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Structural and Magnetic Long-Range Phase Separation in $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ Perovskites

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Neutron diffraction study of $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ shows that with increase of Pr content (decrease of average A-cation radius), the low temperature state of the compound is changing from homogeneous FM to quasi-homogeneous with canted magnetic structure, passing the stage of the two-phase state with FM-metallic and AFM-insulating regions of mesoscopic (> 1000 Å) dimensions. Different atomic structure of the appearing phases and developing field of lattice deformations are the factors stabilizing the two-phase state.

KEYWORDS: manganites, phase separation, neutron diffraction

Phase separation, arising in the structures of perovskite manganites at cooling below the temperature of magnetic ordering, is at present one of the most intensively discussed issues of the physics of compounds with CMR-effect. The tendency to the inhomogeneity of the ground state of CMR-compounds was proved in many experimental works and the conclusion has even been done that it is a generic property of the systems with strong electron correlations.$^{1)}$ In theoretical models of the phenomenon of phase separation at transition from insulating-paramagnetic to ferromagnetic-metallic state (FMM), until the last time, the scenario was discussed, in which the charge (CO) and antiferromagnetic (AFM) ordering initially take place. Further temperature decrease stimulates the concentration of charges, which leads to the appearance of charged FMM clusters. The size of charge-separated regions is regulated by the Coulomb energy and cannot be large. This is why, the observed coexistence of FM and AFM structures in manganites is being interpreted as homogeneous "canted" structure.$^{2)}$ However, during the last two years, the reliable experimental evidences were obtained$^{3-6)}$ for the appearance in some manganite compositions of the two-phase FM+AFM state with regions of mesoscopic dimensions (> 1000 Å). These large regions cannot be charged, implying that the electronic and magnetic properties should be controlled not only by charge carrier concentration, but also by some other parameters.

In the present work, we provide new experimental data obtained with the $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ series of compounds, which show that the exact situation is even more complicated, than just appearance of the two-phase FM+AFM state at the mesoscopic level. Namely, depending on the average A-cation radius, $\langle r_A \rangle$, to which the average valence angle ⟨Mn–O–Mn⟩ is proportional, either two-phase state with mesoscopic region dimensions, or the quasi-homogeneous state with canted magnetic structure, are appearing.

The samples of $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ (LPCM, hereafter) with $0.5 \leq y \leq 1.0$ were prepared as powders with the use of the so-called "paper synthesis" and carefully characterized by various methods. This work was done at Department of Chemistry, Moscow State University (A.R. Kaul's laboratory) and in "Kurchatov Institute", Moscow (N.A. Babushkina's laboratory). The neutron-diffraction experiments were carried out at two neutron diffractometers: DMC in Paul Scherrer Institute at SINQ neutron source and HRFD in FLNP, JINR at the IBR-2 pulsed reactor. At both instruments, the diffraction spectra were measured in the regime of heating the sample in the temperature range from 15 to 293 K. Correspondingly, the values of the phase transition temperatures are given for this particular regime. The results obtained earlier for the effect of isotope exchange and external magnetic field on the composition with $y = 0.75$ have been presented in refs. 3 and 5.

For all the compositions with $y \geq 0.6$, at low temperature the neutron diffraction peaks are observed (the most characteristic of them are (0 0 1/2) and (1/2 0 1/2) peaks), which correspond to the pseudo-CE AFM structure, and also FM contribution to the nuclear peaks, for example (1 0 1) and (0 2 0). With increasing temperature, first the FM ordering disappears, then, after the 10 – 30 K interval, the transition to the paramagnetic state occurs. The temperature dependence of the AFM peaks intensities is completely different for the compositions with $y \geq 0.9$ and $y \leq 0.8$ – monotonous and peak-shaped correspondingly (Fig. 1).

