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Magnetic properties and electronic conduction of superconducting $La_{2-x}Sr_xCuO_4$

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Magnetic susceptibility χ and resistivity were measured in $La_{2-x}Sr_xCuO_4$. Enhancement of χ due to a ferromagnetic correlation, which is inherent in the orthorhombic phase at low Sr concentrations, disappears at around $x=0.05$, near the margin of the superconducting regime. In superconducting samples with $0.1 \lesssim x \lesssim 0.2$, χ exhibits a broad peak at a temperature $T_{\max}$. The T-dependent part of χ, $\chi^s(T)$, follows a single curve F regardless of x when χ^s and T are normalized with the peak value $\chi^s_{\max}$ and $T_{\max}$, as has been reported. However, the present scaling curve F decreases much more at $T \ll T_{\max}$ than the reported one. The resistivity exhibits a T-linear dependence above a temperature T^* and deviates downward from the T-linear dependence below T^*. For $x>0.1$ the temperature T^* agrees well with $T_{\max}$, indicating that the deviation from a T-linear resistivity is related to the decrease of χ below $T_{\max}$. On the other hand, for $x<0.1$ a large reduction of χ is seen below $\sim T^*$ in the data up to 1000 K by Yoshizaki *et al.*, although no peak is seen in the χ-T curve. The T dependence of χ in $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ is also reported for $x=0.16$ and 0.22.

I. INTRODUCTION

The spin system of La_2CuO_4 at $T>T_N$ (~ 250 K) can be treated as a two-dimensional (2D) $S=\frac{1}{2}$ Heisenberg antiferromagnet.[1,2] Neutron-scattering experiments have shown that a 2D antiferromagnetic (AFM) correlation develops among the Cu spins largely above T_N and its correlation length grows up to ~ 200 Å at 300 K.[2] The uniform magnetic susceptibility χ decreases with the development of the 2D AFM correlation at high temperatures. However, χ upturns below ~ 380 K because of a weak ferromagnetic correlation, while it decreases again below T_N. Thio *et al.* have shown that the ferromagnetic correlation originates from an antisymmetric exchange interaction which appears in the orthorhombic phase of this system below $T_0 \approx 530$ K.[3] The long-range AFM order of this system is suppressed drastically by doping of holes into the Cu-O planes. Neutron-scattering experiments on lightly doped nonsuperconducting $La_{2-x}Sr_xCuO_4$ crystals have shown that the spins of doped holes are strongly coupled to the Cu spins and limit the AFM correlation length such that the long-range AFM order is not possible.[4]

In superconducting $La_{2-x}Sr_xCuO_4$ samples with $0.1<x<0.2$, the magnetic susceptibility χ decreases gradually with lowering T after exhibiting a broad peak at a temperature $T_{\max}$.[5-11] It has been shown in the systematic studies by Johnston that the T-dependent part of χ, $\chi^s(T)$, follows the universal curve F regardless of x when it is normalized with its maximum value $\chi^s_{\max}$ and plotted as a function of the reduced temperature $T/T_{\max}$.[5] The decrease of χ below $T_{\max}$ has been understood in terms of the 2D AFM correlation among Cu spins. On the other hand, χ in samples with $x>0.2$, where the superconducting transition temperature T_c decreases rapidly with increasing x, increases monotonically down to T_c.[6-14] It has been reported that the T dependence of χ for $x \gtrsim 0.2$ can be reproduced by adding a Curie term on the T-dependent term which follows the universal curve F.[13,14]

At Sr concentrations ($x \approx 0.16$) for optimum T_c, the resistivity ρ in the Cu-O planes exhibits a linear dependence on T over a wide T range from a high temperature well above room temperature down to near T_c.[15] Nakamura and Uchida have recently shown in $La_{2-x}Sr_xCuO_4$ crystals with $x=0.1$ and 0.12 that ρ deviates downward below a temperature around 600 K from a T-linear behavior at higher temperatures.[16] The deviation of ρ from T-linear behavior becomes marked in lightly doped nonsuperconducting samples.[17] Similar behavior in the T dependence of ρ has been also seen in $YBa_2Cu_3O_{7-\delta}$.[18] In this system, the deviation from a T-linear resistivity is associated with development of a gap in this spin excitations.[18] It is of great interest to clarify whether the deviation from a T-linear resistivity in $La_{2-x}Sr_xCuO_4$ is also related to the magnetic property.

In the present study, magnetic susceptibility and resistivity were reexamined using well-characterized $La_{2-x}Sr_xCuO_4$ samples with $0 \le x < 0.3$. The doping experiments for the in-plane Cu sites of high-T_c cuprates have revealed that impurities on the Cu sites strongly influence the magnetic susceptibility; if impurities exist on the Cu sites, they induce magnetic moments even though they carry no magnetic moments themselves and the magnetic moments give rise to a Curie-like contribution to the magnetic susceptibility.[19-23] Therefore, studies on the magnetic susceptibility of high-T_c cuprates should be made using samples of high purity. It has been also shown that impurities on Cu sites cause a decrease of T_c and a finite T-linear term (γT) of specific heat at $T \ll T_c$ even if the impurity concentration is at a very low level,[24] and therefore the T_c and γ values of high-T_c cuprates are good indicators of sample purity. The T_c value of the present samples of around $x=0.16$ is comparable with the highest one reported so far and the T-linear term of the specific heat is absent at $T \ll T_c$ around $x=0.16$.[24] These results indicate that the amount of impurities on the in-plane Cu sites was extremely small in the present samples. Measurements of magnetic susceptibility were also carried out on $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ samples with $x=0.16$ and 0.22 in order to study doping effects on magnetism and superconductivity.

II. EXPERIMENTS

The $La_{2-x}Sr_xCuO_4$ and $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ samples were prepared using La_2O_3, $SrCO_3$, CuO, and ZnO powders of 99.995–99.999 % purity. These powders were mixed well and fired in flowing oxygen for 24 h in a two-step procedure. First, the mixed powders were fired at 1000–1075 °C by using a furnace with a small temperature gradient. These materials were reground well and pressed into pellets, and refired in flowing oxygen. After the firing, the pellets were cooled to 600 °C and annealed for 24 h, then slowly cooled down to room temperature.

Magnetic susceptibility was measured by using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The magnetic susceptibility of the normal state was measured under a magnetic field of 10 kOe in a T range below 550 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. In the measurements of diamagnetic susceptibility below T_c, samples were cooled under a zero magnetic field down to 5 K or 2 K, and the diamagnetic susceptibility was measured by heating samples under 15 Oe. Resistivity was measured by the conventional four-probe dc method in a T range from 5 to ~820 K. Electrical contacts were made with indium stuck on the surface of the sample below 350 K. In the measurements of resistivity at high temperatures, Au lead wires were bounded to the samples with heat-treated Au paste.

