EVIDENCE FOR THE MAGNETIC PHASE SEPARATION INDUCED BY A STRUCTURAL INSTABILITY IN POLYCRYSTALLINE SAMPLES OF $La_{1-x}Sr_xMnO_{3-\delta}$

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Strong suppression of ferromagnetism and conductivity has been observed in $La_{1-x}Sr_xMnO_{3-\delta}$ polycrystalline samples at the crossover from the monoclinic to rhombohedral phase ($x \approx 0.21$). The results are well described in terms of magnetic phase separation arising as a result of the combined effect of oxygen nonstoichiometry and microstrain, the latter being extremely enhanced in the vicinity of the concentration boundary between two structural phases.

During the last decade, manganite perovskites of the chemical formula $R_{1-x}A_xMnO_3$ (where R is a rare earth, and A is an alkali earth atom) have attracted considerable attention because they exhibit a number of interesting electronic properties, including the colossal magnetoresistance phenomenon. Recent studies show convincingly that a number of the intriguing properties of the manganites cannot be understood through spatially uniform phases and that a tendency toward phase separation, typically involving ferromagnetic metallic and antiferromagnetic charge and orbital ordered insulating domains, plays an essential role in these compounds (for a review see [1]). Recently, short-range charge/orbital correlations were found prevalent in the paramagnetic insulating phase of $R_{1-x}A_xMnO_3$ (R=Pr, Nd, Sm; A=Ca, Sr) systems, especially when the carrier concentration takes the commensurate values, e.g., $x = 1/3, 1/2$, or $2/3$ [1—3]. Interestingly, the high-temperature structural correlations do not necessarily correspond to the low-temperature order, and in some cases the incipient high-temperature ordering is in direct competition with the ground state [1, 2]. The relationship between the low-temperature ground state and high-temperature correlations is at present largely unclear.

Several parameters are known to influence the tendency toward charge/orbital ordering (CO) significantly, among which the most crucial one is the one-electron bandwidth W. The reduction in W favors the CO state, while destabilizing the ferromagnetic ordering [1]. Other factors, such as enhanced oxygen deficiency, structural/magnetic disorder, and mechanical strain, may also hinder the development of ferromagnetism and induce the CO antiferromagnetic state [1, 4—5]. Recently, J. Li et al. found evidence for the oxygen-deficiency-activated CO transition in $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin films prepared by laser pulsed deposition on $LaAlO_3$ substrates [4]. The authors fabricated the films under different oxygen pressures, p_O, and revealed a relatively narrow range of p_O, within which the films exhibited the profoundly unusual behavior. Structural, transport, and magnetic properties of these films convincingly suggested the coexistence of two different phases, a metallic ferromagnet and an insulating, presumably CO, antiferromagnet. Such behavior is in compliance with the recent theoretical views predicting that it is the CO state which is in competition with the ferromagnetic state even in systems with large W and $x < 0.5$ and which may be stabilized in a narrow range of variables [1].

In this paper, we present the evidence that the CO state is likely to occur in the $La_{1-x}Sr_xMnO_{3-\delta}$ system near $x \approx 0.21$ and it might be a result of the combined effect of oxygen nonstoichiometry and microstrain, the latter being extremely enhanced in the vicinity of the concentration boundary between two structural phases [4,6]. While doing our previous work, which was devoted to studying the effect of sintering temperature on the magnetoresistance of the polycrystalline samples of $La_{1-x}Sr_xMnO_{3-\delta}$ [7—9], we revealed that, depending on the synthesis conditions, sharp anomalies in the transport and magnetic behavior of the samples might arise in a relatively narrow concentration region situated between $x = 0.2$ and 0.25. Being quite reproducible, these anomalies were found to be very sensitive to the details of the sintering process. Here, we present the data obtained on the samples which were synthesized in such a regime that the anomalies were most pronounced.

