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LETTER TO THE EDITOR

Metal (M) dopant centred local structures, high-pressure synthesis and bulk superconductivity in $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$: M = Fe, Co, Ni

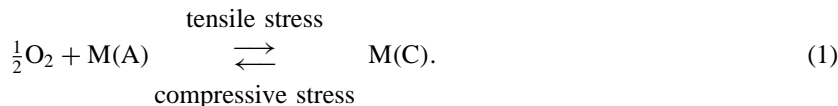
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Abstract. Depression of T_c by the dopants Fe or Co, but not Ni, is spectacularly reversed by synthesis of the titled cuprates at high P instead of ambient P of oxygen with T_c enhanced from 32 to 82 K for M = Fe at $x = 0.10$. With Fe dopant, Mössbauer spectroscopy reveals a conversion of a tetrahedral (A) into a trigonal bipyramidal coordinated (C) Fe chain site by oxygen addition in the chains upon high- P processing. The A \rightarrow C site transformation is elucidated and extended to the case of Co dopant, and its consequences for superconducting behaviour discussed.

High-temperature superconductivity in the cuprates continues to pose challenges. Their unusual physical properties have been ascribed by some to an exotic pairing mechanism. Results of several other experiments suggest that unusual physical behaviour of the cuprates may derive from structural inhomogeneities intrinsic to this class of materials [1, 2]. The short coherence length, the low carrier concentrations and their strong dependence on oxygen content makes it likely that superconductivity in the cuprates may be closely related to structural inhomogeneities. In fact, Phillips [3] has argued theoretically that inhomogeneities on an atomic scale may be directly responsible for the high- T_c values of the cuprates by providing resonant pinning states at E_F through an anti-Jahn–Teller effect [3].

The importance of local structure has also emerged from a voluminous literature [4–9] on rare-earth (RE) and transition-metal (M) doping effects in YBCO. Substitution of a larger RE ion for Y increases the compressive stress on the Cu_3O_7 network (a $\text{Cu}(1)\text{O}_3$ chain between a pair of $\text{Cu}(2)\text{O}_2$ planes). This results in a decrease of the $\text{Cu}(1)$ – $\text{Cu}(2)$ interlayer spacing [10] and an increase in the frequency of the Raman active phonon [11] (500 cm^{-1}) associated with a stretching vibration of the apical oxygen. Furthermore, it has recently been pointed out [7] that the decrease in T_c with increasing metal dopant concentration x , i.e. $|dT_c/dx|$, in $(\text{Y or RE})\text{Ba}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ is also linearly correlated with RE radii (R^{3+}) as well as being dependent on the nature of M. We propose that for M located primarily in the chains, the radius effect is the result of interlayer stress, during sample preparation, on the quasi-equilibrium



Here, M(A) is a four coordinated (pseudo-tetrahedral) dopant (M) site with M slightly displaced from a Cu(1) site; M(C) is a five coordinated (distorted trigonal bipyramidal) M occupying a Cu(1) site [22]. For M = Fe, and at low dopant concentrations ($x = 0.015$), Mössbauer spectroscopy has shown [12] that the observed intrachain site intensity ratio I_A/I_C varies linearly (figure 1) with RE crystal radius R^{3+} . Substitution of a larger RE ion for Y increases the compressive stress on the chains, the quasi-equilibrium of equation (1) moves to the left and results in the dopant selecting the more compact A over the C sites. The role of the A type of local structure in providing stress relief is in harmony with a softening [13] of the 500 cm^{-1} Raman active host phonon upon progressive Fe and Co doping in YBCO. With increasing x , the linear CuO_3 chains along [010] are progressively disrupted and replaced by fragments of corner sharing MO_3 (M = Fe or Co) tetrahedral chains [14] along both $[110]$ and $[1\bar{1}0]$, producing chemical disorder and a reduction of T_c . These chains are akin to GaO_3 chains in the model compound [14] $\text{YSr}_2\text{Cu}_2\text{GaO}_7$.

