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Novel phase transitions in B-site doped manganites

Z.V. Popović[a,*], A. Cantarero[b], W.H.A. Thijssen[c], N. Paunović[a], Z. Dohčević-Mitrović[a], F. Sapiña[b]

[a]*Institute of Physics, P.O. Box 68, 11080 Belgrade/Zemun, Serbia and Montenegro*
[b]*Materials Science Institute, University of Valencia, P.O. Box 22085, 46071 Valencia, Spain*
[c]*Kamerlingh Onnes Laboratorium, Leiden University, Postbus 9504, 2300 RA Leiden, The Netherlands*

Abstract

We have examined the infrared reflectivity and the electrical resistivity of $La_{1-x}[Sr(Ba)]_xMn_{1-z}[Cu(Zn)]_zO_3$ samples in ferromagnetic metallic and insulator regime. Several phase transitions are observed, the most obvious being the transition from a ferromagnetic metallic to a ferromagnetic insulator phase that is related to the formation of short-range orbitally ordered domains. The temperature T_1 of the phase transition is dependent on doping concentration and for optimally doped samples (~32% of Mn^{4+} ions) we have found $T_1 \approx 0.93\,T_C$.

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Pseudocubic manganites like $R_{1-x}A_xMnO_3$ (R = La, Pr, Nd, Dy; A = Sr, Ca, Ba, Pb) have attracted great interest because of their unique spin-dependent magnetotransport properties, suitable for realizing magnetic sensors. The strong interplay between the charge, spin, orbital and lattice degrees of freedom in these materials leads to a variety of phases, such as ferromagnetic (FM) metallic, FM insulator, cluster glass, spin glass, orbitally ordered, antiferromagnetic canted and charge-orbitally-ordered. In this paper, we use infrared and transport measurements to study optimally doped $La_{1-x}[Sr(Ba)]_xMn_{1-z}[Cu(Zn)]_zO_3$ oxides. Details on the preparation of the samples, together with chemical and structural characterization as well as magnetic measurements, can be found in Ref. [1]. Chemical analysis and EDAX results show that the manganese mean oxidation state in studied samples is practically constant, being 3.32 ± 0.01 and the concentration of vacancies at the A and B positions is negligible [1]. On the other side, the B-site doping offers us the possibility to reduce the concentration of free

*Corresponding author. Tel.: +381 11 3161 385; fax: +381 11 3162 190.
E-mail address: zoran.popovic@phy.bg.ac.yu (Z.V. Popović).

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carriers (the Drude term in the optical conductivity) and to suppress the long-range charge/orbital ordering.

Fig. 1 shows the temperature dependence of the electrical resistivity for several A- and B-site optimally doped samples. In general, an increase in the resistivity, a decrease of the Curie temperature (T_C) and a "double peak" structure upon B-site doping are observed, Fig. 1(a). An increase of the electrical resistivity originates from the hole-scattering by the random potential of the B-site impurities. On the other side, a decrease of T_C is a consequence of the weakening of the double-exchange (DE) interaction due to the crystal distortion caused by the B-site doping and/or the perturbation of the connecting paths for the transport of holes across Mn–O–Mn, that substantially prevents the DE interaction. In Fig. 1(b) we show the same spectra as in Fig. 1(a) but in a temperature scale normalized to T_C. The main conclusion that can be drawn from Fig. 1(b) is that T_1 *appears at the same position related to* T_C, *regardless of the A or B site dopants*. We found here that for optimum doping $T_1/T_C = 0.93 \pm 0.02$.

