



## The effect of demagnetization on the magnetocaloric properties of gadolinium

Bahl, Christian Robert Haffenden; Nielsen, Kaspar Kirstein

*Published in:*  
Journal of Applied Physics

*Link to article, DOI:*  
[10.1063/1.3056220](https://doi.org/10.1063/1.3056220)

*Publication date:*  
2009

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Bahl, C. R. H., & Nielsen, K. K. (2009). The effect of demagnetization on the magnetocaloric properties of gadolinium. *Journal of Applied Physics*, 105(1), 013916. <https://doi.org/10.1063/1.3056220>

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# The effect of demagnetization on the magnetocaloric properties of gadolinium

C. R. H. Bahl<sup>1,a)</sup> and K. K. Nielsen<sup>1,2</sup>

<sup>1</sup>*Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark*

<sup>2</sup>*DTU Mechanical Engineering, Building 402, Technical University of Denmark, DK-2800 Lyngby, Denmark*

(Received 4 September 2008; accepted 18 November 2008; published online 9 January 2009)

Gadolinium displays a strong magnetocaloric effect at temperatures close to room temperature making it useful in the field of room temperature magnetic refrigeration. We discuss the importance of including the effects of the demagnetization field when considering the magnetocaloric properties of gadolinium. The adiabatic temperature change  $\Delta T_{\text{ad}}$  of gadolinium sheets upon application of a magnetic field has been measured at a range of applied magnetic fields and sample orientations. A significant dependence of  $\Delta T_{\text{ad}}$  on the sample orientation is observed. This can be accounted for by the demagnetization factor. Also, the temperature dependence of  $\Delta T_{\text{ad}}$  has been measured experimentally and modeled by mean field theory. Corrections to mean field theory modeling due to the demagnetization field are proposed and discussed. © 2009 American Institute of Physics.

[DOI: [10.1063/1.3056220](https://doi.org/10.1063/1.3056220)]

## I. INTRODUCTION

Gadolinium has been the benchmark magnetocaloric material for room temperature magnetic refrigeration since the pioneering work of Brown<sup>1</sup> in 1976. Gadolinium is readily available and has a relatively high magnetocaloric effect and a Curie temperature around room temperature. However, gadolinium easily corrodes and is rather expensive. Recently, other materials displaying a magnetocaloric effect similar in magnitude have been demonstrated.<sup>2</sup> Many of these allow for a tuning of the Curie temperature to a desired value by chemical doping. Although the implementation of gadolinium in commercial magnetic refrigeration devices is not expected, it remains a useful material for testing magnetic refrigeration devices due to the relatively large magnetocaloric effect close to room temperature.

A number of numerical models have been developed to predict and optimize the output of magnetic refrigeration devices. These models are in general configured to calculate the performance using gadolinium as the magnetocaloric material, relying either on mean field theory (MFT) calculations<sup>3,4</sup> or experimental measurements of the gadolinium properties<sup>5,6</sup> generally from extremely pure samples. In the following the difference between results obtained from such pure samples or MFT will be compared to those obtained from commercially available gadolinium, which is generally used in actual magnetic refrigeration devices. For a review of such devices, see Ref. 7.

The effect of demagnetization due to the morphology of the gadolinium samples has not previously been reported. This paper presents a study of the adiabatic temperature change  $\Delta T_{\text{ad}}$  measured by a direct method on commercially obtained gadolinium sheets. The importance of considering the demagnetization field when studying the magnetocaloric properties will be shown in the following and the manner in

which this demagnetization affects the temperature and field dependence of  $\Delta T_{\text{ad}}$  is discussed. Also, it will be discussed in the following how the magnetocaloric properties of Gd published in the literature are affected by the level of impurities. Thus, when using gadolinium as a benchmark material for a magnetic refrigeration device care must be taken to ensure that similar purities of gadolinium are used and that the shape of the Gd is taken into account.

