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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