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Low-temperature nonlinear effects in the conductivity of lightly doped cuprates La$_2$$_{−x}$Sr$_x$CuO$_4$ in antiferromagnetic state

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Low-temperature conductivity of antiferromagnetic cuprates La$_2$$_{−x}$Sr$_x$CuO$_4$ prepared by solid-phase synthesis was investigated. The concentration of strontium in the samples was 0.01, 0.005 and 0.001. In the temperature range $T < 100$ K for all the samples the conduction mechanism corresponded to 3D variable-range hopping. For $T > T_N$ (where $T_N$ is the Neel temperature) a transition to the metallic type of conductivity was observed. Nonlinear effects in low-temperature conductivity, magnetoresistivity, as well as current-controlled negative differential resistance were found. It was established that the nonlinear behavior of conductivity intensified with decreasing the strontium concentration. For temperatures $T < 10$ K, the effect of positive magnetoresistance was observed. It is suggested that this effect can be attributed to the presence of a new low-temperature magnetic phase (spin density waves).

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Introduction

Since the discovery of high-temperature superconductivity, study of cuprate superconductors (HTSC) remains one of the most important fundamental problems of solid state physics. For a long time (over 25 years), the focal point of the study of HTSC cuprates was the quest for the mechanism of high-temperature superconductivity. Despite the significant progress in this area, the exact nature of superconductivity in these compounds is still not clear. In recent years, more attention has been attracted to the cuprates in underdoped state. It is expected that their unusual properties, such as the evolution of the pseudogap state or change in the dynamic coherence length of incommensurate spin fluctuations with changing the doping level, may provide a key to understanding the nature of high-temperature superconductivity. Numerous experiments on neutron scattering and photoemission have provided detailed information on the evolution of the spin and electronic subsystems upon increasing the concentration of charge carriers in copper oxides. Nevertheless, the mechanism of metal-insulator transition in these systems remains a subject of debate. To date, it is generally accepted that the phase separation (PS), which is intrinsic for cuprates, creates optimal conditions for the transition from the insulating state to the normal and superconducting states. However, no consensus on the mechanism and the nature of the PS in cuprates has yet been reached. Different studies have suggested a variety of models: superconducting drops in a dielectric matrix, stripes, as well as more complex mechanisms.

In order to obtain a better idea of the scenario for the transition from a Mott insulator to metallic conductivity, a systematic study of the transport properties of cuprates in the antiferromagnetic (AFM) state with a low concentration of impurity is required. The most complete studies of weakly doped cuprates have been conducted on the La$_2$$_{−x}$Sr$_x$CuO$_4$ system. The lowest concentration of strontium in all the cases known to us was $x = 0.01$. However, most of the studies of lightly doped La$_2$$_{−x}$Sr$_x$CuO$_4$ in the dielectric state have been performed for $x \geq 0.02$, when the long-range AFM order has already been destroyed, and there are only strong AFM correlations.

In the present paper we investigated the low-temperature conductivity of ceramic samples of La$_2$$_{−x}$Sr$_x$CuO$_4$ with lower strontium content: $x = 0.001$, 0.005, and 0.01. The aim of this work is to study the nonlinear effects in the conductivity at low temperatures. The main attention is paid to the potential impact of the structural disorder associated with the spatial distribution of strontium impurities on the low-temperature conductivity. Investigation of the mechanisms of nonlinear effects in the conductivity of the HTSC is of interest not only for solving the fundamental problems of high-temperature superconductivity, but also for a number of applications. For example, the systems in which the current-voltage characteristics (CVC) exhibit a region of negative differential resistance (NDR) are of interest for a number of technical applications. A large body of theoretical and experimental work is devoted to the quest for the conditions at which NDR can arise as well as for the systems in which these conditions can be realized. It is known that one of the conditions for NDR is the presence of impurities, defects, or inhomogeneities of any kind, which create a microscopically inhomogeneous electric field distribution inside the sample. In this regard, alloyed ceramic HTSC...
cuprates are promising materials. Due to the inherent for cuprates thermodynamic PS, these compounds have the so-called intrinsic inhomogeneities, which originate due to the intrinsic nature of a strongly correlated state of the electronic system.

The parent compound of \( \text{La}_2\text{Sr}_x\text{CuO}_4 \) is the stoichiometric lanthanum cuprate \( \text{La}_2\text{CuO}_4 \), which is a hard AFM Mott-Hubbard insulator with a Neel temperature \( T_N \approx 320 \text{ K} \).\(^9\) Alloying \( \text{La}_2\text{CuO}_4 \) with an excess of oxygen or partially substituting the lanthanum atoms with divalent alkaline metals (Ca, Sr or Ba) creates charge carriers (holes) and leads to the suppression of long-range AFM order (decrease in \( T_N \)). According to the phase diagram,\(^{10}\) \( \text{La}_2\text{Sr}_x\text{CuO}_4 \) remains an insulator for \( x < 0.05 \). In the low-temperature limit \( (T \rightarrow 0) \), the AFM ordering persists up to the strontium concentration \( x = 0.02 \). The concentration range \( 0.02 < x < 0.05 \) is the region of strong AFM correlations.

