Fizika Nizkikh Temperatur, 1998, v. 24, No 11, p. 1086–1094B. I. Belevtsev, N. V. Dalakova, and A. S. PanfilovNon-linear effects in hopping conduction of single-crystal $La_2CuO_{4+\delta}$B. I. Belevtsev, N. V. Dalakova, and A. S. PanfilovNon-linear effects in hopping conduction of single-crystal $La_2CuO_{4+\delta}$1086

Non-linear effects in hopping conduction of single-crystal $La_2CuO_{4+\delta}$

B. I. Belevtsev, N. V. Dalakova, and A. S. Panfilov

B. I. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine,
47 Lenin ave, Kharkov, 310164, Ukraine
E-mail: belevtsev@ilt.kharkov.ua

Received June 30, 1998

The unusual non-linear effects in hopping conduction of single-crystal $La_2CuO_{4+\delta}$ with excess oxygen has been observed. The resistance is measured as a function of the applied voltage U (voltage controlled regime) in the temperature range $5\ K \lesssim T \lesssim\ 300\ K$ and voltage range 10^{-3}–25 V. At relatively high voltage (approximately at $U > 0.1$ V) the conduction of sample investigated corresponds well to variable-range hopping (VRH). That is, in the range $0.1\ V < U \lesssim 1$ V the conductivity does not depend on U (Ohmic behavior) and the temperature dependence of resistance $R(T)$ follows closely the Mott's law of VRH [$R \propto \exp(T_0/T)^{1/4}$]. In the range of highest applied voltage the conduction has been non-Ohmic: the resistance decreases with increasing U. This non-linear effect is quite expected in the frame of VRH mechanism, since the applied electric field increases the hopping probability. A completely different and unusual conduction behavior is found, however, in the low voltage range (approximately below 0.1 V), where the influence of electric field and (or) electron heating effect on VRH ought to be neglected. Here we have observed strong increase in resistance at increasing U at $T \lesssim 20$ K, whereas at $T > 20$ K the resistance decreases with increasing U. The magnetoresistance of the sample below 20 K has been positive at low voltage and negative at high voltage. The observed unusual non-Ohmic behavior at low voltage range is attributable to inhomogeneity of the sample, namely, to the enrichment of sample surface with oxygen during the course of the heat treatment of the sample in helium and air atmosphere before measurements. At low enough temperature (below ≈ 20 K) the surface layer with increased oxygen concentration is presumed to consist of disconnected superconducting regions in a poorly conducting (dielectric) matrix. This allows us to explain the observed unusual non-linear effects in the conduction of sample studied. The results obtained demonstrate that in some cases the measured transport properties of cuprate oxides cannot be attributed to the intrinsic bulk properties.

PACS: 72.20.Ht; 74.72Dn; 74.62Dh; **74.80.**-g

1. Introduction

High-temperature (high-T_c) superconductivity of cuprate oxides with perovskite-related structure is still a fascinating problem in solid state physics. Aside from superconductivity the investigations of these materials give also the possibility of studying other fundamental phenomena, for example, magnetism, electron localization and hopping, metal-insulator transition. It is well known that electronic and magnetic properties of cuprate oxides depend essentially on charge carriers density which in its turn depends strongly on chemical composition. Introducing the donor or acceptor impurities into oxides, or changing the oxygen concentration in them it is possible to vary their conductivity over wide limits and to cause the transition from insulating to metallic state in some cases. To judge whether a system is in the metallic, superconducting or insulating state the measurements of transport properties are used in most cases. From these measurements the magnitude, temperature and magnetic-field dependences of resistivity and other conduction characteristics can be obtained. These data are often used for the characterization of prepared samples and evaluation of their «quality». But it is not uncommon that the measured transport characteristics do not correspond to the intrinsic crystal, stoichiometric and, therefore, electronic and magnetic properties of the sample. In the majority of the cases the main reason for it is a sample inhomogeneity due to peculiarities of sample preparation procedure, heat treatment and other related factors. Two main possible sources for cuprate inhomogeneity can be distinguished: intrinsic and extrinsic. Intrinsic source is connected with phase separation of cuprate oxides on two phase with different concentration of charge carriers [1]. The extrinsic one is due to various technological factors of sample preparation. This may lead, among other things, to significant difference in charge carriers density between the surface and inner parts of the sample [2].

In our opinion the investigations of influence of surface or volume inhomogeneity of cuprate oxides on their transport properties are of considerable importance in two following aspects. First, such kind of studies can help to answer the question in what degree the observed transport properties can be attributed to intrinsic properties of the bulk crystal [2]. Second, under gaining enough experimental data on this matter (combined with necessary theoretical considerations and treatments) it is possible to apply the transport measurements not only for revealing of structural inhomogeneity, but also for identification of specific types of surface and volume inhomogeneities. Therefore, study of influence of inhomogeneity on transport properties of cuprate oxides is of both fundamental and applied importance.

In this communication we shall describe some new results of investigation of hopping conduction of single-crystal $La_2CuO_{4+\delta}$ with some amount of excess oxygen ($\delta \neq 0$). In the studies of high-T_c superconductivity these compounds have attracted considerable attention. The stoichiometric La_2CuO_4 ($\delta = 0$) is an antiferromagnetic insulator with Neel temperature T_N in the range 300–325 K [1,3,4]. However, the introducing of excess oxygen (as well as doping with bivalent metals such as Sr) leads to the violation of long-range antiferromagnetic order and to a transition to metallic and superconducting states. Excess oxygen doping introduces additional charge carriers (holes) in Cu-O planes [5]. For high doping level ($\delta \simeq 0.13$) the superconducting transition temperature T_c may be as high as $\simeq 50$ K [6]. For the range of doping $\delta \simeq 0.01–0.055$ the $La_2CuO_{4+\delta}$ compounds undergo a phase separation below room temperature into the two phases with different oxygen content: the oxygen-poor phase is nearly stoichimetric and nonsuperconducting, while the oxygen-rich phase is superconducting [1,5,7–10]. Depending on the δ value, the different (sometimes coexisting) superconducting phases can emerge with T_c values from $\simeq 20$ to $\simeq 45$ K [1,5,7–11].

