

Thermodynamics of the magnetocaloric effect

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The relationship between the behavior of the temperature-dependent heat capacity at constant pressure measured in different magnetic fields and the magnetocaloric effect in magnetic systems with and without discontinuous change of entropy is discussed. It is shown that the two are directly related to each other, and if the behavior of either property (i.e., the heat capacity or the magnetocaloric effect) is known, the general behavior of the second one can be predicted. The derived relationships are illustrated using several sets of experimental data and model examples.

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I. INTRODUCTION

The magnetocaloric effect (MCE) is generally recognized as the heating or the cooling of magnetic solids in a varying dc magnetic field. It was discovered by Warburg¹ and, over the years, the nature and the behavior of the MCE as a function of temperature and magnetic-field change were the subjects of many experimental and theoretical studies.²⁻⁸ The fundamentals of the magnetocaloric effect are developed quite well, e.g., see recent reviews by Pecharsky and Gschneidner,⁹ and Tishin.¹⁰ Nevertheless, even today advanced research on this magnetothermal phenomenon remains important from both basic and practical perspectives. The fundamental significance of the MCE arises from its intimate relationship with both the magnetism and the thermodynamics of solids. This warrants further basic experimental and theoretical studies to bring about a more complete understanding of the thermal behavior of magnetic solids as functions of both temperature and magnetic-field change. The applied importance of the MCE is easily appreciated from the fact that for many years it has been used successfully to reach ultra-low temperatures in a research environment.^{11,12} Furthermore, recent technological advancements^{13,14} strongly suggest that in the near future the MCE may become the keystone for an energy efficient and environmentally safe near-room-temperature solid-state refrigeration and cooling technologies, provided all theoretical and practical aspects of continuous magnetic refrigeration are adequately matured.

In essence, the magnetocaloric effect in solids is the result of the entropy variation due to the coupling of a magnetic spin system with the magnetic field. It is well known that the total entropy S of a magnetic solid, where the magnetism is due to localized magnetic moments, e.g., lanthanide-based materials, is the sum of the electronic, lattice, and magnetic entropies (S_E , S_L , and S_M , respectively). We note that in a magnetic solid with itinerant magnetism and/or $3d$ magnetism, the separation of the three contributions to the entropy is, in general, not straightforward. At constant pressure P , all three are functions of temperature T ,

$$S(T)_P = [S_E(T) + S_L(T) + S_M(T)]_P. \quad (1)$$

Among the three, the magnetic entropy strongly depends on the magnetic field H , while usually the electronic and the lattice entropies are practically magnetic-field independent. However, for materials with high-electronic specific-heat constants, e.g., Sc,¹⁵ CeCu₂Si₂,¹⁶ CeB₆,¹⁶ UBe₁₃,¹⁷ and others, below ~ 10 K the electronic heat capacity (and entropy) exhibit strong nonlinear dependences on both temperature and magnetic field, which are difficult to treat theoretically. The electronic contribution to the magnetocaloric effect in this case, nonetheless, can be calculated from the experimental electronic heat capacity data if they are available. Hence, if the magnetic field around a typical magnetic solid varies from H_1 to H_2 (i.e., it is changed by $\Delta H = H_2 - H_1$), then the magnetic entropy of the solid at a constant T is reduced (or increased) by ΔS_M , and both S_E and S_L remain constant. The value of $\Delta S_M(T)_{\Delta H,P}$ depends on both ΔH and absolute temperature (see Fig. 1) and the magnetocaloric effect at an

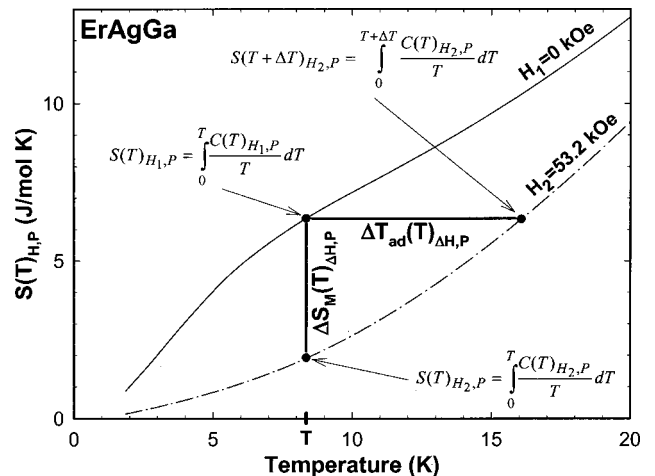


FIG. 1. The total entropy functions of ErAgGa in magnetic fields 0 and 53.2 kOe. The magnetocaloric effect in terms of both the isothermal magnetic entropy change, $\Delta S_M(T)_{\Delta H,P}$, and the adiabatic temperature change, $\Delta T_{ad}(T)_{\Delta H,P}$, for the given temperature T , is shown as thick vertical and horizontal bars, respectively. The corresponding values of the total entropy are indicated by dots and arrows, and are listed in terms of the heat capacity in magnetic fields H_1 and H_2 .

arbitrary and constant T is given in terms of the *isothermal magnetic entropy change* as

$$\begin{aligned}\Delta S_M(T)_{T,\Delta H,P} &= [S_M(T)_{H_2} - S_M(T)_{H_1}]_{T,P} \\ &= [S(T)_{H_2} - S(T)_{H_1}]_{T,P}.\end{aligned}\quad (2)$$

The magnitude, the sign, and the behavior of the $\Delta S_M(T)_{\Delta H,P}$ is therefore dependent on the relationship between $S(T)_{H_1}$ and $S(T)_{H_2}$ at constant pressure. When the magnetic field is changed adiabatically by ΔH (i.e., when S is constant), the combined lattice and electronic entropies must change by $\Delta(S_L + S_E) = -\Delta S_M$ to fulfill the condition that $\Delta S = \Delta S_E + \Delta S_L + \Delta S_M = 0$. The configurational entropy in a solid generally remains constant during a magnetic-field change and therefore only the thermal lattice and electronic entropies vary resulting in the measurable *adiabatic temperature change*, ΔT_{ad} , of the magnetic material. Considering temperature as a function of the total entropy, the magnetocaloric effect in terms of $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ is also a function of temperature (see Fig. 1) and, for a fixed ΔH and an arbitrary T , it is defined as

$$\Delta T_{\text{ad}}(T)_{T,\Delta H,P} = [T(S)_{H_2} - T(S)_{H_1}]_{S,P}.\quad (3)$$

Hence, according to Eqs. (2) and (3), when the behavior of the total entropy of a magnetic solid is known as a function of both temperature and magnetic field, its MCE is fully characterized.

The magnetic entropy change is also related to the change of the bulk magnetization M as a function of temperature and magnetic field, and can be calculated from magnetization data (see Refs. 9, 10, 18) using the well-known Maxwell relationship

$$\Delta S_M(T)_{\Delta H,P} = \int_{H_1}^{H_2} \left(\frac{\partial M(T,H)}{\partial T} \right)_{H,P} dH.\quad (4)$$

The adiabatic temperature change is also given^{9,10,18} as

$$\Delta T_{\text{ad}}(T)_{\Delta H,P} = - \int_{H_1}^{H_2} \left(\frac{T}{C(T,H)} \times \frac{\partial M(H,T)}{\partial T} \right)_{H,P} dH.\quad (5)$$

Equations (4) and (5) are easily derived from general thermodynamics, but both fail to describe the MCE during a truly discontinuous first-order phase transition when $[\partial M(H,T)/\partial T]_{H,P}$ does not exist. Analytical integration of both Eqs. (4) and (5) is impossible since both magnetization and heat capacity are material-dependent and generally unknown functions of temperature and magnetic field. Equation (4) is usually integrated numerically, while numerical integration of Eq. (5) is hardly ever performed because normally the magnetic field and temperature-dependent heat capacity is not known with the required details. Finally, the adiabatic temperature change can be measured directly (see Refs. 9, 10, 18–20).

Although Eqs. (2) and (3) completely define the MCE in solids, the numerical integration involved in evaluating the total entropy functions may result in the accumulation of

errors that can reach 20–30% of the calculated MCE values near the room temperature, and the heat-capacity measurements must be carried out starting as close to the absolute zero as possible.^{18,21} It is of considerable interest therefore to analyze the relationships between the behavior of the heat capacity as a function of temperature in different magnetic fields and the magnetocaloric effect (also as a function of temperature), particularly with respect to the magnitude, the sign, and the positions of the MCE peaks. The relationships between the behavior of the heat capacity and the adiabatic temperature change in the vicinity of the magnetic-phase transition have been recently examined by Tishin, Gschneider, and Pecharsky⁸ by considering a closed reversible thermodynamic cycle on T - S diagram. The results obtained in Ref. 8 are applicable when the magnetocaloric effect is quite large. Here we explore the general relationships between the two characteristics of the MCE, $\Delta S_M(T)_{\Delta H,P}$, and $\Delta T_{\text{ad}}(T)_{\Delta H,P}$, both as the functions of temperature, and the most basic thermodynamic property of solids, i.e., their heat capacity at constant pressure as the function of temperature in constant magnetic fields H_1 and H_2 . First we analyze the magnetocaloric effect associated with second-order phase transitions, which is the most commonly experimentally studied phenomenon and is usually classified as the conventional MCE. Later we consider the magnetocaloric effect in the vicinity of first-order phase transformations, which has recently received much attention in particular with respect to reports of the giant magnetocaloric effect in such materials as FeRh and $\text{Gd}_5(\text{Si}_{1-x}\text{Ge}_x)_4$, see references in Sec. III. As far as we are aware, these relationships were not discussed before.

