LOCAL STRUCTURE STUDIES OF THE UNDERDOPED-OVERDOPED TRANSITION IN YBa$_2$Cu$_3$O$_x$

Measurement of the yttrium x-ray absorption-fine-structure

J. RÖHLER, P. W. LOEFFEN AND S. MÜLLENDER
European Synchrotron Radiation Facility, B.P. 220, F-38043, France

AND

K. CONDER AND E. KALDIS
Laboratorium für Festkörperphysik ETH, CH-8093 Zürich, Switzerland

Abstract. We have measured the extended x-ray absorption-fine-structure (EXAFS) at the Y-K edge of YBa$_2$Cu$_3$O$_x$ for $x=6.801, 6.947, 6.968, 6.984$ at $T=20-300$ K. The Y-Cu$_2$ pairs vibrate harmonically but freeze out in the superconducting phase. The Y-O$_{2,3}$ pairs exhibit strong anharmonicities with a singularity at $T_c$. With increasing oxygen concentration the Cu$_2$ layer shifts along $c$ towards the Ba layer. Optimum doping is a notable point in the phase diagram, also concerning the structural degrees of freedom. Here the O$_{2,3}$-Cu$_2$ spacing is largest, the relative displacements of O$_{2,3}$ and Cu$_2$ layers along $c$ invert upon doping, and the Cu$_2$ position along $c$ is independent on temperature in the superconducting phase.

1. Introduction

Upon doping of the superconducting cuprates, one distinguishes an under- and overdoped regime. Optimum doping defines the unique point in the phase diagram where the critical temperature, $T_c$, is at a maximum. The superconducting phase of YBa$_2$Cu$_3$O$_x$ exhibits a broad but well defined maximum of $T_c$ in the oxygen concentration range $6.8 < x < 7.0$ [1, 2]. From $T_c$ vs. $x$ of homogeneously oxidized powder samples [1] we read the maximum $T_c = 92.5$ K is at $x_{opt} = 6.92 \pm 0.01$.

$^1$Corresponding author. Universität zu Köln, II. Physikalisches Institut, Zülpicherstr. 77, D-50937 Köln, Germany. Email: abb12@RS1.RRZ.Uni-Koeln.de
Optimum doped YBa$_2$Cu$_3$O$_{6.92}$ contrasts with its under- and overdoped neighbours not only by the relatively highest $T_c$, but also by the narrowest width in the superconducting transition (in the electrical resistance, magnetization, specific heat), and the largest superconducting volume fraction. Moreover, at $x_{opt}$ the anisotropy ratio of all electrical and magnetic properties is largest and the normal $a$-$b$ resistivity most linear in temperature. It is generally believed that the maximum of $T_c$ is related to a critical concentration of charge carriers in the CuO$_2$ planes, $n_c(x) \simeq 0.2 - 0.25$ holes/Cu, which may be related to an optimum superconducting condensate density $\rho_s(0) = n_s(0)/m^*_{ab}$ at zero temperature. ($m^*$ is the effective mass of the superconducting carriers in $a$, $b$ direction.) At optimum doping $\partial T_c/\partial n \simeq 0$.

It is important to note that the oxygen isotope shift is smallest at optimum doping [3, 4]. Measurements of the electrical resistivity under high pressure on YBa$_2$Cu$_3$O$_x$ has also established a vanishing pressure dependence of $T_c$, $dT_c/dp \simeq 0.04$ K/kbar [5]. From the currently available experimental data, YBa$_2$Cu$_3$O$_x$ turns out to be the family of cuprate superconductors where optimum doping is most precisely characterized.

The other families of cuprate superconductors have been well defined in their under- and overdoped regimes, but as yet optimum doping could not be determined with the same accuracy as in YBa$_2$Cu$_3$O$_{6.92}$. Carrier concentration is a key variable influencing $T_c$, but in the various compound families, control of the carrier concentration in the CuO$_2$ planes is achieved in a multi parameter space of cation and anion concentrations. At fixed compositions of the dopants, ordering of the inherent defects has been established as playing an important role in the variation of $T_c$. Even in the structurally “simple” compound La$_{2-x}$Sr$_x$CuO$_4$ optimum doping is not completely understood. For instance, La$_{2-x}$Sr$_x$CuO$_4$ exhibits the maximum $T_c$ (38 K) at $x=0.15$, however, application of pressure may enhance $T_c$ at just this concentration up to 49 K. We believe a key for understanding of the narrow range of stoichiometries which allows for optimum doping is in the ordering of the inherent defect structures. The optimum doped superconducting phases have intermediate carrier concentrations with respect to the insulating (antiferromagnetic) parent phases and the overdoped nonsuperconducting metallic phases. It is an important indication that just these intermediate carrier concentrations are most favourable for the superconductivity.

An exceptionally detailed picture of the role of defects in a high-$T_c$ material emerged from the numerous detailed studies of oxygen vacancies in the chain layer of underdoped YBa$_2$Cu$_3$O$_x$, $6.4 < x < 6.92$. For a given $x$, the highest $T_c$ is generally found for samples annealed so that the interstitial oxygen O4 in the chain layer is well ordered. The oxygen ordering is manifested as dramatic increases in $T_c$ with time in samples that
have been quenched from high temperature. Alternatively, application of external pressure to underdoped YBa$_2$Cu$_3$O$_x$ may be used to affect the ordering-disordering of the chain oxygens. Note that 'ordered defects' are not defects at all; instead they have become part of the regular lattice, e.g. the so-called 2$a$ ortho-II superstructure, [6, 7].

But many defects remain after the chain oxygen becomes well ordered creating local lattice distortions. For instance, the copper-oxygen chains are not straight but zigzagged, and the oxygen displacements associated with this distortion are not ordered in three dimensions. It is important to note that even the CuO$_2$ planes, generally believed to be structurally most perfect, are locally distorted by the atomically defined dopant sites located in the nearest or next nearest layers. Are there specific configurations of ordered distortions, which are most favourable for the superconductivity, and which stabilize the compound at optimum doping? To elucidate this problem, experimentally homogeneously oxidized samples and precision measurements of their oxygen concentrations are necessary prerequisites.

The overdoped regime exhibits further intriguing properties. The jump in the specific heat at $T_c$, $\Delta C_p/T_c$ saturates for $x > x_{opt}$. Compared to underdoped YBa$_2$Cu$_3$O$_{6.80}$ it is enhanced by a factor of three [2]. At $x > 6.95$ new features show up in the shapes of the specific heat jumps and of the magnetization. These are interpreted as a double superconducting transition with $T'_c$'s split by 3 K [8]. The splitting cannot be explained by macroscopic oxygen inhomogeneities in the grains [9]. Overdoping tends to suppress the superconducting properties, to dramatically reduce the anisotropy ratio of the normal electric transport properties, and to cause the normal resistivity to evolve a power law dependence.

X-ray and neutron diffraction data recorded as a function of oxygen concentration at 5 K exhibit clear structural anomalies at $x \geq 6.935$ [1]. Further insertion of oxygen was found to invert the $x$-dependency of the $c$ lattice parameter. The spacing between the oxygen and copper layers in the CuO$_2$ plane, $\Delta z_{O2.3-Cu2}$, drops at $x \simeq 6.925$ by 0.02 Å. Recently the in-phase Raman mode of the planar oxygens, O2.3, was found to soften in the overdoped regime [10].

In this lecture, we address the problem of local structural distortions in the CuO$_2$ planes around optimum doping in YBa$_2$Cu$_3$O$_x$, $x=6.801-6.984$, by measurements of the extended x-ray absorption-fine-structure (EXAFS) beyond the yttrium $K$-edge, both, as a function of oxygen concentration, $x=6.801-6.984$, and of temperature $T=20-300$ K.
2. Experimental Details

2.1. X-RAY ABSORPTION-FINE-STRUCTURE

The x-ray absorption-fine-structure beyond the x-ray absorption thresholds of atoms in solids arises from the interference between freely propagating photoelectrons and photoelectrons backscattered from the atomic cluster to the absorbing central atom. X-ray photons are used for generating EXAFS spectra, but it is interfering photoelectrons which give the oscillating absorption pattern used for the analysis of the local structure. Since electrons are strongly scattered by atoms, EXAFS is a very sensitive structural probe, but exhibits strong contributions from complicated multiple scattering (MS). However, strong MS signals are of great advantage for the detection of subtle structural effects and the improvement of the structural analysis. On the other hand, inclusion of MS into the data analysis markedly increases the complexity of the structural refinement, far beyond that of the so-called standard analysis carried out earlier on the Y K-EXAFS of YBa$_2$Cu$_3$O$_x$ by many laboratories [11, 12, 13, 14]. We have recently determined the so-called dimpling angle in the CuO$_2$ planes of BiSr$_2$Ca$_2$Cu$_2$O$_{8+δ}$ [15] from a MS analysis of the Cu K-EXAFS using the FEFF code [16]; MS analysis of the EXAFS from high-$T_c$ cuprates using other codes have been reported in e.g. Ref. [17, 18].

