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**MAGNETISM  
AND FERROELECTRICITY**

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## Magnetic Properties and Phase Transitions in Hexagonal DyMnO<sub>3</sub> Single Crystals

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**Abstract**—DyMnO<sub>3</sub> single crystals of hexagonal modification were grown for the first time by zone melting, and their anisotropic magnetic properties were studied in detail. At  $T \sim 7$  K, a small uncompensated magnetic moment ( $\sim 1 \mu_B$  per formula unit) is shown to occur along the hexagonal axis. At temperatures 7–45 K, a transition from the purely antiferromagnetic state to a state with uncompensated magnetic moment was revealed; the transition is induced by a magnetic field  $\mathbf{H}$  parallel to the  $c$  axis. This transition seems to be due to a ferrimagnetic ordering of the moments of Dy cations located in nonequivalent crystallographic positions.

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### 1. INTRODUCTION

It is known that, under normal conditions, rare-earth manganites  $R\text{MnO}_3$  have either the orthorhombic structure of a distorted perovskite (for  $R = \text{La to Tb}$ ) or a hexagonal structure (for  $R = \text{Ho–Lu}$  and also  $\text{Y}$  and  $\text{Sc}$ ) depending on the rare-earth ion radius [1]. The free energies of these two polymorphic modifications of DyMnO<sub>3</sub> are close to each other. The perovskite modification is more stable at room temperature and undergoes a transition to the hexagonal phase at a temperature of  $\sim 1600^\circ\text{C}$  [2]. Thus, the hexagonal structure can be obtained at room temperature by quenching from a high temperature ( $\geq 1600^\circ\text{C}$ ) [3]. This structure can also be produced in epitaxial films of DyMnO<sub>3</sub> and certain other manganites ( $R = \text{Gd, Eu, Sm}$ ) by choosing suitable substrates [4, 5]. It is also known that excess oxygen (with respect to the stoichiometric composition) favors stabilization of the orthorhombic phase, whereas an oxygen deficit (for example, when the compound is synthesized in a nitrogen atmosphere) favors the formation of the hexagonal phase [6].

The physical (above all, magnetic) properties of the orthorhombic and hexagonal manganites differ substantially. First, as the ionic radius of a cation decreases from La to Ho, the Néel temperature  $T_N$  decreases from 140 to  $\approx 40$  K and the magnetic structure changes from a canted antiferromagnetic (AFM) phase of the  $A$  type to an incommensurable structure with a longitudinal spin-density wave [7–9]. The hexagonal manganites are ferroelectrics with high ( $\sim 900$  K) Curie temperatures

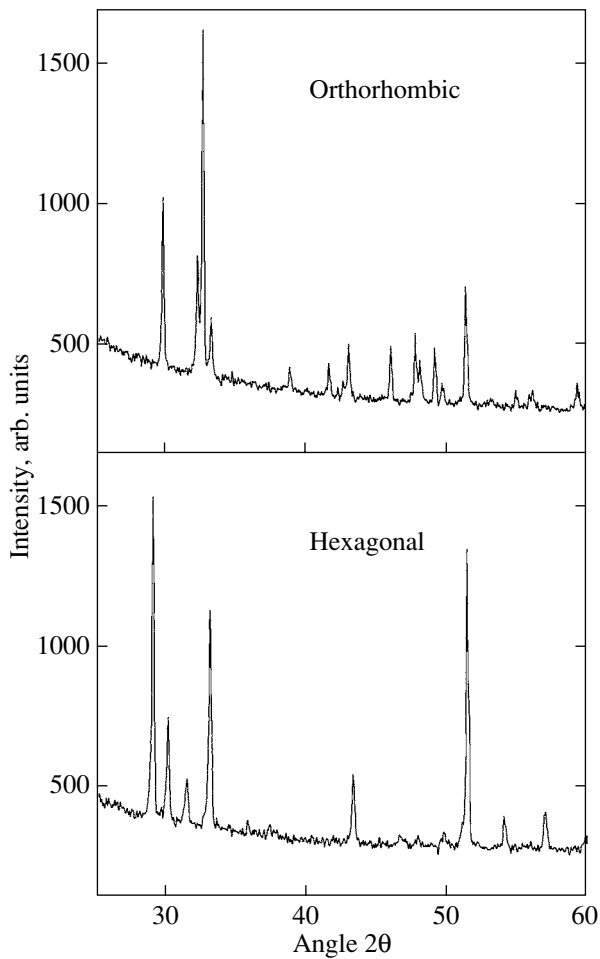
[10]. At low temperatures ( $T_N \sim 80$  K), they are magnetically ordered, with the magnetic moments of  $\text{Mn}^{3+}$  ions forming triangular AFM structures; at  $T \leq 5\text{--}7$  K, the rare-earth ion subsystem is also ordered [11].