II. THE CONVENTIONAL MAGNETOCALORIC EFFECT

In this section we consider a fully reversible magnetocaloric effect in conventional paramagnetic and/or ferromagnetic systems. The total entropy of systems considered below is always a continuous function of temperature regardless of magnetic field. It is also assumed that hystereses, coercive fields, anisotropy, and remanence, are all negligible and therefore have no effect on the magnetocaloric effect. Furthermore, all changes in the magnetic systems are assumed to be equilibrium or quasistatic processes. For convenience we also assume that the magnetic field is always changing by $\Delta H = H_2 - H_1$ and that $H_2 > H_1$. It is easy to see [Eqs. (2) through (5)] that all conclusions remain valid even when $H_2 < H_1$ resulting in the reversal of the MCE sign.

A. Isothermal magnetic entropy change, $\Delta S_M(T)_{\Delta H,P}$

From the second law of thermodynamics,

$$dS(T)_{H,P} = \frac{C(T)_{H,P}}{T} dT,\quad (6)$$

where $C(T)_{H,P}$ is the heat capacity at constant pressure P and magnetic field H ; $S(T)_{H,P}$ is the total entropy at constant pressure and magnetic field; and T is the absolute temperature. Assume that the heat capacity of a magnetic material is measured at constant pressure as the function of temperature

between T_1 and T_2 (where $T_2 > T_1$ and T_1 approaches zero) in two constant magnetic fields H_1 and H_2 (where $H_2 > H_1$ and H_1 is usually zero). When the entropy of such system is a continuous function of temperature, the total entropies at an arbitrary T , where $T_1 < T \leq T_2$, and constant magnetic fields H_1 and H_2 can be easily calculated from Eq. (6) as

$$S(T)_{H_1,P} = \int_{T_1 \rightarrow 0}^T \frac{C(T)_{H_1,P}}{T} dT \quad (7a)$$

and

$$S(T)_{H_2,P} = \int_{T_1 \rightarrow 0}^T \frac{C(T)_{H_2,P}}{T} dT. \quad (7b)$$

According to the third law of thermodynamics, the zero-temperature entropy in Eqs. (7a) and (7b) is assumed to be zero and magnetic-field independent. The magnetocaloric effect as a function of temperature for a given $\Delta H = H_2 - H_1$ in terms of the magnetic entropy change, $\Delta S_M(T)_{\Delta H,P}$, is defined by Eq. (2). Hence, substituting Eqs. (7a) and (7b) into Eq. (2) and integrating between $T=0$ K and an arbitrary T that, as shown in Fig. 1, is the same for both entropy functions at H_1 and H_2 , we get

$$\Delta S_M(T)_{\Delta H,P} = \Delta S(T)_{\Delta H,P} = \int_0^T \frac{[C(T)_{H_2} - C(T)_{H_1}]_P}{T} dT. \quad (8)$$

It is immediately evident therefore that greater difference of the heat capacities in magnetic fields H_1 and H_2 between 0 K and T results in the greater $|\Delta S_M(T)_{\Delta H,P}|$ values at the same T . In other words, a large MCE is expected in the systems where the magnetic field strongly affects the heat capacity. Furthermore, provided that the difference between $C(T)_{H_2}$ and $C(T)_{H_1}$ remains the same, the magnetocaloric effect in terms of $|\Delta S_M(T)_{\Delta H,P}|$ is expected to be gradually lowered as absolute temperature increases.

If $\Delta S_M(T)_{\Delta H,P}$ has a maximum or a minimum, then the peak temperature is found by differentiating Eq. (8) with respect to temperature,

$$\frac{\partial[\Delta S_M(T)_{\Delta H,P}]}{\partial T} = \frac{[C(T)_{H_2} - C(T)_{H_1}]_P}{T} = 0. \quad (9)$$

It is straightforward from Eq. (9) that $\Delta S_M(T)_{\Delta H,P}$ reaches a maximum or a minimum when

$$C(T)_{H_1,P} = C(T)_{H_2,P}. \quad (10)$$

Whether the $\Delta S_M(T)_{\Delta H,P}$ has a maximum or a minimum can be found by calculating its second derivative with respect to temperature

$$\frac{\partial^2[\Delta S_M(T)_{\Delta H,P}]}{\partial T^2} = \frac{\partial}{\partial T} \left[\frac{C(T)_{H_2,P} - C(T)_{H_1,P}}{T} \right]. \quad (11)$$

Expanding the right-hand side of Eq. (11) we obtain for $\Delta S_M(T)_{\Delta H,P}$ being a maximum for

$$\frac{1}{T} \left[\frac{\partial C(T)_{H_2,P}}{\partial T} - \frac{\partial C(T)_{H_1,P}}{\partial T} \right] - \frac{1}{T^2} [C(T)_{H_2,P} - C(T)_{H_1,P}] < 0 \quad (12)$$

and, correspondingly, we have for $\Delta S_M(T)_{\Delta H,P}$ being a minimum for

$$\frac{1}{T} \left[\frac{\partial C(T)_{H_2,P}}{\partial T} - \frac{\partial C(T)_{H_1,P}}{\partial T} \right] - \frac{1}{T^2} [C(T)_{H_2,P} - C(T)_{H_1,P}] > 0. \quad (13)$$

Taking into account Eq. (10), one can see that

$$\frac{1}{T^2} [C(T)_{H_2,P} - C(T)_{H_1,P}] = 0 \quad (14)$$

at both the maximum and the minimum and therefore combining Eqs. (10) and (12) through (14), and noting that $1/T$ is always positive and defined except for $T=0$ K, the maximum in $\Delta S_M(T)_{\Delta H,P}$ is observed when

$$C(T)_{H_1,P} = C(T)_{H_2,P} \quad \text{and} \quad \frac{\partial C(T)_{H_2,P}}{\partial T} < \frac{\partial C(T)_{H_1,P}}{\partial T}, \quad (15)$$

while $\Delta S_M(T)_{\Delta H,P}$ is a minimum when

$$C(T)_{H_1,P} = C(T)_{H_2,P} \quad \text{and} \quad \frac{\partial C(T)_{H_2,P}}{\partial T} > \frac{\partial C(T)_{H_1,P}}{\partial T}. \quad (16)$$

Equation (15) indicates that the magnetic entropy change has the maximum near the temperature at which the heat capacities in different magnetic fields are equal and the slope of $C(T)_{H_2,P}$ as a function of temperature is lower than that of $C(T)_{H_1,P}$. Similarly, Eq. (16) shows that $\Delta S_M(T)_{\Delta H,P}$ has the minimum when the heat capacity in the higher magnetic field rises faster with temperature than the heat capacity in the lower magnetic field when the two are the same (i.e., when the two heat capacity functions cross over).

The relationships between the heat capacity and the magnetic entropy change discussed above are illustrated in Figs. 2, 3, and 4. Figure 2 shows the heat capacity of ErAgGa (Ref. 22) as a function of temperature in three different constant magnetic fields: $H_1=0$, and $H_2'=53.2$ or $H_2''=98.5$ kOe. For both nonzero magnetic fields the slope of the high-magnetic-field heat capacity exceeds that of the zero-magnetic-field heat capacity at the temperature when $C(T)_{H_1,P} = C(T)_{H_2,P}$ [Fig. 2(a)], i.e., the $\Delta S_M(T)_{\Delta H,P}$ in these cases should have a minimum in accord with Eq. (16), which is seen in Fig. 2(b). Furthermore, since the temperature where Eq. (16) holds is rising as the upper magnetic field increases, the $\Delta S_M(T)_{\Delta H,P}$ minima for various ΔH are observed at different temperatures. The heat capacity of Dy Al₂ in 0, 20, and 50 kOe magnetic fields²³ is shown in Fig. 3(a). The temperature where the heat capacity in both 20 and 50 kOe magnetic fields is equal to that in the zero magnetic field remains practically constant due to a well-defined

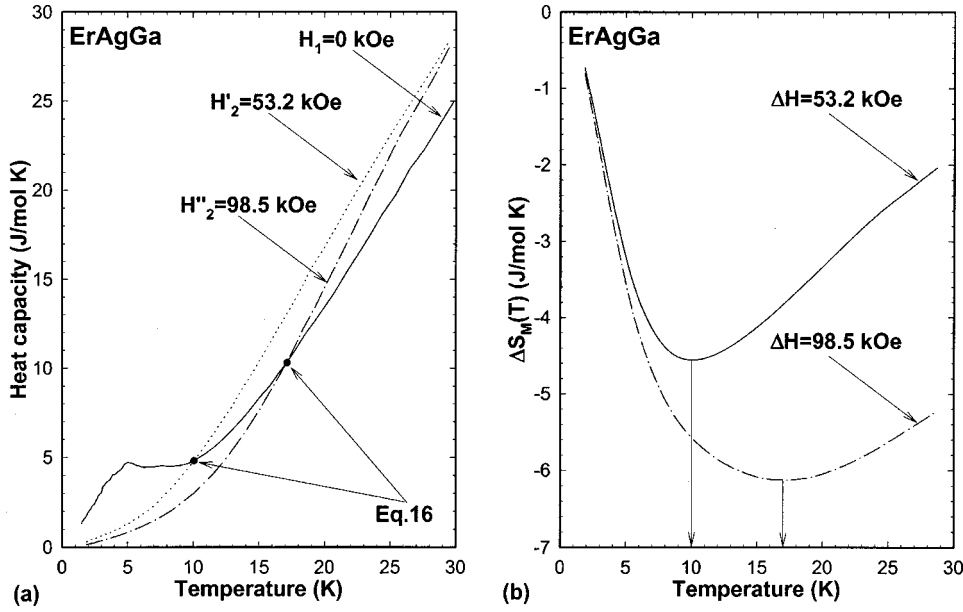


FIG. 2. The heat capacity of ErAgGa in 0, 53.2, and 98.5 kOe magnetic fields as a function of temperature (a) and the corresponding magnetic entropy changes for ΔH from 0 to 53.2 and from 0 to 98.5 kOe (b). The dots in (a) indicate the temperatures where Eq. (16) holds, i.e., the temperatures where, $\Delta S_M(T)_{\Delta H, P}$, is at the minimum [also indicated in (b) by vertical arrows].

