

Weakening of charge order and antiferromagnetic to ferromagnetic switch over in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ nanowires

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We have prepared crystalline nanowires (diameter ~ 50 nm, length \sim a few microns) of the charge-ordering manganite $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ using a low reaction temperature hydrothermal method and characterized them using x-ray diffraction, transmission electron microscopy, superconducting quantum interference device (SQUID) magnetometry and electron magnetic resonance measurements. While the bulk sample shows a charge ordering transition at 245 K and an antiferromagnetic transition at 175 K, SQUID magnetometry and electron magnetic resonance experiments reveal that in the nanowires phase, a ferromagnetic transition occurs at ~ 105 K. Further, the antiferromagnetic transition disappears and the charge ordering transition is suppressed. This result is particularly significant since the charge order in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ is known to be very robust, magnetic fields as high as 27 T being needed to melt it. © 2005 American Institute of Physics. [DOI: 10.1063/1.2125129]

The competition between and the coexistence of charge ordered (CO) and colossal magneto resistive (CMR) ferromagnetic (FM) ground states in the rare earth manganites $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (where R is a trivalent rare earth ion and A is a divalent alkaline earth ion) is currently the subject of intense theoretical¹ and experimental² study. It is generally believed that the two phases are mutually exclusive; e.g., in the prototype manganite $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $0.2 < x < 0.5$ the material is ferromagnetic and metallic while for $0.5 < x < 0.9$ it is antiferromagnetic and charge ordered. Two essentially different mechanisms have been proposed for these two apparently disparate phenomena, namely, Zener double exchange for FM, metallic phase and polaron hopping for the CO, antiferromagnetic (AFM) phase. However, recently a number of experiments have provided evidence^{2,3} for the coexistence of the two phases under certain circumstances, as well as for the fragility of the phase boundaries between them. It was observed that minute perturbations of the system with magnetic fields of the order of a few Tesla, electric field and radiation could cause a “melting” of the CO phase and the appearance of an FM phase.⁴ However, the CO phase in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (PCMO:0.5) has been found to be particularly robust, magnetic fields of the order of 27 T being necessary to cause a transition to FM metallic phase.⁵ In this work we show that for this system the charge order can be suppressed and FM phase be observed when the material is prepared in the form of nanowires. This result has important implications for nano-device applications of manganites and to the best of our knowledge, is the first report of charge order suppression in a one-dimensional manganite system.

The nanowires of PCMO ($x=0.5$) were prepared using the hydrothermal method.^{6–8} High purity $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, KMnO_4 , $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and KOH obtained from Sigma Aldrich were used for the preparation. Stoichiometric proportions of the chemicals were dissolved in de-ionized water. KOH was added to adjust the alkalinity. The solution was vigorously stirred and

poured into a Teflon vessel. The vessel was placed in a sealed stainless steel container, which in turn was heated at 270 °C for 50 h in a furnace. After this, the autoclave was cooled and depressurized, the product of the reaction was washed with de-ionized water and dried in ambient air at 100 °C. Since it is crucial to determine the chemical composition of the nanowires, particular care was taken to establish it by using both energy dispersive x-ray analysis, and inductively coupled plasma atomic emission spectroscopy. The former experiment gave the cation composition as $\text{Pr}_{0.50}\text{Ca}_{0.498}\text{Mn}_{0.98}$ and the latter showed it to be $\text{Pr}_{0.51}\text{Ca}_{0.48}\text{Mn}_{0.99}$. The oxygen content was determined by iodometric titration to be 2.98. The material was further characterized by various techniques such as x-ray diffraction (XRD), transmission electron microscopy (TEM), selective area electron diffraction (SAED), high-resolution electron microscopy (HREM), superconducting quantum interference device (SQUID) magnetometry and electron magnetic resonance (EMR) spectroscopy.

Figure 1 shows the powder XRD pattern recorded with

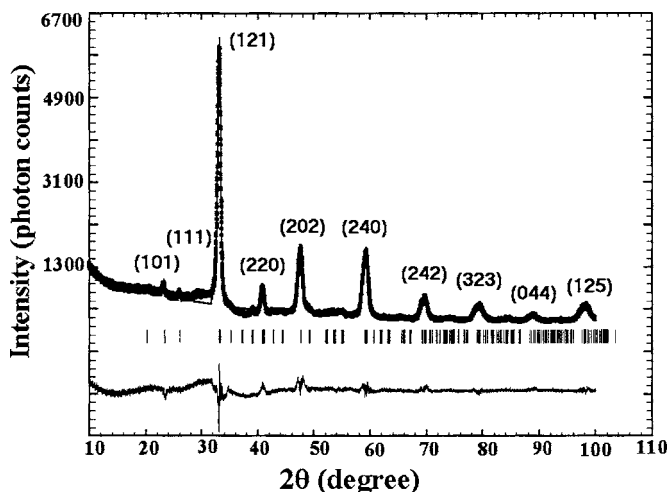


FIG. 1. Observed (dots) and Rietveld fitted (continuous lines) XRD patterns of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ nanowires. ($R_w=8.3\%$).

