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Superconductivity and antiferromagnetism in $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ and $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$

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$La_2CaCu_2O_6$ can be made superconducting by doping Ca or Sr in the form of $La_{2-x}(Sr,Ca)_xCaCu_2O_{6+\delta}$ and by synthesis under high O_2 pressures of more than 4 atm. Superconducting properties of $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ $(0.08 \leq x \leq 0.25)$ and $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ $(0.07 \leq x \leq 0.23)$ as functions of composition (x) and oxygen partial pressure during synthesis (P_{O_2} up to 400 atm) were investigated by measuring their electrical resistivity and magnetic susceptibility. In both compounds, the superconducting transition temperature (T_c) increased with increasing x and P_{O_2}, and showed almost the same maximum T_c (zero) of about 51 K at the solubility limit of Ca or Sr in La $(x \approx 0.25)$ with P_{O_2} at 400 atm, although at a lower P_{O_2}, T_c (zero) was higher in a Sr-doped compound than that of a Ca-doped compound. Nonsuperconducting or weakly superconducting $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ and $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ synthesized under oxygen partial pressures between 0.2 and 10 atm showed cusps in their magnetic susceptibility at around 25 K, which may result from three-dimensional (3D) antiferromagnetic ordering. The superconductivity of these compounds may appear as a result of the frustration of such 3D antiferromagnetic correlation as with other copper oxide superconductors.

INTRODUCTION

The failure to achieve superconductivity in 2:1:2:6-type compounds, typified by $La_2SrCu_2O_6$, has been a mystery since the beginning of research on high-T_c superconductivity. These compounds have the planar CuO_2 network common in high-T_c cuprates and some of these compounds show a metallic nature in their electrical resistivity.[1] Recently, Cava *et al.*[2] and independently Kinoshita, Shibata, and Yamada[3] detected bulk superconductivity in Ca-based compounds such as $La_{1.6}Sr_{04}CaCu_2O_6$ and $La_{1.85}(Ca_{0.86}Sr_{0.14})_{1.15}Cu_2O_{6.03}$ synthesized under high oxygen pressures. More recently, Kinoshita, Shibata, and Yamada[4] succeeded in preparing an isomorphous superconductor $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ $(0.08 \leq x \leq 0.25)$ containing no Sr.

Since the successful synthesis of superconductors by Cava *et al.*,[2] several investigators have analyzed the crystal structure to explain the effect of high-O_2-pressure synthesis and to determine the relationship between the crystal structure and the superconductivity of these compounds.[5–10] A slight amount of interstitial oxygen between the two CuO_2 planes is commonly observed in "2126"-type superconductors, and this is considered to be an important factor in the occurrence of superconductivity.[5,7,10]

A deeper understanding of the superconducting properties of these compounds requires systematic research on the relationship between T_c and the composition and synthesis conditions, as was done for $La_{2-x}Sr_xCuO_4$ by Torrance *et al.*[11] Furthermore, "2126" compounds are the simplest two-CuO_2-layer compounds because they do not have the additional carrier reservoir layers that other compounds such as $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ and $TlBa_2Ca_{n-1}Cu_nO_y$ have. Therefore, systematic studies on T_c would be useful in investigating the nature of the CuO_2 planar network and in obtaining clues concerning the causes of superconductivity in high-T_c cuprates.

One more common feature of high-T_c cuprates is their antiferromagnetism when the number of carriers is reduced.[12] It is of much interest whether "2126" compounds have the same antiferromagnetic characteristics as the other high-T_c cuprates. One way of investigating antiferromagnetism is to measure the magnetic susceptibility. However, very few researchers have measured the normal-state magnetic susceptibility of the "2126" compounds.

In this paper, we report electrical resistivity and magnetic susceptibility measurements on superconducting and nonsuperconducting $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ $(0.08 \leq x \leq 0.25)$ together with $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ $(0.07 \leq x \leq 0.23)$ synthesized under various oxygen partial pressures.

