Journal of Magnetism and Magnetic Materials 433 (2017) 234–238

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

# Magnetocaloric properties of Gd in fields up to 14 T

Yu.S. Koshkid'ko [a], J. Ćwik [a,*], T.I. Ivanova [a,b], S.A. Nikitin [a,b], M. Miller [a], K. Rogacki [a,c]

[a] International Laboratory of High Magnetic Fields and Low Temperatures, PAS, 53-421 Wroclaw, Poland
[b] Lomonosov Moscow State University, Faculty of Physics, 119991 Moscow, Russian Federation
[c] Institute of Low Temperatures and Structure Research, PAS, 50-950 Wroclaw, Poland

ARTICLE INFO

*Article history:*
Received 12 October 2016
Received in revised form 19 February 2017
Accepted 14 March 2017
Available online 15 March 2017

ABSTRACT

The magnetocaloric effect (MCE) of polycrystalline gadolinium was studied in high steady magnetic fields up to 14 T by direct measurements of the adiabatic temperature change ($\Delta T$) using an "extraction method". Large MCE was observed at the ferromagnetic phase transition resulting in $\Delta T$ of 19.5 K at a field change of 14 T. The direct measurements of MCE were performed using the measuring system designed and constructed by the authors. It was shown that near the Curie temperature, the magnetic field dependence of the adiabatic temperature change is far from saturation even in a 14 T field and is adequately described by the thermodynamic Landau theory for magnetic second-order phase transitions.



## 1. Introduction

Magnetocaloric effect (MCE) is defined as the cooling or heating of a magnetic material when it is magnetized or demagnetized in an external magnetic field under adiabatic conditions, i.e. in the absence of heat exchange with the environment. E. Warburg discovered this effect late in the 19th century [1]. Over the last 30 years interest in the study of MCE has grown strongly due to the possibility of its practical application (mainly because of the commercial potential offered by magnetic refrigerators operating at room temperature) and interesting fundamental properties of new materials in magnetic fields [1–7]. One example of the increased interest is magnetic refrigerants for solid-state energy-efficient cooling. Taking into account that large electricity consumption by the entire world population is related to refrigeration and air conditioning, an improvement in the efficiency of these processes via the use of magnetic technologies would translate into a large reduction in energy consumption. Magnetic refrigerators could replace conventional refrigerators because they are economical and environmentally friendly. The fundamental study of MCE is interesting from both points of view of the physics of magnetism and solid state thermodynamics. It should also be noted that MCE is a powerful and widely used tool for the investigation of magnetic phase transitions including their mechanisms. Generally, the MCE reaches maximum values in the region of magnetic phase transitions. Furthermore, large MCE can be observed at the cryogenic temperature range due to the superparamagnetic properties [8] or some magnetic precursor effects of rare earth ions [9].

Metallic gadolinium is promising for magnetic cooling. The magnetic behavior of gadolinium has attracted a lot of attention in the last three decades, and MCE of this metal has been studied by both direct and indirect methods [10–18]. The direct method of MCE measurements, when the sample moves quickly between areas of maximum and minimum (or zero) magnetic field (extraction method), is more effective than the indirect method. The adiabatic temperature change ($\Delta T$) during the magnetization and demagnetization process of bulk gadolinium was directly measured, for magnetic fields up to 2 T in the range 285 K to 305 K [19] and up to 9 T for temperatures between 10 and 325 K [17,20]. Magnetocaloric properties of distilled gadolinium with a composite-like structure have been studied in Ref. [21], for fields up to 1.8 T. The magnetic field dependence of MCE has been investigated by Franco et al. [22] and Kuz'min et al. [23], for fields up to 2 T. Generally, direct MCE measurements in high magnetic fields of up to 14 T are seldom done, since the generation of high magnetic fields in superconducting solenoids requires a considerable amount of time during which the heat emitted/absorbed by a sample is dispersed [17,20,24].

