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EFFECT OF OXYGEN ISOTOPE SUBSTITUTION ON MAGNETIC STRUCTURE OF (La$_{0.25}$Pr$_{0.75}$)$_{0.7}$Ca$_{0.3}$MnO$_3$

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Влияние изотопического замещения кислорода
на магнитную структуру $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$

Методом порошковой нейтронной дифракции исследовано влияние изотопического замещения кислорода на магнитную структуру и зарядовое упорядочение в манганите $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$. Установлено, что при комнатной температуре образцы этого соединения, один из которых содержал естественную смесь изотопов кислорода (99,7 % ^{16}O, металл при $T \leq 100$ K), а другой был обогащен на 75 % изотопом ^{18}O (изолятор во всем температурном диапазоне) являются кристаллографически идентичными. При понижении температуры образец с ^{16}O последовательно испытывает антиферро- ($T_{AFM} = 150$ K) и ферромагнитный ($T_{FM} = 110$ K) переходы, приводящие к установлению неколлинеарной ферромагнитной структуры, в то время как в образце с ^{18}O возникает чисто антиферромагнитный ($T_{AFM} = 150$ K) порядок. Температурные зависимости интенсивностей дифракционных пиков, связанных с зарядовым упорядочением, существенно разные в образцах с ^{16}O и ^{18}O и также коррелируют с поведением их электрического сопротивления. Прямых указаний на наличие фазового разделения с дальним порядком при низкой температуре не обнаружено.

Effect of Oxygen Isotope Substitution
on Magnetic Structure of $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$

The oxygen isotope effect on the magnetic structure and charge ordering in $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ was studied by neutron powder diffraction. At first it was found that two investigated samples, one of those contained the natural mixture of isotopes (99.7 % ^{16}O, metallic at $T \leq 100$ K), and the other one enriched by ^{18}O in 75 % (insulating in all temperature range) are identical at room temperature. At the temperature lowering the sample with ^{16}O undergoes subsequent antiferromagnetic ($T_{AFM} = 150$ K) and ferromagnetic ($T_{FM} = 110$ K) transitions, resulting in the non-collinear FM structure, while in the sample with ^{18}O the pure AFM ordering ($T_{AFM} = 150$ K) is found. The temperature dependencies of the diffraction peak intensities associated with charge ordering are also quite different in the samples with ^{16}O and ^{18}O and correlate with the behavior of the electrical resistivity and the magnetic structure. No indications of long-range phase segregation at low temperature were found.

Recent studies revealed a close interplay between transport (electrical) and magnetic properties of perovskite manganites $A_{1-x}A'_xMn^{3+}_{1-x}Mn^{4+}_xO_3$, where A=La, or a rare earth, A'= Ca, Sr etc. These compounds were widely known since the discovery of the colossal magnetoresistance (CMR) effect [1]. At room temperature these compounds are usually paramagnetic insulators (PI), and their low temperature state is ferromagnetic metal (FMM), or antiferromagnetic insulator (AFI) with a tendency to ordering of manganese charges (CO) (see, for example, Refs. [2–4].) The low temperature state is determined by a subtle balance of several interactions and can be modified by changing the composition or by external forces (pressure or magnetic field). The particular state depends on doping level, i.e. on the proportion of Mn^{3+}/Mn^{4+}, and on the relation between the Mn-O and A-O bond lengths which in turn depends on average A-cation radius ($<r_A>$).

It is clear now that for understanding of manganites physics a particular attention should be paid to the interplay between their electron and phonon subsystems. A variety of examples evidencing the importance of the electron-phonon interaction are discussed in a recent review [5], where this interaction is proposed as a key factor affecting the phase transitions in the CMR compounds. The isotope substitution is a direct experimental method to study the effect of lattice vibrations on physical properties. Several papers have already been published where the strong influence of ^{16}O for ^{18}O substitution on transport and magnetic properties was demonstrated for manganites. In the first papers on this subject (Zhao et al., [6,7]), it was found that the Curie temperature decreases by 21 K when 95% of ^{16}O is substituted by ^{18}O in the $La_{1-x}Ca_xMnO_3$ with x=0.2, which significantly exceeds the temperature shifts of magnetic and electronic phase transitions in the other earlier studied oxides like HTSC, and that magnetization and coefficient of thermal expansion of the series strongly depend on the isotope composition. Moreover, a metal-insulator transition induced by oxygen isotope substitution was reported for $(La_{0.5}Nd_{0.5})_{0.67}Ca_{0.33}MnO_3$ [8] and $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ [9,10]. The obtained results can not be described on the base of the classical double exchange model [11] solely, but should also take into account some additional effects.

