DC transport properties and microwave absorption in bulk ceramic sample and film of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta$: magnetic inhomogeneity effects

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Abstract. The DC transport properties and microwave absorption (at 41 GHz) are measured in a bulk ceramic sample and a film (220 nm thick) of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta$. The bulk sample has been cut from a target from which the film was pulsed-laser deposited. It is found that the temperature behavior of DC resistivity and magnetoresistance of the bulk sample is quite different from that of the film. This is attributed to oxygen depletion of the film as compared with the target. Below Curie temperature $T_C$, the film behaves like a highly inhomogeneous system of weak-connected ferromagnetic grains (or clusters). The microwave study has provided further data about inhomogeneity of the samples. It is found that a surface layer of the bulk sample has very low conductivity compared with the bulk. This can be explained by the oxygen depletion of the surface layer. The most important feature of doped cobaltates revealed in this study is the following: the microwave conductivity, which should be related mainly to the conductivity within the poor-connected grains, increases by the order of the magnitude at the transition to the ferromagnetic state. The increase is much greater than that of found in the reported DC measurements in doped cobaltates of the best crystal perfection. The found microwave effect is attributed to inherent magnetically inhomogeneous state of the doped cobaltates. Relaying on the results obtained it can be suggested that rather low magnetoresistance in the doped cobaltates as compared with that of the manganites is attributable to their more inhomogeneous magnetic state.

PACS numbers: 72.80.Ga, 73.50.Mx, 75.70.Ak, 64.75.+g, 81.15.Fg

Submitted to: J. Phys.: Condens. Matter

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1. Introduction

The hole-doped lanthanum cobaltates of the type La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (0 < $x$ ≤ 0.5) with perovskite-related structure have attracted much attention during the last five decades due to the range of novel magnetic and transport properties they show (see [1, 2, 3, 4, 5, 6, 7, 8, 9] and references therein). The system is important both for fundamental studies and for promising applications [10]. The undoped cobaltate LaCoO$_3$ ($x = 0$) is an insulator. In the intermediate range of Sr doping (0.3 < $x$ < 0.5) it is a high conductive metal, which shows ferromagnetism (FM) below Curie temperature $T_c = 240 \pm 10$ K [2, 3, 4, 6]. An interest in the doped cobaltates has quickened in recent years after discovery of, so called, colossal magnetoresistance (CMR) in the related FM perovskite oxides, named doped manganites, of the type La$_{1-x}$A$_x$MnO$_3$ (where $A$ is a divalent alkaline-earth element like Ca, Sr, Ba) (see reviews [11, 12, 13] as an introduction to the problem). In the doped manganite films, the magnetoresistance (MR), defined as $\delta(H) = [R(0) - R(H)]/R(0)$, was found to be more than 90% at fields $H$ about 60 kOe in the neighbourhood of room temperature. This has triggered intensive theoretical and experimental studies by a large number of scientific groups around the world. In spite of this, a clear understanding of the CMR is not yet available. In the Sr doped cobaltates, the MR magnitude is found to be much less (only a few percents). It is believed that elucidation of reasons of this large difference in MR behavior of manganites and cobaltates can be helpful for understanding of CMR nature.

It follows from the known studies [12, 13] that doped manganites are always magnetically inhomogeneous to some extent. The degree of inhomogeneity depends on the doping level and preparation conditions. More exactly, two main types of inhomogeneity sources in the doped manganites are distinguished at present: extrinsic and intrinsic. Extrinsic sources are due to various technological factors of sample preparation. They can cause chemical-composition inhomogeneity (for example, in an oxygen concentration), structural inhomogeneity (polycrystalline or granular structure) and others. Intrinsic ones are believed to be due to thermodynamical reasons and can lead to phase separation on two phases with different concentration of the charge carriers [12, 13]. The inhomogeneity effect on magnetic and transport properties of manganites is usually minimal at the optimal doping ($x \approx 0.33$) but can be significant at low doping level. Needless to say that any of the above-mentioned types of inhomogeneity is associated with perturbation of the magnetic order and, therefore, with magnetic inhomogeneity.

