

Mössbauer and Magnetic Studies of Doped Lanthanum Manganite $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$): I. Nonstoichiometric Composition

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Abstract—Mössbauer and magnetic studies of Ca-doped lanthanum manganites $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$) of a nonstoichiometric composition are performed. An increase in the Ca concentration and a decrease in the interstitial oxygen quantity results in a decreasing electric-field gradient in the region of the Fe atomic nucleus due to the spatial rearrangement of the charge of surrounding atoms. The Mössbauer spectra of all studied lanthanum-manganite samples demonstrate a relaxation character at low temperatures, which can be associated with the presence of small-sized magnetic clusters. This finding correlates with the results of magnetic investigations. The values of the coercive force, saturation magnetization, and blocking temperature are determined.

Keywords: doped lanthanum manganites, Mössbauer spectroscopy, magnetic properties, superparamagnetism

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INTRODUCTION

The system of perovskite-like lanthanum manganites has been known of for more than 50 years. However, only in recent decades has interest in heterostructure ferromagnetic materials of this kind grown. This interest is a result of their colossal magnetoresistance [1–6]. Doped lanthanum manganites are also used as cathode materials in fuel power production, which should provide the free ingress and egress of oxygen (i.e., a high mobility of oxygen atoms is required). Due to a high diffusion of oxygen ions, these materials can be used as selective oxygen transporting membranes in fuel systems [7–9]. The physical properties of manganites are very diverse and often unusual, and thus they attract much interest of researchers. Varying the type and content of the doping element leads to significant changes in the properties of manganites; phase transitions with different ordering types (magnetic, structural, electronic) occur.

This work presents a study of calcium-doped lanthanum manganites $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$) of a nonstoichiometric composition in a wide temperature range using Mössbauer spectroscopy and magnetic measurements.

EXPERIMENTAL

Polycrystalline samples of $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$) were synthesized by the sol-gel technique in air from lanthanum and calcium nitrates and manganese acetate. An aqueous solution of ^{57}Fe nitrate (2 at %) was added during synthesis to obtain samples for Mössbauer measurements. The synthesis conditions were described in detail in [10].

The Mössbauer studies were carried out using an MS-1104Em spectrometer with a ^{57}Co source in a Rh matrix. The spectrometer operates in the constant acceleration mode with a triangular waveform of the source's Doppler velocity relative to the absorber at temperatures of 300, 80, and 5 K. Spectral processing and analysis were performed via the model interpretation of partial spectra and reconstruction of the distribution of hyperfine parameters using SpectrRelax software [11].

The magnetization measurements were conducted on a Lake Shore vibration magnetometer at 100 K and in fields of up to 16 kOe. The temperature dependences of the magnetization in an external magnetic field of 100 Oe were investigated in the temperature range from 100 to 300 K in the ZFC/FC modes (zero-field cooling and field cooling, respectively).

