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Ca-substitution and O-doping effects in superconducting Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-x}$Ca$_x$)Cu$_2$O$_{6+z}$ obtained from neutron diffraction refinements

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Distinct calcium and oxygen doping effects were studied in the Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-x}$Ca$_x$)Cu$_2$O$_{6+z}$ (Cu-1212:P) system by means of neutron diffraction and superconducting quantum interference device experiments in the wide substitution ranges of $0 < x < 0.35$ and $0 < z < 1$. The effectiveness of the two different ways to introduce holes into the CuO$_2$ planes was compared both in respect to the capability to increase $T_c$ and in terms of the hole production as estimated from neutron-diffraction data via bond-valence-sum calculation. Oxygen doping was found to increase the hole concentration less efficiently, and further, at a certain hole concentration value higher $T_c$ values were obtained with calcium substitution than with oxygen doping. The two different hole-doping methods exhibited also different $T_c$ vs Cu-O bond length relations. As a conclusion, the possible roles of the hole distribution in the in-plane Cu-O bond and the flatness of the CuO$_2$ planes in determining the superconducting properties were recognized. [S0163-1829(99)06929-5]

I. INTRODUCTION

The structures of superconducting cuprates are best described as members of different homologous series expressed by $M_nA_2Q_{n-1}O_{m+2}+2n+\delta$ or $M-Mm(1-n)n$. In these structures the superconductive $Q_{n-1}O_{m}$ ($Q =$ Ca, rare-earth element; $n = 1-7$) “infinite-layer” blocks are sandwiched by AO (A = Sr, Ba, La) layers and $M_{M}O_{m+\delta}$ ($M =$ e.g., Cu, Bi, Pb, Tl, Hg, C; $m = 0-3$) “charge reservoir” blocks. For understanding the phenomenon of high-$T_c$ superconductivity, evaluation of the factors determining the superconducting properties is essential. The observed values of critical temperature $T_c$ are believed to be related to the hole concentration in the CuO$_2$ planes, which is further commonly associated with, e.g., the valence of copper in the CuO$_2$ planes. An open challenge is, however, how to explicitly establish the values of such parameters.

In a common chemical approach the hole concentration in the CuO$_2$ planes is imagined as a mixed valence value of copper and estimated for the layered $M_nA_2Q_{n-1}O_{m+2}+2n+\delta$ cuprate structures by first analyzing the oxygen stoichiometry, i.e., $\delta$ in the $M_{M}O_{m+\delta}$ charge-reservoir block, and then sharing the observed excess oxidation evenly in between the different CuO$_2$ planes in the $Q_{n-1}O_{m}O_{2n}$ infinite-layer block to get a quantity which is best described as a “nominal average copper valence” $V_{Cu,nom}$, i.e.,

$$V_{Cu,nom}=2+[(2-C_{cr})-2C_{rs}+(n-1)(2-V_{Q})]/n,$$  

where $C_{cr}$ and $C_{rs}$ are the nominal charges of the $M_{M}O_{m+\delta}$ charge-reservoir block and the AO layer, respectively, and $V_Q$ is the nominal integer oxidation number of the $Q$ cation (e.g., +II for Ca and +III for Y) in the $Q_{n-1}Cu_{o}O_{2\alpha}$ infinite-layer block. The nominal charge of the $M_{M}O_{m+\delta}$ charge-reservoir block depends on the nominal valence of the metal constituent $M(V_{M,nom})$ and the oxygen stoichiometry $\delta$, i.e., $C_{cr}=mV_{M,nom}-2(m+\delta)$. On the other hand, the rocksalt-type spacing layers between the charge-reservoir and infinite-layer blocks are usually formed by formally neutral $A$ (+II)O units, i.e., $C_{rs}=0$.

Establishment of the oxygen stoichiometry by means of chemical analysis defines the actual hole concentration in an unambiguous way only in the simplest cases such as the (La,Sr)$_2$CuO$_{4+\delta}$ compound (i.e., 0201 phase). In the CuBa$_2$RCu$_2$O$_{7-\delta}$ structure (i.e., so-called “123” compound, or Cu-1212:P phase, where $P$ stands for a perovskite-type charge-reservoir$^1$), for example, even though the calculation of the average copper valence from the chemically analyzed oxygen content value is straightforward, the distribution of holes in between the CuO$_{1-\delta}$ chains (charge-reservoir block) and the CuO$_2$ planes (infinite-layer block) is nontrivial, and cannot be evaluated from the chemical analysis data.

