Enhanced magnetocaloric effect and magnetic phase diagrams of single-crystal GdCrO$_3$

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The crystalline structure, magnetism, and magnetocaloric effect of a GdCrO$_3$ single crystal grown with the laser-diode-heated floating-zone technique have been studied. The GdCrO$_3$ single crystal crystallizes into an orthorhombic structure with the space group $Pbnm$ at room temperature. Upon cooling, under a magnetic field of 0.1 T, it undergoes a magnetic phase transition at $T_{N-Cr} = 169.28(2)$ K with Cr$^{3+}$ ions forming a canted antiferromagnetic (AFM) structure, accompanied by a weak ferromagnetism. Subsequently, a spin reorientation takes place at $T_{SR} = 5.18(2)$ K due to Gd$^{3+}$-$Cr^{3+}$ magnetic couplings. Finally, the long-range AFM order of Gd$^{3+}$ ions establishes at $T_{N-Gd} = 2.10(2)$ K. Taking into account the temperature-(in)dependent components of Cr$^{3+}$ moments, we obtained an ideal model in describing the paramagnetic behavior of Gd$^{3+}$ ions within 30–140 K. We observed a magnetic reversal (positive $\rightarrow$ negative $\rightarrow$ positive) at 50 Oe with a minimum centering around 162 K. In the studied temperature range of 1.8–300 K, there exists a strong competition between magnetic susceptibilities of Gd$^{3+}$ and Cr$^{3+}$ ions, leading to puzzling magnetic phenomena. We have built the magnetic-field-dependent phase diagrams of $T_{N-Gd}$, $T_{SR}$, and $T_{N-Cr}$, shedding light on the nature of the intriguing magnetism. Moreover, we calculated the magnetic entropy change and obtained a maximum value at 6 K and $\Delta S_m \approx 57.5$ J/kg.K. Among all RECrO$_3$ (RE = 4f$^n$ rare earths, $n$ = 7–14) compounds, the single-crystal GdCrO$_3$ compound exhibits the highest magnetic entropy change, as well as an enhanced adiabatic temperature, casting a prominent magnetocaloric effect for potential application in magnetic refrigeration.

I. INTRODUCTION

The GdCrO$_3$ compound was initially synthesized in 1956 [1]. Its crystalline structure was proved to be orthorhombic with the space group $Pbnm$ and lattice constants $a = 5.312$ Å, $b = 5.514$ Å, and $c = 7.611$ Å [2]. Recently, the space group was determined as $Pna2_1$ [3]. Later, its infrared and electronic absorption spectra were studied [4]. Albeit that the GdCrO$_3$ single crystal grown with a flux method may contain $\sim1\%$ impurity, it was proposed that below $\sim7$ K, the ionic Cr$^{3+}$ magnetic sublattice underwent a spin reorientation from the $\Gamma_4$ ($G_x$, $A_y$, $F_z$) to the $F_2$ ($F_x$, $C_y$, $G_z$) magnetic structure. This was driven by the formation of the Gd$^{3+}$ magnetic sublattice and the Gd$^{3+}$-$Cr^{3+}$ couplings [5]. [6]. The behavior of negative magnetization with a minimum centering around 25 K was observed in a polycrystalline GdCrO$_3$ sample, which was ascribed to the interactions between paramagnetic (PM) Gd$^{3+}$ moments and the canted Cr$^{3+}$ antiferromagnetic (AFM) moments [7]. It was reported that the GdCrO$_3$ compound displayed an electric polarization of 0.7 $\mu$C/m$^2$ at $E = 2.25$ kV/cm, appearing simultaneously with the formation of Cr$^{3+}$ magnetic structure below $T_{N-Cr}$ [3] [8]. The distortion in the GdCrO$_3$ structure was proposed to be associated with the off-center displacement of Gd atoms together with octahedral rotations via displacement of oxygen ions [3] [9]. Magnetic refrigeration has risen to be a new civilian refrigeration technology [10, 11]. Beside the ferroelectric property, the GdCrO$_3$ compound has attracted much attention and been believed to be a promising magnetorefrigerator material due to its high effective magnetic entropy change [12, 13].

In this paper, we have grown a GdCrO$_3$ single crystal using laser diodes with the floating-zone (FZ) technique. We characterized the crystalline structure with a room-temperature x-ray powder diffraction (XRPD) study and the magnetic properties with a physical property measurement system (PPMS DynaCool instrument, Quantum Design). Based on our measurements, we studied the magnetocaloric effect (MCE) and found that the GdCrO$_3$ single crystal investigated in this study displayed the highest magnetic entropy change among all RECrO$_3$ compounds (RE = 4f$^n$ rare earths, $n$ = 7–14). Moreover, we have built the magnetic phase diagrams as a function of applied magnetic field around the magnetic phase transitions of Gd$^{3+}$ and Cr$^{3+}$ ions, shedding light...
on a further understanding of the nature of the intriguing magnetism.

