Effect of the crystal structure defectiveness on magnetic state of sodium-doped lanthanum manganites

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Structural, electric, magnetoresistive, and resonance properties of $La_{1-x}Na_xMnO_{3+\gamma}$ samples synthesized by solid phase reactions have been studied. It is shown that the valence state of manganese remains essentially unchanged as x increases from 0.08 to 0.16: the positive charge reduction in lanthanum sublattice caused by the increase in sodium content occurs due to formation of vacancies either in cation sublattices or in both cation and anion ones. In addition to magnetically ordered phases, all the samples have been found to contain the magnetically disordered low-conductive phase even at low temperatures (77 K), and its amount is greater in the samples with the lower x values. The Curie temperature (T_C) for $La_{1-x}Na_xMnO_{3+\gamma}$ system rises monotonically as x changes from 0.08 to 0.16. A correlation is revealed between the characters of concentration induced changes in T_C and number of vacancies in manganese sublattice. It is shown that, as x changes, the change character of the unit cell parameters (the diminution in both the cell volume and rhombohedral distortion angle) is also directed towards an enhancement of the ferromagnetic double exchange interaction and the TC elevation. The magnetoresistance (MR) measured at room temperature in 15 kOe field exhibits a maximum (20 %) in the samples with $x = 0.12$. For the samples of this composition, MR(H) dependence is close to the linear one, which stresses a good utilization prospect of such materials in the magnetic field measurement devices.

Исследованы структурные, электрические, магниторезистивные и резонансные свойства образцов $La_{1-x}Na_xMnO_{3+\gamma}$, синтезированных методом твердофазных реакций. Показано, что валентное состояние марганца практически не изменяется при изменении x от 0,08 до 0,16: снижение положительного заряда в подрешетке лантана при увеличении содержания натрия совершается за счет формирования вакансий в катионных, или одновременно в катионных и анионной подрешетках. Обнаружено, что, кроме магнитоупорядоченных фаз, все образцы содержат магнитно неупорядоченную слабопроводящую фазу даже при низких температурах (77 К), причем ее количество больше в образцах с меньшим значением x. Температура Кюри (T_C) в системе $La_{1-x}Na_xMnO_{3+\gamma}$ монотонно возрастает при изменении x от 0,08 до 0,16. Обнаружена корреляция между величинами роста T_C и уменьшения количества вакансий в подрешетке марганца. Показано, что при изменении x характер изменения параметров элементарной ячейки (уменьшение объема ячейки и угла ромбоэдрической деформации) также направлен на усиление двойного обмена и повышение T_C. Магнитосопротивление (МС), измеренное в поле 15 кЭ при комнатной температуре, имеет максимум (20 %) в образцах с $x = 0,12$. Для образцов этого состава зависимость МС(H) близка к линейной, что перспективно для использования таких материалов в устройствах для измерения магнитного поля.

An intense research interest in complex oxides based on lanthanum manganites $(La,M)MnO_3$ (M is a mono- or divalent element) is associated with the discovery of colossal magnetoresistance effect (CMR) and good prospects of its utilization in magnetoelectronic devices [1, 2]. The CMR in doped manganites results from a competition between oppositely directed interactions among aliovalent (differing in valence) manganese ions [2]. So, so-called double exchange, i.e. electron transfer between Mn^{3+} and Mn^{4+} through the oxygen anions, favors simultaneous appearance of ferromagnetism and metal-like conductivity [1–3]. At the same time, a series of other effects (electron-phonon interaction, antiferromagnetic superexchange, charge and orbital interactions) oppose establishment of the ferromagnetic ordering and favor the charge carrier localization [2]. If the double exchange dominates over the other interactions, both the paramagnetic-ferromagnetic and insulator-metal transitions occur almost simultaneously as the temperature decreases, resulting in a high sensitivity of electric resistance to magnetic field in the vicinity of the Curie temperature T_C [1–3].

To be suitable for competitive applications (magnetic field measurement devices, magnetic sensors, reading elements for devices of ultra-high density magnetic recording, etc.), the CMR materials should be highly sensitive to magnetic fields and have T_C close to room temperature. The Curie temperature value depends mainly on the manganese formal charge (MnFC), i.e. on the mean ionization state of manganese which, for the doped manganites that contain Mn only in 3+ and 4+ states, is determined by the fraction of Mn^{4+} ions. So, an increase in Mn^{4+} content from 15 to 40 % of the total manganese amount (here and below, we imply atomic percentage) gives rise to T_C elevation from 180 to 360 K [3]. The Mn ionization state can be tuned by variation of the oxygen non-stoichiometry or by aliovalent substitutions in cation sublattices. To date, it is just the $La^{3+}_{1-x}M^{2+}_xMnO_3$ that is the most comprehensively studied manganite system, where M^{2+} is an alkaline-earth element (AEE) [2–7]. By contrast, very few works are devoted to investigation of the alkaline elements (AE) substitution for lanthanum. Taking into account the differences in both the valence states and ionic radii between AE and AEE, additional information on the role of both the MnFC and structural changes should be expected to re-

sult from introduction of AE ions into lanthanum sublattice. Among all AE ions, the ionic radius of sodium $(R_{Na1+} = 1.39Å)$ is closest to that of lanthanum $(R_{La3+} = 1.36Å)$ [8], which allows minimizing the local structural perturbations in lanthanum sublattice of $La_{1-x}Na_xMnO_{3\pm\gamma}$ system and makes it possible to concentrate on the role of MnFC and other factors.