Precise structural data obtained from neutron-diffraction experiments and the universal bond valence—bond length correlation, i.e., the concept of bond-valence-sum (BVS) as developed by Brown and Altermatt,$^4,5$ have been successfully utilized to establish the hole concentration vs $\delta$ behavior in...
Ca-SUBSTITUTION AND O-DOPING EFFECTS IN . . .

the CuBa$_2$YCu$_2$O$_{7-\delta}$ compound.\textsuperscript{8,7} Especially, when considering “net holes” which may reside either on copper or on oxygen in the CuO$_2$ planes rather than the valence of copper only, a parameter $p$ (CuO$_2$), see Eq. (7)), which best explains the $T_c$ vs $\delta$ relation in CuBa$_2$YCu$_2$O$_{7-\delta}$ is obtained.\textsuperscript{8,9}

Another interesting question is, which are the optimum ways to fine tune the $p$(CuO$_2$) parameter, i.e., to dope the existing as well as the “not-yet-discovered” cuprate superconductors to reach the “universal maximum $T_c$.” Based on the observation\textsuperscript{10} that in the $p$(CuO$_2$) value the contributions from the in-plane Cu-O bonds are counteracted and only the out-of-plane bonds from copper to the apical oxygen ($O_{ap}$) and from the in-plane oxygen to the $Q$ and $A$ cations have net effects on the hole concentration, three different ways of doping the CuO$_2$ planes were defined in Refs. 2 and 3, i.e., (1) shortening the Cu-O$_{ap}$ bond and (2) lengthening the effective O-A or (3) O-Q bond in the $M_{m}M_{m}^{2}Q_{n}^{-1}Cu_{m}O_{m+2+n+2\delta}^{}$ structure (Fig. 1). It was also shown that these different doping routes may function either separately or in a collaborative manner. In the CuBa$_2$(Y, Ca)Cu$_2$O$_{7-\delta}$ system, for example, incorporation of oxygen into the CuO$_{1-\delta}$ chain is seen as gradual movements of $O_{ap}$ towards the CuO$_2$ plane [route (1)] and Ba away from the in-plane O atoms [route (2)] as the oxidation proceeds, while substitution of trivalent Y by divalent Ca introduces holes into the CuO$_2$ planes by lengthening the effective O-(Y, Ca) bond according to route (3).\textsuperscript{2,3}

In order to clarify the distinctive features of the different doping routes and to study the efficiency of each route, e.g., in terms of hole production and the capability to increase $T_c$, the different doping routes should be facilitated separately in a fixed parent structure in wide doping ranges. The Cu$_{1.2}RCu_{2}O_{7-\delta}$ system is, in principle, a good model structure in which the joint effect of doping routes (1) and (2) achieved by oxygen doping can be compared to the structural changes associated with the Ca substitution, i.e., doping via route (3). However, when $A$ = Ba and $R$ = Y, single phase samples are obtained only up to $x<0.20$.\textsuperscript{11-13} Therefore, the Cu(Ba$_{0.8}$Sr$_{0.2}$)$_{2}(Yb_{1-x}Ca_{x})Cu_{2}O_{6+z}$ system, in which the solubility limit of Ca has been extended up to $x\approx0.4$,\textsuperscript{14} was selected for the present systematic investigation of the Ca substitution and O-doping effects. (Note that for the amount of excess oxygen, $z$ is used instead of “$1-\delta$.”) In the following, essentially single-phase samples with $0<z<1$ and $0\leq x\leq0.35$ are dealt with. All the samples have been characterized by chemical analysis for the oxygen stoichiometry and by means of x-ray diffraction (XRD), neutron powder diffraction (NPD), and superconducting quantum interference device (SQUID) measurements for the structural and superconducting properties. For discussing the effects of the different hole-doping routes, the BVS calculation approach presented in detail in Refs. 2 and 3 and described shortly in Sec. II of the present contribution is utilized.

\section*{II. EXPERIMENTAL}

\textbf{Synthesis and characterization of the samples}

Single-phase Cu(Ba$_{0.8}$Sr$_{0.2}$)$_{2}(Yb_{1-x}Ca_{x})Cu_{2}O_{6+z}$ powders with $x=0.0, 0.10, 0.20, 0.25$, and 0.35 were prepared from Yb$_2$O$_3$, BaCO$_3$, SrCO$_3$, CaCO$_3$, and CuO utilizing the technique developed and described in more detail in Ref. 14.

