Direct-current transport properties of and microwave absorption in a bulk ceramic sample and a film of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$: magnetic inhomogeneity effects

Direct-current transport properties of and microwave absorption in a bulk ceramic sample and a film of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$: magnetic inhomogeneity effects

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Abstract

The DC transport properties of and microwave absorption (at 41 GHz) in a bulk
ceramic sample and a film (220 nm thick) of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ are measured.
The bulk sample was cut from a target from which the film was also produced,
by pulsed-laser deposition. It is found that the temperature behaviours of the DC
resistivity and magnetoresistance (MR) of the bulk sample are quite different
from those of the film. This is attributed to oxygen depletion of the film as
compared with the target. Below the Curie temperature T_C, the film behaves
like a highly inhomogeneous system of weakly connected ferromagnetic grains
(or clusters). The microwave study provides further data on the inhomogeneity
of the samples. It is found that the 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 poorly connected grains,
increases by an order of magnitude at the transition to the ferromagnetic state.
The increase is much greater than that found in the reported DC measurements
on doped cobaltates of the highest crystal perfection. The microwave effect
found is attributed to an inherent magnetically inhomogeneous state of the
doped cobaltates. On the basis of the results obtained, it can be suggested
that the rather low MR in the doped cobaltates as compared with that of the
manganites is attributable to their more inhomogeneous magnetic state.

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1. Introduction

Hole-doped lanthanum cobaltates of the type $La_{1-x}Sr_xCoO_{3-\delta}$ ($0 < x \leqslant 0.5$) with perovskite-related structure have attracted much attention during the last five decades due to the range of novel magnetic and transport properties that they show (see [1–9] and references therein). This system is important both for fundamental studies and in view of its promise for 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 highly conductive metal, which shows ferromagnetism (FM) below the Curie temperature $T_C = 240 \pm 10$ K [2–4, 6]. Interest in the doped cobaltates has quickened in recent years following the discovery of so-called colossal magnetoresistance (CMR) in the related FM perovskite oxides, called doped manganites, of the type $La_{1-x}A_xMnO_3$, where A is a divalent alkaline-earth element like Ca, Sr, Ba (see the reviews [11–13] 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 of about 60 kOe in the neighbourhood of room temperature. This has triggered intensive theoretical and experimental study by a large number of scientific groups around the world. In spite of this, a clear understanding of CMR is not yet available. In the Sr-doped cobaltates, the magnitude of the MR is found to be much less (only a few per cent). It is believed that elucidation of the reasons for this large difference in MR behaviour between the manganites and cobaltates could be helpful for understanding the nature of CMR.

It follows from the existing 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 source in the doped manganites are distinguished at present: extrinsic and intrinsic. Extrinsic sources arise due to various technological factors in the sample preparation. They can cause chemical composition inhomogeneity (for example, in the oxygen concentration), structural inhomogeneity (polycrystalline or granular structure) and other inhomogeneities. Intrinsic sources are believed to arise for thermodynamical reasons and can lead to phase separation into two phases with different concentrations of the charge carriers [12, 13]. The effect of inhomogeneity on the magnetic and transport properties of manganites is usually minimal at optimal doping ($x \approx 0.33$) but can be significant at low doping levels. Needless to say, all of the above-mentioned types of inhomogeneity are associated with perturbation of the magnetic order and, therefore, with magnetic inhomogeneity.

The types of inhomogeneity outlined above for manganites reveal themselves in doped cobaltates as well [2–4, 7–9]. What is more, the cobaltates appear to be more prone to phase separation than doped manganites. The system $La_{1-x}Sr_xCoO_{3-\delta}$ with $0.18 \leqslant x \leqslant 0.5$ shows evidence of phase separation. Beginning at low dopant concentration ($x > 0.1$), an inhomogeneous distribution of the Sr^{2+} ions takes place. This results in 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 a so-called magnetic cluster-glass phase. The cluster glass is a 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, a cluster-glass system is expected to demonstrate spin-glass behaviour with decreasing temperature. This expectation was borne out to some degree by AC susceptibility measurements [2, 7]. For this reason, some scientific groups believed that the cluster-glass state persists up to concentration $x = 0.5$ [2, 7]. By this it is meant that the clusters remain isolated from one another up to this concentration and, therefore, this state does not exhibit a long-range FM order. It is known, however, that the volume fraction of the FM regions increases with the Sr

concentration [4, 9]. At $x > 0.25$ the metallic FM regions percolate magnetically as well as conductively [9]—that is, for high enough Sr concentration, long-range FM order does occur in this system. The authors of [3, 8] arrived at the same conclusion. It should be taken into account, however, that a pervasive hole-poor matrix with some isolated clusters in it persists to $x = 0.50$ [4].

