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TUNNELING SPECTROSCOPY OF MANGANITES WITH NANOSCALE STRUCTURAL NON-UNIFORMITIES

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We report on our recent electron-tunneling studies of bulk manganite samples that provide important information about the structure of the near-surface layers of the material and the nature of the charge transport across them. It is shown that the even part of the differential conductance of contacts formed by a metallic injector with the surface of a manganite is a power function of the voltage bias. High voltages applied to the sample are found to locally modify the conductance of the degraded native surface layer. Experiments aimed to monitor the force applied to a metal tip pressed into the surface of a manganite prove the presence of sub-surface layers with properties significantly different from those near the surface. Experimental data are analyzed and interpreted within the Glazman–Matveev theory taking into account inelastic tunneling through two metallic "drops" inside the insulating barrier.

Keywords: Manganites; tunneling spectroscopy; near-surface layers.

1. Introduction

Numerous phenomena and especially the colossal magnetoresistance effect in the $La_{1-x}A_xMnO_3$ manganites (where A is a divalent metal atom) are determined by a combination of electronic, spin, lattice, and orbital degrees of freedom.[1] In compounds of such type a transition is observed at $x \sim 0.3$ from a ferromagnetic metallic to a paramagnetic dielectric state due to the double exchange mechanism

and a strong Jahn–Teller bond responsible for the polaron nature of charge carriers at high temperatures.[2] Moreover, there are indications of a possible formation of a non-uniform state, phase-separated into nanosize ferromagnetic and paramagnetic domains in the vicinity of the Curie temperature T_C.[3] Although the likelihood of such separation finds experimental and theoretical confirmations, the size of the domains and their dependence on external parameters remain debatable.

One of the most effective techniques for resolving these debates could be the tunneling spectroscopy method, which allows probing state non-uniformities with a nanoscale resolution and reveals influence of external parameters on those non-uniformities in both metallic (ferromagnetic) and dielectric (paramagnetic) phases. The near-surface structure of manganite samples remains one of the most important issues from both fundamental and applied points of view. Several experimental groups have reported on relevant results, yet as of today questions concerning physical properties of the near-surface layers, the character of charge transfer across them, the role of surface inhomogeneities, and changes in their size away from the surface into the bulk remain unresolved. This work offers electron-tunneling data for bulk polycrystalline manganite samples. Analysis of our results within the theory[4] that accounts for inelastic tunneling through two metallic inclusions within the potential barrier provides answers to the questions mentioned above. Some preliminary results were presented earlier in Ref. 5. Here, we provide new data for the $La_{1-x}Ca_xMnO_3$ compound along with results concerning the electromigration effect and experiments that employed monitoring of a mechanical force applied to the metal tip. The new experimental observations clearly support our previous conclusions[5] about the strongly inhomogeneous nature of manganite surfaces.

2. Experimental Details

Below we present tunneling conductivity spectra for the $La_{1-x}Sr_xMnO_3$ (LSMO), $La_{1-x}Ca_xMnO_3$ (LCMO), and $Nd_{1-x}Sr_xMnO_3$ (NSMO) compounds in a ferromagnetic metallic phase, which exhibit for $x \sim 0.3$ a colossal magnetoresistance effect at room temperature. Bulk samples were sintered by a conventional solid-state method from rare-earth oxides, calcium (or strontium) and manganese at $T_s = 1200$–1250°C in air ambient followed by repeated mixing, pressing, and annealing. The time of annealing and sintering was about 12 hours. Saturation with oxygen took place in a laboratory oven during cooling to room temperature. 8 mm × 1.5 mm × 0.4 mm plates obtained by compressing the manganite powder between two flat steel anvil plates have been used as electrodes of the tunneling heterostructures. Copper or aluminium wires, glued parallel to one another on the surface of an anvil, served as a band support for the powder being compressed. Thin films of $La_{0.67}Sr_{0.33}MnO_3$ and $Nd_{0.67}Sr_{0.33}MnO_3$ were obtained on (100)-oriented $LaAlO_3$ substrates (heated up to 760–770°C at the oxygen pressure of 3 mbar) by a high-pressure DC sputtering method. Electrical contacts to manganite samples were formed by soldering with a silver paste at ~ 450°C.