Inspection of our experimental Fourier transform spectra at fixed temperature ($T=100$ K, Fig. 4) shows clearly the structural changes upon variation of the oxygen concentration are most pronounced at $R \geq 3.5$ Å, a

Fig. 1. Atomic cluster projected from the unit cell of YBa$_2$Cu$_3$O$_x$. Shown are two CuO$_2$ plaquettes (Cu: small black circles, O: big dotted circles) separated by the Y-layer (big black circles). On the top we see one Ba layer (hatched circles) including the apical oxygen of the Cu–O pyramid. Arrowed lines indicate schematically some of the important Y EXAFS scattering paths: Y–O$_{2,3}$ ("O2,3"), Y–Cu2 ("Cu2"), and Y–Cu2–Ba ("6.2"), Y–O$_{2,3}$–Ba ("5"), discussed in the text.
regime strongly dominated by MS. Thus extraction of meaningful structural information from our data requires MS to be included in the data analysis.

2.1.1. Single Scattering

The interference function $\chi(k)$ for a single back-scattering (SS) configuration ($\Theta = 180^\circ$) of $l = 1$ photoelectrons ($K$-absorption) can be expressed as

$$k\chi(k) = S_0^2 F(k) \int dr \frac{\rho(R)}{R^2} \exp(-2R/\lambda(k)) \times \sin \left[(2kR + \varphi(k) + 2\delta(k))\right]$$  \hspace{1cm} (1)

Here $k$ is the momentum of the photoelectron, $S_0^2$ is an amplitude reduction factor to account for intrinsic losses at the absorbing atom, $F(k)$ the scattering amplitude, $\rho(R)$ is a radial pair distribution function (RDF), $\varphi(k)$ the scattering phase shift, $\delta(k)$ the final-state phase shift at the absorbing (central) atom. $\lambda(k)$ refers to the decay of the photoelectron wave-function amplitude due to various losses. These losses are taken into account by the imaginary parts of the photoelectron self-energy and the core-hole width.

$\rho(R)dr$ is proportional to the probability of finding an atom of a given shell within $R + dR$ around the absorbing atom, and $\int \rho(R)dr = N$ defines the number of atoms, $N$, in this shell. From Eqn. 1 $\chi k$ is the Fourier transform of an effective RDF, which includes the structural information and the physics of the electron scattering. The true RDF can be expressed in moments of the true RDF writing Eqn. 1 as

$$k\chi(k) = A(k) \sin \Phi(k)$$  \hspace{1cm} (2)

where

$$A(k) = \frac{S_0^2 F(k)}{R^2} N \exp \left[-2R/\lambda(k)\right] \exp(-2\sigma^2 k^2)$$  \hspace{1cm} (3)

and

$$\Phi(k) = 2k \left[R - \sigma^2 \left(\frac{2}{R} + \frac{2}{\lambda(k)}\right)\right] - \frac{4}{3} c_3 k^3 + \phi(k).$$  \hspace{1cm} (4)

$\sigma^2 = \langle (R - R_0)^2 \rangle$ denotes the mean-squared relative displacements from small harmonic disorder of thermal and/or static origin. $c_3$ denotes the mean-cubic relative displacement describing deviations from the Gaussian RDF. Extraction of $c_3$ from the sine argument in Eqn. 2 is particularly useful in measuring the strength of anharmonicities and other non-Gaussian disorder as a function of temperature. The bond lengths and $\sigma_0^2$ listed in
Tabs. 1, 4 were determined by least-squares fitting of the experimental $k$-space and/or $R$-space data to Eqn. 1. $\Delta \sigma^2(T, x)$ was determined from polynomial fits to the ln-ratios of the envelopes

$$\ln \left( \frac{A}{A_0} \right) = -2\Delta \sigma^2 k^2.$$  \tag{5}

Assuming harmonic motion for a diatomic system the vibrational contribution to the disorder is given by

$$\sigma_{vib}^2 = \frac{\hbar}{8\pi^2 \mu \nu} \coth \frac{\hbar \nu}{2k_B T}$$  \tag{6}

where $\mu$ is the reduced mass, and $\nu$ the vibration frequency.

$\Delta c_3(T, x)$ of the anharmonic Y–O2,3 RDF were derived from polynomial fits to differences of Eqn. 4.

\[
\frac{1}{k} (\Phi - \Phi_0) = 2 \left[ (R - R_0) - \Delta \sigma^2 \left( \frac{2}{R} + \frac{2}{\lambda(k)} \right) \right] - \frac{4}{3} \Delta c_3 k^2 \tag{7}
\]

To extract the true RDF from the experimental absorption-fine-structure (carried out for the Y–Cu2 pair at $T$=20 K, cf. sec. 3.1.2), $\sigma^2$ and $c_3$ were determined from least-squares fits and interpolated between $k$=3.5 and 0 Å$^{-1}$. $P(R)$ was then obtained by taking the inverse sine transform from $k_{min}$=0 to $k_{max}$=12 Å$^{-1}$. For details of the “splicing” see e.g. Ref. [19].

2.1.2. Multiple Scattering

The MS contributions to $\chi k$ were calculated using the high-order MS approach of the FEFF 6 code. The theoretical ingredients of this code can be found in Ref. [20]. The multiple scattering paths are expressed in a form analogous to single back-scattering given in Eqn. 1, but which includes all multiple scattering and curved wave effects. For MS configurations the effective path length is given by $R = r_{tot}/2$, where $r_{tot}$ is the total length of the MS path. The geometrical data of the relevant MS configurations are listed in Tabs. 1, 4, 5, 6, 7. Calculated Fourier transform spectra are displayed in Fig. 17. From a total of 598 relevant scattering configurations, found in a $R$=8 Å sized cluster (choosing the default curved wave and plane wave filters of the code), only 33 (1-4 legs) turned out to reproduce qualitatively the experimentally observed spectra.

Application of more elaborate procedures yielding quantitative results from the high-$R$ scattering configurations first of all needs a realistic model, which contains the ”allowed“ distortions of the important MS configurations. In the following sections we shall develop step by step such a model, which in particular describes the static atomic displacements that are at the origin of the alterations of the strongest MS observed on doping and
Fig. 2. Distribution of the relative amplitudes of the Y K-EXAFS as calculated from a cluster of 149 atoms ($R=8$ Å) in YBa$_2$Cu$_3$O$_{6.9}$ using the FEFF6 code and crystallographic data. The $k$-range is 0-20 Å$^{-1}$. Amplitudes are given relative to the "strongest" amplitude ($\equiv O_2$). Plotted are 598 bars corresponding to the filtered scattering configurations out of a total of $\approx 8500$ with up to 8 legs.

variation of temperature ($T < 100$ K). This model might serve as a starting point for a future quantitative analysis of the complete data sets.

The variations in the peak heights of peaks "6.2" and "3.5" are found to depend sensitively on the position of the Cu2 atom in a few MS paths. We have determined quantitatively the correlations between peak heights and Cu2 displacements (listed in Tab. 8) from re-iterated full calculations of the MS within the whole cluster, and by displacing the Cu2 atoms from their nominal position along the $c$-axis. The mean-squared variations in $R$, the so-called path Debye-Waller factors, $\sigma^2_R$, have been chosen to be zero for all paths. The Gaussian broadening in the calculated Fourier transform (Fig. 17) spectra therefore arises solely from the finite transform range (2-16 Å$^{-1}$) and the Gaussian window function (0.2 Å$^{-1}$).

