Spin and lattice dynamics in pure and ^{57}Fe substituted $La_{0.67}Ca_{0.33}MnO_3$

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The optimally doped colossal magnetoresistance (CMR) perovskite $La_{0.67}Ca_{0.33}MnO_3$ exhibits a ferromagnetic to paramagnetic transition and a simultaneous metal to insulator transition at $T_C = 280K$. The Fe-doping into Mn sublattice replaces exclusively Mn^{3+} by Fe^{3+} what suppresses double exchange by reduction Mn^{3+}/Mn^{4+} ratio. In result, both T_C and metal-insulator transition temperature (T_{M-I}) decrease with increasing Fe doping. At T_{M-I} strong electron-phonon coupling was predicted. The Fe-doping dramatically enhances magnetoresistance. The ^{57}Fe isotope as a local probe witnesses the dynamics of the Mn lattice which was the aim of our study. Powder X-ray diffraction (XRD) method has been used to study the structure and lattice parameters *vs*. temperature. The XRD measurements as a function of temperature were performed on Siemens D5000 diffractometer (Cu K_α). Lattice constants *vs*. temperature in a range LHe-RT are presented in Fig. 1b. From these results the volume expansion coefficient α ($\alpha = \Delta V/\Delta T \cdot 1/V$) was calculated. The α *vs*. temperature for $x = 0.01$ has a sharp maximum at T_{M-I}, which diminishes with x, and is very broad and weak for $x = 0.03$ [1].

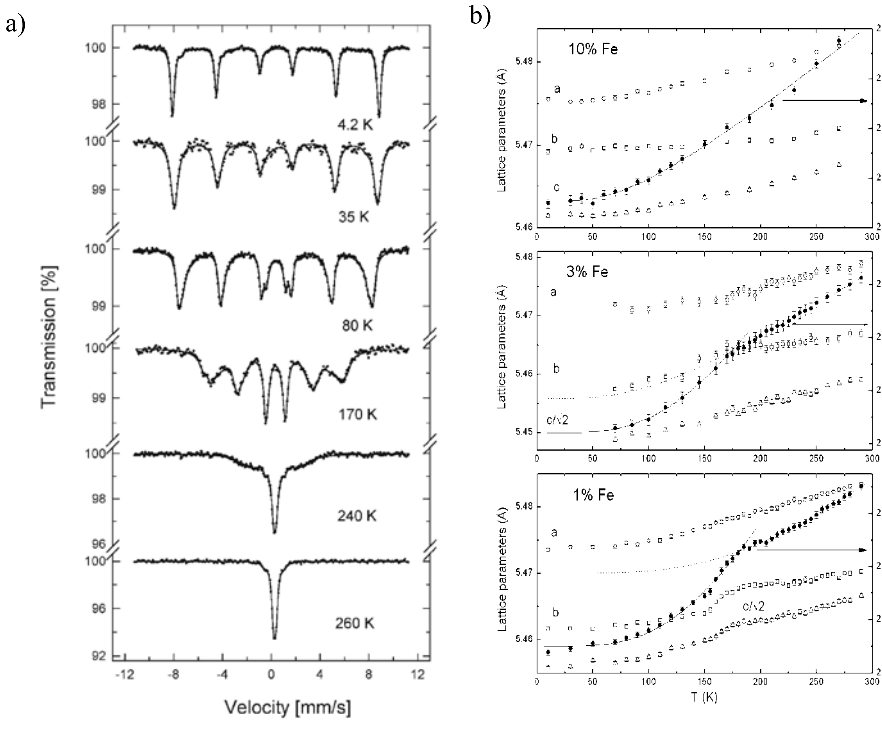

Fig. 1 a) Temperature variation of $La_{0.67}Ca_{0.33}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ Mössbauer spectra. b) Lattice parameters and unit-cell volume *vs*. temperature for $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$ with $x = 0.01$, 0.03 and 0.10.

Mössbauer spectra (MS) of $La_{0.67}C_{0.33}(Mn_{1-x}{}^{57}Fe_x)O_3$ (x = 0.01, 0.03, 0.05) were measured in transmission geometry using ^{57}Co(Rh) source (Fig.1a). Spectra were fitted with arbitrary number of Zeeman patterns to obtain the area over the spectrum with best possible accuracy, and relative value (relative to lowest temperature measured) of the *f*-factor was determined. Results are presented in Fig. 2. The low and high temperature ($-\ln f/f_o$) values were fitted within the Debye approximation and the Debye temperatures θ_D were obtained (Fig. 2). Mössbauer spectra were also fitted with hyperfine field distribution programme. Maximum and average values were determined and are plotted *vs*. temperature in Fig. 3.