Previously, we have investigated the conductivity of single-crystal \( \text{La}_2\text{CuO}_4\delta \) in the AFM state.\(^{11-15}\) The values of \( T_N \) in these samples were in a fairly wide range of temperatures from 160 to 290 K. References 11–15 have noted the anomalies in the low-temperature behavior of conductivity, which has been interpreted as a manifestation of the competition between the localization and conductivity (or superconductivity) associated with the phase separation into the AFM phase with \( \delta = 0 \) and the oxygen-reach \( \delta > 0 \) superconducting phase. As discussed in Ref. 11, the PS in \( \text{La}_2\text{CuO}_4\delta \) cuprates, most probably, does not originate from one particular mechanism. The nature of PS may depend on various circumstances, including the degree of doping. The results of our studies have demonstrated the ability to identify structural heterogeneity in HTSC based on the known phenomena of the competition between localization and superconductivity in inhomogeneous systems.\(^{11-15}\) The same kind of structural heterogeneity can be expected in lightly doped \( \text{La}_2\text{Sr}_x\text{CuO}_4 \) cuprates.

We assume that due to the very low concentration of strontium in addition to the general (intrinsic) heterogeneity originating from the PS, the irremovable heterogeneity associated with an external (extrinsic) factor can appear in the originating from the PS, the irremovable heterogeneity associated with an external (extrinsic) factor can appear in the phenomena of the competition between localization and superconductivity (or superconductivity) associated with the phase separation into the AFM phase with \( \delta = 0 \) and the oxygen-reach \( \delta > 0 \) superconducting phase. As discussed in Ref. 11, the PS in \( \text{La}_2\text{Sr}_x\text{CuO}_4 \) cuprates, most probably, does not originate from one particular mechanism. The nature of PS may depend on various circumstances, including the degree of doping. The results of our studies have demonstrated the ability to identify structural heterogeneity in HTSC based on the known phenomena of the competition between localization and superconductivity in inhomogeneous systems.\(^{11-15}\) The same kind of structural heterogeneity can be expected in lightly doped \( \text{La}_2\text{Sr}_x\text{CuO}_4 \) cuprates.

Method of sample preparation

Samples were produced and tested at the Department of Magnetochemistry at St. Petersburg University. Ceramic \( \text{La}_2\text{Sr}_x\text{CuO}_4 \) samples were prepared by standard solid phase synthesis. Reagents used for production of \( \text{La}_2\text{Sr}_x\text{CuO}_4 \) oxides were \emph{purissimum speciale} grade. Stoichiometric mixture of the starting reagents (lanthanum and strontium carbonate) were preliminarily calcined in air at \( T = 1073 \text{ K} \) to remove the adsorbed water and carbon dioxide. The magnetic susceptibility and emission spectral analysis data confirmed the absence of ferromagnetic impurities, which could distort the measurement results, in the starting reagents. A stoichiometric mixture of the corresponding oxides and carbonates, which was calculated according the reaction equation

\[
(2-x)\text{La}_2\text{O}_3 + 2x\text{SrCO}_3 + 2\text{CuO} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{La}_2\text{Sr}_x\text{CuO}_4 + 2x\text{CO}_2,
\]

was thoroughly grinded in an agate mortar for 1.5 h. Afterwards, the resulting mixture was cold pressed into pellets using a mold made of organic glass. The pellets were placed in a corundum crucible and calcined in air in a muffle furnace at 850°C during 18 h. Since it has been established earlier\(^17\) that a rapid temperature rise leads to melting of the initial mixture of components (copper oxide II \( (3d^9 \) decomposes into \( \text{Cu}_2\text{O} \) and \( \text{O}_2 \)), the first calcination step was performed at low temperature with a gradual temperature increase of \( 0.5 \text{ °C/min} \). The synthesis temperature (850°C) at the first stage was selected to be lower than the generally accepted value in order to ensure decomposition of strontium carbonate while reducing the risk of melting the sample. After the first stage of the synthesis, X-ray phase analysis (XRPA) was carried out using the patterns from the catalog X-Ray Diffraction Data Cards, ASTM. According to the XRPA data, in addition to the reflection lines corresponding to the standard structure of the type \( \text{K}_2\text{NiF}_4 \), two intense lines corresponding to the initial lanthanum oxide were observed in the diffractograms. This indicated that during the first step of the synthesis, complex oxides had already been formed as a result of the solid-phase reaction. However, the reaction was not completed yet. Therefore, further calcination was carried out at a higher temperature. In the second step of the synthesis, the rate of temperature increase remained the same, and the calcination temperature was set to 920°C (4 h). Then the temperature was further raised to 950°C (calcination time at 950°C was 20 h) and then to 960°C (calcination time at 960°C was 24 h). As a result, the total calcination time in the second step of the synthesis was 48 h.