The types of inhomogeneity, outlined for manganites, reveal themselves in doped cobaltates as well [2, 3, 4, 5, 8, 9]. What’s more the cobaltates appear to be more prone to phase separation than doped manganites. The system La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ with 0.18 ≤ $x$ ≤ 0.5 shows evidence of phase separation. Beginning with low dopant concentration ($x > 0.1$) an inhomogeneous distribution of the Sr$^{2+}$ ions takes place. This results in the segregation of the material into hole-rich FM regions and a hole-poor semiconducting matrix. It was suggested [2] that this inhomogeneous state
should appear as, so called, magnetic cluster-glass phase. The cluster glass is some set of clusters, formed due to short-range FM ordering at the Curie temperature \( T_c \). The clusters are embedded in a non-ferromagnetic matrix. Below \( T_c \), cluster-glass system is expected to demonstrate spin-glass behavior for temperature decreasing. This suggestion was justified to some degree by AC susceptibility measurements \[2, 7\]. For this reason some of the scientific groups believed that cluster-glass state persists up to concentration \( x = 0.5 \) \[2, 7\]. By this is meant that the clusters remain isolated from one another up to this concentration and, therefore, this state does not have a long-range FM order. It is known, however, that volume fraction of the FM regions increases with the Sr concentration \[3, 9\]. At \( x > 0.25 \) the metallic FM regions percolate magnetically as well as conductively \[9\], that is a long-range FM order does occur in this system at high enough Sr concentration. The authors of references \[3, 8\] have arrived to the same conclusion. It should be taken into account, however, that inpenetrating hole-poor matrix and some isolated clusters in it persist to \( x = 0.5 \) \[4\].

From the aforesaid, it might be assumed that compound \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3-\delta \) is magnetically inhomogeneous in the whole range \( 0.18 \leq x \leq 0.5 \), where FM ordering manifests itself. This can lead to peculiar magnetic and transport properties. In studies of transport properties of FM perovskites, it is most common to use of direct current (DC) measurements. For doped manganites, however, the microwave studies were undertaken in several groups \[14, 15, 16\]. These have brought some interesting results and, in particular, have revealed that microwave conductivity is more sensitive than DC conductivity to the changes in magnetic state of manganites at the paramagnetic-ferromagnetic transition. In this way the microwave data disclose magnetic inhomogeneity in manganites. It can be expected that in the case of doped cobaltates the microwave study can bring some interesting data about their magnetic inhomogeneity and its sources as well. Some previous microwave studies of cobaltates have not come to our knowledge. All this motivate us to study transport properties in \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta \) not only through the use of DC measurements, but by measurements of microwave absorption as well. A choice of composition \( (x = 0.5) \) was determined to some extent by the fact that this compound is expected to find the most application in advanced technology \[10\].

A bulk ceramic sample and a film (prepared by pulsed-laser deposition) were studied. We have found that DC transport characteristics (magnitude and temperature behavior of the resistivity and these of the MR) are distinctly affected by magnetic inhomogeneity of the samples below Curie temperature \( T_c \). On the strength of these data it is concluded that the film studied is an inhomogeneous system of weak-connected FM grains (or clusters) at \( T < T_c \). The microwave absorption study has provided further data about inhomogeneity of the samples. In particular, it is found that a surface layer of the bulk sample has very low conductivity comparing with the bulk. This is explained by the surface oxygen depletion of the bulk sample. The DC method of transport measurements is not sensitive to this type of inhomogeneity when the oxygen-depleted layer is fairly thin.
The most important feature of doped cobaltates revealed in this study is the following: the microwave conductivity, which should be related mainly to the conductivity within the poor-connected grains, increases by the order of the magnitude at the transition to the FM state. The increase is much greater than that of found in the reported DC measurements in doped cobaltates of best crystal perfection, that is with the minimal effect of extrinsic sources of an inhomogeneity. Thus the found microwave effect can be safely attributed to inherent magnetically inhomogeneous state of doped cobaltates. Relaying on the results obtained it can be suggested that rather low MR in the doped cobaltates as compared with that of the CMR manganites is attributable to their more inhomogeneous magnetic state.

2. Experiment

The samples studied are the pulsed-laser deposited (PLD) film and the bulk sample (cut from a target from which the film was deposited). The disk-shaped ceramic target with a composition \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \) was prepared by a standard solid state reaction technique. The final annealing was done at temperatures 1000°C and 1200°C. X-ray diffraction does not reveal any inclusions of unreacted components in the target, suggesting that it was homogeneous in chemical composition. The target was polycrystalline with rather large grain size (in the range 40-70 \( \mu \)m). It was porous (as it usually is for this type of samples) with void content about 45%. The lattice parameter for the target indexed for a pseudo-cubic perovskite-like cell is found to be \( a_p = 0.383 \pm 0.001 \) nm, that agrees closely with measurements of reference [3].