In brief, stoichiometric mixtures of the starting materials were several times calcined and sintered (as pelletized) in air at 900–940°C, and then oxidized in powder form by annealing in $O_2$ at 350–400°C for 48 h. Oxygen-deficient Ca-free Cu(Ba$_{0.8}$Sr$_{0.2}$)$_{2}(Yb_{1-x}Ca_{x})Cu_{2}O_{6+z}$ samples with varying oxygen content were obtained from the oxygenated Cu(Ba$_{0.8}$Sr$_{0.2}$)$_{2}(Yb_{1-x}Ca_{x})Cu_{2}O_{6+z}$ samples by post-annealing in an Ar atmosphere at the following temperatures: 380°C ($z\approx0.76)$, 480°C ($z\approx0.55)$, 550°C ($z\approx0.38)$, 750°C ($z\approx0.06$), 800°C ($z\approx0$). The Ca-substituted oxygen-deficient ($z\approx0$) Cu(Ba$_{0.8}$Sr$_{0.2}$)$_{2}(Yb_{1-x}Ca_{x})Cu_{2}O_{6+z}$ samples were obtained from the corresponding oxygenated powders by annealing in Ar at 800°C. In order to ensure the homogeneity of the oxygen content in the whole sample all these post-annealings were carried out in powder form in very small batches of $\approx150$ mg in a thermobalance (MAC Science TG/DTA 2000 S) to be able to carefully control the temperature and atmosphere during the oxygen depletion and \textit{in situ} detect the changes in the weight/oxygen stoichiometry. In the thermogravimetric (TG) annealings the heating and cooling rates were 2°C min$^{-1}$, and the isothermal heating period at the final temperatures was 6 h.

The level of excess oxygen in the samples was further confirmed by the coulometric Cu(+I)/Cu(+II) titration method\textsuperscript{15} using the experimental setup described in Ref. 16. In this method, the possible trivalent copper and/or peroxide-type oxygen, i.e., $\alpha$(CuO$^+$), is reduced by Cu(+I) when dissolving the sample [expressed by (Ba, Sr)$_{2}(Yb_{1-x}Ca_{x})(Cu(III))Cu_{2}O_{6+z}$] in HCl solution containing a known excess ($\gamma$) of monovalent copper ions [Eq. (2)]. On the other hand, if the sample itself contains monovalent copper, i.e., $\beta$(CuO$^-$), the Cu(+I) amount in the solution increases upon dissolving the sample [Eq. (3)]. Depending on the balance of $\alpha$(CuO$^+$) and $\beta$(CuO$^-$) in the sample and the initial amount of monovalent copper ($\gamma$) in the solution, different quantities of electricity ($Q=(\gamma-\alpha+\beta)F$; $F$ = Faraday constant) are detected when the coulometric back titration of the excess Cu(+I) is performed [Eq. (4)]. The average valence of copper ($V_{Cu}=2+\alpha-\beta$) and thus the oxygen excess ($z=0.5+0.5\alpha-0.5\beta-0.5x$) in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig1.png}
\caption{The three hole-doping routes $\Pi(1)$, $\Pi(2)$, and $\Pi(3)$ for the pyramidal CuO$_2$ planes in layered $M_{m}A_{2}Q_{n}^{-1}Cu_{m}O_{m+2+n+\delta}$ cuprates and in the Cu(1)(Ba, Sr)$_{2}(Yb, Ca,Cu)_{2}O_{6+z}$ system.}
\end{figure}
Purity and lattice parameters by an x-ray diffractometer. The synthesized samples were characterized for the phase signal. The neutron flux at the sample was approximately $10^6$ cm$^{-2}$ s$^{-1}$. The data were collected at 298 K. The neutron powder diffraction experiments were carried out at the R2 reactor in Studsvik, Sweden. The neutron-diffraction experiments were carried out supposing either the tetragonal $P4/mmm$ (No. 123) or the orthorhombic $Pmmm$ (No. 47) space group, and assuming a full occupancy for all the other atomic positions with the exception of the O(1) site. The cell parameters obtained from the XRD measurements were used as starting values for $a$, $b$, and $c$. Isotropic temperature factors were refined for all the atoms, except for O(1).

