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Magnetocaloric effect from indirect measurements: Magnetization and heat capacity

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Accurate values for the magnetocaloric effect can be obtained from both magnetization and heat-capacity data. A reliable estimate of the experimental errors in the calculated magnetocaloric effect can be made from the known experimental errors of the measured physical properties. Attempts in the past to simplify the basic thermodynamic relation to allow the calculation of the adiabatic temperature change from the heat capacity at constant field and the magnetic entropy change calculated from the magnetization data fail because the assumption that heat capacity is magnetic-field independent is erroneous. A suitable approach to carry out these calculations from the combined heat capacity and magnetization data is suggested. © *1999 American Institute of Physics.* [S0021-8979(99)04013-X]

I. INTRODUCTION

The magnetocaloric effect (MCE) is intrinsic to magnetic solids and is induced via the coupling of the magnetic sublattice with the magnetic field, which alters the magnetic part of the total entropy due to a corresponding change of the magnetic field. It can be measured and/or calculated as the adiabatic temperature change $\Delta T_{ad}(T, \Delta H)$, or as the isothermal magnetic entropy change $\Delta S_M(T, \Delta H)$. The MCE is a function of both temperature T and the magnetic-field change ΔH and is usually recorded as a function of temperature at a constant ΔH. In addition to its fundamental importance, the MCE has a significant technological importance since magnetic materials with large MCE values could be employed as magnetic refrigerants in magnetic refrigerators, air conditioning units, and/or heat pumps which are environmentally safe and energy efficient.[1–13] It is, therefore, not surprising, that worldwide research on the magnetocaloric effect and magnetic refrigeration is on the rise. The number of publications about magnetic refrigerant materials science and magnetic refrigeration technology increased from a total of 11 in 1965 to 1969 to a total of 127 in 1990 to 94, and is estimated to reach 155 in 1995 to 1999.[14] One of the important areas which needs to be advanced before magnetic refrigeration becomes a viable technology is the development of improved solid magnetic refrigerant materials with large MCE to allow the use of permanent magnets instead of superconducting magnets as the magnetic-field source. Thus, experimental characterization of new soft magnetic materials with respect to their MCE still is and will remain an important task for basic and applied physics.

The magnetocaloric effect can be measured directly or it can be calculated indirectly from the experimentally measured heat capacity and/or magnetization. *Direct techniques* always involve measurements of the sample temperatures (T_I and T_F) in magnetic fields H_I and H_F, where the subscripts I and F designate initial and final temperature and magnetic field, respectively. Usually, the initial magnetic field is zero when MCE is measured in the magnetic field rising from H_I to H_F (i.e., when a sample is magnetized). For a fully reversible process, the MCE can also be measured when a sample is demagnetized, and for this case, $H_F = 0$. The $\Delta T_{ad}(T)_{\Delta H}$ is then determined as the difference between T_F and T_I for a given $T_{H=0}$ and $\Delta H = H_F - H_I$.

Indirect techniques allow (1) the calculation of both $\Delta T_{ad}(T)_{\Delta H}$ and $\Delta S_M(T)_{\Delta H}$ from the experimentally measured heat capacity as a function of temperature in magnetic fields H_I and H_F, and (2) the calculation of $\Delta S_M(T)_{\Delta H}$ from the magnetization experimentally measured at a number of different temperatures as a function of H from H_I to H_F. Using the $\Delta S_M(T)_{\Delta H}$ calculated from magnetization data it is also possible to calculate the $\Delta T_{ad}(T)_{\Delta H}$ if the heat capacity at constant field H_I or H_F is available. Both $\Delta T_{ad}(T)_{\Delta H}$ and $\Delta S_M(T)_{\Delta H}$ relate to the total entropy of the system as a function of temperature in magnetic fields H_I and H_F (where $H_F > H_I$), as shown schematically in Fig. 1. For a ferromagnet the $\Delta T_{ad}(T)_{\Delta H}$ is, therefore, the heating (during magnetizing) or the cooling (during demagnetizing) of a solid when the magnetic field is changed adiabatically between H_I and H_F. Consequently, the $\Delta S_M(T)_{\Delta H}$ is the decrease (on magnetizing) or increase (on demagnetizing) of the total entropy of the ferromagnet when the magnetic field is isothermally changed between H_I and H_F. Independent of how the MCE was measured or calculated, it is typically reported in the form of either $\Delta T_{ad}(T)_{\Delta H}$ or $\Delta S_M(T)_{\Delta H}$ for a certain ΔH, as shown schematically in the inset to Fig. 1. It should be noted that these two quantitative characteristics of the magnetocaloric effect are by no means the same (see below), but generally, a large $|\Delta T_{ad}(T)_{\Delta H}|$ corresponds to a large $|\Delta S_M(T)_{\Delta H}|$, and vice versa.

The recent increase of research activity, in particular with respect to characterization of the MCE in new soft magnetic materials, requires a careful analysis of the benefits and the limitations inherent to each of the three mentioned ex-

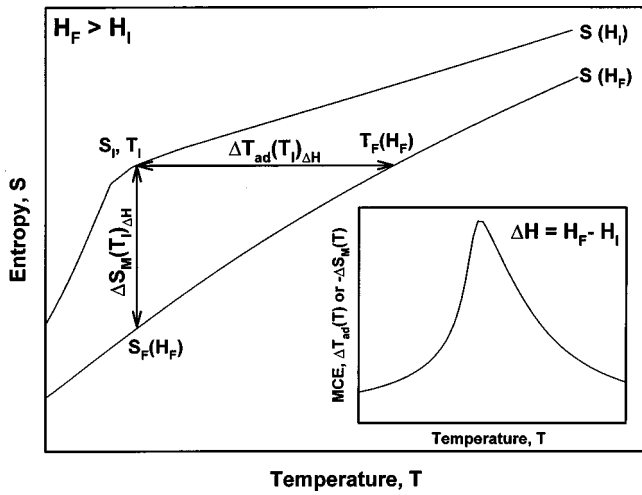[a)]Corresponding author. Electronic mail: vitkp@ameslab.gov

FIG. 1. Magnetocaloric effect as the adiabatic temperature rise, $\Delta T_{\mathrm{ad}}(T_I)_{\Delta H}$, and the magnetic entropy change, $\Delta S_M(T_I)_{\Delta H}$ shown for a single initial temperature T_I and a given magnetic-field change $\Delta H = H_F - H_I$ in a ferromagnetic material. The inset displays MCE typical for a ferromagnet as a function of temperature.

perimental techniques, which currently is either lacking or inaccurate. It is important to recognize that the direct measurements of the magnetocaloric effect may be intrinsically erroneous if the changes in the magnetic structure of a solid are time dependent, i.e., if they exhibit far from instant kinetics, because the experiments are generally carried out in a rapidly varying magnetic field. Hence, if the T_F is measured when a process induced by the application or removal of a magnetic field is incomplete, then the resulting $\Delta T_{\mathrm{ad}}(T_I)_{\Delta H} = T_F - T_I$ would be systematically underestimated. The same could be true when the $\Delta S_M(T)_{\Delta H}$ is calculated from magnetization measurements, although they are usually performed in a much slower varying magnetic field, and therefore, the kinetics of the magnetic phase transformation have almost no effect on the results unless the transformation is extremely slow. The adiabatic or semiadiabatic heat-capacity measurements are usually free from detrimental kinetic effects because the measurements are performed in constant magnetic field at a slowly varying temperature. Unfortunately, the two indirect techniques require extensive processing of the experimental data, which could result in an accumulation of experimental errors and yield inaccurate $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ and $\Delta S_M(T)_{\Delta H}$ values. To the best of our knowledge, little, if any, information is available in the literature analyzing the accuracy (not repeatability) of the indirectly calculated MCE. Finally, there are some examples in the literature where the simplified basic thermodynamic relations have been applied without caution (i.e., authors have made some erroneous assumptions), which yields inaccurately calculated MCE. In this article we consider the evaluation of the magnetocaloric properties by indirect techniques in a fully reversible isobaric process with no kinetic effects impairing experimental results.

II. MAGNETOCALORIC EFFECT AND MAGNETIZATION MEASUREMENTS

The infinitesimal isobaric–isothermal magnetic entropy change is related to the magnetization (M), magnetic-field strength (H), and absolute temperature (T) using one of the Maxwell relations[15]

$$\left(\frac{\partial S_M(T,H)}{\partial H} \right)_T = \left(\frac{\partial M(T,H)}{\partial T} \right)_H, \tag{2.1}$$

which after integration yields

$$\Delta S_M(T)_{\Delta H} = \int_{H_I}^{H_F} dS_M(T,H)_T = \int_{H_I}^{H_F} \left(\frac{\partial M(T,H)}{\partial T} \right)_H dH. \tag{2.2}$$

Hence, $\Delta S_M(T)_{\Delta H}$ could be easily calculated for any T numerically by integrating Eq. (2.2) using the experimentally measured magnetization as a function of magnetic field and temperature.[16,17] Generally, since temperature stabilization is the longest step in the process of collecting magnetization data, the measurements are almost exclusively carried out isothermally by varying the magnetic field.

