

# Existence of cryogenic magnetic entropy change in Gd based nanoparticles

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Magnetic nanoparticles with average diameter of 5–7 nm were prepared by nanocasting method inside of the pores of periodic silica matrix of SBA15 type. The uniform size of the pores limited the particles' growth what resulted in formation of nanocomposite consisting of monodisperse nanoparticles of  $\text{Gd}_2\text{O}_3$  embedded in amorphous silica matrix. Magnetic properties of the material were examined in magnetic fields up to 5 T and in temperature range 2–52 K. The magnetic entropy change of 29 J/kg·K was observed at 2 K for field variation 5 T in the investigated nanocomposite what suggests this material could be feasible for cryomagnetic refrigeration applications.

PACS: 75.30.Sg Magnetocaloric effect, magnetic cooling;  
81.05.Rm Porous materials; granular materials;  
75.20.Ck Nonmetals;  
75.75.Fk Domain structures in nanoparticles.

Keywords: nanoparticles, magnetocaloric effect, magnetic entropy change.

## 1. Introduction

Magnetocaloric effect (MCE) in magnetic materials has been topical from basic and practical points of view for many years. MCE becomes evident as a temperature change of a magnetic material due to the change in magnitude of applied external magnetic field. For a long time, this effect has been called adiabatic demagnetisation, but this phenomenon is only the one of practical applications of the MCE in magnetic materials [1,2]. MCE was discovered for the first time in iron by Emil Warburg in 1881 [3]. In 1926–1927, Debye [4] and Giauque [5] each independently explained the process of reaching very low temperatures using method of adiabatic demagnetization. In the 1930's, when refrigerators became widely used, the MCE became the first method of reaching temperatures below 0.3 K. Beside of this practical application (energy efficient and environmentally friendly magnetic refrigerators, liquefaction of hydrogen or helium [1]), strong relation of MCE with nature of magnetism can give further information

about magnetic phase transitions and spin structures. Several compounds, particularly those based on gadolinium, are now in extensive interest because of the discovery of their new properties that contribute to exhibit large MCE [6,7]. Hong Zeng *et al.* [8] presented a work in which magnetocaloric properties of the as-consolidated nanocrystalline and coarse-grained gadolinium metals were studied. With the decrease of Gd grains from micrometer to nanometer range, magnetic entropy change drops surprising from 10.07 to 4.47 J/kg·K under the magnetic field change of 5 T, and their resultant magnetic entropy change uniformly peaks at 294, 290, and 288 K, respectively, corresponding to the magnetic transition temperature of the three samples. Meanwhile, the nanostructures do not change the magnetic transition and the second-order magnetic transitions still remain. The Curie temperature  $T_C$  of the nanocrystalline Gd shifts by more than 6 K below that of coarse-grained Gd sample. The values of magnetic entropy change of the nanocrystalline metals exhibit a more constant tendency compared with the coarse-grained sam-

ple. This large temperature interval with almost constant value of  $\Delta S$  could be interesting for magnetic refrigeration applications at room temperature [8].

With the rapid progress in nanoengineering, brand new structures and nanoscale systems are currently waiting for profound investigation with respect to their magnetocaloric properties. There are some feasible features in nanostructures which are fundamentally absent in bulk materials. For instance, it is possible to tailor intrinsic properties like magnetization or magnetic anisotropy of nanoparticle by variation of its size, shape or coating layer. Furthermore, nanoparticles are characterised by high surface to volume ratio (in comparison with bulk materials) thus there is an assumption that such structures would transfer the heat with considerably higher efficiency in comparison with bulk materials.

Assuming feasible MCE properties of gadolinium based compounds and nanostructures, we decided to prepare and study nanocomposite consisting of  $Gd_2O_3$  nanoparticles embedded in periodic nanoporous silica matrix of SBA15 type with hexagonal symmetry. Although excellent biomedical applications of  $Gd_2O_3$  nanoparticles are already well known the magnetocaloric response of such material has never been investigated yet.

## 2. Experimental materials and methods

Studied sample consisting of  $Gd_2O_3$  nanoparticles in periodic nanoporous silica matrix of SBA15 type was prepared by nanocasting. The structure and magnetic properties of blank SBA15 matrix have been studied and it was published elsewhere [9,10]. The HRTEM (high-resolution transmission electron microscopy) micrographs were taken with JEOL 2100F microscope. Copper grid coated with a holey carbon support was used to prepare samples for the TEM observation. The bright-field TEM image was obtained at 200 kV. EDX (energy-dispersive x-ray spectroscopy) measurement performed by TEM and XANES (x-ray absorption near edge structure) spectra confirmed the presence of  $Gd_2O_3$  [11]. Nanoparticles inside pores were close to spherical shape with size up to 7 nm. The detailed structural study was described elsewhere [11,12].