In this paper, we present the result of direct MCE measurements of polycrystalline Gd in the region of the magnetic phase transition in high steady magnetic fields of up to 14 T. These MCE measurements were carried out by fast extraction of the sample from the magnetic field. The main goal was to study the correspondence between MCE variations in magnetic fields up to 14 T and thermodynamic relationships following from Landau's theory for second-order phase transitions. This is important, because it was not clear whether the thermodynamic relationships predicted by the Landau theory are still valid for large values of both the magnetocaloric effect, $\Delta T$, and the magnetic field. The results obtained should also

* Corresponding author.
*E-mail address:* jacek.cwik@ml.pan.wroc.pl (J. Ćwik).

http://dx.doi.org/10.1016/j.jmmm.2017.03.027
0304-8853/

have practical importance, as they provide the basis for extrapolation of the adiabatic temperature change for a given field change, $\Delta T/\Delta H$, to the region of high magnetic fields.

## 2. Experimental details

An experimental device has been designed, constructed and developed, that allowed direct MCE measurements in magnetic fields of up to 14 T in the temperature range of 4.2–350 K using the extraction method (see Fig. 1). A Bitter-type magnet generated steady magnetic field. Both the temperature of the sample and the temperature change (due to MCE) were measured using a differential thermocouple. The sample was encased within a thermal screen to minimize heat exchange with the environment. The temperature was controlled by a Lake Shore® thermo-controller. A Hall sensor placed in the sample holder was used to measure the magnetic field. Movement of the sample to and from the region of the maximum magnetic field was forced with a LinMot® actuator [25]. A carbon fiber tube (1 m long, 4 and 6 mm in the inner and outer diameter, respectively) was connected to the actuator with one end and to the sample with the other. The sample was moved during 1 s from the center of the Bitter magnet to the outside (or vice versa) at a distance of 35 cm. It should be noted that the magnetic field values, initially for magnetization and finally for demagnetization, were less than 2 % of the maximum field in the center of the solenoid. Both the temperature of the sample and the temperature change (due to MCE) were measured using differential copper-constantan and chromel-gold (at low temperatures) thermocouples with the accuracy better than 0.1 and 0.05 K, respectively. An influence of the magnetic field on the thermocouples has been tested with a copper block used as the sample and no adiabatic temperature change has been observed within above specified accuracies. We have developed computer software which recorded the adiabatic temperature change ($\Delta T$), sample temperature ($T$), and magnetic field ($H$). To gauge these quantities, voltage from thermocouples and Hall sensor has been measured with Keithley 2010 multimeters. All MCE measurements were carried out on a sample that was made of sublimated dendrite lump polycrystalline gadolinium of 99.99% purity (REacton – Alfa Aser).

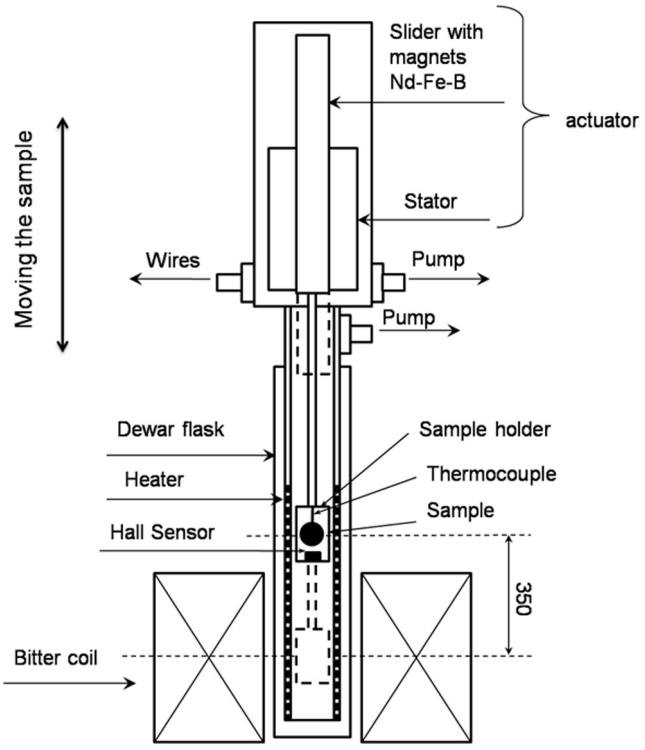


**Fig. 1.** Schematic diagram of the setup used for direct measurements of MCE at temperatures from 4 to 350 K and magnetic field changes up to 14 T.