It is known that low-temperature conduction of nearly stiochiometric $La_2CuO_{4+\delta}$ occurs by variable-range hopping (VRH) of localized holes [12–15] and can be fitted well to Mott's formula [with temperature dependence of resistance $R \propto \propto \exp (T_0/T)^{1/4}$]. In Refs. 14,15 it was found that the transition from VRH to simple activation conduction $R \propto \exp (\Delta/kT)$ occurs at temperatures below 20 K (the similar effect was described also before in Ref.13). In Refs. 14,15 this effect was explained by the influence of sample inhomogeneity, namely, by the presence of superconducting inclusions in the insulating sample due to phase separation of $La_2CuO_{4+\delta}$. As was mentioned in Ref. 2, in each case when some exotic transport behavior of cuprate oxides is found, the reason for it should be sought primarily in the possible influence of inhomogeneity. Our new experimental results support (as we believe) this point of view. We have observed the unusual non-linear behavior of hopping conduction of single-crystal $La_2CuO_{4+\delta}$: at low applied voltages (in conditions where the influence of electric field and (or) electron heating effect on VRH can be neglected) the resistance strongly increases with increasing of applied voltage at $T \lesssim 20$ K, but decreases with voltage increasing at temperatures above 20 K. This unusual non-Ohmic behavior is attributed to inhomogeneity of sample, namely, to the enrichment of sample surface with oxygen during the course of the heat treatment of the sample in helium and air atmosphere before measurements. At low enough temperature (below ≈ 20 K) the surface layer with increased oxygen concentration is presumed to consist of disconnected superconducting regions in a poorly conducting (dielectric) matrix.

2. Sample and experiment

We have studied the hopping conduction of same single-crystal sample of $La_2CuO_{4+\delta}$ as in Refs. 14,15, but with reduced and inhomogeneous oxygen content in it as a result of outlined below heat treatment in helium gas and air. The original sample or, as it is better to say, the original state of this sample is characterized by $T_N \simeq 230$ K and $\delta \approx \approx 0.005$ [14,15]. For reducing the oxygen content the sample was annealed in a furnace in an atmosphere of helium at $T \simeq 330$°C for two hours. It was rather slowly cooled thereafter (about 4 h) in the same inert atmosphere. It is known that annealing in inert gas atmosphere is a very effective way to reduce the oxygen content in cuprate oxides [12].

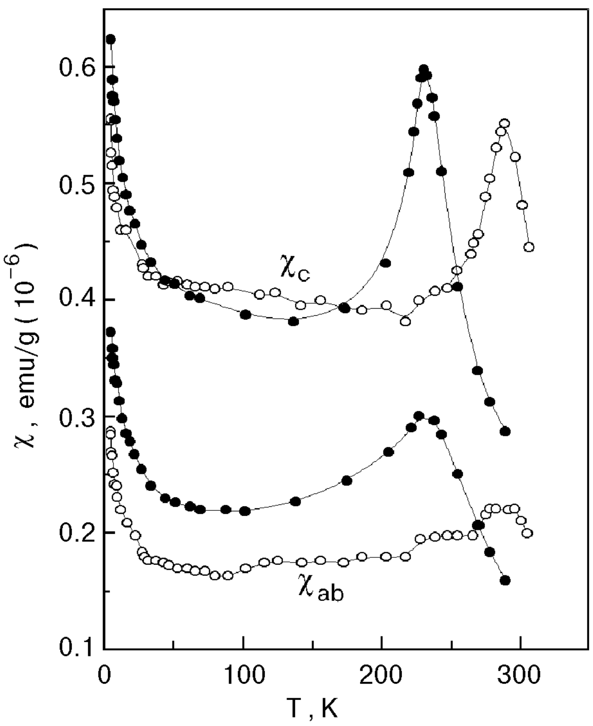

Fig. 1. Temperature dependences of magnetic susceptibility χ in the magnetic field H = 0.83 T of the single-crystal sample of the $La_2CuO_{4+\delta}$ in the initial state (●) and after the outlined heat treatment in helium and air (○). The quantity χ_c corresponds to the measurements in a magnetic field parallel to the crystallographic axis c (the unit cell corresponds to the crystallographic *Bmab* structure in which $a < b < c$, c being the tetragonal axis). The dependences $\chi_c(T)$ are presented by two upper curves. The quantity χ_{ab} is the susceptibility in a magnetic field parallel to Cu-O planes (two bottom curves). The positions of maximums of $\chi(T)$ dependences correspond to Néel temperature T_N.

The resistance of the sample after this procedure (measured by a standard four-probe technique) has appeared however to be too high (about 1.7 kΩ) for intended study of the hopping conduction at low temperatures (down to about 5 K). Therefore it was additionally annealed in air at $T \simeq$ 330°C for 2.5 h and (for lowering the contact resistance) at $T \simeq$ 80°C for 2 h. In the result of such heat and gas treatment the oxygen content in single-crystal sample was reduced significantly. This is evidenced by increase of Néel temperature T_N from 230 to 290 K and very large rise (of more than three order of magnitude at liquid helium temperatures) in resistance (see Figs. 1 and 2, in which the temperature dependences of magnetic susceptibility and resistance are shown for the original state of the sample and for the state after above-described gas and heat treatment). The rather high crystal quality of sample investigated is characterized by the high anisotropy of magnetic susceptibility (Fig.1).

The sample studied has dimensions approximately 3x3x2 mm. For resistance measurement the thin gold contact wires were connected to the sample by a silver epoxy paste which was hardened at $T \simeq$ 80°C for 2 h. The measuring direct current I was parallel to the Cu-O planes. Two techniques were used in resistance measurements: (i) A standard four-probe technique when sample resistance was less than $\approx 4 \cdot 10^6$ Ω; (ii) Two-probe technique for higher sample resistances. For both techniques, actually, the I–V characteristics were measured with applied voltage varying U (voltage controlled regime). From these data we shall present below the obtained dependences $R(T,U)$ and $I(U)$.

