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Relation between Lattice Parameters and Valence State of Cu Ions of $M_xNd_{2-x}CuO_{4-y}$ (M = Na and Ce) Solid Solution

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The lattice parameters, the oxygen content, and the electrical and magnetic properties of $M_xNd_{2-x}CuO_{4-y}$ (M = Na and Ce) with the Nd_2CuO_4 structure have been determined by means of X-ray powder diffraction, thermogravimetry, electrical resistivity, and magnetic susceptibility measurements. The oxidation states of Cu were estimated from the measured y values and the nominal composition x, on the basis of charge neutrality. The composition dependence of the lattice parameters is discussed by taking the oxygen content, the ionic radii, and (Cu^+/Cu) into consideration. The formation of holes and electrons on the Cu–O bond within the basal plane is discussed in terms of the Cu–O bond length in the structure of the host materials.

Introduction

Since the first discovery by Bednorz and Müller (*1*) of a high T_c superconducting copper oxide, $Ba_xLa_{2-x}CuO_{4-y}$, with the K_2NiF_4 structure, extensive efforts have been devoted to synthesizing new superconducting copper oxides having higher T_c. M–La–Cu–O (M = Sr, Ca, and Na) (*2, 3*), Y–Ba–Cu–O (*4*), Bi(Tl)–Sr(Ba)–Ca–Cu–O (*5, 6*), and Ce–Sr–Nd–Cu–O (*7*) systems have been discovered as new bulk superconductors and investigated in detail. Main features which these superconductors have are (1) two-dimensional planes of CuO_6 octahedra or CuO_5 square pyramids in their crystal structure, and (2) metallic conduction by hole carriers which are related to Cu^{3+} ion (or O^- ion) (*8, 9*) in two dimensional copper planes. The structure of the tetragonal Nd_2CuO_4 which was first analyzed by Müller-Buschbaum and Wollschläger (*10*) is called T′-type Nd_2CuO_4 structure and is known for having only two-dimensional CuO_4 square planes. Nd_2CuO_4 shows semiconducting conduction behavior (*11*). However, efforts to introduce holes in two-dimensional CuO_4 square planes of T′-type Nd_2CuO_4 by substitution of Nd by alkaline earth metal ions have been unsuccessful.

Recently, new superconducting copper oxides $Ce_xLn_{2-x}CuO_{4-y}$ (Ln = Pr, Nd, and Sm) were discovered by Tokura *et al.* (*12, 13*). The surprising feature of these compounds is electron (not hole) type superconductivity. In this paper, we report synthesis of $M_xNd_{2-x}CuO_{4-y}$ (M = Na and Ce) and measurements of their lattice parameters, oxygen content, electrical resistivity, and magnetic susceptibility. For comparison, $M_xNd_{2-x}CuO_{4-y}$ (M = La and Sm)

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were also synthesized and their lattice parameters were measured. We estimate P = (Cu^{3+}/Cu) and Q = (Cu^{+}/Cu) from the values of y and the nominal composition x on the basis of charge neutrality and take P and Q as representations of the oxidation states of Cu ions. Finally, we compare both compounds $Na_xNd_{2-x}CuO_{4-y}$ and $Ce_xNd_{2-x}CuO_{4-y}$ with $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca, and Na) compounds and discuss the relation between the Cu–O bond length within the basal plane and the formation of holes or electrons on the bond.