The studies of $La_{1-x}Na_xMnO_{3\pm\gamma}$ solid solutions in [9, 10] were limited to $x = 0.10$ or $x = 0.10$ and 0.30, respectively. According to [10], the T_C of the ceramic samples is highly sensitive to the heat treatment regimes. To date, however, there is no unequivocal opinion about the optimal heat treatment parameters: using the solid phase reaction method, the single phase Na doped manganites were obtained at temperatures from 1290 [11] up to 1470 K [12-14], but the materials prepared differed strongly in properties. Among other factors, the appreciable volatility of sodium at high temperatures also contributes to the ambiguity concerning boundaries of the regions for the $La_{1-x}Na_xMnO_{3\pm\gamma}$ solid solutions existence: $x \le 0.2$ [15], $x \le 0.25$ [11], $x \le 0.30$ [10-13]. The authors [14] succeeded in achievement of the upper limit for the single-phase solid solution, namely, $x = 0.40$, by using sintering of the powders containing excess Na.

In most papers, $La_{1-x}Na_xMnO_{3\pm\gamma}$ solid solutions were reported to be crystallized in the $R\bar{3}c$ rhombohedral space group [10–15]. At the same time, there were reports that the rhombohedral character of distortions occurs only at $x \ge 0.15$ for $Nd_{1-x}Na_xMnO_3$ [16] and $x > 0.065$ for $La_{1-x}Na_xMnO_{3\pm\gamma}$ [17], whereas at lower x values, typical is the orthorhombic structure. It was pointed out in [18] that, as there exist vacancies at lanthanum or oxygen sites, the materials have $R\bar{3}c$ structure, high values of T_C and magnetoresistance, whereas at high concentration of vacancies at manganese sites, orthorhombic Pbnm structure and activated behavior of electric resistance R $(dR/dT < 0)$ take place. According to [15], a decrease in the positive charge of lanthanum sublattice, occurring at substitution of Na for La, causes no changes in the Mn^{2+} charge state, but enhances the occupancy degree of manganese sites. It is noteworthy that in most papers dealing with $La_{1-x}Na_xMnO_{3\pm\gamma}$, no data have been reported on the magnetoresistive response of these materials, a pa-

rameter of particular importance for their practical applications.

The magnetic behavior as well as features of the relationship between electric and magnetic properties of $La_{1-x}Na_xMnO_{3+\gamma}$ compounds were studied in detail in [13]. To explain the results of magnetic and electric measurements, the authors employed a hypothesis stating that the magnetic state of $La_{1-x}Na_xMnO_{3\pm\gamma}$ samples is inhomogeneous and that three phases, namely ferromagnetic metallic (FM), ferromagnetic insulating (FI), and nonmagnetic one, coexist within the sample volume. However, there is no direct confirmation of the existence of those phases. The aim of this work is to clarify the effect of both the Na doping level and the crystal structure defectiveness on magnetoresistive characteristics and magnetic phase composition of $La_{1-x}Na_xMnO_{3+\gamma}$ samples in the composition range where ferromagnetic-to-paramagnetic transition point is near room temperature.

The samples for this investigation were prepared by solid state reaction using appropriate mixtures of extra purity grade La_2O_3 and Mn_2O_3, and reagent grade Na_2CO_3, dried preliminarily at 1120 K, 920 K, and 520 K, respectively. The stoichiometric amounts of starting reagents were mixed and homogenized for 6 to 8 h by ball milling in distilled water. After evaporating the residual water, the mixtures were dried at 380–400 K and passed through a caprone sieve. After preliminary annealing (1170 K, 4 h), wet homogenizing millings were repeated. After adding aqueous solution of polyvinyl alcohol as the binder, the powder was pressed into disks of 10 mm in diameter and 3–4 mm in thickness, which were then sintered for 2 h at 1440 K.

The Mn^{3+} and Mn^{4+} contents were determined by titration with iodine thiosulfate solution. Iodine in the potassium iodide solution was replaced by chlorine resulting from the dissolution of a weighed manganite sample in hydrochloric acid [20]. Na content was determined by flame photometry using dissolved manganite samples. Details of the X-ray and electric studies are described in [23]. Magnetoresistance was measured in fields up to 15 kOe and was determined as $(\rho - \rho_H)/\rho$, where ρ is resistivity in zero magnetic field, and ρ_H, in the external field H.

In this work, we have studied $La_{1-x}Na_xMnO_{3+\gamma}$ solid solutions with $x = 0.08$, 0.10, 0.12, 0.14, and 0.16. Chemical analysis of the samples has shown that absolute losses of sodium, Δx, increase in proportion to x. At the same time, relative losses, $\Delta x/x$, are almost the same for all x values and vary within the range of 23 to 27 %. Absolute and relative sodium losses, the content of manganese (Mn_{total}) being in different valence states (Mn^{3+} and Mn^{4+}), manganese formal charge MnFC as well as oxygen non-stoichiometry coefficient γ, as resulting from the chemical analysis of $La_{1-x}Na_xMnO_{3+\gamma}$ samples, are presented in Table 1. It is seen that a lowering of the positive charge in lanthanum sublattice, occurring upon substitution of Na for La, does not result in a MnFC increase, in accordance with earlier findings [15, 19, 21].