From the aforesaid, it might be assumed that the compound La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ is magnetically inhomogeneous over the whole range $0.18 \leqslant x \leqslant 0.5$ where FM ordering manifests itself. This could lead to peculiar magnetic and transport properties. In studies of transport properties of FM perovskites, it is most common to use DC measurements. For doped manganites, however, microwave studies were undertaken by several groups [14–16]. These have produced 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 microwave study could produce some interesting data about their magnetic inhomogeneity and its sources as well. Previous microwave studies of cobaltates have not been made, to our knowledge. All of this motivates us to study transport properties in La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ not only through the use of DC measurements, but also by means of measurements of microwave absorption. The choice of the 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, PLD) were studied. We have found that DC transport characteristics (the magnitude and temperature behaviour of the resistivity and these of the MR) are distinctly affected by magnetic inhomogeneity of the samples below the Curie temperature T_C. On the strength of these data, it is concluded that the film studied is an inhomogeneous system of weakly connected FM grains (or clusters) at $T < T_C$. The microwave absorption study has provided further data about the inhomogeneity of the samples. In particular, it is found that the surface layer of the bulk sample has very low conductivity compared 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 poorly connected grains, increases by an order of magnitude at the transition to the FM state. The increase is much greater than that found in the reported DC measurements on doped cobaltates of the highest crystal perfection—that is, with the minimal effect of extrinsic sources of inhomogeneity. Thus the microwave effect found can be safely attributed to the inherent magnetically inhomogeneous state of doped cobaltates. From the results obtained, it can be suggested that the 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 a PLD film and a bulk sample (cut from the target which was used for producing the film by deposition). The disc-shaped ceramic target with the composition La$_{0.5}$Sr$_{0.5}$CoO$_3$ was prepared by a standard solid-state reaction technique. The final annealing was done at temperatures of 1000 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 μm). It was porous (as is usually the case for this type of sample) with a void content of about 45%. The lattice parameter for the target indexed with respect to a pseudo-cubic perovskite-like cell is found to be $a_p = 0.383 \pm 0.001$ nm, which agrees closely with the measurements of [3].

The film (220 ± 20 nm thick) was grown on (001)-oriented LaAlO$_3$ substrate. A PLD system with an Nd–YAG laser operating at 1.06 μm 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 of 880 ± 5 °C in an oxygen atmosphere at a pressure of about 8 Pa. The oxygen pressure in the PLD chamber was increased 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 cryostat used, with a rotating electromagnet, makes it possible to measure DC resistance with different directions of H relative to the plane of the film.

The 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 5.2×2.6 mm^2 cross-section. The samples were inclined at a $10°$ angle to the waveguide thick wall (the angle between the normal to the sample and the longitudinal waveguide axis is $\theta = 80°$ in the plane of $\vec{E}$, where $\vec{E}$ is the vector of the microwave electric field in the waveguide) [18]. The technique employed is similar to that used in IR experiments [19], in which a p-polarized beam is incident on a specimen at a grazing angle. Such approaches allow one to enhance the sensitivity of the reflection measurements. It was shown previously [20] that, with a knowledge of the complex refraction coefficients of a film, $n = \sqrt{\epsilon\mu}$, and a substrate, $n_s = \sqrt{\epsilon_s\mu_s}$ (where ϵ, μ and ϵ_s, μ_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 the reflectivity coefficient for a plane wave. We have used the relations $\epsilon = 1 + \sigma_{mw}/i\omega\epsilon_0$ (where σ_{mw} is the microwave conductivity) for the film and $\mu_s = 1$ for the dielectric substrate. Having experimental values of the reflection coefficient R_r, ϵ_s, d and d_s, it is possible to calculate, with the help of backward transformation, the values of σ_{mw} and the corresponding resistivity $\rho_{mw} = 1/\sigma_{mw}$. In microwave studies the microwave surface resistance $R_s = (\omega\mu\mu_0/2\sigma_{mw})^{1/2}$ is often considered an important parameter. This can be calculated from σ_{mw}-data for appropriate values of μ.

