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The Effect of Ca Doping on the Structures of $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{14+x}$ Single Crystals[1]

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IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

The transition temperature of $YBa_2Cu_4O_8$ (124) is increased by about 10 K by doping with calcium, whereas Ca substitution in $Y_2Ba_4Cu_7O_{14+x}$ (247) has no effect on T_c. X-ray structure refinements of 13 $YBa_2Cu_4O_8$ and 12 $Y_2Ba_4Cu_7O_{14+x}$ Ca-doped and undoped single crystals have been performed in order to determine structural changes due to Ca doping. In 124 a major fraction of Ca replaces Y; in 247 Ba1 (single-chain 123 unit) and Y are substituted by Ca in the ratio 3:2. The changes of the charge distribution caused by the substitution of trivalent Y^{3+} by divalent Ca^{2+} and ion size effects lead to structural changes in Ca-doped crystals. One structural consequence of the replacement of the small Y ($r = 1.02$ Å) by the larger Ca ($r = 1.12$ Å) is the increase of the distance between the adjacent oxygen planes in the c direction. In 247 the 123 unit is compressed due to the substitution of Ba1 by the smaller Ca. Ca doping diminishes the buckling of the CuO_2 superconducting layers. The Ba–O sublattices in the double-chain 124 units of 247 and 124 are identical and change in the same way upon Ca doping; differences are observed in the Ba–Y sublattice.

INTRODUCTION

The double-chain compounds $Y_2Ba_4Cu_7O_{14+x}$ (247 or 123.5) and $YBa_2Cu_4O_8$ (124) were discovered (1) and synthesized in bulk form for the first time (2) under high oxygen pressure. The superconducting transition temperatures are $T_c = 80$ K for 124 and $T_c = 95$ K for 247. Miyatake *et al.* (3) succeeded in increasing the T_c of 124 to 90 K by a 10% Ca doping. However, Ca doping in 247 did not increase the transition temperature (4, 5). In 123 two effects occur with Ca doping: The oxygen-poor $YBa_2Cu_3O_6$ becomes superconducting with $T_c = 50$ K (6), and in the oxygen-rich $YBa_2Cu_3O_7$ the transition temperature decreases with increasing Ca content (4). Yttrium is substituted partially by calcium (6–8) in 123. For a long time, it has not been clear which atom sites are substituted in 124 and 247. The T_c enhancement was explained by the generation of additional holes in the CuO_2 plane, due to the partial replacement of the trivalent Y^{3+} by the divalent Ca^{2+} (3). This substitution seems geometrically preferred, because the ionic radius of Ca^{2+} ($r = 1.12$ Å) is much closer to that of Y^{3+} ($r = 1.019$ Å) than to that of Ba^{2+} ($r = 1.42$ Å) (9). On the other hand, NMR, NQR, and EELS measurements show no evidence for an increase of the in-plane hole concentration, and therefore favor the substitution of Ba^{2+} by Ca^{2+} (10–12). Powder diffraction experiments (13), however, indicated Y substitution. Recent X-ray single-crystal structure refinements confirmed this model and showed, in addition, a small partial substitution at the Ba site (14).

Not much is known about Ca-doped $Y_2Ba_4Cu_7O_{14+x}$. Buckley *et al.* (4) and Triscone *et al.* (5) showed that T_c does not increase with Ca doping and that the solubility limit of Ca in 247 is clearly lower than 10%. The latter authors suggested that Ca substitutes at the Ba1 site. Recent single-crystal structure investigations of 247 show that the structural parameters deviate significantly for Ca-doped crystals (15) and that Ba1 and Y are substituted by Ca in the ratio 3:2 (16).

Both $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{14+x}$ crystallize with space group *Ammm*. The crystal structure of 247 in the c direction contains alternating blocks with CuO single

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[1] Additional material for this paper (e.g., lists of structure factors, anisotropic thermal parameters) can be ordered, using numbers CSD 400079-400092 (247 crystals) and CSD 400273-400282 (124 crystals), the names of the authors, and the citation of the paper, from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen, FRG.

