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Effects of Resistance Switching in Niobium Oxides: Metastable Nanochannels

A. V. Mitin[a], V. F. Shamray[b], and A. S. Gordeev[b]

[a] *Kapitza Institute for Physical Problems, Russian Academy of Sciences, ul. Kosygina 2, Moscow, 119334 Russia*
[b] *Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Leninskii pr. 49, Moscow, 119991 Russia*
e-mail: mitin@kapitza.ras.ru

Abstract—The recent experimental data suggest that lattice defects in transition-metal oxides tend to be aligned into chains, which can promote pairing of charge carriers with subsequent formation of bosonic stripes. In this study, possible relationship between the extraordinary manifestations of electronic properties, observed by different methods in niobium oxides, and the processes of formation of metastable nanochannels from bosonic stripes are discussed.

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The importance of finding the reasons for strong spatial modulation of local properties of transition-metal oxides is related both to the internal logic of development of condensed-matter physics and the strong competition in solving engineering problems in the design of optoelectronic cells, holographic matrices, memory cards, fuel cells, sensors, etc. Despite the impressive progress in the development of physical experimental methods, consensus in a number of questions concerning the fundamental aspects of physical processes occurring in transition-metals oxides [1–3] is still absent. In particular, the revived interest in the effects of resistance switching is stimulated not only by the prospects of fabrication of non-volatile terabit memories but also the intention to clarify the microscopic nature of the phenomena occurring in this case [2–7].

The first indications to the effects of resistance switching in transition-metal oxides were revealed in the 1960s in investigations of the current–voltage (*I*–*V*) characteristics of Nb–Nb_2O_5–Bi structures previously exposed to an electric field of ~10^8 V cm^{-1} (see [8] and references therein). The multiple increase in the conductivity of the Nb_2O_5 layer as a result of field application was accompanied by the formation of a kink in the *I*–*V* characteristic at the potential difference $U \sim 0.6$ V, followed by a region with negative differential resistance (NDR). It was found that the transition of the samples to the conducting state through the NDR region is reversible and can be multiply reproduced upon cycling [8]. Subsequent investigations showed that the switching effects can manifest themselves in different transition-metal oxides: from binary to multicomponent ones, including superconducting cuprates [2–6].

Detailed analysis of the microstructure of the switching samples of transition-metal oxides gave suggested that the effects of resistance switching should be related to defect ordering along selected crystallographic directions [2, 3, 6, 7, 9, 10]. Defects of the oxygen sublattice [2, 7], in which weakly bound oxygen ions can migrate at distances much larger than the lattice parameter, are most affected by an external electric field. As a result of the electromigration of a sufficiently large number of defects and localized states generated by them, one would expect the formation of a network of metastable conducting nanochannels; charge carriers can be unstable with respect to pairing at $T < T_{ci}$ in individual fragments of these nanachannels. In other words, conditions for formation of bosonic stripes can be implemented in the extended valleys of the potential extra-relief formed by the chains of defects in transition-metal oxides, as this was considered within the string model applied to $YBa_2Cu_3O_{6+\delta}$ with $\delta < 0.5$ [11, 12]. The main purpose of this study is to justify application of the concept of bosonic stripes for explanation of the general regularities in evolution of electronic properties of cuprates and niobates with an increase in the carrier concentration.

It is pertinent to recall that, among the best-studied transition-metal oxides, it is the $La_2CuO_{4+\delta}$ oxide that is most prone to alignment of extra oxygen ions into chains [13, 14]. It is important that the ordering of hole excitations in the form of superconducting nanochannels [14] (filamentary superconductivity [15]) is related specifically to the formation of chain fragments in these compounds. An increase in the length and concentration of such channels provides conditions for the sample transition to the state of percolation superconductivity upon cooling below the critical temperature $T_{cp}(\delta)$, which is limited by the weakest links on the way of tun-

