A Displacive Structural Transformation in the CuO$_2$ Planes of YBa$_2$Cu$_3$O$_x$ at the Underdoped-Overdoped Phase Separation Line

E. Kaldis,[1] J. Röhler,[2] E. Liarokapis,[3] N. Poulakis,[3] K. Conder,[1] and P. W. Loeffen[4]

[1]*Labor für Festkörperphysik, ETH-Technopark, CH-8005 Zürich, Switzerland*
[2]*II. Physikalisches Institut, Universität zu Köln, D-50937 Köln, Germany*
[3]*National Technical University of Athens, Athens 157 80, Greece*
[4]*European Synchrotron Radiation Facility, F-38043 Grenoble, France*

A structural phase transformation in the CuO$_2$ planes of YBa$_2$Cu$_3$O$_x$ has been observed at the onset of the overdoped regime, $x = 6.95$. We have measured as a function of x the dimpling in the CuO$_2$ planes by EXAFS, and the O(2,3) in-phase (A_{1g}) mode by Raman scattering. The data show for $x \geq 6.95$ anomalously large static displacements of the Cu(2) atoms off the O(2,3) layer and a gap in the distribution of the O(2,3) in-phase Raman shifts. We conclude the structure of overdoped YBa$_2$Cu$_3$O$_x$ to be a martensitic form of the optimum doped crystal. [S0031-9007(97)04809-6]

The so-called 90 K plateau of YBa$_2$Cu$_3$O$_x$ is well established [1–3] to exhibit a broad but clear maximum of $T_c = 92.5$ K at optimum doping around $x_{opt} = 6.92$; see Fig. 1(a). In the T-x phase diagram of the cuprate superconductors x_{opt} indicates the phase separation line between the underdoped and overdoped regimes. While optimum doped YBa$_2$Cu$_3$O$_{6.92}$ exhibits a single superconducting transition various laboratories have reported from measurements of the magnetization [3–7], resistivity [8], and specific heat [7,8] of overdoped YBa$_2$Cu$_3$O$_x$, $x \geq$ 6.95, two superconducting phases with critical temperatures split by about 2.5 K. Optimum doped YBa$_2$Cu$_3$O$_{6.92}$ has an intermediate oxygen concentration with respect to its insulating (antiferromagnetic) parent phase and the overdoped metallic phase. It is an important indication that only a very narrow compositional range is most favorable for the superconductivity. The physical reason for the narrow phase separation line between the underdoped and overdoped regimes to occur just at an intermediate oxygen concentration of $x = 6.92$ is a matter of intense and controversial debates [9].

In this Letter we report evidence for a structural phase transformation in the superconducting CuO$_2$ planes of YBa$_2$Cu$_3$O$_x$ occurring close to optimum doping at the onset of the overdoped regime, $x = 6.95$. Orthorhombic YBa$_2$Cu$_3$O$_x$ is martensitic as evidenced by [110] transformation twins. We show a second martensitic form of the crystal to develop across the underdoped-overdoped phase separation line at $x = 6.95$. We have observed this new martensitic form also in "classically" prepared YBa$_2$Cu$_3$O$_x$ exhibiting no anomaly in the x dependency of the lattice parameters around $x = 6.95$. A lattice instability around optimum doping has been suggested earlier [1,3] from the observation of a minimum in the c-axis lattice parameter, see the open symbols in Fig. 1(b). However, the experimental evidence came exclusively from special samples synthesized by direct

oxidation of the metals (DO) or with Ba obtained from decomposed BaCO$_3$ (BaO) [1,3]. On the other hand hundreds of samples, classically synthesized by direct reaction of BaCO$_3$ with the metal oxides (CAR), all exhibited a linear x dependency of the c axis, extending straight across the boundary between the underdoped and overdoped regimes [10], cf. the closed squares in Fig. 1(b). Therefore the lattice anomalies found in the DO and BaO samples could be possibly an artifact arising from their particular form of carbonate incorporation [15].

The different conditions of synthesis [3,4,6], and the applied method for high precision measurements of the oxygen concentrations [11] have been reported elsewhere. We emphasize that all these methods of synthesis used very slow cooling rates to obtain homogenous samples under near equilibrium conditions. Originally the oxygen diffusion in YBa$_2$Cu$_3$O$_x$ was assumed to freeze at $T \approx$ 350−400 °C, and thus the samples were quenched from 500 °C by various laboratories [7,12]. Detailed studies of the oxygen diffusion process [13,14], however, have unambiguously shown oxygen to diffuse rapidly even at $T < 250$ °C, and consequently slow cooling is a necessary prerequisite to approach the equilibrium state of lattice defects. The CAR samples were found in all laboratories (also when slowly cooled) to exhibit a linear x dependency of the c axis. It is not known at the present time why the use of BaCO$_3$ as a precursor masks the c-axis minimum found in the DO samples. We believe that the chemical history [3,6,15] is as important as the thermal history for the synthesis of homogenous samples near the equilibrium.

