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Magnetocaloric effect in Gd microwires

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In Gd microwires obtained by ultrafast cooling of the melt, a change in the magnetic entropy of 12 J/kg K was determined at a Curie temperature of 293 K in a magnetic field of 5 T. This value coincides with the change in the magnetic part of the entropy in bulk single-crystal samples in the same field. It has been found that in a strong magnetic field of 9 T, the temperature dependence of the entropy exhibits two maxima at temperatures of 292 and 312 K. The appearance of an additional entropy maximum in microstructured samples is caused by high mechanical microstresses retained in the sample after ultrafast cooling.

Keywords: microwires, magnetic entropy, magnetoelastic anisotropy, Curie temperature.

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1. Introduction

Magnetocaloric effect (MCE) has two typical manifestations in experiments: a change in the temperature of the body when switching on−off the magnetic field and a change in magnetic entropy derived from the magnetic moment and its dependence on the field. Pecharsky and Schneidner have discovered an extraordinarily large magnetocaloric effect in gadolinium alloys [1]. Adiabatic change in the temperature of the body under an applied magnetic field or isothermic change in magnetization with changes of the field at the Curie point are especially large in gadolinium and alloys based on it [1–4]. A „magnetic refrigerator", that allows for temperature lowering by 20−30 K, is possible even now with the use of gadolinium-based alloy as the working medium. Also, gadolinium is a convenient option due to the fact that its Curie point of 292 K is close to the room temperature. This addresses the problem of energy consumption while cooling, as well as the environmental problem related to the use of toxic gases in classic cooling devices. Therefore a lot of research teams all over the world are searching for ways to modify gadolinium and optimize its magnetocaloric properties.

Usually, the varied parameters in these studies are chemical and phase composition of the alloy. Addition of various chemical elements and variations of melt heat treatment and cooling mode really result in MCE increase in gadolinium-based alloys and are able to make magnetic cooling devices even more effective in the future. Another way to optimize MCE is the creation of internal stresses that can affect the magnetoelastic anisotropy, change the Curie point. In particular, it was shown that a change in the orientation of Gd film substrate resulting in mechanical stresses in the interface can affect the MCE to a significant extent [5]. It should be expected that in microwires prepared by ultra-fast melt cooling microstresses can be very high and result in a significant MCE change. In addition, microwires are suitable as a working medium of a refrigerator because they have considerable specific surface area and ensure good heat exchange with the environment. This fact is reflected in recent works mainly focused on studying of microwires of binary and triple alloys of gadolinium with transition metals [6–8]. In these studies the entropy addition at the Curie point mainly appeared to be less than in the bulk gadolinium, and Curie points are lowered down to 100−150 K, which is considerably less than the room temperature required for practical applications. Even microwires of pure Gd [9] demonstrate maximum entropy at 80−100 K, that is indicative of MCE lowering in amorphized microwires.

The goal of this study is to obtain information on the magnetocaloric effect in microcrystalline Gd-microwires and to analyze changes in magnetic entropy caused by microstructuring.

2. Procedure and samples

Gadolinium microwires were prepared by melt extraction on a pendent drop (MEPD) [10]. A workpiece in the form of a $5 \times 5 \times 50$ mm Gd ingot was hanged over a rotating water-cooled sharpened extraction sharpened wheel in a vacuum chamber. We used a commercially pure gadolinium ingot with a concentration of 99.4 mass%. The chamber was

