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Features of the Magnetic Properties of $La_{0.7}Sr_{0.3}MnO_3$ Manganite Films Obtained by an Extraction–Pyrolysis Method

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Abstract—We have experimentally studied the magnetic properties of manganite films obtained for first time using an extraction–pyrolysis technique. It is established that the characteristics of samples significantly depend on the conditions of final annealing. The annealing at temperatures $T_a < 970$ K is accompanied by strong thermomagnetic effects, and the resulting films possess properties similar to those of spin glasses. When the annealing temperature is increased to $T_a \geq 1020$ K, the films exhibit magnetic properties typical of ferromagnetic systems.

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Manganites with a perovskite structure have received much attention due to the phenomenon of colossal magnetoresistance (CMR) [1]. The properties of such compounds depend to a considerable extent not only on the composition and external conditions, but on the system dimensions as well [2]. According to modern notions [1, 3, 4], the CMR effects are related to the phenomenon of electron phase separation, which is determined by a quite delicate energy balance between competitive factors, predominantly of lattice and magnetic nature. The transformation of manganites into a granular or quasi-two-dimensional state can substantially change the energy structure of a sample, which provides additional possibilities in obtaining materials with unusual properties. Thin films of granular or polycrystalline manganites were previously obtained by various methods, including cathode sputtering [5, 6], magnetron sputtering [7], and chemical deposition from solution [8], and amorphous manganite films were obtained by means of chemical vapor deposition [9]. It was established that the grain size significantly influences the magnetic and transport properties of film structures. For example, a decrease in the particle size from 60 to 10 nm was accompanied by an almost fivefold increase in the magnetoresistance of samples and led to a change in the character of conductivity from metallic to semiconductor at $T < 300$ K [10]; an increase in the grain size from 14 to 27 nm led to an increase in the Curie temperature from 220 to 234 K [11].

We have attempted to synthesize $La_{1-x}Sr_xMnO_3$ manganite films using an extraction–pyrolysis method and studied the magnetic properties of obtained samples. Initially, we selected a composition with $x = 0.3$, since this compound is characterized by the maximum temperature of magnetic ordering in the system under consideration. The essence of the extraction–pyrolysis method consists in the extraction of components from appropriate aqueous solutions, mixing them in a required proportion, application of the mixed solution onto a substrate, and subsequent pyrolysis of the applied layer. The films were applied onto quartz glass substrates by centrifuging at 300 rpm. The process of oxide layer formation from a solution is strongly influenced by the solution concentration. We prepared manganite films using a solution with a concentration of 2%. After the application of a wetting film, it was dried by heating to 390–410 K. The substrates with deposits were placed into a vertical furnace, subjected to the pyrolysis at 770 K for 5–10 min, extracted from the furnace, and cooled for 2 min. Then, the subsequent layer was formed in the same way and so on. The stage of pyrolysis led to the formation of an amorphous or finely crystalline layer. A total of ten layers were deposited and then the samples were annealed in air at various temperatures.

The chemical composition and thickness of each sample were determined using X-ray fluorescence (XRF) measurements. The X-ray diffraction showed that the films obtained in the stage of pyrolysis (prior to the annealing) exhibited an X-ray amorphous structure. The subsequent annealing in air led to the formation of a polycrystalline single-phase perovskite. The XRF data indicated that the composition of obtained films

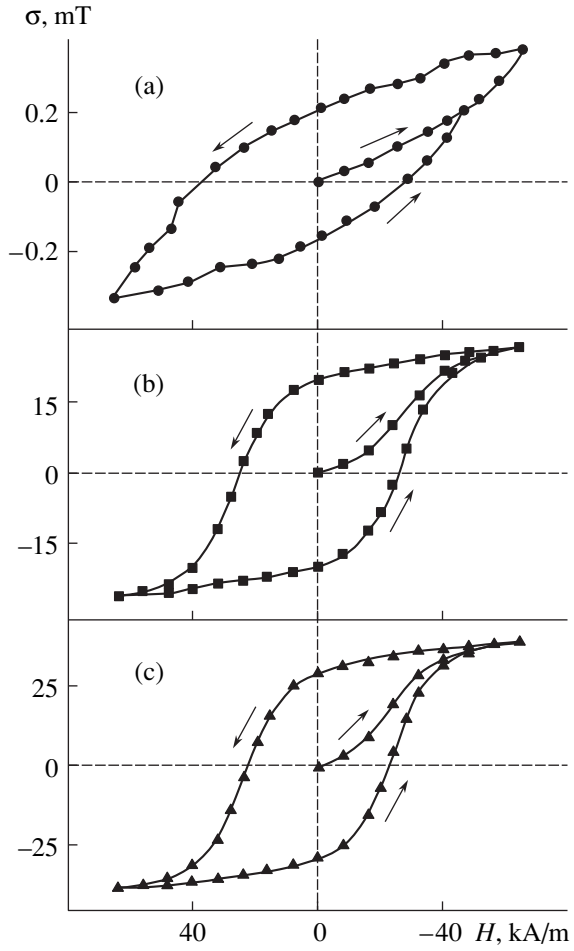

Fig. 1. Magnetization curves of $La_{0.7}Sr_{0.3}MnO_3$: (a) F1, T_a = 870 K; (b) F1, T_a = 1000 K; (c) F2, T_a = 1000 K (all measurements performed at T = 4.2 K).

