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# Evolution of percolating behavior in La<sub>0.325</sub>Pr<sub>0.3</sub>Ca<sub>0.375</sub>MnO<sub>3</sub> micro/nanowires

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#### Abstract

La<sub>5/8-x</sub>Pr<sub>x</sub>Ca<sub>3/8</sub>MnO<sub>3</sub> (LPCMO) is a prototypical electronic phase separation material whose scaling property and size dependence have attracted much attention due to its potential applications in electronic devices. In this study, planar-structured single LPCMO micro/ nanowire devices with diameters ranging from 100 nm to several microns were fabricated using an electro-spinning method. We found that the metal–insulator transition of the LPCMO wire was suppressed and finally disappeared with decreasing diameter. We suggest that such transport behavior originates from the size limitation of the percolating characteristic. Several ferromagnetic percolating paths formed in the micron-sized device, evidenced by step-like jumps in the magnetoresistance measurements. For the submicrometer-sized devices, the percolating behavior was severely decreased, resulting in a significant reduction of magnetic response by more than three orders of magnitude. These results indicate that the scaling limitation of the percolating characteristic plays a key role in performance modulation of phase separation material based nano-devices, and should be carefully considered in device design.

Keywords: manganite, nanowire, electronic phase separation, percolating path

S Online supplementary data available from stacks.iop.org/JPhysD/49/335001/mmedia

(Some figures may appear in colour only in the online journal)

#### Introduction

Perovskite manganites, which are strongly correlated electron systems, have been extensively studied in the past few decades due to their complex phase diagrams and peculiar physical phenomena, such as their metal–insulator transition (MIT), colossal magnetic resistance (CMR), lattice distortion and charge ordering [1–3]. This material provides a proto-typical platform to investigate the interplay of charge, spin, lattice and orbital degrees of freedom. The coexistence and competition of different phases in these materials have been confirmed by various methods [2, 3] and many efforts have been devoted to controlling the phase transition for potential electronic device applications. Among perovskite manganites,  $La_{5/8-x}Pr_xCa_{3/8}MnO_3$  (LPCMO) is a typical electronic phase separation (EPS) material composed of paramagnetic insulator (PMI), charge-ordering insulator (COI) and ferromagnetic

metal (FMM) phases. It is generally believed that the CMR effect in this type of material arises from the competition and transition among these phases. A lower temperature or a higher magnetic field usually cause the nucleation and growth of FMM domains in EPS materials, finally forming several percolating paths in the insulator background. The percolating behavior is very sensitive to external perturbations, such as strain, light and field effects [4–8], indicating the feasibility of multiple field modulation in EPS materials. As reported, the domain size of mixed electronic phases varies from tens of nanometers to submicron meters [2, 9]. It is natural to ask what will happen if the size of the manganite is comparable to a single domain, for example, in terms of the characteristics of nanoscale inhomogeneity and the microscopic nature of EPS. Several groups have reported that LPCMO stripes (from several micrometers to submicron sizes) fabricated using UV-lithography and etching of high quality epitaxial films

[10–12] should demonstrate different electric and magnetic transport behaviors compared to large scale samples. These differences may arise from a break in symmetry at the artificial edge of the LPCMO stripes, i.e. the FMM state occurs at the stripe edge. However, Yanagisawa *et al* [13] found that a nanoscale LPCMO device patterned by atomic force microscope lithography possessed insulating behavior below 0 T and large hysteretic behavior below 5 T. The intrinsic characteristics of nanoscale manganites may be hampered by elements changing on these stripe edges, which is unavoidable when using micro-fabrication techniques.

Electro-spinning has been widely used in chemistry to synthesize binary and complex oxide nanowires such as TiO<sub>2</sub>, ZnO, La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> LaCoO<sub>3</sub> [14–18], and LaSrCuO<sub>4</sub> [19]. The competition between the charge repulsion and surface tension of precursors leads to materials with various nanostructures such as nanobeads, nanowires necklace-like nanowires, etc [20–22]. Their diameters can easily be changed from several micrometers to tens of nanometers by varying the electric field, injection speed, viscosity and surface tension of the precursors [23]. By adopting an appropriate temperature and oxygen pressure in the subsequent calcination, complex oxide nanowires with high crystallization, purity and a smooth surface can finally be obtained.