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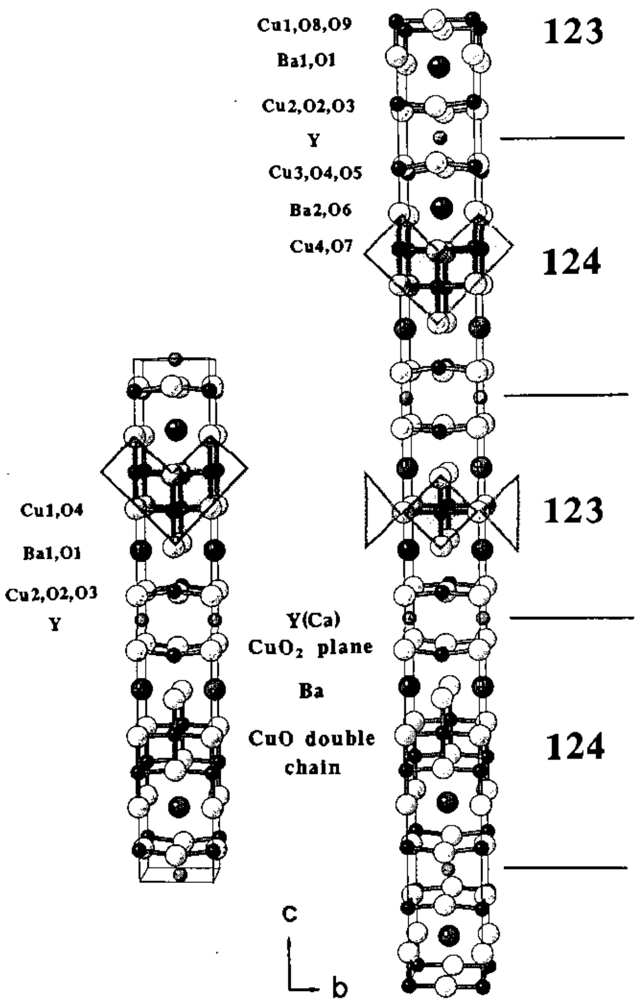

FIG. 1. SCHAKAL plots (22) of the $YBa_2Cu_4O_8$ (left) and $Y_2Ba_4Cu_7O_{14+x}$ (right) crystal structures. The shaded areas represent the single chains in the 123 units and the double chains in the 124 units.

chains (123 units) and with $(CuO)_2$ double chains (124 units), whereas 124 consists completely of double-chain blocks (Fig. 1). This gives an opportunity to study the influence of Ca doping on the same structural units in different crystal structures. In this paper, the X-ray structure refinements of both undoped and Ca-doped 124 and 247 single crystals are reviewed and new results are presented. We discuss the common features as well as the differences in the crystal structures of 124 and 247 due to Ca doping.

EXPERIMENTAL

Single crystals of the YBaCuO double-chain compounds have been grown using a high oxygen pressure flux method (17). Ceramic $YBa_2Cu_3O_{7-x}$ material was synthesized from $BaCO_3$, Y_2O_3, CuO, and CaO in the case of Ca-doped samples, using a standard routine. (Ca-)247 single crystals have been grown from a flux with composition (Ca-)123 : $BaCuO_2$: CuO = 1 : 1 : 3.5, using high oxygen pressures, $60 < pO_2 < 400$ bar, in alumina crucibles. The crystals had transition temperatures lower than 40 K, due to the unavoidable incorporation of impurities from the Al_2O_3 crucible walls at the Cu1 single-chain position in the 247 crystal structure (15). (Ca-)124 crystals have been grown from a flux with composition (Ca-)123 : $BaCuO_2$: CuO = 1 : 1 : 3.5 or 1 : 4 : 8 in the temperature range $1090 < T < 1100$°C at high oxygen partial pressures $700 < pO_2 < 1700$ bar. Undoped 124 crystals, grown in alumina crucibles, had transition temperatures of 70–73 K, also due to Al^{3+} doping. Ca-doped flux-grown 124 crystals showed $77 \leq T_c \leq 79$ K. These values are smaller than those of the corresponding ceramic samples. Substitution of the Al_2O_3 crucible material under high oxygen pressures is very difficult due to mechanical stability problems. In order to avoid Al contamination, we started crystal growth in ZrO_2 crucibles. A large fraction of the melt reacted with the crucible to $BaZrO_3$, but undoped 124 crystals with $T_c = 77.4$ K could be obtained. Ca-doped 124 crystals, grown in a ZrO_2 crucibles, had only small Ca content of less than 4.2%, and $T_c \cong 80$ K. The problem has been solved now with Y_2O_3 crucibles, but the crystals have not yet been structurally investigated.

The superconducting transition temperature T_c was determined from the magnetization, $M(T)$, measured with a BTI SQUID magnetometer. Due to the small sizes of the crystals, the data were taken in the zero-field cooled mode with magnetic field $H < 50$ Oe applied parallel to the c axis. T_c was defined as the onset of the superconducting transition.

