

Structural, electric, and magnetic study of $Y_{0.5}Ca_{0.5}MnO_3$

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Abstract

Correlations between magnetic, structural and transport properties were found in the Y–Ca half-doped manganite. At $T < 500$ K the crystalline structure changes from an orthorhombic O-phase to a more distorted O'-phase. The electron spin resonance behaviour allow us to determine the transition temperatures $T_{CO} = 290$ and $T_N = 130$ K. © 2003 Elsevier B.V. All rights reserved.

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In half-doped manganites $A_{0.5}A'_{0.5}MnO_3$ (A and A' are, respectively, tri- and divalent ions) the A–A' average radius, r_A , is a relevant parameter to determine their magnetic properties [1]. For $r_A \geq 1.39$ Å the low T magnetic state is ferromagnetic (FM) and double-exchange (DE) interactions are predominant. For $r_A < 1.39$ Å, instead, an antiferromagnetic (AFM) order of FM chains was found. Charge localization (CO), orbital ordering, and superexchange were considered essential for the stabilization of this magnetic structure. Recently, an alternative picture [2] explains this magnetic array in terms of Zener polarons where the itinerant electrons are trapped within pairs of Mn sites involving DE interactions and lattice distortions. In this description an unconventional magnetic behaviour in the paramagnetic (PM) phase is expected. It would be interesting to know how this behaviour reflects on other physical properties. With this aim we present an experimental study on electric transport, electron spin resonance (ESR) and crystalline structure performed on the half-doped and low $\langle r_A \rangle$ manganite $Y_{0.5}Ca_{0.5}MnO_3$.

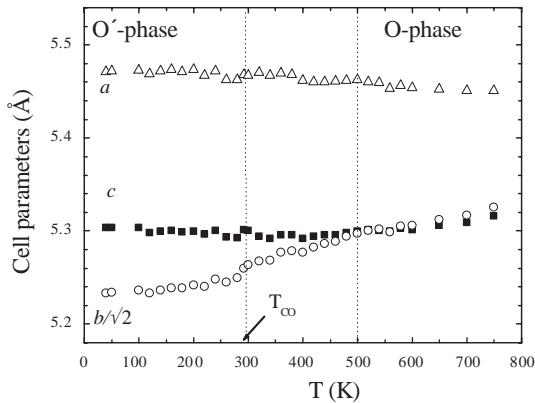
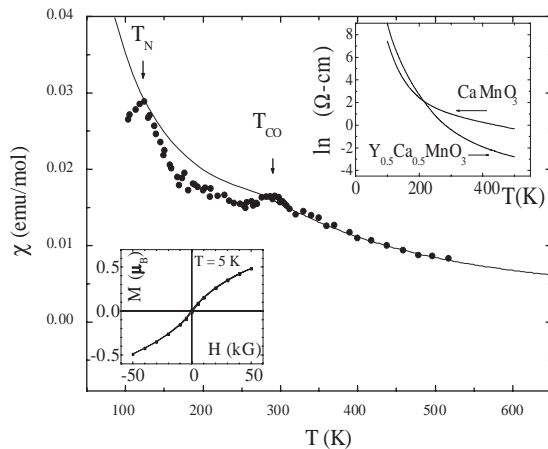
Samples of $Y_{0.5}Ca_{0.5}MnO_3$ were prepared by solid state reaction [3], and studied by X-ray diffraction. We observed that the material is single phase in all the

studied T range (20/750 K). In Fig. 1 we show the evolution of the cell parameters with T obtained for an orthorhombic $Pnma$ structure. The parameters a and c are nearly constant with T while b shows important variations: for $T > 500$ K, $b/\sqrt{2} \approx c$ and for lower T , $b/\sqrt{2} < c$ remaining approximately constant for $T < 250$ K. The resistivity, ρ , is shown in Fig. 2 where we compare $Y_{0.5}Ca_{0.5}MnO_3$ with the insulating $CaMnO_3$. For $T \approx 500$ K (limit of our experimental setup) the $Y_{0.5}Ca_{0.5}MnO_3$ resistivity is one order of magnitude lower than that of the reference compound. In both cases, thermally activated mechanisms, $\rho(T) \propto e^{W/kT}$, may explain the observations. For $CaMnO_3$ $\rho(T)$ is fitted with a single value of W . For $Y_{0.5}Ca_{0.5}MnO_3$, instead, two values of W are necessary: $W/k \approx 1800$ and 1100 K for $T > 200$ K and $T < 140$ K, respectively.