λ -type zero-magnetic-field heat-capacity anomaly. Therefore the $\Delta S_M(T)_{\Delta H, P}$ minima also remain practically temperature independent [Fig. 3(b)]. Also included in Fig. 3(b) is the $\Delta S_M(T)_{\Delta H, P}$ calculated from the magnetization data for DyAl₂ [Eq. (4)], which is in an excellent agreement with the magnetic entropy change determined from the heat capacity using Eq. (8). A different heat capacity and $\Delta S_M(T)_{\Delta H, P}$ behaviors are observed in PrNi₅,²⁴ when the high magnetic field enhances the low-temperature heat capacity and then lowers it to below the zero-magnetic-field heat capacity for certain temperature range as shown in Figs. 4(a) and 4(b), respectively, for 0 and 70 kOe. As a result, there are two temperatures, one where Eq. (15), and another where Eq. (16) hold, i.e., $\Delta S_M(T)_{\Delta H, P}$ has a low-temperature maximum and a high-temperature minimum [see Fig. 4(b)]. The anomalous behavior of the heat capacity in a paramagnetic PrNi₅ has been associated with crossing of the two lowest-

magnetic-energy levels (Γ_4 and Γ_1) in the presence of crystalline electric fields (for more details see Ref. 24).

B. Adiabatic temperature change, $\Delta T_{ad}(T)_{\Delta H, P}$

For simplicity assume that magnetic field suppresses the total entropy and therefore $\Delta S_M(T)_{\Delta H, P}$ is negative resulting in a positive adiabatic temperature change when $H_2 > H_1$ as shown in Fig. 1. The relationship between the adiabatic temperature change, $\Delta T_{ad}(T)_{\Delta H, P}$, and the heat capacity at constant pressure can be analyzed by means of the following considerations. By definition [see Eq. (3) and Fig. 1],

$$S(T)_{H_1, P} = S(T + \Delta T_{ad}(T)_{\Delta H})_{H_2, P} \quad (17)$$

for any T . Hence, by substituting Eqs. (7a) and (7b) into Eq. (17) and integrating between $T = 0$ K and an arbitrary T we get

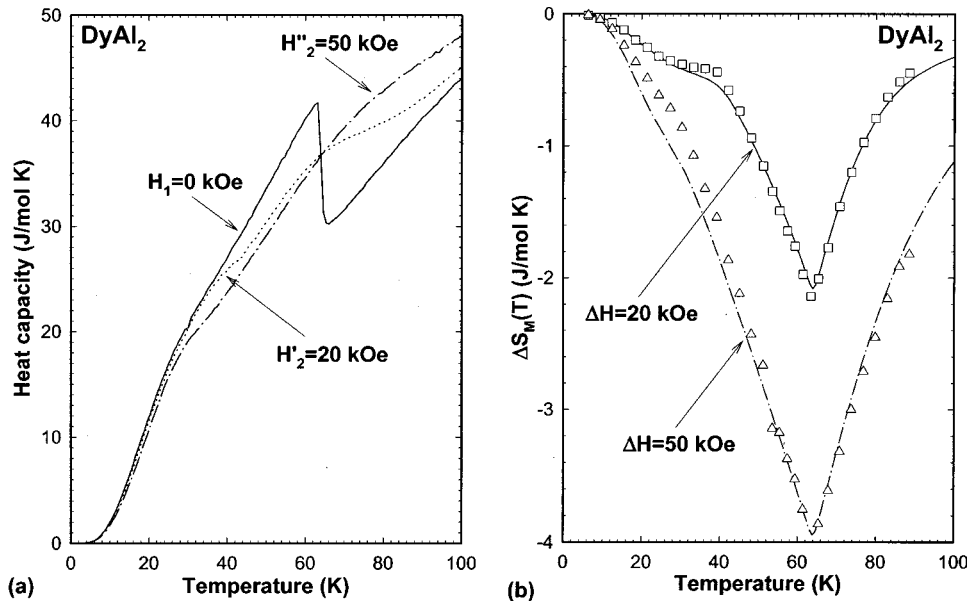


FIG. 3. The heat capacity of DyAl₂ in 0, 20, and 50 kOe magnetic fields as a function of temperature (a) and the corresponding magnetic entropy changes for ΔH from 0 to 20 and from 0 to 50 kOe (b). The lines in (b) represent the $\Delta S_M(T)_{\Delta H, P}$ calculated from the heat capacity using Eq. (8), and the open symbols in (b) represent the same calculated from the magnetization data using Eq. (4).

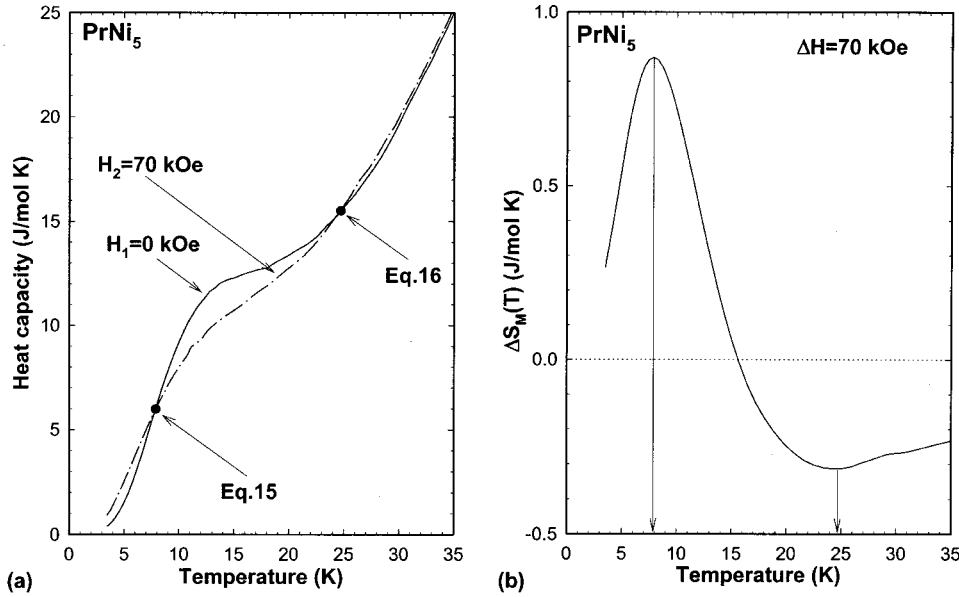


FIG. 4. The heat capacity of PrNi₅ in 0, and 70 kOe magnetic fields as a function of temperature (a) and the corresponding magnetic entropy change for ΔH from 0 to 70 kOe (b). The dots in (a) indicate the temperatures where Eq. (15) or (16) holds.

$$\int_0^T \frac{C(T)_{H_1,P}}{T} dT = \int_0^{T+\Delta T_{ad}(T)_{\Delta H,P}} \frac{C(T)_{H_2,P}}{T} dT, \quad (18)$$

which can be rearranged as

$$\int_0^T \frac{[C(T)_{H_1} - C(T)_{H_2}]_P}{T} dT = \int_T^{T+\Delta T_{ad}(T)_{\Delta H,P}} \frac{C(T)_{H_2,P}}{T} dT. \quad (19)$$

By comparing with Eq. (8) it becomes

$$-\Delta S_M(T)_{\Delta H,P} = \int_T^{T+\Delta T_{ad}(T)_{\Delta H,P}} \frac{C(T)_{H_2,P}}{T} dT. \quad (20)$$

Noting that $1/T$ is always positive and continuous except for $T=0$ K and $C(T)_{H_2,P}$ is positive and defined throughout the limits of integration in Eq. (20), and applying the first mean-value theorem, a specific temperature T_0 exists for any $T > 0$ K where

$$T \leq T_0 \leq T + \Delta T_{ad}(T)_{\Delta H,P} \quad (21)$$

and Eq. (20) becomes

$$-\Delta S_M(T)_{\Delta H,P} = C(T_0)_{H_2,P} \times \int_T^{T+\Delta T_{ad}(T)_{\Delta H,P}} \frac{1}{T} dT. \quad (22)$$

From Eq. (21) it is clear that T_0 is a function of both T and $\Delta T_{ad}(T)_{\Delta H,P}$. We note that when $\Delta T_{ad}(T)_{\Delta H,P}$ is small, which is usually observed at temperatures much higher than absolute zero and far from the magnetic phase transitions, T_0 in Eq. (22) can be approximated by T since $T \cong T + \Delta T_{ad}$. In the vicinity of phase transition temperature the situation becomes much more complex and the location of T_0 within the temperature interval delineated by T and $T + \Delta T_{ad}(T)_{\Delta H,P}$ is impossible to predict. By integrating the right-hand side of Eq. (22) and solving it with respect to $\Delta T_{ad}(T)_{\Delta H,P}$ we get

$$\Delta T_{ad}(T)_{\Delta H,P} = T \times \left\{ \exp \left[-\frac{\Delta S_M(T)_{\Delta H,P}}{C(T_0)_{H_2,P}} \right] - 1 \right\}. \quad (23)$$