The calcium content was checked qualitatively by EDAX on a JEOL JSM/840 scanning electron microscope. Quantitative results were calculated from the results of the structure refinements.

All crystals were black rectangular plates. The main face was always (001) and usually the b axis ran parallel to the longest edge of the crystal. The largest crystals grown had dimensions up to 6 × 1.5 × 0.1 mm^3, and the average dimensions of the crystals used for structure refinements were 0.26 × 0.36 × 0.03 mm^3. The crystals have all been examined for twinning, intergrowth, and superstructures with an X-ray precession camera. Suitable crystals were selected and mounted on a SIEMENS P4 four-circle single-crystal diffractometer. Reflections of the whole or in some cases of the half-Ewald sphere in the range $3 \leq 2\theta \leq 70°$ were collected at room temperature using Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) monochromated by a graphite crystal. Intensities were measured with the ω-2θ scan; in the case of overlap with neighbor reflections the ω scan was chosen. Numerical absorption corrections were applied, and the reflections were averaged in the Laue group *mmm*, corresponding to the space group *Ammm*. Internal $R_i < 0.05$ could be obtained. Reflections with $F \geq 1.5$–$2.5\ \sigma(F)$ were used for full-matrix least-squares refinements with weighted intensities, based on $\sigma(F)$. All calculations were performed with the SHELXTL program (18).

RESULTS

The initial models for the refinements of 124 and 247 were the crystal structures first determined by Bordet *et al.* (19, 20). All refinements converged well with an excellent final $1.65 < R < 4.68\%$ and $1.34 < R_w < 3.95\%$ for (Ca-)124 and $2.82 < R < 6.60\%$ and $2.01 < R_w < 4.79\%$ for (Ca-)247. The partial replacement of Y ($Z = 39$) and Ba ($Z = 56$) by Ca ($Z = 20$) reduces the electron density at that position. The electron density is not a parameter which can be refined directly. A Ca-substituted Ba or Y site, however, has a reduced occupancy factor for the heavy atom. In order to determine the substituted atom positions the Y and Ba occupancies, which usually are fixed at 100%, have been released and refined. Figures 2 and 3 show the refined occupation factors for the undoped and Ca-doped 124 and 247 crystals: they clearly indicate a substitution at the Y site for both 124 and 247, and in addition a partial replacement of Ba1 in the 123 unit of 247. For the structure refinements the occupancies of the undoped crystals have been fixed to 100%. The Ca content was determined by refining the Y/Ba : Ca ratio for each position and constraining the occupancy to 100%. The total Ca concentration is calculated from the sum of the Ca content at the Y site and twice the content at the Ba site in the case of 124, and by addition of the Ca content at the Y and Ba1 positions in the case of 247. In Ca-247 the ratio of Ca content at the Y and the Ba1 sites is 2 : 3. The oxygen nonstoichiometry x in $Y_2Ba_4Cu_7O_{14+x}$ is determined by the occupancies of the O8 and O9 positions in the 123 unit. In order to compare the oxygen content of the different crystals, the isotropic temperature factors of O8 and O9 have been fixed at 0.015 Å^2. The occupancies of Cu1 and O1 in the 123 unit have been released as well, because defects like Al, CO_3, and vacancies accumulate at the single-chain Cu1 position and reduce the electron density (15). All the Ca-247 crystals had Cu1 occupancies of 70–76%; for comparison, the data for undoped 247 in the tables and figures were taken from crystals with a similar level of defects at Cu1.