III. RESULTS AND DISCUSSION

A. Nonsuperconducting $La_{2-x}Sr_xCuO_4$ for $x \leq 0.05$

In Fig. 1, the T dependence of magnetic susceptibility χ is shown for the samples with $x \leq 0.04$. Susceptibility χ of La_2CuO_4 exhibits a T-linear dependence in a T range from ~380 K up to the highest temperature examined, but upturns below ~380 K. The upturn of χ is progressively reduced with increasing x, although it is still marked in the sample with $x=0.02$ where the long-range AFM order no longer appears. Temperature T_a at around which χ clearly deviates upward from the T-linear behavior decreases with increasing x, as shown in Figs. 1 and 2. Susceptibility χ for $x>0.015$ greatly increases below ~60 K, much lower than T_a.

The T dependence of χ for $0.02 \leq x \leq 0.04$ can be reproduced by a phenomenological relation given by

$$\chi(T)=AT-B(T-T_a)+C/T+\chi^0 , \qquad (1)$$

where $A,B>0$ and the second term is defined in the T range below T_a. The first, second, and third terms in Eq. (1) are introduced to describe the T-linear dependence of χ at high temperatures, the upturn of χ below T_a and the steep increase at low temperatures, respectively. The fitting to the experimental results is very good, as shown in Fig. 1. On the other hand, susceptibility χ for $x=0.05$ can be reproduced very well by Eq. (1) without the second term, as shown in Fig. 3. This result indicates that the upturn of χ [the second term Eq. (1)] no longer appears in the sample with $x=0.05$. The Curie term in the low Sr concentration range, which is very small but causes the steep increase of χ at low temperatures, is considered extrinsic for the present system, because the Curie constant depends on the sample preparation conditions.

The spin system of La_2CuO_4 can be treated as a spin-$\frac{1}{2}$ square-lattice Heisenberg antiferromagnet, and a tilt of

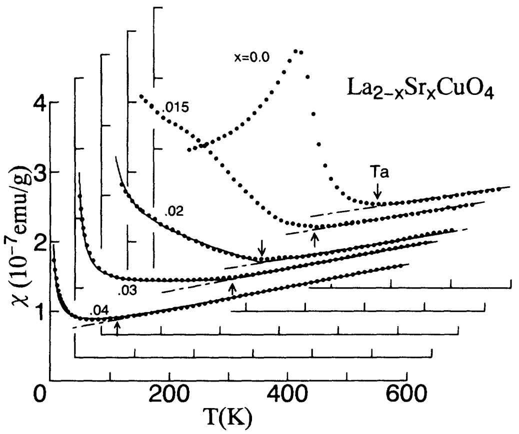

FIG. 1. Magnetic susceptibility χ for the nonsuperconducting samples of $La_{2-x}Sr_xCuO_4$ ($x \leq 0.04$). The dot-dash lines are the linear terms extrapolated from high temperatures. The solid lines for $x=0.02$, 0.03, and 0.04 represent the curves given by Eq. (1).

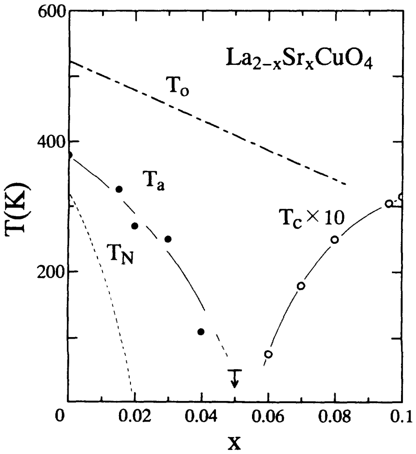

FIG. 2. Dependences of T_a, T_N, T_0, and T_c on x in $La_{2-x}Sr_xCuO_4$. The x dependence of T_N and T_0 are from Refs. 2–4 and from Refs. 44–46, respectively.

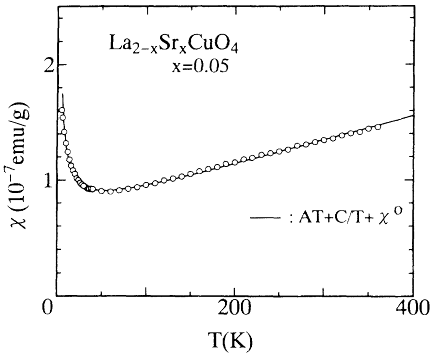

FIG. 3. Magnetic susceptibility χ of $La_{2-x}Sr_xCuO_4$ for $x=0.05$. The solid line represents the curve given by $AT+C/T+\chi^0$.

the CuO_6 octahedron in the orthorhombic phase below $T_0 \approx 530$ K allows an antisymmetric exchange term in the exchange Hamiltonian. Assuming nearest-neighbor Cu-Cu spin interactions alone, the exchange Hamiltonian for the orthorhombic phase may be written

$$H=\sum_i S_i \bar{\bar{J}}_{NN} S_{i+\delta} \tag{2}$$

with

$$\bar{\bar{J}}_{NN}=\begin{bmatrix} J^{aa} & 0 & 0 \\ 0 & J^{bb} & J^{bc} \\ 0 & -J^{bc} & J^{cc} \end{bmatrix},$$

where $|J^{cc}| \approx |J^{aa}| > |J^{bb}|$.[3] Using Eq. (2) and taking the very weak interplane AFM coupling into account, Thio *et al.* have shown that the uniform susceptibility χ at $T>T_N$ is given by

$$\chi=\chi_0+\chi_0^2(2J^{bc})^2\chi_{2D}^{\dagger}(1+J_{\perp}\chi_{2D}^{\dagger}) \tag{3}$$

for an external magnetic field H_b parallel to the b axis.[3] In Eq. (3), $\chi_{2D}^{\dagger}$ and χ_0 are the staggered and uniform susceptibilities of the 2D system with no antisymmetric exchange interaction, and $J_{\perp}$ is the interplane AFM coupling constant. The second term $\Delta\chi$ of Eq. (3) results from the antisymmetric exchange interaction which appears in the orthorhombic phase. Equation (3) holds for the b and c components of an external field, although χ_0 and $\chi_{2D}^{\dagger}$ are different between the b and c directions because of their anisotropies. On the other hand, the second term $\Delta\chi$ of Eq. (3) vanishes for the a component of an external field. The uniform susceptibility χ in the ceramic samples whose crystal axes are randomized is therefore given by an average of the susceptibilities for the three directions. The second term $\Delta\chi$ of Eq. (3), increasing with the increases of $\chi_{2D}^{\dagger}$ and J^{bc}, accounts for the upturn of χ below T_a in La_2CuO_4, as has been shown in the single crystals by Thio *et al.*[3]

Equation (3) is applicable to the orthorhombic phase of $La_{2-x}Sr_xCuO_4$ as long as the Cu-spin system can be described as a 2D Heisenberg antiferromagnet, although the 2D AFM correlation among Cu spins, i.e., $\chi_{2D}^{\dagger}$, is reduced by holes introduced into the Cu-O planes.[4] In $La_{2-x}Sr_xCuO_4$ the antisymmetric component J^{bc} will also decrease with increasing x, because J^{bc} is expected to be proportional to the orthorhombicity of the crystal. However, it is found from the data for the lattice constants in x-ray-diffraction experiments that the orthorhombicity at 150 K in a sample with $x=0.05$ is reduced by 13% in comparison with that in La_2CuO_4.[25] This reduction is not enough to remove the upturn of χ, $\Delta\chi$, entirely in the sample with $x=0.05$. It is therefore strongly suggested that the progressive reduction of $\Delta\chi$ with increasing x is caused mainly through the reduction of $\chi_{2D}^{\dagger}$, i.e., the 2D AFM correlation among Cu spins.