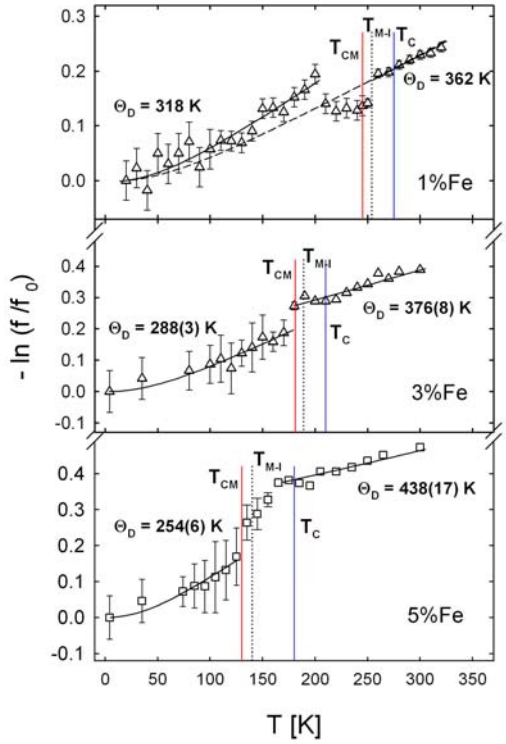

Fig. 2. Temperature variation of the $-\ln(f/f_0)$ for $La_{0.67}Ca_{0.33}Mn_{1-x}{}^{57}Fe_xO_3$ with x = 0.01, 0.03, 0.05

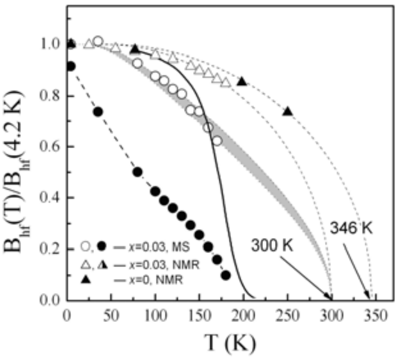

Fig. 3. The normalised maximal values of the ^{57}Fe hyperfine field $B_{hf}^{\max}(T)\,/\,B_{hf}^{\max}(4.2)$ (empty circles) from MS, $B_{hf}(T)/B_{hf}(4.2)$ (empty triangles) from ^{55}Mn NMR measurements *vs*. T for x=0.03 and $B_{hf}(T)/B_{hf}(4.2)$ (full triangles) *vs*. T from NMR measurements for x=0.0. Dashed curves indicate the best fits of the experimental data with Brillouin functions for S = 1.83. Solid line shows normalized magnetization ($M(T)/M(4.2)$) *vs*. T data, measured at H=100 Oe for x=0.03. Filled circles represent the normalised ^{57}Fe mean hyperfine field $\langle B_{hf}(T)\rangle/\langle B_{hf}(4.2)\rangle$

Hyperfine fields on ^{55}Mn were in addition measured with NMR technique. B_{hf} vs. T are presented in Fig.3. In conclusion, our X-ray diffraction results for x = 0.01 and 0.03 samples show that iron doping has strong and negative influence on the sharpness of the M-I transition. Contrary and unexpected effect was found in $-\ln f/f_o$ vs. T dependence (Fig.2) and could be correlated with increasing absorber effective thickness and/or its optical inhomogeneity with increasing ^{57}Fe concentration. This possibility has been excluded by additional experiment on a specially prepared sample with 9 at% natural iron but only 1 at% of ^{57}Fe isotope substitution for Mn (thin absorber limit). Finally, the $-\ln f/f_o$ *vs.* T dependence for x = 0.01, which is related to $\langle u^2\rangle$ *vs.* T dependence and gives information how strongly the Mössbauer probe is bounded to the Mn-O-Mn lattice, does not show any evidence of abnormal increase at T_{M-I} and in result does not reveal any softening of this bound. One can understand this important and rather surprising result by stressing the difference in meaning of Mössbauer $\langle u^2\rangle$ which is probing dynamics (strengths of bonding) of Mn sublattice and $\langle u^2\rangle$ from X-ray/neutron diffraction or

EXAFS measurements which are additionally sensitive to static disorder. In summary no clear anomaly in dynamics of the Mn sublattice was found by ^{57}Fe Mössbauer probe at T_{M-I} what means that instead of dynamics rather static effects (in the time window of Mössbauer Spectroscopy) are responsible for anomalous increase of manganese or oxygen Debye-Waller factors seen by other methods.

