Suppression of the superconducting transition temperature T_c around $x\sim0.115$ in $La_{2-x}Sr_xCuO_4$

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Detailed studies of the superconducting diamagnetism of $La_{2-x-y}Nd_ySr_xCuO_4$ show that the characteristic concentration x_{dip} at which the largest T_c suppression is observed changes from 0.115 to 0.125 on Nd doping around $y\sim0.12$, above which the structural transition to the low-temperature tetragonal (LTT) phase is observed. This indicates that also in $La_{2-x}Sr_xCuO_4$, the x_{dip} value is, in principle, also $\frac{1}{8}$ as in $La_{2-x}Ba_xCuO_4$. We propose that the largest T_c suppression around $x\sim0.115$ in $La_{2-x}Sr_xCuO_4$ is the result of the existence of two competitive factors. One is the local distortion expanding the LTT region around the Sr^{2+} ion, which is largest at $x=\frac{1}{8}$ and acts to suppress T_c. The other is the antiferromagnetic spin fluctuation energy, which might increase with x and acts to increase T_c. On Nd doping, the former factor becomes larger around $x=0.125$ than around $x=0.115$ and the x_{dip} value moves to 0.125.

It is well known that suppression of T_c is observed in a narrow x region around $\frac{1}{8}$ in $La_{2-x}Ba_xCuO_4$ (Ref. 1) and in the rare-earth-doped $La_{2-x}Sr_xCuO_4$.[2,3] Although extensive studies have been performed on this subject, its origin still remains to be solved.[1–10] These compounds exhibit a structural transition at T_{d2} from the LTO1 (low-temperature orthorhombic 1, space group *Bmab*) to LTT (low-temperature tetragonal, space group $P4_2/ncm$) or LTO2 (low-temperature orthorhombic 2, space group *Pccn*) phase around $x\sim\frac{1}{8}$.[4] In $La_{2-x}Sr_xCuO_4$, unlike $La_{2-x}Ba_xCuO_4$, the T_c suppression appears centered around $x\sim0.115$, which was clarified in the Zn-doped samples by Koike *et al.*,[11] and muon spin resonance (μSR) and nuclear quadrupole resonance (NOR) experiments exhibited antiferromagnetic (AF) ordering centered around $x\sim0.115$,[12–14] while the AF ordering in $La_{2-x}Ba_xCuO_4$ is observed centered around $x\sim0.125$.[15,16] Thus the x value where the anomalous T_c suppression is observed is different between $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$. Furthermore, in $La_{2-x}Sr_xCuO_4$, the system is in the LTO1 phase down to low temperatures, while signs of the structural transition to the LTT phase were observed below $\sim$10 K around $x\sim0.12$ by studies of the ultrasonic sound velocity.[17] We define the x value where the largest T_c suppression is observed as the x_{dip} value. The origin of the different x_{dip} values between $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ is still unknown. In order to clarify the origin of the T_c suppression centered around $x\sim0.115$ in $La_{2-x}Sr_xCuO_4$, we have performed detailed studies of the superconducting diamagnetism of samples with low T_{d2} in the $La_{2-x-y}Nd_ySr_xCuO_4$ system. In this system, the critical concentration y_c above which the structural transition to the LTT phase appears at low temperatures is $\sim$0.12, which is relatively high compared with those of the Sm-, Eu-, and Gd-doped systems, and T_{d2} can be as low as $\sim$30 K.[18]

In our previous paper,[18] we proposed the following mechanism for the structural transition from the LTO1 to the LTT phase. Two LTT (or LTO2) and two LTO1 regions are induced around the doped ion by superposition of the isotropic distortion of the CuO_6 octahedra around the doped ion and the cooperative tilts of the CuO_6 octahedra in the LTO1 phase. The structural transition to the LLT phase takes place when the LTT region is connected by percolation in a whole area of the crystal. Coexistence of the LTT and LTO1 regions is inevitable.

In this paper, we show that in $La_{2-x-y}Nd_ySr_xCuO_4$, the x_{dip} value changes from $x=0.115$ to 0.125 around $t\sim0.12$, above which the structural transition to the LTT phase appears. This indicates that the x_{dip} value is, in principle, $\frac{1}{8}$ also in $La_{2-x}Sr_xCuO_4$ and the origin of $x_{dip}\sim0.115$ in $La_{2-x}Sr_xCuO_4$ is the result of the existence of two competitive factors.

