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Superconductivity of $La_{2-x}Nd_xCuO_{4+z}$ Prepared under High Oxygen Pressure: Suppression of the Phase Separation Seen in La_2CuO_{4+z}

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$La_{2-x}Nd_xCuO_{4+z}$ was prepared under oxygen pressures ranging between 0.2 bar and 60 kbar. The oxygen content increased slightly as the Nd content increased; $z \simeq 0.09$ for $x = 0.4$ under 60 kbar of oxygen. The Nd substitution and the introduction of excess oxygen as oxide ion counteract each other from the viewpoint of structure chemistry. For La_2CuO_{4+z} the superconducting transition temperature, T_c, was almost independent of z at around 40 K, while the T_c of the Nd-doped samples showed a strong dependence. The superconductive volume fraction was considerably increased by the Nd doping. The phase separation into the nearly stoichiometric ($z \simeq 0$) semiconductive phase and an oxygen-rich superconductive phase as seen in La_2CuO_{4+z} may be suppressed by the Nd-for-La substitution.

1. Introduction

Oxygen stoichiometric La_2CuO_4 is an antiferromagnet with a T_N around 250–300 K (*1, 2*), while superconductivity has been observed for oxygen-doped La_2CuO_{4+z} ($z > 0$) at around $T_c = 40$ K (*3–5*). The T_c is almost the same as observed for alkaline earth-substituted $La_{2-x}A_xCuO_4$ (A = Ba,Sr,Ca). The superconducting volume fraction of La_2CuO_{4+z} is increased by annealing under oxidizing conditions. Some authors have claimed that a fraction as large as 30% was achieved by annealing at 600°C under 1–3 kbar of oxygen (*3*). Jorgensen *et al.*, on the other hand, proposed a phase diagram of La_2CuO_{4+z} from their powder neutron diffraction work (*6, 7*). According to them, a phase separation into nearly stoichiometric *Bmab* ($z = 0$) and oxygen rich *Fmmm* phases occurs for $0 < z < 0.08$ at relatively low temperature. Mixed-phase samples in this range display both antiferromagnetic and superconducting behaviors.

Such an oxygen excess in the K_2NiF_4 structure has been known for La_2NiO_{4+z} and La_2CoO_{4+z} too (*8*). Two types of ordering modes leading to serial oxygen contents have been found for La_2NiO_{4+n} ($n = 1/2n$: $n > 2$) (*9*), while any such ordering has not been reported for La_2CuO_{4+z}.

The excess-oxygen defect in La_2MO_{4+z} (M = Co, Ni, Cu) may be caused by the bond-length mismatch between the LaO and

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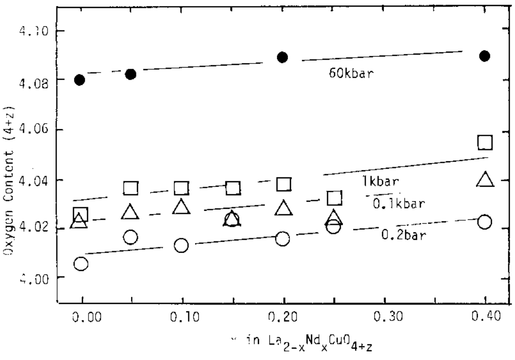

FIG. 1. Variation of oxygen content with oxygen pressure in $La_{2-x}Nd_xCuO_{4+z}$.

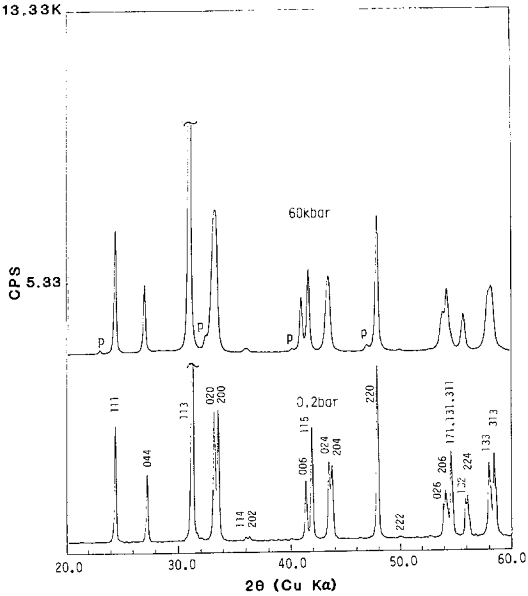

FIG. 3. XRD patterns for $La_{1.8}Nd_{0.2}CuO_{4+z}$. "p" indicates an impurity perovskite phase (La,Nd)CuO_3 formed under 60 kbar of oxygen.

