Antiferromagnet-ferromagnet and structural phase transitions in $La_{0.88}MnO_x$ manganites

I. O. Troyanchuk* and V. A. Khomchenko

Institute of Solid State and Semiconductor Physics, National Academy of Sciences, P. Brovka str. 17, 220072 Minsk, Belarus

M. Tovar

Hahn-Meitner-Institute (BENSC), Glienicker Str. 100, D-14109 Berlin, Germany

H. Szymczak

Institute of Physics, Polish Academy of Sciences, Lotnikov str. 32/46, 02-668 Warsaw, Poland

K. Bärner

IY. Physikalisches Institut der Universität Göttingen, Bunsenstrasse 13-15, D37073 Göttingen, Germany (Received 10 June 2003; revised manuscript received 15 October 2003; published 27 February 2004)

The crystal and magnetic structure as well as elastic, magnetic, and electrotransport properties of $La_{0.88}MnO_x$ ($2.82 \le x \le 2.96$) manganites have been investigated as a function of oxygen content by x-ray, neutron diffraction, Young's modulus, magnetization, and resistivity measurements. The crystal structure of the compounds has been found to be orthorhombic at x < 2.91 and monoclinic at $x \ge 2.91$. The gradual transition from an orbitally ordered state to an orbitally disordered one is observed with increasing temperature or oxygen content. The magnetic properties of the samples have been found to correlate with the type of orbital state. The dynamic orbital correlations favor ferromagnetic state, while A-type antiferromagnetic state is typical for the static Jahn-Teller distortions. The orthorhombic compounds have been found to exhibit a semiconducting behavior, and show a second-order transition into paramagnetic state. The metallic conductivity appears starting from the x = 2.92 monoclinic compound and, simultaneously, a first-order paramagnet-ferromagnet magnetic phase transition is observed. The properties are discussed in the framework of structurally driven phase separation model.

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I. INTRODUCTION

Mixed-valence manganites with a perovskite structure are the model objects for the physics of strongly correlated electronic systems. The interest in the study of manganites is due to a variety of phase states and transitions and intrinsic correlation of the crystal structure, magnetic, and transport properties. The discovery of the colossal magnetoresistance (CMR) effect in lanthanum based hole-doped manganites¹ has renewed the interest in the La-Mn-O system which, in fact, has been known for a long time.^{2,3}

The parent compound LaMnO₃ is an orbitally ordered antiferromagnetic insulator. The antiferrodistortive ordering of the d_{z^2} orbitals is established due to the cooperative Jahn-Teller effect breaking the degeneracy of the electronic configuration of the Mn^{3+} ions $(t_{2g}^3 e_g^1)$. This type of orbital ordering, which removes a first-order phase transition above $T_{JT} = 750$ K,^{4,5} is responsible for the A-type antiferromagnetic structure which is stable below $T_N = 140$ K.³ Hole doping (i.e., the introduction of Mn^{4+} ions), which can be induced by a heterovalent substitution in the A or B sublattice of the ABO₃ perovskite or by oxidation of stoichiometric LaMnO₃, leads to striking changes in the crystal structure, magnetic, and electrotransport properties. At present, the properties of $La_{1-x}A_xMnO_3$ ($A = Ca^{2+}, Sr^{2+}$) and LaMnO_{3+ δ} systems are the most well studied. Under hole doping, the crystal structure of $La_{1-x}Sr_xMnO_3$ as well as LaMnO_{3+ δ} manganites undergoes a number of concentration transitions from orbitally ordered orthorhombic to orbitally disordered orthorhombic and then to a rhombohedral type of unit cell distortion.^{6,7} In contrast, for a $La_{1-x}Ca_xMnO_3$ system, the concentration transition to rhombohedral phase is not observed.⁸ The x-ray and neutron diffraction data indicate that a nonuniform crystal structure can exist in rather large concentration and temperature ranges. For instance, the presence of local Jahn-Teller distortions in $La_{1-x}Sr_xMnO_3$ manganites has been observed even for the metallic compound x = 0.35.⁹

For a small doping concentration, several magnetic phases have been observed at low temperatures. In $\text{La}_{1-x}A_x\text{MnO}_3$ $(A = \text{Ca}^{2+}, \text{Sr}^{2+})$ systems, transitions from an antiferromagnetic to a ferromagnetic insulating state and then to ferromagnetic metallic state take place at $x \sim 0.08$ and 0.16, respectively.^{6,10} Unlike cation-doped manganites, the nonstoichiometric LaMnO_{3+ δ} seems to be insulating at least up to $\delta = 0.15$.¹¹ For large values of δ , the ferromagnetic order is suppressed, and the low-temperature phase exhibits a spin glass behavior.¹²

The nature of the interplay between the crystal structure, magnetic, and transport properties of manganites is still a matter of discussion in spite of numerous investigations. Several models were proposed to explain a magnetic state evolution under hole doping as well as a metal-insulator transition at the Curie point. In the double-exchange model of Zener, simultaneous ferromagnetic and metallic transitions have been qualitatively explained by the fact that electrons tend to move between Mn^{3+} and Mn^{4+} ions having the same spin orientation, therefore electron delocalization favors the

ferromagnetic order.¹³ De Gennes developed the theory of double exchange and predicted that a concentration transition from an antiferromagnetic to a ferromagnetic state occurs via the formation of a canted homogeneous magnetic structure.¹⁴ More recently Millis *et al.* pointed out that double exchange alone cannot account for many of the experimental results.¹⁵ The authors showed that a Jahn-Teller-type electron-phonon coupling plays an important role in explanation of the colossal magnetoresistance effect and argued the possibility of lattice polaron formation above the temperature of ferromagnetic ordering.

Another mechanism of antiferromagnet-ferromagnet phase transitions in manganites was proposed by Nagaev.¹⁶ Taking into account that the energy of charge carriers in a magnetic semiconductor is minimal for a ferromagnetic state and free charge carriers tend to establish a parallel ordering of the magnetic moments, he predicted that the intermediate phase can be described as a nonhomogeneous magnetic state driven by an electronic phase segregation. In this scenario the ferromagnetic regions contain an excess of holes and are metallic. The antiferromagnetic matrix remains insulating. The transition to metallic conductivity, taking place with an increase of the doping level, occurs when ferromagnetic clusters percolate.