Total magnetic moment of Mn atoms defined as $M_{tot} = (\mu_{FM}^2 + \mu_{AFM}^2)^{1/2}$, is also visibly different for these two Pr concentration regions (Fig. 2): for $y \leq 0.8$, M_{tot} is almost equal to the spin-only value, which for the 30% Ca content is about 3.7 μ_B, while for $y = 0.9$ and 1.0, M_{tot} abruptly decreases in value by more than 1/3. With increase of Pr content up to $y = 0.9$, the response of magnetic ordering to the effect of external magnetic field drastically changes. For $y = 0.75$ and 0.8, no synchronism in changing of the intensities of FM and AFM peaks was observed,$^{5)}$ while for $y = 0.9$, the changes be-

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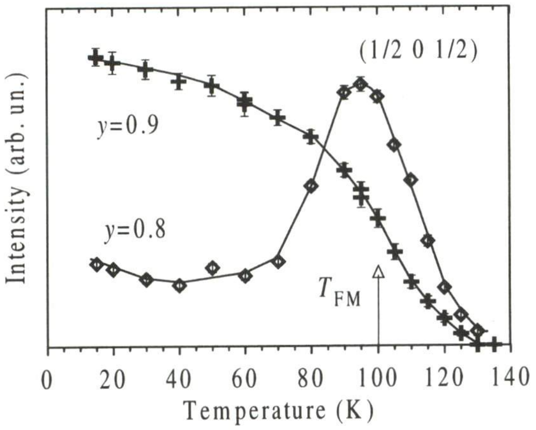

Fig. 1. Temperature dependence of the superstructural (1/2 0 1/2) peak intensity appearing at the AFM ordering, for the compositions with $y = 0.8$ and 0.9. Below $T_{FM} \approx 100$ K, FM contribution in the diffraction intensity is observed in both samples.

come synchronized (Fig. 3).

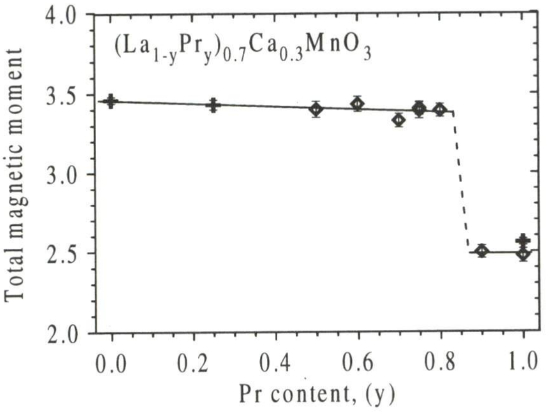

Fig. 2. $M_{tot} = (\mu_{FM}^2 + \mu_{AFM}^2)^{1/2}$ (in Bohr magnetons) as a function of Pr content: (◇) – defined by us, (+) – taken from the literature (refs. 7 and 8).

The above mentioned facts allow to assume that with increasing Pr content up to $y \approx 0.9$, i.e. with decreasing $\langle r_A \rangle$ down to 1.183 Å, the change of the low-temperature behavior of LPCM compositions takes place. The two-phase state (FM metallic matrix with AFM dielectric drops) is replaced by quasi-uniform dielectric state with "canted" magnetic structure. The change of the canting angle naturally explains the dependencies shown in Fig. 3. The significant decrease of the M_{tot} value for $y \geq 0.9$ evidences that not the entire sample volume is in the one-phase state. It agrees with the data presented in[6] for $Pr_{0.7}Ca_{0.3}MnO_3$, for which the coexistence of charge and orbital ordered phase and Jahn-Teller glass phase with different lattice constants was observed. From the values of M_{tot}, we can estimate that significant part of our sample (54 %) was in the homogeneous (canted) state. Correspondingly, in our high resolution neutron diffraction patterns of $Pr_{0.7}Ca_{0.3}MnO_3$, we did not observe such a clear splitting, as in.[6]

For the whole Pr content range investigated, including the region of FM+AFM two-phase state ($0.6 \leq y \leq 0.8$), the width of magnetic peaks is close to nominal and consequently, the phase separation is occurring at the mesoscopic level. Theoretically substantiated already in 70-s (see the review[9] and references therein) electronic phase separation, which occurs at a few tens of angstroms scale, may also take place in LPCM, however, it does not manifest itself in diffraction experiments.

