PHYSICAL REVIEW B VOLUME 43, NUMBER 13 1 MAY 1991

Effects of Fe and Zn substitution upon superconductivity in $YBa_2Cu_4O_8$

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(Received 8 November 1990; revised manuscript received 9 January 1991)

We report experimental data about the influence of Fe and Zn substitution on the T_c of $YBa_2Cu_4O_8$. Dopant occupation sites have been found using Mössbauer spectroscopy for Fe and by x-ray diffraction for Zn. The Fe atoms were found to occupy the Cu(1) site predominantly at low concentration, whereas the Zn atoms possibly reside in the Cu(2) site. Both dopants suppress T_c at the same rate of 23 K/at.% and this phenomenon is completely different from that observed in the $YBa_2Cu_3O_7$ system.

I. INTRODUCTION

Since the discovery of high-T_c superconductivity a large variety of possible explanations concerning the basic interactions and the nature of the superconducting state have been published. A promising way to probe the superconducting state is to study samples with compositional variations. The orthorhombic $YBa_2Cu_3O_7$ phase (denoted 1:2:3) contains both two CuO_2 planes [denoted Cu(2)] and one CuO chain [denoted Cu(1)]. It is commonly accepted that superconductivity is mainly due to the hybridization of the Cu *d* state and O *p* state in Cu(2) sites. Chemical substitution of transition-metal ions for the two Cu sites has proven to be a rich and varied endeavor.

In $YBa_2(Cu_{1-y}M_y)O_7$ substitution for Cu by a magnetic ion like Fe results in an orthorhombic-tetragonal[1,2] structure transition at $y=0.02$–0.03, and produces drastic changes in T_c. Measurements made by us[3] and others[1,2] established that T_c remains constant and equal to 90 K up to the orthorhombic-tetragonal transition and then decreases continuously to less than 4.2 K at $y=0.13$. Several groups have measured the variation of T_c with Fe concentration and the change of T_c with y obtained by different groups differ somewhat from one group to another. The mean values for the concentration dependence of T_c with y for $M=$Fe are shown in Fig. 1. Mössbauer measurements show[4,5] that for low values of y Fe replaces Cu preferentially in Cu(1) sites whereas for higher concentration $y>0.05$, 10–20% of Fe ions also occupy the Cu(2) sites.[6]

On the other hand, x-ray[6] and neutron-diffraction measurements[7] indicate that for $M=$Zn the crystal structure remains orthorhombic up to $y=0.1$. Despite the fact that Zn is not magnetic, the rate of the depression of T_c with Zn substitution in 1:2:3 is the largest known to date. The dependence of T_c with Zn concentration[5] is also shown in Fig. 1. Several measurements have shown that divalent Zn ions preferentially substitute Cu in the Cu(2) sites,[7] or are distributed roughly equally among the Cu(2) and Cu(1) sites.[6]

Bulk samples of the high-T_c superconductor $YBa_2Cu_4O_8$ (hereafter referred to as 1:2:4) have recently been synthesized by various groups and by different methods. Morris *et al.*[8] synthesized bulk 1:2:4 samples by a high-oxygen-pressure technique. These samples exhibited a superconducting transition at around 80 K. Cava *et al.*[9] were successful in synthesizing the 1:2:4 phase in a powder form under one atmosphere oxygen pressure by utilizing a catalyst such as alkali-metal carbonates. X-ray[10,11] and neutron-diffraction studies[12] revealed that the 1:2:4 structure is closely related to 1:2:3 but with one additional Cu-O chain [Cu(1)] in the unit cell. Each unit cell contains therefore two Cu(1) and two Cu(2) sites, and this leads to a much longer c lattice parameter of 27.19 Å and a smaller orthorhombicity (0.8% in the 1:2:4 phase, 1.8% in the 1:2:3 phase). Furthermore, the 1:2:4 compound has excellent thermal stability of oxygen content up to 800°C since oxygen is neither lost nor gained during heating and cooling[8,9] and the well-known tetragonal-orthorhombic phase transition of the 1:2:3 structure at high temperature is absent.

