Hole trapping by Ni, Kondo effect, and electronic phase diagram in nonsuperconducting Ni-substituted $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$

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In order to investigate the electronic state in the normal state of high-T_c cuprates in a wide range of temperature and hole concentration, specific-heat, electrical-resistivity, magnetization, and muon-spin-relaxation measurements have been performed in nonsuperconducting Ni-substituted $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ where the superconductivity is suppressed through the partial substitution of Ni for Cu without disturbing the Cu-spin correlation in the CuO_2 plane so much. In the underdoped regime, it has been found that there exist both weakly localized holes around Ni and itinerant holes at high temperatures. With decreasing temperature, all holes tend to be localized, followed by the occurrence of variable-range hopping conduction at low temperatures. Finally, in the ground state, it has been found that each Ni^{2+} ion traps a hole strongly and that a magnetically ordered state appears. In the overdoped regime, on the other hand, it has been found that a Kondo-type state is formed around each Ni^{2+} spin at low temperatures. In conclusion, the ground state of nonsuperconducting $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ changes upon hole doping from a magnetically ordered state with the strong hole trapping by Ni^{2+} to a metallic state with Kondo-type behavior due to Ni^{2+} spins, and the quantum phase transition is crossoverlike due to the phase separation into short-range magnetically ordered and metallic regions.

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I. INTRODUCTION

In the history of the research of the high-T_c superconductivity (HTSC), studies of impurity-substitution effects have played one of central roles in the elucidation of the mechanism of HTSC. It is widely recognized in the hole-doped high-T_c cuprates that the suppression of the superconductivity through the substitution of magnetic impurities such as Ni for Cu is weaker than through the substitution of nonmagnetic impurities such as Zn for Cu,[1,2] which is a trend opposite to that observed in conventional superconductors.[3] Nuclear magnetic/quadrupole resonance measurements have revealed that Ni operates to weakly scatter holes while Zn operates to strongly do.[4] The so-called dynamical stripe correlations of spins and holes in the CuO_2 plane[5] observed in La-based high-T_c cuprates tend to be pinned and stabilized by Zn more effectively than by Ni.[6–8] These contrasting behaviors suggest that Ni has weak influence on the electronic and magnetic states in the CuO_2 plane. In recent years, moreover, neutron-scattering,[9,10] magnetization,[11] muon-spin-relaxation (μSR),[12] x-ray absorption fine structure (XAFS) (Ref. 13) experiments and a theoretical work using the numerical exact diagonalization calculation[14] have suggested that a hole tends to be bound around a Ni impurity, leading to the decrease in the effective hole concentration. That is, a Ni^{2+} ion with the spin quantum number $S=1$ tends to trap a hole, forming a Ni^{2+} ion with a ligand hole, i.e., a so-called Zhang-Rice doublet state (the effective value of S is 1/2) so as not to disturb the antiferromagnetic (AF) correlation between Cu^{2+} spins with $S=1/2$ so much. These suggest that Ni is no longer regarded as an usual magnetic impurity in the high-T_c cuprates.

The above distinct concept of hole trapping by Ni may pin down the issue whether or not a quantum critical point (QCP) resides in the superconducting (SC) region on the phase diagram of high-T_c cuprates. It has been pointed out that the magnitude of the pseudogap decreases with increasing hole concentration per Cu, p, and seems to vanish at $p \sim 0.19$.[15] Moreover, the electrical resistivity, ρ, has exhibited a T-linear behavior above T_c in a very limited region near the optimally doped regime, suggesting the existence of a quantum critical region.[16–18] To investigate the quantum phase transition, the SC state concealing the normal ground state has to be removed. In the La-based cuprate $La_{2-x}Sr_xCuO_4$ (LSCO) where the superconductivity is suppressed by the application of high magnetic field, in fact, it has been sug-

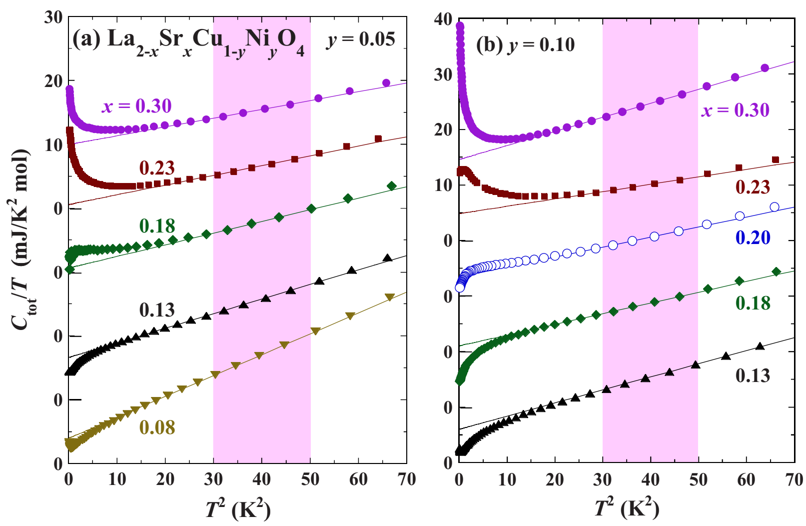

FIG. 1. (Color online) Temperature dependence of the specific heat, C_{tot}, for typical values of x in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ with (a) $y=0.05$ and (b) $y=0.10$ plotted as C_{tot}/T vs T^2. The data are shifted top and bottom. Solid lines indicate the best-fit results obtained using Eq. (3.1). Shaded areas represent the fitting range of $30 \leq T^2 \leq 50$ K^2 where C_{tot}/T is linear as a function of T^2.