## 3. Results and discussion

The change of the magnetic field and the resulting change of the sample temperature during MCE measurements are shown in Fig. 2. The results have been collected as a function of time during the alternating magnetization and demagnetization process of the sample under adiabatic conditions. One can notice the efficiency and reproducibility of the MCE due to minimized heat leaks between the sample and its surroundings. Results of direct MCE measurements for the polycrystalline Gd sample are shown in Fig. 3. The $\Delta T(T_{start})$ dependences, where $T_{start}$ is the initial temperature, obtained for both magnetization and demagnetization processes, are typical peaked curves. The maximum value of MCE measured during magnetization and demagnetization occurred at different initial temperatures (see Fig. 3). The maximum value of MCE obtained for demagnetization was shifted to higher $T_{start}$ by about 20 K, which corresponds to the maximum value of $\Delta T$ = 19.5 K obtained in the magnetic field of 14 T. This is due to the fact that during the magnetization and demagnetization processes, which begin at the same initial temperature $T_{start}$, the sample is in a different thermodynamic state revealing heating and cooling, respectively, as shown schematically in Fig. 4.

The total entropy of a magnetic material at constant pressure can be expressed in general as:

$$S(H,T) = S_M(H,T) + S_L(H,T) + S_e(H,T) \quad (1)$$

where $S_M$ is the magnetic entropy, $S_L$ is the lattice and $S_e$ is the electron contribution to the total entropy. However, in the first approximation we can assume that the lattice and electron parts of the entropy depend only on temperature. In that case, the isothermal magnetic entropy change $\Delta S_M(T,H)$ can be defined as:

$$\Delta S_M(T,H) = S_M(T,H_2) - S_M(T,H_1) = S(T,H_2) - S(T,H_1) \quad (2)$$

where $H_2 - H_1 = \Delta H$ denotes the change of magnetic field.

The adiabatic temperature change $\Delta T(T)$ and the isothermal magnetic entropy change $\Delta S_M(T)$ are shown schematically in Fig. 4 for Gd single crystal in the vicinity of a phase transition. The $S(T)$ curves at constant pressure were determined by the formula:

$$S(H,T) = \int_0^T \frac{C_P(H,T)}{T} dT \quad (3)$$

where heat capacity values $C_p(T,H)$ for $\mu_0 H$ = 0 and 5 T were taken from Ref. [16]. In Fig. 4, AB is $\Delta T_{magn}$ obtained during adiabatic magnetization when the magnetic field changes from zero to 5 T, CD is $\Delta T_{demag}$ obtained during adiabatic demagnetization, and CA is the isothermal magnetic entropy change $\Delta S_M(T)$. Points A and C refer to the same temperature, but belong to different $S(T)$ curves. Thus, $|\Delta T_{magn}| \neq |\Delta T_{demagn}|$ when the magnetization and demagnetization processes start at the same temperature, as in our experiment. The isothermal magnetic entropy change $\Delta S_M(T)$ explains the shift of the peak on the $\Delta T(T_{start})$ dependence (see Fig. 3), as mentioned earlier. Thus, for magnetic refrigerators, which make use of the demagnetization process, magnetic materials with a Curie temperature below room temperature can be used as refrigerants. If, in the case of adiabatic demagnetization process, the temperature of the sample in zero magnetic field $T_{H=0}$ is taken as the reference temperature (point D in Fig. 4), the curve for adiabatic demagnetization process (Fig. 3) shifts to the left by the value of $\Delta T_{demag}$. In this case,