II. EXPERIMENTAL

Polycrystalline samples of GdCrO$_3$ compound were synthesized using the conventional solid-state reaction method \([16, 18]\). Chemically stoichiometric raw materials of Gd$_2$O$_3$ (ALFA AESAR, 99.9\%) and Cr$_2$O$_3$ (ALFA AESAR, 99.6\%) were milled and mixed by a Vibratory Micro Mill (FRITSCH PULVERISETTE 0) with an addition of 5–10\% Cr$_2$O$_3$ compound. The mixture was calcined twice at ambient air pressure: Once was at 1100 °C for 24 h, and the other at 1200 °C for 36 h. We grew GdCrO$_3$ single crystals with a laser diode FZ furnace (Model: LD-FZ-5-200W-VPO-PC-UM) \([19–21]\).

We pulverized a small piece of the single crystal to check the phase purity and determine the room-temperature crystalline structure with XRPD employing copper $K\alpha$1 (1.54056 Å) and $K\alpha$2 (1.544390 Å) with a ratio of 2:1 as the radiation. The XRPD pattern was collected at 2θ = 20–90° with a step size of 0.02°. We used the software FULLPROF SUITE \([22]\) to refine the collected XRPD data. We modeled the Bragg peak shape with a Pseudo-Voigt function and used a linear interpolation between automatically-selected data points to estimate background contribution. The refining parameters are scale factor, zero shift, background contribution, peak shape parameters, asymmetry, preferred orientation, lattice constants, and atomic positions.

The measurements of dc magnetization and specific heat were carried out on a PPMS DynaCool instrument using the vibrating sample magnetometry and the heat capacity options, respectively. The dc magnetization at an applied magnetic field of 500 Oe was measured with two modes at 1.8–300 K: One was after cooling with 0 Oe, i.e., zero-field cooling (ZFC), and the other at $\mu_0H = 500$ Oe, i.e., field cooling (FC). To clearly show the effect of applied magnetic field on magnetic structures of the two modes at 1.8–300 K: One was after cooling with 0 Oe, an applied magnetic field of 500 Oe was measured with increasing magnetic field. In order to gain the adiabatic temperature change, the specific heats were measured at magnetic fields of 0.5, 1, 2, 3, 5, 6, 8, 10, 12, and 14 T.

III. RESULTS AND DISCUSSION

A. Structural study

To study the crystalline structure of our grown GdCrO$_3$ single crystal, we pulverized a small piece of the GdCrO$_3$ single crystal and carried out a XRPD experiment at room temperature. Figure 1(a) shows the collected and refined patterns. Within the present experimental accuracy, the data can be well indexed with space group $Pmnb$. The corresponding crystalline structure in one unit cell was exhibited in Fig. 1(b), and the refined structural information was listed in Table I. The low values of the goodness of refinement validate our FULLPROF refinements. Our refined room-temperature lattice constants of the pulverized GdCrO$_3$ single crystal are $a = 7.6041(3)$ Å, $b = 5.5255(2)$ Å, and $c = 5.3102(2)$ Å, consistent with previously-reported values from a study with the polycrystalline GdCrO$_3$ compound \([17]\).

B. Magnetic phase transitions

Figure 2 shows the measured magnetization as a function of temperature. As shown in the left of Fig. 2(a), as temperature decreases from 300 to 1.8 K, there is a smooth increase in the magnetization with an anomaly appearing around $T_{N-Cr}$ [Fig. 2(d)]. At $T_{N-Cr}$, we observed a small sharp increase [Fig. 2(d)]. This is by far clearer in the inverse magnetic susceptibility $\chi^{-1}$, as shown in the right of Fig. 2(a). The magnetization increases smoothly again until around 25 K. We observed a maximum at $T_{SR}$ [Fig. 2(c)]. Upon further cooling, there exists a kink at $T_{N-Gd}$ [Fig. 2(c)]. These anomalies are attributed to magnetic phase transitions. The first anomaly is related to Cr$^{3+}$ ions, and $T_{N-Cr} \approx 168.97$ K at 0.06 T; the second one is ascribed to the spin reorientation of Cr$^{3+}$ ions due to the gradual formation of Gd$^{3+}$ moments \([6]\), and $T_{SR} \approx 6.74$ K at 0.02 T; taking into account the fact that the ordering of 4f magnetic Gd$^{3+}$ ions requires much lower temperatures \([23, 24]\), the third one thus corresponds to the formation of long-range ordered Gd$^{3+}$ magnetic structure, and $T_{N-Gd} \approx 2.33$ K at 0.02 T. The inverse magnetic susceptibility $\chi^{-1}$ in a pure PM state observes well with the Curie-Weiss (CW) law