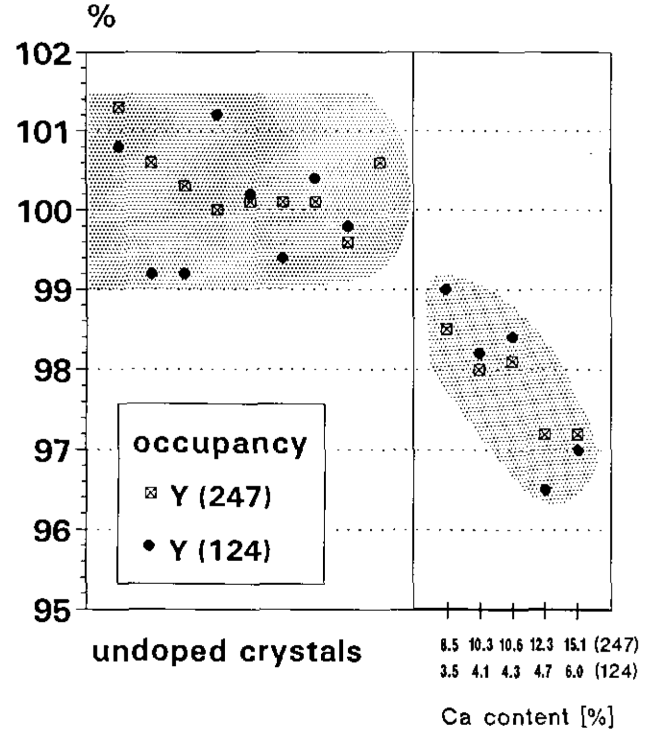

FIG. 2. Refined occupancies of the Y site of undoped and Ca-doped $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{14+x}$ single crystals. Occupancies lower than 100% indicate a Ca substitution. The refined Ca contents at the Y site are 2.1, 4.1, 3.1, 3.5, and 6.0% in 124, and 2.9, 4.3, 3.4, 5.8, and 5.3% in 247.

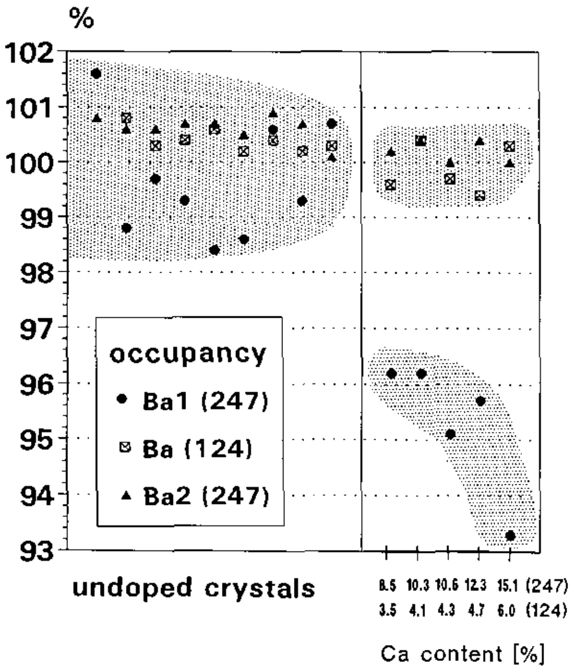

FIG. 3. Refined occupancies of the Ba site of undoped and Ca-doped $YBa_2Cu_4O_8$ and $Y_2Ba_4CuO_{14+x}$ single crystals. Occupancies lower than 100% indicate a Ca substitution. The refined Ca contents at the Ba site are 0.7, 0.0, 0.6, 0.6, and 0.0% in 124, and 5.6, 6.0, 7.2, 6.5, and 9.8% at Ba1 (123 unit) in 247.

The following structural changes can be observed upon Ca doping in 124:

(1) The distance Y(Ca)–O2,3 increases.

(2) The fractional z/c coordinate of Ba decreases, i.e., the distance Y–Ba.

(3) The distance Ba–O2,3 decreases.

(4) The distance Ba–O4 increases.

(5) The buckling—the distance Cu2–O2,3—decreases.

Ca-doping in 247 leads to the following effects:

(1) The distances Y–O2,3 and Y–O4,5 increase.

(2) All fractional z/c coordinates of the metal atoms decrease.

(3) The distances Ba1–O2,3, Ba1–O8,9, and Ba2–O4,5 decrease.

(4) The distance Ba2–O7 increases.

(5) The buckling—the distance Cu2–O2,3 and Cu3–O4,5—decreases.

(6) The size of the 123 unit decreases, and therefore (7) follows.

(7) The lattice constants b and c decrease, and consequently, the unit cell volume, too.

The final refined parameters of the undoped and Ca-doped 124 and 247 crystals are listed in Tables 1 and 2.