In the present paper we present the effect of dopants such as Fe^{3+} and Zn^{2+} on the T_c of 1:2:4. The results are significantly different from those described in 1:2:3. Our Mössbauer spectra of iron doped in 1:2:4 samples show that at low concentrations the irons ions occupy

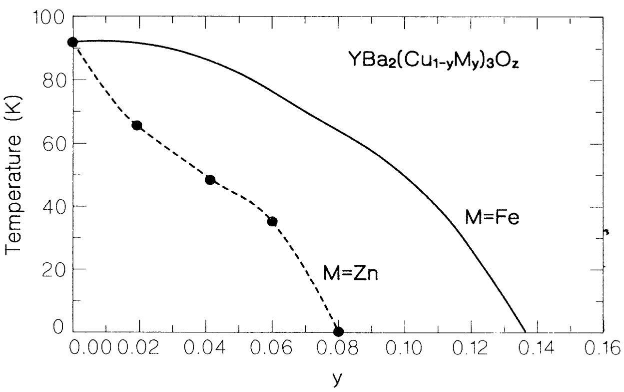

FIG. 1. Concentration dependence of T_c for $YBa_2(Cu_{1-y}M_y)_3O_{7+\delta}$ with $M=$Fe and Zn.

preferentially the Cu(1) sites, whereas we tend to believe that divalent Zn ions reside in the Cu(2) sites. Surprisingly, we find, in general, that T_c in 1:2:4 is extremely sensitive to the impurities regardless of their nature. In both cases a concentration in the order of 3% is sufficient to destroy superconductivity completely.

II. EXPERIMENTAL DETAILS

$YBa_2(Cu_{1-x}M_x)_4O_{8+\delta}$ M=Fe and Zn samples were prepared by a solid-state reaction of stoichiometric mixtures of the constituent oxides, following the procedure described recently by Pooke *et al.*[13] The stoichiometric mixtures, with an addition of 0.2 mol $NaNo_3$ prereacted as a loose powder for 30 min at about 600 °C. The powders were then pressed into pellets, and reacted at 815 for 12 h in flowing oxygen, and then ground. This procedure was applied at least four times. The best materials are obtained when the samples are quenched from 815 °C to ambient temperature, then heated again to 800 °C and furnace cooled under flowing oxygen to room temperature.[14] Powder samples were x-ray analyzed by a Phillips Diffractometer using Ni-filtered Cu K_α radiation, monochromatized by a graphite monochromator. The lattice parameters were determined from least-squares fits, using an average of 24 reflections indexed for the orthorhombic (or tetragonal) phases with the space group *Ammm*. Mössbauer spectroscopy studies were performed using a conventional constant-acceleration spectrometer and a 100-mCi ^{57}Co:Rh source. The spectrum obtained with least-squares fitted to yield the hyperfine parameters. Magnetic dc susceptibility measurements in low fields as a function of temperature were carried out in a PAR vibrating sample magnetometer, to determine T_c of the samples.

A. Crystal structure measurements

Because of the structural complexity of the 1:2:4 phase and the many parameters involved in the fitting process, it is important to be use that the base compound material is providing reliable results. X-ray powder measurements indicate that all the samples mentioned here are essentially phase-pure materials . In some cases, about 3–5 % of undefined lines are also present. The attractive feature in the use of $NaNO_3$ is that by the time the reaction is completed, all the alkali-metal oxide has evaporated from the mixture, leaving a pure 1:2:4 product. The lattice parameters obtained for pure 1:2:4 are $a=3.833(3)$ Å, $b=3.873(3)$ Å, and $c=27.19(1)$ Å in perfect agreement with Refs. 11 and 15.

In $YBa_2(Cu_{1-x}Fe_x)_4O_{8+\delta}$ the ionic radii for Fe^{+3} (0.64 Å) is smaller than that of Cu^{+2} (0.69 Å). From our refinement, the sample with $x=0.025$ is found to remain orthorhombic and a slight decrease of c lattice parameter is observed (Fig. 2). For $x \geq 0.05$ the crystal structure undergoes an orthorhombic-to-tetragonal transition and the c axis does not change in the tetragonal phases. In that respect, the tetragonal phase induced by the doping of Fe in 1:2:4 is very similar to that obtained in the 1:2:3 iron-doped materials.[1,2] In Fig. 3 some examples of x-ray-

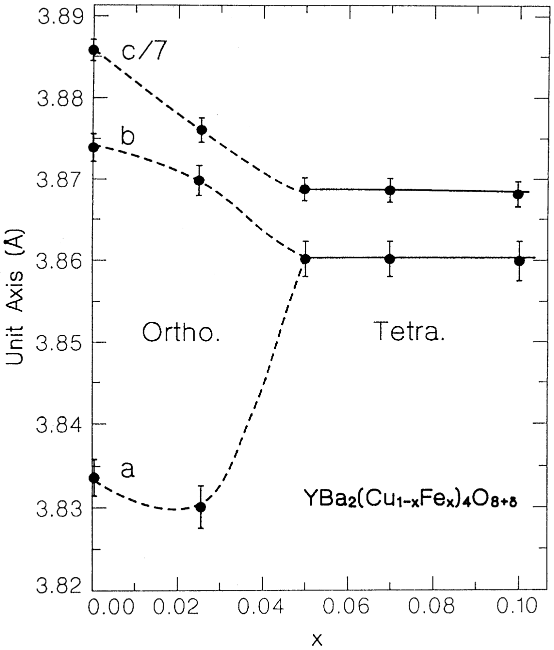

FIG. 2. Concentration dependence of the lattice parameters for $YBa_2(Cu_{1-x}Fe_x)_4O_8$. Doping with Fe induces an orthorhombic-tetragonal phase transition at $x > 0.025$.