$$\chi^{-1}(T) = \frac{3k_B(T - \Theta_{CW})}{N_A\mu_{eff}^2}, \quad (1)$$

where $k_B = 1.38062 \times 10^{-23}$ J/K is the Boltzmann constant, $\Theta_{CW}$ is the PM CW temperature, $N_A = 6.022 \times 10^{23}$ mol$^{-1}$ is the Avogadro’s constant, and $\mu_{eff} = g\mu_B\sqrt{J(J+1)}$ is the effective PM moment. We fit the magnetization in the temperature range of 200–300 K ($> T_{N-Cr} > T_{N-Gd}$) to Eq. 1 and extrapolated the fit down to $M(\Theta_{CW}) = 0$, as shown in the right of Fig. 2(a).
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Though the magnetic frustration parameter for Cr

larger than the corresponding experimental value 8.40(9)

taller GdCrO$_3$ compound. This theoretical value is

∼ reported value

the appearance of

The bottom curve represents the difference between observed and refined XRPD patterns. (b) Crystal structure of GdCrO$_3$ compound in one unit cell (solid lines) with space group $Pmnb$ (No. 62). The Gd, Cr, O1, and O2 ions were labeled.

TABLE I. Refined structural parameters, including lattice constants, unit-cell volume ($V$), atomic positions, and goodness of refinement, from room-temperature XRPD with a pulverized GdCrO$_3$ single crystal. The Wyckoff sites of all atoms were listed. We kept the atomic occupation factors (OCs) during FULLPROF refinements. The numbers in parentheses are the estimated standard deviations of the last significant digit.

| Atom | Site | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ ($Å^3$) | $α(= β = γ)$ (°) | OCs |
|------|------|---------|---------|---------|------------|----------------|-----|
| Gd   | 4c   | 7.6041(3)| 5.5255(2) | 5.3102(2) | 223.12(2) | 90            | OCs |
| Cr   | 4b   | 0.00    | 0.25    | 0.0588(2) | 0.0151(3) | 0.5           | 0.5 |
| O1   | 4c   | 0.25    | 0.4705(19) | 0.1146(19) | 0.5        | 0.5 |
| O2   | 8d   | 0.0530(10) | 0.2784(17) | 0.5       | 1.0        | 1.0 |

$R_B = 3.28$, $R_{wp} = 4.64$, $R_{exp} = 3.43$, and $\chi^2 = 1.84$

This results in an effective PM moment $\mu_{eff} = 8.40(9) \mu_B$ and a PM CW temperature $\Theta_{CW} = -20.33(4)$ K. It is stressed that these values correlate with the PM behaviors of both Gd$^{3+}$ and Cr$^{3+}$ ions. Here, the extracted $\mu_{eff} = 8.40(9) \mu_B$ is a little larger than the previously-reported value $\sim 8.2 \mu_B$ from a study with the polycrystalline GdCrO$_3$ compound [24], indicating a better quality of the single-crystal GdCrO$_3$ sample. For Gd$^{3+}$ ions (shell 4$f^7$, quantum numbers $S = \frac{5}{2}$, $L = 0$, and $J = \frac{7}{2}$), the size of the theoretical (theo.) effective PM moment is 7.94 $\mu_B$, while for Cr$^{3+}$ ions, $\mu_{eff, theo.} = 3.873 \mu_B$ [26], therefore, $\mu_{eff, theo.} = \sqrt{7.94^2 + 3.873^2} \mu_B = 8.834 \mu_B$ for the GdCrO$_3$ compound. This theoretical value is $\sim 5.17\%$ larger than the corresponding experimental value 8.40(9) $\mu_B$, which indicates that there exist probably vacancies in the Gd and/or Cr atomic sites. We calculated schematically the magnetic frustration parameter $f = \frac{|\theta_{CW}|}{T_C}$ [21]; for Cr$^{3+}$ ions at 0.05 T, $f_{Cr} \approx 0.12$. Compared with the YCrO$_3$ compound within which the Y$^{3+}$ ions are non-magnetic, and $f_{Cr} \approx 3.06$ [26], the competing degree of AFM and ferromagnetic interactions in GdCrO$_3$ compound is much weaker. The introduction of magnetic Gd$^{3+}$ ions in GdCrO$_3$ compound has a strong effect on the magnetic structure of Cr$^{3+}$ ions, in agreement with the appearance of $T_{SR}$.

To analyze individually the PM behavior of Gd$^{3+}$ ions, we took the magnetization data in the temperature range of 30–140 K. This thermal range was within the interval ($T_{N,Gd}$, $T_{N,Cr}$) (Fig. 2), and far above $T_{N,Gd}$ (to ensure that Gd$^{3+}$ ions were indeed in a PM state), and $\sim 20$ K below $T_{N,Cr}$ (to weaken the effect of ordered Cr$^{3+}$ ions as much as possible). We first fit tentatively the data with

$$M = M_{BG} + \frac{m}{T - \Theta_{CW}},$$

where $M_{BG}$ is the contribution from background (BG) magnetization that includes actual BG magnetization
The numbers in parentheses are the estimated standard deviations of the last significant digit. Gd

