Oxygen-loss effects on superconductivity of $Bi_2Sr_2CaCu_2O_y$ system

M. Nagoshi and T. Suzuki*

Steel Research Center, NKK Corporation, Kawasaki 210, Japan

Y. Fukuda, K. Terashima,† and Y. Nakanishi

Research Institute of Electronics, Shizuoka University, Hamamatsu 432, Japan

M. Ogita

College of Engineering, Shizuoka University, Hamamatsu 432, Japan

A. Tokiwa, Y. Syono, and M. Tachiki

Institute for Materials Research, Tohoku University, Sendai 980, Japan

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The properties of $Bi_2Sr_2CaCu_2O_y$ annealed at 200–650 °C in vacuum (10^{-4} Pa) are studied by x-ray powder diffraction, ac magnetization, and Hall measurement. The amount of oxygen loss, Δy, was obtained by an integration of the oxygen partial pressure measured by a quadrupole mass spectrometer. The T_c increases from 65 to 92 K, which is accompanied by a small amount of oxygen loss (on the order of 10^{-3}). The a and c axes are extended by the oxygen loss. The change of the hole concentration estimated by Hall measurement is of the same order of magnitude as that for the other superconducting oxides against the change of T_c, however, it is larger by about two orders of magnitude than that expected from the oxygen loss. This discrepancy suggests charge redistribution in the structure.

I. INTRODUCTION

It is one of the most interesting and important studies to elucidate the relationship between carrier concentration and superconductivity. This is unavoidable for understanding the mechanism of high-T_c superconductivity and also for materials designs. For these purposes, the relationship between oxygen content and T_c has recently been studied for various superconducting oxides. It has been reported that T_c is sensitive to oxygen content not only for $YBa_2Cu_3O_{7-\delta}$,[1] but also for $La_{2-x}Sr_xCuO_{4-\delta}$ (Refs. 2 and 3) and Tl systems.[4,5]

Also for $Bi_2Sr_2CaCu_2O_y$, the correlation between oxygen content and T_c was reported by Buckley et al.[6] and has been discussed from the point of the hole concentration on $Cu-O_2$ planes by some groups.[6-13] These investigations show that T_c depends strongly on oxygen content; that is, T_c increases with decreasing in oxygen content in this system. But the amount of oxygen loss Δy for giving maximum T_c is still controversial. Buckley et al.[6] and Morris et al.[8] reported that the Δy estimated by weight loss is about 0.4. By the same method, Zhao and co-workers[10,13] and Imai and Matsuba[11] resulted that the Δy is about 0.1 and 0.05, respectively. In contrast to their results, Groen and de Leeuw[9] reported that the Δy is too small to be measured by the thermogravimetric method. With respect to the crystal structure, although Buckley et al.[6] and Groen and de Leeuw[9] reported that the c axis extends with a decrease in oxygen content and has good correlation with T_c, the others reported no in-

formation on the lattice parameters. Moreover, no Hall measurement has been carried out on the $Bi_2Sr_2CaCu_2O_y$ systems against the oxygen loss, which has not answered the question of whether the hole concentration is changed by the oxygen loss. Therefore, the effects of oxygen loss on the superconductivity is still open to question in this system.

In this paper we report the study on the $Bi_2Sr_2CaCu_2O_y$ annealed in vacuum at various temperatures in order to elucidate the effects of oxygen loss on the structure, hole concentration, and superconductivity in detail. We present the result that the amount of oxygen loss, even if it is very small, can be controlled by annealing in vacuum and can be estimated from the integration of the oxygen partial pressure measured by a quadrupole mass spectrometer.[14] This method can measure only oxygen evolution from the oxides, while the thermogravimetric methods measure the evolution of not only oxygen but also the other gases. The lattice parameters and T_c were measured for the annealed samples. The Hall coefficient was also measured on these samples, which was the first time that the Hall coefficient was measured versus the oxygen loss within our knowledge. From these results, the relationship between oxygen loss and superconductivity in this system will be discussed in view of the charge redistribution.