gested that the quantum critical region deduced from the T-linear behavior of ρ seems not to converge at a singular point of p in the ground state as in the case of a conventional quantum phase transition but seems to spread out over a wide range of p in the overdoped regime at low temperatures.[19] In Zn-substituted $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ (LSCZO) where the superconductivity is suppressed by Zn, on the other hand, μSR measurements[20] have revealed that the development of the Cu-spin correlation through the Zn substitution is weakened gradually with increasing p in the overdoped regime and disappears around $x=0.30$ where the superconductivity in LSCO disappears, suggesting that QCP in the viewpoint of the Cu-spin correlation[21] is not located simply at $p \sim 0.19$ but is extended in the overdoped regime due to the presence of a phase separation into short-range magnetically ordered and metallic regions. Both high magnetic field and Zn suppressing the superconductivity, however, may affect the Cu-spin correlation which is probably indispensable to the appearance of HTSC. Therefore, the exploration of QCP in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ (LSCNO) in which the superconductivity is suppressed by Ni attracts great interest.

In this paper, specific heat, ρ, magnetization, and μSR measurements have been carried out to investigate the electronic state in the normal state of non-SC Ni-substituted LSCNO in a wide range of x and y.[22,23] In particular, we have focused on the temperature-dependent change in the hole dynamics from the underdoped to overdoped regime in order to obtain a whole aspect of the electronic state in the normal state because only separated results in limited ranges of p and temperature have been reported so far.[9–14]

II. EXPERIMENTAL

Polycrystalline samples of LSCNO with $x=0.08-0.30$ and $y=0-0.10$ were prepared by the ordinary solid-state reaction method.[8] All of the samples were checked by the powder x-ray diffraction to be of the single phase. Specific-heat measurements were carried out by the thermal relaxation method in zero magnetic field and 9 T at low temperatures down to 0.4 K, using a commercial apparatus [Physical Property Measurement System (PPMS), Quantum Design]. The ρ measurements were performed by the standard four-probe method in zero field and 9 T at temperatures down to 0.4 K. Magnetization measurements were performed in a magnetic field of 1 T at temperatures down to 2 K, using a superconducting quantum interference device magnetometer [Magnetic Property Measurement System (MPMS-XL5), Quantum Design]. In order to estimate the magnetic transition temperature, T_N, zero-field μSR measurements were performed at temperatures down to 0.3 K at the Paul Scherrer Institute (PSI) in Switzerland and at the RIKEN-RAL Muon Facility at the Rutherford-Appleton Laboratory in the UK.

III. RESULTS

A. Specific heat

Figure 1 shows the temperature dependence of the specific heat, C_{tot}, for LSCNO with $y=0.05$ and 0.10 plotted as C_{tot}/T vs T^2. The data are shifted top and bottom. The specific heat in non-SC samples of LSCNO at low temperatures should be expressed as

$$C_{tot}(T) = \gamma T + \beta T^3. \qquad (3.1)$$

The first term represents the electronic specific heat, C_{el}, and γ is the electronic specific-heat coefficient proportional to the density of states (DOS) of quasiparticles at the Fermi level, described in the Fermi-liquid state. The second term represents the phonon specific heat, C_{ph}, assuming the Debye model. In Fig. 1, every C_{tot}/T shows a T^2 dependence in a range of $30 \leq T^2 \leq 50$ K^2, indicating that every C_{tot} is well expressed by Eq. (3.1). For $T^2 \leq 30$ K^2, on the other hand, it is found that C_{tot}/T tends to deviate upward or downward from the T^2 dependence, suggesting an anomalous change in C_{el} at low temperatures.

After removing the phonon contribution from the total specific heat to investigate the anomalous deviation at low temperatures in detail, the temperature dependence of $(C_{tot} - C_{ph})/T$ for LSCNO with $y=0.05$ and 0.10 is shown in Figs. 2(a) and 2(b), respectively. Here, C_{ph} was estimated from the fit of the data in the temperature range of $30 \leq T^2 \leq 50$ K^2 in