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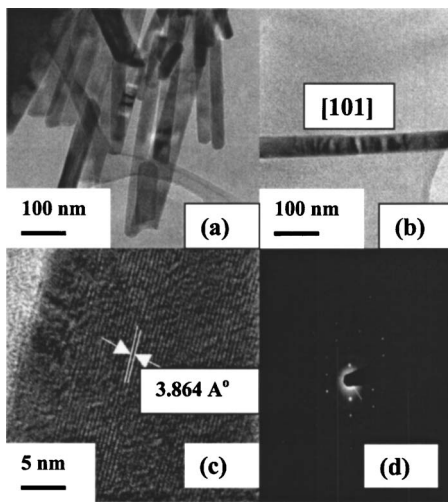


FIG. 2. Typical TEM images [(a), (b)] and HREM and SAED patterns [(c), (d)] of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ nanowires. The scale bar in (a) and (b) is 100 nm and in (c) it is 5 nm. The diameter of most of the wires is ~ 50 nm though a few wires with larger diameter (~ 120 nm) are also seen. The lengths are of the order of a few micrometers. The growth direction is [101]. The amorphous looking region at the top left hand corner of (c) is actually due to the background. The relatively disordered ~ 5 -nm-thick surface region on the nanowires could be due to amorphization/polycrystallization caused by electron bombardment (Ref. 6).

Cu $K\alpha$ radiation in the 2θ scan range from 10 to 100° at the rate of $0.01^\circ/10$ s. The sample is found to be single phasic and free from impurities. The Reitveld analysis of the pattern shows that the unit cell is orthorhombic with the lattice parameters $a=5.4464$ Å, $b=7.6031$ Å, $c=5.3962$ Å and the unit cell volume $V=223.0842$ Å³. The corresponding values for the bulk are $a=5.40428$ Å, $b=7.61275$ Å, $c=5.39414$ Å, and $V=221.92$ Å³ (Ref. 9). Thus there is found to be a small increase in the unit cell volume in nanowires, with an associated contraction along the (b) direction. Figure 2 shows the results of TEM investigations of the nanowires. It is seen that each nanowire is of uniform diameter along its entire length. The diameter of most of the wires is found to be ~ 50 nm though a few wires with larger diameter (~ 120 nm) are also seen. The lengths are of the order of a few micrometers. The SAED pattern shows that the nanowires are single crystalline. HREM lattice imaging confirms the single crystalline nature of the nanowires. The interplanar spacing is found to be 3.864 Å and we conclude that the growth direction is [101].

In Fig. 3 are presented the results of SQUID magnetometry carried out on the nanowires along with those on bulk PCMO:0.5 presented for comparison. The latter was prepared by solid state reaction of Pr_6O_{11} , CaCO_3 and MnO_2 . For the bulk sample, in conformity with the already published behavior,¹⁰ the charge ordering transition at 245 K is clearly seen as a peak in the magnetization and a shallow, broad peak marks the antiferromagnetic transition at ~ 175 K. (The small increase in the magnetization below ~ 50 K for the bulk sample could be attributed to ordering of the Pr^{3+} ions.) In sharp contrast, for the nanowires, the CO peak is greatly suppressed and the AFM peak is absent. At this point, it is not possible to determine whether the weak CO peak is intrinsic to the nanowires or due to any residual bulk PCMO:0.5 present. Further, a rise in the magnetization is observed starting at $T < 125$ K, indicative of ferromagnetism. The inflection point given by the minimum in

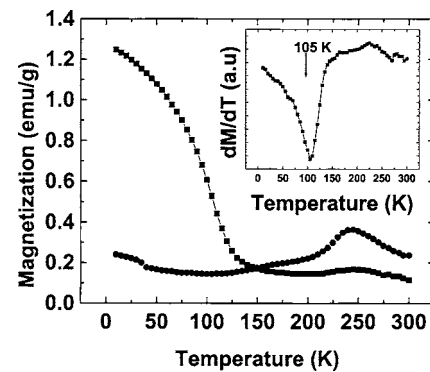


FIG. 3. Temperature dependence of magnetization for the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ nanowires (filled square) and the bulk polycrystalline sample (filled circle) at a constant magnetic field of 0.1 T. The first derivative of M with respect to T is shown in the inset.

dM/dT vs T shown in the inset of Fig. 3 gives the transition temperature T_C to be 105 K.

