GIANT PEAK OF THE 1/f NOISE AT THE METAL-INSULATOR TRANSITIONS IN LOW-$T_c$ CMR MANGANITES:
EVIDENCE OF THE PERCOLATION THRESHOLD AT $T_c$

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ABSTRACT

We observed a dramatic peak in the 1/$f$ noise at the metal-insulator transition (MIT) in low-$T_c$ manganites. This many-orders-of-magnitude noise enhancement is observed for both polycrystalline and single-crystal samples of $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ ($y = 0.35 - 0.4$) in zero magnetic field and $Pr_{1-x}Ca_xMnO_3$ ($x = 0.35 - 0.5$) in magnetic field. This observation strongly suggests that the microscopic phase separation in the low-$T_c$ manganites causes formation of a percolation network, and that the observed MIT is a percolation threshold.

INTRODUCTION

It is well known that the electronic phase diagrams of perovskite manganites are very complex; they exhibit numerous ground states and phase transitions as the carrier concentration is varied [1]. The phase diagram for the system $La_{1-x}Ca_xMnO_3$ in the plane of the doping concentration $x$ and temperature $T$ is reported in [2]. The concentration of charge carriers in this system is proportional to the Ca doping level. At high temperatures, the system is in a paramagnetic phase. In the range $x \simeq 0.3 - 0.5$, the system undergoes a transition into the ferromagnetically-ordered state at $T \simeq 200 - 250K$; this magnetic transition is accompanied by the metal-insulator transition (MIT) [3, 4, 5]. A very high sensitivity of this MIT to the external magnetic field results in the so-called colossal magnetoresistance (CMR) [3, 4]. The change of the resistivity across the transition and, correspondingly, the CMR are more dramatic in compounds with a lower transition temperature $T_c$. The MIT in low-$T_c$ manganites bears many features which are intrinsic to the first-order transitions, including a strong thermal hysteresis of the resistivity $\rho$ and magnetization $M$ [3, 4].

There is a growing theoretical and experimental evidence that transport properties of the insulating state above $T_c$ are dominated by small polarons or magnetic polarons, and that the band-like carriers become important below $T_c$ [3, 4, 5]. However, the details of the MIT remain unclear. The experimental data suggest that the phase separation occurs gradually with decreasing temperature [3]. Appearance of small ferromagnetic (FM) regions in the charge-ordered (CO) phase has been reported at $T >> T_c$, well beyond the conventional fluctuation regime [1]. A very large and temperature-independent resistivity in the FM state, much greater than the Ioffe-Regel limit for a uniform metallic system, also indicates that the insulating CO and metallic FM phases coexist on the ”metallic” side of the MIT [3, 4]. The transition into the FM state is accompanied by an increase of the magnetization $M$, which saturates below $T_c$ (see Fig. 1). In contrast to the resistance, $M$ varies smoothly across the transition. The magnetization is proportional to the volume fraction of the FM phase; this volume fraction is $\sim 15 - 20\%$ at $T_c$, which is close to the percolation threshold.
Figure 1: Temperature dependence of the resistivity in $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ (at $B = 0$) and in $Pr_{1-x}Ca_xMnO_3$ (at $B = 0 - 7T$). The solid lines correspond to cooling, the dashed ones - to heating. The temperature dependence of the magnetization for $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ with $y = 0.35$ is shown for cooling as open circles in the upper panel.

in a three-dimensional percolated system. All these observations suggest that the low-$T_c$ manganites can be viewed as macroscopically inhomogeneous systems, where the metallic FM domains are imbedded into the insulating CO matrix. Percolation phenomena might be important in this situation near the MIT, provided the scale of the phase separation is much smaller than the sample’s dimensions.

The noise measurements can open a new window on the MIT in the CMR manganites. Indeed, it is well known that in classical percolation systems, the $1/f$ noise diverges at the percolation threshold $[12, 13]$. The $1/f$ noise reflects fluctuations of the resistance, and its spectral density $S_V$ is proportional to the fourth power of the bias current density $j$ $[13]$. Close to the percolation threshold, the current density becomes strongly non-uniform, and, with approaching the threshold, the contribution of the regions with a large $j$ to the $1/f$ noise increases more rapidly than their contribution to the resistance $[13]$. We report on the $1/f$ noise measurements in polycrystalline and single crystal samples of low-$T_c$ manganites. The combined transport and noise measurements strongly suggest that the so-called Curie
temperature in the low-$T_c$ materials is, in fact, a percolation threshold temperature rather than the temperature of the long-range ferromagnetic phase transition. The scaling analysis of the $1/f$ noise is consistent with the percolation model of conducting domains randomly distributed in an insulating matrix [14].