All the samples were sintered ones prepared by a standard solid-state reaction method mentioned elsewhere.[10] The dc magnetization measurement was carried out using a superconducting quantum interference device (SQUID) magnetometer. The thermal conductivity was measured by the usual steady-state method.

Figure 1 shows the temperature dependence of the thermal conductivity κ of $La_{1.875-x}Nd_{0.125}Sr_xCuO_4$. A small enhancement or kink is observed in κ below $\sim$30 K in the

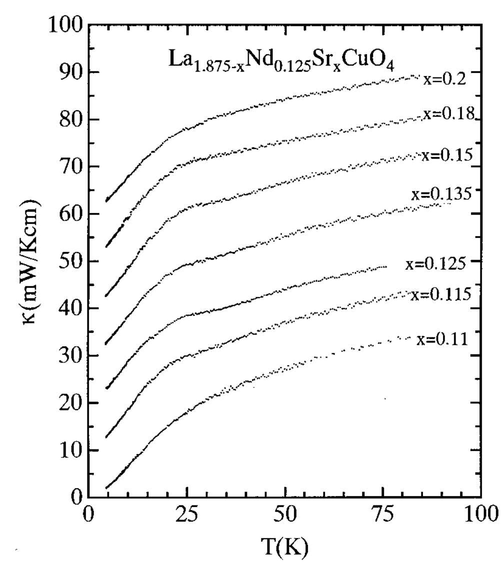

FIG. 1. Temperature dependence of the thermal conductivity of $La_{1.875-y}Nd_ySr_{0.115}CuO_4$. The origin of the y axis is shifted by 10 mW/K cm for each curve. The arrows indicate the structural transition temperature.

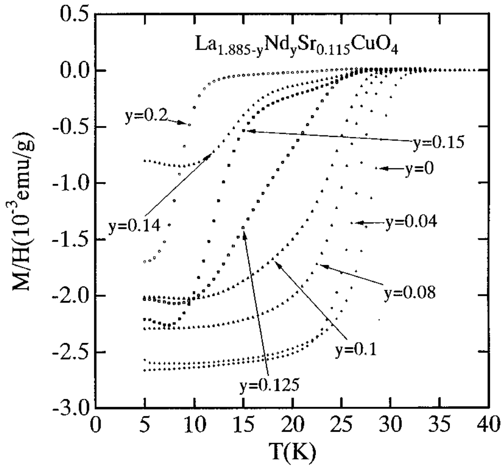

FIG. 2. Temperature dependence of the field-cooled magnetic susceptibility (measured at $H=20$ Oe) of $La_{1.885-y}Nd_ySr_{0.115}CuO_4$.

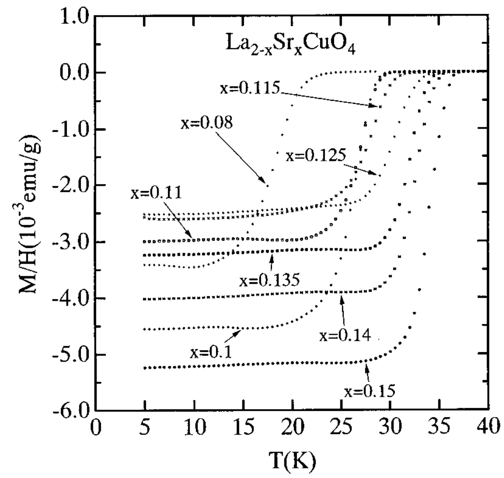

FIG. 4. Temperature dependence of the field-cooled magnetic susceptibility (measured at $H=20$ Oe) of $La_{2-x}Sr_xCuO_4$.

samples with $0.115 \leqslant x \leqslant 0.18$, as shown by the arrows. This anomaly of κ originates in the structural transition to the LTT phase. Previously, we reported that the structural transition to the LTT phase appears at low temperatures above $y \sim \frac{1}{8}$ in $La_{1.875-y}Nd_ySr_{0.125}CuO_4$ (Ref. 18) and the enhancement of κ below T_{d2} increases with y up to ~ 0.2, where it is much larger and more pronounced than those of the present samples with $y=0.125$.[19] In the samples with $x=0.11$ and 0.2, no anomaly is seen in the temperature dependence of κ, which indicates that the structural transition does not exist in these samples.