B. Superconducting $La_{2-x}Sr_xCuO_4$

In Fig. 4, the normal-state magnetic susceptibility χ is shown for the superconducting samples of $La_{2-x}Sr_xCuO_4$, where the results below 50 K are omitted to avoid effects of diamagnetism due to superconducting fluctuations above T_c.[26] Susceptibility χ for $x \lesssim 0.2$ decreases with lowering T at low temperatures, while it tends to be saturated at high temperatures or exhibits a broad peak at a temperature $T_{\max}$. Temperature $T_{\max}$ decreases with increasing x. Yoshizaki *et al.* have systematically examined the T dependence of χ of the present system in a wide T range up to 1000 K.[11] Our results for the T dependence of χ reproduce their results well within the common T range between both measurements, although both results are different by a constant value. According to their results for the χ-T curve, a broad peak is seen down to $x \approx 0.09$, but below $x \approx 0.09$ no peak is seen even at high temperatures of around 1000 K.[11] In the samples with $x<0.09$, it can be seen in their data (Fig. 5) that susceptibility χ decreases largely below a temperature T_b, although the T dependence of χ is almost linear and much weaker above T_b.

The χ-T curves with a broad peak have the following important property, as shown by Johnston;[5] when the T-independent part of χ, χ^0, is treated as a parameter and the T-dependent part $[\chi^s(T)=\chi-\chi^0]$ and T are reduced by the maximum value $\chi_{\max}^s$ and $T_{\max}$, respectively, the reduced $\chi^s(T)$, $\chi^s(T/T_{\max})/\chi_{\max}^s$, falls onto universal

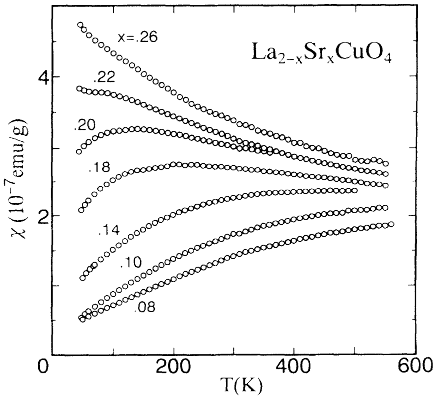

FIG. 4. Magnetic susceptibility χ for the superconducting samples of $La_{2-x}Sr_xCuO_4$.

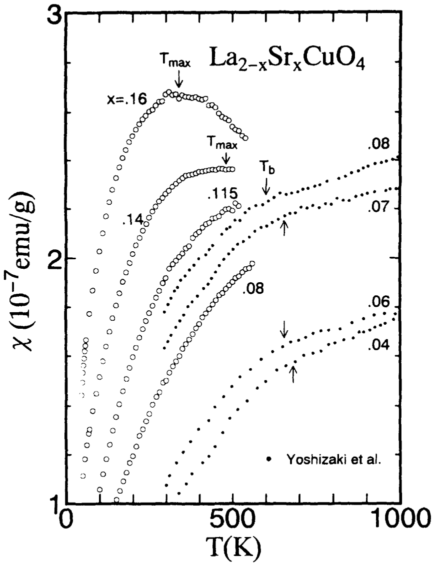

FIG. 5. Magnetic susceptibility χ for the superconducting samples of $La_{2-x}Sr_xCuO_4$. The closed circles show the data by Yoshizaki *et al.* (Ref. 11).

curve F regardless of x (Fig. 6). The T-dependent part of χ which follows universal curve F is hereafter referred to as $\chi_F^s(T)$. On the other hand, susceptibility χ for $x > 0.2$ increases with lowering T over the entire T range examined.[6–14] The T-dependent part of χ for $x > 0.2$ can be reproduced by adding a small Curie term on the T-dependent $\chi_F^s(T)$, as shown in Fig. 7. The T dependence of χ for $x = 0.2$, exhibiting a broad peak, is also reproduced much better by taking a small Curie term into account.[13,14] The value of T_{max}, the T-independent part χ^0, and the Curie constant C determined in the above analyses are shown as a function of x in Fig. 8.

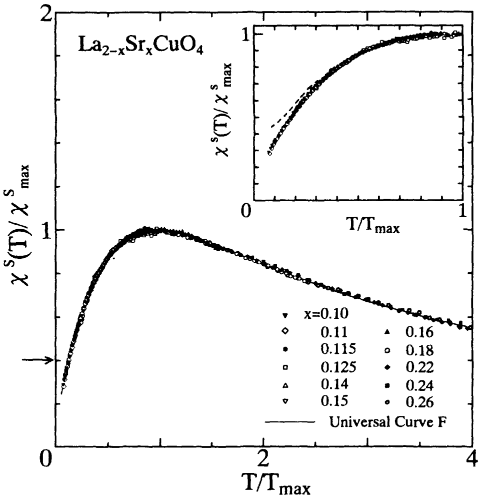

FIG. 6. $\chi^s(T)/\chi^s_{max}$ versus T/T_{max} for the superconducting samples of $La_{2-x}Sr_xCuO_4$. The arrow shows the value of $\chi^s(T)/\chi^s_{max}$ at $T = 0$ K predicted by theoretical works and numerical calculations (Refs. 33–35). The solid line is the universal curve F obtained by the present study. The inset shows that the present universal curve decreases much more largely at $T \ll T_{max}$ from the previous one (the broken line) (Refs. 5 and 8).

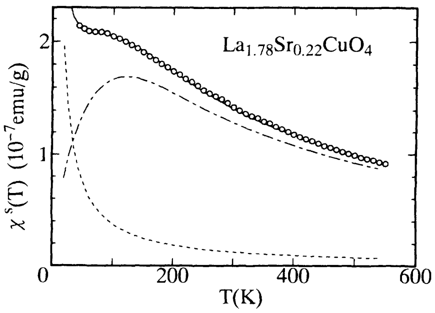

FIG. 7. T-dependent part of magnetic susceptibility $\chi^s(T)$ for $La_{1.78}Sr_{0.22}CuO_4$. The dot-dash and broken lines represent $\chi_F^s(T)$ and a Curie term, respectively. The solid line is the curve given by adding the Curie term on $\chi_F^s(T)$.