The reflectivity, as a function of temperature, has been measured using a microwave phase bridge in the 6 mm wavelength range. In practice, the change of the microwave power of the signal reflected from the samples was measured. This change contains information about the sample conductivity variation. A calibration procedure (which was done using a 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 the range -10 to $+100\%$. The 'asymmetry' of the maximal probable error results from the non-linear dependence of R_r on σ_{mw}. The calculated absolute values of σ_{mw} (or ρ_{mw}) depend strongly on the value used for the permeability μ. We have taken $\mu = 1$ in such calculations. A discussion of the 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 the relative temperature changes in σ_{mw} of about $\pm4\%$ for the bulk sample and $\pm10\%$ for the film.
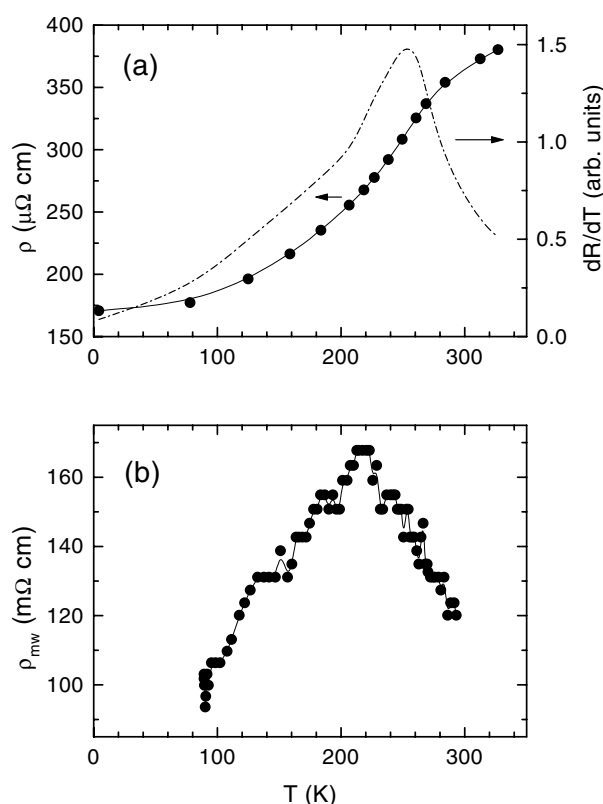
Figure 1. Temperature dependences of the resistivity, ρ, and its derivative, $d\rho/dT$, from DC measurements (*a*) and the microwave resistivity, ρ_{mw}, from the microwave measurements at 41 GHz (*b*) for the bulk sample of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$. The values of ρ_{mw} are deduced taking $\mu = 1$.

3. Results and discussion

3.1. DC transport properties

The temperature dependence of the DC resistivity, $\rho(T)$, of the bulk ceramic sample is presented in figure 1(*a*). The dependence agrees well with the known results on La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ for $0.3 \leqslant x \leqslant 0.5$ [3–5]. The resistivity values correspond to the known data on the doped ceramic cobaltates as well [3]. The ρ-values presented in figure 1(*a*) were calculated taking into account the porosity of the sample[5], so they represent, within certain limits, the resistivity of compact material. For La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ with fairly perfect crystalline structure and δ close to zero, the resistivity values are reported to be about 100 $\mu\Omega$ cm (or even less) at room temperature [1, 4, 21]. The higher value of ρ for the sample studied is to be attributed to its polycrystalline structure and some oxygen deficiency. The ratio of the resistances at 300 and 4.2 K is more than 2, which corresponds to the data of references [4, 6] for samples with fairly good crystal quality. The T_C-value for the sample studied was found to be about 250 K from AC susceptibility measurements [22].