Table II. Fit values of the parameters $M_{BG}$ and $\gamma$ while modelling the temperature-dependent ZFC magnetization data of the GdCrO$_3$ single crystal (measured at 7–30 K and 500 Oe) with Eq. 3. We divided the whole temperature range into five regimes as listed below (see details in the text). During the refinements, we fixed $m = 114.17(51)$ emu.K./g and $\Theta_{CW} = -2.33$ K. The numbers in parentheses are the estimated standard deviations of the last significant digit.

| $T$ regime (K) | $M_{BG}$ (emu/g) | $\gamma$ |
|----------------|------------------|---------|
| 7–10           | 1.312(12)        | 1.229(1) |
| 10–15          | 0.050(8)         | 1.144(1) |
| 15–20          | -0.239(10)       | 1.122(1) |
| 20–25          | -0.306(12)       | 1.115(1) |
| 25–30          | -0.329(15)       | 1.112(2) |

from instrument, sample holder, as well as the glue, the temperature-independent diamagnetism components of Gd$^{3+}$ and Cr$^{3+}$ ions, the temperature-independent net magnetization of Cr$^{3+}$ magnetic sublattice, and $m$ is a constant. Similar modeling strategies were used previously. The values of the diamagnetism of Gd$^{3+}$ and Cr$^{3+}$ ions are $\sim -2.0 \times 10^{-5}$ and $\sim -1.1 \times 10^{-5}$ emu/mol, respectively, which could be neglected reasonably. Since the Gd$^{3+}$ magnetic sublattice seems to form a long-range AFM order below $T_{N,Gd}$, most probably, the frustration parameter of Gd$^{3+}$ ions $f = |\Theta_{CW}| / T_{N,Gd} \approx 1$, from which we deduced $\Theta_{Gd}^{CW} \approx -2.23$ K. By forcing $\Theta_{Gd}^{CW} = -2.23$ K, we refined the data with Eq. 2 and obtained $M_{BG} = -0.473(33)$ emu/g, and $m = 80.823(22)$ emu.K./g, and the resultant fit was shown as fit2 in Fig. 2(b). It is worth noting that in Eq. 2 the net...
magnetization of Cr$^{3+}$ magnetic sublattice is supposed to be temperature independent, which is true only at low enough temperatures. For example, achieving this stage for the YCrO$_3$ single crystal, it requires temperatures at least below $\sim$50 K \[20\].

For ferromagnets, it has been proved that the temperature-dependent magnetic susceptibility observes a power law $\chi_0^{-1} \propto (T - T_C)^\gamma$ at temperatures slightly above the Curie temperature $T_C$, where the exponential parameter $\gamma$ usually acts as a criterion for distinguishing the Heisenberg system ($\gamma = \frac{3}{2}$) from the Ising one ($\gamma = \frac{5}{4}$) \[30, 31\]. When $\gamma = 1$, it correlates with the CW model that is derived from the molecular-field theory; when $\gamma > 1$, it becomes a modified nonlinear formula that relates to the short-range spin correlations during the formation of the spin order \[32, 33\]. For antiferromagnets, there also exists a power-law model in describing the staggered magnetic susceptibility $\chi(Q) \propto \alpha(T - T_N)^{-\gamma}$ below $T_N$. 

FIG. 3. (color online) ZFC $M$ as a function of temperature from 1.8 to 8 K at applied magnetic fields of (a) 300–1000 Oe with a step size of 100 Oe, and (b) 0.2–0.8 T with $\Delta \mu_0 H = 0.1$ T. (c) Applied magnetic-field- and temperature-dependent phase diagram of $T_{N-Gd}$ and $T_{SR}$. (d) ZFC $M$ versus temperature from 150 to 175 K at applied magnetic fields of 50, 150, 400, 600, 800, and 1000 Oe. (e) Slope ($dM/dT$) (symbols) of $M - T$ curve at 1, 2, and 4.7 T. The solid lines are fits with a modified Gaussian function, as guides to the eye. (f) $T_{N-Cr}$ as a function of applied magnetic field (symbols). We fit tentatively the data with a linear function (solid line).
FIG. 4. (color online) (a–d) Representative ZFC isothermal magnetization versus applied magnetic field. (a) The field range is from –14 to 14 T, and the studied temperature points are at 1.8, 5.1, 100, 167, and 300 K. The measured temperature points are (b) 160, 167, and 180 K; (c) 60, 100, and 125 K; (d) 3.2, 5.1, and 8 K. For Figs. (b–d), the magnetic fields are from –1.2 to 1.2 T. (e) Representative ZFC magnetization as a function of applied magnetic field in the range of 0–14 T at temperatures of 2–10 K (step size 2 K) and 10–180 K (step size 10 K). (f) Extracted magnetic entropy versus temperature in the thermal range of 4–180 K (with log2 scale) at \( \mu_0 H = 1–14 \) T with an interval of 1 T. The solid lines are guides to the eye.

\[ \Delta T = 10 \text{ K} \]

When \( \alpha = 1 \), one may get the best fit [35].