**Neutron-diffraction experiments**

Neutron-diffraction experiments were carried out at the R2 reactor in Studsvik, Sweden. The neutron powder diffractometer consisting of a double Cu (220) monochromator system ($\lambda = 1.470$ Å) and 35 $^3$He detectors spaced 4.00° apart from each other, was used for the precise structure determination by scanning in steps of 0.08° over the 2$\theta$ range of 4.00–139.92°. The powder samples (each 2.5–4.0 g) were placed in vanadium sample holders with a diameter of 6 mm, and the data were collected at 298 K. The neutron flux at the sample was approximately $10^6$ cm$^{-2}$ s$^{-1}$.

For the structure refinements a Rietveld program FULLPROF$^{17}$ was used. In Fig. 2, the unit cell of Cu(1)(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-x}$Ca$_x$)Cu$_2$O$_{6+z}$ is shown to illustrate the nomenclature of the atomic positions used in the present study. Since precise detection of very small gradual changes in the structure is crucial for the study, special care was taken to refine all data sets in a consistent way. The refinements were carried out supposing either the tetragonal $P4/mmm$ (No. 123) or the orthorhombic $Pmmm$ (No. 47) space group, and assuming a full occupancy for all the other atomic positions with the exception of the O(1) site. The cell parameters obtained from the XRD measurements were used as starting values for $a$, $b$, and $c$. Isotropic temperature factors were refined for all the atoms, except for O(1).

**Bond-valence-sum (BVS) calculations**

The bond-valence sums for the in-plane Cu(2), O(2), and O(3) atoms were calculated according to the scheme suggested by Brown and Altermatt, $^{4,5}$ i.e., first the bond valence $s_{ij}$ of each $i$-$j$ bond from an empirically determined parameter $R_0$ and from the experimental bond length $R_{ij}$ (in Å) by

$$s_{ij} = \exp[(R_0 - R_{ij})/0.37],$$

and then the bond-valence sum around a species $i$ by summing over the bond valences from all the nearest-neighboring counter ions, as

$$V_i = \sum_j s_{ij}.$$

The calculated $V_i$ sum was given as a positive value for the metal atoms and as a negative value for the oxygen atoms. The $R_0$ values $^{4,5}$ used in the present study are summarized in Table I. For the Cu-O bonds with copper in an intermediate valence state, the $R_0$ values were iterated in a self-consistent manner.

**TABLE I. Values for the parameter $R_0$ (Refs. 4 and 5) used in the present bond-valence calculations.**

<table>
<thead>
<tr>
<th>Bond</th>
<th>$R_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)-O</td>
<td>1.679</td>
</tr>
<tr>
<td>Cu(III)-O</td>
<td>1.730</td>
</tr>
<tr>
<td>Yb-O</td>
<td>1.965</td>
</tr>
<tr>
<td>Ca-O</td>
<td>1.967</td>
</tr>
<tr>
<td>Ba-O</td>
<td>2.285</td>
</tr>
<tr>
<td>Sr-O</td>
<td>2.118</td>
</tr>
</tbody>
</table>

Cu(1)(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-x}$Ca$_x$)Cu$_2$O$_{6+z}$ ($z = 0$) samples. The coulometric titration results are average values of at least five parallel analyses.

**TABLE II. Summary of the coulometric titration, NPD and SQUID results for the oxygen excess and $T_c$ values in the Cu(1)(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-x}$Ca$_x$)Cu$_2$O$_{6+z}$ ($z = 0$) samples.**

<table>
<thead>
<tr>
<th>Ca content $x$ nominal</th>
<th>Oxygen excess $z$, coulometry/NPD</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.03/0.225</td>
<td>&lt;5</td>
</tr>
<tr>
<td>0.10</td>
<td>0.00/0.104</td>
<td>&lt;5</td>
</tr>
<tr>
<td>0.20</td>
<td>0.00/0.166</td>
<td>&lt;5</td>
</tr>
<tr>
<td>0.25</td>
<td>-0.02/0.072</td>
<td>27</td>
</tr>
<tr>
<td>0.35</td>
<td>-0.08/0.075</td>
<td>43</td>
</tr>
</tbody>
</table>
TABLE III. Summary of the coulometric titration, NPD and SQUID results for the oxygen excess and $T_C$ values in the Cu(1)(Ba$_{0.8}$Sr$_{0.2}$)$_2$YbCu$_2$(O$_{6.5}$)$_2$ samples. The coulometric titration results are average values of at least five parallel analyses.