The detailed studies of the doped manganite structure where oxygen content deviates from the ideal stoichiometric value, have shown that formation of manganites having deficiency and excess of oxygen occurs in different ways. So, $La_{1-x}Na_xMnO_{3+\gamma}$ manganites with a negative γ value contain vacancies in oxygen sublattice, the number thereof is equal to γ. On the contrary, oxygen excess with regard to the ideal stoichiometric value results in formation of vacancies in cation sublattices, and thus, for $La_{1-x}Na_xMnO_{3+\gamma}$ compounds with $\gamma > 0$, $(La_{1-x}M_xMn)_{1-\delta}O_3$ formula is more appropriate [15, 24–26]. Basing on the analysis of the data of neutron scattering and X-ray

Table 1. Absolute (Δx) and relative ($\Delta x/x$) sodium losses, content of Mn_{total}, Mn^{3+} and Mn^{4+}, manganese formal charge MnFC, and oxygen non-stoichiometry coefficient γ resulted from chemical analysis of $La_{1-x}Na_xMnO_{3+\gamma}$ samples

x	Δx	$\Delta x/x$	Mn_{total}, %	Mn^{3+}, %	Mn^{4+}, %	MnFC	γ
0.08	0.0216	0.27	23.6	16.1	7.5	3.32	0.068
0.10	0.0240	0.24	23.9	16.5	7.4	3.31	0.043
0.12	0.0288	0.24	24.2	16.9	7.3	3.32	0.016
0.14	0.032	0.23	24.4	17.1	7.3	3.33	−0.006
0.16	0.039	0.24	24.6	17.7	7.6	3.31	−0.027

diffraction, the authors of [24−26] conclude that at $\gamma > 0$, the vacancies are distributed almost equally between the lanthanum and manganese sublattices, and their number, N_V, in each sublattice can be estimated as $N_V = \gamma/(3+\gamma)$. The vacancy numbers for each of the sublattices in $La_{1-x}Na_xMnO_{3+\gamma}$ calculated according to this procedure are shown in Fig. 1. As is seen, N_V in lanthanum sublattice is rather great (~0.04) for all x values. In manganese sublattice, the corresponding number is maximal in $La_{0.92}Na_{0.08}MnO_{3+\gamma}$; as x grows, N_V decreases and reaches zero at $x = 0.14$. On the contrary, the number of vacancies in oxygen sublattice differs from zero only in the samples with $x = 0.14$ and 0.16. The total number of vacancies (N_{Vtotal}) is minimal at $0.12 \leq x \leq 0.14$, which is shown in inset of Fig. 1.

The x-ray diffraction studies have shown that the synthesized materials are single-phase ones and their structure is characterized by the rhombohedrally distorted ($R\bar{3}c$) perovskite cell. The results of the structural parameters refinement for the sodium doped lanthanum manganites are presented in Table 2. The tolerance factor t was determined as
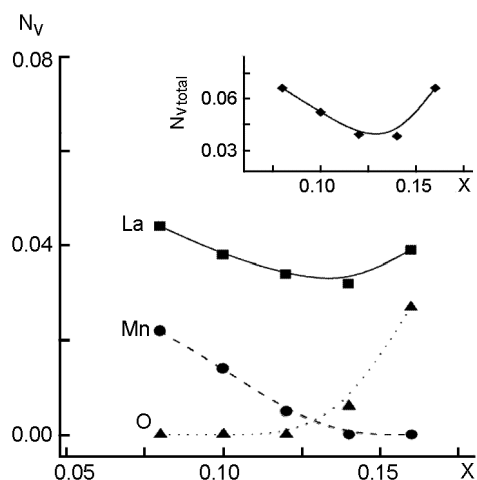

Fig. 1. Number of vacancies in lanthanum, manganese and oxygen sublattices as a function of the nominal sodium content, x. Inset shows total amount of vacancies in all the sublattices.

$$t = \frac{\overline{R}_{La} + \overline{R}_O}{\sqrt{2}\,(\overline{R}_{Mn} + \overline{R}_O)}, \qquad (1)$$

where $\overline{R}_{La}$, $\overline{R}_{Mn}$, and $\overline{R}_O$ are mean ionic radii in lanthanum, manganese and oxygen sublattices, respectively. For calculations, the following radii values were used: $R_{Mn3+} = 0.65$Å, $R_{Mn4+} = 0.54$Å and $R_{O2+} = 1.4$Å [8]. The tol-

