Magnetocaloric effect and heat capacity in the phase-transition region

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The behavior of the magnetic-field and temperature-dependent heat capacity $C(H,T)$ and the magnetocaloric effect $\Delta T(\Delta H,T)$, in the vicinity of magnetic phase transitions is discussed. A simple model allowing calculation of the peak value of the magnetocaloric effect is developed from general principles of thermodynamics. It is shown that a characteristic temperature $\Theta(H)$ where the heat capacity of the magnetic material is independent of the magnetic field, can be defined. The peak value (maximum or minimum) of the magnetocaloric effect occurs near the $\Theta(H)$. Both $\Theta(H)$ and peak value of the magnetocaloric effect approach the magnetic ordering temperature. Experimental measurements of the heat capacity and the magnetocaloric effect of several high-purity lanthanide magnetic materials agree well the theoretical model.
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I. INTRODUCTION

Adiabatic application of a magnetic field to a magnetic material changes its initial temperature by a certain value $\Delta T_{\rm ad}$. This effect was discovered by Warburg[1] late in the 19th century and is known as the magnetocaloric effect (MCE). The size of the MCE depends upon the magnetic-field change and the temperature at which it is measured, and it can be measured directly[2,3] as $\Delta T_{\rm ad}=\Delta T(\Delta H,T)=T_F-T_0$, where T_F is the final temperature of the sample when the magnetic field reaches its maximum (H), and T_0 is initial temperature of the sample before the magnetic field was altered, typically starting from $H_0=0$.[4] MCE can also be determined indirectly from the experimental heat capacity $C(H,T)$ measured as a function of temperature in different magnetic fields.[5] In this study we consider only fully reversible magnetocaloric effect.

The largest magnetocaloric effect in moderate magnetic fields changing from 0 to 1–10 T is observed in the vicinity of a magnetic phase transformation. Usually it is assumed that the maximum MCE in simple ferromagnetic materials occurs at the Curie temperature T_C. It is well known that the Curie temperature is a distinct point on a temperature scale at which magnetic ordering occurs or vanishes spontaneously as the material's temperature decreases or increases, respectively. This definition applies to the change of magnetic order with temperature at ambient pressure and zero magnetic field. It is assumed that when $T>T_C$, then the magnetic order parameter η is equal to zero. As shown by Smith,[6] the transition at T_C has a nearly pointlike nature in some classic $3d$-magnetic materials. Magnetic phase transitions in most common magnetic materials, however, are smeared out over a range of temperature. This broadening is usually associated with chemical impurities, imperfections of the crystal lattice, short-range magnetic order and, perhaps, a more complicated behavior of the thermodynamic potential.[4,7] Various physical properties display different behaviors near the T_C. Heat capacity, magnetic susceptibility, and MCE anomalies may occur above or below the true T_C. For instance, in some Gd-based compounds a heat-capacity maximum is observed below the Néel point T_N,[8] but the inflection point of the heat-capacity anomaly coincides with the true Néel temperature.[9] Impurities and structural imperfections significantly affect the magnetization, heat capacity and other properties of rare-earth metals.[10,11] Therefore, a detailed theoretical and experimental study of the relationships between the heat capacity and the magnetocaloric effect of high-purity materials in the vicinity of magnetic phase transitions is quite important.

In this paper we report on (1) a theoretical analysis of the interrelationship between magnetocaloric effect and heat capacity by examining the behavior of the entropy as a function of magnetic field and temperature, and (2) a comparison of the theory with the experimental thermodynamic measurements of two pure lanthanide metals, Gd and Dy, and two lanthanide intermetallic compounds, GdPd and $(Dy_{0.25}Er_{0.75})Al_2$. This study is an attempt to relate the two important thermodynamic properties of magnetic materials: the magnetic field and temperature-dependent heat capacity with the magnetocaloric effect. A simple thermodynamic model developed theoretically is found to be in excellent agreement with experimental measurements.

II. THEORY

A. General

From the general principles of thermodynamics the following expression exactly defines the infinitesimal change of the magnetic material's temperature dT in an adiabatic-isobaric process:

$$dT=-\frac{T[\partial I(H,T)/\partial T]_H}{C(H,T)}\,dH, \tag{1}$$

where T is the absolute temperature, $I(H,T)$ and $C(H,T)$ are the magnetization and the heat capacity at constant pressure, and H is the magnetic-field strength.[4,7] An exact analytical

solution of Eq. (1) is impossible, because both the magnetization and the heat capacity are magnetic material specific and usually analytically unknown functions of magnetic field and temperature. It can be integrated numerically using the experimentally measured or theoretically predicted magnetization and heat capacity to calculate the MCE:

$$\Delta T(\Delta H,T_0)=T_F-T_0=-\int_{H_0}^{H_f}T(H)\,\frac{(\partial I(H,T)/\partial T)_H}{C(H,T)}\,dH, \tag{2}$$

where $\Delta T(\Delta H,T_0)$ is the magnetocaloric effect, H_0 is the initial magnetic-field strength at which the initial temperature of a magnetic material is T_0, and H_f is the final magnetic-field strength at which the final temperature is T_F. Thus, a temperature where MCE reaches its maximum for magnetic-field change $\Delta H=H_f-H_0$, is dependent on both the behavior of the $T/C(H,T)$ and the behavior of the magnetization derivative with respect to temperature at constant field, $[\partial I(H,T)/\partial T]_H$. Obviously, the MCE is large when $[\partial I(H,T)/\partial T]_H$ is large, and $C(H,T)$ is small at the same initial temperature T. Since the $[\partial I(H,T)/\partial T]_H$ peaks at the magnetic ordering temperature, then the peak of the MCE should correspond (or at least should be close) to the Curie temperature of a simple ferromagnet. However, the heat capacity also is quite large in the vicinity of the magnetic ordering temperature and it appears from Eqs. (1) and (2) that the maximum $|\Delta T_{ad}|$ for a given field change, ΔH, should occur when $[\partial I(H,T)/\partial T]_H$ and $C(H,T)$ peaks do not coincide. The results reported by Schmitt and co-workers,[8,9] and as discussed in the Introduction, support this conclusion at least for the case of an order $\leftrightarrow$ disorder phase transition.

It is difficult to simplify Eq. (2) for further analytical analysis and, therefore, it is unlikely to answer the question: how are the peak values of the MCE, the derivative of the magnetization with respect to temperature, and the heat capacity related to each other?