In this work, LPCMO wires with diameters ranging from several microns to tens of nanometers were fabricated using the electro-spinning method. Although the magnetizationtemperature (M-T) curves indicate that the Tc changed slightly, we found that the electric transport behavior strongly depended on the diameter of the LPCMO wires. The resistance of the micrometer-sized LPCMO wire demonstrated a typical MIT when cooling down, combined with step-like jumps in the magnetoresistance measured at the warming up transition temperature. The nanometer-sized wires retained their insulator properties at very low temperatures and their magnetoresistance was significantly reduced. These results could be understood based on the size limitation of percolating behavior in LPCMO, which gives us some suggestion for the structural design and performance modulation of EPS material based nano-scale devices.

#### **Experimental details**

In the sample preparation, 50 nm thick SrRuO<sub>3</sub> (SRO) films are deposited on (001) SrTiO<sub>3</sub> (STO) substrates by pulsed laser deposition at 650 °C with 15 Pa oxygen pressure. Then the SRO film was patterned to parallel stripes by conventional UV-lithography and etching processes. The electrode bars are 50  $\mu$ m in width with 10  $\mu$ m separations.

The LPCMO wires were fabricated using the electrospinning technique. LPCMO precursors were first prepared by mixing lanthanum (III) nitrate hydrate, praseodymium (III), calcium nitrate tetrahydrate and manganese (II) acetate terahydrate. 0.3 g of polyvinylpyrrolidone (MW 130000), 0.2 ml deionized water and 3 ml N, N-dimethylformamide were added into each solution sample. To change the diameter of the LPCMO wires, three types of precursors were adopted, with LPCMO concentrations of 0.003 mol, 0.002 mol and 0.001 mol. After 10h continuous stirring at room temperature, an injector was filled with the LPCMO precursor with a 15 cm target distance. The spinning voltage was 10 kV and the injection speed was  $1 \text{ ml } 3 \text{ h}^{-1}$ . To prepare a single nanowire device, a concave metal bracket was used as the sample holder as shown in figure S1(a) (stacks.iop.org/JPhysD/49/335001/ mmedia). The concave bracket was quickly placed below the needle for less than one second. Usually only a few nanowires were left hanging on the concave bracket. Thus we could easily choose one nanowire and transfer it to the SRO-covered substrate by electrostatic adherence. To identify the chemical composition, crystallization and magnetic properties, in addition to the single nanowire devices, three types of grid-like LPCMO wires were also spun on STO substrates using corresponding precursor solutions. Finally, all the LPCMO wires were calcinated at 650 °C in 1 bar oxygen pressure for 3h.

#### **Results and discussion**

#### Morphology and structure of LPCMO wires

Figures 1(a) and (b) show scanning electron microscope (SEM) images of the LPCMO wires fabricated on the STO substrate, which demonstrate quite smooth edges without obvious unnatural boundaries or macro-physical defects. To verify the growth quality of the LPCMO wires, figure 1(c)compares the x-ray diffraction (XRD) results of the LPCMO wires spun on the STO substrate and free LPCMO wires that were directly scraped off the concave bracket and calcinated in the same conditions. The results for the free LPCMO wires without a substrate are in agreement with the polycrystalline powder XRD pattern, demonstrating similar peak positions and relative intensities (the highest peak in the (110) orientation). In contrast, the LPCMO wires grown on the (001) STO substrate mainly show a preferred c-axis (001) orientation. The relative intensities of the (110), (111) orientated peaks become much weaker compared to the powder diffraction pattern, which may be due to some indirectly contacted LPCMO wires in the upper layer of the thick sample. Thus, we consider that a single LPCMO wire annealed in the same temperature and oxygen pressure conditions could be epitaxially grown on the STO substrate. To further identify the surface topography, a 3D image of a single LPCMO nanowire was obtained using atomic force microscope (AFM), as shown in figure 1(d). The shape of the nanowire is like a semi-cylinder, the width of which (~460nm) is twice its thickness (~220nm), as shown in the inset cross-section image. The chemical stoichiometry of the as-prepared sample was confirmed using an energy dispersive spectrometer (EDS) (shown in figure S2). The atom percent of the nanowire calculated using EDS software gives a La:Pr:Ca:Mn ratio of 0.32:0.26:0.3:1 (table S1) which deviates slightly from the La<sub>0.325</sub>Pr<sub>0.3</sub>Ca<sub>0.375</sub>MnO<sub>3</sub> precursor. As the huge background interference of the STO substrate should severely reduce the signal-to-noise ratio of the EDS analysis, this deviation of the element ratio is acceptable. What we want to emphasize is the homogeneous distribution of all elements along the nanowire direction (figure S3), indicating that the LPCMO nanowires are single-phase.



