

# Comparison of magnetocaloric properties from magnetic and thermal measurements

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The isothermal change of the magnetic entropy of a magnetically ordered material upon application of external magnetic field can be calculated from the temperature and field dependence of the magnetization or of the specific heat. The adiabatic temperature change, i.e., the magnetocaloric effect (MCE) can be measured directly or can be calculated via different methods using the field-dependent specific heat values, or a combination of data obtained via magnetization and thermal measurements. In the present study, magnetic and thermal measurements were carried out on  $\text{Gd}_{75}\text{Y}_{25}$  ( $T_C = 232$  K) and  $\text{Gd}_{48}\text{Y}_{52}$  ( $T_C = 161$  K) samples, for applied fields ranging between 0 and 7 T. From both datasets, the magnetic entropy change and MCE values were calculated and compared, in order to assess the mutual reliability of the methods applied. The magnetically or thermally deduced specific heat discontinuities show a reasonable agreement within experimental error. Similar comparison of the calculated magnetic entropy changes reveals that the measured transition temperature and the shape of the curve do not depend on the method selected. It is demonstrated that the choice of an integration constant during entropy calculation has a significant impact on the adiabatic temperature change deduced from the field and temperature dependence of the entropies. For the MCE, a better approximation can be obtained using the magnetically acquired magnetic entropy change and the field-dependent specific heat. The results prove that magnetic measurements carried out in high enough magnetic fields provide reliable information on the isothermal magnetic entropy change and, when combined with field-dependent specific heat measurements, on the magnetocaloric effect as well. © 1997 American Institute of Physics. [S0021-8979(97)01313-3]

## I. INTRODUCTION

The magnetocaloric effect (MCE), which is the isothermal change of the entropy or the adiabatic change of the temperature upon the application of magnetic field<sup>1,2</sup> is exploited by several cryogenic applications. The MCE of a paramagnetic salt or of nuclear spins in metals is used for magnetic refrigeration below 4 K or 5 mK, respectively. Other applications, e.g., the magnetic liquefaction of gases in the 4–300 K temperature range require large MCE over a broad range of temperatures. For this purpose, materials with strong magnetic ordering (e.g., ferromagnets) have to be used. As the MCE of ordered magnetic materials is significant only in a relatively narrow temperature range near the ordering temperature, several materials with different transition temperatures are needed to cover broad temperature ranges. Measurements of the field-dependent specific heat,

which can be used to calculate the isothermal entropy change or the adiabatic temperature change, can be time consuming and costly on a large number of samples. Therefore, it would be advantageous if the prescreening and at least part of the characterization could be realized via magnetic methods.

The problem with this approach is that broad temperature range data on the mutual reliability of the two methods are not available in the literature. The only existing data were taken well below 100 K,<sup>3,4</sup> i.e., on samples with low transition temperatures ( $T_C \ll 100$  K), where evaluation of the results does not require long-range integration over the temperature.

In the present study, we investigate samples with transition temperatures  $T_C$  above 100 K, and compare the values of the specific heat discontinuity  $\Delta C_p$ , magnetic entropy change  $\Delta S_M$ , and adiabatic temperature change  $\Delta T$  obtained via different methods. On this basis, we point out problems with numerical processing and their effect on the final result.

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## II. EXPERIMENTAL METHODS

### A. Sample processing

The alloys of gadolinium and yttrium were prepared via conventional metallurgical processing, described in detail elsewhere.<sup>5</sup> Samples of about 10 mg for superconducting quantum interference device (SQUID) magnetometry were cut using a precision diamond saw. Calorimeter samples weighted about 1 g and were diamond polished on one surface.

### B. Materials testing

The homogeneity and correct composition of the samples were tested using conventional metallography followed by scanning electron microscopy with an energy-dispersive composition analyzer. No second phases or significant inhomogeneities were found. The standardless composition analysis qualitatively confirmed the composition and revealed only  $\pm 1.5\%$  deviations as a function of beam location. On the basis of the low loss during melting, the homogeneity of the composition, and the qualitative agreement found by the standardless analysis, the nominal and actual compositions can be considered equal.

### C. Magnetic measurements

The magnetic measurements were carried out in a 7 T quantum design SQUID magnetometer. The susceptibility curves at 0.0025 and 1 T were first measured over the total temperature range. The comparison of the low- and high-field susceptibility curves indicated the nature of the magnetic order present. The low-field susceptibility curve was used to identify the transition region in which a set of about 20 isothermal magnetization curves  $M(H)_{T=\text{const}}$  was measured. The temperature steps were 2.5 K apart closer to the transition and 5 K further away. These magnetization curves were used to calculate the specific heat discontinuity and the magnetic entropy change.