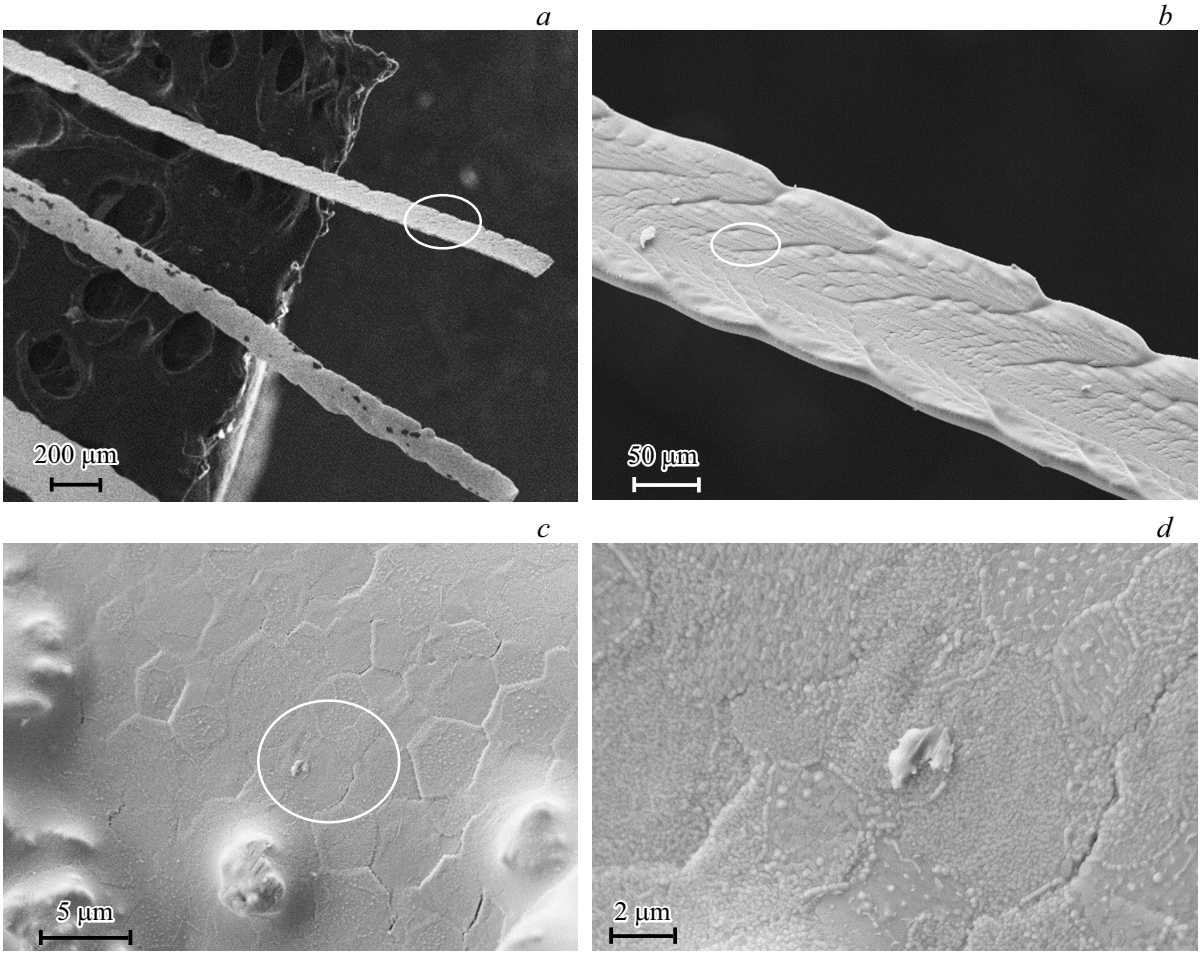

Figure 1. SEM-images of Gd microwire (*a*); surface of the contact with extraction wheel (*c, d*); images in figures *c* and *d* correspond to enlarged scale of the area in ellipse in Fig. *b*.

vacuumed down to a pressure of $1 \cdot 10^{-2}$ Pa. A free part of the sample was heated by a directed electron beam with a diameter of 5 mm, generated by an electron gun. Then the melt was supplied onto the rotating extraction wheel. As a result of contact of a melt drop with the wheel edge the melt was ejected into the free space of the chamber. Microwires prepared in this way were as long as up to 100 mm and had a diameter from 25 to 100 μm (Fig. 1).

It can be seen on the electron microscopic images, that there are different structures of microwires in relation to the free surface and the surface of contact with the extraction wheel (Fig. 1, *a*). There are dark spots on the free surface of microwire that are correspondent to the formation of Gd oxides. In the case of fast quenching the temperature front is directed from the surface of contact with the extraction wheel to the free surface. Therefore, the surface of the microwire with the wheel is almost free from oxidation traces (Fig. 1, *b*–*d*), because the rate of cooling in this area is maximum, i.e., ($\sim 10^5$ K/s). This is evidenced by the shape of the surface of the melt hardened in the flow (Fig. 1, *b*). The free surface has a smoother relief and a round shape since it cools significantly slower in the process of microwave extraction from the wheel. However, the high rate of cooling appeared to be insufficient to form an amorphous phase. The microstructure of the microwire contact surface is composed of grains with a size of 2–5 mkm and dendrites contained in them with a size of 100-200 nm (Fig. 1, *c, d*).