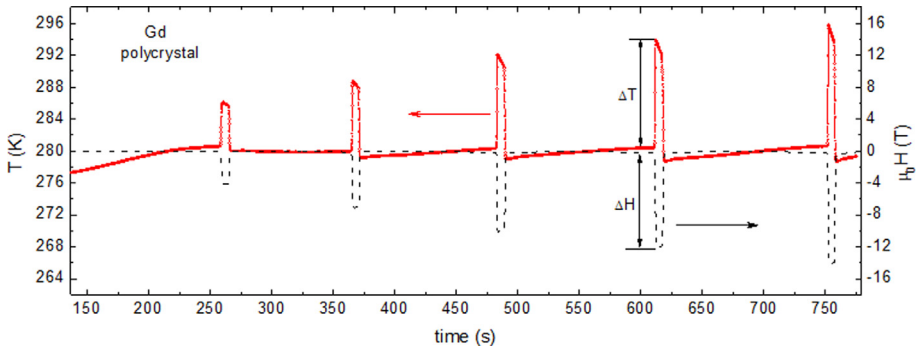


**Fig. 2.** Time dependences of the magnetic field change (dashed line) and the resulting temperature change (solid red line) for a Gd sample in the course of experiment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

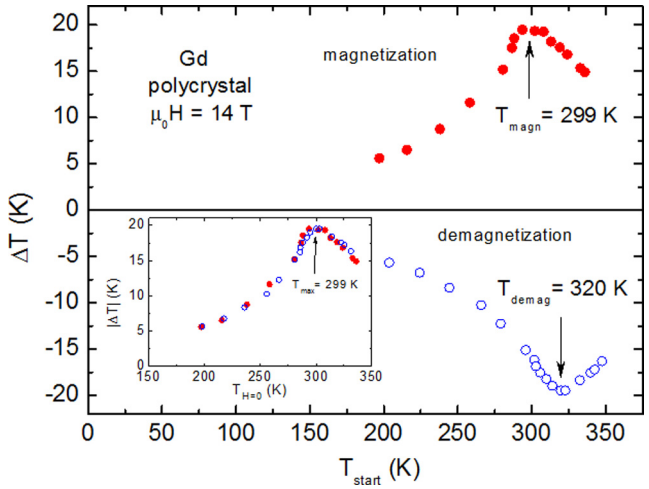


**Fig. 3.** Temperature change $\Delta T$ as a function of the initial temperature, $T_{start}$, for the Gd sample during magnetization (closed red circles) and demagnetization (open blue circles) in 14 T magnetic fields. Arrows point to the temperature corresponding to the maximum $\Delta T$. Inset shows $|\Delta T|$ vs. $T_{H=0}$ obtained from the $\Delta T(T_{start})$ dependence for magnetization and demagnetization processes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

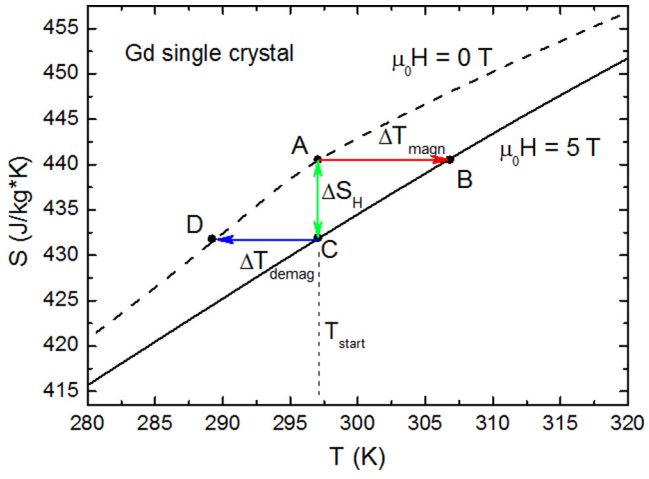


**Fig. 4.** Entropy of Gd single crystal plotted as a function of temperature at 0 (dashed line) and 5 T (solid line) magnetic fields. The results have been obtained using the heat capacity values reported in Ref. [16].