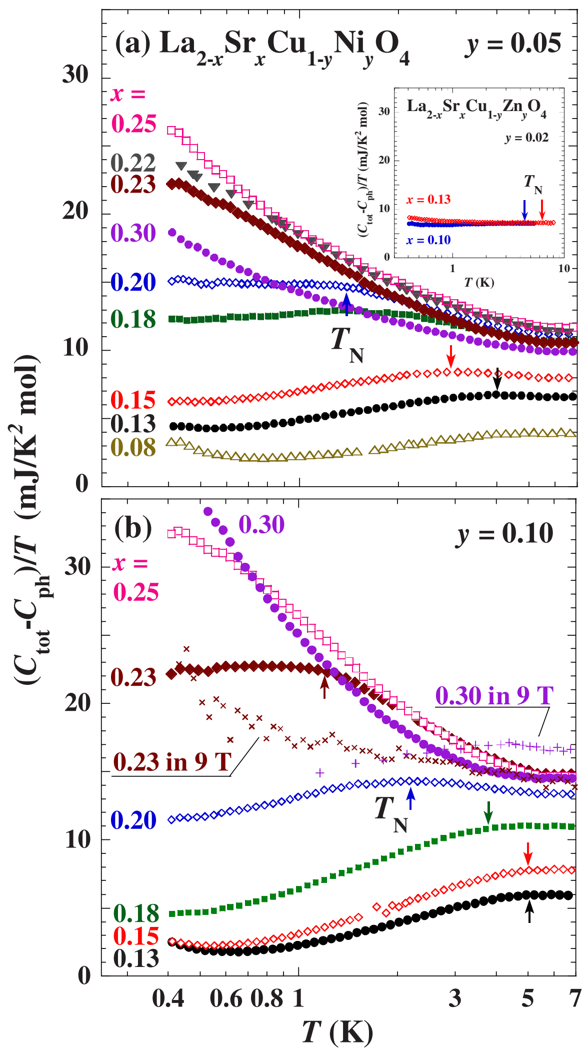

FIG. 2. (Color online) Temperature dependence of $(C_{tot}-C_{ph})/T$ for $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ with (a) $y=0.05$ and (b) $y=0.10$ (Ref. 23) in zero field. Here, C_{ph} is the phonon specific heat estimated from the best-fit results obtained using Eq. (3.1) in the temperature range of $30 \leq T^2 \leq 50$ K^2. Data of $x=0.23, 0.30$ and $y=0.10$ in a magnetic field of 9 T are also indicated by crosses. The inset shows the temperature dependence of $(C_{tot}-C_{ph})/T$ in Zn-substituted $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ with $x=0.10$, 0.13, and $y=0.02$. Arrows indicate the magnetic transition temperature, T_N, estimated from μSR measurements (Refs. 12 and 26).

Fig. 1 to Eq. (3.1). For all the samples, $(C_{tot}-C_{ph})/T$ is found to be almost constant above 5 K while it significantly varies depending on x below 5 K. Here, we define the effective hole concentration per Cu, p_{eff}, in a sample as $p_{eff}=x-y$, which is reasonable in the case that a Ni^{2+} ion traps a hole. For low-p_{eff} samples of $(x,y)=(0.08–0.13, 0.05)$ and (0.13–0.18,0.10), $(C_{tot}-C_{ph})/T$ decreases with decreasing temperature below 5 K while it increases below 5 K for high-p_{eff} samples of $(x,y)=(0.20–0.30, 0.05)$ and (0.25–0.30,0.10). For intermediate-p_{eff} samples of $(x,y)=(0.15–0.18, 0.05)$ and (0.20–0.23,0.10), $(C_{tot}-C_{ph})/T$ once increases with decreasing temperature and then decreases below 5 K. Therefore, the behavior of $(C_{tot}-C_{ph})/T$ at low temperatures are summarized to exhibit a gradual crossover from the decrease to increase with increasing x. It is noted that a small upturn of $(C_{tot}-C_{ph})/T$ around the lowest temperature observed for $(x,y)=(0.08–0.13, 0.05)$ and (0.13–0.15,0.10) is probably due to the so-called Schottky anomaly often observed in high-T_c cuprates.[24]

To make quantitative discussion about C_{el}, values of $(C_{tot}-C_{ph})/T$ before and after the change around 5 K are defined as γ_{HT} and γ_{LT}, respectively, and plotted in Fig. 3(a). Concretely, γ_{HT} is defined as the averaged value of $(C_{tot}-C_{ph})/T$ at 5–7 K for all the samples. The γ_{LT} for $(x,y)=(0.08–0.13, 0.05)$ and (0.13–0.15,0.10) exhibiting the Schottky anomaly is defined as the minimum value at low temperatures below 1 K and γ_{LT} for the other samples of $(x,y)=(0.15–0.30, 0.05)$ and (0.18–0.30,0.10) is defined as the value of $(C_{tot}-C_{ph})/T$ at the lowest temperature of 0.4 K. Normal-state values of γ, γ_N, in Ni-free LSCO obtained by Momono and Ido[25] is also plotted for comparison. It is found that γ_{HT} is in approximate agreement with γ_N at each x. This indicates that values of γ are dependent on the Sr concentration x irrespective of the Ni concentration y at high temperatures above 5 K. Therefore, in comparison with the other experimental results suggesting the occurrence of hole trapping by Ni at high temperatures,[9,10,13] the present results indicate that the complete hole trapping by Ni does not take place at high temperatures above 5 K.

On the other hand, γ_{LT} appears to disagree with γ_N at each x. Figure 3(b) shows the dependence on p_{eff} of γ_{LT} and γ_N. It is found that γ_{LT} is in approximate agreement with γ_N for low-p_{eff} samples of $(x,y)=(0.08-0.15, 0.05)$ and (0.13–0.18,0.10), suggesting that the strong hole trapping by Ni^{2+} takes place resulting in the effective decrease in the hole

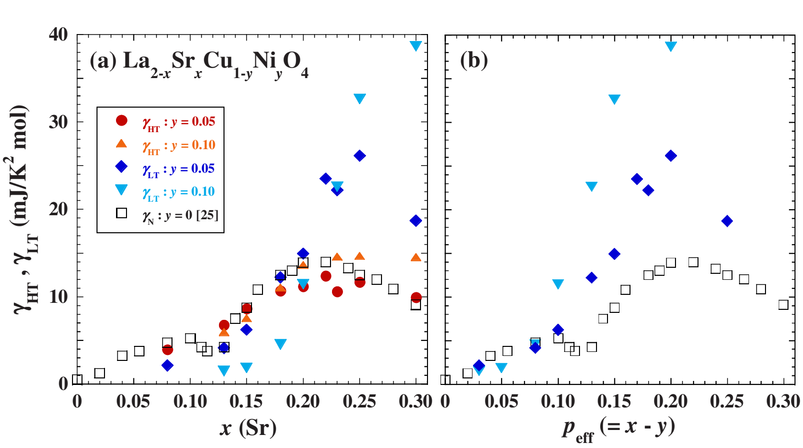

FIG. 3. (Color online) (a) Sr-concentration x dependence and (b) effective hole-concentration, $p_{eff}(=x-y)$, dependence of γ_{HT} and γ_{LT} in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ with $y=0.05$ and $y=0.10$. Normal-state values of γ, γ_N, in Ni-free $La_{2-x}Sr_xCuO_4$ obtained by Momono and Ido (Ref. 25) are also plotted for comparison.

concentration in these samples at low temperatures below 5 K.