In measurements of high-resistive semiconducting samples with non-Ohmic effects it is important to take into account the possible influence of contact resistances. Concerning our sample, we can say the following on this point. First, both of the (four-probe and two-probe) techniques give the same behavior of I–V curves and quite closely values of resistance $R = U/I$ (as a rule, the difference is not more than about 2%) in the resistance range $2 \cdot 10^5$–$4 \cdot 10^6$ Ω. This range corresponds approximately to the temperature range 15–25 K. Second, the special estimation of influence of contact resistances (using different contact places or short-circuiting wires) at $R \geq 10^9$ Ω (this corresponds to temperature below 10 K) has shown that the ratio of contact resistance to measured sample resistance is less than 10%. All this implies (as we believe) that the contact resistance has not much influence on reliability of the obtained results.

The I–V curves and resistance were also recorded in magnetic field H (with magnitude up to 5 T) in the temperature range 5–40 K. The magnetic field was directed along the Cu-O planes at the right angle to the measuring current.

3. Results and discussion

We found that hopping conduction of sample investigated follows closely the Mott's law of VRH:

$$R \propto \exp\left(\frac{T_0}{T}\right)^{1/4}, \qquad (1)$$

where $T_0 \simeq 6.4 \cdot 10^6 K$. It can be seen in Figs. 2 and 3 that this law holds for broad temperature range (10–300 K) in which the resistance is varied up over 7 orders of magnitude. The same exponential $R(T)$ dependence in nearly stoichiometric $La_2CuO_{4+\delta}$ was found previously in Refs. 12–15 but in not as wide temperature and resistance ranges as

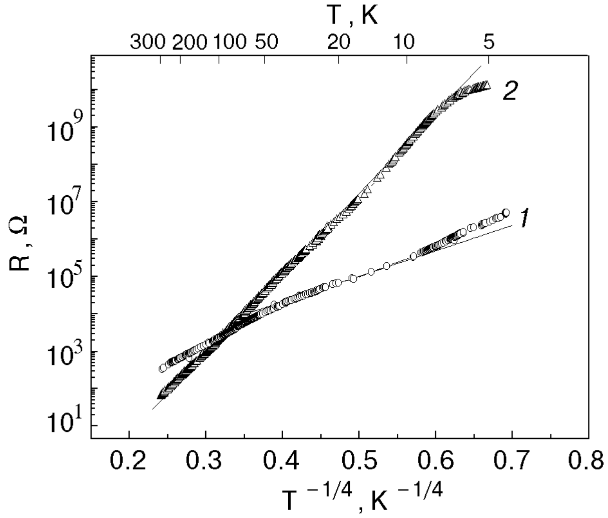

Fig. 2. The dependences of resistance R (on logarithmic scale) on $T^{-1/4}$ of the sample in initial state (curve *1*) and after the outlined heat treatment in helium and air (curve *2*). The dependences were registered at applied voltage $U = 25$ V.

in present study. In the theory of VRH the fractional exponent in Eq. (1) is written in general form as $\alpha = 1/(D + 1)$ where D is the system dimensionality [16]. Therefore, the case $\alpha = 1/4$, observed in our and previous studies, corresponds to behavior of a three-dimensional system. This seems to be contrary to the commonly accepted belief that the cuprate oxides with layered perovskite structure, in which the Cu-O planes are the main conducting units, should behave as electronic quasi two-dimensional systems [17–19]. If this is the case, the VRH behavior should be two-dimensional with $\alpha = 1/3$, and this was indeed observed in some cuprate oxides [17,18]. However, as shown in Ref. 5, in $La_2CuO_{4+\delta}$ owing to special character of the excess oxygen as interstitial atom with weak oxygen-oxygen bonding a hole transfer between Cu-O planes is likely. Therefore, the VRH of this compound behaves as that of three-dimensional system. In passing it should be mentioned that this is not true for Sr or Ba doped $La_2CuO_{4+\delta}$ systems which remain quasi two-dimensional [5].

At $T \lesssim 20$ K, we observed very large deviations of $R(T)$ dependence from Mott's law (Fig.3) which are determined by non-Ohmic effects in the sample conduction. In this temperature range the resistance rise with decreasing temperature is much less than the prediction of Eq. (1) and at low enough temperatures the resistance does not increase at all [approaches some constant value or even decreases with decreasing temperature at fairly low voltage (Fig.4)]. The deviation temperature below which the appreciable deviations of this type take place decreases as the voltage U increases. A quite unusual and unexpected behavior for semiconductor in VRH regime of conduction is connected with this: at low enough temperature ($T \lesssim 20$ K) the resistance increases with U increasing (Fig.3). Indeed, it is well known [16] that conductivity in this

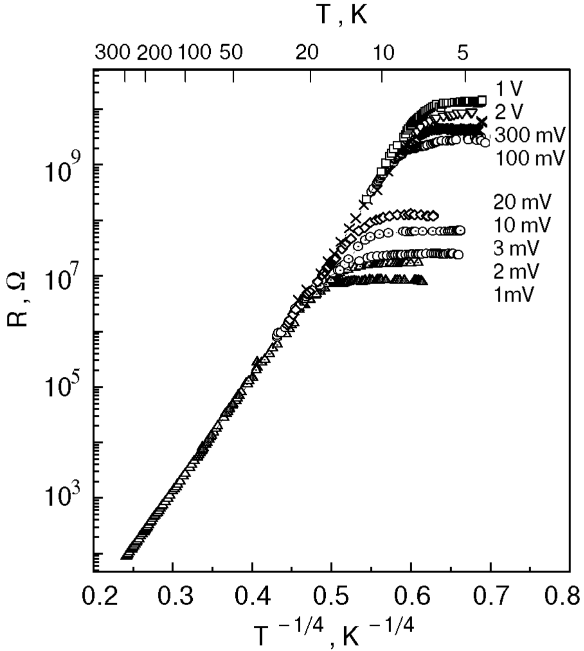

Fig. 3. The dependences of resistance R (on logarithmic scale) on $T^{-1/4}$ of the sample studied at different magnitudes of applied voltage.