DISCUSSION

Figures 2 and 3 show the refined occupancies of the Y and the Ba sites which are proportional to the electron density at those positions. The values for the undoped crystals are 100 ± 1% for the Y site and between 100 and

TABLE 1
Crystal Data of $Y_{1-x}Ca_xBa_{2-2y}Ca_{2y}Cu_4O_8$ Single Crystals

T_c (K)	a (Å)	b (Å)	c (Å)	V (Å^3)	or	R (%)	R_w (%)	Ca(Y) (%)	Ca(Ba) (%)
69.2	3.8385(13)	3.8733(11)	27.200(8)	404.4(2)	4.50	1.65	1.86	0	0
70.0	3.8422(10)	3.8728(9)	27.242(6)	405.3(2)	3.97	1.93	1.93	0	0
72.8	3.8407(6)	3.8746(7)	27.234(6)	405.3(1)	4.39	2.77	2.07	0	0
73.1	3.8430(6)	3.8759(6)	27.247(5)	405.8(1)	4.26	2.55	2.06	0	0
77.4	3.8403(11)	3.8698(16)	27.248(5)	404.9(2)	3.83	1.73	1.34	0	0
78.0	3.8427(5)	3.8736(6)	27.258(4)	405.7(1)	4.00	2.05	2.05	0	0
78.5	3.8429(6)	3.8740(4)	27.250(3)	405.7(1)	4.03	3.31	2.32	0	0
78.5	3.8386(5)	3.8689(6)	27.201(5)	404.0(1)	3.93	2.26	1.77	0	0
80.0	3.8538(23)	3.8661(18)	27.302(17)	406.8(4)	1.59	2.42	2.11	2.1(10)	0.7(4)
79.6	3.8421(5)	3.8718(5)	27.256(4)	405.5(1)	3.85	4.68	3.95	4.1(17)	0
80.0	3.8445(8)	3.8721(8)	27.271(6)	406.0(2)	3.58	2.73	2.41	3.1(9)	0.6(4)
	3.8413(7)	3.8703(6)	27.228(5)	404.8(1)	3.76	2.57	2.29	3.5(12)	0.6(5)
82.0	3.8370(5)	3.8672(5)	27.224(4)	404.0(1)	3.92	2.87	2.23	6.0(13)	0

T_c (K)	Ba1 (z/c)	Cu1 (z/c)	Cu2 (z/c)	O1 (z/c)	O2 (z/c)	O3 (z/c)	O4 (z/c)
69.2	0.13485(1)	0.21295(2)	0.06154(2)	0.1454(1)	0.0524(1)	0.0524(1)	0.2179(1)
70.0	0.13484(1)	0.21294(3)	0.06152(2)	0.1453(1)	0.0524(1)	0.0523(1)	0.2181(1)
72.8	0.13484(1)	0.21298(2)	0.06157(2)	0.1453(1)	0.0521(2)	0.0524(2)	0.2180(2)
73.1	0.13483(2)	0.21297(3)	0.06156(2)	0.1453(2)	0.0526(2)	0.0522(2)	0.2184(2)
77.4	0.13484(1)	0.21298(2)	0.06156(2)	0.1453(1)	0.0526(1)	0.0523(1)	0.2181(1)
78.0	0.13484(1)	0.21298(2)	0.06152(2)	0.1452(1)	0.0523(1)	0.0522(1)	0.2180(1)
78.5	0.13483(2)	0.21298(4)	0.06156(4)	0.1454(3)	0.0524(3)	0.0525(3)	0.2179(3)
78.5	0.13485(1)	0.21299(2)	0.06155(2)	0.1453(1)	0.0525(2)	0.0523(2)	0.2182(2)
80.0	0.13480(1)	0.21299(3)	0.06153(3)	0.1455(2)	0.0524(2)	0.0523(2)	0.2181(2)
79.6	0.13480(3)	0.21293(6)	0.06157(6)	0.1454(3)	0.0529(4)	0.0523(3)	0.2181(4)
80.0	0.13477(1)	0.21294(3)	0.06155(3)	0.1454(2)	0.0525(2)	0.0525(2)	0.2181(2)
	0.13479(2)	0.21293(4)	0.06162(4)	0.1453(2)	0.0527(3)	0.0526(2)	0.2182(3)
82.0	0.13471(3)	0.21288(5)	0.06150(6)	0.1455(2)	0.0528(2)	0.0523(2)	0.2183(2)

Note. Variables shown are T_c; lattice constants a, b, c; volume v; orthorhombicity, or = $(b - a)/(b + a) \times 10^3$; R, R_w; Ca(Y) and Ca(Ba), Ca contents x and y at the Y and Ba sites, respectively; Ba1(z/c), etc., fractional z/c coordinates of the atoms. Standard deviations are given in parentheses. Structural data for 124 are space group *Ammm*; Y ($\frac{1}{2}$, $\frac{1}{2}$, 0); Ba ($\frac{1}{2}$, $\frac{1}{2}$, z); Cu1 (0, 0, z); Cu2 (0, 0, z); O1 (0, 0, z); O2 ($\frac{1}{2}$, 0, z); O3 (0, $\frac{1}{2}$, z); O4 (0, $\frac{1}{2}$, z).