II. EXPERIMENT

The polycrystalline $Bi_2Sr_2CaCu_2O_y$ synthesized by the solid-state reaction method was used as starting materi-

als. The mixture of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO powders with the metal ratio Bi:Sr:Ca:Cu = 2:2:1:2 was fired and reground. This procedure was repeated at 700 °C for 12 hours, 770 °C for 12 hours, and 820 °C for 20 hours in air. Then it was pelletized and fired at 880 °C for 12 hours in air followed by furnace cooling to the room temperature. Small fraction of the $Bi_2Sr_2CuO_y$ (2:2:0:1) phase, which was less that 5%, was observed in some samples by x-ray powder diffraction, although no impurity was detected by scanning electron microscopy equipped with the energy-dispersive x-ray spectrometer (SEMEDS). The T_c of this material measured by ac susceptometor was 65 K. This starting material was annealed at temperatures between 200 and 650 °C for 2 h and furnace cooled to the room temperature in the vacuum chamber (base pressure was about 10^{-4} Pa).

In order to estimate the amount of the oxygen loss caused by annealing in vacuum, the amount of oxygen evolution as a function of sample temperature was measured by a quadrupole mass spectrometer. The base pressure of the vacuum chamber was about 10^{-8} Pa in this experiment. The oxygen partial pressure was calculated from the peak intensities of mass number 32 O_2) and 16 (O), where the fragment ratio and the relative ionization cross section to nitrogen were assumed to be 100:21 for O_2:O and 0.96 for oxygen, respectively. The amount of oxygen loss $q_O(T)$ at annealing temperature T can be calculated by using the following equations:

$$q_O(t) = VP_O(t) + S \int P_O(t)dt , \tag{1a}$$

$$T = 5t + Ts , \tag{1b}$$

where the heating ratio was kept constant at 5 ° C/min, V is the volume of the vacuum chamber, S the exhaust velocity of the vacuum pump, t the heating time, and Ts the temperature at $t = 0$. By combining these and the ideal-gas equation, the oxygen losses from the samples annealed at each temperatures were calculated.

In order to check the suitability of this method, the oxygen loss of $YBa_2Cu_3O_{7-\delta}$ and Δy of $Bi_2Sr_2CaCu_2O_y$ were measured by the same method.[14] After the sample was heated to 500 °C with the constant heating ratio of 5 °C/min, the temperature was kept at 500 °C until the $P_O(t)$ decreased enough to be neglected, in which $VP_O(t) \approx 0$. The oxygen loss of $YBa_2Cu_3O_{7-\delta}$ was also measured by means of an iodometric titration. The total accuracy of this method estimated from the oxygen loss of $YBa_2Cu_3O_{7-\delta}$ systems was within 50%.

The oxygen evolution from the 2:2:0:1 phase was also measured to check the effects of this phase on the oxygen-loss measurements. The oxygen started to be evolved at about 600 °C in the vacuum. This shows that we do not have to take the oxygen loss from the impurity phase into account for that from the 2:2:1:2 phases in the temperature range below about 600 °C.

The samples annealed in vacuum were examined by x-ray powder diffraction with a Rigaku diffractometer, and the lattice parameters were measured by using Al_2O_3 powder (99.999%) as an internal standard in order to obtain the precise values. The T_c was determined by the temperature dependence of the diamagnetic response measured by ac magnetic susceptometer (Sumitomo Heavy Industry). The metal composition of the samples were measured by SEMEDS (JSM-840/LINK-860). The Hall coefficients of these samples were measured by the conventional Hall measurement at room temperature.

III. RESULT AND DISCUSSION

A. Oxygen loss by annealing in vacuum

The change of the oxygen partial pressure measured by the mass spectrometry as a function of annealing temperature is shown in Fig. 1. The oxygen starts to be evolved from the sample at about 220 °C, and the partial pressure has a peak at about 350 °C. It is suggested here that oxygen is evolved at least from two sites in the superconducting oxide structure; one below about 500 °C (site I) and the other above that (site II), although it is difficult to determine where these sites are in the structure. The amount of oxygen loss Δy estimated from Fig. 1 on the basis of Eq. (1) is shown (open circles) as a function of annealing temperature along with T_c in Fig. 2. The Δy increases with increasing the annealing temperature, although it is very small.

