Orthorhombic (II) superstructure phase in oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ prepared by quenching

Y. Kubo, T. Ichihashi, T. Manako, K. Baba, J. Tabuchi, and H. Igarashi
Fundamental Research Laboratories, NEC Corporation, 4-1-1 Miyazaki, Miyamae-ku, Kawasaki 213, Japan
(Received 3 December 1987)

The oxygen-ordered orthorhombic (II) phase in oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ was successfully prepared by a metal-block-quenching method. The orthorhombic (II) phase was found to be a single phase with a T_c of ~60 K at around $\delta=0.5$. Electron diffraction revealed the doubling of the shorter axis (a axis) of the orthorhombic structure in this phase. These results can be interpreted by the structure model that every other Cu—O chain is missing on the Cu(1) plane of the orthorhombic structure at the composition of $\delta=0.5$.

Recently, several reports on a possible new oxygen-ordered phase [we call this the orthorhombic (II) phase] in oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ have appeared based on experimental observations[1-3] or theoretical considerations.[4] This must be very important for understanding the superconducting mechanism because it gives us a new combination of T_c and crystal structure which is different from the ordinary 90-K materials. However, there remain many unanswered questions for the orthorhombic (II) phase as to the oxygen-ordering state, oxygen composition range, and preparation method. Cava *et al.*[2] prepared oxygen-deficient samples using a gettered annealing technique and found the orthorhombic (II) phase with T_c ~60 K in the δ range of 0.3–0.4. They also suggested that the orthorhombic (II) phase has a superstructure with a doubled b axis of orthorhombic structure. Tendeloo *et al.*,[1] however, observed the doubling of the a axis in a part of the sample with a T_c of 84 K, which was not prepared by gettered annealing. Theoretically, such doubled unit-cell superstructures are possible at $\delta=0.5$,[4] a δ value which does not agree with the result of Cava *et al.*[2]

In this report, we present experimental results on the orthorhombic (II) phase in oxygen-deficient samples prepared by a metal-block-quenching method. One of the most interesting results is that the orthorhombic (II) phase was easily obtained without a special preparation technique as described in Ref. 2. Both ac susceptibility and dc resistivity measurements indicated two different superconducting phases with a T_c of 90 K [δ~0.15: orthorhombic (I)] and ~60 K [$\delta=0.45$–0.55: orthorhombic (II)]. Electron diffraction of the orthorhombic (II) phase revealed the doubling of the shorter axis (a axis) in the orthorhombic structure, which coincides with Ref. 1 but is contrary to Ref. 2. The most probable structure is the one where every other Cu—O chain is missing in the Cu(1) plane of the orthorhombic structure.

The starting $YBa_2Cu_3O_{7-\delta}$ pellets were prepared from Y_2O_3, $BaCO_3$, and CuO powders by sintering at 980 °C. The pellets were cut into a bar shape of $1.2\times1.5\times8$ mm^3 for ac susceptibility measurements and $1.2\times1.5\times12$ mm^3 for resistivity measurements. The standard weight of each bar was measured after being oxygen annealed at 950 °C for 1 h and furnace cooled. Then, each bar was heat treated at various temperatures for 30 min in an oxygen atmosphere and quenched on a cold metal block. The relative oxygen deficiency $\delta'=\delta-\delta_0$ was obtained from the weight change of the sample. The amount of the oxygen deficiency for a furnace-cooled sample, δ_0, was measured by a Horiba MEGA-2800 NDIR oxygen analyzer. The ac susceptibility was measured by a self-inductance method using a HP-4274A LCR meter. Calibration was carried out using the same-shaped lead bar at 4.2 K. The dc resistivity was measured by a conventional four-probe method with Au electrodes sputtered on the surface of the bar and fine Au wires wound and fixed by a silver paint. The electron diffraction studies were done on a JEOL 4000 EX transmission electron microscope.