The spin susceptibility of $La_{2-x}Sr_xCuO_4$ has been studied by means of ^{17}O and ^{63}Cu Knight-shift measurements,[27–30] and rather different T dependences of the ^{63}Cu shift have been reported by different groups.[29,30] Results of the ^{17}O shift for $x = 0.15$, together with the $\chi_F^s(T)$ obtained in this study, are shown in Fig. 9, assuming that the spin part of the ^{17}O shift becomes almost zero at $T \ll T_c$ and that the hyperfine coupling constant for ^{17}O is 109 kOe/μ_B. The former assumption is plausible because the superconductivity is that of a spin singlet one[30,31] and the T-linear term of the specific-heat capacity vanishes at $T \ll T_c$, indicating that the spectral weight of the excitation spectrum is almost zero at $E = 0$.[24] The

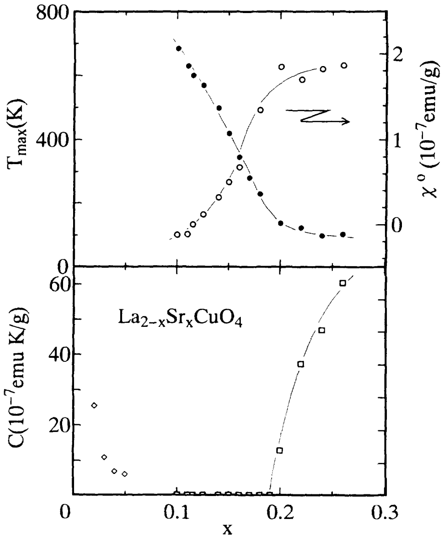

FIG. 8. Dependences of T_{max}, χ^0, and C on x in the superconducting samples $La_{2-x}Sr_xCuO_4$. The diamonds are the Curie term determined from fitting of $\chi(T)$ for $x \leq 0.05$ to the phenomenological relation [Eq. (1)] in Sec. III A.

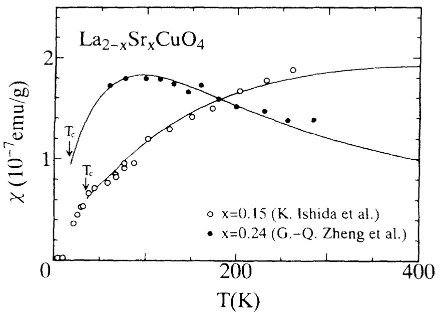

FIG. 9. Comparison between $\chi_F^s(T)$ and ^{17}O Knight shift for $x=0.15$ and 0.24. The open and closed circles are the ^{17}O Knight-shift data for $x=0.15$ and 0.22, respectively (Refs. 28 and 29). The solid lines are the $\chi_F^s(T)$ curves.

hyperfine coupling constant of 109 kOe/μ_B for ^{17}O is smaller by 20 kOe than that obtained by Ishida *et al.*,[27] but very close to that for ^{17}O in $YBa_2Cu_3O_{7-\delta}$.[32] In Fig. 9, the T dependence of the ^{17}O shift is also shown for $x=0.24$,[28] together with the $\chi_F^s(T)$ curve determined in this study. The hyperfine coupling constant for ^{17}O was taken to be the same as that for $x=0.15$ because it is usually independent of x, and the ^{17}O shift at 0 K was assumed here to be 0.076% because of absence of data for the ^{17}O shift at $T<T_c$. It can be noted in Fig. 9 that the T dependence of $\chi_F^s(T)$ is in good agreement with that of the ^{17}O shift in both samples. The agreement for the sample with $x=0.24$ gives support to our analyses for the χ-T curves carried out on the basis of an idea that the susceptibility χ for $x \gtrsim 0.2$ consists of $\chi_F^s(T)$ and Curie term. The T dependence of the ^{63}Cu shift reported by Ohsugi *et al.* can be also fitted to that of the ^{17}O shift, i.e., $\chi_F^s(T)$, for $x=0.15$ and 0.24 above T_c, but it deviates seriously below T_c.[29]

Johnston has shown that the shape of $\chi_F^s(T)$ is in good agreement with the result given by the high-T series-expansion calculations for a spin-$\frac{1}{2}$ square-lattice Heisenberg antiferromagnet within the T range $T>0.7T_{\text{max}}$, although the effective moment per Cu ion and the superexchange coupling between the in-plane Cu spins are both largely suppressed with increasing x.[5] Furthermore, the value of $\chi_F^s(T)$ at 0 K obtained by Johnston reduces to $\sim$40% of χ_{max}^s, consistent with the theoretical predictions for a spin-$\frac{1}{2}$ square-lattice Heisenberg antiferromagnet.[5,33-35] It was therefore suggested that the decrease of $\chi_F^s(T)$ at $T<T_{\text{max}}$ could be due to the development of a 2D AFM correlation among the spins localized on the Cu sites.[5] Our previous data also supported the above result obtained by Johnston.[8,14] However, the present $\chi_F^s(T)$ decreases much more at $T \ll T_{\text{max}}$ the previous one; the present value of $\chi_F^s(T=0)$, estimated by extrapolating the data to 0 K, is less than 20% of χ_{max}^s, as shown in the inset in Fig. 6. As noted in Sec. I, impurities on the in-plane Cu sites of high-T_c cuprates induce magnetic moments even though they carry no magnetic moments themselves, and the magnetic moments give rise to a Curie-like contribution to the magnetic susceptibility.[19-23] The present samples are expected to contain an extremely small number of impurities on the Cu sites, as also noted in Sec. I. It is therefore suggested that the previous samples[5,7,8,14] would contain the magnetic moments induced by impurities on the Cu sites more than the present samples. This result indicates that the exceeding reduction of $\chi_F^s(T)$ at $T \ll T_{\text{max}}$, which is hard to be understood in terms of the development of an AFM correlation in a 2D Heisenberg antiferromagnet, is intrinsic to the superconducting $La_{2-x}Sr_xCuO_4$ system. A possible explanation for the exceeding reduction of $\chi_F^s(T)$ at $T \ll T_{\text{max}}$ is that a kind of spin-singlet state might develop below $\sim T_{\text{max}}$.