The film (220 ± 20 nm thick) was grown on (001) oriented \( \text{LaAlO}_3 \) substrate. A PLD system with Nd-YAG laser operating at 1.06 \( \mu \)m was used to ablate the target. The pulse energy was about 0.39 J with a repetition rate of 12 Hz and pulse duration of 10 ns. A standard substrate arrangement normal to the laser plume axis was used. The other details of the PLD technique employed were described previously [17]. The film was deposited with a substrate temperature 880±5°C in an oxygen atmosphere at pressure about 8 Pa. The oxygen pressure in the PLD chamber was increased up to about \( 10^5 \) Pa after deposition, the film was cooled down to room temperature in this oxygen atmosphere.

The resistance of the samples as a function of temperature and magnetic field \( H \) (up to 20 kOe) was measured using a standard four-point probe technique. The available cryostat with a rotating electromagnet makes it possible to measure DC resistance with different directions of \( H \) relative to the plane of the film.

Microwave conductivity of the samples was determined at frequency \( \nu = 41 \) GHz from measurements of the reflection coefficient \( R_r \) for samples placed in a waveguide with \( 5.2 \times 2.6 \) mm\(^2\) cross-section. The samples were inclined at a 10° angle to the waveguide broad wall (an angle between the normal to the sample and longitudinal waveguide axis is \( \theta = 80^\circ \) in the plane of \( \vec{E} \), where \( \vec{E} \) is the vector of microwave electric field in the waveguide) [18]. The technique employed similar to that used in IR experiments.
in which a \( p \)-polarized beam has been incident on a specimen at a grazing angle. Such approach allows to enhance the sensitivity of reflection measurements. It was shown previously [20] that with a knowledge of complex refraction coefficients of a film, "\( n = \sqrt{\varepsilon \mu} \)\), and a substrate, "\( n_s = \sqrt{\varepsilon_s \mu_s} \)\), where \( \varepsilon, \mu \) and \( \varepsilon_s, \mu_s \) are complex dielectric permittivity and magnetic permeability of the film and the substrate, respectively), and their thicknesses \( d \) and \( d_s \), it is possible to calculate reflectivity coefficient for the plane wave. We have used relations \( \varepsilon = 1 + \sigma_{mw}/i\omega\epsilon_0 \) (where \( \sigma_{mw} \) is the microwave conductivity) for the films and \( \mu_s = 1 \) for dielectric substrate. Having experimental data for reflection coefficient \( R_r, \varepsilon_s, d \) and \( d_s \), it is possible to calculate with help of backward transformation the values of \( \sigma_{mw} \) and corresponding resistivity \( \rho_{mw} = 1/\sigma_{mw} \). At microwave studies the microwave surface resistance \( R_s = (\omega\mu\mu_0/2\sigma_{mw})^{1/2} \) is often considered as an important parameter. This can be calculated, based on \( \sigma_{mw} \) data for appropriate values of \( \mu \).

The reflectivity as a function of temperature has been measured using a microwave phase bridge in the 6 mm wavelength range. In practice, change of the signal microwave power reflected from the samples was measured. This change contains information about the sample conductivity variation. A calibration procedure (which was done by means of the high-\( T_c \) superconducting YBaCuO film at \( T = 77 \) K) allows us to determine the absolute values of the microwave conductivity in the samples studied with an accuracy which is believed to be within range \(-10\% \) to \(+100\% \). An “asymmetry” of maximal probable error results from non-linear dependence of \( R_r \) on \( \sigma_{mw} \). The calculated absolute values of \( \sigma_{mw} \) (or \( \rho_{mw} \)) depend essentially on the used value of permeability \( \mu \). We have taken \( \mu = 1 \) at such calculations. A discussion of appropriateness of this choice is presented in the next section of this paper. On the other hand, the relative temperature changes in \( R_r \) were measured with higher precision, which results in an accuracy of relative temperature changes in \( \sigma_{mw} \) about \( \pm 4\% \) for the bulk sample and \( \pm 10\% \) for the film.