Fuelled by the increasing interest in room temperature refrigeration and the widespread use of Gd for this a large number of papers have been published on the magnetocaloric properties of Gd. A seminal and broadly quoted work is that of Dan'kov *et al.*<sup>8</sup> in which a wide range of measurements on a number of samples is presented. A value of  $\Delta T_{\text{ad}}=3.8$  K was measured at the Curie temperature  $T_C$  in an applied field of 1 T from an extremely pure (99.90 at. %/99.99 wt %) polycrystalline sample of gadolinium prepared by the Materials Preparation Center at the Ames Laboratory. This is similar to the value of 3.6 K previously reported.<sup>9</sup> A significant lowering of the directly measured adiabatic temperature change was observed in less pure samples.<sup>8</sup> The lowering seems to depend on the degree and more importantly on the type of impurities present in the sample. A similar lowering of the magnetocaloric effect when comparing a very pure single crystal Gd sample (made from a polycrystalline starting material of 99.85 at. %/99.98 wt %) prepared at Ames to a commercially obtained sample (99.9%) has been observed.<sup>10</sup> Here a value of  $\Delta T_{\text{ad}}=3.5$  K was measured in an applied field of 1 T and a temperature of 295 K from the single crystal and  $\Delta T_{\text{ad}}=2.8$  K was measured from the commercial sample in the same conditions. Measurements of a 98.0% pure Gd sample at 293 K yielded  $\Delta T_{\text{ad}}=3.5$  K, but in a field of 1.3 T.<sup>25</sup> Generally it has been shown that even small amounts of impurities can have a significant effect on the physical properties of rare earth elements and compounds.<sup>11</sup> An example of this is the change in magneto-

<sup>a)</sup>Electronic mail: christian.bahl@risoe.dk.

caloric properties of the giant magnetocaloric material  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  when prepared from Gd from different sources.<sup>12</sup> Using commercial Gd from two different locations in China, the first order phase transition, characteristic of the giant magnetocaloric material and present when using pure Gd, disappeared.

MFT has previously been successfully used to model the magnetic properties of Gd.<sup>3,9,13-15</sup> The model employed to find  $\Delta T_{\text{ad}}$  is a combination of the Weiss mean field model for the magnetic properties, the Debye model for the lattice entropy, and the Sommerfeld model for the conduction electron entropy. The modeled profiles for the adiabatic temperature change closely resemble those measured experimentally.<sup>3,9,13-15</sup> However, the absolute magnitude of  $\Delta T_{\text{ad}}$  is slightly higher than that measured in purified Gd samples, as the calculated values for a 1 T applied field are around 4.0 K.<sup>3,9</sup> Recently, a Monte Carlo method has been employed to predict a heat capacity in Gd that resembles the experimental data more closely than that predicted by conventional MFT.<sup>16</sup>

## II. EXPERIMENTAL

Sheets of gadolinium with dimensions of  $x=40$  mm,  $y=25$  mm, and  $z=0.9$  mm were obtained commercially from Metall Rare Earth Ltd. with a claimed purity of 99.4 wt % Gd.

The magnetic properties of the gadolinium were measured using a Lake Shore 7407 vibrating sample magnetometer. Magnetization measurements were conducted in applied fields of  $\mu_0 H_{\text{appl}}=0$  T to 1.6 T at temperatures ranging from 240 to 330 K with a  $2 \times 2 \times 1$  mm<sup>3</sup> (33.8  $\mu\text{g}$ ) sample.

A magnetic refrigeration device consisting of a plastic cylinder with a rectangular hole has previously been described in Ref. 17. The hole has grooves into which 13 of the above mentioned sheets of gadolinium can be held at a separation of 0.8 mm between each sheet. The cylinder is held in place in the gap of a Lake Shore EM7 electromagnet with 2 in. diameter pole pieces capable of producing  $\mu_0 H_{\text{appl}}=1.3$  T. By rotating the cylinder within the magnetic field the sheets may be magnetized in any direction within the  $yz$ -plane. A small groove has been cut in the center of the central plate. In this a 0.13 mm type  $E$  thermocouple (chromel constantan) is mounted with thermally conducting epoxy. The temperature increase in the gadolinium is measured when a magnetic field is applied. The field is ramped from zero to between 0.1 and 1.3 T at 0.08 T/s.