Since \( T_{N-Gd} = 2.33 \text{ K} \ll T_{N-Cr} = 168.97 \text{ K} \), when the magnetic structure of \( \text{Cr}^{3+} \) ions establishes below \( T_{N-Cr} \), the staggered magnetization could induce short-range Gd\(^{3+}\) magnetic orders due to possible Gd\(^{3+}\)-Cr\(^{3+}\) couplings [15] [36] [37]. To model these complicated magnetic behaviors, we modified Eq. 2 into

\[ M = M_{BG} + \frac{m}{(T - \Theta_{CW})^\gamma} \]

where \( \gamma \) is a parameter representing both the short-range correlations of Gd\(^{3+}\) ions and the temperature-dependent component of net magnetization of Cr\(^{3+}\) magnetic sub-
lattice. This could be enhanced by the formation of magnetic polarons due to Gd\(^{3+}\)-Cr\(^{3+}\) ionic couplings \[38, 39\]. We took the following strategies for refinements in the thermal range of 30–140 K: (1) First, we kept \(M_{BG} = 0\) and refined \(m\) and \(\gamma\), which resulted in \(m = 618.1(12)\) emu.K./g, and \(\gamma = 1.6219(5)\), and the fitting result was shown as fit3 in Fig. 2(b). (2) While releasing \(M_{BG}\), \(m\), and \(\gamma\), we refined them simultaneously, leading to \(M_{BG} = -0.359(22)\) emu/g, \(m = 114.17(51)\) emu.K./g, and \(\gamma = 1.108(1)\), the best fit1 as displayed in Fig. 2(b). This best refinement is supported by the following facts (a) \(T = 30\) K is a little above the temperature point \(\sim 24.51\) K at which a kink appears in the slope of the \(M-T\) curve and from where ZFC \(M\) increases sharply upon cooling due to the formation of AFM Gd\(^{3+}\) sublattice moments. (b) While extrapolating these fits to the temperature range from \(-2.33\) to 160 K [Fig. 2(b)], the calculated values of \(M(T)\) [short-dash-dotted line (fit2) and dashed line (fit3)] are deviated too much from the measured data below 30 K and above 140 K. It is noted that for the best fit1, the refined \(M_{BG}\) is still negative, which is much smaller than the values of diamagnetism of Gd\(^{3+}\) and Cr\(^{3+}\) ions, and \(\gamma > 1\). As shown in the inset of Fig. 2(b), one possible configuration of spin moments during 30–140 K is (i) The magnetic Gd\(^{3+}\) ions stay in a PM state, i.e., all spins are theoretically aligned randomly with potential short-range correlations induced possibly by the formation of the magnetic order of Cr\(^{3+}\) ions. (ii) The formed Cr\(^{3+}\) AFM sublattice moments (\(M_+\) and \(M_-\)) are canted downward from their AFM axis \(M_0^+\) and \(M_0^-\) with an angle of \(\beta\) so that the net Cr\(^{3+}\) and Gd\(^{3+}\) moments are in opposite directions, leading to a negative value of \(M_{BG}\). It is pointed out that mere the applied magnetic field of 500 Oe itself is hard to make an AFM canting [10] and produce so large net negative magnetization from the Cr\(^{3+}\) magnetic sublattice, consistent with the formation of a canted AFM Cr\(^{3+}\) structure.

To gain an in-depth understanding of the two magnetic

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**FIG. 5.** (color online) (a) Temperature-dependent specific heat measured at applied magnetic fields of 0–14 T. Inset exhibits specific heats within the temperature range of 1.8–20 K with a log2 scale. (b) Temperature-dependent adiabatic temperature change (\(\Delta T_{ad}\)) with applied magnetic fields from 0.5 to 14 T. (c) Maximum of adiabatic temperature change (\(\Delta T_{ad}^{max}\)) versus applied magnetic field. In Figs. (a)–(c), the solid lines are guides to the eye.
transitions occurring at 2.33 and 6.74 K, we further fit the temperature-dependent (from 7 to 30 K) ZFC magnetization data using Eq.[3] The m value in Eq.[3] is determined by the CW constant. We therefore fixed the parameters of m and Θ_{CW} (Table [1]) and released only M_BG and γ for the fits. To explore the detailed temperature-dependent values of M_BG and γ, we divided the temperature range of 7–30 K into five regimes, i.e., 7–10, 10–15, 15–20, 20–25, and 25–30 K. The fit results were listed in Table [1]. It is noted that as temperature decreases from 30 to 7 K, the value of γ increases, consistent with the hypothesis that there exist short-ranged AFM orders of Gd^{3+} ions above T_{N-Gd}. It is more interesting that the value of M_BG changes from negative (15–30 K) to positive (7–15 K). This sign change most probably indicates that the AFM axis of Cr^{3+} ions rotates, consistent with the observed spin-reorientation transition.