3. Results and discussion

3.1. DC transport properties

The temperature dependence of DC resistivity, \( \rho(T) \), of the bulk ceramic sample is presented in figure 1a. The dependence agrees well with the known results on \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3-\delta \) for \( 0.3 \leq x \leq 0.5 \) [3, 4, 5]. The resistivity values correspond to the known data on the ceramic doped cobaltates as well [3]. The \( \rho \) values presented in figure 1a were calculated taking into account the porosity of the sample\( \dagger \), so that they present, within certain limits, the resistivity of compact material. In \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta \) with fairly perfect crystalline structure and \( \delta \) close to zero, the resistivity values are \( \dagger \) This was done in the simplest way using the fractional part (55\%) of actual cross-section of the sample at calculation of the sample resistivity. In the case of fairly homogenous pore distribution (as shown by SEM study of the sample) the error in calculated \( \rho \) values should not exceed about 10\%.
DC transport properties and microwave absorption in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta$

reported to be about 100 $\mu\Omega\text{ cm}$ (or even less) at the room temperature $[1, 4, 21]$. The higher value of $\rho$ in the sample studied is to be attributed to its polycrystalline structure and some oxygen deficiency. The ratio of resistances at 300 K and 4.2 K, is more than 2, that corresponds to the data of references $[1, 4]$ for the samples with fairly good crystal quality. The $T_c$ value for the sample studied was found to be about 250 K by AC susceptibility measurements $[22]$. It is seen in figure 1a that the $\rho(T)$ behavior is metallic ($d\rho/dT > 0$) in the whole temperature range investigated, below and above $T_c$. The $\rho(T)$ dependence exhibits a change of slope at $T_c$ as a result of spin disorder scattering. This is reflected by the temperature behavior of $d\rho/dT$ (figure 1a) which has a maximum near $T_c = 250$ K. Such behavior of $\rho(T)$ is typical in FM metals $[23]$. The point is that the resistivity of FM metal has a quite pronounced contribution from the electron scattering on spin disorder (apart from the usual contributions from crystal-lattice defects and electron-phonon scattering) $[23]$. This contribution represents, so called, magnetic part of the resistivity, $\rho_m(T, H)$, which depends on the magnetization. With a rise of magnetization at the transition to the FM state, $\rho_m$ drops appreciably, which is a reason for an enhanced resistivity decrease below $T_c$, when going from high to lower temperature. This takes place in the sample studied as well (figure 1a). The external magnetic field enhances the spin order, that leads to a decrease in the resistivity. That is why the FM metals are characterized by a negative MR. The negative MR of the ceramic sample is found to have a maximum absolute value at $T = T_c$ [$\delta(H) = 2.15 \%$ at $H = 20$ kOe]. It goes down rather steeply to $\delta(H) \ll 1\%$ for temperature deviating to either side from $T_c$. Such temperature behavior of MR is expected for the FM metals of fairly good crystal perfection.

We turn now to the DC conductivity behavior of the PLD film studied (figure 2a). This is quite different from that of the bulk sample. First, the resistivity is higher than in the bulk sample (compare with figure 1a). Second, $\rho(T)$ curve has a maximum at $T_p \approx 250$ K and a minimum at $T_m \approx 107$ K. A decrease in resistance below $T_c$ is rather small (by about 10 % from the maximum value). Third, the MR of the film is found to be less than in the bulk sample (a maximum value of $\delta(H)$ is about 0.8 % at $T \approx 230$ K and $H = 20$ kOe, as shown in figure 3).

Consider now the temperature behavior of the resistivity of the film more closely. The first thing that catches the eye is that for $T > T_p = 250$ K and for $T < T_m = 107$ K the temperature behavior is non-metallic ($dR/dT < 0$). This type of $\rho(T)$ behavior (that is a maximum near $T_c$ and a minimum about 100 K) is typical for cobaltates $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3-\delta$ with low doping level $0.2 \leq x \leq 0.3$ $[4]$, that is for low charge-carrier concentration. The appearence of this type of dependence in PLD film with a nominal composition $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta$ should be attributed to some considerable oxygen deficiency (large value of $\delta$), that can cause the significant decrease in the charge-carrier concentration $[21, 24]$. Beside reducing the number of carriers, the oxygen deficiency is connected with the presence of oxygen vacancies sites, which hinder the carrier motion. It was shown in studies $[21, 24]$ that for sufficiently high values of $\delta$ the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta$
films can be even insulating.

