Doping Dependence of Pseudogap and Related Charge Dynamics in $Nd_{2-x}Ce_xCuO_4$

Y. Onose,[1] Y. Taguchi,[1] K. Ishizaka,[1] and Y. Tokura[1,2]

[1]*Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan*

[2]*Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-0046, Japan*

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A notable pseudogap (Δ_{PG} as large as 0.2–0.4 eV) has been found below a characteristic temperature T^* in the optical conductivity spectrum for metallic but nonsuperconducting crystals of $Nd_{2-x}Ce_xCuO_4$ ($x < 0.15$). The Δ_{PG} and T^* decrease with doping x, holding the relation of $\Delta_{PG} \approx 10k_BT^*$. The Drude-like component is observed to evolve concomitantly with the pseudogap. The T^* almost coincides with another characteristic temperature T_0 that scales the Hall coefficient. These results indicate that the charge transport in the underdoped region is under the strong influence of the pseudogap state.

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Since the discovery of electron-doped cuprate superconductors [1], their similarity or dissimilarity to the hole-doped superconductors has been under dispute [2]. Quite recently the superconductor order parameter of the prototypical electron-doped cuprate, $Nd_{2-x}Ce_xCuO_4$ (NCCO), was confirmed to be $d_{x^2-y^2}$-like, similar to the hole-doped compounds [3,4]. On the other hand, one of the recent advances in the research on hole-doped cuprates is the discovery of the so-called pseudogap (PG) or spin-gap (SG) phenomena [5]. In the hole-doped compounds, there seem to be two energy-scales that govern the PG and SG behaviors. One is the high-energy-scale PG phenomena appearing with a relatively high crossover temperature ($T^* = 200$–500 K). Below this temperature, Hall coefficient [6,7], magnetic susceptibility, and NMR Knight shift [8] undergo appreciable change, and the photoemission spectral weight near the Fermi energy is suppressed on a high-energy scale (over several hundreds meV) [9]. The other is related to a lower-lying crossover temperature T_{SG}, below which the NMR rate is suppressed [10], the PG feature in the tunneling spectroscopy is discerned [11], and the leading edge shift at around $(\pi, 0)$ is observed in angle-resolved photoemission spectroscopy [12]. The purpose of this paper is to report the finding of an even more notable PG feature, its doping dependence, and its determinate role in the charge dynamics for electron-doped NCCO crystals. While some results of research on the doping and temperature (T) dependence of optical conductivity spectra for NCCO crystals have been reported [13], the PG feature and its important effect on transport properties have seldom been investigated.

To study the doping-dependent behavior of the charge transport and the optical spectrum, we have prepared single crystals of NCCO with various doping levels ($x = 0$, 0.05, 0.075, 0.10, 0.125, and 0.15) by using the traveling solvent floating zone method [14]. To avoid the influence of apical oxygen as interstitial impurities [15], all the crystals except $x = 0$ were annealed in a flowing Ar/O_2 gas mixture with a partial oxygen pressure of $10^{-3} \sim 10^{-5}$ atm at 1000 °C for 100 h. The T dependence of the in-plane resistivity is shown in Fig. 1(a) for the NCCO crystals for various x. In the undoped ($x = 0$) crystal the resistivity is insulating, whereas the electron-doped compounds with $x = 0.05$–0.125 are almost metallic, though not superconducting, over the whole T region. Especially, the crystals with $x = 0.10$ and $x = 0.125$ are obviously metallic: The resistivity is of 10^{-4} Ω cm range, which is below the Ioffe-Regel limit, down to the lowest temperature measured (0.5 K), although it shows a gentle upturn below 50–100 K. The $x = 0.15$ crystal undergoes the superconducting transition at 25 K with 100% volume fraction. To deduce the