Equation (23) relates the magnetocaloric effect as the function of temperature for a given ΔH and an arbitrary T with the magnetic entropy change for the same ΔH and T , and the heat capacity in the magnetic field H_2 at the specific temperature T_0 [see Eq. (21)]. We also note that in Eq. (8) $\Delta S_M(T)_{\Delta H,P}$ is the function of the heat capacities and T , and therefore $\Delta T_{ad}(T)_{\Delta H,P}$ is ultimately the function of $C(T)_{H_1,P}$, $C(T)_{H_2,P}$, and T . Similar to the conclusion based on Eq. (8) for the magnitude of the $\Delta S_M(T)_{\Delta H,P}$, a large value of $|\Delta T_{ad}(T)_{\Delta H,P}|$ is expected to be observed in materials where the magnetic field strongly influences the heat capacity, i.e., when $|C(T)_{H_2,P} - C(T)_{H_1,P}|$ is large between $T=0$ K and a given T . By repeating the above procedure [Eqs. (20)–(23)] and noting that T is always positive and continuous and $C(T)_{H_2,P}/T$ is positive and defined throughout the limits of integration in Eq. (20), a different temperature, $T_1 \neq T_0$ exists, where

$$T \leq T_1 \leq T + \Delta T_{ad}(T)_{\Delta H,P}, \quad (24)$$

when Eq. (20) becomes

$$-\Delta S_M(T)_{\Delta H,P} = \frac{C(T_1)_{H_2,P}}{T_1} \times \int_T^{T+\Delta T_{ad}(T)_{\Delta H,P}} dT. \quad (25)$$

Similar to T_0 [Eqs. (21)–(23)], T_1 [Eqs. (24) and (25)] is also a function of both T and $\Delta T_{ad}(T)_{\Delta H,P}$, and when $\Delta T_{ad}(T)_{\Delta H,P}$ is negligibly small, T_1 in Eq. (25) can be approximated by T but near a phase-transition temperature the value of T_1 remains unique and unknown. Thus, Eq. (25) yields a second obvious solution of Eq. (20) for the adiabatic temperature change

$$\Delta T_{ad}(T)_{\Delta H,P} = -\frac{T_1}{C(T_1)_{H_2,P}} \Delta S_M(T)_{\Delta H,P}. \quad (26)$$

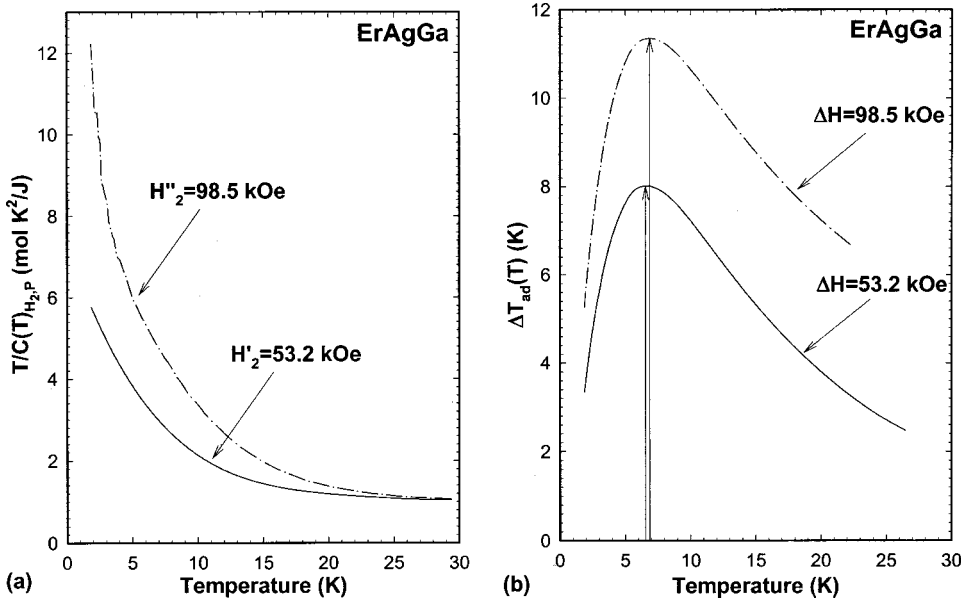


FIG. 5. The behavior of the $T/C(T)_{H_2,P}$ of ErAgGa between ~ 1.5 and 30 K in magnetic fields 53.2 and 98.5 kOe (a) and the adiabatic temperature change of ErAgGa for magnetic field change from 0 to 53.2 and from 0 to 98.5 kOe (b).

Equation (26) relates the magnetocaloric effect as the function of temperature for a given ΔH and an arbitrary T with the magnetic entropy change for the same ΔH and T , a specific value of the absolute temperature, T_1 [see Eq. (24)] and the heat capacity in the magnetic field H_2 at T_1 . Also Eq. (23) can be simplified by recalling that $e^x - 1 \cong x$ when x is small. Hence, when $|\Delta S_M| \ll C_p$, which is a valid assumption at high temperatures (e.g., near the Debye temperature and above), Eq. (23) can be approximated by

$$\Delta T_{\text{ad}}(T)_{\Delta H,P} \cong - \frac{T}{C(T_0)_{H_2,P}} \Delta S_M(T)_{\Delta H,P}. \quad (27)$$

Noting Eq. (8), $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ as given by Eqs. (26) and (27) is, at the end, a function of the heat capacities in two magnetic fields and the absolute temperature. Equations (23) and (26) are general, but unfortunately, the exact values of T_0 or T_1 and therefore $C(T_0)_{H_2,P}$ or $C(T_1)_{H_2,P}$ remain unknown. Furthermore, both T_0 and T_1 are also functions of temperature at fixed magnetic field H_2 .

Several important conclusions can be drawn from an analysis of Eqs. (23), (26), and (27). First, the adiabatic temperature change should increase for the same $\Delta S_M(T)_{\Delta H,P}$ and $C(T)_{H_2,P}$ as temperature increases. Above Debye temperature the lattice heat capacity of solids approaches the DuLong-Petit limit of $3R$ J/mol(atom)K and therefore $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ may be considerable at room temperature and above, provided Debye temperature is near or below room temperature. Second, the adiabatic temperature change is expected to be much larger in solids with lower total heat capacity provided magnetic entropy change and temperature remain the same. In principle, similar conclusions can be derived from an analysis of Eq. (5).

Noting Eq. (9), differentiating the simplest of the two general equations [Eq. (26)] with respect to temperature, and equating $\partial(\Delta T_{\text{ad}}(T)_{\Delta H,P})/\partial T$ to zero, a peak value of the $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ is observed when

$$[C(T)_{H_2} - C(T)_{H_1}]_P = -T \times \Delta S_M(T)_{\Delta H,P} \times \frac{C(T_1)_{H_2,P}}{T_1} \times \frac{\partial}{\partial T} \left(\frac{T_1}{C(T_1)_{H_2,P}} \right). \quad (28)$$

From Eq. (28) it is clear that the maximum (or the minimum) $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ generally should not coincide with the temperature of the corresponding minimum (or maximum) in $\Delta S_M(T)_{\Delta H,P}$. For any $T > 0$ the right-hand side of Eq. (28) becomes zero only when $\Delta S_M(T)_{\Delta H,P} = 0$ or when $\partial/\partial T [T_1/C(T_1)_{H_2,P}] = 0$. It is also obvious that the peak temperatures of both $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ and $\Delta S_M(T)_{\Delta H,P}$ approach each other as the magnetocaloric effect and/or $\partial/\partial T [T_1/C(T_1)_{H_2,P}]$ approach zero. The analysis of the equations derived above [Eqs. (23), (26), and (27)] indicates that the sign of the $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ peak is always opposite to that of the $\Delta S_M(T)_{\Delta H,P}$. Furthermore, since all variables except the differential of $T_1/C(T_1)_{H_2,P}$ with respect to temperature and $\Delta S_M(T)_{\Delta H,P}$ in Eq. (28) are always positive, then the $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ maximum will be observed when

$$C(T)_{H_2,P} \geq C(T)_{H_1,P} \quad \text{and} \quad \frac{\partial}{\partial T} \left(\frac{T_1}{C(T_1)_{H_2,P}} \right) \geq 0, \quad (29)$$

or when

$$C(T)_{H_2,P} \leq C(T)_{H_1,P} \quad \text{and} \quad \frac{\partial}{\partial T} \left(\frac{T_1}{C(T_1)_{H_2,P}} \right) \leq 0. \quad (30)$$

The relationships between the position of the magnetocaloric effect maximum and the behavior of the heat capacity in constant magnetic fields [Eqs. (28)–(30)] is illustrated in Figs. 5 and 6. At low temperatures [Fig. 5(a), ErAgGa], the derivative of $T/C(T)_{H_2,P}$ with respect to temperature is

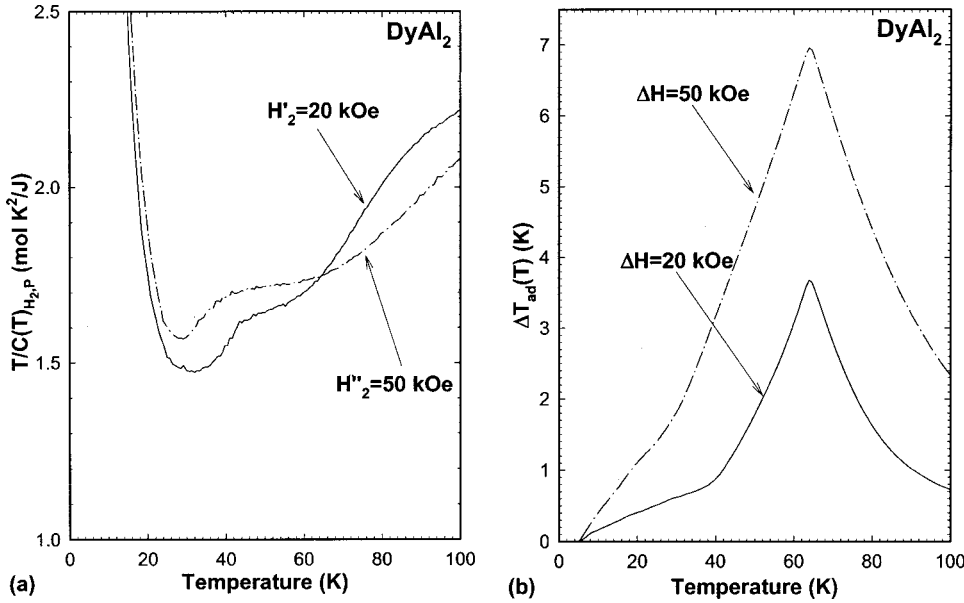


FIG. 6. The behavior of the $T/C(T)_{H_2,P}$ of DyAl_2 between ~ 15 and 100 K in magnetic fields 20 and 50 kOe (a) and the adiabatic temperature change of DyAl_2 for magnetic field change from 0 to 20 and from 0 to 50 kOe (b).