It should be mentioned, that ρ(T) dependence, shown in figure 2a (that is a maximum at $T = T_p$ and a minimum at low temperature) is typical for systems of FM grains (or clusters) with rather weak interconnection. For example, similar dependences were found in polycrystalline manganites [25, 26, 27]. For these compounds, the paramagnetic phase is non-metallic, and for this reason the temperature dependence of resistance has a peak at a temperature $T_p$ at which an infinite percolating ferromagnetic cluster is formed at the transition. The grain boundaries in FM perovskite oxides are usually poorly conductive or can be even dielectric. Therefore, in the limiting case, a polycrystalline sample is just a granular metal, that is a system of metal grains embedded in an insulator. The conductivity of granular metals is determined by the tunnelling of charge carriers through the boundaries between the grains. The tunnelling can be activated or non-activated, depending on the thickness of boundaries and the temperature. Real granular systems are inhomogeneous in strength of tunnelling barriers between grains and, therefore, in the probability of charge-carrier tunneling. These systems are actually percolating and their conductivity is determined by both intragrain and intergrain transport properties.

The conductivity of granular metal is conditioned by two processes: tunnelling and thermal activation of the charge carriers. If the activation energy $E_a$ is rather low, the conductivity at high enough temperature, $kT > E_a$, is non-activated. In this case the system behaves as a (“bad”) metal with a positive temperature coefficient of resistivity ($dR/dT > 0$). Since granular metals are percolating systems, their conductivity is determined by the presence of “optimal” chains of grains with maximal probability of tunnelling for adjacent pairs of grains forming the chain. These “optimal” chains have some weak high-resistive links. At low enough temperature the relation $kT < E_a$ can become true for these links, and, hence, the measured DC conductivity of the system will become activated.

We have considered here the most obvious reasons for appearance of the resistance minimum at low temperature in inhomogeneous FM systems. Some more specific models of this phenomenon in doped manganites are presented in references [26, 27]. The above-mentioned general reasons for the resistance minimum can be applied to the film studied as well. On the basis of our gained experience, we can safely assume that PLD cobaltate films obtained in the above-described conditions are polycrystalline. There is a reason to believe that distribution of oxygen vacancies in perovskite oxides is inhomogeneous. The vacancies are more likely to reside at the grain boundaries [15, 28], that increases the structural and magnetic inhomogeneity. Beside this, the doped cobaltates are believed to have an intrinsic source of inhomogeneity: the phase separation, that is a segregation of material into FM metallic clusters embedded in a hole-poor semiconducting matrix [2, 4, 7] (see discussion in Sec. II). In cobaltates with low charge-carrier concentration, the FM clusters are weakly connected or even isolated, so that the system can behave as a granular FM metal. The $R(T)$ dependences quite similar to figure 2a were observed previously in La$_{1-x}$Sr$_x$CoO$_{3-δ}$ with $0.2 \leq x \leq 0.3$ [4]. The authors of reference [4]
speculate that for this composition the metallic conduction is only established within interval \(100 \text{ K} < T < T_c\), but below \(100 \text{ K}\) the increasing population of low-spin Co(III) ions in the matrix reestablishes a non-metallic temperature dependence. May be this is a reason for the observed \(\rho(T)\) behavior in the film studied. In any case, however, it is evident from figure 2a that the clusters (or FM grains) in the film have a weak connectivity. For this reason the resistance shows only slight (10 \%) decrease at the transition to FM state. This change is far less than that in the bulk sample, which shows a twofold decrease in resistivity (figure 1a).

From the aforesaid, it appears that the film studied behaves as a system of weakly connected FM grains (or clusters). The MR data obtained support this viewpoint. First, a maximum value of the MR in the film near the temperature of transition to the FM state is less than that of in the bulk sample. This is quite reasonable, since the measured MR of a granular FM system near \(T_c\) should be less than an intrinsic intragrain MR in the cases that grains have poor interconnectivity. This obvious effect has been seen previously, for example, in polycrystalline films of doped manganite [29].