2.1.3. The Atomic Cluster Centered at the yttrium Site

The photoexcited yttrium atom in YBa$_2$Cu$_3$O$_x$ is an ideal observer of the atomic structure of the CuO$_2$-planes. Yttrium is located in the electronically inert "separating" layer in between the CuO$_2$ double layers, see e.g Ref. [21]. Its position and the vibrational dynamics are expected to be only weakly affected by the oxygen vacancies at the chain sites and the related order–disorder phenomena. Nearest neighbours of Y are the planar oxygen atoms, O2 and O3, next nearest neighbours the planar copper atoms, Cu2. Their RDF’s are expected to show up in the Fourier transform spectra well isolated from each other. Thus Y-EXAFS yields directly information on the dimples in the CuO$_2$ plane. From the crystalline symmetry we expect
the Y–Cu2 pair to be unaffected by the orthorhombic distortion of the unit cell.

The selection of an “inert” central site is crucial for EXAFS measurements of subtle local distortions. For instance Cu-EXAFS in YBa2Cu3Ox suffers from the two nonequivalent sites of copper. Ba might be considered as an equally well suited candidate for the central site as Y. However, the position of Ba has been shown to be displaced by oxygen vacancies in the chains. Diffraction studies of the ortho-II superstructure in underdoped YBa2Cu3Ox (x=6.40-6.7) report shifts by +0.04 Å along the a-axis [7]. Thus the {100}-mirror plane through the average barium sites is partially removed, at least in underdoped YBa2Cu3O7−δ. Much weaker antiferro-type shifts of ≃ 0.011 Å have been reported for the Y atoms.

Fig. 1 displays a view of a Y–O2,3–Cu–Ba cluster with some of the important scattering paths contributing to the Y EXAFS (arrowed):

- Y–O2, Y–O3 (SS), see Tab. 1
- Y–Cu2 (SS), see Tab. 4
- Y–Cu2–Ba (SS, MS), see Tab. 5
- Y–O2–Ba, Y–O3–Ba (SS, MS), see Tab. 6
- Y–O2–Cu2, Y–O3–Cu2 (MS), see Tab. 7
2.2. SAMPLE PREPARATION

The samples under investigation were polycrystalline powders with oxygen contents: \(x = 6.806\) (“underdoped”), \(x = 6.947\) (“optimum doped”), \(x = 6.968\) (“overdoped”), \(x = 6.984\) (“heavily overdoped”). The samples were from the same batches earlier used for the measurements of the crystallographic, electrical and magnetic properties in the underdoped–overdoped transition [1]. We used preparations which were obtained by direct reaction of BaCO\(_3\) with the metal oxides. The reduction was performed in equilibrium with YBa\(_2\)Cu\(_3\)O\(_{6.05}\) in sealed ampoules (CAR method). For further details of the preparation route and the precision measurement of the oxygen contents see Ref. [1] and references therein. The x-ray absorbers were prepared from about 60 mg of finely ground powders (\(\leq 5\mu m\)) spread onto a metallized Kapton tape and sealed by Kapton foil.

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**Fig. 4.** Yttrium K EXAFS in YBa\(_2\)Cu\(_3\)O\(_x\) as a function of oxygen concentration at \(T=100\) K: co-plotted moduli of the Fourier transforms, \(\mid FT(\chi k^2)\mid\), as obtained from the interference patterns in Fig. 3 using \(k=2–16\) Å\(^{-1}\). Note the reduced height of peak “6.2” for \(x=6.801\).
Fig. 5. Yttrium K EXAFS in YBa$_2$Cu$_3$O$_{6.968}$ as a function of temperature. 18 photo-electron interference patterns, $\chi k^2$, at $T=86-250$ K are co-plotted.

2.3. ABSORPTION SPECTROSCOPY

A stack of 8 such foils was found to yield the optimum absorption contrast, $\Delta \mu d \simeq 0.69 \pm 0.03$. The x-ray absorption measurements were carried out in transmission mode using the double crystal spectrometer at the bending magnet BM29(BL18) at the European Synchrotron Radiation Facility (ESRF). The harmonics were suppressed to $\leq 10^{-3}$ by detuning the flat Si 111 crystals to 50% of the maximum of the rocking curve. Krypton filled ionization chambers served as detectors. The spectrometer broadening was set to match the Y K-core-level width. The scans were extended up to 1500 eV above the Y K-edge at 17033 eV, yielding $\simeq 20$ Å$^{-1}$. $E_0$ was uniquely defined by the inflection point at the onset of the white line. The drifts in energy caused by the thermal load on the first uncooled monochromator crystal were typically $\pm 1.5$ eV.

The low temperature experiments were carried out using a closed cycle He-cryostat. The absorption foils were coupled to the cold head by He gas. The temperature drifts during high temperature scans were $< \pm 0.1$ K, during measurements across the superconducting phase transition $< 0.05$ K. We took care of possible hysteretic effects during the thermal cycle. Each sample was cooled down within about 2 h from room temperature...
to about 18 K, subsequently heated up to room temperature, and again cooled down to 18 K. Possible hysteretic effects turned out to be within the error margins of the data reduction procedure. All data presented in the following sections were recorded at increasing temperature. The time intervals between successive temperature scans were in average about 1 h.

3. Experimental Results

Figs. 3, 5 display typical photoelectron interference patterns, $\chi k^2$, as obtained by data reduction of the raw absorption spectra, $\mu d(E)$, where $\mu$ is the linear absorption coefficient, $d$ the thickness of the absorber and $E$ the photon energy. After subtraction of a linear pre-edge background the spectra were normalized and the atomic absorption, $\mu_0$, was determined from a sequence of four cubic splines. The energy dependence of $\mu_0$ above threshold was taken into account using tabulated numbers. No further corrections to the data were applied, neither to eliminate possible atomic multielectron excitations, nor to smooth the monochromator glitch occurring systematically around $k=8 \, \text{Å}^{-1}$. The accuracy and reproducibility of the data reduction procedure can be appreciated from $\chi(k)k^2$ (Figs. 3,5), from

**Fig. 6.** Yttrium $K$ EXAFS in $\text{YBa}_2\text{Cu}_3\text{O}_{6.968}$ as a function of temperature, $T=86–250 \, \text{K}$: co-plotted moduli of the Fourier transforms, $|\text{FT}(\chi k^2)|$, from the interference patterns in Fig. 5. Transform range $k=2–16 \, \text{Å}^{-1}$. 

the corresponding Fourier transform spectra (Figs. 4, 6), and in particular from the behaviour of $|\text{FT}(\chi k^2)|$ for $R_{\text{eff}} \rightarrow 0$. The tiny bump around 1 Å is an artefact due to deficiencies in the above background definition.

All spectra were recorded up to $k=20$ Å$^{-1}$, but only the window $k=2-16$ Å$^{-1}$ (Gaussian broadened by 0.2 Å$^{-1}$) was used for the structural analysis. Some of the spectra exhibit spikes at $k \geq 16$ Å$^{-1}$ (Fig. 3) degrading the important nearest neighbour Y–O2,3 signal. Scans with an excellent S/N ratio were obtained from the “overdoped” ($x=6.968$) sample, in particular during one synchrotron shift at $86 > T > 105$ K. We have used this set of data to study in greater detail the subtle structural anomalies showing up in the direct vicinity of $T_c$ (Fig. ??).

Within $R_{\text{eff}}=0.8$ Å the Fourier transform spectra, $|\text{FT}(\chi k^2)|$, exhibit 6 prominent peaks. The calculated distribution of scattering amplitudes displayed in Fig. 2 exhibits a similar overall pattern. Single scattering at the oxygen and copper atoms in the CuO$_2$ plane gives rise to the peaks “O2,3” and “Cu2”; at larger $R_{\text{eff}}$ mixtures of single and multiple scattering configurations cause the peaks labelled “3.5”, “4”, “5”, “6.2”. Tabs. 1, 4, 7, 6, 5 list the strongest scattering configurations, their geometries and degeneracies, the atomic coordinates, and the relative amplitudes as calculated from an average of the unit cell parameters [22, 23, 24]. The overall patterns of the Fourier transform spectra are nearly identical for all concentrations at 100 K (Fig. 4). Differences occur in the peak heights, but not in the peak positions. It is important to note that peak “6.2” in the “underdoped” sample ($x=6.801$, short dashed line) is strongly damped. A weaker but clear reduction is observable in peak “3.5”. Seemingly peak “5” is not affected by the oxygen concentration. As a function of temperature, peak “6.2” exhibits the strongest relative variation (Fig. 6) although the temperature also affects the height of peak “5”.

