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 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 [1]. More recently Millis et al. pointed out that double exchange alone cannot account for many of the experimental results [2]. They showed that a JT-type electron-phonon coupling should play an important role in explanation of the colossal magnetoresistance effect. Another mechanism of antiferromagnet-ferromagnet phase transitions in manganites was proposed by Nagaev [3]. He assumed 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. Goodenough et al. argued that the magnetic properties of manganites were determined by the type of orbital state [4]. 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 the case of the static JT effect and ferromagnetic when the JT 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$_x$MnO$_3$ and La$_{1-x}$Ca$_x$MnO$_3$ systems were constructed assuming a homogeneous canted magnetic state in a low doping range [5,6]. On the other hand, there are numerous experimental data which indicate the existence of phase separation in manganites. The results of nuclear magnetic resonance [7-11], neutron diffraction [11,12], muon spin relaxation [13], X-ray absorption [14], scanning tunneling spectroscopy [15], and electron microscopy [16] experiments give evidence of magnetic and structural inhomogeneities, but the driving force of antiferromagnet-ferromagnet transition as well as magnetic phase separation in lightly doped manganites is still not fully clear. We consider the features of orbital ordering occurring in low doping regime of the manganites. We will show that orbital ordering strongly affects magnetic properties of manganites.

1.1. Orbital ordering and magnetic structure of LnMnO$_3$ (Ln=lanthanide) and BiMnO$_3$

The parent compound LaMnO$_3$ of the hole-doped colossal magnetoresistance material La$_{1-x}$A$_x$MnO$_3$ (A=Ca, Sr, Ba) has attracted much interest from condensed matter scientists [17,18]. Stoichiometric LaMnO$_3$ in which Mn ions are formally Mn$^{3+}$, has an antiferromagnetic insulating ground state. Cooperative JT distortion removes the degeneracy of the $e_g$ orbitals in the $t_{2g}^{14}e_{g}^1$ electron configuration of the Mn$^{3+}$ ions, and stabilizes $d_{3x^2-r^2}$/$d_{3y^2-r^2}$ orbitals which are ordered, the so-called $O^I$. 
structural phase. The orbital order consists of the ordering of the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals in the alternate staggered pattern (Fig. 1) in the $a$-$b$ plane. The orbital ordering pattern repeats itself along the $c$ axis. This type of orbital order induces $A$-type antiferromagnetic (A-F) ordering [$19,20$] below $T_N \sim 140$ K. In the $A$-type AF phase the spins in the $a$-$b$ plane are ferromagnetically ordered. The ferromagnetic planes are stacked antiferromagnetically along the $c$ axis (Fig. 1). The orbital order persists in the paramagnetic phase above $T_N$. A complete understanding of the mechanism stabilizing the observed order in the insulating parent compound LaMnO$_3$ is a prerequisite to understanding fully the complex interplay among the spin, charge, orbital, and lattice degrees of freedom in the doped manganites. For this reason a large number of theoretical investigations has already been undertaken on stoichiometric LaMnO$_3$ itself [21].

LaMnO$_3$ crystallizes in the orthorhombic space group $Pbnm$. The MnO$_6$ octahedra in LaMnO$_3$ are distorted due to the Jahn-Teller effects. There are three Mn-O distances called short $s$, medium $m$, and long $l$. LaMnO$_3$ undergoes a transition at $T_{JT} \sim 750$ K from the Jahn-Teller distorted O-orthorhombic phase to a high temperature orthorhombic phase which is nearly cubic [22]. The space group $Pbnm$ remains the same in both phases, but the Jahn-Teller distortion is nearly removed in the high temperature phase. The distortion of the MnO$_6$ octahedra on going through $T_{JT}$ diminishes drastically indicating the disappearance of the static orbital ordering.

The temperature variation of the unit cell volume $V$ of LaMnO$_3$ increases linearly as a function of temperature from room temperature to about 600 K, and deviates from this linear behavior at higher temperatures [23]. It shows a local maximum at about $T=720$ K, then decreases with increasing temperature, and finally drops abruptly at $T_{JT} \sim 750$ K with a volume contraction of about 0.36% at $T_{JT}$. The authors of the [23] interpret this effect as due to the more efficient packing of the MnO$_6$ octahedra in the orbitally disordered or orbital liquid state.