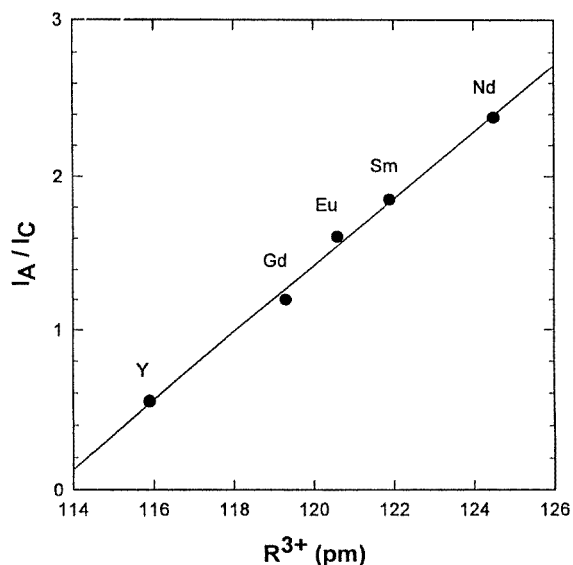


Figure 1. Mössbauer site intensity ratios I_A/I_C deduced from spectra of (Y or RE) $\text{Ba}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$, $\delta \simeq 0$, $x = 0.015$ samples for indicated REs plotted as a function of RE crystal radius (R^{3+}).

In figure 2 we provide observed T_c values at various doping concentrations x for M = Fe, Co and Ni in bulk $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ samples. The *broken* curves represent the $T_c(x)$ variation for samples prepared [5–8] by sintering the precursors at *ambient P* of air or oxygen, and will henceforth be denoted as *usual* samples. If sintering is performed at *high P* (27 MPa) of oxygen and at high T (915 °C), as was done in the present work, the samples not only are stable when brought back to laboratory ambient, but also display a $T_c(x)$ variation shown by the *continuous* curves in figure 2, and these differ significantly from the usual samples for M = Fe and Co. Superconductivity in such high- P processed (HPO) samples occurs at higher T_c values, it is robust and it persists to larger concentrations of Fe. In this letter we show that the microscopic origin of this rather striking behaviour is closely related to the growth of chemical order by selective population of a specific Fe dopant centred local structure (site C) in the chains.

The cuprates were prepared in two steps. First, the precursors Y_2O_3 , BaCO_3 , CuO and