C. Magnetic phase diagrams

Figure [3] shows the measurements of magnetization as a function of temperature at different applied magnetic fields. The values of T_{N-Gd} and T_{SR} were determined with the methods as claimed in Fig. [2] (c). The indications of T_{N-Gd} and T_{SR} were clearly observed at 300–1000 Oe [Fig. [3]a)]. With increasing applied magnetic field, the values of T_{N-Gd} and T_{SR} shift to lower and lower temperatures [Figs. [3] b) and [3] c)]. Temperature-dependent magnetization curves around T_{SR} were previously measured at 0, 50, 500, and 1000 Oe [12]. Unfortunately, due to the presence of impurities [6] [12], the indication of the SR transition disappeared when the strength of applied magnetic field was stronger than 1000 Oe, and the kink indicative of the AFM transition of Gd^{3+} ions at ~2.3 K didn’t appear [12]. By comparison, our study clearly shows both features with the high-quality GdCrO_3 single crystals. This makes us confident to deeply explore the detailed magnetic phase diagram.

As shown in Fig. [3] (c), above ~0.68 T, the value of T_{N-Gd} combines with that of T_{SR}, and the indication of T_{N-Gd} is indistinguishable; above ~0.8 T, the signature of T_{SR} disappears, indicating that there exist applied-magnetic-field driven magnetic phase transitions [40]. We therefore divided the magnetic phase diagram [Fig. [3] c)] into four regimes. Within the regime 1, the ions of magnetic Cr^{3+} form a long-range ordered AFM structure with a small canting [Fig. [2] b)]. With decreasing temperature and increasing applied magnetic field, the AFM easy axis M_{a}^{P} of Cr^{3+} magnetic ions changes from one direction to another (regime 2), depending on the competing degree between anisotropic exchange and single-ion anisotropic energies of Cr^{3+} ions as previously predicted theoretically [40]. While further decreasing temperature, the long-range magnetic order of Gd^{3+} ions forms (regime 3). The regime 4 hasn’t been yet explored owing to the technique limitation. The applied magnetic field shifts T_{N-Gd} to lower temperatures, resembling the behavior of a normal antiferromagnet. It is abnormal that the applied magnetic field also suppresses the values of T_{SR}, which necessitates a further hot-neutron scattering study to solve this puzzle. It is pointed out that the magnetic phase diagram of applied magnetic field and temperature [Fig. [3] c)] has been compiled with the measurements of magnetization, which strongly depends on the relative magnetic contributions of Gd^{3+} and Cr^{3+} ions [7].

As shown in Fig. [3] d), at 50 Oe, the M – T curve behaviors like an antiferromagnet. Upon cooling, the magnetization increases obviously at T_{N-Cr} = 168.86(2) K and reaches a maximum at 168.40(2) K, subsequently, decreases sharply and then becomes negative at 167.99(2)

### Table III. Comparison of the MCE in different RECrO_3 compounds (RE = 4f^{n} rare earths, n = 7–14). Here PC = polycrystal, SC = single crystal, FZM = floating-zone method, FLM = flux method, T = tesla, T = temperature, Ref = reference, and TS = this study.

| Compound | 4f^{n} | Form | From Refs | \(-\Delta S_M\) | From TS | \(\Delta \mu_0 H\) | T | Ref |
|----------|--------|------|-----------|-------------|--------|-----------------|---|-----|
| LaCrO_3 | PC     | 0.1699 | 3.75 | 2107% | 5 | ~37.1 | 41 |
| GdCrO_3 | 7      | SC (FZM) | 57.47 | 14 | 6 | TS |
| GdCrO_3 | 7      | SC (FLM) | 35.52 | 20.4% | 4 | 3 | 12 |
| GdCrO_3 | 7      | PC | 41.24 | 21.1% | 9 | 3.8 | 14 |
| TbCrO_3 | 9      | SC (FLM) | 11.97 | 139.4% | 2 | ~4.5 | 42 |
| DyCrO_3 | 10     | PC | 10.85 | 164.5% | 4 | 5 | 43 |
| HoCrO_3 | 11     | PC | 7.2 | 160% | 7 | 20 | 44 |
| ErCrO_3 | 12     | PC | 10.7 | 113.8% | 7 | 15 | 45 |
| TmCrO_3 | 13     | PC | 4.6 | 260.8% | 5 | ~13.4 K | 46 |
| YbCrO_3 | 14     | PC | ~1.91 | 854.5% | 5 | ~12.33 | 47 |
K, followed by a smooth decrease until \(\sim 162\) K. After that, the magnetization increases again and becomes positive at \(\sim 149.73\) K. Similar magnetic reversal was also observed in \(\text{TmCrO}_3 \) \([46, 48]\), \(\text{EuCr}_0.85\text{Mn}_{0.15}\text{O}_3 \) \([28]\), and \(\text{YbCrO}_3 \) \([49]\) compounds. By contrast, above 150 Oe, the values of the measured magnetization always keep positive [Figs. 3(d) and 3(e)], and the magnetization in the temperature range from \(\sim 140\) K to \(T_{N,\text{Cr}}\) becomes larger and larger with increasing applied magnetic field so that the kink indicative of the appearance of \(T_{N,\text{Cr}}\) [Fig. 2(d)] gets weaker and weaker and finally disappears above \(\sim 4.3\) T [Figs. 3(e) and 3(f)]. The kink may be buried into the higher magnetization signal induced by higher applied magnetic fields, or its disappearance indicates a meltble magnetic state. Utilizing the method claimed in Fig. 2(d), we determined the values of \(T_{N,\text{Cr}}\) as a function of applied magnetic field, as shown in Fig. 3(f). The applied magnetic fields enhance the values of \(T_{N,\text{Cr}}\), consistent with the hypothesis that below \(T_{N,\text{Cr}}\) the magnetic \(\text{Cr}^{3+}\) ions order with a canted AFM structure.