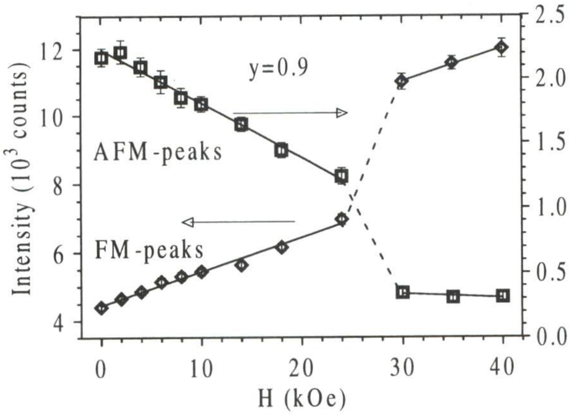

Fig. 3. Changes of the FM and AFM diffraction peaks intensities for the sample with $y = 0.9$ with increase of external magnetic field from 0 to 40 kOe.

Obviously, the regions of mesoscopic dimensions cannot differ much by average charge and consequently, the stabilizing factor for the two-phase state must be another than the Coulomb interactions. Structural mechanism of stabilization[10] can be an alternative one. It assumes the significant differences in atomic structure of the coexisting crystallographic phases and as a result, appearance of the "strain fields in random orientation".[11] In fact, the comparative analysis of the crystal structures of the $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ samples enriched with ^{16}O and ^{18}O oxygen isotopes, first of which transformed at $T \leq 110$ K into mixed FM+AFM metallic state and the second remained dielectric with collinear AFM structure,[3,5] has shown that both the unit cell volume and the average values of the valence angles and interatomic distances $\langle Mn-O-Mn \rangle$ and $\langle Mn-O \rangle$ were visibly different. The analysis of the magnetic diffraction peaks shapes of our samples has shown their pronounced (30 %) broadening with increase of the FM-phase content in the samples, which may be connected with the appearance of inhomogeneous stresses at the grain boundaries.

Magnetic phase diagram of $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$, based on our and literature data, is shown in Fig. 4. The temperature of transition to ordered FM state (almost coinciding with the insulator-metal transition temperature), linearly decreases in the range of y values from 0 to 0.8 with increasing Pr content, or, which is the same, with decreasing $\langle r_A \rangle$. On the contrary, the temperature of AFM peaks appearance is practically independent of y, close to 130–140 K for all compositions, and AFM ordering is observed if $T_{AFM} \geq T_{FM}$. Analogous behavior of AFM and FM components was also observed for some other compositions undergoing I–M transition, for example, for $Pr_{0.65}(Ca_{0.7}Sr_{0.3})_{0.35}MnO_3$.[12] At the same time, if no transition into metal state takes place, i.e. for $y \geq 0.9$, then with decreasing temperature, gradual increase of the average values of ordered moments for both AFM and FM components is observed. Thus, the region of coexistence of FM- and AFM-ordering ($0.6 \leq y \leq 1.0$) is divided into two intervals with conditional border at $y \approx 0.85$ ($\langle r_A \rangle \approx 1.184$ Å). The low-temperature state of LPCM is either two-phase with spatially separated domains possessing metallic and insulating properties, or the major part of the sample volume is occupied by the insulating phase with homogeneous non-collinear magnetic ordering.

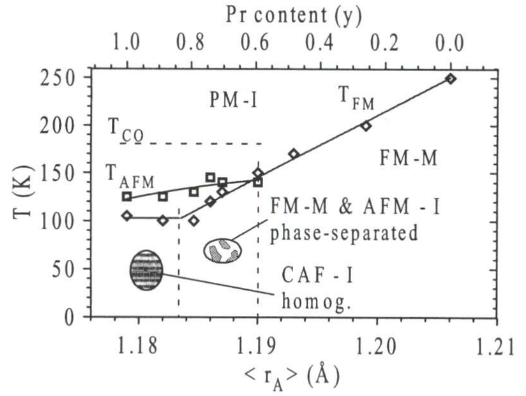

Fig.4. Magnetic phase diagram of $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$. PM-I is paramagnetic insulating region, FM-M is ferromagnetic metallic region, CAF-I is canted, antiferromagnetic region. FM-M & AFM-I is two-phase state.

In the recent paper[13] it was shown that the coexistence of metallic and dielectric clusters of mesoscopic sizes with equal charge density is possible due to the chemical composition fluctuations of the doped manganites. Such fluctuations are affecting, in particular, the conduction bandwidth.

However, our data show that the particular atomic structure of the appearing phases, arising lattice deformations and the possible crossover from two (or, multi phase) state to homogeneous one should also be taken into account.

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