Giant Rotating Magnetocaloric Effect in the Region of Spin-Reorientation Transition in the $NdCo_5$ Single Crystal

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We have investigated the anisotropy of the magnetocaloric effect in a $NdCo_5$ single crystal in a wide range of temperatures, including the spin-reorientation temperature region. In the field $\mu_0 H = 1.3$ T in the spin-reorientation region 250–310 K, we discovered a giant rotating magnetocaloric effect of ~1.6 K, caused by rotation of the magnetization vector. The calculations of the anisotropy magnetocaloric effect for the field $\mu_0 H = 1.3$ T have been carried out.

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Introduction.—The magnetocaloric effect (MCE) refers to a temperature change in a magnetic material due to a reversible release of heat or absorption under its adiabatic magnetization. Applying a magnetic field to a magnetic material changes its magnetic state, internal energy, and entropy, which causes heating or cooling of the magnetic material. The most significant contributions to MCE include (i) changes of exchange energy due to magnetization during a paraprocess [1,2], (ii) changes of magnetic anisotropy energy during rotation of a spontaneous magnetization vector [3,4], and (iii) changes of magnetoelastic energy due to magnetostriction [5].

The majority of studies investigated the first contribution to MCE—i.e., the magnetocaloric effect of a paraprocess, which peaks at the Curie temperature in the ferromagnetic-paramagnetic phase transition. Meanwhile, the second and third contributions to MCE have not been sufficiently investigated. This lack of attention may be explained by the fact that, for most magnetic materials, the contributions at the Curie temperature are considerably lower than MCE induced by a paraprocess. Still, in the region of magnetic spin-reorientation phase transition, the anisotropy and rotating MCE can be quite significant. Today, studies of the magnetocaloric effect are of considerable interest for developing more energy-efficient and ecologically safe chlorofluorocarbon-free refrigerators on the basis of giant MCE materials. Extensive studies of MCE anisotropy can facilitate finding new, constructive solutions in developing magnetic refrigerators [6].

The contribution from the magnetization vector rotation to the total MCE is known to be higher for materials with high values of derivatives of the magnetocrystalline anisotropy (MCA) constants with respect to temperature [7]. This suggests that the highest values of the rotating MCE should be expected at SRT in single crystals of intermetallic compounds of rare-earth magnets with 3*d* metals, where magnetic anisotropy constants have record-high values at room temperatures.

The present study is the first to investigate the rotating MCE in the $NdCo_5$ compound with high values of magnetic anisotropy constants. According to the literature [8–14], two II-type SRTs are observed in $NdCo_5$ compounds. When the temperature is increased to $T_{SR1} = 250$ K, an ''easy-plane''–''easy-cone'' transition occurs. When the temperature is increased to $T_{SR2} = 290$ K, an uniaxial magnetic state with an easy magnetization axis along the hexagonal $\boldsymbol{c}$ axis is observed. The fact that the temperatures for these transitions are close to room temperature makes it possible to use this material as a working body for magnetic refrigerators.

Experimental results and discussion.—The MCE was measured by a direct method. A temperature change of a sample under adiabatic magnetization was determined by the copper-constantan thermocouple. The measurements were taken in the temperature range of 78–700 K in a constant magnetic field of up to $\mu_0 H = 1.3$ T. The angle between the hexagonal axis of the crystal and the magnetic field was set by a rotating electromagnet, which allowed us to measure the MCE along various crystallographic directions.