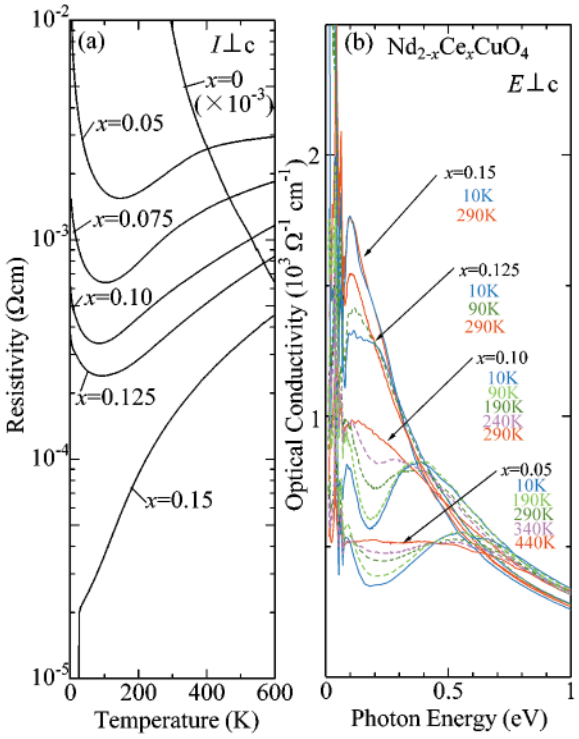

FIG. 1 (color). The T dependence of (a) in-plane resistivity, and (b) the optical conductivity spectra for reduced crystals of NCCO.

optical conductivity spectra, reflectivity spectra were measured on the mirrorlike polished ab faces of the crystals. To remove possible residual stress at the polished surface, we annealed the crystal at 500 °C in the same atmosphere as was employed in the first annealing procedure. The T dependence of the reflectivity was measured for 0.01–3 eV over the T range of 10–540 K. Room-temperature data for 3–32 eV were used to perform Kramers-Kronig analysis and deduce optical-conductivity spectra at respective temperatures. For the analysis, we assumed the Hagen-Rubens relation below 0.01 eV and ω^{-4} extrapolation above 32 eV.

The optical conductivity spectra of the respective crystals at various temperatures are shown in Fig. 1(b). At first glance, one may notice large T-dependent changes of the optical conductivity spectra in the energy region (0–1 eV) except for $x = 0.15$. In particular, for $x = 0.05$ and 0.10, the optical conductivity spectra tend to show notable hollow structures in the region of 0.1–0.4 eV with decreasing T. The T-dependent change of the spectra appears to accompany the isosbetic (equal-absorption) point in the course of the spectral-weight transfer; e.g., around 0.43 eV for $x = 0.05$ and around 0.33 eV for $x = 0.10$. The observed feature indicates the evolution of the gap structure, although a real charge gap with zero conductivity is not observed. Such a distinct PG in the optical spectrum has never been found in hole-doped (underdoped) superconductors in which only a steep change in the scattering-rate spectrum $\tau^{-1}(\omega)$ derived by the extended Drude analysis has been ascribed to the presence of the PG [16]. A similar tendency is also clearly observed in the T dependence of the $x = 0.125$ spectra but is not seen for the superconducting $x = 0.15$ crystal. Here we should mention that a similar PG formation is observed in the as-prepared (or oxygenated) nonsuperconducting $x = 0.15$ crystal and has been assigned to the possible charge-ordering fluctuation [14]. The observed PG of the reduced crystals may have a common origin. However, the feature distinct from those of the oxygenated $x = 0.15$ (and also other oxygenated lower-doped) crystals is that the reduced crystals, perhaps with minimal apical-oxygen impurities, have metallic conductivity down to the lowest temperature and, correspondingly, show a clear Drude-like component in the far-infrared region.

We show in Fig. 2 the T dependence of the conductivity spectra for the $x = 0.10$ crystal on a logarithmic scale of photon energy to scrutinize the low-energy component. A steep rise of the optical conductivity toward zero energy with lowering T is observed as an indication of the Drude-like response, whereas the PG evolves as indicated by the mesh area. This is consistent with metallic T dependence of resistivity above 80 K [17]. The concomitant evolution of the low-energy Drude-like weight and the large-energy PG are commonly observed in such an underdoped region ($x < 0.15$) of NCCO. The spectral weight lost in the course of the PG formation can be estimated as the ω-integrated area of the $\sigma(\omega)$ (termed the effective number of electrons, N_{eff}) of the hollow structure between