EXPERIMENT

Two series of samples with nominal compositions $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ $(0.05 \leq x \leq 0.50)$ and $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ $(0.05 \leq x \leq 0.35)$ were synthesized from La_2O_3, $CaCO_3$, $SrCO_3$, and CuO powders with purities higher than 99.9%. The powder mixture was pressed into pellets and sintered at 1050–1080 °C for 20 to 50 h in air or in flowing O_2 under a pressure of 1 to 8 atm. To obtain superconducting samples, the samples sintered under 2 atm O_2 were pulverized, pressured into pellets, and sintered again at 1080 °C for 100 h in 20% O_2+80% Ar at a total pressure ranging between 50 and 2000 atm (P_{O_2} ranging between 10 and 400 atm) using a furnace for hot isostatic pressing (HIP). Some samples sintered under 2 atm O_2 were heat-treated in Ar or in air, which made it possible to obtain single-phase high-x samples with fewer carriers.

Electrical resistivity was measured using a standard four-probe dc method. Normal-state magnetic susceptibility and Meissner signals were measured with a SQUID magnetometer with field cooling at magnetic fields of 5k Oe and 10 Oe, respectively. The magnetic moment was measured at temperatures of 5, 10, and 20 K for $La_{1.82}Ca_{1.18}Cu_2O_{5.99}$ synthesized under 2 atm O_2 at magnetic fields up to 5 T. The crystal structure and the presence of impurity phases were examined by x-ray powder diffraction. The oxygen content was determined by iodometric titration.

RESULTS AND DISCUSSION

Figure 1 compares the temperature dependence of the electrical resistivity for $La_{1.82}Ca_{1.18}Cu_2O_{6\pm\delta}$ synthesized under various P_{O_2}. Although a sample synthesized under 2 atm O_2 showed metallic behavior in its electrical resistivity between 300 and 70 K, its electrical resistivity began to increase below 70 K and the sample did not show superconductivity, as reported by several investigators.[13–15] The increase in oxygen pressure during synthesis suppressed electrical resistivity upturn at low temperatures, and an 8-atm-O_2-synthesized sample showed a drop in electrical resistivity at around 8 K, indicating the onset of superconductivity. A sample synthesized at 10 atm O_2 showed superconductivity with a T_c (zero) of about 8 K. The superconducting critical temperature increased with an increase in oxygen partial pressure during synthesis, and a 400-atm-O_2 sample had a T_c (onset) of around 60 K and a T_c (zero) of about 49 K.

Figures 2 and 3 compare the electrical resistivity of samples with different compositions synthesized under 10 and 400 atm O_2. In Fig. 2, superconductivity appeared in samples with $x=0.15$ and 0.18, while a sample with $x=0.12$ did not show superconductivity. An increase in T_c (zero) with an increase in Ca concentration is also shown in Fig. 3. The highest T_c (zero) is about 51 K for $x=0.25$. Both figures show that superconductivity appears more easily at a higher Ca concentration.

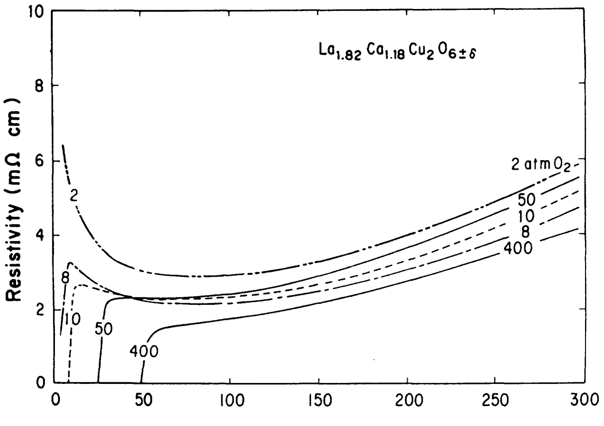

FIG. 1. Electrical resistivity vs temperature for $La_{1.82}Ca_{1.18}Cu_2O_{6\pm\delta}$ synthesized under various oxygen partial pressures.

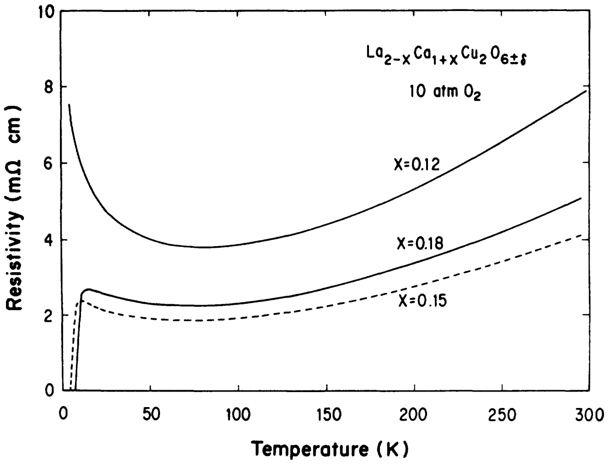

FIG. 2. Electrical resistivity vs temperature for $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ synthesized under 10 atm O_2.