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[5] This was done in the simplest way, using the fractional part (55%) of the actual cross-section of the sample in the calculation of the sample resistivity. In the case of fairly homogeneous pore distribution (as indicated by the SEM study of the sample), the error in the calculated ρ-values should not exceed about 10%.
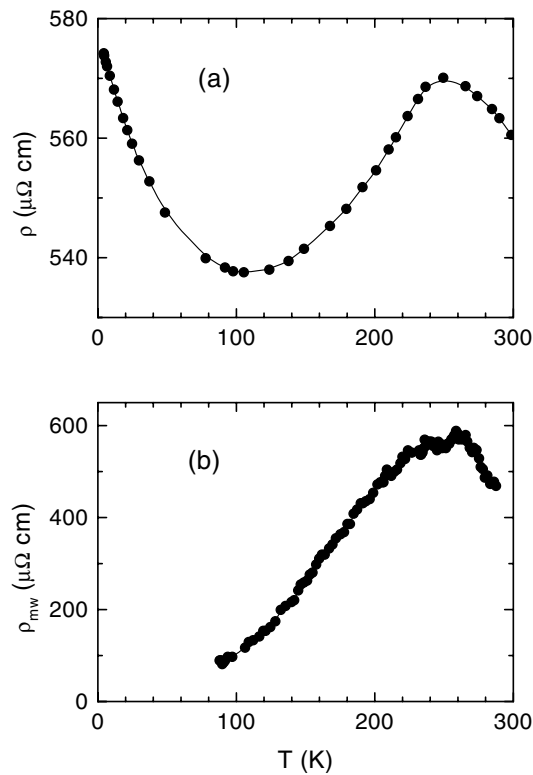
Figure 2. Temperature dependences of the resistivity, ρ, from DC measurements (*a*) and the microwave resistance, ρ_{mw}, from the microwave measurements at 41 GHz (*b*) for the PLD La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ film. The values of ρ_{mw} are deduced taking $\mu = 1$.

It is seen in figure 1(*a*) that the $\rho(T)$ behaviour is metallic ($d\rho/dT > 0$) over 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 behaviour of $d\rho/dT$ (figure 1(*a*)) which has a maximum near $T_C = 250$ K. Such behaviour of $\rho(T)$ is typical of FM metals [23]. The point is that the resistivity of FM metal has a quite pronounced contribution from the electron scattering on the spin disorder (in addition to the usual contributions from crystal lattice defects and electron–phonon scattering) [23]. This contribution represents the so-called magnetic part of the resistivity, $\rho_m(T, H)$, which depends on the magnetization. With the rise of magnetization at the transition to the FM state, ρ_m drops appreciably, which is one reason for the enhanced resistivity decrease below T_C, when going from high to lower temperature. This takes place in the sample studied also (figure 1(*a*)). The external magnetic field enhances the spin order, which 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 behaviour of the MR is expected for FM metals of fairly good crystal perfection.

We turn now to the DC conductivity behaviour of the PLD film studied (figure 2(*a*)). This is quite different from that of the bulk sample. First, the resistivity is higher than in the bulk sample (compare with figure 1(*a*)). Second, the $\rho(T)$ curve has a maximum at $T_p \approx 250$ K
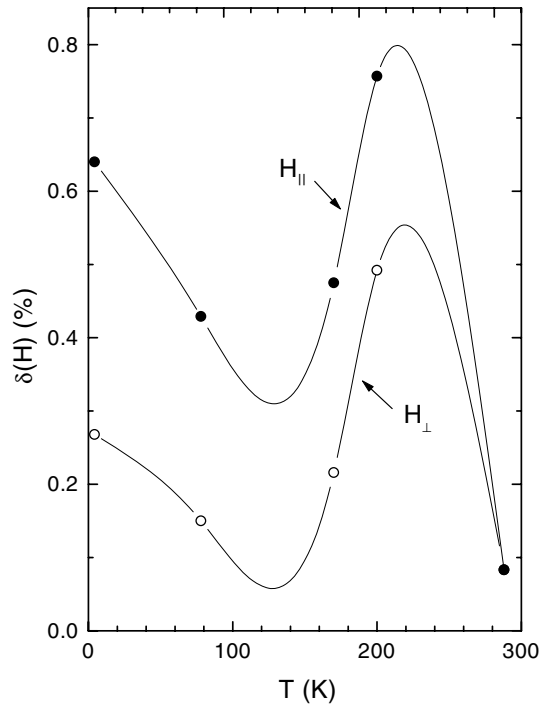
Figure 3. The MR, $\delta(H) = [R(0) - R(H)]/R(0)$, at $H = 20$ kOe for the fields $H_\parallel$ and $H_\perp$, applied parallel and perpendicular to the film plane. In both cases the fields were perpendicular to the transport current. The solid curve presents a B-spline fitting.

and a minimum at $T_m \approx 107$ K. The 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 (the maximum value of $\delta(H)$ is about 0.8% at $T \approx 230$ K and $H = 20$ kOe, as shown in figure 3).

