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MAGNETISM

Magnetic Properties of Polycrystalline Films of $CoCr_2O_4$ and $CoFe_{0.5}Cr_{1.5}O_4$ Multiferroics

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Abstract—This paper reports on the first study of the magnetic properties of polycrystalline films of $CoCr_2O_4$ and $CoFe_{0.5}Cr_{1.5}O_4$ multiferroics. The study covered, in particular, magnetization reversal curves and temperature dependences of the magnetization at temperatures ranging from 4.2 to 300 K in magnetic fields of up to 10 kOe. It has been shown that the Curie temperature and the pattern of the temperature dependence of the magnetization depend on the cation composition of the multiferroic. The temperature dependence of the magnetization of polycrystalline $CoCr_2O_4$ films has revealed an anomaly in the temperature range 10–70 K.

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Multiferroics have become of considerable interest as materials each combining two kinds of ordering, ferromagnetic and ferroelectric. These materials exhibit both the properties inherent in each of the classes separately (spontaneous magnetization, magnetostriction, spontaneous polarization, and the piezoelectric effect) and novel properties deriving from interaction between the magnetic and electrical subsystems [1, 2]. Investigation and application of thin-film multiferroics in the form of single layers, as well as of heterostructures designed on their basis, open up new promising ways to the field of electronic device applications [3, 4].

Ionic compounds in the variable-composition system with the chemical formula $Co_xFe_yCr_{3-x-y}O_4$ reveal a rich variety of magneto-optical [5], magnetic [6–8], and electrical [7, 8] properties making them an extremely attractive material for the fields of pure scientific and applied research. Comparatively recent studies revealed multiferroic properties in the $CoCr_2O_4$ and $CoFe_{0.5}Cr_{1.5}O_4$ spinels [7]. Spinel-based multiferroics are among a few materials whose multiferroic properties are observed in the magnetic ordering region. The $CoCr_2O_4$ spinel having a unique conical spiral magnetic structure [8] is known to be the first example of a multiferroic with spontaneous magnetization and magnetic-field-dependent electrical polarization. Below the Curie temperature $T_C = 94$ K, collinear ferrimagnetic order persists in $CoCr_2O_4$, to transform to long-range helicoidal magnetic order at the temperature $T_S \approx 27$ K. Electrical polarization was shown to exist both in the helicoidal magnetic and collinear ferrimagnetic phases [7, 9]. The $CoFe_{0.5}Cr_{1.5}O_4$ multiferroic differs in a higher Curie temperature (175 K) and a lower temperature of transition to the spiral magnetic structure [7]. The temperature region within which spontaneous electrical polarization persists coincides, just as in $CoCr_2O_4$, with the magnetic ordering region.

We report on the first results of a study into the magnetic properties of polycrystalline films of the $CoCr_2O_4$ and $CoCr_{1.5}Fe_{0.5}O_4$ multiferroics. The polycrystalline films were synthesized by solid-phase reactions in metal/oxide layered structures at temperatures of 870–920 K [5, 10]. As shown by us earlier, solid-phase reactions in such structures can proceed both under isothermal annealing and in self-propagating high-temperature synthesis [5].

Solid-phase synthesis of $CoCr_2O_4$ and $CoFe_{0.5}Cr_{1.5}O_4$ films proceeded in the following reactions:

$$Co + Cr_2O_3 + 1/2O_2 = CoCr_2O_4, \quad (1)$$

$$Co + 0.5Fe + 0.75Cr_2O_3 + 1.25O_2 = CoFe_{0.5}Cr_{1.5}O_4. \quad (2)$$

The reagents of reaction (1) are layers in the Cr_2O_3/Co film structure, and those of reaction (2) are layers in the Cr_2O_3/Co/Fe structure. The metal layers were deposited in the Cr, Co, Fe sequence on fused quartz plates by thermal evaporation in a vacuum of 5×10^{-6} Torr at the substrate temperature of 470 K. Deposition of Co and Fe layers was preceded by oxidation of the Cr layer at 870 K in air in the reaction chamber.

Solid-phase reactions in these film structures were carried out under isothermal annealing at temperatures of 870–920 K in air. As a result, we obtained polycrystalline multiferroic films 150–200 nm thick. The chemical composition and thickness of the films were monitored by X-ray fluorescence spectroscopy. The crystal structure was established by X-ray structural phase analysis. The magnetic properties of the films prepared were measured with the use of the MPMS-XL (Quantum Design) magnetometer within the temperature range from 4 to 300 K in magnetic fields of up to 10 kOe, as well as with a Nano MOKE 2 magneto-optic magnetometer.

The diffraction pattern of a $CoCr_2O_4$ multiferroic film contains only spinel reflections (Fig. 1).