It is well-known that (unless special precautions are exercised) an oxygen-depleted layer occurs naturally at the surfaces of manganites. In our case, this layer served as a potential barrier for tunneling electrons. An injector for the metal–insulator-manganite heterojunctions was formed either with a film deposited on the sample or by a sharp Ag tip pressed against it with an adjustable force. First derivatives $\sigma(V) = dI(V)/dV$ of the tunneling I–V curves were measured by a standard modulation technique in the constant-voltage source regime. Strong chemical modifications of the oxide surface caused by oxygen ion displacements were induced by high voltages (in excess of 1 V) applied directly to the junctions. This effect is believed to be responsible for an enormous growth of inelastic tunneling processes across the transition region. Notably, a large spin-dependent tunneling magnetoresistive effect was observed even when one of the electrodes was a non-magnetic metal. The magnitude of this effect in $La_{0.67}Sr_{0.33}MnO_3$-Pb contacts reached 15%, whereas in symmetric structures, it was 10–30% (for H nearly 100 Oe). The observed magnetoresistive effect can be explained by assuming that the spin-dependent electron tunneling occurs through magnetic states (or clusters of states) localized inside the barrier.

3. Results and Discussion

It has been suggested that, similarly to the case of superconducting cuprates, the oxygen mobility, as well as its weak bonding within the lattice, have a dramatic impact on the formation of subsurface layers in manganite compounds. In this section, we present experimental results illustrating (a) a significant role played by the oxygen migration in the near-surface vicinity for the specimens studied, and (b) oxygen deficiency-mediated formation of isolated microscopic metallic inclusions.

We start with the data obtained for bulk LCMO specimens with an optimized stoichiometry. Their resistance at 4.2 K was several ohms and varied rather slowly with temperature up to 200 K with a characteristic maximum at 280 K related to the metal–insulator phase transition. Tunneling contacts were produced by pressing a silver tip into the surface of the manganite. The tunneling resistances of the junctions at 4.2 K and zero voltage R_0 that varied between tens to several hundred ohms (depending on the tip location on the surface) exceeded resistances of the manganite samples by at least an order of magnitude, indicating a substantial surface energy barrier adequate for the tunneling spectroscopy technique. A significant spread in the values of R_0 reveals the degree of non-uniformity of the near-surface vicinity in our samples. The differential conductance $\sigma(V)$ was measured in a broad range of voltages V, up to several hundred mV. For an ideal square barrier, experimental plots should be symmetric parabolas,[6] whereas in reality the two parts corresponding to different voltage signs differ from each other and their shape is not parabolic (Figs. 1 and 2). Besides, we observed shifts in the positions of the minima along the voltage axis that can be explained by a trapezoidal asymmetry of the potential

barrier as well as its significant non-uniformity due to contamination with different impurities. We shall analyze the latter fact assuming a power dependence V^k of the differential conductance. It is well-known[6] that usually it is a parabola with $k = 2$. At the same time, as suggested by Glazman and Matveev,[4] in heterostructures, where the electronic transport takes place via inelastic tunneling through two metallic "drops" inside the insulating barrier, $k = 4/3$. If the number of such granules participating in the under-barrier tunneling is increasing (due to the increase of either temperature or their number along the electron path inside the barrier) then k should increase from 4/3 to 2.[4] From our data for the LCMO and NSMO samples presented in Figs. 1 and 2, one can see that the conductance curve with $k = 4/3$ agrees well with the experimental results in a wide range of energies, and especially well for the high-resistance samples. For the LCMO manganite with $R = 55\ \Omega$, the agreement with the Glazman–Matveev theory[4] was observed between 20 and 120 meV, whereas for $R = 140\ \Omega$ between 50 and 320 meV, which corresponds to, essentially, the entire voltage range studied [Figs. 1(a) and 1(b)]. In the case of NSMO samples, the range where the theory[4] agrees with the experimental data also grows with the resistance. When $R_0 = 125\ \Omega$, it is approximately between 10 and 160 meV, whereas for $R_0 = 320\ \Omega$, the range increases up to 5–330 meV [Figs. 2(a) and 2(b)]. This observation corraborates the presence of localized states near the junction interface, with their number increasing due to the increasing width of the insulating layer.

