SPECIFIC HEAT AND MAGNETIC PROPERTIES OF Fe SUBSTITUTED MIXED-VALENT MANGANITES $\mathbf{La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3}$*

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The experimental results of AC susceptibility, magnetization, and heat capacity of polycrystalline $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$ (x = 0, 0.01, 0.06, 0.06 ^{57}Fe, 0.10 ^{57}Fe and 0.015 ^{57}Fe) are presented. A nonlinear reduction of the ordering temperature T_C and a diminishing anomaly in heat capacity with increasing Fe contents were found. A similar lowering of the χ_{AC} signal by external magnetic field was observed for all samples but frequency dependent effects are visible for $x \geq 0.06$ and $M(H)$ for those compositions do not show saturation at T close to critical temperatures. The results are discussed based on formation of microscale magnetic clusters.

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Manganite perovskites of the $R_{1-y}Ca_yMnO_3$ type are recently of a great interest due to both the occurrence of colossal magnetoresistance in these materials and the electronic microscale inhomogeneities possibly responsible for CMR. The phase separation can be finely tuned by changing the magnetic order either by partial blocking of double exchange (DE) $Mn^{4+} - Mn^{3+}$ interactions or by chemical pressure. The alteration in magnetic interactions may be achieved *e.g.* by the substitution of Fe^{3+} for Mn cations, the process

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causing partial change of Mn valance [1, 2] yet introducing no additional distortion and the symmetry modification of the system [3]. To precisely evaluate the effect of Mn substitution by iron, we have performed studies of $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$ compounds. In this work, we report the AC magnetic susceptibility, magnetization and specific heat data for the polycrystalline samples with $x = 0$, 0.01, 0.06, 0.06 ^{57}Fe, 0.10 ^{57}Fe and 0.015 ^{57}Fe.

The results of AC susceptibility studies are shown in Fig. 1. The Curie temperature T_C was determined as the inflection point of χ_{AC} *vs* T curve. With increasing Fe concentration T_C was found to decrease nonlinearly indicating a diminishing of magnetic interactions due to the blocking of Mn^{4+}–Mn^{3+} double exchange. The overall shape of χ_{AC} curve is similar for all samples. A significant decrease of the χ_{AC} signal below T_C in applied external DC magnetic field (up to 2 kOe) was observed and the critical temperature was shifted slightly to higher temperature as determined from the position of the specific heat anomaly (the shift is 3 K for 2 kOe in case of $x = 0$ sample). Since both Mn^{4+} and Mn^{3+} ions exist in these materials, and also Fe^{3+} ions are randomly distributed within the lattice the system may be magnetically frustrated, that often leads to spin glass state [4], or to electronic inhomogeneities on the microscale (cluster glasses) [1, 5]. To check for these effects frequency dependence of AC susceptibility was measured and we have found that positions of maxima in χ_{AC} depend on frequency for $x \geq 0.06$. Magnetic order has been further studied in selected samples by magnetization *vs* magnetic field strength H measurements (Fig. 2). All measured samples, at $T < T_C$, display $M(H)$ dependence with the negligible remanence and the apparent lack of saturation, except at 4.2 K. Temperature dependence of magnetic moment per $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$ molecule is shown in the inset of Fig. 2.

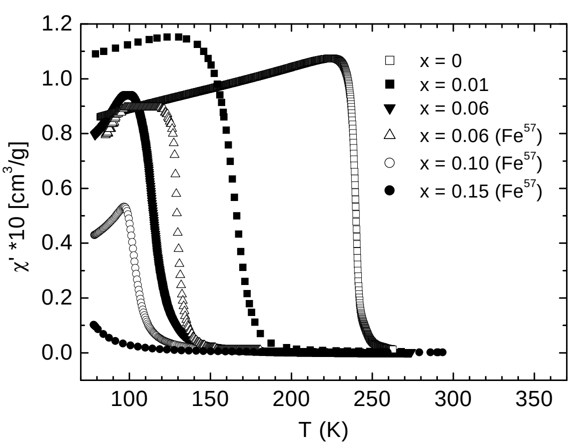

Fig. 1. Temperature dependence of χ_{AC} for $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$.