Table 2. Structural parameters of $La_{1-x}Na_xMnO_{3\pm\gamma}$ manganites

x	0.08	0.10	0.12	0.14	0.16
Unit cell parameters					
a(Å)	5.5206(2)	5.5190(3)	5.5157(2)	5.5102(2)	5.5084(4)
c(Å)	13.3416(3)	13.3414(4)	13.3436(3)	13.3400(3)	13.3393(6)
V(Å³)	352.13(2)	351.93(3)	351.56(2)	350.77(2)	350.52(4)
c/a	2.4167	2.4174	2.4192	2.4210	2.4216
Positions of oxygen ions					
x_O/a	0.456(2)	0.454(3)	0.452(2)	0.454(2)	0.445(2)
Interatomic distances (Å)					
Mn−O	1.959(1)	1.960(2)	1.961(1)	1.958(1)	1.960(2)
Mn−O−Mn angle (degrees)					
	165.4(4)	164.8(5)	164.2(2)	164.8(4)	163.5(6)
Tolerance factor					
t	0.9548	0.9550	0.9548	0.9554	0.9523
Agreement factors					
Rb (%)	5.26	3.86	5.48	5.33	6.86
Rf (%)	7.50	4.53	7.09	7.28	7.84

Note: Atomic positions in the $R\bar{3}c$ structure: La 6a (0 0 1/4); Mn 6b (0 0 0); O 18e (x_O 0 1/4).
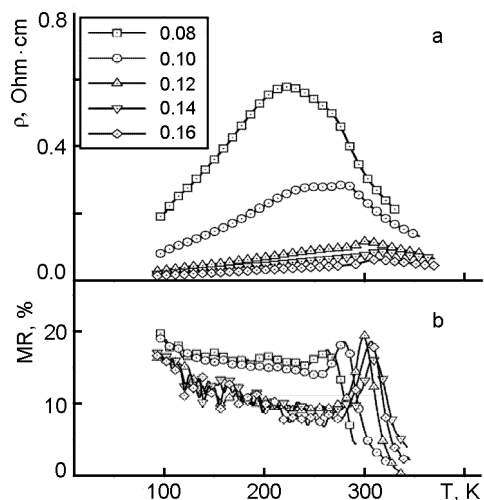
Fig. 2. Temperature dependences of resistivity (a) and magnetoresistance (b) for $La_{1-x}Na_xMnO_{3+\gamma}$ samples.

Fig. 3. Magnetoresistance vs field dependences at 77 and 297 K.

erance factor describes quantitatively the deviation degree of a lattice from the ideal perovskite one, where $t = 1$. As is seen from Table 2, independent of the x value, there is no noticeable changes in t, Mn–O bond lengths and angles in Mn–O–Mn chain, in compliance with the chemical analysis results stating that for $La_{1-x}Na_xMnO_{3+\gamma}$ system, the changes in the manganese valence state are negligible within the range $0.08 \le x \le 0.16$.

Fig. 2 shows temperature dependences of resistivity and magnetoresistance for $La_{1-x}Na_xMnO_{3+\gamma}$ samples. The $\rho(T)$ dependence shows a maximum, its temperature, T_p, rises with increasing sodium content. In the low temperature region ($T < T_p$), the temperature coefficient of resistance exceeds zero ($d\rho/dT > 0$, metallic character of conductivity), that is characteristic of the ferromagnetic state of manganites. At high temperatures ($T > T_p$), the conductivity is of activation type ($d\rho/dT < 0$) which is generally observed in the paramagnetic state of manganites [2, 3]. Analysis of the temperature dependences of magnetoresistance can provide more precise information about magnetic state of the samples. The peak on the $MR(T)$ curve is associated with a transition from para- to ferromagnetic state. An additional contribution to magnetoresistance which becomes especially evident in low temperature region is associated with the spin-dependent charge transfer across the regions which are structurally and magnetically disordered [27–29]. In most cases,
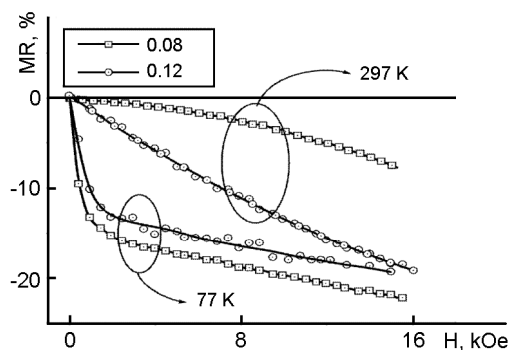
the Curie temperature coincides with that of the peak in $MR(T)$ curve, and in this work, T_C was defined as the peak temperature on MR vs T dependence. A considerable deviation of T_p from T_C for the sample with $x = 0.08$, as well as the double-peak character of $\rho(T)$ dependence for $x = 0.10$ evidence the high magnetic inhomogeneity of these materials [30].