B. The thermodynamic model

Consider the reversible thermodynamic cycle *WXYZ* in the (S,T) coordinates which is shown in Fig. 1, similar to as it was done earlier in Ref. 12. Here S is the total entropy of a magnetic material. When magnetic field is changed by $\Delta H=H-0=H$, the material is magnetized adiabatically, it follows the path *WX*, and its temperature is changed by $\Delta T(H,T_W)=T_X-T_W$ due to the magnetocaloric effect. When the adiabatic part of the cycle is completed, the magnetic material is connected to a hot sink ($T_{hot}<T_X$) and it follows the path *XY* giving up a finite amount of energy and reduces its entropy from S_X to S_Y and its temperature from T_X to T_Y. After that the material is disconnected from the hot sink, the magnetic field is reduced to zero, and the sample is demagnetized adiabatically (the path *YZ*), during which its temperature is reduced from T_Y to T_Z due to the inverse MCE. Finally the material is connected to a cold sink ($T_{cold}>T_Z$), where it absorbs finite amount of energy following the path *ZW* and rises its entropy from S_Z to S_W and its temperature from T_Z to T_W, thus completing the thermodynamic cycle *WXYZ*. For infinitesimal entropy and temperature changes during the *XY* and *ZW* parts of the cycle we can write

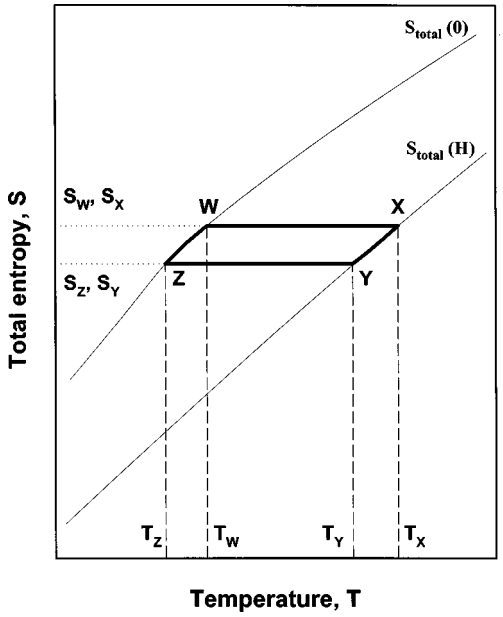

FIG. 1. An example of an ideal reversible thermodynamic cycle. The thin solid lines represent the total entropy curves at zero magnetic field, $S_{total}(0)$, and at an elevated magnetic field, $S_{total}(H)$. The thick solid lines outline the thermodynamic cycle *WXYZ*. S_W, S_X, S_Y, S_Z, and T_W, T_X, T_Y, T_Z represent the entropy and the temperature of the material at the positions *W*, *X*, *Y*, and *Z* of the cycle, respectively.

$$dS_{WX}=0;\;\; dS_{XY}=-C(H,T_X)dT_X/T_X,$$

$$dS_{YZ}=0;\;\; dS_{ZW}=C(0,T_Z)dT_Z/T_Z, \tag{3}$$

where $C(H,T_X)$ and $C(0,T_Z)$, and T_X and T_Z are the heat capacities, and the temperatures of a material at *X* and *Z*, respectively. Also dT_X and dT_Z, are infinitesimal temperature changes at T_X and T_Z, respectively. Furthermore, since the resulting entropy change, *dS*, during the closed reversible thermodynamic cycle equals to zero, we may write

$$dS=dS_{WX}+dS_{XY}+dS_{YZ}+dS_{ZW}=0. \tag{4}$$

Combining Eqs. (3) and (4) yields

$$\frac{C(H,T_X)}{T_X}\,dT_X=\frac{C(0,T_Z)}{T_Z}\,dT_Z. \tag{5}$$

For the conditions described above the magnetocaloric effect equals: $\Delta T(H,T_W)=T_X-T_W\cong T_Y-T_Z\cong T_X-T_Z$. Introducing the following notations: $T_F=T_X\cong T_Y$ and $T_0=T_W\cong T_Z$ and noting that that these conditions are easily achieved in practice particularly near the magnetic phase transition when $WX\cong ZY\gg XY\cong WZ$, we can now write Eq. (5) as follows:

$$\frac{dT_F}{dT_0}=\frac{T_F}{T_0}\,\frac{C(0,T_0)}{C(H,T_F)}. \tag{6}$$

Taking into account that $T_F=T_0+\Delta T(H,T_0)$, we can rearrange Eq. (6) and solve it with respect to $\Delta T(H,T_0)$:

