PHYSICAL REVIEW B VOLUME 61, NUMBER 6 1 FEBRUARY 2000-II

Control of T_c for Ni-substituted $YBa_2Cu_3O_{7-\delta}$ by annealing treatments

S. Adachi, Y. Itoh, T. Machi, E. Kandyel,* S. Tajima, and N. Koshizuka

Superconductivity Research Laboratory, ISTEC, 1-10-13 Shinonome, Koto-ku, Tokyo 135-0062, Japan

(Received 15 June 1999)

Effects of annealing treatments on T_c of Ni-substituted $YBa_2Cu_3O_{7-\delta}$ have been studied. Ceramic samples of $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$ ($x=0.00$, 0.02, 0.05, and 0.10) prepared in 1-atm oxygen atmosphere were annealed at 800–1000 °C in various atmospheres with different oxygen partial pressures, and subsequently oxygenated below 550 °C. The lower the oxygen partial pressure, the lower the T_c. For the samples with a fixed x but different T_c's, no appreciable difference in lattice parameters and oxygen contents was observed. The results clearly indicate that the T_c of Ni-substituted $YBa_2Cu_3O_{7-\delta}$ can be controlled by changing the oxygen partial pressure during annealing treatment. It is likely that the distribution of Ni atoms between the chain and plane sites can be altered by the annealing treatment.

I. INTRODUCTION

Since the discovery of high-T_c cuprate superconductors, much effort has been devoted on the transition-metal substitution effects on their physical properties.[1–38] Especially, the Ni and Zn substitution effects are very interesting because of the contrast in magnetism of the substituents.[5,15,18–22,25,29,30,37,38] The previous reports on the $YBa_2Cu_3O_{7-\delta}$ superconductor informed that Zn suppresses T_c most significantly among the examined transition metals and the effect of T_c suppression by Ni substitution is weaker.[1–25] On these experimental results, some researchers discussed the role of Cu in the CuO_2 plane, assuming that both Zn and Ni atoms enter into the Cu(2) (*planes*) site, not into the Cu(1) (*chain*) one. In fact, Islam and Baetzold[12] suggested that both Zn and Ni preferentially substitute for the Cu(2) site by energy calculation using atomistic simulation techniques. Hoffman *et al.*[19] reported that the substituted Ni were located at the Cu(2) site from their study of anomalous dispersive x-ray-diffraction measurements.

On the other hand, Howland *et al.*[11] and Bridges *et al.*[13] reported a nearly random distribution of Ni atoms at the two Cu sites from the studies of a differential anomalous x-ray scattering and x-ray-absorption fine-structure measurements, respectively. The optical conductivity studies[22,40] suggested the existence of Ni atoms at Cu(1) site. The recent Cu-NQR study (where NQR is nuclear quadropole resonance) indicated that Ni preferentially goes to the Cu(1) site.[39] If a considerable amount of Ni atoms were located at the Cu(1) site, it is likely that the observed weaker effect of Ni substitution on T_c suppression, compared with the case of Zn substitution, is due to a smaller Ni content in the CuO_2 plane than the total amount of substituted Ni. Without information about the location of the substituents, we cannot understand correctly the impurity effects on the superconductivity. For an ideal way to study the impurity effects on superconductivity, it is required to produce samples in which Ni atoms are preferentially substituted for the Cu(2) site in the plane.

The two sites for Cu atoms in the $YBa_2Cu_3O_{7-\delta}$ superconductor have different coordination numbers for oxygen atoms; namely, 2–4 for Cu(1) and 5 for Cu(2). The former is changed, depending on oxygen content, 7-δ. The diagram of oxygen nonstoichiometry against temperature and oxygen partial pressure, $p(O_2)$, for $YBa_2Cu_3O_{7-\delta}$ was well established by the chemical analysis.[41] More directly, Jorgensen *et al.*[42] investigated *in situ* neutron powder diffraction at elevated temperatures in various $p(O_2)$'s. Their results indicate that the occupancy of the oxygen sites next to Cu(1) at a fixed temperature in the range of 400–900 °C can be controlled by changing $p(O_2)$. These results suggest to us a way to control the chemical potential at Cu(1) site by tuning the condition of heat treatments. Assuming that the site selection of substituted Ni is linked with the chemical potential at Cu(1), we may be able to control the ratio of Ni occupancies at the two sites by changing the heat-treatment condition, in which temperature is high enough to move cation atoms but lower for decomposition. It is expected that the samples with different Ni distribution, if obtained, show different T_c values.