negative [i.e., Eq. (30) holds] and the peak of $\Delta T_{ad}(T)_{\Delta H,P}$ should be observed when $C(T)_{H_2,P} < C(T)_{H_1,P}$. As seen in Fig. 5(b) the $\Delta T_{ad}(T)_{\Delta H,P}$ maxima in ErAgGa indeed occur at approximately 7 K, which is lower than the temperatures of the corresponding $\Delta S_M(T)_{\Delta H,P}$ minima [Fig. 2(b)] regardless of the magnetic field. A second example (Fig. 6) shows the behavior of $T/C(T)_{H_2,P}$ and $\Delta T_{ad}(T)_{\Delta H,P}$ of DyAl_2 . As temperature exceeds 23 – 26 K, the sign of the differential [Eqs. (28)–(30)] for DyAl_2 is changed from negative to positive and the locations of the $\Delta T_{ad}(T)_{\Delta H,P}$ peaks are determined from Eq. (29). Furthermore, since the value of the differential is quite small (i.e., $\partial/\partial T[T_1/C(T_1)_{H_2,P}] \cong 0$ near 60 K, see Fig. 6(a), the positions of the magnetocaloric effect (ΔT_{ad}) peaks practically coincide with those of $\Delta S_M(T)_{\Delta H,P}$ [compare Figs. 3(b) and 6(b)], i.e., both adiabatic temperature change and magnetic entropy change peaks are observed when $C(T)_{H_1,P} \cong C(T)_{H_2,P}$ [see Fig. 3(a)]. The latter conclusion fully agrees with the analysis presented in Ref. 8.

III. GIANT MAGNETOCALORIC EFFECT

The relationships between the magnetocaloric effect and the constant magnetic field heat capacity discussed in the previous section were derived assuming that the total entropy of the magnetic material is a continuous function of temperature. This is the case when phase transition(s), which occur in the system, are second order (typically found in magnetic order \rightleftharpoons disorder transformations, see the examples for ErAgGa and DyAl_2 above), or when there is no phase transition at all (see the PrNi_3 example above). When the system undergoes a first-order phase transition, then the behavior of the total entropy as a function of temperature must account for this discontinuity. Figure 7 shows a T - S diagram modeling the system where a magnetic field has small effect on the heat capacity both below and above the first-order phase transition, while the phase-transition temperature increases

with increasing magnetic field. The phase transition in magnetic field H_1 occurs at temperature T_{pt,H_1} , and the enthalpy of this transformation is ΔE_{H_1} . This results in the discontinuous equilibrium change of the entropy at T_{pt,H_1} totaling $\Delta S_{H_1} = \Delta E_{H_1}/T_{pt,H_1}$. Likewise, the phase transition in the magnetic field H_2 occurs at T_{pt,H_2} , the enthalpy of this transformation is ΔE_{H_2} , and the equilibrium entropy change is $\Delta S_{H_2} = \Delta E_{H_2}/T_{pt,H_2}$. A theoretical analysis of the behavior of the MCE in first-order phase-transition materials is of special interest, because, as far as we are aware, no similar analysis has been performed. Furthermore, magnetic first-order phase transitions have been known in some cases to bring about large, i.e., giant, magnetocaloric effects [e.g., see

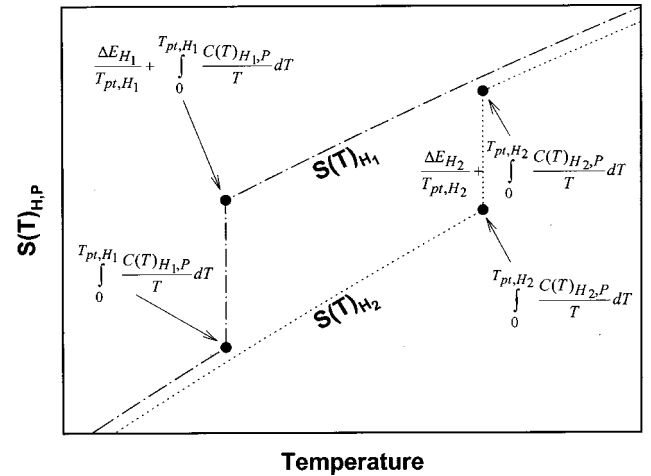


FIG. 7. A schematic T - S diagram of a magnetic system in the vicinity of the first-order phase transition in two magnetic fields, H_1 and H_2 . The corresponding values of the total entropies at critical points (dots) are marked on the plot. It is assumed that the magnetic field has small (but not negligible) effect on the heat capacities both below T_{pt,H_1} and above T_{pt,H_2} and that the heat capacity below T_{pt,H_1} is suppressed by the higher magnetic field.

the experimental data on $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ (Refs. 25, 26) and FeRh (Refs. 27, 28).

The presence of temperature and magnetic field hystereses during first-order phase transitions generally requires the analysis to be performed for a specific direction of the magnetic field change. Just like in the previous section, here we assume that the magnetic field always increases (i.e., $H_2 > H_1$). However, it can be shown that all conclusions remain valid also when $H_2 < H_1$ resulting in the inverted sign of both $\Delta S_M(T)_{\Delta H, P}$ and $\Delta T_{\text{ad}}(T)_{\Delta H, P}$. The presence of hysteresis can be accounted for by introducing different phase-transition temperatures, which are observed during the magnetic field reduction. Similarly, as it was done in the previous section, both magnetizing and demagnetizing and therefore phase changes are assumed to be equilibrium processes with negligible coercive field, anisotropy, and remanence.

A. Magnetic entropy change

When the first-order phase transition occurs at constant temperature and pressure, and proceeds as predicted by thermodynamic theory (i.e., the heat capacity is infinite, and the entropy change is discontinuous at constant temperature), the corresponding analogs of Eqs. (7a) and (7b) are

$$S(T)_{H_1, P} = \int_{T_1 \rightarrow 0}^{T_{\text{pt}, H_1}} \frac{C^l(T)_{H_1, P}}{T} dT + \frac{\Delta E_{H_1}}{T_{\text{pt}, H_1}} + \int_{T_{\text{pt}, H_1}}^T \frac{C^h(T)_{H_1, P}}{T} dT \quad (31a)$$

and

$$S(T)_{H_2, P} = \int_{T_1 \rightarrow 0}^{T_{\text{pt}, H_2}} \frac{C^l(T)_{H_2, P}}{T} dT + \frac{\Delta E_{H_2}}{T_{\text{pt}, H_2}} + \int_{T_{\text{pt}, H_2}}^T \frac{C^h(T)_{H_2, P}}{T} dT, \quad (31b)$$

respectively. Here T_{pt, H_1} , T_{pt, H_2} and ΔE_{H_1} , ΔE_{H_2} are the phase-transition temperatures and the enthalpies of transformation in magnetic fields H_1 and H_2 , respectively, see Fig. 7. Also, $C^l(T)$ and $C^h(T)$ indicate the heat capacities of the low-temperature (i.e., stable below T_{pt}) and the high-temperature (i.e., stable above T_{pt}) phases in their respective magnetic fields since, in general, the heat capacities of the two phases are different. Equations (31a) and (31b) are given for the case when an arbitrary T exceeds both T_{pt, H_1} and T_{pt, H_2} . Following the same approach as in Sec. II and assuming that $T_{\text{pt}, H_2} > T_{\text{pt}, H_1}$, it is easy to see that for any $T < T_{\text{pt}, H_1}$ the magnetic entropy change is

$$\Delta S_M(T)_{\Delta H, P} = \Delta S(T)_{\Delta H, P} = \int_0^T \frac{[C^l(T)_{H_2} - C^l(T)_{H_1}]_P}{T} dT, \quad (32a)$$

i.e., it is exactly the same as for any other magnetic system without the first-order phase transformation [see Eq. (8) for comparison]. When $T_{\text{pt}, H_1} \leq T < T_{\text{pt}, H_2}$, $\Delta S_M(T)_{\Delta H, P}$ becomes

$$\begin{aligned} \Delta S_M(T)_{\Delta H, P} &= \Delta S(T)_{\Delta H, P} \\ &= \int_0^{T_{\text{pt}, H_1}} \frac{[C^l(T)_{H_2} - C^l(T)_{H_1}]_P}{T} dT \\ &\quad + \int_{T_{\text{pt}}}^T \frac{[C^l(T)_{H_2} - C^h(T)_{H_1}]_P}{T} dT - \frac{\Delta E_{H_1}}{T_{\text{pt}, H_1}} \end{aligned} \quad (32b)$$

and when $T \geq T_{\text{pt}, H_2}$, the magnetocaloric effect in terms of $\Delta S_M(T)_{\Delta H, P}$ is

$$\begin{aligned} \Delta S_M(T)_{\Delta H, P} &= \Delta S(T)_{\Delta H, P} \\ &= \int_0^{T_{\text{pt}, H_1}} \frac{[C^l(T)_{H_2} - C^l(T)_{H_1}]_P}{T} dT \\ &\quad + \int_{T_{\text{pt}, H_1}}^{T_{\text{pt}, H_2}} \frac{[C^l(T)_{H_2} - C^h(T)_{H_1}]_P}{T} dT \\ &\quad + \int_{T_{\text{pt}, H_1}}^T \frac{[C^h(T)_{H_2} - C^h(T)_{H_1}]_P}{T} dT \\ &\quad - \left(\frac{\Delta E_{H_1}}{T_{\text{pt}, H_1}} - \frac{\Delta E_{H_2}}{T_{\text{pt}, H_2}} \right). \end{aligned} \quad (32c)$$