Experimental

For the synthesis of $M_xNd_{2-x}CuO_{4-y}$ (M = Na, Ce, La, and Sm), Na_2CO_3 (99.98%), CeO_2 (99.99%), CuO (99.99%), La_2O_3 (99.99%), Sm_2O_3 (99.9%), and Nd_2O_3 (99.99%) were mixed according to the following ratios: $(2 - x)/2$ Nd_2O_3/ $(x/2)$ Na_2CO_3 or La_2O_3 or Sm_2O_3/ x CeO_2/ 1 CuO. Mixtures were prefired at 750°C for the Na series and at 950°C for the Ce series for 12 hr in air. Prefired products for the Na series were ground, pelletized, and sintered at 900°C for 24 hr and then quenched in oxygen atmosphere in order to keep out the occurrence of $NaCuO_2$ (*14*). The Ce series was sintered at 1100–1150°C for 12 hr and then furnace-cooled in air. For the Ce series, sintered products were reground, repelletized, and annealed at 900°C for 12 hr and then quenched in argon atmosphere in order to introduce forcibly the oxygen defect into their structure. Samples were synthesized on a boat made of gold for the Na series and of platinum for the Ce series. $M_xNd_{2-x}CuO_4$ (M = La and Sm) were synthesized by a method similar to that in the case of M = Na and Ce. Both prefiring and sintering conditions were 1100°C for 12 hr in air with the platinum boat.

The samples were examined by X-ray powder diffraction (XRD) using monochromated Cu$K\alpha$ radiation with a Rigaku goniometer. The lattice parameters were refined by the least-squares method to better than 0.01% accuracy.

The oxidation state of copper, i.e., the oxygen content $4 - y$, was determined by thermogravimetry using a Shinku-Riko thermobalance, by heating to about 750°C in 30% hydrogen/argon atmosphere. The heating rate was 5°C/min. In the temperature range 25–500°C, this procedure reduces only copper ion to Cu metal, i.e.,

$$M_xNd_{2-x}CuO_{4-y} \rightarrow x/2Na_2O \text{ (or } xCeO_2) + (2 - x)/2Nd_2O_3 + Cu \quad (M = \text{Na and Ce}) \tag{1.1}$$

The initial weight of samples used for this experiment was about 200 mg and the weight loss was about 8 mg. Complete reduction to Cu metal was confirmed by means of XRD.

The oxidation state of Cu ions, as P or Q, was estimated from the measured y values and the nominal composition x on the basis of charge neutrality. The accuracy of the oxygen content measured by thermobalance was generally better than 0.2% for the single-phase samples.

The resistivity of the sintered samples was measured by the usual dc four-probe method with a current of 1 to 10 mA, depending on the sample dimensions. Electrical contact was made by conducting silver paste or indium tips. Temperature was measured with a previously calibrated germanium resistance thermometer.

The magnetic susceptibility of the sintered samples was measured by ac susceptometer (Sumitomo Heavy Industries, Ltd.) for the Na series and by SQUID susceptometer (Quantum Design MPMS) for the Ce series, under field-cooled conditions, with H = 20 Oe.

Results

(*A*) *X-ray Powder Diffraction*

According to the methods previously described, T′-type compounds corresponding to the nominal composition $Na_xNd_{2-x}CuO_{4-y}$ were synthesized in a composition range $0 < x \leqq 0.4$ and found to be almost single phase with a trace of unknown phases in $x \leqq 0.2$. The diffraction peak intensity of the unknown phases was small but increased with increasing x in $0.2 < x \leqq 0.4$. $M_xNd_{2-x}CuO_4$ (M = La and Sm) were synthesized as single phase in a composition range $0 < x \leqq 0.4$, respectively. The lattice parameters are plotted as a function of the nominal composition x in Fig. 1. The lattice parameter a increased and c decreased with x for the Na series. Both the lattice parameters a and c increased with x for the La series, while they decreased for the Sm series. The cell volume V is plotted as a function of the nominal composition x in Fig. 2. The cell volumes increased with x for the Na and La series, while it decreased for the Sm series.

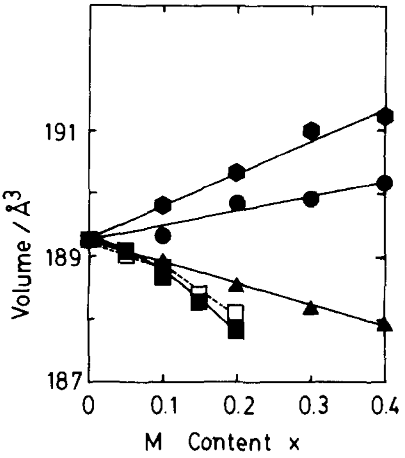

FIG. 2. Composition dependence of the cell volumes of $M_xNd_{2-x}CuO_{4-y}$ (M = Na, Ce, La, and Sm). Circles, Na series; hexagons, La series; triangles, Sm series; solid squares, Ce series with the as-prepared samples; open squares, Ce series with the argon-annealed samples.

