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Magnetic and magnetocaloric properties of Gd-based microparticles at cryogenic temperatures

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The results of a study of the structural, magnetic and magnetocaloric properties of Gd-based microparticles obtained by ball milling of rapidly quenched gadolinium ribbons are presented. Analysis of the structural data revealed the presence of gadolinium oxide and hydride phases. Based on the measurement of magnetic isotherms, a sufficiently high magnetocaloric effect was found at cryogenic temperatures.

Keywords: gadolinium powder, ball milling, structure, magnetocaloric effect, cryogenic temperatures.

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1. Introduction

The need for forced cooling in industry and everyday life requires significant energy costs. The transition to magnetic cooling, which is characterized by higher energy efficiency in comparison with the conventional compressor technology using gas as a working fluid, could reduce the severity of the problem. Moreover, the magnetic cooling technology promises the reduction of the noise and mechanical vibrations of operating devices, the reduction of the environmental risks due to the rejection of gases that destroy the ozone layer [1]. One of the key points in this direction is the search for appropriate magnetocaloric materials. Gadolinium still occupies a leading position as a working material for real devices in the field of room temperatures because of the corresponding value of the Curie temperature, a large magnetic moment and the absence of thermal hysteresis [2,3]. The working fluid of a magnetic refrigerator in the form of powder has additional advantages both in terms of heat transfer efficiency and the design of specific devices. It has recently been shown that grinding of Gd to a powder state makes it possible to increase the degree of field dependence of the change of the magnetic part of the entropy, which suggests an increase of the intensity of the response of the working fluid to an external magnetic field [4]. Currently, the need for the development of cryogenic magnetic cooling is increasing due to the increasing need for liquefaction of gases [5–7]. Until recently, binary and ternary intermetallic compounds based on rare earth elements and gadolinium oxide particles were considered promising materials for this temperature range [8,9]. The magnetocaloric properties of Gd powders at low temperatures have been poorly studied compared to the properties of Gd powders at the room temperatures. The results of studies of the magnetic and magnetocaloric properties of Gd microparticles in the field of cryogenic temperatures are presented in this paper.

2. Study methodology

The process of obtaining Gd powder consisted of two stages. Rapid-quenched Gd tapes were obtained at the first stage by spinning the melt onto a rotating copper disc. The purity of the used Gd was 99.96%, the linear rotation speed of the quenching surface of the disc was 20 m/sec. A Gd tape with a width of 3 mm and a thickness of 70 μm was obtained as a result. The rapid-quenched tape pre-cut into parts with the length of not more than 5 mm and the mass of 10 g at the second stage was subjected to many hours long grinding in a ball mill in an ethyl alcohol medium. The mass ratio of the steel balls and the ground tape was 66 : 1. The tape experienced only plastic deformation during the first hours of grinding in the mill because of high plasticity of gadolinium which was accompanied by growth of the area and reduction of the thickness of the parts of the tape. Preliminary experiments showed that grinding during 6 hours results in the beginning of the process of reduction of the geometric dimensions of the parts of the processed tape. The Gd powder studied in the paper was obtained as a result of grinding of a rapid-quenched tape for 12 h. Figure 1, *a* shows a general view of the powder particles. It can be seen that these particles have an irregular shape with a large size ranging from tens of nanometers to tens of microns, moreover, it can be either a single particle or a conglomerate of particles of different sizes.

The powder structure was studied using X-ray diffraction with automatic diffractometer PHILIPS X'PERT PRO (radiation Cu-Kα) and transmission electron microscopy