After the second stage of the synthesis, according to the XRPA data, only the reflection lines corresponding to the structure of \( \text{K}_2\text{NiF}_4 \) type were observed in the diffractograms. The unit cell parameters of the obtained structure were: \( a = 3.8 \text{ Å}, c = 12.19 \text{ Å} \) (for \( \text{La}_{1.995}\text{Sr}_{0.005}\text{CuO}_4 \)) and \( a = 3.73 \text{ Å}, c = 12.25 \text{ Å} \) (for \( \text{La}_{1.99}\text{Sr}_{0.01}\text{CuO}_4 \)). These values are consistent with those from the catalog Powder Diffraction Files (PDF) for the tetragonal layered structure \( \text{K}_2\text{NiF}_4 \) as well as with literature data for this structure. Thus, according to XRPA, the complex oxides obtained in this work were homogeneous and exhibited a tetragonal
dependence of magnetic susceptibility as well as the conduc-

tivity of the samples was determined using a scanning elec-
tron microscope Cam Scan. The accuracy of determining the

elemental composition of the samples, and the composition

of individual phases were determined using X-ray microanalysis

of three La$_{2-x}$Sr$_x$CuO$_4$ samples. The accuracy of determining the

composition of the samples, and the composition

diameter was 1 μm. The penetration depth of the radiation

was 3–5 μm. A typical micrograph of the sample La$_{1.99}$Sr$_{0.01}$

CuO$_4$, obtained using a scanning electron microscope is

shown in Fig. 1. It can be seen that the average ceramic grain

size is below 1 μm. The beam of radiation scanned the entire

sample surface, followed by integral analysis. The reproduc-
bility of the analysis results at several points on the sample

indicated its high reliability. The lanthanum and copper con-
tent was determined using an EDS spectrometer LINK

AN-10000. The content of strontium was determined by a

highly sensitive WDS spectrometer MIKROSPEC in five

different regions of the sample. Table 1 shows the results of

X-ray microanalysis of three La$_{2-x}$Sr$_x$CuO$_4$ samples with

$x = 0.001, 0.005, \text{ and } 0.01$.

The data presented in Table 1 show that the strontium

content in the sample La$_{1.99}$Sr$_{0.01}$CuO$_4$ matched the specified

value ($x = 0.01$), while in the samples of La$_{1.999}$Sr$_{0.001}$CuO$_4$

and La$_{1.995}$Sr$_{0.005}$CuO$_4$ the strontium content in the test areas

was approximately 0.002. This indicates that the spatial

disorder in these samples is higher than in the samples

with $x = 0.01$.

The pellets of La$_{2-x}$Sr$_x$CuO$_4$ with the diameter of ca. 10

mm obtained in the synthesis were diced into cuboid-shaped

samples using a diamond cutter. The length of the samples

was 7–8 mm with the cross section of ca. 2 × 1.5 mm. These

samples were used for the measurements of temperature
dependence of magnetic susceptibility as well as the conduc-
tivity measurements in zero and finite magnetic fields.

Measurement results

The temperature dependence of the magnetic suscepti-
bility $\chi(T)$ for three samples of La$_{2-x}$Sr$_x$CuO$_4$ was measured

using a Faraday magnetometer in a magnetic field of 0.83 T.

The transition temperature into the AFM state determined by

the peak position on the curve $\chi(T)$ was 212, 265, and 193 K

for the samples with the strontium concentration $x$ equal

$0.001, 0.005, \text{ and } 0.01$, respectively (Fig. 2). The dependence

$\chi(T)$ shown in Fig. 2 indicates that the transition to the AFM

state is smeared in temperature, hence demonstrating certain

magnetic inhomogeneity of the samples. A comparison of the

obtained transition temperature into the AFM state with the

known phase diagram for La$_{2-x}$Sr$_x$CuO$_4$ (Ref. 10)

(Fig. 3) showed that the transition to the AFM state in the

La$_{1.999}$Sr$_{0.001}$CuO$_4$ samples occurred at a significantly lower

temperature (212 K) than that expected from the phase dia-

gram. At the same time, the magnetic state of the samples

with higher strontium contents ($x = 0.005$ and 0.01) corre-
sponds well to the phase diagram. In order to determine the

degree of magnetic homogeneity of the samples, the mag-

netic susceptibility measurements were carried out on five

different samples for each of the three concentrations. For all

the concentrations, a small spread in $T_N$ was observed, which

was ±7% (for $x = 0.001$ and 0.01) and ±4% (for $x = 0.005$).

Substantial deviation of the $T_N$ values downwards from the

AFM transition line on the phase diagram was found only

for the samples with a minimum content of strontium

$x = 0.001$. The deviation was about 90 K and could not be

associated with the magnetic inhomogeneity of the samples,

which was recorded by the magnetic measurements.

Using the obtained values of Neel temperature and the

data from Ref. 18, we can estimate the average number of

holes per copper atom. For samples with $x = 0.001$ and 0.01

it was 0.00552 and 0.00654, respectively (Table II). It seems

surprising that upon a ten-fold decrease in the concentration

of strontium in the furnace charge, the value of $T_N$ and the

FIG. 1. Micrograph of a La$_{1.99}$Sr$_{0.01}$CuO$_4$ ceramic sample obtained using a

scanning electron microscope.

FIG. 2. Temperature dependence of the magnetic susceptibility for three

La$_{2-x}$Sr$_x$CuO$_4$ samples in a magnetic field of 0.83 T.
hole concentration in the sample with $x = 0.001$ were just slightly changed as compared to the sample with $x = 0.01$. The Neel temperature has increased by $10\%$, and the hole concentration decreased by about $16\%$. These data indicate that there are localized regions in the La$_{1.999}$Sr$_{0.001}$CuO$_4$ samples, in which the concentration of strontium may be substantially higher than not only $0.001$, but also $0.002$ measured by X-ray microanalysis (Table 1) in the test parts of the sample. Thus, the results of X-ray microanalysis and magnetic measurements show that the decrease in strontium concentration is accompanied by an increase in the degree of structural disorder associated with non-uniform bulk distribution of strontium. Among the all investigated samples, the samples with a minimum content of strontium ($x = 0.001$) were found to be the most heterogeneous. Manifestation of structural disorder should also be expected in the behavior of the low-temperature conductivity.