In this work, we prepared successfully $YBa_2(Cu,Ni)_3O_{7-\delta}$ samples that have the same cation composition, oxygen content, and unit-cell dimension, but appreciably different T_c values. This provides a new synthetic method for $YBa_2(Cu,Ni)_3O_{7-\delta}$ having different site occupation of Ni.

II. EXPERIMENT

Ceramic samples were prepared by a solid-state-reaction method. Y_2O_3, $BaCO_3$, CuO, and NiO powders were weighed out at the nominal composition of $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$ ($x=0.00$, 0.02, 0.05, and 0.10) and thoroughly mixed. The powder mixture was calcined at 860–920 °C for 3 days in air with intermediate grindings. The calcined powders were pelletized and sintered at 970 °C for 2 days in flowing oxygen gas and then slowly cooled at a rate of 100 °C/h. The obtained ''as-synthesized'' samples were annealed under different conditions as follows:

(i) at 800 °C for 3 days in flowing nitrogen gas, and then quenched,

(ii) at 800 °C for 14 days in flowing nitrogen gas, and then quenched,

(iii) at 900 °C for 3 days in air, and then quenched,

(iv) at 1000 °C for 3 days in a mixture of 80% Ar–20% O_2 gases at 2000 atm, i.e., $p(O_2)=400$ atm.

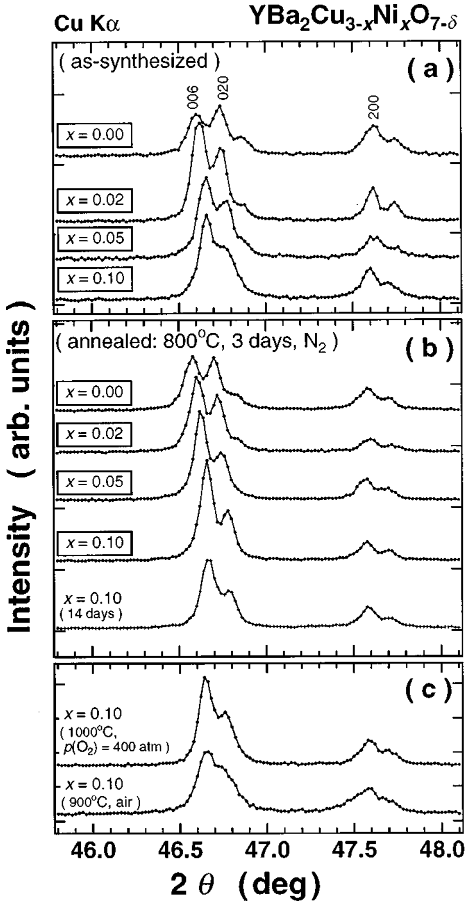

FIG. 1. XRD patterns for $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$ samples; (a) as-synthesized, (b) annealed at 800 °C for 3 or 14 days in nitrogen, (c) annealed at 1000 °C for 3 days in 400-atm oxygen and at 900 °C for 3 days in air.

The annealing treatment of (iv) was carried out using a hot isostatic pressing apparatus. The all-annealed samples were finally oxygenated by heat treatment at 550 °C for 18 days in flowing oxygen gas, and then slowly cooled at a rate of 50 °C/h.

Structural properties were examined by powder x-ray diffraction (XRD) using CuKα radiation. The lattice parameters were determined by calculation using the least-squares method. dc magnetic susceptibility was measured by cooling samples in an external field of 10 or 20 Oe using a superconducting quantum interference device magnetometer. The oxygen contents were determined by a conventional iodometric titration method, assuming valences for Y, Ba, Ni, and O are +3, +2, +2, and −2, respectively.