Goodenough *et al.* argued that the magnetic properties of manganites were determined by the type of orbital state.¹⁷ According to the rules for 180° superexchange, if the electronic configuration correlates with vibrational modes, $Mn^{3+}-O^{2-}-Mn^{3+}$ interactions are antiferromagnetic in case of the static Jahn-Teller effect and ferromagnetic when the Jahn-Teller effect is dynamic. Thus, antiferromagnet-ferromagnet phase transitions can occur going through a mixed state of phases with different orbital dynamics.

The recent magnetic phase diagrams of the $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Ca_xMnO_3$ systems were constructed assuming a homogeneous canted magnetic state in a low doping range.^{18,19} On the other hand, there are numerous experimental data which indicate the existence of phase separation in manganites. The results of nuclear magnetic resonance,^{20–24} neutron diffraction,^{24,25} muon spin relaxation,²⁶ x-ray absorption,²⁷ scanning tunneling spectroscopy,²⁸ and electron microscopy²⁹ experiments give evidence of magnetic and structural inhomogeneities, but the driving force of magnetic phase separation in manganites is still not fully clear. In order to contribute to the solution of this problem we have investigated the features of the antiferromagnet-ferromagnet phase transition in low-doped lanthanum-deficient manganites. Specifically, we carried out a study of structural, magnetic, and transport properties of the La_{0.88}MnO_x system as a function of oxygen content.

The choice of the research object was made due to the following considerations. The lanthanum-deficient compounds show all the interesting properties which are peculiar to the low-doped manganites.^{30–32} However, a systematic study of cation-deficient manganites has not been carried out yet. According to our investigation, a lanthanum deficiency y=0.88 is the largest to realize with single-phase perovskites. Hence, one can expect that the properties of La_{0.88}MnO_x solid solutions will be more pronounced in com-

parison with the properties of other lanthanum deficient series. Moreover, it is known that low-doped manganites are very sensitive to the oxygen stoichiometry. A thorough research of cation-doped $La_{1-x}A_xMnO_3$ manganites would be difficult due to the necessity of continuous control of both oxygen and A-cation contents. In the $La_{0.88}MnO_x$ system, the oxygen concentration is the single varying parameter. Besides, all compositions of $La_{0.88}MnO_x$ series were made from the same parent sample which increases the repeatability and the reliability of the results obtained.

II. EXPERIMENT

The polycrystalline sample $La_{0.88}MnO_x$ was prepared by a solid-state reaction method using high-purity La₂O₃ and Mn_2O_3 reagents. To remove absorbed water, a prefiring of La₂O₃ (1000 °C, 1 h) was carried out. After that, the compacted mixture of reagents taken in stoichiometric cation ratio was annealed at 950 °C for 2 h. Obtained product was ground, pressed into pellets, annealed at T = 1300 °C in air for 6 h and then cooled at a rate of 30 °C/h down to room temperature. The oxygen content of the resulting material has been determined using thermogravimetric analysis, i.e., decomposition of the sample into simple oxides La₂O₃ and MnO in a reducing H_2/N_2 flow. True chemical formula of the obtained compound was La_{0.88}MnO_{2.96} with an estimated error of ± 0.01 oxygen per formula. Reduction of the samples was carried out in evacuated quartz ampoules at T = 1050 $^{\circ}$ C for 24 h. All the samples were quenched. Metallic tantalum was used as reducing agent. The reduction can be described by the following equation:

$La_{0.88}MnO_{2.96} + (2 \delta/5)Ta \rightarrow La_{0.88}MnO_{2.96-\delta} + (\delta/5)Ta_2O_5.$

The oxygen loss has been checked by the weighing of the samples before and after reduction. To verify the correctness of the determination of the oxygen content in the reduced compounds a thermogravimetric analysis was performed for x = 2.93, 2.89, 2.85, and 2.82 samples. In all cases, results showed good agreement with expected values of the oxygen content.

The unit cell parameters as well as the phase purity of the samples were checked by x-ray analysis using a DRON-3 diffractometer with CrK_{α} radiation. The refinement of the unit cell parameters has been carried out using the FULLPROF program. The elastic properties were studied by a resonance method in the sound frequency range using cylindrical samples with a diameter of 6 mm and a length of 60 mm. The differential thermal analysis (DTA) was performed at heating (cooling) rates of 10 °C/min. The temperature dependence of the magnetization was registered using a commercial vibrating sample magnetometer OI-3001, warming from 4 to 300 K in a field of 100 Oe after a field cooling (FC) or zero field cooling (ZFC) procedure. The field dependence of magnetization was measured in the temperature range from 4 to 300 K in fields up to 15 kOe. The study of electrotransport properties was performed using the standard four-probe method using ultrasonically deposited indium contacts. The resistivity data were collected in the temperature range from 80 to 400 K either in the absence of a mag-



FIG. 1. Room-temperature lattice parameters of the $La_{0.88}MnO_x$ samples as a function of the oxygen content.

netic field $[\rho(H=0)]$ or in the field of 9 kOe $[\rho(H)]$. The magnetoresistance Mr has been calculated according to the relation

$$Mr = \{ [\rho(H) - \rho(H=0)] / \rho(H) \} 100\%$$

Neutron diffraction measurements for the $La_{0.88}MnO_{2.84}$ and $La_{0.88}MnO_{2.87}$ samples were performed in the Berlin Neutron Scattering Center using the E9 neutron powder diffractometer (FIREPOD) with a wavelength of neutrons λ = 1.7974 Å. A sapphire single-crystal filter of total thickness of 110 mm in the primary beam was used to reduce the number of epithermal neutrons. In order to increase the neutron flux at the sample a vertically focusing Riso-design Ge monochromator was used. The evolution of the neutron diffraction patterns was followed in the temperature range 2-530 K. The data have been analyzed with the Rietveld method using the FULLPROF program.

III. RESULTS

Crystal structure and elastic properties. Single-phase compounds of $La_{0.88}MnO_x$ manganites were obtained in the oxygen concentration range $2.82 \le x \le 2.96$ which corresponds to the average valence of manganese ions from 3 to 3.28. The reduction below the value of 2.82 leads to decomposition of the samples into La_2O_3 and MnO oxides. This means that $La_{0.88}MnO_x$ perovskite structure cannot accommodate appreciable numbers of Mn^{2+} ions.

