STRUCTURE AND MAGNETIC PROPERTIES OF THE MEDIUM-ENTROPY GdTbDyY ALLOY

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Abstract. A multicomponent rare-earth alloy GdTbDyY with a single-phase HCP crystal structure was synthesized. It was found that this alloy exhibits two magnetic phase transitions at temperatures of 140 and 201 K. Within the temperature range that encompasses both transitions, there was a noticeable magnetocaloric effect. It has been established that trivalent terbium and dysprosium ions contribute significantly to the magnetic properties of the GdTbDyY alloy: there is a correlation between structural and magnetic parameters.

Keywords: *magnetocaloric effect, rare-earth alloys, entropy change, temperature of the magnetic phase transition*

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INTRODUCTION

Magnetic solid-state cooling based on the magnetocaloric effect (MCE) is a promising environmentally friendly technology [1-5]. Numerous comprehensive studies on various magnetic refrigerants show that this cooling strategy has great potential for implementation in the foreseeable future. One of the key challenges towards this goal is to find suitable and efficient magnetic materials with large magnetocaloric effect in rather small magnetic fields (< 20 kE) [6-9]. Previously, magnetic cooling technology has become one of the most competitive and efficient techniques for achieving ultra-low cryogenic temperatures in laboratory devices [10]. In the last decades, great efforts have been made to extend the scope of this technology to near room-temperature applications.

Magnetic refrigeration equipment, the prototypes of which are currently being developed, has great potential to replace the widely used steam-compression devices. However, a number of key problems still remain unsolved. Most of the known magnetic materials exhibit a large caloric effect in a narrow temperature range, near the points of their magnetic transformation (e.g., at the Curie temperature). Moreover, the FEM in such materials, as rule, manifests itself in sufficiently strong magnetic fields. Consequently, one of the main problems on this path is the search for a caloric material with a large FEM in a magnetic field of less than 2 Tesla. It is also important to ensure stable and efficient energy conversion, since the potential magnetocaloric material "works" in the phase transition region. "Good" refrigerant should not exhibit magnetic hysteresis over the operating temperature range to achieve the highest cooling efficiency. Materials with magnetic phase transitions of the second kind, which include

the rare earth metal gadolinium, exhibit weak hysteresis to ensure repeatable results under cyclic magnetization. Currently, there are various approaches and productive ideas that can help to cope with the challenges encountered in the development of magnetic solid-state cooling.

The discovery of a giant magnetocaloric effect in the room temperature region in the three-component compound $Gd_5Si_2Ge_2$, as well as in substituted compositions, was a real breakthrough in the study of FEM [11-16]. It was found that the majority of promising magnetocaloric phases are multicomponent systems that contain several elements, including rare earth elements. Alloys and compounds containing heavy rare-earth metals, such as gadolinium, terbium and dysprosium, demonstrate high magnetocaloric characteristics and, therefore, multicomponent systems consisting of four, five or more REMs (so-called medium- and high-entropy alloys (MEA and HEA)) can also be considered as magnetic refrigerants [17]. At present, SES and HES are the objects of increased attention from scientists and technologists due to their unique combination of different physicochemical properties [18-20].

The main advantages of REM-based SES and HES are the presence of magnetic phase transitions of the second kind in them, as well as high values of the change in the magnetic part of entropy in a much wider temperature range than in traditional alloys. Previously, such compositions were studied: GdTbHoErY, GdTbHoErLa, GdTbHoErLaY, GdTbHoErPr, GdTbDyHoEr, ScGdTbDyHo, and GdTbHoEr, which demonstrated high values of the magnetocaloric effect in a wide temperature range up to 250 K [21-31]. Among them, the last three alloys from the above mentioned ones had the most promising magnetocaloric characteristics [29-31].

The aim of this work was to synthesize a new multicomponent rare-earth alloy GdTbDyY and to study the temperature and field dependences of magnetization and magnetocaloric effect in a wide temperature range, including the region of magnetic phase transitions.

EXPERIMENTAL RESEARCH METHODS

The alloy of rare-earth metals representing equiatomic combinations of elements Gd, Tb, Dy, and Y was obtained by arc melting. After preparation of charge from initial rare earth elements (purity not less than 99.9 wt. %), the alloy was synthesized in an electric arc furnace in argon atmosphere. The obtained alloy was also subjected to high-temperature annealing (at a temperature of 900 °C, lasting 80 h).

Several methods have been used to validate the GdTbDyY alloy and determine its structural parameters. The surface morphology was studied by scanning electron microscopy (SEM) on a LEO EVO 50 XVP™ microscope, the elemental and phase composition was clarified by energy dispersive X-ray spectroscopy (EDX) and X-ray phase analysis (XRD) on an ARLX'TRA™ diffractometer.