Typical susceptibility data are shown in Fig. 1. Perfect diamagnetism is observed with δ' up to 0.52 under a measuring field of ~0.1 Oe. However, this diamagnetism is very sensitive to the measuring field and is strongly suppressed by a field of ~10 Oe as shown in Fig. 1, which is similar to the previous data.[5,6] The most interesting result is that the field dependence of $\delta'=0.19$ and 0.52 is quite different from that of $\delta'=0$ and 0.36, i.e., the former shows a large field dependence from the beginning of the diamagnetic transition while the latter shows no field dependence up to over a midpoint of the transition. This

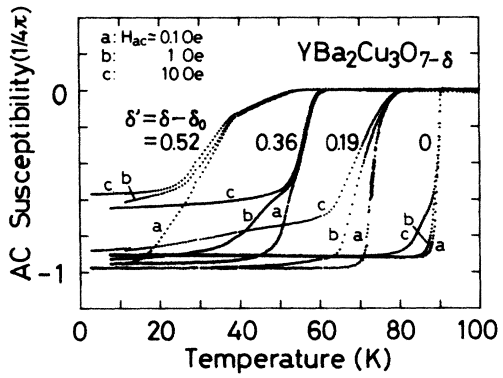

FIG. 1. ac susceptibilities for $YBa_2Cu_3O_{7-\delta}$ samples prepared by a metal-block-quenching method measured in the field of 0.1, 1, and 10 Oe. The amount of the oxygen deficiency is expressed by δ', which is a relative value measured from the furnace-cooled state, $\delta=\delta_0=0.15$.

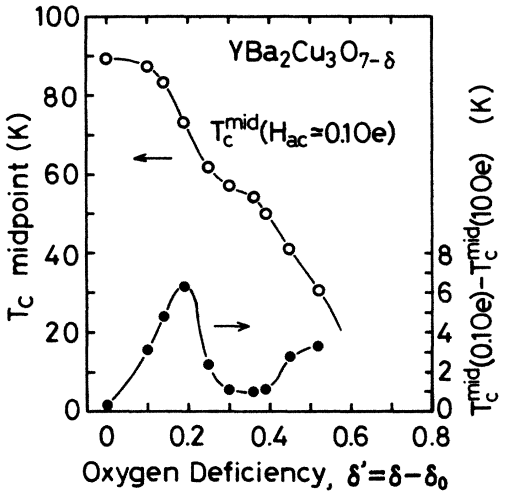

FIG. 2. T_c midpoints for $YBa_2Cu_3O_{7-\delta}$ samples measured by ac susceptibility in the field of 0.1 Oe are plotted against the oxygen deficiency δ', which is a relative value measured from the furnace-cooled state, $\delta-\delta_0=0.15$. The difference between the T_c midpoints measured at 0.1 Oe and at 10 Oe is also plotted.

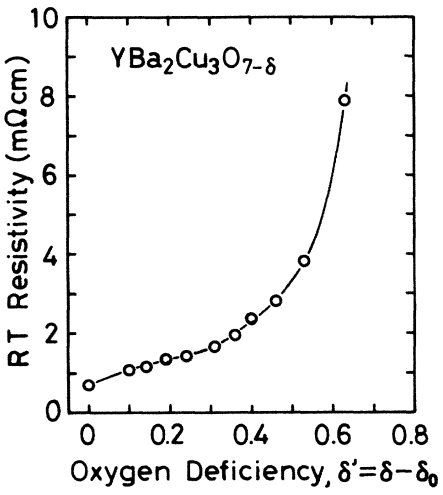

FIG. 4. Room-temperature resistivities for $YBa_2Cu_3O_{7-\delta}$ samples prepared by a metal-block-quenching method. The amount of the oxygen deficiency is expressed by δ', which is a relative value measured from the furnace-cooled state, $\delta-\delta_0=0.15$.