Zhou and Goodenough [23] have reported the observation of a peculiar conductive phase with ferromagnetic interactions and a Curie-Weiss paramagnetism above the cooperative Jahn-Teller orbital-ordering temperature $T_{JT}$ in a single crystal of the single-valent compound LaMnO$_3$. A positive Weiss constant increases discontinuously on raising the temperature through $T_{JT}$, but the Curie constant remains
unchanged. The sudden increase of electroconductivity across the JT transition by factor of ten was observed. Above $T_{JT}$, a nearly temperature-independent resistivity $\rho(T)$ and thermoelectric power $\alpha(T)$ that, unlike below $T_{JT}$, are insensitive to the oxidation state of the MnO$_3$ array are suggestive of charge transport by vibronic charge carriers.

A change in slope of the temperature dependence of the resistivity $\rho(T)$ and of the thermoelectric power $\alpha(T)$ at $T^* \sim 600$ K is due to nucleation of an orbitally disordered phase in a volume fraction of the high-temperature phase; this volume fraction grows monotonically with increasing temperature in the interval $T^* < T < T_{JT}$ but it increases discontinuously on heating across $T_{JT}$. Raman spectroscopy [24,25] has revealed the existence of orbital order-disorder fluctuations in the interval $T^* < T < T_{JT}$. An abrupt jump in the Weiss constant of the paramagnetic susceptibility on heating through $T_{JT}$ signals a change to three-dimensional (3D) ferromagnetic interactions from the 2D ferromagnetic coupling within (001) planes and antiferromagnetic coupling between these planes (type-A antiferromagnetic order found below a Neel temperature $T_N$) in the $O'1$ orthorhombic phase [23]. Gor’kov and Kresin [26] have predicted a metallic ferromagnetism in LaMnO$_3$ above $T_{JT}$ by their revised band calculation. However, the paramagnetic phase above $T_{JT}$ with strong ferromagnetic coupling shows peculiar transport properties which are incompatible with a band electronic model.

Moreover, the spectral weight of optical conductivity moves to lower energy on heating through $T_{JT}$ [27]. However, there is no Drude peak in the optical conductivity, which confirms that the mobile electrons above $T_{JT}$ do not have a momentum described by a well-defined $k$ vector as is to be expected for mobile localized electrons.

The static orbital ordering can be removed not only by temperature, but also applying external pressure. LaMnO$_3$ was studied by synchrotron X-ray diffraction, optical spectroscopies, and transport measurements under pressure up to 40 GPa [28]. The cooperative JT distortion is continuously reduced with increasing pressure. There is strong indication that the JT effect and the concomitant orbital order are completely suppressed above 18 GPa. The system, however, retains its insulating state to ~32 GPa, where it undergoes a bandwidth-driven insulator-metal transition. Delocalization of electron states, which suppresses the JT effect is insufficient to make the system metallic, appears to be a key feature of LaMnO$_3$ at 20-30 GPa.

The observation of an insulating state with suppressed JT effect supports the view that LaMnO$_3$ is a Mott (or charge-transfer) insulator, the JT distortion rather being a consequence of the localization of the $e_g$ electrons than its origin.

Millis [29] based on fits to data of a classical model that included JT and lattice terms, estimated the energy of the JT splitting to be $\geq 0.4$ eV and possibly as high as 2.4 eV. This high energy scale clearly implies that the JT distortions are not destroyed by thermal excitation at 750 K and the $O'1$-$O$ transition is an order-disorder transition where local JT octahedra survive but lose their long-range spatial correlations. This picture is supported by some probes sensitive to local structure, for example XAFS [39, 31] and Raman scattering [24], each of which presents evidence that structural distortions consistent with local JT effects survive above $T_{JT}$. 

Using neutron powder diffraction data a combined Rietveld and high real space resolution atomic pair distribution function analysis has been carried out [32]. The nature of the JT transition around 750 K is confirmed to be orbital order to disorder. In the high temperature orthorhombic (O) and rhombohedral (R) phases the MnO$_6$ octahedra are still fully distorted locally. The data suggest the presence of local orbitally ordered clusters of diameter ~16 Å (~ four MnO$_6$ octahedra) implying strong nearest neighbor JT anti-ferrodistortive coupling.

