reduced spontaneous magnetization ($\tau < 1$),

$$\sigma^2 = \frac{\sqrt{\kappa^2 + 4(1-\kappa)\dfrac{1-\tau^3}{1+p\tau^{3/2}}} - \kappa}{2(1-\kappa)}. \tag{18}$$

At low temperatures, $\tau \ll 1$, this simplifies to

$$\sigma = 1 - \frac{p}{2(2-\kappa)}\tau^{3/2}, \tag{19}$$

which is Bloch's 3/2 power law. By virtue of Eq. (14), the paramagnetic susceptibility, $\chi = M_0/a(\tau)$, is given by

$$\chi = \frac{M_0}{a_0} \frac{1 + p\tau^{3/2}}{\tau^3 - 1}. \tag{20}$$

Let us finally express the characteristic quotient Q in terms of the model parameters. To this end, we expand the dependence $\tau(\sigma)$ defined by Eqs. (16) and (17) with $H = 0$ in a power series,

$$\tau = 1 - \frac{1+p}{3}\kappa\sigma^2 - \frac{1+p}{3}\left(1 - \kappa + \frac{2-p}{6}\kappa^2\right)\sigma^4 - \cdots. \tag{21}$$

By definition, Q is the ratio of the factor of σ^4 to that of σ^2, i.e.,

$$Q = \frac{1-\kappa}{\kappa} + \frac{2-p}{6}\kappa. \tag{22}$$

In realistic situations ($Q > 1$, $0 < \kappa < 1/2$, $p > 0$), the main contribution to Q comes from the first term, which is equal to the ratio c/b of the coefficients in Eq. (4).

B. Comparison to experiment

The equation of state obtained in Sec. III A has been tested by fitting available in the literature data on the four elemental ferromagnets. The most topical one of them is gadolinium metal. The interest in its equation of state is primarily centered around the Curie point, $T_C = 293$ K, and is stimulated by use in room-temperature magnetic cooling devices.[6,7]

A set of single-crystalline Gd data was taken from a classical work of Nigh *et al.*[22] The reduced spontaneous magnetization is plotted against reduced temperature in Fig. 2(a). To compute σ and τ, fixed values of saturation magnetization, $M_0 = 266$ emu/g, and Curie temperature, $T_C = 293$ K, were used, which were both taken from Ref. 22. The data points were fitted to Eq. (18). The two adjustable parameters, p and κ, were determined as follows. First, p was chosen so as to reproduce the low-temperature part of the dependence, which according to Eq. (19) is insensitive to the value of κ.

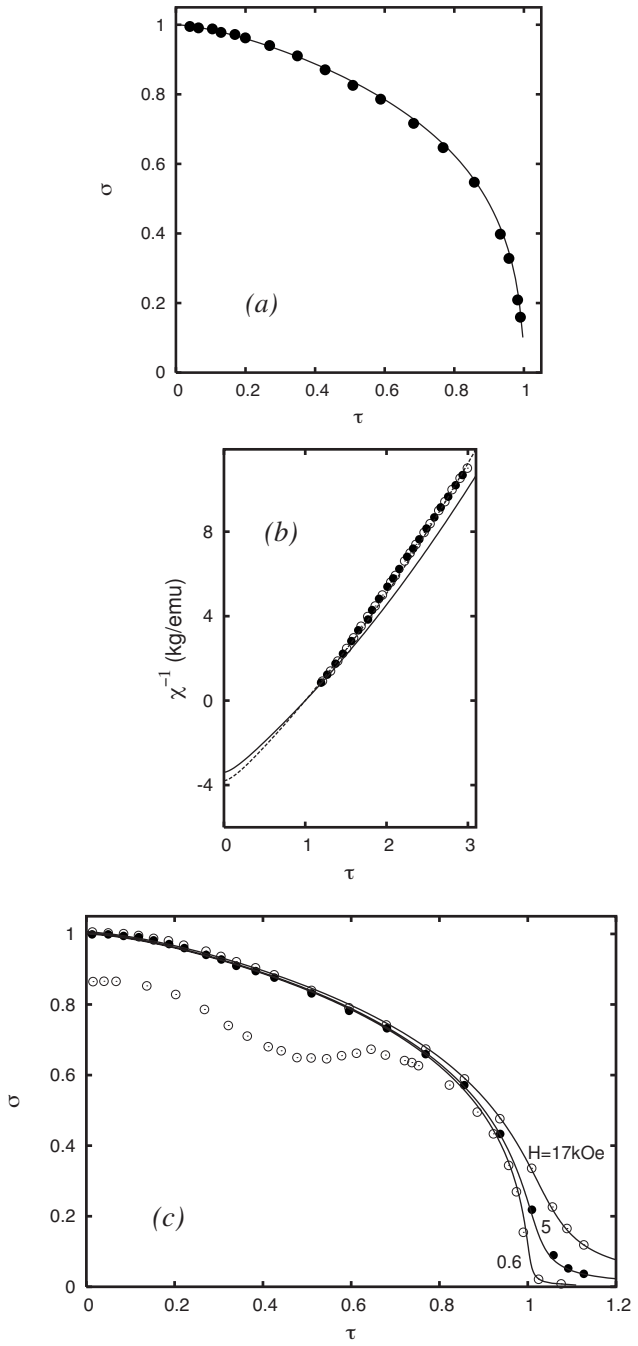

FIG. 2. Fitting experimental data on Gd (Ref. 22). All parameters are as in Table I unless indicated otherwise. (a) Reduced spontaneous magnetization vs reduced temperature: filled circles—experiment; solid line—Eq. (18). (b) Reciprocal susceptibility vs reduced temperature: circles—experiment [(○) a axis, (●) c axis]; solid line—Eq. (20) with $a_0=0.9$ MOe; and dotted line—Eq. (20) with $a_0=1.0$ MOe. (c) Reduced magnetization vs reduced temperature at three indicated values of internal magnetic field: circles—experiment; solid lines—Eqs. (16) and (17).

Then, keeping the found p fixed, κ was adjusted to fit the high-temperature end of the curve. After a few iterations, the process converged at $p=1.5$ and $\kappa=0.35$.