Figures 2–5 show the temperature dependence of the magnetic susceptibility M/H of $La_{1.885-y}Nd_ySr_{0.115}CuO_4$, $La_{1.875-y}Nd_ySr_{0.125}CuO_4$, $La_{2-x}Sr_xCuO_4$, and $La_{1.875-x}Nd_{0.125}Sr_xCuO_4$, respectively. These results show that two superconducting transitions exist in $La_{2-x-y}Nd_ySr_xCuO_4$ above $y \sim 0.125$ and in a narrow x region between 0.115 and 0.135. We define the lower and higher T_c as T_c^l and T_c^h, respectively. In $La_{1.875-x}Nd_{0.125}Sr_xCuO_4$, the x value of 0.115 corresponds to the smallest x concentration where the structural transition to the LTT phase appears, as shown in Fig. 1. This indicates that the above anomalous behavior of the M/H-T curve should be attributed to the entrance into the LTT phase. Previously, we showed that the coexistence of the LTT and LTO1 regions is inevitable below T_{d2},[18] and we propose that T_c^l and T_c^h and the T_c's of the LTT and LTO1 regions, respectively. When T_{d2} is low, a comparable LTO1 region coexists with the LTT region below T_{d2} because the distortion around the substituted ion does not extend far. The existence of two superconducting phases is the result of competition between the size of the LTT or LTO1 regions and the short superconducting coherence length in the present high-T_c cuprates, which depends on x. The present results suggest that the volume fraction of the LTT region increases and that of the LTO1 region decreases rapidly with further increase of y above 0.125.

Here, we discuss the possibility of site-selective substitution in the La-Sr or La-Ba system. The ionic radius of Sr^{2+} is larger than that of La^{3+}. Thus, it is expected that each Sr^{2+} ion is substituted in isolation from other Sr^{2+} ions, because

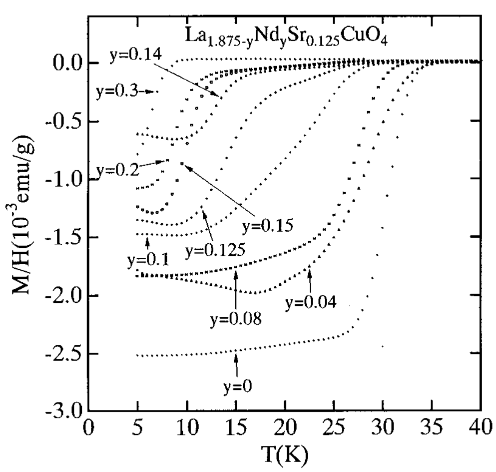

FIG. 3. Temperature dependence of the field-cooled magnetic susceptibility (measured at $H=20$ Oe) of $La_{1.875-y}Nd_ySr_{0.125}CuO_4$.

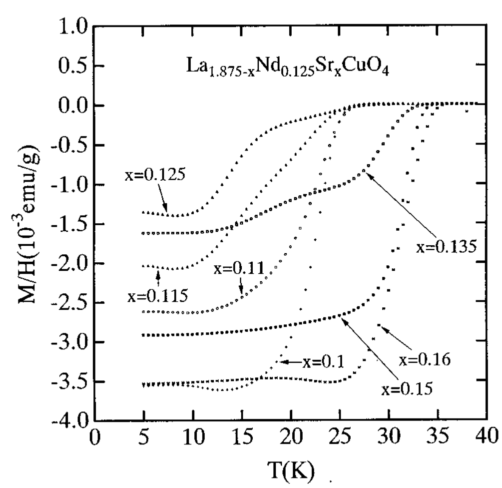

FIG. 5. Temperature dependence of the field-cooled magnetic susceptibility (measured at $H=20$ Oe) of $La_{1.85-x}Nd_{0.125}Sr_xCuO_4$.

