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Scaling behavior of the conductivity of $Nd_2CuO_{4-x-\delta}F_x$ single crystals: Evidence for orthogonal symmetry

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We have measured electrical conductances for single-crystal $Nd_2CuO_{4-x-\delta}F_x$ samples by changing the parameters $x(=0.02–0.30)$ and δ. We confirm that observed conductances can be unifiedly described by a single β function from the weakly to the strongly localized regime. We claim, from our analysis of the data using the β function, that the nonsuperconducting state of $Nd_2CuO_{4-x-\delta}F_x$ systems is the two-dimensional Fermi-liquid system described by orthogonal symmetry.

A great deal of experimental activity has been concentrated on understanding the nature of the normal state of cuprates in connection with the pairing mechanism of high-T_c materials. The *n*-type (electron-doped) cuprates such as $Nd_{2-x}Ce_xCuO_{4-\delta}$ have the simplest structure in the family of high-T_c cuprates, since this structure has only one CuO_2 plane per unit cell without chains and apical oxygen atoms. In particular, $Nd_2CuO_{4-x-\delta}F_x$ is an ideal material with less lattice distortion even when fluorine is substituted for oxygen (the ion radius for F^- is 1.33 Å and for O^{2-} 1.32 Å). The physical properties of *n*-type cuprates exhibit no abnormal behavior, in contrast to those observed in the *p*-type cuprates of $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$.[1] For example, the resistivity of $Nd_{2-x}Ce_xCuO_{4-\delta}$ has a T^2 temperature dependence,[2,3] its magnetoresistance shows typical two-dimensional weak localization behavior,[4,5] the temperature dependence of its penetration depth and the surface resistivity can be explained by assuming a simple *s*-wave BCS function,[6] the angle-resolved photoemission experiments indicate the presence of a large Fermi surface.[7,8] It is important to reveal the *fundamental symmetry* (such as orthogonal, unitary, and symplectic) of the normal state of this cuprate. This paper details our investigation of this issue, when we observed the electronic transport properties of the $Nd_2CuO_{4-x-\delta}F_x$ system, in particular through the localization phenomenon induced by disorder. We have measured the electrical conductance for single-crystal $Nd_2CuO_{4-x-\delta}F_x$ samples by changing the parameters x and δ. The samples were prepared by the CuO self-flux method. The results show that observed conductances can be unifiedly described by a single β function from the weakly to the strongly localized regime. Observed magnetoconductances in the weakly localized regime show the characteristics typically associated with two dimensionality. We claim that $Nd_2CuO_{4-x-\delta}F_x$ is a two-dimensional Fermi-liquid system that can be described by orthogonal symmetry. We draw this conclusion from a detailed analysis of the observed data by the β function.

Single crystals of $Nd_2CuO_{4-x-\delta}F_x$ samples were grown by using a solidification technique. This employs a stationary Al_2O_3 crucible inside a box furnace. CuO was added as a flux to the compound in order to lower the high melting temperature. Starting materials were composed of a mixture of the Nd_2O_3, NdF_3, and CuO powder. The purity of all materials used in this work was 99.9%. The maximum soaking temperature varied between 1200 and 1300 °C. A successful growth condition for $Nd_2CuO_{4-x-\delta}F_x$ single crystals was obtained by adding 50 wt. % of CuO flux. The mixture was soaked at 1250 °C for 2 h in air and then cooled at a rate of 30 °C per hour to 1080 °C, at which temperature the oven was shut off and the crucible was cooled to room temperature over a five hour period. Owing to the evaporation of the melt at high temperatures, it was difficult to optimize the growth parameters of the soaking temperature, soaking time, temperature ramp rate, temperature gradient, and amount of CuO flux. The parameters which we obtained differed for each different NdF_3 concentration. For a typical successful growth, the flux was allowed to flow

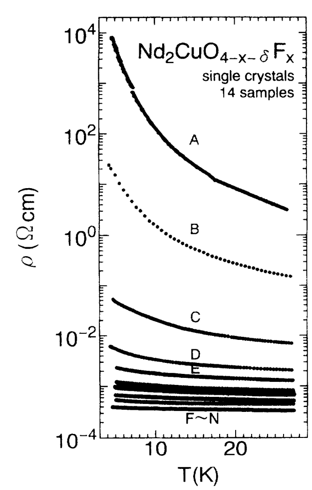

FIG. 1. Temperature dependence of observed resistivities for single-crystal $Nd_2CuO_{4-x-\delta}F_x$ samples by changing x and δ. The value x for samples are 0.02(A), 0.05(B), 0.1(C), 0.15(D–F), 0.2(G–H), 0.25(I–K), and 0.3(L–N), respectively. The reduced conditions corresponding to δ (temperature was constant 700 °C at Ar 0.4 Torr atmosphere and reducing time was altered) are 0 min (B, D, G, N), 30 min (E, H, L), 60 min (I, M), 120 min (J), and 150 min (A, C, F, K), respectively.