Figure 1 shows the MCE temperature dependencies in the $NdCo_5$ single crystal for two principal crystallographic directions: the hexagonal $\boldsymbol{c}$ axis ($\Delta T_{AD,c}$) and the $\boldsymbol{a}$ axis lying in the basal plane ($\Delta T_{AD,a}$). As Fig. 1 shows, the MCE temperature dependencies in the $\mu_0 H = 1.3$ T field are characterized by peaks in the SRT range. When the external magnetic field H is applied along the $\boldsymbol{a}$ axis ($\boldsymbol{H} \parallel \boldsymbol{a}$), the MCE $\Delta T_{AD,a}$ at $T < 250$ K is virtually nonexistent. In the 250–360 K temperature range, which includes the SRT range, the MCE temperature dependence peaks, and $\Delta T_{AD,a}$ reaches its maximum positive value of ≈1.1 K at $T = 290$ K. In the magnetic field $\boldsymbol{H} \parallel \boldsymbol{c}$, the MCE $\Delta T_{AD,c}$

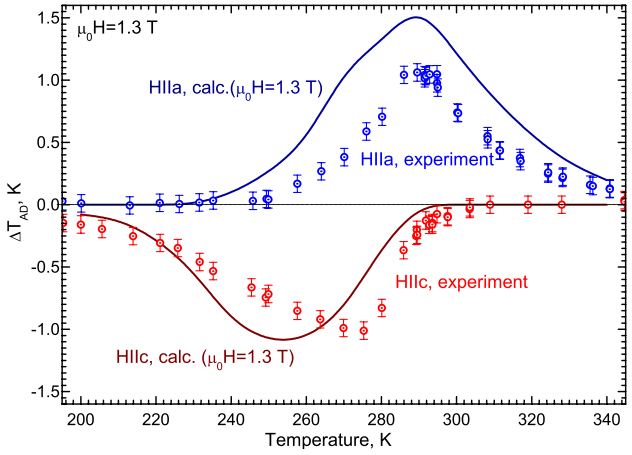

FIG. 1 (color online). Adiabatic change of temperature of the $NdCo_5$ single crystal, measured along the c axis $\Delta T_{\mathrm{AD},c}$ (red symbols) and along the a axis $\Delta T_{\mathrm{AD},a}$ (blue symbols) in the field $\mu_0 H = 1.3$ T. The lines indicate the results of the calculations of the rotating MCE using the expression (4) for the field $\mu_0 H = 1.3$ T and the anisotropy constants from Ref. [10] (solid lines).

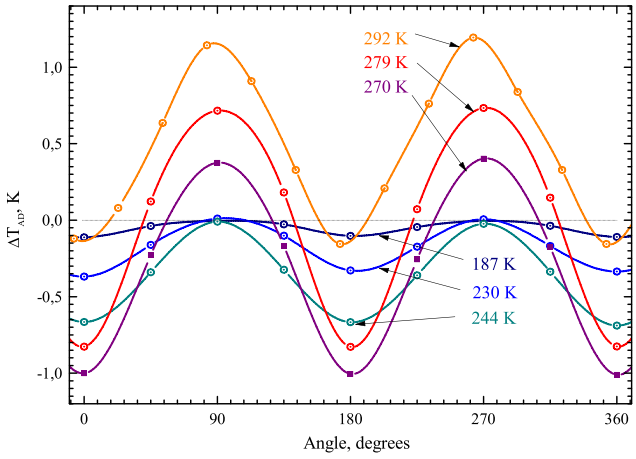

FIG. 2 (color online). The adiabatic change of temperature measured at different angles between the external magnetic field $\mu_0 H = 1.3$ T and the c axis of the $NdCo_5$ single crystal in the spin-reorientation region.

decreases monotonously as the temperature increases and reaches its maximum negative value $\Delta T_{\mathrm{AD},c} \approx -1.1$ K at 275 K.

The MCE anisotropy is clearly observed in the measurements of the adiabatic temperature change as a function of the Θ_H angle between the magnetic field and the hexagonal $\boldsymbol{c}$ axis. Figure 2 shows the MCE angle dependencies in the $NdCo_5$ single crystal measured under various temperatures. As we can see from Fig. 2, depending on the Θ_H angle, the sample can either heat (positive MCE) or cool (negative MCE). For instance, at $T = 270$ K, when $\boldsymbol{H} \parallel \boldsymbol{c}$, $\Delta T_{\mathrm{AD},c} = -1.0$ K. With $\boldsymbol{H} \parallel \boldsymbol{a}$, we observe $\Delta T_{\mathrm{AD},a} = 0.4$ K.