In Fig. 3, compared are dependences of MR on magnetic field H for the manganites with $x = 0.08$ and 0.12. At $T = 77$ K, $MR(H)$ curves exhibit a kink near $H_{cr} = 1.5$ kOe, whereas at $H < H_{cr}$ and $H > H_{cr}$, magnetoresistance is almost linear function of magnetic field. In doped manganites, such character of $MR(H)$ behavior is an evidence of the FM phase coexistence with other one which is simultaneously magnetically disordered and low-conductive or insulating [2, 27–29]. The latter phase is mainly concentrated near intergrain boundaries or vacancies. At high fields ($H > H_{cr}$), the main contribution to magnetoresistance is due to the former phase, whereas the low-field component (LFMR) is caused by spin-polarized tunneling or spin-dependent scattering of charge carriers at the regions of reduced conductivity and provides indirect information on the amount and features of low-conductive inclusions [27–29]. For $La_{0.92}Na_{0.08}MnO_{3+\gamma}$ sample, the value of LFMR determined by extrapolating of the $MR(H)$ curves from a high field region to $H = 0$, equals 14.3 %. As x increases to 0.12, LFMR is lowered to 11.8 %, and then remains almost constant upon further increase in x. These data give additional evidence that amount of the magnetically disordered phase decreases with a rise in x, in full compliance with the results of electric measurements (see Fig. 1). At $T = 297$ K, the magnetoresistance measured in 15 kOe
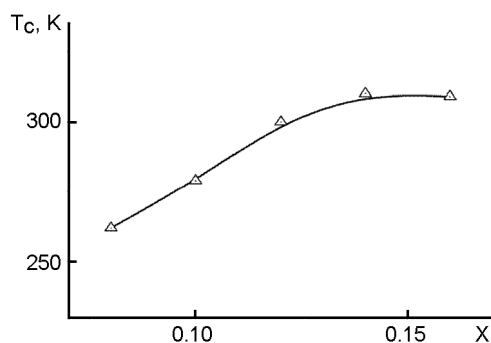
Fig. 4. Curie temperature as a function of the nominal sodium content.

Fig. 5. NMR spectra for $La_{1-x}Na_xMnO_{3+\gamma}$ samples with $x = 0.08$, 0.12, and 0.16.

magnetic field shows a maximum (20 %) in the sample with $x = 0.12$. For this composition, the *MR* vs *H* dependence is almost linear (see Fig. 2). Deviation of x from 0.12 gives rise to both a decrease in *MR* and increase in nonlinearity of *MR(H)* curves. It is noteworthy that, for the bulk samples of other doped-manganite-based systems, the magnetoresistance at room temperature does not exceed 8–15 % in fields up to 15 kOe [2, 23]. Accounting for a high degree of the *MR(H)* linearity in $La_{0.88}Na_{0.12}MnO_{3+\gamma}$ samples, such materials can be used in sensing elements of magnetic field measuring devices.

Despite the fact that MnFC is almost constant, the Curie temperature increases monotonically as x grows from 0.08 to 0.16 (Fig. 4). To understand better a reason for such the behavior of the Na-doped manganites, we carried out NMR studies on manganese nuclei. The analysis of such spectra can give more detailed information about the magnetic phase composition and inhomogeneity in $La_{1-x}Na_xMnO_{3+\gamma}$. It is known that, when placed in magnetic field H_{eff}, a nuclear spin performs a precession around an axis coincident in direction with that of H_{eff}, and thus, using the magnetic resonance technique, it is possible to determine the corresponding resonance frequency. For magnetically ordered media, H_{eff} is the sum of external and internal magnetic fields. The NMR spectra on manganese nuclei measured in zero external field provide the information on local environment and valence state of magnetically ordered Mn ions [31–34]. This results from the fact that the nuclear spins are coupled with surrounding electron moments through the hyperfine field $B_{hf} = (2\pi/\gamma)A<S>$, where γ is the gyromagnetic ratio having the value depending on the nucleus type; A, the hyperfine interaction constant; and $<S>$ is the mean value

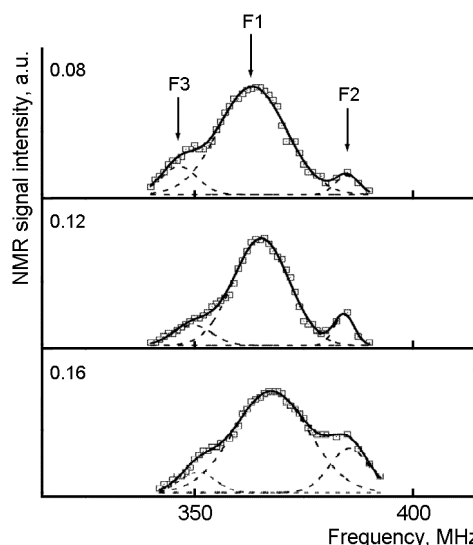of the ion electron spin of [31, 32]. For Mn^{4+} ions ($S = 3/2$) with the t_{2g}^3 electron configuration, the ground state is the ^3F singlet, and this results in zero spin-dipole contribution to hyperfine interaction. In this case, B_{hf}, which is due to the Fermi contact interaction [31–34], is practically isotropic and gives rise to a relatively sharp NMR line centered near 325 MHz at low temperatures (~5 K) [31–36]. Hyperfine field on Mn^{3+} ions ($S = 2$) has a substantial anisotropic contribution from the spin-dipole field of $d_{x^2-y^2}$ or $d_{3z^2-r^2}$ orbital states, and this results in a distribution of the NMR frequencies in a wide range from 370 to 430 MHz [31–36]. For the case where a fast movement of electron from a Mn^{3+} ion to the neighboring Mn^{4+} one occurs, the hyperfine fields on the manganese nuclei are averaged out, with relative contribution from Mn^{3+} and Mn^{4+} ions being dependent on their concentrations. If manganese ions are ferromagnetically ordered, the lines shift towards a low frequency side and their intensity is reduced with the temperature rise.