Here we provide a more detailed analysis of our experimental results for La-based manganites based on the voltage dependence of the even part of the differential conductance $\sigma_+(V) = (\sigma(V) + \sigma(-V))/2$ in the 4.2–77 K temperature range. According to a well-established methodology for tunneling structures,[6] the $\sigma_+(V)$ behavior is determined by the barrier parameters as well as the processes of

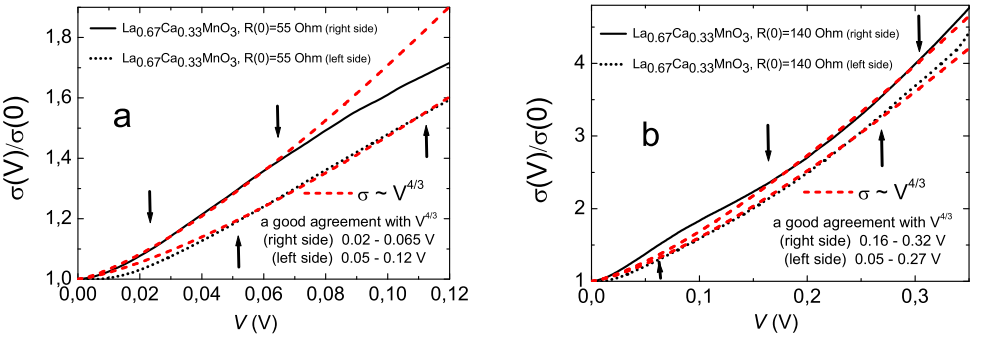

Fig. 1. Barrier characteristics of the Ag/LCMO junctions with the junction resistance R ($V = 0$) equal to (a) 55 Ω and (b) 140 Ω for positive (solid line) and negative (dotted line) voltage signs. The dashed lines represent a conventional voltage dependence on the tunnel conductance predicted by the Glazman–Matveev model for an indirect tunneling. Arrows show voltage regions of the best agreement between the experiment and the theory. The temperature of the experiment was 77 K.

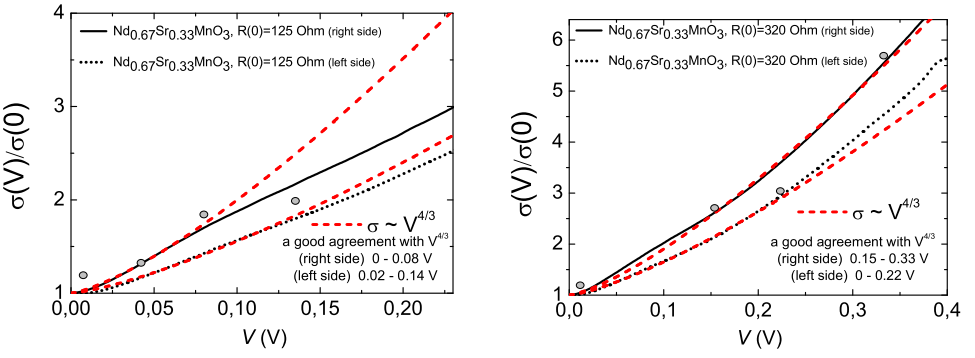

Fig. 2. Barrier characteristics of the Ag/NSMO junctions with the junction resistance $R(0)$ equal to (a) 125 Ω and (b) 320 Ω for positive (solid line) and negative (dotted line) voltage signs. The dashed lines represent a conventional voltage dependence on the tunnel conductance predicted by the Glazman–Matveev model for an indirect tunneling. Arrows show voltage regions of the best agreement between the experiment and the theory. The temperature of the experiment was 77 K.