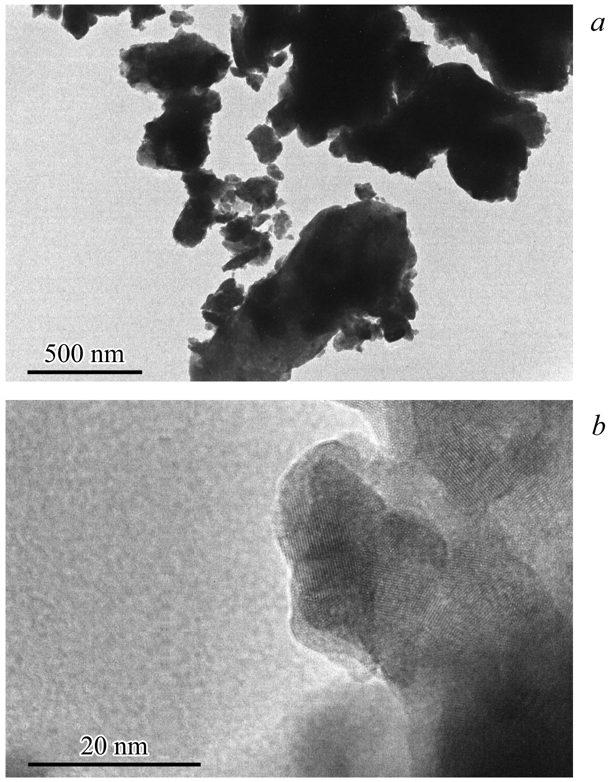

Figure 1. Images of Gd particles obtained using transmission electron microscopy: general view (*a*), high resolution (*b*).

(microscope JEM-2100). Magnetic measurements were performed using SQUID magnetometer. The change of the magnetic part of the entropy ΔS_M was determined using the measurements of magnetic isotherms based on the Maxwell ratio.

3. Results and discussion

The analysis of the results of structural studies suggests the multiphase nature of Gd particles. Figure 2 shows a diffractogram of Gd powder, the parameters of the peaks shown on it are collected in a table where they are compared with diffraction lines of HCP lattice of Gd, HCP lattice of gadolinium oxide Gd_2O_3 and FCC lattice of gadolinium hydride GdH_2. The presence of gadolinium oxide and hydride is most likely a consequence of machining of the powder in an ethyl alcohol medium. It is also necessary to note possible presence of a monoclinic phase of Gd_2O_3 whose most intense diffraction lines are in the range of angles 2θ from 28° to 32.5° (card JSPDS 43-1015) and intersect with the lines of Gd-hcp and Gd_2O_3 fcc in this angle range of angles. The analysis of images obtained using high-resolution electron microscopy (Figure 1, *b*) confirmed the presence of all three crystalline phases in the powder.

The position of the peaks on the diffractogram and their conformance with the diffraction lines of various compounds

Peak	2θ (deg.)	Gd, HCP	Gd_2O_3, FCC	GdH_2, FCC
1	28.8	(100)	(222)	
2	29.4			(111)
3	31.1	(002)		
4	32.6	(101)		
5	33.9			(002)
6	35.4		(411)	
7	42.7	(102)		
8	47.9		(440)	
9	48.7			(022)
10	50.5	(110)		
11	52.4		(611)	
12	56.2	(103)	(622)	
13	57.9			(113)
14	60.5	(112)		
15	64.5		(642)	
16	78.8	(203)		

The features on the temperature dependences of the magnetization $M(T)$ measured using the ZFC-FC protocol, at temperatures below 30 K constitute a definite confirmation of the presence of GdH_2 whose magnetic ordering temperature is approximately 22 K [10] (Figure 3). It is possible to find a correlation of these features with the Curie temperature of the metastable cubic phase of FCC-gadolinium [3], the blocking temperature of superparamagnetic particles of FCC-Gd or HCP-Gd [11], with a phase transition of surface Gd from the paramagnetic state to the spin glass state, which is attributable to the disorientation of spins on the surface of particles [12]. In particular, the blocking temperature of Gd particles of about 50 nm in size was approximately 35 K [13]. Taking into account the very wide variation in particle sizes in our Gd powder, as well as the presence of a high degree of particle surface defects due to the conditions of their preparation, none of the above possible causes of the occurrence of features on the dependencies $M(T)$ at $T < 50$ K cannot be excluded.

