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Orthorhombic structure: a necessity in superconducting 1-2-3 compounds

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Abstract. X-ray and resistivity measurements on $YBa_2Cu_3O_{7-\delta}$ (1-2-3) samples show that for the same but low oxygen concentration, $\delta \simeq 0{\cdot}55$, no superconducting transition down to 4·2 K is observed for the tetragonal phase samples while the orthorhombic phase shows a $T_c \sim 31$ K. The effect of oxygen concentration on T_c is isolated. $T_c = 91 \pm 1$ K has, however, been observed continuously for the normal oxygen annealed samples, $\delta \simeq 0{\cdot}07$. The experimental results suggest strongly the necessity of the 1-2-3 compound to be in the orthorhombic phase for the superconducting mechanism to be operative.

Keywords. High temperature superconductivity; $YBa_2Cu_3O_{7-\delta}$; orthorhombic structure.

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Transport and magnetic susceptibility measurements on structurally well-characterized $YBa_2Cu_3O_{7-\delta}$, 1-2-3 compound, ($\delta \leqslant 0{\cdot}1$) and isostructural $RBa_2Cu_3O_{7-\delta}$ (R = rare earths except Ce, Pr, Pm and Tb) show superconducting (SC) transition temperature, T_c, in the vicinity of 91 K (Cava *et al* 1987b; Siegrist *et al* a, b, 1987; Rao *et al* 1987; Prakash *et al* 1987; Schneemeyer *et al* 1987). In these compounds, the defect perovskite orthorhombic structure with oxygen vacancy seems to play an important role in the SC behaviour. (Hatano *et al* 1987; Jorgensen *et al* 1987; Stavola *et al* 1987). Further, it has been reported that the 1-2-3 compound, $YBa_2Cu_3O_{7-\delta}$ for $\delta > 0{\cdot}5$ does not show SC either due to the sample being in the tetragonal phase or having large number of oxygen vacancies or both. It has also been noted that the 1-2-3 compound in its usual preparation cycle if quenched at high temperature (> 800°C) invariably forms tetragonal phase for the equilibrium oxygen concentration ($\delta \geqslant 0{\cdot}5$). There is just one report, (Manthiram and Goodenough 1987), to our knowledge, where tetragonal phase has conclusively been observed for $\delta < 0{\cdot}5$ although SC transition at lower temperatures in the tetragonal phase samples has been reported (Hatano *et al* 1987; Oda *et al* 1987; Rajarajan *et al* 1988). In this paper we have aimed at isolating and ascertaining the important but not so unambiguous roles of (i) the orthorhombic structure, and (ii) the oxygen vacancies in the SC mechanism in the 1-2-3 compound. The details of our experiment, especially a careful control of the oxygen concentration, are described in what follows.

The samples of $YBa_2Cu_3O_{7-\delta}$ (1-2-3) compound were prepared by the standard ceramic technique (Prakash *et al* 1987). High purity (> 99%) $BaCO_3$ and oxides of Y

and Cu were taken in proportionate quantities as the starting powders. The powders were finely ground and mixed in acetone for 3 h and were calcined in a pressed cake form at ~ 930°C for 24 h in air. The precalcined cake was recrushed to fine powder which was then pressed at 5 MPa into pellets of 6 mm diameter and ~ 2 mm in thickness. The pellets were finally sintered at 930 ± 10°C for 18 h and slowly cooled in oxygen atmosphere down to ~ 550°C where they were subjected to an extended oxygenation for 8 h. These pellets were slowly cooled to about 100°C before taking them out of the furnace. This sample hereafter will be referred to as sample A. The sample A in powder form as well as ruby scraper cleaned pellets were examined at room temperature using an X-ray unit (Phillips PW 1140). All the XRD lines could be assigned only to a single orthorhombic phase within the instrumental accuracy (impurity phase if any ought to be less than 2%). The amount of oxygen in the fresh samples was estimated (Tarascon *et al* 1987) by thermogravimetric analysis (Du Pont TGA 951). The value of δ in $YBa_2Cu_3O_{7-\delta}$ was $0{\cdot}07 \pm 0{\cdot}02$. The DC resistivity of these samples was measured by the standard four-probe technique using a Keithley nanovoltmeter and constant current source.

In order to synthesize 1-2-3 compound in orthorhombic (Pmmm) structure with a large oxygen deficiency ($\delta \geqslant 0{\cdot}5$), which is normally associated with a tetragonal phase, we adopted the following procedure. Oxygen-annealed pure 1-2-3 pellets of sample A were taken as the starting material and placed in a platinum foil inside a quartz tube along with freshly sliced and snapped cerium metal pieces which were in physical isolation from the pellets. Ce metal acts as a highly reactive oxygen absorbent (Prakash *et al* 1982; Ross 1987). The quartz tube was vacuumed and sealed. Three such quartz tubes were prepared and placed in a horizontal tubular furnace for different time durations at ~ 400°C. The samples were slowly cooled to room temperature and were X-rayed and thermogravimetrically analysed. All these pellets show orthorhombic (Pmmm) phase albeit having a varying degree of δ. Only the highly oxygen-deficient ($\delta = 0{\cdot}55 \pm 0{\cdot}02$) pellets, hereafter referred to as sample B, were selected for electrical resistivity measurements.

To obtain the tetragonal (P4/mmm) phase samples, the pellets of sample A were rapidly quenched from different elevated temperatures ranging between 800°C and 920°C. The samples were subjected to XRD and TGA analysis. All the quenched pellets showed tetragonal structure but with a varying degree of oxygen vacancy. The pellet quenched at 840 ± 10°C gave $\delta = 0{\cdot}54 \pm 0{\cdot}02$ and is referred to as sample C. Various physical parameters measured for the samples A, B and C are listed in table 1.

