# Characteristics of the metal–insulator transition in systems based on Ln–Ba–Cu–O and Ln–Sr–Nb–O (where Ln=La, Nd, Gd, Dy, Tm, Lu)

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Our studies of high-$T_c$ superconducting samples belonging to the systems $LnBa_2Cu_3O_{6+\delta}$ and Ln–Sr–Nb–O (where Ln=La, Nd, Gd, Dy, Tm, Lu) have revealed similar patterns in the behavior of their electronic properties as they undergo the transition from insulator to metal. In all of these compounds there is a range of low temperatures $T \leqslant T_{cM}$ in which the global resistance $R_I(T,H,I) \equiv U(T,H,I)/I$ deviates from the Mott law and is dispersive in its temperature dependence, and in which the magnetoresistance $\partial R_I/\partial H$ becomes negative. As the samples become metallic, this region first broadens in $T$. The departure from the Mott law then turns into a maximum, and the derivatives $\partial R_I/\partial I$ and $\partial R_I/\partial H$ are observed to change sign with decreasing temperature. In order to explain these properties, and other features of the cuprates, in a self-consistent way, we invoke stratification, which leads to a regime of localized superconductivity with a broad distribution of local critical temperatures $T_{ci}$. Our data not only indicate that localization effects play a decisive role in the creation of high-temperature superconductivity; they also lend considerable support to the hypothesis that regions of localized superconductivity can exist with $T_{ci}$ up to 160 K and above in the copperless system Ln–Sr–Nb–O. © *1995 American Institute of Physics.*

## 1. INTRODUCTION

In recent years, the investigation of concentration-induced metal–insulator transitions in oxygen-deficient metal–oxide systems has attracted increasing attention. There are two reasons for this: first, these studies address fundamental questions that touch on the interdependence of localization effects and the mechanism for high-temperature superconductivity; and second, they aid in the search for copper-free metal–oxide systems based on transition metals that exhibit superconductivity with $T_c > 50$ K. Data from numerous experiments indicate that the most fully investigated stoichiometric cuprates, e.g., $La_2CuO_{4+\delta}$ and $YBa_2Cu_3O_{6+\delta}$ with $\delta=0$, are antiferromagnetic insulators with well defined insulator gaps of width $\Delta_M = 1.2$–$1.5$ eV. It is assumed that these gaps separate the filled $2p$(O) band from the empty $3d$(Cu) band.[1] The gaps between these bands are apparently caused by strong correlations in the electronic subsystem; therefore, these stoichiometric compounds are usually referred to as Hubbard insulators.

There is reason to believe that when the oxygen content is increased, as long as the value of $\delta$ stays within the range where localized superconductivity does not manifest itself in a significant way the evolution of the electronic properties should recall that of a classical semiconductor (with oxygen playing the role of an acceptor) with roughly the same value of the gap.[2,3] In particular, this agrees with the conclusions of a recent paper[1] on the way the cuprate electronic spectra change: a band of localized states appears above the $2p$O band, while holes appear within the $2p$O band itself that belong to the $CuO_2$ planes. When the specifics of localized states near the Fermi level are taken into account more completely, the cuprates $YBa_2Cu_3O_{6+\delta}$ under discussion should probably be viewed as Fermi glasses for $\delta < 0.3$.[2] At sufficiently low temperatures, the transport properties of these cuprates should be characterized by variable-range hopping conductivity[2] (the Mott law), which is sometimes interpreted as activated conductivity with a monotonically decreasing activation energy.

As $\delta$ increases further, we should expect the system $YBa_2Cu_3O_{6+\delta}$ to exhibit a number of peculiarities, primarily due to the large difference in binding energy of the oxygens at nonequivalent crystallographic positions. Recently, there has been more and more evidence that for intermediate values of $\delta$ the high-$T_c$ superconductor cuprates stratify into homologous phases with differing metal–oxygen ratios, which could be due to the interaction of weakly coupled ("active") O ions with the electron subsystem.[4] Thus, in Ref. 5 it was observed that passing an electric current for a long period of time through samples of $DyBa_2Cu_3O_{6+\delta}$ (with $\delta = 0.3$–$0.7$) immersed in liquid nitrogen leads to a strong change in the function $R(T)$, apparently caused by redistribution of the active oxygen. This type of stratification[6–8] can favor the appearance of a regime of localized superconductivity with broad distributions of local values of the critical temperature $T_{ci} \leqslant T_{cM}$ and energy gap $\Delta_{Si} \leqslant \Delta_{SM}$ (see Refs. 8–10). Thus, we should expect that, in contrast to classical semiconductors, the increased conductivity of the cuprates with increasing $\delta$ should be accompanied by the appearance of nonlinearity over portions of the current–voltage characteristics at temperatures $T < T_{cM}$. As $\delta$ increases and/or $T$

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decreases, we should observe a crossover from a situation where the current–voltage characteristics are determined predominantly by single-particle tunneling between superconducting clusters to one where a decisive role is played by Josephson tunneling of pairs. In the first case, the magnetoresistance should be negative, while in the second case it should be positive.

In this paper we present the results of parallel studies of the distinctive features of transport properties of the systems $LnBa_2Cu_3O_{6+\delta}$ and Ln–Sr–Nb–O near the metal–insulator transition. Based on our data and data previously published, we conclude that phase stratification and superconductivity with $T_c > 50$ K (although in local form) can result from the strong interaction of the electron subsystem with the relatively labile subsystem of ions in the presence of a sufficiently large concentration of the corresponding vacancies. In ideal crystals, this interaction could lead to the appearance of concentration density waves, and, accordingly, to a strong spatial modulation of both the electrostatic potential and the local density of states. Furthermore, it is logical to assume that the strong anisotropy of all known high-$T_c$ superconducting cuprates with $T_c > 50$ K, whose structure can be viewed as consisting of alternating insulating and superconducting layers (metallic for $T > T_c$) with predominantly Josephson coupling between them, is a consequence of the instability of the crystal lattice against the appearance of concentration density waves along one of the directions. Evidence in favor of these considerations is the fact that decreased anisotropy accompanies the appearance of superconductivity[11] in, e.g., $La_{2-x}Sr_xCuO_4$ crystals for $x > 0.2$, although the metallic properties of these compounds improve in this case. The results of our previous investigations of the residual conductivity and diamagnetism of high-$T_c$ superconducting cuprates,[12] and much other data, lead us to conclude that superconductivity with extremely high values of $T_c$ could, in all probability, be realized in local fragments of the structure located near the threshold for crystalline instability. One of the tasks of this paper is to focus more on looking for materials in which the superconductivity has a local character. The growth of interest in such nonuniform systems, besides its practical importance, is consistent with the internal logical development of solid-state physics, one of whose most interesting topics is the physics of superconductivity. In accordance with what we have said, materials with this kind of localized superconductivity should be characterized by a much greater variety of physical properties than, e.g., those of doped semiconductors, the study of whose transport processes has remained, and continues to remain, one of the most important topics in solid-state physics.

## 2. SAMPLES AND METHODS OF INVESTIGATION

X-ray-quality single-phase cuprates with compositions $LnBa_2Cu_3O_{6+\delta}$ (where Ln=La, Nd, Gd, Dy, Tm, Lu) were prepared using the standard method of solid-phase synthesis in an oxygen flux. The value of $\delta$ was decreased by annealing the samples at $T = 500$–$1200$ K in vacuum or in an inert gas.[5,7]

The main group of oxygen-deficient niobate compounds $(Sr_{1-x}Ln_x)_yNbO_{3-\delta}$ were prepared from powders of SrO, $SrCO_3$, $Ln_2O_3$ (exceptionally pure), $Nb_2O_5$, and Nb (chemically pure). Before batching, all the powders (except for Nb) were heated in air at $T \leq 1400$ K in order to purge them of both absorbed and chemically bound water, which could be present, e.g., in the form $Ln(OH)_3$ or $Ln(OH)CO_3$. The Nb powder was ordinarily purified at 1200 K in a mixture of hydrogen and helium. After grinding in an agate mortar, the mixture of powders, which was pressed into the form of tablets with diameter 9 mm and thickness 2 mm, was placed in an alundum crucible and annealed for 10–20 minutes in an atmosphere of helium at $T = 1700$–$1800$ K. The resulting material was carefully ground and once again pressed into tablets. It was then subjected to repeated thermal processing under the same conditions. In order to obtain more homogeneous samples, this procedure was repeated three to five times. At all stages of preparation of the samples, measures were taken to avoid the inclusion of additional copper in the samples, and after each thermal processing the change in the tablet weight was monitored, which ordinarily did not exceed a fraction of a percent.

The samples of the second group had the same composition as those of the first group, with the difference that the second group was prepared from a mixture of "polyfabricates" in the corresponding proportions: $NbO_x$, $Sr_xNbO_{3-\delta}$, and $Ln_xNbO_{3-\delta}$. In this case, we were able not only to vary the preparation conditions of the polyfabricates separately, but also to make a preliminary selection, e.g., according to the parameters of the unit cell of the fundamental phase or the form of the electrical resistivity function $\rho(T)$. As a rule, samples from the second group were characterized by higher reproducibility of their properties.

In determining the phase composition of the samples, we used a Geigerflex diffractometer (using Cu$K_\alpha$ radiation and a graphite bent-crystal monochromator) and a DRON-2.0 (using Cu$K_\alpha$ radiation and a graphite planar monochromator).

The electrical voltage $U(T)$ was measured for samples with cross section 1–2 mm$^2$ and length 6–9 mm by the standard method of four-contact switching of a stabilized constant current $I$ whose magnitude could be varied from $10^{-6}$–0.2 A. In order to decrease the junction resistance at the contact point, an indium–gallium eutectic was rubbed into the sample. The input resistance of the apparatus used to measure $U(T)$ was $10^8$–$10^9$ Ω. In order to reduce sample heating to a minimum while dissipating an electrical power $P > 10^{-3}$ W in the sample, we used rectangular current pulses with an inverse duty cycle of 10 or more. The sample temperatures were controlled by a differential thermocouple made from Cu/Cu+0.01 atomic % Fe, one of whose joints was usually immersed in liquid helium. The current–voltage characteristics of the samples were taken by smoothly scanning the current at fixed temperature.