the $\Delta T$ magnitude during adiabatic demagnetization is equal in value to $\Delta T$ during adiabatic magnetization, i.e., |DC| = |CD| and |BA| = |AB| (Fig. 4). Because of that, when the $T_{start}$ temperature is taken as the reference temperature for both magnetization and demagnetization processes, we observe the shift of the maximum in the $\Delta T(T_{start})$ dependences by 20 K, which is the maximum adiabatic temperature change ($\Delta T$) for a magnetic field change of 14 T. The insert in Fig. 3 shows the temperature dependences $|\Delta T|$ vs $T_{H=0}$ obtained from the temperature dependences of $\Delta T$ measured once during adiabatic magnetization and second time during adiabatic demagnetization. As shown in the Figure, the dependences plotted versus $T_{H=0}$ fully coincide. Similar features of MCE measured for polycrystalline gadolinium at low magnetic fields were reported previously [19].

The magnetic field dependence of MCE was measured in the vicinity of the phase transition in various fields. These plots are shown in Fig. 5. The value of $\Delta T$ increases non-linearly with the magnetic field, however the $\Delta T(H)$ is far from saturation. Thus, a much larger $\Delta T$ is expected in fields higher than 14 T. As one can draw from Fig. 5, with an increasing field the characteristic quantity $\Delta T/\mu_0 H$ decreases from 2.6 K/T in 1 T to 1.4 K/T in 14 T at 294 K. More data are shown in Table 1. In Fig. 6 our $\Delta T(H)$ results are compared with those obtained by other authors and reveal very good correlation. Our results, however, extend the already published data to a region of much higher magnetic fields. Note, that single-crystal gadolinium can also demonstrate high $\Delta T/H$ values [18]. The MCE of single-crystal gadolinium was studied by an indirect method. For Gd magnetized along the [0001] axis in a field of 10 T, $\Delta T$ reached 19.5 K. This value is 25 % higher than that

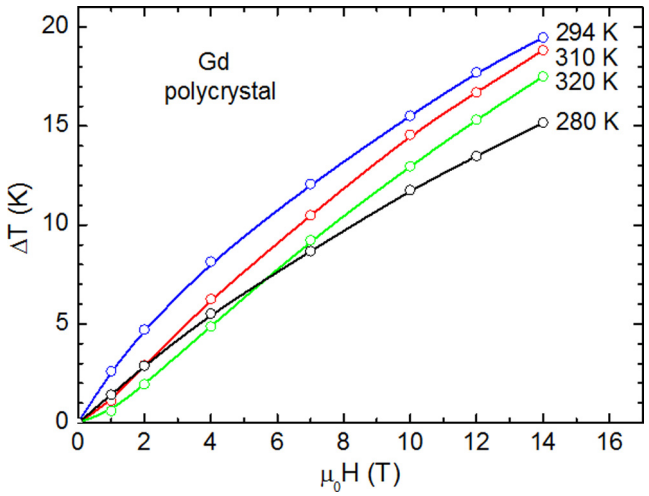


**Fig. 5.** Magnetic field dependences of the adiabatic temperature change $\Delta T$ for the Gd sample measured during magnetization process an initial temperature $T_{start}$ = 280, 294, 310 and 320 K.

**Table 1**
Ratio $\Delta T/\mu_0 H$ for the different magnetic field changes, $\mu_0 H$, for Gd upon its magnetization from zero field to $H$ or demagnetization from $H$ to zero field at temperatures close to the magnetic phase transition temperature ($T_C$ = 293.4 K).

| $\mu_0 H(T)$ | 1 | 2 | 4 | 7 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|
| $\Delta T/\mu_0 H$ (K/T) | 2.6 | 2.4 | 2 | 1.7 | 1.6 | 1.5 | 1.4 |