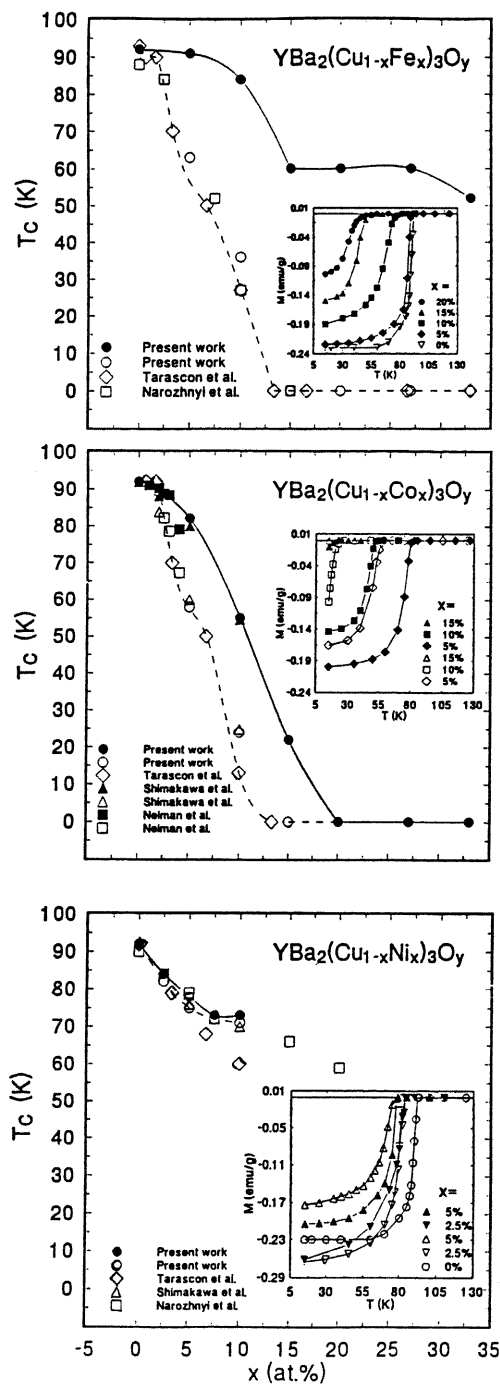


Figure 2. T_c plotted as a function of metal doping concentration x for $M = \text{Fe}$ (top panel), $M = \text{Co}$ (middle panel) and $M = \text{Ni}$ (bottom panel) in YBCO samples synthesized at high P (filled symbols) and at ambient P (open symbols). Lines drawn through data points are guides to the eye. The T_c values determined either magnetically or resistively, $T_c(R \rightarrow 0)$, are taken from [5–8] and are representative of a vast literature. Magnetization measured in a 20 G field, in the zero-field-cooling mode, are displayed in insets.

Fe_2O_3 (or CoO or NiO) of 99.99% purity or better were thoroughly mixed in the desired proportion and sintered in air in the range 925–1000 °C repeatedly for at least 2 days until a single phase was formed, followed by an eventual slow cool (16 h) to room temperature resulting in the usual samples. Second, about 300 mg of the usual sample, wrapped in Au foil, was then sintered at 915 °C in 27 MPa oxygen for 24 h using an autoclave assembly [15], and slow cooled at 1 °C min^{-1} to room temperature, yielding an HPO sample. The oxygen content of the samples was established by a thermo-gravimetric analyser (model TGA-7, Perkin Elmer), the average crystal structure identified by x-ray diffraction (Rigaku D-2000 diffractometer), dc magnetization studied by a vibrating sample magnetometer (model 4500, Princeton Applied Research) and Fe site distributions established by room-temperature Mössbauer spectroscopy.

The T dependence of magnetization at several doping concentrations x is compared to that of a pristine YBCO sample in the insets of figure 2. HPO samples show both higher T_c values and more robust shielding fractions (zero-field cooling). On the other hand, for $M = \text{Fe}$, both HPO and usual samples revealed a systematic smearing (in temperature) of the diamagnetic response with increasing dopant concentration. In select cases we measured magnetization of samples soon (10 min) after retrieval from the autoclave and followed such measurements over the span of a year and failed to detect changes in magnetization, in contrast to pristine YBCO samples which degrade on aging. TGA scans directly confirm the chemical stability of these samples, showing no weight loss up to $T = 400$ °C. X-ray diffraction scans revealed single-phase materials for Fe ($0.05 \leq x \leq 0.22$), Co ($0.05 \leq x \leq 0.33$) and Ni ($0 \leq x \leq 0.10$) with a tetragonal cell for the case of Fe and Co dopants, but an orthorhombic one for Ni dopant. At higher doping concentrations impurity phases begin to appear. The lattice parameters of the usual samples are in good agreement with previous work [5]. For HPO samples, the cell lengths c decreased systematically by 0.18(3)% for $M = \text{Fe}$ and 0.09(3)% for $M = \text{Co}$ in relation to that of the usual samples.