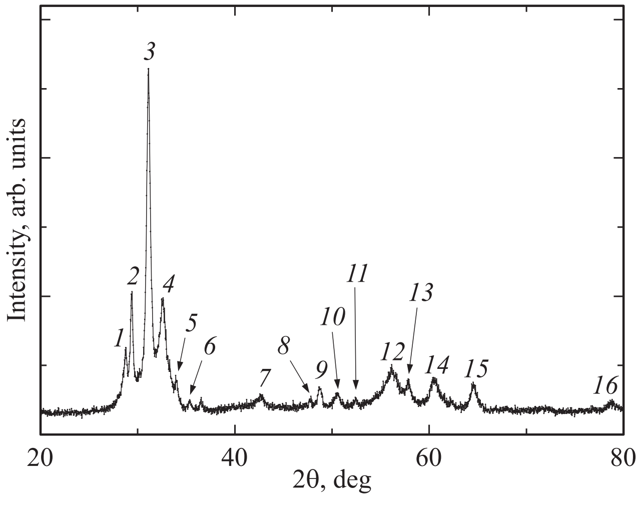

Figure 2. Diffractogram of Gd powder.

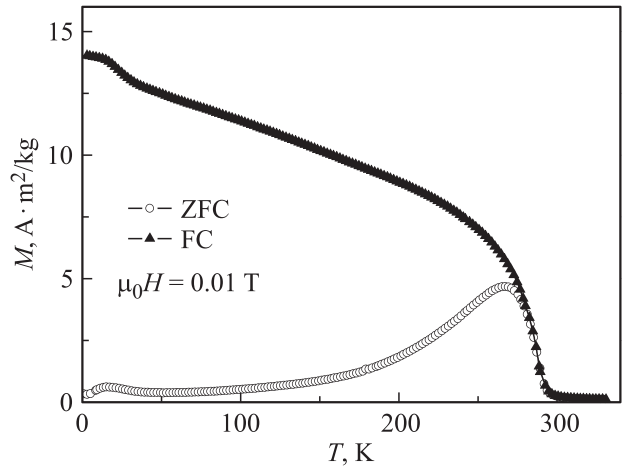

Figure 3. Temperature dependences of the magnetization of the Gd powder.

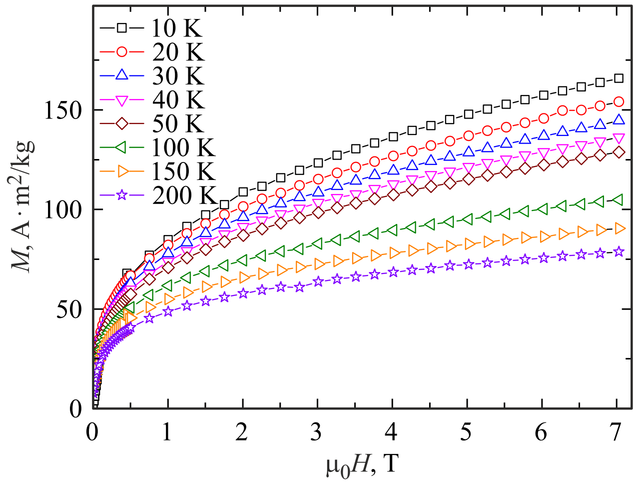

Figure 4. Magnetization curves of Gd powder.

It should also be noted that the dependences shown in Figure 3 $M(T)$ indicate that the hexagonal gadolinium with the Curie temperature of 293 K is the main phase of Gd microparticles.

The magnetic isotherms used to determine the change of the magnetic part of the entropy were measured in temperature increments of 10 K with a change of the magnetic field to 7 T. Figure 4 shows some curves $M(H)$ as an example.