### D. Thermal measurements

The specific heat capacity  $C_p(T)$  up to 320 K was measured in an improved version of a vacuum calorimeter as described in Ref. 6. The quasiadiabatic step heating method (Nerst method) was used. The contribution of the sapphire sample holder, of the Pt100 thermometer, and of a minute amount of grease, which was used to attach the sample, was measured in a separate run and subtracted. The thermodynamic conditions of the  $C_p(T)$  measurements were quasiadiabatic (external  $\delta Q=0$ ), and the measurements were performed at constant fields of 0 and 7 T. The shift  $\Delta T(\Delta R)$  of the temperature calibration of the Pt100 thermometer in the magnetic field of 7 T was small and negligible above about 100 K. A larger relative temperature shift  $\Delta T$  is visible only below about 100 K, becoming more severe with decreasing temperature, reaching the value of  $\Delta T/T \approx 0.4\%$  at liquid-nitrogen temperature (77 K).

## III. THEORETICAL BACKGROUND AND NUMERICAL METHODS

### A. Transition temperature and specific heat anomaly from magnetic measurements

The theory for the second-order phase transitions<sup>7,8</sup> predicts the following relation between the high-field magnetization  $M$  (“approach to saturation”) and the external magnetic-field  $H$  near the transition temperature:

$$\alpha + \beta M^2 = H/M. \quad (1)$$

Consequently, when  $H/M$  is plotted as a function of  $M^2$  (Belov–Goryega plot<sup>8,9</sup>), the relationship is linear in the region above the technical saturation,<sup>10</sup> i.e., where the material is one domain and the rotation of spins toward the field direction is the main mechanism of increasing magnetization (“true” magnetization or paraprocess<sup>8</sup>). Technically, the Belov–Goryega plot<sup>8,9</sup> is equal to the Arrott plot.<sup>11</sup> The calculations leading to the Arrott plot, however, are based on less general assumptions, and allow only for the determination of the Curie point, without deducing the specific heat anomaly. Equation (1) was fitted to the experimental data by the least-squares method. The resulting  $\alpha$  and  $\beta$  parameters were used to calculate the thermodynamic Curie point  $T_C$  and the specific heat anomaly at  $T_C$ . The Curie point is obtained by a linear fit to the  $\alpha = \alpha'_C(T - T_C)$  equation, where  $T_C$  equals the thermodynamic Curie point and  $\alpha'_C$  is a material’s constant. The specific heat anomaly equals  $\Delta C_p = (\alpha'_C)^2 T_C / 2\beta_C$ , where  $\beta_C$  is the value of  $\beta$  at the thermodynamic Curie point  $T_C$ . Details were given elsewhere.<sup>5</sup> With the usual SQUID precision, i.e., 0.1 K in temperature and 0.1% in magnetization, the above calculation gives the Curie point with an error of about  $\pm 1\%$ , while the error estimate for the specific heat discontinuity is about  $\pm 6\%$ .

### B. Magnetic entropy change from magnetic measurements

From the magnetization data, the magnetic entropy change for isothermal magnetization can be calculated as well. Due to the slow increase of the magnetic field in the superconducting magnet, the condition can be considered as isothermal rather than adiabatic. The entropy change associated with the change of the magnetization is given as<sup>12</sup>

$$\Delta S_M = \int_0^H \left[ \frac{\partial M}{\partial T} \right]_H dH. \quad (2)$$

### C. Magnetic entropy change from thermal measurements

The entropy of a material at temperature  $T$  is defined as<sup>12</sup>

$$S_0(T) = \int_0^T \frac{C_{p,0}}{T'} dT' + S_0, \quad (3)$$

where  $C_{p,0}$  is the specific heat at constant pressure  $p$  in zero field, and the value of the constant is chosen as  $S_0 = 0$ , in

order to give zero entropy for  $T=0$ . If the applied field is not zero, the field-dependent specific heat has to be introduced into the above integral.

$$S_H(T) = \int_0^T \frac{C_{p,H}}{T'} dT' + S_{0,H}, \quad (4)$$

where  $C_{p,H}$  is the specific heat measured with a field  $H$  applied, and  $S_{0,H}=0$  as above. We note here that the assumption of a zero integration constant is valid only if both measurement and integration took place between 0 K reference temperature and the temperature in question. If the reference temperature is not zero, the integration constant will be different, and will depend on the reference temperature  $T_{\text{ref}}$ . The magnetic entropy change is the difference of the two entropies above,

$$|\Delta S_M(T)| = S_0(T) - S_H(T) = \int_0^T \frac{C_{p,0} - C_{p,H}}{T'} dT' + \Delta S_0. \quad (5)$$

We note, again, that  $\Delta S_0=0$  only if *both* measurements were started at  $T=0$ . If not, there will be a starting temperature *and* field-dependent constant present.

## D. Adiabatic temperature change, “thermal only,” and combined methods

### 1. “Thermal only” method

This method takes advantage of the definition of the adiabatic (external  $\Delta Q=0$ ) temperature change, i.e., temperature changing with changes in the applied field, while the entropy is kept constant ( $dS=0$ ). In this way, the adiabatic temperature change equals the horizontal distance between the entropy curves  $[\Delta T(S)]$ , which can be determined for a series of constant entropy values and transformed into a temperature-dependent curve. We point out, again, that correct results can be expected only if the  $S(T)$  entropy curves are correct, not just qualitatively, but including the values of the integration constants  $S_0$  and  $S_{0,H}$  as well. Neglecting the constants will shift the two curves in a different way, resulting in incorrect  $\Delta T$  readings.