Second, in polycrystalline samples the significant contribution to MR comes from grain boundaries, and this contribution increases with decreasing temperature. Discussion of possible mechanisms of this extrinsic type of MR can be found in references [30, 31, 32]. The film studied shows indeed a continuous increase in MR for decreasing temperature (for the temperatures fairly below \(T_c\)) (figure 3). This is an expected behavior for polycrystalline samples with poor enough intergrain connectivity [30, 31]. In contrast with it, for cobaltate and manganite samples with fairly good crystal perfection or even for polycrystalline samples of these materials but with a good intergrain connectivity the MR has a peak near \(T_c\) and goes nearly to zero with decreasing temperature [3, 4, 20]. This effect has found a verification in this study as well for the bulk sample (see above). In summary, the DC resistance and MR of the film show that it makes a system of weakly connected grains (or clusters). This inhomogeneous phase state in the (nominally) high-doped cobaltate \((x = 0.5)\) should be attributed mainly to rather significant oxygen deficiency.

At the end of this subsection it should be added that the MR of the film is strongly anisotropic (figure 3). Although (as far as we know) nobody else has yet reported this effect in doped cobaltate films, the anisotropic MR is not surprising for PLD films of FM perovskite oxides [33]. In the present study it is found that the absolute values of the negative MR in fields parallel to the film plane are much above that of in the perpendicular fields (figure 3). Since conductivity of doped cobaltates increases with an enhancement of the magnetic order, this behavior just reflects the point that the magnetization increases more easily in a magnetic field parallel to the film plane. This MR anisotropy is connected with the FM state. For this reason it disappears for \(T > T_c\). This effect (which is not a main goal of this paper) is to be discussed in more detail elsewhere.
3.2. Microwave absorption measurements and comparison with DC transport properties

As stated above, the $\rho_{mw}$ values, obtained in the present microwave study, are deduced taking $\mu = 1$. Although some direct measurements of $\mu$ in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system for $0.2 \leq x \leq 0.5$ have not come to our knowledge, this choice seems to us as the most appropriate and credible. In FM metals $\mu$ is equal to unity above Curie temperature. Below $T_c$ it can be considerably larger than unity, but only for rather low frequencies. For frequency decreasing the value of $\mu$ decreases, so that at high enough frequency it is close to unity. This general for FM metals tendency is found to be true for related perovskite-like oxides as well. For example, in polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ the magnitude of $\mu$ decreases significantly for frequency above 1 MHz, so that at $\nu = 100$ MHz the magnitude of $\mu$ is only moderately greater than unity. It can be expected that at far higher frequency $\nu = 41$ GHz, used in this study, $\mu$ should be quite close to unity. Some additional support to this can be seen in the fact, that the best agreement between the DC and microwave resistivities in the film studied for $T > T_c$ has been found at $\mu = 1$ (see below). For $\mu > 1$ an agreement is much worse. In any case, even if $\mu$ is somewhat larger than unity in the samples studied it cannot effect essentially the main findings and conclusions of this paper outlined below.

A comparison of the temperature dependences of $\rho_{mw}$ and DC resistivity ($\rho$) for the bulk sample and the film can be made with figures 1 and 2. Let us begin with the bulk sample (figure 1). Its $\rho_{mw}(T)$ dependence is non-monotonic with a maximum at $T_p \approx 220$ K, so that the corresponding $R(T)$ behavior is non-metallic at $T > T_p$. This is in sharp contrast to the $\rho(T)$ dependence of the bulk sample (figure 1a). As discussed above, the non-monotonic $R(T)$ dependences with a maximum below $T_c$ are inherent in doped cobaltates with low density of the charge carriers and thus with the high resistivity. Indeed, the $\rho_{mw}$ values, estimated for $\mu = 1$, are found to be more than two orders of the magnitude greater than corresponding DC values of the resistivity, indicated in figure 1a. The skin depth in the bulk sample is about 80 $\mu$m at the used frequency. Therefore, the found $\rho_{mw}(T)$ behaviour is to be attributed to the properties of a rather thin surface layer of the bulk sample, which is poor of the charge carriers, most likely, due to an oxygen depletion. It is known that ceramic samples of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta$ are always oxygen deficient with $\delta$ up to 0.06. But even greater oxygen deficiency can be expected at the surface of the samples comparing with the bulk. This suggestion has been made previously in reference based on the specific features in the temperature curves of the AC susceptibility of ceramic $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta$. The microwave study in this paper supports this suggestion.