To determine the structure of samples we used X-ray diffraction (XRD) and an X-ray fluorescence (XRF) analysis. Spectra of Gd-microwires are shown in Fig. 2 (XRD) and Fig. 3 (XRF), respectively.

XRD-spectrum in Fig. 2 (black line *1*) is an experimental data for a Gd-microwire. Other spectra are simulated using databases and contain peaks close to the obtained experimental spectrum of the sample. The model spectrum *3* includes contributions of hcp- and fcc-phases of gadolinium (curves *2* and *4*, respectively), as well as a contribution of Gd_2O_3 oxide (curve *5*). Positions of peaks in the model spectrum basically match the experimental data. However, peaks of the experimental XRD-spectrum mainly are less intensive as compared with the database of spectra of possible compounds, which is indicative of the fact that microwires have a fine-grain multiphase structure.

The main stable hcp-phase is a hexagonal closely-packed phase with the following parameters: $a = 3.606$ and $c = 5.786$ Å for the bulk material. Another phase, fcc, is a face-centered cubic phase with a lattice parameter of $a = 5.336$ Å. This phase is metastable and often found in thin films and microstructured samples of gadolinium [11].

Phase composition with an appropriate numbers of compounds from the PDF database and derived from peak areas of XRF-spectrum (Fig. 3). Concentrations of detected phases are presented in the table. As a result of quick quenching hcp- and fcc-phases of gadolinium and Gd_2O_3 gadolinium oxide are formed in the Gd-microwires. The presence of Gd oxide is related to the presence of residual oxygen in the chamber while quick-quenching from the melt.

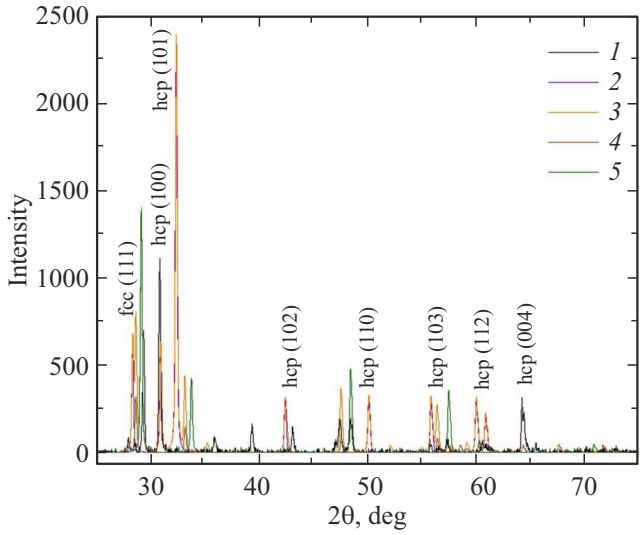

Figure 2. X-ray diffraction analysis of Gd-microwires. *1* — experimental diffraction spectrum of the studied sample of Gd-microwire; *2* — diffraction spectrum of the hcp-phase of Gd from the Pdf № 000-65-7943 database; *3* — sum model spectrum of multiphase material; *4* — diffraction spectrum of the fcc-phase of Gd from the Pdf № 000-45-0912 database; *5* — diffraction spectrum of Gd_2O_3 from the Pdf № 000-86-2477 database.

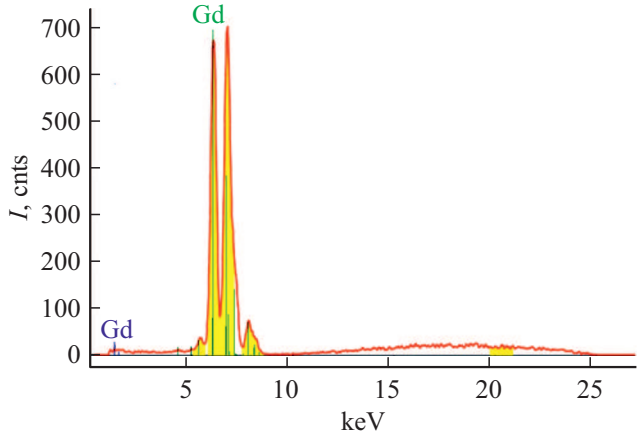

Figure 3. X-ray fluorescence spectrum of Gd-microwire.

