Phaseseparation in overdoped
\(Y_{1-0.8}Ca_{0.2}Ba_{2}Cu_{3}O_{6.96-6.98}\)

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Abstract. The dimpling in the CuO\(_2\) planes of overdoped \(Y_{1-y}Ca_yBa_2Cu_3O_{6.96-6.98}\), \((y=0.02-0.2)\) has been measured by x-ray absorption-fine-structure spectroscopy (Y-K EXAFS). A step-like decrease around 12% Ca indicates a percolation threshold for distorted sites of 5 cells, and thus phase segregation. We conclude the charge carriers added by substitution of \(Y^{3+}\) by \(Ca^{2+}\) to be trapped at the Ca sites and their \(nn\) environment.

INTRODUCTION

The unusual metallic properties of the high \(T_c\) cuprate superconductors are difficult to reconcile with a homogenous electronic state. Since inhomogeneities in the electronic structure may lift the translational invariance of the underlying lattice, it is suggesting to measure both, the atomic structure using short-range (or local) structural probes, and the average crystallographic structure using diffraction techniques [1]. Anomalous atomic displacements may be then extracted from careful comparisons between the local and the crystallographic structure.

The anomalous electronic structure of the cuprate superconductors is frequently discussed in terms of dynamic inhomogeneities, for instance a mixture of microscopically segregated phases. The notorious nonstoichiometry of all known superconducting cuprates, even their optimum doped phases, causes many static inhomogeneities thus adding a constraint to the analysis of anomalous atomic displacements.

Advantageously the metallic CuO\(_2\)-planes of the cuprate superconductors are the structurally most perfect blocks. Thus significant structural anomalies in the planes can be safely related to nontrivial electronic inhomogeneities. We have recently shown that upon oxygen doping of \(YBa_2Cu_3O_x\) the locally measured spacing between the Cu2 and O2,3 layers ("dimpling") in the CuO\(_2\)-planes keeps track of the planar hole concentration [1]. The data from Y K-edge EXAFS comprise the

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atomic structure of the 8 next neighboured CuO$_2$-plaquettes, and thus the effective charge in only 32 Cu–O bonds. Oxygen doping for $x \rightarrow x_{opt}=6.92$ has been found to increase the dimpling, in other words: the increasing number of oxygen holes bends the Cu–O bonds out-of-plane towards the Ba-layer. At the onset of the overdoped regime, $x \simeq 6.95$, the dimpling and thus also the number of holes exhibits a sharp maximum [3]. A concomitant displacive transformation of the crystallographic structure however seems to block a further increase of the dimpling. Although further doping from $x \simeq 6.95 \rightarrow 7$ increases the nominal hole concentration, the dimpling starts to decrease.

In this contribution we report on Y $K$-EXAFS measurements of the dimpling in a series of overdoped compounds, YBa$_2$Cu$_3$O$_{6.96-6.98}$, additionally overdoped by substitution of Y$^{3+}$ with 2–20% Ca$^{2+}$.

![Figure 1](image.png)

**FIGURE 1.** Dimpling of the CuO$_2$-planes in Y$_{1-y}$Ca$_y$Ba$_2$Cu$_3$O$_{6.96-6.98}$ as a function of Ca concentration. Large full circles (thick drawn out line): data from Y-EXAFS at 25 K. Thin open circles (thin dashed line): data from neutron diffraction at 5 K [2]. For convenience the latter are offset by +0.01 Å.

**EXPERIMENTAL DETAILS**

The polycrystalline samples were from the same batches studied previously by diffraction with x-rays and neutrons, and by magnetometry [2]. Up to 20% Ca could be homogenously solved in YBa$_2$Cu$_3$O$_x$ while the oxygen content was kept at the highest numbers possible: $x = 6.96 – 6.98$, i.e. surprisingly always < 7.00. Ca EXAFS of the same samples confirmed that calcium has replaced yttrium (> 97%),
and not barium. The EXAFS spectra \((T = 20 − 60K)\) were recorded at the European Synchrotron Radiation Facility (ESRF) using the double crystal spectrometer at BM29. Details of the spectroscopic technique and of the data analysis are given in [1].

RESULTS

Fig.1 exhibits the dimpling of the CuO\(_2\)-planes in \(Y_{1−y}Ca_yBa_2Cu_3O_{6.96−6.98}\) \((T = 25 K)\) for \(y = 0.02 − 0.2\) as extracted from the Y EXAFS (large full circles, drawn out line). Comparison is made with the results from neutron diffraction (small circles, dashed line) by Böttger et al. [2]. From the Y EXAFS the dimpling is found independent on the Ca concentration up to 9% \((0.281(2) \text{ Å})\), then undergoes a step-like decrease by about 0.015 Å, and flatens around 0.265(4) Å for 14–20 % Ca. The position of the step may be located around 12% Ca (dotted vertical line). The discontinous behaviour of the dimpling from the Y EXAFS is at variance with the continous behaviour obtained from the refinement of the average crystallographic structure [2]. For better comparison the diffraction data are offset by +0.01 Å showing that both methods yield the same overall variations, and that the discontinuity from the EXAFS work is clearly outside the scatter of the data points from the diffraction work.

DISCUSSION

The step-like variation of the dimpling with increasing Ca concentration points to a percolative transition induced by Ca doping. Fig. 2 exhibits a plausible scheme demonstrating the occurrence of percolative paths for concentrations around 16% Ca. Here it is assumed that the holes doped by Ca\(^{2+}\) are predominantly screened by
the $nn$ Y cells thus creating a cross-like cluster of 5 distorted cells. It is suggesting that these holes are trapped and do not contribute to the density of the mobile carriers.

Considering the Ca impurities as percolating sites in a random process, the exact theory for a square 2-D lattice [4] predicts the critical percolation to occur for 59.2746%. Then straightforwardly the critical percolation for the cross-like clusters, each centered at a Ca impurity, is expected for $59.2746%/5 \approx 12\%$ Ca. We conclude that the observed step-like decrease of the dimpling around 12% Ca is connected to this percolation threshold.

The other way around: the observation of a percolation threshold at 12% Ca indicates the percolating sites to be 5 cells large. The solid solution thus segregates into two phases: \textit{i}. the matrix of undistorted Y cells, and \textit{ii}. distorted clusters at the Ca sites.

**CONCLUDING REMARKS**

We conclude that doping of YBa$_2$Cu$_3$O$_x$ with heterovalent cations substituting Y is electronically nonequivalent with oxygen doping in the chain layer. Thus generalized phase diagrams treating Ca$^{+2}$ and O$^{-2}$ dopants in Y$_{1-y}$Ca$_y$Ba$_2$Cu$_3$O$_x$ on an equal footing are questionable. In particular the superconducting transition temperature of dually doped Y$_{1-y}$Ca$_y$Ba$_2$Cu$_3$O$_x$ is not expected to match a parabolic behaviour $T_c$ vs. hole concentration.

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