The NMR and Mossbauer spectroscopy study of $La_{0.67}C_{0.33}(Mn_{1-x}{}^{57}Fe_x)O_3$ compounds provided information on the strength of the Mn-Mn and Fe-Mn exchange integrals. For $x = 0.03$ the Mn-Mn and Fe-Mn exchange integrals amount to 1.24 meV and –0.62 meV, respectively. Such a doping with Fe gives rise to a reduction of the strength of the Mn-Mn double exchange interaction by approximately 13%. Finite values of the Mn hyperfine fields at the magnetic ordering temperatures obtained from magnetisation measurements revealed the coexistence of the DE controlled metallic clusters with a paramagnetic insulating phase. This provides a mixed phase character of the magnetic transition, unlike that in classical ferromagnets. The real Curie temperatures, which correspond to $<S_z>$ decreasing to zero within the ferromagnetic clusters, were derived as 300 K for the Fe doped and 346K for the undoped compound. They are much higher than the Curie temperatures obtained from magnetization measurements, which should rather be called blocking temperatures if the relaxation process observed is approximated with superparamagnetic relaxation (see Fig.3).

The electron photoemission spectra XPS/UPS from core- levels as well as from the valence bands of the (La,Ca)-Mn-O manganese perovskites have been measured in insulating paramagnetic state at 300 K. The results are presented and analyzed in our paper [2]. As examples the low binding energy XP spectra and the Mn 2*p* core–level spectra of $La_{0.67}Ca_{0.33}MnO_3$, $La_{0.63}Ca_{0.37}Mn_{0.92}Fe_{0.08}O_3$ and $(La_{0.57}Tb_{0.10})Ca_{0.33}MnO_3$ are shown in Fig. 4.

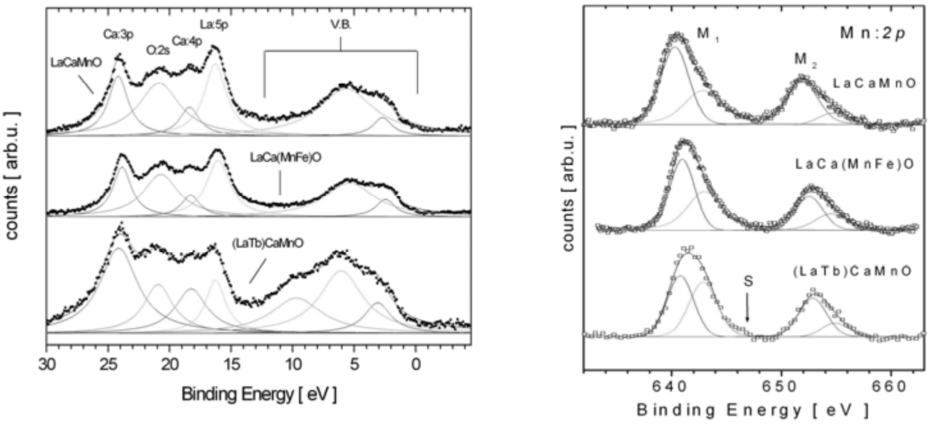

Fig.4. Low binding energy XP (Mg- K_α) spectra and the Mn 2*p* core-level XP (Al- K_α) spectra of the given compounds (for more results see [2])

From those results the following conclusions were drown:

1. Two peaks at 3.5 eV and 5.7 eV in the valence band (VB) spectra arise mainly from the Mn 3*d* states and the O 2*p* states, respectively. Mn $3d$-e_g states and to some extent Mn $3d$-t_{2g} also participate in VB mostly close to the Fermi level, whereas the O *2p* states are important to the lower energy part of VB. These spectral signatures arise most likely from hybridised Mn $3d$-t_{2g} - O 2*p* states. An additional intensity at about 9.5 eV binding energy observed for Tb–doped specimen can possibly be attributed to the Tb 4*f* states and/or some contribution from the La 5*d* electrons. An analysis of the relative changes of the density of states in the gap near the band edges between metallic ferromagnetic state at 80 K and

insulating paramagnetic state at 300K shows that the effect of temperature is very small. A very small intensity at E_F above T_C indicates an insulating phase in the paramagnetic state of the compounds.