### 2. Combined methods

The infinitesimal adiabatic temperature change (magnetoaloric effect) is given by the following equation:<sup>12</sup>

$$dT = - \frac{\mu_0 TV}{C_{p,H}} \left( \frac{\partial M}{\partial T} \right)_{p,H} dH, \quad (6)$$

where  $\mu_0$  equals the permittivity of the free space and  $V$  is the molar volume. The total magnetoaloric effect is given by the integral

$$\Delta T = \int_0^{H_0} \frac{\mu_0 TV}{C_{p,H}} \left( \frac{\partial M}{\partial T} \right)_{p,H} dH. \quad (7)$$

If the field and temperature dependence of the specific heat are known, the numerical calculation can be carried out. Using the rule of integration by parts, the integral on the right-hand side can be rewritten

$$\begin{aligned} & \int_0^{H_0} \frac{\mu_0 TV}{C_{p,H}} \left( \frac{\partial M}{\partial T} \right)_{p,H} dH \\ &= \left[ \frac{\mu_0 TV}{C_{p,H}} \int_0^H \left( \frac{\partial M}{\partial T} \right)_{p,H} dH' \right]_0^{H_0} \\ & \quad - \int_0^{H_0} \left\{ \mu_0 V \frac{d}{dH} \left( \frac{T}{C_{p,H}} \right) \int_0^H \left( \frac{\partial M}{\partial T} \right)_{p,H''} dH'' \right\} dH. \quad (8) \end{aligned}$$

If we assume that  $T/C_{p,H}$  varies much slower with  $H$  than  $(\partial M/\partial T)_H$ , which is a good approximation in the transition range, the second integral can be neglected, and the adiabatic temperature change can be written as

$$\Delta T = \frac{T}{C_{p,H}} \Delta S_M(H). \quad (9)$$

Both the magnetic entropy change and the specific heat have to be introduced at the same field and temperature value. For  $\Delta S_M$ , we can introduce the value calculated from thermal or magnetic measurements, as described in Secs. III B and III C, respectively. As  $C_p(H) - C_p(0)$  can be estimated from magnetic data, too (it is actually the  $T$  derivative of  $\Delta S_M$ ), this calculation can be carried out even if only the zero-field specific heat is known.

## IV. EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of the specific heat for sample Gd<sub>75</sub>Y<sub>25</sub> [Fig. 1(a)] and Gd<sub>48</sub>Y<sub>52</sub> [Fig. 1(b)], in zero or 7 T applied field. In the case of second-order phase transitions, the zero-field specific heat displays a sharp discontinuity. The temperature corresponding to the maximum of this  $\lambda$ -shaped anomaly is the transition temperature. The error in  $T_C$ , as determined from the graph, equals about  $\pm 1$  K. Graphically, the specific heat discontinuity  $\Delta C_p$  can be obtained via linear extrapolation, by calculating the difference between the peak and the “flattened” section above the transition. This method gives a lower limit for  $\Delta C_p$  due to the expected curvature of the lattice contribution to the specific heat. To obtain the upper limit, the temperature dependence of the lattice and electronic contributions to the specific heat is calculated according to the Debye theory (see the dashed curves in Fig. 1) and subtracted from the experimental curves. Reasonable values for the Debye temperature  $\Theta_D$  and electronic specific heat  $\gamma$  for Gd and Y were taken from Ref. 13 and averaged according to the composition of the samples.

On this basis, graphical evaluation of the curves allows us to determine the following transition temperatures, as well as lower and upper limits for specific heat discontinuities, which are summarized in Table I.

Figures 2(a) and 2(b) show the temperature dependence of the 0.0025 and 1 T susceptibility for both alloys. Gd<sub>75</sub>Y<sub>25</sub> [Fig. 2(a)] behaves as a simple ferromagnet, with no obvious low-temperature transition. Gd<sub>48</sub>Y<sub>52</sub> [Fig. 2(b)], on the contrary, displays susceptibility curves characteristic for noncollinear magnetic order, clearly showing a low-temperature transition as well, as predicted by the phase diagram.<sup>14</sup>

