The interplay of superconductivity and localization in Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ single crystal films

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Abstract

The influence of nonstoichiometric disorder on the in-plane resistivity and SC-transition has been investigated for Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ single crystal films ($x = 0.15$ and $0.18$). It is shown that with increasing of $\delta$ the in-plane normal state resistivity increases (the mean free path diminishes) and SC-transition temperature decreases with essential broadening of the transition region. The observed evolution from homogeneous metallic (and superconducting) Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ system to inhomogeneous dielectric one is described as Anderson-type disorder-induced transition in a two-dimensional electron system.

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1 Introduction

Single crystal Nd$_{2-x}$Ce$_x$CuO$_4$ belongs to a class of basically tetragonal copper oxide compounds. All of these crystals have CuO$_2$ planes in their structure separated by buffer layers of other atoms. The conduction process mainly occurs in the CuO$_2$ planes while the other layers act as so called charge reservoirs simply providing carriers [1].

The structure of Nd$_2$CuO$_4$ crystal called T$'$ structure is the simplest among the cuprates: in the T$'$ structure the apical oxygen atoms are displaced so as to make an isolated CuO$_2$ plane (ab-plane). Upon doping Nd$^{3+}$ ions are randomly replaced by Ce$^{4+}$ ions and an excess of electrons is donated to the CuO$_2$ planes resulting in the $n$-type in-plane conduction. The electrons are concentrated within the confines of conducting CuO$_2$ layers separated from each other by a distance $c \cong 6\text{Å}$. Strong resistivity anisotropy ($\rho_c/\rho_{ab} \cong 10^4$) is observed in Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ single crystals mainly caused by the two-dimensional (2D) nature of the system. Due to the highly layered structure Nd$_{2-x}$Ce$_x$CuO$_4$ single crystal may be regarded as a natural super-lattice or more exactly as a selectively doped multi-quantum well system with CuO$_2$ layers acting as wells and buffer NdO layers as Ce - doped barriers [2].

We report here a study of a disorder influence on the in-plane transport and low-temperature localization effects in Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ single crystal films deposited by flux separation technique [3]. The different degree of disorder has been got by varying of annealing conditions or by ion irradiation of a sample. It is of importance that in

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this model two-dimensional system there is an opportunity to vary gradually a disorder in the sample and thus to investigate 2D-localization process in detail. We compare our results with the data of preceding reports on disorder induced insulator-metal (insulator-superconductor) transition in Nd_{2-x}Ce_xCuO_{4+δ} system with x = 0.18 \[4\] and x = 0.15 \[5\].

2 Results and discussion

The transport properties of Nd_{2-x}Ce_xCuO_{4+δ} are extremely sensitive to oxygen content: an as-grown bulk crystal (x = 0.15) is not superconducting and a small amount of oxygen (δ ≈ 0.01 ± 0.03) has to be removed in order to achieve superconductivity \[6, 7\]. It is ascertained now \[5-8\] that as-grown Nd_{2-x}Ce_xCuO_{4+δ} crystals have an excess oxygen atoms (δ > 0) at interstitial out-of-plane sites which random potential substantially disturbs the conductive CuO_2 plane and may cause localization of the electrons provided by Ce doping. The annealing in vacuum gradually reduces the concentration of the oxygen nonstoichiometric defects and the optimal reduction gives the composition close to stoichiometric one (δ → 0).

In the model of autonomous CuO_2 planes the partial 2D - conductivity of a plane may be obtained as \( \sigma_s = \frac{\rho_{ab}}{\ell} \). From the relation \( \sigma_s = (k_F\ell)c^2/h \) (\( \ell \)-mean free path, \( k_F \) - Fermi wave vector) the value of \( k_F\ell \) may be estimated. The parameter \( k_F\ell \) is usually regarded as a measure of disorder in a system \[9\]. Fig.1 shows temperature dependencies of the in-plane resistivity \( \rho_{ab} \) for three samples with x = 0.18: unreduced (as-grown) sample 1, optimally reduced in vacuum (at 800°C during 40 min.) sample 3 and intermediate reduced sample 2. With varying of annealing procedure in our Nd_{1.82}Ce_{0.18}CuO_{4+δ} system the disorder parameter \( k_F\ell \) changes in an order of magnitude from one sample to another (see Fig.1a). Decreasing disorder we first observe superconductivity for sample 2 with \( k_F\ell = 2.5 \) in rather good accordance with the data of Tanda et al. for Nd_{1.82}Ce_{0.18}CuO_{4+δ} single crystal epitaxial films \[4\]. In their work the low-temperature superconductor-insulator transition tuned by disorder introduced at various stages of oxygen reduction was fixed at \( \rho_{ab}(T=18\,\text{K}) = 0.5\,\text{mΩ}\,\text{cm} \), i.e. for \( k_F\ell \approx 3 \).