C. Resistivity of $La_{2-x}Sr_xCuO_4$

The T dependences of resistivity ρ of $La_{2-x}Sr_xCuO_4$ are shown in Figs. 10(a) and 10(b). The present results for the ρ-T curve are consistent with those reported by Takagi *et al.*[17] Resistivity ρ of the samples with $x<0.16$ exhibits a T-linear dependence above temperature T^*, but deviates downward below T^* from the T-linear behavior. Temperature T^* decreases with increasing x. The downward deviation of ρ from a T-linear behavior is progressively reduced with increasing x, and becomes unclear above $x \approx 0.16$ around which T_c reaches the maximum value of this system. In the samples with $x \gtrsim 0.2$, the T dependence of ρ follows a concave function of T even at high temperatures of around 800 K.[12,14,17] It has been shown by Nishikawa, Takeda, and Sato that Hall coefficient R_H of this system increases with lowering T and tends to be saturated at low temperatures, while at high temperatures it is or tends to be independent of T.[36] The increase of R_H is progressively reduced with increasing x and becomes rather small at $x \approx 0.16$, which is very

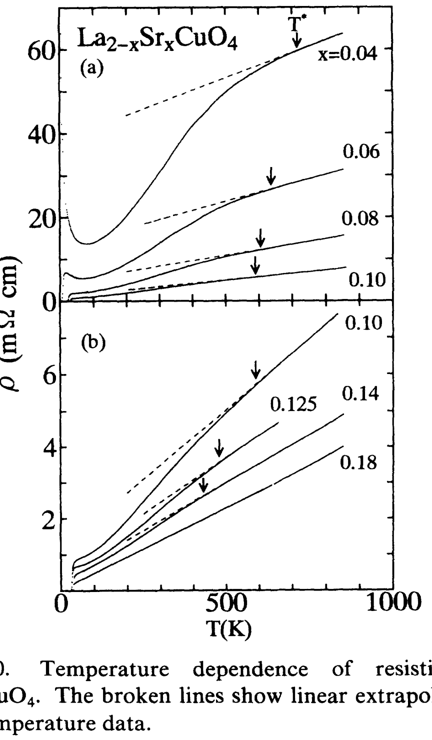

FIG. 10. Temperature dependence of resistivity for $La_{2-x}Sr_xCuO_4$. The broken lines show linear extrapolations of the high-temperature data.

similar to the behavior in the deviation from a T-linear resistivity.

As noted in the preceding section, magnetic susceptibility χ has a broad peak at $T_{\max}$ above $x \approx 0.09$ and temperature $T_{\max}$ decreases with increasing x below $x \approx 0.2$. In Fig. 11, temperature T^* at around which ρ starts to deviate from T-linear behavior, together with $T_{\max}$, is plotted as a function of x. It is clear in this figure that both the characteristic temperatures T^* and $T_{\max}$ agree well with each other for $0.09 < x \lesssim 0.16$. On the other hand, below $x \approx 0.09$ no peak is seen in the χ-T curves examined up to $T = 1000$ K by Yoshizaki *et al.*,[11] although the large deviation of ρ from T-linear behavior is observed below T^* lower than 1000 K. However, it should be remembered that χ decreases greatly below T_b as seen in their data (Fig. 5). For a low Sr-concentration range below $x \approx 0.09$, temperature T^* agrees well with T_b, as shown in Fig. 11. Therefore, the deviations from a T-linear resistivity observed in both x ranges below and above $x \approx 0.09$ of $La_{2-x}Sr_xCuO_4$ are related to some changes in the magnetic property.

As seen in Fig. 11, the x dependence of the characteristic temperatures in the ρ-T and χ-T curves becomes stronger above $x \approx 0.09$, where the χ-T curve is characterized by an existence of a broad peak and scaled by the single curve F regardless of x. According to neutron-scattering experiments, above a Sr concentration near $x \approx 0.09$ an incommensurate modulation appears in the wave-vector dependence of the magnetic excitations, instead of an AFM one which is inherent at low Sr concentrations.[37] It is therefore considered that the magnetic property and/or the electronic state of $La_{2-x}Sr_xCuO_4$ drastically changes at around $x \approx 0.09$, suggesting that the origin of the reduction of χ below T^* may be different between both x ranges below and above $x \approx 0.09$.

Similar behaviors in the T dependence of ρ have been seen in $YBa_2Cu_3O_{7-\delta}$.[18] The resistivity ρ in the deoxygenated crystals of $T_c \approx 60$ K deviates below a temperature of around 300 K from a T-linear behavior. The temperature at which ρ starts to deviate from a T-linear behavior decreases as the hole concentration is increased by oxygenation, and ρ in the fully oxygenated crystals of $T_c \approx 90$ K exhibits a T-linear dependence in a wide T range just above T_c. In this system, the deviation from a T-linear resistivity is associated with development of a gap in the spin excitations (hereafter referred as a spin gap) which has been suggested by NMR relaxation rate and neutron-scattering experiments.[31,38–40] According to these experiments, in the 60-K crystals the formation of a spin gap becomes apparent at ~200 K much higher than T_c. The temperature at around which the spin-gap formation becomes apparent decreases as the hole concentration is increased by oxygenation, and the formation of a spin gap is no longer seen in the normal state of the fully oxygenated 90-K crystals where the deviation from a T-linear resistivity is no longer seen. It has been considered in $YBa_2Cu_3O_{7-\delta}$ that the development of a spin gap suppresses magnetic fluctuations and leads to reduction of electron scattering by the magnetic fluctuations.[18] The uniform susceptibility χ of the 60-K crystals tends to be saturated at high temperatures above ~300 K and decreases with lowering T.[41,42] The decrease of χ at low temperatures is suppressed with increasing hole concentration by oxygenation, and χ is almost independent of T in the 90-K crystals.[41–42] Such a hole concentration dependence of the decrease of χ is quite similar to those in the deviation from a T-linear resistivity and in the development of a spin gap. As mentioned above, the deviation from a T-linear resistivity in $La_{2-x}Sr_xCuO_4$ is also accompanied by the decrease of χ as in $YBa_2Cu_3O_{7-\delta}$. However, it should be noticed in $La_{2-x}Sr_xCuO_4$ that the deviation from a T-linear resistivity is suppressed more rapidly with increasing hole concentration than the decrease of χ below T^* and is not seen for $x > 0.16$ through χ still decreases greatly below $T_{\max}$. The relation between the magnetic property and the deviation from a T-

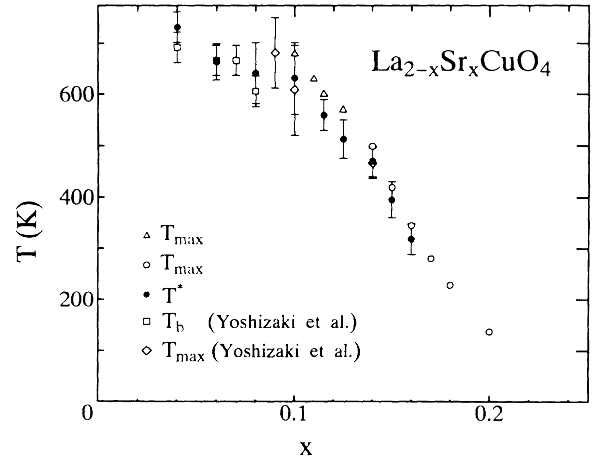

FIG. 11. Dependences of $T_{\max}$, T_b, and T^* on x in $La_{2-x}Sr_xCuO_4$. The triangles are $T_{\max}$ determined from the fitting of $\chi^s(T)$ to the universal curve F. The open circles and diamonds are $T_{\max}$ obtained by the present study and by Yoshizaki *et al.* (Ref. 11), respectively. The squares are the temperatures T_b below which a large reduction of χ is seen in the data by Yoshizaki *et al.* (Ref. 11).