Figure 4 summarizes T_c (zero) as a function of composition x in $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ with the oxygen partial pressure during synthesis as a parameter. T_c values are shown only for single-phase samples. For smaller x values, samples contained $La_{2-x}Ca_xCuO_4$ (214 compound) as a second phase, and for larger x values they contained impurity phases of CaO and $La_xCa_{14-x}Cu_{24}O_{41+\delta}$. As shown in Figs. 1–3, T_c increased with increasing x and the highest T_c was obtained at the highest allowable value of x at a given O_2 pressure. At a given composition, T_c increased with an increase in P_{O_2} during synthesis.

Figure 5 shows a similar summary of T_c (zero) for Sr-doped $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$. It resembles Fig. 4 in that T_c increases with increasing x and P_{O_2} during synthesis. The highest T_c (zero) attained by the synthesis under

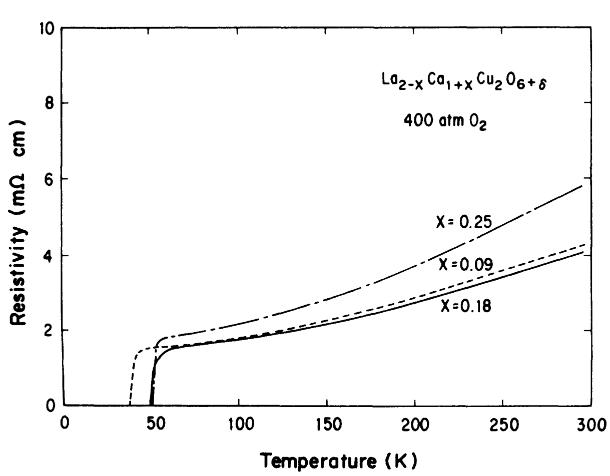

FIG. 3. Electrical resistivity vs temperature for $La_{2-x}Ca_{1+x}Cu_2O_{6+\delta}$ synthesized under 400 atm O_2.

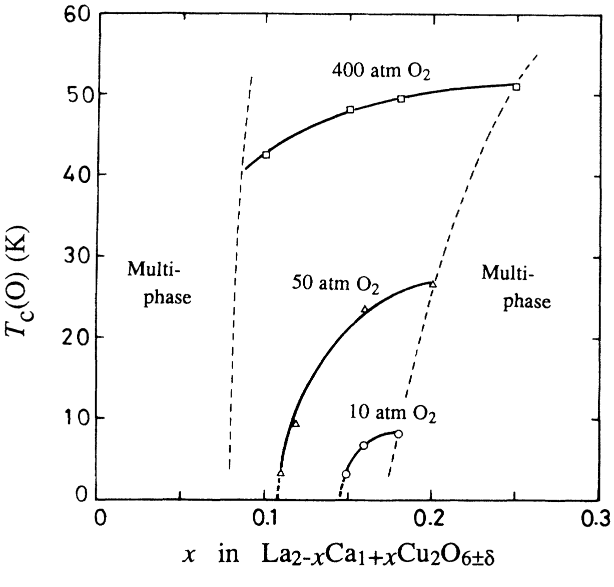

FIG. 4. T_c (zero) of $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ as a parameter of oxygen partial pressure during synthesis.

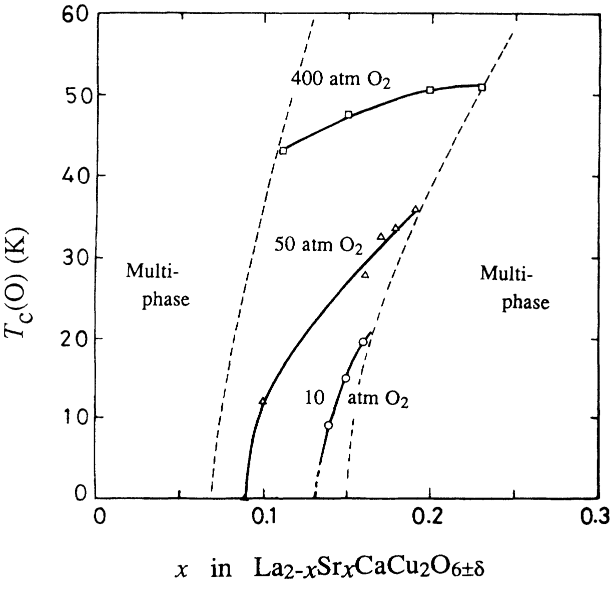

FIG. 5. T_c (zero) of $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ as a parameter of oxygen partial pressure during synthesis.