According to x-ray diffraction data the La_{0.88}MnO_x (2.82 $\leq x \leq$ 2.86) samples are characterized by so-called *O*'orthorhombic type of unit cell distortion $(b/\sqrt{2} < c < a)$, space group *Pnma* (Fig. 1). The unit cell values of the most reduced La_{0.88}MnO_{2.82} compound have been found to be very close to those for LaMnO₃ stoichiometric composition.⁴ The unit cell volume decreases as the oxygen content increases, and the transition to the *O*-orthorhombic crystal structure $(b/\sqrt{2} \approx a < c)$ occurs starting from x = 2.87 (Fig. 1). It is worth to be noted that according to Goodenough



FIG. 2. Temperature dependence of a square of resonance frequency for selected samples. Filled and open symbols are used for measurements of heating and on cooling, respectively.

et al., the *O*'-orthorhombic distortions in manganites are due to an orbital ordering while *O*-orthorhombic structure corresponds to the orbitally disordered state.¹⁷ It is obvious that the transition to an orbitally disordered state as oxygen concentration increases is the result of the appearance of a sufficient number of Mn⁴⁺ ions which remove Jahn-Teller's cooperative static effect. Unlike La_{1-x}A_xMnO₃ ($A = Sr^{2+}$, Ba²⁺, Pb²⁺) and LaMnO_{3+ δ} manganites, which exhibit concentration and temperature-induced transitions to rhombohedral unit cell symmetry,^{6,11} the compounds La_{0.88}MnO_x (2.91 $\leq x \leq$ 2.96) go over to monoclinic symmetry (space group *I2/a*) (Fig. 1).

The temperature dependence of Young's modulus for samples with a different oxygen content (square of resonance frequency is proportional to Young's modulus) are presented in Fig. 2. The most reduced $La_{0.88}MnO_{2.82}$ sample shows a well pronounced structural phase transition around 650 K [Fig. 2(a)]. A large temperature hysteresis and strong damping are observed in the vicinity of 650 K. As the oxygen content increases the temperature of the phase transition lowers gradually and the transition becomes broader [Figs. 2(b)–2(d)]. Besides, a sharp increase of Young's modulus indicating an appearance of another structural transition is observed for the x=2.84 and 2.85 compounds around 630 and 530 K, respectively [Figs. 2(c) and 2(d)]. The hysteresis observed between heating and cooling runs over a wide range of tem-

T (K)	Cell (Å)	Atoms	x	у	Z	R factors (%)
300	a = 5.6275(1)	La 4 <i>c</i>	0.0353(8)	0.2500	0.9944(1)	$R_{p} = 6.91$
Pnma	b = 7.7515(9)	Mn 4b	0.0000	0.0000	0.5000	$R_{wp}^{r} = 9.22$
	c = 5.5534(6)	O1 4 <i>c</i>	0.4938(7)	0.2500	0.0677(2)	$R_B = 8.51$
	$\alpha = \beta = \gamma = 90^{\circ}$	O2 8 <i>d</i>	0.2069(3)	0.5350(9)	0.2285(5)	$\chi^2 = 4.94$
530	a = 5.5457(6)	La 4 <i>c</i>	0.0204(4)	0.2500	1.0062(1)	$R_{p} = 6.48$
Pnma	b = 7.8563(7)	Mn 4b	0.0000	0.0000	0.5000	$R_{wp}^{P} = 8.81$
O-phase:	c = 5.5663(6)	O1 4 <i>c</i>	0.4925(8)	0.2500	0.0705(8)	$R_{B} = 8.80$
56%	$\alpha = \beta = \gamma = 90^{\circ}$	O2 8 <i>d</i>	0.2250(7)	0.5337(2)	0.2299(7)	$\chi^2 = 4.23$
530	a = 5.6139(9)	La 4 <i>c</i>	0.0365(1)	0.2500	0.9960(8)	$R_{p} = 6.48$
Pnma	b = 7.7737(6)	Mn 4b	0.0000	0.0000	0.5000	$R_{wp}^{P} = 8.81$
O'-phase:	c = 5.5531(1)	O1 4 <i>c</i>	0.4945(9)	0.2500	0.0681(3)	$R_{B} = 8.88$
44%	$\alpha = \beta = \gamma = 90^{\circ}$	O2 8 <i>d</i>	0.2047(8)	0.5372(8)	0.2258(1)	$\chi^2 = 4.23$

TABLE I.	Structural	data	of	La _{0.88} MnO _{2.84}	at	300	and	530	Κ.
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perature is evidence of a gradual structural transformation. For the x = 2.86 compound, the temperature dependence of Young's modulus exhibits a broad minimum slightly above room temperature. The temperature of the second anomaly

decreases down to 500 K. In contrast to the $2.82 \le x \le 2.86$ samples, no minimum of Young's modulus temperature dependence is observed for the La_{0.88}MnO_{2.87} compound above room temperature. However, as in the case of $2.84 \le x$

