Substitution of 3d metals for Cu in $Bi_2(Sr_{0.6}Ca_{0.4})_3Cu_2O_y$

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The effect of the substitution of 3d metals (Fe, Co, Ni, and Zn) for Cu in a high-temperature superconductor $Bi_2(Sr,Ca)_3Cu_2O_y$ was investigated by measuring lattice constants, dc resistivity, Hall effect, and magnetic susceptibilities in normal and superconducting phases. For all kinds of impurities, within the composition range where the single-phase samples are synthesized, the superconducting transition temperature T_c was found to decrease with increasing impurity concentration. Even nonmagnetic Zn was found to decrease T_c, as well as, magnetic Fe, Co, and Ni, without changing the hole concentration. These behaviors cannot be explained by the Abrikosov-Gorkov theory for conventional BCS superconductors. Possible explanations are discussed.

I. INTRODUCTION

In the copper-oxide-based superconductors, many studies have been done on the effect of the substitution by impurities on the physical properties.[1] In particular, the substitution of 3d metals for Cu is expected to provide important information on the pairing mechanism of high-temperature superconductivity. For instance, by the substitution of Fe for 5% of Cu in $LBa_2Cu_3O_y$ system (L=Y or some of the lanthanides, hereafter we shall call them 1:2:3 compounds), the superconducting transition temperature decreases by 40 K.[2] Other 3d metals decrease T_c by almost the same magnitude.[3] Furthermore, the substitution of Zn, which has the closed d shell, decreases T_c the most. Thus, it is expected that an unusual mechanism for the pairing may exist in high-T_c Cu oxides.

However, the substitution in 1:2:3 compounds induces a large change of the carrier density,[4] which is most probably due to the existence of the CuO chain.[5] Furthermore, the existence of two kinds of Cu sites[5] makes the problem much more complicated. Thus, it still remains an open question of whether the effect of the impurity, that is, the pair breaking by magnetic[6] or nonmagnetic impurities,[7] exists in high-T_c superconductors or not.

$Bi_2(Sr,Ca)_3Cu_2O_y$ (Ref. 8) (hereafter we shall call it the Bi-Sr-Ca 2:2:1:2 phase) is another material which shows superconductivity above liquid-nitrogen temperature. This material has only one kind of Cu site,[9] and the oxygen deficiency during a heat cycle is very small. Thus, it is expected that the Bi-Sr-Ca system is a more appropriate candidate for the study of substitution experiments in the Cu site. In this paper, we shall present the results of the experiments on the effect of the substitution of 3d metals for Cu in the Bi-Sr-Ca 2:2:1:2 phase (T_c=80-K phase). For all kinds of impurities, within the composition range where the single-phase samples are synthesized, the superconducting transition temperature T_c was found to decrease with increasing impurity concentration. Even nonmagnetic Zn was found to decrease T_c as well as magnetic Fe, Co, and Ni without changing the hole concentration. Possible explanations on these results are presented.

II. EXPERIMENTS

In previous work[10] it was revealed that the superconducting 80-K phase Bi-Sr-Ca-Cu-O system can be obtained most easily at $z=0.4$ in $Bi_2(Sr_{1-z}Ca_z)_3Cu_2O_y$ solid solution. Therefore, we adopted $Bi_2(Sr_{0.6}Ca_{0.4})_3Cu_2O_y$ as the basic material for the substitution. The samples of $Bi_2(Sr_{0.6}Ca_{0.4})_3(Cu_{1-x}M_x)_2O_y$ (M=Fe, Co, Ni, or Zn) were prepared by conventional solid-state reaction methods from Bi_2O_3, $SrCO_3$, $CaCO_3$, and Fe_2O_3 (or CoO, NiO, and ZnO) powders (purity 99.99%). Typical preparation conditions were calcination at 820 °C for 12 h, sintering at 860 °C for 12 h, and slow cooling in a furnace.

The samples obtained were characterized by x-ray powder diffraction, the scanning-electron-microscope–electron-probe-microanalysis (SEM-EPMA) method, magnetic-susceptibility measurements, and resistivity measurements. The Hall coefficient was also measured for these samples. For the resisitivity measurements and Hall-coefficient measurements under the magnetic field of 1.8 T, electrical contacts were made by Dupont 6500 silver paste.

