Electrical Noise
in Colossal Magnetoresistors and Ferroelectrics

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Condensed Matter Physics
Department of Microelectronics and Information Technology
Royal Institute of Technology
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Abstract

Low frequency electrical fluctuations were studied in the pulsed laser deposited epitaxial thin films exhibiting colossal magnetoresistance (CMR) and ferroelectricity.

Electrical fluctuations in micrometer thick CMR manganite films is a sum of the excess noise and thermal (Johnson) noise. Excess noise has $1/f^\alpha$ ($\alpha = 1 \pm 0.2$) spectra and increases quadratically with the bias current. Most of our films has a normalized spectral density $S_R/R^2 \cdot \Omega \cdot f$ around $3 \cdot 10^{-27}$ m$^3$.

Thin and ultra-thin CMR films random telegraph like signals with the Lorentzian spectra appear on a background of $1/f$ noise. Noise spectroscopy revealed the relaxation process is thermally activated with an energy gap of tens of meV.

Transport properties of thin colossal magnetoresistors (thickness below 300 Å) have been effectively tailored in a wide temperature range by changing only the film thickness, while the performance of temperature and magnetic field CMR sensors can be maintained almost constant in the thickness range down to 100 Å. The lowest temperature difference and magnetic field difference which can be resolved: NETD and NEMFD were found to be $3 \mu K/\sqrt{Hz}$ and $5 \text{mOe}/\sqrt{Hz}$.

Solid solution with the composition of La$_{0.7}$(Pb$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ undergoes semiconductor - normal metal (paramagnetic - ferromagnetic) phase transition close to and above room temperature. Films with the composition $x = 0.33$ and thickness of 4500 Å possess maximum temperature coefficient of resistivity (TCR) of 7.4 %K$^{-1}$ at 295 K. These films were used to build uncooled infrared bolometer operating at room temperature. Bolometer performance test yields the responsivity $R = 0.6$ V/W, detectivity $D = 9.8 \cdot 10^6$ cm$\sqrt{Hz}$/W and noise equivalent power NEP of $3 \cdot 10^{-8}$ W$/\sqrt{Hz}$ at 30 Hz frame frequency.

Dielectric relaxation phenomena and low frequency electrical fluctuations have been studied in ferroelectric Au/Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$/La$_{0.67}$Sr$_{0.33}$MnO$_3$/Pt$_{80}$Ir$_{20}$ PLD-made thin film vertical capacitor structures. The current measured in time domain exhibits long-time Curie-von Schweindler relaxation after a voltage step is applied: $j \propto 1/t^{0.8}$. This result qualitatively agrees with a power law frequency dispersion
of the capacitance \( C \propto 1/f^{0.1} \). Amplitude of relaxation currents shows hysteresis behaviour, whereas steady (‘true’) leakage current does not.

Voltage fluctuations across ferroelectric capacitor increase with bias voltage increase and were found to have \( 1/f^{1.5} \) spectra. Approaching the electric breakdown field noise exhibits non-ergodic behavior: fluctuations are non-steady, randomly spike-shaped, and fractal-scalable in time domain.

A brief introduction of the main transport properties of manganite perovskites and simple theoretical explanation of CMR phenomenon is given in \textbf{Chapter 1}.

\textbf{Chapter 2} gives an introduction to ferroelectricity and materials possessing ferroelectric properties. Simple theoretical background is also included.

Description of the most important concepts and relations from the random signal theory is given in \textbf{Chapter 3}.

\textbf{Chapter 4} presents the main models of the fluctuations in the thermodynamic equilibrium systems.

Low frequency noise experimental setup and measurement technique are described in \textbf{Chapter 5}.

Overview of main results found in literature on electrical and magnetic noise in manganites is given in \textbf{Chapter 6} and continued by the detailed report on the original noise measurements.

\textbf{Chapter 7} is devoted to one of the possible future applications of CMR materials - uncooled bolometer.

Finally \textbf{Chapter 8} presents original results on electrical fluctuations in ferroelectric thin films.

Our most important experimental achievements are presented in the appended nine papers and two manuscripts.

\textbf{Keywords:} low frequency noise, colossal magnetoresistance, uncooled bolometer, relaxations and electrical fluctuations in ferroelectrics.
Preface

This thesis is based on results of experimental work carried out from December 1998 to August 2001 at the Condensed Matter Physics, department of Physics (from January 2001 we belong to the department of Microelectronics and Information Technology), Royal Institute of Technology.

The thesis is based on the following publications and manuscripts:


5. "Tailoring the colossal magnetoresistivity: La$_{0.7}$(Pb$_{0.63}$Sr$_{0.37}$)$_{0.3}$MnO$_3$ thin-film uncooled bolometer" Alvydas Lisauskas, S.I. Khartsev, and Alex Grishin, Appl. Phys. Lett. 77, 756 (2000);77, 3302 (2000).

7. "Colossal magnetoresistive La$_{0.7}$(Pb$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ films for bolometer and magnetic sensor applications" A. Lisauskas, J. Bäck, S. I. Khartsev, A.M. Grishin, J. Appl. Phys. 89, 6961 (2001).


10. "Relaxation characteristics of Ag(Ta,Nb)O$_3$ interdigital capacitors" J.-H. Koh, A. Lisauskas, Alex Grishin, manuscript.

11. "Low frequency Noise Measurement setup" A. Lisauskas, manuscript

Comments on My Participation

My work has played an important role for the realization of publications included in this thesis. I have made most of electrical measurements and the analysis, and in most cases also written the paper. Cotributions from the other author can be summarized as follows: A. Grishin, my supervisor, have been involved in most aspects of the work, especially concerning discussions on the manuscripts for publications and manuscript finalization. S. Khartsev made all the thin film samples (except for Paper 10) and assisted me in characterization of transport properties (resistance and magnetoresistance measurements). He helped me much in the designing noise measurement setup presented in Paper 11. The diploma worker J. Bäck took part in the measurements and analysis for Paper 7. The measurements for Paper 10 were carried out together with J.-H. Koh, who also made the sample. V. Palenskis contributed in the discussions writing the Paper 1.
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## Contents

Abstract i  
Preface iv  
Acknowledgements vi  

1 Colossal Magnetoresistors (CMR) 1  
1.1 Manganite perovskites ................................. 1  
1.2 Properties of the manganites ............................ 2  
1.3 Mechanisms of colossal magnetoresistance ............... 6  
1.4 Phase separation and percolation ......................... 9  

2 Ferroelectrics 13  
2.1 Ferroelectricity ........................................... 13  
2.2 Ferroelectric materials ..................................... 15  
2.3 Theory of ferroelectricity .................................. 16  

3 Basics of the random signal theory 20  
3.1 Probability density functions, moments, characteristic function .... 20  
3.2 The correlation function ................................... 24  
3.3 Spectral density, Wiener - Khintchine theorem ............. 25  

4 Fluctuations in equilibrium state and 1/f noise 28  
4.1 Fluctuation-dissipation relations (FDR) .................. 28  
4.2 Applications of FDR ....................................... 32  
4.2.1 Nyquist theorem ....................................... 32  
4.2.2 Equilibrium fluctuations in magnetoresistors ........... 34  
4.2.3 Equilibrium fluctuations in dielectrics ................. 35  
4.3 Temperature fluctuations ................................. 36
Chapter 1

Colossal Magnetoresistors (CMR)

1.1 Manganite perovskites

Complex metal oxides have long been subjects of study, because they exhibit a wide range of exotic and not very well understood structural, magnetic and electronic behavior. Almost in all cases this behavior cannot be explained within a context of the usual one-electron band theory that accounts well for the properties of most other solids, indicating the importance of strong electron-electron and electron-lattice correlations. The properties of these materials continue to surprise, for example, 1986 saw the discovery of high-temperature superconductivity in materials based on copper oxide.

More recently, attention has become focused on a certain class of manganese oxides, the manganite perovskites. Although these materials have been studied for many years [1, 2, 3], the current burst of activity was stimulated by reports of Helmholt et al.[4] and Jin et al.[5] of spectacularly large magnetoresistance which could not be compared with any other form of magnetoresistance. To distinguish this effect from the giant magnetoresistance observed in multilayers [6, 7] it was called 'colossal' magnetoresistance. This discovery raised expectations of a new generation of magnetic devices and sensors, such as magnetic data storage and magnetic read heads. Also, it launched a scientific race to understand the cause of the effect. While the promise of the great stride still remains a challenge, these perovskites are receiving a lot of attention for quite a different reason. In these materials interaction between the electrons and lattice vibrations (phonons) is unusually strong, leading to a wide range of striking physical phenomena and, most crucially, can be 'tuned' over a wide range by varying chemical composition, temperature and magnetic field. Therefore, these materials provide an unprecedented opportunity to study the poorly
Figure 1.1: A simple perovskite manganite structure $\text{AMnO}_3$ ($A = \text{La, Nd or Pr}$) consists of a large central rear-earth cation (in the center) surrounded by manganese (middle sized) and oxygen (small sized) ions.

understood physics of systems in which high density of electrons is strongly coupled to phonons and, in particular, to elucidate the interplay between the local structural deformations and global properties.

High magnetic sensitivity of manganite perovskites is accompanied by a large temperature coefficient of resistivity (TCR) that gives a great potential for temperature sensor applications (bolometers, etc.). One more advantage of a CMR material is its perovskite structure. This fact allows making smart devices, fabricating epitaxial heterostructures with alternating layers that possess identical crystalline structure with different functional properties.

1.2 Properties of the manganites

Manganese oxides that show colossal magnetoresistance (CMR) are compounds based on the $\text{AMnO}_3$ perovskite structure shown in Fig. 1.1. The most widely studied family has the chemical formula $\text{R}_{1-x}\text{A}_x\text{MnO}_3$, where $\text{R}$ is a rare earth element such as La, Nd, Pr and A is a divalent alkali such as Sr, Ca, Ba, Pb. Simple perovskite compounds are insulators. The $\text{Mn}^{3+}$ ion has four electrons in its outermost 3d energy level, out of possible ten. Hund’s atomic rule dictates that spins of the four electrons in manganese ion should point in the same direction to minimize the electrostatic repulsions. As spin-up and spin-down states are separated in energy, four electrons occupy spin state with the lowest energy (see Fig. 1.2). Electrostatic interactions between these four electrons and the neighboring oxygen
ions cause this single spin state to split into a triplet with three electrons and a doublet with one electron. This single electron state is unstable, however, and the system reduces its energy by splitting the doublet state into two hyperfine energy levels. This well-known phenomenon, called the Jahn-Teller effect, is characteristic of Mn$^{3+}$ ions and it has important consequences for the physical properties of the manganites.

Because all energy levels are fully occupied, the solid material is an insulator. However, substituting a divalent alkaline element can modify the electrical properties. This doping changes some Mn$^{3+}$ ions to Mn$^{4+}$ ions, and creates holes in the singlet energy state. If all the lanthanum ions are replaced by an alkaline earth, the charge density in the singlet state will be zero and the material becomes an insulator again. Changing the carrier concentration $x$ produces a variety of phases, which may be characterized by their magnetic, transport and 'charge-ordering' properties. A phase diagram in the doping ($x$) and temperature ($T$) plane for one representative material, La$_{1-x}$Ca$_x$MnO$_3$, is shown in Fig. 1.3. At $x = 0$, the material is 'insulating' at all temperatures. The material is paramagnetic (it has no long-range magnetic order) at high temperature, but below approximately 140 K it becomes antiferromagnetic: in a plane perpendicular to the crystal c-axis the magnetic moments on Mn sites are aligned. The moment direction alternates from plane to plane. The ground state remains insulating for $x < x_{\text{MI}} \approx 0.2$ but the magnetic order changes in a complicated (and still controversial) way, eventually becoming a fully polarized ferromagnet (all spins aligned in the same direction). In the phase diagram presented in Fig. 1.3, this sequence of phases is denoted by CAF (for canted antiferromagnet) and FI (for ferromagnetic insulator). One also notices that
a charge order (CO - a periodic pattern of Mn sites in different valence states) develops inside the ferromagnetic insulator phase. At $x = x_{\text{MI}}$ the ground state changes from insulating to metallic. This is shown in Fig. 1.3 as the vertical dotted line separating the FI (ferromagnetic insulator) and the FM (ferromagnetic metal) phase. For $x_{\text{MI}} < x < 0.5$ the ground state is a ferromagnetic metal. For $x > 0.5$ the ground state becomes insulating and antiferromagnetic again, and it is 'charge-ordered' in addition. As the temperature is raised in the region $x_{\text{MI}} < x < 0.5$, there is a ferromagnetic-paramagnetic transition at $T_C(x) \approx 200 - 250$ K. The magnetic phase boundary also separates the low-temperature 'metallic' phase from the high-temperature 'insulating' phase.

The main properties of one of the representative colossal magnetoresistor, $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$, are presented in Fig. 1.4. The paramagnetic - ferromagnetic transition (top frame) is also accompanied by a sudden reduction in the resistivity (middle frame). Such a drop is well known in other ferromagnetic metallic systems; it is caused by a transition from the state with spin disorder to the one without it. Disorder causes charge carriers with different spin orientations to scatter from each other, which increases the electrical resistivity.

---

Figure 1.3: Phase diagram of manganite perovskite $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (Reproduced from [8]).
Figure 1.4: Top frame: magnetization against temperature of La$_{0.75}$Ca$_{0.25}$MnO$_3$ for various field values. Middle frame: resistivity against temperature. The inset shows the low-temperature resistivity compared to $T^{2.5}$ (solid line) and $T^{4.5}$ (dashed line) behavior. Bottom frame: magnetoresistance against temperature. Open symbols reflect the low-field behavior and solid symbols reflect the high-field behavior. (Reproduced from [9]).
The same loss of resistivity should be observed in an applied magnetic field, since this aligns the electron spins and prevents the scattering caused by the spin disorder. This magnetoresistance effect is commonly defined as $(\rho_H - \rho_0)/\rho_0$, where $\rho_H$ is the resistivity in an applied magnetic field and $\rho_0$ is the resistivity in the absence of the magnetic field (bottom frame of Fig. 1.4). In normal ferromagnetic materials the magnetoresistance effect is just a few percent. But the manganese perovskites have shown magnetoresistance values of close to 100% in magnetic fields of a few Teslas. This truly 'colossal' magnetoresistance is generally observed close to the Curie temperature.

### 1.3 Mechanisms of colossal magnetoresistance

The basis of the theoretical understanding of CMR is usually referred to the double exchange (DE) mechanism proposed by Zener [10] to explain Jonker and Van Santem results [2]. Within the DE model the explicit movement of electrons is schematically written as $\text{Mn}_{11}^{3+}\text{O}_{21,34}\text{Mn}^{4+} \rightarrow \text{Mn}^{4+}\text{O}_{11,34}\text{Mn}_{21}^{3+}$ where 1, 2 and 3 label electrons that belong either to the oxygen between the manganese ions, or to the $e_g$ level of the Mn ions (Fig. 1.5). In this process simultaneous movement of two electrons makes the itinerant charge carrier (hole) to move from Mn$^{4+}$ to Mn$^{3+}$ and provides the mechanism for a ferromagnetic interaction between these ions. The oxygen linking is a crucial factor in the DE initiated ferromagnetism. Ferromagnetic
Curie temperature $T_C$ is related to the strength of the transfer integral $t_{ij}$ between the Mn$^{3+/4+}$ ions which controls the electronic (hole) conductivity. It follows that in this system one should expect a strong interplay between magnetic, transport and structural properties.

The ferromagnetic phase in manganites could also appear due to the large Hund coupling even without the oxygen link. In this situation the $e_g$ level electrons can directly jump from Mn$^{3+}$ to Mn$^{4+}$ ion. Kinetic energy of such jumps is minimized if all the spins are aligned. This mechanism of ferromagnetism is usually also called double exchange although it is very different from the original DE. However, recent computer simulations show that large Hund coupling could indeed be the main reason for ferromagnetism in some compounds.

Understanding of the ferromagnetic phase as a consequence of double exchange was found very satisfactory in the early studies of manganite compounds. However, after the initial theoretical success, further development continued in slow pace. Renewed interest to colossal magnetoresistors also initiated progress in the theoretical understanding of the physics of these compounds. Double exchange, exploited in explanations of properties of colossal magnetoresistors [11, 12, 13, 14] was argued in the latest theoretical studies to be insufficient. The shocking magnitude of magnetoresistance, very rich phase diagram, transport properties of high-temperature paramagnetic state etc., required to supplement DE with additional mechanisms.

Strong interplay between electrons and lattice is a peculiar feature of CMR manganites. As was already mentioned, three of the electrons in the 3d orbital of the manganese ions form a triplet state at lower energy levels (Fig. 1.2). These can be viewed as localized electrons that remain bound to the ion and, because their spins point in the same direction, they have an overall magnetic moment of 3/2. In contrast, the electrons in the highest energy level are shared with the oxygen ions, forming an energy band that extends throughout the solids. The motion of charge carriers through this energy band - and hence conductivity of the material - is largely controlled by the width of the band. This is determined by the overlapping of the manganese and oxygen orbitals, which in turn depends on the geometric arrangement of the ions. The larger the overlap, the wider the band.

To characterize this overlap, the geometrical quantity called the ‘tolerance factor’, is defined as $\Gamma = d_{A-O}/\sqrt{2}d_{Mn-O}$. Here $d_{A-O}$ is the distance between the A site, where the trivalent or divalent non-Mn ions are located, and the nearest oxygen ion $d_{Mn-O}$ is the shortest distance between the manganese and oxygen ions. Since there are two possible ions at ‘A’ site, the tolerance factor for a given compound can
be defined as a density-weighted average of the individual tolerance factors. In an undistorted cube the manganese and six oxygen ions form regular octahedra (Fig. 1.1) thus the Mn-O-Mn link angle is $180^\circ$, with the maximal overlapping of orbitals and $\Gamma = 1$. However, sometimes the A site is too small to fill the space in the cube center and for this reason oxygen ions tend to move towards it. The octahedra buckle, tolerance factor decrease ($\Gamma < 1$), and the Mn-O-Mn bond angle becomes smaller than $180^\circ$. As a consequence the possibility for carriers to move from Mn to Mn decreases and the tendency for charge localization increases. This decreases the overlap between orbitals and narrows the energy band. The relation between the ion size, the energy bandwidth, the resistivity and the Curie temperature provides a simple method of tuning the electronic and magnetic properties of perovskites [15].

There are many arguments that the FM phase in manganites originates from the interplay between strong electron-phonon coupling and large Hund coupling [16, 17, 8, 18]. The strong electron-phonon coupling, called Jahn-Teller (JT) distortion, may localize carriers, because the presence of an electron in a given Mn orbital causes a local lattice distortion, which produces a potential minimum: this minimum tends to trap the electron in that orbital. If the coupling is strong enough, these tendencies lead to the formation of a 'self-trapped' state, called a polaron. It is shown that static JT distortion plays a key role in a regime below $x = 0.2$ whereas dynamical JT effect may persist at higher $x$. Polarons are also important in the explanation of insulator behavior, since only the spin disordered scattering does not provide with enough localized charge carriers [19]. Polarons in manganites could be accompanied by a magnetic cloud or a region with ferromagnetic correlations.

Self-trapping competes with the delocalizing tendency of electron hybridization. The competition is parameterized by a dimensionless quantity $\lambda$, which is the ratio of the energy $E_{JT}$ gained from the electron-phonon coupling in the absence of hybridization, to the 'bare' electron kinetic energy $t_{eff}$; thus $\lambda \approx E_{JT}/t_{eff}$. In the manganites, the nature of the double-exchange and the tolerance factor means that $t_{eff}$, and therefore $\lambda$, may change over a wide range by varying magnetic field and temperature, which change spin correlations, and also by changing main and substituted ions, which change the tolerance factor and concentration of carriers. The change in $\lambda$ may be large enough to dramatically affect the behaviour of materials, causing, for example, the high-temperature 'insulating' behaviour of manganites [16].
1.4 Phase separation and percolation

Although double exchange and electron-phonon coupling effects are commonly accepted to be main ingredients of the CMR phenomenon, all of them are still insufficient to describe correctly the high-temperature transport properties and to quantify the large resistance drop.

Recent theoretical studies suggest that ground states of manganite models tend to be intrinsically inhomogeneous due to the presence of strong tendencies toward phase separation [20], typically involving ferromagnetic metallic and antiferromagnetic charge and orbital ordered insulating domains. Such ideas are strongly supported by observations of charge inhomogeneities in x-ray absorption fine structure measurements (XAFS) at low temperatures [21] and more recently the coexistence of charge localized and delocalized phases was found close to the metal-insulation transition [22]. Electron microscopy studies of polycrystalline La$_{1-x-y}$Pr$_x$Ca$_y$MnO$_3$ ($x = 3/8$) system revealed it to be electronically separated into submicrometer-scale ferromagnetic (FM) metallic regions and insulating regions [23]. Another experimental evidence of spatially inhomogeneous transition is given by high-resolution electron microscopy (HREM) of manganite thin films and single crystals [24]. Ideas of percolative transition are also supported by scaling analysis of magnetization data [25]. Strong evidences of two-phase coexistence at the ferromagnetic phase transition also comes from noise measurement results. Switching between two different states induces telegraph-like signals (TLS) which were observed in thin epitaxial manganite films [26]. Scaling of $1/f$ noise and resistance near Curie temperature $T_C$ [27] proves the percolation nature of transport at the phase transition in polycrystalline samples. Due to all the above given arguments this section is devoted to the basics of percolation theory.

Consider a simple square (2D) or cubic (3D) lattice; metallic (ferromagnetic) or semiconducting bonds are placed on this lattice with probabilities $p$ and $q = 1 - p$, respectively. If $p$ exceeds some critical value, the percolation threshold $p_c$, an infinite metallic (ferromagnetic) cluster is formed, and the resistivity of the network becomes metallic. The system undergoes a second-order phase transition. In this particular case it is also a ferromagnetic phase transition with diverging cluster size $\xi = \xi_0 |1 - p/p_c|^{-\nu}$. Although, besides square or simple cubic lattices there are much more lattice configurations, such as honeycomb, triangular, diamond, face centered cubic (FCC), etc., and even if percolation thresholds $p_c$ are different, the critical behaviour (critical exponents) of a system depend only on dimensionality of the
lattice, but not on the structure itself [28]. The probability $P$ that a bond belongs
to the infinite cluster and the average cluster size $S$ in the vicinity of the percolation
threshold follow the scaling laws

$$P = P_0(p_c - p)^\beta,$$

$$S = S_0(p - p_c)\gamma.$$  

(1.1)

The correlation function $g(r)$, or in other words, the pair connectivity function,
is defined as the probability that a site at distance $r$ away from an occupied site
belongs to the same cluster. Pair connectivity function at the percolation threshold
decays as $r^{-2\beta/\nu}$.