Four experimental series were performed. In the first and second, a single sheet of gadolinium is placed in the center of the cylinder. This is magnetized in a range of applied fields along both the  $y$  and the  $z$  directions, i.e., parallel and perpendicular to the plate. In the third and fourth, the cylinder is filled with 13 sheets and again magnetized along the  $y$  and the  $z$  directions while measuring the temperature change in the central sheet.

In a different experiment the cylinder with 13 plates is placed in a drive mechanism designed to move it in and out of the bore of a permanent magnet assembly. This permanent

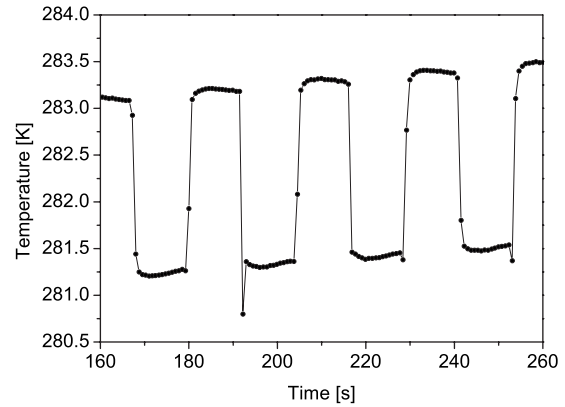


FIG. 1. Sample of the raw data measured by a thermocouple embedded in the central of the 13 Gd sheets. Application and removal of the  $\mu_0 H_{\text{appl}}=1.1$  T field from the permanent magnet assembly is clearly seen to result in a change in temperature.

magnet assembly is of the Halbach-type with a 40 mm diameter and 50 mm long bore, supplying a maximum flux density of around 1.1 T.

The cylinder is precooled by dry ice and allowed to warm to room temperature while repeatedly being moved in and out of the magnet bore. The cylinder is held in and out of the magnetic field for 10 s respectively and the movement in and out of field takes approximately 1 s. The sampling frequency of the temperature measurements is roughly 1.3 Hz. A raw sample of the data measured by the thermocouple is shown in Fig. 1. The magnetocaloric temperature change is determined by averaging the measured temperature in the respective situations (in or out of field) and defining these regions with a tolerance of 0.1 K. The occasional spikes observed in the data are due to induction in the thermocouples during the movement. These do not affect the temperature measurements<sup>18</sup> and are ignored in the calculation of  $\Delta T_{\text{ad}}$ . The adiabatic temperature change is quite evident and it is also seen that the temperature of the Gd sheet does not increase significantly during each 10 s period. When the measured temperature approaches room temperature the Gd sheets are heated and allowed to cool to room temperature in order to measure at the hot side of room temperature. The gap in the temperature measurements, visible in Fig. 1, is due to the very slow approach toward room temperature both from above and below.

## III. RESULTS AND DISCUSSION

### A. Curie temperature

From the magnetization data the Curie temperature  $T_C$  can be determined by the inverse susceptibility method of the mean field Curie–Weiss law. Calculating the inverse susceptibility at each temperature and extrapolating the linear part gives  $T_C=297(2)$  K, see Fig. 2(a). Alternatively the Curie temperature may be found by fitting the susceptibility to an expression with a critical exponent  $\chi \propto (T-T_C)^{-\gamma}$ . This results in a Curie temperature of  $T_C=295.0(2)$  K, see Fig. 2(b). The critical exponent is found to be  $\gamma=1.19(2)$  in correspondence to the published values of around 1.2.<sup>19</sup> In both approaches the data have been corrected for the demagneti-