$T(\mathbf{K})$	Cell (Å)	Atoms	x	У	Z	R factors (%)
2	a = 5.5170(1)	La 4 <i>c</i>	0.0220(2)	0.2500	0.9944(4)	$R_{p} = 4.9$
Pnma	b = 7.7666(9)	Mn 4b	0.0000	0.0000	0.5000	$R_{wp} = 6.7$
	c = 5.5228(7)	O1 4 <i>c</i>	0.4938(5)	0.2500	0.0699(2)	$R_B = 3.64$
	$\alpha = \beta = \gamma = 90^{\circ}$	O2 8 <i>d</i>	0.2199(6)	0.5348(8)	0.2286(7)	$\chi^2 = 1.68$
100	a = 5.5227(1)	La 4 <i>c</i>	0.0228(5)	0.2500	0.9956(1)	$R_p = 5.03$
Pnma	b = 7.7600(5)	Mn 4b	0.0000	0.0000	0.5000	$R_{wp} = 6.75$
	c = 5.5241(1)	O1 4 <i>c</i>	0.4933(8)	0.2500	0.0691(5)	$R_B = 3.83$
	$\alpha = \beta = \gamma = 90^{\circ}$	O2 8 <i>d</i>	0.2186(7)	0.5349(7)	0.2297(5)	$\chi^2 = 1.71$
200	a = 5.5432(1)	La 4 <i>c</i>	0.0262(2)	0.2500	0.9953(4)	$R_p = 6.26$
Pnma	b = 7.7543(1)	Mn 4b	0.0000	0.0000	0.5000	$R_{wp} = 8.08$
	c = 5.5337(1)	O1 4 <i>c</i>	0.4955(2)	0.2500	0.0683(7)	$R_B = 5.87$
	$\alpha = \beta = \gamma = 90^{0}$	O2 8 <i>d</i>	0.2181(3)	0.5336(2)	0.2321(8)	$\chi^2 = 3.78$
300	a = 5.5227(3)	La 4 <i>c</i>	0.0209(3)	0.2500	0.9955(3)	$R_{p} = 4.54$
Pnma	b = 7.7836(8)	Mn 4b	0.0000	0.0000	0.5000	$R_{wp} = 5.8$
	c = 5.5353(3)	O1 4 <i>c</i>	0.4944(7)	0.2500	0.0664(2)	$R_B = 4.79$
	$\alpha = \beta = \gamma = 90^{\circ}$	O2 8 <i>d</i>	0.2215(8)	0.5335(1)	0.2290(9)	$\chi^2 = 1.99$
400	a = 5.5094(5)	La 4 <i>c</i>	0.0178(4)	0.2500	0.9964(6)	$R_{p} = 4.22$
Pnma	b = 7.7991(2)	Mn 4b	0.0000	0.0000	0.5000	$R_{wp} = 5.47$
	c = 5.5400(6)	O1 4 <i>c</i>	0.4946(6)	0.2500	0.0656(3)	$R_B = 4.87$
	$\alpha = \beta = \gamma = 90^0$	O2 8 <i>d</i>	0.2261(5)	0.5337(1)	0.2293(8)	$\chi^2 = 1.78$
500	a = 7.8220(1)	La 4 <i>e</i>	0.2500	0.5040(8)	0.0000	$R_{p} = 4.91$
I2/a	b = 5.5577(3)	Mn 4 <i>a</i>	0.0000	0.0000	0.0000	$R_{wp} = 6.29$
	c = 5.5039(5)	O1 4 <i>e</i>	0.2500	0.0559(9)	0.0000	$R_B = 5.79$
	$\alpha = \gamma = 90^{\circ}; \ \beta = 90.77(9)^{\circ}$	O2 8 <i>f</i>	-0.0223(1)	0.2167(1)	0.2829(8)	$\chi^2 = 2.35$

TABLE II. Structural data of La_{0.88}MnO_{2.87} at different temperatures.

Compound	<i>T</i> (K)	Mn-O1(m)	Mn-O2(s)	Mn-O2(l)	Mn-O1-Mn	Mn-O2-Mn
x = 2.84	2	1.971	1.928	2.103	157.45	158.55
	300	1.974	1.924	2.099	157.94	158.59
	450	1.989	1.950	2.048	158.91	159.63
	530 (O-phase)	2.003	1.972	2.008	157.26	161.58
	530 (O'-phase)	1.980	1.930	2.098	157.90	157.11
x = 2.87	2	1.980	1.947	2.014	157.42	160.40
	100	1.978	1.939	2.024	157.62	160.35
	200	1.975	1.930	2.040	157.87	161.12
	300	1.981	1.953	2.010	158.53	161.16
	400	1.984	1.968	1.989	158.81	161.71
	500	1.980	1.978	1.983	161.92	161.77

TABLE III. Selected interatomic distances (in Å) and angles (in degrees) for x = 2.84 and 2.87 compounds at different temperatures.

 \leq 2.86 samples, significant increase of Young's modulus value is observed above 440 K [Fig. 2(e)]. The monoclinic compounds do not show any sharp changes in the behavior of Young's modulus and exhibit a gradual increase of the resonance frequency in the whole accessible temperature range [Fig. 2(f)]. Usually a resonance frequency decreases with a temperature. This anomalous increase of Young's modulus reflects an instability of the crystal structure which can be related to dynamic Jahn-Teller effect.

In order to refine the structural features of O'- and O-orthorhombic samples and to reveal origin of the anomalies observed on the temperature dependence of Young's modulus value we performed neutron diffraction study of La_{0.88}MnO_{2.84} and La_{0.88}MnO_{2.87} compounds. Diffraction patterns were collected at temperatures of 2, 300, 450, and 530 K for x = 2.84, and at 2, 100, 200, 300, 400, and 500 K for x = 2.87. The structural data as well as selected interatomic distances and angles obtained in the Rietveld refinement are presented in Tables I, II, and III. The crystal structure refinement of La_{0.88}MnO_{2.84} sample at $2 \le T \le 450$ K was successfully carried out in space group Pnma using onephase structural model (Table I). The MnO₆ octahedrons were found to be rather strongly distorted. The bond lengths vary in the range from 1.924 to 2.099 Å at 300 K (Table III). Such distortions are typical for the static ordering of d_{z^2} orbitals. The distortions of MnO₆ octahedrons get smaller with increasing temperature to 450 K. At 530 K, the refinement performed in one-phase model did not allow one to get a satisfactory agreement between the observed and calculated diffraction patterns. In the resulting fit, only the χ^2 =9.64 value [with unit cell a=5.5627(9) Å, b =7.8447(5) Å, and c=5.5474(4) Å] was achieved. The agreement factors were significantly improved (Table I) when an additional orthorhombic phase was introduced (Fig. 3). According to the obtained results the crystal structure of the La_{0.88}MnO_{2.84} sample at T = 530 K is characterized by coexistence of two orthorhombic phases which differ in oxygen octahedrons distortions. While MnO₆ octahedrons in the O' phase are strongly distorted indicating the static d_{z^2} orbital ordering, these octahedrons are almost regular for disordered O phase (Table III).

The crystal structure of La_{0.88}MnO_{2.87} sample at $T \leq 400$ K is characterized by an orthorhombic type of unit cell symmetry. The space group *Pnma* was used for the refinement. At 500 K, the best fitting was obtained for monoclinic space group *I2/a*. The observed and calculated diffraction patterns of the La_{0.88}MnO_{2.87} sample below and above the temperature of the orthorhombic-monoclinic phase transition are shown in Fig. 4. The temperature dependence of the Mn-O distances as well as the local modes Q_2 and Q_3 which characterize the Jahn-Teller distortion are presented in Fig. 5. One can see that the decrease of a temperature down to 200 K leads to an increase of the distortion of the MnO₆ octahedron. This fact indicates the stabilization of the orbitally ordered component. The situation is changed with a further decrease of a temperature.