<table>
<thead>
<tr>
<th>Oxygen excess $z$, coulometry/NPD</th>
<th>$T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-0.03/0.225$</td>
<td>$&lt;5$</td>
</tr>
<tr>
<td>$0.06/0.201$</td>
<td>$&lt;5$</td>
</tr>
<tr>
<td>$0.38/0.248$</td>
<td>$&lt;5$</td>
</tr>
<tr>
<td>$0.55/0.350$</td>
<td>37</td>
</tr>
<tr>
<td>$0.76/0.817$</td>
<td>55</td>
</tr>
<tr>
<td>$0.96/0.999$</td>
<td>82</td>
</tr>
</tbody>
</table>

The net hole concentration $p$(CuO$_2$) in the CuO$_2$ planes was calculated as suggested by Tallon.

$$p$(CuO$_2$) = $V_{Cu(2)}$ + $V_{O(2)}$ + $V_{O(3)}$ + 2. (7)

In order to distinguish the three different doping routes defined in Refs. 2 and 3, and discussed in the previous section, contributions from the Cu(2)-O(4), O(2,3)-CuO$_2$, and O(2,3)-(Yb, Ca) bonds to the $p$(CuO$_2$) value were separated according to Eqs. (8)-(11) into the partial hole concentrations $\Pi$$^1$(1), $\Pi$$^1$(2), and $\Pi$$^1$(3):

$$\Pi$$1(1) = $\Pi$(CuO$_2$) = $\Pi$(1) + $\Pi$(2) + $\Pi$(3).

$$\Pi$$1(2) = $2s_{Cu(2)-O(4)}$.

$$\Pi$$1(3) = $2s_{O(2)-A}$ - $2s_{O(3)-A}$ + 1.

Since the constant ’’+2’’ in Eq. (7) is shared just empirically between $\Pi$(1), $\Pi$(2), and $\Pi$(3) [Eqs. (9)-(11)], it is obvious that the absolute values but only the changes in these parameters are meaningful. Therefore, the $\Pi$(1), $\Pi$(2), $\Pi$(3), and $p$(CuO$_2$) values were standardized against an extrapolated ’’zero sample’’ with $x=0$ and $z=0$ to get the corresponding $\Delta$$\Pi$(1), $\Delta$$\Pi$(2), $\Delta$$\Pi$(3), and $\Delta p$(CuO$_2$) values.

III. RESULTS

Judging from the x-ray-diffraction data, the synthesized Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-z}$Ca$_z$)CuO$_{6+z}$ samples were essentially of single-phase in the whole substitutional range of 0 $\leq x \leq 0.35$ and 0 $< z < 1$. Only in the XRD pattern of the Ca-free Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$YbCu$_2$O$_{6+z}$ samples were traces of

<table>
<thead>
<tr>
<th>$x$</th>
<th>0.10</th>
<th>0.20</th>
<th>0.25</th>
<th>0.35</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (in Å)</td>
<td>3.8314(2)</td>
<td>3.8272(2)</td>
<td>3.8320(2)</td>
<td>3.8334(2)</td>
</tr>
<tr>
<td>c (in Å)</td>
<td>11.745(1.0)</td>
<td>11.735(0.7)</td>
<td>11.736(0.8)</td>
<td>11.734(0.9)</td>
</tr>
<tr>
<td>Yb/Ca</td>
<td>0.90/0.10</td>
<td>0.80/0.20</td>
<td>0.75/0.25</td>
<td>0.65/0.35</td>
</tr>
<tr>
<td>Ba/Sr</td>
<td>0.57</td>
<td>0.50</td>
<td>0.39</td>
<td>0.26</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>0.198 45(40)</td>
<td>0.197 89(30)</td>
<td>0.197 19(30)</td>
<td>0.197 55(30)</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>0.57</td>
<td>0.50</td>
<td>0.39</td>
<td>0.26</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.104</td>
<td>0.166</td>
<td>0.072</td>
<td>0.075</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.380 61(30)</td>
<td>0.380 09(20)</td>
<td>0.378 88(20)</td>
<td>0.378 50(20)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.26</td>
<td>0.63</td>
<td>0.46</td>
<td>0.56</td>
</tr>
<tr>
<td>B (in Å$^2$)</td>
<td>1.00</td>
<td>1.13</td>
<td>1.06</td>
<td>1.19</td>
</tr>
<tr>
<td>B (in Å)</td>
<td>0.30</td>
<td>0.10</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>R$_p$ (%)</td>
<td>3.94</td>
<td>4.41</td>
<td>3.54</td>
<td>3.67</td>
</tr>
<tr>
<td>R$_pp$ (%)</td>
<td>5.37</td>
<td>6.29</td>
<td>4.84</td>
<td>5.06</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>6.80</td>
<td>7.10</td>
<td>4.72</td>
<td>5.74</td>
</tr>
</tbody>
</table>