Numerical integration of Eq. (2.2) is straightforward; however, the experimental errors in the $\Delta S_M(T)_{\Delta H}$ due to the errors in temperature, and the accumulation of errors in the magnetic moment and magnetic field upon numerical integration, have never been carefully analyzed, except an unverified statement that a better than or equal to 0.5% accuracy of the magnetic measurements yields about $\pm7.5\%$ error in the values of $\Delta S_M(T)_{\Delta H}$.[17] Since such an analysis is important to understand the limits of the accuracy of the derived $\Delta S_M(T)_{\Delta H}$, it is described below together with the numerical results obtained using the experimental magnetization data for ErAl$_2$, which orders magnetically at $\sim$14 K, and the pure lanthanide metal Gd, which orders magnetically at $\sim$294 K. Both are well-studied magnetocaloric materials.

Consider the calculation of the magnetic entropy change $\Delta S_M(T=T_{\mathrm{av}})_{\Delta H}$ for an average temperature $T_{\mathrm{av}} = (T_u + T_l)/2$ from the two magnetization isotherms measured at T_u and T_l in a magnetic field changing by $\Delta H = H_F - H_I$ at a constant step δH. Numerically integrating Eq. (2.2), for instance using a trapezoidal rule, we obtain

$$\Delta S_M(T_{\mathrm{av}})_{\Delta H}$$
$$= \int_{H_I}^{H_F} \left(\frac{\partial M(H)_{T_{\mathrm{av}}}}{\partial T} \right)_H dH$$
$$= \frac{1}{2\delta T} \left(\delta M_1 \delta H_1 + 2 \sum_{k=2}^{n-1} \delta M_k \delta H_k + \delta M_n \delta H_n \right). \tag{2.3a}$$

Since δH is a constant, for practical calculations Eq. (2.3a) can be simplified as follows:

$$\Delta S_M(T_{\mathrm{av}})_{\Delta H} = \frac{\delta H}{2\delta T} \left(\delta M_1 + 2 \sum_{k=2}^{n-1} \delta M_k + \delta M_n \right). \tag{2.3b}$$

Here, $\delta T = T_u - T_l$ is the temperature difference between the two isotherms, n is the number of points measured for each of the two isotherms with the magnetic field changing from

$H_1 = H_I$ to $H_n = H_F$ at $\delta H = \Delta H/(n-1)$, and $\delta M_k = [M(T_u)_k - M(T_l)_k]$ is the difference in the magnetization at T_u and T_l for each magnetic-field step from 1 to n. Hence, the full expression for the combined uncertainty of the calculated magnetic entropy change $\sigma|\Delta S_M(T_{av})_{\Delta H}|$ can be written as

$$\sigma|\Delta S_M(T_{av})_{\Delta H}|$$
$$= \frac{|\delta H|}{2|\delta T|}\left(\sigma M_1 + 2\sum_{k=2}^{n-1}\sigma M_k + \sigma M_n\right)$$
$$+ \frac{1}{2|\delta T|}\left((|\delta M_1|\sigma H_1) + 2\sum_{k=2}^{n-1}(|\delta M_k|\sigma H_k)\right.$$
$$\left. + (|\delta M_n|\sigma H_n)\right) + \frac{|\delta H|}{2(\delta T)^2}$$
$$\times\left(\delta M_1 + 2\sum_{k=2}^{n-1}\delta M_k + \delta M_n\right)\sigma T_u$$
$$+ \frac{|\delta H|}{2(\delta T)^2}\left(\delta M_1 + 2\sum_{k=2}^{n-1}\delta M_k + \delta M_n\right)\sigma T_l. \quad (2.4a)$$

Here, $\sigma M_k = [\sigma M(T_u)_k + \sigma M(T_l)_k]$ is the sum of the errors in the magnetization measured at T_u and T_l for magnetic field H_k; $\sigma H_k = [\sigma H(T_u)_k + \sigma H(T_l)_k]$ is the sum of the errors in the magnetic field H_k at T_u and T_l; and σT_u and σT_l are the uncertainties in the temperatures T_u and T_l, respectively. By combining Eq. (2.4a) with Eq. (2.3b) and rearranging, we obtain the following equation, explicitly defining the combined uncertainty in $\Delta S_M(T_{av})_{\Delta H}$ as

$$\sigma|\Delta S_M(T_{av})_{\Delta H}|$$
$$= \frac{1}{2|\delta T|}\left\{|\delta H|\times\left(\sigma M_1 + 2\sum_{k=2}^{n-1}\sigma M_k + \sigma M_n\right)\right.$$
$$+ \left(|\delta M_1|\sigma H_1 + 2\sum_{k=2}^{n-1}(|\delta M_k|\sigma H_k) + |\sigma M_n|\sigma H_n\right)$$
$$\left. + 2|\Delta S_M(T_{av})_{\Delta H}|\times(\sigma T_u + \sigma T_l)\right\}. \quad (2.4b)$$

Analysis of Eq. (2.4b) allows one to predict the effect of the changes in δH and δT on the resulting error in $\Delta S_M(T)_{\Delta H}$, provided the errors in the temperature, magnetic field, and magnetization remain unchanged. The change of δT will affect the first and the third term in Eq. (2.4b), while the second term should remain insensitive to δT because this will inversely change δM. Thus, the combined error in the magnetic entropy will be increased if the δT is decreased, and vice versa. The change in δH should have a small effect on the first term in Eq. (2.4b) because the decrease in δH will be offset by the corresponding increase in n, and the increase in δH will be offset by the corresponding decrease in n. Any change in δH has no effect on the third term in Eq. (2.4b) except that the smaller δH provides a better approximation of Eq. (2.2) by the sum in Eq. (2.3b). However, the reduction of δH will increase the second term in Eq. (2.4b) due to the increased n, thus also rising the combined error,
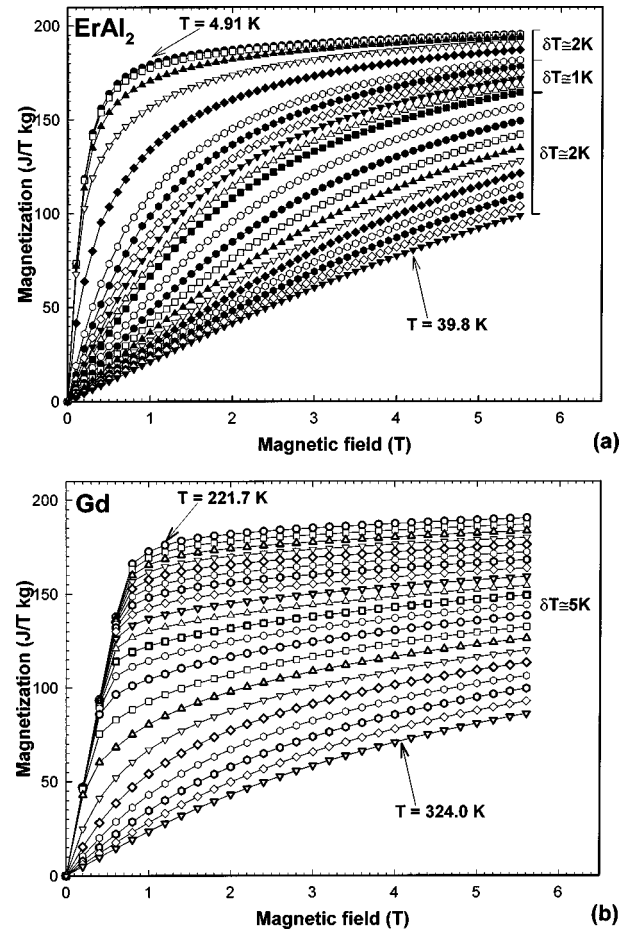

FIG. 2. Magnetization isotherms in ErAl$_2$ (a) and single-crystal Gd (b). For ErAl$_2$ $\mu_0\delta H = 0.1$ T, and $\delta T = \sim 2$ K between ~ 5 and ~ 15 K and between ~ 20 and ~ 40 K, and $\delta T = \sim 1$ K between ~ 15 and ~ 20 K. For Gd the magnetic-field vector was parallel to the [0001] direction, $\mu_0\delta H = 0.2$ T and $\delta T = \sim 5$ K.

and vice versa. Both δT and δH, however, cannot be chosen to be too large because then Eqs. (2.3a) and (2.3b) become invalid.