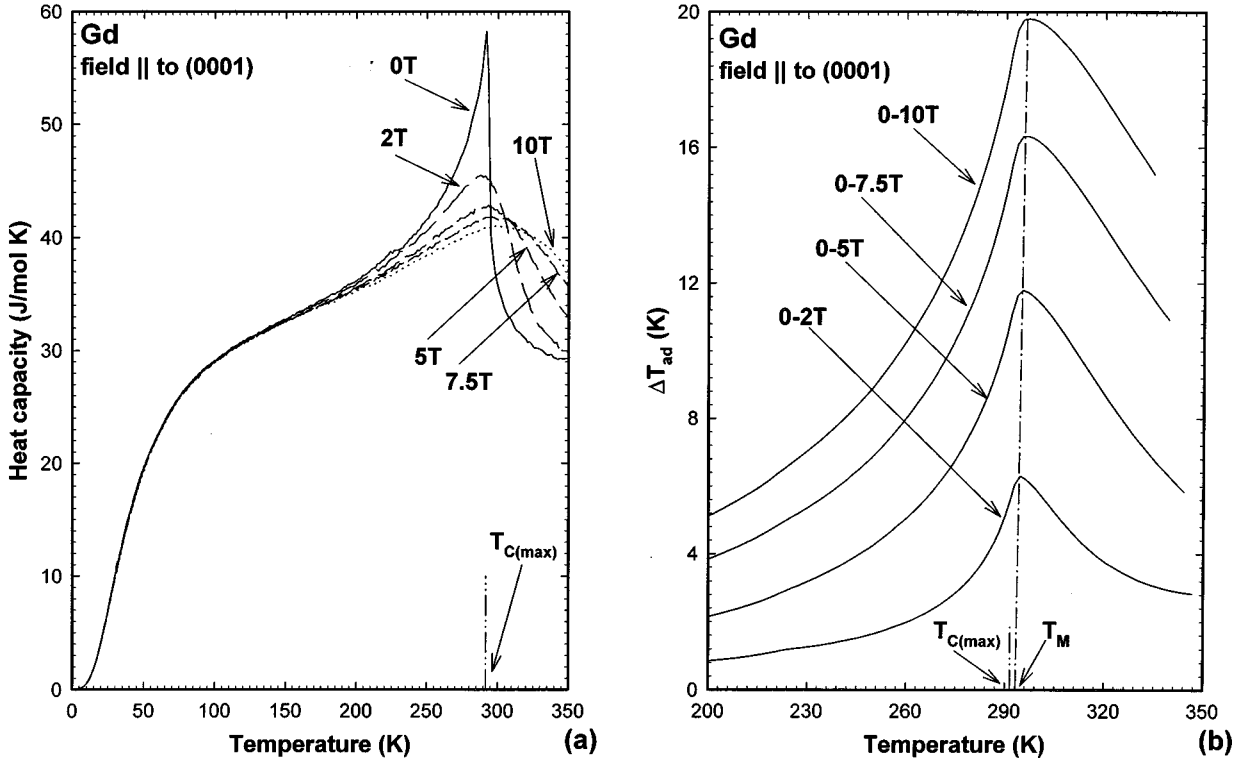

FIG. 2. The heat capacity of single-crystalline Gd from 3.5 to 350 K at 0, 2, 5, 7.5, and 10 T (a) and the magnetocaloric effect for a magnetic field change from 0 to 2, from 0 to 5, from 0 to 7.5, and from 0 to 10 T (b). $T_{c(\max)}$ is the temperature where the heat-capacity maximum is observed in zero magnetic field, and T_M is the temperature where the maximum magnetocaloric effect is observed.

$$\Delta T(H,T_0) = -T_0\left[\Delta C(H,T) - \frac{\partial \Delta T(H,T_0)}{\partial T}\,\frac{C(H,T_F)}{C(0,T_0)}\right], \tag{7}$$

where

$$\Delta C(H,T) = \frac{C(0,T_0) - C(H,T_F)}{C(0,T_0)}.$$

Recalling that $\partial \Delta T(H,T_0)/\partial T = 0$ at the temperature where the magnetocaloric effect reaches its maximum (peak value is positive) or minimum (peak value is negative), we obtain

$$\Delta T(H,T_0)_{\text{Peak}} = -T_0 \Delta C(H,T). \tag{8}$$

It is straightforward from Eq. (8) that the peak value of the magnetocaloric effect is positive (the MCE is maximum) when $\Delta C(H,T) < 0$ and it is negative (the MCE is minimum) when $\Delta C(H,T) > 0$. Analysis of the available experimental data on the heat capacity of simple ferromagnets shows that $\Delta C(H,T)$ is positive at temperatures below and just above the zero magnetic-field heat-capacity peak. It changes sign and becomes negative at slightly higher temperatures [see, for example a variety of experimental data for Fe,[12] the pure lanthanide metals and intermetallic compounds,[13–15] and also Figs. 2(a), and 4(a)]. This leads to the conclusion that the maximum magnetocaloric effect in a simple ferromagnet should occur above the zero magnetic-field heat-capacity peak.

For small magnetic fields and/or for relatively high temperatures, (e.g., when T_0 is close to room temperature) $\Delta T(H,T_0)_{\text{Peak}}/T_0$ is small and can be neglected. Thus Eq. (8) at temperature $T_M(H)$, where the peak (maximum or minimum) magnetocaloric effect occurs can be written as

$$C(0,T_M) \cong C(H,T_F), \tag{9}$$

which indicates that the heat capacity of a magnetic material should be practically independent of the magnetic field at the temperature where the MCE peak occurs. According to Eqs. (8) and (9), the temperature of the MCE peak should be located close to a certain characteristic temperature, $\Theta(H)$, where the values of $C(0,T)$ and $C(H,T)$ are equal. In the generalized case, when the magnetic field varies from H_1 to H_2 and H_1 is not equal to zero, Eqs. (3)–(9) are still valid. Hence, for a magnetic-field change from H_1 to H_2, the temperature where magnetocaloric effect maximum (or minimum) is observed must be located close to the temperature where the values of $C(H_1,T)$ and $C(H_2,T)$ are the same.

Since Eq. (9) was derived assuming negligible $\Delta T_{\text{ad}}/T$, which may not be true for a ferromagnet near the Curie temperature (or, in general, for a magnetic material near its ordering temperature), then for the temperature where MCE has its maximum (or minimum), Eq. (8) can be rewritten as follows:

$$C(0,T_M)\,\frac{T_F}{T_M} = C(H,T_F). \tag{10}$$

For a ferromagnet T_F/T_M is always larger than 1 (i.e., the magnetocaloric effect is positive), and therefore, it is easy to see that the MCE maximum occurs at a temperature higher than $\Theta(H)$. The zero magnetic-field heat capacity in ferromagnets changes sharply with temperature immediately

above its peak [e.g., see Figs. 2(a), 4(a)] and, therefore, the difference between $\Theta(H)$ and $T_M(H)$ may be considered negligible.

As a result of the above relations (3)–(10), the following conclusions can be made:

(1) For a simple ferromagnet and for a given magnetic-field change it is possible to define a certain temperature $\Theta(H)$ in the vicinity of which the maximum magnetocaloric effect should occur. This temperature is higher than the temperature of the zero magnetic-field heat-capacity peak. When magnetic field decreases in the adiabatic process (i.e., when $H\rightarrow 0$), then the maximum magnetocaloric effect approaches the characteristic temperature $\Theta(H)$, where the heat capacity of the material is not affected by the magnetic field [Eq. (9)]. Furthermore, since $[\partial I(H,T)/\partial T]_H$ is the largest at $T\rightarrow T_C$ when $H\rightarrow 0$, and since $T/C(H,T)$ is weakly dependent on temperature, then according to Eq. (1) the maximum magnetocaloric effect in weak magnetic fields also approaches the Curie temperature. Thus, as magnetic field decreases, $\Theta(H)$ also approaches T_C.