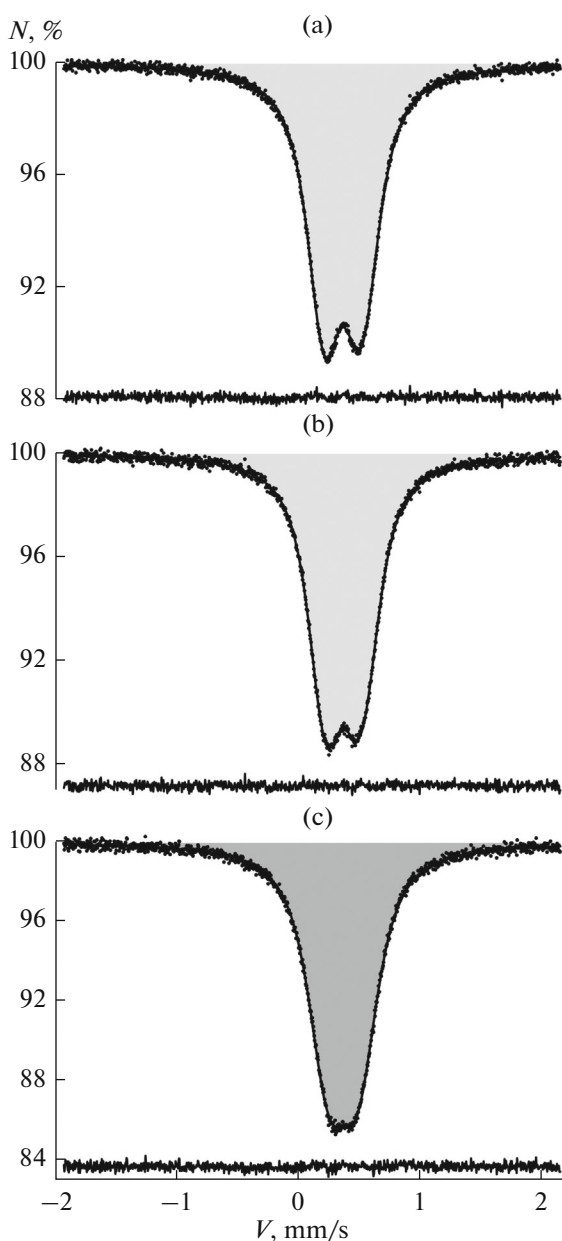


Fig. 1. Mössbauer spectra of calcium-doped nonstoichiometric lanthanum manganites at room temperature with a Ca content of (a) 5, (b) 10, and (c) 20%.

RESULTS AND DISCUSSION

It was shown earlier [10, 12, 13] that lanthanum manganites synthesized in air have a nonstoichiometric composition with an excess of oxygen, which occupies interstitial positions. In the studied lanthanum-manganite samples both Mn^{3+} and Mn^{4+} are present. As the Ca content grows, the fraction of Mn^{4+} ions in nonstoichiometric samples of lanthanum manganite decreases, while the content of Mn^{3+} increases. The amount of interstitial oxygen decreases; for the sample with $x = 0.20$ it is almost zero [10].

According to X-ray studies, the synthesized samples of $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ are single-phase and have a rhombohedral lattice (space group $R\bar{3}c$) at $x = 0.05$ and 0.10 ; when $x = 0.20$, the crystal lattice is rhombic (space group $Pnma$) [10].

Mössbauer Investigations

Mössbauer spectra of doped $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ lanthanum manganites ($x = 0.05, 0.10, 0.20$) with a nonstoichiometric composition were measured first at room temperature in a wide velocity range. The spectra represented slightly broadened quadrupole doublets; no sextets were observed. Therefore, the room-temperature spectra of doped $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$) samples were measured and in a narrower velocity range for further detailed analysis (Fig. 1); they agreed well with the data of [10].

The spectra were processed by reconstructing the quadrupole-shift distributions. Table 1 presents the mean values of the Mössbauer line shift ($\langle\delta\rangle$) (the shifts are given with respect to the α -Fe BCC lattice) and the quadrupole shift ($\langle\varepsilon\rangle$) obtained for the considered experimental spectra. The value of $\langle\delta\rangle$ is almost the same for all three spectra and is typical of trivalent iron atoms in a high-spin state in an octahedral oxygen environment. The value of $\langle\varepsilon\rangle$ decreases as the calcium content grows. The Ca-concentration increase and related reduction in the interstitial oxygen fraction lead to a decrease in the electric-field gradient at the Fe-atom location, which is due to the spatial redistribution of the charge of the surrounding atoms.

To obtain additional information, measurements at 80 K were performed. The spectra of ^{57}Fe nuclei in $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$) are shown in Fig. 2; parameters describing the Mössbauer spectra are listed in Table 2. In the case of $x = 0.10$ and 0.20 , the Mössbauer spectra are sextets with broadened lines having a shape typical of relaxation spectra; and when $x = 0.05$, the spectrum is the combination of a sextet and quadrupole doublet with a relative intensity of the latter of about 25%. The spectra of the samples with 10 and 20% Ca were processed by reconstructing the distribution of the hyperfine magnetic field using the multilevel superparamagnetic relaxation model [14]. The spectrum of the sample with 5% Ca was analyzed using the model containing a sextet in the multilevel superparamagnetic relaxation model [14] and a quadrupole doublet. The Mössbauer spectra of the samples at 80 K have the relaxation character, which is typical of superparamagnetic particles. It is the most prominent for the sample with 5% calcium content, showing also a quadrupole doublet which