As can be seen from Fig. 1, the paramagnetic to FM phase transition is manifested as a peak in resistivity (at T_C). Below T_C the resistivity drops rapidly until the next transition, which occurs for example in the $La_{0.83}Sr_{0.17}Mn_{0.9}Cu_{0.1}O_3$ sample, at $T_1 = 220$ K. At T_1 a sudden increase in the resistivity can be observed, together with an additional increase in the spontaneous magnetization [2]. Several microscopic origins have been proposed to explain this resistivity rise below T_C, among them a long-range polaron (charge) ordering [3], a long-range orbital ordering [4], and a long-range antiferromagnetic order [5]. Recently, it has been shown that insulating ground state in manganites does not require the development of long-range charge or orbital order. The resistivity upturn was associated with a diffuse structural transition characterized by strong reduction of the orthorhombicity [6], or the formation of orbitally ordered domains [7]. Here, the B-site doping destroys the coherence of the long-range orbital and/or charge alternation. On the other side, local lattice distortion created by B-site substitution is accompanied with localization of e_g holes (polarons) and their short-range correlations. The short-range polaron–polaron correlations can also be regarded as short-range charge ordering which, as discussed in Ref. [8], drives the orbital ordering. The insulating behavior below T_1 can be understood in terms of competition between the short-range orbital/charge order and the long-range FM order.

The appearance of new infrared active phonon modes at $T < T_1$ (denoted by * and ** in Fig. 2) is considered as an evidence of phase transition.

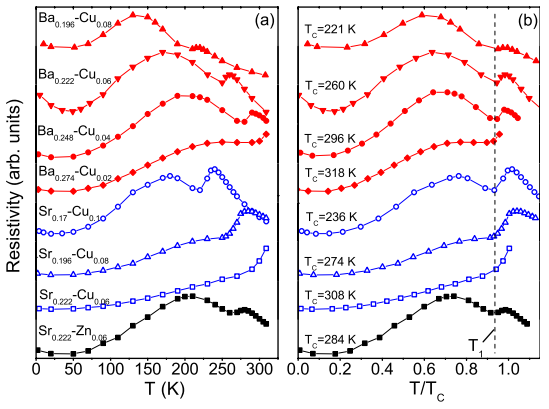

Fig. 1. (a) Temperature dependence of the electrical resistivity of the $La_{1-x}[Sr(Ba)]_xMn_{1-z}[Cu(Zn)]_zO_3$ samples. (b) The same results represented in the temperature scale normalized to T_C. Dashed line denotes the value $T_1/T_C = 0.93$.

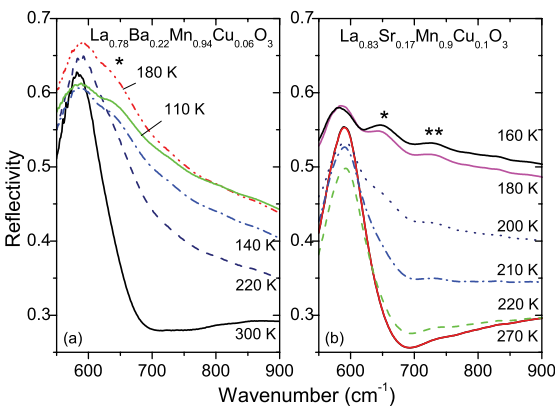

Fig. 2. Temperature dependence of the infrared reflectivity of (a) $La_{0.78}Ba_{0.22}Mn_{0.94}Cu_{0.06}O_3$, and (b) $La_{0.83}Sr_{0.17}Mn_{0.9}Cu_{0.1}O_3$ samples.

These modes can be assigned as antistretching and breathing modes at the R-point of the Brillouin zone in the Pm3m cubic symmetry. Their calculated frequencies [9] 646 and 716 cm^{-1} are very close to our results. Appearance of edge zone phonons derived from the cubic structure of $LaMnO_3$ can be a consequence of doubling the unit cell by a structural change from orthorhombic O* to pseudocubic O** phase [10] or due to their coupling with spin waves, as it has been recently shown [11] for the FM insulator phase in $La_{0.875}Sr_{0.125}MnO_3$, suggesting the complex ground state for the FM insulator phase with mixed magnetic and phononic excitations.

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