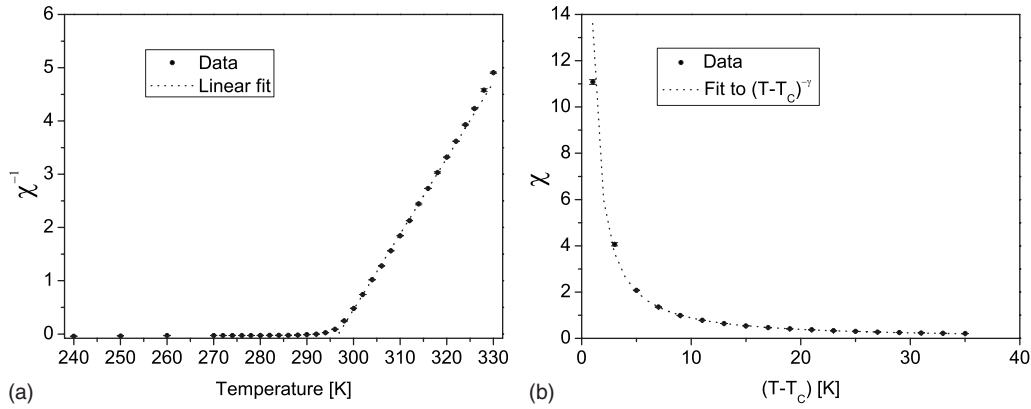


FIG. 2. Determination of the Curie temperature  $T_C$  (a) by the mean field inverse susceptibility method and (b) by the critical exponent method.

zation field as will be discussed below. It has previously been found that the ordering temperature of Gd is strongly dependent on both the experimental technique employed and the purity of the sample.<sup>8,20</sup> Values in the range 290–297 K have been published for low magnetic fields.

## B. Field dependence

The measured adiabatic temperature change in the gadolinium as a function of applied field is shown in Fig. 3. As the Gd sheets are held in the plastic cylinder and not isolated in a vacuum chamber the temperature change is not truly adiabatic. However, as the temperature change in the sheets is isotropic and the thermal conductivity of the surroundings is relatively low, heat loss to the surroundings will not be significant on a short time scale<sup>18</sup> and the term adiabatic temperature change will be used in the following. Each data point in Fig. 3 was obtained from an initial temperature of 294 K. It is observed that magnetizing the sheets along the  $z$  direction results in a significantly lower temperature change than when magnetizing along the  $y$  direction. This is, as expected, due to an increased demagnetization factor  $N_D^{\text{sheet}}$  of the sheets when the magnetization direction is normal to these, as compared to when it is parallel to the sheets.

The average demagnetization factor of a single sheet can be approximated by a relatively simple analytical expression.<sup>21</sup> However for a stack of sheets the calculations

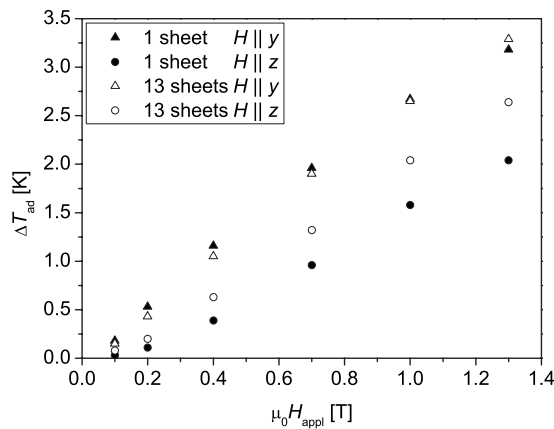


FIG. 3. The temperature change in the Gd sheets measured in the electromagnet at the applied field  $H_{\text{appl}}$  at an initial temperature of 294 K.

become more involved. We have calculated the average demagnetization factor in a single plate and in a stack of 13 plates by a three-dimensional finite element method using the software package COMSOL MULTIPHYSICS.<sup>22</sup>

The calculated average demagnetization factors of the sheets along with those obtained from the analytical expression for a single sheet are given in Table I. Good correspondence is observed between the results of the analytical expression and the numerical calculations.