In our earlier work¹¹ we have observed that the transition to the ferromagnetic state in manganites is accompanied by characteristic changes in the line shapes of EMR signals. This is the consequence of the appearance of exchange and anisotropy fields in the ferromagnetic state. With a view to obtaining additional confirmation of the transition to the ferromagnetic state in the PCMO:0.5 nanowires, we have carried out X-band electron paramagnetic resonance experiments on the nanowires dispersed dilutely in paraffin wax as a function of temperature in the range 10–300 K. The results are presented in Fig. 4. It can be seen that down to about 130 K symmetric Lorentzian signals are observed which, however, become very broad and asymmetric below that temperature, in a way similar to that observed in ferromagnetic manganites. The detailed analysis of the EMR results in terms of the temperature dependence of the g factor, the linewidth and the intensities will be published elsewhere. Here we only wish to point out the additional corroboration obtained by the EMR measurements towards a ferromagnetic phase in the PCMO:0.5 nanowires.

Now we address the question of the likely mechanism of the weakening of the CO and the disappearance of the AFM transition and the appearance of the FM phase in the nanowire system. It is well known that significant changes of the

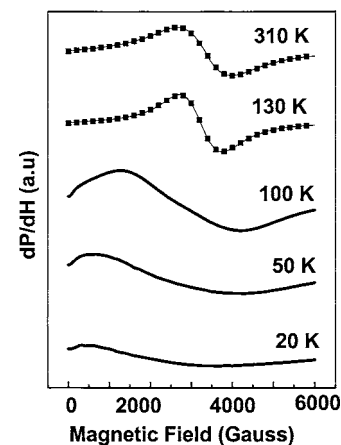


FIG. 4. EMR signals of nanowires at different temperatures. The solid lines are experimental signals and the filled squares on the signals for 310 and 130 K are fits to the field derivative of Lorentzian line shape.

magnetic properties are expected at the nano scale. For example as early as 1962, Néel¹² suggested that fine particles of AFM materials should exhibit weak ferromagnetism and/or superparamagnetism. He argued that this occurs as a result of uncompensated spins on the two sublattices. Since then a number of examples have been reported where nonzero magnetic moments have been observed in nanosize particles of bulk antiferromagnetic materials.¹³ A similar mechanism, in principle, could provide an explanation for our observation, in as much as along the two directions perpendicular to the growth axis of the nanowires, surface effects dominate over the bulk effects, which can result in uncompensated spins. However, recent studies have shown that other factors need to be taken into account in nanometric systems. For example, in a study of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ thin films on LaAlO_3 substrate,¹⁴ a ferromagnetic phase was observed and CO phase suppressed which was attributed to the strain effect caused by the substrate, which also caused a structural change to a monoclinic phase. While our nanowires are free standing, and do not undergo any structural change unlike the thin film, they are still subject to strain effects originating in “surface-coordination deficiency-induced” bond contraction.¹⁵ The latter, together with the profound changes in the band structure expected to be caused by the quantum confinement effects¹⁶ arising out of the one-dimensional nature of the nanowires, could alter the phase diagram drastically. It is established¹⁷ that T_{CO} decreases slowly and linearly and T_C increases much faster in a parabolic dependence with the e_g electron bandwidth. The clarification as to whether any or all of these factors are operative behind our observation is beyond the scope of this present work and will form the subject of future studies.

An important correlate of the FM phase in a large number of manganites is the insulator to metal transition occurring around T_c accompanied by CMR. To find out if the nanowires also show these phenomena, the resistivity of single nanowires as functions of temperature and magnetic field needs to be measured. Our preliminary electrode-less conductivity measurements on the nanowires of $\text{PCMO}:0.5$ indicate that the transition to the ferromagnetic state is accompanied by an enhancement in the conductivity.

In summary, we have prepared nanowires of the charge ordering manganite $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ using a hydrothermal method and characterized them by various techniques. The charge ordered phase is found to be weakened and the antiferromagnetic phase is seen to have disappeared in the nanowires. Instead, a ferromagnetic phase is observed in this one-dimensional phase of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.

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