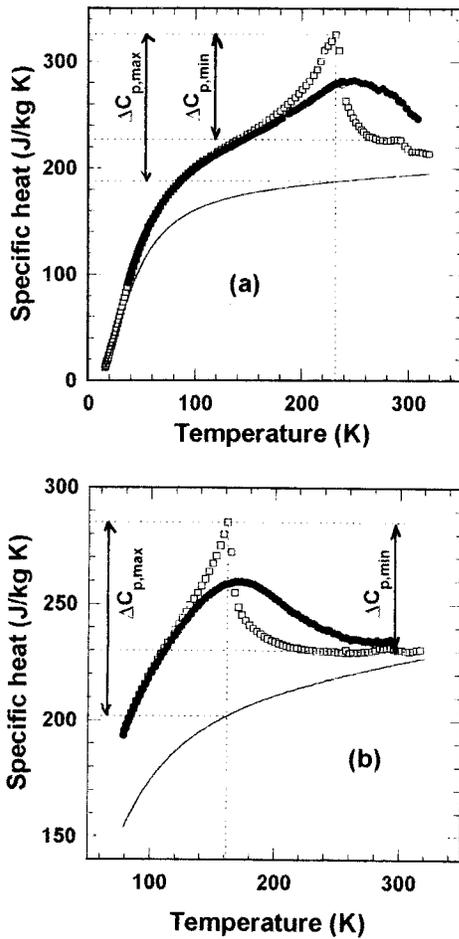


FIG. 1. Specific heat as a function of temperature, for sample Gd<sub>75</sub>Y<sub>25</sub> (a) or Gd<sub>48</sub>Y<sub>52</sub> (b), in zero (□) or 7 T (●) applied field. Solid lines represent the theoretically calculated lattice+electron contribution. Arrows indicate the maximum and minimum values of the specific heat discontinuity.

Figures 3(a) and 3(b) show the transformed magnetization curves (Belov–Goryega plots<sup>8,9</sup>). Gd<sub>75</sub>Y<sub>25</sub> [Fig. 3(a)] displays simple ferromagnetic behavior, while the low-temperature curves of sample Gd<sub>48</sub>Y<sub>52</sub> [Fig. 3(b)] are consistent with a noncollinear magnetic structure.

The thermomagnetic parameters obtained from the transformed curves are summarized in Table II. The numbers display the strengths and limitations of the method. It is a general feature of the processing that the resulting  $T_C$  and  $\Delta C_p$  increase with increasing applied field. The behavior can be attributed to the approximations used in series expansion,<sup>15</sup> i.e., to the neglected higher-order terms in Eq.

TABLE I. Transition temperature and specific heat discontinuity, as determined by thermal methods, as well as parameters used to calculate  $\Delta C_p^{\max}$ .

Alloy	Transition temperature $T_C$ (K)	Specific heat discontinuity $\Delta C_p$ (J/kg K)		Debye temperature $\Theta_D$ (K)	$\gamma$ (mJ/mol K <sup>2</sup> )
		min	max		
Gd <sub>75</sub> Y <sub>25</sub>	232	100	138	170	8
Gd <sub>48</sub> Y <sub>52</sub>	161	55	83	210	8

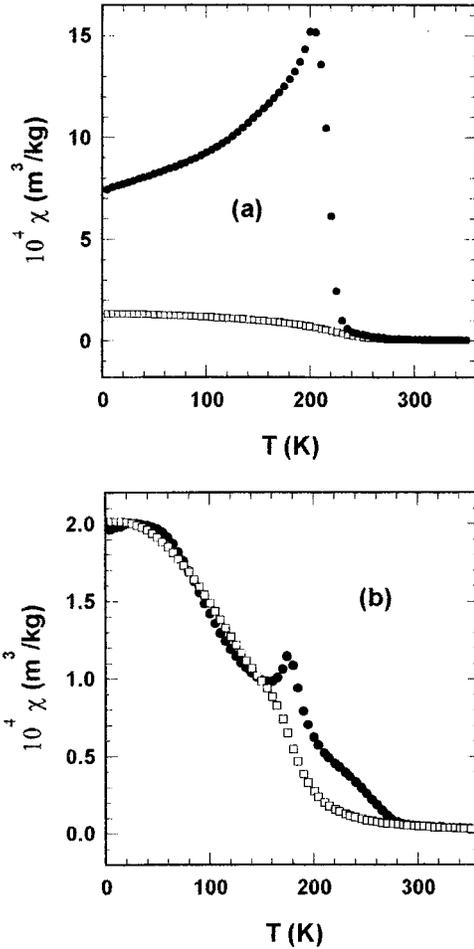


FIG. 2. Magnetic susceptibility as a function of temperature, for sample Gd<sub>75</sub>Y<sub>25</sub> (a) or Gd<sub>48</sub>Y<sub>52</sub> (b) in 0.0025 T (●) or 1 T (□) applied field.

(1). Alloys with simple ferromagnetic order are more affected than noncollinear alloys, which display usually a lower saturation magnetization. Comparison of the values obtained from magnetic and thermal measurements reveals a good qualitative agreement. For the ferromagnetic alloys Gd<sub>75</sub>Y<sub>25</sub>, the agreement of  $T_C$  is better in low field, while the  $\Delta C_p$  obtained from the high-field measurement well approximates the upper limit of the range, deduced from thermal measurements. On the contrary, the noncollinear Gd<sub>48</sub>Y<sub>52</sub> alloy displays good agreement between magnetic and thermal results only when magnetic measurements were carried out up to 7 T.

At the individual measuring temperatures, the field dependence of the isothermal magnetic entropy change of sample Gd<sub>75</sub>Y<sub>25</sub>, as calculated from the magnetization curves, is consistent with simple ferromagnetic order (i.e., a monotonic, almost linear increase is seen) over the total investigated field and temperature range. On the contrary, when plotted the same way, the isothermal magnetic entropy change for sample Gd<sub>48</sub>Y<sub>52</sub> displays the signs of noncollinear order, as positive values at low temperatures and fields, as well as nonmonotonic field dependence [Figs. 4(a) and 4(b), for temperatures below and above the transition, respectively].