The rare earth and yttrium manganites, RMnO$_3$, crystallize in two different crystallographic structures. The compounds with R=La, Ce, Pr,Nd, Sm, Eu, Gd, Tb, Dy have an orthorhombic unit cell of space group $Pbnm$ whereas they have an hexagonal structure of space group $P6_3cm$ when R=Ho, Er, Tm, Yb, Lu or Y [32]. However, these compounds can be obtained in perovskite structure using high pressure and high temperature [33].

According to neutron diffraction data PrMnO$_3$ [34] and NdMnO$_3$ [35] are characterized also with A-type antiferromagnetic structure. However, the temperature of magnetic ordering dramatically decreases as rare-earth ionic radius increases (Fig.2). The small ferromagnetic component arises from the canting of the A-type AFM structure due to Dzyaloshinsky-Moriya interaction which is generated by a buckling of the oxygen octahedral. A crossover from A-type structure to helical AF structur seems to occur in GdMnO$_3$ which is also weak ferromagnet below $T=27$ K. A helical AFM structure has been revealed by neutron diffraction for TbMnO$_3$ [36], YMnO$_3$ [37] and HoMnO$_3$ [35].

![Figure 2. Temperatures of magnetic and orbital ordering as a function of Ln- ionic radius in LnMnO$_3$. wF- weak ferromagnet, hA- helical antiferromagnet, O$^\parallel$- orbitally ordered phase, O- orbitally disordered phase.](image)

The low-temperature magnetic structures of the orthorhombic perovskite HoMnO$_3$ have been studied on a polycrystalline sample from neutron diffraction, specific heat and susceptibility data [38]. With cooling, HoMnO$_3$ exhibits three magnetic phase transitions at $T_N=41$ K, $T\approx26$ K and $T\approx6.5$ K,
which suggests a rich magnetic phase diagram. At \( T_N \), the Mn\(^{3+} \) magnetic moments become ordered in an incommensurate antiferromagnetic (AFM) arrangement, defined by a \((C_x,0,0)\) mode, adopting a modulated sinusoidal magnetic structure which becomes commensurate with the unit cell below 29 K. Finally, below 22 K, an ordered magnetic moment appears on Ho\(^{3+} \) cations in an antiferromagnetic arrangement defined by a \((A_x,0,C_z)\) mode; this moment significantly increases below 6.5 K, reaching a value of 7.27(11) \( \mu_B \) at 1.8 K. The different magnetic structures are interpreted on the basis of competing superexchange interactions of opposite signs.

The thermal expansion of LnMnO\(_3\) was studied by dilatometric method [39]. It was found that all these compound exhibit JT transition at high temperature. The temperature of JT transition increases as ionic radii decrease (Fig. 2). According to dilatometric study JT transition is of martensite type because its connection was observed with a shape memory effect [39]. Moreover two-phase state around JT transition was found by X-ray diffraction method [39].

The magnetic properties and crystal structure of BiMnO\(_3\) strikingly differ from those of LnMnO\(_3\) family. BiMnO\(_3\) has a triclinically distorted perovskite structure. This low symmetry structure has been explained by a highly polarized 6s\(^2\) character of Bi\(^{3+} \) ions. Contrary to LnMnO\(_3\) family this compound shows ferromagnetism below \( T_V \sim 103 \) K.

Structure of ferromagnetic BiMnO\(_3\) synthesized at high pressure has been determined by electron diffraction and high resolution neutron powder diffraction [40]. The MnO\(_6\) octahedra reveal uni-axial elongation. The elongation is about 12-15\% of the mean Mn-O distance of the in-plane Mn-O distances. This should be explained by the JT distortion of the trivalent manganese cation with a \( d^4 \) electronic configuration. This elongation suggests that the degenerated \( e_g \) orbital splits into \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals and the \( e_g \) electron occupies a \( d_{z^2} \) orbital for every manganese cation.

According to orbital ordering picture presented in [40] 1/3 of orbital configurations are favorable for antiferromagnetic interactions while 2/3 of the Mn-O-Mn configurations are favorable for ferromagnetic interactions via superexchange. For every manganese cation four ferromagnetic and two antiferromagnetic interactions occur. The ferromagnetic interaction overcomes antiferromagnetic ones and consequently the ferromagnetism of BiMnO\(_3\) appears.