The remaining free parameter a_0 was deduced from the inverse susceptibility data[22] [Fig. 2(b)]. Equation (20) with $a_0=1.0$ MOe can be seen to agree with experiment at temperatures of up to three times the Curie point [Fig. 2(b), dashed line]. Following Ginzburg's advice,[13] however, a slightly lower value, $a_0=0.9$ MOe, was chosen instead, which better fits the data near (as well as below) the Curie point [see the solid line in Fig. 2(b)].

The best-fit parameters are collected in Table I. These parameters were used to compute the $\tau(\sigma)$ dependences by means of Eqs. (16) and (17). The calculated curves are presented in Fig. 2(c) as σ vs τ together with experimental data.[22] There is good agreement between theory and experiment except in the spin reorientation region, $\tau \lesssim 0.7$, where the low-field data measured along [001] are no longer representative of the full magnetization.

Nickel data are presented in Fig. 3. The spontaneous magnetization [Fig. 3(a)] was taken from two different sources[23,24] and normalized by using $M_0=58$ emu/g and $T_C=631$ K,[23,24] which were regarded as fixed values. The data were fitted to Eq. (18) with $p=0.28$ and $\kappa=0.47$. The inverse susceptibility [Fig. 3(b)] yielded $a_0=1.85$ MOe. Finally, these parameters were used in conjunction with Eq. (15) to generate the magnetization curves displayed in Fig. 3(c). The data points therein are from Table II of Ref. 24. The abscissas were corrected for demagnetization following the prescription of Weiss and Forrer.[24] Some residual curvature in the low-field region is attributable to domain effects in the irregularly shaped sample.

Less detailed data are available for Fe and Co (Figs. 4 and 5, respectively). Similarly to the previous, temperature dependence of spontaneous magnetization (a) and inverse susceptibility (b) was used to determine p, κ, and a_0. The fitting range for $\chi^{-1}(\tau)$ is rather narrow in both cases for different reasons. Iron undergoes a structural phase transition at $\tau \approx 1.1$, where its susceptibility experiences a large discontinuous change, whereas cobalt melts at $\tau \approx 1.27$. Unfortunately, no tabular data on $\sigma(\tau, H \neq 0)$ of iron or cobalt are available in literature. What has been found perfectly fits the description formulated in Sec. III A.

C. *Ab initio* evaluation of the parameters

Let us briefly review the prospects of computing from first principles the model parameters introduced in Sec. III A. As follows from the discussion in Sec. II, in order for the $\sigma(\tau)$ curve to have the right shape on approach to the Curie point, it is crucial to find a realistic value of the characteristic quotient Q or alternatively of the parameter κ. The two quantities are related through

$$Q \approx \frac{1-\kappa}{\kappa}, \tag{23}$$

which is just Eq. (22) without the small second term.

Evaluating Q proves a difficult task. It is no mere chance that most models underestimate it by an order. The one exception is the high-temperature expansion,[16] which suggests that Q (or κ) should be sought in the paramagnetic region. As a rough estimate, one may take $Q \sim 3$ and $\kappa \sim 0.3$.

The parameter p is obtainable from low-temperature calculations. By writing Bloch's law as[4]

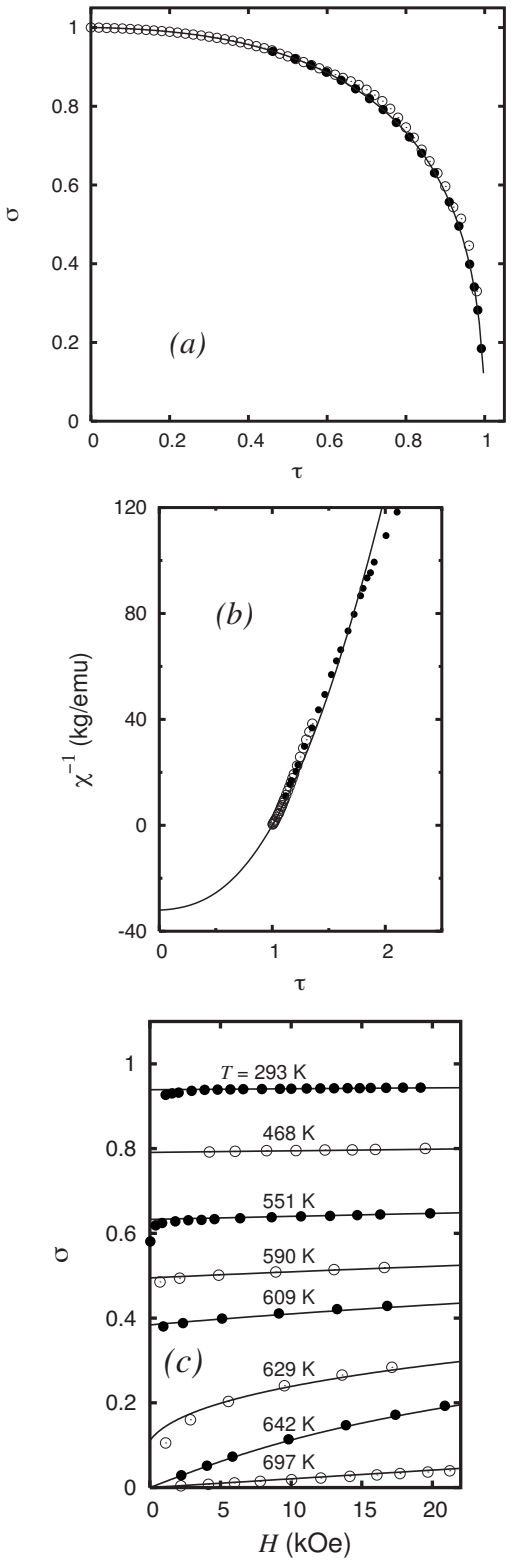

FIG. 3. Fitting Ni data. All parameters are as in Table I. (a) Reduced spontaneous magnetization vs reduced temperature: open circles—experiment (Ref. 23); filled circles—experiment (Ref. 24); and solid line—Eq. (18). (b) Reciprocal susceptibility vs reduced temperature: open circles—experiment (Ref. 25); filled circles—experiment (Ref. 26); and solid line—Eq. (20). (c) Reduced magnetization vs internal magnetic field at various fixed temperatures: circles—experiment (Ref. 24); solid lines—Eq. (15).