III. EXPERIMENTAL RESULTS

Figure 1 shows the lattice constants of Fe-doped and Co-doped samples determined by the powder x-ray diffraction method. Up to $x=0.06$–0.08 for Fe doping, 0.10 for Co doping, 0.015 for Zn doping, and 0.02 for Ni doping, all peaks can be indexed with the 2:2:1:2 phase of Bi-Sr-Ca compounds. When x exceeds these values, diffraction peaks of the impurity phases appear. As is shown in Fig. 1, the c parameter decreases very slightly with increasing x. Thus, it is expected that the oxygen content increases with increasing x. However, what is important is the concentration of mobile holes, which can be monitored by the Hall coefficient. The result of the

Hall-coefficient measurements will be given later.

Here it should be noted that the crystal structure does not change by the doping of impurities. Since the impurity concentration of the current interest is very small, it is almost impossible to decide the precise impurity dopant concentrations even by the SEM-EPMA method. However, the SEM-EPMA observation of these samples showed that there is almost no separation of other phases at the grain boundaries for the samples whose x-ray diffraction patterns showed no impurities. This demonstrates that the impurities are uniformly doped into crystals.

Figure 2 shows the magnetic susceptibility of $Bi_2(Sr_{0.6}Ca_{0.4})_3$ $(Cu_{1-x}Fe_x)_2O_y$ below and near T_c. It shows that the transition temperature T_c (defined by the temperature at which the Meissner signal begins to appear) decreases progressively with x, and the absolute value of the Meissner signal also decreases. The Meissner signal of the sample with $x=0.10$ shows almost the same behavior as that of the sample with $x=0.08$ and has the same T_c. This corresponds to the fact that the samples

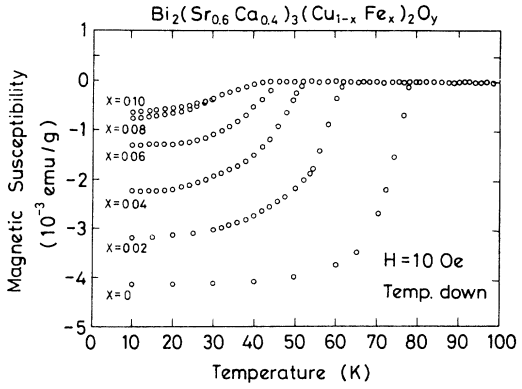


FIG. 2. The Meissner effect of the Fe-doped Bi-Sr-Ca 2:2:1:2 samples.

with x larger than 0.08 cannot be single phase. In the same manner, it was revealed that single-phase samples can be obtained up to $x=0.10$ for Co, $x=0.02$ for Ni, and $x=0.015$ for Zn.

Figure 3 shows the temperature dependence of the resistivity of the Fe-doped samples. Every sample shows the T linear dependence characteristic of Cu-oxide-based superconductors,[1] and the resistivity increases with increasing x. On the other hand, the transition temperature decreases with increasing x up to 8%. With further increasing x, T_c ceases to change. This corresponds to the change in the Meissner effect as a function of the Fe composition, and is also consistent with the result of the powder x-ray diffraction. Thus, it can be said that the superconducting transition temperature decreases by the doping within the compositional range where the single-phase samples can be synthesized in the Bi-Sr-Ca 2:2:1:2 system. In Fig. 3, the magnitude of the resistivity continued to increase in the compositional range where T_c ceases to depend on the impurity concentration. Thus, the increase of the resistivity in the normal state is likely