The effect of the oxygen isotope substitution on ferromagnetic phase transition temperature T_C was studied in Refs. [12,13] for the series of $La_{1-x}Ca_xMnO_3$ with x in the range from 0.2 to 0.43, and it was shown that the value of the negative shift of T_C
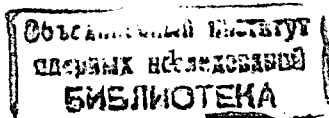
evidently depends on $\langle r_A \rangle$. The influence of oxygen isotope substitution on the insulator-metal transition induced by the external magnetic field was studied in Ref. [14]. The initial insulating state of $Pr_{2/3}Ca_{1/3}MnO_3$ samples with ^{16}O and ^{18}O isotopes was transformed to the metallic one by applied magnetic field, but in the case with ^{18}O the magnitude of magnetic field inducing I-M transition was much higher. Ibarra et al. [15] have carried out the analysis of the oxygen isotope-effect in $(La_{0.5}Nd_{0.5})_{0.67}Ca_{0.33}MnO_3$ compound, which, as it was found before [8], is insulator down to helium temperatures in the case of ^{18}O, while ^{16}O sample undergoes the I-M transition at $T \approx 150$ K. The identical sequence of charge ($T_{CO} \approx 210$ K) and magnetic ordering was found for both isotopic samples: FM at $T_{FM} \approx 200$ K and AFM at $T_{AFM} \approx 170$ K [15]. However strong difference was observed in the magnetic behavior: the FM-contribution to nuclear peaks intensities was much lower in the ^{18}O sample than in the ^{16}O sample.

According to the literature data the insulator-metal (I-M) phase transition is observed in $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$, with natural oxygen isotope content, for $y \leq 0.75$, while for $y = 1$ the compound is insulator in the whole temperature range. It was shown in Ref. [10], that the composition with $y=0.75$ is close to the phase boundary between metal and insulating states, that is conditioned by the critical value of tolerance factor of perovskite structure for this compound ($t \approx 0.91$). As a result, the low-temperature state can be easily modified even by relatively weak effect of the oxygen isotope substitution. It was shown [9], that the composition with natural content of oxygen isotopes (99.7% ^{16}O) becomes metallic at $T \approx 100$ K, while the $^{16}O - ^{18}O$ exchange resulted in the insulating state down to 4 K like it was observed for $(La_{0.5}Nd_{0.5})_{0.67}Ca_{0.33}MnO_3$ [8]. A possible microscopic model of such transition was discussed in Ref. [10] in terms of the isotope dependence of the effective electron bandwidth near the I-M phase boundary.

In our previous neutron diffraction study of $(La_{0.5}Pr_{0.5})_{0.7}Ca_{0.3}MnO_3$ with natural oxygen isotope content [16] it was shown that the phase transition to the metallic state occurs simultaneously with FM ordering, and is accompanied by a jump in the unit cell volume and «melting» of the orbital ordering of Mn-O bonds. In the present paper we continue the study of the $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ system and report new experimental data obtained for the compound with $y=0.75$ by the neutron diffraction technique. Two oxygen isotope samples of this compound have been studied: the first one (O-16 sample hereafter) contained the natural mixture of isotopes (99.7% ^{16}O, metallic at $T \leq 100$ K) and in the other one (O-18 sample hereafter) 75% of oxygen was substituted by ^{18}O (insulating in the whole temperature range). The main goal of the study was to find out the changes in magnetic structure accompanying the colossal isotope-effect in this compound.