Table 1. Parameters of the ^{57}Fe Mössbauer spectra of non-stoichiometric $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$) samples measured at room temperature ($\langle\delta\rangle$ is the average shift of the Mössbauer line relative to BCC Fe at room temperature; $\langle\epsilon\rangle$ is the average quadrupole shift)

Spectral parameters	$T = 300 \text{ K}$		
	5% Ca	10% Ca	20% Ca
$\langle\delta\rangle$, mm/s	0.365 ± 0.001	0.369 ± 0.001	0.366 ± 0.001
$\langle\epsilon\rangle$, mm/s	0.154 ± 0.001	0.145 ± 0.001	0.130 ± 0.001

may arise due to the presence of small particles in the sample. The analysis of X-ray diffraction patterns of the studied samples, however, did not reveal any small-sized particles present in the investigated objects. We may suggest that the relaxation character of the spectra is due to the presence of small magnetic clusters of different sizes and different blocking temperatures (the temperature of the transition from the superparamagnetic state to the ordered magnetic state), which behave similarly to superparamagnetic particles. The blocking temperature T_b exceeds 80 K for all samples; however, the sample with $x = 0.05$ contains smaller clusters which are still in the paramagnetic state at 80 K. The existence of analogous clusters 8–20 Å in size in stoichiometric doped lanthanum-manganite systems was revealed in [15, 16]. All spectra measured at 80 K show a decrease in the quadrupole shift ϵ as the Ca content grows, as well as the spectra recorded at room temperature (Table 2).

An additional spectrum was recorded at a temperature of 5 K for the sample with 5% Ca (Fig. 3). The obtained Mössbauer spectrum is a sextet with broadened spectral lines and possesses the relaxation character. The quadrupole doublet in the spectrum at the considered temperature is absent. Consequently, the blocking temperature T_b for magnetic clusters is above 5 K. The description including a sextet in the multi-

level superparamagnetic relaxation model [14] was also used to interpret the spectrum.

The varied parameter α was calculated within the multilevel superparamagnetic relaxation model; it is the ratio of the magnetic-anisotropy energy to the thermal-oscillation energy: $\alpha = \frac{K_{\text{eff}}V}{k_B T}$ (K_{eff} is the effective magnetic anisotropy constant, V is the particle volume, k_B is the Boltzmann constant, and T is the temperature). For the $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ samples with $x = 0.10$ and 0.20 at 80 K, the value of α was nearly the same, ~ 10 (Table 2). If the magnetic-anisotropy constants are assumed nearly the same, then the sizes of the magnetic clusters should be stated to be nearly equal. The value of α calculated for the sextet in the case of $x = 0.05$ is almost seven times smaller than in the samples with a calcium content of 10 and 20%. It allows the conclusion that the cluster sizes in the sample with 5% Ca are noticeably smaller, which is also proved by the presence of the quadrupole doublet in the Mössbauer spectrum.

Magnetic Investigations

Hysteresis loops at 100 K in a field up to 16 kOe were obtained for each of the studied lanthanum manganite $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$) samples (Fig. 4). The shape of the magnetization-reversal curves is typical of ferromagnetic materials with a low coercive force. The saturation magnetization I_S and coercive force H_C are listed in Table 3. As the Ca concentration grows, the coercive force H_C increases from 46 ± 1 to 69 ± 1 Oe. Such small values of the coercive force are usually characteristic of soft magnetic materials. Moreover, an increase in x is accompanied also by an increase in the saturation magnetization I_S from 29 ± 1 to 72 ± 1 emu/g, which corresponds to known published data on calcium-

Table 2. Parameters of ^{57}Fe Mössbauer spectra of nonstoichiometric $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$) samples measured at 80 K (δ is the shift of the Mössbauer line relative to BCC Fe; ϵ is the quadrupole shift; H_n is the hyperfine magnetic field; α is the parameter of the relaxation model). The average spectral parameters are given for $x = 0.10$ and 0.20

$x, \text{ Ca}$	Parameters of partial spectra					
	sextet				doublet	
	δ , mm/s	ϵ , mm/s	H_n , kOe	α	δ , mm/s	ϵ , mm/s
0.05	0.496 ± 0.011	0.043 ± 0.011	441 ± 3	1.5 ± 0.1	0.415 ± 0.003	0.187 ± 0.002
0.10	0.512 ± 0.008	0.012 ± 0.008	476 ± 4	9.9 ± 0.5	—	—
0.20	0.495 ± 0.005	0.003 ± 0.001	457 ± 4	11.1 ± 0.6	—	—