Conductivity and noise exponents $\mu$ and $\kappa$ are defined as follows. Near the
percolation threshold the averaged conductivity $\Sigma$ (the averaged resistance $\langle R \rangle = 1/\Sigma$) of the random metal-insulator network vanishes as

$$\Sigma \propto (p - p_c)^\mu, \quad p > p_c,$$

(1.3)

and the normalized resistance fluctuations diverge as

$$\frac{\langle \delta R \delta R \rangle}{\langle R \rangle^2} \propto (p - p_c)^{-\kappa}.$$  

(1.4)

For comparison with experiments, where concentration does not appear as a directly
measured value (for example if one measures temperature dependence of transport
properties), it is useful to estimate the critical exponent of normalized resistance
fluctuations versus averaged resistance:

$$\frac{\langle \delta R \delta R \rangle}{\langle R \rangle^2} \propto \langle R \rangle^{-t}.$$  

(1.5)

In reality there are no infinities. Each system is described by a finite linear size $L$. Since the largest cluster is a fractal the properties, which are determined by this
cluster also have fractal behavior. For example, the mass of the largest cluster scales
as $L^D$, where $D > d$ with $D$ is the fractal dimension and $d$ is the spatial dimension.
The conductivity $\Sigma(L, \xi)$ scales as a function of the linear size and the correlation
length of such cluster,

$$\Sigma(L, \xi) \propto \begin{cases} 
\xi^{-\zeta}, & \text{if } L \gg \xi, \\
L^{-\zeta}, & \text{if } L \ll \xi.
\end{cases}$$  

(1.6)

Thus, real fractal behavior could be observed by measuring conductance if the
system size is relatively small or at percolation threshold $p_c$. Numerically found
Exponent  | $d = 2$ | $d = 3$
---|---|---
$\beta$ | 5/36 | 0.41
$\gamma$ | 43/18 | 1.80
$\nu$ | 4/3 | 0.88
$\mu$ | 1.30 | 1.98
$s$ | 1.30 | 0.73
$\bar{\zeta}_R$ | 0.975 | 2.27

Table 1.1: Percolation exponents for 2D and 3D systems. The values are taken from Ref.[28].

values of the critical exponents in the standard percolation problem are listed in Table 1.1.

Instead of averaging over all possible cluster configurations of the random resistor network, one can examine one particular cluster (connecting opposite ends of the sample with voltage applied). The current through bond $b$ is denoted as $I_b$ and the total current is $I$. These currents have a complicated distribution, with $I_b$ varying from full $I$ to very small values. The current distribution moments scale as

$$M_q(L) = \sum_b (I_b/I)^{2q} \propto L^{y(q)}.$$  \hfill (1.7)

There is no linear relation between different exponents $y(q)$, thus one needs an infinite number of independent exponents to characterize the current distribution. The distribution of currents is therefore called multifractal.

If the resistances of each bond are the same, then $M_1(L) = R/r_b$, thus $y(1) = \bar{\zeta}_R$. If we allow the bond resistances $r_b$ to fluctuate, then the total resistance $R$ will also fluctuate. The mean squared deviation $\langle [\delta R]^2 \rangle$, where $\delta R \equiv R - \langle R \rangle$, is equal to

$$\langle [\delta R]^2 \rangle = \langle (\delta r_b)^2 \rangle \sum_b (I_b/I)^4 = \langle (\delta r_b)^2 \rangle M_2 \propto L^{y(2)}.$$  \hfill (1.8)

Using this, one can estimate critical exponent of $\langle \delta R \delta R \rangle / \langle R \rangle^2$ versus sample linear size $L$, which is expected to be $y(2) - 2y(1) < 0$. This means that the amplitude of normalized resistance fluctuations decreases as the a linear size of system is increased.

Standard percolation problem considers an infinite resistivity of the insulating link. In the case of manganites, we have a binary mixture with resistivities $\rho_m$ (metallic phase) and $\rho_s$ (semiconductor phase) with corresponding probabilities $p$ and $q = 1 - p$. The averaged conductivity $\Sigma$ is a function of several parameters,
\[ \Sigma = F_2(p, \rho_m, \rho_s). \]  
\( F_2 \) is a homogeneous function of the bond resistivities such that the conductivity can be written as \( \Sigma = \rho_m^{-1} F_1(p, h) \) with \( h = \rho_m / \rho_s \) and \( F_1(p, h) = F_2(p, 1, h^{-1}) \). For a binary mixture near the critical point \( p_c \), and for \( h \to 0 \), conductivity obeys the following scaling behaviour:

\[
\Sigma = \rho_m^{-1} |p - p_c|^\mu \Phi_\pm |h| |p - p_c|^{-s-\mu}
\]  
\( \Phi_\pm \) with a scaling function \( \Phi_+ \) above the transition and \( \Phi_- \) below. These functions have the asymptotic forms

\[
\Phi_+ (x) \sim x_0, \\
\Phi_- (x) \sim x_0, \\
\Phi_{\pm} (x) \sim x^{\mu/(s+\mu)}.
\]

The percolation problem in the manganite case is even more complicated since there is a wide distribution of the bond resistances. In this case the percolation is the continuum type. As the resistance distribution function is unknown and presumably is unique for different samples, each sample gives a different set of critical exponents and universality is not found yet. Thus a strict comparison of data to theory still can not be done. In spite of this restriction, recently reported scaling results for low-bandwidth [27] and intermediate-bandwidth [25] manganites show an excellent agreement with an oversimplified model of binary mixture.
Chapter 2

Ferroelectrics

2.1 Ferroelectricity

There are four basic mechanisms responsible for dielectric polarization: (i) electronic polarization which occurs due to the distortion of electron cloud, when an electric field is applied, (ii) ionic polarization, which corresponds to the elastic deformation of the bonds between ions (length or angles), (iii) orientational polarization which occurs due to the changes in the orientation of permanent dipole moments, and (iv) interfacial polarization which usually arises from the accumulation of charge at structural interface in heterogeneous materials. Within the orientational polarization mechanism there are two subclasses of polarizabilities. These are the reversible orientational polarization mechanism that reverts back to its original unpolarized state after field removal such as polarization of water, and the spontaneous polarization mechanism, that exhibits a remnant polarization after removal of field. Materials, which posses reversible spontaneous polarization belongs to the class of ferroelectrics.

Thus, ferroelectricity is a property of certain nonconducting crystals, or dielectrics, that exhibit spontaneous electric polarization that can be reversed in direction by the application of an appropriate electric field. Ferroelectricity has also been called (no longer) Seignette electricity, as Seignette or Rochelle Salt (RS) was the first material found to show ferroelectric properties. Besides spontaneous polarization there are more characteristic properties such as ferroelectric domains and a ferroelectric hysteresis loop. Generally due to the similarity of those properties to the major properties of ferromagnetic materials: magnetization, magnetic domains and magnetic hysteresis loop, this phenomenon is called 'ferroelectricity', though physics behind those to phenomenon is completely different.
All ferroelectric crystals necessarily possess both pyroelectric (the value of spontaneous polarization depends on the temperature) and piezoelectric (ability to develop an electrical charge proportional to mechanical stress) properties. However pyroelectrics are not necessary ferroelectrics: the tourmaline shows pyroelectricity (discovered by Teophrast in 314 B.C.) but it is not ferroelectric\(^1\). In accordance the pyroelectrics are a subclass of piezoelectrics (for example quartz is piezoelectric, but it not pyroelectric). Usually material lose its ferroelectric properties at the transition or Curie temperature \(T_C\). The nonpolar phase above \(T_C\) is the so-called paraelectric phase.

Ferroelectric crystals possess regions with uniform polarization called ferroelectric domains. Within a domain, all the electric dipoles are aligned in the same direction. There may be many domains in a crystal separated by interfaces called domain walls. A ferroelectric single crystal, when grown, has multiple ferroelectric domains. A single domain state can be obtained by domain wall motion, which is possible by the application of an appropriate electric field. Strong enough field could lead to the reversal of the polarization in the domain, known as domain switching.

Thus, the most distinguishing feature between ferroelectric and pyroelectric materials is that the direction of the spontaneous polarization in ferroelectrics can be reversed by applying an electric field. The reversal of polarization can be observed by measuring the ferroelectric hysteresis, which is shown in Fig. 2.1. Assume the starting point to be \(H\). As the electric field strength is increased, the domains start to align in the positive direction giving rise to a rapid increase in the polarization (curve HA). At very high field levels, the polarization saturate. The polarization does not fall to zero when the external field is removed. At zero external field, some of the domains remain aligned in the positive direction, hence the crystal will show a remnant polarization \(P_R\) (OD). The crystal cannot be completely depolarized until a field of magnitude \(OE\) is applied in the negative direction. The external field needed to reduce the polarization to zero is called the coercive field strength \(E_C\). If the field is increased to a more negative value, the direction of polarization flips and hence a hysteresis loop is obtained. The value of the spontaneous polarization \(P_s\) (OC) is obtained by extrapolating the curve (BA) onto the polarization axis.

\(^1\)The magnitude of the electric field needed for reversal of polarization is large enough to destroy the material.
Figure 2.1: A Polarization vs. Electric Field (P-E) hysteresis loop for a typical ferroelectric crystal.

2.2 Ferroelectric materials

Ferroelectricity phenomenon was discovered in 1921 by J. Valasek during investigations of the anomalous dielectric properties of Rochelle salt (NaKC₄H₄O₆ · 4H₂O). A second ferroelectric material, KH₂PO₄, was not found until 1935 and was followed by some of its isomorphs. A huge leap in the research on ferroelectric materials came after discovery of BaTiO₃ in 1944. Since then, this small group of ferroelectrics has been joined by approximately 250 pure materials and many more mixed crystal systems.

Ferroelectric materials are grouped according to their structure into four main types such as the corner sharing oxygen octahedron, compounds containing hydrogen bonded radicals, organic polymers and ceramic polymer composites. The three first types (see Table 2.1) mainly refers to single phase materials. The need for piezoelectric composites raises from the fact that not all the desirable properties could be obtained from a single phase materials such as piezoceramics or piezopolymers. For example, optimum material and piezoelectric parameters for medical ultrasound applications are obtained for 20-25 vol. % PZT ceramic embedded in a polymer.

Applications of ferroelectric materials usually utilize their unique dielectric, piezoelectric, pyroelectric, and electro-optic properties. Due to this ferroelectrics both in bulk form and thin film form found applications in many electronic and electro-optic devices and sensors. The list of possible and already exploited applications of
Table 2.1: Ferroelectric materials

<table>
<thead>
<tr>
<th>Type</th>
<th>Subclass</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corner Sharing Oxygen Octahedron</td>
<td>Perovskite</td>
<td>CaTiO₃, BaTiO₃, PbZrₓTi₁₋ₓO₃, KₓNa₁₋ₓNbO₃</td>
</tr>
<tr>
<td>Tungsten-Bronze</td>
<td></td>
<td>PbNb₂O₆, K₃LiNb₅O₁₅, Ba₂Sr₃Nb₁₀O₃₀</td>
</tr>
<tr>
<td>(Bi₂O₂)²⁺ layer structured</td>
<td></td>
<td>Bi₄Ti₅O₁₂, PbBi₂Nb₂O₉</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>KDP-type</td>
<td>KH₂PO₄, KH₂AsO₄, RbH₂PO₄</td>
</tr>
<tr>
<td>Hydrogen Bonded Radicals</td>
<td>Rochelle salt</td>
<td>NaKC₄H₄O₆ · 4H₂O, NaKC₄H₂D₂O₆ · 4H₂O</td>
</tr>
<tr>
<td>Organic Polymers</td>
<td>TGS-type</td>
<td>(NH₂CH₂COOH)₃ · H₂SO₄</td>
</tr>
<tr>
<td></td>
<td>PVDF</td>
<td>(CH₂ – CF₂)ₙ</td>
</tr>
</tbody>
</table>

ferroelectrics in bulk form include ceramic capacitors, ultrasound devices, gas ignitors, displacement transducers, accelerometers, piezoelectric transformers, impact printer heads and many others. Materials in thin film form continue this list and enhance it with nonvolatile memories, thin films capacitors, pyroelectric sensors, surface acoustic wave (SAW) substrates, optical waveguides and optical memories and displays.

2.3 Theory of ferroelectricity

There are two main approaches that can be used to describe and understand ferroelectricity, the phenomenological approach based on Ginsburg-Landau phase transition theory developed by Devonshire [29] and the lattice dynamic approach based upon the concepts of polarization catastrophe [30] and/or soft phonon mode [31]. Both approaches are complementary and each has its merits. Phenomenologi-
Figure 2.2: Free energy curves for the paraelectric (a) and ferroelectric (b, c) phases; b and c correspond to the second and first order phase transitions, respectively.

...cal theories are most used to understand the macroscopic behaviour and the lattice dynamic theory is applied to understand the lattice dynamics of the phase transition on the lattice level. Microscopic theories of ferroelectricity just started to develop by use of recent advances in calculation techniques, that allows first-principles calculations.

Devonshire theory provides a successful phenomenological description of many cubic perovskite ferroelectrics such as BaTiO$_3$ i.e. it explains the observed phases and phase transition sequences quite naturally in terms of a phenomenological Landau-type expansion of the free energy in terms of the ferroelectric order parameter $P$. Making use of cubic symmetry and truncating the expansion to sixth order in $P$, Gibbs free energy change can be expressed as:

$$G = G_0 + \frac{1}{2} \alpha P^2 + \frac{1}{4} \beta P^4 + \frac{1}{6} \gamma P^6.$$  \hfill (2.1)

The coefficients $\alpha$, $\beta$, and $\gamma$ are allowed to be temperature dependent, but generally first and second order ferroelectric transitions can be described by assuming such dependence only for $\alpha = \alpha_0(T - T_C)$ and $\gamma > 0$. The thermodynamic system will be in a stable state when the free energy $G$ is minimized. Differentiation of Eq. 2.1 with respect to $P$ gives the dielectric equation of state:

$$E = \frac{\partial G}{\partial P} = \alpha P + \beta P^3 + \gamma P^5.$$  \hfill (2.2)
With no external field applied \((E = 0)\), at temperatures above the Curie temperature \(T_C\) there is only one solution \(P_S = 0\) and the system is in the paraelectric state (Fig. 2.2 a). If one of \(\alpha\) or \(\beta\) is negative, the system will have nonzero spontaneous polarization which originate from first or second order phase transitions. If the \(\alpha\) is negative and \(\beta\) is positive, there are two minimums at \(P = \pm P_C\) (Fig. 2.2 b) and the transition is second order. If the sign of \(\alpha\) is positive and \(\beta\) is negative, an equilibrium will exist at \(P = 0\), and \(P = \pm P_C\) (Fig. 2.2 c). Phase transition in this case will be of first order.

There are some limitations of such a phenomenological approach. Truncating Gibbs free energy \(G\) to the sixth-order in \(P\) permits only those ferroelectric phases, where polarization is confined along the symmetry axis. Recent discovery of a novel monoclinic ferroelectric phase in which \(P\) is confined only to a symmetry plane in the PZT system [32] requires an extension of the theory up to eight power in order parameter [33]. Expansion in odd powers of \(P\) is appropriate if the unpolarized crystal has a center of inversion symmetry. There are ferroelectric crystals in which odd powers are also important. Also, power series expansion of the free energy do not always exists, especially very close to the phase transition. There are materials in which transition is neither first, nor second order, like the transition in KH\(_2\)PO\(_4\).

The occurrence of ferroelectricity in some systems could be explained as the result of a polarization catastrophe. Polarization catastrophe takes place, when the local electric fields arising from the polarization itself increase faster than the elastic restoring forces on the ions in the crystal. This leads to an asymmetric shift in ionic positions; the shift is limited to a finite displacement by an onset of restoring force.

For crystals where the Lorentz local field obtains the form \(E_{loc} = E + \frac{1}{3\varepsilon_0}P\) the dielectric constant \(\varepsilon\) relates to the electronic polarizability by the Clausius-Mossoti relation. Expressing this relation for \(\varepsilon\), it could be rewritten in the form

\[
\varepsilon = \frac{1 + \frac{2}{3\varepsilon_0} \sum N_j \alpha_j}{1 - \frac{1}{3\varepsilon_0} \sum N_j \alpha_j},
\]

(2.3)

where \(\alpha_j\) the electronic plus ionic polarizability of an ion of type \(j\) and \(N_j\) is the number of ions \(j\) per unit volume. The dielectric constant becomes infinite and permits spontaneous polarization in zero field when

\[
\sum N_j \alpha_j = 3\varepsilon_0.
\]

(2.4)

This is the condition for a polarization catastrophe.

18
In the presence of small departures $s \ll 1$ in $\sum N_j \alpha_j$ from the critical value $3\varepsilon_0$, where $1/3\varepsilon_0 \sum N_j \alpha_j = 1 - 3s$, the dielectric constant becomes

$$\varepsilon \simeq 1/s.$$  \hfill (2.5)

Suppose that near the critical temperature $s$ varies linearly with temperature $s \simeq (T - T_C)/\xi$, where $\xi$ is a constant. Then the dielectric constant has the form

$$\varepsilon \simeq \frac{\xi}{T - T_C},$$  \hfill (2.6)

i. e. follows Curie-Weiss law.

High static dielectric constant $\varepsilon(0)$ also can be associated with a low frequency of the transverse optical phonon following the Lyddane-Sach-Teller relation:

$$\frac{\omega^2 \Theta}{\omega^2 L} = \frac{\varepsilon(\infty)}{\varepsilon(0)}.$$  \hfill (2.7)

Approaching transition temperature from the paraelectric state, transverse optical phonon frequency decreases toward zero since $\varepsilon(0) \to \infty$. Thus in the structural phase transition the order parameter can be associated with this vibrational mode.
Chapter 3
Basics of the random signal theory

1 In physics as everywhere else, together with the expected and strongly deterministic processes we always have to deal with the uncertain and random processes. Notwithstanding the fact that single event of a random process cannot be determined before it occurs, there are some nonrandom measures which can characterize that process. The field of science which treats the laws and relations of random processes is called the probability theory. Random signal theory is one of the applications of probability theory.

3.1 Probability density functions, moments, characteristic function

In everyday terminology, probability can be thought of as a numerical measure of the likelihood that a particular event will occur. Probability values are assigned on a scale from 0 to 1, 0 indicates that an event will never occur and 1 indicates that an event will take place. A probability of 1/2 means that an event is equally likely to occur as not to occur. Let $P\{\ldots\}$ be the probability of an event indicated in the curly brackets. The distribution functions of the first, second, and higher order for a given random process $x(t)$ are defined as

$$W_1(x_1, t_1) = P\{x(t_1) \leq x_1\},$$
$$W_2(x_1, t_1; x_2, t_2) = P\{x(t_1) \leq x_1; x(t_2) \leq x_2\},$$
$$W_2(x_1, t_1; \ldots; x_n, t_n) = P\{x(t_1) \leq x_1; \ldots; x(t_n) \leq x_n\},$$

(3.1)

1This chapter was compiled mostly from Sh. Kogan "Electronic noise and fluctuations in solids"
where \( x_i \) is the value of random quantity at instant \( t_i \). So distribution function is the mathematical expression that describes the probability that a system will take on a specific value or set of values.

For instance, \( W_n(x_1, t_1; ...; x_n, t_n) \) is the probability that random quantity \( x \) at instant \( t_1 \) is less than a given value \( x_1 \), and at instant \( t_n \) is less than \( x_n \).

If \( W_n(x_1, t_1; ...; x_n, t_n) \) are differentiable functions of the variables \( x_1, ..., x_n \), one may introduce the corresponding probability density functions:

\[
\begin{align*}
    w_1(x_1, t_1) &= \frac{\partial W_1(x_1, t_1)}{\partial x_1}, \\
    w_2(x_1, t_1; x_2, t_2) &= \frac{\partial W_2(x_1, t_1; x_2, t_2)}{\partial x_1 \partial x_2}, \\
    w_n(x_1, t_1; ...; x_n, t_n) &= \frac{\partial W_n(x_1, t_1; ...; x_n, t_n)}{\partial x_1 \partial x_2 ... \partial x_n}.
\end{align*}
\]

The functions \( w_n \) are called \( n \)-dimensional probability density functions of the random quantity \( x(t) \).

For example the probability that variable \( x \) at instant \( t \) falls in the interval \( a < x \leq b \) is the integral of the one-dimensional probability density function \( w_1(x, t) \):

\[
P(a < x(t) \leq b) = \int_a^b w_1(x, t)dx.
\]

The probability density functions must be consistent with each other, that is, each \( k \)-dimensional density function can be obtained from any \( n \)-dimensional function with \( n > k \) by integration over 'extra' variables:

\[
w_k(x_1, t_1; ...; x_k, t_k) = \int dx_{k+1}...dx_n w_n(x_1, t_1; ...; x_n, t_n).
\]

Random processes are called stationary if all distributions \( w_n(x_1, t_1; ...; x_n, t_n) \) remain invariable under any identical shift of all time points \( t_1, ..., t_n \). It means that for a stationary process the probability function \( w_1(x_1, t_1) \) does not depend at all on time \( t_1 \), the probability density function \( w_2(x_1, t_1; x_2, t_2) \) depends only on the difference \( t_1 - t_2 \), that is, may be written as \( w_2(x_1, x_2, t_1 - t_2) \), and so on.

The mean value of the random variable \( x(t) \) or in other words its 'expectation' is equal to

\[
    \langle x(t) \rangle = \int_0^1 x(t) dW_1(x, t) = \int_{-\infty}^{+\infty} x(t) w_1(x, t)dx.
\]

In general, the mean value of function \( x(t)^r \) is called \( r \)-th order moment. The mean value of the random quantity \( (\delta x(t))^r \), where \( \delta x(t) = x(t) - \langle x(t) \rangle \) is the deviation of
the random quantity $x(t)$ from its mean value $\langle x(t) \rangle$, is called as $r$-th order central moment.

