

Reemergent Metal-Insulator Transitions in Manganites Exposed with Spatial Confinement

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The metal-insulator transition is characterized as a single peak in the temperature-dependent resistivity measurements; exceptions to this have never been seen in any single crystal material system. We show that by reducing a single crystal manganite thin film to a wire with a width comparable to the mesoscopic phase-separated domains inherent in the material, a second and robust metal-insulator transition peak appears in the resistivity versus temperature measurement. This new observation suggests that spatial confinement is a promising route for the discovery of emergent physical phenomena in complex oxides.

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The striking transport properties of perovskite manganites, manifested in exotic behaviors such as their colossal magnetoresistance (CMR), are believed to be caused in large part by their intrinsic tendency toward the coexistence of competing orders [1–3], a phenomenon often referred to as phase separation (PS). For manganites, PS and its associated percolative transport are generally considered to be responsible for their unusually high magnetoresistance [1,2]. If the spatial dimension of these materials is artificially reduced to the characteristic PS length scale, dramatic changes in their transport properties could occur. For instance, discrete steps in resistivity have been observed in the metal-insulator transitions (MIT) in systems of manganite wires [4,5].

Recent experimental and theoretical investigations have shown that the nanometer is the most typical length scale for PS in manganites [6–12]. However, submicrometer scale PS has also been observed in $\text{La}_{1-x}\text{Pr}_x\text{Ca}_{0.375}\text{MnO}_3$ (LPCMO) system where ferromagnetic (FM) metallic and charge ordered (CO) insulating domains coexist [13,14]. Although the driving mechanisms that cause large scale PS is still under investigation [15–17], the LPCMO system provides an ideal system for studying the effect of spatial confinement as it can be easily accessed by conventional lithographic fabrication processes [18,19]. In this work, we show never before observed emergent transport properties in LPCMO wires that differ vastly from bulk and thin films of the same material. We have found that by reducing a single crystal LPCMO thin film to a wire with a width comparable to the mesoscopic phase-separated domains inherent in this material, a second and robust MIT peak appears in the resistance vs temperature measurement. This phenomenon can be theoretically modeled by describing the system as a resistive network created by local modifications of bandwidth or strain. These findings are anticipated to lead to further experimental and theoretical studies in exploring novel emergent behavior while potentially leading to new functionalities in, not only manganites, but any material where phase competition plays an important role in determining bulk properties.

$\text{La}_{1-x}\text{Pr}_x\text{Ca}_{0.375}\text{MnO}_3$ thin films were grown on single crystal substrates of SrLaGaO_3 (100), LaAlO_3 (100) and NdGaO_3 (110) using laser molecular beam epitaxy under ultrahigh vacuum. Film quality was confirmed by atomic force microscope (AFM), Rutherford backscattering (RBS), and x-ray diffraction. Wires were then fabricated from the epitaxial thin films using conventional wet-etch optical lithography. The detailed growth and etching procedures have been described elsewhere [4,20,21].

Figure 1(a) shows an optical image of a typical $\text{La}_{1-x}\text{Pr}_x\text{Ca}_{0.375}\text{MnO}_3$ wire fabricated from an epitaxial thin film using conventional wet-etch optical lithography. Figures 1(b) and 1(c) show the temperature-dependent resistivity of a 70 nm thick LPCMO film grown on SrLaGaO_4 (100) (SLGO) and a LPCMO wire with dimensions $70 \text{ nm} \times 10 \mu\text{m} \times 50 \mu\text{m}$ on SLGO both having a 0.3 Pr doping which translates to an $\langle r_A \rangle$ of 1.339 Å. The film [Fig. 1(b)] shows the typical MIT expected in CMR thin samples. The CO insulator phase develops and coexists with the low- T FM metallic phase which results in the observed thermal hysteresis. By increasing the magnetic field strength, the transition temperature increases while the magnitude of the warming or cooling hysteresis decreases. In Fig. 1(c), the $10 \mu\text{m}$ wire exhibits a similar behavior but with a notable addition. With cooling, a MIT occurs at roughly the same temperature ($\sim 150 \text{ K}$) as in the film, but after entering a region of metallicity ($\sim 125 \text{ K}$), the resistivity rebounds and forms a *second* MIT ($\sim 75 \text{ K}$). The resistivity difference between cooling and warming (insets) illustrates the dramatic benefits of using spatial confinement in PS materials in order to observe concealed properties. Both resistivity peaks in the wire are strongly sensitive to magnetic fields. With increasing fields, the intensities of both peaks decrease, while the peak positions shift toward higher temperatures. We note that such a reemergent MIT has never been observed in manganite materials in any single crystal bulk or thin-film form and, to our knowledge, has not been observed before in any other single crystal compound [22–24]. Although double peaks in resistivity vs temperature measurements have