The magnetic properties were investigated on a multifunctional measuring complex MagEq 201 (LLC "PMTiK" Russia) in a wide temperature range (77-350 K) in magnetic fields up to 18 kE. The magnetization of the samples was measured by the induction method. The magnetocaloric effect was investigated by the direct method by measuring the temperature change of the sample at adiabatic change of the magnetic field.

RESULTS AND DISCUSSION

X-ray diffraction analysis of GdTbDyY alloy showed that in the studied samples the volume of the main phase with hexagonal densely packed (HPU) structure (space group P63/mmc) is not less than 95%. According to the results of X-ray fluorescence analysis it is shown that in addition to the main phase (equiatomic) in the samples a small amount (up to 5 %) of impurity phase with GPU structure with increased content of yttrium was detected. The lattice parameters *a* and *c of* the main phase are shown in Table 1. For comparison, the parameters for magnetic REMs - Gd, Tb and Dy (according to literature data [32]) are given in the table. Table 1 shows that the lattice parameters and unit cell volume for GdTbDyY are between the values of the unit cell volume Tb and Dy, which is characteristic of lanthanide compression.

Thermomagnetic analysis of GdTbDyY alloy was performed in an external magnetic field of 1 kE (see Fig. 1) to determine the temperatures of magnetic phase transitions, namely, the temperature of transition from the ferromagnetic state to the antiferromagnetic phase (θ_1) and the temperature of transition from the magnetically ordered (antiferromagnetic) to the paramagnetic state ($\theta_{2)}$. The values of the temperatures $\theta_1$and $\theta_2$are 140 and 201 K (Table 1). The observed temperature dependence of the magnetization is quite characteristic of a number of heavy rare earth metals [32]. As is known, in Tb and Dy in the region of low temperatures ferrimagnetic ordering is observed (the light axis lies in the basis plane), and with increasing temperature there is a sharp decrease in magnetization caused by the phase transition from the ferrimagnetic phase to the helicoidal antiferromagnetic phase (GAFM). The region of existence of GAFM in terbium and dysprosium is very different: in Tb this region is only 8 K, while in Dy it is an order of magnitude larger (93 K) [33-35]. As a

result, it can be assumed that in the GdTbDyY alloy, ferrimagnetic ordering also exists in the low temperature region at$T < \Theta_1$ and a GAFM phase appears in the temperature region$\Theta_1 < T < \Theta_2$. In this case, the temperatureΘ_2 is the Neel temperature. In the alloy GdTbDyY atΘ_2 there is a magnetic phase transition from antiferromagnetic phase to paramagnetic phase.

Fig. 2 shows the field dependences of the magnetization in magnetic fields up to 18 kE measured at different temperatures. At a temperature of 300 K, a linear dependence of the magnetization on the magnetic field is observed, which confirms the presence of a paramagnetic state at$T > \Theta_2$. At temperature 140 K, a curve characteristic of a ferromagnetic is observed.

The magnetocaloric effect in this work was studied by direct method by measuring the magnitude of temperature change during adiabatic magnetization of the sample. Fig. 3 shows the temperature dependences of the FEM in magnetic fields up to 18 kE. Two pronounced maxima are observed on the curves$\Delta T_{ad}(T)$, which merge into one broad maximum as the magnetic field increases. The maximum in the low temperature region corresponds to the phase transition from the FM to the AFM state with increasing temperature. The temperature change at FEM corresponds to the region of rapid decrease of magnetization with temperature growth, which follows from Maxwell's relation:

$$\Delta T_{ad} = -\frac{C}{T}\int_0^H \left(\frac{\partial M}{\partial T}\right) dH \quad (1)$$

At magnetic phase transitions from one magnetic state to another at a change in the magnitude of the applied magnetic field, the FEM is observed due to the fact that the entropies of different magnetic phases are not equal to each other [33]. In particular,

considering the antiferromagnetism- ferromagnetism transition in the field as a phase transition of the first kind, we obtain the FEM due to the entropy change at this transition:

$$\Delta T_{\text{ад}} = \frac{-T}{C}\left(S_{\text{ф}} - S_{\text{аф}}\right)1) \quad (2)$$

where $S_f$and $S_{af}$are the entropy values of the ferromagnetic and antiferromagnetic states, respectively,$S_{\text{ф}} - S_{\text{аф}}$ is the entropy jump at the AFM -- FM transition. This type of FEM is observed in a number of rare-earth metals and alloys [33]. In the single crystal Dy in the magnetic field applied in the basis plane, a broad maximum appears on the temperature dependence of the FEM (in the region of existence of antiferromagnetic structure) if the value of the field H does not exceed the critical value H_{kr}. At$H > H_{\text{кр}}$ the antiferromagnetic structure is destroyed and the ferromagnetic structure appears. Similarly, in the investigated SES GdTbDyY in magnetic fields below 7 kE, a negative FEM is observed in the antiferromagnetic ordering region. The appearance of negative FEM is caused by the presence of AFM magnetic ordering near θ_2.