We first analyze the single scattering (SS) paths from the nearest and next nearest neighbours Y–O2,3 and Y–Cu2 pairs in terms of bond lengths, $R$, mean-squared radial deviations, $\sigma^2$, and characteristic vibrational frequencies, $\nu$. Then we study the SS and MS paths contributing to the three high-$R$ peaks “3.5”, “5”, “6.2”, and show their dependence on $x$ and $T$. Finally we discuss the evolution of the static disorder in the Y–Cu2–O2–O3–Ba cluster with $x$ and $T$. In particular we focus on the three-body correlations Y–Cu2–Ba (“6.2”), Y–O2,3–Ba (“5”), Y–Cu2–O2,3, and Y–O2,3–O2,3 (“3.5”), which exhibit significant variations at $T < T_c$. The relatively weak peak “4” here will not be addressed further.
3.1. NEXT AND NEXT NEAREST NEIGHBOURS

The CuO$_2$-planes in YBa$_2$Cu$_3$O$_{7-\delta}$ are not flat but dimpled. In contrast to the buckled CuO$_2$ planes in the 214 compounds the planar oxygen atoms in YBa$_2$Cu$_3$O$_x$ are all displaced from the Cu2 planes in the same direction. Therefore the geometry of the CuO$_2$ planes in YBa$_2$Cu$_3$O$_x$ may be seen as stacked O2,3 and Cu2 layers separated by about 0.27 Å in c direction. The O2,3 layers are located closest to the Y layer, and the Cu2 layers closest to the Ba layer.

The spacing between the O2,3 and Cu2 layers gives rise to a difference of about 0.8 Å between the average Y-O2,3 and Y-Cu2 bond lengths. The Fourier transform spectra of high resolution Y EXAFS ought to exhibit well isolated O2,3 nearest neighbours from the Cu2 next nearest neighbour shell. Since the nearest high order shells are about +0.6 Å further out than the Cu2 shell (cf. Tab. 7), both, the Y–O2,3 and the Y–Cu2 single scattering signals are well isolated from the other scattering contributions, see Figs. 4,6. Standard single scattering analysis is therefore expected to yield straightforward structural information on the O2,3 and Cu2 layers and their interlayer spacing.

3.1.1. The Y–O2,3 Pair

The orthorhombic nature of superconducting YBa$_2$Cu$_3$O$_x$ is manifest in the oxygen layer of the CuO$_2$ plane by the two symmetry equivalent sites O2 and O3, the differences in their thermal vibrations and the differences in their displacements from the Cu2 layer, see e.g. Ref. [22]. The two displacements have been reported to exhibit magnitudes differing by < 0.01 Å, but other diffraction studies have reported flat O2,3 layers.

The average Y–O2,3 bond lengths are 2.40 Å, and depend weakly on

| $R_{avg}$[Å] | scatterer | x  | y  | z  | $\Theta$ [°] | $g$ | Rel. Amp. [%] | # |
|--------------|-----------|----|----|----|--------------|----|--------------|---|
| 2.377        | O2        | -1.911 | 0 | 1.413 | 180.00 | 4 | 100.0 | 1 |
|              | Y         | 0   | 0  | 0  | 180.00       |    |        |   |
| 2.416        | O3        | 0  | -1.943 | 1.436 | 180.00 | 4 | 95.6  | 2 |
|              | Y         | 0  | 0  | 0  | 180.00       |    |        |   |
Fig. 7. Y–O2,3 mean-squared displacements, $\sigma^2$, as a function of temperature. Left: "Underdoped" and "heavily overdoped" samples, Right:"optimum doped" (closed circles) and "overdoped samples" (open circles) of YBa$_2$Cu$_3$O$_x$. The solid lines are fits from the harmonic model of lattice vibrations.

Temperature (4–320 K), see e.g Ref. [22, 23, 24, 25], but strongly on oxygen concentration. Variation of $x$ from 6.6 to 6.97 decreases the average Y–O2,3 bond length by 0.04 Å (at 5 K) [1]. Y–O2 differs from Y–O3 by about 0.02 Å.

Fig. 8. Y–O2,3 mean-cubic relative displacements, $\Delta c_3$, as a function of temperature for $x=6.968$, relative to $T=100$ K. Fits were from 7-10 Å$^{-1}$. Lines connecting the data points are guides to the eyes. Right : Zoom of the region around $T_c$. 
Å. Fits of a single shell absorption fine structure to the filtered \( R_{\text{eff}}=1.1-\)

### TABLE 2. Results obtained from a harmonic single shell fit to the average of the Y–O2,3 pairs.

| \( x \)  | \( R \) [Å] | \( \sigma^2_0 \) (40 K) [Å²] | \( \bar{\nu} \) [cm\(^{-1}\)] | \( E_0 \) [eV] |
|----------|-------------|-----------------|----------------|----------|
| 6.984    | 3.39(4)     | 0.0035(2)       | 253(25)        | 3(3)     |
| 6.968    | 3.39(4)     | 0.0051(2)       | 313(25)        | 3(3)     |
| 6.947    | 3.39(4)     | 0.0048(1)       | 291(25)        | 3(3)     |
| 6.806    | 3.39(4)     | 0.0048(2)       | 270(25)        | 3(3)     |

2.2 Å) Y–O2,3 shell at \( T < T_c \) (40 K) and at \( T > T_c \) (100 K) yielded only coarse agreement with the experimental data, even when narrowing the \( k \)-range to 4–9 Å\(^{-1}\). Inclusion of the orthorhombic splitting (0.02 Å) did not improve these fits, even when the splitting was increased up to 0.2 Å. Obviously the Y–O2,3 pairs are strongly disordered and/or vibrate strongly anharmonically.

The presence of disorder or strong anharmonicities in the Y–O2,3 pairs is directly visible in the imaginary part of the Fourier transform spectra (not shown here). Using the nominal energy zero, \( E_0 \), the maximum of \( \text{Im}(\chi k^2) \) is found markedly shifted apart the maximum of the modulus, and even the best value of \( E_0 = +3 \pm 0.3 \text{ eV} \) (resulting from the harmonic \( k \)-space fits) does not bring them into coincidence. Surprisingly, the average Y–O2,3 bond lengths obtained from these fits (see Tab. 2) are found close to those reported from the diffraction studies. Clearly, applying the harmonic approximation to an anharmonic problem we obtain only approximate parameters, since we put a sufficiently broadened Gaussian RDF on an anharmonic RDF, at best at its centre of gravity.

We have quantified the anharmonicity of the Y–O2,3 RDF’s by the relative mean-cubic relative deviation, \( \Delta c_3 \), extracted from the \( T \)-dependent differences of the sine arguments, \( \Delta \Phi \). In our best set of data \((x=6.968)\) we find a marked singularity of \( \Delta c_3(T) \) exactly at \( T_c \) (Fig. 8). The relative dependence of disorder on the oxygen concentration at 40 K, expressed as \( \sigma^2_0(x) - \sigma^2_0(x = 6.947) \), was determined from the ln-ratios (Eqn. 5) at \( k^2=16-81 \text{ Å}^{-2} \). \( \sigma^2_0 \) is independent of the oxygen concentration for \( x=6.801-6.947 \), but decreases by about 20% in the "heavily overdoped" sample \((x=6.984)\). This finding corroborates the relative heights of peak "5", cf. Fig. 14.

The temperature dependencies of the mean-squared-deviations, \( \sigma^2(T) \), were determined based on the assumption that \( \sigma^2 \) obeys a harmonic model of vibrations (Eqn. 6). The results are displayed in Fig. 7 (drawn out lines) and listed in Tab. 2. Although the characteristic frequencies, \( \nu \), are only
Fig. 9. Y–Cu2 mean-squared displacements, $\sigma^2$, as a function of temperature. Determined from the ln-ratios. Left: The solid line is a fit from the harmonic model of lattice vibrations yielding $\bar{\nu} = 192$ cm$^{-1}$. Right: Same data but zoomed in the superconducting phase. Line connecting the data points is a guide to the eyes.

