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Comparison of isothermal and adiabatic magnetocaloric effects in Gd films and microwires

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A comparative analysis of the temperature and field dependences of the magnetization of Gd films and microwires was carried out, as well as an analysis of isothermal and adiabatic changes in the magnetic part of the entropy and heat capacity at temperatures close to the Curie temperature. The magnetocaloric effect in microwires exhibits two peaks at ~ 290 and ~ 320 K in the temperature dependence of the magnetic part of the entropy, in contrast to one peak in films. In films and microwires, the entropy maximum at ~ 290 K depends on the magnetic field, shifting equally in films and microwires with increasing field. In microwires, the second maximum at ~ 320 K does not change its position as the field increases to 9 T, but its amplitude increases linearly with increasing field. This maximum is due to a spin-reorientation transition in the phase with an increased Curie temperature.

Keywords: microwires, thin films, magnetic entropy, magnetic anisotropy, spin-reorientation transition, Curie temperature.

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1. Introduction

Magnetocaloric effects (MCE) in solids are well known and for a long time ensure high efficiency, the absence of toxic refrigerant, and the simplicity of the design of refrigerating machines based on them (see reviews [1–3]). This direction was further developed when considering other effects of a non-magnetic nature, the cyclic application of which also makes it possible to create a cooling cycle. For example, the strategy of solids cooling using mechanical deformation is currently being actively developed [4]. The possibility of non-magnetic effects use in magnetic cooling devices as an additional channel for increasing efficiency and cooling depth resulted to the creation of hybrid refrigerating machines in which the magnetic thermodynamic cycle is significantly closer to the Carnot cycle during synchronized operation of the magnetic cooling system with the Peltier element [5] or mechanical loading of the working fluid [6].

Gadolinium and its alloys are recognized as the best working fluid for refrigerating machines, because their Curie temperatures are close to room temperature, and there is a strong decrease in the temperature of the working fluid by $20-30$ K [3–6]. The abnormally high change in the magnetic part of the entropy ΔS_M in isothermal cycles and significant cooling ΔT [3–6] make gadolinium and its alloys promising for the development of new technologies of magnetic refrigerating machines. To improve magnetocaloric alloys the modification of the chemical composition is mainly used, varying the concentrations of transition and rare earth metals. Besides, heat treatment is often used to achieve optimal phase composition. These approaches, being used for a long time, largely exhausted themselves. Currently they are rep[laced by another approach to MCE improvement, it consists in the development of nano- and microstructures of the alloys that demonstrate the best properties in the macroscopic state [7–10]. High microstresses, the presence of long-lived nonequilibrium metastable phases that do not exist in macroscopic samples, a significant improvement in heat transfer in medium consisting of micro- or nanostructures — all this significantly increases the applicability of nanostructured alloys to achieve significant MCE values.

In addition, the considerable induced anisotropy of magnetization in microwires and films arising due to the texturing and mechanical deformation of the material can be used to improve the magnetic refrigerating machine design. In particular, in [11,12] it is shown, that a change in the crystal-lattice orientation of the gadolinium film substrate and in appropriate internal stresses created

by the substrate in the film, can result in a significant change in MCE. In [13] authors reported a complicated temperature dependence of magnetic anisotropy found in gadolinium microwires, which contained two maxima of entropy that indicated a complicated-stressed state and a two-phase structure. In nano- and microstructures, a significant magnitude of MCE can be achieved not only by changing the external magnetic field, but also by changing its orientation relative to the sample. Indeed, the MCE estimate should also take into account the factor of demagnetization, which depends on the sample's shape, as it is convincingly demonstrated in [14,15]. The main difference between microstructures and nanostructures in terms of their use in MCE-devices is evidently related to different mechanisms of remagnetization. In nanostructures, as a rule, a single-domain structure is observed, and remagnetization is realized by a coherent remagnetization. In microstructures the limit of single-domain state generally is not achieved, and the remagnetization is realized by means of nucleation of remagnetization nuclei or by domain wall spreading. However, the dynamics of domain walls, the size and type of domains can change significantly under the influence of induced magnetic anisotropy, specific to the highly stressed state of microstructures.

The objective of this study is to compare magnetic properties and parameters of the magnetocaloric effect in Gd submicron films and microwires.

2. Procedure and samples

W—Gd—W—MgO film heterostructures were produced by high vacuum magnetron sputtering deposition as described in [11,12]. Thickness of the gadolinium film was 100 nm. To suppress the oxidation the tungsten layers 5 nm thick were used. MgO with crystal-lattice orientation (111) was used as a substrate. The gadolinium microwires were produced by extraction of a hanging melt drop followed by superfast cooling on a water-cooled rotating disc [13]. As a result of contact of melt droplet with the sharp edge of the rotating disc, the melt was extracted into the free volume of the unit chamber. In this case, the melt was drawn out and solidified in the form of thin threads — metal microwires. The process of microwire formation took ~ 10 ms, which ensured the melt cooling rate $\sim 10^6$ K/s. The chemical and phase compositions of films and microwires were determined in [12] and [13], respectively.