**Figure 1.** (a) SEM image of a group of LPCMO wires spun on the STO substrate. (b) High resolution SEM image of a single wire with diameter of ~1  $\mu$ m. (c) XRD data of the LPCMO wires spun on the STO substrate (top) and free LPCMO wires without substrate (bottom). (d) 3D AFM image of a single LPCMO wire. The inset shows the cross-section image.



**Figure 2.** (a) Optical image of the experimental set up of a planar two-terminal device. (b)–(d) The diameters of three LPCMO wire devices confirmed by SEM are 100 nm, 850 nm and 2.9  $\mu$ m.



**Figure 3.** R-T curves measured in different magnetic fields for the (a) 2.9  $\mu$ m, (c) 850 nm and (e) 100 nm LPCMO wires, and the correspondingly M-T curves of a group of LPCMO wires fabricated by the (b) 0.003 mol, (d) 0.002 mol and (f) 0.001 mol precursors, respectively.

Figure 2(a) shows an optical image of the experimental set up for electric measurement. A single LPCMO wire vertically crosses the SRO electrodes, forming a series of planar devices. To confirm the ohmic contact between SRO electrode and the LPCMO nanowire, we compared the roomtemperature current-voltage (I-V) characteristics of the same device measured using the two-terminal method and fourterminal method (figure S1(b)). Good linearity of the I-Vcurves is observed for both methods, only displaying slight changes in their slopes. Because the resistance of the LPCMO nanowire would become very high at low temperatures, we adopted the two-terminal method in all electric experiments to extend the measureable range of the resistance-temperature (R-T) curves. As mentioned in experimental details section, three types of LPCMO devices with different diameters were prepared using different precursors. The SEM images shown in figures 2(b) and (c) indicate that the diameters of the three wires were 100 nm, 850 nm and 2.9  $\mu$ m, which correspond to the 0.001 mol, 0.002 mol and 0.003 mol solutions, respectively.

#### Transport and magnetic properties

The temperature dependence of the transport and magnetic properties of LPCMO wires was tested in a SQUID-VSM system with an extra Keithley 2601B sourcemeter. The *R*–*T* curves and *M*–*T* curves of these samples are shown in figure 3. The room temperature resistance of the sample with the largest diameter (2.9  $\mu$ m) is ~2.3 × 10<sup>5</sup> Ω. When cooling down, a peak resistance of ~2.1 × 10<sup>8</sup> Ω is observed at 97 K (figure 3(a)), which indicates the transition of insulator to

metal behavior. The warming up R-T curve gives a higher transition temperature of 120K and a lower peak resistance of ~2.3  $\times$  10<sup>7</sup>  $\Omega$ , demonstrating an obvious hysteresis loop with the cooling down curve. These characteristics are very similar to the LPCMO films deposited by pulse laser deposition or molecular beam epitaxy, which are usually explained by the percolating behavior caused by the connection of FMM domains in the COI background. The magnetic response of the R-T curves also confirms the existence of percolating paths in the 2.9  $\mu$ m LPCMO wire. When a magnetic field is applied, the transition point shifts to a higher temperature (up to ~200 K in a 5 T field) and the hysteresis loop of the R-T curves is significantly suppressed and finally disappears, which implies the influence of the magnetic field on the growth and melting of the FMM phase. Note further that, unlike the obvious MIT in the 2.9  $\mu$ m LPCMO wire, the *R*-*T* curves of the 850 nm and 100 nm wires retain insulator behavior in the whole measurement range (20 K-300 K) as shown in figures 3(c) and (e). (The resistance below 150K of the 100nm nanowire reaches the limits of our equipment, and there is no sign of metal behavior at very low temperatures.) In contrast, the magnetic response of the LPCMO submicron wires has been strongly reduced and even a 5 T field cannot turn the R-T curves into metal behavior, which possibly indicates that the growth of FMM phases is greatly confined by the surface of nanowires.