Figure 3 shows the temperature change of the $NdCo_5$ single crystal, caused by the rotation of magnetization with the change in the direction of the magnetic field from the $\boldsymbol{c}$ axis to the $\boldsymbol{a}$ axis ΔT_{ROT} (rotating MCE). Prior to the measurements, the temperature of the sample was stabilized. After that, the magnetic field was turned on, and, following another thermodynamic balancing in the magnetic field, the electromagnet was rotated by 90° over a period of 1 sec. After the magnet was rotated, we measured the temperature change of the single crystal caused by the rotation of magnetization of the sample ΔT_{ROT}, following the change in the direction of the external magnetic field.

As we can see in Fig. 3, ΔT_{ROT} reaches its maximum at 280 K and has a value of 1.6 K, which is significantly higher than the values of the rotating MCE observed before in other materials. This enables us to designate the effect we discovered as the giant rotating MCE. It should be noted that the acquired measurements are comparable with the MCE values observed in intermetallic compounds near the Curie temperature. It is also important to point out that the rotating MCE is reversible. Under the thermal and field cycling, no hysteresis is observed in the $NdCo_5$ single crystal. The absence of energy dissipation is an obvious advantage for technical applications of this material.

To describe the rotating MCE quantitatively, one should take into account the changes of the magnetic part of the entropy and magnetic anisotropy energy at the rotation of the magnetization vector in the SRT region.

The magnetic anisotropy energy depends considerably on the angles that the magnetization forms with the major crystallographic directions of the crystal. For a hexagonal magnetic, when the first two anisotropy constants are taken into account, the MCA energy looks as follows:

$$F_{A,H=0} = K_1 \sin^2\theta_0 + K_2 \sin^4\theta_0, \qquad (1)$$

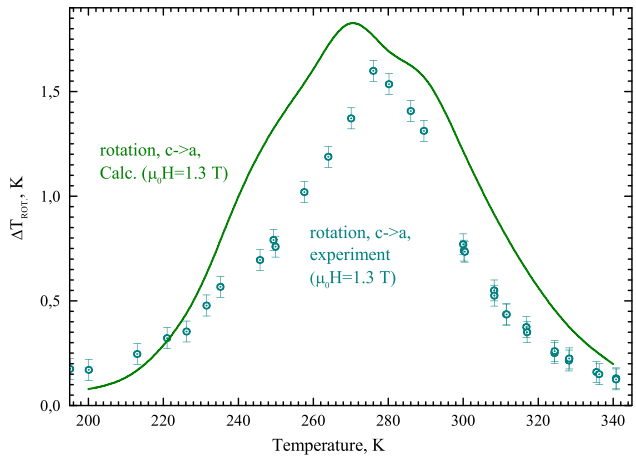

FIG. 3 (color online). The adiabatic change of temperature ΔT_{ROT} caused by the rotation of the $NdCo_5$ single crystal in the magnetic field $\mu_0 H = 1.3$ T from the c axis to the a axis (symbols) and the results of the calculations using the expression (4).

where θ_0 is an angle between the magnetization vector and the $\boldsymbol{c}$ axis of the crystal in the absence of a magnetic field.

The change in the magnetic anisotropy energy of the sample, caused by the magnetization rotation when a magnetic field is applied, equals

$$\Delta F_A = F_{A,H} - F_{A,0} = K_1(\sin^2\theta_H - \sin^2\theta_0) + K_2(\sin^4\theta_H - \sin^4\theta_0), \quad (2)$$

where $F_{A,H}$ and $F_{A,0}$ are MCA energy in the field H and in the zero magnetic field, respectively, θ_0 is the initial value of the angle at $H = 0$, and θ_H is the ending value of the angle in the field H.