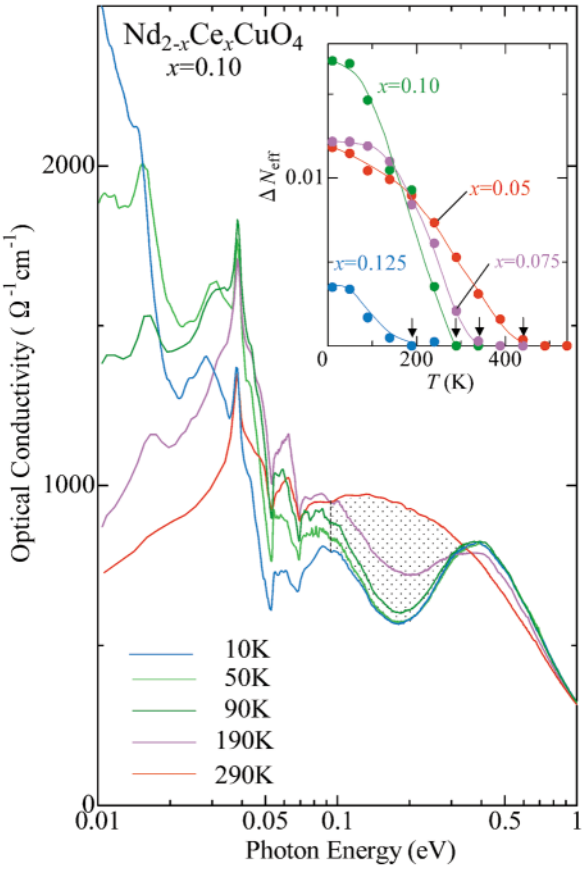

FIG. 2 (color). The T dependence of the optical conductivity spectrum for a reduced NCCO crystal with $x = 0.10$ on a logarithmic scale of photon energy. A mesh region between 0.1 and 0.4 eV indicates the spectral-weight loss due to the PG formation. Spiky structures below 0.06 eV are due to the optical phonons coupled with the electronic excitations. The inset shows the T dependence of the loss of the spectral weight (ΔN_{eff}) due to the formation of a PG for various x. Arrows indicate the onset temperature of the PG evolution (T^*).

0.1–0.33 eV. In an actual procedure, we have estimated the spectral weight change (ΔN_{eff}) from the high-temperature spectrum, e.g., at 540 K, in between the two (lower and upper) isosbetic points as represented by the mesh area in Fig. 2. The upper isosbetic point energy, denoted here as Δ_{PG}, measures the energy of the PG. Similar procedures were also used for the spectral changes at various doping levels. The T dependence of the ΔN_{eff} is shown in the inset of Fig. 2, which clearly indicates the PG evolution temperature T^* (indicated by downward arrows) for the respective crystals. The spectral weight lost upon the opening of the PG is transferred partly to the higher energy region beyond the Δ_{PG} and partly to the low-energy coherent (Drude-like) component, which represents the metallic charge transport. Thus, the obtained T^* and Δ_{PG} are plotted in the lower panel of Fig. 3 as a function of x, together with the previous data for the Néel temperature (T_{N}) measured on the reduced NCCO by means of the muon spin resonance [18]. Both T^* and Δ_{PG} decrease with x in a parallel manner toward $x = 0.15$ or the superconducting region, while holding the relation that $k_B T^* \approx \Delta_{\mathrm{PG}}/10$.