FIG. 3. Results of the Rietveld refinement of the NPD pattern of $La_{0.88}MnO_{2.84}$ obtained at 530 K assuming a two-phase structural model. The inset shows enlarged part of the Rietveld refinement for two-phase (a) and one-phase (b) structural models. The measured data (solid circles) are shown together with the resulting fit (open circles) and their difference plot (continuous line). The ticks show the predicted 2θ positions for the Bragg peaks of the orbitally ordered phase (lower row).



FIG. 4. Observed and calculated powder diffraction patterns of $La_{0.88}MnO_{2.87}$ at T=300 and 500 K (inset).

tion appears starting from the pattern acquired at T = 100 K and, simultaneously, the distortions of the MnO₆ octahedrons get smaller (Fig. 5). In spite of the worsening of the agreement factors which is observed with decreasing temperature from 400 to 200 K for the refinement performed in the one-phase structural model (Table II), the introduction of a second orthorhombic phase does not allow one to improve the agreement between the observed and calculated diffraction patterns.

Thus, neutron diffraction data indicate that the minimum



FIG. 5. MnO₆ bond lengths (upper panel) and Q_2 and Q_3 distortions (lower panel) as a function of temperature for La_{0.88}MnO_{2.87} sample. Q_2 and Q_3 are defined as: $Q_2=2(l-s)/\sqrt{2}$ and $Q_3=2(2m-l-s)/\sqrt{6}$ where *s*, *m*, and *l* are short, medium, and long Mn-O distances.



FIG. 6. Temperature dependence of resistivity for x = 2.89 and 2.90 samples measured on heating (filled circles) and on cooling (open circles). The range of temperature hysteresis is marked by the arrows.

temperature dependence of the Young's modulus value corresponds to the onset of cooperative orbital ordering removal. A two-phase structural state is realized in the temperature range where hysteresis between heating and cooling runs is observed. A sharp increase of the Young's modulus value is associated with the transition from orthorhombic to monoclinic type of unit cell distortion.

The results of both differential thermal analysis and resistivity measurements correlate with the data of study of crystal structure and elastic properties. The DTA shows a thermal effect at temperatures where structural phase transitions have been observed. Resistivity measurements carried out for $2.87 \le x \le 2.90$ samples above room temperature reveal a hysteresis between the heating and cooling runs in the same temperature range where elastic and thermal anomalies occur indicating the orthorhombic-monoclinic phase transition (Fig. 6).

Magnetic structure. The neutron powder diffraction patterns acquired at T=2 K were used for the magnetic structure refinement of x = 2.84 and 2.87 samples. A comparison of diffraction patterns obtained for the La_{0.88}MnO_{2.84} compound at 2 and 300 K is shown in Fig. 7. One can see that a decrease of temperature results in the appearance of a (010)reflection forbidden by the space group Pnma. The permitted (111) reflection increases in intensity. This can be attributed to the long-range layered type antiferromagnetic order with ferromagnetic coupling of the Mn ions within the plane (010)and antiferromagnetic interactions between these planes. At the same time, the additional intensity of the (101), (200), (121), and (002) lines denotes the existence of ferromagnetic component. No additional intensity is observed to the (020)line indicating the orientation of ferromagnetic component along the y axis.

The simultaneous appearance of antiferromagnetic and ferromagnetic contributions can be explained as due to the



FIG. 7. Observed neutron diffraction patterns of $La_{0.88}MnO_{2.84}$ at T=2 K (top) and T=300 K (bottom).

existence of a homogeneous canted magnetic structure or the coexistence of antiferromagnetic and ferromagnetic phases. The magnetic structure refinement was carried out in both models. In the model of canted magnetic structure the refinement gives a value of $1.48\mu_B$ for the ferromagnetic component and of $2.24\mu_B$ for the antiferromagnetic one. The best fitting (R_M =9.5%, χ^2 =4.45) is observed for the magnetic mode $A_x F_y$.

The refinement performed in the model of coexistence of antiferromagnetic and ferromagnetic phases leads to the following magnetic structure: the La_{0.88}MnO_{2.84} sample consists of 63% of an A-type antiferromagnetic phase and 37% of a ferromagnetic one. The magnetic moments of the Mn ions are $3.8\mu_B$ and $3.7\mu_B$ for antiferromagnetic and ferromagnetic phases, respectively. The magnetic moments are ordered along the *x* axis for the antiferromagnetic phase and along the *y* axis for the ferromagnetic one. Discrepancy factors obtained in such magnetic structure refinement are $R_M(AF) = 9.2\%$, $R_M(F) = 6.2\%$, and $\chi^2 = 4.57$.

No long-range antiferromagnetic contribution is observed for the La_{0.88}MnO_{2.87} sample. The refinement of the neutron diffraction data at 2 K shows that magnetic structure of this sample corresponds to the magnetic mode F_y , with R_M = 5.1%. The magnetic moment for the Mn ions is $3.3\mu_B$. The value of the magnetic moment is smaller than that expected for the given ratio of Mn³⁺ and Mn⁴⁺ cations ($3.9\mu_B$). Such a result can be attributed to the existence of a second short-range ordered magnetic phase.

Magnetic and electrotransport properties. The magnetic properties reveal a correlation between the magnetic and orbital states. The magnetization vs field curves for the La_{0.88}MnO_x system at T=5 K are presented in Fig. 8. The La_{0.88}MnO_{2.82} sample (the lowest oxygen content) has a very small magnetic moment (about $0.15\mu_B$ per manganese ion in H=15 kOe) and a very large coercive field—more than 15 kOe. Magnetization vs temperature curves for this sample are shown in Fig. 9(a). A sharp transition to the paramagnetic



FIG. 8. Magnetization vs field for the $La_{0.88}MnO_x$ (2.82 $\leq x \leq$ 2.94) compounds at T=5 K. The inset shows the magnetization H=15 kOe and a coercive field as a function of the oxygen content.

