Nanometer-scale phase separation in a colossal magnetoresistive manganite

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Abstract – Scanning tunneling microscopy and spectroscopy were conducted over a broad temperature range on single crystals of Pr\(_{0.68}\)Pb\(_{0.32}\)MnO\(_3\). Spectroscopic studies revealed inhomogeneous maps of the zero-bias conductance with a broad distribution of the local conductivities only within a narrow temperature range close to the metal-insulator transition. An analysis of the conductance histograms based on these maps gave direct evidence for phase separation into insulating and conducting areas. This phase separation was found to be confined only to the transition region.

There is an intense research going on to understand the remarkable and complex properties shown by a whole family of strongly correlated electron systems. In these materials, an intrinsic instability of the electronic state due to competing interactions may result in the formation of nanometer-sized regions of different phases. Such states have been considered as charge and spin ordered stripes in under-doped cuprates [1], as polar domains in relaxor ferroelectrics [2], or as phase separation between insulating paramagnetic and conducting ferromagnetic regions [3] in mixed-valence manganites of perovskite type A\(\text{MnO}_3\) (A — rare earth or doped divalent ion). In the latter case, evidence for phase separation has been found by various experimental techniques, such as electron microscopy [4], scanning tunneling microscopy/spectroscopy (STM/S) [5,6], magnetic force microscopy [7] and photo-electron spectroscopy [8]. These experiments showed inhomogeneities of random shape on a length scale ranging from nanometers [6] to several hundreds of nanometers [4,5,7,8]. Further, the phase separation persisted deep into the metallic state in some of these manganites. However, computational studies on models of manganites considering double exchange, coupling to Jahn-Teller phonons and long-range Coulomb potential could show only regularly spaced nanometer-scale phase separation [9,10]. The random location and shape of the clusters observed experimentally [4–8] are conjectured to be caused by quenched disorder in the couplings induced by chemical substitution [11,12], whereas mesoscopic phase separation is speculated to result from elastic strain [13]. Recent STS studies combined with transmission electron microscopy [14] on A-site ordered and disordered La\(_{0.73}\)Ca\(_{0.27}\)MnO\(_3\) thin films revealed that phase separation persists in the metallic state only in the disordered film. But, this study does not address the question of phase separation at the metal-insulator transition temperature \(T_{\text{MI}}\). Thus, the origin of the phase separation, the length scale involved, the role of quenched disorder originating from the random A-site substitution, and the temperature range at which phase separation occurs remain all strongly debated.

To resolve some of these issues experimentally, we carried out STM/S on Pr\(_{0.68}\)Pb\(_{0.32}\)MnO\(_3\) (PPMO) single crystals. This compound crystallizes in a pseudocubic, perovskite-type structure with a tolerance factor of 0.97 indicating minimum internal strain. Hence, PPMO constitutes a material highly suitable for the investigation of intrinsic properties. Previously reported [5,6] STS measurements on manganites indicating phase separation were carried out on thin film samples in which substrate-induced strain as well as the granular structure are known to be extrinsic sources for phase separation [15,16], specifically well below \(T_{\text{MI}}\). Further, the STS measurements [5] on thin films of La\(_{0.73}\)Ca\(_{0.27}\)MnO\(_3\) on SrTiO\(_3\), showing coexistence of regions with metallic, insulating as well as intermediate conductivities extending over several

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hundred nanometers, were obtained at a rather high bias voltage $V$ of 3 V (much larger than the semi-conducting gap of 0.2–0.3 V in manganites) and may not reflect the ground-state properties. To overcome this, Becker et al. [6] mapped the zero-bias conductance, $G_0 = dI/dV|_{V=0}$, of thin films $La_{0.7}Sr_{0.3}MnO_3/MgO as a function of temperature $T$ and applied a threshold criterion to distinguish metallic and insulating regions. Such a threshold criterion may not give unambiguous evidence for the existence of phase separation because any statistical distribution of conductance whose average value shifts with temperature will seem to show phase separation [17]. Therefore, in order to provide clear evidence for phase separation, we analyze the entire distribution of $G_0$ and its dependence on temperature. This approach gives direct information on the length scale of the inhomogeneities and the temperature range within which it appears. We discuss the role of disorder or doping and compare the results with macroscopic properties of the very same single crystals.

