Contrasting Ni- and Zn-substitution effects on magnetic properties and superconductivity in $La_{2-x}Sr_xCuO_4$

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Both Ni- and Zn-substitution effects on superconducting and magnetic properties of $La_{2-x}Sr_xCuO_4$ were studied by measuring the magnetic susceptibility χ and the electronic specific heat C_{el} at $T \ll T_c$. In Ni-substituted samples with $x \geq 0.14$, the local nature of the spin correlation among $3d$ spins remains almost unchanged even on Ni sites at low Ni concentrations, where Ni atoms are substituted as Ni^{3+} ions. On the other hand, in Zn-substituted samples the $3d$-spin correlation is seriously disturbed on host Cu sites around each Zn site. The depression of T_c and the residual γ value at $T \ll T_c$ indicate that the suppression of the superconductivity in Zn-substituted samples is much stronger than that in Ni^{3+}-substituted ones. The suppression of the superconductivity in the Ni^{3+}-substituted samples can be understood in the context of a potential scattering of the Cooper pairs in a *d*-wave superconductor. On the other hand, the strong suppression of the superconductivity in the Zn-substituted samples will occur through the local disturbance of the $3d$-spin correlation on host Cu sites around each Zn ion. [S0163-1829(98)07733-9]

I. INTRODUCTION

In typical high-T_c cuprates such as $YBa_2Cu_3O_{7-\delta}$ (YBCO) and $La_{2-x}Sr_xCuO_4$ (LSCO), partial substitution of nonmagnetic ions such as Zn^{2+} and Al^{3+} for Cu leads to stronger suppression of the superconductivity than substitution of nominally magnetic Ni ions, which is in sharp contrast with the conventional superconductors.[1–5] It has been found in NMR experiments that partial substitution of Zn or Al induces localized magnetic moments on host Cu sites neighboring Zn or Al.[6–8] Therefore, the induced local-magnetic moments were invoked to suggest magnetic pair breaking as possible origins of the strong suppression of T_c in Zn- or Al-substituted LSCO and YBCO samples.[1,3,7] However, Ishida *et al.* have performed ^{27}Al NMR studies on Al-substituted LSCO, whose T_c is suppressed to almost the same extent as that in Zn-substituted LSCO, and found that the magnetic pair breaking due to the local magnetic moments induced by the substitution of nonmagnetic ions is too weak to explain the rapid suppression of T_c.[8] It has been reported for both LSCO and YBCO systems that the Zn substitution causes a large residual density of states at E_F at $T \ll T_c$, N_{res}, in addition to the rapid suppression of T_c, ΔT_c. The N_{res} vs ΔT_c relation can be qualitatively explained on the basis of a *d*-wave superconductor by assuming that nonmagnetic Zn ions act as strong potential scatterers in the unitarity limit.[9–13] However, the N_{res} vs ΔT_c relation obtained for LSCO samples with $x \lesssim 0.18$ obviously deviates from the theoretical prediction.[10]

In comparison with nonmagnetic ions such as Zn^{2+} and Al^{3+}, nominally magnetic Ni ions lead to a moderate effect not only on the superconductivity but also on the local magnetism at host Cu sites neighboring Ni in the YBCO system.[2,12–15] It was demonstrated by NMR studies on the YBCO system that the spin-lattice relaxation time $^{63}T_1$ of ^{63}Cu is only slightly modified even on planar Cu sites around Ni ions, whereas $^{63}T_1$ is largely modified on planar Cu sites around Zn ions on account of a local disturbance of spin correlation among Cu $3d$ spins.[12–14] Mendels *et al.* measured the Curie term on Ni-substituted YBCO samples, and found that the Curie constant corresponds to $S=1/2$ rather than $S=1$, though usually $S=1$ is expected for Ni^{2+} ions.[15] They explained the results as follows: an isolated $3d$ spin in the $3d_{3z^2-r^2}$ orbital of Ni^{2+}, whose magnetic channels to neighboring host Cu $3d_{x^2-y^2}$ spins are very weak, will contribute to the Curie term corresponding to $S=1/2$, while a spin in the Ni $3d_{x^2-y^2}$ orbital can couple antiferromagnetically to neighboring Cu $3d_{x^2-y^2}$ spins; that is, the magnetic channel between $3d_{x^2-y^2}$ spins survives at Ni sites. The survival of the magnetic channels will preserve the local nature of the $3d_{x^2-y^2}$-spin correlation on host Cu sites around Ni sites. Recently the superconductivity of cuprates was found to be of a *d*-wave type, and antiferromagnetic interaction within the CuO_2 plane has received more attention than ever as a candidate for the origin of the superconductivity.[10,16–20] Therefore, the preservation of the local nature of the $3d_{x^2-y^2}$-spin correlation has become of interest to explain the milder pair-breaking effect of Ni than that of Zn in the YBCO system.[15] It has also been reported for the LSCO system that the superconductivity is less suppressed in Ni-substituted samples than in Zn-substituted ones.[1,3,5] To understand the reason why the substitution effects on the superconductivity are rather different between nominally magnetic Ni and nonmagnetic Zn, we should clarify their substitution effects on the magnetic properties in the LSCO system as well as the YBCO system. However, the Ni-substitution effect on magnetic properties has not been systematically studied for the LSCO system yet.