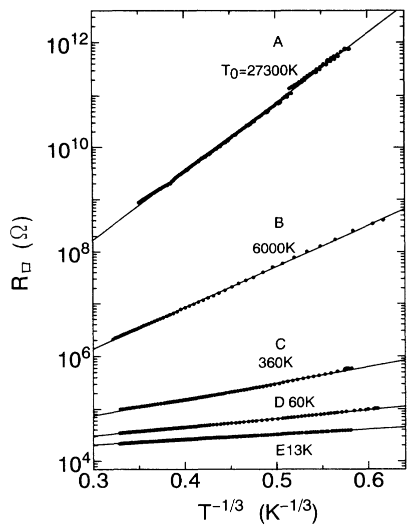

FIG. 2. Logarithmic plot of sheet-resistances $R_\square$ vs $T^{-1/3}$ for samples in the strongly localized regime (A, B, C, D, and E shown in Fig. 1).

out of the crucible at the end of the growth process, so that only a free standing crystal was left at the bottom of the crucible. Crystals with dimensions as large as $8\times8\times0.2$ mm^3 were easily extracted from the crucible. The crystal surfaces were not contaminated by flux and were optically shiny.

The as-grown single crystals were not superconducting. Superconductivity was induced by annealing the crystals in a reducing atmosphere to remove some oxygen atoms. A long time and high-temperature reduction was required to create homogeneous crystals. We observed that long-time reduction, at more than 750 °C in an argon atmosphere, degraded the crystal surface. We used thin crystals (thickness is 5 to 20 μm) for uniform removal of oxygen. The crystal structure of each sample was characterized by x-ray diffraction (XRD). XRD analysis revealed that all the samples of $Nd_2CuO_{4-x-\delta}F_x$ demonstrated a single phase of the Nd_2CuO_4-type tetragonal structure. The composition of the samples were determined by electron-probe microanalysis and comparing the lattice constants c of $Nd_2CuO_{4-x-\delta}F_x$ ceramics, as reported.[9] Electrical resistivities (ρ) of samples were measured by a dc four-probe method. The dc-current density, applied to the samples, was about 10 A/cm^2. The sheet resistances $R_\square=\rho/d$ (d is lattice spacing between CuO_2 layers: $d=6.02$ Å) are plotted in Fig. 1 as a function of temperature for 14 samples of different x and δ. Absolute values $R_\square$ extend over more than 7 orders of magnitude. The superconducting transition takes place at $T_c=20$ K in the low-resistance sample.

Electrical transport in a strongly disordered regime is

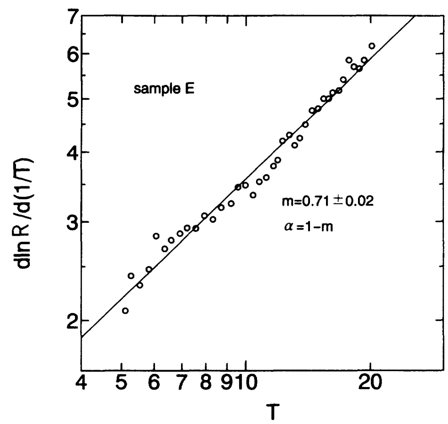

FIG. 3. Plot of $d(\ln R)/d(1/T)$ vs T on a log-log scale for the sample E. The slope m is related to α by the relation $\alpha=1-m$.

characterized by variable range hopping (VRH).[10] The temperature-dependence of their resistances takes the form $R_\square(T)=R_0\exp(T_0/T)^\alpha$. In the VRH transport, the value of α depends on both the dimensionality d of the system and the density of states at the Fermi level. The VRH predicts the value $\alpha=\frac{1}{4}$ in three dimensions (3D) and $\alpha=\frac{1}{3}$ in 2D. The other value of α concerns the effect of correlation between electrons. Altshuler *et al.*[11] have shown that the density of states has a minimum (but finite) at the Fermi level in disordered metals. If the disorder becomes large, the electronic states at the Fermi level are strongly localized. Efros and Shklovskii[12] have claimed that the minimum becomes a gap (Coulomb gap) and the conductivity is described by the VRH with $\alpha=\frac{1}{2}$ independent of dimensionsionality.