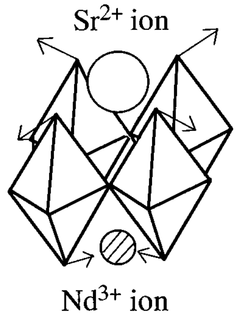

FIG. 6. Schematic picture of the proposed pair substitution of Sr^{2+} and Nd^{3+}ions into La_2CuO_4. The large open circle and small hatched circle indicate the Sr^{2+} ion and Nd^{3+} ion, respectively. See the text for details.

of the difference of the valence and ionic radius between the La^{3+} and Sr^{2+} ions. When Nd^{3+} ions are doped into the La-Sr system, we expect that Sr^{2+} and Nd^{3+} ions are substituted as a pair as shown in Fig. 6 because of the smaller ionic radius of Nd^{3+} compared to La^{3+}. This enhances the LTT distortion around the doped ions. This pair may have a tendency to order so as to make the volume fraction of the LTT region maximum when $x=\frac{1}{8}$. In $La_{2-x}Ba_xCuO_4$, the ionic radius of Ba^{2+} is much larger than that of La^{3+} compared to that of Sr^{2+} and the local distortion around Ba^{2+} is large enough to induce the structural transition to the LTT phase. On the other hand, in $La_{2-x}Sr_xCuO_4$, the difference of the ionic radius between the Sr^{2+} and La^{3+} ions is not so large that the Sr doping can induce the macroscopic structural transition by itself. However, if Nd^{3+} ions are doped, the local distortion around Sr^{2+} is enhanced by the above proposed pairing substitution and the structural transition is induced. However, in $La_{1.75}Nd_{0.125}Sr_{0.125}CuO_4$, T_{d2} is ~30 K, which is half of the value of ~65 K in $La_{1.875}Ba_{0.125}CuO_4$. This means that the range where the local lattice distortion, i.e., the LTT region, around the substituted ion extends is rather smaller in the former than in the latter. Because of this difference, the volume fraction of the LTT region at the lowest temperature may be a few times larger in $La_{1.875}Ba_{0.125}CuO_4$ than in $La_{1.75}Nd_{0.125}Sr_{0.125}CuO_4$. In $La_{1.875-y}Nd_ySr_{0.125}CuO_4$, with further increase of y above 0.125, Nd^{3+} ions may be substituted near Sr^{2+} ions in the same LaO layer, which also enhances the local distortion around the Sr^{2+} ions and such a region where the local distortion is large becomes the core of the LTT region. Thus the LTT region expands with further increase of y. In this way, in the La-Sr or La-Ba system, site-selective substitution possibly plays an important role in various physical properties. La-site or Cu-site substitution effects in these systems should be reexamined carefully from this point of view. We note that if both x and y are smaller than ~0.11, the LTT region is not connected in a whole area of the crystal by percolation.

Figure 7(a) shows the y dependence of T_c^h, T_c^l, and T_{d2} of $La_{1.885-y}Nd_ySr_{0.115}CuO_4$ and $La_{1.875-y}Nd_ySr_{0.125}CuO_4$. T_{d2} is determined from measurements of κ. This figure clearly shows that the superconducting properties are very different below and above y~0.12 between the samples with $x=0.115$ and those with $x=0.125$. In the small-y region, T_c^h is higher in the samples with $x=0.125$ than in those with