In the present study, we investigate both Ni- and Zn-substitution effects on magnetic properties and superconductivity of LSCO by measuring the magnetic susceptibility χ and the electronic specific heat C_{el} at $T \ll T_c$. It was found in

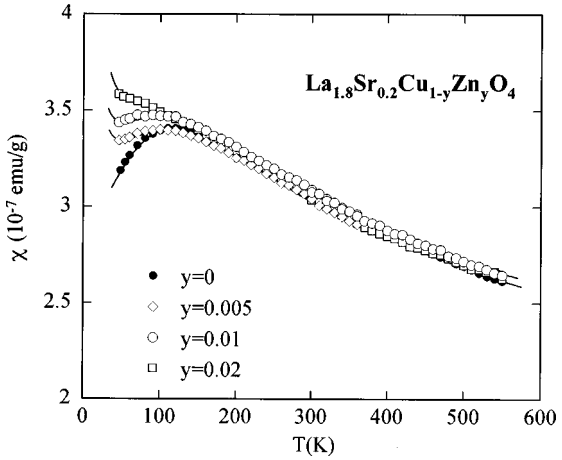

FIG. 1. Magnetic susceptibility χ of $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ with $x=0.2$. The solid lines represent fitting curves.

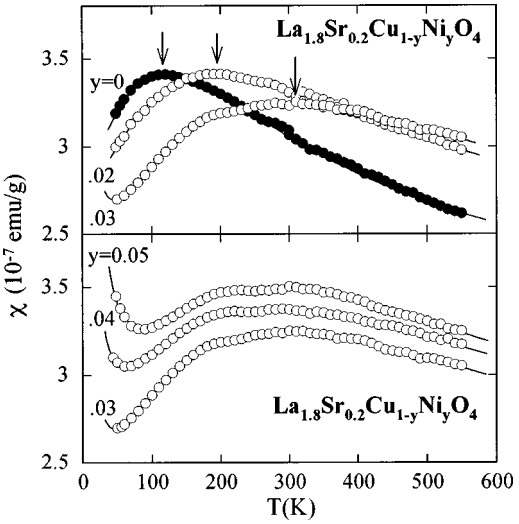

FIG. 2. Magnetic susceptibility χ of $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ with $x=0.2$. The solid lines represent fitting curves.

Ni-substituted LSCO with $x \gtrsim 0.14$ that the spin correlation among $3d_{x^2-y^2}$ spins remains unchanged even on Ni sites below the critical Ni concentration y_0, where Ni atoms are substituted as trivalent Ni^{3+} ions. On the other hand, in Zn-substituted samples the $3d_{x^2-y^2}$-spin correlation is seriously disturbed on host Cu sites around each Zn site because the magnetic channels between $3d_{x^2-y^2}$ spins are disrupted at nonmagnetic Zn ions. It was also found that the depression of T_c and the residual density of states at E_F at $T \ll T_c$ are much smaller in Ni^{3+}-substituted samples than in Zn-substituted ones. We discuss the difference between Ni- and Zn-substitution effects on the superconductivity in terms of the local disturbance of the $3d_{x^2-y^2}$-spin correlation.

II. EXPERIMENTS

A master batch of high-purity $La_{2-x}Sr_xCu_{1-y}M_yO_4$ (M = Ni, Zn) samples was prepared using La_2O_3, $SrCO_3$, CuO, NiO, and ZnO powders of high purity (99.99–99.999 %) at 1050–1150 °C in an oxygen atmosphere with one intermediate grinding, followed by annealing in an oxygen atmosphere at 600 °C for 24 h. Each sample was fully characterized by x-ray diffraction and confirmed to be single phase.

Magnetic susceptibility was measured by using a Quantum Design SQUID magnetometer. The magnetic susceptibility in the normal state was measured under a magnetic field of 10 kOe in a T-range below ~600 K in both courses of heating and cooling. There was no degradation of samples due to oxygen deficiency, at least in the T-range examined. Measurements of the superconducting diamagnetism were carried out under a field of 15 Oe. The specific-heat capacity was measured by a conventional adiabatic heat pulse method within a T^2 range from 4 K^2 to 50 K^2. Details of the measurements have been reported elsewhere.[9,10]

III. RESULTS AND DISCUSSION

A. Substitution effect on the magnetic susceptibility

In Figs. 1 and 2, the magnetic susceptibility χ is shown for the normal state of $La_{2-x}Sr_xCu_{1-y}M_yO_4$ (M = Ni, Zn) with $x=0.2$. The $\chi-T$ curve of $La_{2-x}Sr_xCu_{1-y}M_yO_4$ exhibits a broad peak at temperature T_{max} as well as that of $La_{2-x}Sr_xCuO_4$ (LSCO).[21–29] In Zn-substituted samples, the position of the broad peak weakly depends on Zn concentration y though the broad peak is obscured by the appearance of the Curie term at Zn concentrations of more than 1%. On the other hand, in Ni-substituted samples the position of the broad peak of the $\chi-T$ curve largely shifts to higher temperatures with increase in Ni concentration y at $y<0.03$, and the shift tends to be saturated at $y \gtrsim 0.03$ (Fig. 2). Furthermore, in Ni-substituted samples with $y<0.03$, no evident Curie term was observed at low temperatures though Ni ions are nominally magnetic.