MO_2 layers. A measure of the bond-length matching is the tolerance factor,

$$t = (La - O)/\sqrt{2}(M - O),$$

where the La–O and M–O bond lengths are commonly taken as the sums of the empirically determined ionic radii. The perfect epitaxial matching of the bonds occurs for $t = 1$. However, the values for $La^{3+} + O^{2-}$ and $\sqrt{2}(Cu^{2+} + O^{2-})$, for example, are 2.58 and 2.86 Å, respectively, according to Shannon and Prewitt (*10*). Generally, $t \simeq 0.9$. The CuO_2 planes are thus under compression and the LaO planes under tension. The internal stress within a CuO_2 plane may be relieved by a cooperative tilting of the CuO_6 octahedra making the Cu–Cu distance shorter, when the crystal structure is distorted from tetragonal to orthorhombic symmetry, while introduction of excess oxygen between a pair of LaO planes expands the $(LaO)_2$ lattice and eases the tension (*11*). Moreover, the excess oxygen, if it exists as oxide ions, not as peroxide ions, oxidizes and, thereby, contracts the CuO_2 sheet, thus relaxing the bond-length mismatch (*11*).

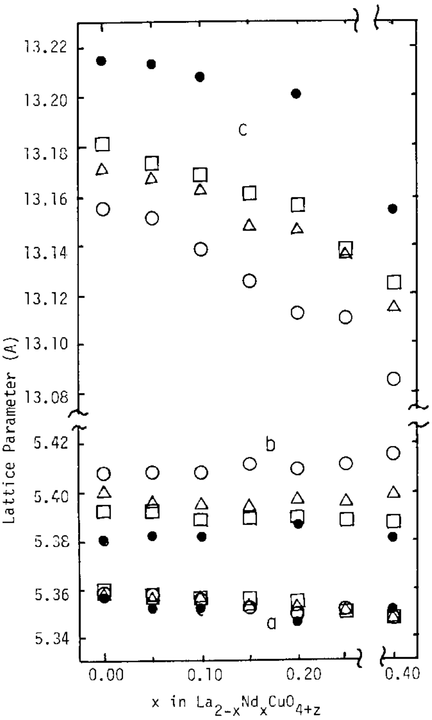

FIG. 2. Lattice parameters for $La_{2-x}Nd_xCuO_{4+z}$ prepared under various oxygen pressures. ○, 0.2 bar; △, 0.1 kbar; □, 1 kbar; ●, 60 kbar.

If La^{3+} ions are partially replaced by smaller rare-earth ions like Nd^{3+}, the bond-