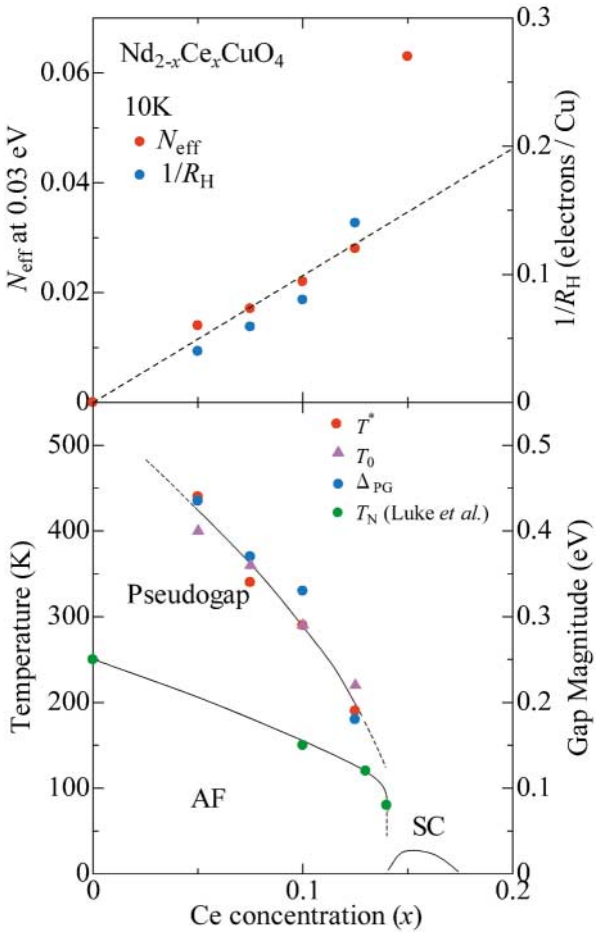

FIG. 3 (color). Upper panel: The x variation of the Drude-like component (measured as $N_{\rm eff}$ at 0.03 eV) and the effective electron-type carrier density (measured as $|R_{\rm H}^{-1}|$) at the ground state (10 K). Lower panel: The electronic phase diagram of reduced NCCO crystals. The PG magnitude $\Delta_{\rm PG}$ (for definition, see text) and its onset temperature (T^*) are shown in comparison with the Néel temperature $T_{\rm N}$ measured previously by Luke *et al.* [18]. T_0 is the crossover temperature of the $R_{\rm H}$ deduced from the scaling plot (see Fig. 4). SC stands for the superconducting region.

The Drude-like component with the fully developed PG (for instance, at 10 K) can be measured by using a low-energy (for instance, $<$0.03 eV) spectral weight. The $N_{\rm eff}$ at 0.03 eV and 10 K as a measure of the Drude-like weight at the ground state is shown by closed circles as a function of x in the upper panel of Fig. 3. The Drude-like weight on this energy scale increases almost linearly with x up to $x = 0.125$. In the same panel, the inverse of absolute value of the Hall coefficient at the same temperature (10 K) that would represent the electron-type carrier density in a conventional sense is also plotted. The carrier density at the ground state linearly increases with x at least up to $x = 0.125$. This feature, which has been considered generic in the underdoped cuprates, has been confirmed most clearly here for the electron-doped cuprate.

Formation of such an anomalous metal state proceeds with the evolution of the PG as the temperature is lowered. The bare T dependence of the Hall coefficient ($R_{\rm H}$) is shown in the inset of Fig. 4. The *negative* $R_{\rm H}$ for $x < 0.15$ shows a large T dependence. This may be characterized by the crossover from a large to a small Fermi-surface feature with the decrease of T [6,7]. In the case of $La_{2-x}Sr_xCuO_4$ (LSCO), it is known that the T-dependent Hall coefficients are scaled with a characteristic temperature (T_0), such as $R_{\rm H}(T,x) = R_{\rm H}^{\infty}(x) + R_{\rm H}^{0}(x) f(T/T_0)$ [7], where f is a scaling function. Then, T_0 was found to correspond to the large-energy scale PG temperature T^*. To check the validity of this empirical rule for the case of NCCO, we attempted to scale the T-dependent $R_{\rm H}$ with T_0 as a scaling parameter. Figure 4 shows the scaling plot where the $R_{\rm H}(T,x)$ normalized by $R_{\rm H}[\frac{2}{3}T_0(x),x]$ is shown against the normalized temperature, $T/T_0(x)$. All the $R_{\rm H}$ curves in the underdoped region of NCCO appear to fall onto a single curve at least in the region of $T \geq 0.4T_0$. Some discrepancy at low temperatures ($T < 0.4T_0$) may be due to antiferromagnetic (AF) long range order. As shown in the lower panel of Fig. 3, the T_0 almost coincides with the T^*, indicating that the PG evolution governs the strong T dependence of $R_{\rm H}$ or the apparent crossover from a large to a small Fermi-surface feature. To our knowledge, this is the first experimental confirmation of the direct link between the generic x- and T-dependent $R_{\rm H}$ and the large-energy PG feature observed by using a spectroscopic experiment.

Although the optical conductivity below the PG energy can be basically viewed as a Drude-like response [17], the lowest energy component shows a deviation from the simple Drude one. This is evident from the resistivity