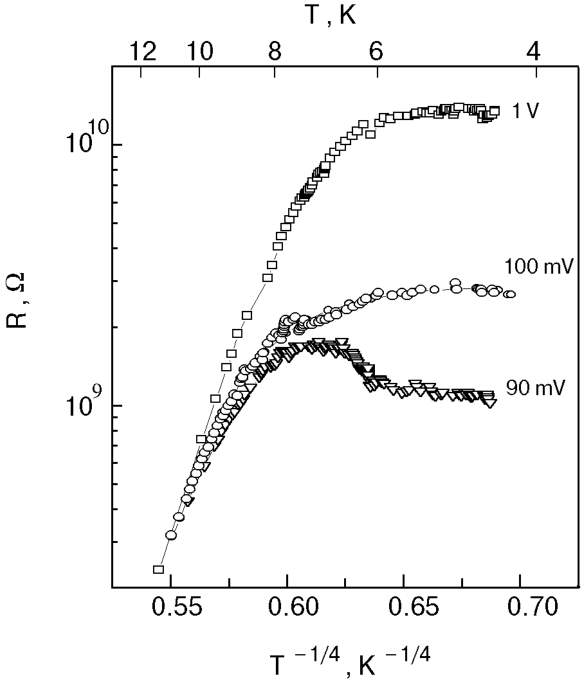

Fig. 4. A selection of dependences of resistance R (on logarithmic scale) on $T^{-1/4}$ presented on an enlarged scale as compared with Fig.3. They demostrate the peculiarities of $R(T)$ behavior at low temperature range at different magnitudes of applied voltage. It can be seen that at high voltage the resistance saturates with decreasing temperature, but at low enough voltage it decreases with decreasing temperature.

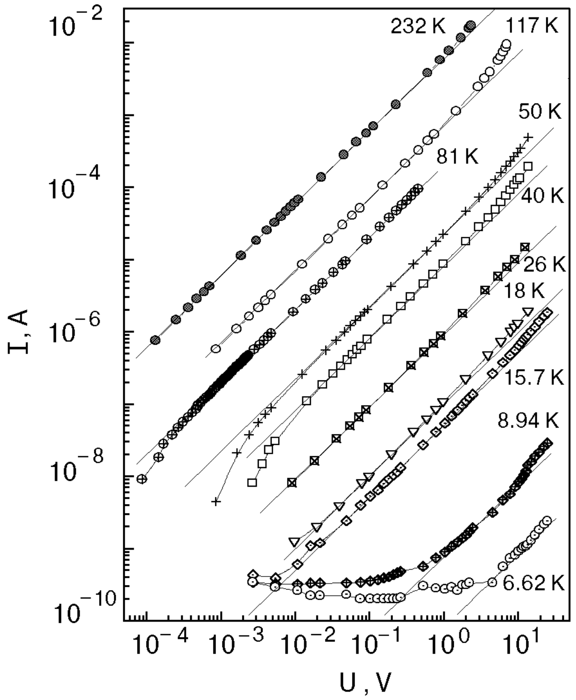

Fig. 5. A set of I-V curves (in logarithmic coordinates) for different temperatures.

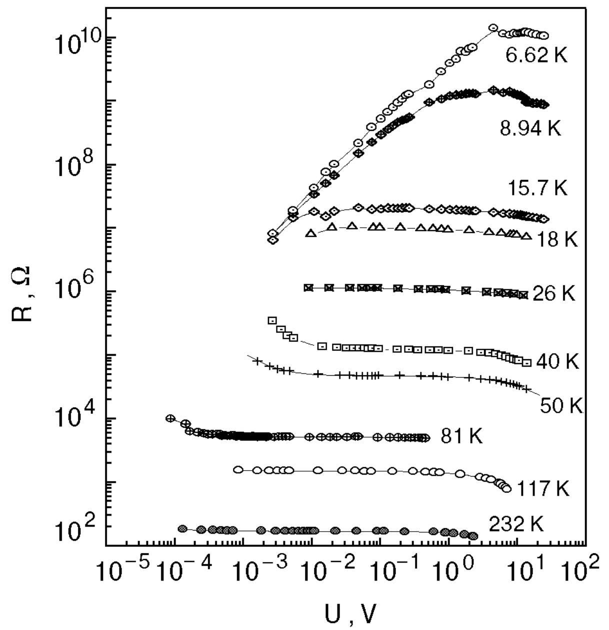

Fig. 6. A set of voltage dependences of resistance R (in logarithmic coordinates) for the same temperatures as in Fig.5.

regime can only increase with the applied electric field E which (when it is large enough) enhances the electron hopping probability. For not very large E values ($eEL_c < kT$, where L_c is the localization length), the effect of electric field on resistance can be described by the following expression [16]:

$$R(T, E) = R_0(T) \exp\left(-\frac{eEr_h\gamma}{kT}\right), \qquad (2)$$

where $R_0(T)$ is the resistance for $E \rightarrow 0$ [described by Eq. (1)]; r_h is the mean hopping distance; γ is a factor of the order of unity. It follows from Eq. (2) that at low enough field ($E << kT/eL_c$) the resistance does not depend on E; that is, Ohm's law holds. With increasing E and decreasing T the influence of electric field must be enhanced and lead to decreasing in R with increasing E; that is quite contrary to what we have observed (Fig. 3).