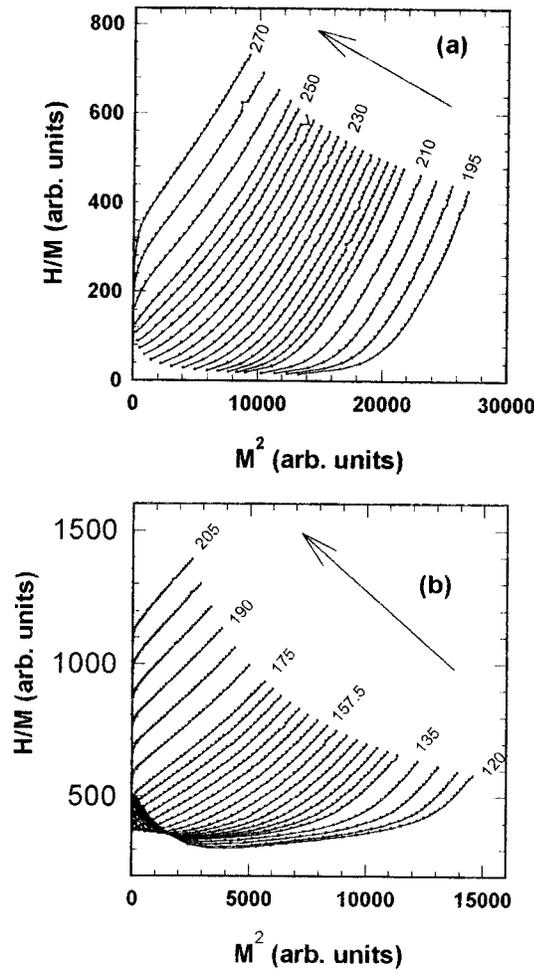


FIG. 3. Below-Goryega plots for sample  $\text{Gd}_{75}\text{Y}_{25}$  (a) or  $\text{Gd}_{48}\text{Y}_{52}$  (b), as calculated from the magnetization curves. The arrow indicates the direction of increasing temperature. For convenience, selected temperatures are shown next to the corresponding curve.

Figures 5(a) and 5(b) show the temperature dependence of the calculated magnetic entropy change from both methods, for an applied field of 7 T. The temperatures corresponding to the maximal change in magnetic entropy (235 K for  $\text{Gd}_{75}\text{Y}_{25}$  and 166 K for  $\text{Gd}_{48}\text{Y}_{52}$ ) are in good agreement with the thermal results, and do not show a significant field dependence. The curves calculated from magnetic or thermal measurements display maxima at identical temperatures (within experimental error) and are also very similar in shape. The most significant difference is a constant shift along the vertical axis; the curves calculated from magnetic measurements are positive over the total temperature range,

TABLE II. Transition temperatures  $T_C$  and specific heat discontinuities  $\Delta C_p$ , as determined from magnetic measurements.

Alloy	Transition temperature $T_C$ (K)		Specific heat discontinuity $\Delta C_p$ (J/kg K)	
	1 T	7 T	1 T	7 T
$\text{Gd}_{75}\text{Y}_{25}$	$235 \pm 3$	$251 \pm 3$	$37 \pm 3$	$123 \pm 7$
$\text{Gd}_{48}\text{Y}_{52}$	$147 \pm 2$	$157 \pm 2$	n/a	$49 \pm 3$

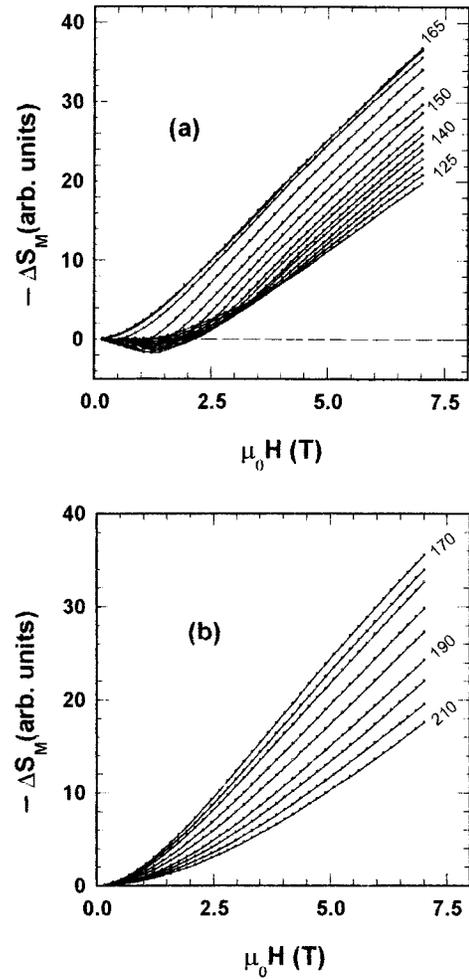


FIG. 4. Isothermal magnetic entropy change vs maximal applied field for sample  $\text{Gd}_{48}\text{Y}_{52}$ , as calculated from the magnetization curves; below {125–165 K, (a)} or above {170–210 K, (b)} the transition. For convenience, selected temperatures are shown next to the corresponding curves.

while the curves obtained from thermal measurements display a negative “tail” at higher temperatures. There is no qualitative difference in the behavior of the samples, thus, the magnetic structure ( $\text{Gd}_{75}\text{Y}_{25}$  is a simple ferromagnet, while  $\text{Gd}_{48}\text{Y}_{52}$  is noncollinear) does not seem to have an impact on the observed discrepancy.