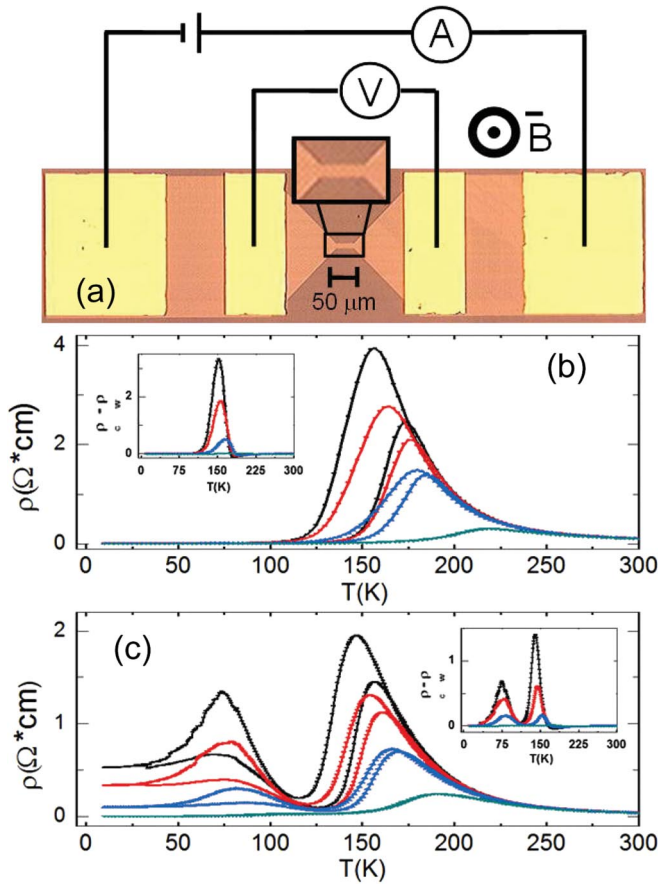


FIG. 1 (color). Transport and magnetic properties of 70 nm $\text{La}_{0.325}\text{Pr}_{0.3}\text{Ca}_{0.375}\text{MnO}_3$ thin film and wire with $\langle r_A \rangle$ of 1.339 Å on lattice matched SrLaGaO_4 on heating and cooling (indicated by arrows) under increasing magnetic fields. (a) Optical image of 10 μm geometry with expanded view of wire and legend of applied magnetic field direction and 4-point probe configuration. (b) Comparison of temperature dependence of resistivity in film at 0 T (black), 0.4 T (red), 1 T (blue), and 3.5 T (green). The film shows a single MIT peak. (c) Comparison of temperature dependence of resistivity in 10 μm wire at 1.5 T (black), 1.75 T (red), 2.25 T (blue), and 3.75 T (green). The wire shows a reemergent, low temperature peak in ρ that is not present in the film. (Insets) Show differences in resistivity between warming and cooling curves.

been observed in polycrystalline samples [25–29], the causes are likely associated with extrinsic factors such as grain boundary effects or chemical defects.