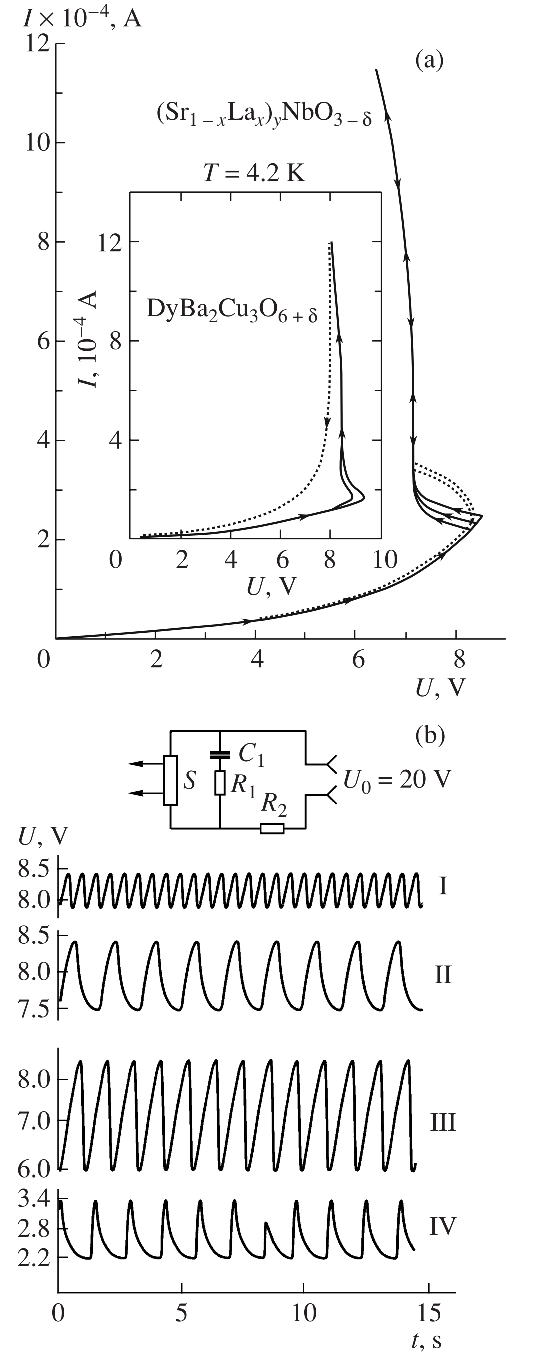

Fig. 1. (a) Examples of current–voltage characteristics of $LnBa_2Cu_3O_{6+\delta}$ and $(Sr_{1-x}La_x)_yNbO_{3-\delta}$ samples; measurements at $T = 4.2$ K. (b) The scheme for measuring the voltage U on the potential contacts of the $(Sr_{1-x}La_x)_yNbO_{3-\delta}$ sample (top part) and (below) examples of oscillations at $C_1 = 10$ μF; $R_2 = 100$ kΩ; and $R_1 =$ (I) 10, (II) 20, (III) 0.1, and (IV) 1 kΩ.

neling of paired carriers, as this occurs in granular superconductors [16]. Similar processes of alignment of oxygen ions in the basal plane of $LnBa_2Cu_3O_{6+\delta}$ (Ln = Y, La, Dy, Gd, Ho, …) should initiate formation of bosonic stripe fragments in clusters of fermion-like hole excitations at $\delta > 1/16$ [11, 12]. Pinning of bosonic stripes may lead to a strong spatial modulation of local properties on a scale of several nanometers [17].

In almost the entire temperature range from 4.2 to 295 K, in which the measurements were performed, the curves $\rho(T)$ for the $LnBa_2Cu_3O_{6+\delta}$ samples with $\delta \approx 0.1$ [18] are approximated well by the Mott law ($\rho_I(T) = \rho_0\exp(T/T_0)^{-1/(1+D)}$) for quasi-two-dimensional systems ($D = 2$) with a variable hop length. The behavior of the samples $(Sr_{1-x}Ln_x)_yNbO_{3\pm\delta}$ with $\rho_I(295\text{ K}) \geq 0.1\ \Omega$ cm [18] is even better described by this law. An increase in the carrier concentration in cuprates and niobates first leads to deviation from the Mott law in the range $T < T_{cM}$, which is accompanied by dispersion of the integral resistance curves $\rho_I(T, I) = \frac{s}{lI}\int_0^I \frac{\partial U}{\partial I} dI \equiv \frac{sU}{lI}$, measured at several values of the stabilized current I, where s is the cross section of the sample and U is the voltage drop on the length l between the potential contacts. Further evolution is related to extension of the range $T \leq T_{cM}$ and $\partial\rho_I/\partial T$ sign inversion, while NDR portions and signs of metastable behavior begin to be observed in the I–V characteristics of cuprates and niobates, which are characteristic of resistance switching effects. Two sets of I–V characteristics shown in Fig. 1a supplement the previous results of comparative study of $LnBa_2Cu_3O_{6+\delta}$ and $(Sr_{1-x}Ln_x)_yNbO_{3-\delta}$ oxides [18]. Connection of a capacitor to the current contacts of the samples leads to U oscillations (Fig. 1b). Note that manifestations of the effects of resistance switching were observed in other cuprates prone to superconductivity, such as $Bi_2Sr_2CaCu_2O_{8+\delta}$ [19].