The described unusual $R(U)$ behavior is one of the major non-Ohmic effects that we have observed. Before trying to explain it we should, however, present more a general picture of found non-Ohmic effects in I–V characteristics and the corresponding $R(U)$ dependences of sample investigated (Figs. 5–7). At low enough voltage the resistance behavior was found to be non-Ohmic in all temperature range investigated (from 5 K to room temperature), but at $T \lesssim 20$ K the resistance increases with increasing U (as was shown above) whereas at $T \gtrsim 20$ K it decreases with increasing U (Figs. 6 and 7)*. These unusual $R(U)$ dependences at low voltage and radical difference between them below and above $T \approx 20$ K are keys to understanding of the conducting state of sample investi-

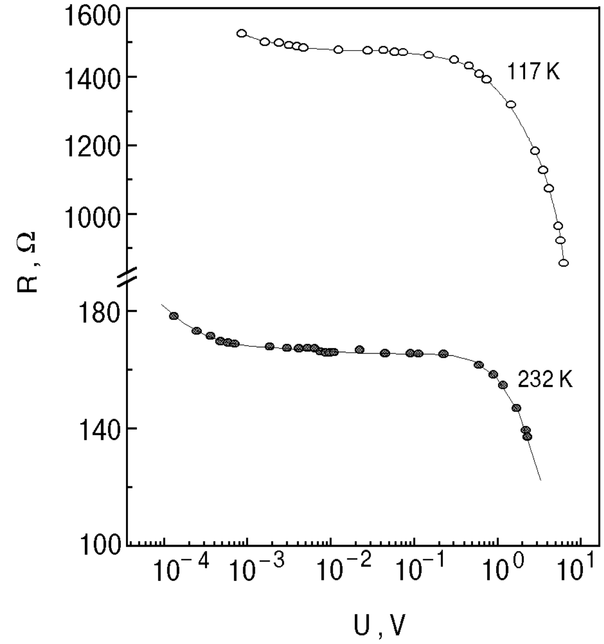

Fig. 7. The semilogarithmic plots of voltage dependences of resistance R for two temperatures above 100 K.

---

* Owing to the logarithmic scales in Fig. 6 the important peculiarities of the $R(U)$ behavior at temperatures above 100 K cannot be seen. Because of this, some examples of $R(U)$ dependences in this temperature range are shown more clearly in Fig. 7 using semilogarithmic coordinates.

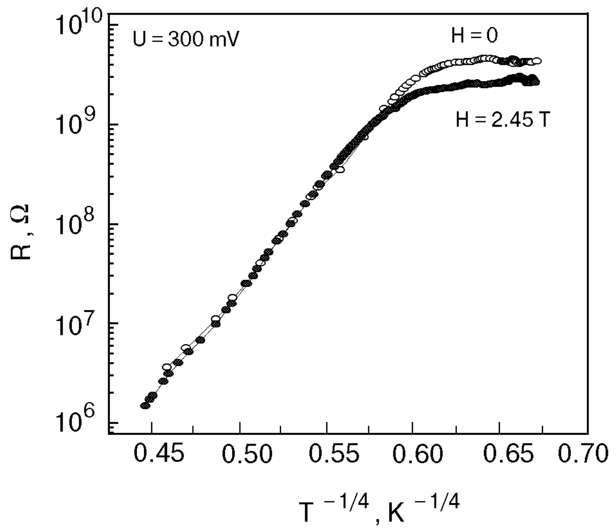

Fig. 8. The dependences of resistance R (on logarithmic scale) on $T^{-1/4}$ at $U = 300$ mV registered in a magnetic fields $H = 0$ and 2.45 T.

gated and will be considered more thoroughly below. At higher voltage the $I(U)$ and $R(U)$ behaviors are basically the same for all temperature range investigated. That is, in some intermediate range of voltage the Ohm law is true and at maximal applied voltage (about 10 V or more) the resistance decreases with increasing U (Figs. 5–7). As it was mentioned above, this type of transition from Ohmic to non-Ohmic regime of conduction at increasing of applied voltage is quite common for semiconductors with VRH and is attributed to the influence of applied electric field [16]. We believe that this is also true for the sample studied and we can substantiate it with some numerical estimates using the Eq. (2). Indeed, it is known [12,28] that electron localization length L_c in nearly stoichiometric $La_2CuO_{4+\delta}$ is about 0.8–1.0 nm. Taking into account that the mean hopping distance r_h in VRH regime of conduction is greater than L_c (say by a factor of 2 or 3), and using the above-indicated sample dimensions, it is easy to see that the electric field effect on hopping conduction is negligible ($eEr_h\gamma/kT << 1$) not only in low-voltage range where the above-mentioned non-linear $I(U)$ behavior and unusual $R(U)$ dependences were observed, but also in higher-voltage range, where Ohmic behavior takes place. Only for the highest applied voltage (10 V and more) the quantity $eEr_h\gamma/kT$ may be about 0.1 and, hence, the influence of electric field E in accordance with Eq. (2) can be appreciable. This can explain the resistance decrease with U increasing at highest applied voltage (Figs. 5–7). Besides, at fairly high field the heating effect is possible at low temperatures. This can also lead to the resistance decrease with U increasing.