MCE was studied in two limit modes:

– in the adiabatic mode, when the change in magnetic field is so fast that the consequent spin reorientation in the sample results in change in its temperature ΔT, and the magnetic part of entropy is kept constant $\Delta S_{\mathrm{M}} = \mathrm{const}$. This method is based on measuring the amount of heat in a calorimetric cell with test sample placed in the interpole space of the electromagnet. When the magnetic field is turned on/off, an amount of heat is released/absorbed, proportional to MCE and inversely proportional to the heat capacity of the sample;

– in the isothermal mode, when the changing in the external magnetic field is as slow as to keep the working medium temperature constant and equal to the temperature of the thermal reservoir where the ferromagnet is located, $\Delta T = \mathrm{const}$. In this case, the magnetic part of the entropy changes significantly. The isothermal mode was implemented in SQUID MPMX Quantum Design magnetometer with a temperature control function with an accuracy of 0.1 K. The magnetic field of $0-5$ T was changing slowly during the transition from one value to another, so the sample temperature always succeeded to equalize when the isothermal field dependencies of magnetization $M(H)$ were recorded. In some experiments we also used a Lake Shore vibration magnetometer where maximum magnetic filed achieved a level of 9 T.

Thus, the temperature dependences of change in temperature ΔT and on the magnetic part of the entropy ΔS for ensembles of gadolinium microwires were obtained by two independent methods of MCE measurement under isothermal and adiabatic conditions. For folms only dependences $\Delta S(T)$ were obrained, since the sensitivity of the calorimeter was not enough to measure MCE in a single film. For comparison, the dependences $\Delta T(T)$ in crystalline bulk gadolinium were obtained.

3. Experimental results

3.1. Isothermal MCE measurement mode

Figure 1 shows dependencies of the magnetization of Gd thin film on a MgO (111) substrate and Gd microwire versus an external magnetic field applied along its axis. These series of dependencies are recorded in the isothermal mode with step of 5 K for sample heating from 250 K followed by heating to 350 K (above the Curie temperature of 294 K). This heating procedure unifies the initial state, from which the recording of dependences $M(T)$ is started. It can be seen, that at high temperatures the magnetization of microwires and films does not reach the saturation, and with the decrease in temperature the level of saturation magnetization in microwires and films is different, which may be explained by different phase composition. The films contain a cubic metastable phase, and the microwires contain gadolinium oxide [12,13].

It is seen from Figure 1 that the maximum of entropy in films at 290 K has almost no shift with increase in field, while its amplitude grows. In microwires the high-temperature maximum at $T_{c1} = 320$ K does not shift, while the low-temperature maximum at $T_{c2} = 290$ K in field 9 T moves towards low temperatures with decrease in the field to 0.5 T.

Approximations of the temperature dependences of Gd microwire magnetization were obtained based on the phe-