EXPERIMENT

The resistance drop at the MIT is more dramatic in the CMR manganites with a lower transition temperature $T_c$. One can decrease $T_c$, for example, by partial substitution of $La$ with Pr, which changes the chemical pressure in the system [3]. Alternately, it is possible to start with a compound that does not demonstrate the MIT even at the lowest $T$ (e.g., $Pr_{1-x}Ca_xMnO_3$), and to induce the MIT by the magnetic field. In this work, we have used both methods. The transport and noise measurements have been carried out on poly- and single crystal bulk samples of $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ ($y = 0.35 - 0.4$) and $Pr_{1-x}Ca_xMnO_3$ ($x = 0.25 - 0.5$). The former compound demonstrates the MIT at zero magnetic field, whereas in the latter compound, the MIT can be induced by the magnetic field (Fig. 1). The sample preparation is described elsewhere [2]. Typically, the polycrystalline samples were $4 \times 1 \times 1$ mm$^3$, single crystals - $3 \times 1 \times 0.5$ mm$^3$. The spectral density of the $1/f$ noise and the resistivity $\rho$ have been measured in the four-probe configuration over the temperature range $T = 4.2 - 300K$ in the magnetic field $B = 0 - 8T$ for both cooling and heating.

The bias current $I$ was driven through the sample by a low-noise current source with the output resistance much greater than the sample’s resistance. Typical values of the bias current were $I \approx 10^{-6} - 10^{-4}A$. All the data discussed below were obtained in the linear regime, where the rms noise was linear in current. The noise signal was amplified by a preamplifier PAR 113 and measured by a lock-in amplifier SR 830 in the mean average deviation mode. This regime allows to measure continuously the spectral noise density $S_V = \langle (V - \bar{V})^2 \rangle$ ( $\bar{V}$ is the average value of the voltage across the sample, $\langle .. \rangle$ stands for the time averaging), while the temperature (or the magnetic field) is slowly varying. Because of a very strong temperature dependence of the resistance in manganites, especially in the vicinity of the MIT, the rate of the $T$ (or $B$) sweep must be very slow (otherwise, the change of $\bar{V}$ during the measurement time will contribute to $S_V$). This also requires a good temperature stabilization (the long-term temperature stability in our measuring set-up was better than $1mK$ at $T = 10 - 300K$). Typically, the noise was measured at $f = 10 - 30Hz$, with the equivalent noise bandwidth $\Delta f = 1 - 5Hz$ and the time constant $\tau = 0.1 - 1s$. It has been verified that the noise spectrum has a power-law form $1/f^\gamma$ in the frequency range $f = 1 - 10^3Hz$ with $\gamma$ close to unity for all temperatures.

RESULTS

Typical temperature dependences of the resistivity for the $LaPrCaMnO$ system at $B = 0$ and for the $PrCaMnO$ system at different magnetic fields are shown in Fig. 1. Qualitatively, the dependencies $\rho(T)$ for these systems are similar: with cooling, the resistivity grows exponentially below the CO transition ($T_{CO} \sim 200 - 220K$), decreases rapidly when the system undergoes the MIT, and remains almost temperature-independent in the FM state. The temperature of the MIT is strongly $y$-dependent: $T_c$ increases from $35K$ for $y = 0.4$ to
75K for $y = 0.35$. For the $LaPrCaMnO$ system, the change of the resistivity is the most dramatic at $y = 0.35 - 0.375$, the "sharpness" of the transition is also the largest for these concentrations of $Pr$. Both systems exhibit a very strong hysteresis upon cooling and heating. The transition into the FM state is accompanied by the increase of the magnetization $M$, which saturates at $T < T_c$ (see Fig. 1). In contrast to $\rho$, $M$ changes gradually across $T_c$ for both poly- and single crystal samples. According to the magnetization data, the fractional volume of the FM phase, on the one hand, always exceeds $\sim 20\%$ on the "metallic" side of the MIT (we recall that the percolation threshold for both discrete and continuum percolation models is $\sim 17\%$ in three dimensions), on the other hand, is significantly smaller than 100%. This observation, as well as an anomalously large and temperature-independent resistivity in the FM state (observed even for single crystal samples), is consistent with the idea of coexistence of the FM and CO phases on the ferromagnetic side of the MIT.