The orbital order-disorder transition in BiMnO\(_3\) occurs around 800 K as first-order transition [41]. The crystal structure at \( T=835 \) K can be indexed by the \( Pbnm \) orthorhombic structure. As for electrical properties BiMnO\(_3\) is an insulator and exhibits ferroelectric hysteresis loop in the ferromagnetic state [42]. A fairly large negative magnetocapacitance effect was observed in the vicinity of the ferromagnetic transition temperature \( T_M \) [41].

1.2. La\(_{0.88}\)MnO\(_x\) system

Tentative magnetic phase diagram of the La\(_{0.88}\)MnO\(_x\) (2.82\( \leq x \leq 2.96\)) manganites is shown in Figure 3 [43]. 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 LaMnO\(_3\). Both compounds have very close unit cell parameters, the same magnetization value, and close temperatures of both magnetic (\( T_{OO} \sim 140K \)) and orbital (\( T_{CO} \sim 750K \)) orderings. The existence of orbital ordering in the A-type
antiferromagnetic structure of La$_{0.88}$MnO$_{2.82}$ is corroborated by neutron diffraction measurements [44]. With increasing oxygen content up to the $x=2.85$ sample, the magnetic and orbital ordering temperatures lower while the magnetization increases slightly. Results of the neutron diffraction measurements carried out for the $x=2.84$ sample confirm the appearance of a ferromagnetic component. A further increase of the oxygen concentration leads to a significant enhancement of the ferromagnetic contribution. The transition temperature to the paramagnetic state begins to increase and the transition becomes broader. Neutron diffraction data obtained for the $x=2.87$ sample 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 relatively large magnetic anisotropy at low temperature 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. No pronounced thermomagnetic irreversibility indicating the anisotropic magnetic interactions is observed starting from the $x=2.92$ sample. The values of magnetization estimated for the monoclinic compounds are close to those expected for full spin alignment. The ground state of all the orthorhombic compounds $2.82 \leq x \leq 2.90$ is insulating. It should be noted that the appearance of metallic conductivity does not coincide with the transition to monoclinic phase. Simultaneous first-order magnetic transition and metal-insulator transition at $T_C$ are observed for $x \geq 2.92$ compounds. 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, neutron diffraction, Young’s modulus, resistivity, and DTA data is shown in Figure 4. For La$_{0.88}$MnO$_{2.82}$, the sharp anomalies of the Young’s modulus and resistivity are associated with the removal of cooperative orbital ordering; it is observed at approximately 650 K. The DTA measurements revealed the release of latent heat in the range 650–730 K. Neutron diffraction data indicate the coexistence of orbitally ordered $O'$ and orbitally disordered O phases at $T=700$ K. Another thermal anomaly connected with the transition to the monoclinic phase is observed in the temperature range $915 \leq T \leq 960$ K. With the increase of the oxygen content to $x=2.83$, the temperatures of both orbital order-disorder and orthorhombic-monoclinic phase transitions significantly decrease. The range of coexistence of $O'$ and $O$ phases becomes broader, while the width of the anomaly associated with the temperature-induced orthorhombic-monoclinic 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 JT distortions at room temperature and two-phase character of the crystal structure above $T \sim 470$ K.

Inhomogeneous structural states are observed up to 650 K. 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. The neutron diffraction study performed for the La$_{0.88}$MnO$_{2.87}$ compound indicates that the value of the MnO$_6$
The temperature of orthorhombic-monoclinic phase transition gradually decreases as the oxygen content increases and starting from the $x=2.91$ sample, the monoclinic phase is stabilized (Fig. 4). It is necessary to mention 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 [45]. Thus, the correlation between the orbital state and magnetic properties of the
La$_{0.8}$MnO$_3$ manganites is prominent. The static JT distortions are responsible for the A-type antiferromagnetic structure, while dynamic orbital correlations lead to ferromagnetism.