New insights into the role of local structure on superconductivity emerge from Fe local environments in the chains differentiated from those in the planes using Mössbauer spectroscopy. In figure 3, we reproduce two spectra at $x = 0.10$: one of the samples was processed at ambient P and the other at high P of oxygen. Several groups [16–18] have reproduced the trimodal distribution of Fe sites shown in figure 3(b) for a usual sample ($T_c = 36$ K and oxygen content of 7.0 ± 0.02). We label [16] the quadrupole doublet with the largest splitting ($\Delta = 1.92(1)$ mm s^{-1}) as site A, the one with the smallest splitting ($\Delta = 0.59(1)$ mm s^{-1}) as site B and the one with an intermediate splitting ($\Delta = 0.98(1)$ mm s^{-1}) at site C. Sintering such a sample at high P increases not only T_c to 82 K and oxygen content to 7.11 ± 0.02 , but also the C-site integrated intensity at the expense of the A- and B-site ones so that an almost unimodal distribution of sites appears (figure 3(a)). The observed site distributions form part of a general trend that is displayed in figure 3(c) as a plot of the site intensity ratio I_n/I ($n = \text{A, B and C}$) against T_c . Parallel results displaying growth of chemical order upon high- P synthesis were also observed at other Fe doping concentrations.

There is a general consensus [14–20] that sites A and C are chain associated while site B is plane associated. The fractional occupancy of chain associated Fe sites of 0.85(2) at $x = 0.10$ for the usual samples (figure 3(c)) is in good agreement with the value 0.85(9) deduced from differential anomalous x-ray scattering (DAXS) [21]. Site A is thought to represent Fe^{3+} that is quasi-tetrahedral in the chains as suggested by Dunlap *et al* [14] and more recently confirmed by Rykov *et al* [20] and Shi *et al* [22]. Site C, known [14, 16–22] to be populated in oxygen rich samples, is thought [22] to represent an Fe^{4+} species present in a distorted trigonal-bipyramidal coordination. Thus, the intrachain site–intensity ratio

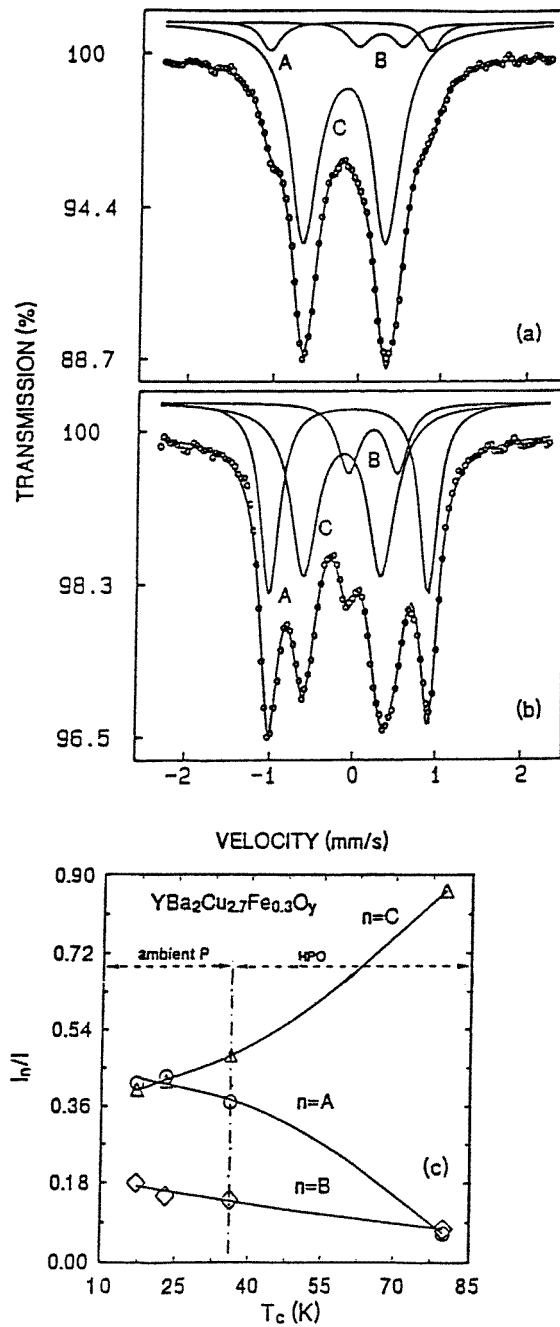


Figure 3. (a, b) Room-temperature Mössbauer spectra of $\text{YBa}_2\text{Cu}_{2.7}\text{Fe}_{0.3}\text{O}_y$ samples: (a) HPO sample; (b) usual sample. (c) Mössbauer site intensity ratios I_n/I of the three Fe sites ($n = A, B$ and C) deduced from the spectra above, plotted as a function of T_c . To obtain usual samples with $T_c < 36$ K, oxygen content y was reduced by quenching the samples equilibrated at elevated temperatures in air.