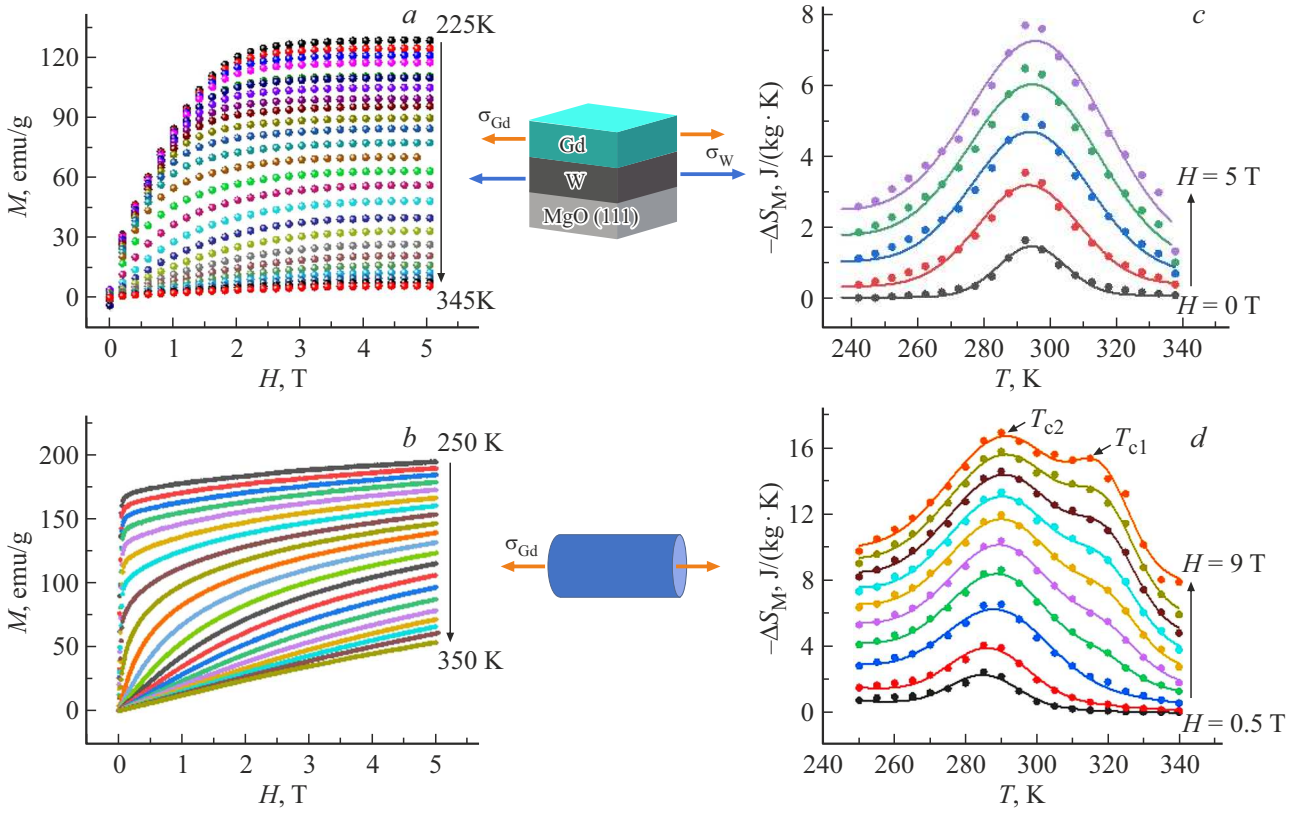

Figure 1. Dependences of magnetization — *a*) — Gd 100 nm film on MgO (111) substrate and *b*) Gd microwire (left column) recorded with steps of 5 K in the temperature range 225–345 K and changes in the magnetic part of the entropy — *c*) of films and *d*) of microwires Gd (right column). Dots show changes in magnetic part of entropy obtained experimentally. Solid lines show approximations by Gaussian functions. The magnetic field lays in the film plane and along the microwire.

nomenological Curie–Weiss theory [16]:

$$M/M_s = L\left(3\frac{T_C}{T}\left(\frac{M}{M_s}+\frac{H}{\omega M_s}\right)\right), \qquad (1)$$

where $L(\alpha) = \coth(\alpha) - 1/\alpha$ — Langevin function, T_C — Curie temperature, M — magnetization, H — external field, $M_s = 2120\,\text{emu/cm}^3$ — saturation magnetization, ω — molecular field coefficient. The molecular field coefficient is expressed in terms of the total angular momentum $J = 7$ of the gadolinium ion, the ion concentration n and the Curie temperature T_C:

$$\omega = 3k_B J T_C/n\mu_0(J+1)(g\mu_B J)^2, \qquad (2)$$

where k_B — Boltzmann constant, μ_0 — magnetic constant, μ_B — Bohr magneton, g — g-factor. Molecular field coefficient ω vs. the external field obtained by approximation for the microwire is shown in Figure 2. The dot at 3 T was obtained for Gd film from the corresponding temperature dependence of its magnetization shown in Figure 3, *b*. The dashed line shows the theoretical value of the coefficient $\omega \approx 630$, calculated using formula (2) for bulk gadolinium.

In the field $H = 3$ T the molecular field coefficients of the film and microwire are the same and equal to 595. The coincidence of these coefficients indicates an almost identical phase composition and a small fraction of foreign phases.

The MCE magnitude in isothermal experiments was calculated by the change in magnetic part of entropy ΔS_M,

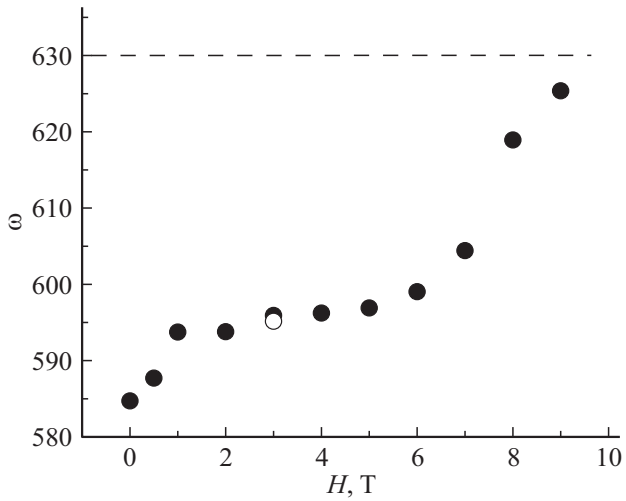

Figure 2. Field dependence of the coefficient ω obtained by approximation for Gd microwire. The dot at 3 T was obtained for the Gd film. The dashed line shows the calculated theoretical value of the coefficient ω.

determined by the magnetization derivative with respect to temperature added at different fields up to the current final value. This relationship is established by the Maxwell relation [17], which is written in discrete form as

$$\Delta S_{\mathrm{M}}(T,H)=\sum_i \frac{M_{i+1},(T_{i+1},H)-M_i(T_i,H)}{T_{i+1}-T_i}\Delta H. \quad (3)$$

Examples of such temperature dependences of the entropy increment $\Delta S_{\mathrm{M}}(T)$ on temperature, calculated by us using formula (3), in a gadolinium film and microwire are shown in Figure 1, *c* and *d*, respectively. In microwires with two maxima on the dependences $\Delta S_{\mathrm{M}}(T)$ the Gaussian functions were used to determine the position of the peaks. In films, where only one peak was observed, the dependence $\Delta S_{\mathrm{M}}(T)$ was approximated by one Gaussian function, and in microwires by two such functions (Figure 4).

