Magnetic-history-dependent nanostructural and resistivity changes in Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.98}$Cr$_{0.02}$O$_3$

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Abstract

We show that nanostructure and resistivity of Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.98}$Cr$_{0.02}$O$_3$ are sensitive to whether the sample is zero-field-cooled (ZFC) or field-cooled (FC) either in the ‘self-magnetic field (H ≈ 2 T)’ of the electron microscope or under the external magnetic field of 2 T. FC resistivity at H = 2 T is lower than ZFC values below 140 K. The average value of the charge-orbital modulation vector (q = 0.44) of the FC crystallites is lower than that of the ZFC crystallites (q = 0.48) and the FC crystallites exhibit numerous defects like discommensuration, dislocations and regions with loss of superstructures compared to the ZFC crystallites.

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The renaissance of interest in charge ordered manganites like Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ is due to insulator-metal transition driven by melting of charges under external magnetic fields. Charge ordering (CO) manifests itself as regular ordering of Mn$^{3+}$:t$_{2g}^3$e$_g^1$ and Mn$^{4+}$: t$_{2g}^3$ ions and ordering of d$_z^2$ orbital at Mn$^{3+}$ sites. The low temperature phase of a perfect CO (Mn$^{3+}$/Mn$^{4+}$ = 1:1) system is a CE-type antiferromagnet, but some of the manganites exhibit phase separation into CO (antiferromagnetic, AF) and non-CO (ferromagnetic, FM) regions. Electron microscopy is one of the powerful techniques to characterize the lattice distortion generated by CO and phase separation. Nevertheless, sample in the electron microscope is under the influence of about 2 T (‘self-magnetic field’) and CO in some of the manganites is sensitive to this ‘self-magnetic field’ as found recently in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$. Coexistence of ordered regions (correlated to the CO-AF phase) and non-ordered regions (correlated to the FM phase) over wide x range (0.01 ≤ x ≤ 0.05) has been reported in Pr$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Cr$_x$O$_3$. In this letter, we report unusual magnetic history dependence of resistivity and nanostructural changes in Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.98}$Cr$_{0.02}$O$_3$.

Resistivity (ρ) and magnetization (M) of polycrystalline Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.98}$Cr$_{0.02}$O$_3$ were measured in two modes: In ZFC and FC modes, data were taken while warming from 5 K in presence of a known field (H) after cooling in zero-field and under H, respectively from 300 K. In order to obtain the ZFC condition in electron microscopy study, the objective lens of the microscope was cut off at 300 K before introducing the sample and the temperature was decreased to 92 K. After one hour at 92 K, the objective lens was switched on. Numerous crystallites have been characterized using electron diffraction (ED) in order to determine the average value of the charge modulation vector q and lattice imaging for the distribution of fringes. Different zones of different crystallites have been located. Then the temperature was raised to 300 K keeping objective lens switched on, again cooled to 92 K keeping exactly the same current density in order to obtain the FC mode. Exactly the same areas of the same crystallites were re-observed and the results are compared to those recorded under ZFC condition.
The temperature dependence of M for H = 0.01 T, 2 T and ρ for H = 0 T and 2 T are shown in Figs. 1(a) and Fig. 1(b) respectively. We use solid curve for the ZFC and dashed curve for the FC modes. The peak in M around 230 K in both H = 0.01 T and H = 2 T signals ordering of charges and orbitals in the paramagnetic phase. A short range FM order is established below T_C = 130 K as suggested by the difference in ZFC and FC magnetization at H = 0.01 T. ρ(0T) starts to decrease not at T_C but around 80 K, close to the temperature where the ZFC magnetization also reaches a maximum. The decrease of ρ(T) below 80 K can be thus considered due to the percolation of FM clusters whose moments are blocked below this temperature. The peak in ρ(T) shifts to 125 K under H = 2 T and the magnetoresistance ([ρZFC(0 T)-ρFC(2 T)] / ρFC(0T) ) at 100 K is as large as 73 %. The surprising result is the deviation of the ZFC and FC-ρ(T) below ≈ 135 K and lower values of the FC-ρ(T). The FC-ρ(T) exhibits a peak at T_p ( = 128 K) which is higher than that of ZFC-ρ(T) (T_p = 116 K). Under H = 2 T, T_C increases to 140 K, the maximum in ZFC-M(T) shifts down ≈ 30 K and, FC-M(T) increases without saturation down to 5 K. This suggests that long-range FM order is not reached even at H = 2 T and canting of spins in the CO-AF phase contribute to non-saturation of M. We find that irreversibility in ρ(T) and M(T) persists even at H = 7 T in this compound but becomes negligible with increasing Cr content but, the details are beyond the scope of this letter.