III. RESULTS AND DISCUSSION

The as-synthesized samples of $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$ had single-phase patterns in XRD spectra. Figure 1(a) shows the XRD patterns of the samples with various Ni contents, x for 006, 020, and 200 reflections. The lattice parameters are plotted as a function of x as shown in the left panels in Fig. 2 (closed circles). With increasing x, the parameters a and b do not change significantly, whereas the parameter c clearly decreases. Figure 3(a) shows the temperature dependences of dc magnetic susceptibility for the as-synthesized samples, indicating quite sharp superconducting transitions. T_c values are lowered with increasing x, which are plotted in Fig. 4 (closed circles). This x dependence of T_c agrees with the results in the previous reports.[6,7,9,10,14,15,17,18,21,23,24] The oxygen contents, 7-δ, for the as-synthesized samples are 6.92–6.95, indicating that almost full oxygenation was attained for the samples. The obtained results of lattice parameters, T_c and oxygen content are summarized in Table I. It is clearly indicated that Ni substitution brings about changes in the lattice parameters and T_c.

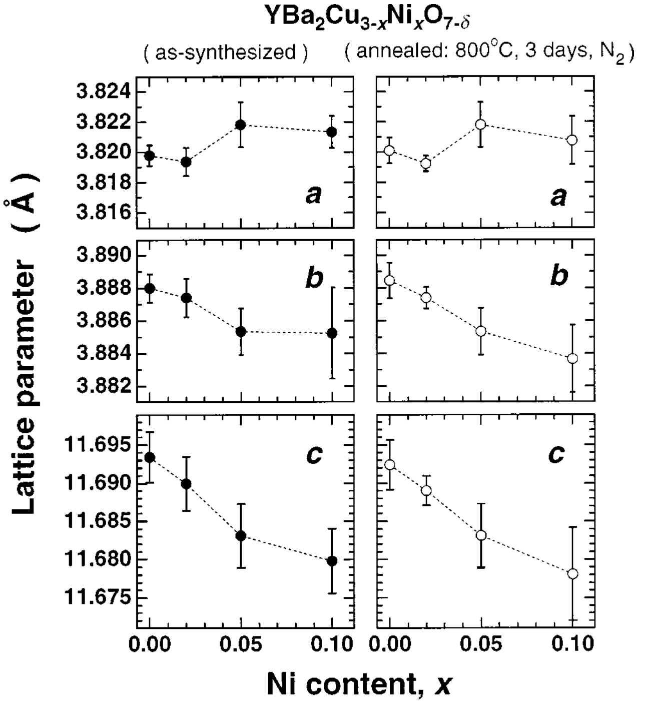

FIG. 2. Lattice parameters against Ni content x for $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$ samples; as-synthesized (left) and for annealed at 800 °C for 3 days in nitrogen (right).

The annealing treatment (i) was performed on the as-synthesized samples. According to the dependence of oxygen content on $p(O_2)$ for various temperatures reported by Kishio *et al.*,[41] this performed annealing condition, i.e., 800 °C in nitrogen, is critical for phase stability of $YBa_2Cu_3O_{7-\delta}$. However, the obtained samples were of single phase in XRD patterns and no appreciable decomposition was detected. The XRD patterns are shown in Fig. 1(b) (the upper-four patterns). We can see the similar peak positions to those for the as-synthesized samples. The lattice parameters are plotted as a function of Ni content, x, in the right panels in Fig. 2 (open circles). No appreciable difference in the lattice parameters can be seen between the as-synthesized and annealed (800 °C, 3 days, N_2) samples. Oxygen contents for the annealed samples (~6.93–6.94) were also almost the same as those for the as-synthesized samples. A clear difference between the two series of samples is seen in T_c suppression. Figure 3(b) shows the temperature dependences of dc magnetic susceptibility for the annealed samples. T_c of the sample with $x=0.00$ is 91 K, which is exactly the same value as that for the as-synthesized sample with $x=0.00$. T_c values are lowered with increasing x. For Ni-substituted samples, T_c suppression in the annealed