In our previous study, the magnetic susceptibility of Zn-substituted LSCO samples was analyzed by assuming that it contains a T-dependent spin component, $\chi^s(T)$, and a T-independent one, χ^0, in addition to the Curie component C/T, i.e.,

$$\chi = \chi^s(T) + \chi^0 + C/T, \tag{1}$$

where component $\chi^s(T)$ is characterized by a broad peak at T_{max}.[22] Both the characteristic temperature, T_{max}, and the size of $\chi^s(T)$ largely depend on the Sr concentration, namely, the hole concentration p within the CuO_2 plane, but the normalized $\chi^s(T)$ vs T curve, $\chi^s(T/T_{max})/\chi^s(T_{max})$ vs T/T_{max}, follows a universal curve, F, which is the same universal curve as that identified for LSCO samples, regardless of p.[22,30] Universal curve F can be understood in terms of an $S=1/2$ square-lattice Heisenberg antiferromagnet at high temperatures ($T \gtrsim 0.7T_{max}$).[22,24,30] In the present study, we fitted the data of Ni-substituted samples to Eq. (1) using the same universal curve F. As seen in Fig. 2, the $\chi-T$ curves of Ni-substituted samples can be reproduced very well.

In Figs. 3 and 4, the Curie constant and temperature T_{max} determined in the above analyses are shown for $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($0.14 \lesssim x \lesssim 0.22$) as a function of y. As seen in Fig. 3, it was confirmed that there exists no additional Curie term in Ni-substituted samples up to a certain value, y_0, while the Curie term appears at $y>y_0$. The details of the Curie term will be mentioned later. It should be noticed in Fig. 4 that T_{max} rapidly increases with increasing y up to the value y_0, while the increase of T_{max} tends to be saturated at

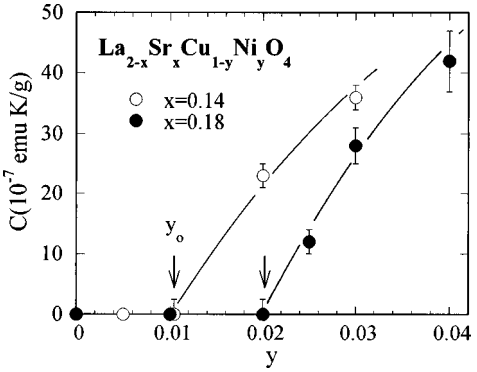

FIG. 3. Dependence of the Curie constant on y for $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$.

$y>y_0$. The characteristic Ni-concentration y_0 increases with increasing x (the inset of Fig. 4). Since T_{max} was found to increase with a decrease in the hole concentration $p(=x)$ in unsubstituted LSCO samples (Fig. 5),[22,24–29] the increase of T_{max} with Ni concentration suggests that the substitution of Ni for Cu may reduce the hole concentration p. A possible origin of the hole reduction is that Ni atoms will be substituted as trivalent Ni^{3+} ions, because the substitution of a Ni^{3+} ion for a Cu^{2+} consumes a hole within the CuO_2 plane. Such a possibility has already been pointed out by Bhat *et al.* on the basis of different T_c-x curves between Ni-free and Ni-substituted LSCO systems.[31] If Ni atoms are substituted as trivalent ions in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$, the hole concentration p should be given by $p=x-y$, instead of $p=x$. In fact, when T_{max} of $La_{1.8}Sr_{0.2}Cu_{1-y}Ni_yO_4$ ($y<y_0$) is plotted as a function of $p=0.2-y$, it agrees very well with the data of Ni-free $La_{2-x}Sr_xCuO_4$ samples with $x=0.2-y$, as seen in Fig. 5. The good agreement supports the possibility that all Ni atoms will be substituted as trivalent Ni^{3+} ions at $y \lesssim y_0$. In this context, the saturation of T_{max} at $y>y_0$ means that p will be fixed at $p=x-y_0$; i.e., some Ni ions, y_0, become trivalent while the rest of them, $y-y_0$, are divalent.

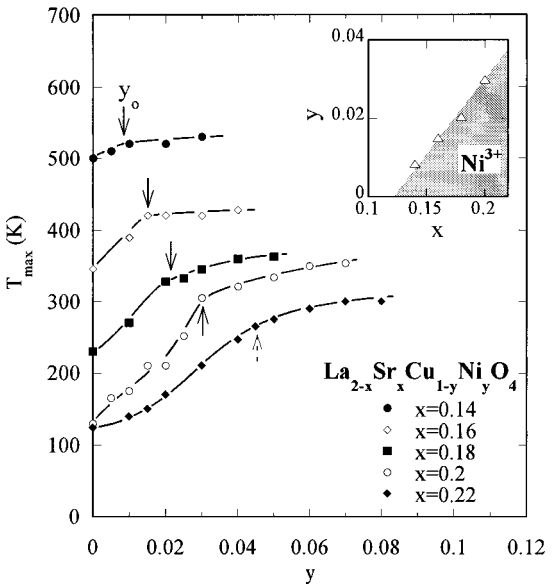

FIG. 4. Dependence of T_{max} on y for $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$. The inset shows the region where Ni is substituted as Ni^{3+}.