Figure 2 shows the magnetization data collected for polycrystalline ErAl$_2$ and a single crystal of Gd (the magnetic-field vector was parallel to the [0001] direction of the single crystal). The data were collected using constant magnetic-field steps, $\mu_0\delta H = 0.1$ T, and $\mu_0\delta H = 0.2$ T for ErAl$_2$ and Gd, respectively. For ErAl$_2$ at temperatures both below and above the magnetic transition (~ 14 K) the δT was ~ 2 K, and it was reduced to ~ 1 K in its immediate vicinity. For Gd the δT was approximately constant at ~ 5 K. These data were used to calculate the $\Delta S_M(T)_{5\,T}$ [Eq. (2.3b)] and $\sigma|\Delta S_M(T)_{5\,T}|$ [Eq. (2.4b)] for the magnetic-field change from 0 to 5 T. Following Foldeaki, Chahine, and Bose[17] we assumed the accuracy of the magnetic-moment measurements at 0.5%. The absolute accuracy of the dc magnetic field is quoted by the manufacturers of commercial magnetometers (e.g., Lake Shore Cryotronics, Quantum Design, Oxford Instruments) at 1% with field stability of an order 0.0005–0.001 T, and field uniformity of 0.1% within the sample volume. For the purpose of this analysis we chose the field uniformity as an error in magnetic field, i.e., the accu-
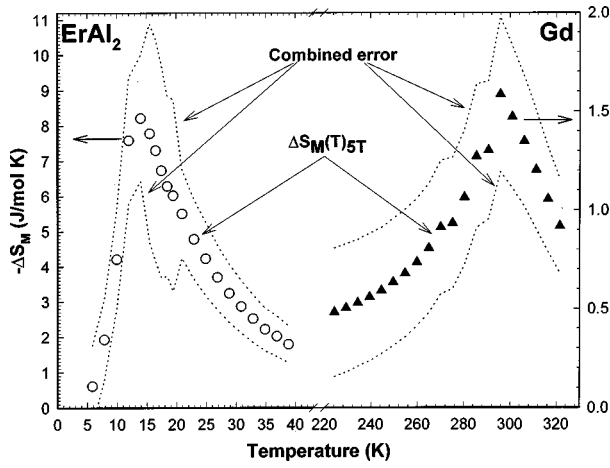
FIG. 3. Magnetic entropy change in ErAl$_2$ (left-hand scale) and Gd (right-hand scale) calculated from magnetization data shown in Fig. 2. The open circles and solid triangles represent the $\Delta S_M(T)_{5\,T}$ [Eq. (2.3b)]. The dotted lines represent the margins of the combined $\sigma[\Delta S_M(T)_{5\,T}]$ [Eq. (2.4b)].

racy of the magnetic field was assumed at 0.1%. It is difficult to estimate the true error in the temperature during the magnetization measurements because the temperature sensor is not in direct contact with the sample. The absolute temperature error in zero-magnetic field is given by the same manufacturers as 0.2 K or 0.5% of T, whichever is greater. The temperature stability is quoted at 0.1 K and the temperature uniformity is 0.1 K + 0.1% of T. Again, we chose the temperature uniformity inside the sample volume as an estimate of the temperature accuracy, i.e., $\sigma T = 0.1\,K + 0.001 \times T$.

Both the magnetic entropy [Eq. (2.3b)] and combined errors [Eq. (2.4b)] in the magnetic entropy of ErAl$_2$ and Gd are presented in Fig. 3. The contribution of different errors (i.e., the errors in magnetic moment, magnetic field, and temperature) and their sum to give the combined relative error of $\Delta S_M(T)_{5\,T}$ is analyzed in Fig. 4. First, it is obvious that the twofold increase of the δH ($\mu_0 \delta H$ in ErAl$_2$ was 0.1 T and it was 0.2 T in Gd), results in an approximate twofold reduction of the contribution from the errors in the magnetic field
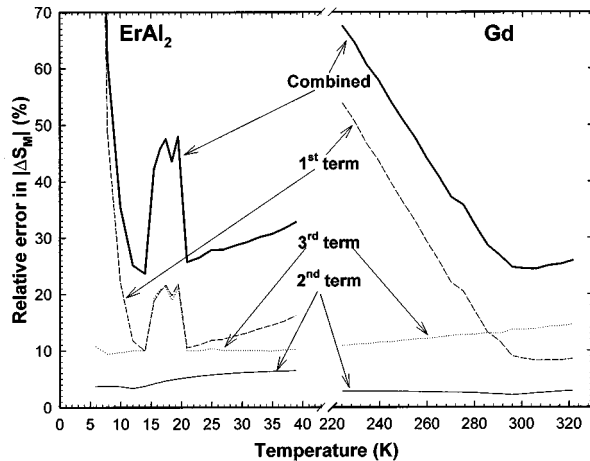

FIG. 4. Relative errors in the magnetic entropy change in ErAl$_2$ and Gd calculated using Eq. (2.4b) from magnetization data shown in Fig. 2. The contribution of each of the three terms in Eq. (2.4b) is shown together with the combined relative error.

[i.e., the second term in Eq. (2.4b)]. Second, the approximate twofold reduction in δT (from ~2 to ~1 K, which occurred at $T = \sim 15$ K and was restored to the original ~2 K step at $T = \sim 20$ K in ErAl$_2$) gives rise to a step-like inversely proportional increase in the errors due to magnetic-moment and temperature uncertainties [the first and third terms of Eq. (2.4b), respectively].

The numerical results presented in Figs. 3 and 4 show that the relative errors due to the errors in the magnetic moment rise rapidly below the magnetic ordering temperature. This happens because below the Curie temperature of a ferromagnet, the MCE decreases, while its magnetization has large absolute values measured with the same relative error, thus leading to a larger $\sigma M(T,H)$. The effect of the magnetic-field errors on the combined relative error in the magnetic entropy change is the smallest and close to a constant rising slightly above the Curie temperature. In fact, this contribution to the combined error can be neglected if the magnetic-field stability (which is considerably better than its uniformity) is taken as a measure of its accuracy. The errors in the temperature give close to a constant contribution provided δT remains unchanged during the experiment, they are significant and obviously may not be neglected. Finally, we would like to note that the statement from Ref. 17 that a 0.5% accuracy in magnetization measurements generally yields ±7.5% accuracy in the calculated magnetic entropy change is unfounded. For the two experiments described above, magnetization data at 0.5% accuracy yield the best accuracy of 10% near the Curie temperature, i.e., where the magnetocaloric effect is the largest, even neglecting the errors in H and T. It rises to ~15% in ErAl$_2$ at higher temperatures and deteriorates rapidly in both materials below the T_c. An account of the contribution of all errors shows that the actual combined relative error in the $\Delta S_M(T)_{5\,T}$ calculated from magnetization data is between ~20% and ~30% above the T_c and is significantly higher below the T_c. Furthermore, the relative error is also dependent on ΔH provided δH is constant, thus reducing the combined error in $\Delta S_M(T)_{\Delta H}$ for smaller differences between H_I and H_F due to the reduction of n in the sums [Eq. (2.4b)], and vice versa. Therefore, the actual errors in the $\Delta S_M(T)_{\Delta H}$ should be analyzed [Eq. (2.4b)] for each experiment, because they depend not only on the relative error in $M(T,H)$, but also on the errors in H and T, and the choice of H_I, H_F, δT, and δH.

III. MAGNETOCALORIC EFFECT AND HEAT-CAPACITY MEASUREMENTS

The heat capacity measured at constant pressure as a function of temperature in constant magnetic fields $C(T)_H$ provides the most complete characterization of solid magnetic materials with respect to their magnetocaloric effect, since the total entropy of a magnetic solid can be calculated from the heat capacity as

$$S(T)_{H_I} = \int_0^T \frac{C(T)_{H_I}}{T} dT + S_{0,H_I} \qquad (3.1a)$$

and

$$S(T)_{H_F} = \int_0^T \frac{C(T)_{H_F}}{T} dT + S_{0,H_F}, \tag{3.1b}$$

where S_{0,H_I} and S_{0,H_F} are *the zero-temperature entropies* (and not the integration constants as is sometimes misrepresented in the literature, e.g., see Foldeaki and co-workers[18,19]). In a condensed system these are the same (i.e., $S_{0,H_I} = S_{0,H_F}$),[20] and therefore, the total entropies $S(T)_{H_I}$ and $S(T)_{H_F}$ can be calculated from the heat-capacity data as

$$S(T_n)_H = 0.5 \left\{ C(T_1)_H + \sum_{i=1}^{n-1} \left[\left(\frac{C(T_i)}{T_i} + \frac{C(T_{i+1})}{T_{i+1}} \right)_H \right. \right.$$

$$\left. \left. \times (T_{i+1} - T_i) \right] \right\}. \tag{3.2}$$

Here, H represents H_I or H_F, and n is the number of heat-capacity data points collected between T_1 and T_n. The term $C(T_1)_H$ accounts for the missing heat-capacity data between the lowest temperature of the experiment T_1 and $T = 0$ K assuming that $C(T=0)_H = 0$. The zero-field entropy is neglected in Eq. (3.2), and because it is the same in different H, this will introduce a small but constant error in the entropy calculated for each magnetic field. If T_1 is close to the absolute zero temperature and $C(T)_{H_I}$ and $C(T)_{H_F}$ were measured starting from the same T_1, the assumption $C(T=0)_H = 0$ will also introduce a small and constant error in both entropy functions. The sign of these two errors (i.e., neglecting the zero-temperature entropy and the approximation that heat capacity at $T=0$ K is zero) will be the same for both $S(T)_{H_I}$ and $S(T)_{H_F}$, which will result in an unknown but constant error δS_0 in both entropy functions with respect to both the temperature and the magnetic field.