Single crystals of PPMO used for the present study were taken from a batch of crystals whose preparation and properties were already reported [18,19]. In Pr$_{1-x}$Pb$_x$MnO$_3$, the Curie temperature $T_C$ and $T_{MI}$ do not coincide, and metal-like conductivity occurs in a paramagnetic state in parts of the phase diagram [18,20], a phenomenon uncommon to mixed-valence manganites. Figure 1 depicts the temperature dependence of magnetization ($M$), resistivity ($\rho$) and magnetoresistive properties of a PPMO sample. The magnetoresistance, $[\rho(9T) - \rho(0)]/\rho(0)$, is found to be $\sim 90\%$ close to $T_{MI}$ in a field of 9 T. From the maximum in slope of the $M$-vs.-$T$ curve, $T_C \sim 210 \text{ K}$ was estimated which is distinctly lower than the corresponding $T_{MI} \approx 255 \text{ K}$. Such an approach to estimate $T_C$ is supported by elaborate investigations on a very similar Pr$_{0.7}$Pb$_{0.3}$MnO$_3$ single crystal ($T_{MI} \approx 235 \text{ K}$ [18]) in which the so-determined $T_C \sim 197 \text{ K}$ agrees well with results from a detailed static magnetization scaling analysis [19] as well as from heat capacity measurements [21].

The scaling analysis surrounding the critical temperature indicated that the underlying magnetic transition is a conventional one, with short-range Heisenberg-like critical exponents. A deviation of the inverse susceptibility from the Curie-Weiss law above $T_C$ [18] and history-dependent transport properties [20] suggest the presence of small magnetic metallic clusters above $T_C$ that form metallic paths through percolation or tunneling upon reducing the temperature below $T_{MI}$. We note the sharpness of the resistive transition at $T_{MI}$ which can be inferred from the logarithmic derivative of the resistance $\left(\frac{d\rho}{dT}\right)/\rho$ plotted in the inset of fig. 1. Such a sharp metal-insulator transition is indicative of a strain-relaxed sample [16].

For the tunneling studies an STM (Omicron Nanotechnology) operating under ultra-high vacuum conditions ($p \leq 10^{-10}$ mbar) was utilized at numerous fixed temperatures, 30 K $\leq T \leq$ 300 K, mostly in the vicinity of $T_C$ and $T_{MI}$. Since crystals with perovskite structure do not cleave easily, the preparation of a clean surface for STM/S is a challenge. Just before inserting the crystal into the UHV chamber the crystal surface was thoroughly cleaned in isopropanol using an ultrasonic bath and then, inside isopropanol, the surface was scraped to rip off some parts of it. This preparation gave locally cleaved surfaces on a length scale of micrometers. STM was conducted using tungsten tips. Typically, a sample bias voltage of $V = 0.8 \text{ V}$ at a current set point of 0.3 nA was applied. This implies that the unoccupied density of states (DOS) of PPMO was probed. Figure 2(a) shows the dependence of the tunneling current $I$ on the relative tip-sample distance $z$ on a semi-logarithmic plot. The exponential nature of $I(z)$ confirms an excellent vacuum tunnel barrier (effective work function $\phi \sim 1.5 \text{ eV}$). Topography within an area of 50 $\times$ 50 nm$^2$ is presented in the inset, fig. 2(b). Terraces with unit cell height ($\sim 0.4 \text{ nm}$) steps, fig. 2(c), indicated a {100} surface of the pseudocubic perovskite crystal.
To map the surface electronic state, we carried out spatially resolved STS measurements at 30 K \(\leq T \leq 300\) K and — for each temperature — at different locations on the sample surface. Typically, an area of \(50 \times 50\) nm\(^2\) with a lateral resolution of 1 nm (2500 pixels) was investigated. Tunneling current and differential conductance, \(G = dI/dV\), were measured simultaneously while ramping \(V\) from \(-1\) to \(+1\) V. For representative temperatures, averaged \(G-V\) curves are presented in fig. 3(a). At \(T \leq T_{MI} \approx 255\) K, the \(G-V\) curves are metal-like with a finite value of \(G_0\) signifying a finite DOS at the Fermi energy \(E_F\). In contrast, at 300 K the \(G-V\) curve around \(V = 0\) is indicative of an insulating gap. The strong asymmetry of the conductance curves at \(T \lesssim T_{MI}\) and their severe change beyond \(T_{MI}\) point at a strongly modified DOS at \(T_{MI}\).