Measurements of the magnetization reversal curves of polycrystalline $CoCr_2O_4$ films with the magneto-optic magnetometer in the temperature range 78–300 K revealed the existence of paramagnetic behavior in the 100–300-K region (Fig. 2, curve *1*). The ferromagnetic magnetization curve was observed at a temperature of 90 K. Figure 2 (curve *2*) demonstrates a magnetization reversal curve obtained for a polycrystalline film of the $CoCr_2O_4$ multiferroic at a temperature of 80 K. We readily see that the hysteresis loop measured in magnetic fields of up to 3 kOe is actually an unsaturated loop and that saturation is apparently reached in a higher magnetic field. The temperature dependence of the magnetization of the synthesized films was studied with MPMS-XL within the temperature range 10–300 K. The temperature dependence of the magnetization measured in a magnetic field of 10 kOe is presented in Fig. 3 (the curve was obtained after field cooling). The temperature dependence curve is seen to follow a complex pattern uncommon for ferrimagnetic spinels. The Curie temperature is ~100 K; the curve transforms, as it does in bulk samples, into a long paramagnetic "tail" persisting in fields of up to 140 kOe. The "height" of the tail was shown to depend on the magnitude of the magnetic field [11]. Another anomaly of the curve is its bend near 70 K. At 50 K, we observe a decrease in the magnetization to about one half of its maximum value. The curve of the temperature dependence of the magnetization fits qualitatively the one obtained for polycrystalline bulk multiferroic $CoCr_2O_4$ [7]. The bend in the temperature dependence near 50 K is traced to formation of short-range order in the conical spiral magnetic structure [7, 8]. This anomaly in the temperature dependence of the magnetic moment coincides with that of the dielectric constant near 50 K reported in [8].

Films of the $CoFe_{0.5}Cr_{1.5}O_4$ multiferroic synthesized by isothermal annealing of the Cr_2O_3/Co/Fe layered structure were shown to have spinel structure. The magnetization reversal curve of the $CoFe_{0.5}Cr_{1.5}O_4$ polycrystalline film measured with MPMS-XL is plotted in Fig. 4. Figure 5 displays the temperature dependence of the saturation magnetization measured in a field of 10 kOe. The temperature behavior of polycrystalline $CoFe_{0.5}Cr_{1.5}O_4$ films follows the classical pattern. The curve plotting temperature dependence of saturation magnetization has a point (70–75 K) of change in the slope, which gives grounds to consider it as a superposition of curves belonging to two phases with different Curie temperatures (200 and 320 K). The temperature 200 K coincides with the Curie temperature of polycrystalline bulk $CoFe_{0.5}Cr_{1.5}O_4$ [7]. At the same time, the magnetization curve (Fig. 4) is considered as that of a single-

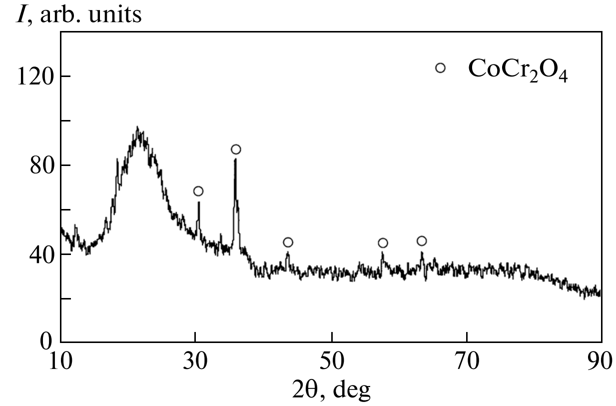

Fig. 1. Diffraction pattern of the layered Cr_2O_3/CoO structure after annealing.

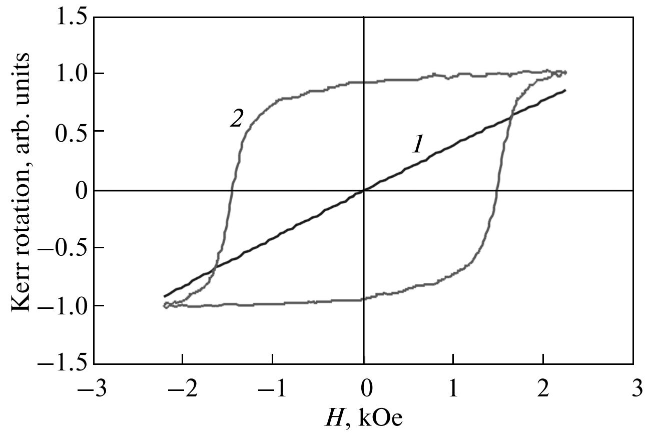

Fig. 2. Magnetization reversal curves of the polycrystalline $CoCr_2O_4$ film at temperatures of (*1*) 120 and (*2*) 80 K.