For the first time, we succeeded in growing DyMnO<sub>3</sub> single crystals of hexagonal modification and studying their anisotropic magnetic properties.

### 2. CRYSTAL GROWTH AND EXPERIMENTAL TECHNIQUE

As initial materials, we used preliminarily annealed Dy<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>. To compensate for a loss of manganese (the most volatile component) during zone melting, we took 1 wt % excess Mn<sub>3</sub>O<sub>4</sub> with respect to the calculated amount. After thorough mixing of a powder, synthesis was carried out at  $1100^\circ\text{C}$  for 10 h. Then, the powder was pressed to fabricate billets in the form of rods 5–6 mm in diameter and  $\sim 10$  cm long; the billets were calcined in air at  $1400^\circ\text{C}$  for 10 h. Single crystals were grown by zone melting with radiation heating both on seeds prepared from the same billets that were used for the crystal growth and on YMnO<sub>3</sub> crystals. The crystals were grown at a rate of  $\sim 7\text{--}9$  mm/h either in air or in an argon flux.

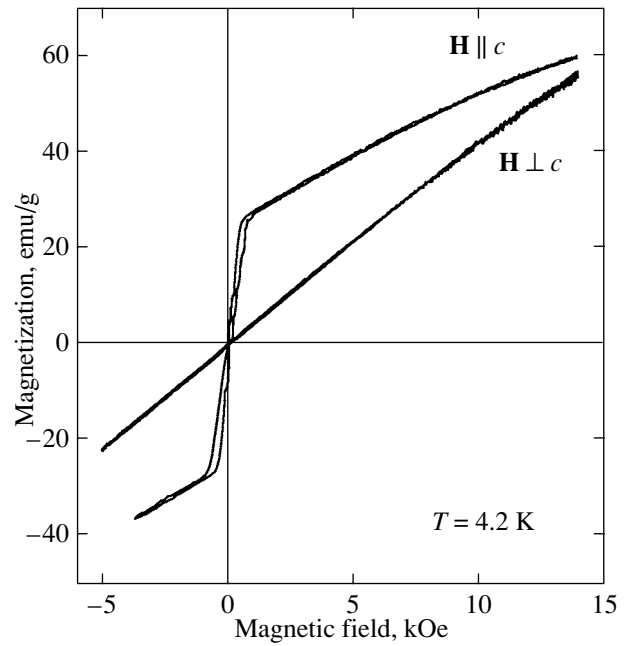
An x-ray phase analysis showed that all samples were single-phase but had various crystalline structures depending on the growth conditions. The crystals grown in air have an orthorhombic structure (space group  $Rb\bar{3}m$ ) with refined lattice parameters  $a =$



**Fig. 1.** X-ray powder diffraction patterns of the orthorhombic and hexagonal modifications of  $\text{DyMnO}_3$ .

5.279(1) Å,  $b = 5.8360(9)$  Å, and  $c = 7.3775(13)$  Å. The crystals grown in argon have a hexagonal structure (space group  $R\bar{6}_3cm$ ) with refined lattice parameters  $a = 6.162(2)$  Å and  $c = 11.37(1)$  Å. When a preliminarily grown  $\text{YMnO}_3$  hexagonal crystal was used as a seed, it was guaranteed that the latter modification would be obtained. The choice of the  $\text{YMnO}_3$  crystal as a seed is explained, on the one hand, by the close values of the crystal lattice parameters and, on the other, by the non-magnetic character of the  $\text{Y}^{3+}$  ion; because of this, the magnetic properties of the  $\text{DyMnO}_3$  crystal remain unchanged even if a small amount of  $\text{Y}^{3+}$  is implanted into the crystal. Figure 1 shows fragments of the x-ray diffraction patterns that illustrate completely different characters of the x-ray reflections of these crystallographic modifications.