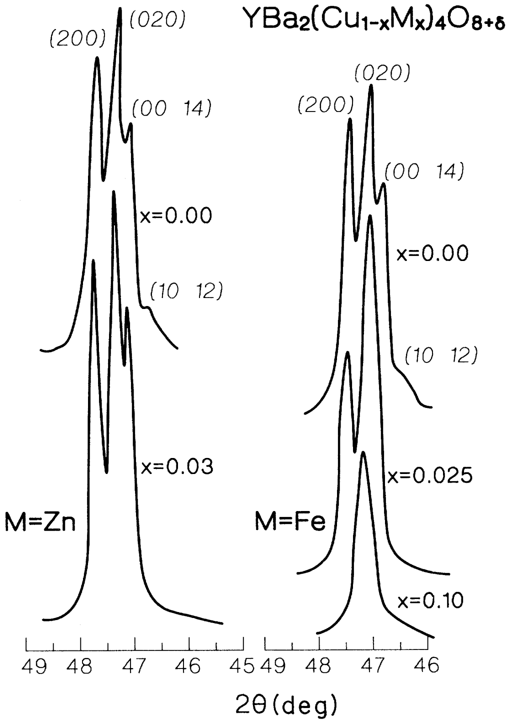

FIG. 3. (0014), (200), and (208) reflections for $YBa_2(Cu_{1-x}M_x)_4)_{8+\delta}$ M=Fe and Zn.

diffraction results in the range $45 < 2\theta \leq 49$ are displayed, embracing the (0014,020,200) group of reflections. For M=Fe a considerable decrease in the c axis of the orthorhombic material for $x=0.025$ leads to overlapping of the two (020) and (0014) reflections. The collapsing of all the three reflections into a unique peak for the tetragonal structure ($x=0.10$) is evident. The oxygen content of Fe substitution samples is not yet clear. In analogy with 1:2:3, it is assumed that, due to the larger valencies of Fe^{3+} ions they attract oxygen to maintain charge neutrality, therefore we assign the oxygen concentration for the iron doped samples as $8+\delta$. The value of δ is proportional to x (one oxygen atom for two Fe atoms) and the positions of these extra oxygens in the crystal structure is not clear yet. Our Mössbauer measurements on iron-doped samples indicate that the solubility limit of Fe in 1:2:4 is higher than $x > 0.10$.[16]

Zn and Cu are next-door neighbors in the Periodic Table and the valence state of Zn is always divalent. Our x-ray measurements indicate that in $YBa_2(Cu_{1-x}Zn_x)_4O_8$ (up to $x=0.07$) the crystal structure remains orthorhombic and all the lattice parameters do not change with x. This means that oxygen stoichiometry, the linear Cu-O chains, and the oxygen-vacancy order are hardly disturbed by Zn substitution and it is believed that (as in the 1:2:3 system[7]) Zn ions preferentially substitute for Cu in the Cu(2) sites. Figure 3 shows that the double peak (020) (200) which is ideally suited for observing the orthorhombic distortion, is not changed by Zn substitution.

B. Mössbauer studies

Figure 4 shows the Mössbauer spectrum obtained at 90 K for the 2.5% ^{57}Fe-doped 1:2:4 system. T_c for this compound is 26 K (Fig. 5). The main information obtained from visual and computer analysis of this spectra is concerned with one doublet with splitting $eqQ/2=0.85(1)$ mm/s [$eqQ/2$ represents the deviation of the local structure, in the iron site, from cubic symmetry] and the isomer shift (IS) of IS=0.41(1) mm/s relative to Fe metal. These parameters can be assigned to Fe^{3+} in a high spin state. We attribute this doublet to iron ions which replace copper in the Cu(1) sites. It appears that all the iron ions in this site are equivalent in terms of oxygen environment.