It is worth noting that there are two alternative models of orbital state corresponding to ferromagnetic ordering in manganites: 3D dynamic $d_{3z^2-r^2}$ orbital correlations and staggered ordering of $d_{x^2-y^2}$ and $d_{z^2}$ orbitals. Neutron diffraction studies have shown that LaMnO$_3$ undergoes a structural transition from $O'$ - orthorhombic to O-orthorhombic phase at $T_{JT} = 750$ K [46]. The MnO$_6$ octahedron in the O-orthorhombic phase becomes nearly regular, i.e. the orbital ordering disappears [46]. However, X-ray absorption near the edge structure and the extended x-ray absorption fine structure at the Mn K-edge measurements have revealed that the MnO$_6$ octahedrons in LaMnO$_3$ remain tetragonally distorted at $T > T_{JT}$ [47]. The empty Mn$^{3+}$ electronic $d$ states were shown to be unaltered through the JT transition. The lowest energy for the $e_g$ electron corresponds to the three possible distortions giving rise to three degenerate vibronic states, $d_{3z^2-r^2}$, $d_{x^2-y^2}$, and $d_{z^2}$, being the electronic orbitals of the vibronic state. The thermally excited electron jumps between these states above $T_{JT}$ and is localized in an ordered state below $T_{JT}$. The orbital ordering proposed for LaMnO$_3$ arises then from the ordering of the local JT distortions. The high temperature (O-orthorhombic) phase can be described as a dynamical locally distorted one with the strong antiferrodistortive first neighbour coupling [47].

The similar situation seems to be observed for Mn$^{4+}$-doped manganites. The atomic pair-density function of La$_{1-x}$Sr$_x$MnO$_3$ manganites (0$\leq x \leq 0.4$), obtained by pulsed neutron diffraction, indicates the existence of tetragonally distorted MnO$_6$ octahedrons even in the rhombohedral metallic phase, when the crystallographic structure shows no JT distortions [48]. This is possible only in the case of the dynamic orbital correlations described above. One can assume that when one puts non-JT Mn$^{4+}$ ions in the background of the Mn$^{3+}$ ions, the $e_g$ orbitals of all the Mn$^{3+}$ ions surrounding the localized hole (Mn$^{4+}$) tend to be directed towards it, forming an orbital polaron [49]. Due to the strong antiferrodistortive Mn$^{3+}$ first neighbour coupling [47], dynamic correlations of the $d_{3z^2-r^2}$ orbitals should arise.

According to the rules for 180° superexchange the dynamic orbital correlations lead to ferromagnetic interaction between the Mn$^{3+}$ ions [30]. Hence, one can expect that ferromagnetism in manganites can arise even in the absence of Mn$^{4+}$ ions, if only the JT effect is dynamic. For instance, Mn substitution with non-JT diamagnetic Nb$^{5+}$, Al$^{3+}$, Sc$^{3+}$, etc, ions should result in the appearance of ferromagnetic order. Below we show this assumption to be correct.

Second possibility lies in description of orbital state as a hybridization of the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals as $\cos(\theta/2)|3z^2-r^2\rangle\pm\sin(\theta/2)|x^2-y^2\rangle$. Such an orbital ordering is recently proposed experimentally and theoretically in the ferromagnetic insulating phase of La$_{0.8}$Sr$_{0.12}$MnO$_3$ and Pr$_{0.75}$Ca$_{0.25}$MnO$_3$ [50-52]. The difficulties in determination of priority of the present models are conditioned by the fact that staggered ordering of $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals can exhibit itself in experiments in the same way as 3D dynamic $d_{3z^2-r^2}$ orbital correlations.

1.3. La$_{1-x}$Sr$_x$(Mn$_{1-x}$Nb$_{x/2}$)O$_3$ system

Hypothetical magnetic phase diagram of La$_{1-x}$Sr$_x$(Mn$_{1-x}$Nb$_{x/2}$)O$_3$ is shown in Figure 5 [53]. The parent LaMnO$_3$ compound shows the spontaneous magnetization value at 5 K corresponding to magnetic
moment of 0.07 $\mu_B$ per $\text{Mn}^{3+}$ ion. The Neel point where spontaneous magnetization develops is 143 K. According to [52] the spontaneous magnetization has a relativistic nature. Substitution of Mn with Nb leads to an enhancement of the spontaneous magnetization whereas the temperature of transition into paramagnetic state slightly decreases. In accordance with the magnetization data the $\text{La}_{0.3}\text{Sr}_{0.7}\text{Mn}_{0.9}\text{Nb}_{0.1}\text{O}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.88}\text{Nb}_{0.12}\text{O}_3$ samples are ferromagnets with the magnetic moment per chemical formula around 2.3 $\mu_B$ and 2.6 $\mu_B$ respectively. Neutron diffraction study has revealed the magnetic moment of $\text{Mn}^{3+}$ in the parent $\text{LaMnO}_3$ antiferromagnetic compound to be close to 3.5 $\mu_B$ [53] whereas $\text{Nb}^{5+}$ is diamagnetic ion, hence the expected moment should be close to 3 $\mu_B$ per formula unit what is in a rather good agreement with the observed one. The Nb doped sample $(x=0.3)$ has a well defined Curie point- 123 K. Both Curie point and spontaneous magnetization start gradually to decrease when Nb content exceeds 15 % from total sites number in the manganese sublattice.