(2) The magnetocaloric effect in a ferromagnet is lowered below and above $\Theta(H)$, i.e., where $\Delta C(H,T)$ is positive or negative, respectively, and $\partial \Delta T(H,T_0)/\partial T \neq 0$ which can be shown from analysis of Eq. (7) and is easy seen in Figs. 2(b) and 4(b). This implies, that one would expect a typical caretlike shape [Figs. 2(b), 4(b)] with just a single maximum for the observed magnetocaloric effect for any material which exhibits a single ferromagnetic ordering. On the contrary, a simple antiferromagnetic material should exhibit a reverse caretlike behavior with a single minimum in the magnetocaloric effect assuming that the magnetic field is not strong enough to quench antiferromagnetism and to flip the magnetic spins to a field-induced ferromagnetism, thus reversing the sign of the $\Delta C(H,T)$ compared to that of a simple ferromagnet.

(3) Furthermore, for a general case, when magnetic order is different from that of simple ferromagnetism or antiferromagnetism, or for the cases when there is more than one magnetic phase transition, the behavior of the magnetocaloric effect as a function of temperature becomes more complicated, featuring maxima and/or minima, depending on how many and where the characteristic points $\Theta(H)$ exist.

III. EXPERIMENT

We have experimentally examined a series of magnetic materials which included high-purity single-crystalline and polycrystalline samples with magnetic ordering temperatures ranging from ~10 to 300 K. Two pure lanthanide metals, Gd and Dy, and two intermetallic compounds, GdPd and $(Dy_{0.25}Er_{0.75})Al_2$, were used in this study. The single-crystalline specimen of Gd was prepared by the Materials Preparation Center (MPC) of the Ames Laboratory and was 99.85 at. % (99.98 wt. %) pure with respect to *all* other elements. The magnetic field was applied parallel to the (0001) direction. The polycrystalline specimen of Dy was purified by the solid state electrolysis (SSE) technique and was 99.95 at. % (99.993 wt. %) pure.[16] Polycrystalline Gd, Dy, and Er, used in the preparation of the intermetallic compounds were prepared by the MPC, Ames Laboratory and were 99.90 at. % (99.99 wt. %), 99.79 at. % (99.98 wt. %), and 99.82 at. % (99.99 wt. %) pure, respectively. Polycrystalline Pd and Al were purchased commercially and were >99.99 wt. % pure. The details of alloy preparation can be found, for example, in Ref. 17.

The heat capacity was measured using an adiabatic heat pulse calorimeter which is described elsewhere[18] over the temperature range from ~3.5 to ~350 K in magnetic fields of 0, 1, 2, 5, 7.5, and 10 T. The accuracy of experimental measurements of heat capacity ranged from 0.3 to 0.7 % over the whole range of temperatures.[18] The magnetocaloric effect was calculated for the different magnetic field changes from the total entropy curves evaluated from the experimental heat-capacity data as described in (Ref. 14). A detailed comparison of the magnetocaloric effect calculated from experimental heat capacity in this study and measured directly in quasistatic and pulse magnetic fields for the same high-purity sample of Gd (Ref. 3) and a different sample of Dy (Ref. 2) shows that they agree with one another within the limits of experimental errors. Therefore, the use of the MCE calculated from heat capacity instead of that measured directly is fully justified. This has also been shown for several other materials—$ErAl_2$ and GdPd.[14]

Figures 2–5 show the heat capacity and the magnetocaloric effect of single-crystalline Gd (Fig. 2), high-purity SSE purified polycrystalline Dy (Fig. 3), and high-purity polycrystalline GdPd (Fig. 4) and $(Dy_{0.25}Er_{0.75})Al_2$ (Fig. 5). The major concern of this experiment was to determine the exact positions of the characteristic temperatures $\Theta(H)$, the heat-capacity peak(s), and the temperature of magnetocaloric effect peak values (maxima or minima), $T_M(H)$, to verify the predictions derived theoretically in the previous section.

A. Ferromagnetic-paramagnetic transition, single-crystalline Gd

The heat capacity and the magnetocaloric effect in single-crystalline Gd for various magnetic-field changes are presented in Fig. 2. Although the heat-capacity maximum in zero magnetic field is observed at $T_{C(\max)}=291\pm 0.7$ K, the maximum magnetocaloric effect occurs at T_M, which is ~2 K higher even for the lowest magnetic-field change from 0 to 2 T [see Fig. 2(a), 2(b)], and this is consistent with the theoretical model. For a field change from 0 to 2 T the temperature of the maximum magnetocaloric effect is very close to the temperature $\Theta(H)$ where $C(0,T)=C(2,T)$, i.e., where these two curves intersect. It is also obvious that both $\Theta(H)$ [Fig. 2(a), Table I] and the maximum magnetocaloric effect temperature [$T_M(H)$, Table I] increase with increasing magnetic field. The experimentally determined values for $\Theta(H)$ and $T_M(H)$ for this Gd specimen and the other materials are listed in Table I.

First, it can be seen that the experimental results for single-crystalline Gd are in excellent agreement with theoretical predictions about the mutual arrangement of the temperatures $\Theta(H)$ and $T_M(H)$ in different magnetic fields. These two temperatures coincide within the accuracy of the experiment in fields up to 7.5 T, and $T_M(H)$ becomes larger than $\Theta(H)$ by ~1.6 K when magnetic field increases to 10 T.

Second, the behavior of the magnetocaloric effect in Gd as a function of temperature has typical caretlike shape, which agrees with the existence of a single temperature $\Theta(H)$ for each pair of magnetic fields [see Figs. 2(a), 2(b)].