No decomposed products were found in the samples annealed up to 600 °C in vacuum by x-ray powder diffraction. Changes of metal composition and of morphology caused by annealing in vacuum were not observed in the 2:2:1:2 phases by the SEMEDS investiga-
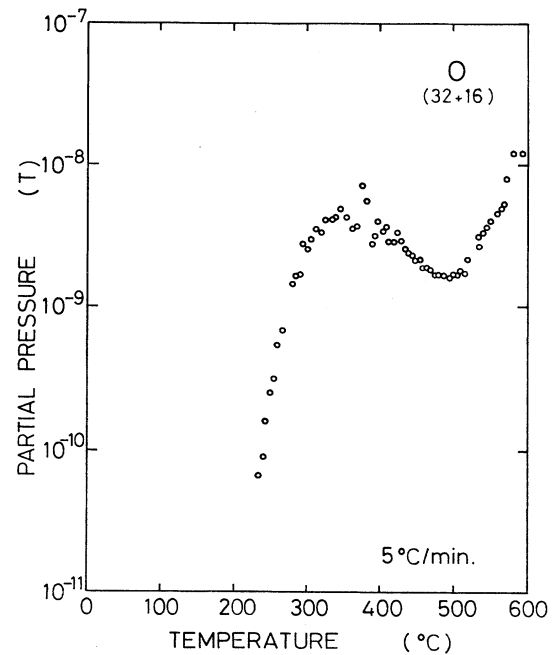

FIG. 1. Change of oxygen partial pressure, in which mass numbers 32 and 16 were measured by quadrupole mass spectrometer, vs annealing temperature. The broad peak is clearly seen around 350 °C. The oxygen is evolved at least from two sites; one is below 500 °C (site I) and the other above 500 °C (site II).
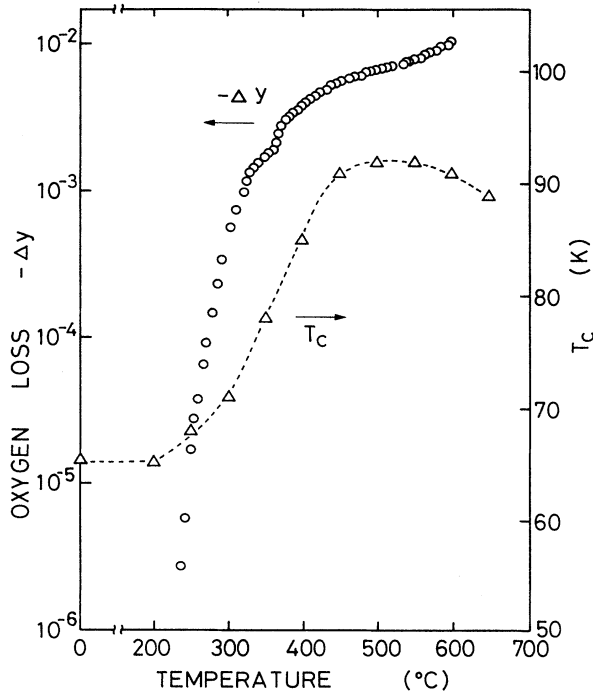
FIG. 2. Oxygen loss Δy (open circles) and T_c (open triangles) as a function of annealing temperature. The oxygen loss is in the order of 10^{-3} within the temperature range lower than 600 °C. Oxygen loss from sites I and II would correspond to increasing and decreasing T_c, respectively.

FIG. 3. Change of lattice parameters vs oxygen loss Δy. Both a and c axes extend monotonically with an increase of the oxygen loss below 600 °C.

tion. These results and the systematic changes of the lattice parameters, which will be mentioned later, confirm the oxygen evolution from the oxide structure.