For the case of magnetic fields below 14 kE, the AFM-FM transition in $\theta_2$corresponds to a point satisfying the condition$\Delta T_{ad} = 0$, and in a field of 16 kE a narrow maximum on the curve$\Delta T_{ad}(T)$. Hence, we can conclude that a magnetic field of 16 kE is sufficient to suppress the helicoidal AFM structure.

The obtained data, in general, coincide with the results of studies of pure REM and binary REM alloys [32,35] and allow us to construct the magnetic phase diagram of the GdTbDyY alloy (Fig. 4). The AFM phase of helicoid type exists in the range ~ 140-201 K in a magnetic field less than 15 kE. The magnetization curves do not show

critical fields as previously found in Tb single crystals, which is probably due to the presence of impurities in the samples that play the role of capture centers and thus prevent the destruction of the weakly bound AFM phase. With increasing magnetic field, the temperature range of the AFM phase decreases significantly. It can be inferred that with increasing magnetic field, the helicoidal phase transforms into a fan structure. The magnetic and magnetothermal properties measured in the present work contain features that can be related to the existence of the fan-type phase. The position of the phase boundaries determined from the FEM anomalies allows the determination of approximate phase boundaries. The fan-type phase exists between the FM and PM ordering regions, i.e., in the temperature range of 150-200 K and the maximum field value of 15 kE. In the low-field region it is replaced by helicoidal AFM ordering. However, the final solution to the question of the existence of the fan-type structure in the GdTbDyY alloy still remains open. Thus, detailed studies on single-crystal samples are needed to determine more precisely the type of magnetic ordering in the specified range.

In this study, the aim was to elucidate the mechanisms responsible for the magnitude of magnetic phase transition temperatures. Table 1 shows the phase transition temperatures for Dy and Tb known from literature data [32]. We can calculate the average value for the temperaturesΘ_1= 154 K andΘ_2 = 205 K. The obtained values are close to the experimentally determined temperaturesΘ_1 andΘ_2 for the GdTbDyY alloy. Note that Y^{3+} ions do not carry an appreciable localized magnetic moment, and Gd^{3+} ions are characterized by the absence of an orbital moment, and, as

a consequence, by a relatively low magnetocrystalline anisotropy and ferrimagnetic ordering in the whole temperature region.

It can be concluded that for multicomponent RZ alloys possessing the region of helicoidal antiferromagnetism, the main contribution to the magnetic phase transition temperatures is made by RZ elements characterized by the presence of the 4f-shell orbital magnetic moment. Also, the interatomic distances between magnetically active ions influence the values of magnetic phase transition temperatures. As mentioned above, the unit cell volume for the alloy GdTbDyY is exactly between the unit cell volumes Tb and Dy. It is known that REMs are characterized by the indirect exchange RKKI interaction (Ruderman-Kittel-Kasuya-Iosida), which is one of the main mechanisms of interaction of magnetic moments in 4f-metals. The RKKI interaction appears due to spin-dependent scattering of electrons in the crystal on magnetic centers and interference of scattered waves from different centers. When the distances between the magnetic moments change, the value of the integral of the indirect exchange interaction changes significantly because it is inversely proportional to the distance to the third degree.

CONCLUSION

The obtained results can be used as recommendations in the search for new magnetocaloric materials among medium-entropic alloys. We have investigated magnetic and magnetocaloric properties of GdTbDyY alloy. The general regularities in the properties of the obtained alloy of GdTbDyY, terbium and dysprosium, as well

as specific features of the GdTbDyY alloy, namely, the absence of a noticeable contribution to the magnetic properties from gadolinium and yttrium. The performed study may be in demand when solving the problem of increasing the performance of magnetic solid-state refrigeration devices based on the magnetocaloric effect.

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FIGURE CAPTIONS

Fig. 1. Temperature dependence of the magnetization of the GdTbDyY alloy in a magnetic field of 1 kE.

Fig. 2. Field dependences of the magnetization of GdTbDyY alloy at different temperatures of 80, 160, 200, 260, 284 and 300 K.

Fig. 3. Temperature dependences of FEM of GdTbDyY alloy in different fields of 3, 7, 10, 14, 16 and 18 kE.

Fig. 4. Magnetic phase diagram of GdTbDyY alloy.

Table 1. Structural and magnetic parameters of medium-entropic alloy GdTbDyY, as well as Gd, Tb, Dy: lattice parameters *a* and *c*, unit cell volume *V*, axial ratio *c/a*, Curie temperature T_C, temperatures of magnetic phase transitions $\Theta_{(1)}$ and $\Theta_{(2)}$.