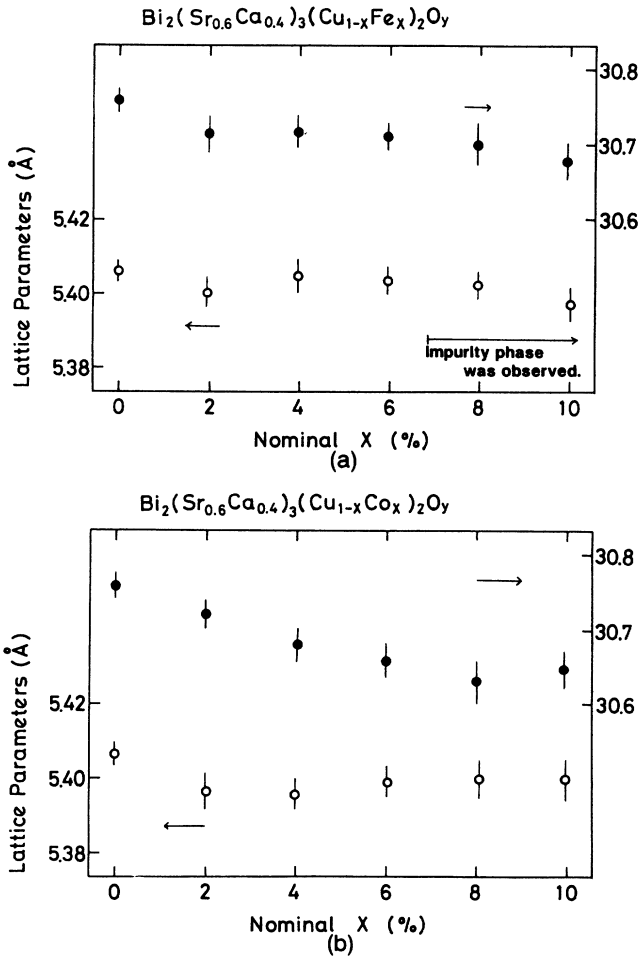


FIG. 1. The lattice parameters of (a) Fe-doped and (b) Co-doped Bi-Sr-Ca 2:2:1:2 samples determined by the powder x-ray diffraction method. Open and solid circles represent the a and c axes, respectively.

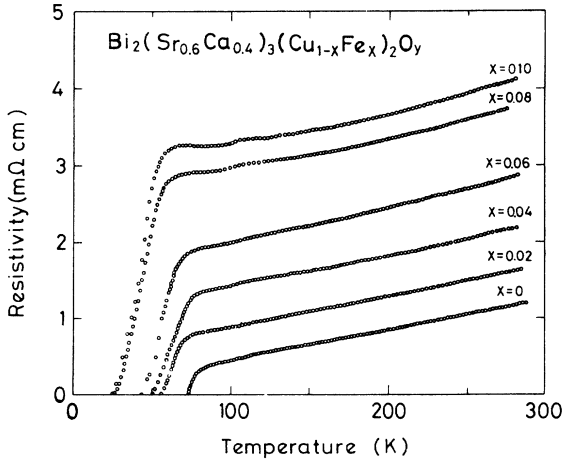


FIG. 3. The temperature dependence of the dc resistivity of the Fe-doped Bi-Sr-Ca 2:2:1:2 samples.

to be due to grain boundaries. Almost the same behaviors were observed in the case of Co, Ni, and Zn doping. We also tried the Ga substitution. However, in this case, Ga did not substitute at all.

Figure 4 shows the superconducting transition temperature T_c versus x for the samples doped with Fe, Co, Ni, and Zn. As was mentioned above, within the composition range where the single-phase samples were obtained, T_c decreases with increasing x. On the other hand, in the range of x where the single-phase sample cannot be obtained, T_c ceases to change with increasing x. Thus, the decrease of T_c seems to be caused by the substitution of the $3d$ atoms. For comparison, we also prepared the Cu-deficient samples $Bi_2(Sr_{0.6}Ca_{0.4})_3$ $(Cu_{1-x}\square_x)_2O_y$ ($\square$=Cu vacancy). In this case, T_c changes only very slightly. This strongly suggests that the change of T_c is not due to the deficiency of Cu but really due to the substitution of $3d$ metals for Cu. It should be also stressed that the substitution of Zn, which has a closed d shell, also decreases T_c as well as Fe, Co, and Ni.

Figure 5(a) shows the magnetic susceptibility in $Bi_2(Sr_{0.6}Ca_{0.4})_3(Cu_{1-x}Co_x)_2O_y$ in the normal state. It clearly shows the existence of local magnetic moments. A small kink observed in $x=0.02$ and 0.04 samples is due to the Meissner effect by the very small amount of the 2:2:2:3 phase, which was not detected by other methods of characterization. With increasing x, the Curie-like component increases monotonically. Thus, it is clear that the local moments are due to the Co ions substituted in the Cu site of Bi-Sr-Ca.