Phase composition and concentrations by volume of phases in Gd-microwires from the data of X-ray diffraction analysis

Phase	№of PDF database	Concentration, rel. unit.
hcp-Gd	000-02-0864	0.375
fcc-Gd	000-65-7943	0.459
Gd_2O_3	000-65-9199	0.166
Sum		1.000

Scanning electron microscope (SEM) images of microwires were obtained using the Tescan Clara super-resolution complex at 15 kV accelerating voltage on a cross section prepared by ion etching and polishing in the Technoorg Linda SEMPrep2 complex. We determined microstructure and chemical composition of microwires using a scanning microscope with a micro-energy dispersive analysis (EDX) attachment. The EDX-spectrum is shown in Fig. 4 together with the image of microwire fragment being analyzed (Fig. 4, *a*) and the distribution of gadolinium in this area (Fig. 4, *b*). In this spectrum the lines of gadolinium are predominantly seen (Fig. 4, *c*), which is indicative of a high purity of the sample under examination.

3. Experimental results

Fig. 5, *a* shows magnetization versus temperature dependencies M(T) for a single microwire recorded in different conditions. Curves *1* and *2* precisely fit each other and are the temperature dependencies recorded in a field of 1 kOe while heating the sample from 2 K after its zero field cooling (ZFC mode) and field cooling (FC mode). An increase in the field up to 9 and 10 kOe (curves *3* and *4*) results in magnetization change at all temperatures, which makes the Curie temperature more distributed over the temperature scale. Fig. 5, *b* shows a series of ZFC temperature dependencies recorded in different magnetic fields of 0–9 T. It can be seen, that as the field of $M(H)$ recording increases, the Curie point T_{c1} shifts from 286 K at the zero field (remnant magnetization) to 292 K in a strong field of 9 T. Also, the presence of the second Curie point T_{c2} can be seen, but its presence will be demonstrated more explicitly in the discussion of the magnetic entropy. Vertical arrows in Fig. 5, *b* show the Curie points determined from maxima on the temperature dependence of entropy at 9 T.

Fig. 6 shows magnetization versus field dependencies $M(H)$, recorded twice: when changing from positive to negative fields and vice versa. Usually, it allows for the detection of the presence of a hysteresis loop. In our experiments we have observed almost no hysteresis, except for the temperature of 2 K, where a coercive force was 10 Oe (not shown in the figure). It is a very important and positive result for the working medium of a magnetic refrigerator. The presence of a magnetic hysteresis results in energy absorption and its transformation to heat, which