Figure 4(a) shows the ZFC magnetization as a function of applied magnetic field from \(-14\) to 14 T at marked temperatures. At 1.8 K, the magnetization increases almost linearly from 0 to \(\sim 2\) T and then approaches towards a saturation magnetic state above \(\sim 4\) T. At 5.1 K, the saturated magnetization at 14 T is \(\sim 4\%\) higher than that at 1.8 K, consistent with the formation of \(\text{Gd}^{3+}\) magnetic structure below \(T_{N,\text{Gd}}\). We transferred the unit of magnetization from emu/g into \(\mu_B\) per chemical formula unit (GdCrO\(_3\)) and obtained that the values of the saturation moments under 14 T were \(\sim 6.43\ \mu_B\) (at 1.8 K) and \(\sim 6.69\ \mu_B\) (at 5.1 K). These values are a little smaller than the theoretical saturation moment of \(\text{Gd}^{3+}\) ions, i.e., \(g_J = 7\ \mu_B\), consistent with the foregoing discussions that the \(\text{Gd}^{3+}\) ions in GdCrO\(_3\) compound form a long-range magnetic order. To check possible magnetic hysteresis effect, we measured the magnetization from \(-1.2\) to 1.2 T in detail as temperature decreases from 180 to 3.2 K [Figs. 4(b)-4(d)]. As shown in Fig. 4(b), no hysteresis loop was observed at 180 K. Upon cooling, it appears at 167 K (below \(T_{N,\text{Gd}}\), consistent with the hypothesis that the \(\text{Cr}^{3+}\) ions in GdCrO\(_3\) compound form a canted AFM structure. Upon further cooling down to 60 K [Fig. 4(c)], the magnetic hysteresis effect gets more and more obvious with enhanced remanent magnetization. As shown in Fig. 4(d), at 8 K, the hysteresis loop becomes very small, and the magnetization shows a nonlinear field dependence, a characteristic feature of ferromagnetism or a short-range AFM state \([40, 50]\). At 5.1, 3.2, and 1.8 K (below \(T_{N,\text{Cr}}\)), the magnetic hysteresis loops are indistinguishable. This may indicate that the canting degree of \(\text{Cr}^{3+}\) magnetic sublattice becomes very small, or there exists a magnetic phase transition for \(\text{Cr}^{3+}\) ions from the canted to a collinear AFM structure.

### D. Magnetocaloric effect

To study the MCE of our grown GdCrO\(_3\) single crystals, we measured field-dependent magnetization from 0 to 14 T at marked temperatures as shown in Fig. 4(e). The magnetic entropy change \(\Delta S_M\) can be calculated by

\[
|\Delta S_M(T, \mu_0H)| = \mu_0 \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i, \quad (4)
\]

where \(\Delta S_M\) is the absolute value of the magnetic entropy change, \(\mu_0\) is the permeability of vacuum, \(M_{i+1}\) and \(M_i\) represent measured values of magnetization at temperatures of \(T_{i+1}\) and \(T_i\), respectively, \(\Delta H_i\) is the differential element of the applied magnetic field. Based on Eq. 4, we calculated the values of \(\Delta S_M\) of single-crystal GdCrO\(_3\) compound, and the results were shown in Fig. 4(f). It is clear that below 9 T, the value of \(\Delta S_M\) reaches a maximum at \(\sim 4\) K; above 9 T, the maximum point shifts to an elevated temperature \(\sim 6\) K. For example, at 6 K and 14 T, \(\Delta S_M \approx 57.47\) J/kg.K, which decreases rapidly upon warming. With the field change of \(\Delta \mu_0H = 9\) T, we calculated the magnetic entropy change \(\Delta S_M = 49.11\) J/kg.K at 4 K for the single-crystal GdCrO\(_3\) sample. This value is \(\sim 19.1\%\) higher than the value \(41.24\) J/kg.K measured with a polycrystalline GdCrO\(_3\) sample under the same conditions at 3.8 K \([13]\). We compared the magnetic entropy changes of GdCrO\(_3\) single crystals grown with two different methods: One was the flux method, where \(\Delta S_M = 29.5\) J/kg.K with \(\Delta \mu_0H = 4\) T at 3 K \([12]\); the second one was the laser-diode-heated FZ technique from the present study where \(\Delta S_M \approx 35.52\) J/kg.K (extrapolated) with the same values of \(\Delta \mu_0H\) and temperature, improved approximately 20.4%. It is obvious that single-crystal GdCrO\(_3\) compound synthesized by the FZ method \([19-21]\) shows a much stronger MCE than the polycrystalline samples, and even much better than the GdCrO\(_3\) compound with enhanced MCE is a promising material for potential application in magnetic refrigerators.