The quantity $U(T)$ was measured in fields $H \leq 10^7$ A/m at the International Laboratory for High Magnetic Fields and Low Temperatures (Warsaw, Republic of Poland). In most cases, we used the Faraday method to measure the magneti-

zation $M(H,T)$ and the function $\chi(T)$ in constant fields up to $3.3\cdot 10^5$ A/m.

### 3. TEMPERATURE DEPENDENCES $R_I(T)$

As we already noted in the Introduction, for intermediate values of $0.1<\delta<0.9$ it is necessary to characterize as multiphase not only polycrystalline samples of $LnBa_2Cu_3O_{6+\delta}$ but also more uniform epitaxial films and single crystals as well.[6–8,10] In the idealized case, we can postulate an invariant structural component of these materials in the form of a perovskite subcell (differing from a cubic perovskite by one oxygen vacancy) whose center contains a Ln ion, adjacent to which are perovskitelike subcells with variable oxygen deficiencies centered around Ba ions. From this point of view, the crystalline structure of the $LnBa_2Cu_3O_{6+\delta}$ system can be viewed as a combination of subcells with compositions $LnCuO_2+BaCu_3O_{2+i}+BaCuO_{2+j}$, where the labels $i$ and $j$ are primarily restricted to the range 0–0.5. In investigating the phase composition and structural features of samples of natural Ln–Sr–Nb–O systems, we also must deal with a cubic perovskitelike cell, but in this case the overall picture obtained is considerably more complicated, probably due to closeness of the phase $(Ln, Sr)_xNbO_{3-\delta}$ at x=0.66 to the threshold for structural instability, which we also associate with nonlinearity of the current–voltage characteristics and other signs of a region of localized superconductivity.

It is clear that in these systems we cannot expect a single-valued relationship between the transport properties and composition, especially if we take into account the tendency of the metal–oxide superconductors to undergo phase stratification;[4,6–10] the maximum discrepancy in values of $\delta$ and, e.g., the resistivity $\rho_r\cong\rho(T=295K)$ in the cuprates $LnBa_2Cu_3O_{6+\delta}$ is usually observed for $\delta=0.3$–$0.5$. In view of the percolation nature of the conductivity in these metal–oxide superconductors and the strong dependence of $\rho_r$ on the specific distribution of oxygen vacancies under conditions of phase stratification, it is more reasonable to associate the electronic properties of the sample not with its composition but rather with global characteristics such as $\rho_r$. We can justify this approach on the basis of the results of a recent study[13] of metastable Cd–Sb alloys where the authors used a quantity directly associated with the electrical resistance as the fundamental parameter to compare with in studying other properties of the sample.[13]

In the majority of samples we investigated, Ohm's law ceased to hold at low temperatures, which made it necessary to use the concept of a global resistance $R_I$ to describe their properties, or its values per unit volume $\rho_I$, which in these measurements are directly determined from the ratio $U/I$:

$$R_I(I,T)=\frac{L}{S}\rho_I(I,T)=\frac{1}{I}\int_0^I R_D(I,T)dI\equiv\frac{U}{I}, \qquad (1)$$

where $L$ is the distance between potential contacts, $S$ is the transverse cross section of the sample, $U$ is the voltage drop across the potential contacts, and $R_D(I,T)=\partial U/\partial I$ is the differential resistance.

Figures 1–3 show examples of the temperature dependences $R_I(T)=U/I$ for high-resistance samples of niobates and cuprates plotted in the coordinates $\log R_I(T)$ and $T^{-1/3}$. Within measurement error, the values of $R_I(T)$ are independent of $I$ for all the samples in Fig. 1 under conditions where $U<10$ V. The increase in $R_I(T)$ by a factor of more than $10^5$ as the temperature decreases is well approximated by an expression of the form:

$$R_I(I,T)=R(T)=R_0\exp(T/T_0)^{-1/(1+D)}, \qquad (2)$$

with the value $D=2$. This value corresponds to variable-range hopping conductivity in a quasi-2D system with a low density of states $N(E_F)$ near the Fermi level[2] and, as we already remarked in the Introduction, is also characteristic for a Fermi glass. The parameters $T_0$ and $R_0$ determined from Fig. 1 vary from $2.4\cdot 10^5$ K and $2.5\cdot 10^{-5}$ Ω from sample 1 to $3.2\cdot 10^4$ K and $8.9\cdot 10^{-3}$ Ω for sample 4. According to the theory of Refs. 2 and 3, the connection between $T_0$ and the localization radius of the carriers $r_l$ for $D=2$ is given by the expression:

$$T_0=\frac{\beta}{k_B N_S(E_F) r_l^2}, \qquad (3)$$

where $\beta=13.8\pm0.8$ (see Ref. 3), $k_B$ is Boltzmann's constant, and $N_S(E_F)$ is the two-dimensional density of states near the Fermi level. Data published previously for cuprates with the various compositions $La_{2-x}Sr_xCuO_{4\pm\delta}$ (Refs. 14, 15), $La_{1.9}Ca_{1.1}Cu_2O_{6+\delta}$ (Ref. 16), $EuBa_2Cu_3O_{6.33}$ (Ref. 17), $YBa_2Cu_{2.76}Nb_{0.24}O_7$ (Ref. 18), and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ (Ref. 19), with $\rho_r\geqslant 0.1$ Ω·cm, also show that in analyzing the functions $R_I(T)$ over a wide interval of temperatures (usually 200 K$>T>$10 K) the Mott law with $D=2$ turns out to be most preferable, although sometimes the exponent can be either larger or smaller, and in addition may vary with temperature.[15,18] Behavior close to the Mott law with $D=2$–$3$ for $R_I(T)$ is also observed for the majority of Ln–Sr–Nb–O samples with the other rare-earth elements Ln=Nd, Gd, Dy, Tm, Lu, if $\rho_r\geqslant 0.2$ Ω·cm. It should be noted that in the high-temperature range ($T>150$ K) the functions $R_I(T)$ are more often than not exponential, just as in doped semiconductors, with well defined activation energies.[18]

Investigations[11,18–20] of systems with various compositions for $T>50$ K primarily confirm the idea[2,21] of Ioffe–Regel–Mott that a change in the functions $R_I(T)$ should take place, accompanied by the sign change of the derivative $\partial R_I/\partial T$, at a certain minimum metallic conductivity that usually lies in the range $\sigma_{\min}=10^2$–$10^3$ $\Omega^{-1}\cdot cm^{-1}$. The decrease in $\rho_r$ for our samples down to values of $\sigma_{\min}^{-1}\approx 10^{-2}$ Ω·cm also leads to an abrupt weakening of the temperature dependence of $R_I(T)$ when $T>100$ K, analogous to what is observed, e.g., in the systems $YBa_2Cu_{3-x}Nb_xO_7$ (Ref. 18) and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ (Ref. 19). As for the low-temperature range, it is clear from Figs. 2 and 3 that a tendency for the sign of $\partial R_I/\partial T$ to change is observed at considerably higher values of $\rho_r\gg\sigma_{\min}^{-1}$. Especially noteworthy is the fact that the deviations from the Mott law are accompanied by dispersion of the functions $R_I(T)$ when $I$ is varied from $10^{-6}$ to $10^{-3}$ A, which ordinarily corresponds to a change of $U$ from 0.1 to 10 V in the range of helium temperatures (Fig. 2). At first glance, we might attribute this

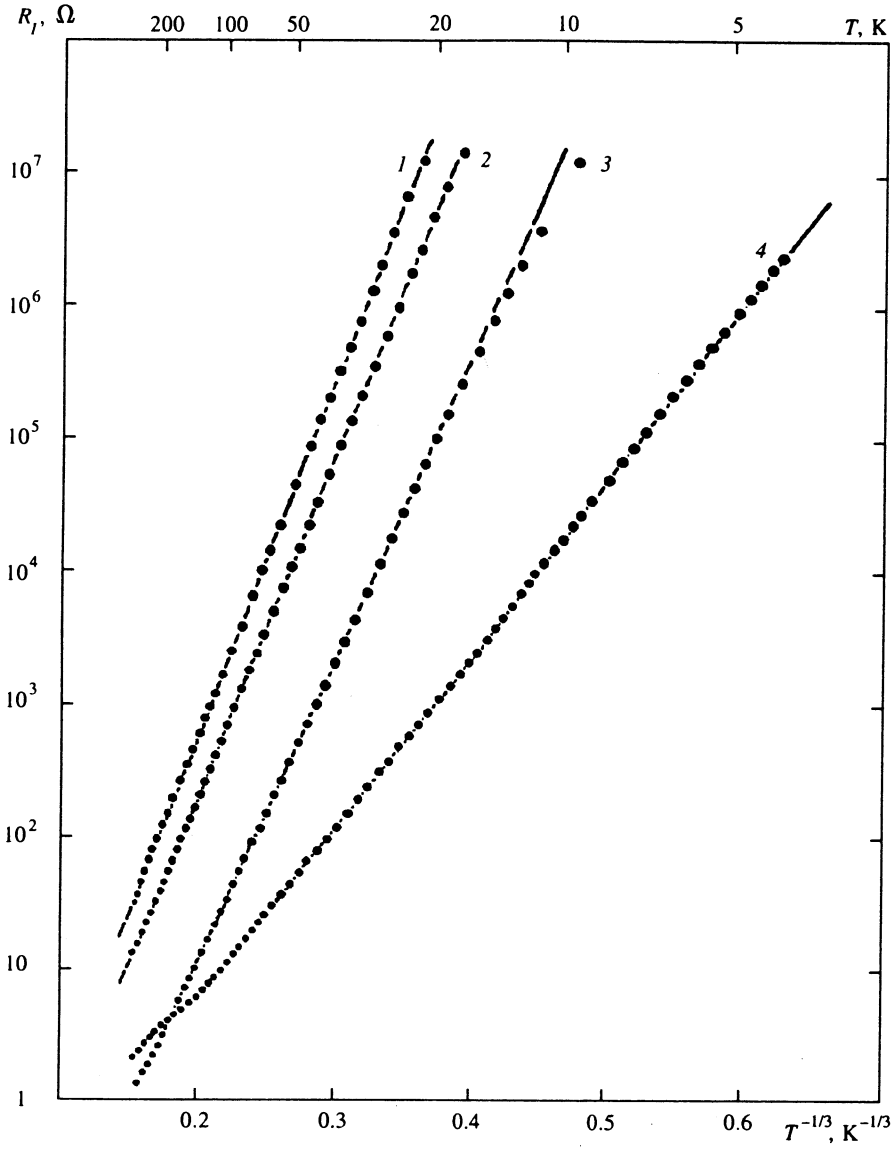


FIG. 1. Temperature dependence of the global resistance $R_I(T)=U/I$ of samples of La–Sr–Nb–O (curves *1–3*) and $ErBa_2Cu_3O_{6+\delta}$ (curve *4*) with various values of the resistivity $\rho_r$: 3, 1.5, 0.1, and 0.2 Ω·cm (curves *1*, *2*, *3*, and *4*, respectively).