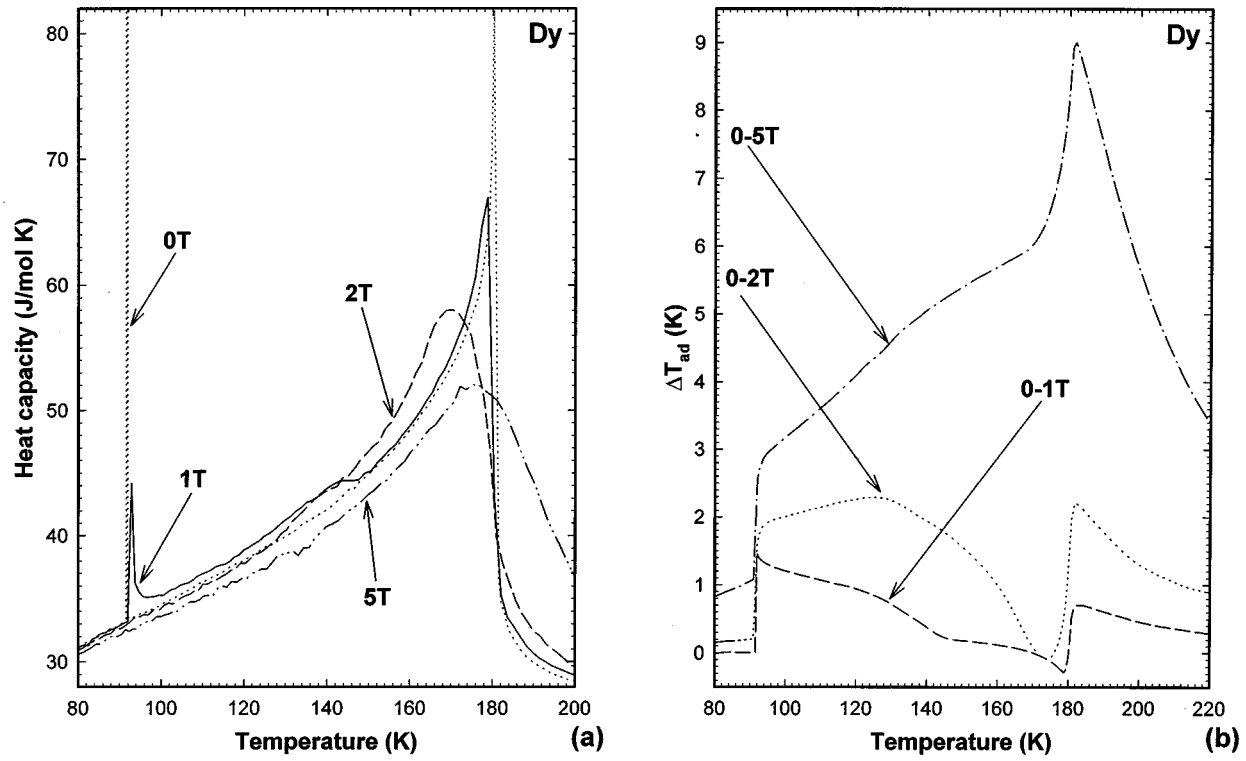

FIG. 3. The heat capacity of polycrystalline Dy from 80 to 200 K at 0, 1, 2, and 5 T (a) and the magnetocaloric effect for a magnetic-field change from 0 to 1, from 0 to 2, and from 0 to 5 T (b).

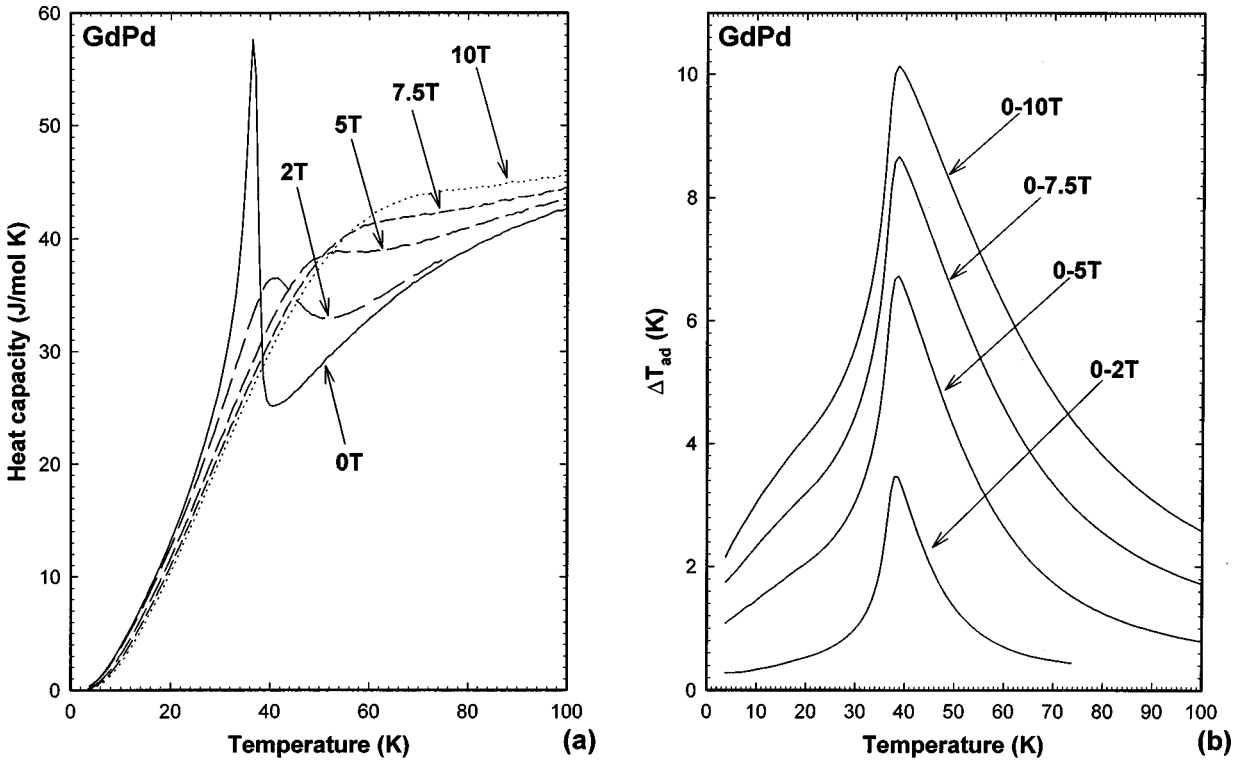

FIG. 4. The heat capacity of polycrystalline GdPd from 3.5 to 100 K at 0, 2, 5, 7.5, and 10 T (a) and the magnetocaloric effect for a magnetic-field change from 0 to 2, from 0 to 5, from 0 to 7.5, and from 0 to 10 T (b).