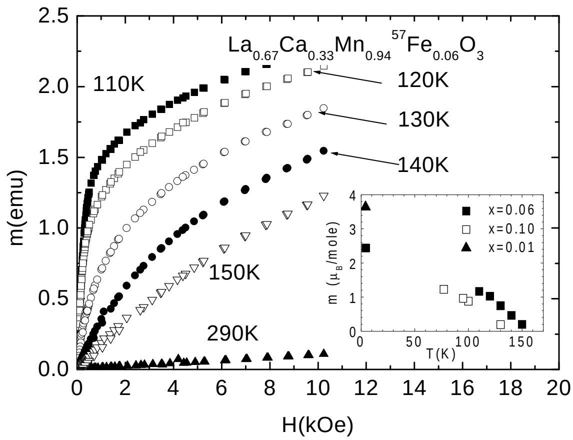

Fig. 2. Magnetic moment $m(H)$ isotherms for $La_{0.67}Ca_{0.33}Mn_{0.94}\,{}^{57}Fe_{0.06}O_3$. The inset shows the temperature dependence of magnetic moment per molecule for selected samples.

Our results suggest that for $x \geq 0.06$ the examined materials do not exhibit typical ferromagnetic structure; in fact the results qualitatively resemble those shown in [4] that were considered a proof of a spin glass behavior. However those effects, especially frequency dependant χ_{AC}, may arise from magnetic domain wall movement [1, 6]. Also, the Arrott plots for $x = 0.06$ sample (Fig. 3) are linear, *i.e.* characteristic for ferromagnet, contrary to those presented in [4]. Critical temperature calculated from those plots match exactly that evaluated from χ_{AC}. Finally for $x = 0.10$, although no long range magnetic order was found, the neutron depolarization technique revealed the presence of *ca.* 2μ m magnetic clusters [1] not a spin glass state. Our results qualitatively confirm those findings, and the following picture may arise. With increasing x magnetic interactions are changed considerably by Fe^{3+} ions blocking DE channels and coupling antiferromagnetically with Mn that may form Mn-rich ferromagnetic clusters linked by Fe-rich antiferromagnetic regions. Assuming that only those ferromagnetic clusters give rise to the observed magnetic moment and that, within a cluster, mean $Mn^{+3} - Mn^{+4}$ moment is present (*i.e.* $3.7\mu_{\mathrm{B}}$), then 0.27 ($x = 0.06$) and 0.35 ($x = 0.10$) Mn ions per each molecule should not contribute to the cluster moments. This would mean that one Fe ion blocks ferromagnetic interactions for *ca.* 4 Mn ions.

The results of the specific heat measurements show the onset of a phase transition for $x = 0$, 0.01 and for 0.06 (^{57}Fe) at temperatures that match the relevant magnetic T_{C}. Under an applied magnetic field of 2 kOe the upward shift of the transition temperature was observed for $x = 0$ and 0.01.

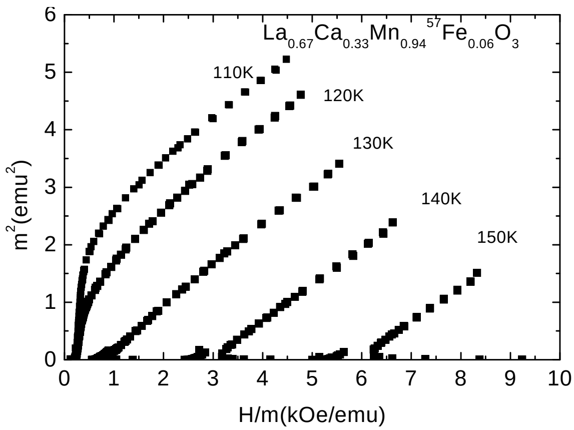

Fig. 3. Arrot plots obtained from the magnetization curve for $La_{0.67}Ca_{0.33}Mn_{0.94}{}^{57}Fe_{0.06}O_3$.

The peaks gradually broaden with x and for $x = 0.06$ (^{57}Fe) only a tiny kink is seen. The entropy released at the transition temperature apparently diminishes with x what suggests that only certain regions within a sample are ferromagnetically ordered, as mentioned above, or the sample is only partially ordered.

In conclusion, we have observed nonlinear T_C reduction with increasing Fe contents and a diminishing anomaly in heat capacity. The results are discussed based on the formation of submicrometer scale magnetic inhomogeneities.

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