inelastic scattering of a tunneling electron inside and in the vicinity of a nanoscale insulating layer. Hence, measurements of $\sigma_+(V)$ alone provide essential information about the structure of the junction barrier regions. In accordance with the observations mentioned above, we found that the functional dependence of $\sigma_+(V)$ has a power dependence of V^k, with k varying between 1 and 2 depending on the value of R_0, the temperature of the experiment, and the studied range of voltages. A linear background ($k = 1$) is observed for the structures with low ohmicity, whereas for contacts with R_0 of several hundred ohms, we observed a quadratic dependence $\delta\sigma_+(V) = \sigma_+(V) - \sigma_0 = \text{const}\,\sigma_0 V^2$, where $\sigma_0 = \sigma\ (V = 0)$. The most interesting intermediate case of $1 < k < 2$ is crucial for understanding a microscopic structure of the interface layer between the injector electrode and the bulk of the manganite, because this structure determines essential properties of the tunneling contacts. For a more accurate estimation of k, we plotted the dependence of $\ln[\delta\sigma(V)/\delta\sigma(1\text{ mV})]$ versus $\ln(V/1\text{ mV})$, the slope of which determines k. Figure 3 demonstrates the $\ln[\delta\sigma(V)/\delta\sigma(1\text{ mV})]$ behavior for the $Ag/La_{0.65}Ca_{0.35}MnO_3$ contacts with a resistance of 140 Ω in the −400 mV to 400 mV range. One can see that this behavior corresponds to $k = 4/3$ at $T = 4.2$ K and $k = 2$ at the liquid nitrogen temperatures. For comparison, in the same figure we provide data obtained for the $La_{0.67}Sr_{0.33}MnO_3$ thin films (with $R_0 = 340\ \Omega$), which demonstrate an identical behavior of the differential conductance, namely, absence of a linear dependence for the high-ohmicity contact case, the 4/3-power dependence at liquid helium temperatures starting with tens of mV, transition to a quadratic ($k = 2$) behavior with temperature increasing to 77 K, etc. This is in perfect agreement with the differential conductance behavior predicted by Glazman and Matveev.[4]

Analysis of our experimental results suggests the following mechanism. An insulating layer appears at the surface of the manganite due to the oxygen

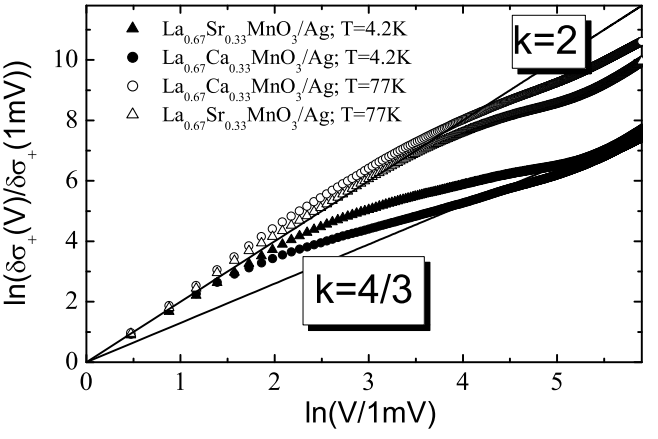

Fig. 3. $\ln[\delta\sigma(V)/\delta\sigma(1\text{mV})]$ versus $\ln(V/1\text{mV})$ dependence for the Ag/LSMO and Ag/LCMO junctions at 4.2 and 88 K. The straight lines correspond to a conventional elastic tunneling with $k = 2$ and an inelastic tunneling through two metallic "drops" inside the potential barrier with $k = 4/3$.