state is observed at a temperature of 140 K. The external magnetic field does practically not shift the temperature of the phase transition. The increase of the oxygen content in the concentration range corresponding to O'-orthorhombic compositions results in a lowering of the Neel point and an increase of the magnetization (Fig. 8). For example, the magnetization of the x = 2.84 compound in H = 15 kOe is $0.76\mu_B/Mn$, the coercive field is 4.2 kOe and the temperature of the magnetic ordering is 125 K. The transition to a paramagnetic state, remains well pronounced. The external magnetic field weakly affects the temperature of the transition to a paramagnetic state, similar to the x = 2.82 composition. This tendency of the magnetic ordering temperature remains up to the La_{0.88}MnO_{2.85} compound [Fig. 9(b)]. One can see that field dependences of the magnetization obtained for the $2.82 \le x \le 2.85$ samples in the field of 15 kOe are far from saturation (Fig. 8). This indicates the large magnetic anisotropy of the samples. The large thermomagnetic irreversibility and coercive field [Figs. 8, 9(a), and 9(b)] confirm that the low-doped orthorhombic La_{0.88}MnO_x samples are strongly anisotropic materials.³³

The magnetic state changes with a further increase of the oxygen concentration in the range of the orthorhombically distorted samples. Starting from the x=2.86 compound, the temperature of magnetic ordering increases from 150 K (x = 2.86) to 202 K (x=2.90). Moreover, a considerable rise of magnetization up to $3.47\mu_B/Mn$ for x=2.90 is observed. Besides, magnetic anisotropy and coercive field decrease significantly [Figs. 8, 9(c), and 9(d)].

Maximal magnetization values (up to $3.55\mu_B/Mn$ in H = 15 kOe) close to that expected for a collinear ferromagnet have been obtained for monoclinically distorted compounds (Fig. 8). FC and ZFC curves indicate that monoclinic samples undergo a paramagnet-ferromagnet transition at temperatures from 212 K for La_{0.88}MnO_{2.91} to 255 K for La_{0.88}MnO_{2.96} [Figs. 9(e) and 9(f)]. In contrast to the *O*'-orthorhombic samples an external field shifts the transi-



FIG. 9. Temperature dependence of the magnetization of the $La_{0.88}MnO_x$ compounds, measured at 100 Oe.

tion rather far to higher temperatures. Note, that the T_C values for La_{0.88}MnO_x compounds are higher than that observed for the LaMnO_{3+ δ} samples corresponding to the same Mn⁴⁺/Mn³⁺ ratios.⁷

It is well known that the transition from the paramagnetic to the ferromagnetic state in $La_{1-x}A_xMnO_3$ manganites can be or first or second-order.³⁴ In order to define the features of a paramagnet-ferromagnet phase transition in $La_{0.88}$ -MnO_x system we used the criterion proposed by Banerjee.³⁵ This criterion allows one to distinguish first-order magnetic phase transitions from second-order ones by purely magnetic methods. It depends on the observation of the slope of isotherms of H/M versus M^2 in the vicinity of T_C . Here M is the experimentally observed magnetization and H is the magnetic field. A positive or negative slope of $H/M(M^2)$ curve indicates a second-order or first-order phase transition, respectively. Before each measurement of a magnetization isotherm, samples were heated above T_C and then cooled down to the measuring temperature under zero field. The results of the measurements for selected samples are shown in Fig. 10. According to the obtained data, the paramagnet-ferromagnet phase transition is second-order one up to the monoclinic compound x = 2.91. Starting from the x = 2.92 sample, the transition from paramagnetic to ferromagnetic states becomes first order.

The change from a first- to a second-order magnetic phase transition was found to correlate with electrotransport properties of La_{0.88}MnO_x manganites. The temperature dependence of the resistivity both under zero field and in a field of 9 kOe as well as the magnetoresistance data are shown in Fig. 11. In the concentration range $2.92 \le x \le 2.96$, the samples are characterized by metallic conductivity below T_C [Figs. 11(a)–11(c)]. A pronounced magnetoresistance peak is observed slightly below the temperature of the metal-insulator transition. The largest value of the magnetoresistance, up to the 96% at T=242 K, was found for the x = 2.94 compound. Starting from monoclinic x=2.91 compound, the semi-conducting type of conductivity is observed [Figs. 11(d) and 11(e)]. The magnetoresistance peak at the

Curie point gradually decreases with the decrease of the oxygen content. While the coincidence of first-order magnetic phase transition and the appearance of metallic conductivity in the samples is obvious here, it is not a common property of CMR manganites. For instance, $La_{0.8}Sr_{0.2}MnO_3$ shows a metal-insulator transition near T_C and a second-order magnetic phase transition.³⁶



FIG. 10. H/M vs M^2 plots of isotherms in the vicinity of the Curie point of x = 2.89 and 2.95 compounds.

0.03

100

100

ρ (Ohm cm)

-90

15 10

250

MR (%)

ρ (Ohm cm)

x=2.95

¹⁵⁰ 200 T (K)

=2.91

0.09

0.06

0.03

10

100

ρ (Ohm cm)

(d) 100 150 200 250 T (K)



100 150 200 250

T (K)

-90 0.08

(b)[.]

MR (%)

250

150 200 T (K)

x=2.89

T (K)

FIG. 11. Temperature dependence of the resistivity and magnetoresistance for selected samples. Filled and open circles are used for measurements in zero field and an applied field of 9 kOe, respectively.

IV. DISCUSSION

100 150 200 250

Traditionally, the evolution of the magnetic properties of manganites under hole doping, namely, the concentration transition from antiferromagnetic to ferromagnetic state is explained by either the formation of a canted antiferromagnetic structure (double exchange model) (Ref. 14) or the appearance of ferromagnetic clusters which contain an excess of holes (electronic phase separation).¹⁶ However, the double exchange or electronic phase separation are capable of explaining the properties of $La_{0.88}MnO_x$ manganites only in the limited range of doping concentration where antiferromagnetic order is associated with insulating behavior ($x \le 2.85$) and ferromagnetism with metallic conductivity ($x \ge 2.92$). Neither the double exchange mechanism nor electronic phase separation can account for the existence of a ferromagnetic but insulating phase $2.86 \le x \le 2.91$. Recently, theoretical works have focused on investigations of the possibility of structurally driven magnetic phase separation in manganites.³⁷ The structural inhomogeneities in manganites seem to result from an intrinsic chemical inhomogeneity of solid solutions. Recent x-ray absorption fine structure measurement of the Sr and La K edges of the lightly doped $La_{1-r}Sr_rMnO_3$ series revealed a consistent deviation from a random distribution of Sr at the La/Sr sites for x < 0.3.³⁸ The local structural disorder on the cation sublattice is also observed to differ in the vicinity of the La-rich and Sr-rich clusters. The local clustering and structural disorder is shown to establish an intrinsic chemical and structural inhomogeneity on the nanometer scale, which may provide a mechanism for the nucleation of magnetic phase separation.³⁸