The grown crystals possessed pronounced anisotropic properties, which are indicative of high crystal perfection. This conclusion is also supported by the x-ray diffraction study. However, it should be noted that the hexagonal  $\text{DyMnO}_3$  crystals were rather brittle and eas-



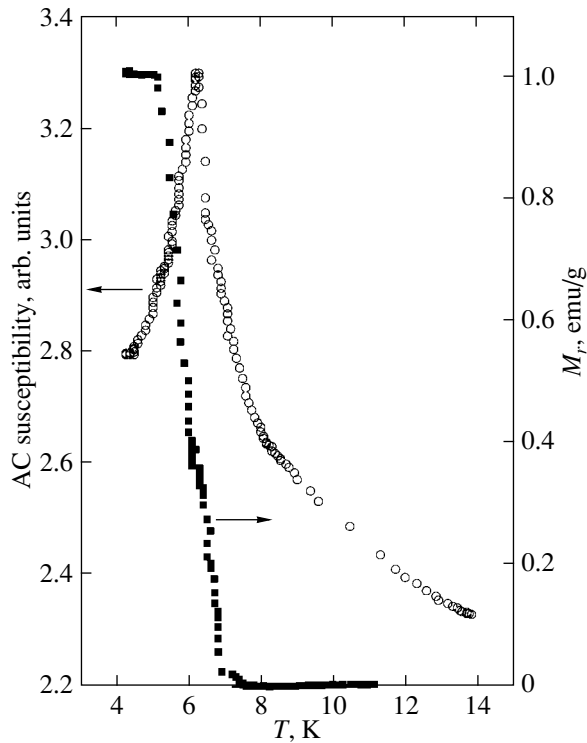
**Fig. 2.** Magnetization curves of a  $\text{DyMnO}_3$  single crystal measured along and perpendicular to the hexagonal axis at 4.2 K.

ily crumbled into small pieces during mechanical treatment, which made it difficult to prepare fairly large (centimeter-sized) crystals.

The magnetization was measured using a vibration-coil magnetometer in fields up to 14 kOe in the temperature range  $4.2 \leq T \leq 300$  K. The ac susceptibility  $\chi_{ac}(T)$  was measured at a frequency of  $\sim 540$  Hz in an ac field with an amplitude of the order of several tenths of an oersted.

### 3. RESULTS AND DISCUSSION

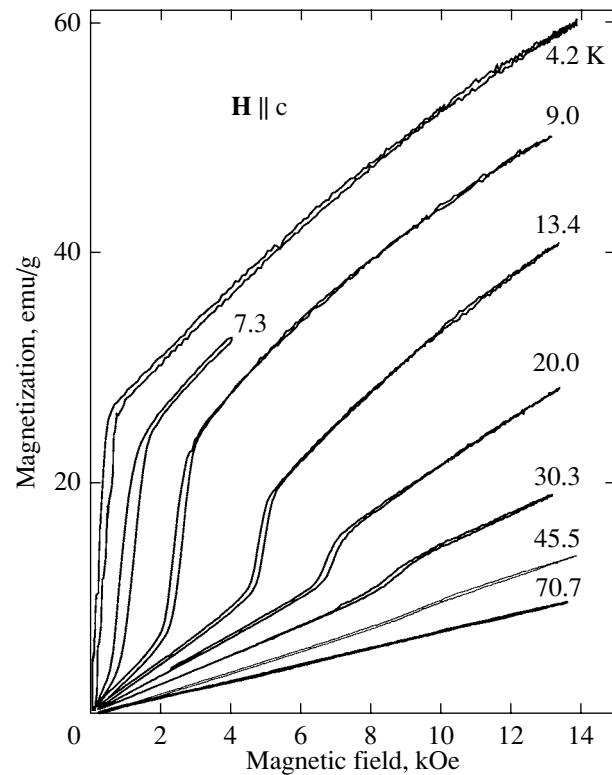
Below, we consider the properties of the hexagonal  $\text{DyMnO}_3$  modification only. Some results of the magnetic measurements for the orthorhombic  $\text{DyMnO}_3$  were reported in [12]. In the paramagnetic temperature range, where the Curie–Weiss law is valid, the magnetic-susceptibility anisotropy of the hexagonal  $\text{DyMnO}_3$  is slight; the Curie–Weiss constants  $\Theta$  along and perpendicular to the hexagonal axis were found to be approximately the same and equal to  $-10 \pm 5$  K. The effective magnetic moment  $\mu_{\text{eff}}$  is also practically independent of the crystallographic direction and is  $(11.0 \pm 0.7)\mu_B$ , which is close to the theoretical value of  $11.7\mu_B$  calculated under the assumption that both free  $\text{Dy}^{3+}$  ions in the  ${}^6H_{15/2}$  state ( $g_J = 4/3$ ) and  $\text{Mn}^{3+}$  ions ( $S = 2$ ) contribute to the paramagnetic susceptibility. Note that the susceptibility does not exhibit notable anomalies at the Néel point; therefore, it is difficult to determine the susceptibility from purely magnetic measurements alone.