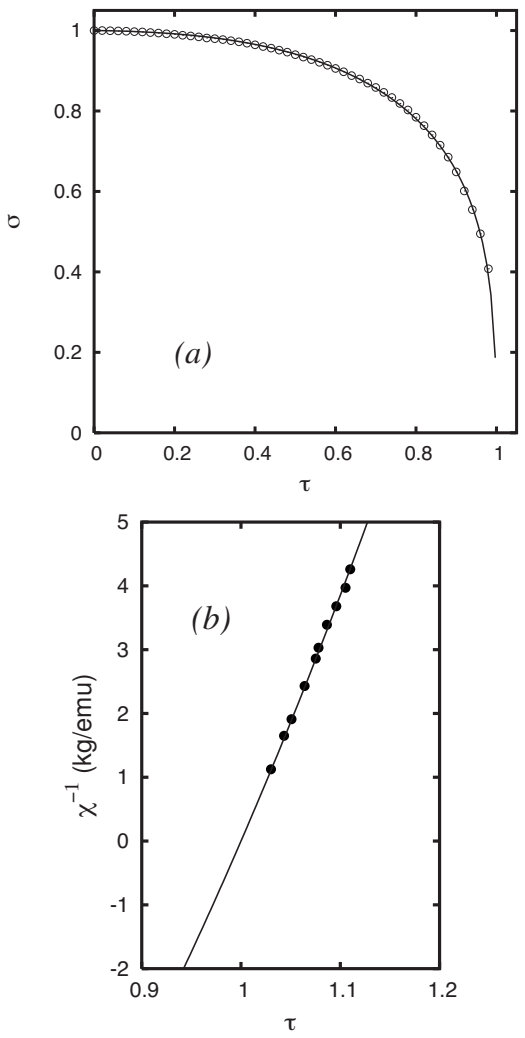

FIG. 4. Fitting Fe data. All parameters are as in Table I. (a) Reduced spontaneous magnetization vs reduced temperature: open circles—experiment (Ref. 23); solid line—Eq. (18). (b) Reciprocal susceptibility vs reduced temperature: filled circles—experiment (Ref. 26); solid line—Eq. (20).

$$\sigma = 1 - \frac{\zeta\left(\frac{3}{2}\right)}{8\pi^{3/2}} \frac{g\mu_B}{M_0} \left(\frac{kT_C}{D}\right)^{3/2} \tau^{3/2} \tag{24}$$

and equating the prefactors of $\tau^{3/2}$ in Eqs. (19) and (24), one gets

$$p = \frac{(2-\kappa)\zeta\left(\frac{3}{2}\right)}{4\pi^{3/2}} \frac{g\mu_B}{M_0} \left(\frac{kT_C}{D}\right)^{3/2}. \tag{25}$$

This expression is not particularly sensitive to the exact value of κ. Calculating the volume saturation magnetization M_0 in the density functional theory (DFT) is a matter of routine. The spin-wave stiffness D is more difficult to evaluate; this requires noncollinear electronic structure calculations. Nonetheless, solving this problem within the DFT can be regarded as an accomplished task.[30–32] The calculated values of D describe well the temperature variation of the spontaneous magnetization of ferromagnetic $3d$ metals (see Fig. 8 of Ref. 33).

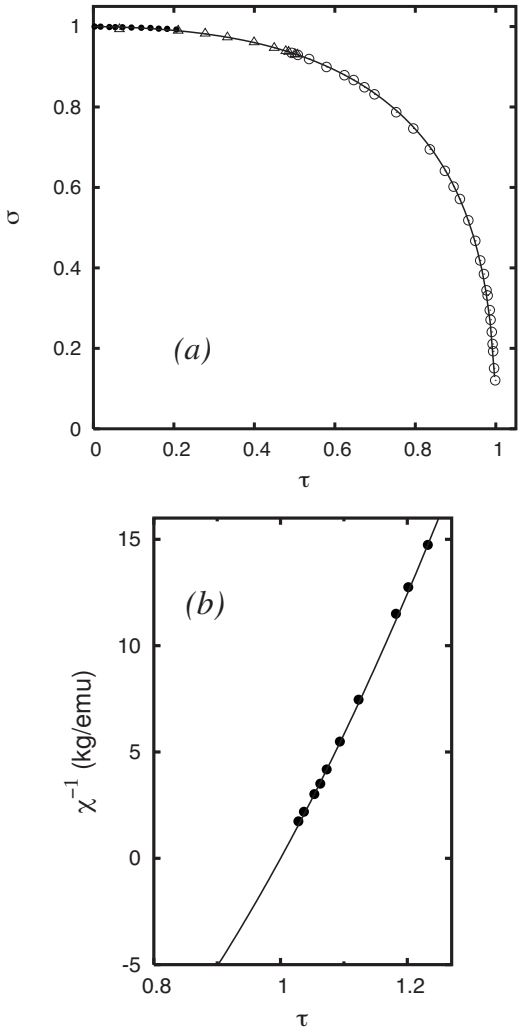

FIG. 5. Fitting Co data. All parameters are as in Table I. (a) Reduced spontaneous magnetization vs reduced temperature: data points—experiment [Refs. 27 (○), 28 (△), and 29 (●)]; solid line—Eq. (18). (b) Reciprocal susceptibility vs reduced temperature: filled circles—experiment (Ref. 26); solid line—Eq. (20).

The susceptibility in the paramagnetic region can be simulated by the classical Monte Carlo technique (prior determination of exchange integrals) and fitted to Eq. (20). This yields the Curie temperature and the parameter a_0. The fitting has to be performed iteratively since the use of Eq. (20) requires the knowledge of p, which in turn depends on T_C through Eq. (25). As regards to practical implementation of this algorithm, we note a recent work of Ruban *et al.*,[34] reporting such Monte Carlo simulations for iron and nickel. The numerical technique is clearly in need of further perfection—only one $\chi^{-1}(T)$ dependence out of five presented in Fig. 7 of Ref. 34 has the correct upward curvature. On the whole, given that Ref. 34 was a first such attempt, the method stands a fair chance of success.