The magnetic state cardinally changes as the concentration of niobium reaches 25 %. We have observed the magnetic susceptibility of the $x=0.5$ sample dramatically decreases. ZFC-magnetization shows a peak at 30 K. Below this temperature FC magnetization practically does not change. Taking into account the character of $\text{M(H)}$ dependence we have concluded that the sample $x=0.5$ can be considered as spin glass with $T_f=30$ K. We can explain the collapse of long range ferromagnetic ordering by a diamagnetic dilution of Mn-sublattice. According to resistivity vs. temperature measurements $\text{La}_{1-x}\text{Sr}_x\text{(Mn}_{1-x/2}\text{Nb}_{x/2})\text{O}_3$ samples are semiconductors. Below Curie point a large value of magnetoresistance is observed.

The results presented here deal with the facts that the Nb-doped $\text{La}_{1-x}\text{Sr}_x\text{(Mn}_{3+}^{3+}\text{Nb}^{5+}_{x/2})\text{O}_3$ samples enriched with $\text{Mn}^{3+}$ ions are ferromagnetic and show a large magnetoresistance. It is worth noting that the possibility of the existence of ferromagnetic ordering in the manganites, despite the absence of $\text{Mn}^{3+}$ ions, reject the double exchange and the electronic phase separation concepts. The result obtained indicates an important role of ferromagnetic superexchange via oxygen scenario of magnetic interactions in manganites. According to the superexchange mechanism the $\text{Mn}^{3+}$-$\text{O}$-$\text{Mn}^{3+}$ and $\text{Mn}^{3+}$-$\text{O}$-$\text{Mn}^{4+}$ 180°

![Figure 5. Magnetic phase diagram for $\text{La}_{1-x}\text{Sr}_x\text{(Mn}_{1-x/2}\text{Nb}_{x/2})\text{O}_3$ series (A- antiferromagnet, F- ferromagnet, P- paramagnet, SG- spin glass; O' and O- orbitally ordered and orbitally disordered phases, respectively).]
magnetic interactions are strongly ferromagnetic for the orbitally disordered state whereas the Mn$^{4+}$-O-Mn$^{4+}$ ones are strongly antiferromagnetic [4]. The Curie point associated with Mn$^{3+}$-O-Mn$^{3+}$ positive superexchange may be close to room temperature for manganites with perovskite structure because our samples contain diamagnetic Nb$^{5+}$ ions which should strongly decrease the Curie point. Stoichiometric LaMn$^{3+}$O$_3$ compound also shows ferromagnetic interactions between Mn$^{3+}$ ions when cooperative JT distortions are vanished at T=750 K. The orbital ordering changes character of superexchange magnetic interactions which in the orbitally ordered state become anisotropic [4, 54].

1.4. Nd$_{1-x}$Ca$_x$MnO$_3$ system
The hypothetical magnetic phase diagram of the Nd$_{1-x}$Ca$_x$MnO$_3$ system at low Ca doping level is presented in Figure 6 [57]. Neutron diffraction shows that the samples with x<0.08 consist mainly of antiferromagnetic phase while at x>0.08 ferromagnetic component dominates. Under hole doping the temperature of the transition into paramagnetic state at first decreases and then around x=0.1 increases. We have observed two magnetic phase transitions in the range 0.06≤x≤0.1 as temperature decreases.