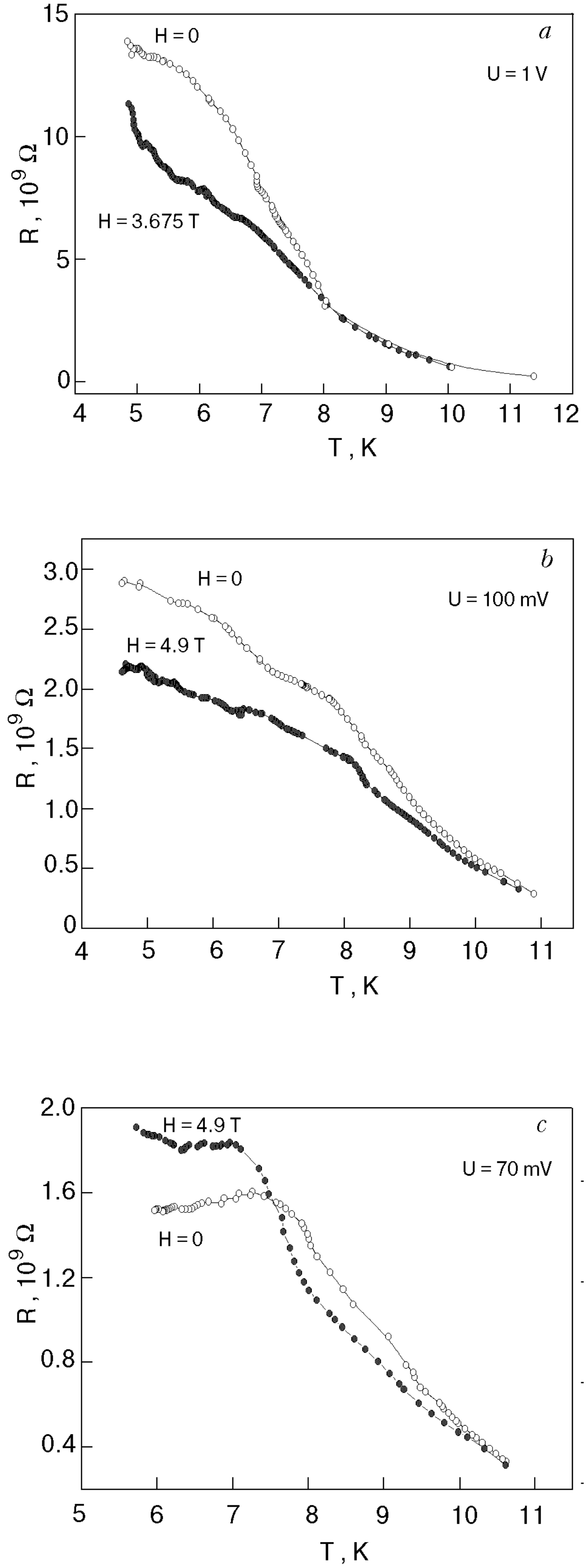

Fig. 9. The temperature dependences of resistance $R(T)$ at $H = 0$ and at some constant magnitudes of H. These dependences were registered at different applied voltages U: 1 V (*a*); 100 mV (*b*); 70 mV (*c*).

The magnetoresistance (MR) of sample studied was found to have appreciable and rather high magnitude only below $T \simeq 10$ K. It was negative at high voltage range, but at low voltage ($U \lesssim 0.1$ V) the MR becames positive at low enough temperatures (Figs. 8 and 9). The negative MR is quite common for insulating $La_2CuO_{4+\delta}$ samples and may be determined by different mechanisms [13–15,21], which we will not discuss here in detail. As far as we know, the positive MR in insulating $La_2CuO_{4+\delta}$ was not observed. Theoretically this phenomenon is considered, however, as quite possible in the VRH regime of conduction and is associated with the shrinking of the impurity wave function in a magnetic field [22]. In this connection we have calculated the possible value of MR using the appropriate equation in Ref. 22 for the case of «weak» magnetic field ($L_H >> L_c$, where $L_H = (\hbar eH)^{1/2}$ is the magnetic length):

$$\ln \frac{R(H)}{R(0)} = t_1 \left(\frac{L_c}{L_H}\right)^4 \left(\frac{T_0}{T}\right)^{3/4}, \qquad (3)$$

where $t_1 = 5/2016$. We have obtained the results that $\ln [R(H)/R(0)]$ is about 0.003 for $H = 4$ T. This is much less than the experimental value of $\ln [R(H)/R(0)] \simeq 0.2$ (Fig. 9). We believe, therefore, that the observed positive MR is not determined by the mechanism proposed in Ref.22.

From the above discussion it appears that the conduction behavior of sample studied at high voltage range, in particular, the transition from Ohmic to non-Ohmic regime of conduction with U increasing, is quite consistent with known properties of semiconductors. This is not the case, however, for the observed non-linear effects in low-voltage range. This raises the two main questions: (i) why this non-Ohmic effects take place at all at so low voltage [in conditions where the influence of electric field and (or) Joule heating on VRH can be neglected]? (ii) what is the cause of radical difference between non-Ohmic effects below and above $T \approx 20$ K in this voltage range? What is more, the observed transition from negative to positive MR at decreasing U should also be considered. After examination of obtained results and taking into account the known properties of cuprate oxides we arrive at the conclusion that the sample inhomogeneity, namely, surface enrichment with oxygen may be responsible for the observed non-linear conduction effects. For the rest of the paper we shall present the points substantiating this conclusion.

First of all we would like to point out that as the result of the above-described heat treatment of the sample in helium and air (see Sec. 2) the oxygen concentration at the surface of sample may be considerably higher than in central (inner) region of it. Indeed, the first step of the treatment was an annealing in helium gas. This should cause [12] an effective reduction in oxygen content in the sample. However, the second step was an annealing in air (partly for the purpose of reducing contact resistance) and this could definitely cause the oxygen enrichment of sample's surface region. This is quite possible if after the helium treatment the oxygen concentration in the sample was low enough. Consider in this connection once again the temperature dependence of the magnetic susceptibility $\chi(T)$ of sample studied (see Fig.1). It can be seen that after the described heat and gas treatment the Néel temperature has increased from ≈ 230 K to ≈ 290 K. The later value of T_N corresponds to nearly stoichiometric $La_2CuO_{4+\delta}$ (very low oxygen content). Therefore, the heat treatment in helium was fairly effective in reducing the of oxygen concentration. At the same time, if a considerable volume part of the sample (in our estimate $1/10$ or more) has gained some additional oxygen after the heat treatment in air, this should be reflected in the form of the $\chi(T)$ curves as well. However, any marked evidence of sample inhomogeneity in this curves, can not be seen. There is only one distinct peak in $\chi(T)$ dependence. But it should be taken into account that in the case, when only fairly thin surface layer has increased oxygen concentration, the influence of it on $\chi(T)$ dependence may be quite negligible. It should be also noted that the marked difference between the surface and inner oxygen content is rather common for the $La_2CuO_{4+\delta}$ and other cuprate oxides [2,6]. For example, in Ref. 6 in $La_2CuO_{4+\delta}$ films, which were oxidized in ozone gas, the increased oxygen concentration in surface layer was found. Taking all this into account and considering the peculiarities of sample treatment we shall assume in the following that the surface region of the sample is enriched with oxygen*. Based on this, it is possible to give a reasonable explanation of all obtained results.