For resistance measurements, four samples with known values of $T_N$ and various degrees of doping strontium were used. The resistance measurements were carried out in four-probe geometry in the current-driven regime. Contacts to the samples were made using silver paste. The data on the temperature dependence of the resistivity for three samples with different content of Sr, which were obtained at a current $J = 100$ $\mu$A, are shown in Fig. 4. At temperatures below $100$ K, all the samples obeyed the Mott law for 3D variable-range hopping conductivity:

$$ R(T) \propto \exp\left((T_0/T)_1/4\right). $$

Upon decreasing temperature, there was a marked deviation from the Mott law towards a lower resistance. For a fixed current of $100$ $\mu$A, as the concentration of strontium decreased, the temperature at which deviation from the Mott law begins was observed to shift toward higher temperatures, and the temperature range of validity of the Mott law narrowed. For $T > T_N$, a transition to the metallic conductivity was observed in all the samples. This transition is consistent with the well-known theoretical concepts and some experiments. According to these concepts, the AFM order enhances the localization of holes, while thermal excitation destroys the AFM order and causes the delocalization of carriers. Therefore, above $T_N$ the system may approach the metallic state upon increasing temperature.

Using the experimental values of $T_0$ and the theoretical expression $kT_0 \approx 16/[N(E_F)L_e]^{1/4}$, it is possible to estimate the localization length $L_e$ from the charge-carrier density of states in La$_2$CuO$_4$ at the Fermi level $N(E_F) = 2.8 \times 10^{26}$ $\text{J}^{-1} \text{m}^{-3}$. Table 2 shows the Neel temperatures, hole concentration, and average localization length $L_e$, which were calculated using the data of resistivity measurements at a current $J = 100$ $\mu$A (Fig. 4). For all the samples, the average length of localization was comparable with the lattice parameters in the plane CuO$_2$.

It should be noted that despite the close values of charge-carrier density in the samples with $x = 0.01$ and $0.001$ obtained from the magnetic measurements, the localization length $L_e$ was considerably different in these samples: $L_e$ in the La$_{1.999}$Sr$_{0.001}$CuO$_4$ samples was substantially smaller than that in La$_{1.995}$Sr$_{0.005}$CuO$_4$. On the other hand, the samples La$_{1.996}$Sr$_{0.004}$CuO$_4$ and La$_{1.996}$Sr$_{0.005}$CuO$_4$ exhibited similar values of $L_e$ (Table 2) as well as similar values of $\rho(T)$ at low temperatures ($T < 100$ K) (Fig. 4). In other

![FIG. 3. Dependence of the Neel temperature $T_N$ on strontium concentration. The dotted line corresponds to the position of the AFM phase-transition line in the phase diagram. Points correspond to the experimental values of $T_N$ obtained in this work for four samples of La$_{2-x}$Sr$_x$CuO$_4$.](image)