We assume that the susceptibility $\chi(T)$ can be expressed as

$$\chi(T)=\chi_0+C/T\ , \tag{3.1}$$

$$C=Np_{\text{eff}}^2\mu_B^2/(3k_B)\ , \tag{3.2}$$

where χ_0 is the temperature-independent term, N is the number density of the impurity atoms. In the Bi-Sr-Ca 2:2:1:2 system, even the susceptibility of undoped materials shows complicated temperature dependence.[10,11] However, when seen in the scale of current interest, we can regard the susceptibility of undoped material almost independent of temperature. Figure 5(b) shows the inverse of the susceptibility as a function of the temperature, together with curves obtained by the fitting to Eq. (3.1).

Figure 6 shows the obtained Curie constants for Fe-doped and Co-doped samples. From the gradient of this plot, we obtained the effective numbers of the Bohr magneton $p_{\text{eff}}=3.6$ for both Fe and Co in the single-phase samples. It is a delicate problem to determine the spin state of the doped impurities from the experimentally obtained p_{eff}. Thus, in the present experiment we cannot definitely understand the magnetic states of Fe and Ni. What is definite from the result of Fig. 6 is that Fe and Co are substituted magnetically for Cu.

For Ni-doped samples, as is shown in Fig. 7(a), susceptibility increases with increasing impurity concentration up to the critical value of x above which the single-phase sample cannot be obtained. However, the x region of the single phase is limited too much to obtain p_{eff}. On the other hand, the effect of the Zn substitution is quite

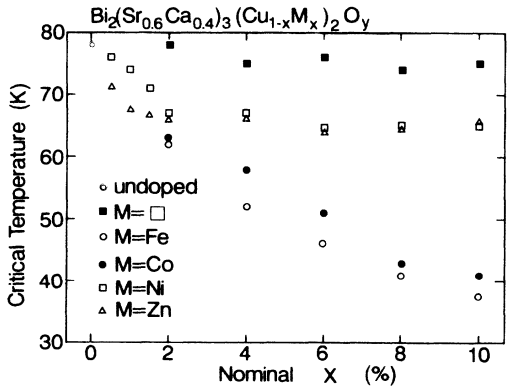


FIG. 4. The superconducting transition temperature T_c as a function of the impurity concentration for Fe-, Co-, Ni-, and Zn-doped samples. The result for the samples with nominally Cu-deficient composition are also included.

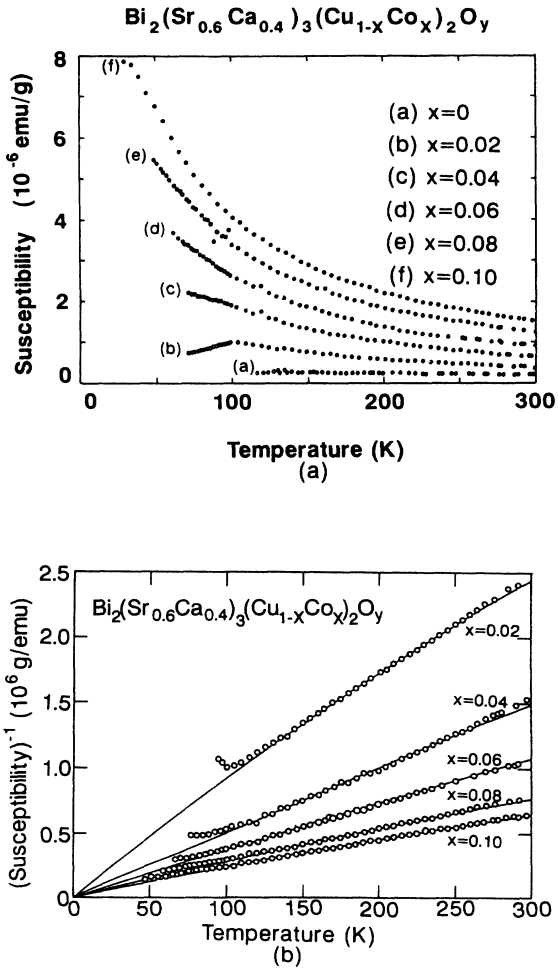


FIG. 5. (a) Magnetic susceptibility in the normal state for the Co-doped Bi-Sr-Ca 2:2:1:2 samples. (b) The inverse of the magnetic susceptibility of the same sample as a function of temperature, together with the fitting curve to Eq. (3.1).