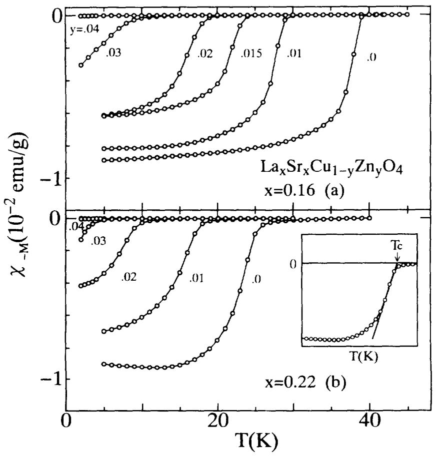

FIG. 12. Diamagnetic susceptibility of $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$: (a) for $x = 0.16$ and (b) for $x = 0.22$. The superconducting transition temperature T_c is defined as shown in the inset.

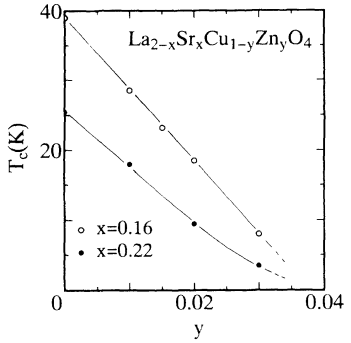

FIG. 13. Dependence of T_c on y for the $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ samples with $x=0.16$ and 0.22.

linear resistivity in $La_{2-x}Sr_xCuO_4$ is rather complicated compared with that in $YBa_2Cu_3O_{7-\delta}$.

D. Zn-substituted samples of $La_{2-x}Sr_xCuO_4$

In Fig. 12, the diamagnetic transition curve of superconductivity is shown for $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ ($x=0.16$ and 0.22). The transition temperature T_c is defined here by extrapolating the steepest part of the transition curve to the zero level (the inset of Fig. 12) and plotted as a function of y in Fig. 13. It should be noted that T_c decreases markedly with increasing y, as has been reported.[19,22,43] Magnetic susceptibility χ at $T>T_c$ is shown for Zn-substituted samples in Fig. 14. In the Zn-substituted samples for $x=0.16$, the broad peak in the χ-T curve shifts to a lower temperature as y is increased, and χ for $y=0.02$ upturns below ~ 50 K. The upturn of χ at low temperatures becomes more prominent as y is increased, and the broad peak in the χ-T curve is no longer observed for $y=0.04$. As shown in Fig. 15, the T dependence of χ in the Zn-substituted samples can be reproduced by adding a Curie term on $\chi_F^s(T)$, as in the $La_{2-x}Sr_xCuO_4$ samples with $x \gtrsim 0.2$. The Curie constant C, $T_{\max}$, and $\chi_{\max}^s$ determined in the present analyses are plotted as a function of y in Figs. 16 and 17. In the Zn-substituted samples with $x=0.16$, the values of $T_{\max}$ and $\chi_{\max}^s$ decrease with increasing y, while the Curie constant increases. These values also decrease with increasing y in the Zn-substituted samples with $x=0.22$, although their dependences on y are rather weak in comparison with those for $x=0.16$.

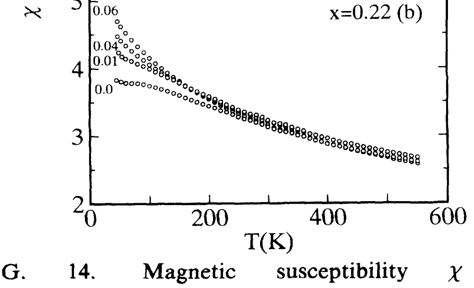

FIG. 14. Magnetic susceptibility χ of the $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ samples with $x=0.16$ and 0.22.

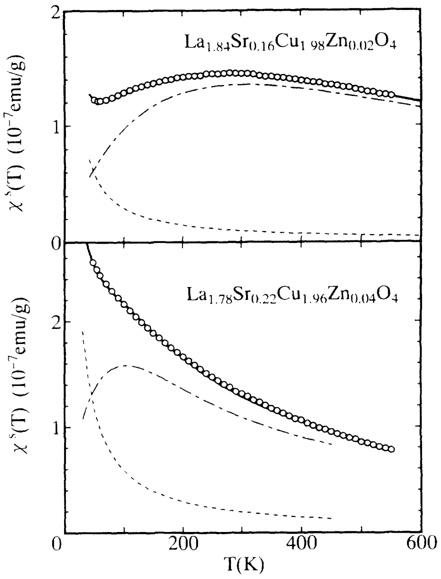

FIG. 15. T-dependent part of magnetic susceptibility $\chi^s(T)$ for the $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ samples with $x=0.16$ and 0.22. The dot-dash and broken lines represent $\chi_F^s(T)$ and a Curie term, respectively. The solid line is the curve given by adding the Curie term on $\chi_F^s(T)$.

It has been reported that the χ-T curve of $La_{1.82}Sr_{0.18}Cu_{1-y}M_yO_4$ (M=Ga, Zn, Ni, and Co) is reproduced by adding a Curie-Weiss term, instead of a Curie term, on a T-dependent term which follows a universal curve.[23] The universal curve used in their analysis is the same as that obtained by Johnston.[5] However, the y dependence of $T_{\max}$ is qualitatively in agreement with the present result, though y dependences of $\chi_{\max}^s$ and C cannot be compared because of absence of their data.

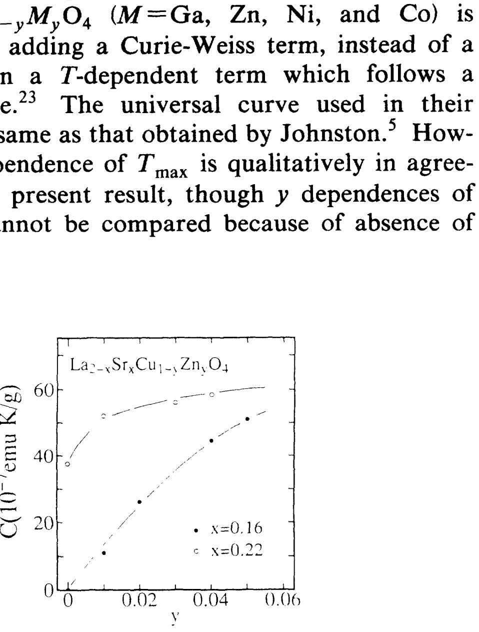

FIG. 16. Dependence of C on y for the $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ samples with $x=0.16$ and 0.22.