Magnetization (M) measurements were performed in the range 5 K/1100 K with SQUID and Faraday balance magnetometers. The PM susceptibility, $\chi_{DC}(T)$, is in reasonable agreement with Ref. [2]. For $T > 400$ K, we observe a Curie–Weiss (CW) behaviour, that we call HTCW, with $C = 3.30$ emu-K/mol and $\theta = 105$ K (C and θ are the Curie constant and the CW temperature, respectively). For lower temperatures, $T < 250$ K, the system follows a new CW regime, the LTCW, with $C = 4.22$ emu K/mol and $\theta = -10$. The charge ordering temperature T_{CO} , where AFM interactions become operative [2], is then between 250 and 400 K. At

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Fig. 1. Cell parameters vs. T .Fig. 2. $\chi_{\text{ESR}}(T)$ (solid circles) and $\chi_{\text{DC}}(T)$ (solid line) vs. T . Bottom inset: M vs. H at 5 K. Top inset: $\rho(T)$ vs. T for CaMnO_3 and $\text{Y}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ as indicated.

$T = 5$ K, as is shown in Fig. 2, M increases continuously with H , showing a negative curvature, up to the limit field of our experiment and $M(H = 5 \text{ T}) \approx 0.5 \mu_{\text{B}}$.

ESR experiments were performed at 9.5 GHz between 100 and 800 K. We observed a single Lorentzian line centred at $g = 1.97(3)$. Comparison of integrated spectra with well-known magnetic samples allow us to determine the ESR susceptibility, χ_{ESR} , shown in Fig. 2 together with χ_{DC} . We found two well-defined peaks at 290 and 130 K.

From inspection of the T dependence of the cell parameters (Fig. 1) we found two regimes: for $T > 500$ K, a pseudo-tetragonal O-phase and for lower temperatures, a more distorted [3] O'-phase (with $b/\sqrt{2} < c$). The cell volume (V) decreases linearly with T but at ≈ 250 K, where a small discontinuity in $b(T)$ is

observed, V stops to decrease and remains constant below this temperature. Combining these structural properties with the $\chi_{\text{DC}}(T)$ behaviour, we conclude that for the more symmetric O-phase, in the HTCW regime for $\chi_{\text{DC}}(T)$, the FM interactions are predominant as indicated by the positive Θ . Decreasing T , the susceptibility abandons the HTCW behaviour and, below 250 K, $\chi_{\text{DC}}(T)$ reaches the LTCW regime. This regime is characterized by a constant cell volume and the weakening of the exchange interactions indicated for the small value of $|\Theta|$. As is seen in Fig. 2, $\chi_{\text{ESR}}(T)$ and $\chi_{\text{DC}}(T)$ coincide above $T \approx 290$ K (near T_{CO} of Ref. [2]) where χ_{ESR} displays a peak. A second χ_{ESR} peak is observed at $T \approx 130$ K. The diminishing of χ_{ESR} for $T < 130$ K is an indication of AFM ordering: in this case the PM resonance cannot be excited. The absence of a maximum in $\chi_{\text{DC}}(T)$ at T_{N} would indicate that the magnetic moments are not completely compensated.

Finally, a word about the transport measurements. The relatively low value of $\rho(T)$, as compared with CaMnO_3 , may be an evidence of the presence of the DE mechanism in $\text{Y}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. Although a change in the activation energy W takes place below T_{CO} , we have not observed the noticeable discontinuities in $\rho(T)$ associated to the CO transitions in other cases [4]. We should notice that our experimental setup does not allow us to determine the transport regime associated to the HTCW susceptibility in the high symmetry O-phase where even lower resistivities would be expected.

In summary, we have found correlations between transport, magnetic and structural properties in the $\text{Y}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ manganite. We relate the unusual PM behaviour found in Ref. 2 to crystalline distortions which increase when T decreases between 500 K and T_{CO} . It is possible to describe this range of T as a broad transition between the pseudo-tetragonal FM phase and the strongly distorted O'-phase where AFM interactions are present. However, a perfect AFM ordering would not take place as indicated for the M vs. H dependence at $T = 5$ K and also for the relatively low values for $\rho(T)$ obtained for $T < T_{\text{CO}}$.

References

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