Contrary to the bulk sample, where the microwave absorption is confined solely to the surface skin-depth layer, the temperature behavior of $\rho_{mw}$ in the film (figure 2b) is determined by response of the whole film volume to the microwave action, since the skin depth is far larger than the film thickness. The maximal values of $\rho_{mw}$ in the film for $T > T_c$ (where $\mu$ is sure equal to unity) are found to be quite close to the
film DC resistivity (figure 2). The $\rho_{mw}(T)$ dependence has a peak at the nearly same temperature $T_p$ as the $\rho(T)$ curve, but it does not show a pronounced minimum at $T_m = 107$ K as the $\rho(T)$ curve does (figure 2). The most sharp distinction between the temperature behaviour of the microwave and DC resistivities, found in this study, is the following. It is seen in figure 2b that for temperature decreasing below $T_c$ the $\rho_{mw}$ magnitude decreases by a factor about ten. This change is really huge in comparison with the 10 % decrease in the film DC resistivity in the same temperature range (figure 2a).

The greater changes in $\rho_{mw}$ at the paramagnetic-ferromagnetic transition when compared with that of in the DC resistivity have been seen previously in the microwave [14, 16, 36] and IR optical [37] studies of polycrystalline doped manganites. It is apparent that this effect is typical of inhomogeneous perovskite oxides for electromagnetic waves of not too high frequency. In some cases [14, 36] the high-frequency resistivity is found to be far less than the DC resistivity in the whole temperature range studied (below and above $T_c$). In other cases [14, 36] the microwave resistivity is found to be nearly equal to the DC resistivity (and their temperature behaviour with a maximum at $T = T_p$ are found to be exactly the same) in the temperature range above and near $T_c$ (or $T_p$), and only below $T_p$ the microwave resistivity becomes far less than the DC one. The latter type of behaviour is found in this study of doped cobaltate $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta$.

The reported results of microwave and optical studies of doped manganites [14, 16, 36, 37] appear, at first sight, as inconsistent and bizarre from standpoint of Drude theory of optical properties of metals [38, 39]. According to that, for electromagnetic waves with low enough frequency ($\omega \ll 1/\tau$, where $\tau$ is the electron relaxation time in a conductor) the optical conductivity should not depend on the frequency and be equal to the DC conductivity. It is true, however, only for homogeneous systems. Consider this question in more detail. In doing so we shall use the more general term “optical conductivity” implying that this has the same meaning as the term “microwave conductivity” for low enough frequency. The point is that the DC and optical conductivities are determined by quite different physical processes. The DC conductivity is defined by the ability of the charge carriers to propagate through a conducting system. It is apparent that this ability is affected profoundly by any kind of structural or phase inhomogeneity, especially when the system is just some disordered mixture of metal and insulator. Take again as an example a granular FM metal with poor intergrain connectivity. At the transition to the FM state the intragrain conductivity of this inhomogeneous system can increase profoundly, but the measured DC conductivity of the whole sample can show only rather weak increasing due to the weak intergrain connectivity (see above an extended discussion of this matter). For this reason the absolute values and temperature dependences of the DC resistivity and MR in FM perovskite oxides depend crucially on preparation conditions, which determine the degree of inhomogeneity of samples. In addition, there can be the intrinsic source

\textsuperscript{§} It should be noted that the main uncertainty in the DC resistivity of the film studied is determined by an accuracy in the film thickness estimation. Taking this into account, the expected accuracy in the film DC resistivity is about $\pm 10\%$. 

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of inhomogeneity (the phase separation) which shows up even in single-crystal samples. And this source, as it appears from the reported studies, is more important in doped cobaltates than in manganites.

The optical conductivity is determined by the ability of metal to absorb the energy of the electromagnetic field. For low frequency $\omega < kT$ (microwave and IR range) the main contribution to it comes from classical absorption, at which the charge carriers are accelerated by the electric field of electromagnetic wave. The absorption ability is characterized by the processes of transformation of energy flux of electromagnetic field to a thermal flux through the scattering of the charge carriers on phonons, impurities and other lattice defects. In FM metals the electron scattering on the spin disorder can give an appreciable contribution to these processes.