Hence, neglecting δS_0, the errors in the total entropy functions calculated using Eq. (3.2) are given as

$$\sigma[S(T_n)_H]$$

$$= 0.5 \left\{ \sigma C(T_1)_H + \sum_{i=1}^{n-1} \left[\left(\frac{\sigma C(T_i)}{T_i} + \frac{\sigma C(T_{i+1})}{T_{i+1}} \right)_H \right. \right.$$

$$\left. \times (T_{i+1} - T_i) \right] \right\} + 0.5 \left\{ \sum_{i=1}^{n-1} \left[\left(\frac{C(T_i)}{T_i^2} \sigma T_i \right. \right. \right.$$

$$\left. \left. \left. + \frac{C(T_{i+1})}{T_{i+1}^2} \sigma T_{i+1} \right)_H \times (T_{i+1} - T_i) \right] \right\}$$

$$+ 0.5 \left\{ \sum_{i=1}^{n-1} \left[\left(\frac{C(T_i)}{T_i} + \frac{C(T_{i+1})}{T_{i+1}} \right)_H \right. \right.$$

$$\left. \left. \times (\sigma T_{i+1} + \sigma T_i) \right] \right\}. \tag{3.3}$$

The errors in temperature for heat-capacity data are much smaller than those for the magnetization data because the temperature sensor is in direct contact with the sample and the typical temperature uniformity and stability is of the order of 0.001–0.003 K with the absolute accuracy better than
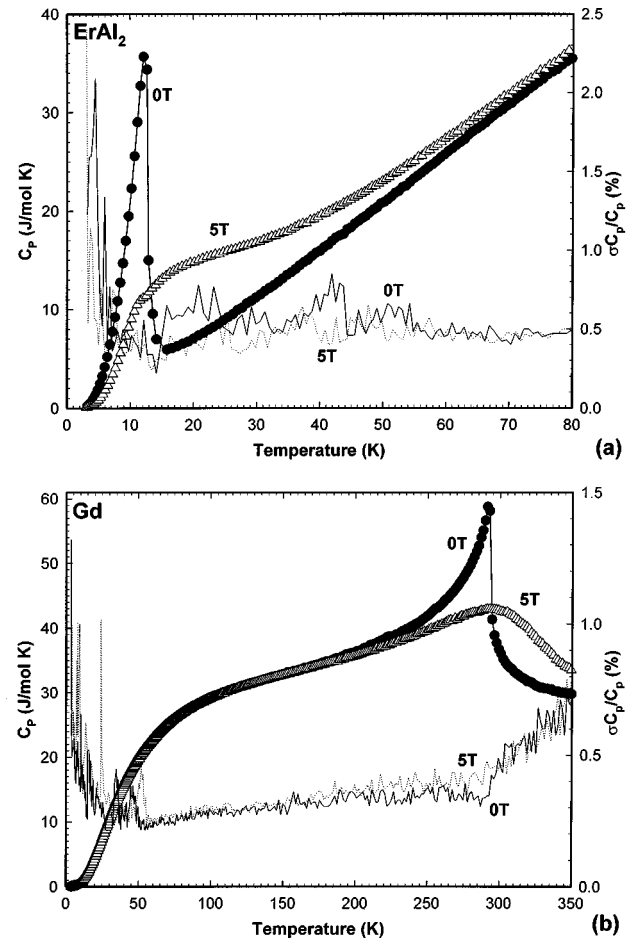

FIG. 5. The heat capacity of ErAl$_2$ (a) and Gd single crystal (b) measured in 0 and 5 T magnetic fields. The magnetic-field vector was parallel to the [0001] direction in the Gd single crystal. The solid and dotted lines without the symbols indicate the relative errors in heat capacity in 0 and 5 T magnetic field (right-hand scale).

0.005 K below ∼100 K and better than 0.05 K between 100 and 350 K.[21] Therefore, it is possible to neglect both the second and third terms in Eq. (3.3) (see below), which leads to an approximate equation

$$\sigma[S(T_n)_H]$$

$$\cong 0.5 \left\{ \sigma C(T_1)_H \right.$$

$$\left. + \sum_{i=1}^{n-1} \left[\left(\frac{\sigma C(T_i)}{T_i} + \frac{\sigma C(T_{i+1})}{T_{i+1}} \right)_H (T_{i+1} - T_i) \right] \right\}. \tag{3.4}$$

Equation (3.4) allows one to calculate the uncertainty in $S(T)_{H_I}$ and $S(T)_{H_F}$ from the known uncertainties in $C(T)_{H_I}$ and $C(T)_{H_F}$. To illustrate the calculation of the MCE and its errors from the heat-capacity data we will use the same magnetocaloric materials as were used above. The heat capacity of the ErAl$_2$ polycrystal and the Gd single crystal together with the corresponding relative errors is shown in Fig. 5. The heat capacity was measured using an adiabatic heat pulse calorimeter with the error in each heat-capacity data point determined individually. Both the calorimeter and evaluation of the heat-capacity errors are described elsewhere.[21] The
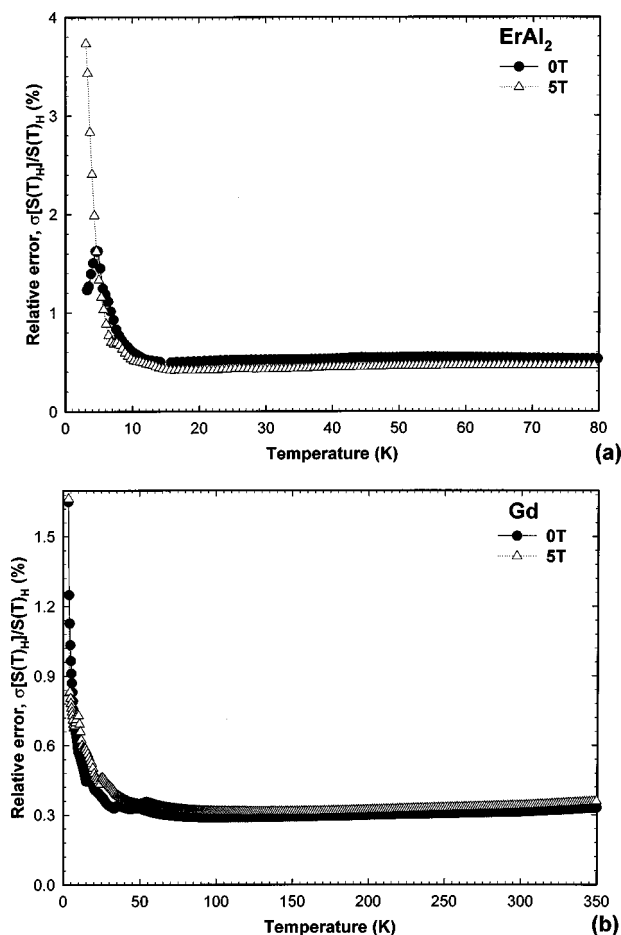
FIG. 6. The relative error of the total entropy in ErAl$_2$ (a) and Gd (b) as a function of temperature in 0 and 5 T magnetic fields.
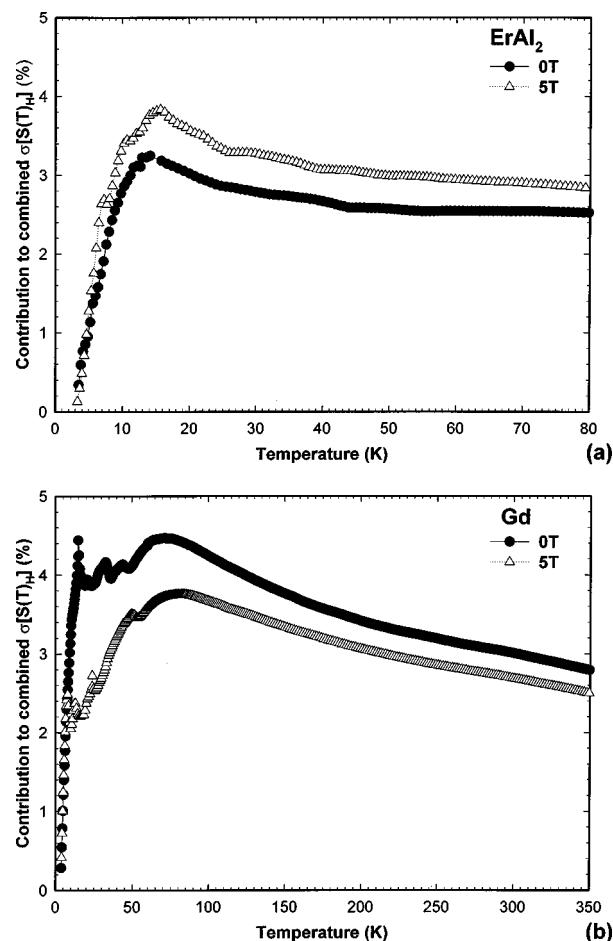