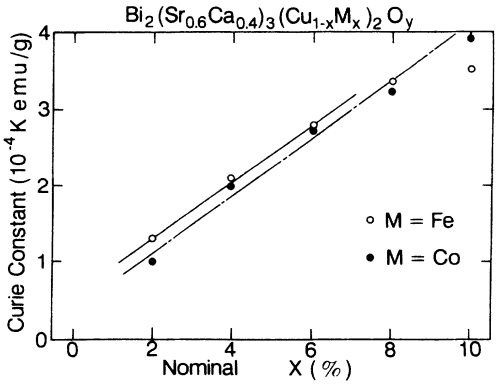
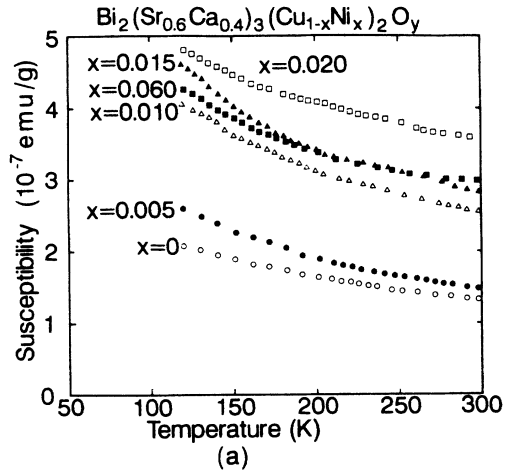


FIG. 6. The Curie constants as a function of the impurity concentration for Fe-doped and Co-doped samples. The solid line and the dashed-solid line are for Fe-doped and Co-doped samples, respectively.

different from others. As is shown in Fig. 7(b), with the Zn substitution the normal-state susceptibility barely changes and, rather, it tends to decrease with x in the x region of single-phase samples. Therefore, we can conclude that the substituted Fe, Co, and Ni atoms really



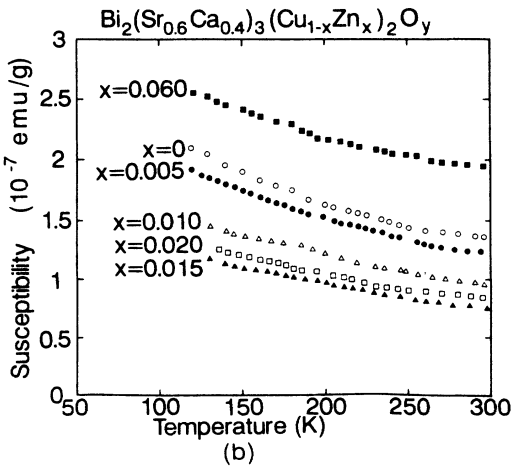


FIG. 7. Magnetic susceptibility in the normal state for (a) Ni-doped and (b) for Zn-doped Bi-Sr-Ca 2:2:1:2 samples.

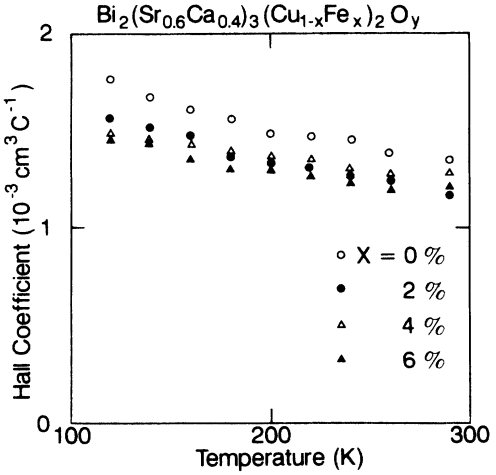


FIG. 8. The temperature dependence of the Hall coefficient of the Fe-doped Bi-Sr-Ca 2:2:1:2 samples.