![Figure 2](image.png)

**Figure 2:** Temperature dependences of the resistivity (solid lines), the spectral noise density (dots, the upper panel), and the normalized spectral noise density corrected on the background (dots, the lower panel) for a polycrystalline sample $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ with $y = 0.35$. All the dependences have been measured for the zero-field cooling.

The upper panel of Fig. 2 shows a typical temperature dependence of the spectral noise density, measured for a polycrystalline sample $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ with $y = 0.35$. The noise exceeds the background level at $T \simeq 150K$ (the preamplifier was not used in this
measurement, which explains a relatively large magnitude of the background), increases by many orders of magnitude with approaching the MIT, and drops sharply below the background level on the FM side of the transition. The frequency dependence of this noise is close to $1/f$. To compare the $1/f$ noise for different samples, it is convenient to use the normalized spectral noise density, $S_V/V^2 = (\delta \rho/\rho)^2$: in the linear regime, this quantity does not depend on the bias current and on the sample’s geometry. The lower panel of Fig. 2 shows that $S_V/V^2$ for this sample is weakly $T$-dependent in the CO state far from the MIT: it varies by a factor of 2-3 over the range $T = 90 – 150K$, though $\rho$ changes by 2-3 orders of magnitude over the same $T$ interval (see also the lower panel of Fig. 3). With approaching $T_c$, the $1/f$ noise exhibits a giant peak. The peak value of $S_V/V^2 = 10^{-10} – 10^{-8}$ $Hz^{-1}$ exceeds by many orders of magnitude $S_V/V^2$ observed for macroscopically uniform metallic or semiconducting samples $(10^{-19} – 10^{-23}$ $Hz^{-1}$ and $10^{-16} – 10^{-19}$ $Hz^{-1}$, correspondingly, for the same frequency and sample’s volume) [13].

The sharp peak of the $1/f$ noise allows to determine $T_c$ with a high accuracy; below we identify $T_c$ with the temperature of the $S_V/V^2$ maximum. There is a correlation between the magnitude of the noise peak and the ratio $\rho(T_c)/\rho(300K)$. For example, for the sample in Fig. 2, $\rho$ increases by 4 orders of magnitude with cooling from room temperature down to $80K$; the normalized noise magnitude at the transition also increases by a factor of $\sim 10^4$. Since the high-temperature portion of the $\rho(T)$ dependences is approximately the same for all compounds $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ with $y > 0.35$ [4], the noise peak is more pronounced for materials with a higher value of $\rho(T_c)$, e. g. with a lower $T_c$.

Qualitatively similar behavior is observed for the $Pr_{1-x}Ca_xMnO_3$ system, where the MIT can be induced by the magnetic field. The upper panel of Fig. 3 shows the $1/f$ noise versus $T$ for the $Pr_{0.025}Ca_{0.375}MnO_3$ sample at zero magnetic field (where the MIT is absent), and for the field cooling at $B = 6T$ (the MIT is observed at $T = 63K$). At $B = 0$, the normalized noise varies weakly with temperature over a range $T = 50 – 80K$. If the sample is cooled down at a fixed $B$, the $1/f$ noise increases sharply at the transition. A "shoulder" on the FM side of the $\rho(T)$ dependence coincides with the second peak of the $1/f$ noise. This shoulder, more or less pronounced, has been observed for all the samples $Pr_{1-x}Ca_xMnO_3$. A very sharp peak of noise is also observed if the sample is initially zero-field-cooled down to a certain $T$, and then the MIT is induced by increasing magnetic field (see Fig. 4). Comparison of Figs. 3 and 4 shows that the field cooling results in the peak magnitude of the $1/f$ noise approximately one order of magnitude greater than that for the isothermic field-induced MIT if the sample was initially zero-field-cooled. In both cases, the magnitude of the noise peak correlates with sharpness of the transition. The noise peak is much smaller for compounds with $x < 0.35$ and $x > 0.4$, where the resistance drop at the transition is less dramatic.