The c-axis contraction upon oxygen doping is usually attributed to the electron-hole charge transfer to the CuO$_2$ planes shortening predominantly the Cu(2)-O(1) apical bond. We may therefore expect a minimum of $c(x)$ around x_{opt} to correlate with a minimum in the x dependency of the apical bond. But standard refinements of neutron
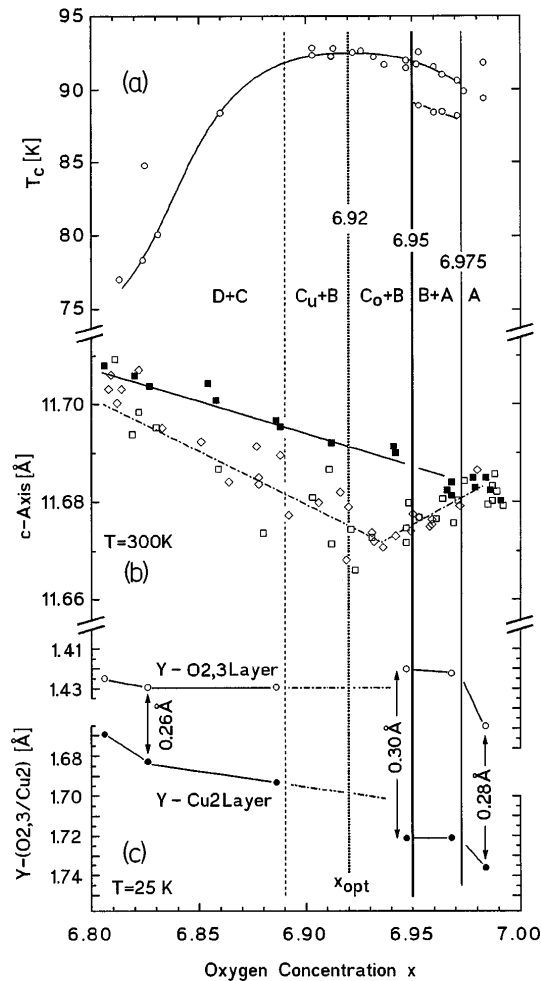
FIG. 1. (a) Superconducting transition temperature T_c of YBa$_2$Cu$_3$O$_x$ around optimum doping x_{opt} as determined from magnetization measurements. Vertical lines indicate the boundaries between the phases analyzed in Fig. 2. (b) c-axis lattice parameter as a function of oxygen concentration from powder x-ray diffraction, by courtesy of Chr. Krüger. CAR samples (filled squares), DO samples (open squares), and BaO samples (open diamonds). The superimposed lines are guides to the eyes. (c) Spacing between the Y-Cu(2) and Y-O(2,3) layers, respectively, as determined from Y-EXAFS. Vertical arrows indicate the dimpling.

diffraction patterns from the DO samples have shown that the shortening of the Cu(2)-O(1) apical bond extends with doping into the overdoped regime, thereby changing very slightly its slope [3]. A steplike discontinuity at $x = 6.947$ has been found to reduce the dimpling of the CuO$_2$ planes by -0.012 Å [3]. However, the negative direction of this discontinuity is hard to reconcile with the inversion of the c-axis parameter and the internal bond lengths. Most likely the structural transformation develops first in small domains of the crystal which are not accessible to standard diffraction techniques.

We have therefore explored the atomic structure of the CuO$_2$ planes on a nanoscale by extended x-ray-absorption

fine-structure spectroscopy (EXAFS) and its dynamics by Raman scattering. We have examined CAR samples from the same batches, all without anomaly in $c(x)$, cf. Fig. 1(b), closed squares.