have localized magnetic moment and the Zn ion is nonmagnetic in $Bi_2(Sr_{0.6}Ca_{0.4})_3(Cu_{1-x}M_x)_2O_y$. Thus, the results in Figs. 4, 5, and 7 clearly show that the decrease of T_c by the substitution is almost the same for impurities with magnetic moments and for those without magnetic moments. This is highly unusual in terms of the ordinary Abrikosov-Gorkov (AG) theory developed for conventional Bardeen-Cooper-Schrieffer (BCS) superconductors.[6]

Figure 8 shows the temperature dependence of the Hall coefficient R_H in $Bi_2(Sr_{0.6}Ca_{0.4})_3(Cu_{1-x}Fe_x)_2O_y$. The change of R_H with x is very small and much smaller than that in the case of the 1:2:3 compounds,[4] and also than that in the L substituted Bi-Sr-Ca.[11-13] This is shown more clearly in Fig. 9, where R_H at 300 K is drawn as a function of the impurity concentration for Fe-doped and Co-doped samples. Within the experimental error, R_H does not depend on the impurity concentration. It was also found that this applies to the substitution of Ni and Zn (not shown as a figure). In the case of Ni and Zn doping where T_c decreases by 15 K, they were substituted up

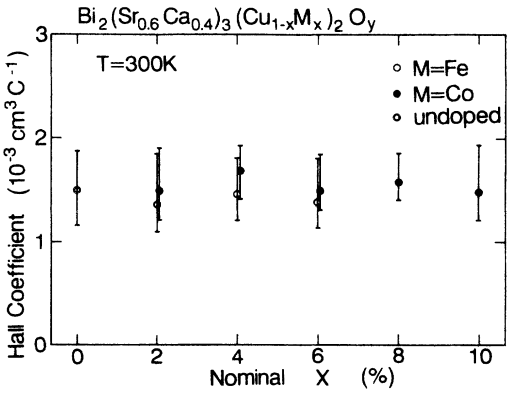


FIG. 9. The Hall coefficient as a function of the impurity concentration for the Fe-doped and Co-doped samples.

to only 1.5–2.0%. Thus, there may remain a suspicion that the change in R_H was not detected in this experiment. In the case of the L substitution for the 2:2:1:2 system, R_H at room temperature changes from 1.4×10^{-3} cm^3/C to 2.4×10^{-3} cm^3/C, when T_c changes from 80 to 65 K.[13] If the change in T_c was caused mainly by the change in the hole concentration, R_H should change in almost the same amount, which can be detected in the present experimental precision. However, the present experimental result shows that the change in R_H (if there is one) is much smaller than this value. Thus, we can say that R_H is also unchanged by Ni and Zn doping. Empirically, in the Bi 2:2:1:2 system the inverse of the Hall coefficient roughly scales with the hole concentration.[13] Thus, we can regard the Hall coefficient as a barometer of the hole concentration. Then, the present result demonstrates that the carrier number does not change with the substitution.

IV. DISCUSSION

The above results clearly show that 3*d* impurities were certainly substituted for Cu without changing the crystal structure. From the magnetic susceptibility measurement in the normal state, Fe, Co, and Ni are found to be magnetic when substituted in the sample, whereas Zn was confirmed to be nonmagnetic. For all kinds of impurities that were investigated, within the compositional range where single-phase samples were synthesized, the superconducting transition temperature T_c was found to decrease with increasing impurity concentration. From the Hall-coefficient measurements, however, the hole concentration was found to be unchanged by the doping. On the other hand, the doping of Y, Lu, or Tm changes R_H by a factor of 2 when T_c decreases from 80 to 40 K.[11–14] As was already pointed out above, in the 1:2:3 compounds, substitution induces a large change in carrier density in many cases. In particular, substitution of Zn, which is nonmagnetic, drastically decreases T_c, which is associated with the large increase of the carrier number.[4,15] Therefore, we cannot tell whether the decrease of T_c is the direct effect of the substitution or is caused indirectly through the change of the carrier density. To our knowledge, there is only one exception, the doping of Ni.[16] Ni is thought to be substituted for Cu on the CuO_2 plane in the 1:2:3 compounds.[17] By the doping of Ni up to 10%, T_c decreases from 92 to 60 K, whereas the Hall coefficient remained unchanged with 1.1×10^{-3} cm^3/C at 100 K. Based on this result, Clayhold *et al.*[16] concluded that the origin of the decrease in T_c caused by Ni doping in the 1:2:3 compounds is different from that caused by other impurities like Co, which is substituted in the CuO chain and induces a large change in R_H. The present experiment shows very clearly that the decrease of the T_c in the Bi-Sr-Ca 2:2:1:2 system caused by the doping of 3*d* impurities is a direct effect of the impurities. In other words, T_c decreases by the pair-breaking effect due to magnetic and nonmagnetic impurities.