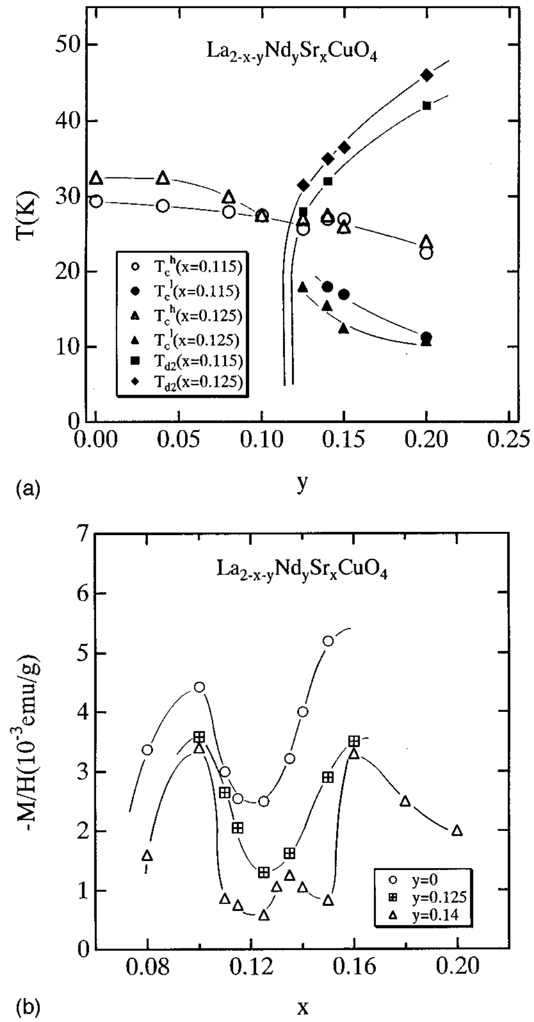

FIG. 7. (a) The y dependence of T_c^h, T_c^l, and T_{d2} of $La_{2-x-y}Nd_ySr_xCuO_4$ ($x=0.115$ and 0.125). (b) The x dependence of the magnitude of the Meissner diamagnetism at 5 K of $La_{2-x-y}Nd_ySr_xCuO_4$ ($x=0$, 0.115, and 0.125).

$x=0.115$. However, T_c^h of the samples with $x=0.125$ begins to decrease with y above ~0.06 and almost coincides with that for $x=0.115$ at $y=0.1$. Above y~0.115, T_c^l appears, and is clearly related to the appearance of the LTT phase. Although T_c^h does not change very much even above y~0.125 in either system, T_c^l shows a clear difference between these two systems. T_c^l of the samples with $x=0.125$ is lower than for those with $x=0.115$ for $x>0.125$. This difference should be related to the difference of T_{d2} between the two systems as shown in Fig. 7(a). That is, the existence of the LTT region is the origin of the lower T_c^l in the samples with $x=0.125$ above y~0.12. This is clearly seen in the M/H-T curves of the $y=0.125$ samples with $x=0.115$ and 0.125 as shown in Figs. 2 and 3, respectively. In this way, the $x_{\rm dip}$ value in $La_{2-x-y}Nd_ySr_xCuO_4$ changes from 0.115 to 0.125 around y~0.12, which indicates that in $La_{2-x}Sr_xCuO_4$, the $x_{\rm dip}$ value is, in principle, $\frac{1}{8}$ as in $La_{2-x}Ba_xCuO_4$. Figure 7(b) shows the x dependence of the magnitude of the Meissner volume fraction at 4.2 K of $La_{2-x-y}Nd_ySr_xCuO_4$ ($y=0$, 0.125, and 0.14). This figure clearly shows that the Meissner volume fraction exhibits a minimum around x~0.12, which is similar to the x dependence of T_c^l observed for $0.115 \leqslant x \leqslant 0.135$. Even in $La_{2-x}Sr_xCuO_4$, the minimum of the Meissner volume fraction at 4.2 K is seen around $x \sim 0.12$. This means that even if the system is in the LTO1 phase, the superconducting state is greatly influenced around $x \sim 0.12$. This is more easily seen in the magnetic susceptibility of $La_{1.775}Nd_{0.1}Sr_{0.125}CuO_4$. In this sample, although the macroscopic transition to the LTT phase does not exist, a small kink is observed at $\sim$22 K in the M/H-T curve, which is a sign of the existence of T_c^l and suggests the existence of a local LTT region with an appropriate size even in the LTO1 phase.