The Nd$_{1-x}$Ca$_x$MnO$_3$ solid solutions contain two types of magnetically active sublattices: neodymium and manganese ones. At first we discuss the Nd contribution into magnetic properties. The f-f exchange interaction in rare-earth sublattice is as a rule rather weak in comparison with d-d interaction between Mn ions. One can expect that neodymium magnetic moments should order as a result of f-d exchange interactions between Nd and Mn sublattices. The study of magnetic properties of Nd$_{1-x}$Ca$_x$MnO$_3$ samples confirm this viewpoint. According to neutron diffraction data the magnetic moments of Nd ions start to be ordered slightly below $T_N$. Magnetic moment of Nd ion is about 1.2 $\mu_B$ at 2 K and directed opposite to weak ferromagnetic vector in NdMnO$_3$ while in the sample x=0.12 the orientation of Nd and Mn magnetic moments is the same. In the range 0.06≤x≤0.10 the metamagnetic behavior was observed in large magnetic fields (triple hysteresis loops with a negative remanent magnetization).
According to our hypothesis, samples in the range $0.06 \leq x \leq 0.10$ consist of antiferromagnetic (weak ferromagnetic) and ferromagnetic phases which are exchange coupled at the boundary. The Nd sublattice in both weak ferromagnetic and ferromagnetic phases orders nearby the Neel point (Curie point). However, the orientation of Nd magnetic moments in both these phases is different: f-d exchange is positive for ferromagnetic phase but negative in weak ferromagnetic one. The ferromagnetic phase strongly affects magnetic properties of weak ferromagnetic phase due to exchange coupling at the boundary. This interaction may induce a reorientational transition from antiparallel orientation of Nd moments and weak ferromagnetic vector to parallel one. We believe that nearby certain temperature the ground state of Nd$^{3+}$ ions becomes degenerate because opposite contributions from exchange coupled ferromagnetic and weak ferromagnetic phases at Nd site become equal. According to theoretical consideration this state should be unstable thus leading to magnetic structure transformation [55]. Results of neutron diffraction study carried out for the $x=0.08$ sample are in agreement with this interpretation of low temperature phase transition.

![Figure 7](image.png)

**Figure 7.** The H-T magnetic phase diagram for Nd$_{0.92}$Ca$_{0.08}$MnO$_{2.98}$ compound.

On the basis of magnetization data we propose H-T magnetic phase diagram of Nd$_{0.92}$Ca$_{0.08}$MnO$_{2.98}$ compound (Fig. 7). Depending on the prehistory in the wide range of magnetic field the phases with parallel or antiparallel orientation of Nd and Mn sublattices in weak ferromagnetic phase can be realized. One can see that the value of magnetic field required for the change of relative orientation of the Nd and Mn magnetic moments in the weak ferromagnetic phase increases as temperature rises. The width of a field range in which the hysteresis is observed practically does not depend on a temperature. This type of magnetic phase diagram is in agreement with crossover of energy sub-levels of Nd ions.

1.5. Bi$_{1-x}$Ca$_x$MnO$_3$ system

Figure 8 presents a magnetic phase diagram of the Bi$_{1-x}$Ca$_x$MnO$_3$ manganites [59]. As the Ca content in the Bi$_{1-x}$Ca$_x$MnO$_3$ system increases, the latter passes through three different magnetic states, namely, ferromagnetic ($x\leq0.1$), spin-glass ($0.15\leq x \leq 0.25$), and antiferromagnetic ($x>0.25$). In the case of antiferromagnetic compositions, the magnetic-ordering and structural-transformation temperatures vary
only weakly within the concentration interval from \( x = 0.25 \) to 0.6. The ferromagnetic ordering in BiMnO\(_3\) is the most likely due to cooperative ordering of the \( d_{x^2-y^2} \) orbitals \([60, 61]\). With orbital ordering of this type, according to the Goodenough-Kanamori rules, ferromagnetic ordering becomes more energetically favorable than antiferromagnetic one. We may recall that rare-earth manganites exhibit orbital ordering of the \( d_{x^2} \) type, which stabilizes the \( A \)-type antiferromagnetic structure \([4]\). Orbital disorder in BiMnO\(_3\) sets in, apparently, at a fairly high temperature, near 760 K. Replacement of Bi ions by Ca results in the formation of quadrivalent manganese ions, which should be accompanied by destruction of orbital ordering due to the appearance of non-JT Mn\(^{4+}\) ions in the lattice. However, the orbitally disordered phase in manganites should be ferromagnetic \([4, 56]\), whereas we observed a state of the spin-glass type. A direct transition from the antiferromagnetic phase to the spin-glass without passing through the ferromagnetic state was observed to occur in the rare-earth manganites \( \text{Sm}_{1-x}\text{Ba}_x\text{MnO}_3 \) and \( \text{Y}_{1-x}\text{Ca}_x\text{MnO}_3 \) (\( x \sim 0.12 \)) \([62, 63]\). It should be pointed out that at approximately this concentration of rare-earth ions, the ferromagnet–spin glass transition takes place in \( \text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3 \).