When the constant magnetic field heat capacity of both the low- and high-temperature phases is essentially the same [i.e., $C^l(T) \cong C^h(T) = C(T)$ as, for example, found experimentally in Dy (Refs. 8, 29)], Eqs. (32a)–(32c) can be simplified as follows [the temperature ranges remain the same as in Eqs. (32a)–(32c)]:

$$\Delta S_M(T)_{\Delta H, P} \cong \int_0^T \frac{[C(T)_{H_2} - C(T)_{H_1}]_P}{T} dT \quad (33a)$$

$$\Delta S_M(T)_{\Delta H, P} \cong \int_0^T \frac{[C(T)_{H_2} - C(T)_{H_1}]_P}{T} dT - \frac{\Delta E_{H_1}}{T_{\text{pt}, H_1}} \quad (33b)$$

$$\begin{aligned} \Delta S_M(T)_{\Delta H, P} &\cong \int_0^T \frac{[C(T)_{H_2} - C(T)_{H_1}]_P}{T} dT \\ &\quad - \left(\frac{\Delta E_{H_1}}{T_{\text{pt}, H_1}} - \frac{\Delta E_{H_2}}{T_{\text{pt}, H_2}} \right). \end{aligned} \quad (33c)$$

Equations (10), (15), and (16) therefore provide a good approximation even for a first-order phase transition since both $\Delta E_{H_1}/T_{\text{pt}, H_1}$ and $\Delta E_{H_2}/T_{\text{pt}, H_2}$ are theoretically temperature-independent constants, and in practice are essentially temperature independent. Furthermore, in materials with first-order magnetic phase transitions, the magnetic field usually

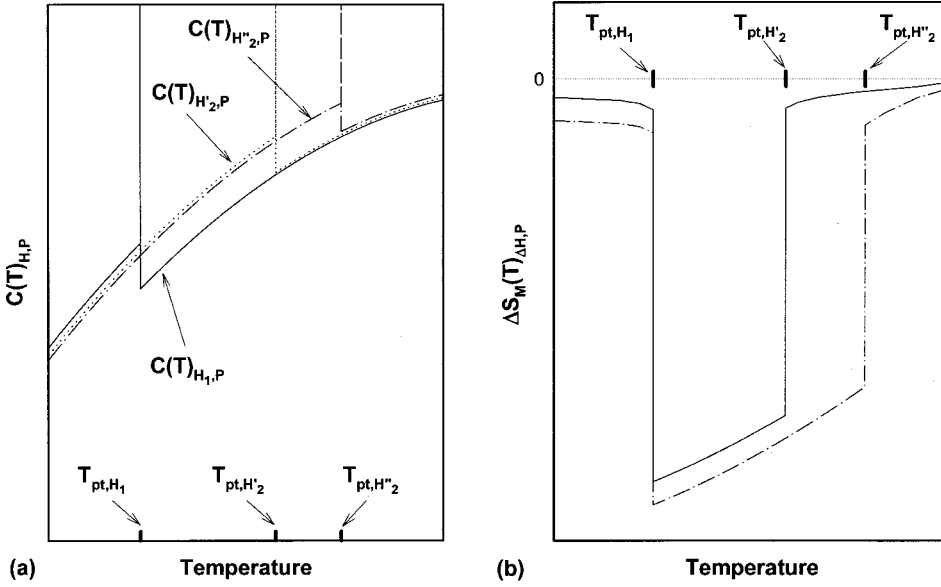


FIG. 8. The schematic behavior of the heat capacity of the magnetic system in the vicinity of the first-order phase transition when the magnetic field increases the phase-transition temperature (a) and the corresponding model behavior of the ΔS_M (b). Both (a) and (b) show the two different magnetic fields H'_2 and H'_1 , such that $H'_2 > H'_1$ and therefore, $T_{pt,H'_2} > T_{pt,H'_1}$.

strongly affects the transition temperature but has much smaller effect on the heat capacity both below T_{pt,H_1} and above T_{pt,H_2} [e.g., see experimental data on Dy,^{8,29} and $Gd_5(Si_xGe_{1-x})_4$ (Refs. 25, 26)]. Thus, it is valid to introduce a further simplification and assume that $C(T)_{H_1} \approx C(T)_{H_2}$ at any temperature except at T_{pt,H_1} and T_{pt,H_2} . Hence, the magnetic entropy change is expected to be much smaller both below T_{pt,H_1} [Eq. (33a)] and above T_{pt,H_2} [Eq. (33c)], but it becomes approximately constant and quite large when $T_{pt,H_1} \leq T < T_{pt,H_2}$ [Eq. (33b)],

$$\Delta S_M(T)_{\Delta H,P} \approx -\frac{\Delta E_{H_1}}{T_{pt,H_1}} \approx -\frac{\Delta E_{H_2}}{T_{pt,H_2}}. \quad (34)$$

We note that as follows from Eq. (33c), in this case $\Delta E_{H_1}/T_{pt,H_1} \approx \Delta E_{H_2}/T_{pt,H_2}$. Equations (32)–(34) indicate that during first-order magnetic phase transitions the major contribution to the magnetic entropy change is due to the entropy of the phase transformation. It is easy to see from Eqs. (32b), (33b), and (34) that ultimately, the value of the enthalpy of the first-order phase transition determines the magnitude of the giant magnetocaloric effect in terms of $\Delta S_M(T)_{\Delta H,P}$ in the temperature range $T_{pt,H_1} \leq T < T_{pt,H_2}$.

An example modeling the relationship between the constant magnetic field heat capacity and $\Delta S_M(T)_{\Delta H,P}$ according to Eqs. (32a)–(32c) is shown in Fig. 8. The heat capacities below T_{pt,H_1} and above T_{pt,H_2} are assumed to be only minimally affected by the magnetic field and $C^h(T)$ is assumed to be slightly lower than $C^l(T)$ [Fig. 8(a)]. At both $T = T_{pt,H_1}$ and $T = T_{pt,H_2}$ the values of the heat capacity are infinite [shown as vertical lines in Fig. 8(a)], i.e., the transition is an ideal first-order phase transformation. Since $C(T)_{H_2,P} > C(T)_{H_1,P}$ between T_{pt,H_1} and T_{pt,H_2} [see Fig. 8(a)], the minimum $\Delta S_M(T)_{\Delta H,P}$ (i.e., the peak value) is observed at T_{pt,H_1} and it is gradually reduced towards T_{pt,H_2} [see Fig. 8(b) and Eqs. (32a)–(32c)]. The model shown in

Fig. 8 describes well the behavior of both the heat capacity and the $\Delta S_M(T)_{\Delta H,P}$ in $Gd_5(Si_xGe_{1-x})_4$ materials where $x \leq 0.5$.^{25,26} In FeRh,^{27,28} the magnetic field reduces the phase-transition temperature (i.e., $T_{pt,H_2} < T_{pt,H_1}$) and therefore the $\Delta S_M(T)_{\Delta H,P}$ here has the sign opposite to that shown in Fig. 8 and is positive.

B. Adiabatic temperature change

Since the largest magnetic entropy changes occur when $T_{pt,H_1} \leq T < T_{pt,H_2}$, the same temperature range represents the most interest with respect to the behavior of the $\Delta T_{ad}(T)_{\Delta H,P}$. Below we show that unlike $\Delta S_M(T)_{\Delta H,P}$, the behavior of the adiabatic temperature change between T_{pt,H_1} and T_{pt,H_2} is critically dependent on T . According to the schematic T - S diagram (Fig. 9) there are two different temperature regions between T_{pt,H_1} and T_{pt,H_2} where the adiabatic temperature change should have fundamentally different behaviors. The two regions are separated by a specific temperature T_m , where $T_{pt,H_1} \leq T_m \leq T_{pt,H_2}$ and T_m can be found from the following integral equation:

$$\int_{T_{pt,H_1}}^{T_m} \frac{C^h(T)_{P,H_1}}{T} dT = \int_0^{T_{pt,H_2}} \frac{C^l(T)_{P,H_2}}{T} dT - \int_0^{T_{pt,H_1}} \frac{C^l(T)_{P,H_1}}{T} dT - \frac{\Delta E_{H_1}}{T_{pt,H_1}}. \quad (35)$$

In other words, T_m is defined as the temperature where the total entropy in the magnetic field H_1 equals to the total entropy of the system in the magnetic field H_2 at the start of the first-order phase transition in this field at temperature T_{pt,H_2} , as shown by the dotted horizontal line in Fig. 9. In the first region, when $T_{pt,H_1} \leq T_1 < T_m$ and T_1 is the temperature at H_1 , the material does not reach T_{pt,H_2} when magnetic field