Coming back to the evaluation of κ, one of the possibilities might be to use the relation

$$\kappa = \frac{M_0^3}{a_0}\frac{\chi_3}{\chi^4}, \tag{26}$$

where χ and χ_3 are the usual (linear) and the nonlinear susceptibilities, which are defined as coefficients in the power expansion of the magnetization, $M=\chi H-\chi_3 H^3-\cdots$. Both quantities can be evaluated simultaneously in the same Monte Carlo simulation, so calculating χ_3 does not involve much extra effort. The advantage of Eq. (26) is that it contains a temperature-independent (within the model) combination of χ and χ_3 and therefore requires no fitting. Instead, it may be averaged over a suitably chosen interval of temperatures above the Curie point. However, no examples of such calculations are yet to be found in literature.

IV. CALORIC EQUATION OF STATE

A. Entropy

We proceed from the thermodynamic potential (1) taken in conjunction with the three assumptions made at the beginning of Sec. III. Namely, expansion (1) is truncated after the term in M^6, the coefficients B and C are independent of temperature, while $A=M_0 a(\tau)$, where $a(\tau)$ is given by Eq. (14). The entropy is the negative derivative of Eq. (1) with respect to temperature, subject to a minimum condition [Eq. (2)]. The latter means that when taking the derivative, only the coefficients in Eq. (1) should be regarded as temperature dependent, but not the magnetization itself. Thus, we write

$$S_{\text{magn}} = -\frac{1}{T_C}\Phi_0'(\tau) - \frac{M_0}{2T_C}a'(\tau)\sigma^2. \tag{27}$$

Of relevance to magnetocaloric applications is the so-called isothermal magnetic entropy change,

$$\Delta S_{\text{magn}} = \frac{M_0 a'(\tau)}{2T_C}(\sigma_{\text{ini}}^2 - \sigma_{\text{fin}}^2), \tag{28}$$

where by convention the initial state is at zero magnetic field and the final state is at $H\neq 0$. Therefore, σ_{ini}^2 as a function of τ is given by Eq. (18). Unfortunately, $\sigma_{\text{fin}}^2(\tau,H)$ cannot be explicitly expressed. Another possibility is a parametric description of the ΔS_{magn} vs τ curves by means of two functions, $\Delta S_{\text{magn}}(\sigma_{\text{fin}})$ and $\tau(\sigma_{\text{fin}})$, where

$$\Delta S_{\text{magn}}(\sigma_{\text{fin}}) = \frac{M_0 a'[\tau(\sigma_{\text{fin}})]}{2T_C}\{\sigma_{\text{ini}}^2[\tau(\sigma_{\text{fin}})] - \sigma_{\text{fin}}^2\}, \tag{29}$$

$\tau(\sigma)$ is given by Eqs. (16) and (17) and σ_{fin} is a parameter running between zero and a nonzero value $\lesssim 1$. The curves displayed in Fig. 6(a) were obtained in this way by using the parameters relevant to Gd from Table I. Each one of these curves has a cuspidate maximum situated at the Curie point, $\tau=1$. The provenance of the cusp is illustrated in Fig. 6(b), which shows two $\sigma^2(\tau)$ curves. One of them, with $H\neq 0$, is smooth, whereas the other one, with $H=0$, has a kink at $\tau=1$. Thanks to the kink, the difference between the two plotted quantities (equal to the length of the hatching in Fig. 6) has a sharp maximum at $\tau=1$. Likewise, the $-\Delta S_{\text{magn}}(\tau)$ curves in Fig. 6(a) have cuspidate maxima at $\tau=1$.

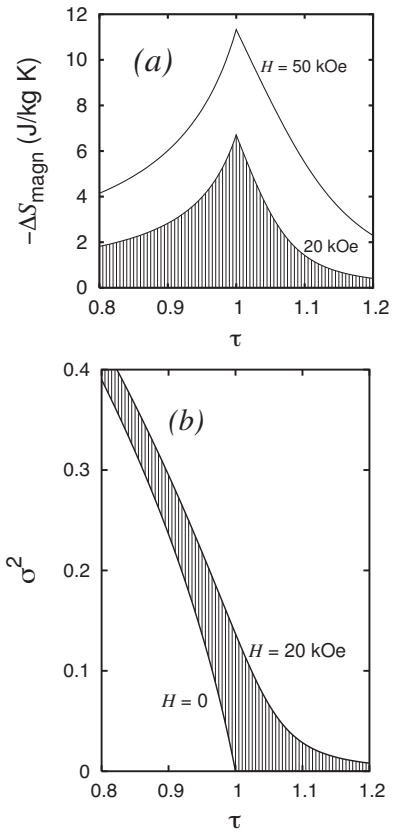

FIG. 6. (a) Negative magnetic entropy change induced in Gd by a change in magnetic field from 0 to 20 or to 50 kOe, computed by means of Eq. (29). (b) Square of reduced magnetization of Gd vs reduced temperature, which is obtained from Eq. (18) for $H=0$ and from Eqs. (16) and (17) for $H=20$ kOe.

The height of the peak is readily evaluated by substituting $\tau=1$ and $\sigma_{\rm ini}=0$ into Eq. (28),

$$\Delta S_{\rm max} = -\frac{M_0 a'(1)}{2T_C}\sigma_{\rm fin}^2. \tag{30}$$

The quantity $\sigma_{\rm fin}$ must satisfy Eq. (15), which at $\tau=1$ simplifies to

$$H = a_0\kappa\sigma_{\rm fin}^3 + a_0(1-\kappa)\sigma_{\rm fin}^5. \tag{31}$$

Setting $\sigma_{\rm fin}$ expressed from Eq. (30) into Eq. (31), we get

$$H = a_0\kappa\Delta\tilde{S}_{\rm max}^{3/2} + a_0(1-\kappa)\Delta\tilde{S}_{\rm max}^{5/2}, \tag{32}$$

where

$$\Delta\tilde{S}_{\rm max} = \frac{2T_C}{M_0 a'(1)}|\Delta S_{\rm max}| = \frac{2(1+p)T_C}{3a_0M_0}|\Delta S_{\rm max}|. \tag{33}$$

Equation (32) sheds some light onto the much discussed question of how $\Delta S_{\rm max}$ depends on magnetic field.[35] According to Eq. (32), the mean-field result, $\Delta S_{\rm max}\propto H^{2/3}$,[36] corresponds to the low-field asymptotic behavior. In order for it to be valid, $\sigma_{\rm fin}$ must be small,

$$\sigma_{\rm fin}^2 \ll \frac{\kappa}{1-\kappa} \tag{34}$$

Here, the right-hand side is roughly the inverse characteristic quotient [cf. Eq. (23)]. Therefore, inequality (34) is equivalent to Eq. (8). In strong fields, the relation $\Delta S_{\rm max}\propto H^{2/3}$ may become inaccurate, as a gradual crossover to $\Delta S_{\rm max}\propto H^{2/5}$ takes place. This is clearly visible in Fig. 3 of Ref. 35, wherein the effective exponent of $LaFe_{10.8}Si_{2.2}$ becomes clearly less than 2/3 when the applied field exceeds 100 kOe. For Gd at $H=100$ kOe, we estimate $\sigma_{\rm fin}^2\approx 0.34$, whereas $\kappa/(1-\kappa)\approx 0.54$. Away from the Curie point, Eq. (32) is not valid due to the emergence of a term in $\Delta S_{\rm magn}^{1/2}$ on the right-hand side.