There is more than one opinion on the nature of exchange interactions in manganites. The antiferromagnetic state certainly forms through oxygen-mediated superexchange interactions of the type Mn-O-Mn. Most researchers believe that the ferromagnetic state in manganites is created through double exchange, i.e., via direct carrier transfer between various lattice sites. In order for such an exchange mechanism to operate, Mn ions in different valence states must be present and the electrical conductivity must be high. The presence of Mn ions of different valences is not a sufficient condition for high electrical conductivity; indeed, the 3d orbitals of manganese and the 2p orbitals of oxygen should also overlap strongly. It is believed that this parameter is controlled by the Mn-O-Mn bond angle \([30, 60]\). The larger the lanthanide ion, the larger should be the Mn-O-Mn angle, the wider the 3d band, and, accordingly, the higher the magnetic ordering temperature and the electrical conductivity. It was observed that the magnetic state of the manganites also depends on the difference between the ionic radii of the rare-earth and the lanthanide ions. A large difference between the radii lowers, as a rule, the magnetic

![Figure 8. Magnetic phase diagram of the Bi\(_{1-x}\)Ca\(_x\)MnO\(_3\) manganites. A- antiferromagnet, F- ferromagnet, P- paramagnet, SG- spin glass, CO- charge-ordered state.](image-url)
ordering temperature as a result of competition between various exchange interactions characterized by a large difference in the Mn-O-Mn angles. This is why the spin-glass state sets in the Sm$_{1-x}$Ba$_x$MnO$_3$ system, wherein the average radius of the Sm and Ba ions is far larger than that between the Y and Ca cations in the Y$_{1-x}$Ca$_x$MnO$_3$ system [62,63]. However, in all the rare-earth manganites, the Mn$^{3+}$-O-Mn$^{4+}$ exchange coupling in the orbitally disordered phase is apparently ferromagnetic. The Mn-O-Mn angles in Bi-based manganites are fairly large, which is supported by structural studies [61] and the quite high Curie temperature of BiMnO$_3$. Hence, in the case of an orbitally disordered phase, one can expect the ferromagnetic part of exchange interactions to be dominant, which is in agreement with experiment. Therefore, we believe that, in contrast to the rare-earth manganites, no orbitally disordered phase forms in the Bi$_{1-x}$Ca$_x$MnO$_3$ system most likely as a result of competition between ferromagnetic interactions in BiMnO$_3$-type clusters and antiferromagnetic coupling in clusters in which the Mn$^{3+}$ orbitals are frozen in random orientations. As the Ca$^{2+}$ concentration increases, a new type of antiferromagnetic clusters, apparently due to charge ordering, appears. The existence in Bi$_{0.75}$Ca$_{0.25}$MnO$_3$ of large clusters, charge-ordered in a similar way to those in Bi$_{0.5}$Ca$_{0.5}$MnO$_3$, is suggested in studies of its elastic properties. Despite the presence of the spin-glass-type ground state, there is a certain fraction of states characterized by short-range order of the type of a charge-ordered phase, which is indicated by the fact that the Young modulus minima for the x = 0.25 and 0.35 compositions are close in temperature. We believe that the extremely high stability of the orbitally and charge-ordered states in Bi-based manganites derives from the strongly anisotropic character of the Bi-O covalent bonding.

Conclusions
The magnetic and structural phase diagrams of a number of lightly doped manganites have been considered. It has been shown that the magnetic properties of the slightly doped manganites are determined by the type of their orbital state. The dynamic correlations of $d_{3z^2-r^2}$ orbitals favor ferromagnetic ordering in the manganites, while A-type antiferromagnetic structure is typical for the static Jahn-Teller distortions. It has been argued that concentrational transition from an antiferromagnetic to a ferromagnetic state occurs via the formation of inhomogeneous state due to structural phase separation mechanism.

References