I_C/I_A provides a local measure of oxygen content [16] in the chains, and is controlled by the interlayer compressive stress in the unit cell (equation (1)) as discussed earlier.

It is tempting to ascribe the increase in T_c from 36 K (ambient P) to 82 K (high P) for $M = \text{Fe}$, $x = 0.10$ samples (figures 2 and 3) to an increase in dopant induced carrier concentration. Using the measured acceptor oxygen contents and taking the Fe charge state to be 3+ for sites A and B, and 4+ for site C, one obtains almost equal hole concentrations of 0.22 and 0.20 holes/[CuO] for the 82 K and the 36 K superconductors, respectively. A more plausible correlation for the increase in T_c is that the use of high P and high T shifts the quasi-equilibrium of equation (1) to the right, and converts all available A into C sites, and further drives some of the dopant from the planes (B sites) to the chains (C sites). For example, one finds the ratio I_B/I to halve in going from the $T_c = 36$ K to the $T_c = 82$ K superconductor (figure 3(c)). The Raman mode frequency of the apical oxygen stretch, which red shifts upon Fe or Co doping in usual samples, shifts back to its pristine value (500 cm^{-1}) upon high- P processing [13]. These changes in local structural order restore planarity in the chains, and hence increase the likelihood that the localized dopant states can pin E_F . They can also reduce some of the global *inhomogeneous strain* between the planes and the chains produced by metal doping in the first place. In HPO samples, the enhanced chemical order of the chains and the reduced dopant site occupancy in the planes both appear to play a role in the enhancement of T_c .

Co as a dopant in YBCO is largely chain associated and exists in multiple sites displaying a propensity for tetrahedral coordination (site A) as revealed by DAXS [21], EXAFS [23] and Mössbauer emission spectroscopy [24]. The $T_c(x)$ results of figure 2 also suggest that Co stabilizes in multiple charge states but it is apparently not as effective as Fe in bringing additional oxygen to the chains probably because the Co charge states (Co^{2+} , Co^{3+}) are lower [20, 21] than those of Fe (Fe^{3+} and Fe^{4+}). In Co doped YBCO samples, the quasi-equilibrium of equation (1) does not move far enough to the right even in HPO samples, and one observes a more modest increase of T_c in relation to that of the usual samples. Nevertheless, the role of the underlying local structural changes in enhancement of T_c is similar to the case of Fe.

Ni as a dopant in YBCO is remarkable in many respects, particularly in that it displays no detectable change in $T_c(x)$ variation between usual and HPO samples, probably because Ni^{2+} is the only charge state populated in both types of sample. The respectable T_c values in the $70 \text{ K} < T_c < 90 \text{ K}$ range (figure 2) at Ni doping concentrations of $0.10 > x > 0$, the metallic nature [7] of transport at $T > T_c$, the closeness of crystal radii of Ni^{2+} (69(4) pm) and Cu^{2+} (71(4) pm) and the lack of a frequency shift [13] of the Raman active apical oxygen mode upon Ni doping all suggest that Ni may be the closest to being a substitutional dopant for Cu in YBCO.

In conclusion we have shown that the T_c values of Fe and Co doped YBCO samples increase unexpectedly on high- P synthesis and that this processing induced enhancement of superconducting behaviour appears to be correlated to the formation of specific dopant centred local structures following equation (1). The present results suggest that theories of high- T_c superconductivity in which specific local structures promote a high density of electronic states at the Fermi level are likely to be the relevant ones [3]. The superconducting–antiferromagnetic phase diagram of the Fe doped YBCO system, particularly in HPO samples, will clearly need examination.

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