It is possible that the decrease in $(C_{tot}-C_{ph})/T$ with decreasing temperature at low temperatures below 5 K is simply caused by the reduction in DOS at the Fermi level accompanied by the formation of a magnetic order, not accompanied by the strong hole trapping by Ni^{2+}. To check the possibility, the temperature dependence of the specific heat was measured for Zn-substituted LSCZO with $x=0.10, 0.13$ and $y=0.02$, in which a stripelike magnetic order is formed at low temperatures below T_N estimated from μSR measurements,[26] as shown in the inset of Fig. 2(a). It is found that no significant decrease in $(C_{tot}-C_{ph})/T$ is observed below T_N, suggesting that the observed decrease in $(C_{tot}-C_{ph})/T$ with decreasing temperature at low temperatures below 5 K for LSCNO is irrelevant to the magnetically induced reduction in DOS.

For high-p_{eff} samples of $(x,y)=(0.18-0.30, 0.05)$ and $(0.20-0.30, 0.10)$, γ_{LT} is apparently larger than γ_N owing to the enhancement of $(C_{tot}-C_{ph})/T$ at low temperatures below 5 K. The enhancement of $(C_{tot}-C_{ph})/T$ is reminiscent of the Kondo effect.[27] As shown in Fig. 2(b), in fact, the enhancement of $(C_{tot}-C_{ph})/T$ at low temperatures for $(x,y)=(0.23, 0.10)$ and $(0.30, 0.10)$ is suppressed by the application of a magnetic field of 9 T, which is also a typical behavior in the Kondo state. Therefore, high-p_{eff} samples with Ni impurities are interpreted as being in a Kondo-type state at low temperatures below 5 K. As for intermediate-p_{eff} samples of $(x,y)=(0.15-0.18, 0.05)$ and $(0.20-0.23, 0.10)$, the enhancement of $(C_{tot}-C_{ph})/T$ with decreasing temperature is followed by the decrease below ~ 1 K. This is regarded as a crossover of the electronic state from the Kondo-type state to the strong hole-trapping state with decreasing temperature.

B. Electrical resistivity

Figure 4 shows the temperature dependence of ρ plotted as $\ln\rho$ vs $T^{-1/3}$ for $(x,y)=(0.13, 0.05)$, (0.20, 0.07), and (0.15–0.23, 0.10). Linear behaviors are observed at low temperatures below T_{VRH} shown by arrows for all the samples, suggesting the occurrence of two-dimensional (2D) variable-range hopping (VRH) conduction. As ρ exhibits a metallic behavior at high temperatures for $(x,y)=(0.13, 0.05)$, (0.20,0.07), and (0.18–0.23,0.10), it is suggested for low-p_{eff} samples that holes tend to be localized gradually with decreasing temperature and turn into a strongly localized state exhibiting VRH conduction below T_{VRH}.

Figure 5(a) shows the temperature dependence of ρ for $(x,y)=(0.30, 0.05)$, (0.20,0.07), and (0.23–0.30,0.10). It is found that the samples except for $(x,y)=(0.30, 0.05)$ exhibit logarithmic temperature dependence below 5–10 K and following saturation below 1–2 K. As shown in Fig. 5(b), moreover, negative magnetoresistance is observed at low temperatures where the logarithmic temperature dependence of ρ is observed. These are characteristic of a Kondo state and/or a 2D Anderson-localized state. In these samples, in fact, a behavior characteristic of a Kondo state is observed also in the specific-heat measurements, as described in Sec. III A.

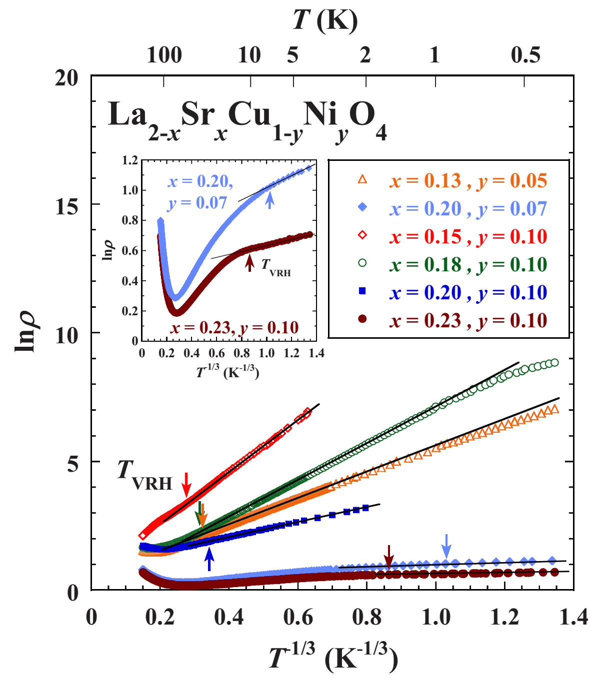

FIG. 4. (Color online) Temperature dependence of the electrical resistivity, ρ, plotted as $\ln\rho$ vs $T^{-1/3}$ for $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ with $y=0.05$, 0.07, and 0.10. The inset shows the data of $x=0.20$, $y=0.07$ and $x=0.23$, $y=0.10$ plotted on a different scale. Arrows indicate T_{VRH} below which $\ln\rho$ changes linearly to $T^{-1/3}$.

Therefore, the logarithmic temperature dependence of ρ in zero field is interpreted as being due to the occurrence of the Kondo-type state, namely, due to screening of localized Ni^{2+} spins by mobile holes.