Coarse approximations, they indicate at least tendencies in the vibrational dynamics on doping. We note that the Y–O2,3 vibrations harden as the oxygen concentration increases up to $x=6.968$, but soften for $x=6.984$. As expected $\bar{\nu} = \nu/c$ is different, but not far from the wavenumber of the infrared active mode reported to be at 312 cm$^{-1}$ for the "oxygen O2,3 mode" [26].

3.1.2. The Y–Cu2 Pair
The Y–Cu2 peak appears in the Fourier transform spectra well isolated from its neighbors. From the crystallographic structure the Y–Cu2 bond lengths are $\simeq 2.2$ Å and are not orthorhombically split. Harmonic single shell fits were performed in $k$-space (5-12 Å$^{-1}$) and the results for 40 K and 100 K are listed in Tab. 3.

For all concentrations we find within the error bars the same energy zero, $E_0$, pointing to the same degree of disorder in the Y-Cu2 pairs, if one exists. Also the bond lengths $R_{Y-Cu2}$ are found to be independent of oxygen concentration and of temperature between 20 and 100 K. However, the temperature dependencies of the mean-squared deviations, $\sigma^2(T)$, exhibit a step-like behaviour around 80 K deviating from the harmonic contribution to the Debye-Waller factor (solid line in Fig. 9). We find $\Delta \sigma^2_{100-40K} \simeq 0.001$ Å$^2$ from the $k$-space fits and $\simeq 0.0006$ Å$^2$ from the ln-ratio.

Since the Y–Cu2 pair is well isolated from its neighbored pairs, and
nominal does not exhibit orthorhombic splitting, we used the so-called splice-method to extract the true pair distribution function, $P(R)$, from the experimental data. Using theoretical phase shifts and envelope functions from the FEFF code, we spliced the phase differences and ln-ratios of the envelope functions from 3.5 to 0 Å$^{-1}$. Fig. ?? exhibits for $x=6.801$ and 20 K the resulting $P(R)$ (thick solid line). We note a weak asymmetry of $P(R)$ towards shorter bond lengths, i.e. a rather weak leakage into the O2,3 layer. For comparison we show an ideal Gaussian (thin dotted line) and a spliced Gaussian (dashed line). The former indicates the broadening introduced by the finite $k$-range and the Gaussian window function. The latter has been calculated from a theoretical and exponentially dampened spectrum using the same splice as for the experimental data. Thus we may estimate the error introduced by the interpolation of the experimental data. We find the true $P(R)$ only slightly outside this margin of error, confirming the absence of strong disorder and/or strong anharmonicities.

We note that the absence of anomalous copper vibrations in YBa$_2$Cu$_3$O$_x$ ($x=6.2$, $x=7$) between 10 and 300 K has been also concluded from neutron resonance absorption spectroscopy [27].

TABLE 3. Results from harmonic single shell fits to the Y–Cu2 peak.

| $x$ | $R$ [Å] | $\sigma^2$ [Å$^2$] | $\bar{\nu}$ [cm$^{-1}$] | $E_0$ [eV] |
|-----|---------|------------------|-----------------|---------|
| 40 K| 100 K   | 40 K             | 100K            |         |
| 6.984| 3.203(5)| 3.204(5) | 0.0023(1)   | 0.0031(1) | 192(25)| 5.93(19)|
| 6.968| 3.204(5)| 3.203(5) | 0.0021(1)   | 0.0033(1) | 192(25)| 5.56(21)|
| 6.947| 3.200(5)| 3.200(5) | 0.0021(1)   | 0.0032(1) | 192(25)| 5.92(22)|
| 6.806| 3.200(5)| 3.200(5) | 0.0021(1)   | 0.0031(1) | 192(25)| 5.88(22)|

TABLE 4. Geometrical data of the Y–Cu2 single scattering configuration giving rise to the isolated 'Cu2 peak'. Calculated from crystallographic data. $R$ is half of the total scattering length. $\Theta$ denotes the scattering angles (180° ≡ back-scattering, 0° ≡ forward-scattering), $g$ the degeneracy of the scattering configurations. Rel. Amp. is the amplitude of the scattering configuration (see text). # is a counter.

| $R$[Å] | scatterer | $x$  | $y$  | $z$  | $\Theta$ [°] | $g$ | Rel. Amp. [%] | # |
|--------|-----------|-----|-----|-----|--------------|----|--------------|---|
| 3.209  | Cu2       | 1.911| 1.943| 1.682| 180.00       | 8  | 96.2        | 1 |
| Y      | 0         | 0   | 0   | 0   | 180.00       |    |             |   |
3.2. PEAKS FROM MIXED SCATTERING CONFIGURATIONS

The peaks at $R \geq 3.5$ Å in the Fourier transform spectra arise from mixed scattering configurations, i.e. 2-leg single scattering paths, which are nearly degenerate with 3- and 4-leg multiple scattering paths, and/or nearly degenerate single and multiple scattering paths from different atomic configurations. Due to the distinguished position of the central yttrium atom at the inversion centre of the unit cell, and due to the particular interlayer spacings in YBa$_2$Cu$_3$O$_x$, the yttrium EXAFS yield many nearly collinear scattering configurations. We take advantage of some of them, in particular of those exhibiting strong or very strong scattering amplitudes. Yttrium in its photoexcited state interferes with the copper and oxygen atoms in the CuO$_2$ plane and through three-body configurations with the Ba atoms in the doping block. The shortest Y–O$_2$.3–Ba and Y–Cu$_2$–Ba scattering configurations deviate from collinear (0°) scattering geometries only by about 14° and 5° and hence give rise to the prominent peaks at 5 Å and 6.2 Å, respectively. Small deviations from collinearity have very strong effects on the three-body scattering amplitude. The results from our MS calculations with adjustable Cu2 position are listed in Tab. 8.

3.2.1. Peak “6.2”

From the calculated distribution of scattering amplitudes displayed in Fig. 2 we expect the spike at $R \approx 6.58$ Å to give rise to the peak “6.2”. The weak side band at the low $R$ side has relative amplitudes up to 13%, and obviously causes the bump between the peaks “5” and “6.2”. It will not be considered further. Table 5 lists the scattering configurations contributing to the “6.2” peak. We find three Y–Ba scattering configurations with...
TABLE 5. Geometrical data of the strongest scattering configurations contributing to peak “6.2”. Calculated from crystallographic data. $R_{\text{avg}}$ is half of the total scattering length. $\Theta$ denotes the scattering angles ($180^\circ$ = back-scattering, $0^\circ$ = forward-scattering), $g$ the degeneracy of the scattering configurations. Rel. Amp. is the amplitude of the scattering configuration (see text). # is a counter.

| $R_{\text{avg}}$ [Å] | scatterer | $x$  | $y$   | $z$       | $\Theta$ [°] | $g$ | Rel. Amp. [%] | # |
|----------------------|-----------|------|-------|-----------|--------------|----|----------------|---|
| 6.583                | Ba        | 3.823| 3.886 | -3.691    | 180.00       | 8  | 17.5           | 1 |
|                      | Y         | 0    | 0     | 0         | 180.00       |    |                |   |
| 6.586                | Ba        | 3.823| 3.886 | -3.691    | 177.70       | 16 | 34.4           | 2 |
|                      | Cu2       | 1.911| 1.943 | -1.682    | 4.71         |    |                |   |
|                      | Y         | 0    | 0     | 0         | 177.57       |    |                |   |
| 6.589                | Cu2       | 1.911| 1.943 | 1.682     | 4.71         | 8  | 19.9           | 3 |
|                      | Ba        | 3.823| 3.886 | 3.691     | 180.00       |    |                |   |
|                      | Cu2       | 1.911| 1.943 | 1.682     | 4.71         |    |                |   |
|                      | Y         | 0    | 0     | 0         | 180.00       |    |                |   |

nearly degenerate scattering lengths centred at $R_{\text{avg}} = 6.586$: single back-scattering Y–Ba (#1), and two nearly collinear Y–Cu2–Ba MS configurations (#2,#3), probing a cluster of 3 × 3 unit cells. Like the Y–Cu2 SS configuration (“Cu2”) these three configurations are not orthorhombically split. The 3-leg MS configuration (#2) contributes nominally by about 47%, the 4-leg configuration by about 27% to the total scattering amplitude at “6.2” (neglecting the $\simeq 8\%$ constant MS background in this region). However it is important to note that the high sensitivity for the detection of subtle Cu2 displacements from the collinear three-body scattering configuration arises from the phase contrast between the 3-leg and 4-leg MS configurations [15].

