

Oxygen order and charge-transfer mechanism in Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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The structural and electronic properties of $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$ have been investigated as a function of δ and at $0 \leq x \leq 0.05$. The oxygen-deficient compounds were obtained with the low-temperature Zr-gettering technique. It was found that the structural characteristics and anomalies, and the oxygen-ordering phenomena, observed in undoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, also occur in Zn-doped compounds at the same oxygen concentration, although they are not related to the corresponding electronic features. This seems to suggest that the charge-transfer mechanism, controlling T_c in pure $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, is modified by the presence of Zn.

Clear evidence has been provided so far by both experiments¹⁻³ and theories⁴⁻⁸ that close correlations exist between the structural ordering of the oxygen atoms and the electronic properties of 1:2:3-type high- T_c superconductors, in addition to the well-established relationship between T_c and oxygen concentration. The first observation that the superconductivity coincides with the orthorhombic structure in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) (Ref. 9) has been further worked on and a closely quantitative agreement has been found between the experimental values of T_c versus oxygen content and the theoretical prediction based on a model proposed by Poulsen *et al.*⁵ They calculate T_c by considering, as a function of the oxygen concentration, the relative abundance of two orthorhombic oxygen ordered phases, orthoI (at $\delta \approx 0$) and orthoII (at $\delta \approx 0.5$), containing, parallel to the b axis, full O-Cu-O chains and alternatively full and empty chains, respectively.⁴ The CuO chains are claimed to act as charge reservoir and to supply holes to the CuO_2 planes through a charge-transfer mechanism. Such a mechanism was supported through calculations of the bond valence sum¹⁰ for the Cu2 atoms by Cava *et al.*,¹ who experimentally evidenced the rearrangement of the atoms in the crystallographic cell and the consequent anomalous increase in the c lattice parameter and cell volume, at precisely the oxygen concentration at which superconductivity disappears. The charge transfer is presently assumed to be the main mechanism controlling the hole concentration in the CuO_2 planes and determining the superconductivity and the T_c in 1:2:3-type materials. There are however a few exceptions, which require further investigations. Besides compounds such as $\text{PrBa}_2\text{Cu}_3\text{O}_7$ (Ref. 11) and $(\text{Y,Ca})\text{Ba}_2\text{Cu}_3\text{O}_7$,¹² which exhibit an anomalous combination of electronic and structural properties when compared to YBCO (the Pr compound is in fact semiconducting, in spite of the orthorhombic structure, while the Ca compound is superconducting, even if tetragonal), also the well-known Zn-doped YBCO system

$[\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}]$ presents interesting peculiarities: Zn doping in fact seems not to affect the structural properties of YBCO, according to what is to be expected on the basis of steric considerations, but it does strongly deteriorate the superconducting properties, being in this respect more effective than any other known substituent for Cu. For these reasons the Zn-doped system has been extensively investigated, from phenomenological¹³ and fundamental^{14,15} points of view, but, in spite of the general interest, a self-consistent explanation for the Zn-induced phenomena has not yet been given and the material itself has still not been thoroughly characterized. Controversial data, for instance, have been reported about the crystallographic site occupancy of Zn substituting for Cu,¹⁶⁻²⁰ which reflect the objective difficulty related to the scarce contrast between the neutron scattering factors of Zn and Cu, and only very few data have been published on the structural and electronic properties of $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$ as a function of oxygen concentration.^{21,22} In this paper we present the results of a systematic study of the properties of the Zn-doped compounds as a function of x and δ , and analyze them within the framework of the current understanding of the 1:2:3-type materials phenomenology. The low-temperature Zr-gettering technique¹ was used for producing oxygen-deficient compounds, since it is expected to yield thermodynamically stable and oxygen-ordered phases.