400 atm O_2 was about 51 K, which is almost the same as with $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$. However, there are some differences. The values of T_c are higher in $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ than in $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ when synthesized under 10 and 50 atm O_2. This may be related to a difference in oxygen content as discussed later. The single-phase region in $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ is narrower than that in $La_{2-x}Ca_{1+x}Cu_2O_{6+\delta}$. This is because the impurity phase of $La_{8-x}Sr_xCu_8O_{20-\delta}$ is easily formed in the Sr-rich side at the present synthesis temperature of 1080 °C. Cava *et al.*[16] synthesized single-phase $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ up to $x=0.45$ at 925 °C. The use of $Ca(NO_3)_2$ and $Sr(NO_3)_2$ and synthesis at lower temperatures may produce Sr-richer single-phased samples.

The oxygen content is shown in Fig. 6 as a function of P_{O_2} during synthesis for $La_{1.82}Ca_{1.18}Cu_2O_y$ and $La_{1.82}Sr_{0.18}CaCu_2O_y$. It increases linearly with increasing oxygen partial pressure for both compounds. Note that oxygen content is always higher in the Sr-doped compound than the Ca-doped compound. This can explained by the difference in ionic radius between Sr and Ca. Since the ionic radius of Sr is larger, the presence of Sr atoms in the interlayer sites increases the interlayer distance, allowing the intercalation of oxygen between the two CuO_2 planes and leading to a higher oxygen content.[17,18] The critical oxygen partial pressures during synthesis for producing superconductivity are 8 atm for $La_{1.82}Ca_{1.18}Cu_2O_y$ and 4 atm for $La_{1.82}Sr_{0.18}CaCu_2O_y$. It is of interest that the oxygen content of both compounds corresponds roughly to the stoichiometric value of 6 at these critical pressures and that a compound with a higher T_c has an excess of oxygen ($y=6+\delta$). Since an increase in oxygen content at a fixed amount of dopant x implies an increase in hole concentration, the increase in T_c with increasing P_{O_2} can be explained by an increase in hole concentration. The higher T_c of the Sr-doped compound synthesized under 10 and 50 atm O_2 may also be explained by the higher oxygen content, i.e., the higher hole concentration. The hole concentration per [CuO_2] is 0.09 for $y=6$ and 0.13 for $La_{1.82}Sr_{0.18}CaCu_2O_{6.04}$ synthesized under 400 atm O_2. These values are lower than the nominal value of 0.2 common to copper-oxide superconductors.[11] Therefore, overdoping of carriers is not attained at such doping level even if the oxygen content exceeds the stoichiometric value of 6.

The increase in T_c with x at a fixed P_{O_2} is also caused by an increase in the hole concentration within the CuO_2 planes, because the replacement of trivalent La atoms by divalent Ca or Sr atoms generates holes. However, the dependence of T_c on the composition is greater for the

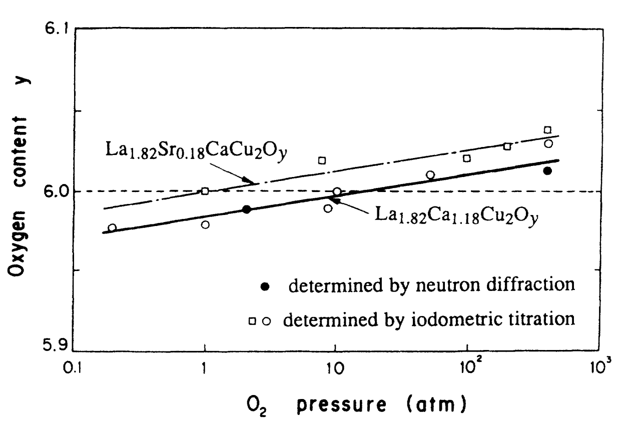

FIG. 6. Oxygen content in $La_{2-x}Ca_{1+x}Cu_2O_y$ and in $La_{2-x}Sr_xCaCu_2O_y$ as a function of oxygen partial pressure during synthesis. Symbol ● shows oxygen content determined by neutron diffraction (Ref. 10).