FIG. 7. The contribution of the two last terms in Eq. (3.3) to the combined error of the total entropy in ErAl$_2$ (a) and Gd (b) as a function of temperature in 0 and 5 T magnetic fields.

errors in all sets of experimental data are generally of the order of 0.5% or less except at the lowest temperature and above $\sim$300 K (see Ref. 21 for more details). The total entropies were calculated using Eq. (3.2) and their combined errors were calculated using Eq. (3.3) (which includes the contributions from all three terms). The combined relative error in the total entropy functions is shown in Fig. 6. Generally, it remains below 0.5% except at very low temperatures ($<\sim$10 K), where the absolute value of the entropy is low. The contribution of the two last terms from Eq. (3.3) into the combined error in the total entropy is shown in Fig. 7. Together they account for less than $\sim$4% of the combined error, and therefore, the approximate Eq. (3.4), is quite valid.

Once the total entropy functions $S(T)_{H_I}$ and $S(T)_{H_F}$ are established, the calculation of both $\Delta T_{\text{ad}}(T)_{\Delta H}$ and $\Delta S_M(T)_{\Delta H}$ is straightforward. The $\Delta S_M(T)_{\Delta H}$ is calculated as the isothermal difference [Eq. (3.5)] and the $\Delta T_{\text{ad}}(T)_{\Delta H}$ is calculated as the isentropic difference [Eq. (3.6a)] between the $S(T)_{H_I}$ and $S(T)_{H_F}$ functions

$$\Delta S_M(T)_{\Delta H} = \{[S(T)_{H_F} + \delta S_0] - [S(T)_{H_I} + \delta S_0]\}_T$$

$$= [S(T)_{H_F} - S(T)_{H_I}]_T, \qquad (3.5)$$

$$\Delta T_{\text{ad}}(T)_{\Delta H} = [T(S + \delta S_0)_{H_F} - T(S + \delta S_0)_{H_I}]_S. \qquad (3.6a)$$

Equation (3.5) indicates that the presence of an unknown but constant δS_0 has no effect on the $\Delta S_M(T)_{\Delta H}$ calculated from the heat capacity. Equation (3.6a), however, requires further analysis because δS_0 is unknown and the $T(S + \delta S_0)_H$ functions are different for H_F and H_I. Expanding the $T(S + \delta S_0)_H$ functions on the right-hand side of Eq. (3.6a) using a Taylor series and neglecting all terms except the first derivative, we obtain

$$T(S + \delta S_0)_{H_F} \cong T(S)_{H_F} + \delta S_0 \left(\frac{dT(S)}{dS}\right)_{H_F}$$

$$= T(S)_{H_F} + \delta S_0 \frac{T}{C(T)_{H_F}}, \qquad (3.6b)$$

$$T(S + \delta S_0)_{H_I} \cong T(S)_{H_I} + \delta S_0 \left(\frac{dT(S)}{dS}\right)_{H_I}$$

$$= T(S)_{H_I} + \delta S_0 \frac{T}{C(T)_{H_I}}, \qquad (3.6c)$$

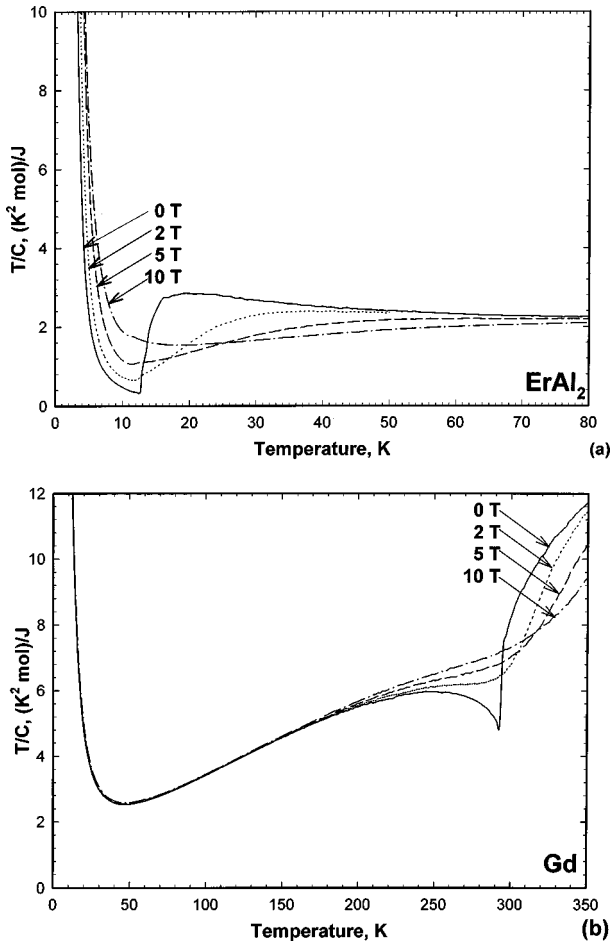because $[dT(S)/dS]_H = [dT/dS(T)]_H = [T/C(T)]_H$. Combining Eq. (3.6a) with Eqs. (3.6b), and (3.6c) we get

FIG. 8. The experimental $T/C(T,H)$ functions of ErAl$_2$ from $\sim$3 to 80 K (a) and Gd from $\sim$12 to 350 K (b) in 0, 2, 5, and 10 T magnetic fields. Note that below $\sim$150 K in Gd the values of $T/C(T, H)$ overlap at the resolution of the plot.

$$\Delta T_{\mathrm{ad}}(T)_{\Delta H} = [T(S)_{H_F} - T(S)_{H_I}]_S$$
$$+ \delta S_0 \left[\frac{T}{C(T)_{H_F}} - \frac{T}{C(T)_{H_I}} \right]_S . \qquad (3.6\text{d})$$

Therefore, in a ferromagnet (see Fig. 8), the effect of the neglected zero-temperature entropy [Eq. (3.2)] may result in a slightly overestimated $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ below the Curie temperature, and it will be slightly underestimated above T_c. As shown in Fig. 8, in both ErAl$_2$ and Gd the difference between the $T/C(T)_H$ values, i.e., the quantity in the square brackets of the second term on the right-hand side of Eq. (3.6d), accounts for the maximum error in $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$, of less than 2 K per each 1000 mJ/mol K (less than 0.002 K per each 1 mJ/mol K) error in δS_0. This error, therefore, can be neglected and Eq. (3.6e) can be used instead of Eq. (3.6a) or (3.6d) to calculate $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ from the heat capacity provided the zero-temperature entropy is small:

$$\Delta T_{\mathrm{ad}}(T)_{\Delta H} \cong [T(S)_{H_F} - T(S)_{H_I}]_S . \qquad (3.6\text{e})$$

We note here that when the $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ decreases, the effect of neglecting δS_0 also decreases, because the difference in

the square brackets in Eq. (3.6d) approaches zero (e.g., see the data for ErAl$_2$ above 50 K and the data for Gd below 200 K, Fig. 8).

