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DYNAMICS OF $La_{2/3}Ca_{1/3}MnO_3$ DOPED WITH ^{57}Fe*

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The lattice dynamics of the $La_{2/3}Ca_{1/3}Mn_{1-x}Fe_xO_3$ system was studied with Mössbauer Spectroscopy in the temperature interval from 4 K to RT. Relative Lamb–Mössbauer factor *vs* T was determined for $x = 0.01$, 0.03 and 0.05. The $-\ln(f/f_0)$ *i.e.* the mean square-displacement of the Mössbauer atom from its equilibrium lattice position shows anomalous behaviour in the vicinity of T_{C} or metal–insulator transition temperature $T_{\mathrm{M-I}}$. In the Debye approximation the $-\ln(f/f_0)$ results give higher Debye temperatures Θ_{D} for the paramagnetic-insulating phase (PI) than for the ferromagnetic-metallic (FM) phase.

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The physical properties of the colossal magnetoresistive (CMR) perovskite $La_{1-x}Ca_xMnO_3$ (LCMO) are still a hot topic in many laboratories. The $La_{2/3}Ca_{1/3}MnO_3$ has the highest Curie temperature ($T_{\mathrm{C}} \approx 289\ K$) [1], which means that the double exchange (DE) with high mobility of electrons between Mn^{3+} ($t^3_{2g}e^1_g$) and Mn^{4+} ($t^3_{2g}e^0_g$) is the dominant process leading to a ferromagnetic order and to metalicity below T_{C}. Above T_{C} this compound is the charge-transfer insulator [2]. Fe-doping into Mn sublattice replaces exclusively Mn^{3+} by Fe^{3+} what suppresses DE by reduction of the Mn^{3+}/Mn^{4+} ratio. As a result magnetisation, T_{C} and metal–insulator transition temperature $T_{\mathrm{M-I}}$ decrease but magnetoresistance dramatically increases with increasing Fe-doping.

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Lattice dynamics of LCMO was studied with elastic neutron diffraction [3] showing anomalous behaviour of the O and Mn Debye–Waller factors at T_C. Also the EXAFS studies [6,7] show an anomalous increase of the Debye–Waller factor (σ^2[Mn–O]) when approaching T_C for $x = 0.33$. Recently, inelastic neutron scattering studies [5] revealed anomalous dumping of the Jahn–Teller (JT) stretching mode when approaching T_C from the FM side. Most probably, this effect is due to the appearance of (short range) dynamic JT distortions in the FM state in the vicinity of T_C.

The aim of our studies is to determine how the relative Lamb–Mössbauer factor changes with temperature, especially when crossing from the FM to PI state. At increasing substitution level we expect also systematic changes of the lattice dynamics of Mn due to a strong Fe doping effect.

Measurements were done on $La_{2/3}Ca_{1/3}Mn_{1-x}{}^{57}Fe_xO_3$ samples with $x = 1, 3, 5$ at. % ^{57}Fe prepared by a wet sol-gel technique and described elsewhere [8]. Another set of samples with $x = 1$ and 3 at. % Fe for XRD studies was prepared by the same method. The oxygen stechiometry was controlled by thermogravimetry and was very close to 3 [9]. Temperature dependent XRD measurements in the temperature range 4–300 K were performed on a Siemens D5000 diffractometer equipped with an Oxford continuous flow cryostat. Mössbauer spectra were measured in transmission geometry with a constant acceleration spectrometer and a ^{57}Co/Rh source. The temperature of the absorber was stabilised in a continuous flow cryostat or a cryodyne refrigeration system with an accuracy better than ± 0.1 K.

The temperature evolution of selected Mössbauer spectra measured between 4.2 K and RT for $La_{2/3}Ca_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ sample is shown in Fig. 1. At 4.2 K they display a normal six-line spectrum for the ferromagnetic state. As temperature increases a line broadening appears which increases gradually with temperature until the spectrum collapses to a paramagnetic single line. To obtain magnetic ordering temperatures T_{CM} the spectra at high temperatures were fitted with a single line. Rapid increase of the fitted FWHM of the line below certain temperature clearly indicates the onset of a ferromagnetic order in the sample. T_{CM} were defined as intersection points between straight lines fitted to FWHM points belonging to paramagnetic and magnetically ordered regions.