depletion in the sub-surface region (akin to the well-established case of superconducting cuprates[7]). Beneath this layer, there is an inhomogeneous area with a lower-than-the-optimum oxygen content, which is again analogous to the case of high-temperature superconductors.[8] In the case, when highly conductive inclusions in this area form metallic contacts with each other, the resistance of the point contacts appears relatively low (tens of Ω in our experiments), most of the potential drop occurs on the tunneling barrier. The linear dependence of conductance versus voltage is stipulated by the inelastic scattering of electrons on magnetic fluctuations in the manganite. If the metallic granules emerging as a result of oxygen out-diffusion do not form a direct contact, and if their amount is relatively small, then the situation is similar to the under-barrier tunneling through conducting inclusions within the barrier.[4] Finally, if the granule-containing region is large, i.e. the flow of current occurs through a substantial number of those granules, then a standard $\sigma(V) = \sigma_0 + \text{const}\,\sigma_0 V^2$ dependence is observed.

The suggested explanation includes a key assumption that the near-surface oxygen migration is responsible for the microscopic structure of the heterojunction. This statement is confirmed indirectly by our experiments on the influence of high voltages on the current–voltage characteristics of manganite-based contacts measured in a wide range up to 2 V. For a point contact formed between a silver tip and a polycrystalline LCMO sample, a sharp resistance decrease was observed at room temperature when a positive potential $V > 0.8$ V was applied to the injector (Fig. 4). In our interpretation, these abrupt changes result from the voltage-driven oxygen out-migration from the manganite's sub-surface region.

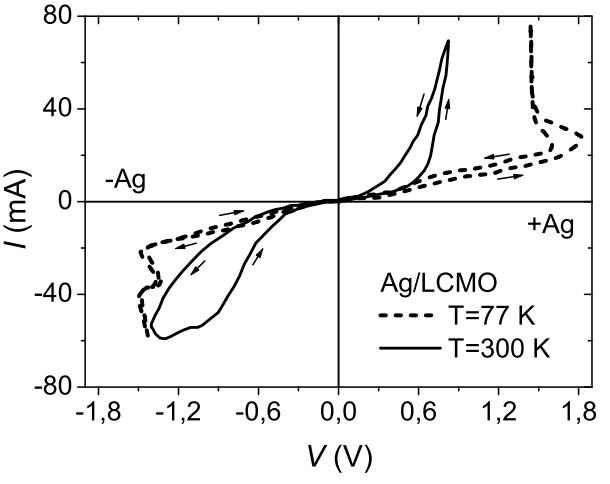

Fig. 4. An impact of high voltage biases applied to the Ag/LCMO junction at 77 and 300 R.

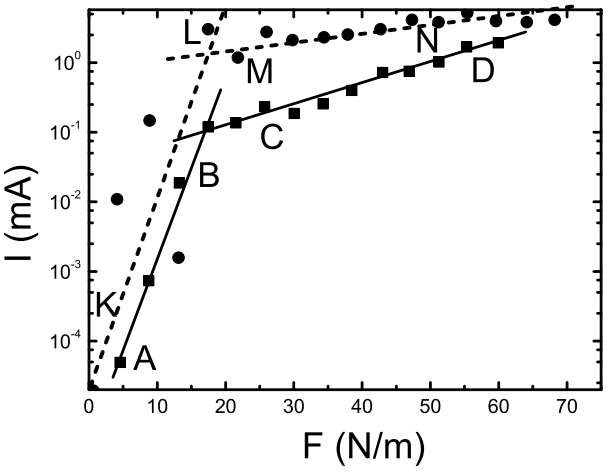

Fig. 5. An effect of increasing the force applied to a metallic tip on the tunneling current across a point contact formed between the tip and the LSMO surface. Squares and circles represent measurements for two different contacts at 0.5 V. Straight lines AB and KL indicate regions of a purely elastic deformation of the near-surface manganite layers whereas lines CD and MN correspond to the damage of the dielectric layer.