B. Specific heat ($H=0$)

Differentiating Eq. (27) with respect to τ and multiplying the result by τ, we arrive at the following general expression for magnetic specific heat:

$$C_{\rm magn} = -\frac{\tau}{T_C}\left[\Phi_0''(\tau) + \frac{M_0}{2}a''(\tau)\sigma^2 + \frac{M_0}{2}a'(\tau)\frac{\partial(\sigma^2)}{\partial\tau}\right] \tag{35}$$

The most characteristic feature of the specific heat of a ferromagnet is a prominent peak near the Curie point, $\tau=1$. The primary responsibility for shaping the peak is borne by the last term in Eq. (35). Its form can be further specified by considering the cases of $H=0$ and $H\neq 0$ separately. In Sec. IV B, we limit ourselves to the former case.

From Eq. (15), with $H=0$, we derive for $\tau<1$,

$$\frac{\partial(\sigma^2)}{\partial\tau} = -\frac{a'(\tau)}{a_0[\kappa+2(1-\kappa)\sigma^2]}, \tag{36}$$

where $a(\tau)$ is defined by Eq. (14). At $\tau>1$, of course, $\partial(\sigma^2)/\partial\tau\equiv 0$. Thus, in the absence of magnetic field, the specific heat of a ferromagnet is described by a conjunction of two explicit expressions,

$$C_{\rm magn}(\tau) = \begin{cases} -\dfrac{\tau}{T_C}\left\{\Phi_0''(\tau) + \dfrac{M_0}{2}a''(\tau)\sigma^2(\tau) - \dfrac{M_0[a'(\tau)]^2}{2a_0[\kappa+2(1-\kappa)\sigma^2(\tau)]}\right\} & \text{if } \tau<1 \\ -\dfrac{\tau}{T_C}\Phi_0''(\tau) & \text{if } \tau>1 \end{cases}, \tag{37}$$

where $\sigma^2(\tau)$ is given by Eq. (18). The usual in LT discontinuity at $\tau=1$ delimits the peak on the right and determines its height,

$$\Delta C = \frac{M_0[a'(1)]^2}{2\kappa a_0 T_C} = \frac{9a_0 M_0}{2\kappa(1+p)^2 T_C}. \tag{38}$$

The low-temperature slope of the peak has a pronounced upward curvature, which gives an impression that the specific heat diverges. This happens because on approach to the Curie point from below, the magnetization behaves as approximately $(1-\tau)^{1/3}$, therefore $C_{\text{magn}} \propto \partial(\sigma^2)/\partial\tau \propto (1-\tau)^{-1/3}$. This is, however, no genuine divergence—very close to the Curie point, the magnetization enters the asymptotic regime, $\sigma \propto (1-\tau)^{1/2}$, and the specific heat tends to a finite limit, quite according to LT. Critical fluctuations play no role here.

The sharp peak of the specific heat, which is brought about by the last term in Eq. (35), stands on a "pedestal" produced by the first term $\propto \Phi_0''(\tau)$. Zeroth-order Landau's coefficient $\Phi_0(\tau)$ appeared as early as in Eq. (1) but was passed over in silence since it entered neither into the magnetic equation of state [Eqs. (2), (4), and (15)] nor into the magnetic entropy change [Eq. (28)]. Nevertheless, $\Phi_0(\tau)$ plays a very important role in the caloric equation of state. It cannot be simply set to zero, as sometimes suggested. Without the first term, the magnetic entropy [Eq. (27)] would be negative in the entire ferromagnetic region, $\tau<1$, which is of course unphysical. Likewise, without the first term, the specific heat [Eq. (35)] would be negative at low temperatures, $\tau \ll 1$, where the term in $a''(\tau)$ would be dominant. In the paramagnetic region, $\tau>1$, both S_{magn} and C_{magn} would be identically zero, which is unphysical too.

It is fair to say that, while the magnetic equation of state hinged on the first Landau's coefficient $a(\tau)$, the caloric equation of state is mainly concerned with constructing Landau's zeroth coefficient $\Phi_0(\tau)$. Without sufficient experimental data in tabular form, we are not in a position to give a definitive solution to this problem. We shall merely state the principles of constructing $\Phi_0(\tau)$ and then demonstrate on Gd that this can be done without introducing new adjustable parameters or changing the ones introduced above, in Sec. III. The basic principle is as follows: the dependence $\Phi_0(\tau)$ should be constructed in such a way as to ensure the correct asymptotic behavior of $S_{\text{magn}}(\tau)$ and $C_{\text{magn}}(\tau)$ away from the Curie point. At low temperatures, $\tau \ll 1$, it should be $S_{\text{magn}} \propto C_{\text{magn}} \propto \tau^{3/2}$.[4] At high temperatures, C_{magn} must monotonically fall off to zero, while S_{magn} must monotonically grow, approaching a nonzero limit S_∞. In the simplest case of localized spins S (relevant in particular to Gd), S_∞ is just $k\ln(2S+1)$ per spin. Restricting ourselves to this special case, we write $\Phi_0(\tau)$ as a two-term expression,

$$\Phi_0(\tau) = \frac{a_0 M_0}{2(1+p\tau^{3/2})} - \frac{pS}{2(2-\kappa)} \frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} NkT_C \tau^{5/2}(1-e^{-\tau_0/\tau})^{3/2}. \tag{39}$$

Here, N stands for the number of spins per unit mass (or volume) and τ_0 is a parameter defined by the following condition:

$$\tau_0^{3/2} = \frac{2(2-\kappa)}{pS} \frac{\zeta\left(\frac{3}{2}\right)}{\zeta\left(\frac{5}{2}\right)} \ln(2S+1). \tag{40}$$