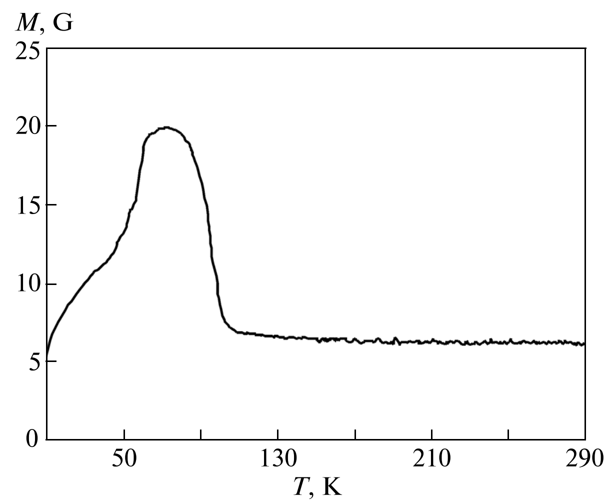

Fig. 3. Temperature dependence of the magnetization *M* of the polycrystalline $CoCr_2O_4$ film.

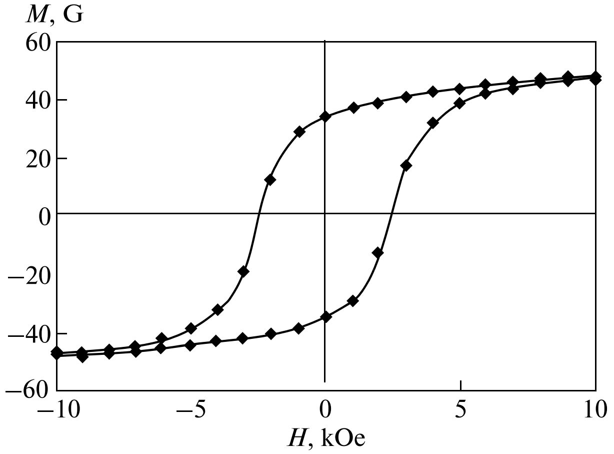

Fig. 4. Magnetization reversal curve of the polycrystalline $CoFe_{0.5}Cr_{1.5}O_4$ film.

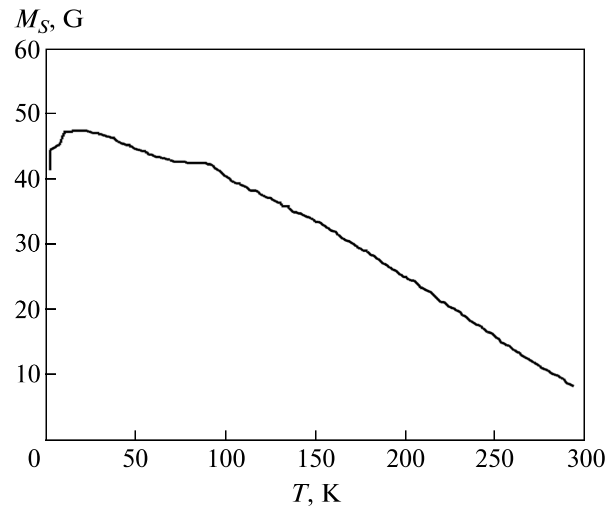

Fig. 5. Temperature dependence of the saturation magnetization M_S of the polycrystalline $CoFe_{0.5}Cr_{1.5}O_4$ film.

phase magnetic material. Assuming the prepared films to be a single-phase ferrimagnet, the difference between our results (the relatively high Curie temperature) can be assigned to the polycrystalline bulk samples and our films having been synthesized at different temperatures. In particular, the temperature of synthesis of the films in our experiments (870–920 K) is markedly lower than that of the polycrystalline samples reported in [6, 7]. Cation distribution influencing the magnetization and the Curie temperature of spinel is known [12] to depend to a considerable extent on the particular conditions of synthesis (temperature, rate). Another point of interest is located in the bend in the low-temperature region (20 K) on the curve of the temperature dependence of saturation magnetization (Fig. 5), which coincides with the temperature of the onset of short-range order in the conical spiral magnetic phase and the anomaly in the dielectric constant of the $CoFe_{0.5}Cr_{1.5}O_4$ multiferroic [7].

The main results obtained in this work can be summarized as follows. Solid-phase synthesis in layered metal/oxide structures was used to obtain for the first time polycrystalline films of the $CoCr_2O_4$ and $CoFe_{0.5}Cr_{1.5}O_4$ multiferroics. Magnetic properties of polycrystalline multiferroic films were likewise studied over a broad temperature range for the first time. The Curie temperature and the pattern of the temperature behavior of the magnetic moment have been demonstrated to depend on the cation composition of the multiferroic. Doping $CoCr_2O_4$ with Fe ions has been found to broaden significantly the temperature domain of existence of ferrimagnetism in $CoFe_{0.5}Cr_{1.5}O_4$ toward higher temperatures (up to 250 K) and, thus, extends the temperature region in which magnetic-field-dependent electrical polarization persists. The specific characteristic (bend) in the temperature dependence curve near 20 K is, however, retained. The magnetic properties of the obtained polycrystalline films of multiferroics agree qualitatively with those of bulk single crystals and polycrystals.

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