The powder samples for neuron diffraction experiments were prepared by means of the so-called «paper synthesis». For this, an aqueous solution of a mixture of La, Pr, Ca, and Mn nitrates taken in the required ratios was deposited on ahs-free paper filters, which were dried (120°C) and then burned. The oxide product thus obtained was annealed in air at 700°C for 2 h. The final thermal treatment consisted of annealing pressed pellets in air at 1200°C for 12 h. Then two pellets of about 5 g weight were placed in alumina boats which were mounted in the furnace inside two quartz tubes. Both samples were treated simultaneously: one sample was heated in natural $^{16}O_2$ atmosphere, the other one was heated in $^{18}O_2$ atmosphere (the molar fraction of $^{18}O_2$ was 85%). The diffusion annealing was carried out at 950°C under oxygen pressure of 1 bar. Oxygen atmosphere in the contour was renewed 11 times. The whole time of annealing was 100 h. The final ^{18}O oxygen content in the O-18 sample was 75%. It was determined from the weight changing and mass-spectroscopy analysis of oxygen atmosphere in the contour.

Neutron diffraction experiments on the magnetic structure determination were carried out on DMC diffractometer at the SINQ spallation neutron source at PSI. The diffraction patterns were measured in the regime of sample heating from 12 K to 293 K. The samples were packed into the vanadium containers filled with helium. The magnetic structure was refined from the diffraction spectra measured at the wavelength $\lambda=2.5616$ Å in the range of scattering angles $10<2\theta<90°$, corresponding to d_{hkl} region from 1.8 to 14.7 Å by the Rietveld method (FullProf program, $Pnma$ space group).

It is evident, that the necessary condition of correct comparison of the results obtained on the samples with isotope substitution is their structural identity. Rietveld refinement of the diffraction patterns at room temperature showed, that the O-16 and O-18 samples are indeed identical, in particular with respect to oxygen content with the accuracy ±0.03. The comparison of the unit cell parameters for both samples gives even better matching for the oxygen content. The unit cell parameters measurement was performed at TOF High Resolution Fourier diffractometer (HRFD) in Dubna [17], and gave for room temperature the following results: $a=5.45657(7)$ Å, $b=7.69294(9)$ Å, $c=5.44788(8)$ Å for O-16 and $a=5.45673(6)$ Å, $b=7.69315(8)$ Å, $c=5.44786(7)$ Å for O-18, i.e. the unit cell parameters coincide within accuracy 0.002 – 0.004%. The comparison of these values with known unit cell parameters dependencies on oxygen content for manganites (for example, see Ref. [18]) gives that the difference in the oxygen content in O-16 and O-18 samples is less than ± 0.002. The result of chemical analysis of O-16 and O-18 samples, performed by the iodometric titration method [19], is in accordance with this estimation: oxygen content corresponds to $x=2.995\pm0.008$ in O-16, and $x=2.996\pm0.005$ in O-18 samples for the general formula $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_x$.
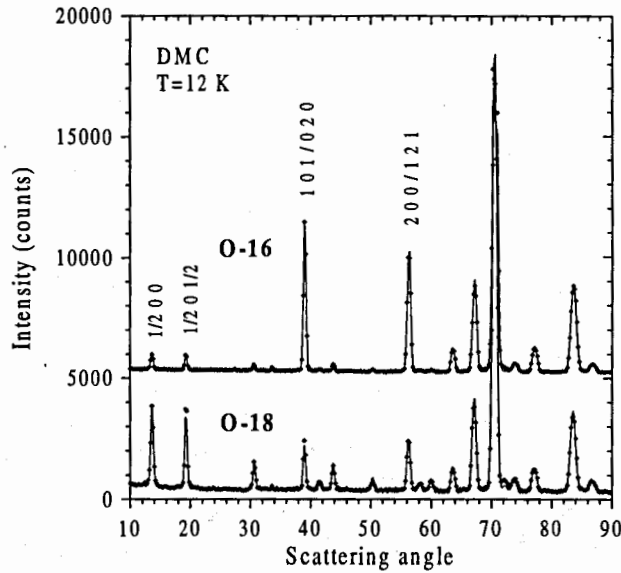
Fig.1. Diffraction patterns of the O-16 (top) and O-18 (bottom) samples measured with DMC at T=12 K. For the O-16 pattern the y-scale is shifted by 5000 counts. The Miller indices highlight the most intensive AFM and FM peaks. At 12 K the AFM intensity, (1/2 0 0) and (1/2 0 1/2) peaks, is much higher for O-18 sample, whereas for O-16 sample the intensity of FM peaks, (101) / (020) and (200) / (121), is high.