Since a reemergent MIT has never been documented in either bulk or thin film form, it is reasonable to assume that this effect is made visible due to the spatial confinement in the wire geometry. In LPCMO, FM and CO phase separation and percolative transport are generally accepted as the governing mechanisms for the observed MIT [1,2]. Within this context, the simplest way to understand a reemergent MIT is to assume that there are two types of regions in the system with their MIT's occurring at distinctly different temperatures. Interestingly, the LPCMO system exhibits a

sharp change in the MIT temperature in the vicinity of a critical $\langle r_A \rangle$ [1,30]. While the $\langle r_A \rangle$ value can be tuned by Pr-doping, it has been shown that the effects of lattice strain act comparably to this “chemical pressure” in influencing the perturbation of the Mn-O-Mn bond angles [31,32]. Considering this fact, a slight spatial variation of Pr-doping or lattice strain can lead to two types of regions with distinctly different MIT temperatures assuming that the effective $\langle r_A \rangle$ has been preset to be close to the critical point, which is the case in our system.

For the LPCMO wire prepared by laser MBE, a spatial variation of Pr doping is rather unlikely to occur due to the nature of the atomic deposition process. However, a slight spatial variation of lattice strain in the LPCMO wire is highly possible due to the presence of steps that are inherent in all thin films. The lattice strain in the regions at the step edges is, in general, slightly different from that at the terrace with the former being only a small fraction of the latter. In the following, we devise a simple model to test if such a spatial variation of strain can indeed give rise to the reemergent MIT behavior.

In this model, a resistive series was created using the known bulk LPCMO resistivities [1] and plotted as $R_t = aR_1 + (1-a)R_2$ where R_t is the total resistance of the series, and R_1 and R_2 are resistances of LPCMO for two similar Pr-dopings (Fig. 2). It is important to point out that, while we justify the existence of R_1 and R_2 by a small fluctuation in the $\langle r_A \rangle$ forming a gate across the wire, R_1

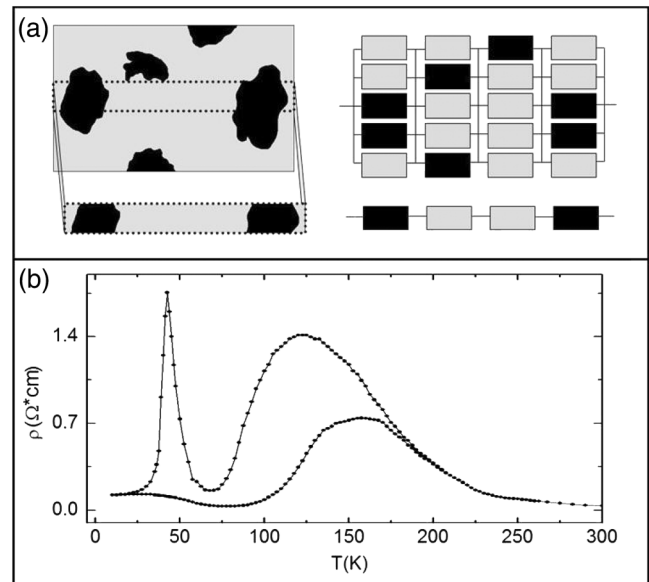


FIG. 2. Theoretical model for the $\text{La}_{0.325}\text{Pr}_{0.3}\text{Ca}_{0.375}\text{MnO}_3$ wire. (a) Schematic diagram of film and wire with corresponding resistive networks. Black and gray areas represent regions of differing resistivity with independent MIT temperatures. (b) Model data for the LPCMO resistivity in a serial resistive network using LPCMO with constituent $\langle r_A \rangle$ of 1.334 and 1.339 Å. The resistivity at 125 K is dominated by the larger $\langle r_A \rangle$, while the low- T peak is contributed by the smaller $\langle r_A \rangle$.