Magnetic properties were studied using commercial MPMS 5XL (Quantum Design). The dependences of magnetization on field magnitude (up to 5 T) were recorded in temperature range 2–52 K with the step of 1 K. The powder sample with the mass of  $m = 3$  mg was encapsulated into a gelatin capsule and inserted into the plastic sample holder. The signals of diamagnetic contributions of gelatin capsule and plastic sample holder were measured and subtracted from experimental data.

Experimental isothermal magnetization data were processed according to Maxwell equation employing Matlab software in order to calculate the dependence of magnetic entropy change on temperature of the investigated material.

## 3. Results and discussion

The structure of Gd based nanoparticles encapsulated inside porous silica matrix was studied in our previous works [11,12]. Figure 1 (left) shows the scheme of the examined nanoparticles inside of porous silica matrix with hexagonal symmetry. The structure of studied sample investigated by transmission electron microscope can be seen in the Fig. 1 (right). After incorporation of Gd based nanoparticles inside of blank periodic matrix, the  $Gd_2O_3$  nanoparticles are visible as black spots and additionally the perfectly ordered porous matrix (can be seen in [9–12]) is disturbing slightly, Fig. 1 (right). Nanoparticles with average size up to 7 nm can be identified from TEM micrographs.

Figure 2 shows the temperature dependence of susceptibility and reciprocal magnetic susceptibility  $1/\chi$  of the composite. Experimental data confirmed almost typical paramagnetic behavior as it was expected.

Isothermal  $M(H)$  data of investigated material are presented in Fig. 3. The curves recorded at lowest temperatures resemble “S” shape with the tendency of becoming almost linear with increasing temperature. Paramagnetic or superparamagnetic materials are characterised by manifest this behavior what is in line with the magnetic susceptibility vs temperature measurements results presented in the Fig. 2.  $M(H)$  data was used for revelation of magnetocaloric properties of the material. Magnetic entropy change ( $\Delta S_M$ ) calculations were carried out employing Maxwell equation and processing the data by Matlab software.

Maxwell relation [13]  $(\partial M/\partial T)_H = (\partial S/\partial H)_T$  express how change in magnetization induces magnetic entropy change, and vice versa. In the case of isothermal-isobaric process after integration we get [14]

$$\Delta S_M = \int \left( \frac{\partial M}{\partial T} \right)_H dH. \quad (1)$$

Refrigeration capacity, RC, which is the measure of the energy that can be transferred between cold and hot reservoirs, is crucial parameter characterizing magnetocaloric

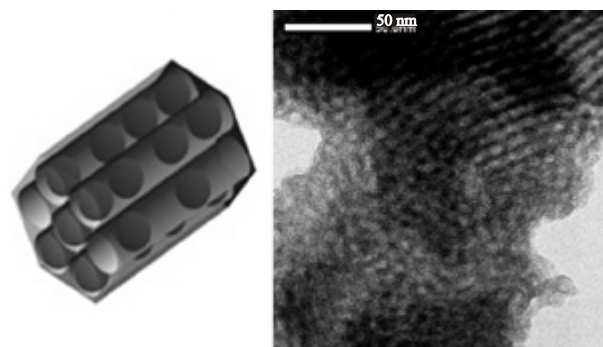


Fig. 1. Scheme (left) and transmission electron microscope micrograph of  $Gd_2O_3$  and  $SiO_2$  nanocomposite (right).

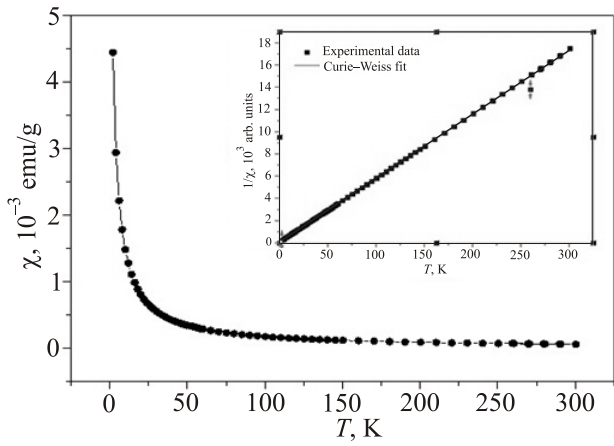


Fig. 2. Temperature dependence of magnetic susceptibility and Curie–Weiss fit of data of  $\text{Gd}_2\text{O}_3$  and SBA15.