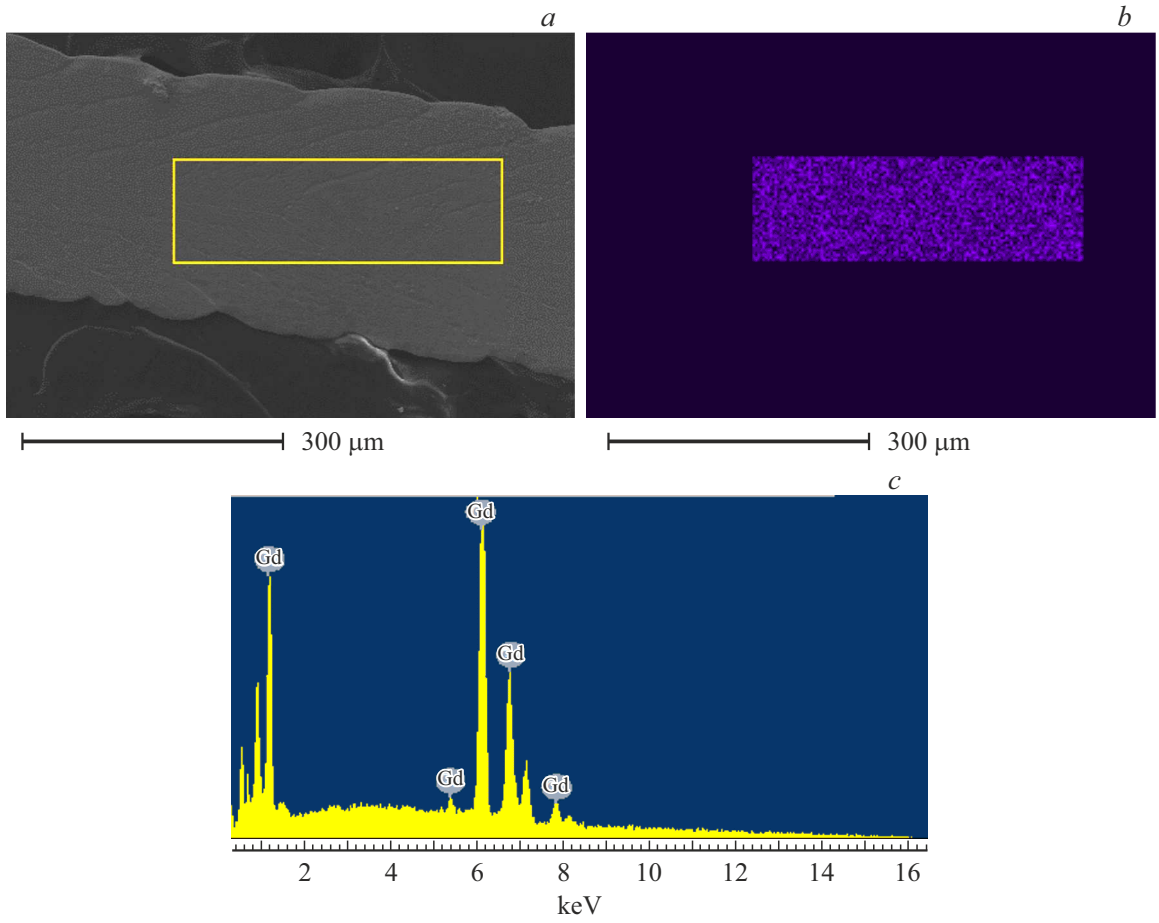

Figure 4. Energy-dispersive analysis of local microarea of the contact surface between the extraction wheel and the Gd-microwire: *a* — the rectangular marks the microwire area under study; *b* — gadolinium distribution in this area; *c* — EDX-spectrum in the highlighted area.

is undesirable at the cyclic change of the field where the working medium is located.

Fig. 7 shows dependencies of Gd-microwire magnetization versus an external magnetic field applied along its axis at temperatures of 247−347 K. The dependecies are recorded with a step of 5 K in isothermal mode, thus, they are suitable to calculate the magnetic entropy.

The value of the MCE is defined by the contribution of magnetic entropy ΔS, which can be derived from the Maxwell relations [12]:

$$\Delta S_M(T, H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH, \qquad (1)$$

where H is positive magnetic field, M is magnetization.

In real practice the calculation of the integral is complicated by the fact that experimental points of the $M(H)$ dependence are recorded in a discrete manner. Therefore, according to [12], the Maxwell formula (1) can be replaced by a discrete formula taking into account the field step of ΔH and summing up the values dependent on the $M_i(T_i, H)$ moment with different numbers i:

$$\Delta S_M(T, H) = \sum_I \frac{M_{i+1},(T_{i+1}, H) - M_i(T_{i,H})}{T_{i+1} - T_i} \Delta H. \qquad (2)$$

The calculated change in magnetic entropy $-\Delta S_M$ as a function of field is shown in Fig. 8, *a*, while temperature dependencies of the $-\Delta S_M$ addition at an applied field of $H = 0-9$ T can be seen in Fig. 8, *b*.

It can be seen from Fig. 8, *a* that at temperatures below 293 K field dependencies in $-\Delta S_{\max}(H^{2/3})$ coordinates proposed for the analysis of the defect structure role in [13] are straightened. Above 293 K the linear character of $\Delta S_{\max}(H^{2/3})$ function is disturbed. Low-temperature parts of the dependencies deviate from straight lines. Weak fields in Fig. 8, *b* have one maximum of entropy at 286 K with 0.5 T. This maximum shifts towards higher temperatures as the field increases, so that at 9 T the position of this maximum corresponds to a temperature of 292 K. At the same time, with an increase in the field the right wing of the $\Delta S_M(H)$ dependence grows gradually and at 7−9 T it becomes evident that one more maximum emerges at a temperature of $T_{c2} = 312$ K with 9 T. This result seems