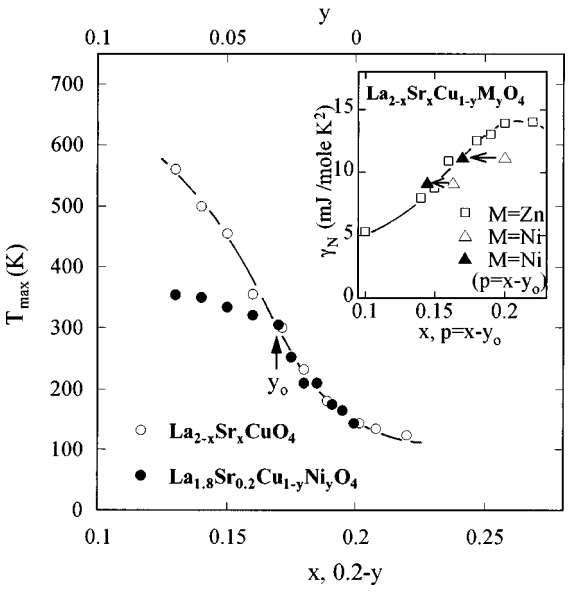

FIG. 5. T_{max} of $La_{2-x}Sr_xCuO_4$ (○) and of $La_{1.8}Sr_{0.2}Cu_{1-y}Ni_yO_4$ (●). T_{max}'s of $La_{2-x}Sr_xCuO_4$ and $La_{1.8}Sr_{0.2}Cu_{1-y}Ni_yO_4$ are plotted as a function of x and $0.2-y$, respectively. The inset shows the x dependence of the γ_N value for $La_{2-x}Sr_xCu_{1-y}M_yO_4$: $M=$Zn (□) and $M=$Ni (△). In the inset, the γ_N value for $M=$Ni (the closed triangle ▲) is also plotted as a function $p=x-y_0$: y_0's are 0.02 and 0.03 for $x=0.16$ and 0.2 samples, respectively.

Studies of the electronic specific heat C_{el} on nonsuperconducting $La_{2-x}Sr_xCu_{1-y}M_yO_4$ ($M=$Ni, Zn) samples also support the possibility that Ni will be substituted as Ni^{3+} at $y<y_0$. In the inset of Fig. 5, the coefficient of the T-linear term of C_{el}, γ_N, is shown for nonsuperconducting $La_{2-x}Sr_xCu_{1-y}M_yO_4$ ($M=$Ni, Zn) as a function of x. The γ_N value is evidently smaller in Ni-substituted samples than in Zn-substituted ones, as has already reported by Hiroi *et al.*[32] Here, to take into account the hole consumption effect of Ni^{3+}, we replot the γ_N value of $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ against $p=x-y_0$ regarding the horizontal axis x as p in the inset of Fig. 5. In this plot, the γ_N values of $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($p=x-y_0$) are in agreement with those of $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ ($p=x$), as expected.

Now we refocus on the result showing that the Ni substitution induces no additional Curie term in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$) samples. Figure 6 shows the $\chi-T$ curve for $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$), whose hole concentration p was kept at 0.16 regardless of y, that is, x was always chosen to hold $p(\equiv x-y)=0.16$ for any given $y(<y_0)$. In Fig. 6, the reduced temperature T/T_{max} is used to correct a small difference of p among different samples, Δp, which was inadvertently introduced; the present $\Delta p(\approx \pm 0.002)$ corresponds to the shift of ± 10 K in T_{max}. Each set of data is shifted as a whole, at most, by ~5% along the vertical axis in order to remove the offset value of χ, which was due to accidental errors characteristic of the apparatus. It should be noticed in Fig. 6 that the $\chi-T$ curves for $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$) agree well with that for the Ni-free sample over a wide temperature range without any correction of the Curie term; that is, no Curie term appears in Ni-substituted samples with $y<y_0$. This indicates that there exist no isolated spins on Ni sites in

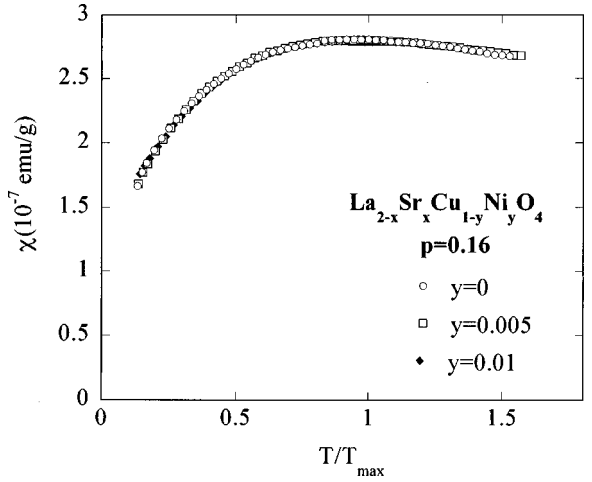

FIG. 6. Temperature dependence of χ for $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$), whose hole concentration p is kept constant ($p=0.16$). The horizontal axis is normalized by T_{max} for each sample.