To elucidate the depth scale of such changes, we modified the contact spectroscopy technique introducing control and monitoring of F, the force applied to the metal tip pressed into the surface of the manganite. Figure 5 illustrates the influence of the force on the magnitude of current I across a heterostructure formed

by a steel tip and a polycrystalline LSMO sample. During these measurements the voltage value was fixed at 0.5 V. From Fig. 5, one can see that the range of the V/I ratio spans several orders of magnitude, from ca. 100 Ω up to hundreds of MΩ. Incidentally, I versus F dependence is not a monotonous function. Moreover, there is a general trend — logarithmic plots for the experimental I-versus-F characteristics reveal two linear sections with different slopes. (See the results of two typical point-contact measurements in Fig. 5.) The first region in the plot shown in Fig. 5 corresponds, most likely, to a purely elastic deformation of the surface layer with the barrier thickness $d = d(F)$ as a key factor determining the tunneling current $I \propto \exp(-\text{const}\, d)$. The second region is related, in our opinion, to the onset of an inelastic deformation and damage of the surface dielectric layer. Besides, we found that for a fixed value of F, the k exponent in the differential conductance $\sigma_+(V)$ also strongly depends on the applied force and changes with F in a step-wise manner. For the voltage bias of 0.5 V, we found that during the transition from one linear section to another with increasing F, the k parameter changes from 1.7–1.8 to ca. 1.3. The $k = 1.75$ value is rather close to the $k = 2$ value predicted by the standard model of tunneling processes in a metal–insulator–metal structure with a high rectangular barrier.[6] It should be stressed that similar measurements carried out by us on a contact formed by a steel tip and an electrolytic aluminum yielded the same value of $k = 1.75$. Thus, our observations reveal that there is a very thin (a few nm) dielectric layer directly at the surface of a polycrystalline manganite sample. Presence of the second linear region in Fig. 5 indicates that the deeper sub-surface layers of the manganite have properties significantly different from those of the near-surface vicinity. In this case, the corresponding power exponent $k \cong 4/3$ is in exact agreement with the theoretical model of Glazman–Matveev.[4] Hence, the sub-surface layers should contain very small conducting grains determining the charge transport across the interface. The grains can form as a result of a nanoscale phase separation of the ferromagnetic and non-ferromagnetic phases with a predominance of the latter due to the deficiency of oxygen in the near-surface region of a manganite.

4. Conclusion

We investigated tunneling charge transport in heterostructures formed by a metallic injector and bulk samples of LSMO, LCMO, and NSMO. In addition, we have modified the contact tunneling spectroscopy technique, augmenting it with measurement and control of the force, clamping the probe tip to the surface of a sample. In our experiments we proved existence of a thin insulating layer at the surface of a polycrystalline manganite sample. In deeper sub-surface layers, we observed a nanoscale phase segregation. High values of the electrical conductivity, which correspond to the ferromagnetic phase, were reached only in the bulk of the manganites studied.

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References

1. V. M. Loktev and Yu. G. Pogorelov, *Low Temp. Phys.* **26** (2000) 171.
2. M. B. Salamon and M. Jaime, *Rev. Mod. Phys.* **73** (2001) 583.
3. E. Dagotto, *Nanoscale Phase Separation and Colossal Magnetoresistance* (Springer-Verlag, Berlin, 2002).
4. L. I. Glazman and K. A. Matveev, *Sov. Phys. JETP* **67** (1988) 1276.
5. V. Svistunov, Y. Revenko, M. Belogolovskii, A. Gerasimenko, Y. Pashkevich, H. Szymczak, P. Przyslupski and I. Komissarov, *Acta Physica Polonica A* **105** (2004) 87.
6. E. L. Wolf, *Principles of Electron Tunneling Spectroscopy* (Oxford University Press, 1985).
7. A. Plecenik, M. Grajcar, P. Seidel, S. Takács, A. Matthes, M. Zuzcak and Ś. Beňačka, *Physica C* **301** (1998) 234.
8. M. Naito, H. Yamamoto and H. Sato, *Physica C* **335** (2000) 201.