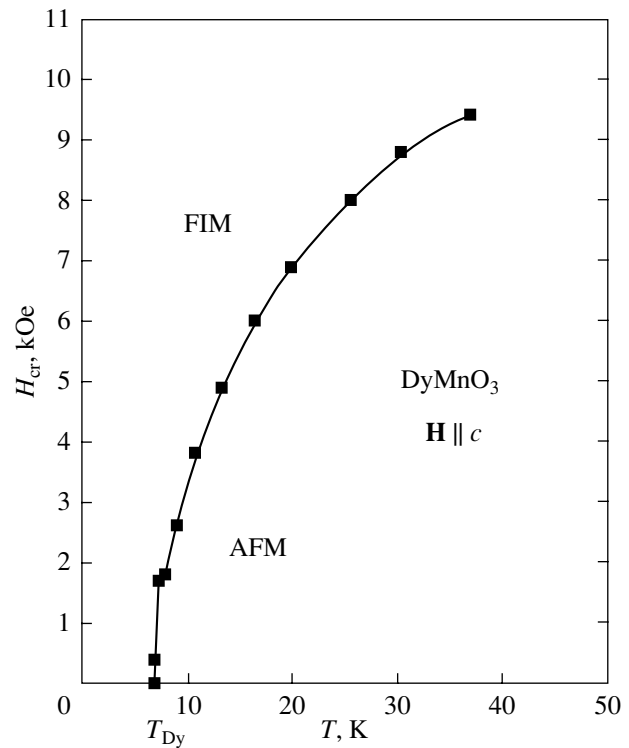
**Fig. 3.** Temperature dependences of the ac susceptibility (left scale) and remanent magnetization (right scale) of  $\text{DyMnO}_3$  measured along the hexagonal axis.

Figure 2 shows the magnetization curves of a  $\text{DyMnO}_3$  crystal measured along and perpendicular to the hexagonal ( $c$ ) axis at 4.2 K. The magnetization measured along the  $c$  axis at low temperatures indicates the existence of a state with a spontaneous magnetic moment of  $\sim 20$  emu/g ( $1 \mu_B$  per formula unit). From the temperature dependence of the remanent magnetization, it follows that this state occurs below  $T_{\text{Dy}} \approx 7$  K (Fig. 3). Near this temperature, the ac magnetization exhibits a peak (Fig. 3). Above  $T_{\text{Dy}}$ , a transition induced by a magnetic field  $\mathbf{H} \parallel c$  is observed to occur into the same state with an uncompensated magnetic moment (Fig. 4). This transition is accompanied by a jumpwise increase in the magnetization. As the temperature increases, the value of the magnetization jump decreases and the transition becomes more diffuse and cannot be distinguished above  $\sim 45$  K. Based on the measured  $M(H)$  curves, we plotted the temperature dependence of the critical magnetic field that induces this transition (Fig. 5).

The temperature and field dependences of the magnetization in the hexagonal  $\text{DyMnO}_3$  crystal described above are observed for the first time. A qualitatively similar behavior of the magnetization was observed in  $\text{ErMnO}_3$  crystals [11]. In [11] and also in [13], where Faraday rotation and second-harmonic generation were studied, the conclusion was drawn that the low-temperature and field-induced states are ferrimagnetic and are



**Fig. 4.** Magnetization curves of  $\text{DyMnO}_3$  along the hexagonal axis measured at various temperatures.



**Fig. 5.**  $H_{\text{cr}}-T$  phase diagram of  $\text{DyMnO}_3$ . AFM stands for the antiferromagnetic phase, and FIM, for the ferrimagnetic phase.

caused by the antiparallel orientation (along the  $c$  axis) of the magnetic moments of the Er ions occupying non-equivalent crystallographic positions  $4(b)$  and  $2(a)$ . According to [13], on this transition, the Mn magnetic moments lying in neighboring layers ( $z = 0$  and  $z = c/2$ ) change from the parallel to the antiparallel orientation, with the AFM triangular structure of the magnetic moments in each layer remaining unchanged. In this case, an effective exchange field is induced along the  $c$  axis at the rare-earth ion sites due to the anisotropic  $R$ -Mn exchange. We believe that the phase transitions in the hexagonal  $\text{DyMnO}_3$  and in  $\text{ErMnO}_3$  are the same in character.

#### 4. CONCLUSIONS

Thus, we have developed a technology for growing  $\text{DyMnO}_3$  single crystals in the orthorhombic and hexagonal modifications. The anisotropic magnetic properties of  $\text{DyMnO}_3$  single crystals in the hexagonal modification have been studied for the first time. We have revealed a magnetic-field-induced transition to a state with an uncompensated magnetic moment, which is likely associated with the ferrimagnetic ordering of the magnetic moments of Dy ions occupying nonequivalent crystallographic positions.

#### ACKNOWLEDGMENTS

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