The static displacements of the planar Cu(2) and O(2,3) atoms upon doping have been determined by yttrium K-edge EXAFS. The photoexcited Y atoms are ideal observers of the local CuO$_2$ structure. In particular we have exploited the high sensitivity of the nearly collinear three-body electron scattering configurations Y-Cu(2)-Ba and Y-O(2,3)-Ba for displacements of the intervening Cu(2) and O(2,3) atoms, respectively. Since both multiple scattering paths refer to the same Ba layer, and show up extremely well isolated in real space, the dimpling of the CuO$_2$ planes may be directly read from the magnitudes of the Fourier transform spectra at 5 and 6.2 Å. The spectra have been recorded in transmission geometry from finely grained polycrystalline absorbers. Details of the experiments and the data analysis are given elsewhere [16]. Figure 1(c) displays the spacings between the Y layer and the O(2,3) and Cu(2) layers, respectively, as a function of x ($T = 25$ K). Their differences yield the x dependency of the dimpling. On doping from the underdoped side, $6.8 < x \to x_{opt}$, the Cu(2) position is found to move along c by about 0.025 Å off the O(2,3) layer, while the average O(2,3) positions remain almost unaffected. Around $x = 6.95$ the dimpling increases by another 0.04 Å to its maximum value of 0.30 Å, nearly entirely due to displacements of the Cu(2) atoms. At $x = 6.984$ both the O(2,3) and Cu(2) layers shift off the Y layer, thereby reducing the dimpling to 0.28 Å.

The Raman shifts, $\bar{\nu}$, of the O(2,3) in-phase mode (A_{1g}) plotted in Fig. 2 (bottom) have been recorded at 300 K in the scattering configuration $y(zz)\bar{y}$ from a total number of 97 microcrystallites (≈ 15 μm sized), on the average, about eight at each measured concentration between $x = 6.438$ and 6.984. The x dependency of the O(2,3) in-phase Raman shift at 300 K has been shown earlier to decrease with increasing oxygen content, and, most important, to soften strongly around x_{opt} [17,18], cf. the diagonal lines in Fig. 2 (bottom). A similar behavior has been found recently also at 200 and 77 K [18]. Figure 2 (top) exhibits the normalized distribution function, $P(\bar{\nu}, x)$, of the observed Raman shifts, $\bar{\nu}$. It is clearly visible that $P(\bar{\nu}, x)$ peaks at six characteristic wave numbers, labeled $A-F$. Therefore $\bar{\nu}(x)$ is better described by staircases than by straights. In the underdoped regime we identify single-phase regions (F, E, D) alternating with two-phased regions ($F + E$, $D + E$). The single-phase regions can be correlated with the particular stability of the superstructures: $2a_0$ around $x_{2a} = 6.5$ (F), $3a_0$ around $x_{3a} = 6.66$ (E), and $5a_0$ around $x_{5a} = 6.8$ (D). Here a_0 denotes the a-lattice parameter of the fundamental unit cell.

For oxygen concentrations $6.8 \leq x \leq 6.89$ we find a multiphase region composed of the underdoped phase D, the optimum doped phase C (subdivided into C_u at the
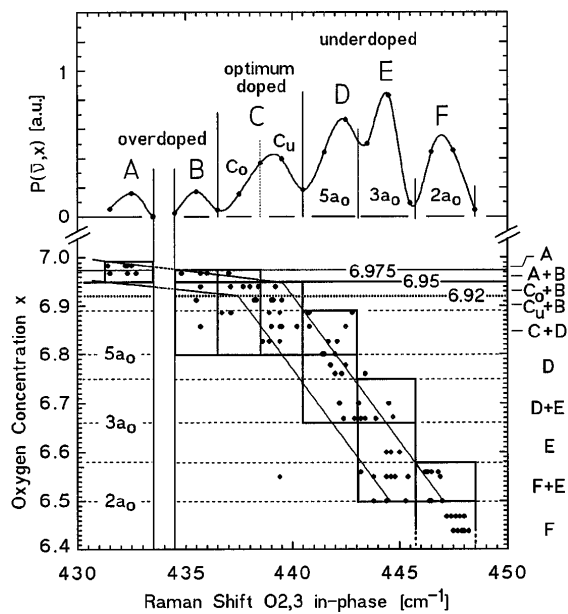
FIG. 2. (bottom) Raman shifts of the O(2,3) in-phase mode in $YBa_2Cu_3O_x$ for oxygen concentrations between $x = 6.438$ and 6.984. Dashed horizontal lines indicate the phase boundaries between coexisting phases, the drawn out horizontal lines (6.95) indicate the miscibility gap in the overdoped regime. The thick drawn boxes emphasize the sequence of phases occurring on doping. (top) Distribution function of the Raman shifts normalized to a constant number of measurements in evenly spaced doping intervals. The maxima A–F are attributed to the different phases. Peak C labeling the optimum doped phases is subdivided into C_o (at the overdoped side of x_{opt}) and C_u (at the underdoped side of x_{opt}).

underdoped flank and C_o at the overdoped flank), and possibly a weak admixture of the overdoped phase B.

