

Charge ordering in the electron doped $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ manganites

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Abstract

Structural studies on the electron doped $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ are presented. At 300 K, orthorhombic O-phase was observed in all cases, associated to low electric resistivity and high Curie–Weiss temperature. For samples with $x > 0.07$, structural phase transitions to more distorted orthorhombic and monoclinic phases were found at $T < 170$ K. In these phases only weak ferromagnetic interactions were observed. © 2002 Elsevier Science B.V. All rights reserved.

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The magnetoresistant manganites series $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ was studied in the electron doped region ($x < 0.5$) by magnetic, structural and electric transport techniques. In a previous report [1] we found that, at $T = 5$ K, magnetization, M , and electric conductivity, σ , increase when Y substitutes for Ca in CaMnO_3 up to $x = 0.15$. This is a signature of the ferromagnetic double-exchange (FM-DE) importance in this range of doping. For $x > 0.15$, the ferromagnetism suddenly weakens and M and σ drop. This behavior has also been observed for other $\text{Ca}_{1-x}\text{R}_x\text{MnO}_3$ series [1] and attributed to charge ordering (CO). In this work, we focus on electron doped samples of $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ with $0.15 \leq x \leq 0.25$ in order to associate structural, magnetic, and transport properties.

Ceramic polycrystalline samples of $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ were prepared by solid state reaction [2]. All samples were studied by X-ray diffraction using a Philips X-Pert system at 300 K and a He-cryogenerator attached to a Rigaku X-ray diffractometer between 15 and 300 K. For dilatometric experiments we used a three terminal capacitance dilatometer described in Ref. [3]. The thermal expansion coefficient, $\alpha(T) = (1/L) dL/dT$, was determined averaging the point-to-point derivative over different temperature ranges, from 1 K near $\alpha(T)$ anomalies, up to ~ 20 K for smooth regions behavior. Electric resistivity, ρ , was measured using a 4-probe method and DC-magnetization, M , was measured with a SQUID magnetometer between 5 and 300 K and, above 300 K, with a Faraday balance magnetometer.

Rietveld refinement shows that the 300 K X-ray diffractograms of $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ can be indexed in the orthorhombic O-phase for $x < 0.5$. However,

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the cell distortion increases continuously [1,2] and the diffractogram for $x = 0.5$ corresponds to an orthorhombic O' -phase. From structural studies as a function of T , we derived the cell parameters shown in Fig. 1. For $x = 0.07$, the behavior corresponds to a typical thermal expansion dependence for a single phase material without structural changes. For $x = 0.25$, when T decreases, a continuous lattice distortion is observed in the range 260–160 K that can be associated to a broad cooperative Jahn–Teller transition between the high T (>260 K) O-phase and the low T (<160 K) O' -phase. The samples with $x = 0.15$ and 0.20 have similar structural behaviors. In both cases, phase separation is observed when the temperature is diminished. For $x = 0.15$ a new, very distorted, orthorhombic O' -phase appears at 140 K coexisting with the less distorted O-phase down to 15 K. Evaluation of the intensities confirms that the new phase grows from the original one. Between 100 and 15 K, about 80% of the sample has the orthorhombic O-phase. For $x = 0.20$, similar phase separation is observed but, in this case, additional distortions (monoclinic and O' type) were also observed (see Fig. 1). All the described characteristics are schematized in the structural phase diagram shown in Fig. 2.

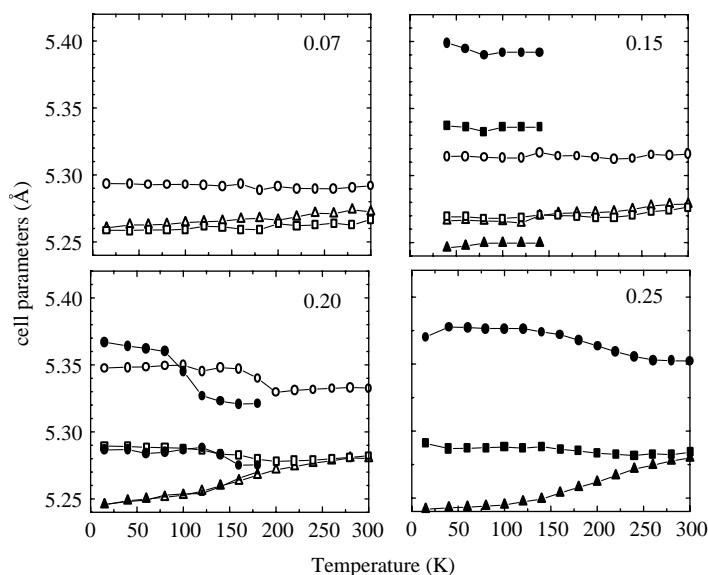


Fig. 1. T -dependence of the cell parameters a (circle), $b/\sqrt{2}$ (triangle) and c (box) for $x = 0.07, 0.15, 0.20$, and 0.25 . Open and solid symbols indicate O- and O' -phases.