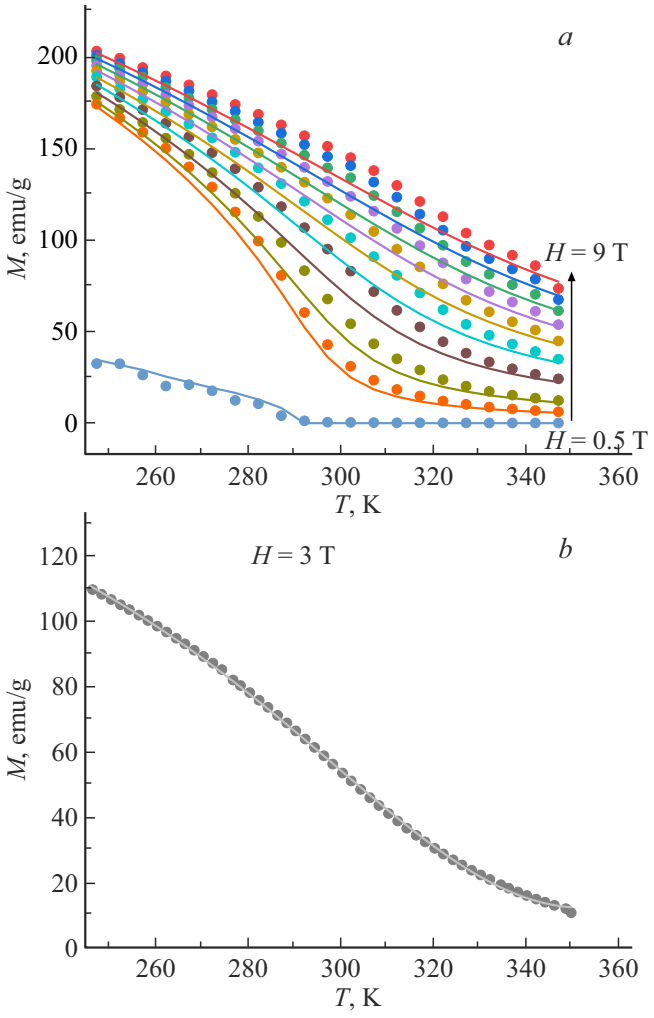

Figure 3. *a*) Temperature dependences of magnetization of Gd microwire, measured in magnetic fields 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 T; *b*) Temperature dependences of magnetization of Gd film, measured in magnetic field $H = 3$ T. Dots show experimental values, solid lines show approximations by formula (1) within the framework of the Curie–Weiss model [16].

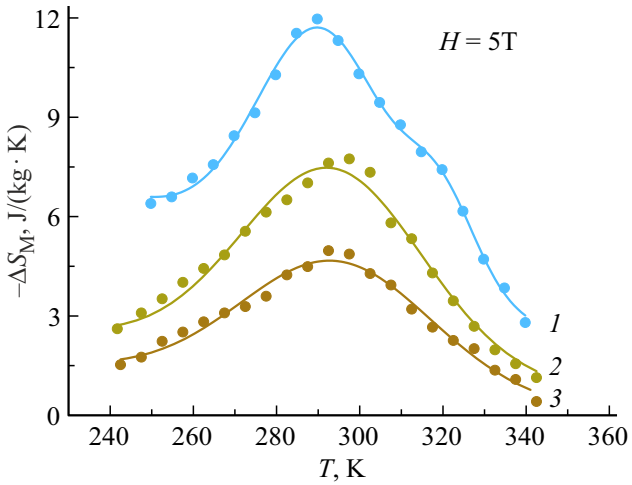

Figure 4. Temperature dependences of the change in the magnetic part of entropy in the field $H = 5$ T in microwire (curve *1*), in film with orientation (111) (curve *2*), in film on MgO substrate (100) (curve *3*). The dots show the experimental values of the change in magnetic entropy, the solid lines show their approximations by two Gaussian functions.

From Figure 4 it follows that in films the change in the substrate orientation (100) with low mechanical stresses (curve *3*) to the orientation (111) with high mechanical stresses (curve *2*) leads to increase in the MCE maximum by 1.5 times and to the appearance of an asymmetry in the dependence $\Delta S_{\mathrm{M}}(T)$. If we consider the curve *1* in microwires as a continuation of this trend, then we can assume that microwires differ from films in even greater mechanical stresses.

3.2. Adiabatic MCE measurement mode

MCE values in the adiabatic mode were determined using a method based on determining the amount of heat released as a result of MCE in a calorimetric experiment Q_{MCE}. This heat was compared with the Joule amount of heat Q_{J} introduced into the calorimeter using a calibration heater

$$Q_{\mathrm{MCE}} = Q_{\mathrm{J}}\Delta T_{\mathrm{MCE}}/\Delta T_{\mathrm{J}}, \quad (4)$$

where ΔT_{MCE} — temperature change in the calorimeter as a result of turning on/off the magnetic field; ΔT_{J} — change in temperature in the calorimeter as a result of transfer of a known amount of heat. The calculation of MCE adiabatic value, expressed as a temperature increase ΔT at a sharp change in the magnetic field, was carried out according to the formula

$$\Delta T = Q_{\mathrm{MCE}}/(m_{\mathrm{M}}C_{\mathrm{M}}), \quad (5)$$

where m_{M} — mass of the magnetic; C_{M} — specific heat capacity of a magnetic.

Figures 5, *a* and *b* show the temperature increase of the sample ΔT_{MCE} vs. temperature at which the magnetic field increased to values 0.2–1 T for bulk crystalline gadolinium

Table 1. The magnitude of the magnetocaloric effect ΔT and the heat capacity of crystalline Gd and Gd microwire

	Magnitude of adiabatic of temperature change when field is switched on $H = 1$ T, K	Position of maximum temperature change, K	Heat J/(gK) capacity,	Position of maximum of heat capacity, K
Crystal bulk material	3.6	295	0.31	287
Microwire	3.8	289.5	0.32	283

and for microwires, respectively. For films, it was not possible to obtain similar dependence, since their small thickness and mass excluded the possibility to determine the amount of heat transferred to the film at the available sensitivity of the calorimeter.