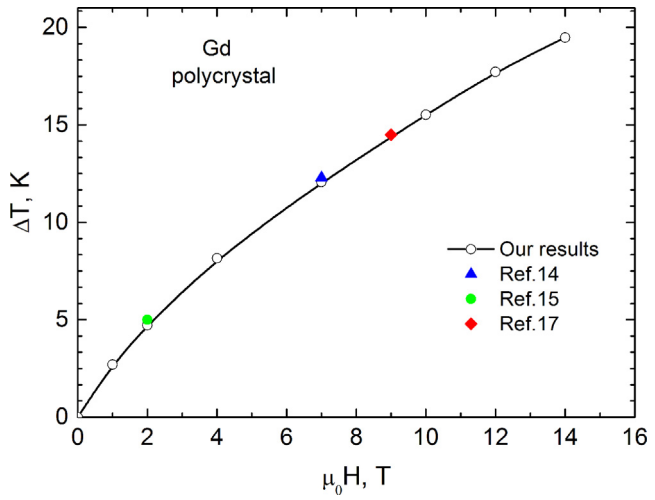


**Fig. 6.** Comparison of the $\Delta T(\mu_0 H)$ data obtained in this work with those reported by other authors at temperatures close to the magnetic phase transition temperature of Gd ($T_C$ = 293.4 K).

observed for polycrystalline Gd in our studies. Such a difference can be related to the random grain orientation in polycrystalline Gd. Anisotropic properties of MCE in single crystalline Gd have been shown previously in [12].

Experimental results can be interpreted within the framework of the thermodynamic Landau theory. According to this theory, the equation for the magnetization of paraprocess near the Curie temperature can be written as [26]:

$$\alpha \cdot I + \beta \cdot I^3 = H \tag{4}$$

where $\alpha$ and $\beta$ are the thermodynamic Landau coefficients, and $I$ is the volume magnetization. The expression for MCE caused by an adiabatic change of magnetization is:

$$dT = -\frac{T}{C_{I,P}}\left(\frac{\partial H}{\partial T}\right)_I dI \tag{5}$$

Near the Curie temperature, the $\beta$ coefficient is only weakly dependent on temperature and therefore the temperature derivative from Eq. (4) equals to:

$$\left(\frac{\partial H}{\partial T}\right)_I = \alpha_1 I \tag{6}$$

Substituting Eq. (6) into Eq. (5) we obtain:

$$dT = -\frac{\alpha_1 T}{C_{I,P}} I dI \tag{7}$$

Integration of the expression (7) leads to:

$$\Delta T = \int_0^I \frac{\alpha_1 T}{C_{I,P}} I dI = \frac{\alpha_1 T}{2C_{I,P}} I^2 \tag{8}$$

Thus MCE must obey the law of proportionality to the square of the magnetization in the region of paraprocess [26]:

$$\Delta T = k \cdot I^2 \tag{9}$$

where $k = \frac{\alpha_1 T}{2C_{I,P}}$. This was confirmed by the experiment of Weiss and Piccard [27].

The magnetic field dependence of $\Delta T$ can be described by the equation of state following from the thermodynamic Landau theory:

$$\frac{\alpha + \gamma P}{k^{1/2}} + \frac{\beta}{k^{3/2}}\Delta T = \frac{H}{\Delta T^{1/2}}, \tag{10}$$

As one can see from Eq. (10), $\Delta T \sim H/\Delta T^{1/2}$ or $\Delta T \sim H^{2/3}$. The $H/\Delta T^{1/2}$ vs. $\Delta T$ and $\Delta T$ vs $H^{2/3}$ dependences obtained for the MCE results are shown in Fig. 7. Adiabatic temperature change for a given field change, $\Delta T/\Delta H$, is dropping with increasing field due to the nonlinear dependence of $M(H)$ and beginning of the saturation process. Note that the experimental points fit a straight line well, confirming the complete applicability of Landau's thermodynamic theory to the description of MCE of Gd near the Curie point. It is important to note that this theory also works accurately in high magnetic fields, up to at least 14 T. It is known that the maximum magnetic entropy can be calculated by expression:

$$S_M^{max} = R\ln(2J+1) \tag{11}$$

where $R$ is the universal gas constant, $J$ is the total angular momentum, which, for Gd, is 7/2. Thus, the maximum magnetic entropy of Gd is 17.3 J/mol K. Assuming that the maximum magnetic field which can be reached under laboratory conditions is 100 T [28,29] and using magnetization data available in [5], an entropy change