Fig.1b demonstrates the low-temperature up-turn of resistivity owing to localization of carriers. It will be seen that the effect of localization becomes less pronounced with the decrease of disorder (increase of \( k_F\ell \)); in sample 3 with \( k_F\ell = 25 \) only marginal effect of weak localization is observed at \( T < 4\,\text{K} \) in magnetic field of 1.3 T \[10\].

In Figs.2 the results of magnetoresistance measurements for sample 2 are presented at magnetic fields \( B \) both parallel and perpendicular to ab-plane. As seen the parallel field up to 5.0 T suppressing superconductivity does not influence on the localization up-turn of normal state resistivity at \( 14 < T < 20\,\text{K} \). In contrast to it the perpendicular field of 2 T to a great extent suppresses localization effect (so as superconductivity). Such behaviour is typical just for 2D system with weak localization as only magnetic field perpendicular to plane may destruct an interference of electron diffusion loops leading to localization.

The in-plane resistivity data for five Nd_{2-x}Ce_xCuO_{4+δ} single crystals with x = 0.15 are shown in Fig.3. These films of thickness t = 2000Å are annealed at various conditions: sample 2 is as-prepared, sample 1 is oxygenated (1 atm., 60 min., 780°C C). The annealing procedure for sample 5 (10^{-2} mm Hg, 60 min., 780°C C) is close to optimal one \( (T_c = 23.5\,\text{K} \text{ with } \Delta T_c = 1.5\,\text{K}) \) and sample 3, 4 are reduced at intermediate conditions.

Fig.3a shows the decreasing of normal state resistivity value at all temperatures in about of two orders of magnitude due to process of deoxygenation. The values of
parameter $k_F\ell$ estimated from the values of $\rho_{ab}(T = T_{min})$ for samples 1-3 and from the values of $\rho_{ab}(T = T_c)$ for samples 4 and 5 are presented in Table. The appearance of SC-transition on the $\rho_{ab}(T)$ dependence with decreasing of disorder in our single crystal films corresponds to $k_F\ell = 10$ (sample 2 with $\rho_{ab}(T_{min} \approx 100 \text{ K}) = 0.15 \text{ m}\Omega \text{ cm}$, $\rho_{ab}(T_c = 12.5 \text{ K}) = 0.2 \text{ m}\Omega \text{ cm}$) just as for bulk single crystal Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ with $x = 0.15$ [5] where $\rho_{ab}(T_c = 11 \text{ K}) = 0.2 \text{ m}\Omega \text{ cm}$ at the border of insulating and superconducting phases.

It should be emphasized that superconducting sample 2 is as-prepared in contrast to the situation for bulk Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ system where as-grown samples are non-superconducting [5-7] and, in particular, the sample with $T_c = 11 \text{ K}$ in [5] is reduced in Ar atmosphere at 1000°C for 30 h in order to induce superconductivity. As it is argued by Xu et al. [11] in a film besides the normal diffusion channels along c-axis and ab-plane additional diffusion channels exist due to grain boundary effects and strains caused by lattice mismatch between the film and the substrate. Thus it is easier to remove oxygen in a film than in a bulk crystal of Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$.