---

* The possible influence of this type of inhomogeneity on the conduction will be considered below. We exclude the phase separation in the inner part of sample as other source of inhomogeneity. Indeed, the Néel temperature $T_N \approx 290$ K for the sample studied means that $\delta \leq 0.003$ [10,23]. This value of δ is far outside of δ range (between $\delta \simeq 0.01$ and $\delta \simeq 0.055$) in which the phase separation occurs [1,5,7–10,23].

The oxygen-enriched surface layer of sample can undergo a phase separation [1,5,6–10] with the resulting formation of considerable volume fraction of superconducting phase. In this case the surface layer would consist of disconnected superconducting regions in a poorly conducting (dielectric) matrix. We believe, that critical temperature T_c of superconducting phase is about 20 K in the case being considered. It is at this temperature that the radically change in non-linear behavior of conduction takes place (Figs.5 and 6)*. Consider, at first, the conduction below $T \simeq 20$ K. In the specified conditions, for driving electric field the system provides at least two main channels for the response: the low-resistive surface layer (with disconnected superconducting regions) and high-resistive core. The measured conductivity of these composite system should be much higher than «intrinsic» conductivity of the core. The increasing U leads to the increase in the current and this must induce the depression of surface superconductivity and, hence, the increasing of the sample resistance. This corresponds to the observed $R(U)$ behavior in low-voltage range (Figs. 3, 5, and 6).

One of the obvious reasons for the superconductivity depression at increasing U is the increase in the current density (this leads to a reduction in T_c). It must not be ruled out, however, in this case the possible influence of Joule heating in low-resistive surface layer on the conductivity of whole system since the Joule heat (as well as current) is much more in this layer than in the core. It is known that Joule heating plays a crucial role in the breakdown of superconductivity in composite or inhomogeneous superconductors [24]. The Joule heating may result (among other things) in resistive domains and negative differential conductance [24]. The latter can be actually seen in the measured $I-V$ characteristics at low enough temperatures (Fig. 5). It cannot be excluded that the observed negative differential conductance is connected with some of the described in Ref. 24 mechanisms of heat breakdown of superconductivity. The results obtained do not provide reason enough to consider this question in detail. In any case, however, we believe that increasing U leads to superconductivity depression and, hence, to the resistance increase.

The magnetic field should also reduce the superconductivity. In this connection the observed positive MR at low-voltage range and the transition to negative MR with increasing U (Fig. 9) can be considered as the important argument to support the existence of oxygen-enriched surface layer (with superconducting inclusions) in the sample. A close look at Fig. 9,*c* shows that when temperature drops, the MR is first negative and then becomes postive. It is significant that the positive MR is combined with decreasing resistance with decreasing temperature at $H = 0$, whereas the negative MR is combined with increasing resistance as the temperature decreases. The resistance decrease with decreasing temperature takes place only at low-voltage range where surface superconductivity is not depressed (Fig.9, see also Fig.4). This decrease can be explained by enhancing of Josephson coupling within some confined groups of superconducting regions with decreasing temperature. Such an effect is quite typical for granular metals in which the competition of the hopping conduction and Josephson coupling takes place [25]. All these effects (especially, the positive MR combined with resistance decreasing with decreasing temperature) can be considered as a direct evidence of superconductivity effect in the sample studied.

It is reasonable to expect that at high enough voltage the surface superconductivity will be depressed completely after which the non-linear conductance of the whole system would change over to Ohmic behavior (Figs. 5 and 6). At the highest applied voltage the non-linear behavior appears again for the reasons that we have mentioned above.

Above $T \simeq 20$ K, where the superconductivity effect should not take place, the non-linear behavior of conduction at low-voltage range still remains. It is weaker than at $T < 20$ K, and appears in radically changed form: the resistance decreases with increasing U (Figs. 6 and 7), at high enough voltage the resistance seems to saturate, that is, the transition to Ohmic behavior occurs (Fig. 5). This type of non-linearity can also be adequately explained in the context of our main conjecture (oxygen-enriched surface layer). The low-resistive surface layer is inhomogeneous. It consists of disconnected (dispersed) high-conducting regions in dielectric matrix. Generally the surface layer would constitute a percolation system with tunneling (or hopping) between disconnected conducting regions. It is just the tunneling that is responsible for the non-linearity of this type of composite system [26,27]. The distinctive feature of these systems is the transition from non-Ohmic to Ohmic behavior of conduction at increasing applied electric field (or temperature). The transition of this type was observed on Ag particles in KCl matrix [28]

---

* The stable superconducting phase with $T_c \simeq 20$ K can emerge due to phase separation of $La_2CuO_{4+\delta}$ at rather low oxygen doping level ($\delta \simeq 0.01$) [11].

and in a semicontionuous gold film near the percolation threshold [29]. In Ref. 29 such behavior was attributed (in line with theory of Ref. 30) to increase in the probability of tunneling with increasing applied voltage U or temperature. The percolation approach of Refs. 26,27 leads to essentially the same result. Thus we believe that the observed change-over from non-linear conductance to Ohmic behavior at low-voltage range (Fig. 5–7) with increasing U is connected with the percolating structure of the oxygen-enriched surface layer and should be attributed to theoretical mechanisms similar those of Refs. 26,27,30. Once the conduction of this layer becomes Ohmic beyond some voltage, the behavior of the whole sample also becomes Ohmic up to the highest voltage, where the influence of electric field (or Joule heating) on hopping conduction becomes perceptible.