nonohmic behavior of $R_I(T)$ to, e.g., Joule heating (at the locations of the current contacts or in locally conducting channels within the sample) and/or heating of the carriers above the temperature of the phonon subsystem; however, if this were the case, increasing $I$ from $10^{-5}$ to $10^{-4}$ A should probably have a considerably greater effect on $R_I(T)$ (by factors of ten) than a similar increase of $10^{-6}$ to $10^{-5}$ A, which contradicts the data of Fig. 2. The estimates given in Ref. 15 also show the untenability of heating effects as an explanation for nonohmic behavior of $R_I(T)$ when $T\leqslant 12$ K in samples of $La_{2-x}Sr_xCuO_{4\pm\delta}$. A connection between the dispersion of $R_I(T)$ and a change in the regime of hopping conductivity is highly improbable for the values of $U$ used in our measurements, since the electric fields achievable in the samples are many times lower than those required.[22] On the other hand, a similar evolution of the function $R_I(T)$ with decreasing $\rho_r$ is also observed in samples of the cuprates $LnBa_2Cu_3O_{6+\delta}$ for $\delta>0.3$. In Fig. 2 we show two families of functions $R_I(T)$ for samples of La–Sr–Nb–O and $DyBa_2Cu_3O_{6+\delta}$ (where $\delta\approx 0.4$) with similar values of $\rho_r\approx 0.3\Omega\cdot$cm (for convenience, the family of curves of $R_I(T)$ for samples of La–Sr–Nb–O is shifted upward by one decade). From Fig. 2 it is clear that the deviation from the Mott law and the dispersion of $R_I(T)$ both begin to appear at approximately the same temperature $T_{cM}$, below which the effect of a field $H=10^7$ A/m on the quantity $R_I(T)$ becomes appreciable. Meanwhile, the magnetoresistance is negative both for the cuprates and the niobates, and for $T\leqslant 4.2$ K can reach 5–10 %. A negative magnetoresistance was observed previously in investigations of samples of $Bi_2Sr_2CuO_6$ ($T<15$ K; see Ref. 23) and $La_{2-x}Sr_xCuO_{4\pm\delta}$ ($T<30$ K); see Ref. 15).

The subsequent evolution of the family of curves $R_I(T)$, both for cuprates and niobates with Ln=La, Nd, Gd, Dy, Tm, and Lu, is accompanied by the appearance of maxima. Figure 3 shows one such family of La–Sr–Nb–O samples with $\rho_r\approx 0.2$ Ω·cm. Our use of DC or pulsed current with inverse duty cycles of $\geqslant 10$ in measurements of $U(T)$ (the light and dark symbols, respectively) shows that the effect of Joule heating on the value of $R_I(T)$ begins to appear in the low-temperature region only for $I\geqslant 10^{-3}$ A, which corresponds to dissipation of a DC power $P\geqslant 10^{-3}$ W

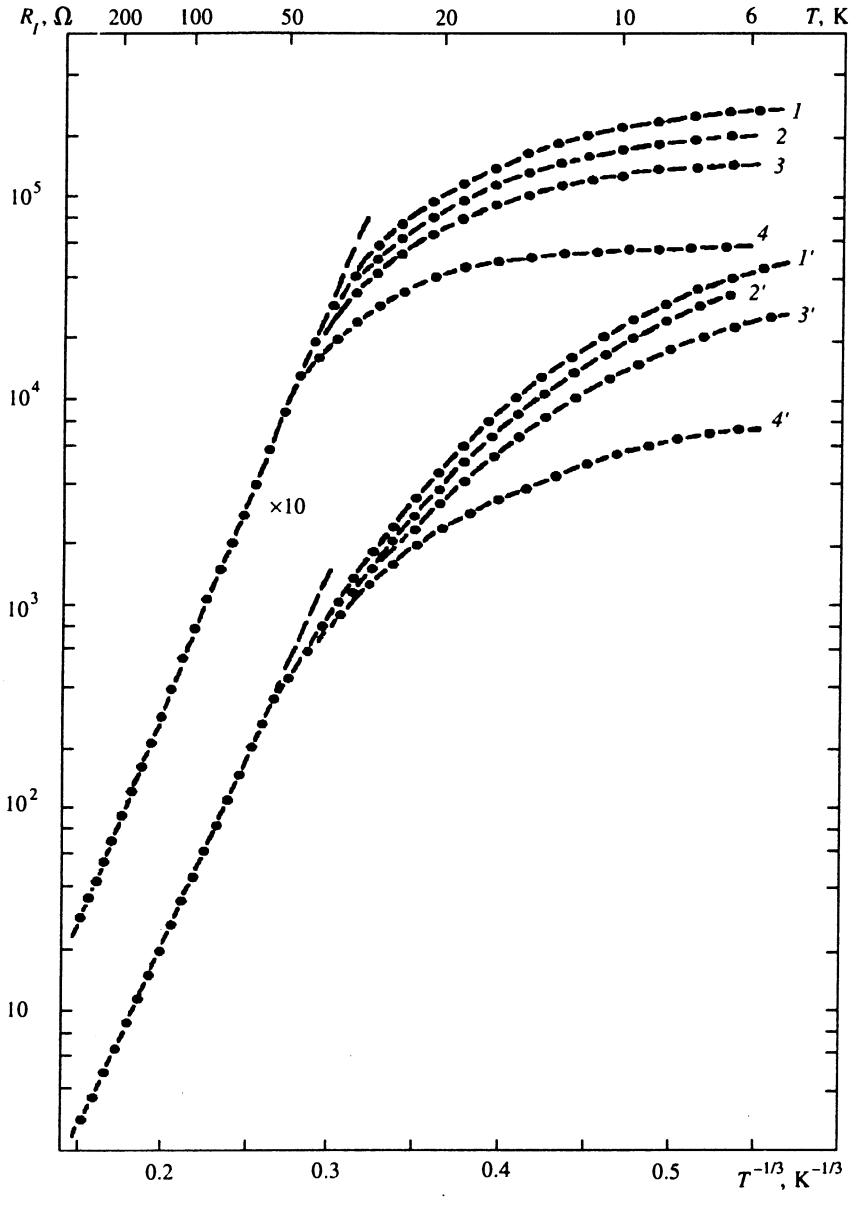


FIG. 2. Temperature dependences $R_I(T)$ for samples of La–Sr–Nb–O($\rho_r = 0.3$ Ω·cm (curves *1–4*) and $DyBa_2Cu_3O_{6+\delta}$ ($\rho_r = 0.25$ Ω·cm (curves *1'–4'*) plotted for various values of the DC measurement current $I_d$ (the family of curves for the La–Sr–Nb–O samples is shifted upward by one decade): *1,1'*—$10^{-6}$ A; *2,2'*— $10^{-5}$ A; *3,3'*—$10^{-4}$ A; and *4,4'*—$10^{-3}$ A.

in the sample. As a result of this heating, the function $R_I(T)$ becomes flatter, and the nonlinearity of the current–voltage characteristics decreases (Fig. 3). With increasing $I$, we observe a tendency for the derivatives $\partial R_I/\partial T$ and $\partial R_I/\partial I$ to decrease for $T \leqslant 30$ K, and the maxima of the functions $R_I(T)$ to shift to higher temperatures (Figs. 3 and 4). Cooling these samples in a field $H = 10^7$ A/m below the temperature of the maximum reveals a tendency in the negative derivative $\partial R_I/\partial H$ to change sign. It should be noted that the functions $R_I(T,H)$ are reversible during thermal cycling of the samples up to 273 K, i.e., they coincide upon heating and cooling, unless $I \leqslant 0.05$ A. In the opposite case, prolonged passage of current through a sample immersed in liquid nitrogen can lead, as in the case of the cuprates,[5] to a change in the shape of the function $R_I(T,H)$. A result of one trial ($I = 0.1$ A, $\Delta t = 1$ hour) is shown in Fig. 4 by the dashed curve.