The evolution of low-temperature part of $\rho_{ab}$ dependencies from localization to superconductivity in tight correlation with $k_F\ell$ value is demonstrated on Fig.3b. A strong nonmetallic ($d\rho/dT < 0$) dependence at $T \leq 100 \text{ K}$ in sample 1 with $k_F\ell < 1$ and almost completely metallic ($d\rho/dT > 0$) dependencies at all temperature interval $T > T_c$ in samples 3 - 5 ($k_F\ell \geq 25$) with only slight upturn of $\rho(T)$ with decreasing of $T$ at $T \leq 50 \text{ K}$ in sample 3 are observed. The most interesting behavior of $\rho(T)$ is demonstrated by sample 2 which is on the low-temperature border of insulating and superconducting phases. The logarithmic upturn of $\rho(T)$ in the temperature interval $13 \leq T \leq 100 \text{ K}$ takes place (Fig.4a) but the superconductivity comes to light at $T < 13 \text{ K}$.

It may be treated as a coexistence of superconductivity and localization or, more exactly, such a behaviour gives an evidence of the existence of localization effects in the normal state of material which from the superconductivity develops. It is of importance that the parameter $k_F\ell > 1$ for sample 2 and thus this normal state is a two-dimensional metal with weak localization corrections due to quantum interference effects. Magnetic field up to 5.5 T suppresses superconductivity and reveals localization effects at $T < T_c$ (see the inset on Fig.4b).

The problem of the mutual interplay of Anderson localization and superconductivity in a disordered system is extensively discussed in literature (see recent review of Sadovskii [12]). For 3D Anderson insulator a condition for coexistence of superconductivity and localization was obtained [13]: the Cooper pairing is possible in localized phase if only superconducting coherence length (the size of a Copper pair) $\xi$ is much smaller than localization length: $R_{loc} \gg \xi$.

It is known [9] that in a two-dimensional system with random disorder the radius of electron localization is of a finite size even in the limit $k_F\ell \gg 1$ (“metallic” state) and the following estimate is valid:

$$R_{loc} = \ell \exp \left( \frac{\pi}{2} \times k_F\ell \right). \quad (1)$$

For small mean free path, in the so called “dirty” superconductor with $\ell \ll \xi_0$ ($\xi_0$ is the coherence length of a pure substance) we have $\xi = (\xi_0\ell)^{1/2}$. As the disorder diminishes in a 2D-system the coherence length increases with $\ell$ according to power law while the localization length increases exponentially and thus the condition $R_{loc} > \xi$ may be attained for $k_F\ell$ of the order of several units. Really, an analysis of effects of disorder introduced by doping or annealing on electrical properties of Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ and the other copper-oxide superconductors [14] reveals that low-temperature insulator-superconductor transition is closely related to insulator-metal transition or, more ex-
actly, to transition from strong to weak localization in a 2D system, which takes place at \( k_F \ell \geq 1 \).

Fig. 4b shows the dependencies of temperature \( T_c \) defined both as the onset of superconducting transition, \( T_c^{\text{onset}} \), and as its completion, \( T_c(\rho = 0) \), on the parameter \( k_F \ell \) for samples 2 - 5 of \( \text{Nd}_{2-\delta} \text{Ce}_\delta \text{CuO}_{4+\delta} \) with \( x = 0.15 \). It is seen that \( T_c^{\text{onset}} \) gradually diminishes with an increase of disorder but a more vital effect is the broadening of the transition: for the sample 2, for example, \( \Delta T_c \approx T_c^{\text{onset}} \).

Much experimental information has revealed that sufficiently large disorder always suppresses superconductivity but the ways of \( T_c \) degradation may be different. From a theoretical point of view [12, 15] either amplitude reduction or phase breaking for the pair wave function will result in suppression of superconductivity. In the case of amplitude reduction, \( T_c \) decreases remaining well defined, while in the case of phase breaking \( T_c^{\text{onset}} \) remains unchanged but the transition width increases until the material has no region of zero resistance. It a 2D - system a realization of this two limiting cases depends on the length scale of a disorder, \( R \): either homogeneous or inhomogeneous it is on a scale of the coherence length \( \xi \).

Two idealized classes of 2D - materials: “homogeneous” and “granular” disordered superconductors were considered [15 - 17], the “homogeneous” system being disordered in an atomic length scale (e.g. solid solutions) and the “granular” system being composed of regions of relatively clean material (with \( R > \xi \)) which are separated by regions of normal conductivity or insulating material. In a “homogeneous” system the superconductivity is believed to be destroyed by a suppression of the pair wave function amplitude while in a “granular” system due to increasing fluctuations of its phase. Real systems usually lie in between these idealized cases.