The total magnetic entropy change for full ordering of the alloys can be estimated as follows:  $S_{\text{mag, total}} = x_{\text{Gd}} R \ln(2S+1)$ , where  $x_{\text{Gd}}$  is the concentration of Gd,  $R$  the universal gas constant and  $S=7/2$ , the Gd spin. Assuming Y does not contribute and does not influence the Gd ordering, the values are 95.5 J/kg K for  $\text{Gd}_{75}\text{Y}_{25}$  and 68.2 J/kg K for  $\text{Gd}_{48}\text{Y}_{52}$ . The observed magnetic entropy changes (11 and 7 J/kg K, respectively), are much smaller than the values above, showing that the alloys were far from full ordering.

Integration of the specific heat curves give a total entropy ( $S_{\text{total}} = S_{\text{lattice}} + S_{\text{electron}} + S_{\text{magnetic}}$ ) of about 300 J/kg K for the  $\text{Gd}_{75}\text{Y}_{25}$  and 200 J/kg K for  $\text{Gd}_{48}\text{Y}_{52}$  at the temperature of the magnetic transition. The observed magnetic entropy change is very small as compared to these total entropies, only about 3% of the values given above. Conse-

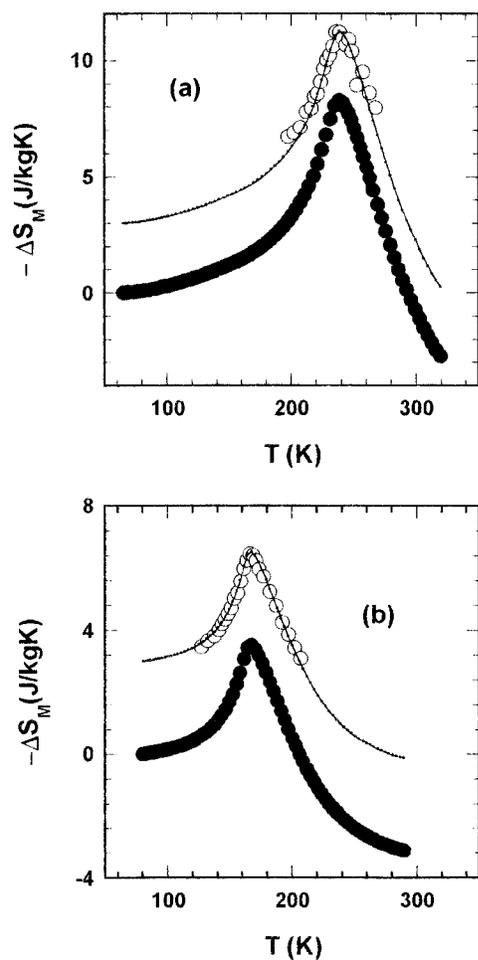


FIG. 5. Magnetic entropy change as a function of temperature for 7 T applied field, from thermal (●) or magnetic measurements (○); for sample  $\text{Gd}_{75}\text{Y}_{25}$  (a) or  $\text{Gd}_{48}\text{Y}_{52}$  (b). The solid line corresponds to a  $-3 \text{ J/kg K}$  shift of the thermal data.

quently, the experienced difference between the results of the magnetic and thermal measurements is well within the error margins of both methods. In case of a random error, no further considerations would be necessary. However, the difference is systematic, thus, it deserves further investigation. As it does not seem to depend on temperature or on sample, it probably results from a difference in integration constants used in both methods. In an empirical approach, we shifted the thermal curve by  $3 \text{ J/kg K}$  for both samples [shown as a solid line in Figs. 5(a) and 5(b)], which resulted in a reasonably good overlap with the results obtained from magnetic measurements. As the magnetization measurements were performed in an isothermal way (adiabatic measurements would be hard to realize) and the thermal measurement under adiabatic conditions, the measurements have different external constants, even if they both arrive at the isothermal entropy change as the final result, and these different constants might have contributed to the observed shift.

### A. Assessment of derived data reliability

In order to calculate the magnetic entropy change from magnetic measurements, we integrate  $\partial M/\partial T$  from  $H=0$  to

$H=H_{\text{max}}$ . This calculation (based on the definition of the magnetic entropy change) is valid only for the saturation regime of the magnetization curve, where changes in magnetization result from moment orientation, and not from domain-wall displacement as is the case for low fields. Consequently, far below the transition, the calculated entropy contains a contribution corresponding to hysteresis losses. The domain-wall contribution and the hysteresis rapidly decrease upon approaching the transition from the lower temperature side, and disappears above the transition (i.e.,  $T > T_C$ ). Its importance increases with decreasing temperature, consequently, magnetic measurements deliver reliable magnetic entropy change data only in the vicinity of the transition. We made efforts to correct for hysteresis loss contribution, by considering only the  $(M, H)$  values consistent with the linear section of the Belov–Goryega plot in the entropy integral [Eq. (1)]. This method has three flaws:

- (i) The Belov–Goryega plot<sup>9</sup> is in itself an approximation, well demonstrated by the field dependence of the delivered parameters (Ref. 15, as well as Table II).
- (ii) It is impossible to give an objective criteria for the cutoff point; it is a subjective decision.
- (iii) Above the transition, all points of the magnetization curve have to be considered, thus, the result of a correction is often a distorted curve for the magnetic entropy change.