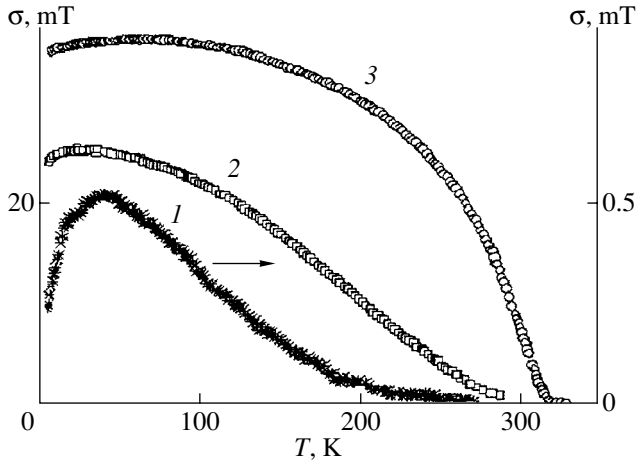

Fig. 2. The temperature dependences of the magnetization of manganite films: (*1*) F1, T_a = 870 K; (*2*) F1, T_a = 1000 K; (*3*) F2, T_a = 1000 K (all measurements performed at H = 64 kA/m).

corresponded to the chemical formula $La_{0.7}Sr_{0.3}MnO_3$ [12]. The magnetic measurements were performed on a SQUID magnetometer in a broad range of magnetic fields H = 0–64 kA/m and temperatures T = 4.2–350 K.

We have studied the magnetic properties of films as a function of the conditions of final annealing. All samples were deposited in a single cycle and had a thickness of t = 270 nm. It was found that the magnetization of films obtained using the same temperature of pyrolysis was dependent on both the temperature and the duration of annealing. Figure 1 shows the typical magnetization curves of two films (F1 and F2). The F1 film sample was first annealed at T = 870 K and measured (Fig. 1a); then, the second annealing was performed at T = 1000 K, after which the sample was measured again (Fig. 1b). The F2 film sample was annealed only at T = 1000 K (Fig. 1c). The duration of each annealing was 2 h. As can be seen, the F1 film sample does not exhibit saturation in fields H < 80 kA/m after the first annealing and the hysteresis loop appears as a superposition of two loops. After the second annealing of this sample, the magnetization increases, the saturation is reached, and the hysteresis loop becomes narrower and acquires the form characteristic of the ferromagnet. However, the final parameters of the magnetization curve of the F1 sample differ (the loop is wider and saturation magnetization is lower) from the analogous parameters for the F2 films (cf. Figs. 1a and 1b).

An even stronger difference between the F1 and F2 films is manifested in the temperature dependence of the magnetization (Fig. 2). The F1 sample after the first annealing exhibits strong thermomagnetic effects (curve *1*), and the temperature dependence of σ has a shape similar to that known for spin glasses. Such a behavior was also observed for the magnetic properties of diluted crystals of lanthanum manganites [6]. The situation is significantly improved after the second annealing, but the $\sigma(T)$ curve still has a cusp (curve *2*), albeit less pronounced than that in the first case. In contrast, the strong thermomagnetic effects in the F2 film are much less pronounced and the behavior of the magnetization is close to that known for ferromagnets (Fig. 2, curve *3*). Note also a significant difference in the values of Curie temperatures (T_C) and the behavior of magnetization in the vicinity of T_C for the F1 and F2 film samples. After the annealing at 1000 K, the Curie temperature increases and the transition becomes more pronounced.

The results of the electric conductivity measurements in a broad range from liquid-nitrogen temperature to room temperature showed that both F1 and F2 films are high-ohmic and (in agreement with published data [1]) fall in the region of existence of a dielectric phase.

The results of preliminary investigations in an atomic force microscope showed that the films possessed a granular structure. The initial films (after

pyrolysis) had a fine-grained structure; after the annealing, the grains increased in dimensions and even merged together and covered macroscopic areas of the substrate surface. Thus, we may conclude that a manganite film immediately after the pyrolysis occurs in an X-ray-amorphous state, while the annealing in air leads to the formation of grains with dimensions dependent on the annealing temperature. Small crystallites form an ensemble of weakly interacting grains. The magnetic characteristics of such films are determined primarily by the properties of individual grains, for which it is known [5] that the Curie temperature and the saturation magnetization decrease with the grain size. This circumstance explains the relatively low magnetization, the shape of the hysteresis loop, and the spin-glass-like behavior of the F1 film after the first annealing (Fig. 1a; Fig. 2, curve *1*). Repeated annealing of this film leads to an increase in the grain size and, probably to an additional enrichment with oxygen. In the F2 film, the structure formation and the oxygen saturation take place at the same temperature. As a result, the grains nucleate, grow to dimensions at which the bulk material properties are manifested, and even merge together to form continuous regions. Although the final regimes of annealing for the F1 and F2 samples are the same, the properties of these films are different. This difference can be related to dissimilar conditions at the onset of structure formation and oxygen saturation. The primary annealing determines the crystallization centers and sets the degree of structural disorder, while the high-temperature annealing more significantly influences the saturation with oxygen and determines the chemical disorder [13].

In conclusion, we have (i) developed a new method for obtaining manganite films and (ii) showed that the conditions of final annealing influence the film structure formation and allow the properties of the films to be controlled by varying the temperature and duration of annealing.

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