A typical example of “homogeneous” disorder in high-temperature superconductor is, e.g., the degradation of \( T_c \) due to Zn substitution into the \( \text{CuO}_2 \) plane for \( \text{La}_{2-\delta}\text{Sr}_\delta \text{CuO}_4 \) or \( \text{YBa}_2\text{Cu}_3\text{O}_4 \) [18], where a gradual displacement of a well defined SC-transition is observed. An intriguing examples of “granular” superconductors are very thin films of Sn and Pb [16] where the high resistivity is probably due to weak coupling between small particles of clean metal evaporated onto glass substrates. With increasing sheet resistance of the films, the temperature of a sharp onset of superconductivity is apparently not changing but below \( T_c^{\text{onset}} \) a long tail with finite resistance develops.

From Fig. 4b we see that an oxygenation of \( \text{Nd}_{2-\delta}\text{Ce}_\delta \text{CuO}_{4+\delta} \) system leads to essential broadening of SC transition and thus the induced disorder is, in a great extent, of the “granular” type (with typical length scale of the order of \( \xi \)). It is in accordance with the conception of random impurity potential introduced by excess oxygen atoms which may cause carrier localization. Electrons are concentrated in wells near random potential minima (“metallic” regions) while insulating regions are located near the potential maxima.

A following sequence of regimes may be outlined as the amplitude of random potential \( \gamma \) diminishes relative to electron Fermi energy \( \varepsilon_F \):

1. **Strong localization regime**, \( \gamma \gg \varepsilon_F \) \( (h\sigma_s/e^2 \ll 1) \). It is highly inhomogeneous system with small localization radius of electrons, \( R_{\text{loc}} < \xi \). Superconductivity is absent.

2. **A vicinity of insulator - “metal” transition**, \( \gamma \approx \varepsilon_F \) \( (k_F \ell \approx 1) \). It is still inhomogeneous system. Regions with \( R_{\text{loc}} > \xi \) are formed, but they do not cover all the plane. Superconducting state with broad SC - transition develops. A coexistence of superconductivity and localization on the same \( \rho(T) \) dependency is most probable just in this region.
3. “Metallic” (weak localization) regime, $\gamma \ll \varepsilon_F (k_F\ell \gg 1)$. It is homogeneous, superconducting system with well defined SC-transition.

Fig. 5a shows the in-plane resistivity data for Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ samples ($x = 0.15$) with different degree of disorder induced by ion irradiation of a sample. The irradiation of the optimally reduced Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ sample (with $T_{\text{onset}} = T_0 = 22.5$ K and $R(30\,\text{K})=R_0 = 1\,\Omega$) was carried out in circular accelerator by He$^+$ ions ($E = 1.2$ MeV) step by step up to $\Phi = 10^{16}$ cm$^{-2}$ [19]. It will be seen that the insertion of radiation defects leads to substantial increase of the resistivity, to destruction of superconductivity and also provokes a transition to insulator-like low-temperature behaviour. The dependencies both of the critical SC-temperature and normal state resistance at $T = 30\,\text{K}$ on fluence $\Phi$ are presented in Fig.5b. It is seen that $T_c(R_0)$ tends to zero at $\Phi_c \approx 1 \times 10^{15}$ cm$^{-2}$. The degree of $T_c$ decreasing ($dT_c/d\Phi$) becomes especially appreciable in the region of substantial resistivity increase. Such a correlation of $T_c$ degradation due to irradiation with the value of $R$ has been observed as well in hole-doped cuprates [20, 21].

3 Concluding remarks

We have investigated temperature dependencies of the in-plane resistivity, $\rho_{ab}$, for two series of Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ single crystal films ($x = 0.15$ and $x = 0.18$) for variable annealing conditions. In accordance with the data of the other authors [4-7] we have observed that deoxygenation of a sample results in decrease of a value of resistivity as a whole, i.e. a degree of disorder diminishes in process of reducing. The evolution of low-temperature behaviour of $\rho_{ab}(T)$ from localization to superconductivity takes place in tight correlation with the degree of disorder (estimated as a value of the parameter $k_F\ell \equiv \hbar c/e^2\rho_{ab}$).