The Δy obtained here is very small against the change of T_c compared with the previous results.[6,8,10,11,13] In our results, the Δy is about 0.006 at 500 °C, which corresponds to the change of T_c from 65 K (starting value) to 92 K (maximum value). On the other hand, Buckley et al.[6] and Morris et al.[8] reported that Δy is about 0.4 for the change of T_c from 72 to 89 K and from 63 to 80 K, respectively. Zhao and co-workers[10,13] and Imai and Matsuba[11] reported that Δy are about 0.1 and 0.05 for the change of T_c from 68 to 95 K and from 80 to 94 K, respectively.

The partial pressures of other gases were also measured during the annealing. The gases, especially those such as CO_2 and H_2O, were evolved from the sample during annealing. The total amount of these gases was at least several times larger in weight than that of oxygen, even if gases evolved from the sample holder were taken into account.[14] The evolution of these gases probably overestimates the amount of the oxygen loss obtained by the thermogravimetric methods.

In Fig. 3 the changes of lattice parameters are shown as a function of the oxygen loss Δy. The lattice parameters were surprisingly changed by the small amount of oxygen loss. The a and c axes both extend in proportion to the oxygen loss. The behavior of the latter is in good agreement with previous results,[9,10] while there have been
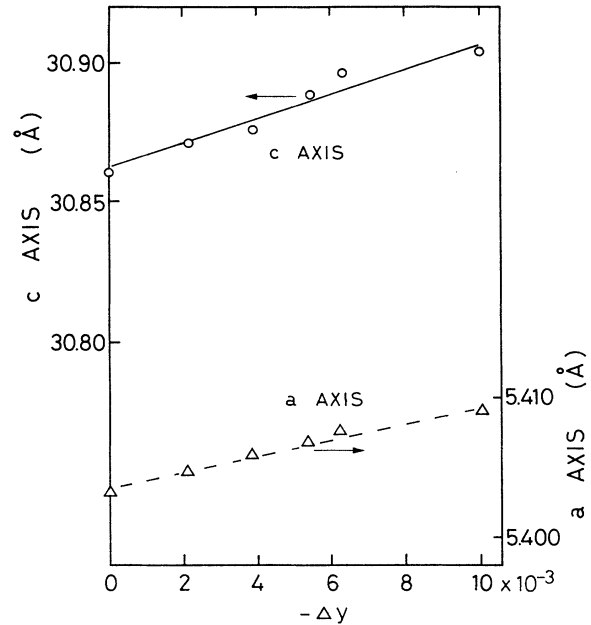
reports on the a-axis extension due to the oxygen evolution.

B. Effects of oxygen loss on the superconductivity of the $Bi_2Sr_2CaCu_2O_y$ system.

The change of the T_c measured by ac magnetization is shown as a function of the annealing temperature in Fig. 2 (open triangles) along with the change of the oxygen loss Δy. The T_c starts increasing at about 220 °C, where the oxygen begins to be evolved (from the site I). It increases with an increase in the annealing temperature, takes the maximum value (92 K) at around 500 °C, and then tends to slightly decrease above 500 °C, where another oxygen evolution occurs.

Figure 4 shows the change of T_c versus the oxygen loss Δy in order to make clear the relationship between oxygen loss and T_c. It increases linearly with increasing the Δy up to about 0.006, and then decreases above that. The ratio of the T_c and the oxygen loss is about 5000 K $/\Delta y$ within the linear region in Fig. 4. This value is remarkably larger than 43 (Refs. 6 and 8) and 270 (Refs. 10 and 11) obtained by thermogravimetric measurements which would include other gases, such as H_2O and CO_2, as mentioned in Sec. III A. Our results show that the T_c of $Bi_2Sr_2CaCu_2O_y$ is extremely sensitive to the change of the oxygen content, which is caused by the oxygen evolution below about 500 °C.