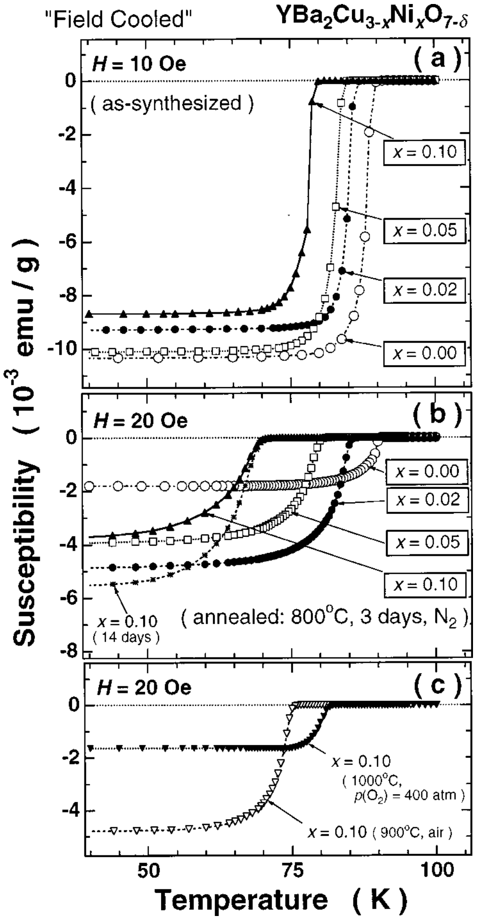

FIG. 3. Temperature dependences of dc magnetic susceptibility for $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$ samples; (a) as-synthesized, (b) annealed at 800 °C for 3 or 14 days in nitrogen, (c) annealed at 1000 °C for 3 days in 400-atm oxygen and at 900 °C for 3 days in air.

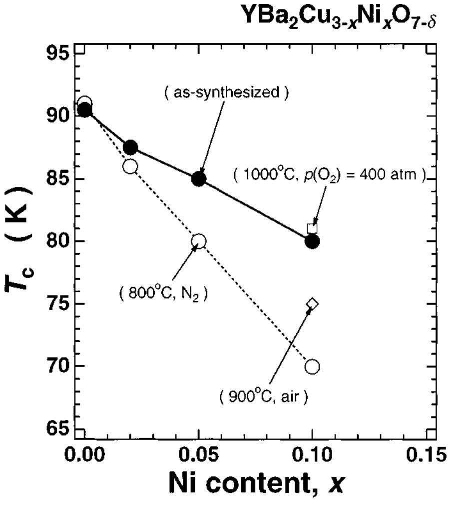

FIG. 4. T_c versus Ni content x for as-synthesized and annealed $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$ samples.

samples is more pronounced, compared with the case of the as-synthesized ones, as shown in Fig. 4 (open circles). It should be noted that two series of Ni-substituted samples with the same compositions and lattice parameters exhibited different x dependence of T_c. This strongly suggests that the conducted annealing treatment altered the distribution of substituted Ni; more concretely, the high-temperature annealing in the reducing atmosphere moved Ni atoms from Cu(1) site to Cu(2) one. The coordination number of Cu(1) site approaches to 2 by the annealing at 800 °C at a lower $p(O_2)$.[42] The atomic site with twofold coordination by oxygen is not a suitable one for substituted Ni from the viewpoint of chemical potential.[43] Ni atoms prefer the atomic site with larger coordination number than Cu atoms.[44] Consequently, it is likely that substituted Ni at the Cu(1) site tends to move to the Cu(2) site.

As mentioned above, the annealing treatment at 800 °C for 3 days in flowing nitrogen gas could change the x dependence of T_c for $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$. To check whether the 3-days annealing is enough to attain an equilibrium condition or not, a longer annealing duration of 14 days was examined [the annealing treatment (ii)]. The obtained samples with $x = 0.00$, 0.02, and 0.05 contained impurities, $Ba_2Cu_3O_{5+\delta}$ (Ref. 45) and Y_2BaCuO_5,[46] as displayed in the XRD patterns of Fig. 5. This implies that these samples started to decompose at 800 °C in flowing nitrogen gas. Therefore, the results obtained by the annealing treatment (i), as described above, are on the samples prepared in a transient condition. However, we can see in Fig. 5 that the impurity peaks become weaker with increasing x. The sample with $x = 0.10$ was of

TABLE I. Summary of lattice parameters, T_c and oxygen content for $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$

Sample		Lattice parameters (Å)				Oxygen content
Processing condition	x	a	b	c	T_c (K)	$7-\delta$
(As-synthesized)	0.00	3.819(1)	3.888(1)	11.693(3)	90.5	6.93
	0.02	3.819(1)	3.887(1)	11.690(3)	87.5	6.95
	0.05	3.822(1)	3.885(1)	11.683(4)	85	6.94
	0.10	3.821(1)	3.885(3)	11.680(4)	80	6.92
800 °C, N_2	0.00	3.820(1)	3.888(1)	11.692(3)	91	6.93
	0.02	3.819(1)	3.887(1)	11.689(2)	86	6.94
	0.05	3.821(1)	3.886(1)	11.685(4)	80	6.93
	0.10	3.821(2)	3.884(2)	11.678(6)	70	6.93
(14 days)	0.10	3.822(1)	3.884(1)	11.678(5)	70	6.95
900 °C, air	0.10	3.821(1)	3.885(1)	11.679(3)	75	6.93
1000 °C, $p(O_2)=400$ atm	0.10	3.823(2)	3.884(2)	11.679(7)	81	6.92