In Fig. 3 we present dilatometric results. For CaMnO_3 , $\alpha(T)$ shows a second-order-type anomaly at $T_N \sim 122$ K with a very sharp peak similar to what should be expected in specific heat [3]. Similar anomalies in $\alpha(T)$ for the $x = 0.10$ and 0.15 samples show a significant reduction of the magnetic ordering temperature, T_{mo} , as was reported in Ref. [1] from magnetization measurements. For $x = 0.15$, above the magnetic transition ($T \approx 150$ K), departures of $\alpha(T)$ relative to the behavior for $x = 0$ and 0.10 samples were observed. This is consistent with the growth of a larger volume secondary phase, as observed by X-ray diffraction. This second phase increases in percentage as T is lowered, leading to a smaller anomaly at the magnetic ordering temperature for $x = 0.15$ as compared with the $x = 0.10$ case. The T range where anomalous behavior in $\alpha(T)$ was observed is strongly broadened for $x > 0.15$ and the *normal* dependence is not recovered within our experimental T -range. The minimum of $\alpha(T)$ is observed at $T \approx 130$ K (200 K) for $x = 0.18$ (0.25).

Magnetic properties in electron doped $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ are a consequence of the competition between FM-DE and antiferromagnetic superexchange (AF-SE) interactions [1]. Measure-

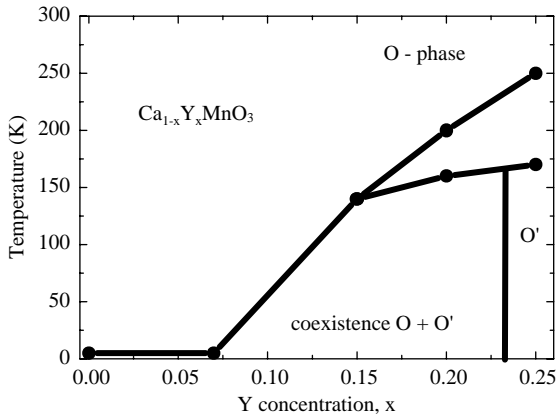


Fig. 2. Structural phase diagram T vs. x for $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$.

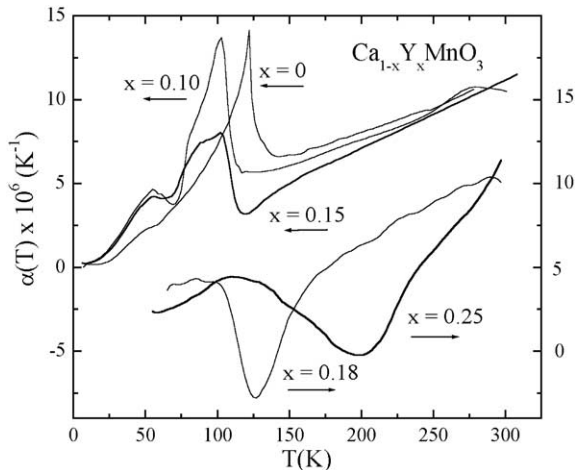


Fig. 3. T -dependence of $\alpha(T)$ for $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$. Values of x are indicated.

ments of $M(T)$ in the paramagnetic (PM) regime, allow us to determine the Curie–Weiss temperatures, Θ . Strongly x -dependent values were reported [1], ranging from $\Theta \approx -400$ K (AF) for $x = 0$ to $\Theta \approx 100$ K (FM) for $x = 0.10$. For $x = 0.15, 0.20$ and 0.25 we have determined $\Theta = 105, 115,$ and 118 K, respectively, indicating that FM-DE interactions are still present in these samples. Despite the similar values of Θ , differences in the saturation magnetization, M_S , at 5 K were measured [2] for this group of samples. While $M_S = 0.9 \mu_B/\text{f.u.}$ for $x = 0.15$, only a weak-FM M_S , of

the same order as that of the AF $x = 0$ compound, was measured for $x = 0.25$. In the T -range close to 300 K low resistivity values were found [4] for all doped samples ($0 < x \leq 0.25$). At $T = 5$ K, instead, a large ρ increase (≈ 5 orders of magnitude) was observed for $x > 0.15$.

In summary, at room temperature, where all the samples have low distorted O-phases, similar electric and magnetic properties are found and FM-DE interaction is predominant. At low T , in the magnetic ordered state, the sample with $x = 0.15$ is 80% O-phase and shows low ρ and high M_S . On the other hand, the $x = 0.25$ sample, with 100% of distorted O'-phase is the less magnetic and conductive compound within the group. The anomalies in $\rho(T)$ and $M(T)$ associated to CO, reported in Ref. [4] for this series of samples, were observed at temperatures in coincidence with the structural transitions (Figs. 2 and 3). Our results are compatible with those found in other electron doped manganites [5]. In all cases, the CO process takes place at $T_{\text{CO}} > T_{\text{mo}}$ as discussed in Ref. [6] for the moderate electron doping regime.

Acknowledgements

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