In Fig. 2, we have plotted $\log_{10}(R_\square)$ vs $T^{-1/3}$ for samples in the strongly localized regime (A, B, C, D, and E shown in Fig. 1). It can be clearly seen that sheet resistances are expressed by $R_\square\propto\exp(T_0/T)^{1/3}$ over a wide range of temperatures. Figure 2 indicates that the observed resistances increase rapidly with decreasing x and δ. In order to determine the precise value of α, we have transformed the expression of the sheet resistance, $R=R_0\exp(T_0/T)^\alpha$, into

$$\log\left[\frac{d(\ln R)}{d(1/T)}\right]=(1-\alpha)\log T+\log(\alpha T_0^\alpha)\,, \qquad (1)$$

where $d(\ln R)/d(1/T)$ corresponds to the characteristic hopping energy or generalized activation energy. In Fig. 3, we have plotted $d(\ln R)/d(1/T)$ vs T on a log-log scale for sample E. The straight line represents least-squares fitting to the data. The slope m is related to α by the relation $m=1-\alpha$. The observed value of m gives rise to $\alpha=0.29\pm0.02$. We have analyzed other samples (A–D) in the same way. The results are shown in Table

TABLE I. The value of parameters for samples in the strongly localized regime.

Sample	A	B	C	D	E
α	0.33±0.02	0.35±0.03	0.40±0.03	0.36±0.02	0.29±0.02
T_0 (K)	27 300	6000	360	60	13
ξ (Å)	8±5	15±5	32±5	85±10	180±20

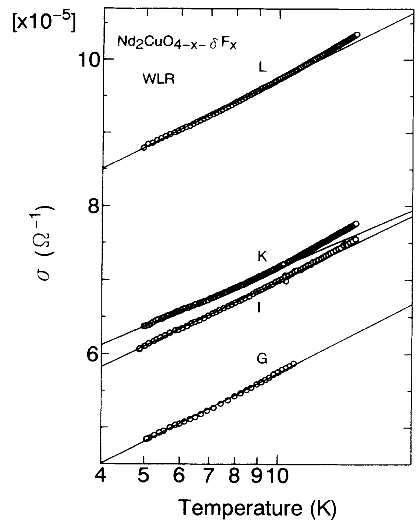

FIG. 4. Conductance per CuO_2 plane in units of $e^2/\pi h$ as a function of temperature in logarithmic scale.

I. These results demonstrate that samples (A–E) of $Nd_2CuO_{4-x-\delta}F_x$ have the characteristics of the 2D strong localization that has been induced by disorder, not by the Coulomb correlation effect. The localization length (ξ) was estimated from the value of T_0 and from the density of states obtained by specific-heat measurements,[13] namely, $\gamma = 30-40$ mJ/mol K^2. These results are given in Table I.

We have also investigated the transport properties of samples (F–N) in the weakly localized regime. The observed conductances show the logarithmic temperature dependence (see Fig. 4). Measurements under magnetic fields are useful to probe the details of weakly localized states. The open circles in Fig. 5 are data under magnetic fields applied perpendicularly to the *ab* plane of sample I. These data clearly exhibit *positive* magnetoconductances

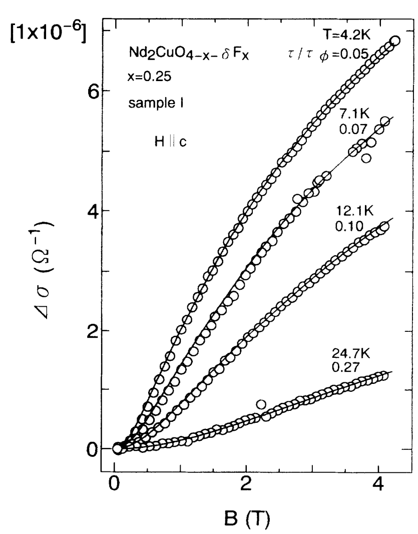

FIG. 5. Conductances under magnetic fields applied perpendicularly to CuO_2 layers for the sample I ($x = 0.25$). The solid lines are obtained by Eq. (2) using the values of parameters given in the text.