Next, we discuss the origin of the suppression of T_c around $x \sim \frac{1}{8}$. Which is more important for the anomalous T_c suppression: the carrier concentration of $x \sim \frac{1}{8}$ or the lattice distortion induced by Sr or Ba doping with $x \sim \frac{1}{8}$? The present results show that the superconducting properties change drastically accompanying the appearance of the LTT phase. In the samples with $x = 0.125$, T_c decreases rapidly above $y \sim 0.06$, and above $y \sim 0.125$ T_c^l is lower than that of the sample with $x = 0.115$ as shown in Fig. 7(a). It is difficult to imagine that the carrier concentration is changed abruptly by the Nd doping above $y \sim 0.06$ only in the samples with $x = 0.125$. It is natural to ascribe the change to the enhancement of the lattice distortion induced by the Nd doping, which is larger in the system with $x = 0.125$ than in the system with $x = 0.115$. That is, the Sr concentration of $x \sim \frac{1}{8}$ is more important for the T_c suppression around $x \sim \frac{1}{8}$ than the carrier concentration of $x \sim \frac{1}{8}$. We propose that Sr^{2+} ions have a tendency to order as one Sr^{2+} ion for 4×4 La sites and the LTT region around the Sr^{2+} ion is most easily connected by percolation when $x = \frac{1}{8}$. The shift of the $x_{\rm dip}$ value from 0.115 to 0.125 caused by the Nd doping indicates the existence of two competitive factors. One suppresses T_c the most at $x \sim \frac{1}{8}$ and the other increases T_c with increasing x. The origin of the former factor is the existence of the LTT phase whose volume fraction is largest around $x \sim \frac{1}{8}$. As the origin of the latter factor, the increase of the antiferromagnetic spin fluctuation energy Γ_Q or the superconducting coherence length with an increase of x can be considered. Here, we discuss the importance of the AF spin fluctuation. Kitaoka *et al.* discussed the importance of Γ_Q based on the results for $(T_1T)^{-1}$ of ^{63}Cu in $La_{2-x}Sr_xCuO_4$.[20] Here, T_1 is the nuclear spin-lattice relaxation time. Tou *et al.* reported that $1/T_1$ of Cu in $La_{2-x}Ba_xCuO_4$ increases below T_{d2}, showing a tendency to diverge toward $T_N \sim 35$ K in a sample with $x = 0.125$,[21] which indicates that the AF spin fluctuation is drastically affected by the structural transition around $x \sim \frac{1}{8}$. These results indicate that Γ_Q decreases below T_{d2}. The AF ordering is observed only around $x = \frac{1}{8}$ where the volume fraction of the LTT region is largest. In the LTT phase where the LTT and LTO1 regions coexist, Γ_Q is expected to be smaller in the LTT region than in the LTO1 region. This may be related to the existence of two superconducting transition temperatures T_c^l and T_c^h in the present system. That is, T_c^l and T_c^h are the T_c's in the LTT and LTO1 regions, respectively. In $La_{2-x}Sr_xCuO_4$, local LTT regions are expected to exist above $x \sim 0.11$ and are largest at $x \sim \frac{1}{8}$, and the LTT distortion effect suppressing T_c should be largest at $x \sim \frac{1}{8}$. However, this distortion effect is not very large because of the small difference of the ionic radius between La^{3+} and Sr^{2+} ions. On the other hand, Γ_Q is expected to increase with x. It is expected that the smaller the x value, the more easily Γ_Q is affected by the LTT distortion. As a result of these two competing effects, the $x_{\rm dip}$ value is observed around $x \sim 0.115$ in $La_{2-x}Sr_xCuO_4$. It is noted that when x is smaller than 0.11, the LTT distortion effect is very small as mentioned above. In $La_{2-x-y}Nd_ySr_xCuO_4$ or $La_{2-x}Ba_xCuO_4$, the LTT distortion effect induced by the doped ion is large enough to greatly suppress Γ_Q at $x \sim \frac{1}{8}$. In this way, the shift of the $x_{\rm dip}$ value from 0.115 to 0.125 on Nd doping in $La_{2-x-y}Nd_ySr_xCuO_4$ can be understood as the result of the existence of two factors. The x-dependent coherence length may also correlate with the shift of the $x_{\rm dip}$ value.

Recently, the possibility that the stripe correlations of spins and holes play an essential role in the T_c suppression around $x \sim \frac{1}{8}$ was discussed based on neutron diffraction experiments on $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ ($x \sim 0.12$).[22] At present, we do not know if the same situation is realized in samples with smaller y values, i.e., lower T_{d2}. However, as pointed out by the authors of Ref. 22, even in the LTO1 phase, similar stripe correlations as in the LTT phase can possibly be realized dynamically and the present results should be examined from this point of view. Neutron-scattering experiments on samples with low T_{d2} in $La_{2-x-y}Nd_ySr_xCuO_4$ are desirable.

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