On this basis, we decided that instead of arbitrary corrections, we would integrate from zero field, and compromise with the possible presence of a small error below the transition.

The calculation based on thermal measurements has similar problems. The integrals (3), (4), and (5), calculating the total entropies with or without applied magnetic field, as well as their difference, should all be carried out from  $T=0 \text{ K}$ , in which case the integration constant can be considered zero. In our case, the measurements have started at a reference temperature of 37 and 80 K, respectively. Thus, the integrals all carry a constant representing the contribution of lower temperatures. The constant is not essentially the same in Eqs. (3) and (4), thus, there is a nonzero constant in Eq. (5) as well. For sample  $\text{Gd}_{75}\text{Y}_{25}$ , Fig. 6(a) illustrates the extreme sensitivity of the calculated entropy curves to the reference temperature. Figure 6(b) displays the effect of the reference temperature on the magnetic entropy change, as calculated from the entropy curves of Fig. 6(a). It clearly shows that the shape of the curves is not distorted by changing the reference temperature, neither is the temperature of the transition influenced. The only impact, a parallel shift along the vertical axis. Well below the transition temperature ( $T < 0.4T_C$ ) and for materials with no low-temperature transitions, the shift could be calculated approximately from the spin-wave theory. Unfortunately, Gd–Y alloys do not retain the simple ferromagnetic behavior of gadolinium, thus, as the susceptibility curves demonstrate, there are low-temperature transitions present. This way, an empirical correction is the only choice, e.g., by determining the constant using the criteria that the magnetic entropy change should not change sign. As the structure of Gd and Y is very similar,

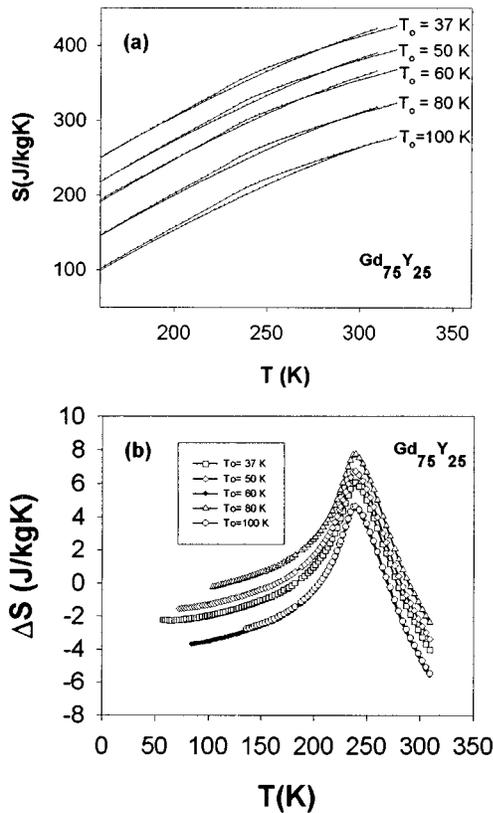


FIG. 6. Entropy curves integrated from different reference temperature (a) and their impact on the resulting magnetic entropy change (b) for sample  $Gd_{75}Y_{25}$ .

it is not surprising that the same constant applies to both alloys: the low-temperature behavior is expected to be similar.

The magnetic entropy change corrected this way agrees well with the values obtained from magnetization measurements, especially above the transition. For sample screening, both measurements carry the same information; while the thermal measurements are clearly superior in that sense that they deliver the specific heat values necessary for further calculations and refrigerator design, should the material be selected. We would like to stress here, that values of the specific heat, or magnetization, as raw data, are not influenced by the above ambiguities. They are introduced in the course of the numerical processing.

### B. Reliability of $\Delta T$ (adiabatic temperature change=magnetocaloric effect) calculations

$\Delta T$  can be calculated from the approximate Eq. (9) or directly from the entropy curves. If the corrected  $\Delta S_M$  is introduced into Eq. (9), the  $\Delta T$  value carries only as much error as the approximation in the equation, which was considered negligible. This calculation gives a  $\Delta T(T_C)$  of 9.5 and 4.3 K for samples  $Gd_{75}Y_{25}$  and  $Gd_{48}Y_{52}$ , respectively. It can be seen that although the magnetic entropy change of  $Gd_{75}Y_{25}$  is not yet significantly reduced as compared to pure Gd, the adiabatic temperature change is smaller, obviously due to the increased specific heat of the alloy in comparison to pure Gd.<sup>16</sup>