Fig. 5 shows NMR spectra at 77 K for $La_{1-x}Na_xMnO_{3+\gamma}$ with $x = 0.08$, 0.12, and 0.16. The complex shape of the spectra indicates that there are several processes that make contributions to the resultant curve. For all the samples, the spectra are well described by a superposition of three Gaussian lines. An attempt to limit the decomposition only to two lines has given unsatisfactory results. The position of the most intense peak F1 corresponds to the frequency at which the nuclear magnetic reso-
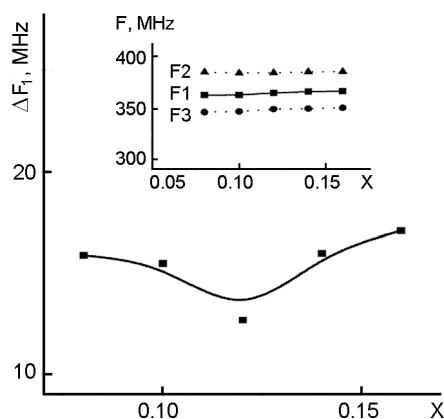
Fig. 6. Dependence of the F1 linewidth on x. Inset shows resonance frequencies of the F1, F2 and F3 lines as functions of x.

nance was observed at 77 K in other manganites with MnFC 3.3 [31−36]. This evidences that the peak F1 belongs to the FM phase, for which hyperfine fields are averaged out due to the fast motion of electrons between the manganese sites. Two other peaks can be ascribed to localized states of the tri- and tetravalent Mn ions belonging to the F phase, its appearance in $La_{1-x}Na_xMnO_{3+\gamma}$ samples being predicted in [13]. For each line, both the position and relative intensity change only slightly with changing x, thus indicating that the properties of the magnetically ordered phases coexisting within a sample volume are practically independent of the sodium content. As is seen from inset in Fig. 6, for each line, a maximum frequency deviation observed upon x variation does not exceed 4 MHz. These data, while agreeing well with the chemical and X-ray structure analysis results stating that MnFC is almost independent of the sodium content, do not explain the ascending character of the T_C vs x dependence. The only parameter that is varied essentially with x is the width of the line corresponding to the FM phase: ΔF_1 decreases as x changes from 0.08 to 0.12 and increases upon further rise in x (Fig. 6). The ΔF_1 vs x dependence correlates with the behavior of the total number of vacancies, $N_{Vtotal}(x)$, and these data show that at 77 K the FM phase is quite well homogeneous in manganites with $x = 0.12$ and less homogeneous in the rest of the samples. These changes, however, are not so essential to be able to explain the whole complex of the magnetotransport properties of the Na doped manganites, especially at $x < 0.12$.

It was noted above that the NMR spectra obtained in the absence of any external magnetic field provide information only on the properties of the magnetically ordered phases. However, it follows from the $MR(H)$ dependences that already at 77 K all the samples contain the magnetically disordered low-conductive phase and the smaller is x, the higher is its content (see Fig. 2). Taking into account the results of both chemical analysis and NMR studies, the same conclusion follows from the analysis of resistivity behavior: at constant MnFC and insignificant parameter change of magnetically ordered phases, the increase in the absolute ρ value at x lowering is only possible if the amount of the magnetically disordered low-conductive phase increases. In compliance with this picture is also the behavior of the temperature dependence of resistivity evidencing the highly inhomogeneous magnetic state of the samples with $x \leq 0.12$.

Returning now to Fig. 1, we can see that in the samples with $x \leq 0.12$, the total number of vacancies increases with x and that the most part thereof is localized in the manganese sublattice. Taking into account the fact that the Curie temperature of a ferromagnet is reduced as the number of magnetic ions in the nearest neighborhood of a specific ion decreases [2, 13], the reduced T_C values should be expected in the vicinity of the vacancies in manganese sublattice. For this reason, as x decreases in $La_{1-x}Na_xMnO_{3+\gamma}$ samples with $x \leq 0.12$, the following processes are expected to occur: the magnetic transition becomes broadened, the amount of the magnetically disordered phase gets increased, and, thus, the mean T_C value is reduced. It is just this picture that is observed in experiment: the concentration dependences of T_C and number of vacancies in manganese sublattice correlate well with each other. It is pertinent to note that oxygen ions also play an important role in exchange interactions between the manganese ions. However, for the samples under investigation, T_C depends slightly on the number of the oxygen vacancies. Such an effect may be caused by the fact that the relative amount of the vacancies is far smaller in oxygen sublattice than in manganese one.