Zn-doped compounds with $x = 0, 0.02, 0.03, 0.05$, and $0 \leq \delta \leq 1$, were prepared by solid-state reaction of oxides and BaCO_3 . Stoichiometric amounts of reagents were homogenized and milled under ethanol, in an agate container. Repeated and alternate thermal heating in air at 930°C and mechanical grinding were performed, until homogeneous and x-ray impurity-free materials were obtained. Powders were then pressed and sintered in air at 930°C. Annealing was carried out in flowing oxygen at 480°C, for 150 hours: oxidized compounds were obtained, whose oxygen content ranged from 6.92 to 6.94

atoms per unit formula (apuf), independently of the Zn content. Reduction was done in vacuum, by gettering oxygen with metallic zirconium. 2–3 pellets of similar weight (about 0.7 gram each) and 2.5-cm-high zirconium strips of various lengths (from 1 to 15 cm) were sealed in evacuated pyrex ampoules, 35–40 cm³ in capacity, and treated at 448°C for 120 hours; an inverse proportionality was reproducibly found between the zirconium surface and the residual content of oxygen in the compounds, independently of x . Within the experimental error limits, the specimens from the same ampoule exhibited uniform stoichiometry and electronic and structural characteristics.

Oxygen concentration in the compounds was determined by iodometric titrations,²³ with an amperometric dead-stop end-point detection,²⁴ and by assuming a constant +2 valence for zinc. The measurement reproducibility was better than 0.02 apuf. The structural analysis was performed by x-ray diffraction on a Siemens D-500 diffractometer, with a CuK α radiation, in steps of 0.05°, between 20° and 60°. The lattice parameters were determined by a least-square fitting to the relevant diffraction lines. Resistivity as a function of temperature was measured between 300 and 12 K, in a closed-cycle helium cryostat, with the four-point probe and by applying a pulsed 0.1–1 mA ac current. Electron-diffraction experiments on ground powders, dispersed in isopropyl alcohol, were performed on a Philips CM30 transmission electron microscope, at 300 kV. In order to correlate the different properties exactly, the complete characterization was done on a single pellet in most of the experiments: the resistivity was measured first, and, after crushing, the powders were used for the other analyses.

The lattice parameters and the orthorhombic strain, $S=(b-a)/(b+a)$, of undoped and Zn-doped compounds, are reported in Figs. 1 and 2, respectively, as a function of the oxygen stoichiometry. Data shown in Fig. 1 indicate that the a - and b -lattice dimensions are independent of Zn content and that the orthorhombic-to-tetragonal phase transition occurs at $\delta \approx 0.65$ for any x . Such a result is also confirmed by the orthorhombic strain annihilation, occurring at the same oxygen value and independently of x . In Fig. 3 the c -lattice parameter

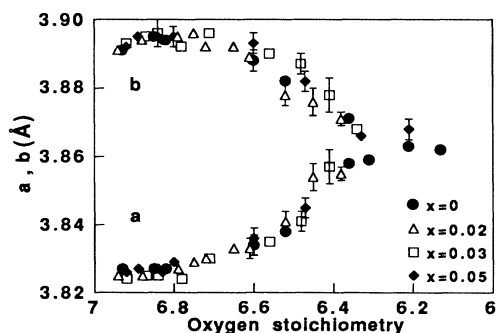


FIG. 1. a - and b -lattice parameters vs δ in $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$. Where not indicated, errors are within the symbol dimensions.

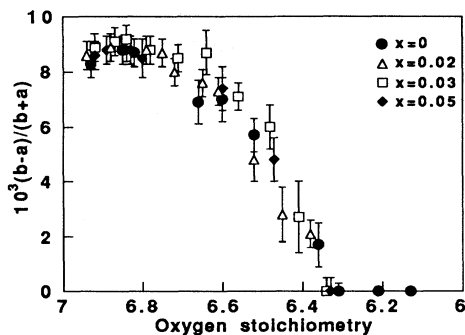


FIG. 2. Orthorhombic strain, $S=(b-a)/(b+a)$, vs δ in $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$.