The similarity of both sets (Fig. 1a) suggests that the physical processes responsible for the occurrence of NDR portions and regions of metastable behavior in the I–V characteristics of cuprates and niobates have the same nature. Analysis of the experimental data shows [18] that, to self-consistently explain the regularities in evolution of the electronic properties observed in cuprates and niobates with an increase in the carrier concentration, it is necessary to take into account the possibility of formation of superconducting nanochannels, as this occurs in $La_2CuO_{4+\delta}$ with an increase in δ [15]. The conclusions of [18] about the possibility of superconducting ordering of paired hole states at $T \leq 800$ K in extended valleys of the potential extra-relief, which are formed by basal-oxygen chains in $YBa_2Cu_3O_{6+\delta}$ samples with $\delta < 0.5$, were developed in the string model [11, 12]. The five-level $T^*_{c\eta}(\delta)$ diagram, proposed within this model to clarify the contradictory situation with the origin of pseudogap anomalies and upper temperature limit of their manifestation in $YBa_2Cu_3O_{6+\delta}$, was soon confirmed by the experimental results obtained in the temperature range up to 1280 K [11, 20]. In particular, the dependences $\rho_I(T)$ for $YBa_2Cu_3O_{6+\delta}$ with $\delta < 0.18$ revealed the predicted maxima at $T \leq 1200$ K, whose shape resembles steep kinks in the curves $\rho_I(T)$ for $La_2CuO_{4+\delta}$ [15] and $(Sr_{1-x}Ln_x)_yNbO_{3-\delta}$ near $T \approx 40$ K [18]; these kinks were interpreted as the result of formation of superconducting filaments.

Since the publication of the Bednorz and Müller's historical study [21], the question of the possibility of implementing high-temperature superconductivity in copperless transition-metal oxides remains to be one of the most intriguing. Among only niobates, more than ten of compounds have been found that are prone to a certain extent to superconducting pairing. For example, monoxide NbO, having the simplest composition, along with the transition to the superconducting state at $T \leq 1.5$ K [22], has interesting transport properties at high temperatures, which are generally attributed to superconducting cuprates. One of such properties is the strong temperature dependence of the Hall coefficient with sign inversion near 100 K [22] and rectification of the quadratic portion $\rho_I(T) \sim T^2$ above 90 K, as this occurs for the cuprates $Tl_2Ba_2CuO_{6+\delta}$ with $\delta > 0.1$. Moreover, cooling of $Tl_2Ba_2CuO_{6+\delta}$ and $NbO_{1-\delta}$ samples below 60 K leads to "sagging" of the $\rho_I(T)$ curves as a result of the excess conductivity caused by the formation of superconducting inclusions in the regions of local defect ordering [23]. This conclusion is confirmed by the nonlinearity of the *I–V* characteristics upon sample cooling below 60 K [23]. Measurements of the dependence $\rho_I(T)$ for the $NbO_{1+\delta}$ samples with $\delta \approx 0.25$ revealed the presence of kinks at $T \approx 150$, 200, and 275 K, which are generally observed for the cuprates $LnBa_2Cu_3O_{6+\delta}$ with $\delta \approx 0.6$ and correspond to the upper temperature limit of existence of bosonic stripes of the sixth, fifth, and fourth ranks on the five-level $T^*_{c\eta}(\delta)$ diagram [12], where the index η corresponds to the stripe rank. The dependences $\rho_I(T)$ for the $NbO_{2\pm\delta}$ and $Nb_2O_{5-\delta}$ samples contain kinks at $T \approx 1100$ K, which can be related to the processes of formation of second-rank bosonic stripes with the width $w_\eta = \eta a = 2a$, where a is the average distance between Nb cations.