For quantifying the STS results and their temperature evolution, the local \(G_0\) values are presented in color-coded conductance maps, figs. 3(b)–(e), with a color scale covering \(0 \leq G_0 \leq 0.64\) nS as shown on the left of fig. 3(b). As outlined, these conductance maps represent locally the slopes of the individual \(I-V\) curves at \(V \to 0\). The distribution of the local \(G_0\) values can be inferred from the corresponding histograms figs. 3(g)–(j) which show the frequency of the observed \(G_0\) values using the same color code. A sharp distribution of \(G_0\) around \(0.37\) nS at 30 K confirms a homogeneous conducting state at low \(T \ll T_C\). Similarly, the conductance map at 300 K (in the insulating regime) is also highly homogeneous, fig. 3(e), with most of the \(G_0\) values very close to zero (fig. 3(j) and inset which, for clarity, zooms into the range of very low \(G_0\) values) confirming an overall insulating state.

On the other hand, as the temperature is raised through \(T_C\) and approaches \(T_{MI} \approx 255\) K, inhomogeneities start to develop at a length scale of 2–3 nm, as seen in figs. 3(c) and (d). A few representative \(I-V\) curves taken at \(T = 199\) K are shown in fig. 3(f). These curves clearly indicate both metallic and insulating behavior at different points on the surface. A bimodal distribution of \(G_0\) at \(T = 199\) K is visible in fig. 3(h), with two maxima in \(G_0\) frequency located at similar \(G_0\) values as for low (\(\sim 0.3\) nS) and high (\(\sim 0\) nS) temperature, respectively. The increasing weight at \(G_0 \to 0\) while retaining a peak at \(G_0 \sim 0.3\) nS provides a direct observation of coexisting insulating and conducting regions and hence, nanometer-scale phase separation.

In the following we focus our investigation on the two transitions, i.e., on the metal-insulator transition at \(T_{MI}\) and the magnetic transition at \(T_C\). The relevant conductance histograms are compared in fig. 4: the histograms shown in (a) and (b) were obtained at temperatures near \(T_C\) whereas those in (c) and (d) enclose \(T_{MI} \approx 255\) K. In both cases the observed changes in the conductance histograms are dramatic. When the temperature is reduced and passes \(T_{MI}\), a large number of conducting areas appears which seem to form conducting paths, as expected for a sample that becomes metallic. Apparently, the surface conductance closely follows the bulk metal-insulator transition. Despite some efforts, we were not able to observe a state at which only a small number of unconnected metallic areas was present. This lack of observation is certainly consistent with the sharp...
metal-insulator transition, fig. 1 and its inset. In comparison, the transition around \( T_C \) does not appear as sharp. It can be seen that the portion of metallic regions increases at the expense of the insulating ones with decreasing temperature. The conductance map at 177 K, fig. 4(a), was found to reveal largely metallic sample areas, with very few instances of \( G_0 \equiv 0 \). We note that this picture is in accord with the broad transition around \( T_C \) in this material: the increasing magnetization with decreasing temperature appears concomitant to the growing portion of the metallic (ferromagnetic) phase at the cost of the insulating (paramagnetic) phase. From this point of view, \( T_C \) represents a mean value of the sample volume and it is easily conceivable that phase separation is found even at a somewhat lower temperature (\( T = 199 \) K in case of the \( G_0 \) map of fig. 3(c)) compared to the mean \( T_C \sim 210 \) K. As to be expected, at 199 K most of the sample is conducting (see discussion of fig. 5 below). Most importantly, however, for our largely strain-free sample no sign of the presence of an insulating phase well below \( T_C \) is found. Our measurements indicate (as far as we can tell from the finite number of measured temperatures) that at \( T \equiv 177 \) K insulating areas can just be detected. Hence, one might speculate that the appearance of an insulating phase well below \( T_C \) \([5,6,22]\) could be the result of an extrinsic effect — possibly strain. Our measurements indicate that the phase separation is confined to a temperature range limited by \( T_{MI} \) and roughly \( T_C \).