tendency is clearly shown in Fig. 2, in which solid circles present the difference between the midpoints of the transition at 0.1 and 10 Oe, and a remarkable minimum of the field dependence exists at $\delta'=0.3$–0.4. Also, the T_c midpoint has a plateau in this δ' region. These facts indicate that two bulk superconducting phases exist at $\delta'=0$ and $\delta'=0.3$–0.4, and that superconducting percolation occurs at the other δ' region. This is also supported by the result of the resistivity measurement as shown in Fig. 3. Sharp transitions and no current dependence are observed for $\delta'=0$ and 0.40, but the sample of $\delta'=0.24$ shows a broad transition from near 90 to 70 K and has a relatively large current dependence. Also, the samples of $\delta'=0.53$ and 0.63 show large current dependence and broad transitions with the same onset temperature of $\sim$60 K as that of $\delta'=0.40$. All these results strongly support the existence of a 60-K superconducting single phase, orthorhombic (II) phase, in the δ' range of 0.3–0.4. Normal resistivity at room temperature plotted against the oxygen deficiency does not show an obvious minimum, but a small depression is recognized at $\delta'=0.2$–0.4 (Fig. 4).

Successive annealing in an evacuated quartz capsule at 400 °C for 60 h scarcely changed the superconductivity of the quenched samples as shown in Fig. 5. This means that the low-temperature equilibrium state is nearly achieved by the present metal-block-quenching method in spite of the high quenching rate of several hundred degrees per second. Therefore, the present results are considered to be very close to the equilibrium behavior. It should be noted,

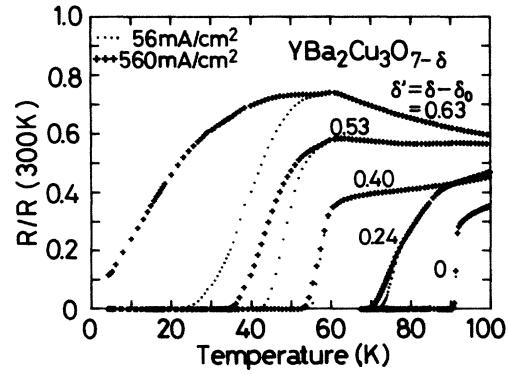

FIG. 3. Resistive transitions for $YBa_2Cu_3O_{7-\delta}$ samples. The amount of the oxygen deficiency is expressed by δ', which is a relative value measured from the furnace-cooled state, $\delta-\delta_0=0.15$.

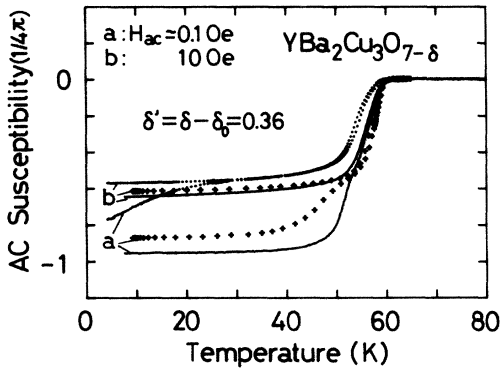

FIG. 5. Superconducting transitions for various $YBa_2Cu_3O_{7-\delta}$ samples of $\delta'=0.36$ measured by ac susceptibility under the measuring field of 0.1 and 10 Oe. δ' is a relative oxygen deficiency measured from the furnace-cooled state, $\delta-\delta_0=0.15$. Solid lines are for the as-quenched sample, cross marks are for the sample annealed at 400 °C for 60 h in an evacuated quartz capsule after the quenching and dots are for the sample left in the ambient atmosphere for ten days after the quenching.

however, that the oxygen-deficient samples are much more unstable as compared with the furnace-cooled sample. Figure 5 demonstrates that the sample left in the ambient atmosphere for 10 days after quenching does not show the perfect diamagnetism even at a low field. So, we kept the samples in a dry oxygen atmosphere after quenching and took all data within a few days after quenching.