TABLE IV. NPD refinement results for the Cu(1)(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-z}$Ca$_z$)CuO$_{6+z}$ samples (z=0) with x=0.10, 0.20, 0.25, and 0.35. Space group P4/mmm (No. 123): Yb/Ca at (0.5, 0.5, 0.5), Ba/Sr at (0.5, 0.5, z), Cu(1) at (0, 0, 0), Cu(2) at (0, 0, z), O(1) at (0, 0.5, 0), O(2) at (0.5, 0, z), and O(4) at (0, 0, z).
the Yb$_2$BaCu$_5$ impurity phase detected. Since the used FULLPROF Rietveld program allows simultaneous refinement of several phases, the neutron-diffraction data of the Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$YbCuO$_{6+z}$ samples were in preliminary refinements to check for the possible existence of the Yb$_2$BaCu$_5$ phase. However, the contribution from the Yb$_2$BaCu$_5$ structure was found to be less than 1%, and in the refinement to Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$YbCuO$_{6+z}$ samples treated as single-phase materials. On the other hand, the solubility limit of calcium in Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-x}$Ca$_x$)$_6$Cu$_3$O$_{6+z}$ is at $x = 0.35$–0.40, and in samples with $x > 0.35$ an increasing amount of BaCuO$_2$ impurity appears with increasing Ca concentration. However, the present $x = 0.35$ sample was totally free from BaCuO$_2$ within the detection limits of XRD and NPD.

According to the results of several parallel coulometric titrations, post-annealing of the Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-x}$Ca$_x$)$_6$Cu$_3$O$_{6+z}$ samples in Ar at 800 °C resulted in a slightly negative oxygen stoichiometry value $z$ for some of the samples with $0 < x < 0.35$ (Table II). The negative values can be explained by a presence of trace amounts of an impurity phase of monovalent copper (Cu$^+$). In order to obtain a reliable estimation for the oxygen excess $z$ from the neutron-diffraction data as well, the isotropic temperature factor of the O$_{4.73}$ was fixed according to the well-occupied oxygen sites of Yb$_2$BaCu$_5$ and Cu$_2$O. A negative value of $z$ was observed in the very low occupancy of the site in the oxygen-deficient samples annealed in Ar at 800 °C ended up to values of $0.35$–0.40, and in samples with $x = 0.27$–0.35 the value of $z$ was slightly higher than the coulometric titration results. In the following discussion of the efficiencies of the doping routes the $z$ values refined from NPD data are assumed.

As the last steps of the NPD refinements, the partial occupancies of Yb and Ca at the $R$ (i.e., $Q$) site and Ba and Sr at the $S$ site were allowed to vary from the nominal values.
However, since no improvements in the reliability factors were seen, the partial occupancies were fixed to the nominal values in the final refinements. The final results obtained from the refinements are shown in Tables IV and V. In general, the obtained $R_p$, $R_w$, and $\chi^2$ values are small, indicating a good reliability of the results.

In Ref. 14, the full series of Ca-substituted and O-doped $\text{Cu}_{\text{Ba}_{0.8}\text{Sr}_{0.2}}\text{Yb}_{1-\text{Ca}_x}\text{Cu}_2\text{O}_6$ samples were characterized for the superconducting properties. In brief, without Ca substitution (i.e., $x=0$) the $\text{Cu}_{\text{Ba}_{0.8}\text{Sr}_{0.2}}\text{YbCu}_2\text{O}_6$ phase becomes superconducting when $z$ exceeds 0.45. With increasing oxygen excess $z$, $T_c$ increases in the same two-step manner as that commonly known for the $\text{CuBa}_2\text{YCu}_2\text{O}_6$ system. On the other hand, in the samples with $z'=0$, superconductivity appears at $x'=0.20$.