Based on Eq. (3.5), the error in $\Delta S_M(T)_{\Delta H}$ due to accumulation of random errors in the total entropy is given[22] as

$$\sigma |\Delta S_M(T)_{\Delta H}| = [\sigma S(T)_{H_I} + \delta S(T)_{H_F}]_T . \qquad (3.7)$$

Here, $\sigma S(T)_{H_I}$ and $\sigma S(T)_{H_F}$ are the errors in the total entropy in initial and final magnetic fields, respectively [Eq. (3.4)]. The error in $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ due to the accumulation of random errors in the total entropy is also easily derived from Eq. (3.6e), as was done earlier,[22]

$$\sigma |\Delta T_{\mathrm{ad}}(T)_{\Delta H}| = \left[\left(\frac{dT(S)_{H_F}}{dS} \right) \sigma S(T)_{H_F} \right.$$
$$\left. + \left(\frac{dT(S)_{H_I}}{dS} \right) \sigma S(T)_{H_I} \right]_S$$
$$= \left[\frac{\sigma S(T)_{H_F}}{(dS(T)_{H_F}/dT)} + \frac{\sigma S(T)_{H_I}}{(dS(T)_{H_I}/dT)} \right]_S$$
$$= \left[\sigma S(T)_{H_F} \frac{T}{C(T)_{H_F}} + \sigma S(T)_{H_I} \frac{T}{C(T)_{H_I}} \right]_S . $$
$$(3.8)$$

The error in adiabatic temperature change is also proportional to $\sigma S(T)_H$, but inversely proportional to the derivatives of the corresponding total entropy functions with respect to temperature, i.e., to the corresponding $T/C(T)_H$ functions. Equation (3.8) indicates that the errors in $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ are reduced when the heat capacity increases rapidly with temperature, for instance, at low temperatures and also near the Curie temperature, provided $\sigma S(T)_H$ are the same. The error in the $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ begins to rise above the T_c due to the intrinsic decrease of the heat capacity (Fig. 5), i.e., the increase of $T/C(T)_H$ (Fig. 8). Figure 9 shows that the magnetic entropy change in ErAl$_2$ and Gd calculated from the magnetization and heat capacity are in excellent agreement with one another. In ErAl$_2$ the errors from the heat capacity [Eq. (3.7)] are much smaller than the errors from magnetization [Eq. (2.4b)], which is expected since at low temperatures the contribution from lattice and electronic entropies to the total entropy is minimal. The $\Delta S_M(T)_{5\,\mathrm{T}}$ in ErAl$_2$ is, therefore, a large difference of the two relatively small values, and the effect of accumulated random errors [Eq. (3.8)] is not present. Even at much higher temperatures, where the $\Delta S_M(T)_{5\,\mathrm{T}}$ in Gd is a much smaller difference of the large total entropies, and therefore, accumulation of random errors could have a deleterious effect, precise heat-capacity data still provide an accuracy similar to that obtained from the magnetization data [Fig. 9(b)]. It should be noted, however, that unlike the magnetization data, the absolute errors from the heat capacity do not decrease for smaller ΔH, and therefore, the relative errors will rise proportionally to the reduction of $|\Delta S_M(T)_{\Delta H}|$. Figure 10 illustrates the $\Delta T_{\mathrm{ad}}(T)_{5\,\mathrm{T}}$ values calculated from the heat capacity for both
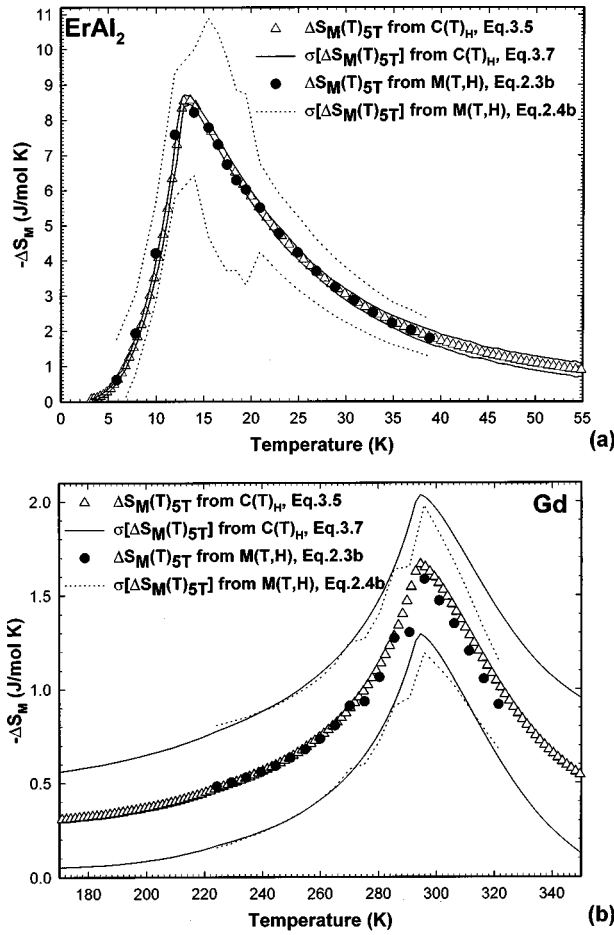
FIG. 9. Comparison of the magnetic entropy change and the corresponding absolute errors in ErAl$_2$ (a) and Gd (b) calculated from the magnetization (Fig. 2) and the heat capacity (Fig. 5) data.

ErAl$_2$ and Gd. The behavior of errors is similar to what was observed when calculating the magnetic entropy change, i.e., they become larger with the increasing temperature, but still allow a reasonable accuracy near 300 K.
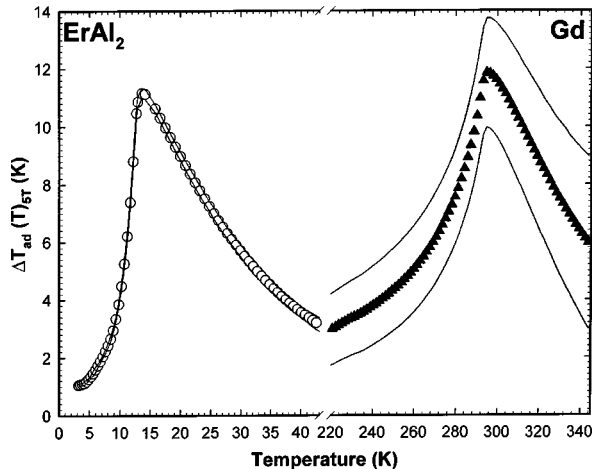

FIG. 10. Adiabatic temperature change in ErAl$_2$ and Gd calculated from the heat-capacity data shown in Fig. 5. The open circles and solid triangles represent $\Delta T_{ad}(T)_{5\,T}$ [Eq. (3.6)]. The solid lines represent the margins of $\sigma[\Delta T_{ad}(T)_{5\,T}]$ [Eq. (3.8)].

An analysis of the errors in $\Delta T_{ad}(T)_{\Delta H}$ calculated from the heat-capacity data was recently mistreated by Foldeaki and co-workers,[18,19] who used a geometrical approach to derive an analogue of the δS_0 term in Eq. (3.6d) and then applied it as Eq. (3.8). They assumed that δS_0 is different in $S(T)_{H_I}$ and $S(T)_{H_F}$ in an attempt to analyze the sign of the "systematic" error in the $\Delta T_{ad}(T)_{\Delta H}$ from the heat capacity. This resulted in mixing together two entirely different effects: (1) a systematic error due to an intrinsic unknown—a small and constant δS_0 in both $S(T)_{H_I}$ and $S(T)_{H_F}$, which allows the use of Eq. (3.6e) instead of Eq. (3.6d), and (2) a random absolute error due to a random but different $\sigma S(T)_{H_I}$ and $\sigma S(T)_{H_F}$. Therefore, the authors of Refs. 18 and 19 make the wrong conclusion that neglecting the "integration constants" (which is indeed the same unknown δS_0, see above) always leads to a negative contribution in Eq. (3.6d) and that the $\Delta T_{ad}(T)_{\Delta H}$ calculated using Eq. (3.6e) will be always systematically underestimated. First, as we showed above [Eq. (3.6d), and the discussion following this equation], the effect of small unknown δS_0 can be either positive or negative dependent on the sign of the difference $[T/C(T)_{H_F} - T/C(T)_{H_I}]$. We note again that *since this effect is small it can be neglected* and the use of Eq. (3.6e) is fully justified. Second, if for some reason *other than neglecting the zero-temperature entropy*, the $S(T)_{H_I}$ and $S(T)_{H_F}$ functions have different systematic errors, δS_{H_I} and δS_{H_F}, respectively, then Eq. (3.6d) becomes

$$\Delta T_{ad}(T)_{\Delta H} = [T(S)_{H_F} - T(S)_{H_I}]_S$$
$$+ \left[\delta S_{H_F} \frac{T}{C(T)_{H_F}} - \delta S_{H_I} \frac{T}{C(T)_{H_I}} \right]_S, \quad (3.9)$$