A correlation between the number of vacancies in manganese sublattice and Curie temperature was observed in [13] devoted to investigation of Na-doped manganites. The authors also pointed out that, although

MnFC keeps constant with the increasing sodium content, the change character of the unit cell parameters (decreasing both the cell volume and rhombohedral distortion angle) is also directed towards enhancement of the double exchange interaction and T_C elevation. For the samples studied in the present work, the change character of the unit cell parameters agrees with the results of [13]. However, the size of these changes does not exceed 0.5 % as x increases from 0.08 to 0.16. It should also be noted that at constant MnFC, the change of the unit cell parameters is a result of the vacancy concentration change, and thus that of N_V, particularly in Mn sublattice, is thought to be the actual origin of the strong dependence of T_C on x. This idea agrees with the data obtained on the manganites of other systems. So, investigation of the oxygen nonstoichiometry parameter, γ, effect on T_C of La$_{0.815}$Sr$_{0.185}$MnO$_{3+\gamma}$ ($\gamma \geq 0$) samples has shown that the increase in $\gamma/(3+\gamma)$ ratio by 1.6 % results in T_C lowering by 10 % even for the case where T_C should increase due to the change in MnFC [37].

To conclude, the structure of La$_{1-x}$Na$_x$MnO$_{3+\gamma}$ samples synthesized by the solid phase method is characterized by rhombohedrally distorted perovskite cell. The valence state of Mn remains essentially unchanged as x varies from 0.08 to 0.16: the reduction in the positive charge of lanthanum sublattice caused by the increase in sodium content occurs due to the formation of vacancies either in cation sublattice or in both cation and anion ones. The number of vacancies in manganese sublattice is concluded to be maximal in La$_{0.92}$Na$_{0.08}$MnO$_{3+\gamma}$; it diminishes with increasing x and reaches zero at $x = 0.14$. The number of vacancies in oxygen sublattice differs from zero only in the samples with $x = 0.14$ and 0.16. NMR spectra on the manganese nuclei are well described by a superposition of three lines corresponding to different magnetically ordered phases. The most intense peak F1 belongs to the FM phase where hyperfine fields are averaged out due to the fast motion of electrons between the neighboring manganese sites. Concentration dependence of this peak width correlates with the behavior of the total amount of vacancies and exhibits a minimum in the manganites with $x = 0.12$. It is shown that the change in properties of the magnetically ordered phases is insufficient to explain the whole complex of the magnetotransport properties of Na doped manganites, especially at $x < 0.12$.

It follows from the $MR(H)$ dependences that all the samples contain a magnetically disordered low-conductive phase and its amount is greater in the samples with lower x values. It is shown that the rise in absolute resistivity value occurring as x increases is also associated with the increase in the amount of the magnetically disordered low-conductive phase. The behavior of the resistivity temperature dependence evidences a high magnetic inhomogeneity of the manganite samples with $x \leq 0.12$. It is concluded that inhomogeneous magnetic state especially characteristic of the samples with smaller x values is caused by the increased amount of vacancies in manganese sublattice. The Curie temperature in the La$_{0.92}$Na$_{0.08}$MnO$_{3+\gamma}$ system increases monotonically as x changes from 0.08 to 0.16. A correlation is established between the character of concentration-induced T_C changes, on the one hand, and N_V in manganese sublattice, on the other hand. It is shown that the change character of the unit cell parameters (decrease in both the cell volume and rhombohedral distortion angle) is also directed towards the enhancement of double exchange and T_C elevation. The data are presented which show that the contribution to the T_C increase caused by the N_V change in manganese sublattice is more important than that caused by the change of the unit cell parameters. Magnetoresistance measured at room temperature in 15 kOe field exhibits a maximum (20 %) in the samples with $x = 0.12$. For the samples of this composition, $MR(H)$ dependence is close to the linear one, which stresses good prospects for utilization of such materials in the magnetic field measurement devices.

References

1. E.O.Wollan, W.C.Koehler, *Phys. Rev.*, **100**, 545 (1955).
2. A.-M. Haghiri-Gosnet, J.-P.Renard, *J. Phys. D: Appl. Phys.*, **36**, R127 (2003).
3. Y.Takura, A.Urushibara, Y.Moritomo et al., *J. Phys. Soc. Jap.*, **63**, 3931 (1994).
4. J.Nowotny, M.Rekas, *J. Am. Ceram. Soc.*, **81**, 67 (1998).
5. V.A.Cherepanov, L.Yu.Barkhatova,V.V.Voronin, *J. Solid State Chem.*, **134**, 38 (1997).
6. Y.Takeda, S.Nakai, T.Kojima et al., *Mat. Res. Bull.*, **26**, 153 (1991).
7. R.A.Lewis, *J. Supercond.*, **14**, 143 (2001).
8. R.D.Shannon, *Acta Crystallogr. Sect. A.*, **32**, 751 (1976).