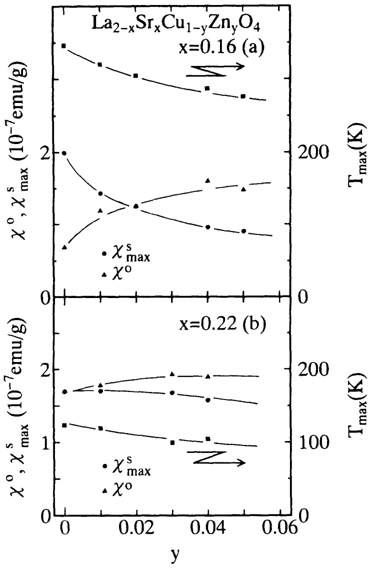

FIG. 17. Dependences of $T_{\max}$, $\chi^s_{\max}$, and χ^0 on y for the $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ samples: (a) for $x=0.16$ and (b) for $x=0.22$.

The $T_{\max}$ and $\chi^s_{\max}$ values decrease with increasing y in $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ ($x=0.16$), as mentioned above. The $T_{\max}$ value of the sample with $x=0.16$ and $y=0.05$ is almost the same as that for the $La_{1.83}Sr_{0.17}CuO_4$ sample (Figs. 8 and 17). Therefore, the comparison of $\chi^s_F(T)$ between the two samples is interesting for studying Zn-doping effects on magnetism. In Fig. 18, $\chi^s_F(T)$ is shown for these samples. It is evident in Fig. 18 that the $\chi^s_{\max}$ value of the Zn-substituted sample is much smaller than that of the nonsubstituted sample. This fact suggests that the regions of a sample whose magnetism follows the universal curve F may decrease in Zn-substituted samples. It has been found in studies of specific-heat capacity that the superconductivity of $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ ($x=0.16$ and 0.19) is destroyed locally around Zn atoms,[24] which accounts for the decrease of diamagnetism in the Zn-substituted samples (Fig. 12). Such a local destruction of superconductivity must be accompanied by a drastic change of the local magnetism and/or the electronic structure around Zn atoms. In the $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ sample with $x=0.16$, the local magnetism around the Zn atoms will follow the Curie law instead of universal curve F. This change in local magnetism can account for the reduction of $\chi^s_{\max}$ in the Zn-substituted samples. On the other hand, the y dependence of $\chi^s_{\max}$ as well as $T_{\max}$ is rather weak in the $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ sample with $x=0.22$. In the region for $x>0.2$, Zn-doping effects on magnetism may be rather different from those for $x<0.2$.

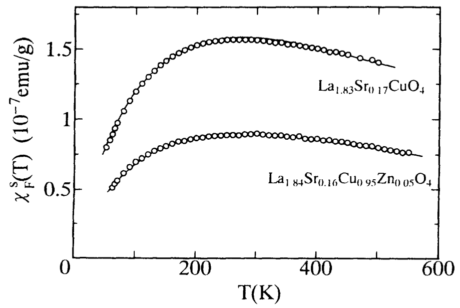

FIG. 18. $\chi^s_F(T)$ for the samples of $La_{1.83}Sr_{0.17}CuO_4$ and $La_{1.84}Sr_{0.16}Cu_{0.95}Zn_{0.05}O_4$.

IV. SUMMARY

Magnetic susceptibility χ and resistivity ρ were measured on well characterized samples of $La_{2-x}Sr_xCuO_4$ and the Zn-substitution effects on the magnetic susceptibility and the superconductivity were also examined in $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ ($x=0.16$ and 0.22). The results are summarized as follows.

(1) The upturn of χ, which results from the development of 2D AFM correlation and the appearance of an antisymmetric exchange interaction in the orthorhombic phase, was observed in a low Sr-concentration range. The upturn of χ was progressively reduced with increasing x and disappeared above $x\approx 0.05$, indicating that the development of 2D-AFM correlation among the Cu spins is greatly suppressed above $x\approx 0.05$ near the margin of the superconducting regime.

(2) In the superconducting $La_{2-x}Sr_xCuO_4$ samples with $0.1<x<0.2$, the T-dependent part of χ, $\chi^s_F(T)$, which exhibits a broad peak $\chi^s_{\max}$ at $T_{\max}$ and follows a universal curve F regardless of x, was found to be greatly reduced to a value of less than 20% of $\chi^s_{\max}$ at $T \ll T_{\max}$. A kind of spin singlet state might develop below $\sim T_{\max}$.

(3) It was confirmed that in the $La_{2-x}Sr_xCuO_4$ samples with $x \gtrsim 0.2$ the T-dependent part of χ contained a small Curie term in addition to $\chi^s_F(T)$. The Curie constant increased with increasing x and T_c decreased greatly with the increase of the Curie constant.

(4) The downward deviation of ρ from a T-linear dependence, which is evident at low Sr concentrations, was observed below a characteristic temperature T_b or $T_{\max}$ in the χ-T curve; for $x<0.09$ χ decreases greatly below T_b,[11] while for $x>0.09$ χ exhibits a broad peak at $T_{\max}$. The deviation from a T-linear resistivity was largely suppressed with increasing x and was unclear at $x\approx 0.16$ at which T_c reached the maximum value in the present system.

(5) The T-dependent term χ for the Zn-substituted samples was reproduced by adding a Curie term on the T-dependent part which follows universal curve F, as in the $La_{2-x}Sr_xCuO_4$ samples with $x \gtrsim 0.2$. With increasing Zn concentrations, the values of $\chi^s_{\max}$ and $T_{\max}$ decreased, while the Curie constant increased.

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[1] G. Shirane, Y. Endoh, R. J. Birgeneau, M. A. Kastner, Y. Hidaki, M. Oda, M. Suzuki, and T. Murakami, Phys. Rev. Lett. **59**, 1613 (1987).

[2] Y. Endoh, K. Yamada, R. J. Birgeneau, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, T. R. Thurston, J. M. Tranquada, G. Shirane, Y. Hidaka, M. Oda, Y. Enomoto, M. Suzuki, and T. Murakami, Phys. Rev. B **37**, 7443 (1988).

[3] T. Thio, T. R. Thurston, N. W. Preyer, P. J. Picone, M. A. Kastner, H. P. Jenssen, D. R. Gabbe, C. Y. Chen, R. J. Birgeneau, and A. Aharony, Phys. Rev. B **38**, 905 (1988).

[4] R. J. Birgeneau, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, P. J. Picone, T. R. Thurston, G. Shirane, Y. Endoh, M. Sato, K. Yamada, Y. Hidaka, M. Oda, Y. Enomoto, M. Suzuki, and T. Murakami, Phys. Rev. B **38**, 6614 (1988); B. Keimer, N. Belk, R. J. Birgeneau, A. Cassanho, C. Y. Chen, M. Greven, M. A. Kastner, A. Aharony, Y. Endoh, R. W. Erwin, and G. Shirane, Phys. Rev. B **46**, 14 034 (1992).