The experimental results obtained in the present work can be successfully explained in the framework of a structurally driven magnetic phase separation model. Tentative magnetic phase diagram of the La_{0.88}MnO_x ($2.82 \le x \le 2.96$) manganites is shown in Fig. 12. The most strongly reduced sample La_{0.88}MnO_{2.82} is antiferromagnet with a Neel temperature of 140 K. Its properties are found to be similar to the properties of stoichiometric LaMnO₃. Both compounds have very close unit cell parameters (Fig. 1), the same magnetization value (Fig. 8), and close temperatures of both magnetic and

orbital orderings [Figs. 9(a) and 2(a)]. The existence of orbital ordering in the *A*-type antiferromagnetic structure of La_{0.88}MnO_{2.82} is corroborated by neutron diffraction measurements.³⁹ With increasing oxygen content up to the x = 2.85 sample, the magnetic and orbital ordering temperatures lower while the magnetization increases slightly [Figs. 2(a)–2(d), 8, 9(a), and 9(b)]. Results of the neutron diffraction measurements carried out for the x = 2.84 sample con-



FIG. 12. Magnetic phase diagram of the La_{0.88}MnO_x ($2.82 \le x \le 2.96$) system. Orth-orthorhombic crystal structure, *M*-monoclinic crystal structure; PI, AFI, FI, and FM-paramagnetic insulating, antiferromagnetic insulating, ferromagnetic insulating, and ferromagnetic metallic states, respectively. Filled circles present the temperatures corresponding to the onset of magnetic ordering. Cross symbols indicate the temperatures of the most pronounced changes of the FC magnetization measured in 100 Oe (were determined as inflection points on the FC curve). Areas 1 and 2 correspond to the concentration regions where an antiferromagnetic or ferromagnetic phase predominates, respectively.

firm the appearance of a ferromagnetic component (Fig. 7). A further increase of the oxygen concentration leads to a significant enhancement of the ferromagnetic contribution (Fig. 8). The transition temperature to the paramagnetic state begins to increase and the transition becomes broader [Fig. 9(c)]. Neutron diffraction data obtained for the x = 2.87sample indicate that ferromagnetic coupling becomes predominant. No long-range antiferromagnetic order has been observed for this compound. At the same time, the refined magnetic moment is lower than that expected for the full spin arrangement. Besides, the large difference between ZFC and FC curves at low temperature [Fig. 9(d)] assumes the presence of an anisotropic magnetic coupling which differs from the isotropic ferromagnetic one. This can be attributed to existence of either short-range antiferromagnetic clusters or a spin-glass phase. However, no spin-glass behavior has been detected for the nominal La_{0.93}MnO₃ sample which is characterized by the same magnetic properties as La_{0.88}MnO_{2.87}.³² No pronounced thermomagnetic irreversibility indicating the anisotropic magnetic interactions is observed starting from the x = 2.92 sample [Fig. 9(f)]. The values of magnetization estimated for the monoclinic compounds in H=15 kOe are close to those expected for full spin alignment (Fig. 8). The ground state of all the orthorhombic compounds $2.82 \le x \le 2.90$ is insulating [Fig. 11(e)]. The appearance of metallic conductivity does not coincide with the transition to monoclinic phase [Fig. 11(d)]. Simultaneous first-order magnetic transition (Fig. 10) and metalinsulator transition at T_C [Figs. 11(a)–11(c)] are observed for $x \ge 2.92$ compounds.

It is necessary to note that a change from two-dimensional ferromagnetic interactions characteristic of LnMnO₃ to 3D ones may be induced not only by Mn⁴⁺ but also by diamagnetic Nb⁵⁺, Al³⁺, Sc³⁺ doping of parent LnMnO₃ (Ln lanthanide).^{40,41} The appearance of ferromagnetic order in spite of the absence of Mn⁴⁺ ions contradicts both double exchange and electronic phase separation scenarios. According to Goodenough et al.¹⁷ and Zhou et al.⁴² removal of static Jahn-Teller distortions should lead to an appearance of isotropic ferromagnetic interaction. In the cases, when one dopes the $LnMnO_3$ with non-Jahn-Teller ions such as Mn^{4+} (Nb⁵⁺, Sc³⁺, etc.) the e_g orbitals of all the Mn³⁺ sites surrounding the Mn⁴⁺ (Nb⁵⁺, Sc³⁺, etc.) ion tend to be directed toward the central ion forming orbital polaron.⁴³ According to Goodenough-Kanamori-Anderson rules, an important consequence of such a type of orbital ordering is ferromagnetic exchange interactions between Mn³⁺ and Mn^{4+} ions in this cluster. The diamagnetic doping (Nb⁵⁺, Sc³⁺, etc.) also favors ferromagnetism converting a 2D-type orbital ordering intrinsic to LnMnO₃ into a 3D clusterlike one with much more fast orbital dynamics. An interaction of ferromagnetic clusters may lead to long-range ferromagnetic order if Mn-O-Mn angle is enough large.

A strong correlation between the magnetic and structural properties of $La_{0.88}MnO_x$ (2.82 $\leq x \leq$ 2.96) manganites is observed. The hypothetical structural phase diagram of $La_{0.88}MnO_x$ (2.82 $\leq x \leq$ 2.96) constructed using x-ray, neuron diffraction, Young's modulus, resistivity, and DTA data is



FIG. 13. Hypothetical crystal structure phase diagram of the $La_{0.88}MnO_x$ system. *O'*, *O*, and *M* orbitally ordered orthorhombic, orbitally disordered orthorhombic, and monoclinic phases, respectively. Areas 1 and 2 correspond to the concentration regions where the static Jahn-Teller distortions or dynamic orbital correlations predominate, respectively. The dark area corresponds to the concentration and temperature range where a coexistence of orbitally ordered and orbitally disordered orthorhombic phases is corroborated by diffraction data coupled with DTA and elastic properties study.