As an example the variance, i.e., the mean value of the fluctuation squared is the second-order central moment. It shows how closely packed about its mean value a distribution is.

$$\langle (\delta x(t))^2 \rangle = \int_{-\infty}^{+\infty} (\delta x(t))^2 w_1(x,t)dx. \quad (3.6)$$

A distribution is not uniquely specified by its moments, but is uniquely specified by its characteristic function. The characteristic function of a random quantity is defined as the mean value of the function $e^{iux}$, where $x$ is the random variable and $u$ is a real parameter. If the distribution function $W_1(x,t)$ is differentiable, the characteristic function is simply the Fourier transform of the probability density function (Eq. 3.2):

$$\phi_x(u) \equiv \langle e^{iux} \rangle = \int_{-\infty}^{+\infty} dxe^{iux} w_1(x,t). \quad (3.7)$$

The characteristic function has a very useful property: if the random variable is the sum of $N$ independent random variables, i.e.,

$$X = \sum_{i=1}^{N} x_i, \quad (3.8)$$

then the characteristic function of $X$ is simply product of the characteristic functions of the variables $x_i$: 

$$\phi_x(u) = \phi_{x_1}(u) \cdot \phi_{x_2}(u) \cdots \phi_{x_n}(u). \quad (3.9)$$

There are more functions which are used in characterization of the distribution, such as the moment-generating function and the cumulant-generating function, whose purpose is clearly indicated in their names.

Many random processes are similar to electron emission from the cathode of a thermionic tube. The instances of the emission of individual electrons are random because emission events are uncorrelated. Such random processes are called Poissonian. Let $n_1$ be the mean rate of individual events that is the mean number of events per unit time. The mean number of such events during a definite time $t_m$ is obviously $\bar{n} = n_1 t_m$. Of cause, the actual number $n$ of events that happen to occur during the time $t_m$ is a random quantity, which fluctuates around its mean value $\bar{n}$. Let us divide the time $t_m$ into $N$ equal intervals. If $N$ is taken so large, or equivalently, the intervals $t_m/N$ are taken so small that occurrence of more then one event in one interval is improbable. Then for each interval two alternatives are
possible: either one individual event or no event may occur. The corresponding 
probabilities are \( \frac{n}{N} \) and \( 1 - \frac{n}{N} \), respectively. This is the binomial distribution 
and the probability of \( n \) events to occur equals

\[
\frac{N!}{n!(N-n)!} \left( \frac{n}{N} \right)^n \left( 1 - \frac{n}{N} \right)^{N-n}.
\] (3.10)

In the limit when \( N \to \infty \), (3.10) approaches the distribution with probability 
function:

\[
P(n) = \frac{n}{n!} e^{-n},
\] (3.11)

which is called the Poisson distribution.

In the random signal theory one of the most important distributions is the normal 
(Gaussian) distribution. The one-dimensional Gaussian probability density function is

\[
w_1(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\bar{x})^2}{2\sigma^2}},
\] (3.12)

where \( \delta x = x(t) - \langle x(t) \rangle \) is the fluctuation and \( \sigma^2 \) is the variance. The importance 
of that distribution is defined by central limit theorem which says that the data of 
many small and unrelated random effects tends to be normally distributed, so often 
random signals with unknown distributions in a good approximation are assumed to be Gaussian.

Strictly speaking a random process is called Gaussian if all its probability density 
functions are normal for all \( n \). The \( n \)-dimensional normal distribution reads:

\[
w_1(x_1, ..., x_n) = \frac{1}{\sqrt{(2\pi)^n det \lambda}} e^{-\frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \lambda_{ij}^{-1} \delta x_i \delta x_j}.
\] (3.13)

Here \( \delta x_i = x_i - \langle x_i \rangle \). The matrix \( \lambda \) is called the covariance matrix with elements \( \lambda_{ij} = \langle \delta x_i \delta x_j \rangle \).

The statistical characteristics of a random process are nonrandom quantities, 
which can be, in principle measures by a corresponding averaging of the random 
quantity or quantities. There are two possible procedures of averaging:

1. Averaging over time, i.e., over a sufficiently long record of the random process. 
In this case the distribution function \( W_1(x_1) \) of a stationary process is equal to that 
part of the total time \( t_m \) of measurement of this process during which random 
quantity \( x < x_1 \). The mean value of the random quantity is then

\[
\overline{x(t)} = \lim_{t_m \to \infty} \frac{1}{t_m} \int_{t_m/2}^{t_m/2} dt \cdot x(t).
\] (3.14)
2. Averaging over an ensemble of a large number $N$ of identical systems, i.e., a systems in which identical conditions for the random process and identical means of $i$-ths measurement are provided. In this case distribution function, $W_1(x_1, t_1)$ is equal to the fraction of the total number of ensemble systems in which at instant $t_1$ the random quantity $x < x_1$. The mean value in this case (denoted by angle brackets) equals:

$$
\langle x(t) \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} x_i(t). 
$$

(3.15)

Here $x_i(t)$ is the value of random quantity at instant $t$ in the $i$-th system of the ensemble.

It is not obvious that both procedures yield identical mean values. For instance if we will measure magnetization in an ensemble of randomly chosen ferromagnets, expected mean value is zero, while single ferromagnet could maintain its magnetization value nonequal to zero for an indefinite period of time. The random process is called \textit{ergodic} only if both procedures yield identical mean values.

### 3.2 The correlation function

The correlation function is one of the most important characteristics of any random process. It is a nonrandom characteristics of the kinetic of the random fluctuations $\delta x(t) = x(t) - \langle x(t) \rangle$ and shows how those fluctuations evolve in time on average.

Consider an ensemble of a large number $N$ of systems at identical conditions. Let $\delta x_i(t_1)$ and $\delta x_i(t_2)$ be the fluctuations in the $i$-th system of the ensemble at instant $t_1$ and $t_2$, respectively. The correlation function is defined by following equation

$$
k_x(t_1, t_2) \equiv \langle \delta x(t_1) \delta x(t_2) \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} \delta x_i(t_1) \delta x_i(t_2).
$$

(3.16)

In a \textit{stationary} system the correlation function remains invariable if both instances $t_1$ and $t_2$ are shifted identically. In such systems $k_x$ depends only on the difference $t_1 - t_2$.

The correlation function may also be determined by averaging over a sufficiently long record of random process $x(t)$ in one system.

$$
k_x(t_1, t_2) \equiv \overline{\delta x(t_1) \delta x(t_2)} = \lim_{t_m \to \infty} \frac{1}{t_m} \int_{-t_m/2}^{t_m/2} dt \cdot x(t_1 + t) x(t_2 + t).
$$

(3.17)
The two correlation functions (3.16) and (3.17) coincide if the system is ergodic. In stationary systems, function \( k_x \) depends only on the time difference \( \tau = t_1 - t_2 \). Function \( k_x(\tau) \) is often called autocorrelation function. At \( \tau = 0 \) the autocorrelation function is simply the variance, i.e., the average fluctuation squared, \( k_x(0) = \langle (\delta x)^2 \rangle \). As \( |\tau| \to \infty \) the autocorrelation function of fluctuation in stationary systems drops to zero. The decay of \( k_x(\tau) \) to zero may be viewed as if system 'forgets' its initial fluctuation. This time is usually called the relaxation time. In real systems a number of kinetic processes and, consequently a number of relaxation times exist.

### 3.3 Spectral density, Wiener - Khintchine theorem

Let \( \delta x(t) \) be a record of the fluctuations measured during a sufficiently long time interval \( t_m \), say, from \( t = -t_m/2 \) to \( t = t_m/2 \). The spectral density is one of most important nonrandom characteristics of a random signal, which gives information about distribution of random signal amplitude in the frequency domain.

\[
S_x(f) = 2 \lim_{t_m \to \infty} \frac{1}{t_m} \left| \int_{-t_m/2}^{t_m/2} dt \cdot e^{i2\pi ft} \delta x(t) \right|^2. \tag{3.18}
\]

Relations between spectral density and correlation function are called Wiener - Khintchine theorem and were derived by Wiener (1930) and Khintchine (1934).

Consider the sample function of a random process \( x(t) \). This is a continuous and infinite signal and cannot be evaluated in the frequency domain unless we make it periodic. We can define a periodic function \( x_T(t) \) that has a period \( T \) and is \( x(t) \) between \(-T/2\) and \( T/2\). Thus, we can define the Fourier series of \( x_T(t) \) by the Fourier coefficients

\[
C_n = \frac{1}{T} \int_{-T/2}^{T/2} dt \cdot x_T(t) e^{-i\frac{2\pi nt}{T}}. \tag{3.19}
\]

The periodic function can then be defined in terms of the Fourier basis functions as

\[
x_T(t) = \sum_{n=-\infty}^{\infty} C_n e^{i\frac{2\pi nt}{T}}. \tag{3.20}
\]

This expression must satisfy the Parseval’s equation, which states that

\[
\frac{1}{T} \int_{-T/2}^{T/2} |x(t)|^2 dt = \sum_{n=-\infty}^{\infty} |C_n|^2. \tag{3.21}
\]
This equation is the time average of the squared sample function or the 'mean-
squared value'. This is the integral power of the signal. Note that at this point, the
power is a random variable since it depends on what sample function of an ensemble
that is chosen. Thus, if we explicitly show the dependence on \( t \), Eq. 3.21 becomes

\[
P(t) = \frac{1}{T} \int_{-T/2}^{T/2} |x(t, t')|^2 dt' = \sum_{n=-\infty}^{\infty} |C_n(t)|^2. \tag{3.22}
\]

Thus, the power in the \( n \)-th frequency is also a random variable. Now we must
tie this result with the correlation function. It can be shown that if a signal has a
periodic component, then its autocorrelation function is also periodic over the same
interval (i.e. \( k_{xT}(T) = k_{xT}(0) \)). Thus, we can define it in terms of a Fourier series

\[
k_{xT}(\tau) = \sum_{k=-\infty}^{\infty} b_n e^{i2\pi n\tau/T}, \tag{3.23}
\]

where

\[
b_n = \frac{1}{T} \int_{-T/2}^{T/2} d\tau k_{xT}(\tau) e^{-i2\pi n\tau}. \tag{3.24}
\]

Now consider the Fourier coefficients of two of our periodic sample functions as
defined in (Eq. 3.19). If we perform the complex multiplication of two coefficients
we will get

\[
C_m^*C_n = \frac{1}{T^2} \int_{-T/2}^{T/2} \int_{-T/2}^{T/2} dt_1 dt_2 x_T(t_1)x_T(t_2)e^{-i2\pi(m_1-n_1)T/T}. \tag{3.25}
\]

Define \( \tau = t_2 - t_1 \) and recall the definition of correlation function (Eq. 3.17). Then
for \( m = n \)

\[
\lim_{T \to \infty} |C_n|^2 = \lim_{T \to \infty} \frac{1}{T} \int_{-T/2}^{T/2} d\tau k_{x}(\tau) e^{-i2\pi n\tau/T} = b_n. \tag{3.26}
\]

Thus, the autocorrelation and the power spectrum are a transform pair and

\[
k_{x}(\tau) = \sum_{n=-\infty}^{\infty} |C_n|^2 e^{i2\pi n\tau/T} \tag{3.27}
\]

Consider the power spectrum made up of a set of discrete expected power terms
(i.e. \( |C_n|^2 \)). The power spectrum density function can be defined as

\[
S_x(f) = \frac{1}{T} \sum_{n=-\infty}^{\infty} \langle |C_n|^2 \rangle \text{rect}(f - n/T) \tag{3.28}
\]

where \( \text{rect} \) is the standard unit function defined as 1 between \( n/T-1/2 \) and \( n/T+1/2 \)
and 0 everywhere else and \( f \) is a continuous frequency variable. Thus, we have
created a continuous power spectral density defined for all $f$. If we integrate the power spectral density over all frequency we get

$$
\int_{-\infty}^{\infty} S_x(f) = \sum_{n=-\infty}^{\infty} \langle |C_n|^2 \rangle \frac{1}{T} \int_{-\infty}^{\infty} \text{rect}(f - n/T) df = \sum_{n=-\infty}^{\infty} \langle |C_n|^2 \rangle = \langle P(t) \rangle. \quad (3.29)
$$

Thus, the Wiener-Khintchine theorem is

$$
S_x(T) = \int_{-\infty}^{\infty} d\tau \cdot k_x(\tau) e^{-i2\pi f\tau}, \quad (3.30)
$$

which indicates that the spectral density function is the Fourier transform of the autocorrelation function.
Chapter 4

Fluctuations in equilibrium state and 1/f noise

4.1 Fluctuation-dissipation relations (FDR)

In any physical system the dependence of the fluctuations correlation function on time or, equivalently, the frequency dependence of spectral density, on one hand, and the response of the same system to external perturbation, on the other hand, are governed by the same kinetic processes, and one can expect that there is some relationship between the two kinetic characteristics of the system. However, for equilibrium systems an exact relationship holds between the spectral density of fluctuations at any given frequency \( f \) and that part of the linear response of the same system to an external perturbation of the same frequency \( f \), which corresponds to the dissipation of the power of the perturbation. This fundamental relation is called the fluctuation-dissipation relation (FDR), or theorem (FDT). It was first derived by Nyquist in 1928 [34] for fluctuations of current and voltage in quasi-stationary electric circuits, and subsequently, in a far more general form, by Callen and coworkers [35, 36] in 1951.

Consider a system, which weakly interacts with a thermal bath with a temperature \( T \) and is in equilibrium with this thermal bath. The probability of the equilibrium system being in its \( m \)-th eigenstate with an energy \( E_m \) is given by the Gibbs distribution:

\[
    w_m = e^{\frac{F - E_m}{k_BT}}.
\]

Here \( F \) is the free energy of the system. It is convenient to describe properties of such a system using a density matrix \( \rho \), which is diagonal in the basis of the
eigenstates $\Psi_m$ of the system Hamiltonian. The diagonal elements of $\rho$ are just the Gibbs probabilities $w_m$ of these eigenstates.

The correlation function of a fluctuating quantity $x(t)$ in quantum-mechanical notation is given by

$$k_x(t_1 - t_2) = Tr[\rho \cdot \{\hat{x}(t_1)\hat{x}(t_2) + \hat{x}(t_2)\hat{x}(t_1)\}] = \sum_{mn} w_m \cdot (x_{mn}(t_1)x_{mn}(t_2) + x_{mn}(t_2)x_{mn}(t_1)).$$

(4.2)

Here $x_{mn}(t)$ is the matrix element of the Heisenberg operator between the states $\Psi_m$ and $\Psi_n$. It satisfies the equation

$$\frac{\partial x_{mn}(t)}{\partial t} = i\hbar\omega_{mn}x_{mn}(t),$$

(4.3)

where $\hbar\omega_{mn} = E_m - E_n$. The solution of Eq. 4.3 is

$$x_{mn}(t) = e^{i\hbar\omega_{mn}t}x_{mn}(0).$$

(4.4)

The matrix element $x_{mn}(0)$, which is time independent, may be considered as a matrix element of a common (Schrödinger) operator and denoted simply by $x_{mn}$. In accordance with Wiener-Khintchine theorem the spectral density of fluctuations of $x(t)$ in an equilibrium system is given by

$$S_x(\omega) = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 k_x(t_1 - t_2)e^{i\omega(t_1-t_2)} =$$

$$= 2\pi \sum_{mn} (w_m + w_n)|x_{mn}|^2\delta(\omega_{mn} - \omega).$$

(4.5)

In deriving this equation, the integral representation of the delta-function was used.

The spectral density of fluctuations of the quantity $x(t)$ at angular frequency $\omega$, as is evident from Eq. 4.5, is determined by the matrix elements of the operator $\hat{x}$ of this quantity between states which energies differ by the $E_m - E_n = \pm \hbar\omega$.

Let us substitute Eq. 4.1 into Eq. 4.5. In the case of equilibrium systems, the ratio of probabilities of two states $m$ and $n$ depends only on the difference of the corresponding energies $(E_m - E_n) \equiv \hbar\omega_{mn}$:

$$w_n = e^{\frac{-\hbar\omega}{k_BT}} w_m$$

(4.6)

due to the delta-function of frequency in Eq. 4.5. Therefore

$$S_x(\omega) = 2\pi[1 + e^{\frac{-\hbar\omega}{k_BT}}] \sum_{mn} w_m|x_{mn}|^2\delta(\omega_{mn} - \omega).$$

(4.7)
Equation 4.7 has to be compared with the equation for the response of the system to external perturbation. This response must be expressed in terms of the same quantities: $w_m$, $x_{mn}$ and $\omega_{mn}$.

Suppose that the quantity $x$ interacts with the field $F(t)$. Let $\hat{x}$ be the quantum-mechanical operator of $x$ and the interaction energy be $\hat{H}_F = -\hat{x}F$. Let $F(t)$ be a periodic 'force' with angular frequency $\omega = 2\pi f$ and amplitude $F_0$. It must be real:

$$F(t) = \frac{1}{2}(F_0 e^{-i\omega t} + F_0^* e^{i\omega t}) \quad (4.8)$$

Under this 'force' the system undergoes transitions between its states. It absorbs the energy of perturbation $F(t)$ and dissipates it. According to rules of quantum mechanics the rate of transitions from a state $m$ to a state $n$ under a periodic perturbation equals:

$$W_{mn} = \frac{\pi}{2\hbar} |F_0|^2 |x_{mn}|^2 \delta(\omega_{mn} - \omega) + \delta(\omega_{mn} - \omega)]. \quad (4.9)$$

Each such transition is accompanied by absorption or emission of an energy quantum $\hbar\omega$ (the first and second terms in rectangular brackets, respectively). The mean power $\bar{Q}$, transferred to the system is obtained by averaging over the initial states, taking into account their probabilities $w_{mn}$:

$$\bar{Q} = \sum_{mn} w_m W_{mn} \hbar \omega_{mn}. \quad (4.10)$$

Using Gibbs distribution for equilibrium systems Eq. 4.1 and Eq. 4.9 one obtains:

$$\bar{Q} = \frac{\pi \omega}{2\hbar} |F_0|^2 [1 - e^{-\frac{\hbar \omega}{kBT}}] \sum_{mn} w_m |x_{mn}|^2 \delta(\omega_{mn} - \omega). \quad (4.11)$$

This power may also be expressed in terms of response of the quantity $x$ to a given external force $F(t)$. The expected linear change of $x$ in a stationary system may be written as

$$\langle x(t) \rangle = \int_{-\infty}^t dt' A(t - t')F(t'). \quad (4.12)$$

Here the real function $A(t)$ may be called the response function. By virtue of the causality principle, the response $\langle x(t) \rangle$ is determined by the force $F(t')$ at instant $t'$ preceding $t$. This is why the upper limit of integration in Eq. 4.12 is $t$. If $F(t)$ is a harmonic function of time given by Eq. 4.8, then

$$\langle x(t) \rangle = \frac{1}{2} \{F_0 A(\omega) e^{-i\omega t} + F_0^* A(-\omega) e^{i\omega t}\}, \quad (4.13)$$

where

$$A(\omega) = \int_0^\infty dt A(t) e^{-i\omega t} = A^*(\omega). \quad (4.14)$$
is the frequency dependent susceptibility of the entire system. The power absorbed
by the system and dissipated by it, after averaging over a period $2\pi/\omega$, equals:

$$\bar{Q} = -\langle x(t)F \rangle = \langle \dot{x}(t)F \rangle =$$

$$\frac{i}{4}(-\omega F_0 A(\omega)e^{-i\omega t} + \omega F_0^* A^*(\omega)e^{i\omega t})(F_0 e^{-i\omega t} + F_0^* e^{i\omega t}).$$

(4.15)

Here the upper dot denotes the time derivative, the bar and over line denote averaging over time. Only those products of exponential functions, which are independent of time, contribute to dissipated power. Therefore,

$$\bar{Q} = \frac{1}{4} |F_0|^2 \omega [A^*(\omega) - A(\omega)] = \frac{1}{2} |F_0|^2 \omega A''(\omega).$$

(4.16)

Here $A''(\omega) \equiv \text{Im} A(\omega)$ is the imaginary part of the complex susceptibility $A(\omega)$. Comparing Eq. 4.7 for $S_x(f)$ with Eqs. 4.11 and 4.16 for $\bar{Q}$, one obtains the FDR that is, the relationship between the spectral density of noise $S_x(f)$ and that part of response at the same frequency ($A''(\omega)$) which determines the dissipated power

$$S_x(\omega) = 2\hbar \coth \left( \frac{\hbar \omega}{2k_B T} \right) A''(\omega).$$

(4.17)

In many cases it is more convenient to use not the susceptibility $A(\omega)$ but the
generalized conductance $G(\omega) = -i\omega A(\omega)$, which is defined as the response of the
time derivative of $x$, i.e., $\dot{x}$, to the 'force' $F(t)$. Therefore $G' = \text{Re} G = \omega A''$. The
spectral density of the quantity $\dot{x}$ is $S_{\dot{x}}(\omega) = \omega^2 S_x(\omega)$. Then

$$S_{\dot{x}}(\omega) = 2\hbar \omega \coth \left( \frac{\hbar \omega}{2k_B T} \right) G'(\omega).$$

(4.18)

At the extreme case $k_B T >> \hbar \omega$, the quasi-classical approximation holds. Even
at $T = 1$ K, the quasi-classical approximation remains valid at high frequencies up
to $f = \omega/2\pi > 4 \cdot 10^{10}$ Hz. In this quasi-classical limit $\coth(\hbar \omega/2k_B T) \approx 2k_B T/\hbar \omega$ and

$$S_{\dot{x}}(\omega) = 4k_B T G'(\omega).$$

(4.19)

FDRs express the spectral density of fluctuations in the equilibrium state of any
system in terms of the dissipative part of the linear response of the same system
to a small enough force. FDRs hold even if the response of this system to a strong
force is arbitrarily nonlinear. In this sense FDRs are quite general.

FDRs (Eqs. 4.17 and 4.18) may be applied only to equilibrium systems. Of
course, the spectral densities of the fluctuating parameters can be found, in principle,
also for nonequilibrium systems. However, in these systems the spectral densities
are not directly related to the linear response of the corresponding system. It means that in nonequilibrium systems the linear response and the spectral density of the noise yield independent information of the kinetic of the system and complement each other.

A 'force' applied to the system removes it from its equilibrium state and, at the same time, reveals such fluctuation processes which, due to their symmetry, are not observable in an equilibrium noise. Often this nonequilibrium noise exceeds the equilibrium one even when the 'force' is so small that the deviation from equilibrium is negligible in all other respects.