The neutron diffraction patterns for O-16 and O-18 measured at room temperature at DMC diffractometer are identical in the range of reached statistical accuracy (about 50000 counts in the most intensive peaks). Superlattice reflections such as (1/2 0 0) at $2\theta=13.6°$ and (1/2 0 1/2) at 19.2° associated with antiferromagnetic (AFM) ordering appeared with the decreasing temperature (Fig. 1) for both samples. The intensities of these peaks are significantly higher for the O-18 sample at $T=12$ K. In the neutron diffraction pattern of O-16 sample at $T=12$ K an increased contribution to the nuclear Bragg peaks (101)/(020) and (200)/(121) at $2\theta =39°$ and 56° due to the ferromagnetic (FM) ordering is clearly observed. The temperature dependencies of AFM and FM peak intensities for the both samples are displayed in Fig. 2. The intensity monotonically increases with decreasing temperature for the O-18. For O-16 sample this dependence is non-monotonic with a maximum at $T≈110$ K, which correlates with appearance of FM component in respective Bragg peaks. The intensity of (101)/(020) peak for O-16 sample has (Fig. 2b) small decrease below 50 K, which can be interpreted as a result of magnetic ordering of Pr atoms like in Refs. [20] and [4]. For the O-18 sample, FM-contribution to the diffraction peaks is absent in the whole temperature range within reached statistical accuracy (~1.3%).
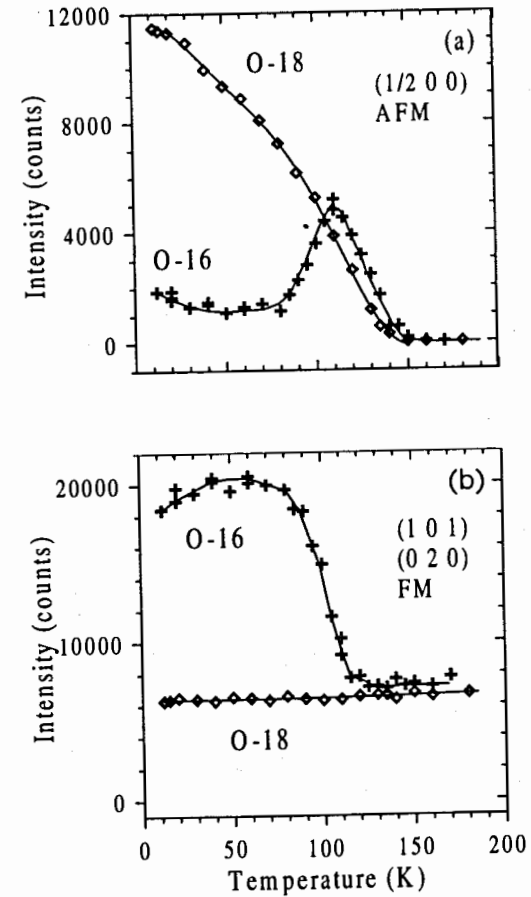

Fig.2. Temperature dependencies of the intensities for the characteristic diffraction peaks of the O-16 and O-18 samples: (1/2 0 0) AFM-peak (a), (101)/(020) FM-peaks (b). Decreasing of the (101)/(020) intensities at T < 40 K for the O-16 sample is believed to be connected with the Pr magnetic moments ferromagnetic ordering. The lines are guides to the eye.

The refinement of the O-16 sample magnetic structure was performed in the model of two antiferromagnetic phases (AFM1 and AFM2) and ferromagnetic phase (FM) with magnetic moments on Mn-atoms. The AFM1-phase peaks can be indexed using the k=(1/2 0 0) or k=(0 0 1/2) propagation vectors (doubling of the a or c unit cell directions), AFM2-phase peaks can be described using the k=(1/2 0 1/2) propagation vector (both a and c parameters are doubled). The refinement of the O-18