with increasing magnetic fields. At each temperature, the observed magnetoconductances show a crossover from negative curvature ($\propto H^2$) at low fields to positive curvature ($\propto \ln H$) at high fields. In the weakly localized regime, quantum interference causes spatially localized states which produce a quantum correction to the classical Drude conductivity. This weak-localization correction is sensitive to perturbations which destroy time-reversal symmetry. This suggests that a magnetic field suppresses the quantum interference effect and give rise to *positive* magnetoconductance. For 2D systems, the correlation $\Delta\sigma$ to the conductivity, not taking into account electron correlation effect, is given by[14]

$$\Delta\sigma = -\frac{Ae^2}{2\pi^2\hbar}\left[\Psi\left[\frac{1}{2}+\frac{1}{a\tau}\right]-\Psi\left[\frac{1}{2}+\frac{1}{a\tau_\phi}\right]-\ln\left[\frac{\tau_\phi}{\tau}\right]\right]. \tag{2}$$

where Ψ is the digamma function, τ_ϕ the dephasing time, τ the elastic scattering time, $a = 4eHD/\hbar$, D the diffusion constant, and A a constant of order of unity. The solid curve in Fig. 5 was obtained from least-square fitting using Eq. (2). These results indicate that samples (F–N) show typical behavior of 2D weak localization.

Let us try to analyze the observed data described so far in terms of the conventional β function: $\beta(g) \equiv d(\ln g)/d(\ln L)$, where L is the sample size and g the dimensionless conductance $[g = (\hbar/e^2)\sigma]$. The sample size L is regarded as a cutoff length due to inelastic scattering: $L^2 = DT^{-p}$. The value of p is obtained as a unity from both the data in Figs. 4 (the temperature dependence of conductances) and 5 (that of magnetoconductances). The β function is written down as

$$\beta(g) = -2\frac{d(\ln g)}{d(\ln T)} = -\frac{2\hbar}{e^2}\frac{d(\ln\sigma)}{d(\ln T)} . \tag{3}$$

Using this form, we have plotted in Fig. 6 the data of the conductances mentioned so far. We can see that all the

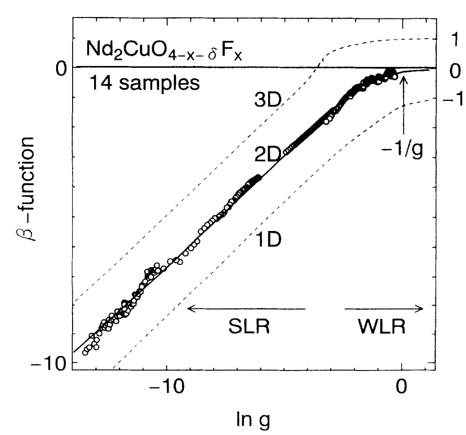

FIG. 6. Scaling behaviors of conductivities for 14 samples of single-crystal $Nd_2CuO_{4-x-\delta}F_x$. Solid line is due to the β function for the 2D system, and experimental data show the $-1/g$ dependence in the weakly localized regime and $\ln(g)$ dependence in the strongly localized regime. Dotted lines are due to β functions for 1D or 3D.

data fall on a single universal curve. For $g \ll 1$, the β function is linearly proportional to lng. For $g > 1$, the β function is proportional to $-1/g$, and $\beta=0$ for $g \gg 1$. The β function for $g > 1$ is expressed as $\beta(g)=(d-2)-b_1/g+b_2/g^2$,[15] where d is dimensionality. The parameter b_1 takes the values 1, 0, $-\frac{1}{2}$ depending on whether the system has orthogonal, unitary, or symplectic symmetry.[14] The value of b_2 becomes -1 for the unitary symmetry, and 0 from the orthogonal case.[14,15] Our observed results ($b_1=1$, $b_2=0$) are consistent with the disorder Fermi-liquid system described by *orthogonal symmetry.*

In summary, we have confirmed that the observed conductances for single-crystal $Nd_2CuO_{4-x-\delta}F_x$ are described unifiedly by a single β function from the weakly to the strongly localized regime. Detailed analysis of the β function indicates that $Nd_2CuO_{4-x-\delta}F_x$ is a 2D Fermi-liquid system that can be described by orthogonal symmetry. An important feature of our findings is that they could play a role in investigating the nature of pairing or the normal-properties of high-T_c oxide superconductors.

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