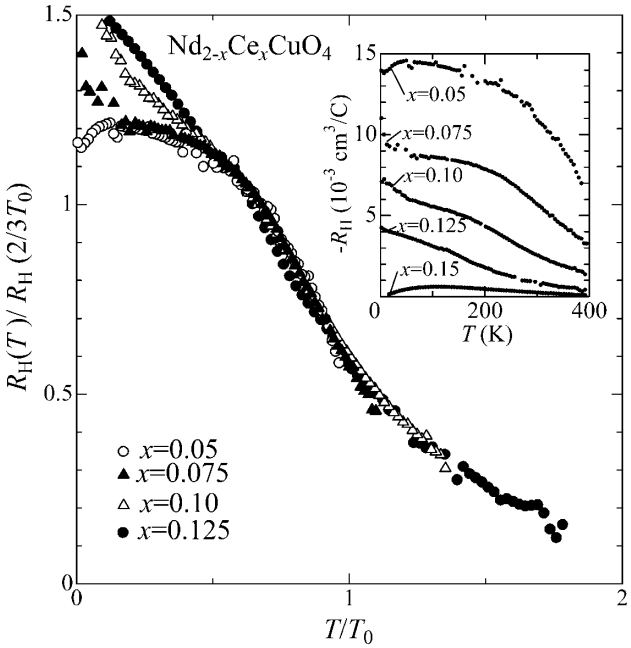

FIG. 4. The scaling behavior of T- and x-dependent $R_{\rm H}$ in reduced NCCO crystals ($x = 0.05$, 0.075, 0.10, and 0.125). The bare data of $R_{\rm H}$ are shown in the inset. The $R_{\rm H}(T)$ data normalized by $R_{\rm H}(T = 2/3T_0)$ are plotted against the normalized temperature T/T_0, where T_0 is the only scaling parameter.

upturn below 80 K [Fig. 1(a)] for a $x = 0.10$ compound, for example. Such a behavior may be interpreted in terms of the weak localization in a disordered metal. Recently, the evolution of typical metallic behavior with doping manifesting itself in a Drude-like conductivity has been studied in a series of flux-grown single crystals of NCCO by Lupi *et al.* [13]. A similar, or even stronger, deviation from the simple Drude response has been observed also in Ref. [13], although their interpretation is based on a small-polaron picture and is different from ours.

As for the observed large-energy PG behavior, there may be several scenarios to explain it. From the distinct gap feature and associated phonon anomaly in the oxygenated NCCO, we formerly proposed the possibility of the charge ordering as the origin of the large-energy PG [14]. However, a recent neutron scattering study [19] has ruled out the presence of the charge-spin stripe in NCCO, but showed only the (π, π) component of the AF spin order and fluctuation. Apart from the vertical stripe state, the charge ordering or the lattice-coupled self-localized state can hardly be reconciled with the metallic charge transport as observed for the present reduced crystals. Therefore, the strong AF spin correlation in the barely metallic state is most probable as the origin of the PG. The idea of the electronic phase separation into the spin-ordered insulating region and the metallic one is apparently contradictory with the concomitant growth of the PG and the Drude-like weight (or metallic conductivity). Thus, we should seek the possibility that the strong AF spin correlation opens up the gap structure in the optical conductivity spectrum while maintaining the metallic state. The situation reminds us of the spin-density-wave (SDW) gap in Cr metal [20] in which the PG feature appears in the metallic optical conductivity spectrum with the magnitude of $\sim 5k_B T_N$ ($T_N = 308$ K being the SDW transition temperature). In the present NCCO, the ground state in the underdoped region has a long-range AF spin order, but we do not detect any steep change in the spectral-weight transfer around T_N (~ 150 K at $x = 0.10$) (see the inset of Fig. 2). Although the weak coupling theory of SDW cannot explain the present experimental features, such as a large value ($\sim 20T_N$) of PG and a high evolution temperature ($\sim 2T_N$) compared with T_N, the strong two-dimensional AF fluctuation that starts below T^* is likely to cause the gap feature. The notable evolution of the Drude-like part with the opening of the PG is still not straightforwardly explained by such a naive picture of the SDW-gapped metal, but requires a more elaborate theory. Another question is why such a strong AF gap feature shows up only in the electron-doped NCCO. The anomalous stability of the AF long-range order up to $x = 0.15$ in NCCO as compared with the case of LSCO (up to $x = 0.02$) may be responsible for this [21]. In fact, a recent angle-resolved photoemission measurement on the superconducting $x = 0.15$ NCCO crystal has revealed the clear gapping at the cross section between the actual Fermi surface and the magnetic (AF) Brillouin zone [4].

In conclusion, the notable PG feature on a large energy scale ($\Delta_{PG} = 0.2$–0.4 eV) is observed directly in the optical conductivity spectra of reduced crystals of NCCO in the underdoped (metallic but nonsuperconducting) region ($x < 0.15$). The PG evolves with a Drude-like component with decreasing T below a characteristic temperature T^*. The T^* steeply decreases, while keeping the relation that $\Delta_{PG} \sim 10k_B T^*$, toward the onset ($x = 0.15$) of the superconductivity as x increases. The T^* almost coincides with the characteristic temperature T_0 that scales the strongly T- and x-dependent R_H. The T^* is ascribed to the onset of the AF spin correlation. The ground state of NCCO in the underdoped region is thus characterized by a barely metallic state with a huge PG and a Drude-like spectral weight proportional to x.

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