For $(x,y)=(0.23, 0.10)$, it is found that the logarithmic increase in ρ with decreasing temperature tends to be saturated around 1–2 K and then increases again below 1 K. The saturated behavior of ρ may be regarded as the one toward the unitary limit of the Kondo state. To understand the increase below 1 K, however, another mechanism is required, as discussed later. It is noted for $(x,y)=(0.30, 0.05)$ that no logarithmic increase in ρ is observed at low temperatures, although $(C_{tot}-C_{ph})/T$ increases with decreasing temperature below 5 K as shown in Fig. 2(a). Since negative magnetoresistance is observed as shown in Fig. 5(b), it is inferred that a Kondo-type state is realized at low temperatures for $(x,y)=(0.30, 0.05)$ as well.

C. Magnetization

Figure 6 shows the temperature dependence of the magnetization divided by the magnetic field, M/H, for LSCNO with $y=0.05$ and 0.10. The data are shifted top and bottom. The characteristics are as follows. (i) All the samples exhibit Curie-type behavior more or less. (ii) For $(x,y)=(0.08-0.18, 0.05)$ and $(0.13-0.20, 0.10)$, downward deviation of M/H from the Curie-type behavior is observed at low temperatures below ~ 10 K. (iii) The M/H due to the so-called 2D-AF correlation between Cu^{2+} spins,[28] χ_{AF}, is invisible for all the samples because probably the variation in the

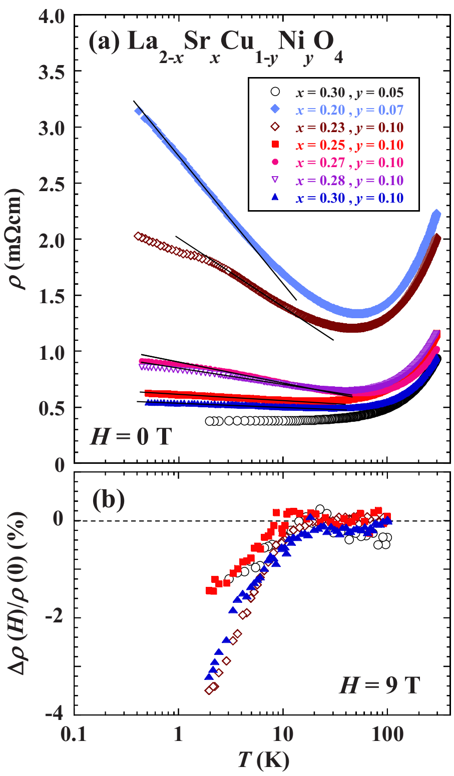

FIG. 5. (Color online) Temperature dependence of (a) the electrical resistivity, ρ, in zero field and (b) the magnetoresistance, $\Delta\rho(H)/\rho(0) \equiv \{\rho(H,T)-\rho(0,T)\}/\rho(0,T)$, in a magnetic field of 9 T in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ with y=0.05, 0.07, and 0.10.

Curie-type M/H with temperature is much larger than that of χ_{AF} in the measured temperature range.

The temperature dependence of M/H is fitted using the following equation:

$$M/H = \chi_0 + \chi_{AF} + C/(T-\theta). \tag{3.2}$$

The first term represents a temperature-independent one originating from the van Vleck paramagnetism, ion-core diamagnetism, etc. The third term is a Curie-Weiss one due to Ni^{2+} spins. The θ is the Weiss temperature and C the Curie constant given by

$$C = Ng^2S(S+1)\mu_B^2/3k_B. \tag{3.3}$$

Here, N is the number of Ni^{2+} spins, g the g factor, μ_B the Bohr magneton, and k_B the Boltzmann constant. Early measurements of M/H in LSCNO by Xiao *et al.*[2] have suggested that the Curie-type behavior is caused by the substituted Ni^{2+} spins.

For underdoped and highly Ni-substituted samples of LSCNO, it has been reported that χ_{AF} exhibits a broad maximum above room temperature and monotonically decreases with decreasing temperature below room temperature,[28] allowing us to express χ_{AF} being linearly dependent on temperature. For optimally doped and overdoped samples of LSCNO, on the other hand, the broad maximum in χ_{AF} has been observed below room temperature.[28] In fact, the fitting of the data of (x,y)=(0.15–0.30,0.05) to Eq. (3.2) in which χ_{AF} is linearly dependent on temperature has failed. On the other hand, the data of (x,y)=(0.08,0.05) and (0.13–0.30,0.10) have been fitted to Eq. (3.2) at high temperatures above T_N, as shown in Fig. 6. Estimated values of S using Eq. (3.3) are plotted in the inset of Fig. 6. It is found that the values of S are between 0.1 and 0.3 and much smaller than the expected value of S=1 in the Ni^{2+} state. This suggests that holes tend to be localized around Ni^{2+} forming Zhang-Rice doublet states even at high temperatures for comparatively low-p_{eff} samples so that each Ni^{2+} spin is antiferromagnetically coupled with a hole spin, resulting in the decrease in S of Ni^{2+} spins. It is noted that the smaller values of S than 1/2 expected from the AF coupling between a Ni^{2+} spin with S=1 and a hole spin with S=1/2 may be due to the mixing of Ni 3d and O 2p orbitals.

As to the downward deviation of M/H from the Curie-type behavior at low temperatures for comparatively low-p_{eff} samples, the onset temperature of the deviation of M/H is found to be in rough agreement with T_N estimated from μSR measurements.[12] This suggests that the deviation of M/H is due to the development of the magnetic correlation between Ni^{2+} and Cu^{2+} spins toward the formation of a magnetic order.