4.2 Applications of FDR

4.2.1 Nyquist theorem

The thermal motion of charge carriers in any conductor is a source of random fluctuations of current. Due to the randomness of the thermal motion, the current created by those charge carriers that are moving in a given direction is, in general, not counterbalanced by the current of those moving in the opposite direction. The net current is therefore not zero even in the absence of any external current sources, i.e., electromotive forces. The mean value of this random, fluctuation, current is, of course, zero. The random current stems from the randomness of the thermal motion of charge carriers, which is analogous to Brownian motion. This noise is universal, i.e., exists in any conductor, irrespective of the type of conduction (electronic, ionic) or type of material (metal or semiconductor).

The random current, $\delta I(t)$, that passes through the conductor in a circuit and which can be measured in principle differs. In general, the random current form that is directly induced by thermal motion of charge carriers and may be called intrinsic current, $\delta I^{\text{int}}(t)$. Let us denote the impedance of the conductor under consideration by $Z(\omega)$, and that of the circuit that closes the conductor (load) by $Z_L(\omega)$. Let us also assume that the only sources of fluctuations are the charge carriers in the conductor. The current $\delta I(t)$ induces a voltage across the load impedance. Its Fourier component is

$$ \delta U_L(\omega) = Z_L(\omega) \delta I(\omega). \quad (4.20) $$

Let us consider quasi-stationary circuits, the linear dimensions of which $L \ll \lambda$, where $\lambda = 2\pi c/\omega$ is the wavelength of the electromagnetic wave with angular frequency $\omega$ and $c$ is the speed of light. According to the Kirchhoff law, the fluctuation
of voltage across the electrodes of the conductor is $\delta U(\omega) = -\delta U_L(\omega)$. The current in the conductor and, hence, in quasi-stationary circuit, is the sum of the source current $\delta I^{\text{int}}(\omega)$ and the current $Z^{-1}(\omega)\delta U(\omega)$ induced by the voltage $\delta U(\omega)$, i.e.,

$$
\delta I(\omega) = -[Z_L(\omega)/Z(\omega)]\delta I(\omega) + \delta I^{\text{int}}(\omega). \tag{4.21}
$$

It means that

$$
\begin{align*}
\delta I(\omega) &= [1 + Z_L(\omega)/Z(\omega)]^{-1}\delta I^{\text{int}}(\omega), \tag{4.22a} \\
\delta U(\omega) &= -Z_L(\omega)[1 + Z_L(\omega)/Z(\omega)]^{-1}\delta I^{\text{int}}(\omega). \tag{4.22b}
\end{align*}
$$

In a short-circuited conductor ($Z_L \to \infty$) the current $\delta I = \delta I^{\text{int}}$ and, obviously, $\delta U = 0$. In a disconnected conductor, on the contrary, $\delta I = 0$, $\delta U = -\delta U^{\text{int}}$, where the voltage

$$
\delta U^{\text{int}} \equiv Z(\omega)\delta I^{\text{int}}(\omega) \tag{4.23}
$$

can be viewed as a random electromotive force (emf) applied across the conductor. It can be considered and used in calculations, on the same footing as $\delta I^{\text{int}}$ as the source of equilibrium noise.

Equations for the spectral densities of current $\delta I^{\text{int}}(t)$ and emf $\delta U^{\text{int}}(t)$ have been derived in a very fundamental way by Nyquist [34]. He analyzed the experiments made by Johnson [37], who observed the equilibrium noise in conductors and proved experimentally that spectral density of $\delta U^{\text{int}}(t)$ is proportional to the resistance of the conductor and to its absolute temperature. Now one can derive the generalized Nyquist theorem from one of the fluctuation-dissipation relations (Eq. 4.18). However, one must keep in mind that these relations may be viewed as the generalization of the Nyquist theorem.

Since the dissipated power in the conductor is $\bar{Q} = \overline{UU}$ (Eq. 4.15), the FDR in form Eq. 4.18 must be used. In our case the conductance $G(\omega)$ is the inverse impedance $Z^{-1}(\omega)$:

$$
\begin{align*}
S_I^{\text{int}}(\omega) &= 2\hbar \omega \coth \left( \frac{\hbar \omega}{2k_BT} \right) \text{Re}Z^{-1}(\omega), \tag{4.24a} \\
S_U^{\text{int}}(\omega) &= 2\hbar \omega \coth \left( \frac{\hbar \omega}{2k_BT} \right) \text{Re}Z(\omega). \tag{4.24b}
\end{align*}
$$

Owing to the Nyquist relationship, the measurement or calculation of the equilibrium noise can not give any additional information besides that which is obtained by measurement or calculation of the real part of the impedance or real part of inverse impedance.
As was emphasized above, the random motion back and forth of the charge carriers generates the equilibrium current noise, i.e., by the fluctuations of directions of the charge carrier velocities. In the same equilibrium systems many other physical quantities fluctuate: the temperature, the number of scattering centers and their orientation in the crystal, the distribution of charge carriers in energy, and so on. However, these fluctuations, due to their symmetry, are not measured (revealed) in the current or voltage noise unless a mean current, generated by an external current source, is passed through the conductor. The magnitude of the mean current, which is sufficient to reveal the ‘hidden’ fluctuations and generate a measurable ‘excess’, nonequilibrium noise is often so small that the conductor in all other respects can be considered as equilibrium one. This sensitivity of the noise is the basis of fluctuation spectroscopy, i.e., of studying the kinetic properties by measurements of noise spectra.

4.2.2 Equilibrium fluctuations in magnetoresistors

Equations 4.24 relates equilibrium electric fluctuations with the resistance of material. However there are many cases when resistance itself can fluctuate. At equilibrium those fluctuations could be revealed by measuring higher order moments of voltage (or current) distribution function or by applying a small external force (for example bias current) not enough to drive a system far from equilibrium state (more detailed discussion is given in section 4.4). Thus magnetoresistance implies a direct coupling between fluctuations in sample magnetization $M$ along the field direction and resistance $R$:

$$ S_R(\omega) = S_M(\omega) \left( \frac{dR}{dM} \right)^2, \quad (4.25) $$

where $S_R(\omega)$ and $S_M(\omega)$ are resistance fluctuations spectral density and magnetization fluctuation spectral density correspondingly. From fluctuation-dissipation relation $S_M(f)$ (Eq. 4.17) one could find

$$ S_M(\omega) = \frac{4k_B T}{\Omega \omega} \chi''', \quad (4.26) $$

where $\chi'''$ is the imaginary part of magnetic susceptibility, $k_B$ is Boltzmann’s constant, $T$ is temperature and $\Omega$ is the sample volume.

Thus, insertion of Eq. 4.26 into Eq. 4.25 leads to

$$ S_R(\omega) = \frac{4k_B T}{\Omega \omega} \chi'' \left( \frac{dR}{dM} \right)^2. \quad (4.27) $$
This is quite interesting result since magnetoresitive systems are expected to exhibit $1/\omega$ ($1/f$) type equilibrium fluctuations. Indeed there are reports with remarkable agreement between theory and experiment [38]. For films which exhibit a significant hysteresis in $M(H)$ dependence, a differentiation between small field saturation and high field saturation of magnetization is introduced: [39]

$$
\left( \frac{\delta R}{R} \right)^2 = \left( \frac{M'_s}{\rho} \frac{\delta \rho}{\delta M} \right)^2 \frac{2\pi k_B T \chi''}{\Omega \omega M_s}
$$

(4.28)

where $M'_s$ is the small field saturation magnetization, and $M_s$ is the large field saturation magnetization.

Generally speaking, external magnetic field drives the system out of equilibrium and fluctuation dissipation relations in the form of Eq. 4.17 and Eq. 4.18 may not longer valid. As example of definitely nonequilibrium noise in magnetoresistors comes Barkhausen noise.

### 4.2.3 Equilibrium fluctuations in dielectrics

Thermal equilibrium noise in the electric polarization of a leaky dielectric material is a direct application of a Nyquist relation. Thus, consider the dielectric as a capacitor $C$ and loss resistor $R$ connected in parallel. In a quasi-classical limit voltage fluctuations spectral density in this system is

$$
S_V(\omega) = 4k_B T \Re Z(\omega) = 4k_B T \Re \frac{R}{R + j\omega C} = 4k_B T \frac{R}{1 + (\omega RC)^2}.
$$

(4.29)

Having complex dielectric permittivity $\varepsilon = \varepsilon' - j\varepsilon''$, the capacitance $C = \varepsilon' \varepsilon_0 A/L$ and the loss resistance $R = L/(\omega \varepsilon'' \varepsilon_0 A)$, where $A$ is a plate area of capacitor and $L$ is a spacing between plates. Finally one will obtain a relation for open circuit voltage fluctuations spectral density:

$$
S_V(\omega) = 4k_B T \frac{L/(\omega \varepsilon'' \varepsilon_0 A)}{1 + (\varepsilon' / \varepsilon'')^2} = 4k_B T \frac{\varepsilon' / (\omega \varepsilon'' C)}{1 + (\varepsilon' / \varepsilon'')^2} \approx 4k_B T \frac{\tan \delta}{\omega C},
$$

(4.30)

where $\tan \delta$ defines the ratio $\varepsilon'' / \varepsilon'$ and $\varepsilon' \gg \varepsilon''$.

In the case when loss tangent and capacitance have weak frequency dispersion, voltage fluctuations according to the fluctuation dissipation relations are expected to have $1/f$ type spectra\(^1\). However this noise differs from excess $1/f$ noise, which will be discussed later, since it could be directly observed in thermodynamic equilibrium.

\(^1\)Although the angular frequency $\omega$ was used in all derivations, for noise spectra characterization it is more convenient to use frequency $f$ notation.
4.3 Temperature fluctuations

Any body, if it is not specially thermally isolated, exchanges heat with other bodies, and each part exchanges heat with other parts of the same body by a thermal conduction e.g. by phonons. Since phonon flow is a random process, the heat flow as well as the quantity of transferred heat is random processes. This produces fluctuations of the energy, or at constant pressure, the enthalpy \( H \). The fluctuations of enthalpy \( \delta H \) are usually considered as the fluctuations of the temperature of body \( \delta T = \delta H/C \), where \( C \) is the thermal capacity of the entire body, or of that part to which the change of enthalpy is related. The time dependent temperature fluctuations result in fluctuations of resistance

\[
\delta R(t) = \left( \partial R/\partial T \right) \delta T(t)
\]

of conductors, and appear at nonzero mean current as voltage noise.

According to the theory of thermodynamic fluctuations [40], the variance of the temperature fluctuations in a body or in part of it equals:

\[
\langle (\delta T)^2 \rangle = \frac{k_B T^2}{C}. \tag{4.32}
\]

Here \( T \) is the absolute temperature of the body. Let assume that at an initial instant of time heat \( \Delta H \) is imparted to the body in form of a short pulse. The initial increment of temperature is \( \Delta T(0) = \Delta H/C \). Owing to the heat conduction, this change of temperature decays in time. In the linear limit the ratio \( \Delta T(t)/\Delta H \) is independent of \( \Delta H \). The correlation function of the temperature fluctuations in the absence of external sources of heat and the relaxation function \( \Delta T(t)/\Delta H \) are related:

\[
k_T(t) \equiv \langle \delta T(t)\delta T(0) \rangle = k_B T^2 \frac{\Delta T(t)}{\Delta H}. \tag{4.33}
\]

This relationship means that the calculation or measurement of the correlation function or spectral density of temperature fluctuations can be reduced to the calculation of the temperature response \( \delta T(t) \) to a heat pulse produced, for instance by a current pulse.

The power introduced into sample may be periodical in time, i.e., \( \Delta P(t) = \Delta P(\omega) e^{-i\omega t} \). Using Eq. 4.33 and the Wiener-Khintchine relation (Eq. 3.30), one can express the spectral density of temperature fluctuations in terms of the response of the temperature to this power, i.e., (analogue of the fluctuation-dissipation relation Eq. 4.19):

\[
S_T(\omega) = 4k_B T^2 Re\left( \frac{\Delta T(\omega)}{\Delta P(\omega)} \right). \tag{4.34}
\]
In experiments it is convenient to measure the sample’s resistance \( R \). Using relation Eq. 4.31 one could find the temperature produced resistance fluctuations spectral density:

\[
S_R(\omega) = S_T(\omega) \left( \frac{\partial R}{\partial T} \right)^2 = 4k_B T^2 \left( \frac{\partial R}{\partial T} \right)^2 \operatorname{Re} \left( \frac{\Delta T(\omega)}{\Delta F(\omega)} \right).
\]  

(4.35)

There was the hypothesis that temperature fluctuations are the source of fluctuations with \( 1/f \) spectrum [41]. Verification gave, in general, negative conclusion: \( 1/f \) noise is not generated by the temperature fluctuations.

The equilibrium temperature fluctuations have been examined above (Eqs. 4.34 and 4.35). When temperatures at the ends of a conductor differ considerably, and mean gradient of temperature and thermal flow between these ends appears, a more general approach to the calculation of temperature fluctuations is required.

### 4.4 General features of the \( 1/f \) noise

In general \( 1/f \) noise is observed when system is driven out of equilibrium. However, there were a lot of discussions related to the question does this noise exist in equilibrium or not [42, 43, 41, 44, 45]. Finally there was an agreement reached that, in homogeneous conductive materials, this noise persists in the equilibrium and under some special experiment conditions it can be observed without introducing any external force (current, magnetic field and etc.) into the system.

History of investigations of noise with \( 1/f \) type spectrum in electron devices continues from Johnson report in 1925 [46]. Despite some very fundamental disagreements among workers in \( 1/f \) noise field, there are agreements on a number of basic features of this phenomenon.

The actual observed spectra are usually of the form \( S(f) \propto f^{-\gamma} \), \( 0.8 < \gamma < 1.4 \) over an extensive frequency range. This type of spectra were reported down to \( 5 \times 10^{-7} \) Hz with no presence of saturation. The phenomenon is that the integral over all frequencies of such a spectrum would diverge. The high-frequency divergence is not generally troublesome; finite scattering times, intrinsic capacitance roll-offs, etc., cause a natural high-frequency cut-off regardless of the specific noise mechanism. No such general argument avoids the low-frequency divergence for \( \gamma \leq 1 \). Despite of this one must keep in mind that some low-frequency cut-off must be present, because the power of the modulated noise cannot exceed the power of source. Such cut-offs can arise from some inherent feature of the model, from limitations imposed by the finite system size, or because the theory describes some nonequilibrium system in
which things actually do break down on a sufficiently long time scale (e.g., a glass may crystallize).

In nearly all resistors, several lines of evidence indicate that resistance fluctuations are present in the absence of a driving current. Thus, for small currents, the spectral density of the measured voltage fluctuations is proportional to the square of the current, since $\delta V = I\delta R$. The same resistance fluctuations are obtained regardless of whether they are measured with dc or ac current probes. For some resistors with particularly large $1/f$ noise, the spectral density of Johnson noise (equilibrium noise required by the fluctuation - dissipation theorem) may be used as sufficiently accurate and fast ohmmeter, which allow determination of the $1/f$ fluctuation with no applied bias.

In many cases it is shown that $1/f$ noise is a statistically stationary process with Gaussian [Eq. 3.12] distribution e.g., fluctuation power measured over some frequency range has an average value, which does not change in time. In some systems additional pulse (telegraph-like) noise persists, which distribution differs from Gaussian and can be non-stationary. This type of noise can be observed in not annealed films and etc.

In stationary systems with Gaussian $1/f$ noise distribution, fluctuations have no long-range correlation. Correlation range must be at least shorter then one micrometer, and very likely that it must be equal to the mean free of scattering path of charge carriers in the material. There is the question: is $1/f$ noise a bulk or surface effect. In many cases it is shown that noise power scales with volume and to consider noise origin as surface phenomenon is correct as long, as close to the surface could be higher defect concentration.

Nowadays it is most common to characterize $1/f$ type noise in homogeneous conducting materials with the empirical Hooge relation:

$$\frac{S_R(f)}{R^2} = \frac{\alpha_H}{N_c f^{\gamma}},$$

(4.36)

where $\alpha_H$ is the materials Hooge’s parameter (originally proposed $\alpha_H = 2 \cdot 10^{-3}$), $N_c$ is the number of charge carriers in a homogeneous sample, $R$ is resistance, and $S_R(f)$ is the power spectral density of the resistance fluctuations at frequency $f$. While in real cases $\gamma$ is not exactly 1, $\alpha_H$ cannot be a dimensionless parameter and the physical meaning of relation (Eq. 4.36) is questionable. There are experiments showing that proportionality to $N_c$ is obeyed only when the total number of free charge carriers is varied via the sample volume, but not when the free carriers density $n$ is changed. So there is no fundamental proportionality of the $1/f$ noise
intensity exactly to $N_c$, but often this approximation occurs and can be considered as inverse proportionality to the sample volume because fluctuations correlation length is very small and all parts of the sample fluctuate almost independently. After many discussions around the meaning of this relation it still gives a useful role of thumb in estimation of resistance fluctuations in many materials.

In the range of linear conductance, in which relation (Eq. 4.36) could be used, the normalized spectral densities of voltage, current and resistance fluctuations have the same value and are independent on $V$, $I$ and $R$:

$$\frac{S_V(f)}{V^2} = \frac{S_I(f)}{I^2} = \frac{S_R(f)}{R^2}. \quad (4.37)$$

This relation is experimentally proved and cannot be interpreted as obvious. Relation (Eq. 4.37) allows a statement that voltage and current fluctuation spectral densities are determined by the resistance fluctuations spectral density.

There are many models, which try to explain $1/f$ noise properties, as mentioned above, but just defect related can explain wide spreading of Hooge’s parameter in a series of samples with approximately same resistance, or even in the different parts of the same sample [47]. One way to prove the fairness of those models is upon noise measurements in very small structures, where resistance switching dynamics produced by individual traps could be observed. Such fluctuations are referred as a random telegraph signals (RTS) with Lorentzian type of spectra. Its superposition can cause $1/f^\gamma$ spectrum with $0 \leq \gamma \leq 2$:

$$\frac{S_R(f)}{R^2} = \sum_i a_i \tau_i \propto \frac{1}{f^\gamma}, \quad (4.38)$$

where $\tau_i$ is relaxation time and $a_i$ is some parameter of $i$-th fluctuator. Real material contains various complex defects (fluctuators) that produce distortions of the energy band and are randomly located in a space. Low-frequency noise level is caused by the effective part of sample volume, which such defects occupy. In order for electron to take part in trapping processes in defects their energy must be higher than height of the barrier, so the effective density of charge carriers that can take part in the trapping processes is much lower than $N_c$, which is obtained from Hall effect measurement. It can in principle explain very long relaxation times and has low-frequency saturation that limits the power of fluctuations.
Chapter 5

Low frequency noise measurement technique

5.1 Noise measurement setup

Measurements of noise involve both statistical analysis, which were described in chapter 3, and experimental setup. Dealing with very small signals, the apparatus part for noise measurements has some special requirements to be fulfilled to gain the required sensitivity. Those involve not only the sensing part to have good noise performance, but also the whole measuring system to be at maximum restricted from external influence, which can affect on the measurement results.

A Schematic presentation of low frequency noise measurement setup used for noise investigations in colossal magnetoresistive manganites films is shown in Fig. 5.1. It consists of three basic parts: sample under test, low noise preamplifier with dc current supply, temperature controller (Keithley 2002 multimeter), and a computer with external spectrum analyzer (SR760 FFT analyzer) or the amplified signal comes directly via a sound card (in this case hand written FFT spectrum analyzer program was used). Each of those parts will be described in details in this chapter.

5.2 Low noise preamplifier

The minimum level of noise, which can be measured in some system under test, does not depend on the type of noise source and is set by the Johnson fluctuations of resistances present in the system. Flicker noise or any other non-thermal noise acts
as additional noise to this thermal noise level. For precise characterization of any additional (or excess) noise, at first one needs to be able to determine the magnitude of thermal fluctuations. This gives the possibility to extract the thermal noise part and leave only the interesting excess noise.

Noise performance of a device is usually characterized with equivalent voltage and current noise generators $e_n^2$ and $i_n^2$, the product of those quantities some times is called quality coefficient. Mean value of voltage fluctuations squared is often represented in terms of equivalent noise resistance $R_{eq}$ that is the Nyquist representation of voltage fluctuations in the short-circuited measuring system:

$$e_n^2 = 4k_B T R_{eq} \Delta f$$

(5.1)

where $k_B$ - Boltzmann’s constant, $T$ - temperature and $\Delta f$ is a frequency range. Possibilities to characterize thermal noise magnitude are limited by the noise of the measuring system itself. To measure fluctuations in the systems with low resistance by dc, measurement systems with lower equivalent input resistance $R_{eq}$ is needed.

The most critical part of a low-frequency low-noise measurement system is the preamplifier, which usually establishes the sensitivity of the entire system. The type of low-noise preamplifier is determined by the elements used in the first cascade. Two groups of active devices are commonly used: bipolar transistors and field effect transistors (FET). Every sort of those devices has its unique features and the choice is determined by the electric behavior of the testing system. Noise equivalent
resistance for bipolar transistors with including sources of $1/f$ noise is equal to [48]:

$$R_{eq} = r_b + \frac{r_e}{2} + \frac{(R_s + r_e + r_b)^2}{2\beta r_e} + \frac{B I_m}{4k_B T} (R_s + r_b)^2,$$

(5.2)

where $\beta$ is transistor small signal current gain in the common emitter connection, $r_b$ is equivalent basis resistance, $r_e = k_B T/e I_e$ is differential emitter junction resistance, $I_e$ and $I_b$ are emitter and basis dc currents, $B$ - transistor excess noise coefficient, and $m \approx 1$. Low equivalent noise resistances could be achieved in transistors with low $r_b$ and high $\beta$. The best field effect transistors demonstrate $R_{eq}$ in the range from 10 $\Omega$ to 50 $\Omega$. It maintains almost constant if $R_s \leq \sqrt{3} r_e$. If source resistance is high, bipolar transistor amplifier equivalent noise resistance significantly depends on $R_s$ and this creates difficulties in subtraction of the measurement system noise. The best commercial low-noise preamplifiers with bipolar transistors have $R_s$ approximately of 60 $\Omega$ (SR554 from Stanford Research, PAR113 from Princeton Applied Research or Brookdeal 5003 from EG&G) 80 $\Omega$ (SR552). In the case when source impedance of measuring system changes during the measurement, FET preamplifiers are required. Usually $n$-type silicon FET’s are used.