Fig. ?? displays the concentration and temperature dependence of the maxima of $|\text{FT}(\chi k^2)|$ at $R_{\text{eff}} \simeq 6.2$ Å. Within the scatter of the data the peak heights from the “optimum doped” and both overdoped samples (closed symbols) exhibit congruent temperature dependences at $\simeq 70 – 300$ K, and saturation for $T \to 20$ K. Seemingly there is a curvature at high temperatures, which deviates from the inverted $\cosh(1/T)$ (see Eqn. 6) behaviour expected for harmonic Y–Ba vibrations. The saturation behaviour of the peak heights in the superconducting phase is different for the “heavily overdoped” and the two others. The former starts to saturate at $T \leq 40$ K, whereas the latter two saturate at $T \leq 60$ K and level out at values $\simeq 10\%$ lower, see Fig. ??.
The peak heights of the “underdoped” sample (open rectangular symbols) have a significantly weaker temperature dependence but exhibit distinct “staircases” at $\simeq 160$ K and $\simeq 100$ K. At $T > 250$ K we find that the temperature dependencies for all concentrations converge. In the superconducting phase the peak height is relatively decreased by $\simeq 15\%$, and a broad maximum seems to evolve around $\simeq 40$ K.

3.2.2. Peak “5”
Peak “5” arises from similar Y-Ba scattering configurations as peak “6.2”. But the species of the intervening atoms are orthorhombically split oxygens, O2 and O3, the average scattering length is shorter ($\simeq 5.354$ Å), and the
bridging angle of $\simeq 15^\circ$ is larger compared to $\simeq 5^\circ$. Fig. 2 shows two closely neighboured spikes sitting in a narrow distribution of scattering amplitudes. Tab. 6 lists the geometrical data of the strongest scattering configurations contributing to the peak “5”. Due to the orthorhombic splitting we expect two triplets (#1-3, #4-6), each with one Y–Ba SS configuration and two Y–O–Ba MS configurations. #7 labels a Y–Y single scattering path. Since this particular Y–Y path is not orthorhombically split and comparatively weak, we simply consider it as a constant contribution to the background.

| $R_{\text{avg}}$[Å] | scatterer | $x$  | $y$  | $z$  | $\Theta$ ['] | $g$ | Rel. Amp. [%] | #  |
|-------------------|-----------|-----|-----|-----|---------------|----|--------------|----|
| 5.314             | Ba        | -3.823 | 0   | -3.691 | 180.00        | 4  | 17.7         | 1  |
|                   | Y         | 0    | 0   | 0    | 180.00        |    |              |    |
| 5.332             | Ba        | 0    | 3.886 | -3.691 | 173.99        | 8  | 31.7         | 2  |
|                   | O2        | -1.911 | 0   | -1.413 | 13.51         |    |              |    |
|                   | Y         | 0    | 0   | 0    | 172.48        |    |              |    |
| 5.350             | O2        | 1.911 | 1.682 | 1.413 | 13.51         | 4  | 14.5         | 3  |
|                   | Ba        | -3.823 | 0   | 3.691 | 180.00        |    |              |    |
|                   | O2        | -1.911 | 0   | 1.413 | 13.51         |    |              |    |
|                   | Y         | 0    | 0   | 0    | 180.00        |    |              |    |
| 5.359             | Ba        | 0    | 3.886 | -3.691 | 180.00        | 8  | 17.28        | 4  |
|                   | Y         | 0    | 0   | 0    | 180.00        |    |              |    |
| 5.376             | Ba        | 0    | 3.886 | -3.691 | 174.28        | 8  | 31.1         | 5  |
|                   | O3        | 0    | 1.943 | -1.436 | 12.76         |    |              |    |
|                   | Y         | 0    | 0   | 0    | 172.95        |    |              |    |
| 5.392             | O3        | 0    | -1.943 | -1.436 | 12.76         | 4  | 14.3         | 6  |
|                   | Ba        | 0    | -3.886 | -3.691 | 180.00        |    |              |    |
|                   | O3        | 0    | -1.943 | -1.436 | 12.76         |    |              |    |
|                   | Y         | 0    | 0   | 0    | 180.00        |    |              |    |
| 5.451             | Y         | 3.823 | -3.886 | 0   | 180.00        | 4  | 12.9         | 7  |
|                   | Y         | 0    | 0   | 0    | 180.00        |    |              |    |
Fig. 13. Modulus of the Fourier transform at the maximum of peak "5" as a function of oxygen concentration and temperature. For details see text. Lines connecting the data points are guides to the eyes.

Due to the relatively large bridging angle of $\simeq 14^\circ$ we expect the sensitivity of the peak height to displacements of the intervening oxygens to be relatively decreased. However, model calculations (not shown here) yielded clearly resolved variations of the peak height by $\geq 4\%$ for oxygen displacements of $\geq 0.01\,\text{Å}$ in $c$ direction.

For all oxygen concentrations under investigation the heights of peak “5” are found to collapse into a single line (Fig. 13) for temperatures $80 \leq T \leq 300\,\text{K}$ (within the scatter of the data points). Seemingly in the normal phase and close to $T_c$ the average position of the oxygen layer in the CuO$_2$ plane is not appreciably altered by variations of the oxygen concentration from...

Fig. 14. Modulus of the Fourier transform at the maximum of peak "5" as a function of oxygen concentration at $T \leq 120\,\text{K}$. For details see text. Lines connecting the data points are guides to the eyes. Zoomed from Fig. 13.
Furthermore (within the limited accuracy of our analysis) the characteristic vibrational frequencies of the Y–Ba pairs do not depend on doping either.

Discrepancies up to 10% in the heights of peak “5” are found in the superconducting phases at \( T < 80 \) K, between the “heavily overdoped” sample on one hand, and the three others on the other hand (cf. Fig. 14).

3.2.3. Peak “3.5”
A number of EXAFS works attribute peak “3.5” exclusively to Y–Ba and Y–Y single scattering [11, 12]. However, our multiple scattering calculation finds three MS configurations to contribute strongly to the total scattering amplitude at “3.5”, nominally by up to \( \approx 42\% \) ! The geometrical data of the 6 scattering configurations causing peak “3.5” are listed in Tab. 7. The Y–Y single scattering is found to be strongest and orthorhombically

| \( R_{avg}[^\text{Å}] \) | scatterer  | \( x \) | \( y \)  | \( z \)  | \( \Theta \) [°] | \( g \) | Rel. Amp. [%] | # |
|-----------------|---------|------|------|------|---------|------|-------------|---|
| 3.691           | Ba      | 0    | 0    | -3.691| 180.00  | 2    | 26.1        | 1 |
|                 | Y       | 0    | 0    | 0    | 180.00  |      |             |   |
| 3.759           | O3      | 0    | -1.943| 1.436| 125.32  | 16   | 17.2        | 2 |
|                 | O2      | -1.911| 0    | 1.413| 123.97  |      |             |   |
|                 | Y       | 0    | 0    | 0    | 110.70  |      |             |   |
| 3.770           | Cu2     | -1.911| -1.943| 1.682| 132.28  | 16   | 13.6        | 3 |
|                 | O2      | -1.911| 0    | 1.413| 85.32   |      |             |   |
|                 | Y       | 0    | 0    | 0    | 142.38  |      |             |   |
| 3.773           | Cu2     | 1.911| -1.943| -1.682| 131.20  | 16   | 13.7        | 4 |
|                 | O3      | 0    | -1.943| -1.436| 85.65   |      |             |   |
|                 | Y       | 0    | 0    | 0    | 143.13  |      |             |   |
| 3.823           | Y       | 3.823| 0    | 0    | 180.00  | 2    | 17.8        | 5 |
|                 | Y       | 0    | 0    | 0    | 180.00  |      |             |   |
| 3.886           | Y       | 0    | -3.886| 0    | 180.00  | 2    | 17.0        | 6 |
|                 | Y       | 0    | 0    | 0    | 180.00  |      |             |   |
split (#5, #6), followed by the Y–Ba single scattering (#1) perpendicular to the planes. The three triangular MS configurations: Y–O2–O3 (#2),

**Fig. 15.** Modulus of the Fourier transform at the maximum of peak “3.5” as a function of oxygen concentration and temperature. For details see text. Lines connecting the data points are guides to the eyes.