To obtain the temperature dependence of Lamb–Mössbauer factor f the spectra were fitted by an arbitrary number of components with the main purpose to reproduce in the best possible accuracy the shape of the spectra. To take into account the absorber effective thickness the fitting program based on transmission integral was used. For a given spectrum the parameter $-\ln(f/f_0)$ was calculated, where f_0 denotes f at the lowest temperature measured. It represents the mean square displacement (msd) difference $\langle u^2\rangle - \langle u_0^2\rangle$, where $\langle u_0^2\rangle$ stands for msd of ^{57}Fe atom corresponding to f_0

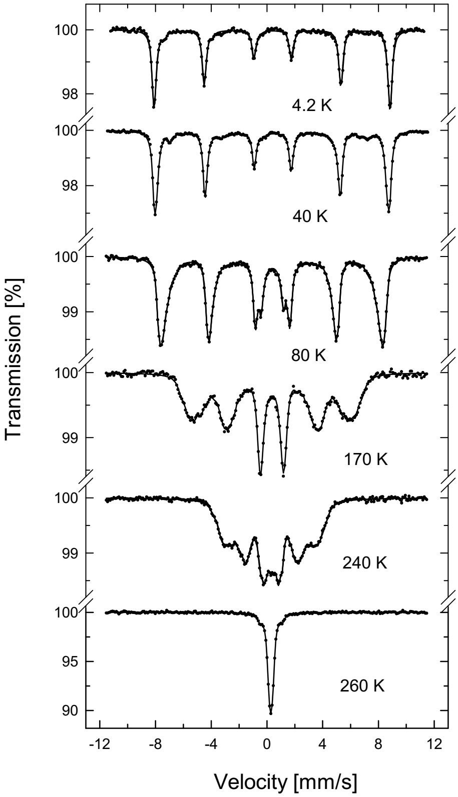

Fig. 1. Temperature variation of $La_{0.67}Ca_{0.33}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ Mössbauer spectra.

(the lowest temperature measured, which was 4.2 K for 3 and 5 at. % ^{57}Fe and 12 K for 1 at. % ^{57}Fe).

We believe that Mn ions undergo the same (or very similar) msd at the same sample temperature. The temperature variation of $-\ln(f/f_0)$ is presented in Fig. 2. It can be seen that the $-\ln(f/f_0)$ *vs* T in the FM state differs from the dependence in the PI state. In the Debye approximation the f factor is described by the formula:

$$f=\left\{-\frac{6E_0}{k\theta_\mathrm{D}}\left[\frac{1}{4}+\left(\frac{T}{\theta_\mathrm{D}}\right)^2\int\limits_0^{\frac{\theta_\mathrm{D}}{T}}\frac{x\,dx}{(\mathrm{e}^x-1)}\right]\right\},$$

where E_0 is the resonance energy and θ_D is the Debye temperature. Fitting this formula to the experimental points for the FM and PI states separately one obtains θ_D values for these two states. The fitted curves (continuous lines) together with corresponding θ_D values for the FM and PI states are presented in Fig. 2. It can be seen that the FM state has a lower Debye temperature then the PI state. It is also evident that with increasing Fe concentration θ_{D} increases for PI state. In addition, for the $x = 1$ at. % ^{57}Fe, the common $\theta_{\mathrm{D}} = 360$ K was obtained by fitting the above formula (dashed line in Fig. 2) to all experimental points. The vertical lines denote T_{C} and $T_{\mathrm{M-I}}$ obtained from magnetisation and resistivity measurements [8] and T_{CM} obtained from Mössbauer Spectroscopy. It should also be noted that T_{CM} is very close to $T_{\mathrm{M-I}}$ whereas $(T_{\mathrm{C}} - T_{\mathrm{M-I}})$ increases with increasing substitution level.

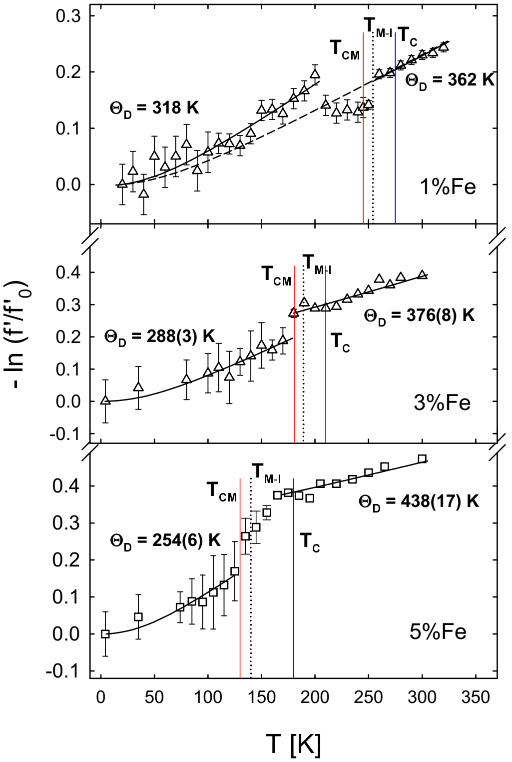

Fig. 2. Temperature variation of the $-\ln(f/f_0)$ for $\mathrm{La_{0.67}Ca_{0.33}Mn_{1-x}{}^{57}Fe_xO_3}$ with $x = 0.01$, 0.03 and 0.05.