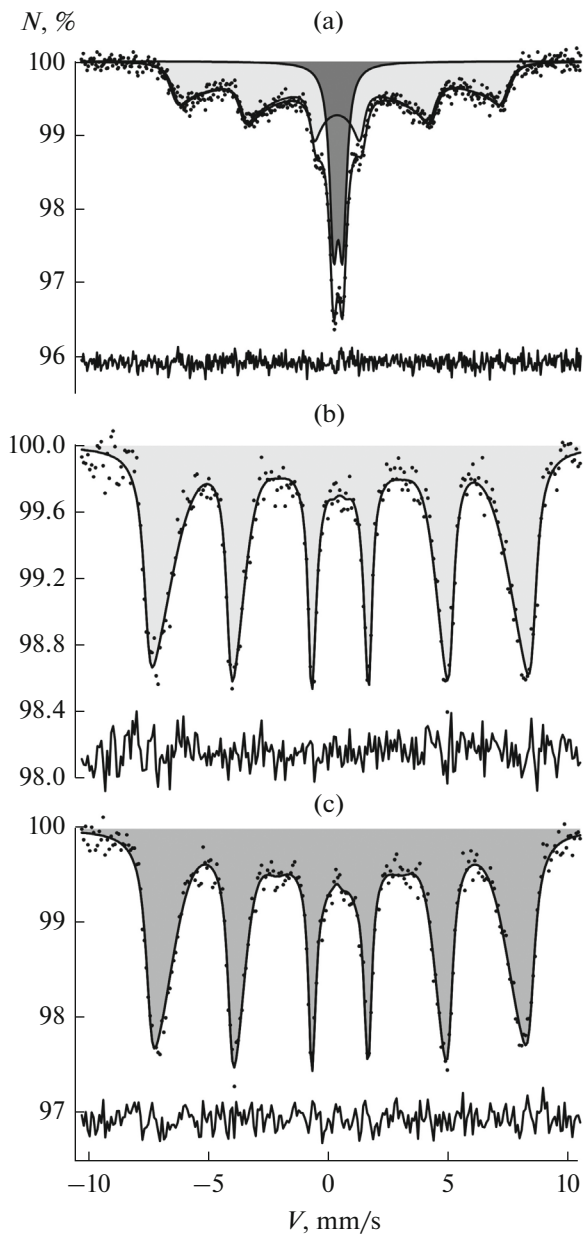


Fig. 2. Mössbauer spectra of calcium-doped nonstoichiometric lanthanum manganites at a temperature of 80 K with a Ca content of (a) 5, (b) 10, and (c) 20%.

doped lanthanum manganites [17]. For instance, the saturation magnetization for $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Fe}_{0.05}\text{O}_3$ at 5 K was found to be 86.7 emu/g in [17]. The increase

Table 3. Saturation magnetization I_S at 100 K in a field of 16 kOe; coercive force H_C , blocking temperature T_b for nonstoichiometric $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$)

x, Ca	$I_S, \text{emu/g}$	H_C, Oe	T_b, K
0.05	29 ± 1	46 ± 1	147 ± 2
0.10	35 ± 1	57 ± 1	184 ± 2
0.20	72 ± 1	69 ± 1	283 ± 1

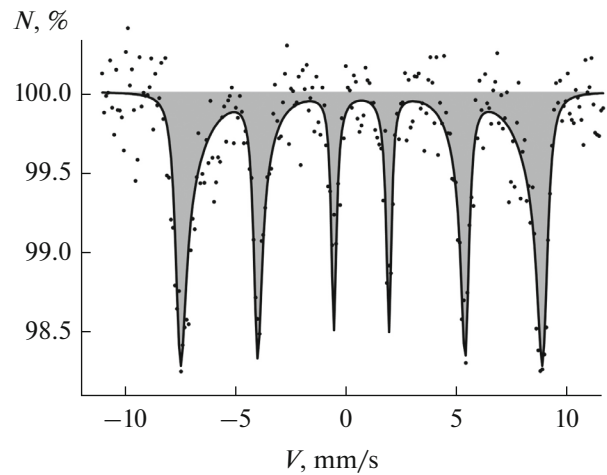


Fig. 3. Mössbauer spectrum of lanthanum manganite doped with 5% Ca measured at 5 K.