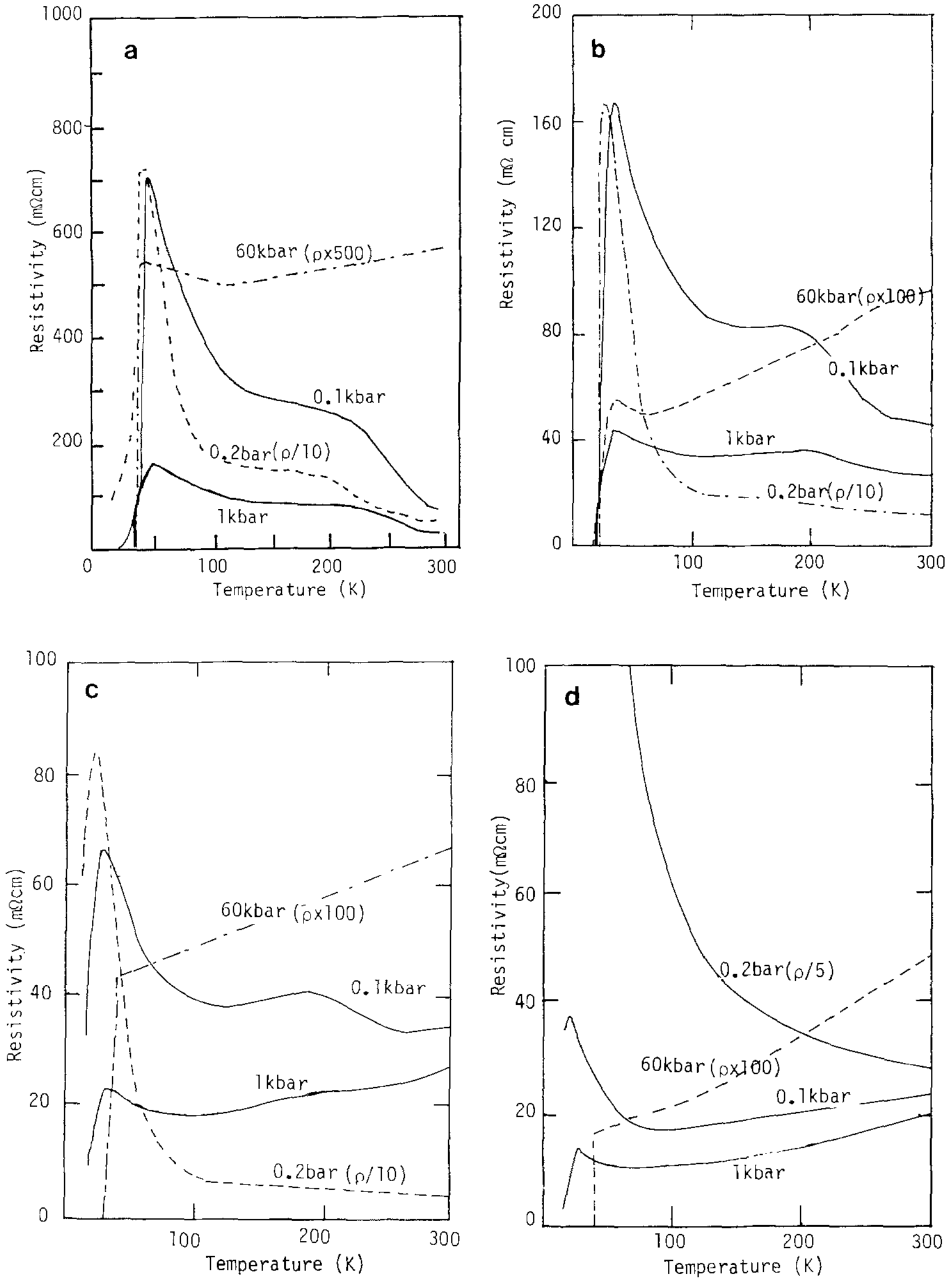

FIG. 4. Variation of electrical resistivity on the oxygen pressure for $La_{2-x}Nd_xCuO_{4+z}$. (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, (d) $x = 0.2$.

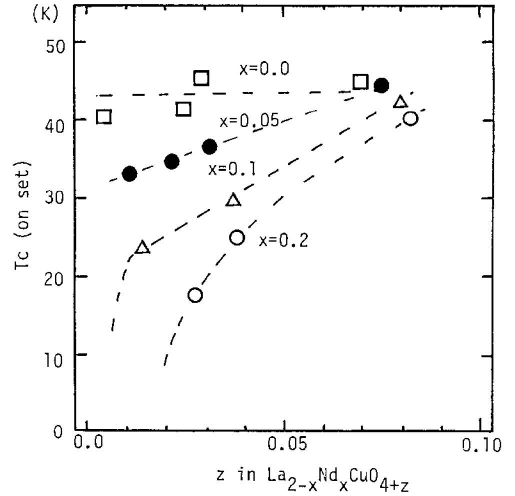

FIG. 5. Variation of the on-set T_c with excess oxygen content for $La_{2-x}Nd_xCuO_{4+z}$.

length mismatch will be further enhanced. It may then be expected that excess oxygen is more easily introduced within the double rock salt layer. We prepared $La_{2-x}Nd_x CuO_{4+z}$ under various oxygen pressures and examined the relations among the excess oxygen content, the structure, and the electrical properties.

2. Experimental

Intimate mixtures of La_2O_3, Nd_2O_3, and CuO were calcined at 950°C for 18 hr in air. The rare-earth oxides were dried at 1000°C for 1 hr just before use. The samples were then ground, pelletized, heated for 18 hr at 1050°C in air, and then furnace-cooled. The process was repeated two times. The pellets thus obtained were annealed at 600°C for 60 hr under 0.1 kbar of oxygen, at 600°C for 80 hr under 1 kbar of oxygen, or at 1050°C for 30 min under 60 kbar of oxygen. For the treatments under pressures below 1 kbar of oxygen, a test-tube-type autoclave made of stellite 25 was used. For the treatment under 60 kbar of oxygen, samples sealed in Au capsules with an oxygen supplier $KClO_4$ were compressed in a belt-type solid high pressure apparatus. Oxygen contents of the final products were determined by iodometric titration.

Electrical resistivity of the sintered pellets was measured by the four-probe method over a temperature range $10 \leq T \leq 300$ K. Magnetic data were obtained with a SQUID magnetometer (SHE 905) in a temperature range between 4 and 100 K, when powdered samples were cooled in a field of 10 G.