properties of material, and serves for a comparison of the qualities of different refrigerants. It is defined as [13]

$$RC(\Delta H) = \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S_M(T, \Delta H) dT \quad (2)$$

where  $\Delta H$  is the difference between minimum and maximum applied fields. Usually, its approximated value calculated as full width at half maximum of the  $\Delta S_M(T)$  peak times the peak value  $\Delta S_M^{pk}$  is reported in the literature. However, our  $\text{Gd}_2\text{O}_3$  and  $\text{SiO}_2$  nanocomposite does not exhibit peak in  $\Delta S_M(T)$  dependences (Fig. 4), thus we were not able to establish the RC value which we could compare with other materials. Due to this, we focused on the evaluation of magnetic entropy change on temperature dependence.

There is a suitable approximation of the Eq. (1) for the discrete measurements [14]

$$\Delta S_M \left( \frac{T_{n+1} + T_n}{2}, H \right) = \sum \frac{(M_{n+1} - M_n) H \Delta H}{T_{n+1} - T_n}, \quad (3)$$

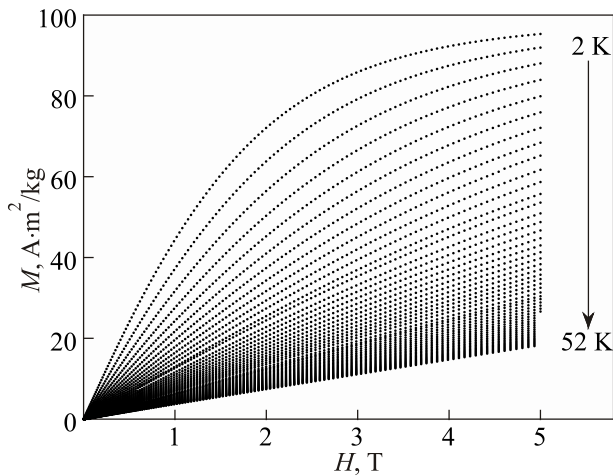


Fig. 3. Isothermal magnetization data of  $\text{Gd}_2\text{O}_3$  and  $\text{SiO}_2$  nanocomposite up to applied field of 5 T obtained at temperature range 2–52 K with the step 1 K.

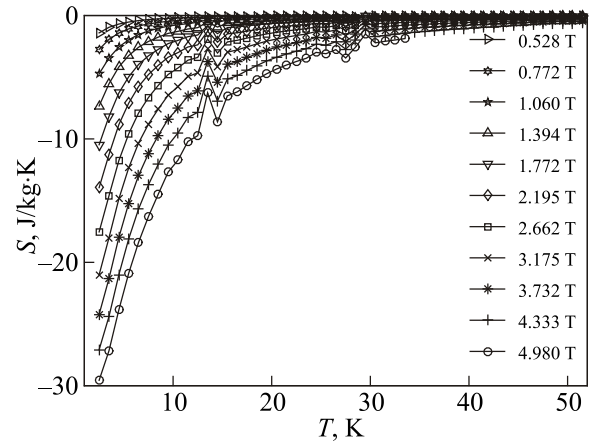


Fig. 4. Magnetic entropy change vs temperature dependences of  $\text{Gd}_2\text{O}_3$  and  $\text{SiO}_2$  nanocomposite for the applied field variations from 0.5 T to almost 5 T. For the sake of transparency, only each 10 of 150 curves is displayed.

where  $M_n$  and  $M_{n+1}$  are the magnetization values measured in magnetic field  $H$  at temperatures  $T_n$  and  $T_{n+1}$ , respectively.

The temperature dependence of  $\Delta S_M$  at different magnetic field variations (up to 5 T) calculated from isothermal magnetization data is shown in Fig. 4. Only slight increase of  $|\Delta S_M|$  with decreasing the temperature can be seen at higher temperature region. On the other hand,  $|\Delta S_M|$  enhances steeply with decreasing the temperature to lowest region of 2–10 K. The maximal value established for the studied material was  $|\Delta S_M| \sim 29 \text{ J/kg}\cdot\text{K}$  at 2 K for field variation 5 T. This behavior is characteristic of paramagnetic salts and observed maximal value of  $|\Delta S_M|$  can be considered as significantly large [6,15].