10- and 50-atm-O_2-synthesized samples than for the 400-atm-O_2-synthesized sample. This implies that T_c does not have linear relation with hole concentration: the derivative of T_c with respect to hole concentration will become small when T_c approaches the maximum.

In $La_{2-x}Sr_xCuO_4$, the maximum T_c is at about $x \approx 0.15$ and T_c decreases when x increases beyond that value.[19] However, the maximum T_c was not attained in the present systems $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ and $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$. This is because the solubility of Ca or Sr at La sites is limited by the present synthesis conditions. Synthesis at a higher oxygen partial pressure or at a lower temperature will be necessary to obtain Ca- or Sr-richer samples. Single-phase $La_{1.7}Ca_{1.3}Cu_2O_6$, whose T_c (onset) was reported to be around 70 K, was synthesized by applying a pressure of 6×10^4 atm, using $KClO_3$ as a source of oxygen.[20] The maximum T_c was reported at a composition of around $La_{1.6}Sr_{0.4}CaCu_2O_6$ with synthesis at a relatively low sintering temperature using $Ca(NO_3)_2$ and $Sr(NO_3)_2$ instead of $CaCO_3$ and $SrCO_3$ (Refs. 2 and 16). This corresponds to Sr doping of 0.2 and hence a hole concentration of 0.2 per CuO_2 layer. The T_c's were maximum for the stoichiometric oxygen content and were lower when the oxygen content exceeded 6 for such highly doped compounds.[16] This suggests that overdoping can also be attained by introducing excess oxygen at a very high doping level.

The bulk nature of superconductivity was confirmed by measuring Meissner effect for $La_{1.82}Ca_{1.18}Cu_2O_{6+\delta}$ (Fig. 7). Meissner signals were stronger for a higher P_{O_2}, and the sample synthesized under 400 atm O_2 showed a Meissner volume fraction of more than 20%.

Figure 8 shows the temperature dependence of the magnetic susceptibility for $La_{1.82}Ca_{1.18}Cu_2O_{6\pm\delta}$ synthesized under various P_{O_2} and annealing conditions. The susceptibility is not corrected for the paramagnetic Curie-Weiss contribution. A major feature in the data is the cusps in the magnetic susceptibility around 25 K for samples synthesized under 2 and 10 atm O_2 and for a sample annealed in air. These cusps may correspond to the three-dimensional (3D) antiferromagnetic long-range ordering as observed in $La_2CuO_{4-\delta}$ (Refs. 21–23). The falls in χ below 10 K may result from a trace amount of a superconducting phase. The sharp falls in χ around 20 K for the sample synthesized under 50 atm O_2 and around 50 K for the sample synthesized under 400 atm O_2 correspond to the onset of superconductivity. The magnetic susceptibility of the sample annealed in Ar is different from the rest of the samples: its value is smaller than the others and χ is minimum around 150 K, and an upturn of χ is observed for temperatures approaching 0 K. The χ of the Ar-annealed sample shows a paramagnetic character rather than an antiferromagnetic character.

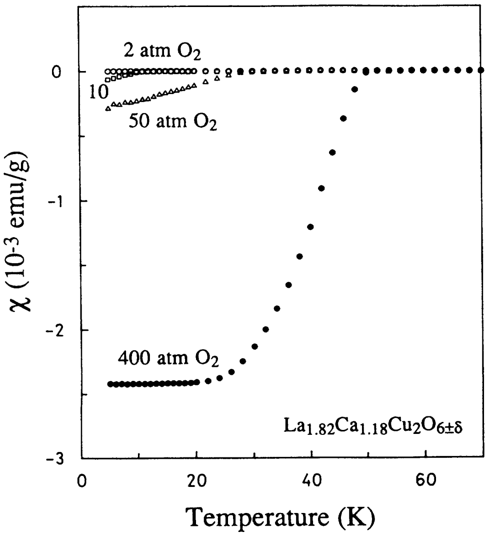

FIG. 7. Meissner signals for $La_{1.82}Ca_{1.18}Cu_2O_{6\pm\delta}$ synthesized under various oxygen partial pressures.