From Figure 5 it follows that, as a result of the magnetocaloric effect, the maximum temperature change when the magnetic field changes by a value in the range 1 T is 3.6 K in microwires (Figure 5, *a*). This is close to the

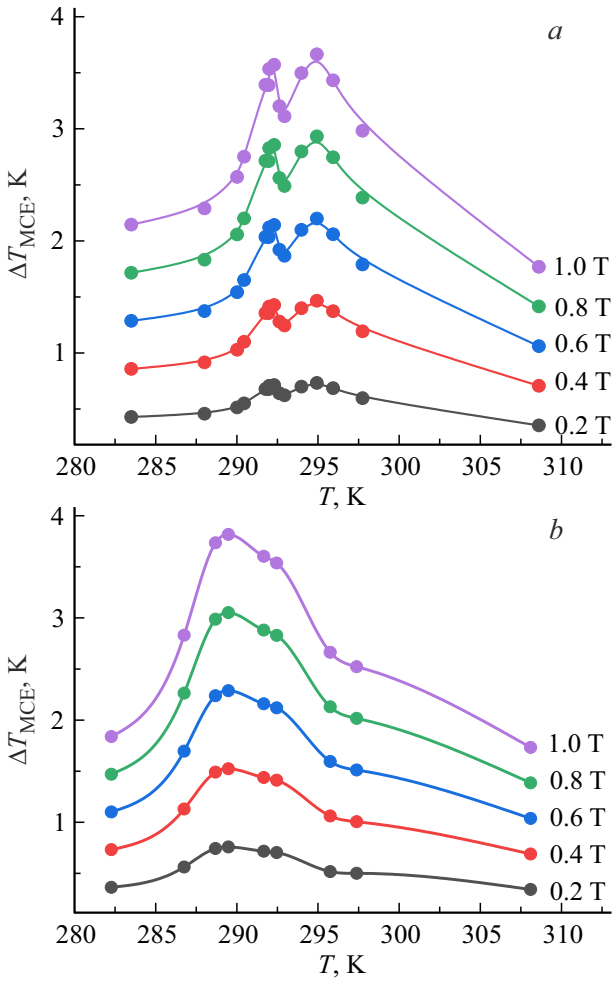

Figure 5. Temperature dependences of the magnetocaloric effect (ΔT_{MCE}) *a*) crystalline Gd and *b*) Gd microwire, measured by the calorimetric method in adiabatic mode at abrupt switching on of magnetic field $H = 0.2-1$ T.

results obtained in the paper [18], where the temperature change as a result of MCE at the same change in the magnetic field (1 T) is 3.1 K. In Gd microwire samples the maximum temperature change in the magnetic field $H = 1$ T is 3.8 K (Figure 5, *b*). This is consistent with Figure 4, where the magnitude of the isothermal MCE turns out to be higher in microwires than in films.

In the dependences $\Delta T_{MCE}(T)$ in Figure 5 two maxima are observed, as in microwires during isothermal MCE measurements. In microwires the first maximum at 290 K (Figure 5, *b*) coincides in temperature with the maximum detected from the change in entropy. However, the second maximum is found in microwires at 293 K instead of 320 K. In crystalline Gd these maxima are centered at 292 and 295 K, respectively. It can be assumed that the difference in the position of MCE maxima in adiabatic measurements compared to isothermal measurements is associated with the anisotropy of the microwire shape. For Gd it was established [19] that in the cylindrical sample the temperature of MCE maximum shifts when the field orientation changes relative to the main axis of the cylinder. Besides, the unconventional behavior of the curves $\Delta T_{MCE}(T)$ in Figure 5, *a* may be due to the inhomogeneous phase composition. For example, the presence of micro- and nanocrystalline phases can lead to different positions of entropy maxima. It can be assumed that there is a similarity with the paper [20], in which the magnetocaloric properties of nanocrystalline and coarse-grained metallic Gd were studied. As Gd grains size decrease from the micron to nanometer range, the maximum of changes in magnetic entropy are observed at 294, 290 and 288 K. Moreover, the shape of the dependence clearly indicates the presence of two or even three entropy peaks simultaneously.

Since in adiabatic measurements a single microwire was used, and the field was directed along its axis, and in isothermal measurements the chaotically directed multiple microwires were used, the magnitude of the demagnetization field was different, which could change the positions of the maxima in the dependences $\Delta T_{MCE}(T)$.

The temperature dependences of the heat capacity of microwires (curve *1* Figure 6) and crystalline Gd (curve *2* Figure 6) were also determined.