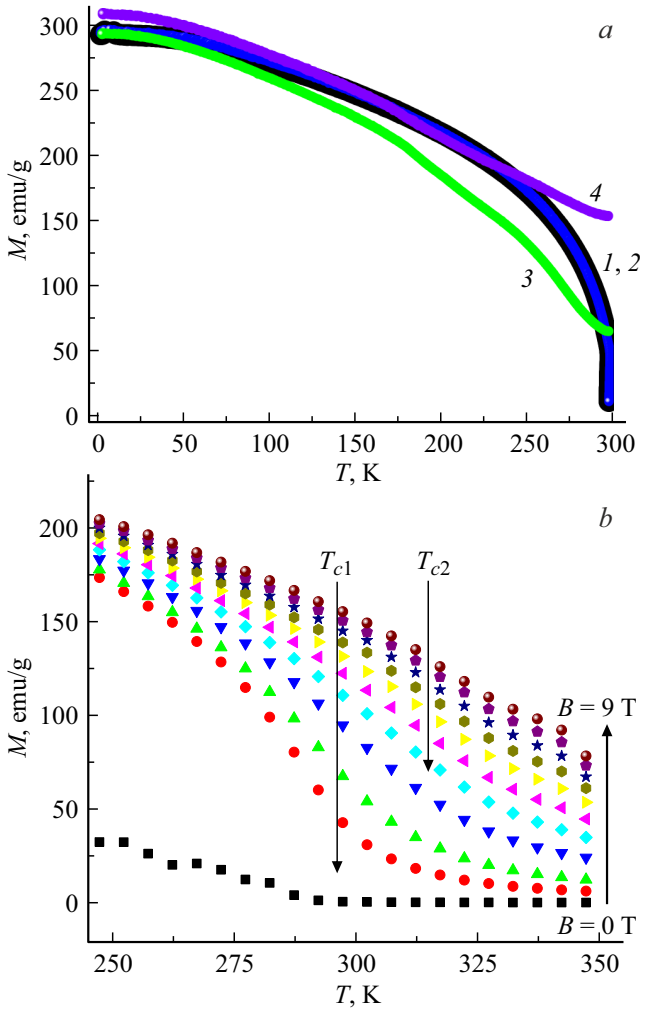

Figure 5. *a* — dependencies of magnetization versus temperature in FC and ZFC cooling modes of microwire recorded in the fields of 1 (1 ZFC and 2 FC), 9, 10 kOe (FC); *b* — dependencies of Gd-microwire magnetization versus temperature measured in a magnetic field with inductions of 0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 T.

to be intriguing because previously no presence of two maxima on the entropy dependence was observed in bulk and microstructured samples of gadolinium.

4. Discussion

The defects of the structure emerged during fast crystallization create a distribution of the Curie temperatures T_c and, thus, increase the width of ferromagnetic-paramagnetic transition. It defines the dependencies of magnetic entropy versus field (Fig. 8, *a*) that describe the position of entropy maximum for the samples with defects by the following formula [13]:

$$-\Delta S_{\max} = AH^{2/3} + B, \qquad (3)$$

where $A = \alpha/(4b)^{2/3}$ and $B = -\alpha^2 T_c/(18b)$ are constants of the material that are classified as expansion ratios.

Fig. 8, *a* shows an approximation of the magnetic entropy increment dependencies versus field by formula (3). The field dependencies of magnetic entropy increment are straightened in $-\Delta S_{\max}(H^{2/3})$ coordinates up to 293 K. Then, at temperatures of 295–312 K, the field dependencies start to deviate from this law, because at least a defect-free part of the sample has transited to the paramagnetic state. This confirms that there is a defect-free part of the sample that has the classic Curie point typical for bulk perfect crystals and a part with an increased Curie point controlled by remnant mechanical stresses.

Now let us discuss the temperature dependencies of the entropy maximum at 293 K. The temperature corresponding

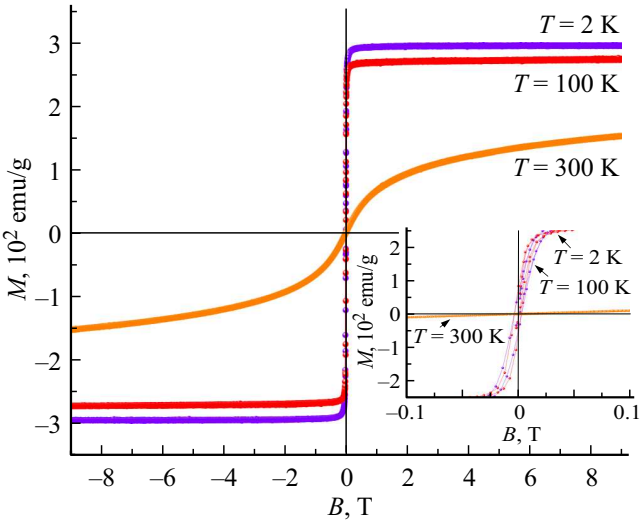

Figure 6. Dependencies of Gd-microwire magnetization versus field recorded at an increasing and decreasing field at temperatures of 2, 100, 287 K. Superposition of the field dependencies at direct and inverse field sweep indicates the absence of hysteresis.