The first term in Eq. (39) is constructed so as to achieve the cancellation of the nonphysical negative contributions to S_{magn} [Eq. (27)] and C_{magn} [Eq. (35)] coming from the terms in $a'(\tau)$ and $a''(\tau)$, respectively. The second term in Eq. (39) ensures the correct high-temperature limit, $S_{\text{magn}} \to Nk\ln(2S+1)$ as $\tau\to\infty$, as well as the spin-wave behavior at $\tau \ll 1$,

$$C_{\text{magn}} = \frac{15}{4} Nk \frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \frac{pS}{2(2-\kappa)} \tau^{3/2}. \tag{41}$$

The ratio of the two ζ functions is needed to correctly relate the prefactors of $\tau^{3/2}$ in Eq. (41) and in Bloch's law [Eq. (19)].[4]

Equation (39) is constructed in such a way as to provide the right asymptotic behavior at $\tau\to 0$ and $\tau\to\infty$, while keeping the function $\Phi_0(\tau)$ possibly smooth and featureless, as proper to a background. The latter is important, e.g., to guarantee the monotonic decreasing of $C_{\text{magn}}(\tau)$ at $\tau>1$. Equation (39) is one of the simplest expressions endowed with such properties, but is certainly not the only one. Its second derivative—too cumbersome to be reproduced here—forms in conjunction with Eqs. (18) and (37), a closed expression for $C_{\text{magn}}(\tau)$.

This dependence calculated for Gd with the parameters from Table I and $S=7/2$ is shown in Fig. 7(b) (solid line). Figure 7(a) displays the total specific heat of Gd, $C_{\text{magn}}(\tau) + C_{\text{lat}}(\tau)$, at $H=0$. The lattice contribution is $C_{\text{lat}}(\tau) = Nkf_D(1.73\tau)$, where $f_D(x)$ is Debye's function defined as follows:

$$f_D(x) = 9x^3 \int_0^x \frac{t^4 e^t dt}{(e^t-1)^2}, \tag{42}$$

and 1.73 is the ratio T_C/T_D computed with the known Debye temperature of Gd, $T_D=169$ K.[6]

The calculated specific heat of Gd [solid line in Fig. 7(a)] bears close resemblance to that measured on Gd single crystals (see Fig. 6 of Ref. 20). The dotted curve in Fig. 7(a)—a convolution of the solid curve with a Lorentzian of semiwidth $\Delta\tau=0.005$—simulates the smearing out of the peak observed in less pure samples.[20]

C. Specific heat in a nonzero magnetic field

If $H\neq 0$, Eq. (36) is no longer valid and has to be replaced by

$$\frac{\partial(\sigma^2)}{\partial\tau} = -\frac{2a'(\tau)\sigma^2}{a(\tau) + 3a_0\kappa\sigma^2 + 5a_0(1-\kappa)\sigma^4}. \tag{43}$$

As a result, Eq. (35) becomes

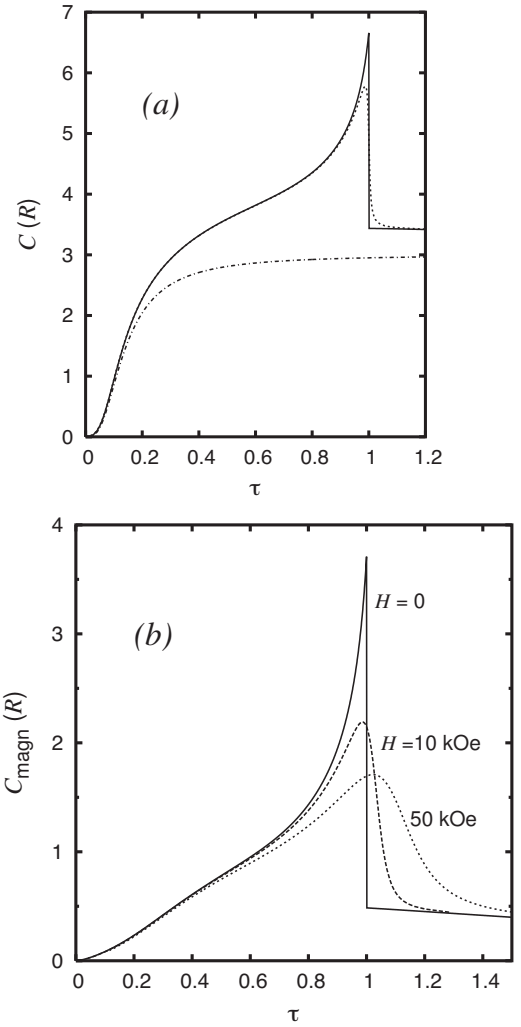

FIG. 7. Calculated molar specific heat of gadolinium. (a) $H=0$, lattice specific heat (dashed-dotted line), total specific heat (solid line), and total specific heat smeared out by inhomogeneities (dotted line). (b) Magnetic specific heat at various values of applied magnetic field.

$$C_{\text{magn}} = -\frac{\tau}{T_C}\left\{\Phi_0''(\tau) + \frac{M_0}{2}a''(\tau)\sigma^2 - \frac{M_0[a'(\tau)]^2\sigma^2}{a(\tau) + 3a_0\kappa\sigma^2 + 5a_0(1-\kappa)\sigma^4}\right\}, \quad (44)$$

where $\Phi_0(\tau)$ and $a(\tau)$ are defined by Eqs. (39) and (14), respectively.

Now, the magnetization σ cannot be expressed explicitly as a function of τ. However, the inverse dependence $\tau(\sigma)$ is given by Eqs. (16) and (17). Therefore, the C_{magn} vs τ curves can be described parametrically by means of a pair of explicit expressions, $\tau(\sigma)$ and $C_{\text{magn}}[\tau(\sigma),\sigma]$, where σ is a parameter running between 0 and 1.