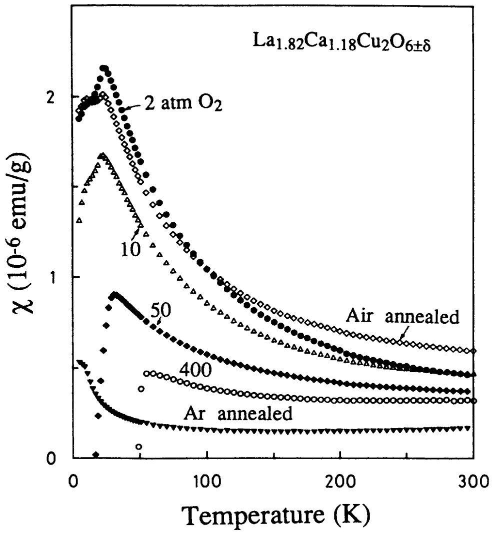

FIG. 8. Magnetic susceptibility vs temperature for $La_{1.82}Ca_{1.18}Cu_2O_{6\pm\delta}$ synthesized under various oxygen partial pressures.

If the susceptibilities are fitted to $\chi = \chi_0 + C/(T+\Theta)$, the sample synthesized under 2 atm O_2 gives $C = 7.27 \times 10^{-2}$ emu K/mol and $\Theta = 35$ K. Similarly, C and Θ can be derived for the rest of the samples (Table I).

TABLE I. Magnetic properties of $La_{1.82}Ca_{1.18}Cu_2O_{6\pm\delta}$ synthesized under different P_{O_2}.

Synthesis or annealing conditions	Curie constant[a] (10^{-2} emu K/mol)	Moment (μ_B)	Θ[a] (K)
Ar annealed	0.37	0.16	0
Air annealed	8.74	0.83	56
2 atm O_2	7.27	0.76	35
10 atm O_2	6.85	0.73	55
50 atm O_2	5.49	0.66	84
400 atm O_2	5.02	0.63	141

[a] Susceptibilities are fit to the form $\chi = \chi_0 + C/(T+\Theta)$.

Assuming that the Curie term is due solely to Cu, the effective Cu moment is calculated to be 0.76 μ_B for the 2-atm-O_2 sample. The effective Cu moments calculated in this way are also listed in Table I. Except for the small value of the Ar-annealed sample, the effective Cu moments are a little larger than those deduced from the magnetic susceptibility of $La_2CuO_{4-\delta}$, which are in the range of 0.2 to 0.6 μ_B.[21,22] They are also larger than those obtained from neutron scattering for $La_2CuO_{4-\delta}$.[24–26] Nevertheless, the moments are smaller than the calculated value of about 1 μ_B for Cu^{2+} ions with a Lande g factor of ≈ 2. The paramagnetic nature of the Ar-annealed sample may be due to the presence of isolated Cu^{2+} ions which are caused by oxygen defects around Cu. If so, we can estimate the contribution of such isolated impurities to the effective Cu moment. It may be in the range between 0.1 and 0.2 μ_B judging from the 0.16 μ_B effective Cu moment of the Ar-annealed sample (Table I). Then, the net effective Cu moments in $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ compounds can be regarded as 0.4–0.6 μ_B if we subtract the moments of isolated Cu^{2+} ions. This is on the same order as those of $La_2CuO_{4-\delta}$ obtained by magnetic measurements or by neutron-scattering experiments. Therefore, the larger moments in $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ than in $La_2CuO_{4-\delta}$ may result from trace amounts of isolated Cu^{2+} ions.

Positive Θ values for all of the samples except the Ar-annealed sample show that the magnetic interaction is antiferromagnetic. The presence of magnetic ordering in nonsuperconducting and weakly superconducting $La_{1.82}Ca_{1.18}(Cu_{0.99}Fe_{0.01})_2O_{6\pm\delta}$ synthesized under 2 and 50 atm O_2 and the frustration of magnetic ordering in superconducting $La_{1.82}Ca_{1.18}(Cu_{0.99}Fe_{0.01})_2O_{6\pm\delta}$ synthesized under 400 atm O_2 have been observed by measuring the Mössbauer effect using ^{57}Fe (Ref. 27). Quasistatic magnetic order is also revealed by the muon spin resonance (μ^+SR) of $La_{1.9}Ca_{1.1}Cu_2O_6$ synthesized in air, whose T_N is reported to be about 20 K.[28] Therefore, we conclude that the χ peaks are caused by the antiferromagnetic transition.