![FIG. 4. Temperature dependence of the resistivity for three samples of La$_{2-x}$Sr$_x$CuO$_4$.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_N$, K</th>
<th>n/atom Cu</th>
<th>$T_0$, $10^4$ K</th>
<th>$L_e$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{1.999}$Sr$</em>{0.001}$CuO$_4$</td>
<td>212</td>
<td>0.00552</td>
<td>1.25</td>
<td>0.32</td>
</tr>
<tr>
<td>La$<em>{1.999}$Sr$</em>{0.005}$CuO$_4$</td>
<td>203</td>
<td>0.00608</td>
<td>1.757</td>
<td>0.287</td>
</tr>
<tr>
<td>La$<em>{1.996}$Sr$</em>{0.004}$CuO$_4$</td>
<td>265</td>
<td>0.00257</td>
<td>1.996</td>
<td>0.275</td>
</tr>
<tr>
<td>La$<em>{1.996}$Sr$</em>{0.005}$CuO$_4$</td>
<td>193</td>
<td>0.00654</td>
<td>0.36</td>
<td>0.478</td>
</tr>
</tbody>
</table>
words, the La$_{1.999}$Sr$_{0.001}$CuO$_4$ and La$_{1.995}$Sr$_{0.005}$CuO$_4$ samples exhibited similar electrical properties. However, unlike La$_{1.995}$Sr$_{0.005}$CuO$_4$, the sample of La$_{1.999}$Sr$_{0.001}$CuO$_4$ showed no correlation between the magnetic (the values of $T_N$ and $n$) and electrical ($I_c$) measurements. This discrepancy may be due to the fact that the applied expression for $T_N(n)$ was obtained in Ref. 18 for the case of very homogeneous samples. Since the sample La$_{1.999}$Sr$_{0.001}$CuO$_4$ exhibits strong structural disorder, it is not correct to apply the dependence $T_N(n)$ from Ref. 18 for the estimation of charge-carriers density in this sample. Thus, the above discrepancy between the results of resistive and magnetic measurements supports the assumption of a higher degree of inhomogeneity (and thus structural disorder) in the ceramics with $x = 0.001$. The mechanism of such a strong suppression of the AFM order depends on the current (Figs. 5 and 6). It can be seen that (Fig. 6) show that for measuring current of 0.03 mA, the temperature $T$ may be due to the fact that the applied expression for $T_N(n)$ is accompanied by a slight decrease in the slope of the curves $\rho(T^{-1/4})$ in the region where the Mott law is obeyed and a corresponding increase in the localization length (Fig. 7). When the current is reduced, the temperature of the onset of deviation of $\rho(T)$ from the Mott law decreases. The $\rho(T)$ data for the sample La$_{1.999}$Sr$_{0.001}$CuO$_4$ ($T_N = 201$ K) (Fig. 6) show that for measuring current of 0.03 $\mu$A, the Mott law holds down to 5 K. We believe that the minimum critical current at which the Mott law is obeyed down to helium temperatures depends on the concentration of charge carriers and the quality of the sample (degree of structural disorder). The low-temperature behavior of $\rho(T)$ shown in Figs. 5 and 6 corresponds to that of percolative conductivity. Regardless of the nature of structural disorder in heterogeneous granular systems, the conductivity is determined by the optimal chains of grains with the maximum probability of tunneling between the adjacent grains separated by intergranular barriers. In the case of thermally activated conductivity, the number of conducting chains gradually decreases with decreasing temperature and, at a sufficiently low temperature, the percolation network can be reduced to a single conducting channel. These optimum chains have several high-resistance tunnel junctions with high activation energy, which determine the thermally activated character of the measured total conductivity. At a fixed temperature the spatial distribution of the optimal chains and the position of high-resistance contacts, which determine the system impedance, constantly change with external electric field (current). Furthermore, upon increasing the external field, additional transport channels appear. In this scenario, $\rho(T)$ in Fig. 6 first
Nonlinear behavior of this type is determined by the tunneling of carriers between isolated conductive chains near the percolation threshold, when a continuous conducting cluster has not yet formed. In this regime, an increase in electric field (and the corresponding increase in current) leads to a higher tunneling probability (or higher jumping probability) and an increase in conductivity. With a further increase in current, a transition to a close-to-ohmic regime takes place. At low temperatures ($T \leq 10\, \text{K}$), a nearly linear dependence of $U/J$ was observed in a very narrow range of low currents. For the more homogeneous sample $\text{La}_{1.999}\text{Sr}_{0.001}\text{CuO}_4$ at $4.4\, \text{K}$, this interval was approximately 2–40 $\mu\text{A}$ (Fig. 8).

In all investigated samples, the NDR regime was only observed at low temperatures. The transition temperature to the NDR regime increased with decreasing the concentration of strontium. According to the dependences shown in Figs. 9 and 10, for the more homogeneous sample with $x = 0.01$ the NDR regime is observed for $T \leq 10\, \text{K}$. For less homogeneous samples, the transition to the NDR regime occurs at higher temperatures: 20 $\text{K}$ for $x = 0.005$ and 30 $\text{K}$ for $x = 0.001$. At a fixed temperature, the current $J_{c1}$, at which the transition to the NDR regime occurs, depends on the concentration of strontium and decreases with decreasing the concentration $x$ (inset Fig. 8). For the samples with the concentrations $x = 0.005$ and 0.001, the currents $J_{c1}$ are similar and roughly an order of magnitude smaller than the current of NDR transition for the sample with $x = 0.01$.

Therefore, an increase in structural disorder upon decreasing the concentrations of strontium leads to a reduction in the threshold current $J_{c1}$ and increase in the threshold temperature for the transition to the NDR regime. For a given concentration of strontium, the current $J_{c1}$ increases with temperature (Figs. 9 and 10).

We evaluated the effect of electric field on conductivity in the regime of variable-range hopping

$$ R(T, E) = R_0(T)\exp\left(-eE_0\gamma/kT\right), $$

where $R_0(T)$ is the resistance at $E \to 0$, $E_0$ is the average length of a jump, and $\gamma$ is a numerical factor of the order of unity. It follows from this expression that at sufficiently low fields when $eE_0\gamma/kT \ll 1$, the resistance does not depend on the field. Estimates have shown that this inequality holds for...
the studied samples even at the highest fields we could achieve. Thus, the observed nonlinear behavior of CVC and the presence of the NDR region (Figs. 9 and 10) cannot be explicitly linked to the influence of the average electric field. It should be noted that for the investigated samples of La$_{2-x}$Sr$_x$CuO$_4$ the transition to the NDR regime occurs in a relatively low field, when the field strength in the sample reaches $E_c \sim (5-10)$ V/cm. In conventional semiconductors the NDR region begins at significantly higher threshold fields. (For example, estimates for the threshold field in GaAs give value $E_c \sim 3000$ V/cm.$^{24}$ With increasing temperature, the threshold field $E_c$ in La$_{2-x}$Sr$_x$CuO$_4$ decreases (Fig. 9), whereas the threshold current $J_{c1}$ increases (Fig. 10).