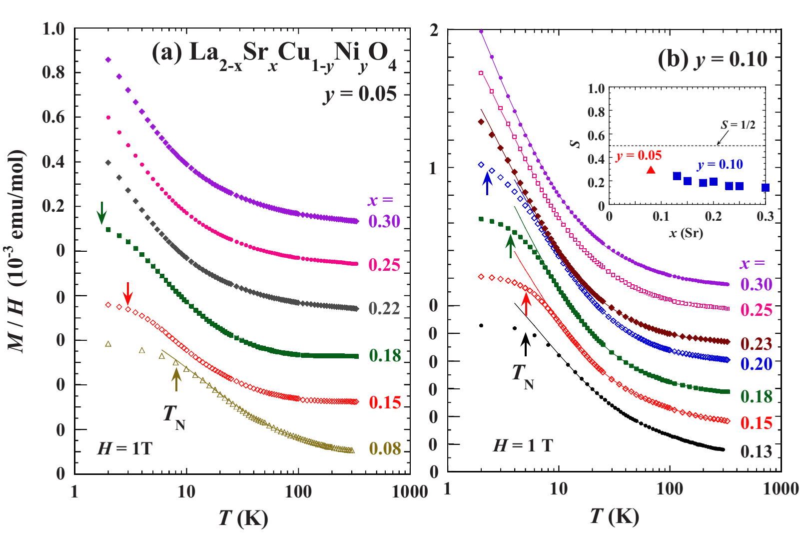

FIG. 6. (Color online) Temperature dependence of the magnetization divided by the magnetic field, M/H, in a magnetic field of 1 T for $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ with (a) y=0.05 and (b) y=0.10. The data are shifted top and bottom. Solid lines indicate the best-fit results obtained using Eq. (3.2) at high temperatures far from the magnetic transition temperature, T_N, estimated from μSR measurements (Ref. 12) shown by arrows. The inset shows the Sr-concentration x dependence of the spin quantum number, S, estimated from the best-fit results.

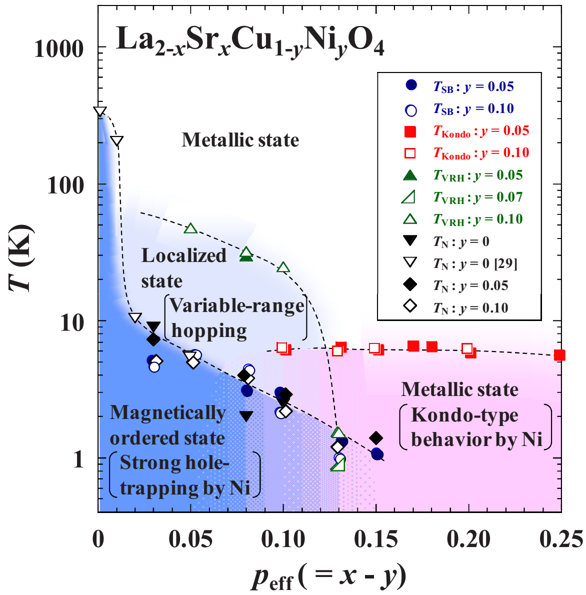

FIG. 7. (Color online) Electronic phase diagram of nonsuperconducting Ni-substituted $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ (Ref. 23). T_{SB} is defined as the temperature below which $(C_{tot}-C_{ph})/T$ decreases with decreasing temperature. T_{Kondo} is the onset temperature of the Kondo-type state where $(C_{tot}-C_{ph})/T$ increases with decreasing temperature. T_{VRH} is defined as the onset temperature of the variable-range hopping conduction. The magnetic transition temperature, T_N, estimated from μSR measurements (Ref. 12) is also plotted, together with the reported data of $y=0$ (Ref. 29). Dashed lines are to guide the reader's eyes.

IV. DISCUSSION

A. Phase diagram of non-SC Ni-substituted $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$

Figure 7 displays the phase diagram of LSCNO in which the temperatures where $(C_{tot}-C_{ph})/T$ shown in Fig. 2 starts to decrease and increase with decreasing temperature, T_{SB} and T_{Kondo}, respectively, the temperature below which ρ shown in Fig. 4 exhibits VRH conduction, T_{VRH}, are plotted as a function of p_{eff}. For high-p_{eff} samples, it is unclear whether or not holes tend to be localized around Ni^{2+} at high temperatures so that p_{eff} may be meaningless. In the Kondo-type state at low temperatures, on the other hand, holes are localized in the ground state so as to screen Ni^{2+} spins so that p_{eff} is meaningful at low temperatures.

In Fig. 7, T_N estimated from μSR measurements[12] is also plotted, together with the reported data of $y=0$.[29] For $p_{eff}<0.10$, a long-range magnetic order is formed in the ground state, confirmed by the muon-spin precession. For $p_{eff}\geq 0.10$, on the other hand, both the presence of fast depolarization of muon spins and the absence of muon-spin precession at low temperatures suggest the formation of a short-range magnetic order, which is discussed later. It is found that T_{SB} is in good agreement with T_N, suggesting that the decrease in the electronic specific heat at low temperatures is deeply related to the formation of the magnetic order. That is, supposed that a hole is strongly bound by a Ni^{2+} ion, the effective value of S of the Ni^{2+} ion with a ligand hole is