3. Results and Discussion

As shown in Fig. 1, the oxygen content increases with increasing oxygen pressure and reaches 4.08–4.09 under 60 kbar of oxygen pressure. Under a given oxygen pressure, it increases with increasing Nd content as expected, but the degree is not so large as to change the doped hole content drastically. The variation of the orthorhombic lattice parameters with Nd content, x, at room temperature are plotted in Fig. 2. The orthorhombic La_2CuO_4 structure was found for $0 \leq x \leq 0.4$, while a T′-Nd_2CuO_4 phase coexisted for $x > 0.40$. Within the monophasic region, the c parameter considerably decreases as a size effect of the Nd ions, while the a and b parameters show, respectively, a slight decrease and increase. The enhanced orthorhombic distortion is another aspect of the size effect because the Nd-substitution makes the tolerance factor smaller. On the other hand, the introduction of excess oxygen makes the c parameter increase and the b parameter decrease as typically seen in Fig. 3. The oxidation may thus be said to counteract the Nd-substitution from the viewpoint of structure chemistry as expected. However, the XRD data measured at 300 K show no evidence of such a transformation from *Bmab* to *Fmmm* with increasing oxygen content as proposed for $La_2 CuO_{4+z}$ by Jorgensen *et al.* Neither was any separation into nearly stoichiometric La_{2-x}

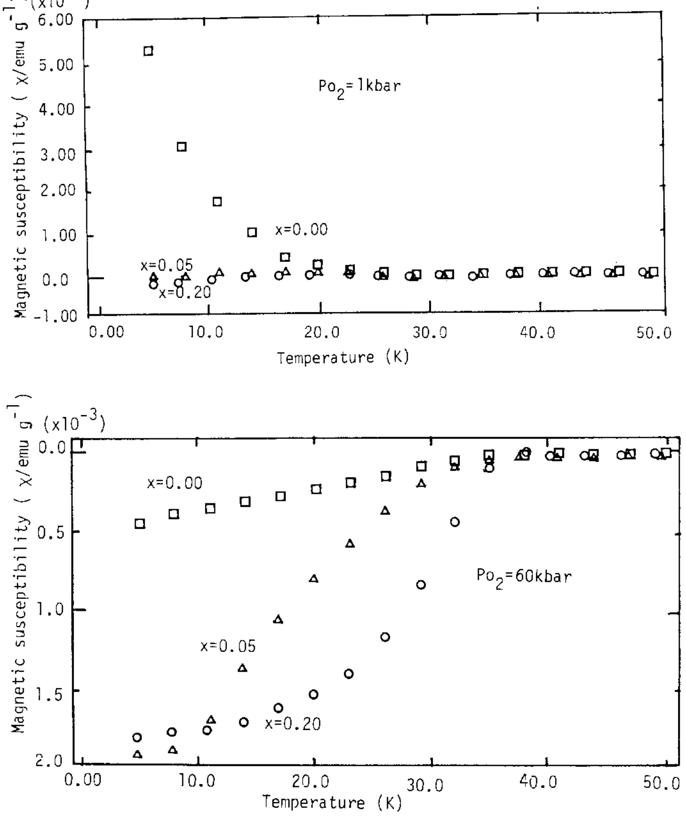

FIG. 6. Magnetic susceptibility of $La_{2-x}Nd_xCuO_{4+z}$ measured on cooling in a field of 10 G.

Nd_xCuO_4 and oxygen-rich $La_{2-x}Nd_xCuO_{4+z}$ observed at room temperature.

Figure 4 shows the electrical resistivity data for $La_{2-x}Nd_xCuO_{4+z}$ with $x = 0$, 0.05, 0.1, and 0.2 prepared under various oxygen pressures. Typical features revealed here are as follows. (i) All the La_2CuO_{4+z} samples after the present oxygen pressure treatments are, at least partially, superconducting. The onset transition temperature where resistivity begins to drop is almost invariant whatever the oxygen pressure is, though the normal-state resistivity decreases and becomes more metallic with increasing oxygen content. The resistance anomaly in the 150- to 300-K range, which has been attributed to the phase separation involving oxygen diffusion (*12*), gradually disappears. (ii) In the Nd-substituted samples, the normal-state resistivity tends to decrease with increasing Nd content under the same preparative conditions (that is, at almost the same oxygen content). For example, even after the treatment under 1 kbar of oxygen, nonsubstituted $La_2CuO_{4.025}$ shows semiconductive behavior with a broad resistive anomaly in the 150- to 300-K range, while at $x = 0.2$, the normal state resistivity is almost metallic. (iii) In spite of the more metallic behavior in the normal state, T_c decreases as the Nd content increases. $La_2CuO_{4.005}$ prepared in air shows a sign of superconductivity at around 40 K, but $La_{1.8}Nd_{0.2}CuO_{4.01}$ shows no superconductivity down to 10 K.