Therefore, we found that increasing the degree of structural disorder upon decreasing the concentrations of strontium leads to an increase in the non-linear effects in the conductivity of La$_{2-x}$Sr$_x$CuO$_4$ ceramic samples. Compositional heterogeneity of the samples leads to an inhomogeneous spatial distribution of charge carriers, which creates a non-uniform electric field distribution inside the sample. This may result in the appearance of regions where the local electric field substantially exceeds the average value (5-10) V/cm. In such regions a local overheating of the charge carriers can occur. The temperature of the charge-carriers then becomes higher than the temperature of the phonons if the carriers are not able to transfer the energy acquired from the field to the crystal lattice fast enough. The heating of the charge carriers leads to a change in mobility hence resulting in a violation of Ohm’s law.

Spatial inhomogeneity of the field distribution is always greater in the samples with a higher degree of structural disorder, so the overheating of electrons is also stronger there. As a result, the transition to the NDR regime in these samples may occur at lower currents and higher temperatures, as was observed in our experiments.

The behavior of magnetoresistance (MR) in the investigated La$_{2-x}$Sr$_x$CuO$_4$ samples also exhibits a strong dependence on the transport current (Fig. 11). The MR is positive for $T \leq 10$ K at relatively low currents. When the temperature and (or) current increases, the positive MR decreases and becomes negative (Figs. 12 and 13). The positive MR is higher for the sample with a higher concentration of Sr ($x = 0.01$). For example, in a field of 1.3 T at $T = 4.4$ K and current $J = 1$ $\mu$A, the positive MR was 9.5% ($x = 0.01$) and 1.6% ($x = 0.001$). The same ratio was demonstrated by the dependence of the MR on the current at $T = 7$ K (Fig. 13). For all the values of measurement current the positive MR was higher for the less resistive sample with $x = 0.01$. The current at which the transition to the negative MR occurs is significantly higher for the sample with $x = 0.01$ (Figs. 11 and 13).

**Discussion**

It is of interest to compare the results obtained in this paper with earlier studies of nonlinear effects in conductivity of single-crystal La$_2$CuO$_{4+d}$. For instance, in Refs. 14 and 15 the features of the low-temperature behavior of $\rho(T)$ in the two investigated La$_2$CuO$_{4+d}$ single crystals have been explained by the presence of superconducting inclusions$^{15}$ or isolated superconducting chains in a dielectric matrix.$^{14}$ In the both La$_2$CuO$_{4+d}$ single-crystals the behavior of $\rho(T)$ and $U(T, J)$ at low temperatures was nonlinear. Upon increasing
the current to a certain temperature-dependent critical value $J_c$, the transition to the NDR regime occurred.

To explain the experimentally observed deviations from Ohm’s law in doped semiconductors, the theory of “hot” electrons is often engaged.\textsuperscript{25} For example, in Ref. 26 for doped Ge in the regime of hopping conductivity, a satisfactory quantitative description of the nonlinear behavior of experimental CVCs has been obtained. The calculation has been performed with the electron overheating and the “thermal model” of the energy transfer from the electron to phonon subsystem taken into account. It has been assumed that the resistance of the sample depends only on the electron temperature $T_e$ whatever current is applied. In the case discussed in Ref. 26, the nonlinear CVCs are due to the fact that the sample resistance $R(T_e)$ decreases upon heating the charge carriers to $T_e$. As a result, the voltage on the sample $U = JR(T_e)$ may decrease with increasing the current. Below a certain critical temperature $T_c$, an extremal point $dU/dJ = 0$ appears on the CVCs, followed by an NDR region. The NDR region is an area of instability, current and resistance oscillations, and non-equilibrium transitions. As has been shown in well-known theoretical studies, one of the possible causes of NDR is inhomogeneous distribution of impurities and defects, which creates regions with a different strength of electric field in the crystal.\textsuperscript{25}

In single-crystal La$_2$CuO$_{4+x}$ samples with Neel temperature $T_N = 182$ K (Ref. 14) and 269 K,\textsuperscript{15} superconducting inclusions in a dielectric matrix have been considered as the inhomogeneities responsible for the emergence of NDR. It was found that the qualitative shape of the CVCs for La$_2$CuO$_{4+\delta}$ matches the dependences calculated with the electron overheating taken into account in Ref. 26. The critical temperature of the transition to NDR regime in Ref. 14 was approximately (5–6) K. The estimates based on the thermal model\textsuperscript{27} have resulted in a value close to 1 K. However, this discrepancy may be due to the phase separation into superconducting and insulating regions. The model of Refs. 26 and 27 has been developed for semiconductors and hence does not comprise superconducting inclusions acting as inhomogeneities. Nevertheless, the main conclusions of the model\textsuperscript{26,27} are consistent with the experimental results obtained in Refs. 14 and 15.

The MR behavior in the temperature range 5–30 K and current range 0.1–100 $\mu$A (Ref. 14) correlates with the behavior of $R(T, J)$ and CVCs and corresponds to the presence of sufficiently long superconducting chains in a
dielectric matrix. At low temperatures ($T \leq 8$ K) and relatively low currents, the positive magnetoresistance associated with the suppression of superconductivity by a magnetic field has been observed in Ref. 14. Upon increasing the current to $J \geq 10$ $\mu$A there was a transition from positive to negative MR.