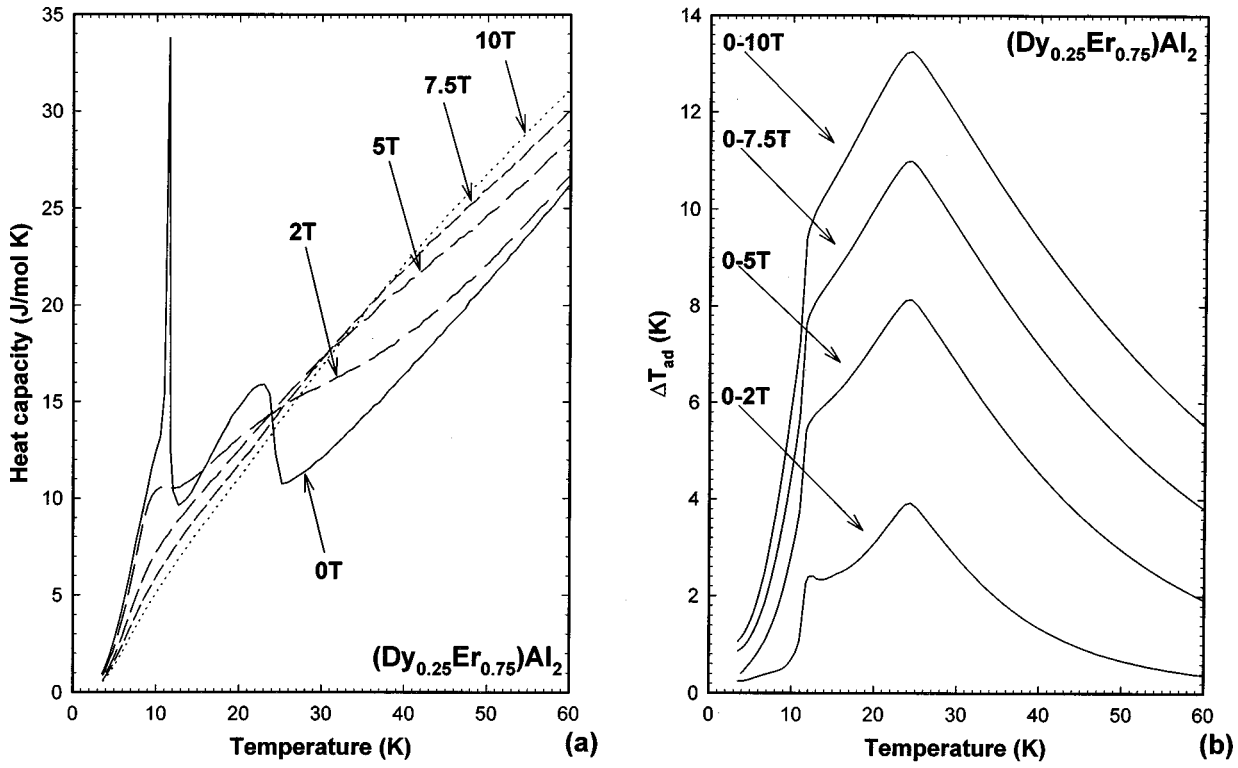

FIG. 5. The heat capacity of polycrystalline $(Dy_{0.25}Er_{0.75})Al_2$ from 3.5 to 60 K at 0, 2, 5, 7.5, and 10 T (a) and the magnetocaloric effect for a magnetic-field change from 0 to 2, from 0 to 5, from 0 to 7.5, and from 0 to 10 T (b).

B. Ferromagnetic-antiferromagnetic and antiferromagnetic-paramagnetic transitions, high-purity polycrystalline Dy

It is well known that upon cooling in zero-field Dy undergoes a transition from a paramagnet to a helical antiferromagnet at ~180 K and then from this helical antiferromagnet to a ferromagnet at ~90 K.[19] Depending on the magnetic field there are from 1 to 3 characteristic temperatures, $\Theta(H)$ [see Table I and Fig. 3(a)]. There are a total of three temperatures where zero-field heat capacity is the same as 1 T field heat capacity. The lowest one is at $\Theta_1(1)=91.9$ K and is due to the shifting of a first-order ferromagnetic-antiferromagnetic phase transition to slightly higher temperature by the 1 T magnetic field. The second $[\Theta_2(1)=178.8\ \text{K}]$ and third $[\Theta_3(1)=181.3\ \text{K}]$ appear due to the suppression of the antiferromagnetic-paramagnetic phase transition to a lower temperature by the 1 T magnetic field. When the magnetic field increases to 2 T it becomes strong enough to quench the first-order ferromagnetic-antiferromagnetic phase transition and it induces noncollinear magnetic structure which yields the lower characteristic temperature $\Theta_1(2)=126.9$ K. Since a 2 T magnetic field is not strong enough to destroy this noncollinear structure, the upper heat-capacity maximum continues to be shifted to

TABLE I. Observed characteristic temperatures [maximum uncertainty in determination of $\Theta(H)$ and $\mathbf{T_M(H)}$ is ±0.7 K]: $\Theta(H)$ [normal type]; and maximum (or minimum) magnetocaloric effect temperatures, $\mathbf{[T_M(H)]}$ [boldface type], for several pure lanthanides metals and lanthanide intermetallic compounds.

Material	0–1 T $\Theta(1)/\mathbf{T_M}(1)$ (K)	0–2 T $\Theta(2)/\mathbf{T_M}(2)$ (K)	0–5 T $\Theta(5)/\mathbf{T_M}(5)$ (K)	0–7.5 T $\Theta(7.5)/\mathbf{T_M}(7.5)$ (K)	0–10 T $\Theta(10)/\mathbf{T_M}(10)$ (K)
Gd		294.2/**294.4**	294.4/**294.8**	294.6/**295.1**	294.7/**296.3**
(max)	91.9/**91.9**	126.9/**126.0**			
Dy (min)	178.8/**178.8**	173.9/**174.0**			
(max)	181.3/**181.5**	181.2/**182.0**	181.0/**181.2**		
GdPd		38.0/**38.1**	38.3/**38.4**	38.4/**38.6**	38.5/**38.7**
$(Dy_{0.25}Er_{0.75})Al_2$		12.0/**12.2** 15.6/**13.8** 23.9/**24.1**	23.9/**24.2**	24.1/**24.3**	24.1/**24.3**

lower temperatures and this preserves the two upper characteristic temperatures, $\Theta_2(2)=173.9$ K and $\Theta_3(2)=181.2$ K. Upon increasing magnetic field to 5 T it becomes strong enough to suppress all magnetic structures except the ferromagnetic phase. Thus at this field just a single characteristic temperature, $\Theta(5)=181.0$ K remains. It is noted that the exact interpretation of the magnetic phase transitions in magnetic fields below ~2 T between ~90 and ~180 K is difficult because the exact magnetic phase diagram of high-purity Dy is not well established.