The maximum value of the heat capacity of crystalline Gd is 0.31 J at the temperature $T = 287$ K; for Gd microwire samples the maximum is observed at the temperature $T = 283$ K and is equal to 0.32 J/(gK) (Figure 6). The

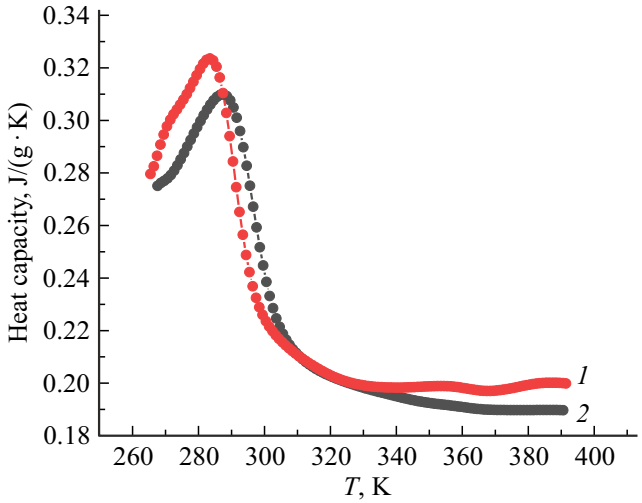

Figure 6. Temperature dependences of the heat capacity of microwires (curve *1*) and crystalline gadolinium (curve *2*).

observed shift of the maximum of heat capacity to the low-temperature region, relative to the Curie temperature for crystalline gadolinium and microwire made from it is consistent with the data presented in [21]. The reason for this shift may be the presence of microstresses in the microwire that occur during ultra-fast cooling of the melt. Table 1 summarizes the results of MCE measurements in the adiabatic mode and the results of the heat capacity measurement of bulk sample and the ensemble of microwires.

From Table 1 it follows that the differences between microwires and bulk crystalline Gd in the MCE value, heat capacity and position of the temperature rise maximum are small. The main difference is observed in the position of the maximum in the temperature dependence of the heat capacity. The differences also lie in the fact that besides the main maximum there is another low-temperature maximum at 270 K, as well as high-temperature maximum at 355 K. Thus, the main regularities distinguishing microwires from bulk material turn out to be similar to those discovered when comparing microwires with Gd films.

4. Discussion

For the results obtained analysis it is necessary to analyze the nature of magnetic ordering in microwires and films. Mechanical stresses, which presumably create differences in the magnetic properties of microwires and films, can create magnetic anisotropy and change the type of spin ordering. For these purposes the Arrott method is used, which is based on the Weiss molecular field theory [22,23]. This analysis is based on Arrott–Noakes equation:

$$(H/M)^{1/\gamma} = \frac{(T - T_c)}{T_c} + \left(\frac{M}{M_r}\right)^{1/\beta}, \qquad (6)$$

where γ and β — critical parameters characterizing the nature of spin ordering in ferromagnet. Plotting the field dependences of magnetization in the coordinates $M^{1/\beta}(H/M^{1/\gamma})$ allows one to determine the parameters γ and β, and, based on their values, make conclusions about the two-dimensional or three-dimensional ordering of spins. To do this, from a series of field dependences of magnetization one is found that is straightened in the mentioned coordinates, and then the values γ and β are determined for it. Figures 7 and 8 show the field dependences in Arrott coordinates and the obtained values of the parameters $\beta = 0.325$, $\gamma = 1.24$ for films and $\beta = 0.365$, $\gamma = 1.368$ for microwires.

The values of these parameters indicate that the ordering in films is close to two-dimensional, which corresponds to

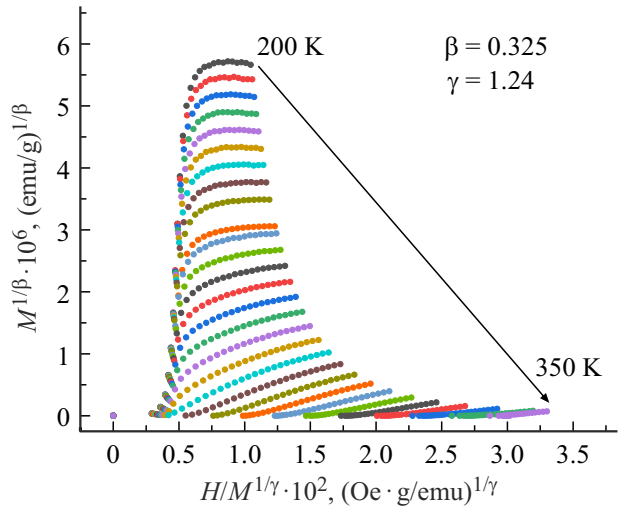

Figure 7. Arrott curves in the temperature range 200–350 K for Gd film sample. The critical coefficients $\beta = 0.325$, $\gamma = 1.24$ correspond to the Ising model. Straightening occurs at temperature $T = 295$ K.

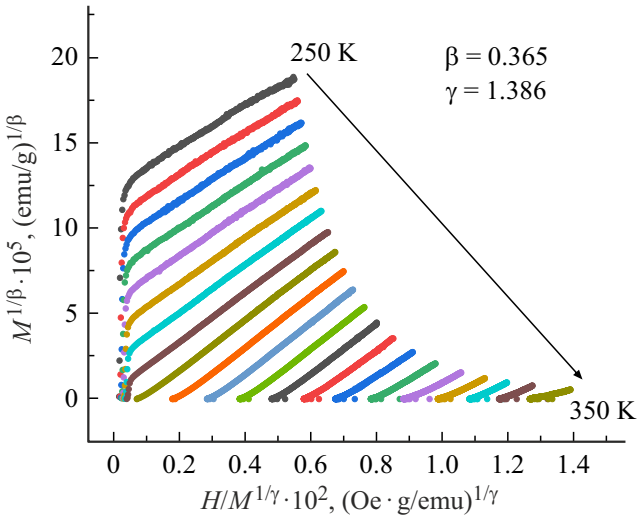

Figure 8. Arrott curves in the temperature range 250–350 K for Gd microwire sample. The critical coefficients $\beta = 0.365$, $\gamma = 1.368$ correspond to the Heisenberg model. The curves straightening occurs at temperature $T = 290$ K.