Noise equivalent resistance in the saturation region of characteristic curve, where those devices operates efficiently as amplifiers, is inversely proportional to the transconductance $g_m$ [49]:

$$R_{eq} = \frac{A}{g_m},$$

(5.3)

where $A \approx 2/3$ and

$$g_m = \frac{2}{|V_p|} \sqrt{I_{DSS} I_{DS}}.$$  

(5.4)

Here $V_p$ is the channel narrowing voltage, $I_{DSS}$ is drain bias current, if the gate is zero biased, $I_{DS}$ is drain offset current. Increaseament of transistor transconductance leads to decrease of noise voltage, but this requires increase of $I_{DSS}$. The possibility to minimize noise voltage is limited by the requirement to keep FET with maximum amplification in the saturation regime for all voltages. Minimum drain-source voltage with saturation $V_{DSAT}$ and drain offset current $I_{DS}$ must be such, that dissipating power will be lower then maximum allowed. This limits maximum $I_{DSS}$. Values of $I_{DSS}$, $V_{DSAT}$ and $g_m$ are predetermined with the gate dimensions. Increasing of gate dimensions will lead to decrease of noise voltage, but this will increase the gate capacitance, that will limit working frequency range of FET. As a consequence of Eq. 5.3 and Eq. 5.4 noise equivalent resistance does not depend on source impedance in a very wide resistance range. This feature and also very
small current noise [50] makes field effect transistors very useful for noise measurements if the source impedance is high or changes during measurements. The best reported values of noise in single FET gives $R_{eq} \approx 100\Omega$ for 2SK117. Commercial amplifiers with FET demonstrates $R_{eq} \approx 1k\Omega$ (SR570). There is always a scattering of the performance in the series of the same type of transistors. Researchers report noise results on the best transistors selected both with minimum excess noise, which persists at low frequencies, and thermal noise of the channel. This is the reason why commercial amplifiers do not reach the minimum reported noise values. Also in hand-made preamplifiers parallel connection of several FET in the input of preamplifier is often used [51]. This allows to limit the maximum allowed dissipation power with decreasing $R_{eq} N$ times ($N$ is the number of transistors) and enables operation in a wide frequency range. Thermal noise of the channel is proportional to temperature and can be reduced by cooling the FET.

If the source resistance is lower then $10\Omega$, it is appropriate to use the transformer input. Transformers have the minimum $R_{eq}$ because it directly equals to the input resistance. The main limitation of transformer amplifier is very narrow working frequency range and dependence of transformation coefficient $K$ on the source impedance $R_s$. Preamplifiers with transformers are mostly used in noise measurements near the superconducting transition. $R_{eq}$ of some commercial low-noise preamplifiers is $0.5\Omega$ (SR565 from Stanford Research System).

The power supply system is very important to ultra-low-noise measurements since it should generate as low $1/f$ noise as possible. Noise of power supply system adds to the amplifier input divided by the amplification coefficient of the first cascade. This requirement appears more strongly at low ($< 1$ Hz) frequencies which are difficult to filter. Carefully selected batteries or high capacity accumulators exhibit low level of $1/f$ noise and are usually used in low noise measurements. Whole measurement system, including power supply, must be well grounded both from surrounding electric and magnetic interference. A reliable solution for this problem is to use a permaloy box for shielding.

Resistance of manganite perovskites, undergoing the phase transition in temperature range from liquid nitrogen to 370 K, changes in several orders of magnitude (from $10\Omega$ to $10k\Omega$). Noise measurements in material with such wide dynamic range of resistance changes, can be performed only using FET preamplifiers with low equivalent noise resistance. As it was mentioned above, commercial FET preamplifiers can provide only $R_{eq} \approx 1k\Omega$, thus to increase measurement accuracy hand-made amplifier with selected field effect transistors is required.
The circuit diagram of low noise amplifier with $R_{eq}$ of 90Ω is presented in Fig. 5.2 and Table 5.1. It consists of two amplification cascades. The first cascade is built of three transistors connected into cascade and supplied with 100% negative feedback by ac. The second cascade is made of low noise operational amplifier OP27. Voltage fluctuations are supplied to the gate of FT1 via capacitor C1. FET transistor 2SK117 unlike many other field effect transistors has a maximum transconductance when the gate is biased with $0.3 \div 0.4$ V. This voltage is supplied with resistors R1 and R2. Capacitor C2 is applied to minimize power source noise in the amplifier input. Transistor FT2 is connected in cascade with FT1. This type of connection provides FT1 with constant drain current, which in this case equals to 3 mA ($S_{3m_A} = 14$ mA/V). Transistor BT1 is connected to a common emitter circuit. Since basis dc voltage is 9 V, the amplification by dc is set less then one with the ratio of resistors $(R6 + R7)/(R8 + R10)$. AC amplification of this cascade is fully determined with
negative feedback (capacitor C3) and equals R6/R7 +1 (201 times). Finally the signal is amplified with a low noise operational amplifier with amplification of 11 times. This results in 66.8 dB total amplification of testing signal. The dynamical frequency range from the low frequencies mainly is determined by the time constant C1R3 and equals to 0.1 Hz. Cutoff from high frequencies is made by operational amplifier and equals to 800 kHz. Linearity of amplification due to negative feedback maintains until amplitude of input signal reaches of 4 mV level.

5.3 Noise estimation technique

Measured noise power is mainly produced by three non-correlated noise sources: the measured material noise, noise of preamplifier and noise of spectrum analyzer. Because of non-correlation between those processes, the noise power of last two devices could be estimated separately and subtracted from the measured noise signal. This estimation requires additional measurement, when preamplifier input is short-circuited.

\[
S_V(f) = \frac{\Delta V^2}{\Delta f} = \frac{n_1 - n_2}{K^2 \Delta f},
\]

where \(n_1\) and \(n_2\) are the noise power of the sample and short input amplifier correspondingly, measured at frequency band \(\Delta f\), \(K\) is the amplifier gain.

To estimate the amplifier gain \(K\) and frequency band \(\Delta f\), we used a calibrated noise source - resistor with known resistance \(R_{calib}\), which noise spectral density in very wide range does not depend on frequency and current (Eq. 4.24)

\[
S_V(f) = 4k_B T_{calib} R_{calib}.
\]

The noise power \(n_3\) of calibration resistor is a noise of resistor itself plus the noise of amplifier:

\[
n_3 = n_2 + K^2 4k_B T_{calib} R_{calib}.
\]

Finally taking \(K^2 \Delta f\) from Eq. 5.7 and substituting this into Eq. 5.5, the voltage fluctuations spectral density of sample could be estimated

\[
S_V(f) = \frac{\Delta V^2}{\Delta f} = \frac{n_1 - n_2}{n_3 - n_2} 4k_B T_{calib} R_{calib}
\]

In many cases we need to estimate the additional (excess noise) to thermal noise part. It can be estimated by subtraction of Johnson noise using \(R(T)\) measurement results

\[
S_V^{\text{excess}}(f) = S_V(f) - 4k_B T_{sample} R(T)
\]
or it could be calculated considering noise power $n_4$ of the sample measured at zero bias

$$S_V^{excess}(f) = \frac{\Delta U^2}{\Delta f} = \frac{n_1 - n_4}{n_3 - n_2} 4k_B T_{calib} R_{calib}$$ \hspace{1cm} (5.10)

The accuracy of this noise measurement technique depends on the measuring time. Noise power measuring time must be more than 100 periods (with precision approximately in 10%) of frequency $f$ in which noise spectral density estimating. It is appropriate to use resistor as calibrating noise source when there are many measurements at many frequencies in one time. For very precise measurements (about 1%) at fixed frequency it is better to use a calibrated generator for $K$ determination and also the measuring time must be increased.

Nowadays digital FFT spectrum analyzers are often used for noise measurements instead of the selective microvoltmeters or lock-in amplifiers. This allows getting noise spectral density in a wide frequency range in one or few realizations. Nevertheless, the noise estimation technique described above is still useful, because it automatically produces calibration by the amplitude. In reality, noise measurements at higher frequencies do not require same time as at lower frequencies, thus the estimation error can be lowered as many times, as those frequencies differs (almost in all published papers noise spectra, measured with FFT analyzers, is presented with the same error in whole frequency range). One can introduce relative frequency window $\Delta f$ to improve the accuracy of presentation of measurement results. The advantages of such presentations are shown in Fig. 5.3. Data were taken over 10 seconds with the sampling rate of 48000 Hz. Line was calculated from $2^{18}$ discrete points with standard Cooley-Turkey FFT algorithm. The cutoff at frequencies 20 Hz and 20 kHz corresponds to dynamical frequency range of input circuits but not related with signal. Open points were obtained with integration in frequency domain ($\Delta f/f = 0.05$) calculated for 100 points equally spaced in logarithmic scale. The deviation from dash line, which represents Johnson $(4k_B T R)$ noise, at frequency 1 kHz is 16 % and at the 10 kHz frequency takes only 6 %. This example clearly demonstrates the advances of introducing such integration in final presentation of measured results, what is appropriate for $1/f$ type and white noise estimations.

To investigate properties of low frequency noise, a hand written FFT spectrum analyzer programs run on the PC. This have several advantages comparing with commercial ones. First is the computer memory, which allows storing the data of several seconds with high sampling rate. Second: numerical processors in new computers are faster then were used in commercial FFT analyzers, this allows to obtain spectra in wider frequency range in one realization (many commercial analyzers in
Figure 5.3: Noise spectra of 10 kΩ resistor recorded by one 10 s long realization and analyzed with FFT. Open points were obtained with integration in frequency domain ($\Delta f / f = 0.05$). Dash line is the calculated Johnson noise ($4k_BT_R$).

Single operation covers less than 2.5 octaves of frequency, while with PII 266 MHz computer is possible in real time operate with 4 octaves). If there is no interest in ultra low frequency range, good solution for data acquisition is an ordinary sound card, which can provide with 16-bit or 18-bit resolution, with signal-to-noise ratio of 90 dB. Possibility to apply averaging not only by realizations but also in frequency domain, makes such system very flexible to obtain accurate results in short time. Finally such measurement system is much cheaper than commercial.
Chapter 6

Electrical fluctuations in manganites

6.1 Introduction

For the applications of CMR, the investigation of low frequency fluctuations has the same importance as the dependence of resistance on the magnetic field and temperature. The magnitude of low frequency fluctuations sets the limits to the minimum detectable signal for the CMR sensor and it carries the information about the quality of the film processing technique. From the theoretical point of view, resistance fluctuations in the transition region reveal a new features of the charge transport, supplementing the results from conventional resistance measurements.

In this chapter we overview basic properties of low frequency noise in ultra-thin and sub-micron series of manganite films exhibiting CMR.

6.2 Overview of published results

Starting from 1994, colossal magnetoresistors were considered as promising material for many types of applications. However, several factors complicating its development were found. For example, very high values of temperature coefficient of resistivity (TCR) and magnetoresistance ratio (MR) occurs at the cost of reducing the Curie temperature $T_C$. It is also known that giant MR multilayer structures present their appreciable changes in resistivity with fields as small as 0.01 Tesla, while manganites typically need larger fields of about 1 Tesla or more for equivalent resistivity changes, which appear too large for potential use in magnetic recording.
Early studies of electrical noise in manganites reported very high magnitude of noise, which was considered as a serious obstacle for sensor applications.

Besides a sensitivity determination, electrical fluctuations in manganites revealed interesting physics behind it. The following section is dedicated to overview main published results from these studies.

One of the first report on noise in manganites was made by Alers et all [39]. The spectral density of the noise had a power law form with exponent $\alpha = 1 \pm 0.2$ at all temperatures, except near the transition. An abrupt increase in the normalized noise below maxima of resistance is attributed to the formation of domains, which is similar to behavior observed in other magnetic systems that undergo an increasing of order parameter such as spin glasses. The magnitude of the normalized noise in the ferromagnetic metallic phase was found to be many orders of magnitude larger than the typically observed in metals, that can’t be explained by any conventional defect mediated mechanism.

Special attention was given for the region near the transition. It was observed that peak in the normalized noise versus temperature is accompanied by a peak in the frequency domain. This detail is taken as confirmation that this peak is an intrinsic feature and is not an artifact of the normalization. Authors conclude that electrical fluctuations are determined by the resistance fluctuations, which originates from fluctuations in magnetic domains. In more detail: resistance fluctuations are related to the imaginary portion of the magnetic susceptibility, $\chi''$, through the fluctuation-dissipation theorem and the sensitivity of resistivity to local magnetization:

$$\left( \frac{\delta R}{R} \right)^2 = \left( \frac{M'_s}{\rho \delta M} \right)^2 \frac{kT \chi''}{\Omega f M_s}$$

(6.1)

where $M$ is the internal local magnetization, $M'_s$ is the small field saturation magnetization, and $M_s$ is the large field saturation magnetization. In this form, the expression in brackets is fairly as a function of temperature below the transition and most of the temperature dependence in the normalized noise occurs from the temperature dependence of $\chi''$. The effect of a magnetic field on magnetization fluctuations is to align the domains and suppress spontaneous fluctuations of the relative alignment of neighboring domains. Decrease of noise peak amplitude indeed was observed under applied magnetic field. As authors note, such behavior is identical to what is observed for $\chi''$ in ferromagnetic materials due to domain wall fluctuations at a ferromagnetic transition.

Paper presented by Hardner et all [52] continues discussion on the origin of
noise in manganites. They found that voltage fluctuations spectral density $S(f)$ was typically close to $1/f$ as long as very large individual resistance steps were not occurring. Electrical noise is interpreted as noise, which arises from thermal fluctuations of magnetic domains. Authors argues if, for example, deviation in resistance $\delta R$ came from fluctuations in interdomain hopping rates but $R$ came primarily from other processes, it would be surprising for $(\delta R/R)^2$ to change by only a factor of 3 upon reducing $H$ from 5 T to zero at 115 K while $R(H)$ changes by a factor of 80. In fact, in a simple series-resistance picture, if the noise came from a weakly $H$-dependent component one would expect a change in the fractional noise power of a factor of 6400. Thus, authors also believe that the noise is not probing some minor component of the transport but rather the main process responsible for the CMR in this material.

Individual steps in resistance had amplitude $(\delta R/R) \approx 10^{-3}$. Even when steps were not resolvable, the noise was generally non-Gaussian, in that sense that the variance in repeated measures of the noise power in each octave was higher than for a Gaussian. If one would relate those steps to the domains in homogeneous conductor, the fluctuating domains would have to have areas on the order of $10^{-4}$ cm$^2$, that is a quite unrealistic. However, such estimations also created doubts on the current homogeneity in colossal magnetoresistors. Later on, almost all works supposed the intrinsic inhomogeneities in manganites. Thus, inhomogeneities were recognized as the general property of material but not the film manufacturing peculiarity.

Merithew et al. [53] discuss the equilibrium conductivity fluctuations measured both in film and bulk single-crystal manganites. The individual steps in noise were frequently observed. Fluctuations in manganites were related to the fluctuations of mesoscopic domains. The average statistical properties of the noise were found independent of whether it was measured below or well above coercive field $H_C$, and independent of field cooling versus zero-field cooling. These results are expected if the fluctuations arises not between the states with different magnetization orientation but rather between the ones with different magnetization magnitudes, with the preferred orientation set by local and applied symmetry-breaking fields. However, authors do not rule out the possibility that magnetization orientation fluctuations are also involved.

The discrete resistance steps $\delta R/R$ were found of order $10^{-4}$. In homogeneous current model it would correspond to approximate domain volume equal $10^{-9}$ sample volume, that indicate that a homogeneous current model is not correct.

The Boltzmann factors (ratio of the times spent in the two states) of fluctuators
in the film have the unexpected temperature dependencies, strongly indicating that
the stability of the mixed phase comes from a term in the free energy favoring
mixture of the two microphases.

Switches in resistance fluctuations named as random telegraph noise (RTN)
were detailed studied by Raquet et all [26]. Authors emphasize that in the tem-
perature range 4 to 180 K the noise had a strong non-Gaussian character, i.e., the
resistance fluctuations were dominated by 'few' fluctuators. In fact, at certain tem-
peratures only a single fluctuator dominated, giving rise to the RTN.

Except such specific temperatures where single fluctuator have dominated, the
power spectral density of the resistance fluctuation has mainly a $1/f$ dependence.
The fractional resistance steps of the RTN varied from 0.01% to greater than 0.2%,
that is in agreement with previous studies.

Magnetic nature of the switching entities was proved by the magnetic field de-
pendence of the noise. Within the framework of the telegraph-like fluctuations model,
the effect of the magnetic field can be explained by including a field-dependent en-
ergy barrier. The temperature dependence of relaxation times results purely from
thermal activation.

Thus, authors argue, that those fluctuators, even though they have a strong mag-
netic character, cannot originate from magnetic domains. Instead, authors believe
that the rapid variation of the energy configuration with temperature, as inferred
from the RTN at high temperature, suggest the dynamic coexistence of two phases:
a ferromagnetic metallic phase and a phase with relatively depressed magnetic and
electrical properties. The RTN occurs when a cluster, the fluctuator, switched back
and forth between the two phases. The magnetic field will always stabilize the ferro-
magnetic state, which is the low-resistance one. At low temperature the conductivity
is dominated by the ferromagnetic metallic phase; by increasing the temperature,
some clusters will switch to the depressed state, increasing the total resistance of
the sample by the RTN quanta. Summarizing this, the conduction is a mixed-phase
percolation process. In this picture, the location of the noise peak well below $T_C$
and its amplitude is a direct consequence of the mixed phase: near the percola-
tion threshold for the metallic state, the conduction is dominated by the narrowest
current paths. A few switching clusters located in these critical bonds will have
dramatic effect on the overall connectivity of the metallic network, which results in
a large increase of the noise level.

Finally authors emphasized that the final state was never exactly the same upon
thermal cycling: the RTN could disappear altogether and, if present, displays differ-
different characteristics. This again let to conclude, that the mixed phase is not related to any chemical inhomogeneity or physical disorder.

The most convincing results for percolation model in manganites is given by Podzorov et all [27]. They measured $1/f$ noise in the poly- and single-crystal bulk samples of $\text{La}_{5/8-x}\text{Pr}_x\text{Ca}_{3/8}\text{MnO}_3$ with $x = 0.35$. Clearly diverging behavior of the $1/f$ noise was observed. In accordance to the percolation theory, transition temperature $T_C$ were determined with high accuracy. Critical exponents, found from scaling analysis of $S_V$ and $R$ on the ‘metallic’ side of the CO-FM transition gave values of critical exponents in consistency with the predictions of the inverted random-void model of the continuum percolation.

The magnitude of $R$ was found to be similar for both types of samples but $R$ for the single crystal exhibited reproducible steps as a function of $T$ in the vicinity of $T_C$.

It is noticeable that observed normalized noise magnitude was about $10^{-10} \div 10^{-7}\text{cm}^{-3}$ and is the largest reported normalized magnitude of the $1/f$ noise for the condensed-matter systems.

Almost all results, discussed above, were obtain for low-bandwidth or for intermediate-bandwidth manganite compounds with reduced Curie temperature. Noise measurements made in epitaxial $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ film grown onto NdGaO$_3$ substrate with perfect lattice match showed very low normalized noise magnitude, which is to that of a conventional metal [54]. This result confronts with previous statements that high noise level is the intrinsic property of manganites. In contrast to previous works, no increase of the $1/f$ resistance noise in the ferromagnetic regime was observed. The magnitude of the normalized resistance fluctuations was found to decrease with temperature decreasing, except for a sharp peak at $T_C$. This peak disappears when external magnetic field of about 2 T is applied. However, its existence indicates that could be a phase separation phenomenon at the metal-insulator transition.

Normalized noise was found to increase also in paramagnetic regime. Such behaviour is explained by authors explains as there is an additional noise source in the paramagnetic regime which is not directly linked to the magnitude of the resistance, e.g., extended disordered regions adjacent to some small ferromagnetically ordered regions. In this scenario, noise due to scattering on defects is supplemented by fluctuations in domain magnetization or large fluctuations in disordered regions at domain boundaries. That could explain the significant reduction of normalized noise in the paramagnetic regime under applied magnetic field.

Authors note, that the negligible magnetic field dependence of the normalized
resistance noise in the ferromagnetic regime (despite the significant field dependence of the resistance) strongly suggests that the measured noise is arising from the same component of the resistance which accounts for the magnetoresistance.

Extended analysis of noise in $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ system is given by Raquet et all [55]. Here noise experimental results were examined using Dutta-Dimon-Horn (DDH) model. In all measured temperatures, slope of noise spectra seemed to follow predicted line with some external bias. To explain this bias a generalization of DDH was proposed, i.e. the net mean-square fractional resistance fluctuation (integrated over all frequencies) assumed to be temperature dependent and energy distribution function should be multiplied by a temperature dependent function $g(T)$. This function expected to be dependent on temperature in power low. Best fit gave it to be proportional to $T^{1.2}$, what was found to be closely related to the term $T^{4.5}$ in temperature dependence of resistance that is associated to the electron-magnon scattering in the DE theory. Thus, authors argue, temperature dependence of the resistivity may be linked to the $g(T)$ function via the number and the strength of the fluctuators. In other words, the fluctuators could be associated with spin fluctuations whose coupling to the resistivity varies as $T^{4.5}$. Such explanation of noise in the ferromagnetic phase of LSMO is supported by the decrease of the noise magnitude as a magnetic field is applied. Moreover, established link between the noise behavior and the resistivity data within the framework of the DDH model provided a direct interpretation of the similarity between the temperature dependence of the electrical noise and the resistivity, as the same scattering centers seem to be responsible for the resistivity and its fluctuations.

Mathieu et all have studied electrical noise, which originates from grain boundaries [56]. Magnetoresistance and resistivity noise measurements have been performed on a $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film deposited on a bicrystal substrate with a misorientation angle of $8.2^\circ$. It was found that noise spectra could be characterized by a contribution of $1/f$ and Lorentzian spectrum. The magnitude of Lorentzian part of the noise wasn’t proportional to the magnetic-field derivative of the dc resistance that means that noise does not originate from random domain wall motion. Estimations of energy barrier and resulting domain size, let authors to conclude, that domain-wall fluctuations with energy barriers determined by the pinning energy of defects are at the origin of the Lorentzian resistivity noise contribution.

Magnetic-field dependence of the noise level for low fields in both orientations (perpendicular and parallel to the grain boundary) plotted against film resistance, was found to have hysteresis. Thus a two-level fluctuator, which is responsible for
the Lorentzian noise contribution is a precursor of larger and more dramatic changes in the domain configuration occurring when the resistance switches between low- and high-resistance states.