There are grounds to believe that, as a result of the increase in the number of components in niobates and careful choice of their synthesis conditions, more favorable conditions can be provided for the formation of superconducting channels composed of bosonic stripes of different ranks; the narrowest of them, at a low (volume-averaged) carrier concentration can withstand heating up to 1200 K [11]. However, as was mentioned above, the temperature T_{cp} of the transition to the percolation superconductivity state is limited by the weakest links between bosonic stripes rather than their "heat resistance". It is quite possible that, as in the situation with underdoped cuprates, specifically the percolation character of superconductivity is responsible for low values of $T_{cp} \approx 5.5$ K in Li_xNbO_2 [24]. Replacement of Li by Ca, Sr, or Ba leads to an increase in T_{cp} for the oxygen-deficient three-component niobate $ANb_2O_{6-\delta}$ (A = Ca, Sr, Ba) to ≈12 K [25]. It was noted in [25] that partial (5–10%) replacement of Sr with a lanthanide (Ln = La, Nd, Pr, Ce, Dy, Gd, Ho) is accompanied by a multiple increase in the diamagnetic signal; this fact indirectly confirms the percolation character of superconductivity in this compound, which is an insulator in the stoichiometric composition ($\delta \to 0$).

Niobates $CaNbO_{3.5-\delta}$ and $SrNbO_{3.5-\delta}$ at $\delta \to 0$ are also insulators, whose magnetic susceptibility $\chi(T)$ in the range from 4.2 to 280 K is temperature-independent [26]. Removal of 3–5% oxygen ions leads to deviation of the curves $\chi(T)$ for the $CaNbO_{3.35}$ and $SrNbO_{3.42}$ samples toward diamagnetism upon their cooling below 120 K and 220 K, respectively. The dependence $\rho_I(T)$ acquires thermally activated character in this case [26]. For the samples of similar composition, Sr_xNbO_3 (x = 0.9), a convexity arises in the curve $\rho_I(T)$ near 200 K; a decrease in temperature is accompanied by an increase in the slope $\partial\rho_I/\partial T$ [27]; this feature is characteristic of systems in which excess conductivity is caused by the formation of superconducting inclusions with a wide distribution function T_{ci} [18]. The peaks in the curves $\rho_I(T, I)$ for the $(Sr_{1-x}Ln_x)_yNbO_{3\pm\delta}$ samples are much more pronounced; in addition, the dependences $\rho_I(T, I)$ measured at different I are characterized by variance up to 160 K [18]. It should be added that, as in the case of $LnBa_2Cu_3O_{6+\delta}$ cuprates [18], the shape and position of these peaks depend not only on the heat treatment conditions but also on the current amplitude I; its increase above some threshold leads to oxygen redistribution [28] with generation (annihilation) of bosonic stripes of particular rank. Within the string model [11, 12], such a network allows formation of extended metastable channels composed of bosonic stripes with $\eta \leq 4$, which can provide almost dissipationless charge transport at $T > 300$ K. Because of extremely low probability of formation and poor reproducibility of such channels in lightly doped oxides, apparently, only a small part of superconductivity signs observed above room temperature have been reported by researchers, who were courageous enough to give examples of $\rho_I(T, I)$ curves with a sharp falloff beginning with 300 K and higher temperatures. Generally, the transition of niobate and cuprate samples to the low-resistance state ("instrumental" zero) was accompanied by the formation of a weak diamagnetic response and other characteristics [29–33] indicating a fairly small volume fraction that could be involved (in the form of channels) in dissipationless charge carrier transport.

On the basis of the above data, we can conclude that scattered experimental data on the electronic properties of niobates give rise to an unified a physical pattern based on the scenario of stripe ordering of charge carriers in extended valleys of the potential extra-relief formed by the defects aligned into chains. The proposed scenario should fill the existing gaps in understanding the microscopic nature of the observed phenomena and choose new ways in purposeful study of peculiar characteristics of transition-metal oxides, which cover the range from antiferromagnetically ordered insulators and ferroelectrics with record critical temperatures to high-temperature superconductors.

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