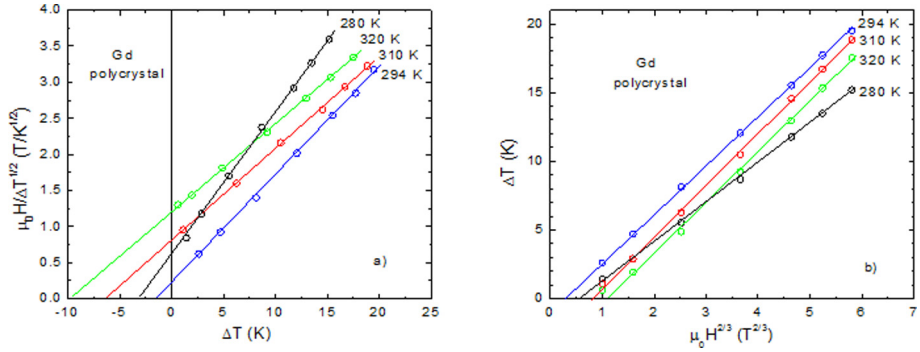


**Fig. 7.** Experimental data (circles), obtained for the Gd sample from MCE measurements and the functional dependences (solid lines) derived from Eq. (9): a) $\mu_0 H/\Delta T^{1/2}$ vs $\Delta T$, and b) $\Delta T$ vs $\mu_0 H^{2/3}$.

of 8.5 J/mol K is expected in this field. Taking into account expression $\Delta T \sim H^{2/3}$, we determine that to reach the maximum magnitude of MCE, magnetic fields of ~ 300 T should be applied.

## 4. Conclusion

In conclusion, the specificity of the MCE measuring system, which was designed and assembled by the authors, is described. It allows the adiabatic temperature change, $\Delta T$, to be measured directly using fast moving of a sample from or into a magnetic field. The application of a stationary magnetic field allows one to reach the thermodynamic equilibrium between a temperature sensor and a sample, whereas, in using pulsed magnetic fields, such equilibrium can't be obtained. The proposed technique was used to measure MCE parameters of polycrystalline Gd in steady magnetic fields up to 14 T. It was shown that the MCE arising in Gd in high magnetic fields results in the adiabatic temperature change $\Delta T$ = 19.5 K for a field change of 14 T. Similar values of the adiabatic temperature changes obtained for the magnetization and demagnetization processes confirm accuracy of the experimental method being developed. Moreover, it has been experimentally proved that the relationships derived from the Landau theory for second-order phase transitions provide the adequate description of the $\Delta T$ vs $H$ dependence in high magnetic fields, around the Curie temperature. This fact demonstrates also the practical importance of experimental results since $\Delta T$ can be calculated for a wide magnetic field range when experimental $\Delta T$ is available for any particular magnetic field.

The research was supported by RFBR Grant 13-02-00916 (T.I.I, S.A.N), and the project No. 146-MAGNES of the ERA.Net RUS Plus initiative of the EU 7th Framework Programme (Yu.S.K, J.Ć, M.M, and K.R).