Figure 5 shows the change of the hole concentration n_H estimated from the Hall coefficient as a function of the oxygen loss Δy. The n_H decreases from 4×10^{21} to about 2×10^{21} cm^{-3} with increasing in the oxygen loss up to about 0.006, which corresponds to the change of T_c from the starting to the maximum values. The relation-
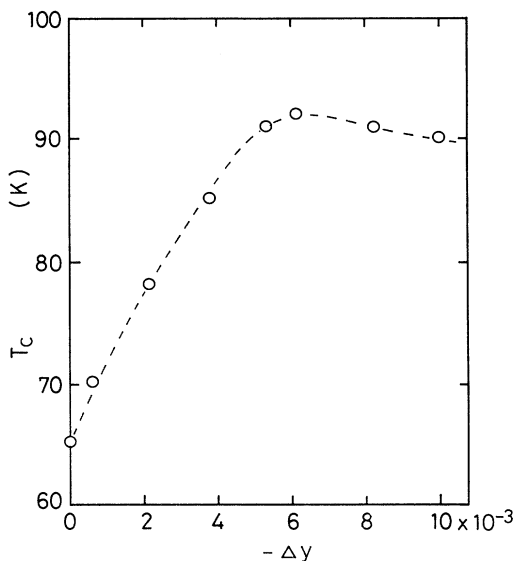
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FIG. 4. Change of T_c as a function of the oxygen loss Δy. The T_c increases linearly with an increase in the oxygen loss up to about 0.006, and then tends to decrease slightly.

ship between T_c and the hole concentration obtained in this study agrees with the results for the Bi-Sr-Ca-Cu-O system,[15−17] in which the hole concentration were controlled by some atomic substitutions. The similar relationship has also been reported for $La_{2-x}Sr_xCuO_{4-\delta}$ (Ref. 18) and $YBa_2Cu_3O_{7-\delta}$.[19] These similarities show that the relationship between T_c and the hole concentration in the 2:2:1:2 system studied here would be put into the same category with the other high-T_c superconducting oxides.

It has been pointed out that T_c of high-temperature superconductors depends strongly on the a axis.[20,21] The re-
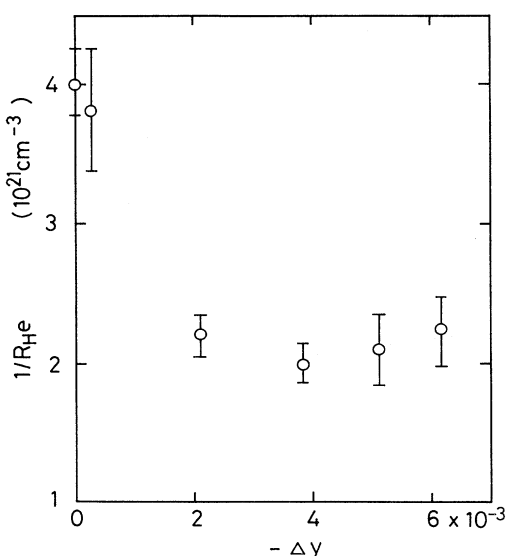

FIG. 5. Change of hole concentration n_H estimated from Hall coefficient vs oxygen loss Δy.

lation between the T_c and the Cu-O length (r) for La, Y, and Tl superconductors was summarized; the T_c increases as increasing in r for $r < r_{op}$ (r_{op} denotes the optimum value which gives a maximum T_c for each oxides) and decreases for $r > r_{op}$, respectively. The ratio of T_c to r for $r < r_{op}$ is in the order of 7 000–12 000 K/Å for the Cu-O_2-based superconductors.[20] We have obtained the value about 15 000 K/Å from Figs. 2 and 3, where $r = a/2\sqrt{2}$, which is the same order as the above value for the other oxide superconductors. This shows that the relationship between the a axis and T_c of the $Bi_2Sr_2CaCu_2O_y$ system annealed in vacuum is also valid for the high-T_c superconducting oxide. The extension of the a axis by oxygen loss would be explained by the extension of Cu-O distance in the Cu-O_2 planes along with decreasing the hole concentration shown in Fig. 5.