Our $1/f$ noise measurements provide strong evidence of the percolation nature of the CO-FM transition in the polycrystalline bulk samples of low-$T_c$ manganites. Indeed, a diverging behavior of the $1/f$ noise is typical for the percolation metal-insulator transition [12, 14]. On the insulating side of the MIT, the $1/f$ noise is relatively small (it is still greater than in macroscopically homogeneous metals and semiconductors), and almost temperature-independent. The concentration of disconnected FM domains increases with approaching $T_c$ on cooling. Switching of these domains between FM and CO states [13], results in a rapid growth of the $1/f$ noise with $T \to T_c$. This can be especially clearly seen for single crystals [14]. The noise intensity exhibits a giant maximum at $T_c$, where the concentration of the FM phase reaches the percolation threshold, and a cluster of connected FM domains
extends through the whole sample. Further strengthening of the backbone of the infinite cluster on the "metallic" side of the MIT causes a rapid fall of the $1/f$ noise. Note that $T_c$ is lower than the temperature of the maximum resistivity; instead, $T_c$ coincides with the maximum of $d\rho(T)/dT$. This is expected for a percolating mixture of two phases where the "insulating" phase has a finite $\rho$ which increases rapidly with cooling.

A clearly diverging behavior of the $1/f$ noise allows to determine $T_c$ with a high accuracy and to perform the scaling analysis of $S_V$ and $\rho$ on the "metallic" side of the MIT. In the vicinity of a percolation metal-insulator transition, the scaling behavior of $\rho$ and $S_V/V^2$ is expected [12, 13, 14]:

Figure 3: Temperature dependences of the resistivity (solid lines), the spectral noise density (dots and open circles, the upper panel), and the normalized spectral noise density corrected on the background (dots and open circles, the lower panel) for a polycrystalline sample $Pr_{1-x}Ca_xMnO_3$ with $x = 0.375$. All the dependences have been measured for cooling. At $B = 0$, this compound does not exhibit the MIT. The normalized $1/f$ noise measured for several fixed $T$ at $B = 0$ coincides with the data at $B = 6T$, measured with a slow temperature sweep far from the transition. This indicates that the sweep rate ($4mK/s$) was sufficiently low to exclude contribution of the time-dependent $\overline{\nu}$ to $S_V = \langle (V - \overline{V})^2 \rangle$. 

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Figure 4: Magnetic field dependences of the resistivity (solid lines), the spectral noise density (dots, the upper panel), and the normalized spectral noise density corrected on the background (dots, the lower panel) for a polycrystalline sample $Pr_{1-x}Ca_xMnO_3$ with $x = 0.375$. All the dependences have been measured at $T = 75K$ after zero-field cooling from room temperature. The magnetic field sweep rate was $2 \cdot 10^{-4}T/s$.

$$S_V/V^2 \propto (p - p_c)^{-k},$$  \hspace{1cm} (1)$$

$$\rho \propto (p - p_c)^{-t}. \hspace{1cm} (2)$$

Here $p$ is the concentration of the metallic phase, $p_c$ is the critical concentration, $k$ and $t$ are the critical exponents of the noise and resistivity, correspondingly. It is convenient to represent $S_V/V^2$ as a function of $\rho$ (in this case, no assumption on the value of $p_c$ is necessary):

$$S_V/V^2 \propto \rho^{k/t}. \hspace{1cm} (3)$$
Figure 5: The scaling dependence of the normalized spectral density of the 1/f noise on $\rho$ for the polycrystalline sample $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ with $y = 0.35$ ($f = 10Hz, \Delta f = 1Hz$). Solid line is a power-law fit with the exponent $k/t = 2.9$.

The normalized magnitude of the 1/f noise versus $\rho$ for the polycrystalline sample $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ with $y = 0.35$ is shown in the double-log scale in Fig. 5. Within the experimental accuracy, this dependence can be fitted by the power law (3) with $k/t = 2.9 \pm 0.5$. For the other samples, the values of $k/t$ fall into the range 1.2 – 3. These values of $k/t$ are consistent with the result $k/t = 2.4$ obtained for the continuum percolation model of conducting regions, randomly placed in an insulating matrix (the so-called inverted random-void model)\[14\]. Previously, similar values of $k/t = 2 – 3$ have been observed experimentally for the mixed powders of conducting and insulating materials [16, 17].