## References

[1] E. Warburg, Ann. Phys. 13 (1881) 141.
[2] A.S. Andreenko, K.P. Belov, S.A. Nikitin, A.M. Tishin, Sov. Phys. Usp. 32 (1989) 649 (in Russian).
[3] V.K. Pecharsky, K.A. Gschneidner Jr., A.O. Pecharsky, A.M. Tishin, Phys. Rev. B. 64 (2001) 144406.
[4] O. Tegus, E. Brück, K.H.J. Buschow, F.R. de Boer, Nature 415 (2002) 150.
[5] A.M. Tishin, Y.I. Spichkin, The Magnetocaloric Effect and Its Application, IoP, Bristol, 2003.
[6] G.J. Miller, Chem. Soc. Rev. 35 (2006) 799.
[7] E. Brück, Handbook of Magnetic Materials, chapt. 4, 2007, p17.
[8] R. Paul, T. Paramanik, K. Das, P. Sen, B. Satpati, I. Das, J. Magn. Magn. Mater. 417 (2016) 182.
[9] K. Das, T. Paramanik, I. Das, J. Magn. Magn. Mater. 374 (2015) 707.
[10] K.P. Belov, Magneto thermal phenomena in the rare-earth magnetic, ed. Nauka, Moscow, 1990 (in Russian).
[11] S.A. Nikitin, Magnetic properties of rare-earth metals and their alloys, ed. MGU, Moscow, 1989 (in Russian).
[12] S.A. Nikitin, E.V. Talalaeva, L.A. Chernikova, G.E. Chuprikov, T.I. Ivanova, G.E. Kazakov, G.A. Yarkho, Zh. Eksp, Teor. Fiz. 74 (1978) 205 (in Russian).
[13] S.M. Benford, G.V. Brown, J. Appl. Phys. 52 (1981) 2110.
[14] B.K. Ponomarev, J. Magn. Magn. Mater. 61 (1986) 129.
[15] S.Yu. Dan'kov, A.M. Tishin, V.K. Pecharsky, K.A. Gschneidner Jr., Rev. Sci. Instrum. (1997) 2432.
[16] V.K. Pecharsky, K.A. Gschneidner, J. Appl. Phys. 86 (1999) 565.
[17] B.R. Gopal, R. Chahine, T.K. Bose, Rev. Sci. Instrum. 68 (1997) 1818.
[18] S.Yu. Dan'kov, A.M. Tishin, V.K. Pecharsky, K.A. Gschneidner, Phys. Rev. B 57 (1998) 3478.
[19] M. Ghahremani, H.M. Seyoum, H. ElBidweihy, E. Della Torre, L.H. Bennett, AIP Adv. 2 (2012) 032149.
[20] S.A. Nikitin, A.S. Andreenko, A.M. Tishin, A.M. Arkharov, A.A. Zherdev, Phys. Met. Metall. 60 (1985) 56 (in Russian).
[21] G.S. Burkhanov, N.B. Kolchugina, E.A. Tereshina, I.S. Tereshina, G.A. Politova, V. B. Chzhan, D. Badurski, O.D. Chistyakov, M. Paukov, H. Drulis, L. Havela, Appl. Phys. Lett. 104 (2014) 242402.
[22] V. Franco, A. Conde, J.M. Romero-Enrique, Y.I. Spichkin, V.I. Zverev, A.M. Tishin, J. Appl. Phys. 106 (2009) 103911.
[23] M.D. Kuz'min, K.P. Skokov, D.Yu. Karpenkov, J.D. Moore, M. Richter, O. Gutfleisch, Appl. Phys. Lett. 99 (2011) 012501.
[24] A.P. Kamantsev, V.V. Koledov, A.V. Mashirov, E.T. Dilmieva, V.G. Shavrov, J. Cwik, I.S. Tereshina, Solid State Phenom. 233 (2015) 216.
[25] http://www.linmot.com/.
[26] K.P. Belov, Magnetic Transitions, Consultants Bureau (eds.), New York, 1961.
[27] P. Weiss, A. Piccard, Compt. Rend. 166 (1918) 352.
[28] J.R. Sims, D.G. Rickel, C.A. Swenson, J.B. Schillig, G.W. Ellis, C.N. Ammerman, IEEE Trans. Appl. Supercond. 18 (2008) 587.
[29] T. Peng, F. Jiang, Q.Q. Sun, Y. Pan, F. Herlach, L. Li, IEEE Trans. Appl. Supercond. 26 (2016) 4300504.