The magnetization measurements were performed with the  $2 \times 2 \times 1$  mm<sup>3</sup> sample oriented such that the field is parallel to one of the 2 mm directions. This results in an average demagnetization factor of  $N_D^{\text{sample}} = 0.25$  by both the analytical expression and numerical calculations. Taking this into account the average internal field  $H_{\text{int}}$  of the sample can be calculated as

$$H_{\text{int}} = H_{\text{appl}} - N_D^{\text{sample}} M. \quad (1)$$

This gives the pure dependence of the magnetization on the internal magnetic field independent of the size or shape of the sample. Now, the relation between the actual average internal field of the gadolinium sheets  $H_{\text{int}}$ , the equivalent applied field of the sheets in the various orientations  $\tilde{H}_{\text{appl}}$ , and the magnetization of the sheets may be written as

$$\tilde{H}_{\text{appl}} = H_{\text{int}} + N_D^{\text{sheet}} M. \quad (2)$$

Figure 4 shows the temperature change data from Fig. 3 plotted versus the internal field in the sheets. The similarity of the data from each of the four experiments when plotted versus  $H_{\text{int}}$  indicates the validity of the demagnetization factor approach. The effect of a change in the demagnetization factor when the sheets are stacked compared to that from a single sheet is clearly seen when comparing Figs. 3 and 4.

TABLE I. Demagnetization factors  $N_D^{\text{sheet}}$  of the Gd sheets calculated by numerical simulations using COMSOL and the analytical expression given in Ref. 21.

Number of sheets	Field orientation	COMSOL $N_D^{\text{sheet}}$	Analytical $N_D^{\text{sheet}}$
1	$H \parallel y$	0.05	0.05
1	$H \parallel z$	0.93	0.92
13	$H \parallel y$	0.16	...
13	$H \parallel z$	0.63	...

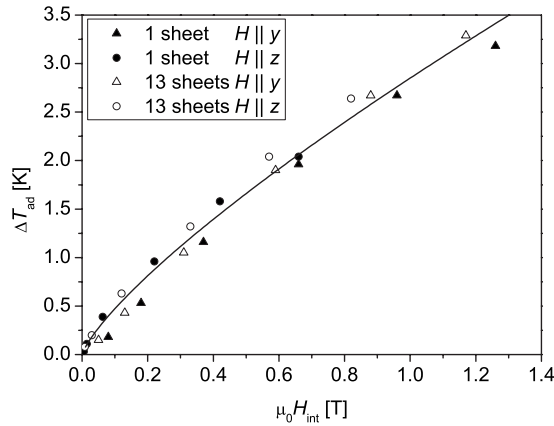


FIG. 4. The temperature change in the Gd sheets vs the internal magnetic field  $H_{\text{int}}$  at an initial temperature of 294 K. The data have been corrected for the demagnetization field using magnetization data measured from the same Gd. The solid line is a fit to the data as described above.

Thus, when using Gd in any magnetocaloric application it is important to take into account the demagnetization factor of the actual configuration of the Gd.

In Fig. 4 the data are observed to pass through the origin as would be expected. MFT calculations predict that near the Curie temperature  $T_C$ , the adiabatic temperature change  $\Delta T_{\text{ad}}$  in Gd upon magnetization or demagnetization is proportional to  $H^{2/3}$  (Ref. 23). Compiling a range of experimental data from the literature Pecharsky and Gschneidner<sup>2</sup> find the relation  $\Delta T_{\text{ad}}[\text{K}] = 3.675(\mu_0 H[\text{T}])^{0.7}$  in good accordance with the MFT result.<sup>9</sup> These data were mainly collected from very pure samples and high field experiments.