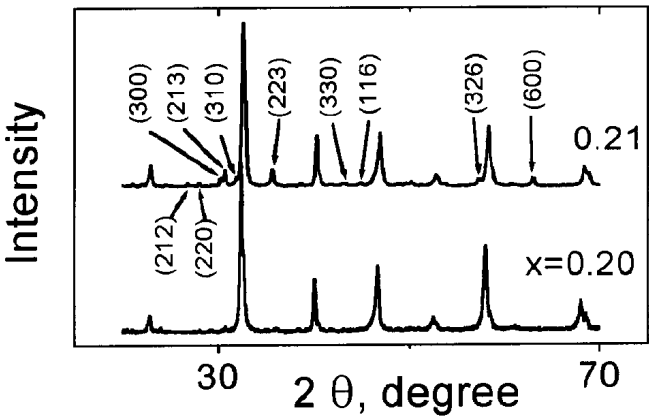

Fig. 1. X-ray powder diffraction patterns for the samples with $x = 0.20$ and 0.21. Arrows show the rhombohedral ($R1$) phase reflections which are not present in the sample with $x = 0.20$

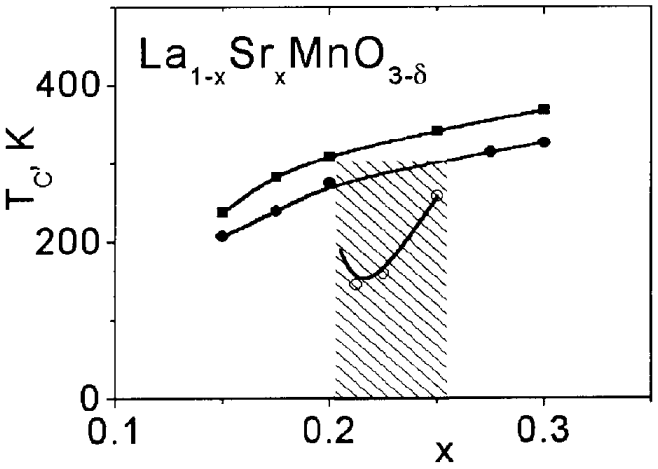

Fig. 2. Curie temperature as a function of x for the single-phase (solid circles) and two-phase (open circles) samples of $La_{1-x}Sr_xMnO_{3-\delta}$. Solid squares show T_C vs x adopted from [10]

Polycrystalline samples of $La_{1-x}Sr_xMnO_{3-\delta}$ (LSMO) with $x = 0.15 \div 0.30$ were prepared through a conventional solid-state reaction in air [7—9]. Representative samples were synthesized repeatedly, and they showed reproducible results. X-ray fluorescence analysis has conformed that, across the series of samples, the atomic ratio between the constituent metal elements (La, Sr and Mn) keeps close to the nominal one. Iodic titration, however, has showed that the fraction of Mn^{4+} ions is by about 4% less than that expected for stoichiometric samples. These results allow us to conclude that the peculiarities described below are mainly caused by oxygen non-stoichiometry of our samples. Details of the measurement procedure were described in [7—9].

As follows from the X-ray powder diffraction measurements, the crystalline structure at room temperature changes with increasing x from monoclinic ($x < 0.21$) to rhombohedral ($x > 0.25$), with a mixture of two different perovskite phases occurring in the intermediate region ($0.21 \leq x \leq 0.25$). The results of investigation of the single-phase samples were reported earlier [8—10]. Here we mainly concentrate on the behavior of $La_{1-x}Sr_xMnO_{3-\delta}$ within the intermediate region.