Figure 5 shows two families of functions $R_I(T)$ for samples of La–Sr–Nb–O and $DyBa_2Cu_3O_{6+\delta}$ (with $\delta \approx 0.5$), which are characterized by lower and almost identical values $\rho_r \approx 0.05$ Ω·cm. It is well known that for $\delta \approx 0.5$ samples of the system $DyBa_2Cu_3O_{6+\delta}$ are on the threshold of percolation superconductivity. For these values of $I$, the contact resistances do not exceed 1 Ω, and no significant heating effects are observed down to the lowest temperatures ($P < 10^{-3}$ W). It is clear from Fig. 5 that, just as in the previous samples, the value of $R_I(T)$ decreases as $I$ increases in the high-temperature range. In this case, we should add that, whereas in the cuprates the nonlinearity of the current–voltage characteristics becomes noticeable only for $T < 60$ K, it is noticeable in niobates at 100 K or higher. The maxima of the functions $R_I(T)$ are located at considerably higher temperatures. In the low-temperature range, an increase is observed in $R_I(T)$ as $I$ increases and for magnetic fields $H > 10^6$ A/m. In principle, this is typical of systems that are near the threshold for percolation superconductivity under conditions where the coupling between superconducting regions becomes predominantly Josephsonlike.[24]

As $\rho_r$ is further decreased to values $\leqslant 0.3$ Ω·cm, differences in the behavior of $R_I(T)$ for the samples of cuprates

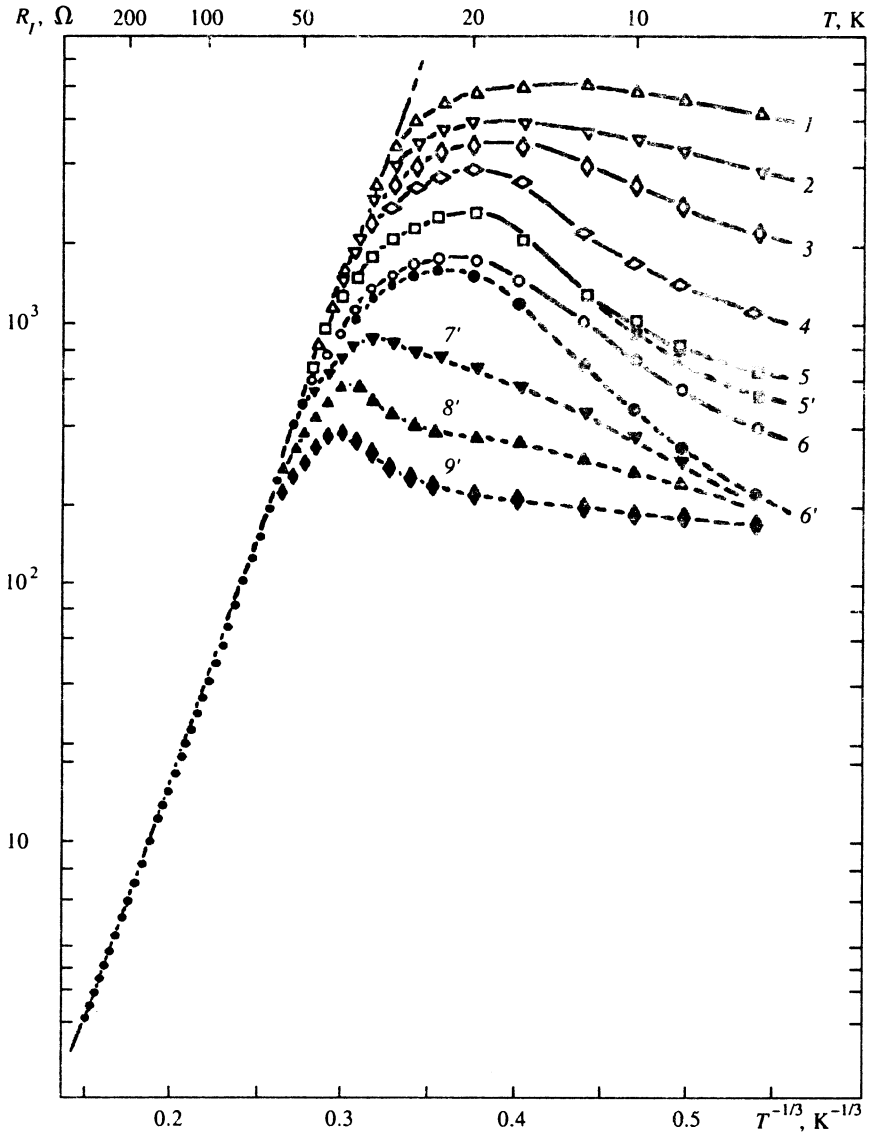


FIG. 3. Family of dependences $R_l(T)$ for a sample of La–Sr–Nb–O with $\rho_r = 0.2$ Ω·cm for various values of the DC measurement current $I_d$ and pulsed current $I_p$ with an inverse duty cycle ≥ 10 (the light and dark symbols, respectively): *1*—$10^{-5}$ A; *2*—$10^{-4}$ A; *3*—$2\cdot10^{-4}$ A; and *4*—$4\cdot10^{-4}$ A; *5,5'*—$10^{-3}$ A; *6,6'*—$2\cdot10^{-3}$ A; *7'*—$5\cdot10^{-3}$ A; *8'*—$10^{-2}$ A; *9'*—$2\cdot10^{-2}$ A.

and niobates under discussion here become more and more marked. Thus, e.g., in the cuprates $LaBa_2Cu_3O_{6+\delta}$ with $\delta \geq 0.5$, the temperature dependence $R_l(T)$ becomes metallic for $T > 150$ K, and the local maximum (which is gradually smoothed away) shifts towards higher temperatures. In the final stage of evolution, samples of this system with $\rho_r \leq 0.005$ Ω·cm and $\delta \approx 1$ exhibit an almost linear decrease of $R_l(T)$ down to the point where the superconducting transition takes place abruptly at $T = 92$–$95$ K.[12]

In samples of Ln–Sr–Nb–O (Ln=La, Nd, Gd, Dy, Tm, Lu), decreasing $\rho_r$ down to <0.03 Ω·cm is accompanied by a shift of the maxima of the functions $R_l(T)$ towards lower temperatures. Simultaneously, there is a decrease in the temperature at which dispersion of the curves $R_l(T)$ begins to occur; in order to observes this, it is necessary to increase $I \geq 10^{-3}$ A. It should also be noted that for these samples, the values of $R_l(T)$ increase as $I$ and $H$ increase over the entire range of temperatures $T < 80$ K where nonohmic behavior of the current–voltage characteristics is observed.

Out of the total number of Ln–Sr–Nb–O samples we obtained and studied (>100), the majority were characterized by nonlinear current–voltage characteristics when $T < 100$ K, with dependences $R_l(T)$ similar to those shown in Fig. 2. While there is no problem obtaining samples in which the behavior of $R_l(T)$ is metallic, samples with high-temperature ($T > 30$ K) maxima for the functions $R_l(T)$ are much less common. This is probably connected with the extreme sensitivity of the transport characteristics of Ln–Sr–Nb–O samples to the slightest fluctuations in composition or conditions of sample preparation over a comparatively narrow intermediate range near the metal–insulator transition. It is likely that this is the region where superconductivity can occur most readily, albeit in localized form. Thus, e.g., in the system $La_{2-x}Sr_xCuO_{4-\delta}$ increasing $x$ leads to monotonic changes in sample properties for the insulating (up to $x < 0.05$) and normal metallic ranges (starting with $x > 0.25$), whereas maximum values of $T_c$ are achieved in the intermediate region $0.1 < x < 0.2$.[11] For some high-$T_c$ superconducting cuprates, the concentration range where superconductivity exists can be extremely narrow. In particular, a decrease in the oxygen content of only 1.5% in samples of $Tl_2Ba_2CuO_{6+\delta}$ is accompanied by an abrupt weakening of

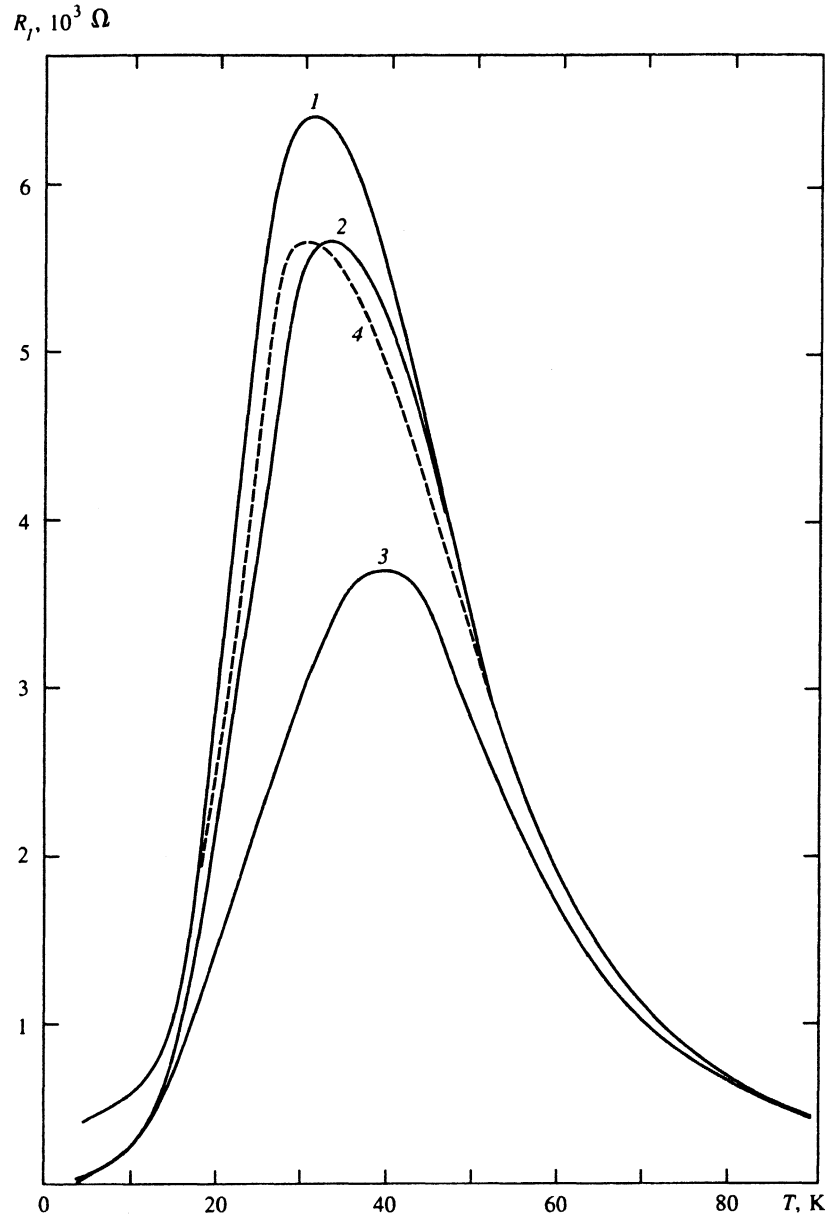


FIG. 4. Temperature dependences $R_l(T)$ for samples of La–Sr–Nb–O ($\rho_r \approx 0.15$ Ω·cm). The dashed curves show the change in the shape of the function 2 after a current of 0.1 A is passed through the sample, which is placed in liquid nitrogen, for a period of one hour: *1*— $I_d = 10^{-4}$ A; *2*— $10^{-3}$ A; *3*—$4 \cdot 10^{-3}$ A; and *4*— $10^{-3}$ A.

the temperature dependence $R(T)$ in the normal state; as this happens, $T_c$ increases from practically zero to 90 K for these compounds.[25]

## 4. CURRENT–VOLTAGE CHARACTERISTICS

In the majority of cases, we took as the current–voltage characteristics the voltage function $U(I)$ measured across the potential contacts of the sample, obtained by smoothly scanning the DC or pulsed current passing through the sample while stabilizing the temperature. In certain samples, the functions $U(I)$ were measured by the method of tunneling contacts, which was previously used to study the high-$T_c$ superconducting cuprates.[12] In this case the samples were attached to a silver mount, and a silver spike was pressed against the sample from above. In order to ensure reliable electrical contact, an indium–gallium eutectic was rubbed into the sample from the mount side. The mount and spike were simultaneously used as current and potential electrodes.