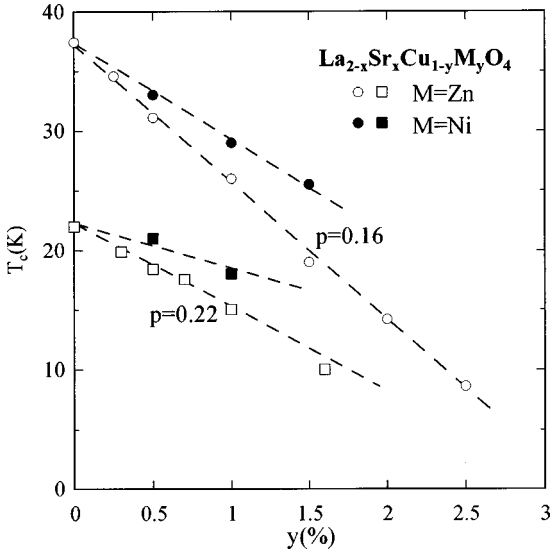

FIG. 7. Dependence of T_c on y for the $La_{2-x}Sr_xCu_{1-y}M_yO_4$: $M=$Zn (open symbol) and $M=$Ni (closed symbol). The hole concentration p is kept constant: $p=0.16$ (circles) and 0.22 (squares).

$La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$) samples and the local nature of spin correlation among $3d_{x^2-y^2}$ spins is not seriously changed on Cu sites around Ni. Such a Ni^{3+}-substitution effect on the $3d_{x^2-y^2}$-spin correlation is in sharp contrast to the Zn-substitution effect; in Zn-substituted samples the $3d$-spin correlation is seriously disturbed on Cu site around each Zn because the magnetic channel among $3d_{x^2-y^2}$ spins is disrupted at nonmagnetic Zn sites, and a resultant Curie term appears.[3,6–8,21–23]

It is noteworthy that the absence of the Curie term in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$) samples can not be understood in terms of divalent Ni^{2+} ions. The reason is as follows. There are two different possible $3d$ configurations for divalent Ni^{2+} ions in the present case: magnetic configuration $d_{x^2-y^2}{}^1d_{3z^2-r^2}{}^1$ and nonmagnetic one $d_{x^2-y^2}{}^0d_{3z^2-r^2}{}^2$ (or $d_{x^2-y^2}{}^2d_{3z^2-r^2}{}^0$). In the magnetic configuration, a spin in the Ni d_{3z2-r2} orbital will be almost isolated because the magnetic channels between the Ni $d_{3z^2-r^2}$ spin and neighboring host Cu $3d_{x^2-y^2}$ spins are very weak. Thus, $d_{3z^2-r^2}$ spins would cause a Curie term, as reported by Mendels *et al.* for $YBa_2Cu_{3-y}Ni_yO_{7-\delta}$.[15] On the other hand, the nonmagnetic configuration of Ni^{2+} is essentially the same as that of nonmagnetic Zn^{2+} or Al^{3+} in that there exists no spin in the $3d_{x^2-y^2}$ orbital. In the nonmagnetic configuration, the $3d_{x^2-y^2}$-spin correlation is seriously disturbed on Cu sites around each Ni^{2+} ion because the magnetic channel among $3d_{x^2-y^2}$ spins is disrupted at the nonmagnetic Ni^{2+} sites. Thus the Curie term would appear, as observed in Zn- or Al-substituted LSCO samples.[3,6–8,21–23] Therefore, it is difficult from the point of view of divalent Ni^{2+} ions to explain the absence of the Curie term in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$).

To explain the experimental result in which no additional Curie term appears in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$), it is reasonable to assume that Ni atoms will be substituted as trivalent Ni^{3+} and they will take the low spin state $S=1/2$ with configuration $d_{x^2-y^2}{}^1d_{3z^2-r^2}{}^0$. In this configuration, since Ni $3d_{x^2-y^2}$ spins are expected to magnetically interact with neighboring host Cu $3d_{x^2-y^2}$ spins, no isolated spin will remain on Ni^{3+} sites and the $3d_{x^2-y^2}$-spin correlation will not be disturbed even on neighboring host Cu sites. The present experimental results are exactly this case, as mentioned above. Unfortunately this configuration of Ni^{3+}, i.e., $d_{x^2-y^2}{}^1d_{3z^2-r^2}{}^0$ might be objected to for the LSCO system because the Cu $3d_{x^2-y^2}$ orbital is higher in energy than the $3d_{3z^2-r^2}$ one owing to the Jahn-Teller effect. However, it was reported in experiments of polarization-dependent x-ray-absorption spectroscopy on films and on single crystals of LSCO that the level difference between $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ orbitals becomes smaller as $p(=x)$ is increased at $p\gtrsim 0.14$; i.e., the probability of hole occupancy for the Cu $3d_{3z^2-r^2}$ orbital increases with p relative to that for the $3d_{x^2-y^2}$.[33,34] Khomski and Neimark also showed theoretically that the crystal field at Cu sites upheaves the $3d_{3z^2-r^2}$ level relative to the $3d_{x^2-y^2}$ level as the average number of holes at O sites within the Cu-O plane is increased.[35] Probably, in the overdoped region of $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$, the $3d_{x^2-y^2}$ level of Ni^{3+} will be so lowered as to cross the $3d_{3z^2-r^2}$ level with an assist of the energy gain in the magnetic interaction between the Ni $3d_{x^2-y^2}$ spin and neighboring host Cu $3d_{x^2-y^2}$-ones.