T′-type compounds corresponding to the nominal composition $Ce_xNd_{2-x}CuO_{4-y}$ were synthesized and found to be single phase with one diffraction peak of unknown phases whose diffraction intensity was in less than 1% in a composition range $0 < x \leqq 0.2$. The lattice parameters are plotted as a function of the nominal composition x in Fig. 3. The lattice parameter a increased and c decreased with x. This tendency was similar to that of the compounds $Na_xNd_{2-x}CuO_{4-y}$. The lattice parameter c of the argon-annealed samples became larger than that of the as-prepared samples in $x \geqq 0.1$. The cell volume V is plotted as a function of the nominal composition x in Fig. 2. The cell volume decreased with x. The cell volume of the argon-annealed samples became larger than that of the as-prepared samples in $x \geqq 0.1$. The cell volume of Nd_2CuO_{4-y} did not change appreciably by the argon annealing.

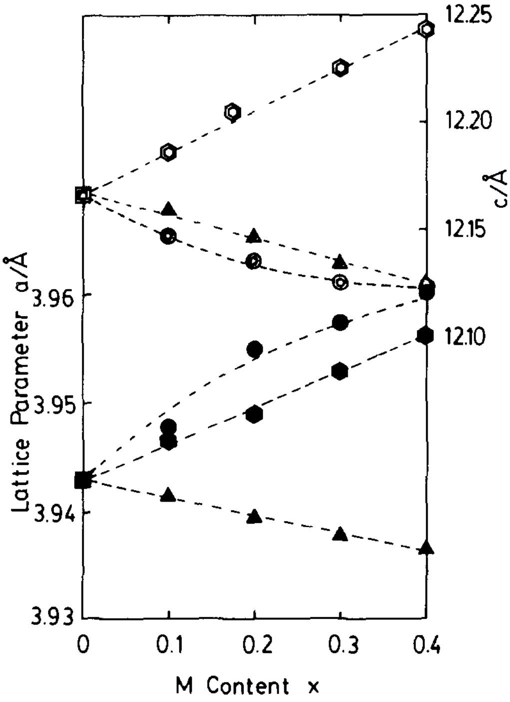

FIG. 1. Composition dependence of the lattice parameters of $M_xNd_{2-x}CuO_{4-y}$ (M = Na, La, and Sm). Circles, Na series; hexagons, La series; triangles, Sm series. Solid and double symbols correspond to the lattice parameters a and c, respectively.

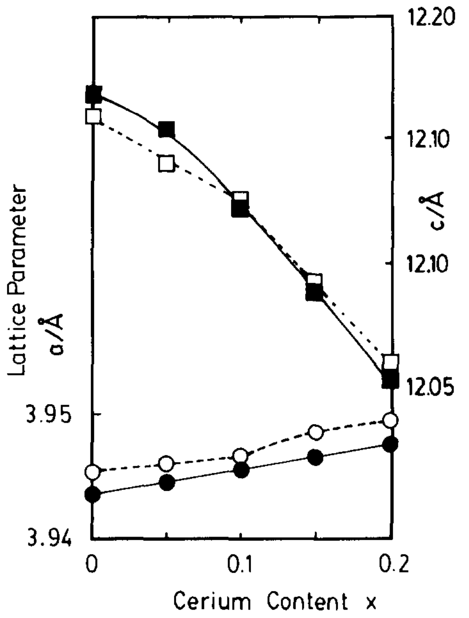

FIG. 3. Composition dependence of the lattice parameters of $Ce_xNd_{2-x}CuO_{4-y}$. Solid symbols, as-prepared samples; open symbols, argon-annealed samples.