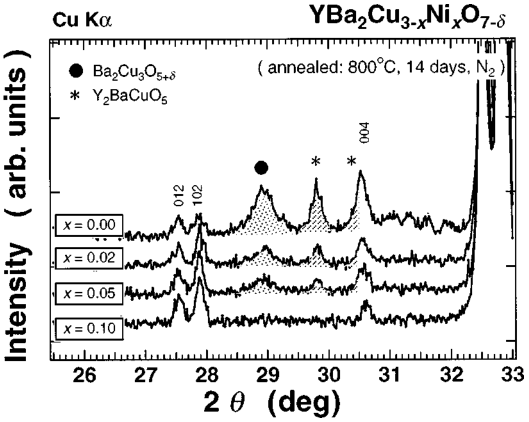

FIG. 5. XRD patterns for $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$ samples annealed at 800 °C for 14 days in flowing nitrogen gas.

single phase. This result indicates that the Ni substitution enhances the phase stability and increases the decomposition temperature. The XRD peaks of 006, 020, and 200 reflections for the 14-days-annealed sample with $x=0.10$ are located at the same 2θ position as those for the 3-days-annealed sample with $x=0.10$, as shown in Fig. 1(b) (the lowest pattern), indicating the same lattice parameters. Moreover, the T_c value of 70 K [see Fig. 3(b)] and the oxygen content of 6.95 are almost identical to the values for the 3-days-annealed sample. Lattice parameters, T_c and oxygen content are listed in Table I. No appreciable difference is seen between the two 800 °C-annealed samples with $x=0.10$. Therefore, it is concluded that an equilibrium condition was attained in the 3-days-annealed sample with $x=0.10$.

In order to confirm the effect of $p(O_2)$ during high-temperature annealing, we attempted annealing treatments in different atmospheres, i.e., in air (iii) and in a mixture of 80% Ar–20% O_2 gases at 2000 atm (iv) for $x=0.10$. It is expected that the decomposition temperature becomes higher, when the $p(O_2)$ is higher. Therefore, we chose the temperatures of 900 and 1000 °C for the annealing treatments (iii) and (iv), respectively, to accelerate the cation movement. In the obtained samples, no decomposition was detected in XRD. Figure 1(c) shows the XRD data of the obtained samples. In the peak position for 006, 020, and 200 reflections, no appreciable difference from other samples with $x=0.10$ given in Figs. 1(a) and 1(b) is seen, indicating no difference in lattice parameters. The temperature dependence of dc magnetic susceptibility of these samples are plotted in Fig. 3(c). Systematic decrease in T_c of samples with $x=0.10$ is observed with decreasing $p(O_2)$ during the annealing treatments, as is plotted in Fig. 4. Here, the highest $p(O_2)$ is examined in the treatment (iv). The $p(O_2)$ for the as-synthesized condition, i.e., 1 atm (flowing oxygen), is higher than that in the treatment (iii), i.e., 0.2 atm. The oxygen contents for the samples processed through the treatments (iii) and (iv) are 6.93 and 6.92, respectively. These results are summarized in Table I. By changing $p(O_2)$ during the annealing treatments, only T_c is substantially changed in the samples with $x=0.10$.