Since ρ(T) values are lower when it is field–cooled, we can expect charge-ordering to be less stable in the FC state than in the ZFC state. The periodic lattice distortion due charge-orbital ordering generates satellites in Electron Diffraction (ED) patterns. The charge-orbital modulation vector exhibit a value q = 0.5-ε , where the incommensurability (ε) is zero for a perfect 1 : 1 charge ordering. Fig. 2(a) and Fig. 2(b) respectively show the ED patterns at 92 K for the ZFC and FC modes. The average q value of the FC crystallites is close to 0.44 which is significantly lower than the average value q = 0.48 of the ZFC crystallites. This is clearly observed in the [010] ED patterns through the amplitude of the satellite splitting (see small black arrows). The satellites of the ZFC crystallites are also more intense than the ones
observed in the FC crystallites. The corresponding lattice images are compared in Fig. 3(a) and 3(b). In the ZFC case (Fig. 3(a)), in addition to majority fringes of periodicity \(2a_p\sqrt{2} = 10.8 \text{ Å}\), we also find a few fringes of higher periodicity with \(3a_p\sqrt{2} = 16.2 \text{ Å}\) at irregular positions in agreement with average \(q = 0.48\). However, in the FC case (Fig. 3(b)), numerous defects are observed in the arrangements of fringes: discommensurations (for example, area noted D) which are easily seen by viewing the images at grazing incidence and local losses of superstructure (for example, area within open arrows). To our best of knowledge, this is the first time influence of magnetic field on nanostructure has been reported. It is important to recall that artefacts due to bad stabilization of the temperature or hysteresis effect can generate the difference in the \(q\) values observed for exactly the same area. We repeated our experiments several times and all our results are identical. The satellites are stable under electron beam with long exposure contrary to what was found in \(\text{Pr}_0.7\text{Ca}_{0.3}\text{MnO}_3\). This suggests that \(\text{CO}\) is more stable in the present compound.

The above results unequivocally suggest that magnetic history of the sample affects not only the resistivity but also nanostructure. Why is it so? Recently, we have suggested that \(\text{Cr}^{3+}:t^3_{2g}\) ions randomly occupy \(\text{Mn}^{3+}:t^3_{2g}e^1_g\) sites with their \(t^3_{2g}\) spins opposite to the replaced \(\text{Mn}^{3+}\) ions. The random substitution of \(\text{Cr}^{3+}\) ions brings about \(e_g\)-orbital deficiency at the original \(\text{Mn}^{3+}\)-sites and affects cooperative Jahn-Teller distortion of \(\text{Mn}^{3+}\text{O}_6\) octahedras. Hence, \(\text{Cr}^{3+}\) ions act as random impurities for spin as well as lattice degrees of freedom. Antiferromagnets with random impurities (‘diluted Ising antiferromagnets’) show long range AF order when they are zero field cooled but break into domains upon field cooling. While the sizes of the domains in theoretical models are purely determined between volume and magnetic surface energies, spin-charge-lattice coupling also plays important role in manganites. Hence, the long range \(d_{z^2}\) orbital ordering is also broken by the formation of AF spin domains which also causes orbital domains to form. Such orbital domains lead to discommensuration and dislocations observed experimentally. Field cooling is also found to enhance the size of FM domains which are clearly visible in lattice images as regions
without superstructure. The breaking of CO-AF matrix into domains and growth of FM domains lead to low resistivity under field cooling.

In conclusion, we have shown that nanostructure and resistivity of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.98}\text{Cr}_{0.02}\text{O}_3$ are strongly magnetic field history dependent. Our study clearly suggests that electron microscopy can be used to tune nanostructure in phase separated manganites.

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FIGURE CAPTIONS

**Fig.1**: (a) Temperature dependence of magnetization at $H = 0.01$ T and 2 T in ZFC (solid curve) and FC (dashed curve). (b). $\rho(T)$ under ZFC (solid curve) and FC (dashed curve) for $H = 2$ T and in absence of field ($H = 0$ T) modes. $T_{CO}$: Charge ordering temperature, $T_C$: ferromagnetic Curie temperature.

**Fig.2**: [010] ED patterns at 92 K under ZFC (a) and FC (b) modes. Note that satellites marked by double arrows are clearly splitted and less intense in FC mode than in ZFC mode.

**Fig.3**: [010] lattice images at 92 K under ZFC (a) and FC (b) modes. Regions with loss of superstructures are denoted by open arrows and one region with discommensuration is marked by D.
FIG. 1
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