B. Substitution effect on the superconductivity

As mentioned in Sec. III A, the Ni substitution reduces the hole concentration p within the CuO_2 plane in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$) samples because Ni is substituted as Ni^{3+}. Since the superconducting properties of the present system largely depend on p, the Ni-substitution effect on the superconductivity was examined under a constant hole concentration in the present study; that is, x was changed to hold $p(\equiv x-y)=$constant for a given $y(<y_0)$ in preparation of $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ samples.

In Fig. 7, the superconducting critical temperature T_c of $La_{2-x}Sr_xCu_{1-y}M_yO_4$ ($M=$Ni, Zn) with $p=0.16$ and 0.22 is plotted as a function of y. The temperature T_c is defined here as the temperature at which the diamagnetism due to the superconductivity is half of the low-temperature saturated

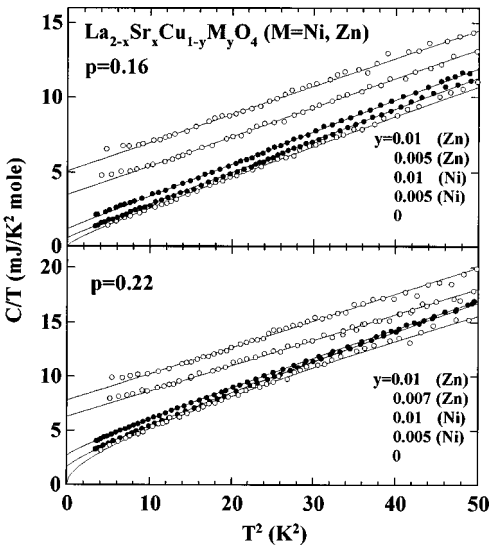

FIG. 8. Specific heat of the $La_{2-x}Sr_xCu_{1-y}M_yO_4$ ($M=$Zn or Ni) in a C/T vs T^2 plot: (a) for $p=0.16$ and (b) for $p=0.22$. The solid lines represent the results of fitting the data to Eq. (2) in the text.

value.[10] The decrease of T_c is slower in Ni-substituted samples than in Zn-substituted ones, as reported by Tarrascon *et al.* and Xiao *et al.*[1,3]

In Fig. 8, typical results of the specific heat at $T<T_c$ are shown for $La_{2-x}Sr_xCu_{1-y}M_yO_4$ ($M=$Ni, Zn) with $p=0.16$ and 0.22 with C/T versus T^2 plot. The low-temperature specific heat of unsubstituted LSCO samples fits to the sum of an electronic T^2 term and a phonon T^3 term at $T\ll T_c$.[9,10] The quadratic behavior of the electronic specific heat $C_{\rm el}$ is peculiar to superconductors with line nodes in the gap structure, such as *d*-wave and extremely anisotropic *s*-wave superconductors.[9,10,36,37] On the other hand, as shown in Fig. 8, the low-temperature specific heat C of Ni-substituted samples fits to the following equation:

$$C=C_{\rm el}+C_{\rm ph}, \tag{2}$$

where $C_{\rm el}=\gamma T+bT^n$ with exponent n, which increases from 2 ($y=0$) to ~2.7 ($y=0.01$) upon increasing y. The phonon term $C_{\rm ph}$ determined in the previous work was used in the present fitting.[9,10] The good fit indicates that the electronic T^2 term observed for unsubstituted LSCO samples changes into $\gamma T+bT^n$ ($2<n<3$) in Ni-substituted samples. On the other hand, the electronic T^2 term changes into $\gamma T+bT^3$ in Zn-substituted samples, as previously reported.[10] In Fig. 9, the γ value at $T\ll T_c$ obtained in above fitting is shown for $La_{2-x}Sr_xCu_{1-y}M_yO_4$ ($M=$Ni, Zn) with $p=0.16$, 0.2, and 0.22 as a function of y. The residual γ value at $T\ll T_c$, i.e., the residual density of states at E_F, $N_{\rm res}$, is obviously recovered from zero as Ni or Zn atoms are substituted for Cu.[9,10] The recovery of the γ value is much weaker in Ni-substituted samples than in Zn-substituted ones.