The oxygen analysis was carried out using a well-annealed 99.9999% Y_2O_3 powder as a standard, and each sample was analyzed ten times. The oxygen content for the furnace-cooled sample was 6.85 ± 0.04 which well agrees with the results of Rietvelt analysis of neutron diffraction data.[7] Therefore, we take the δ_0 value as 0.15, which indicates that the orthorhombic (II) phase occurs at around $\delta = \delta' + \delta_0 = 0.5$ at which half of the oxygen atoms on the Cu(1) plane are lost.

Electron diffraction showed very weak streaks elongated in the a^* direction at the half-way point of the a^* reflections. This superlattice ($2a_0 \times b_0$) was very often observed for samples of $\delta' = 0.3$–0.45 ($\delta' = 0.45$–0.6). Moreover, the orthorhombic distortion ($b_0 - a_0$) of the samples showing the superstructure was always $\sim \frac{2}{3}$ of that of the furnace-cooled sample. This distortion corresponds to the composition of $\delta \sim 0.37$ ($\delta \sim 0.52$) judging from our previous data.[5] This means that the superstructure is strongly related to the narrow oxygen composition range around $\delta \sim 0.5$. The details will appear elsewhere.

Considering that the oxygen deficiency of the orthorhombic (II) is ~ 0.5, the most possible superstructure of $2a_0 \times b_0$ is that every other Cu–O chain is missing on the Cu(1) plane of the orthorhombic structure. Recently, two of the present authors (Y.K. and H.I.) proposed the possible oxygen-ordered superstructure by considering the second-nearest-neighbor interaction of 2D oxygen lattice on Cu(1) plane.[4] If we assume the two kinds of the second-nearest-neighbor oxygen interactions are not the same, that is, the O–O direct interaction is repulsive and the O–Cu–O interaction is attractive, the same superstructure as the orthorhombic (II) phase is derived through similar discussion. Superconducting properties can be explained as follows. Oxygen defects introduced in the orthorhombic (I) phase first destroy the Cu–O chain at random, and divide the 90-K region into small islands which are weakly connected to each other through oxygen-deficient low-T_c boundaries. This situation leads to field-sensitive percolative superconductivity as observed at $0.15 < \delta < 0.5$. Further introduction of oxygen defects ($\delta \sim 0.5$) gives rise to the oxygen-ordering over the whole sample and homogeneous 60-K superconductivity [orthorhombic (II)] occurs, which does not show any percolative behavior. In the δ range larger than 0.5, oxygen defects divide the 60-K region into small islands which will again show the percolative behavior.

In summary, the oxygen-ordered superstructure, orthorhombic (II) phase, in the oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ was successfully prepared by the metal-block-quenching method. Both ac susceptibility and dc resistivity measurement revealed that the orthorhombic (II) is a 60-K superconducting single phase at around $\delta = 0.5$. Also, an electron diffraction study showed the doubling of the a axis in this phase. Therefore, we conclude that the most probable structure of the orthorhombic (II) phase is one where every other Cu–O chain is missing on the Cu(1) plane. Such an alternately lined up Cu–O chain structure seems responsible to the 60-K superconductivity while the full lined-up Cu–O chain structure gives rise to the 90-K superconductivity.

We would like to thank M. Yonezawa for his guidance.

[1] G. Van Tendeloo, H. W. Zandbergen, and S. Amelinckx, Solid State Commun. **63**, 603 (1987).

[2] R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Phys. Rev. B **36**, 5719 (1987).

[3] R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Nature **329**, 423 (1987).

[4] Y. Kubo and H. Igarashi, Jpn. J. Appl. Phys. **26**, L1988 (1987).

[5] Y. Kubo, T. Yoshitake, J. Tabuchi, Y. Nakabayashi, A. Ochi, K. Utsumi, H. Igarashi, and M. Yonezawa, Jpn. J. Appl. Phys. **26**, L768 (1987).

[6] E. Takayama-Muromachi, Y. Uchida, M. Ishii, T. Tanaka, and K. Kato, Jpn. J. Appl. Phys. **26**, L1156 (1987).

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