For high-quality single crystals of $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ ($y \sim 0.35$) [18], a dramatic increase of the 1/f noise at the transition has been observed as well [19]. In contrast to the polycrystalline samples, the temperature dependence of $\rho$ for single crystals exhibits reproducible steps and switching in the vicinity of the MIT. The step-like behavior and switching of $\rho$ at the transition indicates that the scale of the phase inhomogeneity is considerably greater in single crystals than in polycrystalline samples and the contribution of each individual metallic domain to the transport is noticeable. The percolation approach is not applicable in this case, because the inhomogeneous system is probed at the scale comparable with the scale of the phase inhomogeneity. Consequently, the critical behaviour of the 1/f noise and resistivity could not be observed.

CONCLUSIONS

To summarize, we observed the dramatic peak of the 1/f noise in low-$T_c$ CMR manganites $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ and $Pr_{1-x}Ca_xMnO_3$ at the transition between the charge-
ordered insulating and ferromagnetic metallic states. The peak value of the normalized noise density is by several orders of magnitude greater than that in macroscopically homogeneous metals and semiconductors. The combination of these data with the temperature dependence of $\rho$ and $M$ provides a strong evidence that the metal-insulator transition in these compounds is, in fact, a percolation crossover in the system of intermixed FM-metalic and CO-insulating regions. The metal-insulator transition corresponds to the formation of a critical cluster of connected metallic FM domains which extends through the whole sample. In other words, the metal-insulator transition temperature, or the ferromagnetic Curie temperature $T_c$, is the temperature of the percolation threshold. The percolation theory describes adequately the $1/f$ noise in the vicinity of the MIT in polycrystalline samples, where the size of the FM domains is much smaller than the sample’s dimensions. A well-pronounced step-like temperature dependence of the resistivity, observed for high-quality single crystals, suggests that the scale of the phase separation in single crystals is much greater than in polycrystalline samples.

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References

[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
[2] S-W. Cheong and H. Y. Hwang, in Colossal Magnetoresistance Oxides, edited by Y. Tokura (Gordon & Breach, London, 1999), ch. 7.
[3] R. M. von Helmholt et. al., Phys. Rev. Lett. 71, 2331 (1993).
[4] S. Jin et. al., Science 264, 413 (1994).
[5] E. L. Nagaev, Sov. Phys.-Uspekhi, 39, 781 (1996).
[6] N. A. Babushkina et. al., Phys. Rev. B 59, 6994 (1999).
[7] M. Uehara, S. Mori, C. H. Chen, and S-W. Cheong, Nature (London) 399, 560 (1999).
[8] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. 74, 5144 (1995).
[9] H. Röder, Jun Zang, and A. R. Bishop, Phys. Rev. Lett. 76, 1356 (1996).
[10] J.-S. Zhou and J. B. Goodenough, Phys. Rev. Lett. 80, 2665 (1998).
[11] J. M. De Teresa et al., Nature 386, 256 (1997).
[12] R. Rammal et. al., Phys. Rev. Lett. 54, 1718 (1985).
[13] Sh. Kogan, Electronic Noise and Fluctuations in Solids, Cambridge University Press 1998.
[14] A.-M. S. Tremblay, S. Feng, and P. Breton, Phys. Rev. B. \textbf{33}, 2077 (1986).

[15] R. D. Merithew, M. B. Weissman, J. O’Donnel, and J. Eckstein ”Mesoscopic Fluctuations in Colossal Magnetoresistance”, preprint, 1999.

[16] D. A. Rudman, J. J. Calabrese, and J. J. Garland, Phys. Rev. B \textbf{33}, 1456 (1986).

[17] C. C. Chen and Y. C. Chou, Phys. Rev. Lett. \textbf{54}, 2529 (1985).

[18] The $Pr$ concentration for the single crystal, estimated from the $T_c(y)$ dependence, was close to 0.35 (the nominal concentration was $y = 0.42$).

[19] V. Podzorov, M. Uehara, M. E. Gershenson, T. Y. Koo, and S-W. Cheong, \texttt{cond-mat/9910220} 14 Oct 1999.