In Figs. 6 and 7 we show isotherms of the current–voltage characteristics for samples of the system La–Sr–Nb–O with $\rho_r \approx$ 0.2 and 0.5 Ω·cm, respectively, obtained by the first (four-contact) and second methods. Although the argument is the current $I$, the isotherms of the current–voltage characteristic are shown in the form of functions $I(U)$. From Fig. 6 it is clear that, when $T \leqslant$ 12 K, the curves obtained recall tunneling characteristics of ordinary superconductors. The difference lies in the fact that, for the current–voltage characteristics, there are regions where the differential resistance $R_D = \partial U / \partial I$ changes sign and becomes negative. As the temperature decreases, these regions disappear, and the curves themselves are smoothed out and become similar to current–voltage characteristics of high-$T_c$ superconducting cuprates.[12] Above 70–80 K, we observed practically complete linearization of the current–voltage characteristics in the majority of cuprates and niobates.

The isotherms of the current–voltage characteristics ob-

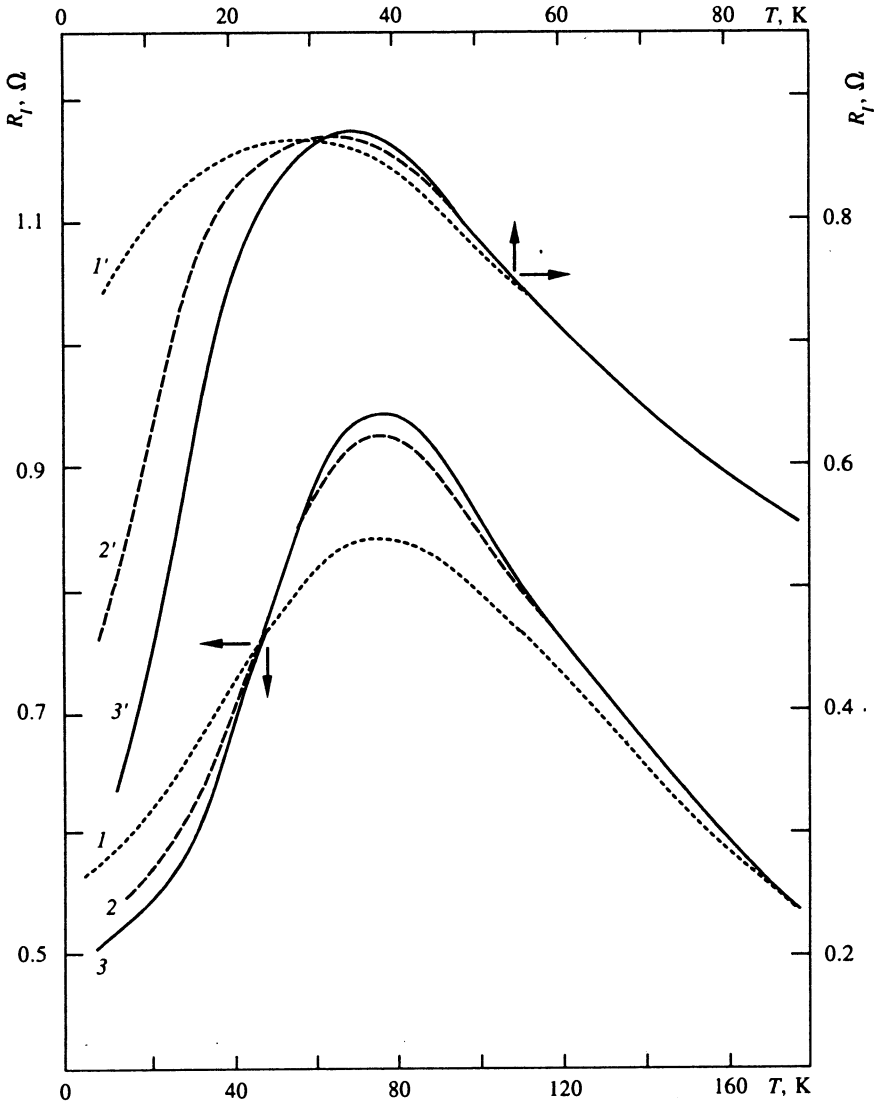


FIG. 5. Temperature dependences $R_l(T)$ for samples of La–Sr–Nb–O ($\rho_r \approx 0.05$ Ω·cm; curves *1–3*) and $DyBa_2Cu_3O_{6+\delta}$ ($\rho_r = 0.05$ Ω·cm; curves *1'–3'*) obtained for various values of the DC measurement current $I_d$: *1,1'* —$25 \cdot 10^{-3}$ A; *2*—$5 \cdot 10^{-3}$ A; *2'*— $10^{-2}$ A; *3*—$0.5 \cdot 10^{-3}$ A and *3'*— $5 \cdot 10^{-3}$ A.

tained by the method of tunneling contacts have portions where the sign of $R_D$ changes; however, they are more extended (Fig. 7), and appreciable nonlinearity of the current–voltage characteristics is preserved up to 160 K. It should be noted that, in the interval of $I$ from $2 \cdot 10^{-4}$ to $3 \cdot 10^{-4}$ A, the values of $U$ change by less than 0.1%. This feature of the current–voltage characteristics can be used, e.g., to design stabilizers for voltage in cryoelectronics. For all the samples we investigated, we never saw even the slightest asymmetry of the current–voltage characteristics when the direction of the current was changed. For certain samples of La–Sr–Nb–O with $\rho_r \geqslant 1$ Ω·cm, along with highly reproducible and stable portions with negative $R_D$ we observed zones of metastable behavior on the current–voltage characteristics, apparently caused by switching effects. Similar features were also observed in the cuprates $LnBa_2Cu_3O_{6+\delta}$ with $\rho_r \approx 0.3$ Ω·cm. Connecting a capacitor to such samples led to stable generation of an AC voltage. It is our hope that, in the course of further investigations, we will not only refine our picture of the physical nature of these features, but that we will also identify promising applications for these systems, e.g., as fundamentally new elements in cryoelectronics.

## 5. DISCUSSION OF RESULTS

It is clear from a comparison of Figs. 1 and 2 that the increase in conductivity of the samples of Ln–Sr–Nb–O and $LnBa_2Cu_3O_{6+\delta}$ at first leads to a deviation of the temperature dependences of $R_l(T)$ from the Mott law at low temperatures, accompanied by dispersion of the curves $R_l(T)$ (Fig. 2) and negative magnetoresistance. In the course of further evolution, the functions $R_l(T)$ develop maxima. The dispersion of $R_l(T)$ caused by nonlinearity of the current–voltage characteristics can extend up to temperatures considerably higher than the maximum (Figs. 3 and 4), whereas at low temperatures we begin to see a tendency for the relative effect of the current $I$ and field $H$ on $R_l(T,H)$ to decrease. As a logical extension of this tendency, upon cooling the samples with lower $\rho_r$ (Fig. 5) we observe a change in the sign of the derivatives $\partial R_l/\partial I$ and $\partial R_l/\partial H$. Finally, at the next stage of decreasing $\rho_r$ down to values that approach the threshold for metallic conductivity $\sigma_{\min}^{-1} \approx 10^{-2}$ Ω·cm, these derivatives become positive over practically the entire temperature interval.