The resistivity curve for the normal annealed sample A (see figure 1, curve a) shows a small drop at ~ 160 K. This drop could be repeated only for three thermal cycles and it then began to wither away indicating unstable structural aspects responsible for this fall. Moreover, out of six pellets of the type A from the same batch, only two showed a small resistivity anomaly in the vicinity of 160 K. The samples show non-measurable low resistance ($\rho = 0$) at $T_c = 91 \pm 1$ K. The transition width has been observed to be less than 2 K (see the inset, figure 1). In sample B, the resistivity behaviour above 92 K is weakly semiconducting-like. A little sharp drop at ~ 92 K and a further larger drop around 60 K is observed (figure 1, curve b). The resistivity eventually disappears at $T_c \simeq 31$ K with a very wide transition width unlike the one observed by Cava *et al* (1987a). The resistivity behaviour in the vicinity of 91 K and 60 K repeats itself indicating the possibility of a few granules in the pellet having a higher T_c of ~ 90 K and a few of ~ 60 K. The tetragonal phase sample C was tested for resistivity only at room

Table 1. Lattice parameters (a, b, c), T_c and room temperature resistivity (ρ) of $YBa_2Cu_3O_{7-\delta}$ prepared under different conditions.

$\delta \pm 0.02$	a(Å)*	b(Å)*	c(Å)*	$\rho(10^{-3}\Omega\,\text{cm}) \pm 5\%$	$T_c \pm 1$(K)
0.07[a]	3.825	3.892	11.683	2.1	91
0.55[b]	3.849	3.884	11.774	23.6	31
0.54[c]	3.866	3.866	11.796	485	—

a, Oxygen annealed, slowly cooled to ~ 100°C.
b, Slow cooling to room temperature from 390 ± 10°C (see text).
c, Rapid quenching to room temperature from 840 ± 10°C, non-SC.
*, Uncertainty in lattice parmeters = 0.005 Å.

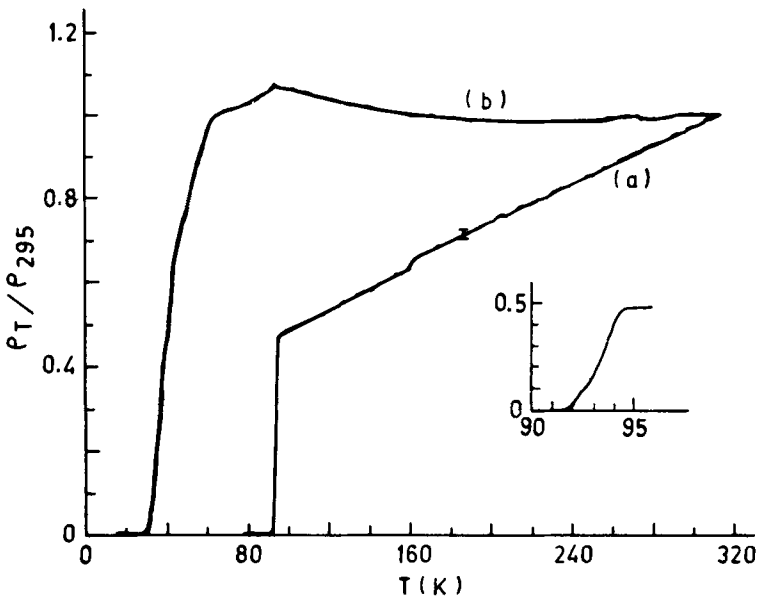

Figure 1. Temperature dependence of normalized resistivity of the ortho-rhombic $YBa_2Cu_3O_{7-\delta}$ samples: curve a—oxygen annealed ($\delta \simeq 0.07$); curve b—oxygen deficient ($\delta \simeq 0.55$). The inset shows the curve a, magnified near T_c.

temperature, ~ 77 K and 4.2 K. The sample did not show SC down to 4.2 K and remained semiconducting.

From our experimental results, we conclude that for the same oxygen concentration ($\delta \sim 0.55$) the orthorhombic structure shows superconductivity albeit at low temperature ($T_c \sim 31$ K) while the tetragonal phase remains non-SC down to 4.2 K. In the 1-2-3 type (Y, La) compositions where superconductivity is reported for the tetragonal phase (Rajarajan *et al* 1988), the XRD structural data are taken only at room temperature. In such compositions a strong possibility of structural phase transition cannot be ruled out at low temperatures at or above T_c. It is interesting to note in this context that $La_{1.85}Ba_{0.15}CuO_4$ with $T_c \sim 30$ K is tetragonal at room temperature but undergoes a structural phase transition to orthorhombic below 150 K (Paul *et al* 1987). It, therefore, appears that the orthorhombic distortion in 1-2-3 compound is essential for the

existence of the SC mechanism and the oxygen concentration plausibly provides the total number of SC interactions analogous to the number of spin interactions in a magnetic system. This view, however, needs to be taken with extreme caution. It should be of great significance to diagnose the local site of the oxygen depletion in the two types of structures of 1-2-3 compound with $\delta > 0{\cdot}5$. For a direct experimental evidence, the high resolution electron microscopy holds some promise (Ourmazd and Spence 1987). Presently, we are conducting detailed XAS and XPS studies on the above samples to investigate the copper and oxygen valence states. The preliminary investigations on $YBa_2Cu_3O_{6{\cdot}93}$ show that Cu is predominantly in 2^+ valence state and about 13% of oxygen in O^{1-} (Mehta *et al* 1988; Padalia *et al* 1988).

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