It was reported that the concentration of Sr in $La_{2-x}Sr_xCuO_{4-\delta}$ almost corresponds to the hole concentration estimated from Hall coefficients.[18] For $YBa_2Cu_3O_{7-\delta}$, the change of the hole concentration is nearly equal to that expected from the change of oxygen content δ.[19] In the case of $Bi_2Sr_2CaCu_2O_y$, by the substitutions of Tm (Ref. 17) and Y (Ref. 16) for Ca, the linear decreases of the hole concentration n_H with Tm and Y contents were observed. However, the change of n_H for $Bi_2Sr_2CaCu_2O_y$ obtained in this study is two orders larger than that expected from the oxygen loss if one oxygen loss removes two holes from the Cu-O_2 planes. This difference may be due to the different mechanism of the charge transfer from hole donors to the Cu-O_2 planes.

The change of the hole concentration estimated by the amount of the oxygen loss is extremely smaller than that obtained here. Therefore, the change of the hole concentration would be achieved by the redistribution of charges in the structure. It has been suggested that there exists an excess oxygen in the Bi-O layers for $Bi_2Sr_2CaCu_2O_y$ prepared in air or under a high-pressure oxygen stream.[22−24] The origin of the hole formation in the Bi-layered oxides was discussed based on the band structure of the Bi-O rocksalt structure. Some calculations[25−28] showed that the bottom of the Bi 6p band in this structure lies below the Fermi level. This implies that Bi can form $Bi^{(3-\delta)+}$ and oxidize Cu^{2+}, which make holes in the Cu-O_2 planes. But Ren *et al.*[29] reported that the bottom of the Bi 6p band lies more that 1 eV above the Fermi level from the band calculation, if the distortion of the Bi-O layers[30] was taken into account; accordingly, Bi forms Bi^{3+}. These results suggest that the band structure of the Bi-O double layers is very sensitive to the distortion of this structure. If the small amount of the oxygen loss changes the distortion of the Bi-O layers, the large change of hole concentration in the Cu-O_2 planes would be anticipated by the shift of the Bi 6p level. The redistribution of holes between the Bi-O and Cu-O_2 planes would lead to changes in the lattice parameters and the hole concentration in the Cu-O_2 planes.

We consider another mechanism as the origin of the hole redistribution; the extension of the c axis caused by the oxygen loss. If the extension of the c axis (in Fig. 4) is due to the stretch of the distance between the Cu-O_2

planes and the Bi-O layers, the transfer integral t between O $2p_z$ bands on the Sr-O layers and Cu $3d_{z^2-r^2}$ bands on the Cu-O$_2$ planes and/or Bi $6s$ or $6p$ bands in the Bi-O layers could decrease. This would reduce the charge (holes) transfer from the Bi-O layers to the Cu-O$_2$ planes exponentially and n_H strongly, if we assume that the hole concentration on the Cu-O$_2$ planes depends on the transfer integral t between the Cu-O$_2$ planes and hole donors. The hole concentration estimated from the Hall measurement seems to decrease exponentially (in Fig. 5) against the monotonous extension of the c axis (in Fig. 3). This suggests that the reduction of the hole concentration would be related to the change of the transfer integral between the Bi-O layers and the Cu-O$_2$ planes. This scenario seems to be the same as that discussed on the YBa$_2$Cu$_3$O$_{7-\delta}$ substituted Cu(I) by Co.[31]

The mechanisms of the hole redistribution proposed here are both related to the change of the crystal structure of Bi$_2$Sr$_2$CaCu$_2$O$_y$ system. In order to elucidate these mechanisms, more research, especially studies on the change of the local structure caused by oxygen loss and on the location of the oxygen, will be needed.