It should be remembered here that Ni atoms are substituted as trivalent Ni^{3+} ions in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$) and no Curie term appears (Sec. III A). This means that Ni^{3+} ions will act as charged impurities, and cause potential scattering of the Cooper pairs. This feature of the Ni^{3+} substitution offers a good opportunity to confirm

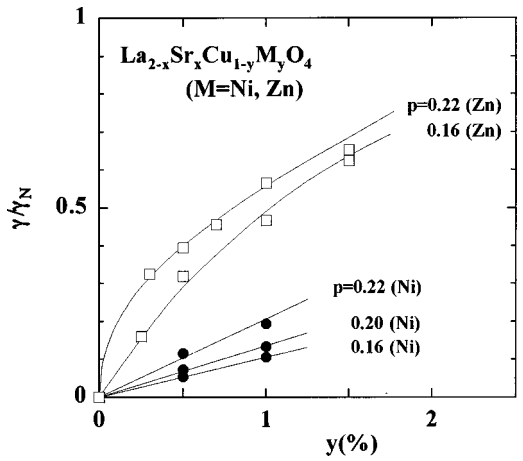

FIG. 9. Dependence of the residual γ value on y for $La_{2-x}Sr_xCu_{1-y}M_yO_4$: $M=$Zn (□) and $M=$Ni (●). The hole concentration p is kept constant ($p=0.16$, 0.2, and 0.22).

whether the order parameter of the present superconductor is of a *d*-wave type or of an extremely anisotropic *s*-wave one. This is because in *d*-wave superconductors the potential scattering of the Cooper pairs suppresses the energy gap $\Delta(k)$ around the nodes in the k space, and causes a residual density of states at $T\ll T_c$, $N_{\rm res}$.[9,10,37–44] On the other hand, in extremely anisotropic *s*-wave superconductors the potential scattering enhances the energy gap $\Delta(k)$ at the nodes, and causes no $N_{\rm res}$.[40,41] Therefore, the present experimental result indicating that $N_{\rm res}$ becomes finite in $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ ($y<y_0$) shows that the present superconductor is of a *d*-wave type.

Now we refocus on different Zn- and Ni-substitution effects on the superconductivity. As mentioned above, the depression of T_c and the recovery of the residual γ value at $T\ll T_c$ is much weaker in Ni-substituted samples than in Zn-substituted ones (Figs. 7 and 9). This means that the pair-breaking effect of the Ni^{3+} substitution is rather moderate in comparison with that of the Zn substitution. The moderate pair-breaking effect of Ni^{3+} is consistent with a characteristic T dependence of $C_{\rm el}$ of $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ at $T\ll T_c$; i.e., the T dependence of $C_{\rm el}$ changes from αT^2 to $\gamma T+bT^n$ with $2\leqslant n<3$ as Ni atoms are substituted for Cu in $La_{2-x}Sr_xCuO_4$, as mentioned above (Fig. 8). Such a change can be understood in terms of a moderate potential scattering of Cooper pairs in *d*-wave superconductors.[39] On the other hand, the change of $C_{\rm el}$ from αT^2 to $\gamma T+bT^3$, observed for the Zn substitution, is characteristic of the pair-breaking in the unitarity limit.[10,37]

As mentioned in Sec. III A, the spin correlation among $3d_{x^2-y^2}$ spins is seriously disturbed on Cu sites neighboring Zn in Zn-substituted samples, while the disturbance is not significant around Ni in Ni^{3+}-substituted ones. The magnetism within the CuO_2 plane has been suggested as one of the most plausible origins for the *d*-wave superconductivity of cuprates.[10,16–20,45–52] In that case, the serious disturbance of $3d_{x^2-y^2}$-spin correlation around each Zn ion will be quite unfavorable to the superconductivity; i.e., the superconductivity will be seriously suppressed over the magnetically disturbed region around each Zn ion. In fact, such a local suppression of the superconductivity around each Zn ion can be demonstrated by analyzing the Zn dependence of the residual

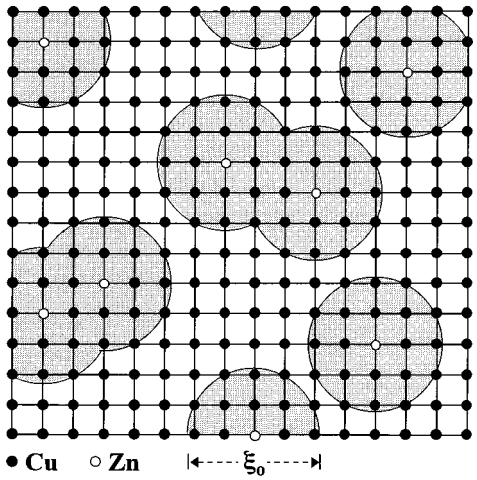

FIG. 10. Schematic diagram for the model: the superconductivity is completely suppressed within a circle centered at each Zn with a diameter ξ_0 on each CuO_2 plane. Only the Cu sites are represented. The closed and open circles are Cu and Zn ions, respectively. The normal states are recovered over the shaded region with the diameter ξ_0.

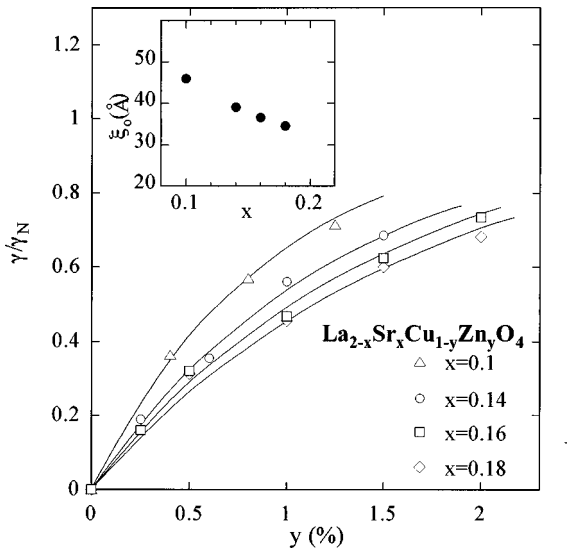

FIG. 11. Dependence of the residual γ value on y for the $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$: $x=0.1$ (△), 0.14 (○), 0.16 (□), and 0.18 (◇). The solid lines represent the residual density of states calculated on the basis of the model schematically shown in Fig. 10. The inset shows the x dependence of ξ_0.