Rajeswari et al. [57] emphasize a striking correlation between the magnetic homogeneity, TCR, and the electrical noise characteristics. As-grown films of LCMO with wide FMR line widths (\( \Gamma > 500 \text{ Oe} \)) and broad resistive transitions as indicated by low maximum of TCR values (5%-6%/K) were also characterized by a very large magnitude of electrical noise. After postdeposition thermal annealing in oxygen, authors found that the \( \Gamma \) values are reduced to 40 Oe and the maximum of TCR increase to 15%-17%. These changes were accompanied by a dramatic decrease in the normalized noise magnitude, both in the paramagnetic insulating state and the ferromagnetic metallic state.

In conclusion they state that structural and magnetic inhomogeneity, results in low performance of designed films.

The same conclusion could be drawn from results presented by Arora et al. [58]. In this study, La\(_{0.75}\)Ca\(_{0.25}\)MnO\(_3\) film was irradiated by 250 MeV \(^{107}\text{Ag}\) ions. In general, irradiation decreased transition temperature except for \(10^{11}\) ions/cm\(^2\), where improvement of transport properties were observed: resistance decreased and transition temperature increased by 10 K. Whereas noise results show a monotonic increase in the normalized noise as a function of ion fluence. The observed modifications in the noise properties of the irradiated LCMO thin films discussed to be consistent with the general expectation concerning the effect of swift heavy ions irradiation induced lattice defects.

6.3 Thin films preparation

Thin (less than one micrometer thick) complex oxide films can be produced by such advanced techniques as physical vapor deposition (PVD) and chemical vapor deposition (CVD) [59]. PVD methods include laser ablation, in which a high-energy laser blasts material from a target and throws a vapor to a substrate, where the material is deposited. Another PVD approach involves sputtering, in which energetic ions bombard the surface of a target, removing material as a vapor that is deposited on an adjacent substrate. CVD involves passing a carrier gas over a volatile organometallic precursor; the gas and organometallic react, producing a ceramic compound that is deposited downstream on an appropriate substrate.

Pulsed Laser Deposition (PLD) uses a laser (usually an excimer such as XeCl,
KrF, ArF) to ablate a target. The target material is vaporized and ejected from the surface of the target when irradiated by a laser beam. Vaporized material then condenses on the substrate forming a thin coating. Resulted films usually have the same composition as that of the target. The PLD system consists of several parts: vacuum chamber with a target and heating substrate holders, an excimer laser, beam scanning and focusing system.

The focused excimer laser beam pulse usually has energy density of a few J/cm². Residual gas pressure less then 10⁻⁶ Torr must be maintained inside the chamber prior to deposition. By carefully choosing the process parameters e.g. pulse repetition and energy density, oxygen pressure and substrate temperature, high quality oxide films can be grown in situ. The laser wavelength is determined by the absorption characteristics of the material to be evaporated. A simple schematic diagram of the PLD system is shown in Fig. 6.1

Advantages of PLD systems are the capability of fast producing the epitaxial layers, precise preserving of the stoichiometry and simple implementation of constituents.

There are several limitations of the PLD technique. First, beam scanning and focusing systems are complex and expensive. Second, it is not always possible to find a laser having a wavelength compatible with the absorption characteristics of the material to be evaporated. The system has low energy efficiency and the size of the uniformly deposited film is small (10 to 20 mm) in diameter. Nevertheless,
all the above mentioned obstacles have been successively overcome in the novel big area deposition PLD systems.

Ultra-thin LSMO film series with the thickness of 42, 50, 100, and 600 Å was produced by a 248-nm KrF pulsed laser ablation of stoichiometric La$_{0.75}$Sr$_{0.25}$MnO$_3$ ceramic target [60]. Films were grown on (001) SrTiO$_3$ (STO) single crystal substrates (5x5 mm$^2$), laser radiation energy density was 3-4 J/cm$^2$, pulse repetition rate was 30 Hz, and target-to-the-substrate distance was 55 mm. Depositions were carried out in an oxygen pressure of 200 mTorr and finalized by in situ annealing in an oxygen pressure of 500 Torr for 10 minutes. The background pressure did not exceed 10$^{-7}$ Torr. Thickness of films was determined by deposition time while the deposition rate was calibrated by AFM.

Comprehensive x-ray diffraction study (Fig. 6.2) shows these films are highly c-axis oriented with the (001) rocking curve FWHM $\sim 0.2^\circ \div 0.3^\circ$. Oscillations, which can be seen on the 300 Å curve, demonstrates very uniform distribution of thickness. Film processing was very reproducible and there was no aging effect observed.

Thin, sub-micron thick La$_{0.7}$(Pb$_x$Sr$_{1-x}$)$_{0.3}$MnO$_3$ (LPSMO) film series were prepared by 248-nm KrF pulsed laser ablation of superposed La$_{0.7}$Sr$_{0.3}$MnO$_3$ and La$_{0.7}$Sr$_{0.3}$MnO$_3$ ceramic targets at substrate temperature of 750°C. Depositions were
done at oxygen pressure of 200 mTorr and finalized by in situ annealing in an oxygen pressure of 600 Torr for 10 minutes. All $La_{0.7}(Pb_{x}Sr_{1-x})_{0.3}$MnO$_{3}$ films have thickness of 4500 Å. One $La_{0.8}Sr_{0.2}$MnO$_{3}$ film was additionally annealed in an oxygen atmosphere at 800°C for 1 hour. $La_{0.7}Pb_{0.3}$MnO$_{3}$ (LPMO) film has same thickness of 4500 Å. All those thin films were grown on (001) $LaAlO_{3}$ single crystal substrates.

To avoid contacts phenomena four-probe technique was used both for resistance and noise measurements. Four 2 mm thick silver contacts with the diameter of 1 mm have been thermally evaporated at 100°C. Probes were soldered to the contact pads using indium solder.

The measured noise spectral density consists of two parts: thermal noise (Johnson noise), which is independent on current and frequency, and excess noise which basically has $1/f^{\alpha}$ dependence where $f$ is the frequency and exponent $\alpha$ is close to 1. As the origin of thermal noise is clearly understood and its magnitude is easily estimated from resistance measurements, there will be focused only on the excess noise. Everywhere in figures thermal noise part is subtracted (otherwise it is mentioned in the figure caption).

### 6.4 Electrical fluctuations in sub-micron thick CMR films

The analysis of excess noise in sub-micron thick epitaxial CMR films with the compositions of $La_{0.75}Sr_{0.25}$MnO$_{3}$, $La_{0.8}Sr_{0.2}$MnO$_{3}$, $La_{0.7}Sr_{0.3}$MnO$_{3}$, $La_{0.7}Pb_{0.3}$MnO$_{3}$ and solid solution $La_{0.7}(Pb_{0.63}Sr_{0.37})_{0.3}$MnO$_{3}$ in low frequency (2 Hz ÷ 20 kHz) range shows, that voltage fluctuations has $1/f^{\alpha}$ spectra with $0.7 \leq \alpha \leq 1.2$, and $\alpha$ monotonically increases with temperature increasing. Such spectral behavior is common for all films, which we have studied. While resistivity and accompanying voltage fluctuations are higher in thin films, for demonstration the thinnest (0.06 µm) film with composition of $La_{0.75}Sr_{0.25}$MnO$_{3}$ was chosen. Exponent $\alpha$ varies from 0.92 at 80 K, where material is in ferromagnetic (FM) metallic state, to 1.0 at 290 K in the transition region and 1.16 at temperature 395 K, where material is in paramagnetic (PM) state (Fig. 6.3). For thicker films (0.45 µm) such measurements were done at the transition region and PM state because voltage fluctuation spectral density in the FM metallic state appears to be smaller then $10^{-18}V^{2}$/Hz that is out of our measurement technique sensitivity range.

The dependence of the excess noise voltage fluctuations spectral density (taken at
Figure 6.3: Frequency dependence of voltage fluctuations spectral density at different temperatures. Johnson noise was subtracted.

30 Hz) on the bias current density, measured in the current range where conductance is linear (ohmic region, and there is no overheating), is shown in Fig. 6.4. For all the films studied it has almost quadratic dependence on the bias current in whole temperature range where material is in FM (80 K), transition region (290 K) and PM (400 K).

Temperature dependence of resistance fluctuations spectral density has a regular behavior for all measured films with thickness more then 600 Å: noise increases with the temperature increase. The temperature dependencies of resistance fluctuations and resistivity at zero and 7 kOe magnetic field in the transition temperature region are shown in Fig. 6.5. In the transition region incline of the resistance fluctuation spectral density changes. It happens at slightly lower temperature than one where the resistance starts drop down. Applying of external magnetic field results lowering the magnitude of resistance and noise power. Maximum of the magnetoresistivity \((R_{7kOe} - R_0)/R_0\) at the applied magnetic field of 7 kOe is reached at 318 K and equals to 17 % (Fig. 6.6). Excess noise power \(S_R/R^2\) in the transition decreases with temperature decrease indicating that relative noise in PM state is higher than in FM metallic state. Both temperature dependencies at zero magnetic field and at the 7 kOe almost coincides.

The main trend of the resistance fluctuation spectral density is the same for all tested sub-micron thickness films, however there is no one general dependence for \(S_R = f(R)\) except \(S_R = R^2 + \delta\) with \(\delta > 0\) in the ferromagnetic state (Fig. 6.7). We
Figure 6.4: Voltage fluctuations spectral density versus bias current density at different temperatures.

Figure 6.5: Temperature dependencies of the resistance and noise at zero magnetic field and with applied magnetic field of 7 kOe.
Figure 6.6: Temperature dependencies of the magnetoresistance ratio $MR = (R_{7kOe} - R_0)/R_0$ and noise $SR/R^2$.

notice that noise data, shown for both ultra-thin (42 Å and 100 Å) films, where strain induced structural disorder plays crucial role for transport properties, demonstrates completely different behavior from sub-micron thick ones.

Normalized noise $f \cdot V \cdot SR/R^2$ dependence on temperature in the PM - FM transition region in Fig. 6.8 demonstrates the role of CMR film heat treatment. Transport properties of manganites perovskites are extremely sensitive to the oxygen content, Mn-O bond length and Mn-O-Mn bond angles, which in turn are influenced by oxygen vacancies. We point out that film processing technique was properly chosen and main transport characteristics (resistivity and magnetoresistivity) have not changed after additional 1h ex situ annealing in oxygen. However annealing in oxygen reduces normalized noise magnitude by one order of magnitude from $2 \cdot 10^{-27}$ to $2 \cdot 10^{-28} m^2$ and proves that investigation of electrical noise in CMR films is very sensitive to crystalline quality and film composition.

6.5 Electrical fluctuations in ultra thin La$_{0.75}$Sr$_{0.25}$MnO$_3$ films

We have made systematic study of the low frequency conduction noise as a function of frequency, bias current and temperature in ultra thin epitaxial CMR films. Frequency dependence were measured in a wide (2 Hz ÷ 20 kHz) frequency range. It was observed that excess noise has $1/f^\alpha$ spectra with $0.8 \leq \alpha \leq 1.2$. For ultra thin
Figure 6.7: Resistance fluctuations spectral density $S_R$ normalized by sample volume versus resistance for films with different thickness and compositions.

Figure 6.8: Temperature dependencies of the resistivity and normalized noise for as prepared and annealed $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ film.
Figure 6.9: Frequency dependence of voltage fluctuations spectral density at different temperatures.

(100 Å) film with composition La$_{0.75}$Sr$_{0.25}$MnO$_3$ exponent $\alpha$ monotonically increases from 0.88 at 80 K where material is in ferromagnetic (FM) metallic state to 1.09 at 294 K temperature where material is in transition region to paramagnetic (PM) state (Fig. 6.9). Increasing of $\alpha$ was observed for all films we have studied. For the thinnest (42 Å, 50 Å and 100 Å) films in the lower temperature region random telegraph like signals (TLS) appears. For ultra-thin 42 Å film we do not observe typical $1/f$ spectral behavior in a wide temperature range from 90 K to 270 K (Fig. 6.10 a). Noise spectra showed its Lorentzian-type origin, with the considerable contribution of single time constant. To prove this statement made fitting of measured noise spectra at different temperatures by following formula:

$$S_R(f) = \frac{A_1}{f^\alpha} + \frac{A_2\tau}{1 + (2\pi f\tau)^2} \quad (6.2)$$

where $A_1$, $A_2$, $\alpha$ and $\tau$ are fitting parameters. In Fig. 6.10 b we show, how superposition of those two terms from right sight of Eq. 6.2 results into solid line, which fits experimental data. All fitting parameters were found to be temperature dependent: $A_2$ was found to have a maximum at 190 K, relaxation time $\tau$ decreased with the temperature increase. Dependence of inverse value of relaxation time from the temperature is shown in the inset of Fig. 6.10 b as the Arrhenius plot. Fitting
revealed that TLS process is thermally activated with an energy gap of 20 meV at the temperatures below 155 K and 79 meV at the temperatures above 155 K, almost where starts a rapid resistivity increase.

Appearance of TLS is accompanied with sharp peaks in the temperature dependence of resistance fluctuations (Fig. 6.11 a). However these peaks show non-reproducible character i.e. appears in different places at different temperature scans. We notice that the data shown at Fig 6.11 c TLS appear as two peaks in the time domain at the begin and the rest of the signal could be attributed to the 1/f type fluctuations as it follows from the spectral analysis of given realizations. With increasing the thickness of films, the role of single defect in a current flow paths decreases and TLS in noise have not been observed for CMR films thicker than 600 Å.

Fig. 6.12 shows excess noise voltage fluctuations spectral density (taken at 10 Hz) dependence on bias current density, measured in the current range where conductance is linear (ohmic region, and there is no overheating). For all films studied it has quadratic dependence on the bias current in whole temperature range where material is in FM state (80 K) and transition to PM state (294 K). This corresponds to Eq. 4.37 for normalized fluctuations and indicate that observed voltage fluctuations arise due to resistance fluctuations.
Figure 6.11: Non-reproducibility of noise in 100 Å thick film at lower temperatures. Figures (b) and (c) shows typical time dependencies of voltage fluctuations.

Figure 6.12: Voltage fluctuations spectral density versus bias current density at different temperatures.
Temperature dependence of resistance fluctuations spectral density for films with different thickness has irregular behavior (Fig. 6.13). For film with thickness of 600 Å noise increases with the temperature increase, for 100 Å film noise decreases with the temperature increase and for film with thickness of 42 Å there is wide noise peak in the 150 ± 200 K region. To parameterize noise Hooge’s empirical relation is often used (Eq. 4.36). Since in many experimental cases there is an uncertainty in the number of charge carriers, the ratio

$$\alpha_H/n = f \cdot V \cdot S_R/R^2,$$

where $S_R$ is the resistance fluctuations spectral density, $f$ is the frequency and $V$ is the sample volume is an appropriate material parameter. We found that normalized noise $\alpha_H/n$ varies for different films: for 42 Å from $5 \cdot 10^{-26}$ to $10^{-22}$m³, for 50 Å from $10^{-25}$ to $10^{-23}$m³, for 100 Å from $10^{-26}$ to $10^{-22}$m³ and for 600 Å variation is the smallest ranging from $10^{-25}$ to $10^{-24}$m³. Those results are in good agreement with the results reported for manganites [61, 39, 57], and about 4 - 8 orders larger than the value $10^{-30}$m³ observed in high temperature superconductors and normal metals [62].
6.6 Noise performance of thin CMR films

In addition to commonly used normalized noise parameter $\gamma/n$ (Eq. 6.3), which in many cases gives information about the crystalline quality of grown films there are several figures of merit introduced to characterize the sensor material performance. Material sensitivity usually is parameterized with noise equivalents: the magnitude of input signal equals to electrical fluctuations in material. For temperature applications it is Noise Equivalent Temperature Difference (NETD) and by analogy for magnetic field sensors - Noise Equivalent Magnetic Field Difference (NEMFD). Inverse value of noise equivalent is called Signal-to-Noise Ratio (SNR). Also very often, the Temperature Coefficient of Resistivity (TCR) is used to describe sensor material. It can be easily shown how TCR is related to the noise equivalents (actually to the SNR).

Let us consider the resistive temperature sensor. Then, the bias current is $I_b$ and temperature deviation $\Delta T$ produces the voltage response $I_b\Delta T(\frac{dR}{dT})$. In the presence only of thermal noise (Eq. 4.24) the noise amplitude in the frequency band $\Delta f$ will be proportional to the $\sqrt{R}$. With the constant electric power supply $P_0$, maximum bias current is limited $I_b = \sqrt{\frac{P_0}{R}}$. Finally SNR:

$$\text{SNR} = \frac{\sqrt{P_0} (\frac{dR}{dT}) \Delta T}{\sqrt{R} \sqrt{4k_B T \Delta f}} \propto \frac{\frac{dR}{dT}}{R} = \text{TCR} \quad (6.4)$$

will be proportional to the temperature coefficient of resistivity.

In opposite limiting case, when thermal noise spectral density is many times lower then excess noise caused by the resistance fluctuations, the noise equivalents are:

$$\text{NETD} \left( \frac{\text{K}}{\sqrt{\text{Hz}}} \right) \approx \frac{\sqrt{T_c S_R}}{I_b dR/dT} = \frac{\sqrt{S_R}}{dR/dT} \quad (6.5)$$

and

$$\text{NEMFD} \left( \frac{\text{Oe}}{\sqrt{\text{Hz}}} \right) \approx \frac{\sqrt{S_R}}{dR/dH} \quad (6.6)$$

For practical applications it is important to have a possibility to tune basic transport properties of colossal magnetoresistors and to have maximum of response on the thermal or magnetic signal at the desired temperature. It was shown in [60] that strain induced due to the lattice mismatch between film and substrate can give one of such solution. Fig. 6.14 shows thickness dependence of the transition temperature $T_c$ and introduced figures of merit NETD, and NEMFD for LSMO films with different thickness. Maintaining film preparation conditions the same and just changing film thickness FM-PM transition temperature has been tailored from 332...
Figure 6.14: Thickness dependence of the transition temperature $T_c$, Noise Equivalent Temperature Difference (NETD), and Noise Equivalent Magnetic Field Difference (NEMFD) for the LSMO films with different thickness.

K for films with thickness over 300 Å to 225 K for 42 Å thin film. Despite the remarkable difference in temperature behavior of resistance fluctuations $S_R$ (Fig. 6.12), we found that the NETD and NEMFD factors do not experience significant change with the thickness decrease. The values of NETD = 3 mK/$\sqrt{Hz}$ and NEMFD = 5 mOe/$\sqrt{Hz}$ can be maintained almost constant in a wide thickness range above 100 Å, and transition temperature can be tuned by film thinning down to 100 Å in the range of 40 K without losing of sensor performance. These ultimate limits of NETD and NEMFD are about two orders of magnitude smaller then earlier published [39, 57].

It was shown in previous sections that sub-micron thin films demonstrate better noise performance then ultra thin films. Normalized noise magnitude for 0.45 µm films at the temperature where temperature coefficient of resistance (TCR) has maximum usually was $\alpha_H/n = 3 \cdot 10^{-27} m^3$, while the best result from ultra-thin film series was observed to be $5 \cdot 10^{-25} m^3$, that is more then two orders higher. Thus NETD and NMFD for sub-micron films must be lower then in ultra-thin films.

We found weak field magnetoresistance does not depend on frequency, thus it allows to use film in a wide frequency range. At frequencies beyond 1 kHz excess noise does not affect, and the ultimate limit of NEMFD is set only by driven current and film resistance and for $La_{0.8} Sr_{0.2} MnO_3$ annealed film has been found to be $75 \mu Oe/\sqrt{Hz}$. Thin $La_{0.7} Pb_{0.3} MnO_3$ film has higher magnetoresistance with
the same noise and exhibits the NEMFD of 50 \mu\text{Oe}/\sqrt{\text{Hz}}. However, the maximum response occurs at temperatures close to 0°C, thus La$_{0.7}$Pb$_{0.3}$MnO$_3$ film is less convenient for uncooled applications than La$_{0.8}$Sr$_{0.2}$MnO$_3$ one. As an evidence of high magnetic sensitivity, the temperature dependence of weak field magnetoresistance \(dR/dh\) (modulation field \(h = 1\) mOe and bias field of 130 mOe) is presented in Fig. 6.15. Since resistance depends on material magnetic moment, which has hysteresis dependence on magnetic field, the \(dR/dh\) also exhibits the hysteresis shown in the insert of Fig. 6.15. We point out the importance to adjust the optimum bias magnetic field to achieve maximum of weak field magnetoresistance.

Temperature dependence of NETD for annealed La$_{0.8}$Sr$_{0.2}$MnO$_3$ film is shown in Fig. 6.16. Extremely low NETD \(\approx 100\) nK/\sqrt{\text{Hz}} can be maintained almost constant in a wide temperature range (of 20 K beyond room temperature). It occurs because the noise and the signal \(dR/dT\) have almost the same temperature dependencies. This makes manganite films to be very promising candidates for applications in two-dimensional staring focal plane arrays for uncooled IR imaging. NETD achieved for our films appears to be 50 times lower than NETD value of 5-6 mK/\sqrt{\text{Hz}} obtained for VO$_x$ and semiconductor YBa$_2$Cu$_3$O$_{7-x}$ microbolometers. [63]

The threshold current, at which excess noise at the frame frequency of 30 Hz crosses over the Johnson noise, is one of the important thermistor characteristic. At 320 K 1 k\(\Omega\) resistor produces Johnson voltage noise with the spectral density of \(1.76 \cdot 10^{-17}\) V$^2$/\sqrt{\text{Hz}}. $S_R$ obtained from our experiments was approximately of
Figure 6.16: Temperature dependence of NETD for annealed $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (0.45 $\mu$m) film. Frequency dependence of voltage fluctuations at the maximum of TCR (317 K) is shown in the insert.