We consider now the temperature behaviour of the resistivity of the film in more detail. The first thing that catches the eye is that for $T > T_p = 250$ K and for $T < T_m = 107$ K the temperature behaviour is non-metallic ($dR/dT < 0$). This type of $\rho(T)$ behaviour (that is, a maximum near T_C and a minimum at about 100 K) is typical for the cobaltates La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ with low doping levels, $0.2 \leqslant x \leqslant 0.3$ [4]—that is, for low charge-carrier concentrations. The appearance of this type of dependence in PLD film with a nominal composition La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ should be attributed to considerable oxygen deficiency (a large value of δ), which is known to be able to cause a 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 vacancy sites, which hinder the carrier motion. It was shown in the studies [21, 24] that for sufficiently high values of δ the La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ films can even be insulating.

It should be mentioned that the $\rho(T)$ dependence, shown in figure 2(a) (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 interconnections. For example, similar dependences were found for polycrystalline manganites [25–27]. For these compounds, the paramagnetic phase is non-metallic, and for this reason the temperature dependence of the resistance has a peak at the 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 even be 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 as regards the strengths of the tunnelling barriers between the grains and, therefore, also the probabilities of charge-carrier tunnelling. 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 ($\mathrm{d}R/\mathrm{d}T > 0$). 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 highly 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 the 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 [26, 27]. The above-mentioned general reasons for the resistance minimum can be applied to the film studied as well. On the basis of the experience that we have gained, we can safely assume that PLD cobaltate films obtained under the above-described conditions are polycrystalline. There is reason to believe that the distribution of oxygen vacancies in perovskite oxides is inhomogeneous. The vacancies are more likely to reside at the grain boundaries [15, 28], which increases the structural and magnetic inhomogeneity. Beside this, the doped cobaltates are believed to have an intrinsic source of inhomogeneity: phase separation—that is, a segregation of material into FM metallic clusters embedded in a hole-poor semiconducting matrix [2, 4, 7, 9] (see the discussion in section 1). In cobaltates with low charge-carrier concentration, the FM clusters are weakly connected or even isolated, so the system can behave as a granular FM metal. $R(T)$ dependences quite similar to those in figure 2(a) were observed previously in $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{CoO}_{3-\delta}$ with $0.2 \leqslant x \leqslant 0.3$ [4]. The authors of [4] speculate that for this composition the metallic conduction is only established within the interval $100\ \mathrm{K} < T < T_C$, but below 100 K the increasing population of low-spin Co(III) ions in the matrix reestablishes a non-metallic temperature dependence. Perhaps this is a reason for the observed $\rho(T)$ behaviour of the film studied. In any case, however, it is evident from figure 2(a) that the clusters (or FM grains) in the film have a weak connectivity. For this reason the resistance shows only a slight (10%) decrease at the transition to the FM state. This change is far less than that in the bulk sample, which shows a twofold decrease in resistivity (figure 1(a)).

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, the maximum value of the MR in the film near the temperature of transition to the FM state is less than that for 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 where grains have poor interconnectivity. This obvious effect has been seen previously, for example, in polycrystalline films of doped manganite [29]. Second, in polycrystalline samples a significant contribution to the MR comes from grain boundaries, and this contribution increases with decreasing temperature. Discussion of the possible mechanisms for this extrinsic type of MR can be found

in the references [30–32]. The film studied does indeed show a continuous increase in MR for decreasing temperature (for the temperatures well below T_C) (figure 3). This is an expected behaviour for polycrystalline samples with poor enough intergrain connectivity [30, 31]. In contrast, for cobaltate and manganite samples with fairly good crystal perfection and 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 [5, 6, 30]. This effect has been verified in this study for the film as well as for the bulk sample (see above). In summary, the DC resistance and MR of the film show that it is a system of weakly connected grains (or clusters). This inhomogeneous phase state in the (nominally) highly 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 observing 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 considerably above those in the perpendicular fields (figure 3). Since the conductivity of doped cobaltates increases with enhancement of the magnetic order, this behaviour 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 topic of this paper) will be discussed in more detail elsewhere.