9. M.K.Gubkin, T.M.Perkalina, A.B.Bykov, V.A.Chubarenko, *Fiz. Tverd. Tela*, **35**, 1443 (1993).

10. T.M.Perekalina, L.Ya.Shapiro, I.E.Lipinski, S.A.Cherkizyan, *Fiz. Tverd. Tela*, **33**, 681 (1991).

11. I.O.Troyanchuk, O.S.Mantytskaya, E.F.Shapovalova, S.N.Pastushonok, *Fiz. Met. Metallogr.*, **83**, 161 (1997).

12. H.Xu, Q.Cao, Y.Shen, S.Zhang, *Nanjing University Gongeng Caliliao*, **32**, 147 (2001).

13. S.L.Ye, W.H.Song, S.G.Wang et al., *J. Appl. Phys.*, **90**, 2943 (2001).

14. A.Yu.Ganin, *Lomonosov Internet J.*, Sect.12, Commun. 1151932 (2000).

15. T.Shimura, H.Toshimura, M.Yoshiykil et al., *J. Solid State Chem.*, **124**, 250 (1996).

16. E.A.Filonova, N.A.Zaytseva, A.N.Petrov, *Zh. Fiz. Khim.*, **76**, 278 (2002).

17. G.A.Bychkov, V.I.Pavlov, A.K.Bogush, G.I.Kartashova, in: Abstr. Book of XVIII All-Union Conf. on Physics of Magnetic Phenomena, Kalinin (1988), p.431 [in Russian].

18. R.N.Singh, C.Shivakumara, N.Y.Vasanthacharaya et al., *J. Sol. St. Chem.*, **157**, 19 (1998).

19. S.Zouari, L.Ranno, A.Cheikh-Rouhou, *Solid State Communus*, **119**, 517 (2001).

20. L.V.Borovskikh, G.A.Mazo, V.M.Ivanov, *Vestn. Mosk. Univ. Ser. 2. Khimiya*, **40**, 373 (1999).

21. W.Boujelben, A.Cheikh-Rouhou, M.Ellouze, J.C.Joubert, *J. Magn. Magn. Mater.*, **242–245**, 662 (2002).

22. S.Jin, T.H.Tiefel, M.McCormack et al., *Science*, **264**, 413 (1994).

23. A.G.Belous, O.I.V'yunov, E.V.Pashkova et al., *Inorg. Mater.*, **39**, 161 (2003).

24. B.C.Tofield, W.R.Scott, *J. Solid State Chem.*, **10**, 183 (1974).

25. J.A.M.Van Roosmalen, E.H.P.Cordfunke, R.B.Helmholdt, H.W.Zandbergen, *J. Sol. St. Chem.*, **110**, 100 (1974).

26. J.Toepfer, J.B.Goodenough, *Chem. Mater.*, **9**, 1467 (1997).

27. R.Gross, L.Alff, B.Buchner et al., *J. Magn. Magn. Mater.*, **211**, 150 (2000).

28. A.Gupta, G.Q.Gong, G.Xiao et al., *Phys. Rev. B*, **54**, 15629 (1996).

29. H.Y.Hwang, S.-W.Cheong, N.P.Ong, B.Batlogg, *Phys. Rev. Lett.*, **77**, 2041 (1996).

30. A.I.Tovstolytkin, A.N.Pogorily, S.M.Kovtun, *Low Temp. Phys.*, **25**, 962 (1999).

31. A.Anane, C.Dupas, K.Le Dang et al., *J. Phys: Condens. Matter*, **7**, 7015 (1995).

32. B.Dabrovski, K.Rogacki, X.Xiong et al., *Phys. Rev. B*, **58**, 2716 (1998).

33. M.M.Savosta, P.Novak, Z.Jirak et al., *Phys. Rev. Lett.*, **79**, 4278 (1997).

34. G.Papavassiliou, M.Fardis, M.Belesi et al., *Phys. Rev. Lett.*, **84**, 761 (2000).

35. M.M.Savosta, E.E.Solovyov, *Pis'ma Z.Eksp.Teor. Fiz.*, **70**, 522 (1999).

36. M.M.Savosta, A.S.Karnachev, S.Krupicka et al., *Phys. Rev.*, **B62**, 545 (2000).

37. Z.Bukovski, B.Dabrovski, J.Mais et al., *J. Appl. Phys.*, **87**, 5031 (2000).

Вплив дефектності кристалічної структури на магнітний стан легованих натрієм манганітів лантану

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Досліджено структурні, електричні, магніторезистивні та резонансні властивості зразків $La_{1-x}Na_xMnO_{3+\gamma}$, синтезованих методом твердофазних реакцій. Показано, що валентний стан марганцю практично не змінюється при зміні x від 0,08 до 0,16: зниження позитивного заряду в підгратці лантану при збільшенні вмісту натрію відбувається за рахунок формування вакансій у катіонних, або одночасно у катіонних і аніонній підгратках. Виявлено, що, крім магнітно впорядкованих фаз, всі зразки містять магнітно невпорядковану слабопровідну фазу навіть при низьких температурах (77 К), причому її кількість більша у зразках із меншим значенням x. Температура Кюрі (T_C) у системі $La_{1-x}Na_xMnO_{3+\gamma}$ монотонно зростає при зміні x від 0,08 до 0,16. Встановлено кореляцію між величинами збільшення T_C і зменшення кількості вакансій у підгратці марганцю. Показано, що при зміні x характер зміни параметрів елементарної комірки (зменшення об'єму комірки і кута ромбоедричної деформації) також спрямований на підсилення подвійного обміну і підвищення T_C. Магнітоопір (МО), виміряний при кімнатній температурі в полі 15 кЕ, має максимум (20 %) у зразках з $x = 0,12$. Для зразків цього складу залежність МО(H) близька до лінійної, що є перспективним для використання таких матеріалів у пристроях для вимірювання магнітного поля.