Fig. 1 contrasts the X-ray diffraction patterns for the samples with $x = 0.20$ and 0.21. In the former, the observed peaks can be indexed according to a monoclinic perovskite structure with $a_0 = 0.546$ nm, $b_0 = 0.552$ nm, $c_0 = 0.780$ nm and $\alpha = 90.58°$. The diffraction picture for $La_{0.79}Sr_{0.21}MnO_{3-\delta}$, however, is composed of large monoclinic phase peaks and small rhombohedral phase ones. The parameters of the first phase are close to the $La_{0.80}Sr_{0.20}MnO_{3-\delta}$ case, while the latter has $a_{R1} = 1.547$ nm $\approx 2c_0$ and $\gamma_{R1} = 91.54°$. Similar two-phase picture holds for all the samples within the concentration region $0.21 \leq x \leq 0.25$, although the relative amount of the rhombohedral ($R1$) phase changes from about 10% ($x = 0.21$) to $3 - 4\%$ ($x = 0.25$). The samples with $x = 0.275 \div 0.30$ are single-phase and reflections correspond to the rhombohedral ($R2$) phase with $a_{R2} \approx 0.546$ nm and $\gamma_{R2} \approx 60.44°$, in good agreement with the data for single crystalline materials of the same composition [10].

Fig. 2 compares the Curie temperature, T_C, of the samples studied (circles) with that of the single crystalline $La_{1-x}Sr_xMnO_3$ (squares) [10]. Here, we have defined T_C as a temperature, at which the temperature derivative of the in-phase ac susceptibility, χ, displays a peak. For all the single-phase samples, the paramagnet to ferromagnet transition is sufficiently sharp, and both the resistivity and magnetoresistance exhibit maxima in the close vicinity of T_C [7, 9]. The samples within the 'anomalous' region show the extremely broadened magnetic/resistive transition and reduced magnetization, M (Fig. 3). For these samples, there are two pronounced peaks on the dM/dT vs T dependence, one at $\approx$ 50 K, and the other at a temperature close to the peak on the χ vs T dependence, but not necessary coinciding with it. In the extreme case ($x = 0.21$), the saturation magnetization at $T = 5$ K is almost twice less than that of $La_{0.80}Sr_{0.20}MnO_{3-\delta}$, and the coercive field ($H_c \approx 125$ Oe) is far greater than H_c of the latter sample (≈ 10 Oe). All these data suggest that the magnetic state of the 'anomalous' samples is

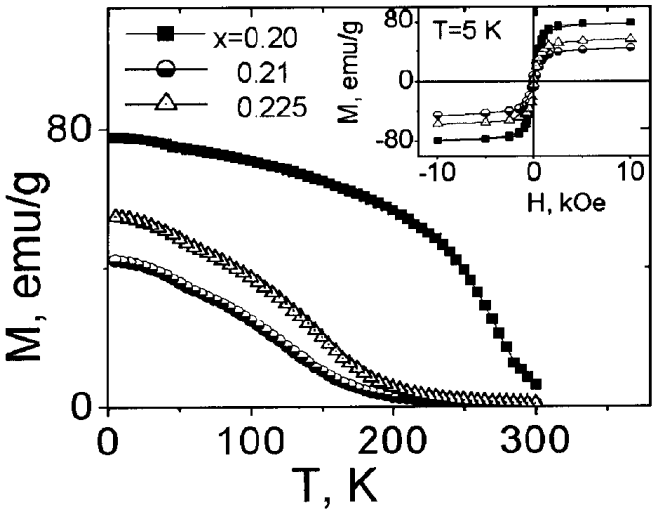

Fig. 3. Temperature dependence of magnetization in a field of 5 kOe for the samples with $x = 0.20 \div 0.225$. Inset shows M vs H dependences measured at $T = 5$ K

sufficiently inhomogeneous, and other mechanism, beside well-known double exchange, is at play.

To shed further light on the peculiar magnetic state of the samples, we have studied the temperature dependence of ESR spectra from 300 K down to 77 K. Let us consider the case of $La_{0.79}Sr_{0.21}MnO_{3-\delta}$ in detail. A strong symmetric ESR signal with a line shape close to Lorentzian is observed at room temperature. When the temperature is lowered, the linewidth decreases, passes through a minimum at $T_{\min} \approx 200$ K, and increases on further cooling. Evidence for ferromagnetic ordering becomes noticeable at around 140 K, but the spectrum is not characteristic of the homogeneous ferromagnetic state even at the lowest temperature measured (77 K) (detailed results of ESR measurements will be reported elsewhere).