In Fig. 5, the variation of T_c with excess oxygen content z is shown. The T_c of La_2CuO_{4+z} is independent of z, while that of $La_{2-x}Nd_xCuO_{4+z}$ depends strongly on z.

Figure 6 shows the temperature dependence of magnetic susceptibility (magnetization divided by applied field) measured on cooling. For samples of low excess oxygen content, it is difficult to find a well-defined, sharp transition because the superconducting volume fraction is small. The substitution of Nd for La and the use of higher oxygen pressures increase the volume fraction of the superconducting phase. For $La_2CuO_{4.08}$ and $La_{1.8}Nd_{0.2}CuO_{4.09}$ prepared under 60 kbar of oxygen, the susceptibility is -4.9×10^{-4} emu/g and -1.8×10^{-3} emu/g at 4 K, respectively.

Since the oxygen content prepared under the same oxygen pressure shows no large dependence upon x, i.e., the doped hole content is considered to be nominally almost the same, it is surprising and interesting that the superconducting volume fraction is largely increased by the Nd substitution. The relatively low resistivity for the Nd-doped samples in their normal state can also be explained by the increase of the fraction of the superconductive phase. In contrast with La_2CuO_{4+z}, the Nd-doped samples show an oxygen-content dependence of T_c. All these data lead us to assume that the phase separation into a nearly stoichiometric phase with $z \simeq 0$ and an oxygen-rich phase tends to be suppressed by the Nd substitution. The monophasic range of the latter superconducting phase is widened toward the low-oxygen-content side, and the dependence of T_c upon the hole concentration is unmasked.

For further discussion, low-temperature structural data are needed. For comparison, we are now preparing other systems such as $La_{2-x}Pr_xCuO_{4+z}$ and $La_{2-x}Gd_xCuO_{4+z}$ and studying their structural, electrical, and magnetic properties below room temperature.

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References

1. D. C. Johnston, J. P. Stakes, D. P. Goshrn, and J. T. Lewandowski, *Phys. Rev. B* **36,** 4007 (1987).
2. R. L. Greene, H. Maletta, T. S. Plaskett, J. G. Bednortz, and K. A. Muller, *Solid State Commun.* **63,** 379 (1987).
3. J. E. Schirber, B. Morison, R. M. Merrill, D. E. Hlava, E. L. Venturini, J. F. Kwak, D. J. Nigrey, B. J. Baugham, and D. S. Gingley, *Phys. C* **158,** 183 (1989).
4. C. Chaillout, S-W. Cheng, Z. Fisk, M. S. Lehman, M. Marezio, B. Morosin, and J. E. Schirber, *Phys. C* **158,** 824 (1988).
5. G. Demazeau, F. Tresse, Th. Plante, B. Chevalier, J. Etourneau, C. Michel, H. Hervieu, B. Raveau, P. Lejay, A. Sulpice, and R. Tournier, *Phys. C* **153–155,** 824 (1988).
6. J. D. Jorgensen, B. Dabrowski, Shiyou Pei, D. G. Hinks, L. Sederholm, B. Morosin, J. E. Schirber, E. L. Venturini, and D. S. Ginley, *Phys. Rev. B* **38,** 11377 (1988).
7. B. Dabrowski, J. D. Jorgensen, D. G. Hinks, Shiyou Pei, D. R. Richards, H. B. Vanfllet, and D. L. Deker, *Phys. C,* **162–164,** 99 (1989).
8. J. D. Jorgensen, B. Dabrowski, Shiyou Pei, P. R. Richards, and D. G. Hinks, *Phys. Rev. B* **40,** 2187 (1989).
9. Z. Hiroi, T. Obata, M. Takano, Y. Banndo, Y. Takeda, and O. Yamamoyo, *Phys. Rev. B* **41** 11, 665 (1990).
10. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B* **25,** 925 (1969); *Acta Crystallogr. Sect. B* **26,** 1046 (1970); *Acta Crystallogr. Sect. A* **32,** 751 (1976).
11. J. B. Goodenough and A. Manthiram, *J. Solid State Chem.* **88,** 115 (1990).
12. M. F. Hundley, J. D. Thompson, S-W. Cheong, Z. Fisk, and J. E. Schirber, *Phys. Rev. B* **41,** 4062 (1990).