It is important that SC-transition is observed only for samples with not high disorder, $k_F\ell > 1$ ($k_F\ell \geq 2.5$ for $x = 0.18$ and $k_F\ell \geq 10$ for $x = 0.15$) as well as for MBE films with $x = 0.18$ [4] and for bulk single crystals with $x = 0.15$ [5]. The appearance of superconductivity just in a vicinity of transition from strong to weak localization (insulator - "metal" transition) as well as the essential broadening of SC - transition in the process of $T_c$ degradation may be described in the model of disorder two-dimensional system with random impurity potential induced by nonstoichiometric oxygen defects.

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Table.

| Sample | $T_{\text{min}}, K$ | $\rho_{ab}(T_{\text{min}}), \text{m}\Omega\text{cm}$ | $k_F\ell$ |
|--------|-------------------|------------------------|----------|
| 1      | 125               | 2.3                    | 0.7      |
| 2      | 100               | 0.148                  | 10.5     |
| 3      | 50                | 0.068                  | 22.8     |
| 4      | $T_{\text{onset}} = 19$ | 0.051                  | 30.4     |
| 5      | $T_{\text{onset}} = 23.5$ | 0.0283                  | 54.8     |
Captions to figures

Fig.1 (a) Temperature dependencies of the in-plane resistivity for three Nd$_{1.82}$Ce$_{0.18}$CuO$_{4+\delta}$ samples with different degree of disorder. The values of parameter $k_F\ell$ are: 1 - 0.25; 2 - 2.5; 3 - 25;

(b) The relative resistivity values as a function of temperature for the samples 1 and 3. The inset shows the low-temperature data for sample 2. The dashed line shows the data in magnetic field $B = 1.3\, \text{T}$

Fig.2 The in-plane resistivity of Nd$_{1.82}$Ce$_{0.18}$CuO$_{4+\delta}$ sample 2 as a function of temperature in different magnetic fields parallel (a) and perpendicular (b) to $ab$-plane

Fig.3 (a) Temperature dependencies of the in-plane resistivity for Nd$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ samples with different degree of disorder;

(b) The relative resistivity values as a function of temperature for the same samples. The dashed line shows the data in magnetic field $B = 5.5\, \text{T}$

Fig.4 (a) The low-temperature data of the in-plane resistivity for Nd$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ sample 2. The inset shows the data in perpendicular to $ab$-plane magnetic fields $B$ up to $5.5\, \text{T}$;

(b) The temperatures of the onset of SC-transition and of its completion as functions of disorder parameter $k_F\ell$ of Nd$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ samples 2 - 5

Fig.5 (a) Temperature dependencies of the in-plane resistivity for Nd$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ single crystal films at different irradiation fluence $\Phi(\text{cm}^{-2})$: $\Phi = 0$ (curve 1); $10^{14}$ (2); $5 \times 10^{14}$ (3); $10^{15}$ (4) and $2 \times 10^{15}$ (5);

(b) The relative values of resistance and the SC-transition temperature as functions of the irradiation fluence for Nd$_{1.85}$Ce$_{0.15}$CuO$_{4+\delta}$ film
$\rho_{ab}$ (m$\Omega$ cm)

$T$ (K)

$B \parallel ab$

$B, T$

- ■ 0
- ▼ 0.6
- ● 1.0
- ○ 2.0
- △ 3.0
- ◊ 5.0

$B \perp ab$

$B, T$

- ■ 0
- ● 0.2
- ★ 0.4
- ▼ 0.6
- ● 1.0
- ◊ 2.0
The graph shows the temperature dependence of the resistivity $\rho$ in arbitrary units. The data is represented by various symbols and lines, indicating different curves labeled 1 to 5. The x-axis represents the temperature $T$ in Kelvin, while the y-axis represents the resistivity $\rho$ in units of mΩ cm. The graph illustrates how the resistivity changes with temperature for different samples or conditions.
