Critical chain length and superconductivity emergence in oxygen-equalized pairs of YBa$_2$Cu$_3$O$_{6.30}$

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Abstract

The oxygen-order dependent emergence of superconductivity in YBa$_2$Cu$_3$O$_{6+x}$ is studied, for the first time in a comparative way, on pair samples having the same oxygen content and thermal history, but different Cu(1)O$_x$ chain arrangements deriving from their intercalated and deintercalated nature. Structural and electronic non-equivalence of pairs samples is detected in the critical region and found to be related, on microscopic scale, to a different average chain length, which, on being experimentally determined by nuclear quadrupole resonance (NQR), sheds new light on the concept of critical chain length for hole doping efficiency.

74.25.Dw; 61.14. x; 76.60.Gv;

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The peculiarity of YBa$_2$Cu$_3$O$_{6+x}$(123), the superconductor that still plays an important role in ongoing efforts to elucidate the mechanism of high-$T_c$ superconductivity, is the existence of a charge reservoir, the ...-Cu-O-Cu-... chain system in the Cu(1)O$_x$ plane, far removed from the superconducting Cu(2)O$_2$ sheets. Its structural order drives the whole crystal structure in a variety of superstructures which have been observed and modeled theoretically in the whole compositional $x$-range. Beside the tetragonal (T, empty chain) and orthorhombic-I (OI, full chain) structures that characterize the end members of the compositional $x$-range ($x$=0 and 1 respectively), at least two orthorhombic modifications, ortho-II (OII) and ortho-III (OIII), occurring around the ideal $x$=0.5 and $x$=0.67 compositions and characterized by a ...-full-empty-... and a ...-full-full-empty-... chain sequence along the a direction, are considered thermodynamically stable. The superstructures arising from an ordering between oxygen-poor and oxygen-rich chains are well described by a simple lattice gas model, called ASYNNNI, first introduced by de Fontaine et al. Despite its simplicity the ASYNNNI model, which considers only second nearest neighbor interactions, can account for the stability region of the OII phase. Extensions of the model to include longer range interactions predict the occurrence of more complex superstructures (e.g. the OIII phase), even if they become significant only for very well equilibrated samples, as it was systematically verified in the range 0.67 ≤ $x$ ≤ 0.75.

The understanding of oxygen ordering in the Cu(1)O$_x$ plane and its effects on superconductivity in 123 systems has been greatly enriched during the last eleven years. It is by now clearly established that the charge transfer process in 123 systems and the related superconducting properties are a rather sensitive function not only of the oxygen content, but also of the oxygen ordering in the Cu(1)O$_x$ plane through its induced effects on hole density in the Cu(2)O$_2$ planes and consequently on $T_c$. The connection between oxygen ordering in the chains and hole behavior in the planes was already clearly manifested in the time dependent increase of $T_c$ during room temperature annealing of samples produced by fast quenching. The formation of the OII superstructure is responsible for the 60K plateau typically observed in the $T_c$ dependence from oxygen content in 123 and more recently the influence of OIII ordering on $T_c$ has been shown.

The variety of possible superstructures has raised the question of the existence, for each different ordering scheme, of a characteristic $T_c$ of their own. However, as stressed by Shaked et al., experiments that unambiguously prove this hypothesis are difficult or impossible as a result of the difficulty of stabilizing an entire sample in a particular ordered state and comparing such sample with those having the same oxygen content but a different ordering. The major limitation is the utilization of single samples, prepared one at a time in conditions that make a comparative study extremely difficult, owing to a lack in reproducibility produced by the significant influence of experimental conditions and thermal history on the 123 properties.

To investigate the effects of oxygen ordering we recently proposed a novel strategy based on oxygen-equalized pair-samples, prepared simultaneously in the same thermal conditions, one by intercalation and the other by deintercalation of oxygen, the fully oxygenated and reduced (OI and T) end-terms of the YBa$_2$Cu$_3$O$_{6+x}$ system acting as oxygen donor and acceptor respectively, to arrive at the final oxygen content $k$ in both samples. This topotactic-like technique for low-temperature processing of oxygen-equalized ($k$) deintercalated [D]$_k$ and intercalated [I]$_k$ pair samples of YBa$_2$Cu$_3$O$_{6+x}$ allowed us to investigate
unanswered questions about the relationship between structure and superconductivity in this
system. On the basis of the acquired experience in controlling the process reproducibility we are now able to explore, for the first time in comparative way, the most important (and at the same time the most difficult to study) region in 123 system: the transient T-O boundary around \( k = 0.30 \), characterized by the vanishing of semiconducting antiferromagnetic (SAF) behavior and the emergence of superconductivity (SC).