**Fig. 16.** Modulus of the Fourier transform at the maximum of peak “3.5” as a function of oxygen concentration at $T \leq 120$ K. For details see text. Lines connecting the data points are guides to the eyes. Zoomed from Fig. 15.
Y–O2–Cu2 (#3) and Y–O3–Cu2 (#4) contribute significantly due to their high degeneracies, \( g = 16 \). It is important to note that these highly degenerate MS configurations are nearly as sensitive to copper and oxygen displacements in the CuO\(_2\) plane as the quasi collinear MS configurations Y–O2,3–Ba (peak “5”), and Y–Cu2–Ba (peak “6.2”). It is clearly visible that the temperature and concentration dependencies of the heights of peak “3.5” and peak “6.2” are strongly correlated, in agreement with our model calculations discussed further below.

Figs. 15, 16 show the concentration and temperature dependencies of peak “3.5”. Both turn out to be very similar to those of peak “6.2” (cf. Figs. 11, 12), but not to those of peak “5” (cf. Figs. 13, 14). The similarity includes the relatively weaker and staircase like temperature behaviour of the “underdoped” sample, and the congruent temperature behaviour of the optimum/overdoped samples for \( T > 80 \) K. It would thus appear that displacements of Cu2 are the common origin of the similarities in Fig. 15 and Fig. 11. However, there are also significant differences: i. the heights of peak “3.5” exhibit a dip around 100 K, at least for the optimum/overdoped samples, ii. a plateau occurs between 100 K and 130 K, and iii. at \( T \leq 60 \) K the order of peak heights changes. In Fig. 12 x=6.968 has the weakest peak amplitude of the overdoped samples, whereas in Fig. 14 it has the strongest.

In the superconducting phase, saturation behaviour evolves for the optimum/overdoped samples (closed symbols); saturation behavior starts closest to \( T_c \) for the “optimum doped” sample. The “underdoped” sample is found to exhibit still at 20 K a finite temperature dependence of the peak height.

4. Discussion

To summarize, we combine the structural results from the quantitative analysis of the nearest and next nearest neighbours peaks, “O2,3” and “Cu2”, with the qualitative information deduced from the inspection of the mixed scattering configurations “6.2”, “5”, and “3.5”. Here we restrict ourselves to the static changes of the local geometry at low \( T \), and to overall tendencies. A detailed analysis of the apparent and interesting anomalies occurring at \( T_c \) and at other characteristic temperatures has to include the vibrational dynamics of the many body scattering configurations, and will be reported in forthcoming papers.

We start with the assumption that the position of the Cu2 atoms is the key variable that controls the relative variations of the peak heights at \( R \geq 3.5 \) Å for the different oxygen concentrations. To understand the effect of Cu2 displacements on the Fourier transform spectra we carried
out a series of model calculations. We have been able to reproduce qualitatively the experimental Fourier transform spectra and their variations with doping at low temperatures. Although vibrational displacements were completely neglected in these calculations ($\sigma^2=0$), we believe that the results are indicative of the response of the Fourier transform spectrum to such displacements.

Some of the calculated Fourier transform spectra are displayed in Fig. 17. Parameters and numerical results are listed in Tab. 8.

### 4.1. THE Cu2 LAYER

Displacing the Cu2 atoms towards the O2,3 layer we dampen the peaks “6.2” and “3.5”, but do not affect peak “5”. Variations of the height of peak “6.2” by about 20% are found to correspond to Cu2 displacements by $\approx 0.07 \, \text{Å}$ along the c-axis. In the range under investigation the height of peak “6.2” turns out to respond almost linearly to the Cu2 positions along c, z(Cu2). But the variations of the height of peak “3.5”, which arise from the non-collinear Y–O2,3–Cu2 MS configurations (#3 in Tab. 7), not unexpectedly, behave mildly non linearly.

| $\delta R$ [Å] | $z$(Cu2) | Dimpling [°] | Height "3.5" | Height "6.2" |
|----------------|---------|--------------|---------------|---------------|
| 0.146          | 0.365   | 4.4          | 128.4         | 100.5         |
| 0.169          | 0.363   | 5.0          | 139.6         | 107.5         |
| 0.204          | 0.360   | 6.1          | 154.2         | 118.3         |
| 0.260          | 0.356   | 7.7          | 171.7         | 134.0         |
| 0.320          | 0.350   | 9.5          | 181.9         | 150.1         |

In Fig. 17 we note that the position of the “Cu2” peak shifts with the heights of peaks “6.2” and “3.5”. However, a correlation between the position of peak “Cu2” and the heights of peaks “6.2” and “3.5” is experimentally not observed (see Figs. 4, 6). From the experiment we find the Y–Cu2 distances are independent on the oxygen concentration (cf. Tab. 3, Y–Cu2 SS configurations). Therefore the Cu2 displacements along c have to be constricted by fixed Y–Cu2 bond lengths, and the Cu2 atoms may be seen to rotate with fixed radii around the central Y sites in the [111] plane of the Y–Ba blocks. Thereby the basal planes of the cationic sublattices
Fig. 17. Calculated Fourier transform spectra, $|\text{FT}(\chi_k^2)|$, $(2-16 \text{ Å}^{-1})$ for different spacings Cu$_2$–O$_{2,3}$ ranging from 0.146-0.321 Å. No Gaussian broadening added. Only Cu2 is displaced along the $c$-axis. The other atomic positions are fixed. Note that the height of peak “5” is not affected. Note also the shift of peak “Cu2” due to the varying Y–Cu2 bond lengths.

(Y, Cu2, Ba) are expanded/contracted along [110] (*cf.* Fig. 18). Correspondingly also the $a, b$ lattice parameters expand/contract, preserving or changing given local orthorhombic distortions. As discussed in Sec. 3.1.1. we are unable to extract numbers of the orthorhombic splittings from peak “O2,3”, because the Y–O2,3 signal exhibits strong non-Gaussian disorder. The Y–Cu2 SS configuration is insensitive to orthorhombic distortions by reasons of rotational symmetry. The absence of non-Gaussian disorder in the Y–Cu2 SS signals (*cf.* Fig. 10) indicates that the rotational symmetry of the Y–Cu2 SS configurations is maintained upon doping.

According to the crystallographic data, see *e.g.* Ref. [1], the $a$ axis expands upon oxygen depletion, $x_{\text{opt}} > x \rightarrow 6.5$, whereas the $b$ axis contracts. The orthorhombicity of the unit cell decreases correspondingly. We have included the orthorhombic distortion and its variation with doping in Figs. 18,19.

The congruent $T$-dependencies ($T > 80$ K) of peak “5” for all concentrations (*cf.* Fig. 13) lead to the conclusions, that not only the distribution of Y–O2,3–Ba forward scattering angles (#2–#6 in Tab. 6) remain unaffected upon doping, but also the Y–Ba vibrational frequency.
**Fig. 18.** *Top:* View from the top on the Y–Ba block in the unit cell of underdoped and optimum YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{x} (schematic). Y (small open circles) forms the top-most, Ba (large black circles) the lowest layer. The Cu\textsubscript{2} and O2.3 layers are located in between. The orthorhombic distortion is exaggerated for reasons of clarity. The increase of the orthorhombicity on doping occurs by contraction of the a-, and expansion of the b-axis. Arrowed lines connect the atoms of the Y–Cu\textsubscript{2}–Ba three body scattering configurations (Peak “6.2”).

*Bottom:* Side view of the doped Y–Ba blocks along [110] with constant Y–Cu\textsubscript{2} bond lengths. On doping Cu\textsubscript{2} moves along c towards the Ba layer thereby decreasing the forward scattering angle from 6° to 4°. The weak expansion along c with doping is expected from the crystallographic structure.

Therefore we may safely attribute the variations of peak “6.2” observed on doping to different forward scattering geometries in the Y–Cu\textsubscript{2}–Ba MS configurations, and we may discard effects from the doping dependence of the Y–Ba vibrational dynamics. Moreover, if we take into account the static Ba displacements from crystallographic work, we find peak “6.2” of the underdoped sample even more strongly dampened than in the case of unaltered Ba positions.