The present experimental data clearly indicate that T_c of Ni-substituted $YBa_2Cu_3O_{7-\delta}$ can be controlled by varying $p(O_2)$ during annealing treatments without changing the lattice parameters and the oxygen content. As an origin of T_c reduction by the heat treatment in low $p(O_2)$, a decrease in hole concentration and the structural change can be ruled out, because of the unchanged oxygen content and lattice parameters. A plausible candidate for the change in T_c is a change in the Ni occupancies at the two Cu sites. In this work, samples were prepared through three steps as follows: (1) sintering at 970 °C for 2 days in flowing oxygen gas, (2) annealing treatment at 800–1000 °C and various $p(O_2)$'s, and (3) oxygenation at 550 °C in flowing oxygen gas, accompanied by slow cooling. Phase formation and oxygen absorption occur at the first and third steps, respectively. At the second step, cation atoms move to the preferable atomic sites. The $p(O_2)$ at the second step must be crucially important to determine the substitution site of substituted Ni. Therefore, it is highly possible that substituted Ni atoms are distributed at both two Cu sites in the as-synthesized samples, and the annealing treatment (of the second step) at lower $p(O_2)$ drives substituted Ni atoms from Cu(1) site to Cu(2) site, giving rise to a stronger pair breaking effect in the predominant superconducting layers.

IV. SUMMARY

For the samples of $YBa_2Cu_{3-x}Ni_xO_{7-\delta}$ ($x=0.00$, 0.02, 0.05, and 0.10) prepared in 1-atm oxygen atmosphere, x dependence of T_c was similar to the previously reported data. These as-synthesized samples were annealed at temperatures higher than 800 °C in various atmospheres (N_2, air and 400-atm O_2), and subsequently well-oxygenated below 550 °C. At a fixed x, the values of T_c decreased with decreasing $p(O_2)$ during high-temperature annealing, keeping lattice parameters and oxygen contents almost unchanged. This suggests the annealing treatment at lower $p(O_2)$ moves substituted Ni atoms from the Cu(1) site to the Cu(2) one. The present work provides a new technique to control the occupation site of substituted Ni in $YBa_2Cu_3O_{7-\delta}$.

ACKNOWLEDGMENT

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) as a part of its Research and Development of Fundamental Technologies for the Superconductor Applications Project under the New Sunshine Program administrated by the Agency of Industrial Science and Technologies M.I.T.I. of Japan.

---

*Permanent address: Department of Chemistry Faculty of Science, Tanta University, Tanta, Egypt.

[1] J. T. Markert, B. D. Dunlap, and M. B. Maple, MRS Bull. **14**, 37 (1989).

[2] Y. Maeno, T. Nojima, Y. Aoki, M. Kato, K. Hoshino, A. Minami, and T. Fujita, Jpn. J. Appl. Phys., Part 2 **26**, L774 (1987).

[3] G. Xiao, F. H. Streitz, A. Gavrin, Y. W. Du, and C. L. Chien, Phys. Rev. B **35**, 8782 (1987).

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

[5] J. M. Tarascon, L. H. Greene, P. Barboux, W. R. McKinnon, G.

W. Hull, T. P. Orlando, K. A. Delin, S. Foner, and E. J. McNiff, Jr., Phys. Rev. B **36**, 8393 (1987).

[6] E. Takayama-Muromachi, Y. Uchida, and K. Kato, Jpn. J. Appl. Phys., Part 2 **26**, L2087 (1987).

[7] H. Adrian and S. Nielsen, Europhys. Lett. **5**, 265 (1988).

[8] J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, G. W. Hull, M. Eibschutz, and S. A. Sunshine, Phys. Rev. B **37**, 7458 (1987).

[9] J. F. Bringley, T.-M. Chen, B. A. Averill, K. M. Wong, and S. J. Poon, Phys. Rev. B **38**, 2432 (1988).

[10] Y. Shimakawa, Y. Kubo, K. Utsumi, Y. Takeda, and M. Takano, Jpn. J. Appl. Phys., Part 2 **27**, L1071 (1988).

[11] R. S. Howland, T. H. Geballe, S. S. Laderman, A. Fischer-Colbrie, M. Scott, J. M. Tarascon, and P. Barboux, Phys. Rev. B **39**, 9017 (1989).

[12] M. S. Islam and R. C. Baetzold, Phys. Rev. B **40**, 10 926 (1989).

[13] F. Bridges, J. B. Boyce, T. Claeson, T. H. Geballe, and J. M. Tarascon, Phys. Rev. B **42**, 2137 (1990).

[14] B. Ullmann, R. Wördenweber, K. Heinemann, and H. C. Freyhardt, Physica C **170**, 71 (1990).

[15] R. Liang, T. Nakamura, H. Kawaji, M. Itoh, and T. Nakamura, Physica C **170**, 307 (1990).

[16] R. Kubiak and K. Westerholt, Physica C **173**, 232 (1991).