Bulk polycrystalline [D]\( _k \) and [I]\( _k \) pair-samples, hereafter referred to as \( k \)-pairs, were prepared in a reproducible way starting with fully oxygenated OI bar-shaped samples of (3.0x2.0x14.0)mm\(^3\), weighing each one about 0.5 g, prepared twenty at a time by following conventional solid-state reactions and sintering, and fully reduced T samples obtained from the former by dynamic vacuum annealing at 650 °C. From iodometric and weight-loss analyses, the quoted oxygen content in the reference (OI, \( x = 0.96 \)) and in the derived (T, \( x = 0.07 \)) samples was estimated to be accurate within 0.02 oxygen atom per formula unit. Individually weighed OI and T bars were equilibrated at a given temperature (\( T_e \)) and order-stabilized at composition-dependent temperatures (\( T_s \)) within the thermal stability domain of OII and OIII superstructures.\(^{21,22}\) By varying the OI/T mass ratios it is possible to prepare \( k \)-pairs in a wide range of equalized oxygen stoichiometry \( k \). The OI (T) mass loss (gain) is due solely to a change in oxygen content in the Cu(1)O\(_x\) plane, and excellent agreement between calculated and experimental oxygen content at equilibrium was systematically obtained. Details on starting materials and \( k \)-pair processing were reported elsewhere.\(^{14}\) This topotactic-like procedure yields pairs of 123 specimens under equilibrium conditions with equal oxygen content and thermal history. The \( k \)-pairs under investigation (0.28 \( \leq k \leq 0.32 \)) were obtained by thermal equilibration of OI and T samples at \( T_e = 670^\circ C \) for 1 day, slow cooling at 0.2°C/min to \( T_s = 75^\circ C \) followed by order-stabilization at this temperature for 3 days and final cooling (0.2°C/min) to room temperature. Several batches were prepared in this way and comparatively characterized by resistive (\( \rho(T) \)), electron diffraction (ED) and NQR studies.

Displayed in fig.1 are the evolution of the \( \rho(T) \) curves (A) and the representative densitometer traces of an ensemble of ED patterns (B) recorded independently on several fragments of three typical samples. Panels 1 in fig.1 show the transport (\( A_1 \)) and structural (\( B_1 \)) characteristics of the \( k = 0.28 \) samples. Resistivity is thermally activated and only tetragonal peaks show up in the diffraction pattern. Both [I] and [D] are therefore characteristic of a non-superconducting tetragonal phase, for which \( k = 0.28 \) defines the upper limit of existence in both samples. Panels 4 likewise show the corresponding lower limit (\( k = 0.32 \)) for the existence of a partially OII-ordered superconducting phase. Note the diffuse (\( \frac{1}{2}00 \)) peak in diffraction patterns B\(_4\) (in agreement with the doubling of the a axis produced by a ...full-empty.... chain sequence in the Cu(1)O\(_x\) plane) and the coincidence of \( T_c \) in the [I] and [D] curves A\(_4\). The situation is totally different in \( k = 0.30 \) pairs, which display a phase separation. Resistivity is shown in panels A\(_2\) and A\(_3\). The [D] sample is insulating, but its curve (A\(_2\)) displays a kink precisely at the same temperature where the corresponding [I] sample shows (A\(_3\) curve) the onset of the SC transition, which percolates the bar. [D] grains invariably show the two kinds of patterns displayed in panel B\(_2\): most of them tetragonal (solid line) and a minority fraction OII (dotted line) characterized by very diffuse spots. A similar separation is observed for the [I] samples: most grains are characterized by diffuse OII superstructure spots (solid line) or by diffuse (dotted line) extra peaks at (\( \frac{1}{2}00 \)),
whereas only few are tetragonal.

These data indicate that the T-O phase transition in the $k = 0.30$ pairs displays the coexistence of tetragonal and orthorhombic domains. This result is consistent with the prediction by de Fontaine et al from a lattice-gas model. However the systematic observation of the $(\frac{2}{3}, 0, 0)$ spots adds a new detail to this picture. We believe that these spots result from domains of an orthorhombic anti-III (OIII*) structure characterized by an ideal ...-empty-empty-full-... periodic arrangement of chains along the $a$ direction. Such a sequence gives rise to a tripling of the $a$ axis in analogy with the ...-empty-full-full-... configuration for the ideal composition $x = \frac{2}{3}$ of the OIII superstructure. To our knowledge the OIII* structure is reproducibly observed around the ideal stoichiometry $x = \frac{1}{3}$ for the first time by means of our equilibration technique. After long-term aging (one year) of [I]$_{0.30}$ samples at room temperature the $(h, 0, 0)$ spots disappear, the original two-phase orthorhombic state (OII + OIII*) stabilizes in the OII single-phase state and the resistive SC transition broadens considerably. Hence the OIII* ordering appears to be a metastable precursor in the emergence of OII ordering in the [I]$_{0.30}$ SC samples.