Table 2. Curie temperature obtained from the value of derivative dM/dT and Arrott curves

	Critical coefficients β, γ	Curie Temperature, obtained from value of derivative dM/dT, K	Curie Temperature, obtained from Arrott curves, K
Gd film	$\beta = 0.325$ $\gamma = 1.24$	293	295 ± 2.5
Gd microwire	$\beta = 0.365$ $\gamma = 1.368$	292	290 ± 2.5

the Ising model. In microwires the spin ordering is closer to the Heisenberg model, i. e. has a three-dimensional nature.

The obtained numerical values of the temperature, at which the Arrott curves are straightened and pass through the origin of coordinates, make it possible to determine the Curie temperature to within 1 K. For the gadolinium film sample straightening occurs at temperature $T = 295 \pm 2.5$ K, which is consistent with the result obtained based on the position of the maximum of change in magnetic entropy. For Gd microwire samples straightening occurs at the temperature $T = 290 \pm 2.5$ K, which also coincides with the position of one of the peaks in the dependence of the entropy increase on temperature (Table 2).

Double maxima of the increment of magnetic part of entropy in alloys with gadolinium are not uncommon in the literature. For example, in [24] authors reported the presence of a double peak in $Gd_{1-x}Ho_xNi$ alloy that was produced by the rapid cooling melt-spinning process. The authors have found, that an additional maximum of entropy arises as Ho is added, and this maximum is absent at a zero concentration of Ho. Since Ho has a symmetry of single-ion anisotropy different from that of Gd, a competition of magnetic anisotropies of two rare-earth sublattices takes place. With change in temperature the dominant symmetry of Gd is replaced by the symmetry of Ho ions. As a result, spin-flip transition occurs, which, like the transition at the Curie temperature, gives increase in the magnetic part of the entropy.

In a zero magnetic field the Curie temperature of the bulk gadolinium single-crystal T_C is equal to 294 K, and temperature of the spin reorientation T_r is equal to 227 K. Authors of this paper found that there are two closely located maxima of anisotropy, one of which corresponds to the Curie temperature of gadolinium, and another — corresponds to the spin-flip transition in gadolinium. At the same time, in the range of 2–7.5 T the value T_C in Gd increases linearly with coefficient of 6 K/T, the spin-flip transition is extinguished completely by magnetic fields higher than 2–2.5 T.

In [4] it is noted that the chemical purity of gadolinium plays an important role in MCE and strongly affects both the Curie temperature and the temperature of the spin-flip transition T_r. Impurities decrease the Curie temperature and also broaden the temperature range of the paramagnetic–ferromagnetic transition, masking the spin-flip transition, which can be easier detected in monocrystal samples of high quality. Therefore, the critical temperatures found by us for microwires and films can be shifted in relation to their values in perfect crystals of gadolinium.

It can be expected that peak *1* at 320 K corresponds to the spin-flip transition shifted from 235 K as a result of microstresses and high percentage of impurity in microwires (Figure 1, *b*). The low-temperature peak *2* in microwires changes its position monotonously from 286 to 293 K in a field range of 3–9 T (curve *2* in Figure 1, *d*), i. e. approximately with a coefficient of dT_C/dH 1.17 K/T, which is considerably lower than the coefficient $dT_c/dH = 6$ K/T determined in [4], where the entropy maximum corresponded to the Curie temperature. In this paper peak *2* at 286–293 K, probably corresponds to the Curie temperature shifted to toward higher temperatures due to high anisotropy of shape and strong microstresses arising at a high rate of melt cooling.

In films with MgO substrate orientation (111) that provides maximum Gd stretching, a growth of the Curie temperature is observed in field range of 1–5 T with a coefficient of $dT_C/dH = 1.25$ K/T close to that observed in microwires (Figure 1, *c*). Changes in the substrate orientation to (110) or (100) or its thickness from 100 to 300 nm decrease the stresses in gadolinium, thus lead to a zero coefficient. The temperature of peak *1* does not depend on field and remains equal to 320 K at field up to 9 T.

Spin-flip transition in bulk samples of Gd is well-known and reliably verified by the neutron diffractometry method (see, for example, [25]). The easy magnetization axis in Gd is parallel to the hexagonal axis *c* between the Curie temperature ($T_C = 293$ K) and the spin-flip temperature ($T_r = 235$ K). The easy axis moves away of the axis *c* below T_r and lays on the surface of the cone of axis c at some angle, which is equal to 30–40° at low temperatures, increases approximately up to 70–90° in the region of 150–200 K, then decreases abruptly down to 0° at T_r.