Fitting the same type of expression to the data presented in Fig. 4 gives the relation  $\Delta T_{\text{ad}}[\text{K}] = 2.85(5)(\mu_0 H[\text{T}])^{0.78(3)}$ , as indicated by the solid line in Fig. 4. Thus the exponent is close to the ones found both by MFT and in Ref. 2 while the prefactor is somewhat less.

### C. Temperature dependence

The magnetocaloric temperature change in the gadolinium sheets was measured as a function of initial temperature in the applied field of 1.1 T supplied by the permanent magnet assembly. The temperature increase and decrease in response to the movement of the gadolinium sheets into and out of the magnetic field region are shown in Fig. 5; for convenience the sign of the temperature decrease has been changed, such that both data sets appear positive.

The data show a peak in the temperature change in the data recorded during magnetization at about 293 K, which is slightly below the Curie temperature determined above. A difference in the transition temperature depending on the method of measurement has previously been reported in Refs. 8 and 24. The peak in the data recorded during field removal is at a higher temperature, 296 K. This is expected due to the reversibility of the magnetocaloric effect, which requires the distance between the peaks to be the same as the peak adiabatic temperature change.

As the magnetization of the Gd sheets decreases with an increase in temperature, the internal magnetic field of the sheets at a fixed applied field increases as the temperature is

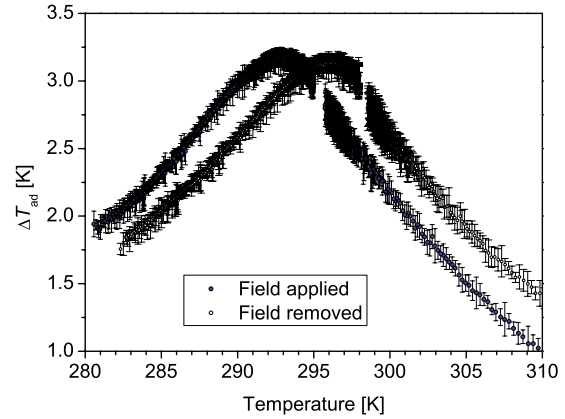


FIG. 5. (Color online) The temperature change in Gd upon application (filled symbols) and removal (open symbols) of the field from the permanent magnet assembly yielding  $\mu_0 H_{\text{appl}} = 1.1$  T. Thirteen sheets were used in the orientation with the field in the plane of the sheets,  $H \parallel y$ . The error bars indicate the standard deviations of the data used to calculate  $\Delta T_{\text{ad}}$ , see Fig. 1.

increased, see Eq. (2). Thus  $\Delta T_{\text{ad}}$  cannot be plotted at a fixed internal field. The temperature dependence of the internal field of Gd sheets at an applied field of  $\mu_0 H_{\text{int}} = 1.1$  T is shown in Fig. 6 for a number of different demagnetization factors. Even a modest value of the demagnetization constant leads to a significant temperature dependence of the internal field.

A temperature increase of around 3.1 K is observed upon magnetization at 294 K. This is larger than around 2.8 K increase that may be interpolated from the data in Fig. 3. This difference is presumably due to a difference in the ramping rate of the magnetic field. The slower field ramping of the electromagnet will allow the Gd to lose heat before the ramp is finished. This is not the case for the permanent magnet device, as the field is ramped fast compared to the rate of heat loss. An equivalent difference in the measured magnetocaloric effect due to the ramping rate of the magnetic field is reported in Ref. 10. Here, changing the ramp rate of the magnet from 0.05 to 0.5 T/s also resulted in an increase in the measured temperature change of about 0.3 K.