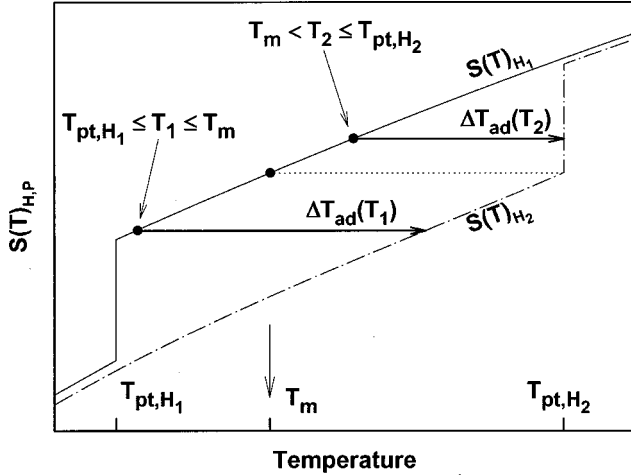


FIG. 9. A schematic T - S diagram in the vicinity of the first-order phase transition in two different magnetic fields, H_1 and H_2 . The specific temperature, T_m , is defined by Eq. (35) as the temperature where the total entropy of the material in magnetic field H_1 equals to the total entropy of the material in the magnetic field H_2 at the start of the first-order phase transition at T_{pt,H_2} . The two horizontal arrows show the ΔT_{ad} in two different regions: $T_{pt,H_1} \leq T_1 \leq T_m$ and $T_m < T_2 \leq T_{pt,H_2}$.

is changed from H_1 to H_2 regardless of the value of $\Delta T_{ad}(T)_{\Delta H,P}$. On the contrary, when $T_m < T_2 \leq T_{pt,H_2}$, the material's temperature rises to T_{pt,H_2} before the magnetic field reaches H_2 due to magnetocaloric effect starting from any T_2 , see Fig. 9. As we show below, in the case of an ideal first-order phase transformation, the final temperature of the sample in this second region ($T_m < T_2 \leq T_{pt,H_2}$) cannot exceed T_{pt,H_2} .

Consider the simplest case when the magnetic field affects the phase transition temperature but has practically no effect on the heat capacity both below T_{pt,H_1} and above T_{pt,H_2} . Furthermore, for simplicity we assume that the heat capacities of both low- and high-temperature phases are the same [see Eq. (34) indicating that in this case $\Delta S_M(T)_{\Delta H,P}$ remains practically constant for any $T_{pt,H_1} \leq T < T_{pt,H_2}$]. This is shown in Fig. 10(a). Taking into account that

$$C^l(T)_{H_1} \cong C^h(T)_{H_1} \cong C^l(T)_{H_2} \cong C^h(T)_{H_2} = C(T), \quad (36)$$

the relationship between $\Delta T_{ad}(T)_{\Delta H,P}$ and heat capacity when $T_{pt,H_1} \leq T \leq T_m$ can be analyzed similarly as done above, and Eqs. (17)–(27) remain valid even for the first-order phase transformation. Noting Eqs. (34)–(36), Equation (20) becomes

$$-\Delta S_M(T)_{\Delta H,P} = \int_T^{T+\Delta T_{ad}(T)_{\Delta H,P}} \frac{C(T)_P}{T} dT \cong \frac{\Delta E_{H_1}}{T_{pt,H_1}}, \quad (37)$$

and therefore the corresponding analog of Eq. (26) is

$$\begin{aligned} \Delta T_{ad}(T)_{\Delta H,P} &= -\frac{T_1}{C(T_1)_P} \times \Delta S_M(T)_{\Delta H,P} \cong \frac{T_1}{C(T_1)_P} \\ &\times \frac{\Delta E_{H_1}}{T_{pt,H_1}}. \end{aligned} \quad (38)$$

It is straightforward from Eq. 38 that since the entropy of the first-order phase transformation in zero magnetic field (i.e., $\Delta E_{H_1}/T_{pt,H_1}$) remains essentially constant, the behavior of $\Delta T_{ad}(T)_{\Delta H,P}$ is determined by the behavior of $T/C(T)_{H,P}$. At low temperatures $T/C(T)_{H,P}$ decreases with increasing temperature [e.g., see Figs. 5(a) and 6(a)] and $\Delta T_{ad}(T)_{\Delta H,P}$ should also decrease proportionally. When the temperature exceeds 20–100 K (depending on the Debye temperature), $T/C(T)_{H,P}$ begins to increase slowly [e.g., see Fig. 6(a)], and therefore $\Delta T_{ad}(T)_{\Delta H,P}$ is also expected to rise proportionally between T_{pt,H_1} and T_m . When temperature exceeds T_m , i.e., when $T_m < T \leq T_{pt,H_2}$, the value of $\Delta T_{ad}(T)_{\Delta H,P}$ becomes dependent only on the difference between T and T_{pt,H_2} [see above and the arrow marking $\Delta T_{ad}(T_2)$ in Fig. 9], i.e., above T_m the magnetocaloric effect is nothing else than the difference between the temperature of the material in the magnetic field H_1 and the phase-transition temperature in the magnetic field H_2 :

$$\Delta T_{ad}(T)_{\Delta H,P} = (T_{pt,H_2} - T)_{S,P}. \quad (39)$$

Hence, regardless of the fact that $\Delta S_M(T)_{\Delta H,P}$ remains large (giant) and approximately constant between T_{pt,H_1} and T_{pt,H_2} , the magnetocaloric effect in terms of $\Delta T_{ad}(T)_{\Delta H,P}$ should be rapidly reduced above T_m . This drastic reduction of the $\Delta T_{ad}(T)_{\Delta H,P}$ is easily understood because as the magnetic system approaches the phase-transition temperature, T_{pt,H_2} , its heat capacity becomes infinite (or in reality, extremely large) and practically no further temperature change occurs in response to the changing magnetic field as long as the two different phases coexist. Unlike in the case of the conventional magnetocaloric effect for a second-order phase transition, the total entropy remains constant when material's temperature reaches T_{pt,H_2} during the magnetic field increase by equilibrating the corresponding fractional change of $\Delta S_M(T)_{\Delta H,P}$ by $-\Delta E_{H_2}/T_{pt,H_2}$, rather than by the increased thermal lattice and electronic entropies.

The example modeling the behavior of both $\Delta S_M(T)_{\Delta H,P}$ and $\Delta T_{ad}(T)_{\Delta H,P}$ according to Eqs. (37)–(39) is shown in Fig. 10. Hence, as the magnetic field change (ΔH) increases, the peak values of the magnetocaloric effect in terms of both magnetic entropy change and adiabatic temperature change remain essentially constant, while the peak width [for both the giant $\Delta S_M(T)_{\Delta H,P}$ and the giant $\Delta T_{ad}(T)_{\Delta H,P}$] increase due to the rising difference between T_{pt,H_1} and T_{pt,H_2} , and T_{pt,H_1} and T_m , respectively.

Equations (35) and (39) result in another important consequence characterizing the giant MCE behavior in some

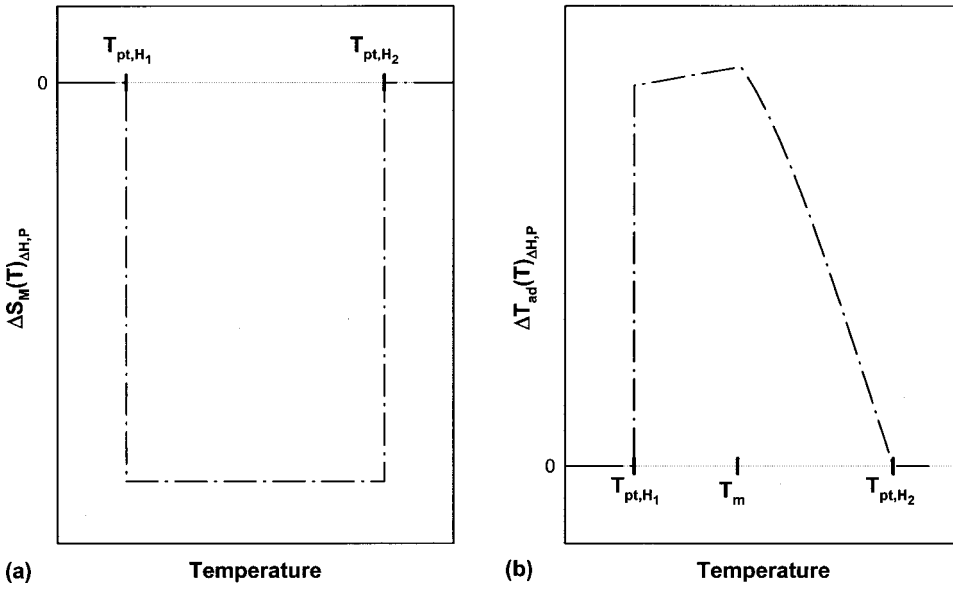


FIG. 10. A schematic behavior of the ΔS_M (a) and ΔT_{ad} (b) in the vicinity of the first-order phase transition. It is assumed that the magnetic field affects only the phase-transition temperature and that the heat capacities of both low- and high-temperature phases are the same and are completely magnetic-field independent.

magnetic systems undergoing a first-order magnetic phase transition. Assume that either the magnetic field change is small, or its effect on the phase-transition temperature is small. Then, the difference between T_{pt,H_1} and T_{pt,H_2} is not large enough for equation (35) to be valid. In this case

$$T_m = T_{pt,H_1}. \quad (40)$$

Therefore regardless of the value of the $\Delta S_M(T)_{\Delta H,P}$, the maximum $\Delta T_{ad}(T)_{\Delta H,P}$ occurs at T_{pt,H_1} and its value straightforwardly determined from Eq. (39) as

$$\Delta T_{ad}(T = T_{pt,H_1})_{\Delta H,P} \cong (T_{pt,H_2} - T_{pt,H_1})_{S,P}, \quad (41)$$

providing an easy estimate of the maximum adiabatic temperature change without thermodynamic or magnetic measurements as long as both T_{pt,H_1} and T_{pt,H_2} are known. Moreover, a larger giant adiabatic temperature change in small

magnetic fields is expected in materials in which the magnetic field strongly influences the magnetic ordering temperature. This conclusion provides a guideline supporting the search for best magnetic refrigerant materials, i.e., those that may have the largest possible $\Delta T_{ad}(T)_{\Delta H,P}$ in the smallest magnetic fields.