Compound	*a*, Å	*c*, Å	*c/a*	*V*, Å^3	$\Theta_{(1)}$, K	$\Theta_{(2)}$, K	T_C, K
GdTbDyY	3.594	5.670	1.58	63.17	140	201	-
Gd	3.636	5.782	1.59	65.93	-	-	293
Tb	3.601	5.694	1.58	63.68	222	230	-
Dy	3.593	5.654	1.57	62.95	87	180	-

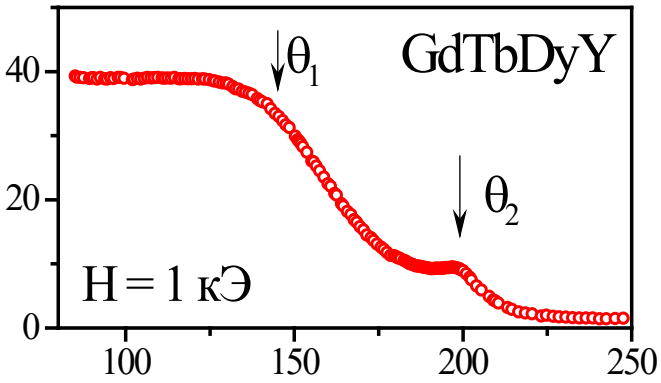

Fig. 1.

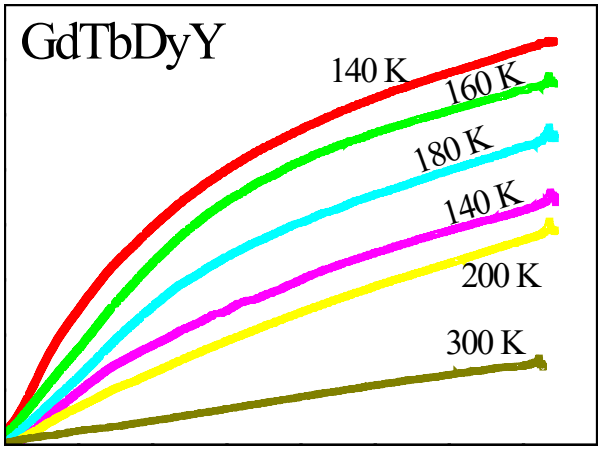

Fig. 2.

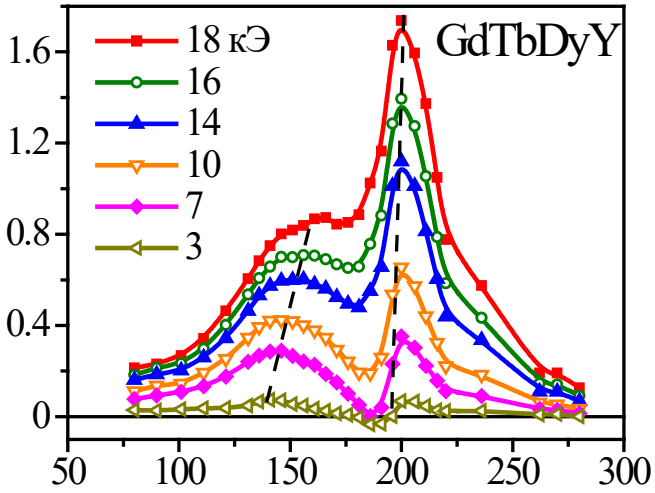
18 кЭ
16
14
10
7
3
GdTbDyY
1.6
1.2
0.8
0.4
0
50
100
150
200
250
300

Fig. 3.

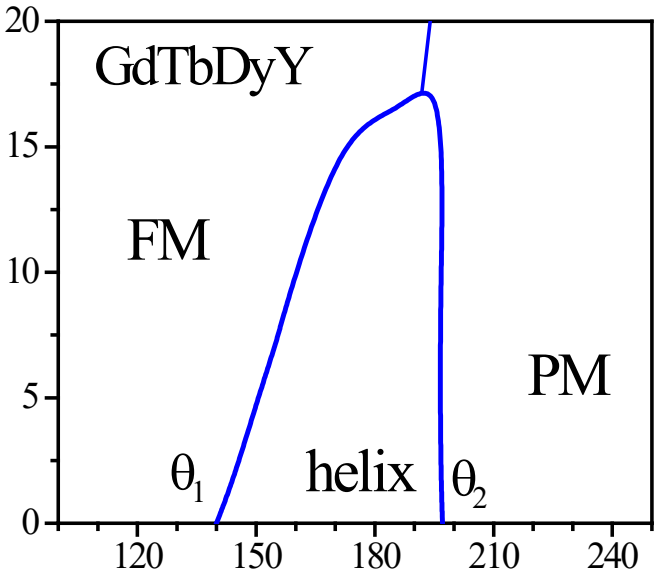
GdTbDyY
FM
PM
θ1
helix
θ2
20
15
10
5
0
120
150
180
210
240

Fig. 4.