and R_2 are likely caused by local modifications of epitaxial strain as mentioned above. Figure 2(a) shows a simple schematic for this model where the unmodified film can be represented as a two-dimensional resistive network, while the etched wire geometry effectively reduces the system to a serial network. The resistive differences of these two dopings can be attributed to the chemical pressure differences resulting from the change in $\langle r_A \rangle$ [33]. Figure 2(b) shows R_T for a serial LPCMO system comprised of 99.9997% LPCMO with an $\langle r_A \rangle$ of 1.339 Å and 0.0003% LPCMO with a smaller $\langle r_A \rangle$ of 1.334 Å. These were selected due to the fact that, while the $\langle r_A \rangle$'s only differ by 0.002%, their transport properties are vastly altered [1,30]. This configuration produces hysteretic differences at 45 and 125 K, and we can plainly see a double-peak formation similar to that experimentally observed. Markedly, only a very small amount of the component with the smaller $\langle r_A \rangle$ is needed to create the reemergent MIT, as a larger percent would totally dominate at low temperatures. This is consistent with the fact that the regions associated with the step edges are only a small fraction of the whole wire.

The pair of LPCMO compositions ($\langle r_A \rangle = 1.339$ Å and $\langle r_A \rangle = 1.334$ Å [1,30]) emphasized here, and the relative amount 0.0003% of the composition with the smaller $\langle r_A \rangle$, leads to a deep valley in between the resistivity peaks, in agreement with experiments. Several other compositional pairs were tried, such as 1.336 and 1.339 Å, but it was not possible to reproduce such a deep valley, although the effective resistivity also had two peaks as in the experiments. Other pairs, such as 1.338 and 1.344 Å, can again produce two peaks, but it is difficult to have those peaks at the correct temperatures or with the correct intensities to match experiments. It is in this sense that the presented results are considered to be optimal to reproduce the experimental resistivity vs temperature curve.

Because of strain effects, it may be suspected that the wire's edge is the likely location for phase differences that vary from the bulk. Moreover, investigations of nanosize manganites have identified a difference between the surface and the center of those clusters [34], again suggesting that the edge could behave differently from the wire's center. If this is the case, a parallel configuration of resistances for two different $\langle r_A \rangle$ compositions could describe the manganite wire. However, the reemergent MIT peaks do not occur if R_1 and R_2 are in parallel since the charge will always flow through the lower resistance; the parallel combination will only exhibit a MIT at the highest temperature. Therefore, it is understandable why the reemergent MIT behavior has never been seen in thin films, nanoscale clusters, or bulk. In these systems, the electrons would have more lanes of lower resistivity to follow. But, by limiting the dimensions of the film to be comparable to the PS scale, we force the electrons to travel across both high- and low- T MIT regions in the center of the wire. So

while the wire in the experiment is 10 μm wide, edge effects reduce the true lane of electrical transport down to a scale that is of the same order as the inherent phase domains. This unveils the reemergent MIT which provides us with a view of otherwise hidden regions that can only be seen by reducing the electronic transport lanes to a serial resistive network. Previous theoretical work remarked on the potential importance of quasi one-dimensional manganite systems [35]. Since bulk quasi-1D manganites do not exist, our LPCMO confined configuration is the closest to a realization of those theoretical expectations.

Since chemical pressure and epitaxial strain both act comparably within this system [31,32], one would expect a strong variation of the reemergent MIT behavior when either the $\langle r_A \rangle$ or the substrate induced strain is varied. Indeed, when $\langle r_A \rangle$ is increased from 1.339 to 1.342 Å, the LPCMO wire on SLGO only exhibits a single MIT. However, if the epitaxial (compressive) strain in the wires is systematically increased by fabricating the wires on NdGaO_3 (110), SrLaGaO_4 (100), and LaAlO_3 (100) substrates, with nominal LPCMO lattice mismatches of +0.5%, <0.1%, and -1.6%, respectively, the reemergent MIT *reappears* in the wire under the higher compressive strain of the LAO substrate [Figs. 3(a)–3(c)].