With our measured temperature-dependent specific-heat data at different applied magnetic fields as shown in Figure 5(a), the adiabatic temperature change \((\Delta T_{ad})\) can be calculated according to \([21, 32]\)

\[
\Delta T_{ad} = \int_0^{\mu_0H} \frac{T}{C_p(T, \mu_0H)} \left(\frac{\partial M}{\partial T}\right) d\mu_0H. \quad (5)
\]
We calculated the temperature dependence of $\Delta T_{ad}$ as well as the applied magnetic-field-dependent maximum $\Delta T_{ad}^{\text{max}}$, as shown in Figs. 5(b) and 5(c), respectively. Figure 5(b) shows an applied-magnetic-field driven enhancement of $\Delta T_{ad}$ when $\mu_0H \geq 10$ T. The grown GdCrO$_3$ single crystal in this study holds large values of adiabatic temperature change, e.g., $\Delta T_{ad}^{\text{max}} \approx 16.40$ K at 8 T, and 24.69 K at 14 T. The $\Delta T_{ad}^{\text{max}}$ value of single-crystal GdCrO$_3$ compound is much larger than that of other Gd-based perovskites such as GdMnO$_3$ and GdAlO$_3$ [52]. It is also larger than that of some lanthanides-based oxides such as EuHo$_2$O$_4$ ($\Delta T_{ad}^{\text{max}} \approx 12.7$ K) and EuDy$_2$O$_4$ ($\Delta T_{ad}^{\text{max}} \approx 16$ K) [53].

IV. CONCLUSIONS

In summary, we have investigated the structural and magnetic properties of the GdCrO$_3$ single crystal. The collected XRPD pattern was well indexed with the space group $Pmnb$, from which we extracted the lattice constants and atomic positions. The magnetization data at 500 Oe from 200 to 300 K observes well with the CW law, which results in a PM CW temperature $\Theta_{CW} = -20.33(4)$ K and an effective PM moment $8.40(9)$ $\mu_B$. Taking into account both the temperature-dependent and independent net-magnetization of Cr$^{3+}$ ions, we can fit well the magnetization data at 30–140 K. We clearly observed the indications of the formation of canted AFM structure of Cr$^{3+}$ ions at $T_{N,\text{Cr}}$, the spin reorientation of Cr$^{3+}$ moments at $T_{SR}$, and the formation of long-range ordered Gd$^{3+}$ magnetic structure at $T_{N,\text{Gd}}$. We have constructed the magnetic phase diagrams of $T_{N,\text{Cr}}$, $T_{SR}$, and $T_{N,\text{Gd}}$ as a function of applied magnetic field and proposed magnetic configurations in the corresponding temperature regimes. The magnetic phase diagrams of $T_{N,\text{Gd}}$ and $T_{N,\text{Cr}}$ are well consistent with the corresponding magnetic structures, whereas, the magnetic phase diagram of $T_{SR}$ seems to be abnormal. When $T_{SR} < T < T_{N,\text{Cr}}$, obvious magnetic hysteresis loops were observed. Below $T_{SR}$, the hysteresis loop becomes very weak, probably indicating a decrease in the canting degree of the Cr$^{3+}$ magnetic structure or a phase transition from the canted to a collinear AFM structure. We calculated the magnetic entropy change $-\Delta S_M$. For example, $-\Delta S_M \approx 35.52$ J/kg.K at $\Delta \mu_0H = 4$ T and 3 K, improved $\approx 20.4\%$ than that of the GdCrO$_3$ single crystal grown by the flux method [12]. We summarized the MCE of RECrO$_3$ compounds ($RE = 4f^{n}$ rare earths, $n = 7$–14) and found that our grown GdCrO$_3$ single crystal displayed the highest value of magnetic entropy change and an enhanced adiabatic temperature change. This indicates that the single-crystal GdCrO$_3$ compound is a potential candidate for magnetic cooling.

The natural Gd atom is a very strong neutron absorber. Therefore, uniquely determining the interest-ing magnetic structures, as well as the magnetic phase-transition diagrams explored in this study, necessitates a single-crystal neutron-diffraction study with a hot neutron source.

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