Taking into account the DC transport properties of the film studied and results of the previous studies of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$, it can be safely assumed that the film is oxygen-depleted and inhomogeneous. With approaching and crossing $T_c$ when going from high to lower temperature the film transforms into magnetically inhomogeneous state of weakly connected FM clusters (or grains) together with some isolated FM clusters and an inpenetrating hole-poor insulating matrix. It is clear that the main contribution to the changes in light (or microwave) absorption and thus in the optical conductivity at this transition will be determined by formation of metallic FM regions even when they are not or poor connected to one another. In this way the changes in the optical absorption in doped cobaltates at the transition to the FM state reflect rather closely the corresponding changes in the intragrain (or intracluster) conductivity. In this study the approximately tenfold increase in the microwave conductivity is found at this transition, although the reported DC measurements of doped cobaltates have shown about threefold increase in the DC conductivity at most. This difference in the DC behavior is quite reasonable, since even cobaltate samples of the best crystal perfection are magnetically inhomogeneous owing to the above-mentioned inherent sources of inhomogeneity.

In summary, the changes in microwave conductivity at the transition to the FM state reflect more closely the real changes in intragrain conductivity of doped inhomogeneous perovskite oxides than their DC conductivity. At first glance the large (by the order of the magnitude) increase in the microwave conductivity at the transition to the FM state which is found in this study in La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ film should involve the corresponding high magnitude of the MR. This is not the case, however, since, as was mentioned above, the MR in inhomogeneous granular or cluster system, obtained by DC measurements, is always less than the actual intragrain (or intracluster) MR. This can be a plausible reason for the much lower MR magnitude in cobaltates in comparison with that of in CMR doped manganites. The known studies testify that doped cobaltates are prone to different types of inhomogeneity to a much greater extent than manganites.
Conclusions

We have studied DC transport properties and microwave absorption in the bulk ceramic sample and the film of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$. It is found that DC transport characteristics (magnitude and temperature behavior of the resistivity and these of the MR) are distinctly affected by magnetic inhomogeneity of the samples below Curie temperature $T_c$. Under gaining enough experimental and theoretical data on this matter, it is possible to apply the DC transport measurements to reveal a structural and magnetic inhomogeneity in FM perovskite oxides. Among other things, analysis of the DC transport data can be used for an assessment of the degree of inhomogeneity and for identification of specific types of inhomogeneities (such as the granular structure). It follows clearly from our DC measurements that the film studied is an inhomogeneous system of weakly connected FM grains (or clusters) at $T < T_c$.

On the other hand, however, a single method should not be enough for characterization of the inhomogeneity in FM perovskite oxides. The study of the microwave absorption has provided an expected support for this apparent truth. It is found, in particular, that a surface layer of the bulk sample has very low conductivity comparing with the bulk. This can be explained by the oxygen depletion of the surface layer. The DC method of transport measurements is not sensitive enough to this type of inhomogeneity when the oxygen-depleted layer is fairly thin. The most important feature of doped cobaltates revealed in this study is the following: the microwave conductivity, which should be related mainly to the conductivity within the poor-connected grains, increases by the order of the magnitude at the transition to the FM state. The increase is much greater than that of found in the reported DC measurements in doped cobaltates of the best crystal perfection, that is with the minimal effect of extrinsic sources of an inhomogeneity. Thus the found microwave effect can be attributed to magnetically inhomogeneous state which is believed to be inherent in the doped cobaltates for any doping level. Relaying on the results obtained it can be concluded that significantly lower MR in the doped cobaltates as compared with that of the CMR manganites can be attributed to their more inhomogenous magnetic state.

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DC transport properties and microwave absorption in $La_{0.5}Sr_{0.5}CoO_3-\delta$ 

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DC transport properties and microwave absorption in La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$

**Figure 1.** Temperature dependences of the resistivity, $\rho$, and its derivative, $d\rho/dT$, from DC measurements (a), and the microwave resistivity, $\rho_{mw}$, from the microwave measurements at 41 GHz (b) for the bulk sample of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$. The values of $\rho_{mw}$ are deduced taking $\mu = 1$.

**Figure 2.** Temperature dependences of the resistivity, $\rho$, from DC measurements (a) and the microwave resistance, $\rho_{mw}$, from the microwave measurements at 41 GHz (b) for the PLD La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ film. The values of $\rho_{mw}$ are deduced taking $\mu = 1$.

**Figure 3.** Magnetoresistance $\delta(H) = [R(0) - R(H)]/R(0)$ at $H = 20$ kOe for the fields $H_{||}$ and $H_{\perp}$, applied parallel and perpendicular to the film plane. In both cases the fields were perpendicular to the transport current. The solid line presents a B-spline fitting.

**Figures**
DC transport properties and microwave absorption in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta$
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Fig. 2 to paper Belevtsev et al.
Fig. 3 to paper Belevtsev et al.