These regularities, which characterize the change in

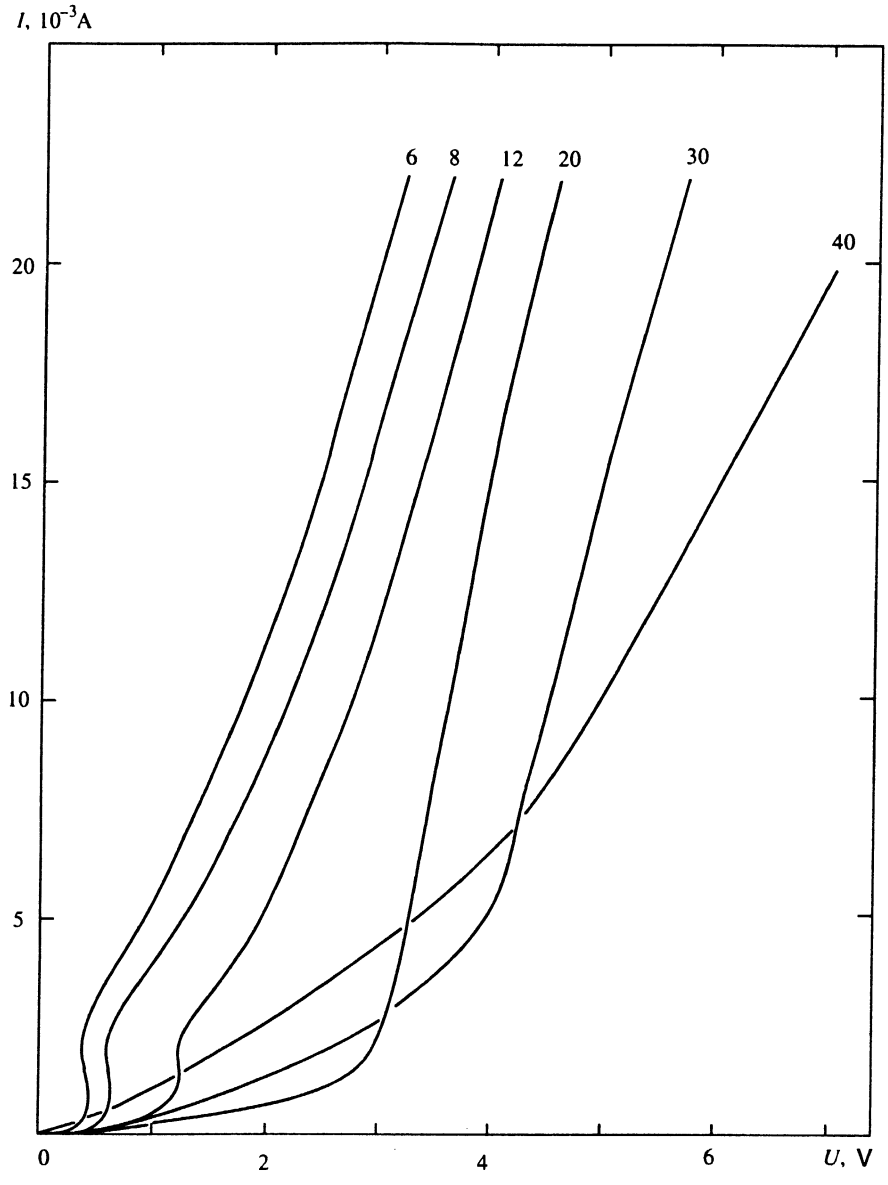


FIG. 6. Isotherms of the current–voltage characteristics for a sample of La–Sr–Nb–O ($\rho_r \approx 0.2\ \Omega\cdot$cm) obtained by the four-contact method. The numbers on the curves are temperatures in K.

transport properties of the samples as we move away from the insulating state, will be analyzed first for the most fully studied system $LnBa_2Cu_3O_{6+\delta}$. In Ref. 26, the assertion was made that the band of carriers in the $CuO_2$ layers arises from direct overlap of the $2p$ orbitals of oxygen, while the electronic states of copper should consequently be localized. This assertion is in agreement, in particular, with the results of recent photoconductivity studies,[1] from which it follows that the transport properties of the system as $\delta \to 0$ are determined almost entirely by the occupied $2p$(O) band, which is separated from the empty $3d$(Cu) band by a gap of $\simeq 1.5$ eV. As we have already mentioned in the Introduction, in the range of small concentrations of active oxygen ($\delta \leqslant 0.1$), the change in electronic properties of the system $LnBa_2Cu_3O_{6+\delta}$ should recall the situation in semiconductors doped with acceptors. In this case the appearance of localized impurity levels at the O ions in the basal planes leads to an outflow of a portion of the electrons from the $2p$(O) band. Due to the large compressibility of the $2p$ orbitals, which usually is manifest in compounds with chalcogenides, it becomes energetically favorable in this case to form localized bipolarons.[27] In this case the Fermi level should be located within a band of localized states, and should, in our view, simultaneously overlap the upper protrusions of the $2p$(O) band, which is warped in space. The radius of localization of holes in the $2p$(O) band due to interaction with bipolarons scarcely exceeds twice the period of the structure $2a \approx 7.6$ Å, whereas for $\delta \leqslant 0.1$ the average distance between holes (and bipolarons) comes to no less than $3a$. Thus, we should expect that when $T < 300$ K the conductivity of samples with $\delta \leqslant 0.1$ will be determined primarily by a hopping mechanism, which, as is observed in traditional doped semiconductors, is characterized by linear current–voltage characteristics and positive magnetoresistance.[3] The quasi-two-dimensional character of the Mott law is probably a consequence of anisotropy of the structure, and indicates that hopping conductivity of holes interacting with bipolarons should occur predominantly along the layers. If we use Eqs. (2), (3) to analyze the functions $R_l(T)$ for the cuprates $LnBa_2Cu_3O_{6+\delta}$ with $\delta \leqslant 0.1$, then for $r_l \leqslant 2a$ we obtain for

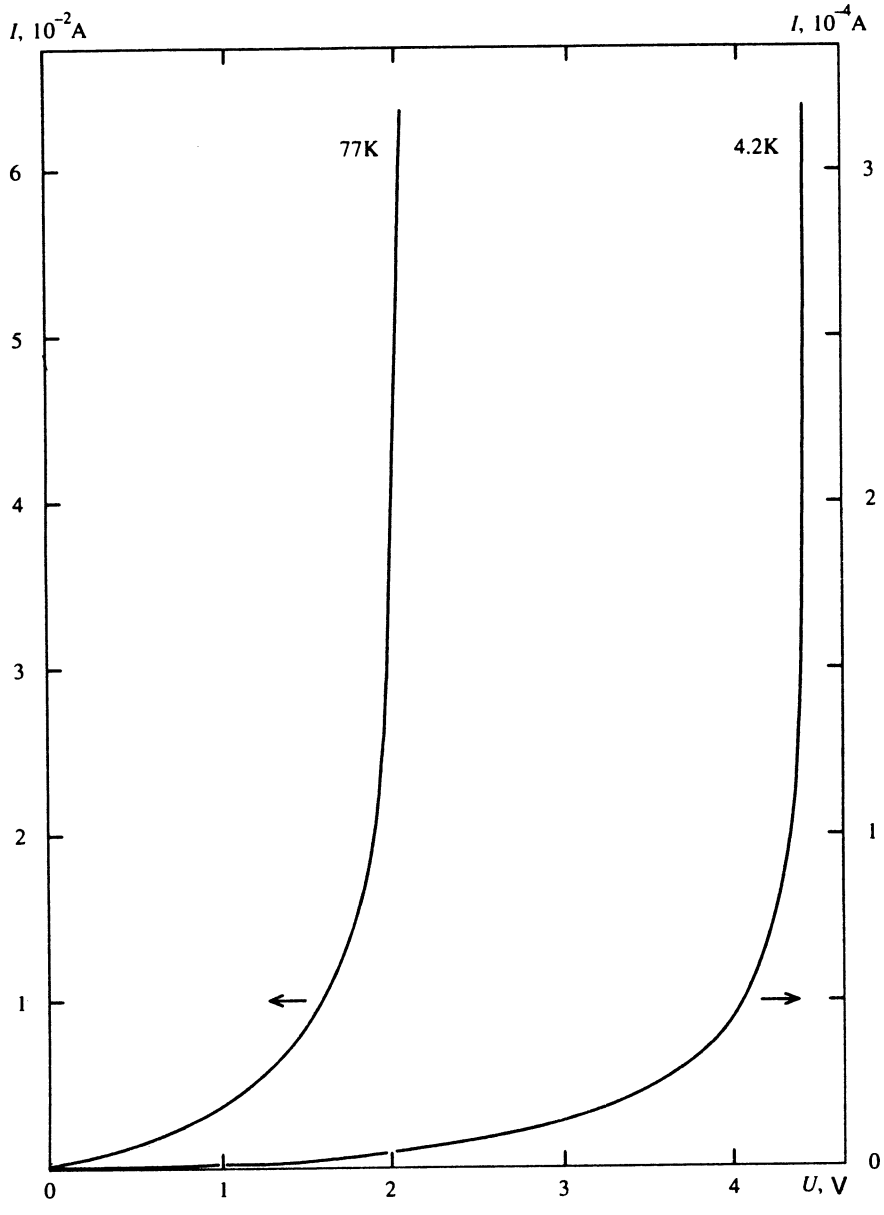


FIG. 7. Isotherms of the current–voltage characteristics for a sample of La–Sr–Nb–O ($\rho_r \approx 0.5\Omega \cdot$ cm) obtained by the two-contact method.

the two-dimensional density of states the reasonable estimate $N_S(E_F) \geqslant 0.1(\text{eV} \cdot \text{cell})^{-1}$, which is 10–100 times smaller than the usual values quoted in publications, i.e., $N(E_F) = 1-12\ (\text{eV} \cdot \text{cell})^{-1}$ for $\delta \approx 1$.[18] If there were no strong interaction between the active oxygen ions and the electronic subsystem,[4,5] the holes could be delocalized even for $\delta \geqslant 0.3$. In reality, the interaction of the subsystem of mobile O ions with the electronic subsystem leads to phase stratification[4–8,10] with a characteristic size $d_m \sim 30$ Å of the metallic regions (superconducting when $T < T_{ci}$; see Ref. 7) in samples with the intermediate values $\delta = 0.1-0.5$. These regions are most likely rather extended clusters of length $l \gg d_m$ ("filamentary" superconductivity; see Refs. 28–30). Calculations show that in this case, for samples with $\delta = 0.5$ the average thickness of the insulating interlayers between clusters should be about 10 Å, which is close to the average of published estimates of the coherence length as $T \to 0$ from $\xi_\parallel = 2-7$ Å along the c-axis to $\xi_\perp = 15-20$ Å perpendicular to it.[12,31] Thus, for intermediate $\delta$ and temperatures $T_{cM} < T < 400$ K, even single crystals should be regarded as granular metals, and for sufficiently low temperatures as a variety of granular superconductor with a broad distribution of local values of $T_{ci}$ and gap $\Delta_{Si}$.[8–10] In principle, this stratification recalls the situation in strongly doped and strongly compensated semiconductors, where it is energetically favorable for the carriers to form isolated "droplets" with a certain characteristic size $r_q$ that greatly exceeds the average distance between impurities.[3] This dimension is bounded from below by the Pauli principle, while from above there are charge-related bounds. As $T$ decreases, the probability of activation of the carriers at the percolation level drops abruptly, and tunneling in the vicinity of the Fermi level begins to play a dominant role, i.e., as before, the transport properties should be determined by a hopping mechanism, but between multicharged droplets. For weak overlap of the wave functions of electrons from neighboring droplets (in the Anderson sense), such a material is customarily regarded as a Fermi glass.[2]