As was noted in [11], the minimal peak-to-peak ESR linewidth, $\Gamma_{\min}$, which is usually achieved at temperatures slightly higher than T_C, may be considered as an indicator of a degree of quality and homogeneity of the sample. In our case, $\Gamma_{\min}$, which is about 30 mT for $La_{0.79}Sr_{0.21}MnO_{3-\delta}$, is comparable to $\Gamma_{\min}$ of the bulk polycrystalline samples synthesized by other researchers [11—12]. It is interesting that $\Gamma_{\min}$ keeps close to 30 mT for all the samples studied, suggesting that the chemical homogeneity and the features of the high-temperature ($T > T_C$) magnetic state of the samples within and beyond the 'anomalous' region do not differ noticeably.

Returning to Fig. 2, we see that, even within single-phase regions, the Curie temperature of our samples differs from that of single crystalline materials, which may be easily understood taking into account that oxygen deficiency gives rise to a reduction of T_C in manganites [13—15]. To explain the behavior within the "anomalous" region, however, we should consider the combined effect of oxygen nonstoichiometry, structural disorder, and microstrain, all of the factors being inevitably present in polycrystalline samples and strongly dependent on synthesis conditions [1, 4, 6, 13].

In our opinion, the behavior of the samples within the 'anomalous' region might be well described within the scenario of inhomogeneous picture where two phases with different structural, transport, and magnetic properties coexist over a wide temperature range. As was noted above, it is the CO state which is expected to be in competition with the ferromagnetic metallic phase in manganites and which is likely to be induced by oxygen non-stoichiometry and microstrain [1, 4, 6]. This state which is characterized by both an increased unit cell (including several primitive perovskite cells) and low-temperature antiferromagnetic ordering seems to dominate the properties of our samples at the crossover between the two structural phases. As follows from the detailed studies on polycrystalline samples of the $La_{1-x}Sr_xCoO_{3-\delta}$ system [6], the microstrain is extremely enhanced in the vicinity of the structural transition ($x \approx 0.35$). If this picture is applicable to the $La_{1-x}Sr_xMnO_{3-\delta}$ samples, the enhanced strained state that, in turn, favors stabilization of CO is expected just in that concentration region where we have revealed the profound anomalies. This remarkable scenario remains to be confirmed by temperature-dependent structural and NMR studies which are in progress now.

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ІНДУКОВАНЕ СТРУКТУРНОЮ НЕСТАБІЛЬНІСТЮ РОЗДІЛЕННЯ МАГНІТНИХ ФАЗ У ПОЛІКРИСТАЛІЧНИХ ЗРАЗКАХ $La_{1-x}Sr_xMnO_{3-\delta}$

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Р е з ю м е

У полікристалічних зразках $La_{1-x}Sr_xMnO_{3-\delta}$ виявлено значне подавлення феромагнетизму і електропровідності в області концентраційного переходу від моноклінної до ромбоедричної фази ($x \approx 0,21$). Одержані результати добре описуються з позиції розділення магнітних фаз, спричиненого комбінованим впливом кисневої нестехіометрії та значно підсилених поблизу концентраційного переходу мікронапружень.

ИНДУЦИРОВАННОЕ СТРУКТУРНОЙ НЕСТАБИЛЬНОСТЬЮ РАЗДЕЛЕНИЕ МАГНИТНЫХ ФАЗ В ПОЛИКРИСТАЛЛИЧЕСКИХ ОБРАЗЦАХ $La_{1-x}Sr_xMnO_{3-\delta}$

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Р е з ю м е

В поликристаллических образцах $La_{1-x}Sr_xMnO_{3-\delta}$ обнаружено сильное подавление ферромагнетизма и электрической проводимости в области концентрационного перехода от моноклинной к ромбоэдрической фазе ($x \approx 0,21$). Полученные результаты хорошо описываются с позиции разделения магнитных фаз, вызванного комбинированным эффектом кислородной нестехиометрии и значительно усиленных вблизи концентрационного перехода микронапряжений.