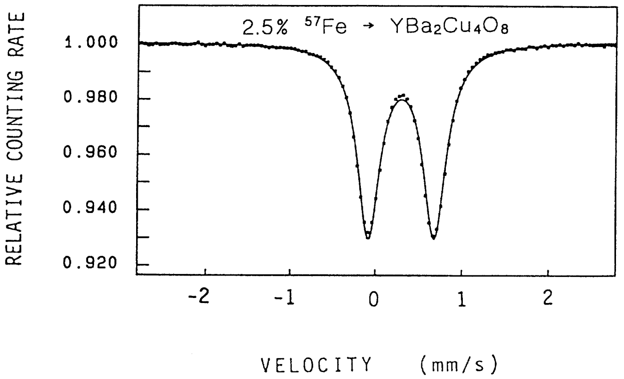

FIG. 4. Mössbauer spectrum of 2.5 ^{57}Fe doped in $YBa_2Cu_4O_8$ at 90 K which is attributed to Fe in the Cu(1) site.

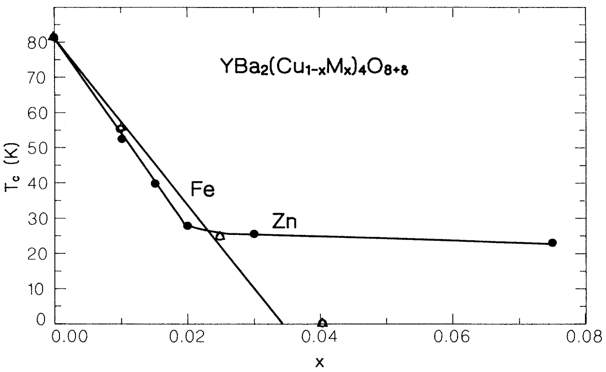

FIG. 5. Concentration dependence of T_c for $YBa_2(Cu_{1-x}M_x)_4O_{8+\delta}$ with M=Fe and Zn.

As already mentioned the 1:2:4 system permits two equally populated types of Cu sites, namely, Cu(1) and Cu(2). Fe as a dopant can be expected to replace both sites and display at least two quadrupole splittings. Moreover, the Mössbauer spectra of ^{57}Fe doped in oxygen-rich 1:2:3 samples is composed of (at least) four quadrupole doublets, corresponding to inequivalent iron sites, due to different oxygen neighbor configuration in the Cu(1) sites.[4,5] None of the doublets observed in the 1:2:3 system resembles the single doublet obtained in the 1:2:4 compound reported here. Upon increasing Fe concentration in 1:2:4, a fraction of Fe atoms enter also into the Cu(2) sites and order antiferromagnetically.[16]

C. dc magnetization measurements

The variation of T_c in $YBa_2(Cu_{1-x}M_x)_4O_{8+\delta}$ (M=Fe and Zn) with x was studied in the field of about 20 Oe in the field-cooled process. The data obtained are exhibited in Fig. 5. Clearly T_c in both systems decreases with x at a rate of 23 K/at. % and for $x > 0.03$ the compounds are not superconducting anymore. The present data for M=Fe agree perfectly with the values of T_c for $0 < x < 0.02$ published in Ref. 17.

In the Zn system for $x > 0.03$ a plateau at about 25 K is observed. Behavior like that is also found in Zn-doped 1:2:3 samples. It probably arises from the limited solubility range of Zn and to the inability to prepare single-phase materials for $x > 0.03$. The main finding of the present paper is that in spite of the different site occupation of the Fe and Zn in the 1:2:4 structure, and in spite of the difference in valency of both ions, the general result is that substituting small amounts of Zn or Fe for Cu strongly inhibits superconductivity and for $x > 0.03$, T_c vanishes (Fig. 5). This implies that in 1:2:4 T_c is decreased at the same rate whether substitution occurs in the CuO_2 planes by nonmagnetic ions or in the CuO chains by magnetic ions. This behavior is completely different from that observed for the 1:2:3 system (see Fig. 1).

To summarize, we have presented the results of an exhaustive experimental study of the effect of Fe and Zn substitution on T_c on the 1:2:4 superconducting system. Our most significant finding in the materials is that the same sharp depression of T_c with increasing doping concentration occurs whether the doping ion is trivalent (Fe) or divalent (Zn). For trivalent Fe^{3+} an orthorhombic-tetragonal phase transition takes place at $x < 0.05$, whereas for divalent doping Zn orthorhombicity is maintained. We provide evidence that Fe substitutes Cu mainly in the Cu(1) site and it is assumed that Zn occupies the Cu(2) sites, but our data cannot be conclusive for Zn substitution. The suppression of T_c by Fe and Zn is much stronger in 1:2:4 than that observed in 1:2:3. For the sharp decrease of T_c obtained no explanation is given at present.

ACKNOWLEDGMENTS

This research was supported by a grant from the German–Israel Foundation (GIF) for Scientific Research and Development No. I-40-100.10/87, and by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel.

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