$2 \cdot 10^{-11} \, \Omega^2/\sqrt{\text{Hz}}$. From this one can estimate the threshold bias current to be around 1 mA. The crossover from excess to the Johnson noise occurring at 30 Hz frame frequency is shown in the insert of Fig. 6.16.
Chapter 7

CMR thin film uncooled bolometer

7.1 Introduction

The highest sensitivity of bolometer response could be achieved at low temperatures exploiting the superconducting resistive transition. Since it requires cooling, those bolometers are expensive to operate. In additional to cryogenic bolometers there are those that do not require cooling. Examples include the detectors based on amorphous silicon [64], amorphous silicon germanium alloys (a-SiGe) [65, 66], hydrogenated amorphous silicon carbide (a – Si$_{1-x}$C$_x$: H) [67], vanadium oxide (VO$_x$) and semiconducting YBCO compounds. Although easy to fabricate and integrate with CMOS technology, obtained by plasma enhanced chemical vapor deposition (PECVD) alloys of a-Si exhibit large 1/f noise [68, 69], which limits bolometer sensitivity. On other hand sputter deposited a-Si:H films demonstrate 1/f noise magnitude more than two orders less than PECVD obtained [66]. However, with this fabrication method, the advantages of entire integrated circuitry are lost. VO$_x$ bolometers have been relatively more successful. Fully integrated microbolometers with on-chip read-out circuitry have been fabricated as high performance and sensitive focal plane arrays [70, 71, 72]. Recently reported bolometers, made on semiconducting YBCO [63, 73] also show relatively high TCR and is easy to deposit via rf-sputtering at ambient temperature. However, those microbolometers detectivity are one order of magnitude less then in VO$_x$ microbolometers and could be compared with PECVD a-Si microbolometers (Table 7.1). According to authors, detectivity could be increased with decreasing of thermal conductance, but normalized
Detector Material | TCR (% K$^{-1}$) | $D$ (cm$\sqrt{\text{Hz/W}}$) at 30 Hz
--- | --- | ---
PECVD a-Si:H [66] | -4.5 | $1.7 \cdot 10^{7}$
Sputtered a-Si [66] | -1.8 | $3.2 \cdot 10^{8}$
Sputtered a-Ge [66] | -1.8 | $4.7 \cdot 10^{8}$
$\text{VO}_x$ [71] | $-1.5 \div -2$ | $4.4 \cdot 10^{8}$
YBCO [63] | -3.2 | $2 \cdot 10^{7}$

Table 7.1: TCR and detectivity of microbolometers reported for different materials.

Detector Material | TCR (% K$^{-1}$) | $\gamma/n (m^3)$ | SNR ($\sqrt{\text{Hz/K}}$)
--- | --- | --- | ---
a-Si [68] | -2.2 | $2 \cdot 10^{-25}$ | $2.7 \cdot 10^{3}$
$\text{VO}_x$ [74] | -1.7 | $2.7 \cdot 10^{-27}$ | $1.8 \cdot 10^{4}$
YBCO [73] | -3.2 | $1.7 \cdot 10^{-27}$ | $4.2 \cdot 10^{4}$

Table 7.2: Material properties and calculated SNR (volume of $10^{-16} m^3$ and $f = 30$ Hz) for materials used in microbolometers.

$1/f$ noise magnitude $\gamma/n$ is comparable with $\text{VO}_x$ films and will limit sensitivity of fabricated microbolometers at the same value. In the table 7.1 the main properties of materials, used for uncooled bolometric applications, are shown.

Mixed valence manganites with basic formula $\text{A}_x\text{M}_{1-x}\text{MnO}_3$ (with $\text{A} = \text{La, Nd}; \text{M} = \text{Ca, Sr, Pb, Ba}$) have attracted our attention as promising bolometric material due the highest, in comparison with above mentioned, TCR value which maximum is close to the room temperature and could be maintained as high as 8 % K$^{-1}$. Recent considerable advances in CMR film processing technique dispersed doubts on previous reported high level of $1/f$ excess noise and made possible to reduce electrical noise down to the ordinary for bolometric materials normalized noise value. With introducing those advances it becomes possible to make thin epitaxial films which performance are comparable and even better than the materials are already used for bolometric applications. Based on those assumptions we have explored CMR thin films as a material for uncooled bolometer.

Infra-red radiation may be detected either by observing the change in temperature of a body exposed to the radiation (thermal detectors) or by measuring effects due to the direct interaction of infra-red photons with electrons present in the detector (photon detectors). Several physical mechanisms could be involved to made thermal detector: thermal expansion, thermal electro moving force, piro-electric effect, dependence of resistance on the temperature, etc. Bolometers are thermal...
detectors which explore the temperature dependence of resistance.

Due to the temperature dependence of resistance $R$, deviation of temperature $\Delta T$ leads to the deviation of the resistance (Fig. 7.1), which could be detected by measuring voltage across the current biased bolometer:

$$\Delta V = I_b \frac{dR}{dT} \Delta T.$$  \hspace{1cm} (7.1)

### 7.2 Bolometer responsivity

A simple model describes a bolometer as an absorber with heat capacity $C$ connected to a thermal bath at temperature $T_c$ by a thermal conductance $G$. The temperature of absorber changes in response on changes in incident power. These temperature fluctuations are converted into voltage fluctuations by means of a current biased thermistor. Thermistor is thin layer of material possessing high temperature coefficient of resistivity (TCR). Relation between temperature changes and incident power could be found from heat transfer equation:

$$C \frac{d(T - T_c)}{dt} + G(T - T_c) = \eta W + W_J(T),$$  \hspace{1cm} (7.2)

where $T$ is the absorber temperature, $T_c$ is the temperature of thermostat, $W$ is incident radiation power and $\eta$ is absorptivity; $R$ is the thermometer resistance and $W_J(T)$ is the energy released in the absorber due to the Joule heat. If the incident
radiation is harmonically modulated $W = W_0 e^{i\omega t}$ and $W_j(T) \ll \eta W$, Eq. 7.2 gives solution for thermometer temperature:

$$T = T_c + \frac{\eta W_0 e^{i\omega t}}{G(1 + i\omega \tau)},$$

(7.3)

where $\tau = C/G$ is the thermal time constant. Responsivity of a bolometer, i.e., the output signal voltage per unit incident infrared power is given by:

$$\mathcal{R}_V = \frac{\Delta V}{W_0} = I_b \frac{dR}{dT} \frac{\Delta T}{W_0} = \frac{\eta I_b dR/dT}{G \sqrt{1 + (\omega \tau)^2}}.$$  

(7.4)

where $I_b$ is a bias current. Therefore, to get high responsivity, high $dR/dT$, low $G$ with $\omega \tau \ll 1$, and maximum allowed $I_b$ are required. The last requirement points out that Joule heating can not be neglected. Within the linear approximation the resistance of thermometer can in the presence of small temperature changes could be written as $R(T) = R_0 + dR/dT \cdot (T - T_c)$. Dissipated power for current and voltage biasing can be presented with this approximation:

$$W_j(T) = I_b^2 R_0 + I_b^2 \frac{dR}{dT} (T - T_c),$$

$$W_j(T) = \frac{V_b^2}{R_0} - \frac{V_b^2}{R_0^2} \frac{dR}{dT} (T - T_c).$$

(7.5)

Heat transfer equation (7.2) becomes:

$$C \frac{d(T - T_c)}{dt} + G_{eff} (T - T_c) = \eta W + W_{j0},$$

(7.6)

where $G_{eff} = G \mp W_{j0} TCR$, sign "-" corresponds to current biasing and sign "+" - to voltage biasing and $W_{j0}$ is Joule heat energy of resistance $R_0$. Including Joule heating, the responsivity for **current biased** bolometer is:

$$\mathcal{R}_V = \frac{\eta I_b dR/dT}{(G - I_b^2 dR/dT) \sqrt{1 + \left(\frac{\omega \tau C}{G - I_b^2 dR/dT}\right)^2}},$$

(7.7)

It reaches the maximum value at optimum of the bias current:

$$I_{opt} = \sqrt{\frac{G^2 + \omega^2 C^2}{(dR/dT)^2}} \approx \sqrt{\frac{G}{|dR/dT|}},$$

(7.8)

if TCR is negative.

Temperature deviations in **voltage biased bolometer** with positive TCR produces current fluctuations and the responsivity must be defined as output signal current per unit incident infrared power what is given by:

$$\mathcal{R}_I = \frac{V_b}{R_0^2 \frac{dR}{dT} W_0} = \frac{\eta V_b TCR}{(G + TCR \frac{V_b^2}{R_0}) R_0 \sqrt{1 + \left(\frac{\omega \tau C}{G + TCR V_b^2 / R_0}\right)^2}}.$$  

(7.9)

73
The responsivity reaches the maximum value at the optimum bias voltage:

\[ V_{\text{opt}} = \sqrt[4]{\frac{G^2 + \omega^2 C^2}{(\text{TCR}/R_0)^2}} \approx \sqrt{\frac{GR_0}{\text{TCR}}} \]  \hspace{1cm} (7.10)

Joule heating sets the stability requirements biased thermistors due to the thermal feedback: to obtain local stability (negative feedback) the thermistor with a positive TCR must be voltage biased while the thermistor with a negative TCR must be current biased \cite{75}. In spite of requirement for local stability, current biased thermistor also can work with some reasonable positive feedback. So thermistor with positive TCR can be current biased if bias current does not exceed value which is set by "thermal runaway" inequality: \( I_b^2 \leq 0.3G(dR/dT)^{-1} \) \cite{76}. Power dissipated by Joule heat leads to thermistor temperature increase, which can be found from steady state solution of Eq. 7.2, then there in the absence of incident radiation:

\[ \Delta T = \frac{W_{j0}/G_{eff}}{I_{\text{opt}}R_0} = \frac{V_{\text{opt}}^2}{R_0G_{eff}}. \] \hspace{1cm} (7.11)

This temperature increase usually called "thermal overheating". The shift of the operating temperature due to the thermal overheating for current biased thermistor with negative TCR (same as the voltage biased thermistor with positive TCR), at the optimum bias conditions (Eq. 7.8, 7.10) can be estimated as:

\[ \Delta T = \frac{I_{\text{opt}}^2R_0}{G + I_{\text{opt}}^2|dR/dT|} = \frac{V_{\text{opt}}^2/R_0}{G + V_{\text{opt}}^2\text{TCR}/R_0} = \frac{0.5}{|\text{TCR}|}. \] \hspace{1cm} (7.12)

For current biased thermistor with positive TCR overheating will be:

\[ \Delta T = \frac{0.3GR_0}{dR/dT(G - 0.3G)} = \frac{0.43}{|\text{TCR}|}. \] \hspace{1cm} (7.13)

Estimation of thermal overheating gives useful information for seeking the materials with optimum TCR at the desired operating temperature. With introducing of optimum current \( I_{\text{opt}} = \sqrt{G/(dR/dT)} \) for current biased bolometer with negative TCR, and optimum bias voltage \( V_{\text{opt}} = \sqrt{GR_0/\text{TCR}} \) responsivities (Eqs. 7.7, 7.9) can be presented as follows:

\[ \Re_V = \frac{\eta \sqrt{R_0|\text{TCR}|}}{2\sqrt{G + \omega^2 C^2}} \hspace{0.5cm}; \hspace{0.5cm} \Re_I = \frac{\eta \sqrt{|\text{TCR}|}}{2 \sqrt{R_0 G + \frac{(\omega C)^2}{4G}}}. \] \hspace{1cm} (7.14)

Eqs. 7.14 points out that optimum voltage responsivity increases only as a square root of increasing resistance or decreasing thermal conductance since there is a
limit on maximum current due to Joule heating. Despite the sign of TCR the main difference between bolometers biased by voltage and current is the opposite requirement for material resistivity. Voltage biased bolometer will respond higher if material with the same TCR will have lower resistivity unlike the current biased bolometer, which has higher response if material has higher resistivity.

The responsivity for current biased bolometer with positive TCR appears to be:

$$\mathcal{R}_V = \frac{0.78\eta\sqrt{R_0\text{TCR}}}{\sqrt{G + \frac{(\omega C)^2}{0.9G}}}.$$  \hspace{1cm} (7.15)

Here there is a maximum of responsivity at the optimum thermal conductance $G = 1.42\omega C$. For commercial room temperature bolometer with thermal capacity $C = 10^{-9}$ J/K maximum responsivity (Eq. 7.15) at 30 Hz chopping frequency could be achieved with the thermal conductance of $G = 2.7 \cdot 10^{-7}$ W/K. Further decreasing of thermal conductivity is not reasonable since it will decrease bolometer responsivity at chosen frequency.

### 7.3 Noise equivalent power and detectivity

The sensitivity of an optimized bolometer to fluctuations in incident power is often expressed as a noise equivalent power (NEP), which is defined as the incident power that provides a signal at the output equals to the noise per unit of frequency band. There are several main noise sources which limit sensor performance: phonon fluctuations, thermal fluctuations, excess noise ($1/f$ noise), photon fluctuations and sometime the preamplifier noise (noise of measuring system itself). Usually for uncooled applications last two noise sources could be omitted.

Phonon fluctuations produce temperature fluctuations (Chapter 3.3), which modulate the resistance. If there is no constant thermal gradient inside the film or parts of it (in other words if system is close to thermodynamic equilibrium), the temperature fluctuations are an analogue of fluctuation dissipation relations and its voltage fluctuation spectral density with bias current $I_b$ can be found by substituting Eq. (7.2) to Eq. (4.35):

$$S_V^{\text{phonon}} = 4k_B T \left( \frac{dR}{dT} \right)^2 \frac{I_b^2}{G(1 + (\omega T)^2)}.$$  \hspace{1cm} (7.16)

Noise equivalent power for phonon fluctuations under such conditions is equal to:

$$\text{NEP}_{\text{phonon}} = \sqrt{\frac{S_V^{\text{phonon}}}{\mathcal{R}_V}} = \sqrt{\frac{4k_B T^2 G}{\eta^2}}.$$  \hspace{1cm} (7.17)
With decreasing the thermal conductance, phonon fluctuations NEP decrease. This appears because responsivity increases faster than the noise voltage.

Voltage fluctuations spectral density of the thermal noise of bolometer resistive element is represented by Nyquist formula Eq. (4.24). Noise equivalent power of thermal fluctuations at current and voltage biasing maintains the same value due to the relation \( R_V = R \cdot R_I \). It can be presented in both forms, accordingly to the biasing conditions:

\[
\text{NEP}_{\text{therm}} = \sqrt{\frac{4kTR}{R_V^2}} \equiv \sqrt{\frac{4kT}{R_R^2}}. \tag{7.18}
\]

With the increasing of bolometer responsivity, noise equivalent power produced by thermal fluctuations will decrease. Depending on thermistor biasing excess noise equivalent power equals:

\[
\text{NEP}_{\text{excess}}^2 = \frac{S_V(f)}{R_V^2} \equiv \frac{S_I(f)}{R_I^2}, \tag{7.19}
\]

where \( S_V(f) \) and \( S_I(f) \) are excess noise voltage and current fluctuation spectral density. Total noise equivalent power equals:

\[
\text{NEP} = \sqrt{\text{NEP}_{\text{excess}}^2 + \text{NEP}_{\text{therm}}^2 + \text{NEP}_{\text{phonon}}^2}. \tag{7.20}
\]

When film demonstrates the absence of excess noise, bolometer sensitivity is still limited by phonon and Johnson noise. At \( T = 300 \text{ K} \), \( \eta = 0.8 \) and \( G = 10^{-7} \text{ W/K} \), phonon noise term could be found to be of \( 8.8 \cdot 10^{-13} \text{ W/Hz} \). For typical room temperature microbolometer with \( R = 1 \text{ M}\Omega \) and \( R_V = 10^4 \text{ V/W} \), contribution of Johnson noise gives \( 1.3 \cdot 10^{-11} \text{ W/Hz} \). Further optimization of bolometer material requires to minimize the magnitude of electrical fluctuations down to the ultimate limit, which in the ideal case is set by phonon fluctuations [77].

To normalize bolometer performance per area unit, the detectivity \( D \) is introduced which is determined as the ratio of square root of detector area \( A \) to the noise equivalent power \( \text{NEP} \):

\[
D = \frac{\sqrt{A}}{\text{NEP}}. \tag{7.21}
\]

### 7.4 Responsivity of thin film bolometer made onto the substrate

In the paragraph 6.2, the bolometer was described as an absorber connected to a thermal bath by a thermal conductance. This simple picture cannot be used if thin
bolometer film absorbs only the part of incident infrared radiation, which is characterized by the absorbance coefficient $\eta_f$. The rest part of radiation is absorbed by a substrate with absorbance coefficient $\eta_s$. Since radiation in substrate is absorbed in accordance with Burger law, there is a temperature distribution in substrate. For simplicity let us solve a problem for a system with allocated parameters. Let film and substrate effective temperature to be $T_f$ and $T_s$ correspondingly. Substrate is connected to thermal bath with constant temperature $T_{th}$ via thermal conductivity $G_{st}$. Effective thermal conductance between film and substrate let be $G_{fs}$. Film and substrate has thermal mass $C_f$ and $C_s$. When incident radiation power $W_0$ is applied by a pulse, heat transfer equation Eq. (7.2) transforms to the system of coupled equations for $T_f$ and $T_s$:

$$
\begin{align*}
C_f \frac{d(T_f - T_s)}{dt} + G_{fs}(T_f - T_s) &= \eta_f W_0 \sigma(t); \\
C_s \frac{d(T_s - T_{th})}{dt} + G_{st}(T_s - T_{th}) &= \eta_s G_{fs}(T_f + T_s) + \kappa_f \eta_s W_0 \sigma(t),
\end{align*}
$$

(7.22)

where two terms in the right part of the second equation correspond to the power which comes to the substrate from the film and directly from the radiation due to the film permeability $\kappa_f$. Solutions of this system of equations could be found in such form:

$$
\begin{align*}
T_f - T_s &= A_1 e^{-\frac{t}{\tau_{fs}}} + A_2; \\
T_s + T_{th} &= B_1 e^{-\frac{t}{\tau_{fs}}} + B_2 e^{-\frac{t}{\tau_{st}}} + B_3,
\end{align*}
$$

(7.23)

where $\tau_{fs} = C_f/G_{fs}$ and $\tau_{st} = C_s/G_{st}$ are effective thermal time constants of film-substrate and substrate-thermostat interfaces correspondingly. For a steady state constants $A_2 = \frac{\eta_f W_0}{G_{fs}}$ and $B_3 = \frac{\eta_s W_0 (\kappa_f + \eta_f)}{G_{st}}$.

Using the boundary condition $T_{f0} = T_{s0} = T_{th}$, one can find intermediate solution for the first equation of the system (7.23):

$$
T_f - T_s = \frac{\eta_f W_0}{G_{fs}} \left(1 - e^{-\frac{t}{\tau_{fs}}} \right),
$$

(7.24)

Substituting Eq. (7.24) into the second equation of system (7.23) and again using boundary condition for temperatures, one finds the solution of film temperature versus time. In the case when incident power is applied by pulse:

$$
T_f = T_{th} + \frac{\eta_f W_0}{G_{fs}} \left(1 - e^{-\frac{t}{\tau_{fs}}} \right) + \frac{\eta_s (\eta_f + \kappa_f) W_0}{G_{st}} \left(1 - e^{-\frac{t}{\tau_{st}}} \right) + \frac{\tau_{st} \eta_f \eta_s W_0}{(\tau_{st} - \tau_{fs}) G_{st}} \left(e^{-\frac{t}{\tau_{fs}}} - e^{-\frac{t}{\tau_{st}}} \right),
$$

(7.25)
While simple heat transfer model of bolometer is an equivalent to the electric circuit with resistance and capacitance giving time constant $\tau = RC$, in the model with two interfaces two thermal time constants appear.

In order to find the bolometer responsivity we should apply incident power in form of harmonic function $W = W_0 e^{i\omega t}$, then the system of heat transfer equations (7.2) is:

$$\begin{align*}
C_f \frac{d(T_f - T_s)}{dt} + G_{fs}(T_f - T_s) &= \eta_f W_0 e^{i\omega t}; \\
C_s \frac{d(T_s - T_{th})}{dt} + G_{st}(T_s - T_{th}) &= \eta_s G_{fs}(T_f + T_s) + \kappa_f \eta_f W_0 e^{i\omega t}.
\end{align*}$$

This system of equations is satisfied with the following film temperature dependence:

$$T_f - T_{th} = \frac{\eta_f W_0 e^{i\omega t}}{G_{fs}(1 + i\omega \tau_{fs})} + \frac{\eta_s \kappa_f W_0 e^{i\omega t}}{G_{fs}(1 + i\omega \tau_{st})} + \frac{\eta_s \eta_f W_0 e^{i\omega t}}{G_{st}(1 - \omega^2 \tau_{fs} \tau_{st} + i\omega (\tau_{fs} + \tau_{st}))}.$$  

(7.26)

As we have already learnt, the presence of Joule heating changes the thermal conductance $G_{fs}$ to the effective one $G_{fs}^*$, where $G_{fs}^* = G_{fs} - I_b^2 \cdot dR/dT$. Therefore, the temperature variation of film will be:

$$|\Delta T| = \frac{\eta_f W_0}{G_{fs}^* \sqrt{1 + (\tau_{fs}^*)^2}} + \frac{\eta_s \kappa_f W_0}{G_{st} \sqrt{1 + (\tau_{st})^2}} + \frac{\eta_s \eta_f W_0}{G_{st} \sqrt{(1 - \omega^2 \tau_{fs}^* \tau_{st})^2 + \omega^2 (\tau_{fs}^* + \tau_{st})^2}},$$

(7.27)

where $\tau_{fs}^* = C_f/G_{fs}^*$. Responsivity of a bolometer, i.e., the output signal voltage per unit incident infrared power in the case when $\tau_{fs}^* << \tau_{st}$ and $\omega^2 \tau_{fs}^* \tau_{st} << 1$, is given by:

$$\Re = \frac{I_b dR}{dT W_0} = \frac{\eta_f}{G_{fs}^* \sqrt{1 + (\tau_{fs}^*)^2}} + \frac{\eta_s (\kappa_f + \eta_f)}{G_{st} \sqrt{1 + (\tau_{st})^2}}.$$  

(7.28)

As the consequence of two interfaces and two different temperatures in the film-substrate structure, two thermal time constants in time and frequency domains appear in the responsivity. As the conclusion we can generalize, that in the system with $n$ interfaces responsivity will have $n$ time constants and in general can be presented in the form:

$$\Re(t) = \sum_{i=1}^{n} A_i e^{-\frac{t}{\tau_i}}.$$  

(7.29)

(7.30)
Figure 7.2: Voltage response versus frequency. Data are represented by points and solid lines show results of fitting to the Eq. 7.31 with three relaxation times.

In the frequency domain the responsivity can be expressed as a sum of relaxors:

$$\Re(\omega) = I_b \frac{dR}{dT} \sum_{i=1}^{n} \frac{B_i}{\sqrt{1+(\omega \tau_i)^2}},$$  \hspace{1cm} (7.31)

if the relaxation times very differ from each other: $\tau_1 << \tau_2 << \ldots << \tau_n$.