Around optimum doping, $x_{opt} = 6.92$, C_u dominates within the -0.03 wide region below, and C_o in the $+0.03$ wide concentration region above. While the underdoped phase D vanishes completely, some admixtures of the overdoped phase B start to appear. The latter contribute strongly at the overdoped flank, $x = 6.92-6.975$.

The overdoped regime exhibits the phases A and B. Most important, while for $x < 6.95$ all phases transform continuously, a frequency gap at 434 cm^{-1} (drawn out vertical lines) suggests for $x > 6.95$ a miscibility gap between the overdoped phases A and B.

We relate the anomalous softening of the O(2,3) Raman shifts and the miscibility gap in the overdoped regime to the anomalously large displacements of the Cu(2) atoms off the O(2,3) layer observed by EXAFS around $x = 6.95$, cf. Fig. 1(c). It is intuitively plausible that the increase of the dimpling in the CuO$_2$ planes softens the Cu(2)-O(2,3) bonds, and thus may decrease the wave number of the O(2,3) in-phase vibrations. The drop of the Raman shift by -5 cm^{-1} within an extremely narrow concentration range of $\Delta x \simeq 0.025$ gives strong evidence that the deformation of the CuO$_2$ planes is of the displacive type. The gap in

the Raman shift indicates a first order transition. From the relatively few data points in Fig. 1(c) evidencing the static anomaly in the dimpling we may also infer a first order transition, at least of the moderate type.

From the structural data displayed in Fig. 1(b), open symbols, and Fig. 1(c) we conclude that the x dependency of the c-axis lattice parameter scales inversely with the dimpling of the CuO$_2$ planes, correlated with the electron-hole charge transfer along c. In the underdoped phase mixture the dimpling increases with decreasing c and exhibits its maximum value of 0.30 Å close to the c-axis minimum. In the overdoped regime, $x \geq 6.95$, $c(x)$ increases while the dimpling decreases, but the possible correlation is weaker than in the underdoped regime.

The a- and b-axis changes above x_{opt} are different in the CAR [3,10] samples on one side and in the DO [3] and BaO [19] samples on the other side. In the latter the significant upturn in c by $\simeq +0.012$ Å, cf. the open symbols in Fig. 1(b), is correlated with a downturn in a by about $\simeq -0.01$ Å [3,19]. The b axis exhibits an almost flat behavior across x_{opt} such that the orthorhombicity increases through shortening of the a axis. The opposite behavior of the deformations along c and a confirms the martensitic nature of the phase transformation. Clearly, further structural examinations using optical and electron microscopy are required to establish the mesostructures of the overdoped martensitic phase. Investigations of their response to ultrasonic applied stresses are expected to yield further important insight into the diffusionless nature of the phase transformation [20].

Our findings on the discontinuity of the dimpling at $x \geq 6.95$ are in conflict with the results from the neutron diffraction patterns of the DO samples [3]. However, it is well known that the crystallographic structure of martensitic phases, cf., e.g., Ref. [20], is not reliably accessible from standard refinements of the diffraction data and consequently further diffraction work is invoked.

The important contribution of this work in the field of cuprate superconductivity is in showing that the phase separation line between the underdoped and overdoped regimes is accompanied by a structural phase transformation deforming the CuO$_2$ planes. Whereas the concentration region around optimum doping is composed of many coexisting intermediate phases, the overdoped regime exhibits a miscibility gap and a martensitic structural transformation. It is a widely known fact that all superconducting compounds including the old intermetallic high-T_c materials (e.g., A15's) and "old oxides" undergo martensitic structural transformations [20,21]. In many A15's double superconducting transitions have been observed, and by applying stress the lower transition temperature has been shown to arise from the deformed martensitic phase [21]. A large coupling between atomic displacements and the shape of the superconducting transition exists also in the heavy fermion compound UPt$_3$, where annealing treatment of as-grown crystals causes the

specific heat anomaly to evolve from a broad bump into a sharp double peak feature [22].

Our results support the idea that the dimpling of the CuO_2 planes is an intrinsic property of the superconducting cuprates and that local coherent distortions of the CuO_2 planes and the superconductivity are coupled [20,23,24]. We hope that proposals for the driving force of the reported martensitic phase transformation at the underdoped-overdoped phase separation line of $YBa_2Cu_3O_x$ might be available in the near future.

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