The experimental results of the magnetic susceptibility in the normal state clearly shows that the magnetic states are different between the two groups (Fe, Co, Ni) and Zn. On the other hand, the decrease of T_c with the substitution is almost the same between the two groups in the single-phase regions. This may exclude the possibility that the decrease of T_c is caused by the simple magnetic impurity effect proposed by Abrikosov and Gorkov[6] for the BCS-type superconductors. From these arguments, it can be said that the conventional AG theory does not apply to high-T_c superconductors. This may indicate that the pairing mechanism of the high-T_c superconductor is fairly different from the conventional one.

Here it should be noted that the magnitude of the Meissner signal decreases with decreasing T_c. Nakamichi *et al.*[18] showed that this is not due to the local destruction of superconductivity around the doped impurities. According to their NMR and Mössbauer experiments, the doped impurity is considered to strongly affect the antiferromagnetic spin correlations. It has been established that the superconducting phase of high-T_c superconductor is located close to the antiferromagnetically ordered phase.[1] Even in the sample exhibiting superconductivity, the large-scale spin fluctuation was observed in the normal state.[19] If we assume that the attractive interaction is mediated by the magnetic fluctuation, we can imagine that the doping of the impurity with magnetically different spin configurations may strongly affect the pairing interaction, irrespective of whether the doped impurities are magnetic or nonmagnetic. However, if this is the case, it may be expected that the magnetic moment increases, even for the Zn doping, because the fluctuation of Cu spins is expected to be suppressed. However, the present experimental result is in sharp contrast to the expectation from the simple discussion above. It should also be noted that in Fe-doped and Co-doped samples the magnetic moment is thought to be due to the doped ions, as was already discussed. Thus, the simple idea of the suppression of the spin fluctuation between Cu spins seems to be unable to explain the decrease of T_c.

In conventional BCS superconductors, the randomness of the periodic potential is known to affect the superconductivity as a result of the higher-order interaction.[7] This kind of decrease in T_c should also be examined theoretically for oxide superconductors, as is already begun by Coffey and Cox.[20]

Nothing has been mentioned above on the effect of 3*d*-metal substitution in the $(La,Sr)_2CuO_4$ system (2:1:4 system) because of the absence of the comprehensive study on the physical properties. In the early work by Hasegawa *et al.*[21] and by Tarascon *et al.*,[22] it was found that T_c also decreases by the doping of Zn in this system. Park *et al.*[23] reported that the Hall coefficient remained constant with increasing impurity concentration for Fe, Co, and Zn. All of these are similar to the results reported above. However, the normal susceptibility was reported to increase even for Zn doping,[22] which is different from the present experimental result in the Bi-Sr-Ca 2:2:1:2 system. Further studies are necessary to resolve this controversy.

At present, the detailed mechanism of the suppression of T_c in the present experiment is quite puzzling. Phenomenologically, however, it can be said that there are

three routes to change T_c in Bi-Sr-Ca system. One is the T_c change with the change of the number of CuO_2 sheets. In this case, "the plasma frequency" in the infrared reflection spectrum increases with the increasing number of CuO_2 sheets.[13,24] The second case is the change in T_c with the change of the hole concentration. In this case, the Hall coefficient changes, whereas "the plasma frequency" does not change.[13,24] In the third case, which is the present case, neither the plasma frequency nor the hole concentration changes. Thus, it can be said that the decrease of T_c observed in this study is due to the effect of the impurity. In this sense, the Bi-Sr-Ca 2:2:1:2 system is much more appropriate than the 1:2:3 compounds for the study of the effect of the impurities in the CuO_2 plane.