sample magnetic structure was done in the same way, but without FM-component. The values of the Mn magnetic moments practically do not depend on their orientation within experimental accuracy. Testing of different variants of moment orientation along the basic directions of the unit cell gave the best matching between measured and calculated intensities for the orientation of the Mn-moment along b-axis in AFM-phases, and along c-axis in FM-phase. The temperature dependencies of the μ_{AFM1}, μ_{AFM2}, μ_{FM} magnetic moments are presented in Fig. 3. The magnetic structure in O-16 sample may be described as noncollinear canted structure, like it was observed for $Pr_{0.7}Ca_{0.3}MnO_3$ [4] and $Pr_{0.65}(Ca_{0.7}Sr_{0.3})_{0.35}MnO_3$ compositions [21]. The complete suppression of the ferromagnetic component in the O-18 sample means that isotope substitution does not lead to a simple shift of transition temperature along magnetic phase diagram $T_{FM}(<r_A>)$, but results in the completely new magnetic state. This type of ordering has not been observed before in Pr manganites with 30% doping level and natural oxygen isotopes content.
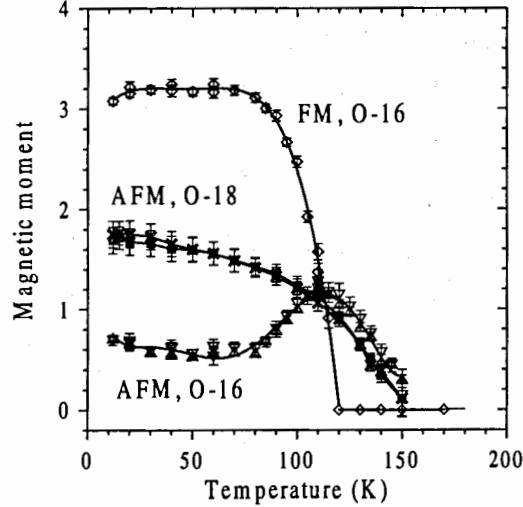

Fig.3. Temperature dependencies of the Mn magnetic moments (in Bohr magnetons) for the FM- and AFM-components of the O-16 sample and for the AFM-components of the O-18 sample. For O-16 sample some of the points were measured twice. The values of the AFM-moments for the O-18 sample for both propagation vectors coincide within the error bars. The lines are guides to the eye.

In both samples, appearance of weak superlattice reflections of (3/2 0 2) type at $T_{CO} \approx 180$ K (Fig. 4) precedes AFM-ordering ($T_{AFM} \approx 150$ K). Appearance of these reflections is believed to be connected with the charge ordering (CO) of Mn^{3+}/Mn^{4+} cations, leading to the doubling of the a axis and lowering of the symmetry to the

monoclinic $P2_1/m$ space group [22]. This effect was thoroughly studied in $Pr_{0.7}Ca_{0.3}MnO_3$ [4,23] and $La_{0.5}Ca_{0.5}MnO_3$ compositions [22].
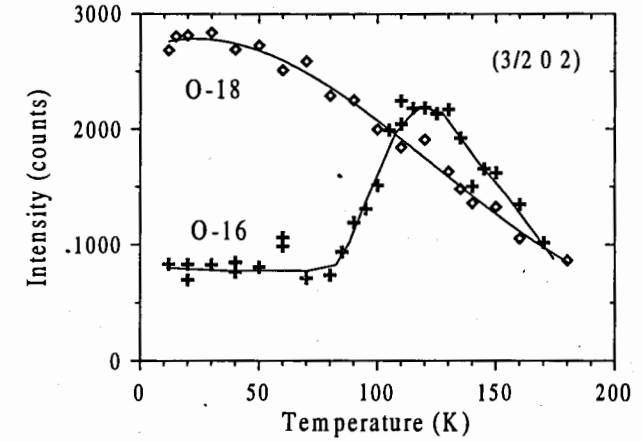

Fig.4. Temperature dependencies of the (3/2 0 2) CO-peak intensity for the O-16 and O-18 samples. At room temperature this peak is absent. For the O-16 sample some of the points were measured twice. The lines are guides to the eye.

The temperature dependencies of the unit cell parameters for both samples were measured at HRFD instrument in Dubna, which high resolution ($\Delta d/d \approx 0.0015 - 0.0018$ in the working range of wavelengths) allowed to obtain high precision data. Several distinctive features are easily seen in the dependencies presented in Fig. 5, which correlate with behavior of the magnetic structure and the electrical properties. In both samples the temperature dependencies of the unit cell parameters are identical between the room temperature and the transition temperature of O-16 sample to metallic state. Moreover, their absolute values are practically the same. Any anomalies of the behavior of unit cell volume are absent, although a and b parameters have non-linear dependencies close to T_{CO} charge ordering temperature. Similar behavior of a and b parameters was found and qualitatively interpreted by Cox et al. [4] for $Pr_{0.7}Ca_{0.3}MnO_3$ compound. Antiferromagnetic ordering at $T_{AFM} \approx 150$ K is not revealed in the temperature dependencies of lattice parameters. At the temperature of FM ordering, $T_{FM} \approx 110$ K, b parameter, and to some extent, c parameter of O-16 sample have well observed sharp jump which is also well visible in $V_c(T)$ dependence. This behavior corresponds to the transition from a high-volume to a low-volume state at phase transition from insulating to metallic state as it was pointed in Ref. [15].