In previous work, LPCMO with $\langle r_A \rangle = 1.339$ Å was grown on LaAlO_3 (100) and spatially confined to similar scales as that used in this work without a double peak in the temperature-dependent resistivity measurements [4]. Taking this data with what has been presented above, we can see that the reemergent MIT appears to arise in a narrow window of strain which could be created by a balance between the chemical pressure related to $\langle r_A \rangle$ and the epitaxial strain contributed from the substrate [31,32]. The double peak observed in the wire on the SLGO substrate at $\langle r_A \rangle = 1.339$ Å can be destroyed by increasing the $\langle r_A \rangle$ of the LPCMO wire which increases the internal chemical pressure. LAO exerts a compressive strain on the wire with $\langle r_A \rangle = 1.339$ Å and shows no reemergent behavior; but by increasing $\langle r_A \rangle$ to 1.342 Å, the change in internal chemical pressure acts to counter-balance the strain and push the transport properties into something roughly similar to those observed on SLGO with a larger $\langle r_A \rangle$. This suggests that there is a critical regime in which the reemergent MIT resides which can be reached through a subtle balancing of strains.

While the underlying mechanism of the proposed simple model needs to be confirmed using imaging techniques and more refined theoretical calculations, our experimental findings already demonstrate the usefulness of reduced dimensionality for the study of PS systems. By forcing electrons to travel through multiple phases, a fuller view of all the phases residing in a material can be obtained via transport measurements. This can effectively be thought of as increasing the “resolution” of electronic transport measurements in phase-separated materials. These develop-

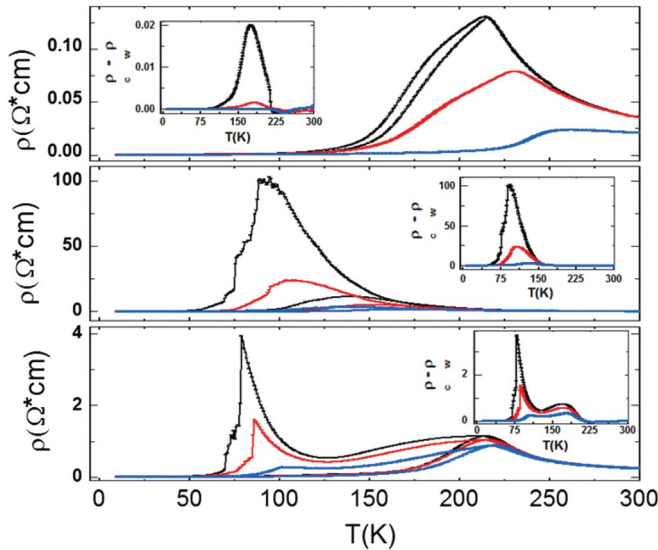


FIG. 3 (color). Transport and magnetic properties of $10 \mu\text{m}$ $\text{La}_{0.391}\text{Pr}_{0.234}\text{Ca}_{0.375}\text{MnO}_3$ wires with $\langle r_A \rangle$ of 1.342 \AA on substrates of varying compressive strain. (Top) LPCMO wire on SrLaGaO_4 ($<0.1\%$ lattice mismatch) for 0 T (black), 1.5 T (red), and 3 T (blue). Hysteretic behavior is never present at lower temperature and is quickly suppressed with application of magnetic fields. (Center) LPCMO wire on NdGaO_3 ($+0.5\%$ lattice mismatch) for 2.5 T (black), 2.75 T (red), and 3 T (blue). The slight increase in tensile strain pushes the MIT to a lower temperature but does not spawn a clear separation into two distinct MIT areas, which could be due to overlap. (Bottom) LPCMO wire on LaAlO_3 (-1.5% lattice mismatch) for 0 T (black), 0.2 T (red), and 0.4 T (blue). Independent metal-insulator transitions are visible at both high and low temperatures with some overlap. (Insets) show differences in resistivity between warming and cooling curves.

ments can be applied to improve our understanding of PS in CMR materials and to establish new functionalities for potential uses in oxide electronics. More generally, for any material with an intrinsic length scale on the order of tens of nanometers, quasi-one-dimensional behavior could be observed by the spatial confinement analysis employed here, which could render properties substantially different from those in bulk and thin-film forms.

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