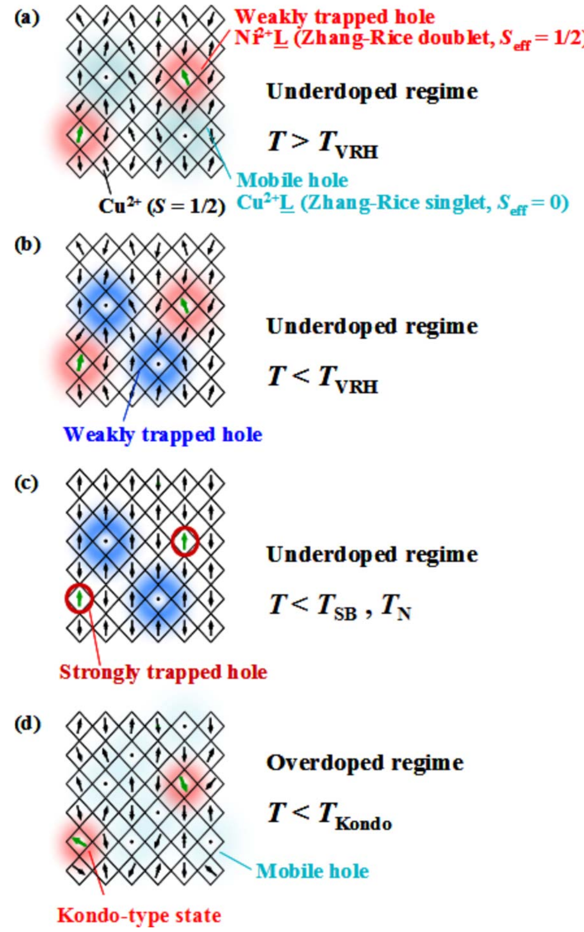

FIG. 8. (Color online) Schematic drawing of the CuO_2 plane (a) in the underdoped regime at high temperatures of $T>T_{VRH}$ where both weakly localized holes around Ni^{2+} and itinerant holes exist, (b) in the underdoped regime at $T<T_{VRH}$ where localized holes exhibit variable-range hopping conduction, (c) in the underdoped regime at low temperatures below $T_N \sim T_{SB}$ where holes are strongly bound by Ni^{2+}, (d) in the overdoped regime at low temperatures below T_{Kondo} where screening of localized Ni^{2+} spins by conducting holes takes place forming a Kondo-type state.

regarded as being roughly the same as that of Cu^{2+} spins, tending to the recovery of the $S=1/2$ network of Cu^{2+} spins.[14] Moreover, the strong hole trapping by a Ni^{2+} ion is expected to reduce the frustration effect between Cu^{2+} spins. Therefore, it is guessed that each Ni^{2+} ion traps a hole strongly so as not to disturb the AF correlation in the network of Cu^{2+} spins.

B. Temperature dependence of the electronic state in the underdoped regime

Here, we discuss the temperature-dependent change in the electronic state in the underdoped regime, as schematically shown in Fig. 8. In the case of $x>y$, that is, p is larger than the Ni concentration, y, there exist two kinds of hole in the CuO_2 plane; one is weakly localized around Ni^{2+} forming a Zhang-Rice doublet state and the other is mobile forming a Zhang-Rice singlet state with Cu^{2+} spins at room temperature, as shown in Fig. 8(a). It has been suggested from XAFS experiments by Hiraka *et al.*[13] that holes tend to be localized around Ni even at room temperature. The present result of M/H that the value of S of Ni^{2+} spins is much smaller than 1 suggests the localization of holes around Ni^{2+} at high temperatures. On the other hand, relatively good conduction occurs at high temperatures, judged from ρ shown in Fig. 4. These results naturally draw the conclusion that the two kinds of hole, namely, weakly localized holes around Ni^{2+} forming a Zhang-Rice doublet state and mobile holes forming a Zhang-Rice singlet state with Cu^{2+} spins reside in the CuO_2 plane at high temperatures.

As shown in Fig. 8(b), mobile holes moving around in the CuO_2 plane at high temperatures tend to be localized below T_{VRH}, leading to the occurrence of VRH conduction. On the other hand, holes around Ni^{2+} are maintained in its original form, supported by the constant value of S in the moderate range of temperature as shown in Fig. 6 and by the good coincidence of γ_{HT} with γ_N at each x.

With further decreasing temperature, each Ni^{2+} ion strongly traps a hole, resulting in the formation of the magnetic order of Cu^{2+} spins and in the decrease in $(C_{tot}-C_{ph})/T$ at low temperatures below $T_N \sim T_{SB}$, as shown in Fig. 8(c). Below T_N, moreover, the suppression of M/H is observed due to the participation of Ni^{2+} spins in the AF order of Cu^{2+} spins. No significant anomaly is detected in ρ around T_{SB}, implying that the state of holes except for ones around Ni^{2+} does not change so much.

C. Temperature dependence of the electronic state in the overdoped regime

In the overdoped regime, ρ exhibits a metallic behavior at high temperatures. At low temperatures below T_{Kondo}, on the other hand, Kondo-type behavior is observed in the specific-heat and ρ measurements. In this case, mobile holes are scattered by Ni^{2+} spins, leading to the screening of the Ni^{2+} spins toward the ground state, as shown in Fig. 8(d). It attracts interest that the ground state of the Kondo-type state due to Ni^{2+} spins in the overdoped regime is more or less analogous to the hole-trapping state due to Ni^{2+} in the underdoped regime. Very recently, a logarithmic increase in ρ and negative magnetoresistance have been observed also in the overdoped Bi-based cuprate in which Fe with a large magnetic moment is partially substituted for Cu,[30] suggesting the occurrence of the Kondo effect. Here, it should be stressed that the Kondo state generally appears in metallic samples. Therefore, the present result is one of significant evidences for the occurrence of a Fermi-liquid state in the overdoped regime.