indicating that the sign and the magnitude of the systematic error becomes critically dependent on the relation between δS_{H_I} and δS_{H_F} and Eq. (3.6e) is no longer valid. To illustrate this, consider the following example. Case 1: both entropy functions $S(T)_{H=0\,T}$ and $S(T)_{H=5\,T}$ in Gd are calculated using Eq. (3.2) with the zero-temperature entropy neglected, i.e., $\delta S_0 = 0$. Case 2: rather large but still constant zero-temperature entropy $\delta S_1 = 50C(T_1)_{H=0\,T}$ [Eq. (3.2)], is added to both $S(T)_{H=0\,T}$ and $S(T)_{H=5\,T}$. Case 3: half of the zero-temperature entropy as in case 2 is added to $S(T)_{H=0\,T}$ but subtracted from $S(T)_{H=5\,T}$. Case 4: opposite to case 3, i.e., half of the zero-temperature entropy as in case 2 is subtracted from $S(T)_{H=0\,T}$ but added to $S(T)_{H=5\,T}$. The $\Delta T_{ad}(T)_{\Delta H=5\,T}$ was then calculated using Eq. (3.6e) and the results are shown in Fig. 11. It is easy to see that as long as both $S(T)_{H_I}$ and $S(T)_{H_F}$ are affected by the *same systematic error*, the value and the sign of this error *has no effect* on the MCE calculated using Eq. (3.6e) [case 1 (open circles) and case 2 (solid line) in Fig. 11]. As we also show in Fig. 11 (filled triangles), the effect of *different systematic errors* on the MCE can be severe. We note that the resulting MCE can be *either underestimated or overestimated dependent on the sign and the magnitude of systematic errors in the two entropy functions*, and not always underestimated as claimed in Refs. 18 and 19. Unlike its value, the position of the
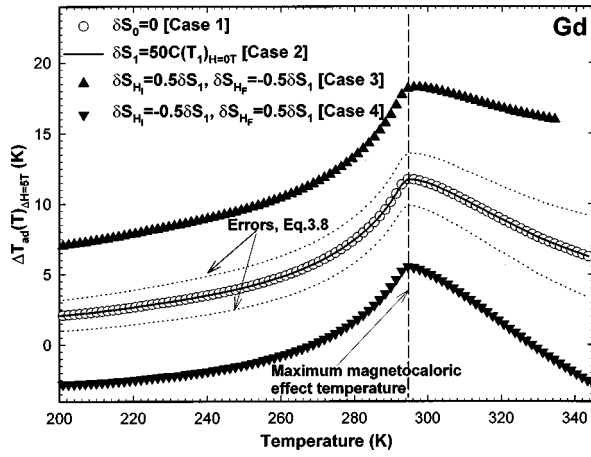
FIG. 11. The $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ in single-crystal Gd for a magnetic-field change from 0 to 5 T calculated using Eq. (3.6e) illustrating the effect of systematic errors on the resulting $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$. The dotted lines show $\sigma\Delta T(T)_{\Delta H}$ calculated using Eq. (3.8).

$\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ maximum remains insensitive to the presence of small systematic errors in the total entropy (Fig. 11).

IV. MAGNETOCALORIC EFFECT AND THE COMBINED MAGNETIZATION AND HEAT-CAPACITY MEASUREMENTS

By combining Eqs. (2.1) and (3.1) with the $TdS = T(\partial S/\partial T)_H dT + T(\partial S/\partial H)_T dH$, it easy to show[15] that the infinitesimal adiabatic temperature rise for the reversible adiabatic–isobaric process is

$$dT(T,H) = -\left(\frac{T}{C(T,H)}\right)_H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH, \qquad (4.1)$$

where $C(T,H)$ is the temperature and magnetic-field-dependent heat capacity at constant magnetic field. The $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ is obtained by integrating Eq. (4.1) as

$$\Delta T_{\mathrm{ad}}(T)_{\Delta H} = \int_{H_I}^{H_F} dT(T,H)$$

$$= -\int_{H_I}^{H_F} \left(\frac{T}{C(T,H)}\right)_H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH. \qquad (4.2)$$

Numerical integration of Eq. (4.2) is impractical because the $C(T,H)$ measurements are slower than the $M(T,H)$ measurements and it is unrealistic to collect the former with H varying at the resolution typical for the latter. Furthermore, if the $C(T)_H$ data are available, Eq. (4.2) is not necessary because the heat capacity alone yields both $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ and $\Delta S_M(T)_{\Delta H}$ (see the previous section). Equation (4.2), therefore, is unsuitable for the calculation of $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ from combined $M(T,H)$ and $C(T,H)$ at constant magnetic field without simplification. Unfortunately, its simplification requires certain assumptions and the improper use of the simplified equation has led to some controversy in recent literature.

One of the simplest approaches, which was proposed by Romanov and Silin,[23] is to use Eq. (4.2), the available zero-magnetic-field heat capacity (or the heat capacity at any given constant magnetic field) and the magnetization data to calculate $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$. They assumed that close to T_c it is possible to neglect the dependence of C on both T and H, which allows one to exclude the term $T/C(T,H)$ from the integration. Thus, Eq. (4.2) combined with Eq. (2.2) is easily transformed into

$$\Delta T_{\mathrm{ad}}(T)_{\Delta H} = -\frac{T}{C_{H,T}} \int_{H_I}^{H_F} \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH$$

$$= -\frac{T}{C_{H,T}} \Delta S_M(T)_{\Delta H}, \qquad (4.3)$$

where $T/C(T,H)$ is treated as a constant. But, it is clearly evident in Figs. 5 and 8 that $T/C(T,H)$ is anything but constant, especially at low temperatures and near the magnetic phase transition, which makes both the assumption[23] and Eq. (4.3) inapplicable, except at temperatures far from $T=0$ K and far from T_c where ΔT_{ad} is essentially zero.

Another erroneous approach is that proposed by Foldeaki and co-workers.[17–19] They claim that the following equation [numbered as Eq. (17) in Ref. 17 and Eq. (9) in both Refs. 18 and 19]:

$$\Delta T = -\frac{T}{C(T)_H} \Delta S_M(T)_{\Delta H}, \qquad (4.4)$$

is a ''more accurate approximation'' compared to Eq. (4.3) because it ''only requires the assumption that the variation of $T/C(H,T)$ is slow compared with the variation of magnetization with temperature.'' The function $C(T)_H$ in Eq. (4.4) indicates that the heat capacity is taken at constant pressure and at the high magnetic field H_F. First, it is rare (if ever) that the non-zero-magnetic-field heat capacity is available without the zero-magnetic-field heat capacity [which, if they are both known, again allows one to calculate both $\Delta T_{\mathrm{ad}}(T)_{\Delta H}$ and $\Delta S_M(T)_{\Delta H}$ using just the heat capacity, see the previous section]. Second, it is easy to prove that Eqs. (4.3) and (4.4) are, in fact, equivalent equations and both are only *valid* if $T/C(T)_{H_I} = T/C(T)_{H_F} = $ const. This has been done below. Again, we note that generally this assumption is incorrect, except over a limited temperature range where these functions vary only slightly with magnetic field and temperature (Fig. 8).

By rearranging Eq. (2.1)

$$dS_M(T,H) = \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH, \qquad (4.5)$$

and substituting it into Eq. (4.2), we obtain

$$\Delta T_{\mathrm{ad}}(T)_{\Delta H} = \int_{H_I}^{H_F} dT(T,H)$$

$$= -\int_{H_I}^{H_F} \left(\frac{T}{C(T,H)}\right)_H dS_M(T,H). \qquad (4.6)$$

Using the Foldeaki and co-workers[17–19] approach and integrating the right-hand side of Eq. (4.6) by parts, we obtain

$$\int_{H_I}^{H_F} \left(\frac{T}{C(T,H)} \right)_H d[S_M(T,H)]$$

$$= \left[\frac{T}{C(T,H)} S_M(T,H) \right]_P \Bigg|_{H_I}^{H_F}$$

$$- \int_{H_I}^{H_F} [S_M(T,H)] \frac{d}{dH} \left[\frac{T}{C(T,H)} \right]. \tag{4.7}$$

Further, following Foldeaki and co-workers[17–19] we neglect the second term on the right-hand side of Eq. (4.7) by assuming that $T/C(T,H)$ is weakly magnetic-field dependent, and combining Eqs. (4.6) and (4.7) we obtain

$$\Delta T_{ad}(T)_{\Delta H} \cong - \left[\frac{T}{C(T)_{H_F}} S_M(T)_{H_F} - \frac{T}{C(T)_{H_I}} S_M(T)_{H_I} \right]. \tag{4.8}$$

Equation (4.8), however, is of no use because the functions $S_M(T)_{H_I}$ and $S_M(T)_{H_F}$ are generally unknown. Both Eqs. (4.3) and (4.4) are easily obtained from Eq. (4.8) *only after making a second assumption* that $C(T)_{H_F} = C(T)_{H_I} = C(T)_H$, which is acknowledged by Romanov and Silin,[23] but ignored by Foldeaki and co-workers,[17–19]

$$\Delta T(T)_{\Delta H} \cong - \frac{T}{C(T)_H} [S_M(T)_{H_F} - S_M(T)_{H_I}]$$

$$= - \frac{T}{C(T)_{H_F}} \Delta S_M(T)_{\Delta H}$$

$$= - \frac{T}{C(T)_{H_I}} \Delta S_M(T)_{\Delta H}. \tag{4.9}$$

Hence, integrating by parts, as suggested by Refs. 17–19, to overcome the inconvenience of Eq. (4.2) is useless because at the end it still requires the same assumption [that $C(T,H)$ is magnetic-field and temperature independent], which allows the immediate exclusion of $T/C(T,H)$ from integration,[23] leading directly to Eqs. (4.3) or (4.4).