as a function of oxygen concentration for $x \geq 0$ is reported. A linear increase of the c -lattice dimension at increasing δ occurs at any x , and the slope variation, already observed at $\delta \approx 0.65$ in the undoped material,^{1,9} is also evident in the Zn doped compounds, even if it is reduced at high Zn concentration ($x=0.05$). Electron-diffraction patterns of Zn-doped YBCO ($x=0.03$) are shown in Fig. 4 for various δ . When compared with those of the undoped materials at similar oxygen concentration, such patterns exhibit identical features: no defects (but twinning) or superstructures in highly oxygenated samples [Fig. 4(a)], elongated spots, indicating short-range ordered domains in the a - b plane, at intermediate oxygen concentration [Fig. 4(b)] and sharp spots, with doubling of the a -lattice parameter, at oxygen ≈ 6.5 apuf [Fig. 4(c)]. Such features, already reported for undoped 1:2:3 compounds,^{1,25,26} were attributed to relatively long-range orthoII structures, determined by the ordering of the oxygen atoms in alternatively empty and full chains, running parallel to the b axis, which occurs at an oxygen stoichiometry ≈ 6.50 . T_c values as a function of oxygen and Zn content are reported in Fig. 5; bars indicate the width of the resistive transition (10–90%). At any x T_c decreases with increasing δ , and, for compounds with similar δ , it decreases with increasing x . The compound with $x=0.02$ still exhibits the “two-plateaus” T_c vs δ curve which has been widely reported¹ for low-temperature annealed YBCO; the plateau width is re-

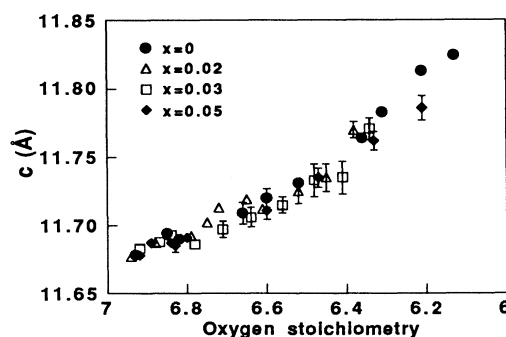


FIG. 3. c -lattice parameter vs δ in $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$.

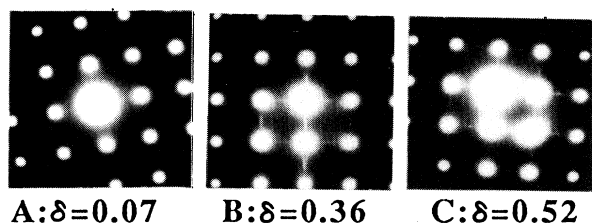


FIG. 4. Electron diffraction patterns of $\text{YBa}_2\text{Cu}_{2.91}\text{Zn}_{0.09}\text{O}_{7-\delta}$ at various δ .

duced, but their position with respect to the abscissa (i.e., oxygen concentration) is practically unchanged with respect to that of the undoped YBCO. At increasing x the T_c curves further smear: the compound with $x=0.05$ is not superconducting down to 12 K, when oxygen stoichiometry is ≈ 6.8 . The superconducting transitions broaden with increasing x , and, for the same x they are sharper in the composition range where the temperature plateaus would be expected in the T_c vs δ curves (even for those compounds which actually do not exhibit plateaus, i.e., $x=0.03$ and 0.05). According to what has been reported for the undoped compound,¹ such a behavior can be explained by assuming that stable oxygen ordered phases exist in the plateau regions, while short-range, differently ordered phases, with distinct T_c , progressively occur in the intermediate oxygen concentration ranges, giving rise to the observed broadening of the resistive transition.

The most interesting feature which emerges from our data is that the structural behavior of pure YBCO as a function of oxygen is not modified by the Zn doping; on the contrary, the electronic effects which were associated with the structural anomalies in the undoped YBCO are not observed in the Zn-doped compounds. Namely (i) the disappearance of superconductivity in the Zn-doped compounds is not connected with the structural, orthorhombic-to-tetragonal phase transition. At any $x > 0$, in fact, orthorhombic semiconducting materials exist, at appropriate δ . (ii) The discontinuity in the c -lattice dimension observed in undoped YBCO simultaneously with the disappearance of the superconductivity and at

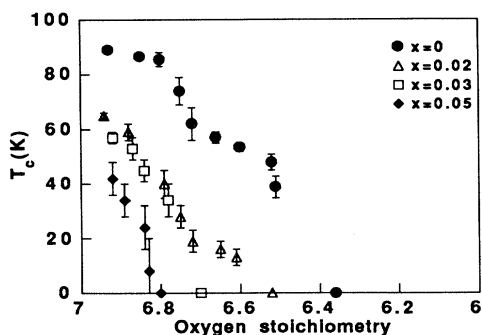


FIG. 5. T_c vs δ in $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$. Bars indicate 10–90% of the resistive transition.