Also the significant difference between the temperature behaviours of peak “6.2” in the “underdoped” sample on the one hand side, and the optimum/overdoped samples on the other hand side (*cf.* Fig. 11), may be at-
Fig. 19. Top: View from the top on the Y–Ba block in the unit cell of underdoped and optimum YBa$_{2}$Cu$_{3}$O$_{x}$ (schematic). Same cell as in Fig. 18, but rotated by $\simeq 45^\circ$. Arrowed lines connect the atoms of the Y–O$_{2}$O$_{3}$–Ba three body scattering configurations (Peak “5”). Bottom: Side view of the doped Y–Ba blocks along [010] with an Y–O$_{2}$,3–Cu$_{2}$ forward scattering angle $\simeq 13^\circ$ kept fixed on doping. Upon doping the positions of the planar oxygens do not move (or only very weakly) along c towards the Ba layer, but perpendicular to b, a. Thereby the Y–O$_{2}$,3 bond lengths expand/contract within the margins of the orthorhombic distortion. Dashed horizontal lines indicate the positions of Cu$_{2}$ from Fig. 18. Same expansion along c as in Fig. 18.

4.2. THE O$_{2}$,3 LAYER

The height of peak “5” is expected to depend sensitively on the forward scattering angle in the Y–O$_{2}$,3–Ba MS configurations, but weaker than in the Y–Cu$_{2}$–Ba MS (peak “6.2”) configurations. However, due to the orthorhombic unit cell the height of peak “5” measures a distribution of Y–O$_{2}$,3–Ba forward scattering angles. It turns out that the distribution of Y–O$_{2}$,3–Ba forward scattering angles is almost unaffected upon doping, if we allow the Y–O$_{2}$,3 distances to expand/contract within the large error margins of $\simeq 1\%$ (c.f. Tab. 2) set by the SS analysis of peak “O2,3”. The

distributed to different Cu$_{2}$ positions along c. The staircase-like $T$-dependence of peak “6.2” in the “underdoped” sample indicates from the Cu$_{2}$ displacements another characteristic temperature than $T_{c}$. Around $T^{*} = 160$ K (close to the so-called spin gap temperature) the Cu$_{2}$ atoms approach more closely to their positions in the optimum/overdoped samples.
resulting displacement of e.g. O2 along c is negligibly weak and indicated in Fig. 19 (bottom) by the drawn out horizontal lines labelled δz ≃ 0. The other way round, if we fix the average Y–O2,3 distance, the average forward scattering angle varies upon doping by ≃ 3°, which clearly pushes the height of peak “5” beyond the error limits of the experimental data. From the congruent data sets in Fig. 13 we conclude that the O2,3 layer does not move along c for 6.801 < x ≤ x_{opt}. But the O2,3 atoms have large degrees of freedom parallel to the Y–O2,3–Ba scattering geometry, i.e. along a and b, respectively (Fig. 19).

It should be noted that a constant distribution of Y–O2,3–Ba forward scattering angles, given as an experimentally given constraint, might be also achieved by rotating the Y–O2,3–Ba scattering triangle around the base Y–Ba path. Such rotations, however, would lift, at least partially, the degeneracies of the forward scattering configurations and alter their angular distributions. It is interesting to note that the shapes of peaks “O2,3” and “5” in the calculated Fourier transform spectra (Fig. 17) show appreciable differences in comparison with the experimental ones (Figs. 6, 4). Apparently the geometry of the Y–O2,3 cluster is only poorly described by the crystallographic data used for the calculations and listed in Tabs. 1, 6.

4.3. THE CU2–O2,3 LAYERS

In Fig. 20 (Left) we plot the heights of peaks “6.2” and “5” at T = 25 ± 5 K vs. the oxygen concentration x. Peak “6.2” increases strongly with x indicating that the Cu2 layer shifts along c towards the Ba layer. Up to x ≃ x_{opt} the height of peak “5” is almost independent on x, but it increases by ≃ 10 % at x = 6.984. From the preceding discussion it is tempting to relate the difference of the two peak heights directly to the spacing of the Cu2–O2,3 layers. However, the configurational average of the Y–O2,3–Ba MS scattering signals and thus the height of peak “5” were shown to depend sensitively on the orthorhombicity and the anharmonic O2,3 dynamics, which also depend on x. If we assume negligible changes of the anharmonic O2,3 dynamics in the underdoped regime, we may read from Fig. 20 (Left) the average Cu2–O2,3 spacing (or dimpling of the CuO₂ planes) to increase for x → x_{opt}.

A recent Raman study of the oxygen vibrations across the underdoped-overdoped transition [29] reports for the overdoped regime, x > 6.93, a relative softening of the O2,3 in-phase vibrations in z-direction (440 cm⁻¹, A_{g}) by ≃ 40%. Taking into account such strong changes of the anharmonic vibrational O2,3 dynamics we expect the relationship between the height of peak “5” and average O2,3 position along c to be quantitatively but not qualitatively different from that in the underdoped regime. Therefore we
read from the data at $x = 6.984$ that the heavily overdoped O2,3 layer moves along $c$ in the same direction as the Cu2 layer and thus reduces the Cu2–O2,3 spacing. The ratio of the peak heights depicted in Fig. 20 (Right) exhibits a clear maximum at optimum doping. It indicates a structural phase transformation of the displacive type at this notable point in the phase diagram. Doping in the overdoped regime displaces the average position of the O2,3 layer along $c$ towards the Cu2 layer and thereby reduces the Cu2–O2,3 spacing. In the underdoped regime the Cu2–O2,3 spacing is reduced by oxygen depletion, but inversely by displacements of the Cu2 layer along $c$ towards the O2,3 layer.

5. Concluding Remarks and Summary

We have extracted local structural information from systematic measurements of the Y-K EXAFS of YBa$_2$Cu$_{3-x}$O$_x$ for $x = 6.801 - 6.984$ and at $T = 20 - 300$ K. The structural analysis was focussed on the Y–O2,3 and Y–Cu2 single scattering configurations, and the multiple scattering configurations Y–O2,3–Ba (peak “5”) and Y–Cu2–Ba (peak “6.2”). With respect to the large amount of structural anomalies, directly visible in the Fourier-transform spectra as a function of doping and of temperature, the structural analysis presented in this lecture is far from being complete, and in part
still preliminary. In particular the important multiple scattering signal demand for a quantitative analysis including the vibrational dynamics. To summarise, we emphasise the following results:

1. The Y–Cu2 bondlengths are independent on doping. In the normal phase the Y–Cu2 pairs vibrate harmonically, but in the superconducting phase the Y–Cu2 vibrations freeze out. On doping the Cu2 atoms shift along the \( c \) direction towards the Ba layer.

2. The Y–O2,3 pairs exhibit strong anharmonicities. The degree of non-Gaussian disorder and the strong anharmonic vibrational dynamics depend significantly on the oxygen concentration. The average Y–O2,O3 bondlengths are almost independent on doping (within the error limits set by our harmonic analysis). The Y–O2,3 mean-squared deviations do not freeze out in the superconducting phase as the Y–Cu2 vibrations. But the mean-cubic deviations of the Y–O2,3 pairs are large, depend on doping, and exhibit a clear singularity at \( T_c \) (shown for \( x=6.968 \)).

3. In the underdoped regime the average spacing O2,3–Cu2 increases with oxygen concentration, \( x \to x_{\text{opt}} \), due to relative displacements of Cu2 towards Ba. The position of the O2,3 along \( c \) is almost unaffected by doping. Staircase-like displacements of Cu2 along \( c \) occur at characteristic temperatures other than \( T_c \). The average position of the O2,3 layer along \( c \) behaves monotonously as a function of temperature.

4. In the overdoped regime increasing oxygen concentration displaces the Cu2 layer along \( c \) further towards Ba. But the O2,3 layer exhibits a clear tendency to shift in the same direction along \( c \) thus decreasing the average O2,3-Cu2 spacing. No staircase-like Cu2 displacements are observed in the normal phase.

5. Optimum doping is a notable point in the phase diagram of YBa\(_2\)Cu\(_3\)O\(_x\), also concerning the structural degrees of freedom. Here the O2,3–Cu2 spacing is largest, and the relative displacements between O2,3 and Cu2 invert upon doping. In the optimum doped superconducting phase the Cu2 position along \( c \) is independent on temperature for \( T < 80 \) K.

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