In conclusion, it may be said that our conjection about the oxygen-enriched surface layer enables us to explain all the observed unusual non-linear effects and magnetoresistance behavior of studied sample of $La_2CuO_{4+\delta}$. The results obtained demonstrate that transport properties of cuprate oxides may be determined to an essential degree by structural or stoichimetric inhomogeneities. This circumstance should be taken into account at evaluation of «quality» of high-temperature superconductors on the basis of transport properties.

We are very grateful to S. I. Shevchenko for critical reading of the manuscript and helpful comments.

1. *Phase separation in Cuprate Superconductors*, E. Sigmund and K. A. Müller (eds.), Springer-Verlag, Heidelberg (1994).
2. V. M. Browning, E. F. Skelton, M. S. Osofsky, S. B. Qadri, J. Z. Hu, L. W. Finger, and P. Caubet, *Phys. Rev.* **B56**, 2860 (1997).
3. D. C. Johnston, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski, *Phys. Rev.* **B36**, 4007 (1987).
4. R. J. Birgeneau and G. Shirane, in: *Physical Properties of High Temperature Superconductors I*, D. M. Ginsberg (ed.), World Scientific, Singapore (1989), Ch. 4, 151.
5. R. K. Kremer, A. Simon, E. Sigmund, and V. Hizhnyakov, in: *Phase Separation in Cuprate Superconductors*, E. Sigmund and K. A. Müller (eds.), Springer-Verlag, Heidelberg (1994), pp. 66-81.
6. H. Sato, M. Naito, and H. Yamamoto, *Physica* **C280**, 178 (1997).
7. J. D. Jorgensen, B. Dabrowski, S. Pei, D. G. Hinks, L. Soderholm, B. Morosin, J. E. Schirber, E. L. Venturini, and D. S. Ginley, *Phys. Rev.* **B38**, 11337 (1988).
8. M. F. Hundley, R. S. Kwok, S.-W. Cheong, J. D. Thompson, and Z. Fisk, *Physica* **C172**, 455 (1991).
9. J. Ryder, P. A. Midgley, R. J. Beynon, D. L. Yates, L. Afalfiz, and J. A. Wilson, *Physica* **C173**, 9 (1991).
10. A. A. Zakharov and A. A. Nikonov, *JETP Lett.* **60**, 348 (1994).
11. E. L. Vavilova, N. N. Garif'yanov, E. F. Kukovitsky, and G. B. Teitel'baum, *Physica* **C264**, 74 (1996).
12. M. A. Kastner, R. J. Birgeneau, C. Y. Chen, Y. M. Chiang, D. R. Gabbe, H. P. Jenssen, T. Junk, C. J. Peters, P. J. Picone, Tineke Thio, T. R. Thurston, and H. L. Tuller, *Phys. Rev.* **B37**, 111 (1988).
13. A. A. Zakharov, E. P. Krasnoperov, B. I. Savel'ev, A. A. Teplov, M. B. Tsetlin, and A. A. Shikov, Sverkhprovodimost': *Fiz., Khim., Tekh.* 4, 1906 (1991).
14. B. I. Belevtsev, N. V. Dalakova, and A. S. Panfilov, *Low Temp. Phys.* **23**, 274 (1997).
15. B. I. Belevtsev, N. V. Dalakova, and A. S. Panfilov, *Physica* **C282–287**, 1223 (1997).
16. N. F. Mott and E. A. Davis, *Electron Processes in Noncrystalline Materials*, Clarendon Press, Oxford (1979).
17. Y. Iye, in: *Physical Properties of High Temperature Superconductors III*, D. M. Ginsberg (ed.), World Scientific, Singapore (1992), Ch. 4, P. 285.
18. L. Forro, *Int. J. of Mod. Phys.* **8**, 829 (1994).
19. V. M. Loktev, *Fiz. Nizk. Temp.* **22**, 3 (1996). [*Low Temp. Phys.* **22**, 1 (1996)].
20. C. Y. Chen, R. J. Birgeneau, M. A. Kastner, N. W. Preyer, and T. Thio, *Phys. Rev.* **B43**, 392 (1991).
21. T. Thio, C. Y. Chen, B. S. Freer, D. R. Gable, H. P. Jenssen, M. A. Kastner, P. J. Picone, and N. W. Preyer, *Phys. Rev.* **B41**, 231 (1990)
22. B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors*, Springer-Verlag, New York (1984).
23. R. J. Birgeneau, F. C. Chou, Y. Endoh, M. A. Kastner, Y. S. Lee, G. Shirane, J. M. Tranquad, B. O. Wells, and K. Yamada, in: *Proc. of 10th Anniversary HTS Workshop on Physics, Materials and Applications*, March 12–16, 1996, Houston, Texas, USA, B. Batlog, C. A. Chu, W. K. Chu, D. U. Gubster, and K. A. Müller (eds.), World Scientific, Singapore (1996), P.421.
24. A. V. Gurevich, R. G. Mints, and A. L. Rakhmanov, *Fizika kompozitnykh svekhprovodnikov (Physics of composite superconductors)*, Nauka, Moscow (1987).
25. B. I. Belevtsev, *Sov. Phys. Uspekhi* **33**, 36 (1990).
26. A. K. Sen and A. Kar Gupta, in: *Non-linearity and Breakdown in Soft Condensed Matter*, K. K. Bardhan, B. K. Chakrabarti and A. Hansen (eds.), *Lecture Notes in Physics*, 437, Springer-Verlag, Berlin (1994), P. 271.
27. A. Kar Gupta and A. K. Sen, *Phys. Rev.* **B57**, 3375 (1998).
28. I-G. Chen and W. B. Johnson, *J. Mat. Sci.* **27**, 5497 (1992).
29. B. I. Belevtsev, E. Yu. Belyaev, Yu. F. Komnik, and E. Yu. Kopeichenko, *Low Temp. Phys.* **23**, 724 (1997).
30. M. Mostefa, D. Bourbie, and G. Olivier, *Physica* **B160**, 186 (1989).