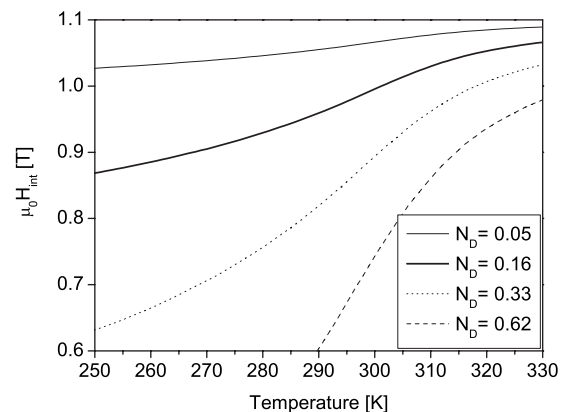


FIG. 6. The temperature dependence of the internal field of the Gd sheets in an applied field of  $\mu_0 H_{\text{appl}} = 1.1$  T determined from the magnetization data. The demagnetization factor  $N_D = 0.16$  (the broad solid line) is equivalent to the 13 sheet situations with the field in the plane of the sheets,  $H \parallel y$ .

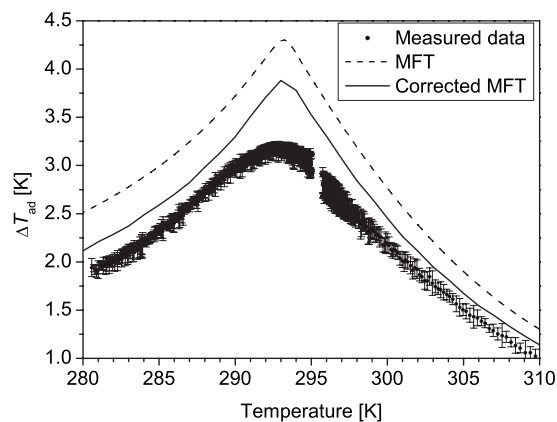


FIG. 7. The temperature change in Gd upon application of the field from Fig. 5 compared to the equivalent MFT results using  $\mu_0 H = 1.1$  T as the input (dashed line) and the corrected MFT results, where the internal field, calculated by the demagnetization, is used at each temperature to calculate (solid line).

The adiabatic temperature change in Gd has been calculated by the MFT, as detailed in Ref. 3. The results of this calculation performed in an applied field of 1.1 T are shown in Fig. 7 by a dashed line. However, the input to MFT is the internal magnetic field. To correct for this the MFT value of  $\Delta T_{ad}$  has been calculated at each temperature using the internal magnetic field given in Fig. 6, resulting in the solid line in Fig. 7. For clarity only the data associated with the application of the field are shown. It is seen that the corrected MFT approach yields a temperature dependence of  $\Delta T_{ad}$  that closely resembles the experimentally measured one. The experimental data have a less pronounced peak around  $T_C$  and are generally below the corrected MFT data. A 10% reduction in the corrected MFT data set results in a profile that, except close to the peak, closely resembles the experimentally measured one. This reduction in the experimental data may be explained by impurities in the commercial grade Gd used for the experiments as discussed above.

#### IV. SUMMARY AND CONCLUSION

The dependence of the measured magnetocaloric effect on the demagnetization factor of a number of thin sheets of gadolinium has been studied. The demagnetization factor was varied by changing the orientation and number of sheets used in the experiments. The average internal field in the Gd sheets is calculated for each of the experiments. When correcting for the effect of demagnetization in this way, consistent values for the adiabatic temperature change  $\Delta T_{ad}$  are found for each of the experiments.

The measured peak value of  $\Delta T_{ad}$  in the present commercial grade Gd is somewhat below that reported for purified samples and that predicted by conventional MFT. Some of this lowering may be explained by demagnetization and indeed a corrected MFT calculation has been shown to model the data more closely. However, the major contribution to the lowering seems to be due to impurities in the commercial Gd, as has previously been reported in the literature.

#### ACKNOWLEDGMENTS

The authors would like to thank Dr. A. Smith and Dr. N. Pryds for fruitful discussions. Also, the authors would like to acknowledge the support of the Programme Commission on Energy and Environment (EnMi) (Contract No. 2104-06-0032), which is part of the Danish Council for Strategic Research.