In the single crystal La$_{2-x}$Sr$_x$CuO$_{4+\delta}$ with $T_N = 269$ K (Ref. 15) no correlation between the behavior of $R(T,J)$ and MR has been observed. In Ref. 15 a transition from the Mott law to simple thermally-activated conductivity $R(T) \propto \exp(\Delta/kT)$, where $\Delta = 32.4$ K and $k$ is the Boltzmann constant, has been observed at $T < 25$ K and $J < 0.2$ $\mu$A. As has been shown in Ref. 11, such a transition at low temperatures indicates the formation of isolated superconducting inclusions in a dielectric matrix. In this case the suppression of local superconductivity by magnetic field should lead to the unpairing of charge carriers and a resistance decrease. However, in Ref. 15 only positive MR has been observed in this range of temperatures and currents. To explain the positive MR, Ref. 15 has used the hypothesis$^{28}$ on the formation of a new low-temperature magnetic phase coexisting with the superconductive phase. As has been shown by the studies of phase separation in the lanthanum cuprate samples with excess of oxygen, the dielectric phase in the mixed state below 40 K is not a Neel phase but represents a new magnetic state—spin density waves (SDW). $^{28}$ The relative amount of this phase increases with decreasing the excess of oxygen (and the corresponding decrease in $T_c$). Therefore, the content of the magnetic phase is higher in a weakly doped La$_{2}$CuO$_{4+\delta}$ and, respectively, the content of the superconducting phase is lower. Magnetic field stabilizes the magnetic phase by reducing the volume fraction of the superconducting phase, hence mimicking changes in the doping level. $^{28}$ Such collective excitations as SDW carry thermal energy and, when propagating, scatter on each other, phonons, impurities and crystal boundaries. At the same time they serve as scattering centers for other quasiparticles, including electrons and holes. Scattering of charge carriers by spin excitations gives an additional contribution to the resistivity. Thus, since magnetic field stabilizes the magnetic phase, it should also induce positive MR. In the vicinity of a defect (e.g., strontium or oxygen atom), there is an additional spin density redistribution. As a result, positive MR may depend on the concentration and distribution of impurities in the crystal.

In the present study of La$_{2-x}$Sr$_x$CuO$_{4}$ ceramic samples, the $\rho(T)$ dependences are fundamentally different those observed previously in single-crystalline La$_{2}$CuO$_{4+\delta}$. $^{14,15}$ At low temperatures, these dependences cannot be explained by the presence of superconducting inclusions at currents $J \geq 0.5$ $\mu$A (Figs. 4 and 5) and even $J \geq 0.03$ $\mu$A (Fig. 6). This is surprising since the parameters determining the conductivity and the temperature dependence of resistivity (hole concentration $n$ and the carrier localization length $L_z$) in the studied La$_{2-x}$Sr$_x$CuO$_4$ ceramic samples and La$_{2}$CuO$_{4+\delta}$ single crystals are similar. $^{14,15}$ For example, for La$_{2}$CuO$_{4+\delta}$ (Ref. 15) $n = 0.0024$ and $L_z \approx 0.262$ nm, while for La$_{1.995}$Sr$_{0.005}$CuO$_4$ $n = 0.00257$ and $L_z \approx 0.275$ nm (Table 2). And, for the La$_{1.995}$Sr$_{0.005}$CuO$_4$ sample the estimated value of hole concentration and the average localization length were even higher than those for the single crystal La$_{2}$CuO$_{4+\delta}$ studied in Ref. 15. The $\rho(T)$ dependence for La$_{2-x}$Sr$_x$CuO$_4$ was qualitatively different from those for La$_{2}$CuO$_{4+\delta}$ (Refs. 14 and 15) also at high temperatures. For $T > T_N$, all the La$_{2-x}$Sr$_x$CuO$_4$ samples exhibited the transition to the metallic type of the $\rho(T)$ dependence (Figs. 4–6), whereas in La$_{2}$CuO$_{4+\delta}$ the insulator-metal transition has not been observed. Thus, the comparison of experimental data on conductivity for two closely related systems, La$_{2-x}$Sr$_x$CuO$_4$ and La$_{2}$CuO$_{4+\delta}$, shows that the features of the transport properties of cuprates in the AFM state are determined not only by the density of charge carriers and their degree of localization. We believe that various kinds of correlation effects related to the nature of structural disorder have a significant impact on conductivity as well. A particular role can be played by the so-called non-universal disorder, i.e., strongly correlated structural fluctuations. Examples of the non-universal disorder are the precursors of another phase, accumulation of impurities inherent to HTSC cuprates, and orientational disorder occurring at the grain boundaries in ceramics. In single crystals, dislocations and (or) twin boundaries are additional sources of the non-universal structural disorder. In addition, structural differences between La$_{2-x}$Sr$_x$CuO$_4$ and La$_{2}$CuO$_{4+\delta}$ arise due to the fact that the excess oxygen and strontium atoms occupy different positions in the lattice of La$_{2}$CuO$_4$. At the same time, the disturbances produced by the excess oxygen and strontium atoms in the lattice of La$_{2}$CuO$_4$ have significant differences. These perturbations depend both on the structure factor (position of the impurity in the lattice of the matrix) and the form factor of the impurity potential. Since strontium is a substitutional element, its atoms should produce a stronger perturbation in the periodic lattice potential than oxygen, similar to the case of substitutional impurities in the metals. For example, it has been noted in Ref. 29 that the substitution of La by Sr leads to the interaction potential Sr–O in the direction perpendicular to the CuO$_2$ layers of about 25 eV. This is 30 times higher than the interaction potential La–O and 100 times higher than that in Cu–O. Molecular dynamics calculations have shown that as a result of substitution of La atoms by Sr, there occurs an excitation of local high-frequency oscillations (LHFO) of four oxygen atoms in the CuO$_2$ layer in the vicinity of Sr atoms with an energy of about 0.4 eV. $^{29,30}$ Some fraction of the thermal oscillation energy is localized in small areas due to “capture” of the LHFO by defects. In the vicinity of Sr atoms “hot spots” appear, while the rest of the system is efficiently cooled. The degree of localization of the energy of thermal oscillations depends on the concentration of “defects,” i.e., the concentration of Sr. In this case the characteristic size of the “hot spots” can reach 10 Å. Similar calculations performed under the assumption that the impurities are uniformly distributed throughout the crystal have not shown the excitation of LHFO. In summary, the calculations$^{29,30}$ have shown that the lattice dynamics and transport properties of HTSC are affected not only by the type of impurity and its concentration, but also by the particular nature of structural disorder.