(*B*) *Thermogravimetry*

A typical TG curve chart of $M_xNd_{2-x}CuO_{4-y}$ (M = Na and Ce) is shown in Fig. 4. The weight loss began at about 230°C and seemed to finish with a sharp break in TG curve at about 500°C. We assumed that the weight loss ΔW in this process corresponded with reaction (1.1). Although the reduction from CeO_2 to CeO_{2-a} might be possible for the Ce series samples in this reduction process, there seemed to be no influence on the analysis because the Ce series samples contained only a small amount of cerium and the 500°C temperature was too low for the reduction of CeO_2, which was confirmed by Brauer and Holdschmidt (*15*) and by our thermobalance experiment. The gradual weight loss in the temperature range above 570°C was due to instrumental drift of the thermobalance apparatus because this tendency was observed for Nd_2CuO_{4-y} samples.

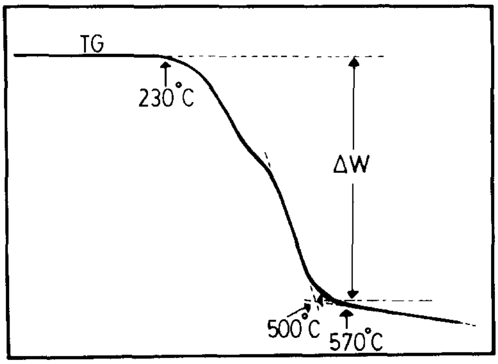

FIG. 4. A typical TG curve chart for $M_xNd_{2-x}CuO_{4-y}$ (M = Na and Ce).

The weight loss of single phase Nd_2CuO_{4-y} in a reduced atmosphere of 30% H_2–Ar was measured several times by thermobalance. The values of $4 - y$ were close to 4 within an experimental error. Figure 5 shows the relation between the sodium content x and the oxygen content $4 - y$ for the Na series. The result showed that the value of $4 - y$ linearly decreased with increasing x and $P = 2x - 2y$ was kept constant at 0 due to the charge compensation by the oxygen defect; that is, the oxidation state of Cu

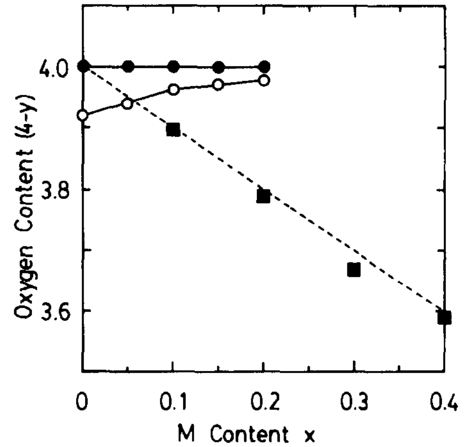

FIG. 5. Composition dependence of oxygen content of $M_xNd_{2-x}CuO_{4-y}$ (M = Na and Ce). Solid squares, Na series; circles, Ce series (solid, as-prepared samples; open, argon-annealed samples).

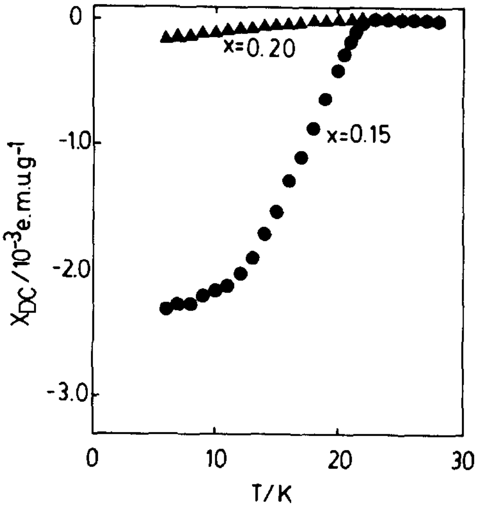

FIG. 6. Temperature dependence of magnetic susceptibility of argon-annealed $Ce_xNd_{2-x}CuO_{4-y}$. Circles, $x = 0.15$; triangles, $x = 0.20$.