The optimum hole concentration[15] and carrier density[32] for the maximum T_c of Bi$_2$Sr$_2$CaCu$_2$O$_y$ have been reported. It would be generally acceptable that a sufficient carrier density is necessary for the samples to be metallic. However, the experimental results indicated that T_c decreases over the optimum hole concentration. The increase of T_c, due to the small amount of oxygen loss shown here, is probably explained by the relaxation of the over-doping state in the Bi$_2$Sr$_2$CaCu$_2$O$_y$ synthesized in air. It was pointed out[15] that if the attraction force between Cooper pairs in high-T_c superconductors were caused by some kind of fluctuation such as spin fluctuation[33] and charge fluctuation,[34] the excess holes would weaken fluctuation and the attraction force, which would lead to suppression of the superconductivity. The high-hole concentrations were also discussed for La-Sr-Cu-O[35]; the disappearance of high-T_c superconductivity at the high concentration could be associated with the change in the value of electronic conduction, namely, from a

highly correlated "Mott conductor" (at low-hole concentrations) to a broadband metal (at high-hole concentrations) due to the band-broadening effects and consequentially, the vanishing of the Coulomb gap. This disappearance of Coulomb gap in the c direction in the oxide structure would lead to a dimensional crossover from two-dimensional to quasi-three-dimensional metallization, which suppress the T_c.[35] The relationship between the optimum hole concentration and the maximum T_c for Bi$_2$Sr$_2$CaCu$_2$O$_y$ is still open to question. This problem would be closely related to the mechanism of high-T_c superconductivity, which is thus far unclear. Theoretical and precise experimental studies on the electronic structures are necessary to solve the problem.

IV. SUMMARY

We measured the oxygen loss, lattice parameters, T_c and Hall coefficient for Bi$_2$Sr$_2$CaCu$_2$O$_y$ annealed in vacuum. It is found that the T_c and the lattice parameters are strongly affected by the small amount of oxygen loss which is in the order of $10.^{-3}$ The relationship between the T_c, a axis, and the hole concentration, which was estimated from the Hall measurement, is similar to those of the other superconductive oxides. However, the decrease of hole concentration is about two orders larger than expected from the oxygen loss in this system. It is suggested that the charge redistribution in the structure is the origin of the large change of the hole concentration in the Cu-O$_2$ planes. The changes of the crystal structure, such as the distortion of the Bi-O layers and the extension of the distance between hole donors and the Cu-O$_2$ planes caused by the oxygen loss, are proposed for the origin of this charge redistribution.

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*Present address: Electronics Research Center, NKK Corporation, Toyama 934, Japan.

†Present address: LSI Project Center, NKK Corporation, Tokyo 101, Japan.

[1]Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzal, Phys. Rev. B **38**, 7156 (1988).

[2]J. M. Tarascon, L. H. Greene, W. R. Mckinon, G. W. Hull, and T. H. Geballe, Science **235**, 1373 (1987).

[3]J. E. Shirber, B. Morosin, R. M. Merrill, R. F. Hlava, E. L. Venturini, J. F. Kuak, P. J. Nigry, R. J. Baughman, and D. S. Ginley, Physica C **152**, 121 (1988).

[4]Y. Shimakawa, Y. Kubo, T. Manako, T. Satoh, S. Ijima, T. Ichihashi, and H. Igarashi, Physica C **157**, 279 (1989).

[5]S. Nakajima, M. Kikuchi, T. Oku, N. Kobayashi, T. Suzuki, K. Nagase, K. Hiraga, Y. Muto, and Y. Syono, Physica C **160**, 458 (1989).

[6]R. G. Buckley, J. L. Tallon, I. W. Brown, M. R. Presland, N.

E. Flower, P. W. Glberd, M. Bowden, and N. B. Milestone, Physica C **156**, 629 (1988).

[7]T. Ishida, Jpn. J. Appl. Phys. **28**, L573 (1989).

[8]D. E. Morris, C. T. Hultren, A. M. Markelz, J. Y. Wei, N. G. Asmar, and J. H. Nickel, Phys. Rev. B **39**, 6612 (1989).

[9]W. A. Groen and D. M. de Leeuw, Physica C **159**, 417 (1989).

[10]J. Zhao and Mohindar S. Seehara, Physica C **159** 639 (1989).