The fact that the low-temperature behavior of $\rho(T)$ in the La$_{2-x}$Sr$_x$CuO$_4$ samples with strontium content $x \leq 0.01$ cannot be explained by the presence of superconducting inclusions, can be attributed to a very small size of the precursors of the phase with a high content of strontium. It is known that the properties of a superconducting grain
significantly change when its size is reduced to a few nanometers. Superconductivity might not be observed if the distance between the size-quantization levels in a grain exceeds the superconducting gap $\Delta$ of the bulk material. Another scenario for suppression of superconductivity in La$_2$-Sr,CuO$_4$ is related with the possible formation of “hot spots.” At sufficiently low concentrations of strontium, the size of the region rich in strontium (and in charge carriers) can be comparable with the size of the “hot spots.” Superconducting pairs are not formed in the “hot” region due to the heating of carriers, while the “cold” region is depleted of charge carriers. It is also possible that in the case of extremely low concentration of Sr ($x < 0.01$) there is no macroscopic PS. It is known that the PS occurs only for a sufficiently high degree of doping. Due to the high mobility of excess oxygen atoms in the La$_2$-Sr,CuO$_4$ cuprate, which is due to the oxygen segregation on various structural and interphase boundaries, in samples with low oxygen content the aggregations of the embedded oxygen atoms near the boundaries can favour PS in a limited region of space. In lanthanum-strontium cuprate, the strontium ions are practically immobile, so impurity or thermodynamic phase separation may not occur.

Regardless of the mechanism of the suppression of local superconductivity in La$_2$-Sr,CuO$_4$, the current-controlled NDR effect observed in the present paper can be attributed to a known type of NDR in percolation systems, in which an increase in the electric field (current) leads to the elongation of the existing or even the formation of new non-continuous percolation paths with high conductivity. A further current increase under the condition of strong heterogeneity may lead to the local heating of charge carriers and an increase in their mobility. Both of these mechanisms lead to a decrease in the electrical resistance. The extent of heating will be stronger, the higher is the degree of structural disorder. This leads to a decrease in the number of charge carriers and the resistance decreases. The same effect is also caused by structural fluctuations. Therefore, in less homogeneous samples with lower strontium content, the positive MR is lower and disappears for lower values of the current (Figs. 11 and 13) and (or) temperature. Upon the complete suppression of SDW, the magnetoresistance becomes negative.

This mechanism for the low-temperature positive MR is in line with the general idea that the spin ordering enhances localization of carriers, while the destruction of the SDW leads to the delocalization of charge carriers and a decrease in the resistance.

Comparison of the results of resistance and magnetoresistance measurements on three samples with different concentrations of strontium (Figs. 4, 8, 9, and 11) suggests that the non-linear effects in conductivity increase with decreasing the concentration of strontium.

Conclusion

In the present paper, the low-temperature conductivity of the AFM La$_2$-Sr,CuO$_4$ cuprates with strontium concentration $x \leq 0.01$ obtained by solid phase synthesis was studied for the first time.

It was shown that in the temperature range $T < 100$ K the conductivity mechanism corresponds to 3D variable-range hopping conductivity. Once the AFM order is destroyed, a transition to the metallic conductivity type occurs.

The results of the magnetic and resistive measurements showed that with decreasing the concentration of strontium impurity, the degree of “extrinsic” disorder and the degree of structural disorder increase.

For all samples with the concentration of strontium $x \leq 0.01$, nonlinear effects in low-temperature conductivity and current-controlled NDR were found. Nonlinear effects in conductivity were observed to increase with the degree of structural disorder upon decreasing the concentration of strontium. Nonlinear behavior of the $U(J,T)$ dependence is qualitatively consistent with the mechanism of electron overheating and the “thermal model” of energy transfer from the electron to phonon subsystem.

We discovered low-temperature positive magnetoresistance, the magnitude of which depends on the current, temperature, and the degree of structural disorder. It is assumed that the mechanism of positive MR may be linked to the formation of a low-temperature magnetic phase—spin density waves.

Results of the study of lowly doped La$_2$- Sr,CuO$_4$ cuprates revealed that the role of internal disorder and local inhomogeneities in the behavior of the conductivity of cuprates is not yet fully understood and further study of the influence of disorder on the properties of HTSC cuprates is required.

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Translated by L. Gardt