3.2. Microwave absorption measurements and comparison with DC transport properties

As stated above, the ρ_{mw}-values obtained in the present microwave study are deduced taking $\mu = 1$. Although no direct measurements of μ in the La$_{1-x}$Sr$_x$CoO$_3$ system for $0.2 \leqslant x \leqslant 0.5$ have been made, to our knowledge, this choice seems to us the most appropriate and credible. For FM metals, μ is equal to unity above the Curie temperature. Below T_C it can be considerably larger than unity, but only for rather low frequencies. As frequency increases, the value of μ decreases, such that at high enough frequency it is close to unity [23]. This tendency, general for FM metals, is found to hold for related perovskite-like oxides as well. For example, for polycrystalline La$_{0.7}$Sr$_{0.3}$MnO$_3$ the magnitude of μ decreases significantly with frequency for frequencies above 1 MHz, such that at $\nu = 100$ MHz the magnitude of μ is only moderately greater than unity [34]. At the far higher frequency $\nu = 41$ GHz used in this study, μ can be expected to be quite close to unity. Some additional support for this expectation can be drawn from the fact that the best agreement between the DC and microwave resistivities for the film studied for $T > T_C$ has been found at $\mu = 1$ (see below). For $\mu > 1$ the agreement is much worse. In any case, even if μ is somewhat larger than unity for the samples studied, it cannot fundamentally affect the main findings and conclusions of this paper, outlined below.

A comparison of the temperature dependences of ρ_{mw} and the DC resistivity (ρ) for the bulk sample and the film can be made using 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 the corresponding $R(T)$ behaviour is non-metallic at $T > T_p$. This is in sharp contrast to the $\rho(T)$ dependence of the bulk sample (figure 1(a)). As discussed above, a non-monotonic $R(T)$ dependence with a maximum below T_C is inherent to doped cobaltate with a low density of charge carriers and thus with high resistivity. Indeed, the ρ_{mw}-values estimated for $\mu = 1$ are found to be more than two orders of magnitude greater than the corresponding DC values of the resistivity, indicated in figure 1(a). The skin depth in the bulk sample is about 80 μm at the frequency used. Therefore, the $\rho_{mw}(T)$ behaviour found is to be attributed to the properties of a rather thin surface layer of the bulk sample, which is poor in charge carriers, most probably

due to oxygen depletion. It is known that ceramic samples of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ are always oxygen deficient for δ up to 0.06 [4,9,35]. But even greater oxygen deficiency can be expected at the surface of the samples compared with the bulk. This suggestion has been made previously in [35] on the basis of the specific features of the temperature curves of the AC susceptibility of ceramic $La_{0.5}Sr_{0.5}CoO_{3-\delta}$. The microwave study in this paper supports the suggestion.

Contrary to the case for the bulk sample, where the microwave absorption is confined solely to the surface skin-depth layer, the temperature behaviour of ρ_{mw} in the film (figure 2(*b*)) is determined by the 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 ρ_{mw} in the film for $T > T_C$ (where μ is certainly equal to unity) are found to be quite close to the film DC resistivity (figure 2)[6]. The $\rho_{mw}(T)$ dependence has a peak at nearly the 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 sharpest distinction between the temperature behaviour of the microwave and DC resistivities found in this study is the following. It is seen in figure 2(*b*) that for temperature decreasing below T_C, the ρ_{mw}-magnitude decreases by a factor of about ten. This change is huge in comparison with the 10% decrease in the film DC resistivity in the same temperature range (figure 2(*a*)).

Greater changes in ρ_{mw} at the paramagnetic–ferromagnetic transition when compared with that in the DC resistivity have been seen previously in 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 [16, 37] the high-frequency resistivity is found to be far less than the DC resistivity over 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 behaviours, each 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 does the microwave resistivity become far less than the DC one. The latter type of behaviour is found in our study of doped cobaltate $La_{0.5}Sr_{0.5}CoO_{3-\delta}$.

The reported results of microwave and optical studies of doped manganites [14, 16, 36, 37] appear, at first sight, inconsistent and bizarre from the standpoint of the Drude theory of optical properties of metals [38, 39]. According to that, for electromagnetic waves with low enough frequency ($\omega \ll 1/\tau$, where τ is the electron relaxation time in a conductor), the optical conductivity should not depend on the frequency and should be equal to the DC conductivity. This is true, however, only for homogeneous systems. We consider this question in more detail. In doing so we shall use the more general term 'optical conductivity', taking this to have 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 governed 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 enormously, but the measured DC conductivity of the whole sample can show only a rather weak increase due to the weak intergrain connectivity (see above for 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 the preparation

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[6] It should be noted that the main uncertainty in the DC resistivity of the film studied is governed by the accuracy in the film thickness estimation. Taking this into account, the expected accuracy in the film DC resistivity is about ±10%.

conditions, which determine the degree of inhomogeneity of samples. In addition, there can be an intrinsic source 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 governed by the ability of the 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, in which the charge carriers are accelerated by the electric field of the electromagnetic wave [38, 39]. The absorption ability is characterized by the processes of transformation of the energy flux of the electromagnetic field to a thermal flux through the scattering of the charge carriers on phonons, impurities and other lattice defects [39]. In FM metals the electron scattering on the spin disorder can make an appreciable contribution to these processes.