Two curves generated in such a way for Gd are shown in Fig. 7(b) along with the zero-field specific heat. Apart from the expected disappearance of the discontinuity and broadening of the peak, we observe that the position of the maximum shifts in a rather peculiar fashion. Namely, in a relatively weak field, $H=10$ kOe, the maximum is situated at $\tau_{\text{peak}}<1$, i.e., at a lower temperature than without the field. However, in a stronger field, $H=50$ kOe, the maximum is at $\tau_{\text{peak}}>1$. The nonmonotonic dependence of τ_{peak} on H obtained in our calculations for Gd is summarized in Fig. 8 (solid line). For small H, the function $\tau_{\text{peak}}(H)$ decreases. It reaches a minimum at about $H=4$ kOe and starts to increase. At about 24 kOe, it crosses the $\tau_{\text{peak}}=1$ level and continues to grow further.

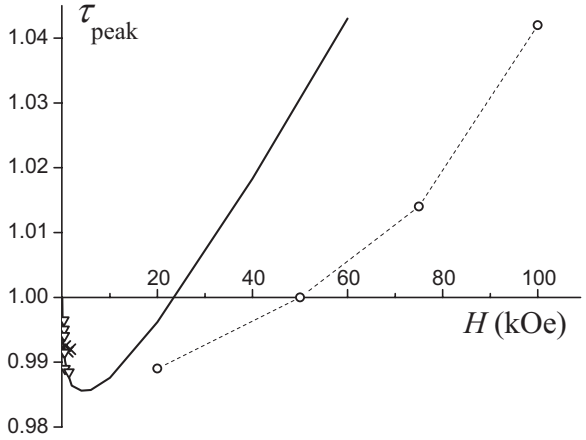

FIG. 8. Position of the maximum in the specific heat of Gd as a function of applied magnetic field. Solid line—calculations, this work. Data points—experiment, Refs. 37 (∇), 38 (×), and 20 (○···○).

Remarkably, the nonmonotonic behavior of the peak position is corroborated by experimental data on Gd from various sources, as displayed in Fig. 8. However, the data have not been analyzed in their entirety by the earlier workers, and the change of trend has not been noticed so far. Thus, Dan'kov *et al.*[20] remarked that the peak shifts toward higher temperatures in stronger fields but made no comment on the fact that the 20 kOe dependence in their Fig. 7 peaks at a distinctly lower temperature than the $H=0$ curve does.

Checking the literature on other ferromagnets, one finds surprisingly little information on whither the maximum of the specific heat shifts under a magnetic field. Thus, Korn and Kohlhaas[39] saw it move toward lower temperatures in iron and nickel in a field range of $H \leq 22.5$ kOe, whereas Ahn *et al.*[40] observed the opposite trend in EuO, although in stronger fields, 10 kOe $\leq H \leq 100$ kOe.

Going back to Fig. 8, we note a systematic overestimation of τ_{peak} in strong fields, which is clearly attributable to the too gently sloping background $\Phi_0''(\tau)$. Constructing for $\Phi_0(\tau)$ a better expression than Eq. (39) is certainly desirable. As regards to the nonmonotonic shape of the $\tau_{\text{peak}}(H)$ dependence, it should be common to all ferromagnets. This is demonstrated in Sec. IV D.

D. Whither the heat-capacity peak?

The aim of Sec. IV D is to demonstrate that the nonmonotonicity of the field-induced shift of the heat-capacity peak is proper to all ferromagnets. To this end, we shall use LT in its simplest form,[8,13] in which $c=0$ is nil, b is positive and in-

dependent of temperature, and $a(\tau)$ is given by $a'(\tau-1)$, where a' is also positive and temperature independent. Equilibrium condition (4) can now be solved for τ,

$$\tau = 1 + \frac{H - b\sigma^3}{a'\sigma}, \tag{45}$$

and this expression be used to eliminate τ from the last term of Eq. (44), which then becomes

$$C_{\text{magn}} = C_0 + \frac{M_0 a'}{T_C}\sigma^2 \frac{H + a'\sigma - b\sigma^3}{H + 2b\sigma^3}. \tag{46}$$

Here, C_0 stands for the background term, $-\tau T_C^{-1}\Phi_0''(\tau)$, and we note the disappearance of the term in a''.

It is convenient to introduce new variables, a dimensionless magnetic field,

$$h = \left(\frac{b}{a'}\right)^{3/2}\frac{H}{b}, \tag{47}$$

and a new running parameter x,

$$x = \frac{b}{a'}\sigma^2. \tag{48}$$

Equations (45) and (46), rewritten in terms of the new variables,

$$\tau = 1 - x + hx^{-1/2}, \tag{49}$$

$$C_{\text{magn}} = C_0 + 2\Delta C \frac{hx + x^{3/2} - x^{5/2}}{h + 2x^{3/2}}, \tag{50}$$

are now regarded as a parametric description of the dependence of C_{magn} on τ. Here, ΔC is the jump in the specific heat at $H=0$,

$$\Delta C = \frac{M_0 (a')^2}{2bT_C}. \tag{51}$$

The position of the maximum in the specific heat τ_{peak} is determined from the condition $\partial C_{\text{magn}}/\partial x = 0$. Neglecting the weak temperature dependence of the background term C_0, this results in

$$h = \tfrac{1}{4}x^{1/2}(7x - 3 + \sqrt{81x^2 - 42x + 9}). \tag{52}$$

The plus sign before the square root has been chosen to ensure that $hx^{-1/2} \to 0$ as $x \to 0$ and $\tau_{\text{peak}} \to 1$ [cf. Eq. (49)].

Setting Eq. (52) into Eq. (49) and solving for x, we get

$$x = \tfrac{1}{6}(2 - \tau_{\text{peak}} \pm \sqrt{9\tau_{\text{peak}}^2 - 8\tau_{\text{peak}}}), \tag{53}$$

which in conjunction with Eq. (52) provides a closed expression for $h(\tau_{\text{peak}})$. It is a universal relation, independent of a' or b. In Fig. 9, it is presented in a more digestible form as τ_{peak} vs h. (An explicit expression for $\tau_{\text{peak}}(h)$ is, in principle, obtainable but too cumbersome to be useful).