Unlike to Ref. [4], we did not observe significant effects of diffraction peak broadening, in spite of high resolution of the HRFD instrument. Small peak broadening (at a level of 10%) was observed in the temperature range from 110 K to 200 K for O-16 sample, i.e. between T_{FM} and T_{CO}, whereas the O-16 and O-18

samples peak widths are identical at room and $T<T_{FM}$ temperatures. This fact allows us to conclude that in both samples no long-range phase segregation takes place in the whole studied temperature interval. Also, the FM moment of the O-16 sample is too large to be consistent with a simple two-phase model, but we cannot exclude the existence of the liquid-like ferromagnetic clusters as discussed in Ref. [24].
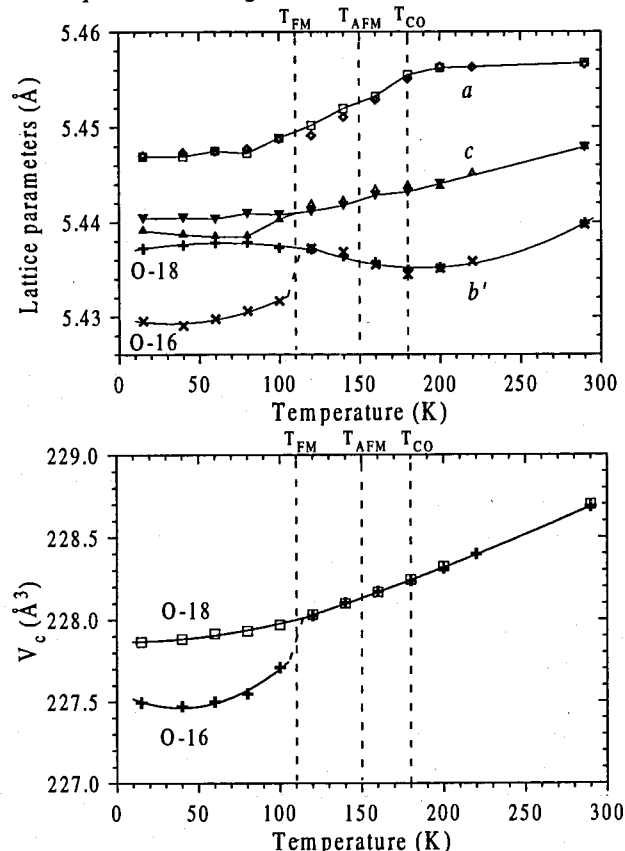

Fig.5. Temperature dependencies of lattice parameters (top) and unit cell volume (bottom) for the O-16 and O-18 samples ($b'=b/\sqrt{2}$). Between T_{FM} and room temperature, there is practically no difference between the parameters. The identity of the a unit cell parameter is preserved in the whole temperature range. The solid lines are guides to the eye.

In conclusion, the results of neutron diffraction study of two $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ samples enriched by oxygen ^{16}O and ^{18}O isotopes are presented. It is shown, that at room temperature the samples are structurally identical. Below $T = T_{CO} \approx 180$ K, charge ordering develops in both samples. Antiferromagnetic

ordering of manganese magnetic moments is observed below $T = T_{AFM} \approx 150$ K with propagation vectors (1/2 0 0) or (0 0 1/2) and (1/2 0 1/2). CO- and AFM-ordering processes are developed identically in both samples down to 110 K. Below $T_{FM} \approx 110$ K the magnetic structure changes in O-16 sample, leading to the appearance of FM component of ordered manganese magnetic moments, decreasing of AFM-components, and partial destroying of the charge ordered state. We emphasize that oxygen isotope substitution did not affect T_{CO} and T_{AFM}. We did not find any traces of long-range phase segregation in both O-16 and O-18 samples at low temperature. Moreover, the width of diffraction peaks and saturated value of magnetic moments indicate that the samples are macroscopically uniform. These results prove, that the low temperature state of the $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ is indeed governed by the strong electron-phonon interaction. And thus we suggest that the sole variation of oxygen mass is responsible for both the change in electronic state (metal-insulator) and alteration of correlated magnetic state (noncollinear ferromagnetic - pure antiferromagnetic).