[11]K. Imai and H. Matsuba, in *Advances in Superconductivity II*, Proceedings of the 2nd International Symposium on Superconductivity (ISS'89), Tsukuba, 1989, edited by T. Ishiguro and K. Kajimura (Springer-Verlag, Tokyo, 1990), p. 149.

[12]Y. Motoi, Y. Ikeda, H. Uwe, and T. Sakudo, Physica C **162 - 164**, 929 (1989).

[13]J. Zhao, M. Wu, W. Abdul-Razzaq, and M. S. Seehara, Physica C **165**, 135 (1990).

[14]M. Nagoshi, T. Suzuki, Y. Fukuda, J. Murata, J. Sanada, A. Tokiwa, Y. Syono, and M. Tachiki, *Advances in Superconduc-*

tivity III, Proceedings of the 3rd International Symposium on Superconductivity (ISS'90), Sendai, 1990 (Springer-Verlag, Tokyo, in press).

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

[16]T. Tamegai, K. Koga, K. Suzuki, M. Ichinohara, F. Sakai, and Y. Iye, Jpn. J. Appl. Phys. **28**, L112 (1989).

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

[18]J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Benzing, T. C. Huang, and S. S. P. Pakin, Phys. Rev. Lett. **61**, 1127 (1988); N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Greene, and W. R. Mckinnon, Phys. Rev. B **35**, 8807 (1987); S. Uchida, H. Takagi, H. Ishii, H. Esaki, T. Yabe, S. Tajima, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L440 (1987).

[19]Z. Z. Wang, J. Clayhold, N. P. Ong, J. M. Tarascon, L. H. Greene, W. R. Mckinnon, and G. W. Hull, Phys. Rev. B **36**, 7222 (1987).

[20]M.-H. Whangbo, D. B. Kang, and C. C. Torardi, Physica C **158**, 371 (1989).

[21]C. C. Torardi, D. Jung, D. B. Kang, J. Ren, and M.-H. Whangbo, in *High Temperature Superconductivity, Relationship between Properties, Structures, and Solid State Chemistry,* Vol. 156 of *MRS Symposium Proceedings,* edited by J. D. Jorgensen, K. Kitazawa, J. M. Tarascon, M. P. Thompson, and J. B. Torrance (Materials Research Society, Pittsburgh, 1989).

[22]S. A. Sunshine, T. Siegrist, L. F. Schneemeyer, D. W. Murphy, R. J. Cava, B. Batlogg, R. B. van Dover, R. M. Fleming, S. H. Glarum, S. Nakahara, R. Fallow, J. J. Krajewski, S. M. Zahurak, J. V. Waszczak, J. H. Marshall, P. Marsh, L. W. Rupp, Jr., and W. F. Peck, Phys. Rev. B **38**, 893 (1988).

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

[24]C. C. Torardi, J. B. Parise, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, Physica C **157**, 115 (1989).

[25]S. Massidda, J. Yu, and A. J. Freeman, Physica C **152**, 251 (1988).

[26]M. S. Hybertsen and L. F. Mattheiss, Phys. Rev. Lett. **60**, 1661 (1988).

[27]H. Krakauer and W. E. Pickett, Phys. Rev. Lett. **60**, 1665 (1988).

[28]F. Herman, R. V. Kasowski, and W. Y. Hsu, Phys. Rev. B **38**, 204 (1988).

[29]J. Ren, D. Jung, M.-H. Whangbo, J.-M. Tarascon, Y. Le Page, W. R. Mckinnon, and C. C. Torardi, Physica C **158**, 501 (1989).

[30]Y. Le Page, W. R. Mckinonn, J.-M. Tarascon, and P. Barboux, Phys. Rev. B **40**, 6810 (1989).

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

[32]M. Rateau, R. Suryanarayanan, O. Gorochov, and H. Pankowska, Phys. Rev. B **41**, 857 (1990).

[33]P. W. Anderson, Science **235**, 1196 (1987).

[34]M. Tachiki and S. Takahashi, Phys. Rev. B **38**, 218 (1988).

[35]K. Sreedhar and P. Ganguly, Phys. Rev. B **41**, 371 (1990).