Taking into account the DC transport properties of the film studied and the results of the previous studies of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ [2–4, 7–9], it can be safely assumed that the film is oxygen depleted and inhomogeneous. On approaching and crossing T_C when going from high to lower temperature, the film transforms into a magnetically inhomogeneous phase of weakly connected FM clusters (or grains) together with some isolated FM clusters and a pervasive 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 the formation of metallic FM regions even when they are not or are poorly 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 an approximately tenfold increase in the microwave conductivity is found at this transition, although the reported DC measurements on doped cobaltates have shown about a threefold increase in the DC conductivity at most [4–6]. This difference in DC behaviour 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, it appears that the large (by an order of 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 an inhomogeneous granular or cluster system, obtained by DC measurements, is always less than the actual intragrain (or intracluster) MR. This is a plausible reason for the much lower magnitude of the MR in cobaltates in comparison with that in CMR-doped manganites. The existing studies attest that doped cobaltates are prone to exhibiting different types of inhomogeneity to a much greater extent than manganites.

4. Conclusions

We have studied DC transport properties and microwave absorption in a bulk ceramic sample and a film of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$. It is found that the DC transport characteristics (the magnitude and temperature behaviour of the resistivity and these of the MR) are distinctly affected by the magnetic inhomogeneity of the samples below the Curie temperature T_C. When one has gained enough experimental and theoretical data on this matter, it is possible to apply the DC transport measurements to reveal 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 inhomogeneity (such as 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 relied upon for characterization of the inhomogeneity in FM perovskite oxides. The study of the microwave absorption has provided the anticipated firm support for this statement. It is found, in particular, that the 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 DC method of transport measurement 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 poorly connected grains, increases by an order of magnitude at the transition to the FM state. The increase is much greater than that found in the reported DC measurements on doped cobaltates of the best crystal perfection—that is, with the minimal effect of extrinsic sources of inhomogeneity. Thus the microwave effect found can be attributed to a magnetically inhomogeneous state which is believed to be inherent to the doped cobaltates for any doping level. From the results obtained, it can be concluded that the significantly lower MR in the doped cobaltates as compared with that of the CMR manganites can be attributed to their more inhomogeneous magnetic state.