It is easy to see from Table I and Figs. 3(a), 3(b), that the predictions of the thermodynamic model are in excellent agreement with the experiment for all of the characteristic temperatures for the three magnetic fields. For a magnetic-field change from 0 to 1 T and from 0 to 2 T there are total of three characteristic temperatures in each case. Correspondingly, the magnetocaloric effect in these fields exhibits two maxima and one minimum. For a higher magnetic-field change, from 0 to 5 T, where just one characteristic point remains, the magnetocaloric effect retains a single peak. Overall, the behavior of the magnetocaloric effect as a function of temperature of Dy is much more complicated compared to a simple caretlike shape observed for Gd, which is due to significant differences in their magnetic structures.

C. High-purity polycrystalline intermetallides, GdPd and $(Dy_{0.25}Er_{0.75})Al_2$

The binary intermetallic compound GdPd orders ferromagnetically at ~38 K,[20] while the magnetic structure of pseudobinary $(Dy_{0.25}Er_{0.75})Al_2$ is more complicated. Upon cooling the latter orders ferromagnetically at ~24 K and then a first-order phase transition associated with the change of an easy magnetizing axis occurs at ~12 K.[21]

As can be seen from Fig. 4(a), in GdPd there is a single characteristic temperature, $\Theta(H)$, which appears to increase slightly with increasing magnetic field up to 10 T but considering the experimental error (Table I), $\Theta(H)$ is independent of field. Correspondingly, there is a single maximum in magnetocaloric effect for all magnetic fields, see Fig. 4(b). A comparison of the characteristic temperatures $\Theta(H)$ with $T_M(H)$ shows that again there is an excellent agreement between the two, see Table I.

In a 2 T magnetic field for the compound $(Dy_{0.25}Er_{0.75})Al_2$ theory and experiment agree with an accuracy of ~0.2 K for the 2 out of 3 crossover points of the $C(0,T)$ and $C(2,T)$ curves. The apparent deviation between $\Theta(2)$ and $T_M(2)$ (as large as 1.8 K) for the middle characteristic point, $\Theta_2(2)=15.6$ K, is most likely associated with the low thermal energy associated with the spin-reorientation transition [see Fig. 5(a)].

It should be noted that the suggested thermodynamic model does not provide any details on the possible mechanisms leading to the existence of maxima and/or minima in the magnetocaloric effect in the vicinity of each characteristic temperature, $\Theta(H)$. It is obvious, however, that there is an excellent agreement between the theoretical predictions derived from general thermodynamic approach and the experimental results discussed in this paper, which were obtained using high-quality single-crystalline and polycrystalline magnetic materials.

IV. PHASE-TRANSITION TEMPERATURE FROM MAGNETOTHERMAL PROPERTIES

As shown above, the temperatures of the heat capacity and the MCE peaks are different even in weak magnetic fields. However the characteristic temperature, $\Theta(H)$, corresponds to the temperature of the magnetocaloric effect peak and as discussed in Sec. II it approaches the magnetic phase-transition temperature when H approaches 0. Taking into account a generally excellent agreement between $\Theta(H)$ and $T_M(H)$ in different materials and moderately strong magnetic fields (Table I, Figs. 2–5), it can also be assumed that even in nonzero fields the characteristic temperature $\Theta(H)$ corresponds to the temperature of the magnetic phase transition.

According to Schmitt and co-workers[8,9] the zero-field heat-capacity inflection point most accurately describes the temperature of magnetic phase transition in Gd-based compounds. Analysis of the experimental results[22] obtained on single-crystalline Gd show that the temperatures of the inflection point of the zero-field heat capacity and the characteristic point $\Theta(H=2\text{ T})$ agree within 0.2 K, i.e., the difference is smaller than the experimental error. Magnetic field shifts the heat-capacity inflection point towards higher [see Figs. 2(a), 4(a) and 5(a)] or lower [see Fig. 3(a)] temperatures depending on the magnetic structure of the samples and the magnetic-field strength. The heat capacity measured in a high magnetic field shows that in pure Gd the inflection point is shifted by almost 50 K in 7.5 T magnetic field [see Fig. 2(a) and Ref. 22]. However, in GdPd and $(Dy_{0.25}Er_{0.75})Al_2$ the inflection point becomes almost indistinguishable in high magnetic fields [see Figs. 4(a), 5(a)]. Therefore, the use of the heat-capacity inflection point to estimate the temperature of the magnetic phase transition in strong magnetic fields becomes unreliable. Nonetheless, the temperatures where the heat-capacity curves in different magnetic fields intersect, are well defined [see Figs. 2(a)–5(a)]. At this temperature the magnetic part of heat capacity is magnetic-field independent and it should be located close to the temperature of the magnetocaloric effect peak. Therefore, it seems that the $\Theta(H)$ is quite specific on the temperature scale, and its properties make it possible to assume that it indicates the approximate temperature where the magnetic phase transition occurs in nonzero magnetic fields.

To verify this assumption we calculated the magnetocaloric effect when the magnetic field changes from a nonzero value to H for the two simple ferromagnetic materials studied here. The magnetocaloric effect in Gd when the initial magnetic field is 2 T, i.e., the MCE for a magnetic-field changes from 2 to 5, from 2 to 7.5, and from 2 to 10 T, is shown in Fig. 6(a). The same for another simple ferromagnet, GdPd, is shown in Fig. 6(b). As one can see, the temperatures where the maximum magnetocaloric effect is observed are quite close to the characteristic temperatures, $\Theta(H)$, where the 5, 7.5, and 10 T heat capacities are the same as the heat capacity in a 2 T magnetic field. Furthermore, if one extrapolates the behavior of both $T_M(H)$ and $\Theta(H)$ to an infinitesimal magnetic-field change from 2 T to $2\text{ T}+\delta$ [dotted and dashed lines, respectively, in Figs. 6(a) and 6(b)] the difference between them becomes considerably smaller. The two temperatures agree almost exactly for GdPd