To clarify the underline physics of the size dependence of transport behavior, we also compared the M-T curves of the LPCMO micro/nanowires. Figures 3(b), (d) and (f) are the results for the three groups of LPCMO wires corresponding to the 0.003 mol, 0.002 mol and 0.001 mol solutions, respectively. We can see that the different-sized LPCMO wires



**Figure 4.** (a) *MR*–*T* curves under a 5 T magnetic field for 2.9  $\mu$ m, 850 nm and 100 nm LPCMO wires. (b) The *R*–*H* curve of the 2.9  $\mu$ m wire measured at 120 K. The scanning sequence for the magnetic field was 0, +5 T, -5 T, and +5 T. The black, red and blue curves correspond to an initial increasing field from 0 T to 5 T, a decreasing field from 5 T to -5 T, and an increasing field from -5 T to 5 T. (c)–(f) Shows the *R*–*H* curve of the 2.9  $\mu$ m wire measured at 35 K, 97 K, 120 K and 150 K, respectively. (g) The *R*–*H* curve of the 2.9  $\mu$ m LPCMO wire measured under a vertical magnetic field (red and purple curves) and a parallel magnetic field (dark and light blue curves). The inset shows a sketch of the field direction.

demonstrate a similar paramagnetic–ferromagnetic (PM–FM) transition ( $T_c$ ) at ~200 K and then tend to be saturated below 100 K. The only difference lies in the small up-turn at 30 K, which is the signal of the residual PM phases. This bending becomes more distinct in the smaller LPCMO nanowires. This may indicate that the proportion of residual PM phases at very low temperature will increase with decreasing wire diameter.

We cannot obtain a numerical estimate for the magnetic moment per Mn atom because the detailed mass of these LPCMO wires for the three samples is unknown. However, the consistent magnetic properties of the LPCMO micro/ nanowires imply that the different electric transport behaviors are not due to the suppression of the intrinsic PM-FM transition but other reasons, i.e. the size dependence of percolating characteristics. In our consideration, although the MIT is still observed in the 2.9  $\mu$ m wire sample, only a few FM phase based percolating paths are formed in this case. The defects, nonstoichiometry and broken bonds of micro/ nano-scaled LPCMO wires cause spin disorder in the sample surface, which destroys the FM ordering and results in a magnetically dead layer. Thus, the growth of the FM phase will be suspended on the wire surface. As the domain size of the electronic phases is in the order of tens of nanometers, the number of connected percolating paths confined within the 2.9  $\mu$ m LPCMO wires should be countable. And when further shrinking the diameter to the submicron scale, neither a low temperature nor a high magnetic field can lead to any percolating paths in the LPCMO nanowires. To confirm the size limitation of the percolating behavior, the magnetoresistances of the three samples were measured at different temperatures. Figure 4(a) shows the *MR*-*T* curves of the three wires. The magnetoresistance of the 2.9  $\mu$ m wire under the 5 T field reaches the largest value of  $\sim 3 \times 10^5$ % at 97 K, whereas it shrinks to ~300% for the 850nm wire and to even less than 10% for the 100 nm wire. More interestingly, the countable percolating paths in the 2.9  $\mu$ m sample are clearly demonstrated by the step-like resistance–magnetic field (R-H)dependence at 120 K. As shown in figure 4(b), after cooling down the sample to 120 K, the resistance quickly reduces from  $\sim 3 \times 10^7 \Omega (0 \text{ T})$  to  $\sim 1 \times 10^5 \Omega (5 \text{ T})$ , which indicates that the percolating paths have already been formed in the LPCMO microwire by the external magnetic field. A small hysteresis also exists during the decreasing and increasing magnetic field, in particular in the low field, which indicates the same process for the formation and melting of percolating paths with temperature variation. The important point to note is



**Figure 5.** (a) R-T curve of a 1.67  $\mu$ m wire composed of tens of nanowires measured in 0 T and 5 T fields. The inset shows the SEM image of this LPCMO wire, indicating clear boundaries between each nanowire. (b)–(d) Show percolating diagrams for the wires in order of decreasing thickness. The white and black lattices represent COI phases and FMM phases, respectively.