The change of the magnetic part of the entropy ΔS_M was determined using the measurements of magnetic isotherms based on the Maxwell ratio

$$\Delta S_M = -\int_{H_2}^{H_1} \left(\frac{\partial M}{\partial T}\right)_H dH, \qquad (1)$$

where H — magnetic field, M — magnetization, T — temperature. The temperature dependence $\Delta S_M(T)$ for the field change amplitude of 7 T is shown in Figure 5. A rather sharp increase of the value of $-\Delta S_M(T)$ is observed at temperatures below 100 K. The maximum value of the change of the magnetic part of the entropy $-\Delta S_M^{\max} = 5.2$ J/kgK at $T = 15$ K for $\Delta\mu_0H = 7$ T, which is significantly less than the similar parameter of intermetallic compounds based on rare earth elements and particles of Gd_2O_3 [8,9]. However, $\Delta S_M^{\max}$ is not the only important indicator of a magnetocaloric material that determines its efficiency. Another significant characteristic is the relative cooling capacity (RCP) [14], which is determined as the product of $-\Delta S_M^{\max}$ and the temperature difference ΔT_{FWHM} at half height of the peak of dependence $-\Delta S_M(T)$:

$$RCP = -\Delta S_M^{\max}\Delta T_{\mathrm{FWHM}}. \qquad (2)$$

The value of RCP can be estimated in our case very approximately by making a number of assumptions [15]. We assume that the value $-\Delta S_M$ at $T = 15$ K corresponds to the peak on the dependence $-\Delta S_M(T)$, and the peak is symmetric relative to this temperature. Then half width of the peak $-\Delta S_M(T)$ at its half height is 45 K. As a result, we obtain $RCP \approx 470$ J/kg. This value RCP is less than for pure polycrystalline Gd near the phase transition temperature of 293 K ($RCP = 556$ J/kg for $\Delta\mu_0H = 5$ T) [16], but comparable with a similar parameter for complex oxides of rare earth elements, considered as a promising working material for cryogenic cooling devices [15].

At the moment, we do not have an unambiguous answer about the source of the magnetocaloric effect (MCE) in the studied Gd powder in the field of cryogenic temperatures. Our samples, as shown by structural studies, may contain antiferromagnetic phases of Gd_2O_3 and GdH_2 with the Neel temperature of 2–3 K and 22 K accordingly [10,18]. In addition, a phase transition of strongly deformed amorphous surface parts of Gd particles from the paramagnetic state to the spin glass state is possible at $T < 50$ K. Any of the mentioned phase transitions will result in an increase of the magnetic part of the entropy.

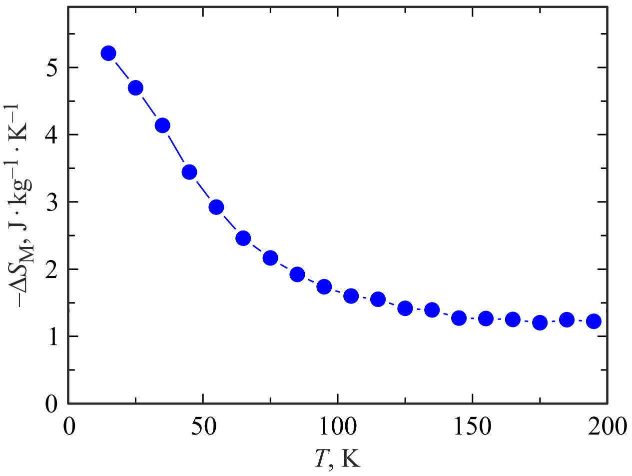

Figure 5. The temperature dependence of the change of the magnetic part of the entropy of the Gd powder. $\Delta\mu_0H = 7$ T.

4. Conclusion

A sufficiently high magnetocaloric effect was found in Gd-based microparticles at cryogenic temperatures ($\Delta S_M^{\max} = 5.2\,\text{J/kg·K}$ for $\Delta\mu_0 H = 7\,\text{T}$ at $T = 15\,\text{K}$). Its cause has yet to be determined. Taking into account the fact that the largest value of ΔS_M is observed near the phase transition temperature [6], it can be assumed that the main contribution to the MCE in this case is made by the phases of gadolinium oxide and hydride, whose magnetic ordering temperatures are below 30,K, the presence of which was discovered by structural studies. It is also not necessary to exclude the possibility of a phase transition from the paramagnetic state to the spin glass state, which is caused by the disorientation of spins on the strongly deformed surface of Gd particles.

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Conflict of interest

The authors declare that they have no conflict of interest.

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