References

[1] Raccah P M and Goodenough J B 1968 *J. Appl. Phys.* **39** 1209
[2] Itoh M, Natori I, Kubota S and Motoya K 1994 *J. Phys. Soc. Japan* **63** 1486
[3] Ganguly P, Anil Kumar P S, Santhosh P N and Mulla I S 1994 *J. Phys.: Condens. Matter* **6** 533
[4] Señaris-Rodriguez M A and Goodenough J B 1995 *J. Solid State Chem.* **118** 323
[5] Yamaguchi S, Taniguchi H, Takagi H, Arima T and Tokura Y 1995 *J. Phys. Soc. Japan* **64** 1885
[6] Mahendiran R and Raychaudhuri A K 1996 *Phys. Rev.* B **54** 16 044
[7] Mukherjee S, Ranganathan R, Anil Kumar P S and Joy P A 1996 *Phys. Rev.* B **54** 9267
[8] Anil Kumar P S, Joy P A and Date S K 1998 *J. Phys.: Condens. Matter* **10** L487
[9] Caciuffo R, Rinaldi D, Barucca G, Mira J, Rivas J, Señaris-Rodriguez M A, Radaelli P G, Fiorani D and Goodenough J B 1999 *Phys. Rev.* B **59** 1068
[10] Wu Wenbin, Wong K H, Mak C L and Choy C L 2001 *J. Phys. D: Appl. Phys.* **34** 1587
[11] Kaplan T A and Mahanti S D (ed) 1999 *Physics of Manganites* (New York: Kluwer)
[12] Dagotto E, Hotta T and Moreo A 2001 *Phys. Rep.* **344** 1
[13] Nagaev E L 2001 *Phys. Rep.* **346** 387
[14] Dominguez M, Bhagat S M, Lofland S E, Ramachandran J S, Xiong G C, Ju H L, Venkatesan T and Greene R L 1995 *Europhys. Lett.* **32** 349
[15] Yates K A, Cohen L F, Watine C, Tay T-N, Damay F, MacManus-Driscoll J, Freitas R S, Ghivelder L, Haines E M and Gehring G A 2000 *J. Appl. Phys.* **88** 4703
[16] Solin N I, Naumov S B and Samokhvalov A A 1998 *Fiz. Tverd. Tela* **40** 1881
[17] Usoskin A I and Chukanova I N 1992 *Sov. J. Low Temp. Phys.* **18** 233
[18] Gubin A I, Lavrinovich A A and Cherpak N T 2001 *Tech. Phys. Lett.* **27** 336
[19] Somal H S, Feenstra B J, Schützmann J, Kim Jae Hoon, Barber Z H, Duijin V H M, Menovsky A A, Palumbo M and van der Marel D 1996 *Phys. Rev. Lett.* **76** 1525
[20] Cherpak N T, Gubin A I and Lavrinovich A A 2001 *Telecommun. Radioeng.* **55** 81
[21] Sucharita M, Aggarwal S, Dhote A M, Ramesh R, Krishan A, Keeble D and Poindexter E 1997 *J. Appl. Phys.* **81** 3543
[22] Beznosov A B, Pal-Val P P, Belevtsev B I, Pal-Val L N, Ishchuk V M, Chukanova I N and Deineka T G 2001 *Euro-Asia Symp. on Trends in Magnetism (Ekaterinburg, Russia)* p 365 (book of abstracts)
[23] Vonsovsky S V 1971 *Magnetism* (Moscow: Nauka)
[24] Liu J-M and Ong C K 1998 *J. Appl. Phys.* **84** 5560
[25] Mahendiran R, Mahesh R, Raychaudhuri A K and Rao C N R 1996 *Solid State Commun.* **99** 149
[26] de Andrés A, Garcia-Hernández M and Martinez J L 1999 *Phys. Rev.* B **60** 7328

[27] Auslender M I, Rozenberg E, Kar'kin A E, Chaudhuri B K and Gorodetsky G 2001 *J. Alloys Compounds* **326** 81

[28] Akhter Hossain A K M, Cohen L F, Kodenkandeth T, MacManus-Driscoll J and Alford N McN 1999 *J. Magn. Magn. Mater.* **195** 31

[29] Rivas J, Hueso L E, Fondano A, Rivadulla F and López-Quintela M A 2000 *J. Magn. Magn. Mater.* **221** 57

[30] Gupta A 1998 *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides* ed C N R Rao and B Raveau (Singapore: World Scientific) pp 189–205

[31] Hwang H Y, Cheong S-W, Ong N P and Batlogg B 1996 *Phys. Rev. Lett.* **77** 2041

[32] Evetts J E, Blamire M G, Mathur N D, Isaac S P, Teo B-S, Cohen L F and MacManus-Driscoll J L 1998 *Phil. Trans. R. Soc.* A **356** 1593

[33] Belevtsev B I, Krasovitsky V B, Naugle D G, Rathnayaka K D D, Parasiris A, Surthi S R, Pandey R K and Rom M A 2001 *Phys. Status Solidi* a **188** 1187

[34] Wang J, Ni G, Gao W, Gu B, Chen X and Du Y 2001 *Phys. Status Solidi* a **183** 421

[35] Anil Kumar P S, Nair S P N, Alias J P and Date S P 1998 *J. Mater. Chem.* **8** 2245

[36] Lofland S E, Dominguez M, Tyagi S D, Bhagat S M, Robson M C, Kwon C, Trajanovic Z, Takeuchi I, Ramesh R and Venkatesan T 1996 *Thin Solid Films* **288** 256

[37] Kim K H, Gu J Y, Choi H S, Eom D J, Jung J H and Noh T W 1997 *Phys. Rev.* B **55** 4023

[38] Ziman J M 1972 *Principles of the Theory of Solids* (Cambridge: Cambridge University Press)

[39] Noskov M M 1983 *Opticheskie i Magnetoopticheskie Svoistva Metallov (Optical and Magneto-Optical Properties of Metals)* (Sverdlovsk: Ural Scientific Centre of the Academy of Sciences of the USSR)