Another striking feature in the χ data is a weak dependence of the Néel temperature T_N on the oxygen partial pressure during synthesis. Assuming that the cusps in χ correspond to T_N, the T_N of about 25 K was almost independent of P_{O_2} between 0.2 and 10 atm. This is in contrast to $La_2CuO_{4-\delta}$, whose T_N is greatly sensitive to annealing conditions and hence to the oxygen deficiency δ (T_N changes from ≈ 300 K for $\delta \approx 0.03$ to ≈ 0 K for $\delta \approx 0$).[21,29]

A similar temperature dependence of χ for $La_{1.82}Ca_{1.18}Cu_2O_{6-\delta}$ annealed in Ar has been reported for hydrogenated $La_{1.9}Ca_{1.1}Cu_2O_6H_x$ with $0.16 \le x \le 0.48$,[30] and long-range antiferromagnetic ordering has been observed in these hydrogenated samples by μ^+SR at room temperature.[28] Therefore, the minimum χ of around 150 K and a positive temperature coefficient from 150 to 300 K for Ar-annealed $La_{1.82}Ca_{1.18}Cu_2O_{6-\delta}$ imply that a peak exists above 300 K where χ was not measured, and that T_N is higher than 300 K.

Figure 9 shows the temperature dependence of the magnetic susceptibility for the series of Ca-doped compounds with various compositions. Samples with x smaller than 0.12 were synthesized in air, and samples with x larger than 0.18 were synthesized under 2 atm O_2 and annealed in air at 1000 °C for 50 h. All samples show peaks at around 30 K, indicating that T_N is also not sensitive to composition. This is also in strong contrast to the $La_{2-x}Sr_xCuO_4$ system, whose T_N is very sensitive to Sr concentration. From the magnetic susceptibility measurements on the $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ series samples, T_N is determined to be about 20 K, and is also not sensitive to P_{O_2} or composition. This weak dependence of T_N on oxygen pressure and on composition means that antiferromagnetism is more stable in $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ and in $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ than in $La_2CuO_{4-\delta}$. These might explain the difficulty in obtaining "2126" superconducting compounds.

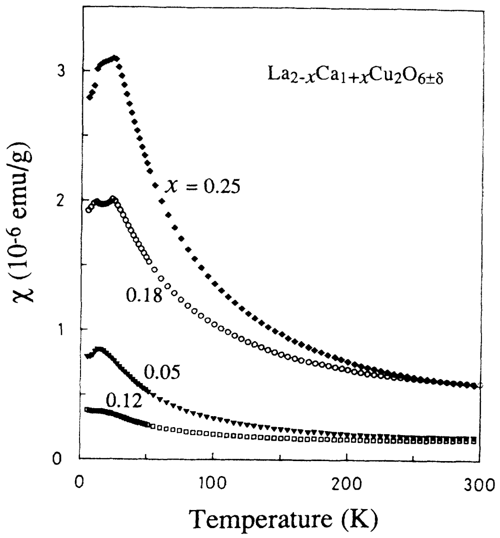

FIG. 9. Magnetic susceptibility vs temperature for $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ synthesized in air or annealed in air.

As shown in Figs. 1 and 2, even the nonsuperconducting $La_{2-x}Ca_{1+x}Cu_2O_{6-\delta}$ shows metallic behavior in its temperature dependence of electrical resistivity from room temperature down to about 100 K, and the values are almost the same for superconductors and nonsuperconductors in the same temperature range. Such a feature in electrical resistivity might correlate to the low Néel temperatures in the $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ system (about 25 K) and the insensitivity of T_N to the synthesis conditions and composition.