[17] M. J. Sumner, J.-T. Kim, and T. R. Lemberger, Phys. Rev. B **47**, 12 248 (1993).

[18] K. Ishida, Y. Kitaoka, N. Ogata, T. Kamino, K. Asayama, J. R. Cooper, and N. Athanassopoulou, J. Phys. Soc. Jpn. **62**, 2803 (1993).

[19] S. A. Hoffman, M. A. Castro, G. C. Follis, and S. M. Durbin, Phys. Rev. B **49**, 12 170 (1994).

[20] D. A. Bonn, S. Kamal, K. Zhang, R. Liang, D. J. Baar, E. Klein, and W. N. Hardy, Phys. Rev. B **50**, 4051 (1994).

[21] P. Mendels, H. Alloul, G. Collin, N. Blanchard, J. F. Marucco, and J. Bobroff, Physica C **235-240**, 1595 (1994).

[22] C. C. Homes, Q. Song, B. P. Clayman, D. A. Bonn, R. Liang, and W. N. Hardy, Proc. SPIE **2696**, 101 (1996).

[23] Y. Tokunaga, K. Ishida, Y. Kitaoka, and K. Asayama, Solid State Commun. **103**, 43 (1997).

[24] F. Shi, R. Harris, W. J. Bresser, D. McDaniel, and P. Boolchand, J. Phys.: Condens. Matter **9**, L307 (1997).

[25] R. P. Gupta and M. Gupta, Phys. Rev. B **59**, 3381 (1999).

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

[27] H. Harashina, T. Nishikawa, T. Kiyokura, S. Shamoto, M. Sato, and K. Kakurai, Physica C **212**, 142 (1993).

[28] A. Maeda, T. Yabe, S. Takebayashi, M. Hase, and K. Uchinokura, Phys. Rev. B **41**, 4112 (1990).

[29] T. Kluge, Y. Koike, A. Fujiwara, M. Kato, T. Noji, and Y. Saito, Phys. Rev. B **52**, R727 (1995).

[30] D. Goldschmidt, Y. Direktovitch, A. Knizhnik, and Y. Eckstein, Phys. Rev. B **54**, 13 348 (1996).

[31] I. Felner and B. Brosh, Phys. Rev. B **43**, 10 364 (1991).

[32] T. Miyatake, K. Yamaguchi, T. Takata, N. Koshizuka, and S. Tanaka, Phys. Rev. B **44**, 10 139 (1991).

[33] Y. Kodama, S. Tanemura, Y. Yamada, and T. Matsumoto, Physica C **199**, 1 (1992).

[34] Ratan Lal, S. P. Pandey, A. V. Narlikar, and E. Gmelin, Phys. Rev. B **49**, 6382 (1994).

[35] T. H. Meen, F. L. Juang, W. J. Huang, Y. C. Chen, K. C. Huang, and H. D. Yang, Physica C **242**, 373 (1995).

[36] G. V. M. Williams, J. L. Tallon, R. Meinhold, and A. Jánossy, Phys. Rev. B **51**, 16 503 (1995).

[37] G.-Q. Zheng, T. Odaguchi, Y. Kitaoka, K. Asayama, Y. Kodama, K. Mizuhashi, and S. Uchida, Physica C **263**, 367 (1996).

[38] N. Watanabe and N. Koshizuka, Phys. Rev. B **57**, 632 (1998).

[39] K. Morita, H. Yamagata, and M. Matsumura, in *Meeting Abstracts of the Physical Society Japan, Higashi-Hiroshima, 1999*, Vol. 54, p. 559 [in Japanese].

[40] N. L. Wang, S. Tajima, V. Zelezny, and K. Tomimoto, in Ref. 39, p. 603 [in Japanese].

[41] K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa, and K. Fueki, Jpn. J. Appl. Phys. **26**, L1228 (1987).

[42] J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).

[43] R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).

[44] A. Navrotsky and O. J. Kleppa, J. Inorg. Nucl. Chem. **29**, 2701 (1967).

[45] J. G. Thompson, J. D. Fitz Gerald, R. L. Withers, P. J. Barlow, and J. S. Anderson, Mater. Res. Bull. **24**, 505 (1989).

[46] C. Michel and B. Raveau, J. Solid State Chem. **43**, 73 (1982).