that when the magnetic field drops below 2000 Oe, as shown in the enlargement of figure 4(e), several step-like jumps of  $\sim 5 \times 10^5 \Omega$  are observed in both directions of the *R*-*H* curve. Considering the enormous difference in the conductivities of the insulating and metal phases, here each step may arise from the melting of a single percolating path. These tiny steps of the *R*-H curve are most obvious at 120 K. For other temperatures (such as 35 K, 97 K and 150 K shown in figures 4(c), (d) and (f)), the resistance gradually changes with the magnetic field. This is because 120K is the MIT temperature for the warming up R-T curve in a 0 T field, which indicates that the percolating paths are both ruptured at this point. In the R-H measurement, although the temperature remains at the critical point of 120K, the thermal fluctuation would become strong enough to cause the rupture of the percolating paths at a very low magnetic field. In contrast, if the temperature is much lower than 120 K, the FM paths are very stable even in a 0 T field. If the temperature is higher than 120 K, the FM paths are already ruptured.

We should point out that the magnetic fields are both inplane and transverse to the LPCMO wires in the above resistance measurements. Considering the intrinsic anisotropy of 1D wires, we also compared the step-like R-H behavior measured under transverse and parallel magnetic fields (figure 4(g)). The parallel R-H curve is basically coincident with that of the transverse case, despite a smaller number of steps and a larger coercive force (200 Oe) causing a more obvious butterfly shape. The more smooth dependence indicates that the percolating paths are more stable in the parallel magnetic field than in the transverse direction, which may be caused by the oriented growth of FM domains in 1D wires.

To further prove the influence of surface states and grain boundaries on the percolating behavior, we synthesized a 1.67  $\mu$ m thick LPCMO wire by gathering tens of small wires with nanometer diameters, as can be seen in the inset of figure 5(a). In this situation, a lot of grain boundaries will be formed inside the LPCMO microwire after calcination. The R-T curve (figure 5(a)) shows totally insulating behavior in the whole measurement range and even in a 5 T magnetic field (only a slight bending at ~80 K), which is quite different from the 2.9  $\mu$ m single wire. This result indicates that the absolute diameter of the LPCMO wires is not the key factor determining percolating behavior, as the growth of the FM phase is restricted by the surface states and grain boundaries.

The schematic phase diagram of LPCMO wires evolving with decreasing diameter is given in figures 5(b)-(d). The black and white lattices correspond to the FMM and COI domains, respectively. Due to surface effects, the nucleation and growth of the FM phase are suppressed in the surface layer. This means that the random growth of FM paths will be terminated at the wire surface and all consecutive percolating paths will be confined within the inner layer. Naturally, when scaling the sample size to microns, the number of percolating paths decreases accordingly (similar to large-scale thin films), and eventually fail in the nanometer-sized LPCMO wires. This is why the MIT can only be observed in the 2.9  $\mu$ m LPCMO wire. For the 100 nm sample, the nanowire diameter is commensurate with the size of the FM/COI domains. Some insulative COI domains still exist at very low temperatures, which block the nanowire and contribute substantially to the transport behavior.

#### Conclusion

In summary, different-sized LPCMO wires with diameters ranging from the micrometer- to nanometer-scale were synthesized using the electro-spinning technique and prepared as single nanowire devices. We observed clear MIT behavior in the 2.9  $\mu$ m LPCMO wire, with step-like jumps in the *R*–*H* curve measured at the warming up transition temperature. However, for the 850 nm and 100 nm wire samples, the *R*–*T* curves show fully insulating behavior and the magnetoresistance is reduced by as much as three orders of magnitude. The similar PM–FM transition temperatures obtained from the *M*–*T* curves imply that the magnetic properties of the LPCMO wires change slightly with wire diameter. Thus we suggest that the different transport characteristics are due to the size dependence of the percolating behavior. Only few percolating paths occurred in the 2.9  $\mu$ m wire, resulting in a step-like *R*–*H* dependence. In contrast, no connected path was formed in the nanometer-sized wires with significantly reduced magnetoresistance. Our results imply the scaling limitations of the percolating characteristic for manganites, which gives us some suggestion for the device design of phase separation material based nanoscale devices.

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