For LCMFO samples with $x = 0.01$ and 0.03 the lattice parameters a, b, c *vs* temperature were precisely measured and the unit-cell volume V calculated (Fig. 3). The b, c and V show clear anomalies at $T_{\mathrm{M-I}}$ for the $x = 0.01$ sample but much smaller ones for the $x = 0.03$ sample. From these results the volume expansion coefficients α ($\alpha = \frac{\Delta V}{\Delta T}\frac{1}{V}$) were calculated. The α *vs* temperature for $x = 0.01$ has a sharp maximum at $T_{\mathrm{M-I}}$ which is very broad and weak for $x = 0.03$.

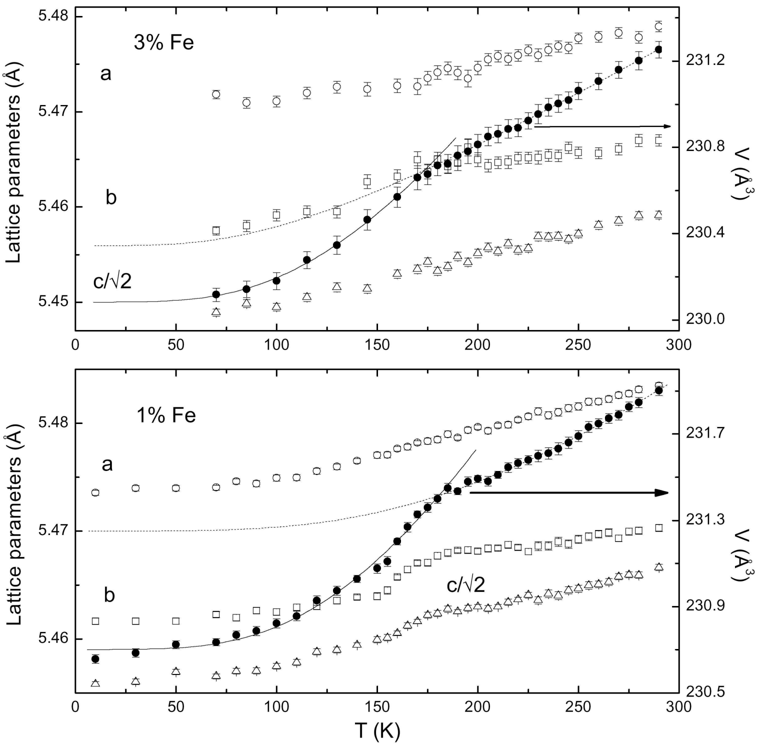

Fig. 3. Lattice parameters and unit-cell volume *vs* temperature for $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$ with $x = 0.01$ and 0.03.

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. A different and unexpected effect was found in $-\ln(f/f_0)$ *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 to be excluded by additional experiment on a specially prepared sample with high iron concentration but low concentration of the ^{57}Fe isotope (thin absorber limit).

Finally, the $-\ln(f/f_0)$ *vs* T dependence for $x = 0.01$, which is related to $\langle u^2\rangle$ *vs* T dependence and yields information how strongly the Mössbauer probe is bounded to the Mn–O–Mn lattice, does not show any evidence of an abnormal increase at $T_{\mathrm{M-I}}$ and therefore does not reveal any softening of this bond. One can understand this important and rather surprising result by stressing the difference in the meaning of Mössbauer $\langle u^2\rangle$ which is probing the dynamics (strengths of bonding) of the Mn sublattice and $\langle u^2\rangle$ from X-ray/neutron diffraction or EXAFS measurements which are additionally sensitive to a static disorder. In summary no clear anomaly in the dynamics of the Mn sublattice was found by ^{57}Fe Mössbauer probe at $T_{\mathrm{M-I}}$ which means that instead of dynamic rather static effects (in the time window of Mössbauer Spectroscopy) are responsible for the anomalous increase of Mn or O Debye–Waller factors seen by other methods.

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