D. Change in the ground state upon hole doping

In the ground state of the underdoped regime, each Ni^{2+} ion traps a hole strongly and a magnetically ordered state appears. In the ground state of the overdoped regime, on the other hand, a metallic state with Kondo-type behavior due to Ni^{2+} spins is realized. It is found that T_N decreases gradually with increasing p_{eff} and tends to disappear around $p_{eff}=0.18-0.19$ as shown in Fig. 7. This is reminiscent of the possible existence of QCP around p_{eff}=0.18–0.19, as formerly suggested from various experiments.[15] As shown in Fig. 2, in fact, $(C_{tot}-C_{ph})/T$ exhibits a logarithmic increase with decreasing temperature down to the lowest temperature of 0.4 K for $(x,y)=(0.22-0.23,0.05)$, which is consistent with the theoretical prediction by Moriya and Ueda in the 2D-AF quantum critical region.[31]

For $(x,y)=(0.15-0.18,0.05)$ and (0.20–0.23,0.10), on the other hand, $(C_{tot}-C_{ph})/T$ increases with decreasing temperature due to the occurrence of the Kondo-type state, followed by a decrease at lower temperatures accompanied by a magnetic transition. Moreover, γ_{LT} is apparently larger than γ_N for these samples. These are inconsistent with the concept of the simple QCP at which two adjacent phases in the ground state are definitely separated in the phase diagram. Therefore, the present results conflict with the simple QCP physics.

It has been suggested from the magnetization,[32–37] specific heat,[38–40] and μSR (Refs. 41–43) measurements that a microscopic phase separation into SC and normal-state regions takes place in a sample of the overdoped high-T_c cuprates. Based on these results, it is possible in Ni-substituted LSCNO that a phase-separated state consisting of the magnetically ordered region observed in the underdoped regime and the metallic region observed in the overdoped regime is realized in a sample around the boundary between the magnetically ordered and metallic phases in the phase diagram. These explain the specific-heat results around $p_{eff}=0.10-0.13$ exhibiting an enhancement of $(C_{tot}-C_{ph})/T$ due to the occurrence of the Kondo-type state in the metallic region and a suppression of $(C_{tot}-C_{ph})/T$ due to the strong hole trapping by Ni^{2+} in the magnetically ordered region. Moreover, the above explanation is also supported by larger values of γ_{LT} shown in Fig. 3 than the expected ones assuming the strong hole trapping by Ni^{2+}. That is, as only the magnetically ordered region in a phase-separated sample is characterized by p_{eff}, the value of γ_{LT} tends to be larger than that in the complete hole-trapping state. Furthermore, the distinctive behavior of ρ for $(x,y)=(0.23,0.10)$ shown in Fig. 5 is well explained taking into account the phase separation. That is, both the increase and following saturation of ρ with a decrease in temperature below ~5 K are characteristic of a Kondo-type state in the metallic region of a sample while the further increase in ρ with decreasing temperature below 1 K is due to the strong hole trapping by Ni^{2+} in the magnetically ordered region of a sample.

The occurrence of the phase separation around the boundary between the magnetically ordered and metallic phases appears to be consistent with the results in LSCO where the superconductivity is suppressed by the application of high magnetic field[19] or by the Zn substitution.[20] In-plane ρ measurements in high magnetic fields in LSCO have revealed that a T-linear behavior characteristic of the quantum critical region is observed not only in a limited region of $p \sim 0.19$ but also in an extended one in the overdoped regime and coexists with the T^2 behavior. The μSR measurements for 3% Zn-substituted LSCZO have revealed that the Zn-induced development of the Cu-spin correlation does not vanish around $p=0.19$ as formerly indicated by Panagopoulos *et al.*[21] but is weakened gradually with increasing p in the overdoped regime and disappears around $x=0.30$.[20] These results are understood in terms of a phase separation into a quantum critical region with the T-linear resistivity and the developed Cu-spin correlation and a Fermi-liquid region with the T^2 resistivity. Accordingly, it is much convinced that the quantum phase transition in LSCO occurs not at a single point of p in the ground state but in an extended region of p, that is, the change in the ground state upon hole doping is crossoverlike due to the phase separation. Since the T-linear behavior of ρ has been observed in various high-T_c cuprates[16–18] and the occurrence of the phase separation has been proposed in various overdoped cuprates,[32–43] the present results together with former ones[19,20] strongly suggest that HTSC emerges around the quantum critical region affected by the phase separation.

V. SUMMARY

We have carried out specific heat, ρ, magnetization, and μSR measurements in non-SC Ni-substituted LSCNO, in order to investigate the temperature-dependent change in the electronic state and the ground state inside the pristine SC dome of LSCO without disturbing the Cu-spin correlation in the CuO_2 plane so much. In the underdoped regime, it has been found that at high temperatures there exist two kinds of hole, that is, weakly localized holes around Ni^{2+} forming a Zhang-Rice doublet state and itinerant holes forming a Zhang-Rice singlet state, deduced from the metallic behavior of ρ and the reduced value of S below 1 of Ni^{2+} spins. With decreasing temperature, itinerant holes tend to be localized and both kinds of hole exhibit VRH conduction at low temperatures. Finally, in the ground state, each Ni^{2+} ion traps a hole strongly and that a magnetically ordered state appears, evidenced from the decrease in DOS at the Fermi level in the specific-heat measurements and from the appearance of a magnetic transition in the μSR measurements. In the overdoped regime, on the other hand, it has been found that a metallic state is realized at high temperatures while a Kondo-type state is formed around Ni^{2+} spins at low temperatures, confirmed by the increase in C_{el}/T, the logarithmic increase in ρ and the negative magnetoresistance. It has been concluded that the ground state of non-SC LSCNO changes upon hole doping from a magnetically ordered state with the strong hole trapping by Ni^{2+} to a metallic state with Kondo-type behavior due to Ni^{2+} spins and that the quantum phase transition is crossoverlike due to the phase separation into short-range magnetically ordered and metallic regions. Since the T-linear behavior of ρ has been observed in various high-T_c cuprates[16–18] and the occurrence of the phase separation has been proposed in various overdoped cuprates,[32–43] it is suggested that HTSC emerges around the quantum critical region affected by the phase separation.

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