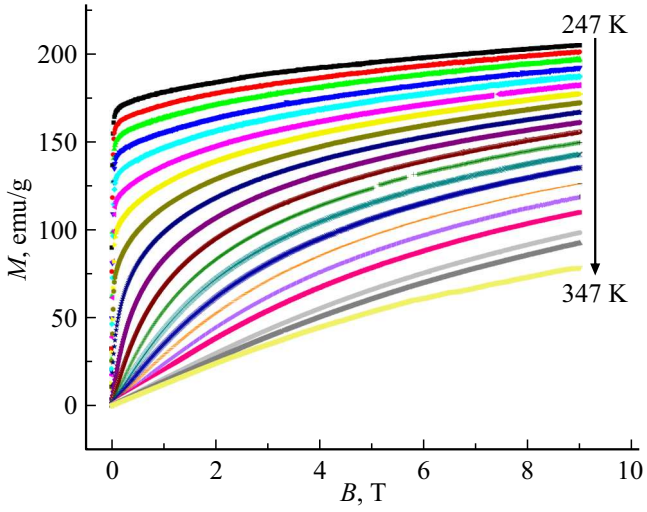

Figure 7. Dependencies of Gd-microwire magnetization versus an external magnetic field applied along its axis at temperatures of 247–347 K and with a step of 5 K.

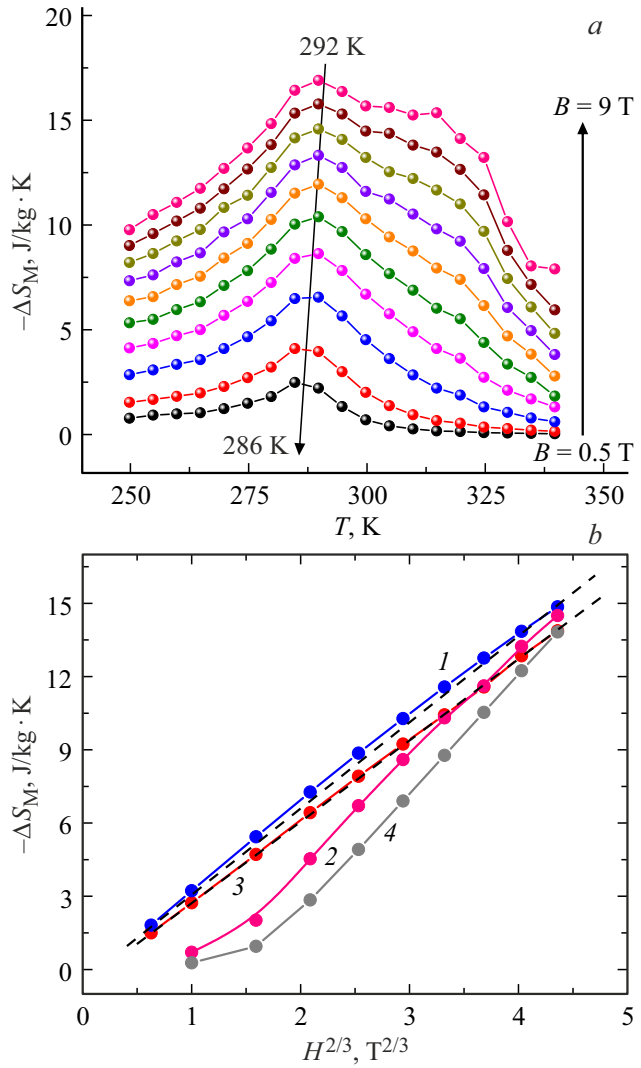

Figure 8. *a* — dependencies of magnetic entropy change versus temperature at changes of an external magnetic field induction 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 T; *b* — dependencies of magnetic entropy increment versus field at temperatures of 275 (*1*), 284 (*2*), 300 (*3*), 310 K (*4*) (top to bottom). dashed lines show approximations of dependencies 1 and 2 by formula (1).