was held at Cu^{2+}. For the Ce series, the relations between x and $4 - y$ of both the as-prepared and argon-annealed samples are shown in Fig. 5. The oxygen content $4 - y$ of the as-prepared samples was kept constant at 4, while $4 - y$ of the argon-annealed samples slightly increased with x. The fact that the measured values of the oxygen content of the as-prepared samples for the Ce series were kept at 4 despite increasing cerium content in $Ce_xNd_{2-x}CuO_{4-y}$ confirmed that there was no influence of the reduction of CeO_2 on the ΔW of reaction (1.1). $Q = (Cu^+/Cu)$ increased linearly with x for the as-prepared samples and nonlinearly as $Q = x + 2y$ for the argon annealed samples.

(C) Electrical Resistivity

The resistivity of the Na series samples of $x = 0.3$ and 0.5 increased in a semiconducting fashion with decreasing temperature. Superconductivity was not realized. The Ce series samples showed much smaller resistance (several ohms) than that of Nd_2CuO_4 (several kilohms) at room temperature.

(D) Magnetic Susceptibility

Diamagnetism was not detected for the Na series samples. For the Ce series, diamagnetism was clearly observed for the argon-annealed samples of $x = 0.15$, while the small amount of diamagnetism was observed for the argon annealed sample of $x = 0.2$. The results are shown in Fig. 6. The volume fraction of the diamagnetism was about 25 and 1% for the argon-annealed samples of $x = 0.15$ and 0.20, respectively. Diamagnetism was not detected for the as-prepared samples of $x = 0.15$ and 0.20 and the argon-annealed sample of $x = 0.10$.

Discussion

$Na_xNd_{2-x}CuO_{4-y}$ Compounds

If Nd^{3+} ions were substituted by similar trivalent lanthanoid ions such as La^{3+} or Sm^{3+}, the lattice parameters a and c and the cell volume V simply increase or decrease in accordance with the difference between the ionic radii of Nd^{3+} and of La^{3+} and Sm^{3+}, as shown in Figs. 1 and 2 ($r_{La^{3+}} = 1.18$ Å, $r_{Nd^{3+}} = 1.12$ Å, $r_{Sm^{3+}} = 1.09$ Å (*16*)). For the Na series, on the other hand, the lattice parameter a increases with x, while c and the oxygen content $4 - y$ drastically decrease with x. The oxygen defect is considered to be on the O_{II} site between the Nd–O layers, since the Nd–O_{II} bond length (2.32 Å (*10*)) is larger than the Cu–O_I bond length (1.97 Å) within the basal plane. Hence, the decrease of c with x may be caused by the oxygen defect. The increasing rate of a with x of the Na series is also anomalously large, compared with that of the La series despite $r_{La^{3+}} > r_{Na^{3+}} = 1.16$ Å and the existence of the oxygen defect of the Na series, while the effect of the substitution on V is smaller in the Na series than that in the La series. The cell volume of the Na series increases with x despite the oxygen defect. For Nd_2CuO_{4-y}, there is no difference between the cell volumes of the as-prepared sample and the argon-annealed sample due to volume compensation of expansion in a and contraction in c. The increase in a with x of the Na series is suggested to be caused by both the substitution of Nd^{3+} by larger Na^+ and the volume compensation against the contraction of c caused by the oxygen defect.