The spin-flip transition as cause of MCE was investigated in detail in [4] in gadolinium samples of different purity and different structural perfection (from poly- to monocrystal). The temperature of the spin-flip transition T_r varies in different papers: 227 K in [4], 232 K in [25]. It was previously established that the temperature of this transition

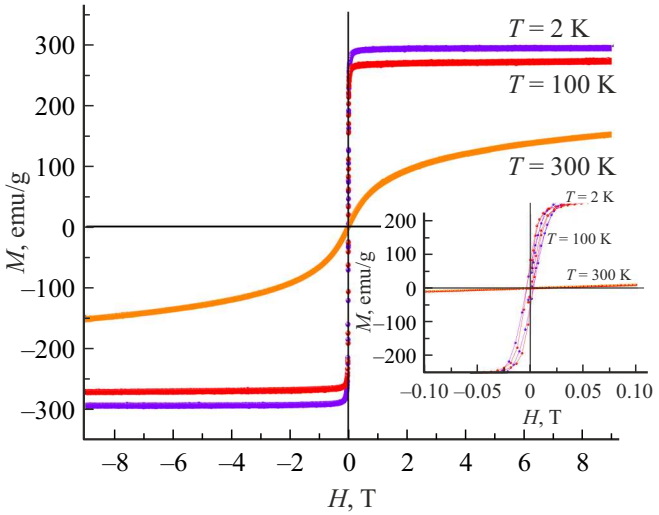

Figure 9. Magnetic hysteresis of Gd microwire sample at temperature of 2, 100, 300 K. The insert shows a section of the hysteresis loop in low fields.

can vary significantly under the influence of mechanical stresses [26]. The theoretical value of coefficient of temperature shift T_r under the applied hydrostatic pressure P is $dT_r/dP = -4.9$ K/kbar, which is close to the experimental value $dT_r/dP = -4.3$ K/kbar [26]. Negative value of this coefficient does not allow for explanation of T_r temperature shift to 320 K in our study under hydrostatic pressure, however the stresses in microwire are not of hydrostatic nature and significantly vary probably creating a mosaic of areas with stresses of different directions. Gradients of these stresses can cause a significant shift toward higher temperatures, as it is found in our experiments. Note that in gadolinium there is a significant influence of the magnetic field on the Young's modulus and elastic constants [27], which can change the magnetoelastic anisotropy and, accordingly, the temperature of the spin-flip transition.

Note that the important factor for assessing the prospects of the material used in magnetic cooling is the magnitude of magnetic hysteresis in the working fluid. For example, the paper [28] notes that hysteresis is a real obstacle on the way from existing laboratory prototypes of magnetic refrigerators to the commercialization of this potentially revolutionary cooling technology. Indeed, the reversibility of the magnetocaloric effect, essential for magnetic heat pumps, is highly dependent on the width of the thermal hysteresis, and therefore it is necessary to understand the mechanisms causing the hysteresis and find solutions to minimize losses associated with thermal hysteresis in heat pumps in order to maximize the efficiency of magnetic refrigerating devices. The main problem associated with giant MCE materials is transition hysteresis of first kind, one of the main factors delaying the development of this new and revolutionary cooling technology. In most cases, thermal hysteresis near the Curie point is studied. However, magnetic hysteresis also plays an important role. The energy absorbed in the cycle is transformed into heat and degrades the achieved magnetic cooling values. In gadolinium samples the area of the hysteresis loop is usually small. For example, in our experiments at temperatures of 300 K the area of the hysteresis loop was practically equal to zero. A small coercive force at the level of 50 Oe appeared at low temperatures only (Figure 9). There was also no magnetic hysteresis in the films at 300 K.

Thus, from the point of view of the small coercive force and small energy losses during magnetic hysteresis, the gadolinium samples are convenient objects for the development of a magnetocaloric environment and obtaining ideas about the pure magnetocaloric effect without distortions caused by hysteresis.

5. Conclusion

1. Two peaks (low-temperature and high-temperature) are observed on the temperature dependence of the magnetic part of entropy received in isothermal mode in microwires in contrast to one peak in Gd films.

2. In Gd films and microwires the low-temperature maximum of the change in the magnetic part of entropy is observed near the Curie temperature of 286−293 K. Upon magnetic field increasing this maximum in microwires is shifted toward higher Curie temperatures with a coefficient of 1.17 K/T, which is considerably less than the coefficient of 6 K/T determined for bulk Gd. In films a differently directed shift of the maximum is observed with an increase in field depending on the crystal-lattice orientation of the substrate and the magnitude of stresses caused by it. The supposed cause of the multidirectional shift of the maximum is the lack of magnetization saturation up to the highest fields and the growth of the demagnetization field as the external field increases.

3. A significant effect of magnetic field on the position of maximum of the entropy dependence on temperature is found in films in contrast to microwires, where this dependence is only observed for one of peaks. The highest effect of magnetic field on the position of entropy maximum in films is observed for the MgO substrate orientation of (111) at the lowest thickness of the Gd film, i.e. in the conditions of maximum stresses created by the substrate. At the same time, the coefficients of linear shift of the entropy maximum with field growth coincide in films and in microwires within the accuracy of the experiment.

4. In Gd microwires the high-temperature peak does not change its position and is located at 320 K, but its amplitude increases linearly with the field, changing in the range 4−15 J/(kg · K) with a coefficient of 1.83 J/(kg · K). The probable mechanism for the appearance of the high-temperature peak is a spin-flip transition, significantly shifted from low temperatures to high temperatures under the influence of high internal stresses and with an increase in the demagnetization field in microwires up to 9 T.

5. The Arrott parameters were determined in films and microwires, which indicate the two-dimensional ordering of spins, described by the Ising model in films, and the three-dimensional nature of their ordering in microwires, where the Heisenberg model is applicable.

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Conflict of interest

The authors declare that they have no conflict of interest.

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