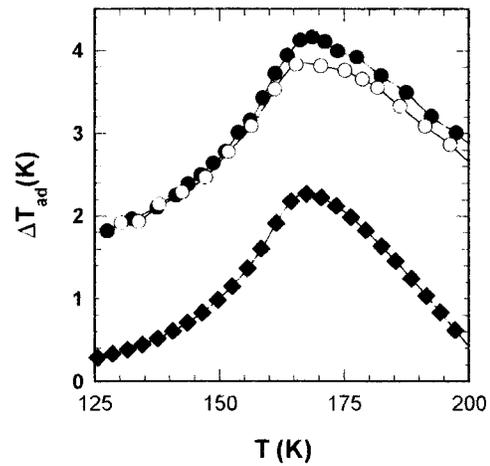


FIG. 7. Temperature dependence of the adiabatic temperature change for sample  $Gd_{48}Y_{52}$ , as obtained from the uncorrected (■) or corrected (●) magnetic entropy change value and the 7 T specific heat, as well as the experimentally determined adiabatic temperature change (○). Solid lines are guides to the eye.

In Fig. 7, we show the directly measured  $\Delta T$  of sample  $Gd_{48}Y_{52}$  in comparison to the values calculated from the magnetic entropy change, as obtained from magnetic or uncorrected thermal measurements, respectively. Figure 7 demonstrates that the experimentally determined data of the adiabatic temperature change  $\Delta T$  show a better agreement with the  $\Delta T$  values calculated from the magnetically obtained magnetic entropy change, which justifies the correction of the thermally obtained magnetic entropy change values.

Similar discrepancies arise if we calculate  $\Delta T$  directly from the entropy curves. The effect of the neglected integration constant appears again and has a non-negligible impact on the results. In the case of the isothermal magnetic entropy change, the shift, as shown above, represent a constant contribution over the total temperature range. For the case of the adiabatic temperature change, however, the correction is not an additive constant, but depends on the temperature. An approximation can be obtained from Eq. (9) as

$$\delta\Delta T = \frac{T}{C_{p,H}(T)} \delta\Delta S_M(H), \quad (10a)$$

or it can be derived geometrically from Fig. 8,

$$\delta\Delta T = \frac{\partial T}{\partial S} \Big|_0 \delta S_H + \frac{\partial T}{\partial S} \Big|_H \delta S_H, \quad \Delta T_{\text{corr}} = \Delta T_{\text{app}} + \delta\Delta T, \quad (10b)$$

where  $\delta S_0$  and  $\delta S_H$  correspond to the shift of the  $S_0$  and  $S_H$  curve, respectively, and  $\Delta T_{\text{corr}}$  and  $\Delta T_{\text{app}}$  correspond to the correct or erroneous value of the adiabatic temperature change, respectively.

The equation clearly shows that the correction depends on the differentials of both curves, and as they are neither linear nor parallel, it will not be constant. Its value is, however, always positive, thus,  $\Delta T_{\text{app}} < \Delta T_{\text{corr}}$  in the total temperature range. Consequently, neglecting the integration constants will result in an underestimated adiabatic temperature change. For sample  $Gd_{75}Y_{25}$ , the estimated error equals 3.7

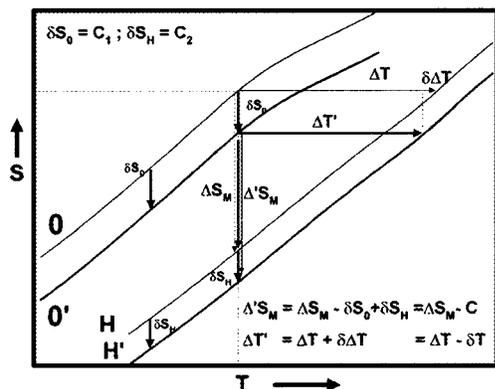


FIG. 8. Schematic figure illustrating the errors and corrections when calculating the adiabatic temperature change from shifted entropy curves.

K. Similarly to the magnetic entropy change, a negative tail at higher temperatures might indicate the presence of numerical problems.

## V. CONCLUSIONS

- (1) Both magnetic and specific heat measurements represent powerful tools in materials' research for magnetic refrigeration.
- (2) The material parameters, significant for the evaluation of the magnetocaloric effect, show reasonable agreement when determined via magnetic or thermal methods.
- (3) Specific heat measurements present the advantage of delivering values necessary for further refrigerator design, should the material in question be selected.
- (4) Values of the entropy, integrated from specific heat data, depend sensitively on the reference temperature. Consequently, magnetic entropy curves contain a field-dependent additive constant, resulting in parallel shift of the curves along the vertical axis.
- (5) The magnetic entropy change is more reliable when calculated from magnetic measurements, as integration from zero field under isothermal conditions does not represent any experimental or numerical difficulty.

Simultaneously, magnetic measurements have the advantage of being fast and less costly than specific heat measurements in magnetic fields, thus, prescreening of a large number of candidate materials does not present a problem.

- (6) Assumptions and approximations used in numerical methods have the most significant impact on the calculation of the adiabatic temperature change; the presence of such an influence should be checked carefully *before* coming up with final conclusions regarding the material's performance.

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