IV. DISCUSSION

Concerning the three possible hole-doping routes shown in Fig. 1, the hole produced in $\text{Cu}_{\text{Ba}_{0.8}\text{Sr}_{0.2}}\text{Yb}_{1-\text{Ca}_x}\text{Cu}_2\text{O}_6$ by the excess oxygen are transferred into the CuO$_2$ plane for the most part via the gradual movements of the apical oxygen atoms towards the plane [route II(1)] and barium atoms away from the in-plane oxygen atoms [route II(2)], while doping with calcium substitution increases the hole concentration by lengthening the effective bond length, i.e., $R_{ij} - R_0$ in Eq. (5), from the in-plane oxygen to the (Yb,Ca) site [route II(3)]. The contributions of the different routes with increasing doping levels, i.e., the $\Delta\Pi$ vs $\Delta p$(CuO$_2$) curves, are illustrated in Figs. 3(a) and 3(b) for Ca substitution and O doping, respectively.

When considering the capability of the two different doping ways to generate holes into the CuO$_2$ plane, the hole concentration $p$(CuO$_2$) as established by the bond-valence sum calculation was found to increase less efficiently with O doping than with Ca substitution, as is seen in the $\Delta p$(CuO$_2$) vs $\Delta V_{\text{Cu},\text{nom}}$ correlations shown in Fig. 4. This is understand-
able, since the excess oxygen atoms are located in the empty site around the chain-site Cu atoms, and are thus supposed to oxidize the CuO$_2$ charge reservoir more efficiently. However, two less obvious observations were made from the data. Both of these observations are supported by our recent results obtained from O K-edge x-ray-absorption near-edge-structure measurements for the site-specific hole concentrations in the same sample powders. First, not only O doping but also Ca substitution leads to smaller than nominal $\Delta p$(CuO$_2$) values, i.e., $\Delta p$(CuO$_2$) $< \Delta V_{\text{Cu,nom}}$. This means that the Cu atoms in the charge-reservoir block are also partly oxidized with the Ca-to-Yb substitution. Since in the Ca-substituted samples practically no O atoms are present in the partly oxidized chain-site Cu atoms. The second observation is that, the $\Delta p$(CuO$_2$) values obtained for O-doped Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$YbCu$_2$O$_{6+\delta}$ samples are quite large as compared to values calculated in the present way from NPD data reported for CuBa$_2$YCu$_2$O$_{6+\delta}$ (Refs. 6 and 7) [\$\Delta p$(CuO$_2$) = 0.15–0.20 when $z$ increases from $\sim$0 to $\sim$1]. It is noted that our preliminary measurements of the Seebeck coefficient for the Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$YbCu$_2$O$_{6+\delta}$ samples indicated that with O doping overdoped state is reached at quite a low excess-oxygen value ($z$$\approx$0.8), in accordance with the observed high $\Delta p$(CuO$_2$) vs $V_{\text{Cu,nom}}$ rate.

When plotting the critical temperature as a function of the change in $p$(CuO$_2$), i.e., against $\Delta p$(CuO$_2$), it is seen (Fig. 5) that at a certain hole-concentration value higher $T_c$ values are obtained with calcium substitution. The two different hole-doping ways also seem to result in different $T_c$ vs (Cu-O bond length) relations [Fig. 6(a)]. In other words, increasing the hole concentration in the CuO$_2$ plane, i.e., the increase in $p$(CuO$_2$), shortens the in-plane Cu-O bond length as a general trend since antibonding electrons are removed, but the rate of shortening is different for the two hole-doping ways [Fig. 6(b)]. This suggests that other parameters besides the hole concentration have to be considered in terms of determining the superconducting properties. One possible additional parameter is the hole distribution in the in-plane Cu-O bond. That is, whether the holes have more Cu(3$d$) or O(2$p$) character. In that respect, note that the Cu(+III)-O(−II) and Cu(+II)-O(−I) bonds have different characteristic lengths, i.e., $R_0$[Cu(+III)-O(−II)]$\approx$1.73 and $R_0$[Cu(+II)-O(−I)]$\approx$1.59. Therefore, according to a bond-valence interpretation, within a certain amount of net holes being accommodated in the Cu-O bond, i.e., $s_{ij}$ is fixed, the shorter the $R_{ij}$ value is, the smaller the $R_0$ should be [cf. Eq. (5)], and consequently the more the holes would be on oxygen.