The corresponding change in the magnetic part of the sample's entropy due to rotation processes under adiabatic magnetization of a single crystal can be written as follows:

$$\Delta S_M = -\left[\left(\frac{\partial F_{A,H}}{\partial T}\right) - \left(\frac{\partial F_{A,0}}{\partial T}\right)\right] = -\left(\frac{\partial \Delta F_A}{\partial T}\right). \quad (3)$$

In the few existing papers on MCE anisotropy, the calculations were performed under the condition that the magnetic field is higher than the anisotropy field and $\theta_H = \Theta_H$. While this condition simplifies calculations when $\Theta_H = 0$ ($\boldsymbol{H} \parallel \boldsymbol{a}$) or $\Theta_H = \frac{\pi}{2}$ ($\boldsymbol{H} \parallel \boldsymbol{c}$), it often does not allow researchers to describe correctly the MCE anisotropy in the fields $\mu_0 H = 1$–2 T. However, in the existing prototypes of magnetic refrigerators, the systems based on the NdFeB permanent magnets are typically used, and these magnets create magnetic fields precisely of this value. For small magnetic fields, we took into account the fact that, at $\mu_0 H = 1$–2 T, the magnetization direction of the $NdCo_5$ single crystal does not coincide with the direction of the external magnetic field [13,14], and the angle $\theta_H \neq \Theta_H$ has to be taken into account as well. If we take into account this angle, the expression for the rotating MCE in the field below the anisotropy field should be written as follows:

$$\Delta T = -\frac{T}{C_p}\Delta S_M = \frac{T}{C_P}\left(\frac{\partial K_1}{\partial T}(\sin^2\theta_H - \sin^2\theta_0) + \frac{\partial K_2}{\partial T}(\sin^4\theta_H - \sin^4\theta_0)\right), \quad (4)$$

where θ_0 is the initial value of the angle at $H = 0$ and θ_H is the ending value of the angle in the field H.

The θ_H was calculated according to the method described in detail in Refs. [15,16]. This method was chosen because it takes into account the presence of the magnetic domain structure in a sample, which should be considered in the fields $\mu_0 H = 1.3$ T for the case when the field is not applied along the easy magnetization axis. This is the first time this approach to calculating the MCE in the fields below the anisotropy field has been used. The experimental evidence available for $NdCo_5$ reveals differences in the observed MCA constants [8–11]. For qualitative calculations of the rotating MCE, we used K_1 and K_2 constants reported in several research papers. The best correspondence with our experiment occurred when we used the constants from [11]. Below, we report only on the results of calculations involving these constants and the heat capacity from [12].

Figures 1 and 3 show the results of the calculations using (4) and the MCA constants from Ref. [11]. From Figs. 1 and 3, we can see that there is some degree of correspondence between the calculated dependencies and the experimental data. Under temperatures below T_{SR1}, the $\boldsymbol{a}$ axis of the $NdCo_5$ single crystal is an easy magnetization axis. Accordingly, at $T < T_{SR2}$, $\theta_0 = \theta_H = \frac{\pi}{2}$ and, in the case when the magnetic field is directed along the a axis, the rotating MCE $\Delta T_{AD,a}$ equals zero (Fig. 1). At $T > T_{SR2}$, the $\boldsymbol{c}$ axis is an easy magnetization axis. Then, $\theta_0 = \theta_H = 0$, and $\Delta T_{AD,c}$ in this temperature range also equals zero, which is clearly seen in Fig. 1.

In the case when the angle between the direction of the external field θ_H and the initial position of the magnetization vector θ_0 does not equal zero, and when rotation processes take place, the sign of the MCE is determined by the sign of the derivatives of the first and second anisotropy constants with respect to temperature and by the direction of the rotation of the magnetization vector. For instance, in the 150–400 K temperature range, $\frac{\partial K_1}{\partial T} + \frac{\partial K_2}{\partial T} > 0$. When the field is applied along the $\boldsymbol{a}$ axis, the difference is as follows: $\theta_H - \theta_0 \geq 0$; with the field applied along the $\boldsymbol{c}$ axis, $\theta_H - \theta_0 \leq 0$. With the magnetization along the $\boldsymbol{a}$ axis, the expression (4) produces a positive MCE, while with the magnetization along the $\boldsymbol{c}$ axis, it produces a negative MCE. Certain discrepancies with the experiment may be due to the fact that the MCA constants were determined by other researchers on a different single crystal, and, apparently, there is a certain difference between the samples.