nearly the composition where the orthorhombic-to-tetragonal phase transition occurs, is observed also in Zn-doped compounds at a constant $\delta \approx 0.65$, independently of x . In the doped materials such discontinuities still occur in coincidence with the orthorhombic-to-tetragonal phase transition, but they are not related to the superconducting-to-semiconducting electronic transition, as in the case of pure YBCO. (iii) The ordering of the oxygen atoms in alternatively empty and full chains parallel to the crystallographic b axis, giving rise to the orthoII phase at $\delta \approx 0.5$ in the undoped YBCO, was observed through the electron diffraction experiments also in Zn-doped materials with the same oxygen content. However, in the pure YBCO, the orthoII structure is associated with a plateau in the T_c curve, contrary to what has been found in the Zn-doped compounds with $x > 0.02$. Such results on one hand could seriously weaken the recent findings concerning the relationship between structural and superconducting properties in 1:2:3 materials, or, more likely, they can be interpreted by assuming that the charge-transfer mechanism, controlled by the oxygen concentration and ordering, is modified by the chemical doping with Zn. The effect of Zn seems to be a weakening of the effectiveness of the charge transfer, as suggested by the smearing of the discontinuity in the c axis, well evident when comparing $x=0$ and $x=0.05$ plots (Fig. 3), and the disappearance of superconductivity at relatively low δ values, where long-range ordered oxygen structures still exist, according to the experimental data (Fig. 4) and to theoretical predictions.^{4,5} Such statements do not contradict recent reports, which relate T_c and superconductivity in 1:2:3 materials to the content of holes introduced in the CuO_2 planes and which are claimed to be proportional to the chain fragments of sufficient length^{6,7} or to the oxygen ordered domains of orthorhombic structure⁵ in the basal CuO planes. The presence of Zn at Cu sites is, in fact, expected to reduce the number of units active in the charge transfer (either chain fragments or square domains). If Zn substitutes for Cu at Cu1 sites,^{19,20} it, of course, modifies the O-Cu-O electronic network (see, for instance, the two-dimensional anisotropic next-nearest-neighbor interaction "ASYNNNI" lattice-gas model⁴), making ineffective the substituted units with respect to the charge-transfer phenomenon. But, even in the case Zn replaces Cu at CuO_2 planes,^{16–18} it is likely to prevent the transfer of charge by interacting with the out-of-plane, apical oxygen (O_c , according to Ref. 10), which has been indicated to play a key role in the charge transfer mechanism.²⁷ On the other hand, even if direct evidence of the Zn occupancy in YBCO cannot be provided by our results, the electron diffraction data in our opinion support the hypothesis that Zn is preferentially substituting for Cu2 in the CuO_2 planes. The rate of occupancy of oxygen at the O_b (Ref. 10) positions is, in fact, unperturbed by the Zn substitution, in contrast to what would be expected if some disorder were introduced at the CuO planes by the presence of Zn. In this respect, and due to the recognized difficulties in finding an experimental solution to the question concerning the Zn occupancy, we think that the development of a theoretical model, taking into ac-

count the Zn-induced variation of the number of minimal structures concurring to the charge transfer in the two cases (i.e., substitution of Zn for Cu1 or Cu2), would be of considerable interest for both purposes: proving the correctness of the model itself, by comparison with the experimental T_c values, and providing definite proof of the Zn occupancy.

In conclusion, the analysis of the properties of Zn-doped YBCO as a function of oxygen content indicates that structural properties and oxygen ordering phenome-

na are not affected by the presence of Zn, thus suggesting that Zn is not perturbing the Cu1 positions, directly involved in the oxygen dynamics. On the contrary, the Zn-induced disorder quickly abates T_c , thus implying a sensible perturbation of the CuO-CuO₂ charge transfer process.

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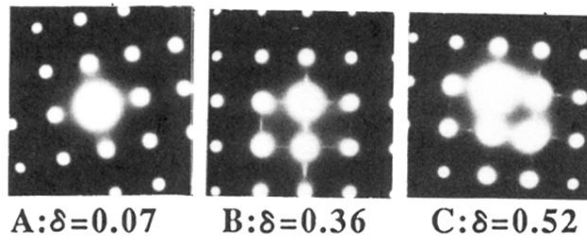


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