[5] D. C. Johnston, Phys. Rev. Lett. **62**, 957 (1989).

[6] M. Oda, T. Ohguro, N. Yamada, and M. Ido, J. Phys. Soc. Jpn. **58**, 1137 (1989).

[7] M. Oda, T. Ohguro, H. Matuki, N. Yamada, and M. Ido, Phys. Rev. B **41**, 2605 (1990).

[8] M. Oda, H. Matsuki, and M. Ido, Solid State Commun. **74**, 1321 (1990).

[9] H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, and Y. Tokura, Phys. Rev. B **40**, 2254 (1989).

[10] J. B. Torrance, A. Bezinge, A. I. Nazzal, T. C. Huang, S. S. P. Parkin, D. T. Keane, S. J. LaPlaca, P. M. Horn, and G. A. Held, Phys. Rev. B **40**, 8872 (1989).

[11] R. Yoshizaki, N. Ishikawa, H. Sawada, E. Kita, and A. Tasaki, Physica C **166**, 417 (1990).

[12] Y. Ando, M. Sera, S. Yamagata, S. Kondoh, M. Onoda, and M. Sato, Solid State Commun. **70**, 303 (1989).

[13] M. Oda, T. Nakano, Y. Kamada, and M. Ido, Physica C **185-189**, 1157 (1991).

[14] M. Oda, T. Nakano, Y. Kamada, and M. Ido, Physica C **183**, 234 (1991).

[15] M. Gurvitch and A. T. Fiory, Phys. Rev. Lett. **59**, 1676 (1987).

[16] T. Nakamura and S. Uchida, Phys. Rev. B **47**, 8369 (1993).

[17] H. Takagi, B. Batlogg, H. L. Kao, J. Kwo, R. J. Cava, J. J. Krajewski, and W. F. Peck, Jr., Phys. Rev. Lett. **69**, 2975 (1992).

[18] T. Ito, K. Takenaka, and S. Uchida, Phys. Rev. Lett. **70**, 3995 (1993).

[19] J. M. Tarascon, L. H. Greene, P. Barboux, W. R. Mckinnon, G. W. Hull, T. P. Orlando, K. A. Delin, S. Foner, and E. J. NcNiff, Jr., Phys. Rev. B **36**, 8393 (1987).

[20] W. Kang, H. J. Schulz, D. Jerome, S. S. P. Parkin, J. M. Bassat, and Ph. Odier, Phys. Rev. B **37**, 5132 (1988).

[21] H. Fujishita and M. Sato, Solid State Commun. **72**, 529 (1989).

[22] G. Xiao, M. Z. Cieplak, J. Q. Xiao, and C. L. Chien, Phys. Rev. B **42**, 8752 (1990).

[23] N. Ishikawa, N. Kuroda, H. Ikeda, and R. Yoshizaki, Physica C **203**, 284 (1992).

[24] M. Momono *et al.* (private communication).

[25] T. Kajitani, K. Hiraga, T. Sakurai, M. Hirabayashi, S. Hosoya, T. Fukuda, and K. Oh-Ishi, Physica C **171**, 491 (1990).

[26] W. C. Lee, R. A. Klemm, and D. C. Johnston, Phys. Rev. Lett. **63**, 1012 (1989). M. Hase, I. Terasaki, A. Maeda, K. Uchinokura, T. Kimura, K. Kishio, I. Tanaka, and H. Kojima, Physica C **185-189**, 1855 (1991).

[27] K. Isida, Y. Kitaoka, G. Q. Zheng, and K. Asayama, J. Phys. Soc. Jpn. **60**, 3516 (1991).

[28] G.-Q. Zheng, T. Kuse, Y. Kitaoka, S. Ohsugi, K. Asayama, and Y. Yamada, Physica C **208**, 339 (1993).

[29] S. Ohsugi, Y. Kitaoka, K. Ishida, S. Matumoto, and K. Asayama, Physica B **186-188**, 1027 (1993).

[30] Y. Q. Song, M. A. Kennard, K. R. Poppelmeier, and W. P. Halperin, Phys. Rev. Lett. **70**, 3131 (1993).

[31] M. Takigawa, A. P. Reyes, P. C. Hemmel, J. D. Thompson, R. H. Heffner, Z. Fisk, and K. C. Ott, Phys. Rev. B **43**, 247 (1991).

[32] Y. Yoshinari, H. Yasuoka, Y. Ueda, K. Koga, and K. Kosuge, J. Phys. Soc. Jpn. **59**, 3698 (1990).

[33] L. J. de Jongh and A. R. Miedema, Adv. Phys. **23**, 1 (1974).

[34] A. Auerbach and D. P. Arovas, Phys. Rev. Lett. **61**, 617 (1988).

[35] Y. Okabe and M. Kikuchi, J. Phys. Soc. Jpn. **57**, 4351 (1988).

[36] T. Nishikawa, J. Takeda, and M. Sato, J. Phys. Soc. Jpn. **62**, 2568 (1993).

[37] G. Shirane, Physica C **185-189**, 80 (1991); Y. Endoh, K. Yamada, M. Matsuda, K. Nakajima, K. Kuroda, Y. Hidaka, I. Tanaka, H. Kojima, R. J. Birgeneau, M. A. Kastner, B. Keimer, G. Shirane, and T. R. Thurston, Jpn. J. Appl. Phys. **7**, 174 (1992).

[38] T. Machi, I. Tomeno, T. Miyatake, N. Koshizuka, S. Tanaka, T. Imai, and H. Yasuoka, Physica C **173**, 32 (1991).

[39] J. Rossat-Mignod, L. P. Regnault, C. Vettier, P. Burlet, J. Bossy, J. Y. Henry, and G. Lpertot, Physica C **185-189**, 86 (1991).

[40] J. M. Tranquada, P. M. Gehring, G. Shirane, S. Shamoto, and M. Sato, Phys. Rev. B **46**, 5561 (1992).

[41] Y. Nakazawa and M. Ishikawa, Physica C **158**, 381 (1989).

[42] D. C. Johnston, S. K. Sinha, A. J. Jacobson, and J. M. Newsam, Physica C **153-155**, 572 (1988).

[43] G. Xiao, A. Bakhshai, M. Z. Cieplak, Z. Tesanovic, and C. L. Chen, Phys. Rev. B **39**, 315 (1989).

[44] R. M. Fleming, B. Batlogg, R. J. Cava, and E. A. Rietman, Phys. Rev. B **35**, 7191 (1987).

[45] M. Kato, Y. Maeno, and T. Fujita, Physica C **152**, 116 (1988).

[46] R. Moret, J. P. Pouget, C. Noguera, and G. Collin, Physica C **153-155**, 968 (1988).