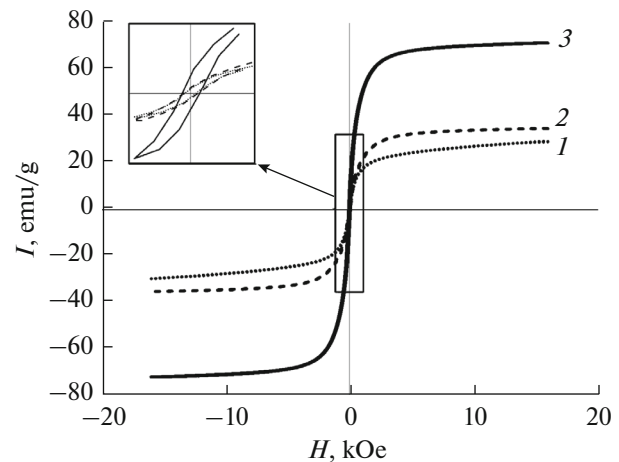


Fig. 4. Hysteresis loops obtained at 100 K for calcium-doped nonstoichiometric lanthanum manganites with x being (1) 0.05, (2) 0.10, and (3) 0.20.

in I_S accompanying the growth in the calcium content is evidently due to an increase in the amount of Mn^{3+} ions, which possess a larger magnetic moment ($2\mu_B$) as compared to Mn^{4+} ($1.5\mu_B$).

The temperature dependences of the magnetization in the external magnetic field of 100 Oe were obtained in the ZFC/FC modes in the temperature range from 100 to 300 K (Fig. 5). The cooling curves in the field and without the field differ for all samples, which proves the superparamagnetic behavior of the magnetic clusters observed in Mössbauer studies. The

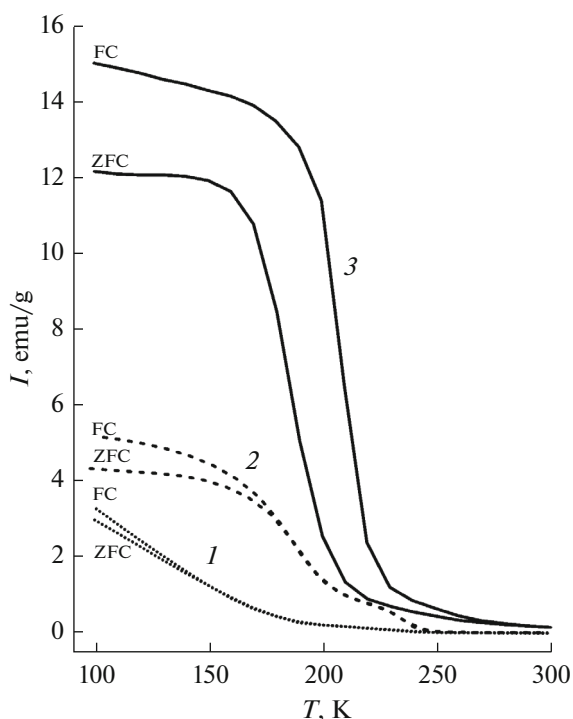


Fig. 5. The temperature dependence of the magnetization (ZFC/FC measurements) in the field of 100 Oe for calcium-doped nonstoichiometric lanthanum manganites with x being (1) 0.05, (2) 0.10, and (3) 0.20.

blocking temperature T_b grows as the Ca content increases (Table 3), and this also correlates with the Mössbauer data.

CONCLUSIONS

The Mössbauer and magnetic investigations of doped lanthanum manganites $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.98-x}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05, 0.10, 0.20$) with a nonstoichiometric composition showed that increasing the Ca concentration and decreasing the amount of interstitial oxygen lead to a decrease in the electric-field gradient at the location of the Fe atom due to a redistribution of the charge of the surrounding atoms. At temperatures below the magnetic-ordering point, the studied lanthanum manganites demonstrate the relaxation behavior which may be attributed to small-sized magnetic clusters present in the samples. As the Ca

content grows, the coercive force, saturation magnetization, and blocking temperature also increase.

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