Another factor which also may affect the $T_c$ value is the buckling of the CuO$_2$ planes. From the (flatness of the CuO$_2$ plane) vs $\Delta \Pi$(1) data summarized for the both hole-doping ways in Fig. 7 it can be concluded that the more the holes are doped via $\Pi$(1) the stronger is the buckling of the CuO$_2$ planes. The fact that, at a certain $p$(CuO$_2$) value a lower $T_c$ value is obtained when the increase in $p$(CuO$_2$) is achieved via $\Pi$(1), is consistent with the observation of Jorgensen et al. that among the different cuprate phases the highest $T_c$ values can be assigned to the structures with the longest Cu-O$_{\text{app}}$ distances. An interesting question is, whether this interpretation can be extended to square-planar CuO$_2$ planes, e.g., the inner CuO$_2$ planes in the $M_{m}A_{n}$[$Q_{n-1}$Cu$_{3}$O$_{m+2n+2\delta}$] phases with $n$ $\approx$ 3, in which the Cu-O$_{\text{app}}$ distance can be thought to be infinite.

V. CONCLUSIONS

In the present study, the distinct calcium-substitution and oxygen-doping effects were established in the Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-x}$Ca$_x$)$_2$Cu$_2$O$_{6+\delta}$ system. The two different hole-doping ways were found to exhibit different $T_c$ vs $p$(CuO$_2$) and (Cu-O bond length) vs $p$(CuO$_2$) characteristics. Also, calcium substitution diminished the buckling of the CuO$_2$ plane while oxygen doping increased the buckling. In an $M_{m}A_{n}$[$Q_{n-1}$Cu$_{3}$O$_{m+2n+2\delta}$] system in general, the hole concentration $p$(CuO$_2$) in the (CuO$_2$) planes is determined as a delicate balance within the exact oxygen content $\delta$ and the nature (valence and size) of the cations $M$, $A$, and $Q$, and the results obtained for the Cu(Ba$_{0.8}$Sr$_{0.2}$)$_2$(Yb$_{1-x}$Ca$_x$)$_2$Cu$_2$O$_{6+\delta}$ system cannot be directly adapted to each different combination of $\delta$, $M$, $A$, and $Q$ even at a fixed $n$. However,
as a general conclusion the present study demonstrated that, not only the hole concentration but also other parameters such as the hole distribution among the Cu and O atoms and the degree of buckling are important in determining the superconducting properties of the CuO$_2$ planes. We believe that considering the distinct contributions of the different hole-doping routes is essential for understanding the superconducting cuprate materials and to be able to explain why, e.g., $T_c$ optimized varies from one cuprate phase to another. Also, in terms of improving the irreversibility field ($H_{irr}$) properties, possibility to control the hole distribution between the infinite-layer and charge-reservoir blocks by guiding the holes in the desired part of the layered cuprate structure would be most attractive.\textsuperscript{24,25}

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\begin{thebibliography}{99}
\bibitem{10} Based on the nomenclature given in Fig. 2 and in Eqs. (5)–(7):

$\rho(CuO_2) = V_{Cu(2)} + V_{O(2)} + V_{O(3)} + 2$

$= s_{Cu(2)-O(1)} + 2s_{Cu(2)-O(2)} + 2s_{Cu(2)-O(3)} - 2s_{Cu(1)-O(2)}$

$- 2s_{Cu(2)-O(3)} - 2s_{A-O(2)} - 2s_{A-O(3)}$

$- 2s_{Q-O(2)} - 2s_{Q-O(3)} + 2$

$= s_{Cu(2)-O(1)} - 2s_{A-O(2)} - 2s_{A-O(3)} - 2s_{Q-O(1)}$

$- 2s_{Q-O(3)} + 2.$

\bibitem{14} K. Fujinami, M. Karppinen, and H. Yamauchi, Physica C \textbf{300}, 17 (1998).
\bibitem{20} T. Nakane, K. Isawa, M. Karppinen, and H. Yamauchi (unpublished).
\end{thebibliography}