The hole concentration P (or the amount of Cu^{3+} or O^-) of the $Na_xNd_{2-x}CuO_{4-y}$ compounds is described as $P = 2x - 2y$ on the basis of charge neutrality of the substitution of Nd^{3+} by Na^+. P depends on both the sodium content x and the oxygen defect y. The measured data were found close to the broken line (Fig. 5) which shows the relation between x and $4 - y$ in the case of $P = 0$. Thus, the effects of y and x compensate each other and P is kept at 0. The result is consistent with the absence of superconductivity and similar to the results in La_2CuO_4 (*8, 9*). The longer Cu–O_I bond within the basal plane in Nd_2CuO_4 is disadvantageous for the formation of hole (Cu^{3+}, O^-) whose amount is to be reflected on the contraction of the Cu–O_I bond (*9*).

$Ce_xNd_{2-x}CuO_{4-y}$ *Compounds*

If the cerium ion exists as larger Ce^{3+} ($r_{Ce^{3+}} = 1.14$ Å $> r_{Nd^{3+}}$) in $Ce_xNd_{2-x}CuO_{4-y}$, both the lattice parameters a and c should increase with increasing x, as in the case of the La^{3+} substitution. However, a increases and c decreases with x. The decrease in c suggests that the cerium ion exists as the smaller Ce^{4+} ion ($r_{Ce^{4+}} = 0.97$ Å) in the structure.

In this case, the electron concentration Q which is equal to the increase of the amount of Cu^+ is described as $Q = x + 2y$ by charge neutrality. As $y = 0$ for the as-prepared samples, the amount of Cu^+ increases linearly with x. This linear relation between the amount of Cu^+ and x has been confirmed by XPS measurements (*17*). Since the ionic radius of Cu^+ is larger than that of Cu^{2+} and the expansion of Cu ion affects the Cu–O_I bond length, the lattice parameter a increases linearly with the increasing amount of Cu^+. The fact that the value of a of the argon-annealed samples was larger than that of the as-prepared samples can be explained by larger Q values of the argon-annealed samples than those of the as-prepared samples at the same Ce content because of the nonzero y values. The composition dependences of a and c change their slope around $x = 0.10$ and the cell volume and c of the argon-annealed samples become larger than those of the as-prepared samples in $x < 0.10$. For the Na series, the oxygen defect causes the contraction of c because the valence state of Cu ions does not change. This suggests that the oxygen defect mainly causes a geometrical contraction of c. For the Ce series, however, both the oxygen defect and the change in the valence state of Cu ions are induced. There is a competition between the geometrical contraction due to the oxygen defect and expansion due to the generation of larger Cu^+ ions. In comparison of the as-prepared samples and the argon-annealed samples, the contraction of c observed in $0 < x < 0.10$ seems to be explained by a relatively large amount of y, while the expansion of c observed in $0.10 \leqq x \leqq 0.20$ might be due to Cu^+ production.

Takagi *et al.* (*13*) reported that (1) bulk superconducting state was realized in only argon-annealed samples and in a narrow region $0.14 \leqq x < 0.18$ and (2) Meissner fraction and T_c decreased with x in a region $0.15 \leqq x < 0.18$ and bulk superconducting state disappeared at $x = 0.18$. Our result is consistent with that of Takagi *et al.* Although the argon-annealed sample of $x = 0.15$ and the as-prepared sample of $x = 0.20$ have almost the same Q values, the superconducting state is realized only in the former, which contains oxygen defects. This suggests that the oxygen defect is very important and necessary for superconductivity in this system (*13*).

Finally, we compare two systems, the La

system ($M_xLa_{2-x}CuO_{4-y}$, M = Ba, Sr, Ca, and Na) and the Nd system ($M_xNd_{2-x}CuO_{4-y}$, M = Na and Ce). For the La system, the Cu–O_I bond within the basal plane contracts with the formation of hole (Cu^{3+}) by the substitution of La^{3+} by M, and the contraction is necessary for superconductivity (*8*). For the Nd system, the contraction of the Cu–O_I bond and the formation of hole cannot be realized in the $Na_xNd_{2-x}CuO_{4-y}$ compounds, while the Cu–O_I bond expands with the introduction of electron (Cu^+) by the substitution of Nd^{3+} by Ce^{4+}, and the superconducting state is realized only in $Ce_xNd_{2-x}CuO_{4-y}$ which contain oxygen defects. Nd_2CuO_4 has four relatively long Cu–O_I bonds (Cu–O_I = 1.97 Å), while La_2CuO_4 has four short Cu–O_I bonds (Cu–O_I = 1.90 Å) plus two longer Cu–O_{II} bonds. The results suggest that the short and long Cu–O_I bond lengths in the structure of the host materials could be advantageous for the formation of holes and electrons on the bonds, respectively (*18*).