In recent years, there have been more and more reasons to suppose that strong spatial modulation of the density of states is an important prerequisite for the appearance of high-temperature superconductivity, even in its localized form.[32] In droplets, the carriers are almost free, i.e., their kinetic energy is large and greatly exceeds the fine-scale fluctuations of the electrostatic potential. This leads to a large set of wave vectors **k**, and thus ensures a rather high probability of pairing in **k**-space in the presence of suitable interactions, e.g., via the "heavy" bipolarons mentioned above.[27,33] This is associated with the fact that in thermodynamic equilibrium the energy levels of the upper occupied states of the droplets should be close to the majority of localized states in the insulating fragments of the structure ($\Delta E < 0.1$ eV; see Ref. 34). It is worth noting that even before the discovery of high-temperature superconductors there was speculation that local values of $T_{ci}$ could be greatly increased by introducing impurities into a uniform material.[35] A number of other considerations lead us to conclude that as researchers attempt to achieve higher and higher values of $T_c$, they will inevitably be drawn to methods that enhance dielectric correlations in the electron subsystem. This fact strongly limits the usefulness of traditional approaches, which are based entirely on the assumptions of band theory. Under these conditions, pairing in **k**-space must be accompanied by enhanced localization of the pairs in real space; this is impossible for homogeneous metallic systems, whose carrier densities are practically constant with volume (when their kinetic energy significantly exceeds the modulation of the lattice potential screened by them). Under ordinary (terrestrial) conditions, the minimum coherence length $\xi_{\min}$ of such pairs will be bounded from below by the dimensions of the minimum subcell $a$. As $\xi$ approaches $\xi_{\min}$, the average concentration of the most mobile carrier-fermions should decrease, since it becomes energetically favorable for more and more of them to be paired with their adjacent partner and wrapped up in an overall "jacket" of polarization, thereby replenishing the ranks of the low-mobility bipolaron-bosons. Equilibrium between the two carrier subsystems will be maintained by reverse fluctuation-induced transitions. Localized superconductivity in the boson subsystem can manifest itself as condensation into droplets and a transition to the superfluid state. Estimates of the negative correlation energy show that when the average amplitude of the electric field modulation is 0.2–0.4 V with a period $2a$, the region of existence of the most "heat-resistant" superconducting boson droplets could extend up to temperatures $T = 400$–$800$ K and to fields $H = (2\text{–}5)\cdot 10^9$ A/m. However, in this case it is necessary to take into account that, unlike traditional superconductors, the $T$–$H$ phase diagram will be strongly washed out, due not only to the scatter of $T_{ci}$ in the various droplets, but also due to the fluctuation-induced instability of the bosons themselves.

There is reason to suppose that favorable conditions for realizing localized superconductivity with $T_{ci} > 50$ K within the framework of this scenario can be created even in binary systems,[32] if their composition includes such key elements as a chalcogen X (preferably oxygen) and a transition metal T. The choice of a chalcogen, as we have already noted above, is due to the high degree of polarizability of the $2p$ orbitals[27] and the favorable conditions for localization of electron pairs to form a bipolaron. The role of the second element T, in addition to that of "supplier" of a sufficient quantity of electrons (potentially more than two), is to ensure the stability of fragments of the structure as the coordination number $n$ with respect to the nearest chalcogen ions varies over a wide range. For $n \leqslant 5$, $TX_2$ planes can be present, analogous to those that exist in the high-temperature superconducting cuprates. In order to form these planes, an important requirement is the presence of a high density of vacancies (primarily in the X positions). If we limit our discussion to the oxygen-deficient T–O oxides, we find that they share an important feature with the high-temperature superconducting cuprates: instability with respect to phase stratification[6] for homologous series of the type $T_nO_{2n-1}$, $T_nO_{3n-1}$, $T_nO_{3n-2}$,... This concept was first introduced by Magneli in his studies of the Mo–O system.[36] This stratification is probably a consequence of strong autocorrelations in the two interacting subsystems, i.e., electrons and mobile O ions (in the presence of a large number of vacancies).[4] If we activate the phonon subsystem by heating the sample up to a certain optimal temperature, we can accelerate the process of stratification considerably.

Binary systems based on lanthanides Ln and a number of metals that exhibit variable valence such as Bi, Pb, Tl,... are less promising. However, we should add here that there is considerable interest within the context of this approach to the problem of high-temperature superconductivity in systems consisting of finely dispersed granules or flakes of oxidized metals. As the calculations of Ref. 37 show, the ground state of these systems is characterized by the presence of potential differences between the granules and a dip in the density of states in the neighborhood of the Fermi level (dielectric correlations). In more complicated structures, which include (along with the basic elements X and T) the elements Ln and M mentioned above as well as alkali metals from groups I and II, there is hope that by suitably choosing the composition and conditions for synthesis we can increase the probability of forming structures in which the modulation of the bare potential contour is optimal for high-temperature superconductivity. The final form of this contour will be determined by the level of filling, i.e., the average number of valence electrons per single anion or cation.[38]

Thus, the discussion above indicates that in order to analyze the evolution of transport properties of the system $LnBa_2Cu_3O_{6+\delta}$ with $\delta > 0.1$ we must include not only the possible appearance of metallic droplets, but also the fact that the electrons in some of these droplets can enter into a phase-coherent paired state at low temperatures. Meanwhile, as we have already noted, the local values of $T_{ci}$ and $\Delta_{Si}$ for the droplets should be characterized by broad distribution functions. For intermediate temperatures $100\text{ K} < T < 300$ K, the transport properties will be determined primarily by hopping conductivity between droplets, which implies a positive magnetoresistance and linear current–voltage characteristics[3] as is observed in experiments. As $\delta$ increases and $T$ decreases, the concentration of regions of localized superconductivity in the samples will increase, and some of them will

join into extended chains (clusters). In this case, we should expect the resistance to increase more slowly (Fig. 2) or even decrease as the sample is cooled (Figs. 3–5). In such samples, the value of $R_I(T)$ for $T<100$ K and a preset $U$, will be primarily determined by a sum of local tunneling currents $i_{i,j}$ of unpaired quasiparticles (above-condensate excitations). It is well known that when this type of tunneling dominates, the current $i_{i,i+1}$ between neighboring localized superconducting regions (or between localized superconducting regions and normal droplets) is a nonlinear function of $T$, $H$, and the local values of $\Delta_{Si}$ and the potential differences $u_{i,i+1}$. In particular, the current $i_{i,i+1}$ should increase abruptly when $u_{i,i+1}\geqslant(\Delta_{Si}+\Delta_{Si+1})/e$. Increasing the voltage $U$ applied to the sample at a fixed temperature $T$ and field $H$ increases the number of tunnel contacts for which this condition holds. As a result, it is not unusual to see an abrupt decrease in the differential resistance $R_D$ or even a change in its sign, behavior which is characteristic of circuits with nonlinear elements. For the majority of cuprates we studied with $\delta=0.2$–$0.5$, the functions $I(U)$ were similar to those shown in Figs. 6 and 7 for the niobates. The decrease of $R_D$ with increasing $U$ (and accordingly with increasing $I$) leads to a decrease in $U/I$; consequently, below a certain temperature we observe dispersion of the curves $R_I(T)$ (Fig. 2) and negative values of the derivative $\partial R_I/\partial I$. A magnetic field $H>H_{c1}$ decreases the pair binding energy, which increases the number of above-condensate excitations. This tends to rectify the current–voltage characteristics, which in principle explains the negative magnetoresistance, which can reach 5–10 % in the low-temperature range for $H=10^7$ A/m; in the high-temperature region it is positive and usually does not exceed a fraction of a percent. As we have mentioned above, a similar magnetic field effect is also observed for cuprates with other compositions, i.e., $La_{2-x}Sr_xCuO_{4\pm\delta}$ ($T<30$ K; see Ref. 15) and $Bi_2Sr_2CuO_6$ ($T<15$ K; see Ref. 23). According to our description of the properties of these cuprates in the range $\delta=0.2$–$0.3$, where single-particle tunneling is decisive, increasing $U$ or $H$ for $T=$ const is equivalent to increasing the number of multicharged centers that can participate effectively in the charge transfer process. With this in mind, we call the reader's attention to the similarity between the families of curves of $R_I(T)$ for the cuprates and niobates (see Figs. 2 and 3) and the family of temperature dependences $R(T)$ for semiconductors with various degrees of doping (see, e.g., Fig. 4.2 in Ref. 3). This means that by varying the voltage applied to the cuprate and niobate samples we can directly control their level of doping within certain limits. Furthermore, such comparisons could turn out to be useful for extracting information about the distribution of local values of $\Delta_{Si}$ and $T_{ci}$.

As $\delta$ increases, the current–voltage characteristics of the cuprates develop a smoothed-out step in the low-voltage range $U\leqslant0.01$ V for temperatures $T\leqslant10$ K, indicating that the relative contribution of Josephson tunneling to the conductivity process is increasing. This change in the current–voltage characteristics is due to the increased concentration of regions of localized superconductivity, which in turn implies a smaller average distance—comparable to $\xi_\perp$—between these regions. Therefore, an increase in $I$ is accompanied by an increase in $R_I(T)$. In a sufficiently strong magnetic field $H\approx10^7$ A/m, the step disappears,[39] and as a result $R_I$ increases. We will argue that the only consistent explanation for the sign change of the derivatives $\partial R_I/\partial I$ and $\partial R_I/\partial H$ observed in the cuprates $LnBa_2Cu_3O_{6+\delta}$ as $\delta$ increases and/or $T$ decreases, and for a number of other similar patterns in the evolution of their properties as they depart from the insulating state, is the following:

1) An increase in the concentration of regions of localized superconductivity with a broad distribution of local values of $T_{ci}$ and $\Delta_{Si}$;

2) The joining of an increasing number of these regions into extended clusters;

3) A crossover[40] from current–voltage characteristics with predominantly single-particle tunneling between superconducting clusters to a situation where an important part of the conductivity comes from Josephson tunneling of pairs.