Examined material combines several features feasible for potential magnetocaloric refrigerants. As it was demonstrated on nanoscaled gadolinium iron garnets ( $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ ) by Phan *et al.* [16], decrement in the diameter of the particles can lead to the magnetic entropy change magnitude enhancement along with the shift of the maximum towards lower temperatures. Baldomir *et al.* [17] and Shull *et al.* [18] showed that wide size distribution of nanoparticles has deleterious effect on the magnitude of magnetic entropy change of the system. Considering relative high  $|\Delta S_M|$  along with the fact that our system consists of uniform nanoparticles of low diameter, the perspectives of its applications can be found in cryogenic refrigeration.

### 3. Conclusions

In this work we studied magnetic entropy change of  $\text{Gd}_2\text{O}_3$  and  $\text{SiO}_2$  nanocomposite prepared by nanocasting of  $\text{Gd}_2\text{O}_3$  nanoparticles in periodic nanoporous silica matrix with hexagonal symmetry. Calculations carried out applying Maxwell equation on experimental isothermal magnetization data obtained at temperature range 1.8–52 K at external magnetic fields up to 5 T revealed large cryo-

genic (at 2 K) magnetic entropy change  $|\Delta S_M| \sim 29 \text{ J/K}\cdot\text{kg}$  of the material. Results of the study suggest that  $\text{Gd}_2\text{O}_3$  and  $\text{SiO}_2$  nanocomposites could be promising material for low temperature refrigeration technology.

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1. A.M. Tishin and Y.I. Spichkin, *Int. J. Refrig.* **37**, 223 (2014).
2. A.M. Tishin, in: *Handbook of Magnetic Materials*, K.H.J. Buschow (ed.), North Holland, Amsterdam (1999), p. 395.
3. E. Warburg, *Ann. Phys.* **13**, 141 (1881).
4. P. Debye, *Ann. Phys.* **81**, 1154 (1926).
5. W.F. Giaque, *J. Amer. Chem. Soc.* **49**, 1864 (1927).
6. S. Ma, W.F. Li, D. Li, D.K. Xiong, N.K. Sun, D.Y. Geng, W. Liu, and Z.D. Zhang, *Phys. Rev. B* **76**, 144404 (2007).
7. Y. Meng, Y. Chen, Z. Zhang, Z. Lin, and M. Tong, *Inorg. Chem.* **53**, 9052 (2014).
8. H. Zeng, J. Zhang, C. Kuang, and M. Yue, *Appl. Nanosci.* **1**, 51 (2011).
9. V. Zeleňák, A. Zeleňáková, and J. Kovac, *Colloids Surf. A Physicochem. Eng. Asp.* **357**, 97 (2010).
10. A. Zeleňáková, V. Zeleňák, J. Bednarcik, P. Hrubovcak, and J. Kováč, *J. Alloy Comp.* **582**, 483 (2014).
11. V. Zeleňák, A. Zeleňáková, J. Kovac, and U. Vainio, *Nanocasting of  $\text{Gd}_2\text{O}_3$  in Porous Silica Matrix* (2011). [http://photon.science:desy:de\\_annual\\_report\\_files\\_2011](http://photon.science:desy:de_annual_report_files_2011)
12. A. Zeleňáková, O. Kapusta, and V. Zeleňák, *Acta Phys. Pol. A* **126**, 218 (2014).
13. H.B. Callen, *Thermodynamics*, Wiley, New York (1981).
14. V.K. Pecharsky and K.A. Gschneidner, Jr., *J. Magn. Magn. Mater.* **200**, 44 (1999).
15. S. Ma, W.B. Cui, D. Li, N.K. Sun, D.Y. Geng, X. Jiang, and Z.D. Zhang, *Appl. Phys. Lett.* **92**, 173113 (2008).
16. M.H. Phan, M.B. Morales, C.N. Chinnasamy, B. Latha, V.G. Harris, and H Srikanth, *J. Phys. D:* **42**, 115007 (2009).
17. D. Baldomir, J. Rivas, D. Serantes, M. Pereiro, J.E. Arias, M.C. Bujan-Nunez, and C. Vazquez-Vazquez, *J. Non-Cryst. Solids* **353**, 790 (2007).
18. R.D. McMichael, R.D. Shull, L.J. Swartzendruber, L.H. Bennett, and R.E. Watson, *J. Magn. Magn. Mater.* **111**, 29 (1992).