The falling portion of the curve in Fig. 9 is obtained if one takes the lower sign in Eq. (53). It is a finite arc starting at the point $h=0$, $\tau_{\text{peak}}=1$. [According to Eqs. (52) and (53), h is undefined for $x<0$ or $\tau_{\text{peak}}>1$]. In very weak fields,

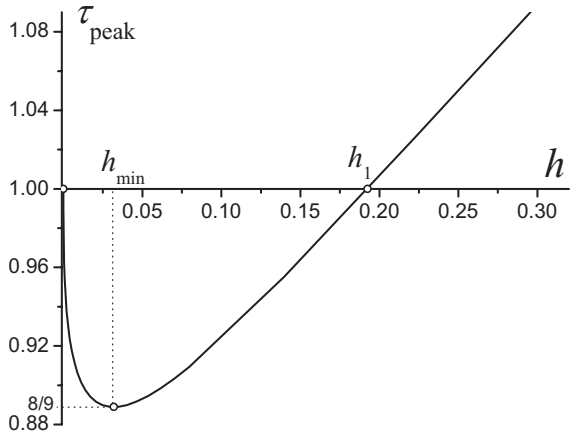

FIG. 9. Position of the maximum in the magnetic specific heat of a ferromagnet against rescaled magnetic field, which is computed by using Eqs. (52) and (53).

$$\tau_{\text{peak}} = 1 - \left(\tfrac{3}{4}\right)^{2/5}h^{2/5} \tag{54}$$

and

$$C_{\text{magn}} = C_0 + \Delta C\left(1 - \frac{5}{3^{3/5}4^{2/5}}h^{2/5}\right), \tag{55}$$

i.e., the decrease in the peak's abscissa and height is proportional to $H^{2/5}$.

The growing part of the curve corresponds to the upper sign in Eq. (53). Setting $\tau_{\text{peak}}=1$ into Eq. (53), we get $x=1/3$ and find, hence, the abscissa of the crossing point, $h_1=3^{-3/2}\approx 0.19$. At this field value, the heat-capacity peak is back to its initial position, where it was without the field. According to Eq. (50), at this point, $C_{\text{magn}}=C_0+\frac{2}{3}\Delta C$, i.e., the elevation of the peak above the pedestal has reduced by a third in comparison to what it was at $h=0$.

Both branches join together at $\tau_{\text{peak}}=8/9$, as the radicand in Eq. (53) vanishes. This corresponds to the minimum in Fig. 9. Its abscissa is $h_{\text{min}}=\frac{2}{81}\sqrt{5/3}\approx 0.03$, i.e., about one-sixth of h_1. The height of the maximum at this stage amounts to $C_0+\frac{20}{27}\Delta C$.

A cartoon explanation of the nonmonotonic behavior of the heat-capacity peak is presented in Fig. 10. An applied magnetic field lowers the peak in a systematic way. The demolition of the summit (hatched) produces extra entropy, which is dumped where room permits—at the foot of the peak on its high-temperature side. The net effect on the po-

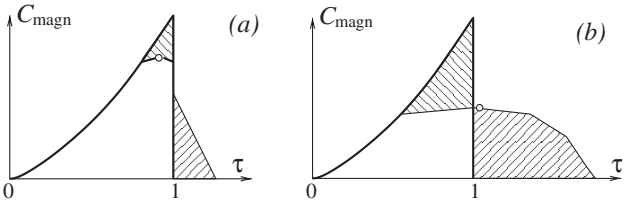

FIG. 10. Lowering of the heat-capacity peak in a magnetic field. The redistribution of the entropy content leads to a shift of the maximum to the left in a weak field (a), but to the right in a strong field (b).

sition of the maximum depends on whether the top of the displaced entropy heap reaches the level of the new summit. If it does not [weak fields, Fig. 10(a)], the maximum is to the left of its initial zero-field position. If it does [strong fields, Fig. 10(b)], then the displaced entropy plays a role in the shaping of the new summit, pulling it eventually toward higher temperatures. (It is essential that the specific heat is integrated with a weight factor $1/T$, so the hatched areas in each panel are *not* equal).

In this simple picture, the maximum shift of the peak to the left can be estimated as the half-width of the zero-field peak at 0.74 of its height above the background. (Recall that the height of the peak in the leftmost position was $20/27 \approx 0.74$ of its height at $H=0$). Accordingly, the rather broad peak contemplated by the simplest version of LT shifts by as much as 11% (or by $\frac{1}{9}T_C$). In the more refined approach of Sec IVB, the peak is much narrower [see Fig. 7(b)]; therefore, under an applied field, it moves to the left by no more than 1.5% (Fig. 8).

Summarizing, the nonmonotonic field-induced displacement of the maximum in the specific heat of ferromagnets is an effect common to all of them. The $\tau_{\text{peak}}(h)$ dependence obtained within the simplest version of LT (Fig. 9) is similar to that calculated from the complete equation of state (Fig. 8). Yet the resemblance is merely qualitative, the minimum in Fig. 9 being much deeper.

V. CONCLUSION

We have constructed an equation of state suitable for ferromagnets in a broad interval of temperatures ($T \lesssim T_C$) and magnetic fields. Properly speaking, these are two distinct but associated equations of state, a magnetic one, which relates M with H and T, and a caloric one, for S vs H and T. Expressions derived for the former are in fair agreement with available experimental data. Crucial to the success of the new magnetic equation of state is a feature that mean-field models usually lack—the ability to handle realistically high values of the characteristic quotient Q.

As regards to the caloric equation of state, here, an important role is played by a background containing the derivatives of Landau's zeroth-order coefficient $\Phi_0(\tau)$ (which is of no relevance to the magnetic equation of state). This term is, in particular, responsible for the short order above the Curie point, which is observed as a high-temperature "tail" in the specific heat. The proposed expression for $\Phi_0(\tau)$ contains no fitting parameters in addition to those already present in the magnetic equation of state and leads to qualitatively correct results. Thus, the heat-capacity peak bears close resemblance to that experimentally observed. There is still room for quantitative improvements—the background slopes off too gently above and is not high enough at the Curie point. As a result, the calculated zero-field peak is somewhat too low.

Among other properties strongly affected by $\Phi_0(\tau)$, one should mention the field-induced displacement of the heat-capacity peak. It has been demonstrated that such displacement in ferromagnets is nonmonotonic with respect to the intensity of the field. In weak fields, the maximum shifts toward lower temperatures, the size of the shift being principally determined by the shape of the upper part of the peak. In strong fields, the maximum moves toward higher temperatures. This rising part of the dependence $\tau_{\text{peak}}(H)$ is very sensitive to the background term in the magnetic specific heat, which can be utilized for fine tuning $\Phi_0(\tau)$.

ACKNOWLEDGMENT

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