### 7.5 Uncooled bolometer demonstrator

To measure voltage response on the incident radiation we used 900 nm IR light emitting diode. Harmonic signal from the internal generator of SR850 Lock-In amplifier was amplified with current amplifier and with additional minimum bias current was applied to the diode. This allows to get harmonically modulated IR power. Voltage response from bolometer was measured with the same Lock-In amplifier. To avoid electromagnetic coupling, diode wires were twisted and shielded and background signal without incident radiation was subtracted. For recording of voltage response in the time domain the low noise DC input amplifier was used. Diode current in this case has rectangular shape. Voltage signal from bolometer was amplified and recorded with the digital the oscilloscope DS 6411.

Fig. 7.2 represents the measured voltage response for LPSMO film bolometer. Three thermal time constants of 0.8 s, 2.6 ms and 80 $\mu$s could be observed in the
Figure 7.3: Time dependencies of voltage response (at \( t = 0 \) the incident radiation was switched off)

line 1 for bolometer suspended in the air. Providing better thermal contact of the bolometer with the thermostat, the heat conductance between substrate and thermostat increases and the longest time constant decreases to 0.5 s, while two others maintaining approximately the same 2.1 ms and 90 \( \mu s \) values. The shortest time constant is related to heat transfer through the contacts pads and connecting wires. The voltage response on the incident radiation pulse in time domain is shown in Fig. 7.3. Heat time constants were estimated by fitting experimental data to the Eq. 7.30. The increase of thermal conductance between substrate and thermostat results in decrease of the longest time constant \( \tau_1 \) approximately two times and slight change of the time constant \( \tau_2 \) between film and substrate. Time constants estimated from the voltage response on the harmonically modulated incident radiation in frequency domain and from the response on the laser pulse measured in time domain coincide with good accuracy.

Bolometer response on 30 Hz modulated 940 nm radiation from LED appears as a sharp peak in Fig. 7.4 on the noise background which experiences crossover from \( 1/f \) to a white Johnson noise. At 295 K for the 1.2 mA bias current the crossover frequency was 260 Hz. The main bolometer characteristics: responsivity \( \mathcal{R} \), noise equivalent power NEP and detectivity \( D \) can be estimated directly from Fig. 7.4. Thus, the responsivity \( \mathcal{R} \) was found to be 0.6 V/W, \( \text{NEP} = 3 \cdot 10^{-8} \text{W/}\sqrt{\text{Hz}} \), and detectivity \( D = 0.9 \cdot 10^7 \text{cm}\sqrt{\text{Hz/W}} \) at 30 Hz of the frame frequency.
Figure 7.4: Noise spectra for La$_{0.7}$(Pb$_{0.63}$Sr$_{0.37}$)$_{0.3}$MnO$_3$ 0.45 µm thick film bolometer. Peak at 30 Hz is the response on incident radiation.
Chapter 8

Fluctuations in ferroelectric thin films

8.1 Introduction

Ferroelectric thin films have a very wide range of applications such as thin film capacitors in high density DRAMs (dynamic random access memories), nonvolatile FERAMs (ferroelectric random access memories) [78], ferroelectric FETs (field effect transistors) [79], as alternative gate dielectrics in transistors with reduced dimensions, and as voltage tunable capacitors in phased array antennas for mobile communication and HRDD (high rate data delivery) technology. In many of those applications, ferroelectric materials are supposed to operate under static or quasi-static electric field. There are several different physical processes which affect the stability of impedance and thus determine the reliability of ferroelectric devices. Such processes are a dielectric relaxation [80], leakage current [81], time dependent dielectric breakdown [82] etc. Although they have been observed in a variety of dielectrics and even generalized as 'laws', the microscopic identification of the mechanisms responsible for these effects is still not clear so these 'laws' are mostly empirical descriptions of charge transport in ferroelectrics. Furthermore, most measuring techniques widely used to characterize impedance of the ferroelectric give only the mean values of the measured physical parameters, whereas the deviations from these mean values are usually left nonquantified. We believe that fluctuations in impedance are a source of intimate information on ferroelectric domain nucleation and switching, ionic transport and electromigration processes in thin ferroelectric films.
The complexity of physical effects involved in electrical transport in ferroelectrics makes noise measurements a difficult task. As a matter of fact, even in materials exhibiting only dielectric properties, electrical fluctuations are not well explored. In this chapter, we present our experimental approach to fluctuations in impedance of ferroelectric thin films. All presented results are measured on Au/PZT/La$_{0.7}$Sr$_{0.3}$MnO$_3$/Pt$_{80}$Ir$_{20}$ thin film vertical capacitor structures.

### 8.2 Experimental

A 248-nm KrF excimer laser (Compex-102) was used to ablate stoichiometric ceramic targets of the following compositions: La$_{0.7}$Sr$_{0.3}$MnO$_3$/Pt$_{80}$Ir$_{20}$ (LSMO) and Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT). Both layers were deposited at a laser radiation energy density of 2-3 J/cm$^2$, pulse repetition rate of 10 Hz, and distance between target and substrate of 60 mm. The background pressure did not exceed $10^{-6}$ Torr. Deposition of a 100 nm thick LSMO film onto polycrystalline Pt$_{80}$Ir$_{20}$ substrate was carried out at an oxygen pressure of 250 mTorr and a substrate temperature of 700 °C and was followed by deposition of a 500 nm thick PZT layer at 580 °C and the same oxygen pressure. The whole heterostructure was annealed in an oxygen pressure of 600 Torr at 580 °C for 20 min and then cooled down to room temperature.

In order to fabricate test capacitor structures for ferroelectric and electrical transport measurements, circular Au electrodes with an area of $6.4 \times 10^{-3}$ cm$^2$ and $1.9 \times 10^{-3}$ cm$^2$ (00.9 mm and 00.5 mm) were deposited at room temperature using a shadowing mask. Additional annealing for two hours was performed at 200 °C in air after deposition of top electrodes.

Ferroelectric properties (hysteresis $P - E$ loops) were recorded using a 1pC resolution electrometer, which was initially calibrated with the Radiant Technology RT66A pulsed tester. The electrometer circuit was driven by a triangular wave at 50 Hz frequency. Capacitance and dielectric losses in the frequency range from 400 Hz to 100 kHz ($C - f$, $\tan \delta - f$ and $C - V$) were characterized using a PM6403 LCR meter. For current-voltage ($I - V$) and current-time characteristics we used either Keithley 2410 Sourcemeter both as a stable voltage supply and as a nano-ampmeter.

Instantaneous impedance was recorded in time domain up to 600 s with a sampling rate of 25 ksample/s under applied dc bias, which did not exceed the breakdown field. The fluctuating discharge current has been limited by a ballast resistor connected in series. To characterize fluctuations spectra, the data sets of $2^{14}$ points of instantaneous impedance have been acquired and Fast Fourier Transformed.
8.3 Dielectric test

Vertical Au/PZT/LSMO/PtIr capacitors show remnant polarization of 20 mC/cm$^2$, induced polarization of 40 mC/cm$^2$ at 380 kV/cm, and coercive field of 52.5 kV/cm (Fig. 8.1). Due to the difference in the work functions of the top and bottom electrodes, the hysteresis loops are slightly asymmetric with the offset to forward electric field (the direction of electric field was denoted as positive when positive potential was applied to the top Au electrode).

The $C-f$ test has revealed a weak frequency dispersion of the capacitance shown in Fig. 8.2. Capacitance, thus dielectric permittivity $\varepsilon$, was found to decrease in the frequency range from 400 Hz to 100 kHz from 925 to 800. Dielectric loss tan$\delta$ takes the minimum value of 3.1% at 10 kHz.

Fig. 8.3 gives an example of $C-V$ and $Q-V$ plots recorded at 1 kHz frequency, which shows tunability of the ferroelectric film. It should be pointed out that the maxima of the $C-V$ curve are reached at the electric field of about 14.4 kV/cm, which is much lower than the coercive field of 52.5 kV/cm obtained from the $P-E$ loop in Fig. 8.1. We address this difference to relaxation of polarization, thus different results are caused by higher sweeping rate and higher electric field used in $P-E$ tracing.

The relaxation of polarization after steep change of bias electric field was observed recording $C-V$ characteristics in time domain. Two curves broken to pieces
Figure 8.2: Frequency dispersion of the capacitance $C$, dielectric permittivity $\varepsilon$, and loss $\tan\delta$. Solid line is the best fit of the experimental $C - f$ data ($\circ$ symbols) to the power law.

Figure 8.3: Capacitance and quality factor $Q = 1/\tan\delta$ at 1 kHz versus bias electric field. Electric field was swept with the step ramp of 4.8 kV/cm per 9 sec.
Figure 8.4: $C - V$ characteristics recorded in the time domain by sweeping electric field with: 4.8 kV/cm per 120 sec step voltage ramp (two curves broken to pieces) and 4.8 kV/cm per 9 sec (solid line with symbols o stands for ascending branch and dashed line for descending branch of hysteresis loop taken from Fig.8.3)

in Fig. 8.4 show ascending (symbols ▶) and descending (◁) branches of instantaneous capacitance measured with 4.8 kV/cm per 120 sec step voltage ramp. After a step of dc-bias voltage was applied, it takes hundreds of seconds to get steady value of the capacitance. Ascending and descending branches of $C - V$ characteristics measured with the step ramp of 4.8 kV/cm per 9 sec (from the area marked as a dashed box in Fig.3) are also shown in Fig. 8.4 by symbols 'o', solid and dashed line, respectively. In this case electric field was swept approx ten times faster, thus $C - V$ characteristic gives overestimated value of the capacitance. It was observed that dielectric losses at moderate electric fields has the same relaxations as capacitance.

8.4 Relaxation phenomenon

Dielectric relaxation process in response to the steps of applied electric field also could be studied by recording instantaneous leakage current in time domain (Fig.8.5). There are four distinct regions in the transient current. 1) Very fast dielectric response is caused by charging/discharging the capacitor under the test. This transient current is too fast to be distinguished in the time scale shown in Fig.8.5 2) Long time transient emphasizes non-Debye type polarization current re-
Figure 8.5: $j - E$ characteristics of Au/PZT/LSMO/PtIr capacitor in time domain: a) ascending field sweep from -120 kV/cm to +120 kV/cm; b) descending sweep from +120 kV/cm to -120 kV/cm. Envelope curve $j_{\text{envelope}}(E)$ is a steady (“true”) leakage current shown by solid line.

Relaxation. Its time dependence follows Curie - von Schweindler law [80]:

$$j(t) = j_{\text{leak}} + j_0 \left( \frac{t}{1 \text{sec}} \right)^{-n}$$

(8.1)

where $j_{\text{leak}}$ is a steady (‘true’) leakage current density at $t \to \infty$, $j_0$ and $n$ are fitting parameters. 3) Steady leakage current regime is reached within

$$t = \left( 10 \frac{j_0}{j_{\text{leak}}} \right)^{1/n},$$

(8.2)

when time deviation of transient current becomes less than 10% of saturated value $j_{\text{leak}}$. 4) In steady leakage current regime after awhile (the time depends on applied electric field) current through the capacitor increases exhibiting effect of resistance degradation.

As it is clearly seen in Figs. 8.5, the steady state leakage $j - E$ characteristic in test capacitors can be obtained only after sufficient delay time, then the relaxation current becomes negligible compared with the steady leakage current shown as an envelope curve. We found that for ferroelectric capacitor this settling time is much dependent on the applied electric field and the direction of electric field sweep. The amplitude of relaxation current density $j_0$ was found to possess distinct hysteresis...
Figure 8.6: Electrical noise in 500 nm thick PZT capacitor voltage supplied through the 40 kΩ series resistor: (a) - voltage fluctuations at forward electric field of 180 kV/cm; (b) - reverse electric field of -180 kV/cm. Panels (c) and (d) at the right hand side present the Fast Fourier Transform of the 2^14 data points at the selected time instants.

behavior, whereas the ‘true’ leakage current \( j_{\text{leak}} \) and the exponent \( n \), experienced 12% variations around the mean value of 0.8, can be considered to be hysteresis-free. The exponent \( n = 0.8 \pm 0.1 \) within the experimental scattering corresponds to the power law \( C \propto f^{n-1} \) governing the frequency dispersion of the capacitance in Fig.8.2.

### 8.5 Electrical noise

To quantify electrical noise, we recorded voltage fluctuations across the ferroelectric capacitor connected in series with the ballast 40 kΩ resistor and autonomous battery. Ballast resistor was used to estrange dielectric breakdown and allowed keep sample under bias long enough to collect statistics. Figs.8.6a and 8.67b present instantaneous voltage across the ferroelectric capacitor in the forward and reverse
bias, respectively, while Figs. 8.6c and 8.6d show voltage fluctuations spectra at time instants \( t_1 \) and \( t_2 \) shown by arrows in the ‘quit’ and ‘noisy’ time domains, respectively. The first domain is the case when the resistance degradation was not occurred, and the second one is when it took place. In both cases voltage fluctuation spectral density \( S_V \) was found to follow universal \( 1/f^\alpha \) law with \( \alpha \approx 1.5 \).

The short-term spectral density analysis of ‘instantaneous’ Fourier harmonic at 300 Hz acquired from \( 2^{14} \) data points by FFT with 22.1 kHz sampling frequency is shown in Fig.8.7. It looks similar to Figs.8.6a and 8.6b indicating fractal character of the noise at high fields close to electric breakdown.

### 8.6 Discussion and summary

When a system is in thermodynamic equilibrium, its linear response function (e.g., susceptibility) and its equilibrium fluctuations are related by the fluctuation dissipation relation (FDR). In accordance to FDR, the spectra of dielectric polarization in the state of thermodynamic equilibrium should exhibit a \( 1/f^\alpha \) type behavior with \( \alpha \approx 1 \). Deviations from unity are determined by the weak frequency dependence of the ratio between dielectric losses and capacitance \( \tan \delta(f)/C(f) \).

Long relaxation times obtained in \( C-V \) and \( j-E \) time dependencies (Figs. 8.4,
8.5) clearly indicate, that system experiences equilibration process, which is often termed as physical aging. We found, that long time transient currents emphasizes non-Debye type polarization current relaxation. Its time dependency was nicely fitted by the Curie-von Schweindler law $j(t) = j_{\text{leak}} + j_0(t/1\text{sec})^{-n}$, where $n \approx 0.8$. It is natural to expect that FDR will not hold in such systems. In our measurements, voltage fluctuation spectral density $S_V$ was found to follow universal (voltage independent) $1/f^\alpha$ law with $\alpha \approx 1.5$. Since noise measurements were performed in times shorter than the equilibration time, short-term spectral analysis was also used to characterize 'instantaneous' Fourier harmonics. Analysis revealed that at fields close to dielectric breakdown, electrical noise was found strongly nongaussian.
Summary of enclosed papers


This paper presents the noise investigation results in a series of ultra thin giant magnetoresistors. We succeed in growing of La$_{0.75}$Sr$_{0.25}$MnO$_3$ with reproducible transport characteristics down to 40 Å. We believe that the internal stress caused by film-substrate lattice parameters mismatch is responsible for decreasing of metal-semiconductor transition temperature and relative broadening of transition region with the film thickness decreasing. Excess noise in all tested samples shows $1/f^\gamma$ spectral dependency, where $\gamma \approx 1 \pm 0.2$ and power of two dependency on bias current. In comparison with other metal oxide films, extremely high magnitude of normalized noise were observed. While noise magnitude and magnetoresistance increase with thickness decreasing, noise dependence on temperature shows very irregular behavior. Despite this, estimation of noise figures of merit - Noise Equivalent Temperature Difference (NETD) and Noise Equivalent Magnetic Field Difference (NEMFD) gives NETD of 3mK/$\sqrt{\text{Hz}}$ and NEMFD of 5mOe/$\sqrt{\text{Hz}}$ at 10 Hz in a wide thickness range above 100 Å. This observation allows to report about the possibility to tailor functional properties of the sensor material within 40 K range without loosing in performance.


In this paper we are presenting detailed study of $1/f$ type noise in La$_{0.8}$Sr$_{0.2}$MnO$_3$, La$_{0.75}$Sr$_{0.25}$MnO$_3$ and La$_{0.7}$Pb$_{0.3}$MnO$_3$ pulse laser deposited thin epitaxial films. We
chose those materials as most promising for uncooled sensors since they experience metal-semiconductor phase transition close to the room temperature. Similar to the other homogeneous conductors, excess noise has been found to be caused by resistance fluctuations. In this study we are demonstrating the effective reducing of electrical noise by ex situ annealing, while change in resistance or magnetoresistance was not observed. It was found that magnetic field of 7 kOe was not sufficient enough to change noise magnitude, while 17 % magnetoresistance were observed. Due to the similar temperature behaviour of resistance fluctuations and resistance in wide range near the phase transition the signal to noise ratio was found to be almost temperature independent. Film La$_{0.8}$Sr$_{0.2}$MnO$_3$ exhibits superior performances: the noise equivalent temperature difference (NETD) and magnetic field (NEMFD) difference are 100nK/$\sqrt{\text{Hz}}$ at 30 Hz and 75$\mu$Oe/$\sqrt{\text{Hz}}$ at 1 kHz correspondingly. The experimental observation of such sensitivity to the small magnetic field oscillations is presented.


This work was dedicated to exploitation of colossal magnetoresistive thin epitaxial films with basic formula of La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.2, 0.25$) and La$_{0.7}$Pb$_{0.3}$MnO$_3$ as the uncooled infra-red (IR) radiation sensors. La$_{0.8}$Sr$_{0.2}$MnO$_3$ 450 nm thick film was pulsed laser deposited onto LaAlO$_3$ single crystal substrate. It has been found to be optimum to make uncooled bolometer prototype due to the lowest excess noise magnitude. Bolometer possesses the responsivity $R = 1.9$ V/W, NEP = $3 \cdot 10^{-8}$W/$\sqrt{\text{Hz}}$, and detectivity D = $5 \cdot 10^6$cm$\sqrt{\text{Hz}}$/W at 30 Hz of the frame frequency. Prospective detectivity in micromachined microbolometer implied to be higher then $10^8$cm$\sqrt{\text{Hz}}$/W at 30 Hz frame frequency.

**Paper 4.** "Epitaxial La$_{0.7}$(Pb$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ thin CMR film room temperature bolometer" S.I. Khartsev, **Alvydas Lisauskas**, and Alex Grishin, in Magnetoresistive Oxides and Related Materials, edited by M. Rzchowski, M. Kawasaki, A.J. Millis, M. Rajeswari, S. von Molnar, Mat. Res. Soc. Proc. 602, JJ10.6 (1999).
With this paper we report on the method to obtain material with the maximum of TCR close to the room temperature by controlling the ratio $x$ in PLD made solid solution with basic formula of $\text{La}_{0.7}(\text{Pb}_{1-x}\text{Sr}_x)_{0.3}\text{MnO}_3$. The film of optimum composition $x = 0.37$ exhibits maximum of TCR = 7.4% K$^{-1}$ at 295 K. The epitaxial quality of films provides with relatively low excess noise magnitude.

As the result of this work, room temperature bolometer demonstrator was made. There is an observation, that bolometer made onto substrate exhibits complex responsivity behaviour with several relaxation times in the frequency and time domains. Bolometer possesses the responsivity $\mathcal{R} = 0.6$ V/W, NEP = $3 \cdot 10^{-8}$W/√Hz, and detectivity $D = 0.9 \cdot 10^7$cm√Hz/W at 30 Hz of the frame frequency.

**Paper 5.** "Tailoring the colossal magnetoresistivity: $\text{La}_{0.7}(\text{Pb}_{0.63}\text{Sr}_{0.37})_{0.3}\text{MnO}_3$ thin-film uncooled bolometer" **Alvydas Lisauskas**, S.I. Khartsev, Alex Grishin, Appl. Phys. Lett. 77, 756 (2000); 77, 3302 (2000).

With this paper we generalize our experience in tailoring of the material performance of colossal magnetoresistors towards the uncooled temperature sensor. The sensor performance of colossal magnetoresistors was compared with the best results published for modern materials used for uncooled bolometric applications.


In this paper we give more extended discussion about the utilization of CMR thin films as a room temperature bolometers. To compare the performance of different temperature sensors, we introduce, as a figure of merit, the ratio between temperature coefficient of resistance and normalized noise power $|\text{TCR}|/(\gamma/n)$.

**Paper 7.** "Colossal magnetoresistive $\text{La}_{0.7}(\text{Pb}_{1-x}\text{Sr}_x)_{0.3}\text{MnO}_3$ films for bolometer and magnetic sensor applications" **A. Lisauskas**, J. Bäck, S. I. Khartsev, A.M. Grishin, J. Appl. Phys. 89, 6961 (2001).

With this paper we show, that colossal magnetoresistor with good noise perfor-
mace could be also utilized as a weak magnetic field sensor.


We report on measurements of impedance of Au/PZT/LSMO/PtIr thin film vertical capacitors performed in the time domain. Instantaneous $C-V$ and $I-V$ characteristics have been recorded to study the relaxation of polarization. Transient current exhibited non-Debye type relaxation and been fitted to Curie-von Schweindler law with an exponent $n \approx 0.8$, while the power law $C \propto f^{-0.1}$ has been found in frequency dispersion of capacitance. Impedance fluctuation spectrum in the 'true leakage' and resistance degradation regimes was found to follow $f^{-1.5}$ dependence. The increase of voltage fluctuations in ferroelectric capacitor was observed approaching break down fields.


This paper extended results presented in Paper 1 with the study low frequency (10 Hz - 10 kHz) noise spectra. We found that for films, thicker than the critical thickness, excess noise spectra has $1/f^\alpha$ dependence with $\alpha = 1 \pm 0.2$. In films thinner than the critical one, on a background of $1/f$ noise, random telegraph like signals (TLS) with the Lorentzian spectra appear. Noise spectroscopy revealed that the relaxation process in 4.2 nm thick film is thermally activated with an energy gap of 20 meV at temperatures below 156 K and 78 meV at $T > 156$ K.

Paper 10. "Relaxation characteristics of Ag(Ta,Nb)O$_3$ interdigital capacitors" J.-H. Koh, A. Lisauskas, Alex Grishin, manuscript, to be submitted.

Relaxations of polarization currents and capacitance was studied in this work. We observed that the power low behavior of relaxation of polarization currents (Curie von Schweindler law) is followed up by power law in capacitance spectra and relaxations of capacitance in time domain. The power exponent for relaxation
in capacitance $m = 1 - n$ was found to be related with an exponent $n$ in current relaxation.

**Paper 11.** "Low frequency Noise Measurement setup” A. Lisauskas, *manuscript*

This is the report made for student laboratory work on noise measurements in manganite thin films. Paper describes low frequency noise measurement setup, noise calculation technique and gives instructions for $1/f$ noise measurements and briefly introduces to the main types of electrical fluctuations.
References


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