shown in Fig. 13. For La_{0.88}MnO_{2.82}, the sharp drop of the Young's modulus value must be associated with the removal of cooperative orbital ordering; it is observed at approximately 650 K [Fig. 2(a)]. The DTA measurements revealed the release of latent heat in the range 650-730 K, indicating the coexistence of orbitally ordered and orbitally disordered phases up to the temperature of 730 K. Another thermal anomaly connected with the transition to the monoclinic phase is observed in the much narrow temperature range $915 \le T \le 960$ K. According to dilatometric investigations the temperature-induced structural transitions in manganites are martensite-type.44 With the increase of the oxygen content to x = 2.83, the temperatures of both orbital orderdisorder and orthorhombic-monoclinic phase transitions significantly decrease. The range of coexistence of O' and Ophases becomes broader, while the width of the anomaly associated with the temperature-induced orthorhombicmonoclinic transition remains practically constant. Starting from the x = 2.84 sample, the differential thermal analysis does not show any significant heat effect, which could be interpreted as a transition to a pure orbitally disordered state; however, the anomaly related to the transition from an orthorhombic to a monoclinic phase remains well pronounced. Neutron diffraction data coupled with Young's modulus measurements indicate the existence of predominantly static Jahn-Teller distortions at room temperature and two-phase character of the crystal structure above $T \sim 470$ K [Fig. 2(c) and Tables I and III]. Inhomogeneous structural states are observed up to 650 K [Fig. 2(c)]. Above this temperature the monoclinic phase is stabilized. A further increase of the oxygen concentration leads to the broadening and gradual disappearance of the anomaly which relates to the transition to the orbitally ordered state [Figs. 2(d) and 2(e)]. However, the weak hysteresis observed for the x = 2.87 sample below the temperature of monoclinic-orthorhombic phase transition can be attributed to the conservation of a minor amount of an orbitally ordered phase [Fig. 2(e)]. The neutron diffraction study performed for the La_{0.88}MnO_{2.87} compound indicates that the value of the orbitally ordered phase increases with decreasing temperature to 200 K (Fig. 5). However, even in the case of T = 200 K, where the worst agreement factors for one-phase structural model have been observed (Table II), the introduction of the second orthorhombic phase was unsuccessful. Apparently, even at 200 K, the orbitally ordered clusters are still too small and separate to distinguish the O' phase in the diffraction experiment. The temperature of orthorhombic-monoclinic phase transition gradually decreases as the oxygen content increases [Figs. 2(c)-2(e) and 6], and starting from the x=2.91 sample, the monoclinic phase is stabilized (Fig. 1). It is necessary to note that the x-ray and neutron diffraction experiments can reveal a two-phase structural state rather in the case of macroscopic structural phase separation. In the cases of local structural inhomogeneities or nanometer scale structural clusters, these experiments give only an average picture of a structural state. For instance, the atomic pair-density function of $La_{1-x}Sr_xMnO_3$ (x < 0.4) manganites obtained by pulsed neutron diffraction indicates that their local atomic structure significantly deviates from the average structure, and that the local Jahn-Teller distortion persists even when the crystallografic structure shows no Jahn-Teller distortion.⁹

Thus, the correlation between the orbital state and magnetic properties of the $La_{0.88}MnO_x$ manganites is prominent (Figs. 12 and 13). The static Jahn-Teller distortions are responsible for the *A*-type antiferromagnetic structure, while dynamic orbital correlations lead to ferromagnetism.

Summarizing, the evolution of magnetic and orbital states in the La_{0.88}MnO_x system is presented as follows. The increase of oxygen concentration above x = 2.82 value leads to an appearance of holes in the 3d states of Mn ions (i.e., Mn⁴⁺ ion appearance). Orbital ordering is removed nearby Mn⁴⁺ ions and the exchange interactions between Mn ions become ferromagnetic. The number of orbitally disordered ferromagnetic clusters increases with increasing oxygen content. This leads to a lowering of the Neel point [Figs. 9(a) and 9(b)] and an increase of the magnetization (Fig. 8). Simultaneously, the temperature of orbital disordering decreases [Figs. 2(a)-2(d)]. A significant decrease of the coercive field and an increase of magnetization are observed for the x = 2.86 compound (Fig. 8). This denotes a change of the predominant magnetic interaction. Indeed, the refinement of magnetic structure performed for the x = 2.87 sample reveals the long-range ferromagnetic order. At the same time, x-ray and neutron diffraction (Fig. 1, Table III) and elastic properties [Fig. 2(e)] indicate the removal of cooperative orbital ordering. The anisotropic contribution concluded from the temperature dependence of the ZFC and FC magnetization for the $x \le 2.91$ samples [Figs. 9(a)-9(e)] suggests a conservation of antiferromagnetic clusters up to concentration range of the monoclinically distorted compounds. The value of the spontaneous magnetization of the monoclinic samples $x \ge 2.92$ is consistent with a collinear ferromagnetic state (Fig. 8). One could infer that the enhancement of the covalent component of the Mn-O-Mn bond which would occur for orbitally disordered state leads to the crossing of the wide valence and the narrow 3d bands and, starting from the x=2.92 compound, the metallic conductivity appears (Fig. 11). The strong dependence of the ferromagnetic order on the external magnetic field results in the colossal magnetoresistance effect near the Curie temperature.

V. CONCLUSIONS

A detailed study of crystal structure, magnetic, and electrotransport properties of La_{0.88}MnO_x (2.82 $\leq x \leq$ 2.96) manganites was carried out. The most reduced La_{0.88}MnO_{2.82} sample which contains only Mn³⁺ ions was deduced an orbitally ordered antiferromagnet with $T_N = 140$ K. Its properties are very similar to those of the LaMnO₃ stoichiometric compound. The crystal structure of investigated samples was found to undergo a number of concentration- and temperature-induced transitions: from an orbitally ordered orthorhombic to an orbitally disordered orthorhombic and then to a monoclinic type of unit cell distortion. It was shown that the magnetic properties of the samples of $La_{0.88}MnO_{r}$ system strongly correlate with the type of their orbital state. Compounds with an antiferromagnetic component exhibit the features of cooperative orbital ordering, while the pure ferromagnetic samples, with T_{C} up to 255 K for x = 2.96, are orbitally disordered. The antiferromagnetferromagnet phase transition was described in the framework of a magnetic phase separation model, taking into account the key role of the structural inhomogeneities. It was found that the monoclinic samples $x \ge 2.92$ are metallic and show a first-order magnetic phase transition, while the $x \le 2.91$ compounds are characterized by a semiconducting behavior and exhibit a second-order transition to the paramagnetic state. From the analysis of the experimental data the magnetic and structural phase diagrams were constructed.

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^{*}Electronic address: troyan@ifttp.bas-net.by