Summary

For the Na-doped Nd system, the lattice parameter c was controlled by the concentration of the oxygen defect, while a was controlled by both the substitution of Nd^{3+} by larger Na^+ and volume compensation against the contraction of c. Hole concentration P was kept at 0 due to the charge compensation between the substitution of Nd^{3+} by Na^+ and formation of the oxygen defect. Superconductivity was not realized in this system because of no hole formation.

For the Ce-doped Nd system, the lattice parameter a was controlled by the amount of Cu^+ corresponding to electron concentration. The lattice parameter c was controlled by the substitution of Nd^{3+} by smaller Ce^{4+} for the as-prepared samples, while for the argon-annealed samples it was controlled not only by substitution but also by formation of the oxygen defect. Electron concentration Q increased as $Q = x + 2y$. Bulk superconductivity was realized only in the argon-annealed samples of $x = 0.15$ containing oxygen defects.

The Cu–O_I bond length in the structure of the host materials seemed to determine whether they become hole- or electron-type conductors.

Acknowledgments

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References

1. J. G. Bednorz and K. A. Müller, *Z. Phys. B: Condens. Matter* **64,** 189 (1986).
2. K. Kishio, K. Kitazawa, N. Sugii, S. Kanbe, K. Fueki, H. Takagi, and S. Tanaka, *Chem. Lett.,* 635 (1987).
3. M. A. Subramanian, J. Gopalakrishnan, C. C. Torardi, T. R. Askew, R. B. Flippen, A. W. Sleight, J. J. Lin, and S. J. Poon, *Science* **240,** 495 (1988).
4. M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Q. Wang, and C. W. Chu, *Phys. Rev. Lett.* **58,** 911 (1987).
5. H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, *Japan. J. Appl. Phys.* **27,** L209 (1988).
6. Z. Z. Sheng and A. M. Hermann, *Nature (London)* **332,** 138 (1988).
7. J. Akimitsu, S. Suzuki, M. Watanabe, and H. Sawa, *Japan. J. Appl. Phys.* **27,** L1859 (1988).
8. J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. Parkin, *Phys. Rev. Lett.* **61,** 1127 (1988).
9. K. Oh-ishi, M. Kikuchi, Y. Syono, N. Kobayashi, T. Sasaoka, T. Matsuhira, Y. Muto, and H. Yamauchi, *Jpn. J. Appl. Phys.* **27,** L1449 (1988).
10. H. Müller-Buschbaum and W. Wollschläger, *Z. Anorg. Allg. Chem.* **414,** 76 (1975).
11. P. Ganguly and C. N. R. Rao, *Mater. Res. Bull.* **8,** 405 (1973).
12. Y. Tokura, H. Takagi, and S. Uchida, *Nature (London)* **337,** 345 (1989).

13. H. Takagi, S. Uchida, and Y. Tokura, *Phys. Rev. Lett.* **62,** 1197 (1989).

14. K. Hestermann and R. Hoppe, *Z. Anorg. Allg. Chem.* **367,** 261 (1969).

15. G. Brauer and U. Holdschmidt, *Z. Anorg. Allg. Chem.* **279,** 129 (1955).

16. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B* **25,** 925 (1969).

17. S. Uji, M. Shimoda, and H. Aoki, *Jpn. J. Appl. Phys.* **28,** L804 (1989).

18. E. Takayama-Muromachi, F. Izumi, Y. Uchida, K. Kato, and H. Asano, *Physica C* **158,** 449 (1989).