The OIII* phase cannot be justified by the original ASYNNI model, due to the neglect of long range interactions. These interactions were later introduced in an extended model, limited to the $6.5 \leq x \leq 7$ range, to account for the observation of the OIII phase. Our carefully equilibrated samples, which reproducibly develop both the OIII* ($k \sim 0.7$) and the OIII* ($k=0.3$) phase, call for an extension of the long range interaction models to the oxygen poor region of the phase diagram.

We investigated the local structure by NQR to determine the degree of short range order in $k=0.3$ samples at the SAF-SC boundary. The NQR resonance frequency, proportional to the electric field gradient (EFG) at the nucleus, is characteristic of each distinct copper site in the lattice. Since there are two Cu isotopes (63 and 65) each lattice site gives rise to an isotope doublet, at fixed frequency ($\nu_{63}/\nu_{65} = 1.082$) and intensity ($I_{63}/I_{65} = 2.235$) ratios. The Cu NQR spectra of the pair [D]$_{0.30}$ and [I]$_{0.30}$ are plotted in fig. 2 in the range 22-33 MHz, corrected for frequency dependent sensitivity and relaxation. Each sample shows two isotope doublets, the solid line being the best Gaussian fit to the above mentioned isotopic constrains. The EFG values of the two doublets identify them as two distinct Cu(1) sites: the 28.05-30.35 MHz doublet is 2-Cu(1), linearly coordinated with apical oxygen and neighbored by oxygen vacancies (v-Cu$^{1+}$-v) in the plane, while the 22.1-23.9 MHz doublet corresponds to the chain-end configuration (O-Cu$^{2+}$-v) of the 3-fold coordinated 3-Cu(1). The few 4-Cu(1) (O-Cu$^{2+}$-O) contribute negligibly to the spectra because of their much larger EFG inhomogeneity.

The area $A_i$ ($i=2,3$) under each doublet yields the average number of oxygen atoms in the inter-Cu(1) sites (i.e. the average chain length) as $\ell = \frac{2}{7}(2A_2/A_3 + 1)$, and we obtain $\ell_D = 3.9(1)$ and $\ell_I = 1.9(1)$ for the two samples of the pair. The short average chain length found in [D]$_{0.30}$ is consistent with its broad NQR lines, since a short correlation length implies a broad distribution of EFG values. These results outline the role of the chain length in determining the chain hole-doping efficiency and confirm directly the theoretical prediction by Uimin et al. that there is essentially no charge transfer from chain fragments shorter than three oxygen atoms.

The $k$-pair method proves itself as an effective tool to extract more detailed information (inaccessible to single sample experiments) on the mechanism of short range oxygen-chain...
ordering which characterizes the transient SAF-SC region. The experimentally demonstrated inequivalence of the $[D]_{0.30}$ and $[I]_{0.30}$ samples of a pair agrees with previous analogous results obtained around the OII-OIII and the OIII-OI transition boundaries $^{14,19}$. This leads us to conclude that different metastable states exist near the thermodynamic equilibrium at a given oxygen content and are connected with the vacancy ordering in the Cu(1)-O$_x$ chain system. Different kinetic and thermodynamic reaction paths are realized during intercalation or deintercalation of oxygen and result in inequivalent chain growth processes revealed by ED and NQR. Moreover we point out that with our equilibration scheme structurally distinct domains occur in the same sample in the transient region around $k=0.3$, while the SC transition in $[I]_{0.30}$ and the resistive kink in $[D]_{0.30}$ (fig.1 A$_2$-A$_3$) systematically occur at the same temperature. This suggests that a simultaneous electronic and structural phase separation takes place at the SAF-SC boundary, where orthorhombic (SC) and tetragonal (SAF) domains coexist. They originate nanoscopically and are critically dependent on the chain growth process. We believe that the different chain lengths observed in $[I]$ and $[D]$ samples represents an experimentally determined critical borderline between the vanishing of SAF behavior and the emergence of SC in 123.
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FIGURES

FIG. 1. Resistivity vs. temperature (A) and representative densitometer traces of ED patterns along the $a^*$ direction of the reciprocal lattice (B) for [D]$_k$ and [I]$_k$. Panel 1 and 4: data from $k$=0.28 and $k$=0.32 pairs respectively; panel 2 and 3: [D] and [I] samples of a $k$=0.30 pair.

FIG. 2. NQR spectra of sample [I]$_{0.30}$ and [D]$_{0.30}$. The area under each isotope doublet, indicated as 3-Cu(1) and 2-Cu(1) respectively, is proportional to the number of Cu ions in that local environment.