In fig. 5, the \( G_0 \) values of the main peak in the histograms in dependence on temperature are plotted (marked by \( \times \)). It shifts to lower conductance values as temperature is increased and, importantly, an increasing weight at \( G_0 \rightarrow 0 \) is observed for \( T \gtrsim 199 \) K. The existence of a finite number of instances with \( G_0 \equiv 0 \), i.e. of insulating areas, above 199 K is marked by \( \Delta \) in fig. 5. The drastic change in \( G_0 \) very close to the bulk \( T_{MI} \) (see \( \rho(T) \) in fig. 5) indicates that our STS results are not dominated by surface effects.

However, the distributions measured at intermediate temperatures \( T_C \lesssim T < T_{MI} \) (cf. figs. 3(h), (i)) are significantly broadened compared to the sharply peaked distributions at both low temperature (\( 30 \) K \( \ll T_C \), fig. 3(g)) and high temperature (\( 300 \) K \( \gg T_{MI} \), fig. 3(j)). The sharp distributions at \( T = 260 \) K, fig. 4(d), and 300 K, fig. 3(j), clearly indicate that the broadening at intermediate temperature reflects a sample property rather than an instrumental influence. The temperature dependences observed in STS arise mainly from a strongly changing DOS of PPMO at these temperatures. This change of electronic properties may result from the release of some lattice distortions around \( T_{MI} \), where the immobilized polaronic carriers become successively mobile producing inhomogeneous spatial conductance distributions. Apparently, polaronic lattice distortions continue to exist below \( T_{MI} \), as inferred from the insulating areas found in figs. 3(c) and (d). This is in consistence with the persistence of local lattice distortions in the metallic state of manganites observed in pulsed neutron diffraction \([23]\) and extended X-ray absorption fine-structure investigations \([24]\). These local distortions may also contribute to the broadening of the histograms at intermediate temperatures, figs. 4(a)–(c). Moreover, the inhomogeneities due to phase separation may directly influence the DOS on a local scale: nanometer-size particles are known for a modified DOS with respect to the bulk.

Recent models have successfully explained phase separation assuming two distinct states of the Mn \( e_g \) electrons, one type is more localized due to the Jahn-Teller effect.
whereas the others form broad band states [25,26]. Specifically if realistic parameters for doped manganites are taken into account [10], nanometer-scale phase separation is predicted which is in good agreement with our experimental findings. However, the theoretical predictions were made for the electronic ground state, whereas, in our case, the phase separation is restricted to finite temperatures close to the transition. It remains an open question, whether the particular properties of PPMO with a metallic paramagnetic state for $T_C \lesssim T < T_{MI}$ are responsible for the clear observation of this nanometer-scale phase separation, and whether the result can be generalized to other mixed-valence manganites. Further, the specific pattern of electronic inhomogeneity in the local surface DOS is certainly affected by unavoidable intrinsic disorder in the associated length scale, similar spatially resolved STS studies on different manganites are called for.

In summary, spatially resolved STS on single crystals $\text{Pr}_{0.68}\text{Pb}_{0.32}\text{MnO}_3$ has been performed and the local zero-bias conductance $G_0$ as well as its histograms have been analyzed. At both low temperature $T \ll T_C$ and high temperature $T > T_{MI}$, homogeneous $G_0$ distributions were found. Only for the intermediate temperatures nanometer-scale phase separation was inferred from the appearance of two maxima in the zero-bias conductance histograms. The restriction of this phase separation to temperatures close to the metal-insulator transition suggests that it is related to the non-coincidence of $T_C$ and $T_{MI}$. A strong broadening of the zero-bias conductance distribution in this regime is likely related to the phase separation and its impact on the local DOS.

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