γ value at $T \ll T_c$, i.e., $N_{\rm res}$ on the basis of a following simple model. It is assumed in this model that the superconductivity is completely suppressed within a circle centered at each Zn atom with diameter ξ_0 on each CuO_2 plane, but little affected outside the circles. The suppressed region $\pi(\xi_0/2)^2$ contributes to γ, i.e., $N_{\rm res}$. In the present study, to make calculations simple we assumed a sharp boundary between the normal and superconducting regions although the real boundary is of course rather sluggish. This simplified model schematically shown in Fig. 10 is identical with the ''swiss cheese'' model, which was introduced by Nachumi *et al.* to explain the reduction of the superconducting carrier density in μSR experiments on Zn-substituted LSCO and YBCO samples.[53]

The result of $N_{\rm res}$ calculated using the present model is shown in Fig. 11, where Zn atoms are assumed to be randomly distributed over the CuO_2 planes. The calculated $N_{\rm res}$ increases linearly with y at low y concentrations while it tends to be saturated at high y concentrations because the neighboring normal regions begin to overlap each other. The experimental results of the γ value at $T \ll T_c$ are also shown in Fig. 11. Since unsubstituted LSCO samples with $x \lesssim 0.15$ exhibit a small residual γ value, γ_0, at $T \ll T_c$, we subtract γ_0 from the observed γ value of Zn-substituted samples: $\gamma_0 = 1$ and 0.5 mJ/mole K^2 for $x=0.1$ and 0.14 samples, respectively. As seen in Fig. 11, the γ values for $x=0.1$, 0.14, 0.16, and 0.18 fit very well to the results of $N_{\rm res}$ calculated for $\xi_0 = 46$, 39, 36.5, and 34.5 Å, respectively.

If ξ_0 is relevant to the superconducting correlation length $\xi_s \propto (2\Delta_0)^{-1}$, ξ_0 should increase with x because the superconducting energy gap $2\Delta_0$ was found to decrease with x at least at $x \geqslant 0.14$ in the present system.[10,54] However, in the present experimental results this is not the case; ξ_0 monotonically decreases with increasing x between $x=0.10$ and 0.18 (the inset in Fig. 11). This implies that ξ_0 is not inherent in the superconductivity. It should be noted here that the characteristic length $\xi_0 = 39$ Å for samples with $x=0.14$ is comparable to the antiferromagnetic correlation length $\xi_{\rm AF}$ (~ 35 Å) at low temperatures, which is reported in inelastic neutron scattering experiments on $La_{2-x}Sr_xCuO_4$ ($x=0.14$).[55] Furthermore, the $\xi_{\rm AF}$ has a trend similar to that of ξ_0 with x, namely, it decreases with increasing x.[56] Therefore, ξ_0 can be considered as the characteristic length relevant to $\xi_{\rm AF}$ rather than ξ_s. This means that the superconductivity will be seriously suppressed over a magnetically-disturbed region ($\sim \xi_{\rm AF}$) around each Zn ion.

IV. SUMMARY

In the present study, we measured the magnetic susceptibility and the electronic specific heat on Zn- and Ni-substituted $La_{2-x}Sr_xCuO_4$ samples. It was found that Ni atoms are substituted as trivalent Ni^{3+} ions below a critical Ni concentration, y_0, in an x range above $x \sim 0.14$. The substitution of Ni^{3+} for Cu causes a prominent hole-consumption effect, leading to an increase of $T_{\rm max}$ and a reduction of the γ_N value. The Ni^{3+} substitution causes no Curie term though Ni^{3+} is nominally magnetic, indicating that magnetic channels among $3d_{x^2-y^2}$ spins survive even at Ni^{3+} sites. On the other hand, in Zn-substituted samples, the spin correlation among $3d_{x^2-y^2}$ spins is seriously disturbed on host Cu sites around each Zn ion because the magnetic channels are absent at nonmagnetic Zn ions.

It was confirmed that the superconductivity is suppressed much more strongly in Zn-substituted samples than in Ni^{3+}-substituted ones; the depression of T_c and the residual density of states at $T \ll T_c$ is much larger in Zn-substituted samples than in Ni^{3+}-substituted ones. The suppression of superconductivity in Ni^{3+}-substituted samples can be understood in the context of a potential scattering of Cooper pairs in a *d*-wave superconductor. On the other hand, in the Zn-

substituted samples the superconductivity is seriously suppressed through disturbance of the $3d_{x^2-y^2}$-spin correlation on host Cu sites around each Zn ion. This implies that the $3d_{x^2-y^2}$-spin correlation within the CuO_2 plane will play a crucial role in causing superconductivity.

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