References

1. S.Jin, M.McCormac, T.H.Tiefel, and R.Ramesh, J. Appl. Phys. **76**, 6929 (1994).
2. C.N.R.Rao, A.K.Cheetham, and R.Mahesh, Chem. Mater. **8**, 2421 (1996).
3. A.P.Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1997).
4. D.Cox, P.G.Radaelli, M.Marezio, and S.-W. Cheong, Phys. Rev. **B57**, 3305 (1998).
5. A.J.Millis, Nature (London) **392**, 147 (1998).
6. G.M.Zhao, K.Conder, H.Keller, and K.A.Muller, Nature (London) **381**, 676 (1996).
7. G.M.Zhao, M.B.Hunt, and H.Keller, Phys. Rev. Lett. **78**, 955 (1997).
8. G.M.Zhao, H.Keller, J.Hofer, A.Shengelaya, and K.A.Muller, Sol. St. Comm. **104**, 57 (1997).
9. N.A.Babushkina, L.M.Belova, O.Yu.Gorbenko, A.R.Kaul, A.A.Bosak, V.I.Ozhogin, and K.I.Kugel, Nature (London) **391**, 159 (1998).
10. N.A. Babushkina, L.M.Belova, V.I.Ozhogin, O.Yu.Gorbenko, A.R.Kaul, A.A.Bosak, D.I.Khomskii, and K.I.Kugel, J. Appl. Phys. **83**, 7369 (1998).

11. C.Zener, Phys. Rev. **82**, 403 (1951)

12. I. Isaac and J.P. Franck, Phys. Rev. **B57**, R5602 (1998).

13. J.P. Frank, I. Isaac, W.Chen, J. Chrzanowski, and J.C. Irwin, Phys. Rev. **B58**, 5189 (1998).

14. B.Carcia-Landa, M.R.Ibarra, J.M.De Teresa, G.M.Zhao, K.Konder, and H.Keller, Solid St. Comm. **105**, 567 (1998).

15. M.R. Ibarra, G.M.Zhao, J.M.De Teresa, B. Garcia-Landa, Z.Arnold, C.Marquina, P.A.Algarabel, H.Keller, and C.Ritter, Phys. Rev. **B57**, 7446 (1998).

16. A.M.Balagurov, V.Yu.Pomjakushin, V.L.Aksenov, N.M.Plakida, N.A.Babushkina, L.M.Belova, O.Yu.Gorbenko, A.R.Kaul, P.Fischer, M.Gutmann, and L.Keller, JETP Letters **67**, 705 (1998).

17. V.L.Aksenov, A.M.Balagurov, V.G.Simkin, A.P.Bulkin, V.A.Kudriashev, V.A.Trounov, O.Antson, P.Hiismaki, and A.Tiitta, J. Neutron Research, **5**, 181 (1997).

18. C.Ritter, M.R.Ibarra., J.M.De Teresa, P.A.Algarabel, C.Marquina, J.Blasco, J.Garcia, S.Qseroff, and S.-W.Cheong, Phys. Rev. **B56**, 8902 (1997).

19. I.G.Krogh Andersen, E.Krogh Andersen, P.Norby, and E.Skou, J. Solid State Chem., **113**, 320 (1994).

20. Z.Jirak, S.Vratislav, and J.Zajicek, phys. stat., sol. (a) **52**, K39 (1979).

21. H.Yoshizawa, R.Kajimoto, H.Kawano, Y.Tomioka, and Y.Tokura, Phys. Rev. **B55**, 2729 (1997).

22. P.G.Radaelli, D.E.Cox, M.Marezio, and S.-W. Cheong, Phys. Rev. **B55**, 3015 (1997).

23. H.Yoshizawa, H.Kawano, Y.Tomioka, and Y.Tokura, Phys. Rev. **B52**, R13145 (1995).

24. M.Hennion, F.Moussa, G.Biotteau, J.Rodriguez-Carvajal, L.Pinsard, and A.Revcolevschi, Phys. Rev. Lett. **81**, 1957 (1998).