V. CONCLUSION

The effect of the substitution of 3d metals (Fe, Co, Ni, and Zn) for Cu was investigated for the Bi-Sr-Ca 2:2:1:2 system. For all kinds of impurities, within the composition range where the single-phase samples were synthesized, the superconducting transition temperature T_c was found to decrease with increasing impurity concentration. Even nonmagnetic Zn was found to decrease T_c as well as magnetic Fe, Co, and Ni, without changing the hole concentration. These features are quite different from those expected by the conventional AG theory. Thus, this may indicate that the pairing mechanism in cuprate superconductors is quite different from those in conventional BCS superconductors.

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[1]For example, *Physical Properties of High-Temperature Superconductors I,* edited by D. M. Ginsberg (World-Scientific, Singapore, 1989).

[2]Y. Maeno, M. Kato, Y. Aoki, and T. Fujita, Jpn. J. Appl. Phys. **26**, L1982 (1987).

[3]Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. Aoki, K. Hoshino, A. Minami, and T. Fujita, Nature (London) **328**, 512 (1987).

[4]N. Okazaki, S. Kambe, A. Kishi, N. Kanazawa, A. Ohtomo, A. Fukuoka, T. Hasegawa, K. Kishio, K. Kitazawa, and K. Fueki, Proceedings of the 1988 MRS International Meeting on Advanced Materials, Tokyo, 1988, edited by K. Tachikawa and K. Kitazawa (unpublished).

[5]F. Izumi, H. Asano, T. Ishigaki, E. Takayama-Muromachi, Y. Uchida, N. Watanabe, and T. Nishikawa, Jpn. J. Appl. Phys. **26**, L649 (1987).

[6]A. A. Abrikosov and L. P. Gorkov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1961) [Sov. Phys.—JETP **12**, 1243 (1961)].

[7]S. Maekawa and H. Fukuyama, J. Phys. Soc. Jpn. **51**, 1380 (1982).

[8]H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. **27**, L209 (1988).

[9]J. M. Tarascon, Y. LePage, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Huang, Phys. Rev. B **37**, 9382 (1988).

[10]A. Maeda, T. Yabe, H. Ikuta, Y. Nakayama, T. Wada, S. Okuda, T. Itoh, M. Izumi, S. Uchida, K. Uchinokura, and S. Tanaka, Jpn. J. Appl. Phys. **28**, L112 (1988).

[11]T. Tamegai, K. Koga, K. Suzuki, M. Ichihara, F. Sakai, and Y. Iye, Jpn. J. Appl. Phys. **28**, L1112 (1989).

[12]J. Clayhold, S. J. Hagen, N. P. Ong, J. M. Tarascon, and P. Barboux, Phys. Rev. B **39**, 7320 (1989).

[13]A. Maeda, M. Hase, I. Tsukada, S. Takebayashi, K. Noda, and K. Uchinokura, Phys. Rev. B (to be published).

[14]Y. Koike, Y. Iwabuchi, S. Hosoya, N. Kobayashi, and T. Fukase, Physica C **159**, 105 (1989).

[15]M. W. Shafer, T. Penney, B. L. Olson, R. L. Greene, and P. H. Koch, Phys. Rev. B **39**, 2914 (1989).

[16]K. Clayhold, S. Hagen, Z. Z. Wang, N. P. Ong, J. M. Tarascon, and P. Barboux, Phys. Rev. B **39**, 777 (1989).

[17]T. Kajitani, K. Kusaba, M. Kikuchi, Y. Shono, and M. Hirabayashi, Jpn. J. Appl. Phys. **27**, L354 (1988).

[18]Y. Nakamichi, K. Kumagai, H. Nakajima, and T. Fujita, Physica C **162-164**, 185 (1989).

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

[20]L. Coffey and D. L. Cox, Phys. Rev. B **37**, 3389 (1988).

[21]T. Hasegawa, K. Kishio, M. Aoki, N. Ooba, K. Kitazawa, K. Fueki, S. Uchida, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L337 (1987).

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

[23]K. Park, S. Kambe, N. Ooba, N. Okazaki, T. Hasegawa, K. Kishio, and K. Kitazawa (unpublished).

[24]A. Maeda, K. Noda, S. Takebayashi, and K. Uchinokura, Physica C **162-164**, 1205 (1989).