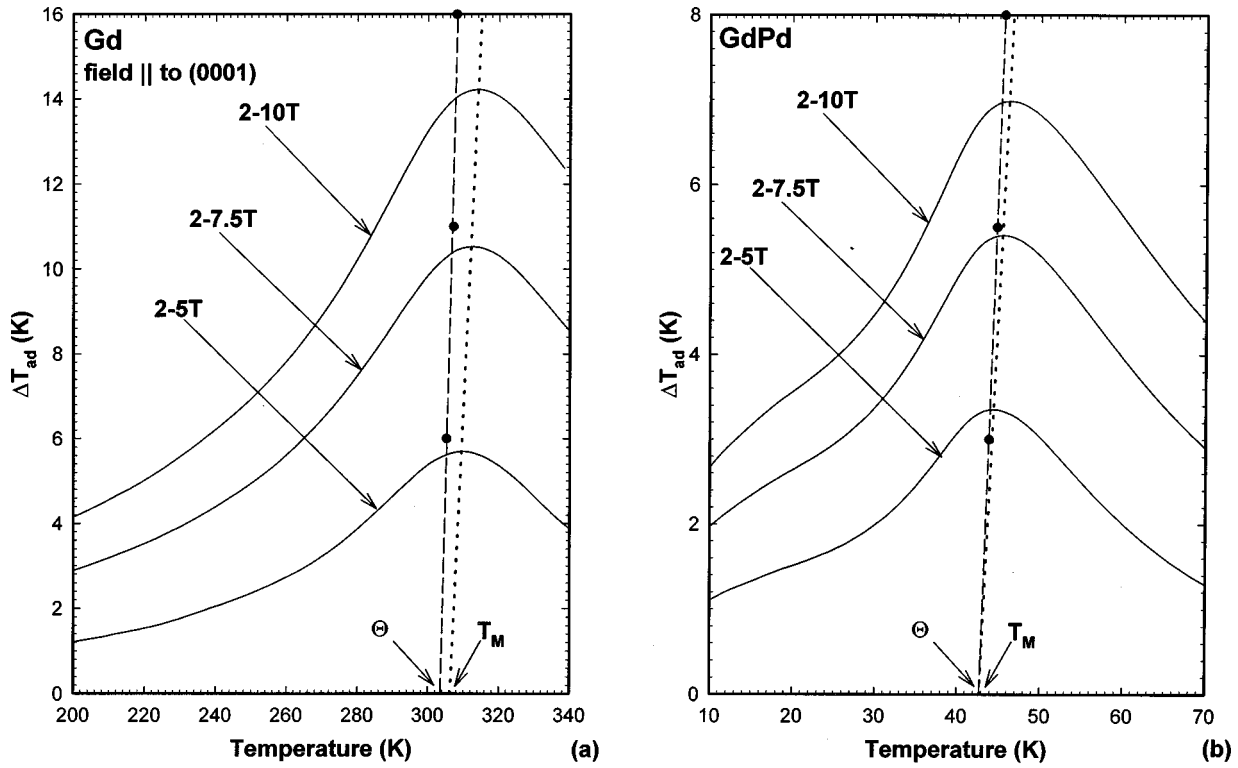

FIG. 6. The magnetocaloric effect in single-crystalline Gd (a) and polycrystalline GdPd (b) for a magnetic-field change from 2 to 5, from 2 to 7.5, and from 2 to 10 T. The dotted lines are a least-squares fit of the maximum magnetocaloric effect temperature $T_M(H)$. The solid points are the corresponding characteristic points $\Theta(H)$ and the dashed lines are a least-squares fit of $\Theta(H)$ as a function of temperature.

when extrapolated to infinitesimal magnetic-field change [Fig. 6(b)]. However, the difference between $T_M(H)$ and $\Theta(H)$ does not become negligible in Gd. Note that the larger differences between $\Theta(H)$ and $T_M(H)$ in Gd were also observed when MCE was calculated for magnetic field changing from 0 T, while in GdPd these temperatures agree quite well (see Table I). Hence, the results of the calculation of the magnetocaloric effect shown in Figs. 2(b) and 6(a) suggest that the difference between the $\Theta(H)$ and $T_M(H)$ in Gd is not negligible and should not be dismissed without an attempt to explain the discrepancy. It seems that the high magnetic ordering temperature in Gd yields a low $\Delta T_M/T \cong 5.7/309 \cong 0.018$ when compared to that in GdPd, $\Delta T_M/T \cong 3.4/44 \cong 0.077$ for a field change from 2 to 5 T and therefore, in the case of Gd the conditions for which Eq. (9) was derived (i.e., $\Delta T/T \cong 0$) are better satisfied. However, the fact that the Curie temperature of Gd is quite high implies that large thermal fluctuations contribute significantly to the smearing of the magnetic phase transition compared to that in GdPd, and hence, even moderate fields of 2 to 5 T, are too large and thus the approximation used to derive Eq. (9) from Eq. (8) no longer holds. The presence of larger spin fluctuations in Gd is well evident from the overall widths of the λ-type heat-capacity anomalies in zero magnetic field [it is significantly smaller in GdPd, Fig. 4(a) compared to Gd, Fig. 2(a)]. It should also be noted that in the case of Gd (i.e., at higher temperatures), the determination of the magnetic phase-transition temperature in general becomes more difficult.

V. CONCLUSION

The proposed thermodynamic model predicts that a certain characteristic temperature, $\Theta(H)$, where the heat capacity of the magnetic material is not affected by the magnetic field can be defined in the vicinity of a magnetic phase transition. The maximum (or minimum) magnetocaloric effect is also observed near this characteristic temperature. In the case of simple ferromagnetic ordering the maximum magnetocaloric effect occurs at temperatures higher than the maximum heat capacity. However, both $\Theta(H)$ and $T_M(H)$ approach the temperature at which magnetic ordering occurs as $H \rightarrow 0$. If the magnetic ordering is different from that of simple ferromagnetism or antiferromagnetism, or for the cases when there is more than one magnetic phase transition, then the behavior of the magnetocaloric effect as a function of temperature becomes more complicated, featuring multiple maxima and/or minima, depending on how many and where the characteristic points $\Theta(H)$ exist. The experimental measurements of the heat capacity and calculations of the magnetocaloric effect for two high-purity lanthanide metals (Gd and Dy) and for two high-purity intermetallic compounds [GdPd and $(Dy_{0.25}Er_{0.75})Al_2$] are in excellent agreement with the theoretical conclusions derived from the model.

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