In the La_2CuO_4 system, weak ferromagnetism is observed in addition to antiferromagnetic spin correlations.[31] This is because the spins do not lie exactly in the CuO_2 plane, but are canted out of the plane at a small angle. Below the critical magnetic field (H_c), the net moment becomes zero due to canting in opposite directions, but a net moment appears above H_c because the canting is only in one direction. To check whether or not the "2126" compounds have hidden ferromagnetism, we measured the magnetic moment for $La_{1.82}Ca_{1.18}Cu_2O_{5.99}$

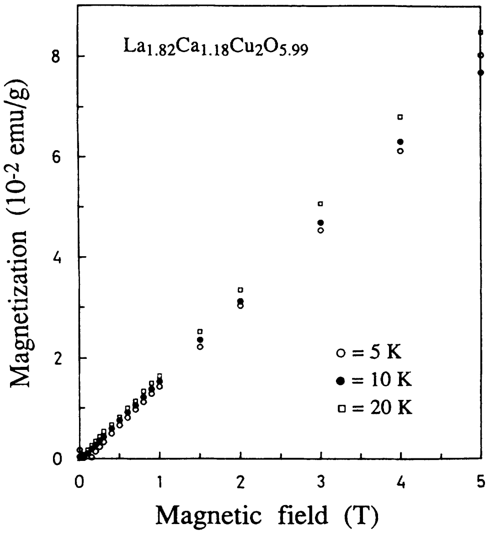

FIG. 10. Magnetic moment for $La_{1.82}Ca_{1.18}Cu_2O_{5.99}$ synthesized under 2 atm O_2 at temperatures of 5,10, and 20 K.

synthesized under 2 atm O_2, which has a T_N of around 25 K. As shown in Fig. 10, no ferromagnetic contribution to the moment was observed at magnetic fields up to 5 T. This is natural because the spin canting caused by the rotation of the CuO_6 octahedron will not occur in two-layered "2126" compounds, in which a CuO_2 planar network is formed by vertex sharing of CuO_5 pyramids.

The appearance and disappearance of antiferromagnetism, and the appearance of superconductivity in "2126" compounds, can be understood in the same way as in the La_2CuO_4 system. The two-dimensional (2D) Cu^{2+}-Cu^{2+} spin correlations within CuO_2 planes develop into 3D long-range antiferromagnetic ordering as a result of interaction between planes. When carriers are doped on the CuO_2 plane, the Cu^{2+}-Cu^{2+} spin-correlation length decreases and antiferromagnetic order is frustrated.[12,32] Another origin of frustration of 3D long-range antiferromagnetic order in "2126" compounds can also be explained by the fact that interstitial oxygen atoms intercalated between two CuO_2 planes destroy the 3D long-range antiferromagnetic correlations by bridging the CuO_2 planes.[10] Since magnetic ordering breaks down only in superconductors, we can conclude that superconductivity appears as a result of the frustration of 3D antiferromagnetic spin correlations in the two-CuO_2-layered "2126" compounds as with other copper oxide superconductors.

CONCLUSIONS

We have examined the resistive and magnetic properties of superconducting and nonsuperconducting $La_{2-x}Ca_{1+x}Cu_2O_{6\pm\delta}$ $(0.08 \le x \le 0.25)$, and $La_{2-x}Sr_xCaCu_2O_{6\pm\delta}$ $(0.07 \le x \le 0.23)$, as functions of composition (x) and the oxygen partial pressure during synthesis (P_{O_2}, up to 400 atm). The superconducting transition temperatures (T_c) increased with an increase in x and P_{O_2} for both compounds. The maximum T_c (onset) and T_c (zero) (about 60 and 51 K) were almost the same for $La_{1.75}Ca_{1.25}Cu_2O_6$ and $La_{1.77}Sr_{0.23}CaCu_2O_6$ synthesized under 400 atm O_2. Although the maximum solubility of Ca or Sr in La increased with increasing P_{O_2}, the maximum value of x, about 0.25, was the highest possible with P_{O_2} up to 400 atm. Antiferromagnetic 3D ordering was observed in nonsuperconducting or weakly superconducting compounds of Ca- or Sr-doped $La_{2-x}(Ca,Sr)_xCaCu_2O_{6\pm\delta}$ synthesized under an oxygen pressure between 0.2 and 10 atm, and an antiferromagnetic ordering was not observed in the superconductors. It can be concluded that in two-CuO_2-layered "2126" compounds the superconducting phase adjoins the antiferromagnetic phase, similar to most high-T_c cuprates. However, the dependence of T_N on P_{O_2} or the composition (x) is greatly different from other high-T_c cuprates.

ACKNOWLEDGMENT

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