An example of the experimental behavior of both the heat capacity and the total entropy in the system with first-order phase transformation, $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$, is shown in Fig. 11. The sample was prepared by arc melting of pure components (Gd, 99.95+ wt.%; Si and Ge, both 99.99+ wt.% pure) and then heat treated at 1300 °C for 1 h. The heat capacity in magnetic fields 0, 20, 50, and 75 kOe and the direct $\Delta T_{ad}(T)_{\Delta H,P}$ measurements were carried out in an adiabatic heat-pulse calorimeter.³⁰ In zero magnetic field, the phase transition (determined from the temperature of the heat capacity peak) occurs on heating at $T_{pt,H_1} \cong 269$ K [Fig. 11(a)].

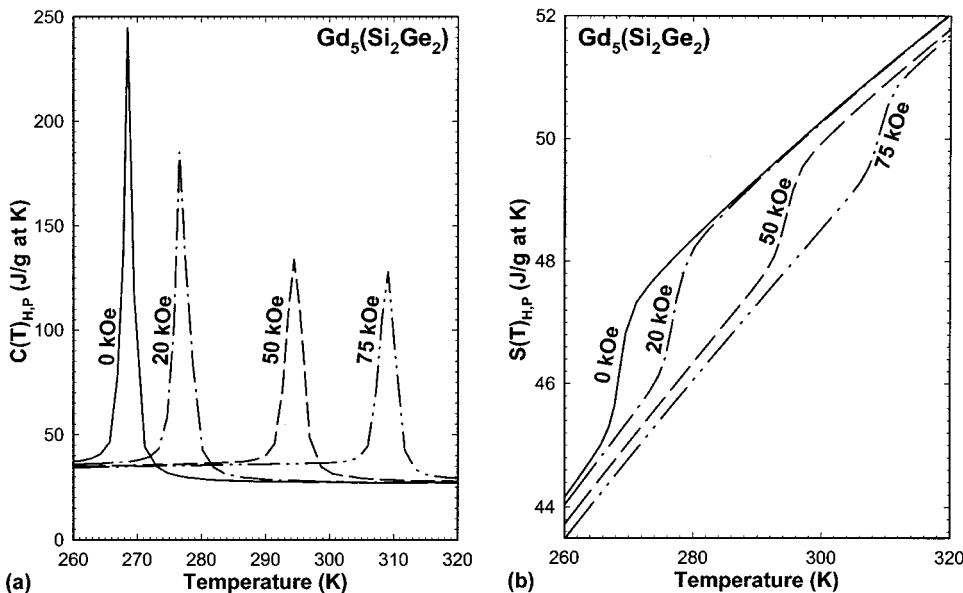


FIG. 11. The heat capacity (a) and total entropy (b) of $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ at constant pressure in magnetic fields 0, 20, 50, and 75 kOe. Note that although the heat capacity at the phase-transition temperature is theoretically infinite, during actual experimental measurements large, but finite values of the heat capacity are usually recorded.

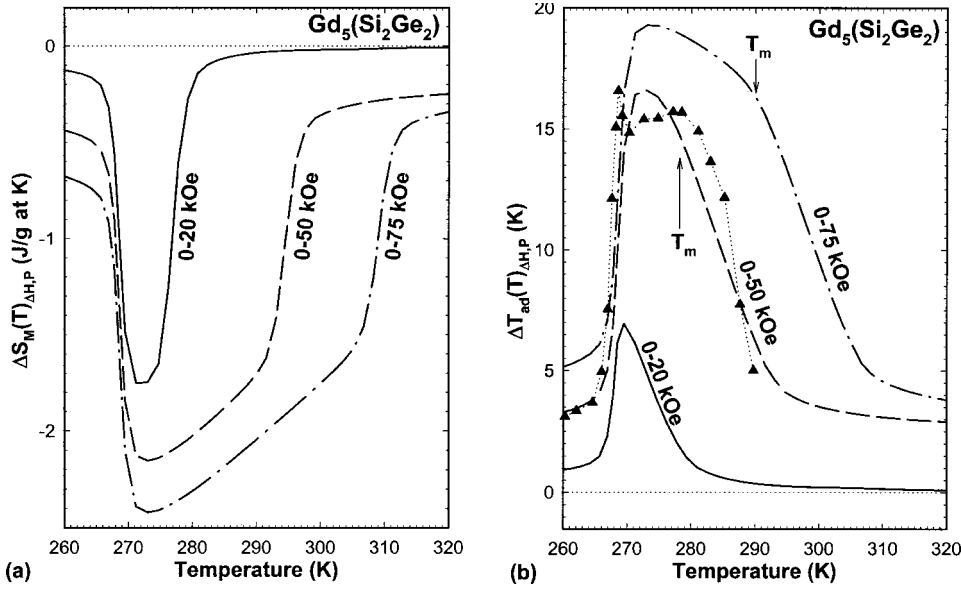


FIG. 12. The magnetic entropy change (a) and adiabatic temperature change (b) of $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ for magnetic field changes from 0 to 20, 50, and 75 kOe. The lines in both (a) and (b) represent the values calculated from heat capacity (Fig. 11), the symbols in (b) represent ΔT_{ad} directly measured for magnetic-field change from 0 to 50 kOe.

The phase-transition temperature in 20 kOe magnetic field is at $T_{\text{pt},H_2} \cong 277$ K. As also seen from Fig. 11(b), for the smallest magnetic field change ($\Delta H = 20$ kOe), the behavior of $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ is defined by Eqs. (39)–(41), i.e., the temperature T_m coincides with P_{pt,H_1} . For larger magnetic field changes (50 and 75 kOe) the specific temperature T_m , is located above T_{pt,H_1} and therefore the behavior of $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ is defined by Eqs. (35), (37)–(41). We note that since Eq. (36) is only approximately valid for the $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ material [i.e., $C^l(T)$ is not exactly equal to $C^h(T)$, see Fig. 11(a)], Eqs. (35) and (37)–(41) only provide an approximate description of the magnetocaloric-effect behavior. The major difference is that the MCE both below T_{pt,H_1} (~ 269 K at $H = 0$ kOe) and above T_{pt,H_2} (~ 277 , ~ 295 , and ~ 308 K at $H = 20$, 50, and 75 kOe, respectively) in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ is not reduced to zero compared to the idealized behavior, i.e., when the heat capacity follows Eq. (36).

Experimental behavior of $\Delta S_M(T)_{\Delta H,P}$ [Fig. 12(a)] closely resembles that predicted theoretically [Eqs. (32) and (33), and Fig. 8(a)]. Despite only approximate validity of Eqs. (35)–(41) for $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$, the behavior of $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ (Fig. 12(b)) also follows the model described above. First, for the lowest magnetic-field change ($\Delta H = 20$ kOe) the observed maximum $\Delta T_{\text{ad}}(T)_{\Delta H,P} \cong 7$ K, while that predicted from Eq. (41) should be ~ 8 K. The small difference can be attributed to a nonideal first-order phase-transition process (i.e., the phase transition does not occur at constant temperature, see Fig. 11). When ΔH increases to 50 and 75 kOe the two different regions of $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ behavior are clearly distinguished in Fig. 12(b). Below ~ 279 K (for 50 kOe) and ~ 290 K (for 75 kOe) $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ varies slowly [also see Fig. 10(b)] while above these temperatures the MCE decreases rapidly indicating that the T_m values are approximately 279 and 290 K for the respective magnetic field changes. The slow reduction of $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ between T_{pt,H_1} (~ 269 K) and T_m instead of the predicted increase

[see Fig. 10(b)] is associated with the fact that $\Delta S_M(T)_{\Delta H,P}$ is not a constant (Fig. 10(a)) but slowly decreases with temperature [Fig. 12(a)].

IV. CONCLUSIONS

The behavior of the magnetocaloric effect both in terms of the isothermal magnetic entropy change, $\Delta S_M(T)_{\Delta H,P}$, and the adiabatic temperature change, $\Delta T_{\text{ad}}(T)_{\Delta H,P}$ is closely related to the behavior of the heat capacity at constant magnetic field and pressure. The thermodynamic analysis indicates that when the heat capacity in two different magnetic fields, $C(T)_{H_1,P}$ and $C(T)_{H_2,P}$ is known, the temperature of the MCE peak(s) can be easily predicted from the relationship between the two. Conventional magnetocaloric effect, which is observed in magnetic systems without discontinuous entropy changes, depends on the degree to which the heat capacity is effected by the magnetic field. A large magnetocaloric effect is expected to occur in systems where the heat capacity is strongly influenced by the magnetic field. In systems with discontinuous magnetic entropy changes, the magnitude of the magnetocaloric effect is largely defined by the difference in the entropies (or the enthalpies) of the low- and high-magnetic-field phases. This explains the macroscopic origin of the giant magnetocaloric effect observed experimentally in some magnetic systems. Generally, the large magnetocaloric effect is expected to occur in the systems with large enthalpy discontinuities, and in the systems in which magnetic field strongly influences the temperature of the first-order phase transition rather than the heat capacity below and above the phase transformation. Although the thermodynamic analysis presented above does not explain the microscopic origin of the anomalous behavior of the magnetocaloric effect in first-order phase-transition materials, it may be combined with a more detailed mean-field calculations of the free energy (e.g., see Ref. 31) in the future to gain better insights on both the nature of the first-order phase transitions and the existence of the giant magnetocaloric effect.

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