In attempting to explain analogous features in the evolution of the electronic properties of the system Ln–Sr–Nb–O, we are driven to postulate the presence of regions of localized superconductivity with $T_{ci}$ as high as 160 K or higher, although we realize that this hypothesis cannot yet be regarded as beyond challenge. On the other hand, at low temperatures ($T\leqslant12.4$ K) the evidence for percolation superconductivity in Ln–Sr–Nb–O samples is incontrovertible.[41,42] The functions $R_I(T)$ shown in Fig. 4 (which, incidentally, are almost exact copies of resistance curves for samples of the ternary system $La_2CuO_{4+\delta}$ published in one of the first papers on this material,[29]) give us cause to hope that the percolation limit may be surmounted at sufficiently high temperatures.

If we are justified in postulating high-temperature localized superconductivity in the system Ln–Sr–Nb–O (see Ref. 43), then juxtaposing the changes in the electronic properties with data from x-ray analysis leads us to conclude that the origin of these localized regions is most likely associated with the perovskite phase of the compound $(Ln,Sr)_xNbO_{3-\delta}$, whose unit-cell parameters (or subcell) vary from 3.97 to 4.03 Å, depending on composition and conditions of preparation; the phase for $x=0.66$ is found to be close to the threshold for stability of the structure.[41] The majority of Ln–Sr–Nb–O samples that exhibit nonlinearity of the current–voltage characteristics up to 50 K and higher are characterized by the parameter $a=3.99$ Å. Note that in a number of high-$T_c$ superconducting cuprates with hole conductivity the increase in $T_c$ from 40 to 125 K is accompanied by an increase in the average distance between O ions in the $CuO_2$ planes from 3.78 to 3.85 Å. If we assume that this increase in $T_c$ is primarily associated with an increase in localization effects due to the decrease in overlap of the $2p$ orbitals, then it follows from our previous discussion that we have a right to expect higher $T_c$ in the niobates, albeit in localized regions.

The usual way to verify the presence of a superconducting state in a sample is to investigate its magnetic characteristics. However, this approach turns out to be rather unproductive for the case of finely dispersed regions of localized superconductivity. Elementary estimates show that if these regions have the form of nonoverlapping extended clusters

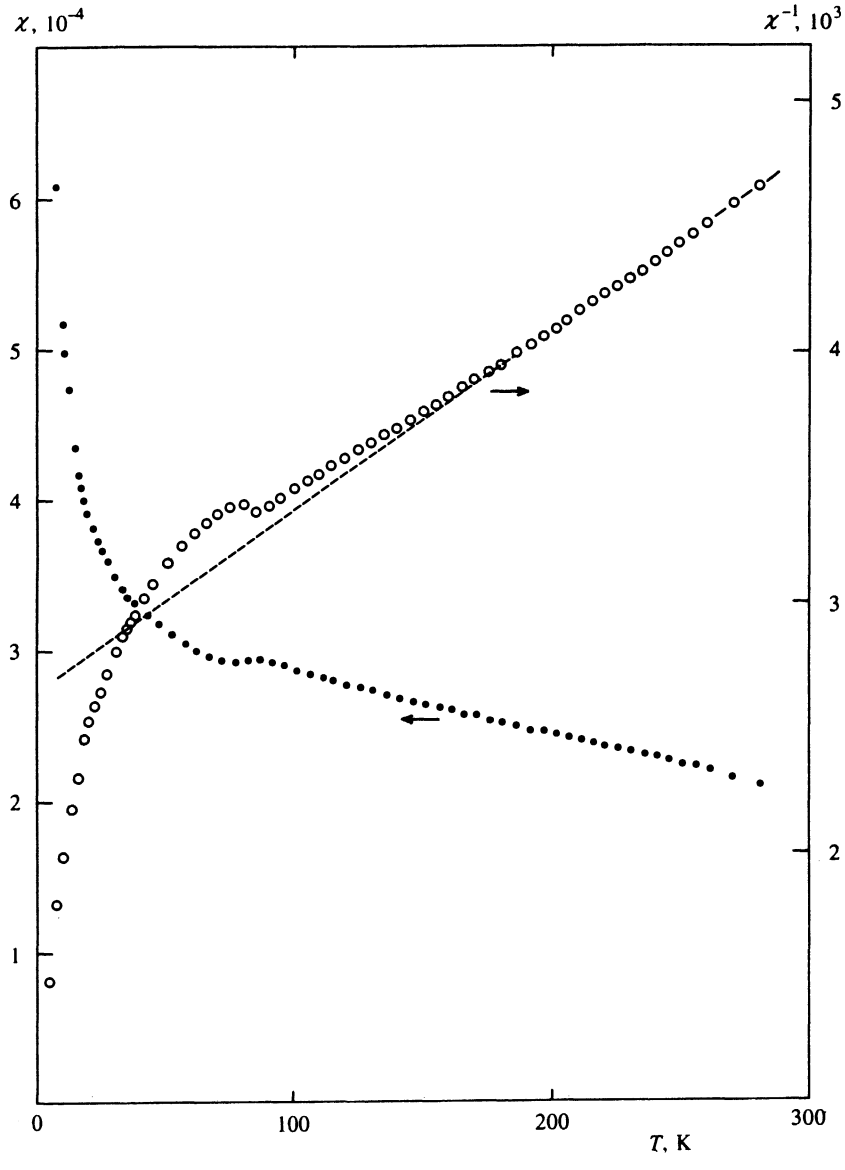


FIG. 8. Temperature dependence of the magnetic susceptibility $\chi(T)$ and its inverse $\chi^{-1}(T)$ (in SI units) for a sample of La–Sr–Nb–O with $\rho_r \approx 0.05$ $\Omega$·cm whose curve for $R_I(T)$ exhibits a maximum at $T \approx 80$ K (Fig. 5).

of the corrugated-cylinder type, with average diameters $d_m \approx 50$ Å (see Ref. 7), we can take values of $\xi \sim 10$ Å and penetration depth $\lambda \sim 2000$ Å that are characteristic of the high-temperature superconducting cuprates to obtain the coefficient $\eta \approx c(d_m - \xi)^2/40\lambda^2$, which characterizes the attenuation of a signal compared to an ideal diamagnet. When the relative concentration of these cylinders $c \sim 0.1$, the value of this coefficient is only $\sim 10^{-6}$. It is therefore not astonishing that the authors of Ref. 29, having observed an abrupt change in the character of the functions $R_I(T)$ for $T \leqslant 40$ K in samples of $La_2CuO_{4\pm\delta}$, chose to explain the vanishingly small diamagnetism ($\sim 10^{-5}$ of the ideal value) as a manifestation of the filamentary character of the superconductivity. In Fig. 8 we show the temperature dependence of the magnetic susceptibility $\chi(T)$ and its inverse $\chi^{-1}(T)$ for a Ln–Sr–Nb–O sample with curves $R_I(T)$ that have a maximum at 80 K (Fig. 5). From a comparison of Figs. 5 and 8 it is clear that a local minimum of $\chi(T)$ is observed at roughly this temperature, and that the deviation of the function $\chi^{-1}(T)$ from its high-temperature behavior (the dashed curve) correlates with the beginning of dispersion of the curves $R_I(T)$. We note here a previous observation[44] of the appearance at $T \sim 290$ K of a diamagnetic response, along with a simultaneous decrease in the resistance, in samples of the systems La–Sr–Nb–O. These samples, whose component ratios were unspecified, were obtained by high-rate magnetron sputtering of a target with composition $LaSrCuO_4$ onto a thin niobium foil. Along with this report, we should also mention the results of comparatively recent studies of samples of the system Sr–Nb–O (see Ref. 45) in which a decrease in the oxygen content was accompanied by the appearance of a diamagnetic deviation from the high-temperature behavior of $\chi(T)$ for $T \leqslant 200$ K.

Summarizing the basic results and ideas of this paper, we can conclude that our methodological approach, which is based on parallel investigation of the evolution of properties of two oxygen-deficient metal–oxide systems, allows us not only to reveal more clearly the fundamental role of dielectric correlations in well known high-temperature superconducting compounds, but also to map out important reference

points for further investigations of one of the most intriguing questions on the modern scene—the possibility of superconductivity with $T_c > 100$ K (at least in localized form) in copperless systems.

## 6. FUNDAMENTAL CONCLUSIONS

1. We have observed and analyzed common patterns and distinctive features in the evolution of the electronic properties of samples of the systems Ln–Sr–Nb–O and $LnBa_2Cu_3O_{6+\delta}$ as they leave the insulating state.

2. We have shown that in samples of $LnBa_2Cu_3O_{6+\delta}$, the deviation of the functions $R_I(T)$ from the Mott law at low temperatures, which is accompanied by their dispersion and subsequent sign changes in the derivatives $\partial R_I/\partial I$ and $\partial R_I/\partial H$, is caused by the appearance of regions of localized superconductivity with a broad distribution of local values of $T_{ci}$ and $\Delta_i$.

3. The analysis given here implies that the sign change in these derivatives is due to a decrease in the average distance between regions of localized superconductivity as $\delta$ increases and $T$ decreases, which in turn leads to crossover from tunneling-dominated current–voltage characteristics to charactieristics of Josephson type.

4. In explaining analogous features in the evolution of properties of samples from the systems Ln–Sr–Nb–O, we are driven to postulate regions of localized superconductivity with $T_{ci}$ up to 160 K or higher, especially because there is practically no doubt that the superconductivity in samples of this system is percolationlike when $T \leqslant 12.4$ K. The results we have obtained for magnetic measurements and data from other authors also may be considered as additional arguments in favor of this assumption.

5. In investigating the current–voltage characteristics of samples of both systems, we observed sections with negative differential resistance and zones of metastable behavior, which may be of interest from the perspective of practical applications.

6. We have analyzed specific features in the variation of properties of the metal–oxide systems near the metal–insulator transition, comparing them with doped and strongly doped semiconductors, and also granular metals. This analysis has helped to further clarify the fundamental role of spatial modulation of the electrostatic potential (and therefore modulation of the carrier density) in creating high-temperature superconductivity, and has pointed the way for more directed searches for new high-$T_c$ superconducting systems.

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