2. The exchange energy ΔE_{ex} = 5.2 eV deduced from Mn 3*s* spectra is in between those of Mn_2O_3 and of MnO_2 that is for Mn^{3+} and Mn^{4+} ions, respectively. It proves the existance of 3+ and 4+ manganese valency in these compounds rather than high- spin configurations of both manganese ions.

3. From the combined analysis of Mn- 2*p* spectrum M_1 and its satelitte S together with the Mn- $L_{2,3}M_{2,3}M_{4,5}$ Auger spectrum the on-site Coulomb correlation energies U_{dd}, U_{pp} and the charge transfer energy Δ have been estimated to be $U_{dd} \cong 6.4$ eV, $U_{pp} \cong 8.7$ eV and $\Delta \cong 3.5$ eV assuming the hybridisation energy $T \cong 2$ eV . Since $U_{dd} > \Delta$ the charge- transfer insulator-like description of the compounds rather than the Mott- Hubbard insulator-like behaviour is favoured according to Zaanen- Sawatzky - Allen phase diagram.

Recently, we have performed also the electron spin resonance (ESR) studies, at 9.5 GHz ($\tau \cong 10^{-10}$ s), on the iron-substituted manganite polycrystalline samples $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_{3+\delta}$ with x = 0, 0.01, 0.03, 0.06, 0.10 and 0.15 prepared by the wet sol-gel method and solid state reaction [3]. The aim was to search for dynamic properties of the clusters coupled via double exchange (D-E) interaction between Mn^{3+} and Mn^{4+} ions. Up to now, we have restricted the analysis of our measurements to the electron paramagnetic spectra (EPR) shown as examples below.

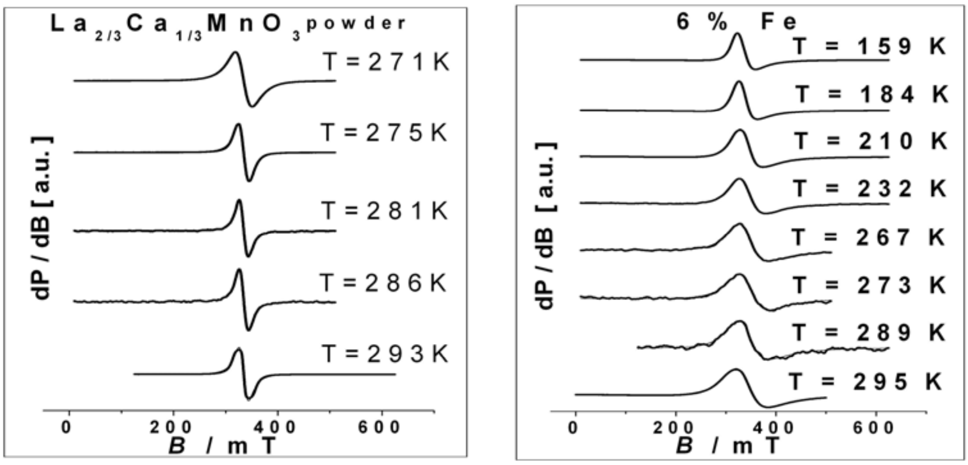

Fig. 5 Examples of temperature dependence of ESR spectra for $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$ for x = 0 and 0.6. Solid lines show the fitting (see [3])

The main conclusion from the data was that the EPR line comes entirely from the clusters and that the EPR measures an average Mn^{3+}- Mn^{4+} state due to the jumping of an electron between them. With increasing concentration of Fe, which is in the Fe^{3+} ionic state, the concentration of the Mn^{3+}ions decreases mainly within the ferromagnetic clusters. Because the EPR line width increases with temperature and concentration of Fe, *i.e.* the cluster spin - lattice relaxation time decreases, we conclude that the substitution by iron weakens the double exchange interaction.

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[1] J. Żukrowski, J. Przewoźnik, E. Japa, K. Krop, K. Kellner and G. Gritzner, *Dynamics of* $La_{2/3}Ca_{1/3}MnO_3$ *doped with* ^{57}Fe, Acta Physica Polonica B 34 (2003) 1521-1526.

[2] R. Zalecki, A. Kolodziejczyk, C. Kapusta and K. Krop, *Electronic states of* $La_{1-x}Ca_xMnO_3$ *from photoemission spectroscopy,* J. of Alloys and Compounds, **328** (2001) 175-180 and references cited therein.

[3] T. Zając, L. Folcik, A. Kołodziejczyk, H. Drulis, K. Krop, G. Gritzner, *Electron Spin Resonance in iron-substituted manganites* $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$, J. Magn..Magn.Matter. (2004) (in print).

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