- <sup>1</sup>G. V. Brown, *J. Alloys Compd.* **47**, 3673 (1976).
- <sup>2</sup>V. K. Pecharsky and K. A. Gschneidner, Jr., *Int. J. Refrig.* **29**, 1239 (2006).
- <sup>3</sup>T. F. Petersen, N. Pryds, A. Smith, J. Hattel, H. Schmidt, and H.-J. H. Knudsen, *Int. J. Refrig.* **31**, 432 (2008).
- <sup>4</sup>P. Li, M. Gong, G. Yao, and J. Wu, *Int. J. Refrig.* **29**, 1259 (2006).
- <sup>5</sup>J. Dikeos, A. Rowe, and A. Tura, *AIP Conf. Proc.* **823**, 993 (2006).
- <sup>6</sup>A. Sarlah, A. Kitanovski, A. Poredos, P. W. Egolf, O. Sari, F. Gendre, and Ch. Besson, *Int. J. Refrig.* **29**, 1332 (2006).
- <sup>7</sup>K. A. Gschneidner, Jr. and V. K. Pecharsky, *Int. J. Refrig.* **31**, 945 (2008).
- <sup>8</sup>S. Y. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Jr., *Phys. Rev. B* **57**, 3478 (1998).
- <sup>9</sup>S. M. Benford and G. V. Brown, *J. Appl. Phys.* **52**, 2110 (1981).
- <sup>10</sup>Y. I. Spichkin, A. V. Derkach, A. M. Tishin, M. D. Kuz'min, A. S. Chernyshov, K. A. Gschneidner, Jr., and V. K. Pecharsky, *J. Magn. Magn. Mater.* **316**, e555 (2007).
- <sup>11</sup>K. A. Gschneidner, Jr., *J. Alloys Compd.* **193**, 1 (1993).
- <sup>12</sup>W. Wu and D. W. Lu, First IIF-IIR International Conference on Magnetic Refrigeration at Room Temperature, Montreux, Switzerland, 2005, p. 127.
- <sup>13</sup>T. Hashimoto, *Cryogenics* **21**, 647 (1981).
- <sup>14</sup>A. M. Tishin, *Cryogenics* **30**, 127 (1990).
- <sup>15</sup>G. J. Liu, J. R. Sun, J. Z. Wang, T. Y. Zhao, and B. G. Shen, *J. Phys.: Condens. Matter* **19**, 466215 (2007).
- <sup>16</sup>E. P. Nobrega, N. A. de Oliveira, P. J. von Ranke, and A. Troper, *J. Magn. Magn. Mater.* **320**, e147 (2008).
- <sup>17</sup>C. R. H. Bahl, T. Petersen, N. Pryds, and A. Smith, *Rev. Sci. Instrum.* **79**, 093906 (2008).
- <sup>18</sup>B. K. Ponomarev, *Instrum. Exp. Tech.* **26**, 659 (1983).
- <sup>19</sup>P. Hargraves, R. A. Dunlap, D. J. W. Geldart, and S. P. Ritecy, *Phys. Rev. B* **38**, 2862 (1988).
- <sup>20</sup>L. B. Robinson and F. Milstein, *Solid State Commun.* **13**, 97 (1973).
- <sup>21</sup>A. Aharoni, *J. Appl. Phys.* **83**, 3432 (1998).
- <sup>22</sup><http://www.comsol.com>.
- <sup>23</sup>H. Oesterreicher and F. T. Parker, *J. Appl. Phys.* **55**, 4334 (1984).
- <sup>24</sup>A. M. Tishin, K. A. Gschneidner, Jr., and V. K. Pecharsky, *Phys. Rev. B* **59**, 503 (1999).
- <sup>25</sup>J. H. Huang, J. F. Qiu, J. R. Liu, P. Y. Jin, L. Z. Xu, and J. X. Zhang, First IIF-IIR International Conference on Magnetic Refrigeration at Room Temperature, Montreux, Switzerland, 2005, p. 179.