Knowing the heat capacity of the $NdCo_5$ single crystal [12] and its adiabatic temperature change, we can estimate the magnetic entropy change at SRT for the given compound. Thus, in the magnetic field $\mu_0 H = 1.3$ T, when the single crystal is rotated by 90°, the maximum entropy change equals $\Delta S_M = 1.9$ J/(kg K), or more than 1.5 J/(kg K) in the field $\mu_0 H = 1$ T [for Gd, this value is 3 J/(kg K) in the field of 1 T [17]].

In the low temperature area, it is possible to achieve the rotating MCE due to high values of the magnetic anisotropy constants of the rare-earth-metal $4f$ sublattice and their sharp change with temperature [expression (4)] in the case of a low Curie temperature. As reported in Ref. [18], for the $DyAl_2$ compound for the field $\mu_0 H = 2$ T, the authors calculated the entropy change by means of Maxwell's equations in the SRT region and received a high value of $\Delta S_M = 4.2$ J/(mol K) (or 19.4 J/kg K) at $T = 24.4$ K. However, when a magnetic $3d$ sublattice is

absent, it is impossible to realize this effect in the room temperature region. Besides, the width of the maximum on the temperature dependence curve of the MCE for $DyAl_2$ is only 20 K, while for $NdCo_5$ it is 60 K.

The estimates of the maximum MCE caused by the rotation of the magnetization vector are given in Ref. [19]. For RCo_5 compounds, the value of the maximum entropy change was determined as $\Delta S_M = 4.3$ J/(kg K). This value can be achieved in magnetic fields of $\mu_0 H = 1$ T under the condition that in this field it is possible to realize the rotation of the magnetization vector from one crystallographic axis to another. This exceeds the value of the magnetic entropy change for Gd in this field. Thus, the results presented in Ref. [19] show that it is possible to realize the values of the MCE in the fields of 1 T that are higher than the MCE of Gd, under the condition that the high gradients of the magnetic anisotropy constants are realized near room temperature.

Conclusion.—The present work has discovered the giant rotating MCE at room temperature in the $NdCo_5$ single crystal. This compound is a ferromagnetic with two magnetic sublattices, $3d$ and $4f$. Each sublattice has high MCA constants. The rare-earth-metal sublattice is in a strong exchange field of the cobalt sublattice. As a result, the high values of the magnetic anisotropy constants and high speeds of change of these constants with temperature can be realized in the area of room temperatures.

The results of the present study of the anisotropy of the magnetocaloric effect in the $NdCo_5$ single crystal show the following: (i) The MCE at the magnetization of the single crystal along the $\boldsymbol{c}$ axis has a negative sign. In the field $\mu_0 H = 1.3$ T, it reaches -1.1 K at 275 K temperature. At magnetization along the $\boldsymbol{a}$ axis, the MCE has a positive sign and reaches 1.1 K at 290 K temperature. (ii) By rotating the single crystal in the magnetic field 1.3 T, we can achieve the temperature change in the sample of 1.6 K. (iii) It has been shown that, to determine the rotating MCE correctly in the fields under the anisotropy field ($\mu_0 H = 1.3$ T), it is necessary to take into account the domain structure that occurs in the sample.

The experimental and theoretical results of our Letter point at the possibility of using the rotating MCE in magnetic refrigerators, working at close to room temperature. The advantage of such systems is that the temperature change is caused by the rotation of the magnetic material in a magnetic field, which is easier to realize from a technological standpoint than the translational motion of the magnetic material into the magnetic field area and out of it.

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