to the entropy maximum can be described by the following relationship: $T_{\max} = T_{c1}(1-\gamma)$, where γ is a coefficient depending on the shape of distribution T_{c1}. That is the maximum of $\Delta S(T)$ dependence in a strict sense does not correspond to the Curie temperature, but can be converted to it. This maximum in our experiments shifts as the magnetic field increases from 0.5 to 9 T (Fig. 8, *b*). This phenomenon is well known and described in details in [14–16]. The temperature shift of the entropy maximum is linearly related to the shift of the Curie point. The shift of this maximum towards higher temperatures is related to the change of the real effective field inside a ferromagnetic due to the contribution of the demagnetization magnetic field. Maximum theoretic deviation of the Curie point from the true Curie point ΔT_c can be calculated by the formula presented in [14]:

$$\Delta T_{c1} = (J+1)\mu N M_S/3Jk, \qquad (4)$$

where $J = 7/2$ — total angular moment of Gd, $\mu = 7$ — magnetic moment of Gd, $M_S = 2120$ emu/cm^3 — saturation magnetization, k — Boltzmann constant, $N = 4\pi \cdot 0.1$ — demagnetization factor of the rod. The estimate of the Curie temperature deviation from the „true temperature" T_{c1} 290 K by formula (4) yields a value at a level of 5 K, which matches well the difference $\Delta T_c = 6$ K between the Curie temperatures of 286 K in a weak field of 0.5 T and 292 K in a strong field of 9 T (Fig. 8, *b*) experimentally determined by us.

Now let us discuss the cause of emergence of the second peak on the $\Delta S(T)$ dependence. It is known that the shift of the Curie point may be caused by the demagnetization field in gadolinium [14–16]. Form-factor should be taken into account, because the real internal field in a ferromagnetic appears to be different as compared with the external field. The magnitude of this effect (ΔT_{c2} Curie point change) in experiments varies in a range of 2–6 K/T, therefore at the maximum field of 9 T in our experiments this could be quite sufficient to explain the shift of the Curie point from 290 K (true Curie point [14]) to 312 K. However, this interpretation could be reasonable only in the case when only one entropy maximum was observed that shifts with an increase in the field, as observed in [14–16]. It is impossible to explain the presence of two entropy maxima and two Curie temperatures, $T_{c1} = 293$ K and $T_{c2} = 312$ K on the same $\Delta S(T)$ dependence using the demagnetization field.

Other causes for the emergence of an additional maximum on the $\Delta S(T)$ curve can be: 1) the presence of a metastable allotropic fcc-modification of gadolinium and gadolinium oxides, confirmed by us using XRD-analysis; 2) the presence of high internal mechanical stresses that emerged during ultra-fast cooling of the melt and are able to change locally the interatomic distances and the corresponding Curie temperature in the area of structural defects [5].

Since gadolinium oxides have an extremely low Curie temperature and can not explain the entropy peak at 312 K [17], it could be possible to take into account the existence of two ferromagnetic phases of gadolinium, hcp and fcc, in microstructures [11]. However, the Curie temperature of fcc-phase is 280–285 K [11] (i.e., less than the Curie temperature of the main hcp-phase), and therefore the presence of this metastable phase can not explain the entropy peak at 312 K.

It is known from [5], that mechanical stresses in gadolinium shift the Curie temperature with a coefficient of $\sim 1.5 \cdot 10^{-8}$ K/Pa. It means, that a change of the Curie temperature in microstressed areas by $\Delta T_c = 19$ K can be achieved even at mechanical stresses of 1.3 GPa, which is ~ 1.5–2% of the Young modulus of 55–80 GPa (depending on the applied field [18]). Such internal mechanical stresses are typical for quickly cooled alloys.

Therefore the hypothesis on the role of microstresses in the shift of the Curie temperature seems to be realistic. Such stresses may well arise in the areas with an increased concentration of dislocations or in a partly amorphized phase.

5. Conclusions

1. A magnetocaloric effect is found in gadolinium microwires, that consists in magnetic entropy increase at temperatures of 293 and 312 K in a field of 9 T.

2. At 5 T the magnetic entropy change at 293 K is 12 J/kg K, that matches the known data for bulk crystalline gadolinium. A shift of the Curie temperature is observed from 286 K in a field of 0.5 T to 292 K in a field of 9 T. This shift is caused by the impact of the scattering field and can be calculated using form-factor.

3. With an increase in the magnetic field up to 9 T, an additional peak at 312 K emerges on the dependence of magnetic entropy versus temperature, which is associated with the mechanical internal stresses in the microwire emerged during ultra-fast cooling of the melt.

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Conflict of interest

The authors declare that they have no conflict of interest.

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