The total heat capacity of a magnetic solid, which is the sum of the lattice $[C_{lat}(T)]$, electronic $[C_{el}(T)]$, and magnetic $[C_{mag}(T,H)]$ heat capacities, is dependent on both the magnetic field and the temperature. From Eq. (4.1) it is obvious that when the magnetic field changes adiabatically by dH the temperature of the magnetic system will change by dT and its heat capacity will change by $dC(T,H)$ because *it remains a function of temperature* even if $C(T)_{H_F} = C(T)_{H_I}$. Thus, Eq. (4.9) may have a limited applicability only at high temperatures and when there is a weak magnetic-field dependence of the heat capacity. It becomes inapplicable when $C_{lat}(T)$ varies sharply with T (i.e., at low temperature), and when $C_{mag}(T,H)$ changes abruptly with T and H (i.e., near a magnetic phase transition). Hence, before Eq. (4.9) can be used, the behavior of the $T/C(T,H)$ must be carefully analyzed. The latter requires knowledge of the $C(T)_H$ in several fields, which allows the use of Eqs. (3.1)–(3.8) and makes Eq. (4.9) worthless.

Referring to Fig. 8 it is easy to see that using $C(T,H = 0$ T) in Eq. (4.9) may never yield a reasonable approxima-

tion for $\Delta T_{ad}(T)_{\Delta H}$ near its maximum value since $T/C(T, H = 0$ T) changes sharply near T_c independent of the absolute temperature. Equation (4.9) using $C(T, H = H_F)$ is also inapplicable at low T [e.g., ErAl$_2$ where $T/C(T, H \neq 0$ T) varies sharply with T] and/or at low H and high T [e.g., Gd where $T/C(T, H = 2$ T) remains strongly temperature dependent]. However, it may yield a reasonable approximation for $\Delta T_{ad}(T)_{\Delta H}$ as both the temperature and ΔH increase because the effect of H and T on $T/C(T, H)$ becomes less pronounced. For instance, $T/C(T, H)$ in ErAl$_2$ varies between 5 and 25 K by as much as ~700% for $H = 0$ T, by ~400% for $H = 2$ T, and by ~350% for $H = 5$ and 10 T (see Fig. 8). At $T = 12$ K the magnetic field increases $T/C(T, H)$ in ErAl$_2$ by ~90% between 0 and 2 T, by ~50% between 2 and 5 T, and by ~60% between 5 and 10 T. In Gd, $T/C(T, H)$ between 270 and 310 K varies: by about 90% for $H = 0$ T, by ~30% for $H = 2$ T, by ~15% for $H = 5$ T, and by ~10% for $H = 10$ T. Also, the effect of the magnetic field is less pronounced: at $T = $ ~291 K the $T/C(T, H)$ in Gd is increased by ~30% between 0 and 2 T, by ~7% between 2 and 5 T, and by ~4% between 5 and 10 T. Thus, for magnetic fields exceeding 5 T the use of Eq. (4.9) together with $C(T, H = H_F)$ could be justified for Gd. In some antiferromagnetic systems, where the heat-capacity peak remains sharp until the antiferromagnetism is destroyed when the magnetic field exceeds a certain critical value, the use of Eq. (4.9) is inapplicable for any magnetic field below the critical.

Nevertheless, it is possible to use the combined heat capacity (measured at constant magnetic field H_I or H_F) and the magnetization data to correctly calculate the adiabatic temperature change in any range of temperatures. The experimental total entropy function of the magnetic system, $S(T)_{H_I}$ or $S(T)_{H_F}$, can be calculated from the heat capacity at H_I or H_F using Eq. (3.2). The magnetization measurements then are used to calculate the experimental $\Delta S_M(T)_{\Delta H}$ function. Now the missing $S(T)_{H_F}$ [or $S(T)_{H_I}$] can be easily calculated from Eq. (3.5). Evaluation of $\Delta T_{ad}(T)_{\Delta H}$ using the combined constant magnetic-field heat capacity and magnetic-field-dependent magnetization measurements, therefore, becomes trivial (see the previous section). We note that if the combined heat-capacity and magnetization data are used in this manner, the accumulation of errors in the entropy function calculated from heat capacity can be neglected, and the errors in the $\Delta T_{ad}(T)_{\Delta H}$ would be determined by the errors in the $\Delta S_M(T)_{\Delta H}$. Figure 12 illustrates the MCE in ErAl$_2$, where it can be seen that the $\Delta T_{ad}(T)_{\Delta H = 5}$ T calculated from the heat-capacity data using Eqs. (3.2) and (3.6e), or from the combined heat-capacity and magnetization data using Eqs. (2.3b), (3.2), (3.5), and (3.6e), are essentially the same and correct [see Fig. 9(a)]. However, the use of Eq. (4.9) results in the wrong MCE for both cases when the $H = 0$ or 5 T heat capacity was used in combination with the magnetization data.

V. CONCLUSION

The indirect calculation of the magnetocaloric effect from magnetization, heat capacity, or the combined magnetization and heat-capacity data can be effectively used to
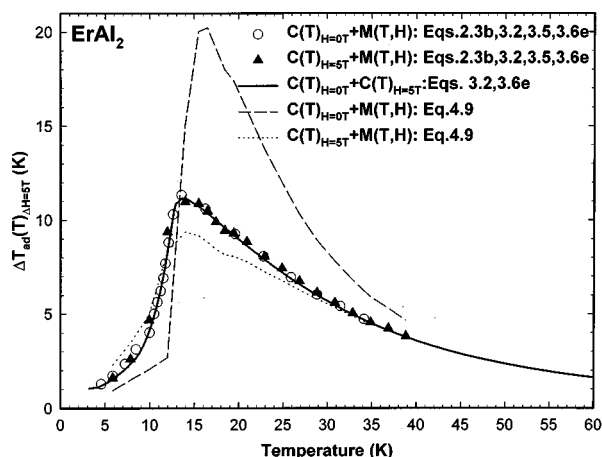
FIG. 12. The value of $\Delta T_{\text{ad}}(T)_{\Delta H=5\ T}$ for ErAl$_2$ correctly calculated using the combined heat-capacity and magnetization data (open circles and solid triangles) compared with that calculated only from the heat capacity (thick solid line), and the erroneous results obtained using Eq. (4.9).

characterize magnetic refrigerant materials with respect to their magnetocaloric properties. Magnetization data allow calculation of the $\Delta S_M(T)_{\Delta H}$ as a function of the temperature and the magnetic-field change. Heat capacity measured at constant magnetic fields provides both $\Delta S_M(T)_{\Delta H}$ and $\Delta T_{\text{ad}}(T)_{\Delta H}$. In addition to accurate magnetocaloric properties as a function of temperature for a given magnetic-field change ΔH, both types of experimental data allow an accurate estimate of the experimental uncertainties in the calculated MCE based on the known experimental uncertainties of the measured physical properties. A numerical analysis of the derived equation for the experimental errors in the calculated MCE shows that they should be used for both magnetization and heat-capacity data to properly estimate the reliability of the calculated MCE. An analysis of recent literature shows that attempts to simplify the basic thermodynamic relation for the infinitesimal adiabatic temperature change to allow calculation of the $\Delta T_{\text{ad}}(T)_{\Delta H}$ from the heat capacity at constant field and $\Delta S_M(T)_{\Delta H}$ calculated from the magnetization data fail, except in the unlikely case when $C(H,T)$ is temperature and magnetic-field independent. While this assumption is approximately valid at high temperatures and high magnetic fields, it is inapplicable at: (1) low temperatures where the lattice heat capacity changes rapidly, and (2) near magnetic phase transitions where the largest magnetocaloric effect is usually observed and the mag-

netic heat capacity changes sharply with both T and H. The combined heat capacity at constant field and $\Delta S_M(T)_{\Delta H}$ from the magnetization data can be used to accurately calculate $\Delta T_{\text{ad}}(T)_{\Delta H}$ if the heat capacity is used to calculate the total entropy at constant field (H_F or H_I) and is combined with $\Delta S_M(T)_{\Delta H}$ to calculate the total entropy for the missing magnetic field (H_I or H_F, respectively).

ACKNOWLEDGMENTS

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