TABLE 2
Crystal Data of $Y_{2-2x}Ca_{2x}Ba_{4-2y}Ca_{2y}Cu_7O_{14+z}$ Single Crystals

T_c (K)	a (Å)	b (Å)	c (Å)	V (Å^3)	or	R (%)	R_w (%)	Cu1 (occ)	O1 (occ)	Ca(Ba1) (%)	Ca(Y) (%)
<4	3.857(1)	3.877(1)	50.44(1)	754.4(2)	2.59	5.05	4.79	76(1)	96(3)	0	0
17.0	3.858(1)	3.876(1)	50.40(1)	754.5(3)	2.30	3.57	2.73	75(1)	85(2)	0	0
17.5	3.864(2)	3.872(2)	50.47(2)	755.0(6)	0.98	2.86	2.04	74(1)	96(2)	0	0
18.2	3.859(1)	3.880(1)	50.48(1)	755.8(3)	2.62	6.60	4.61	72(1)	100.0	0	0
22.4	3.857(1)	3.877(1)	50.44(1)	754.3(4)	2.61	3.40	2.49	73(1)	92(3)	0	0
23.8	3.858(1)	3.878(1)	50.37(1)	753.6(3)	2.48	2.82	2.01	76(1)	94(2)	0	0
40.0	3.851(1)	3.869(1)	50.29(2)	749.3(5)	2.33	5.73	5.73	77(1)	86(8)	0	0
24.0	3.857(1)	3.873(1)	50.35(1)	752.2(2)	2.08	3.14	2.35	73(1)	84(2)	5.6(3)	2.9(6)
30.6	3.854(1)	3.870(1)	50.33(1)	750.7(2)	2.05	3.48	2.84	75(1)	96(3)	6.0(4)	4.3(7)
29.0	3.855(1)	3.869(1)	50.37(1)	750.1(4)	1.83	4.67	4.07	76(1)	87(3)	7.2(4)	3.4(9)
29.7	3.850(1)	3.863(1)	50.18(1)	746.3(4)	1.65	3.58	2.87	73(1)	98(3)	6.5(3)	5.8(4)
22.9	3.853(1)	3.871(1)	50.33(1)	750.6(3)	2.42	6.71	4.98	70(1)	54(4)	9.8(8)	5.3(16)

T_c (K)	Ba1 (z/c)	Ba2 (z/c)	Y (z/c)	Cu2 (z/c)	Cu3 (z/c)	Cu4 (z/c)
<4	0.04353(1)	0.18802(1)	0.11552(2)	0.08305(3)	0.14844(3)	0.23005(3)
17.0	0.04309(1)	0.18795(1)	0.11538(1)	0.08283(2)	0.14839(2)	0.22998(2)
17.5	0.04304(1)	0.18796(1)	0.11538(1)	0.08283(2)	0.14836(2)	0.23002(2)
18.2	0.04326(2)	0.18801(2)	0.11545(4)	0.08303(5)	0.14834(4)	0.23004(4)
22.4	0.04306(1)	0.18797(1)	0.11542(2)	0.08284(2)	0.14841(2)	0.23000(2)
23.8	0.04290(1)	0.18790(1)	0.11527(1)	0.08266(1)	0.14828(1)	0.22998(1)
40.0	0.04311(2)	0.18798(1)	0.11539(2)	0.08294(3)	0.14827(3)	0.23004(3)
24.0	0.04300(1)	0.18782(1)	0.11521(1)	0.08256(2)	0.14819(2)	0.22996(2)
30.6	0.04264(1)	0.18773(1)	0.11503(2)	0.08227(2)	0.14808(2)	0.22991(2)
29.0	0.04262(1)	0.18772(1)	0.11494(2)	0.08218(3)	0.14801(2)	0.22992(3)
29.7	0.04262(1)	0.18768(1)	0.11503(2)	0.08223(2)	0.14806(2)	0.22996(2)
22.9	0.04281(2)	0.18776(2)	0.11513(2)	0.08245(4)	0.14818(3)	0.22985(3)

T_c (K)	O1 (z/c)	O2 (z/c)	O3 (z/c)	O4 (z/c)	O5 (z/c)	O6 (z/c)	O7 (z/c)	O8 (occ)	O9 (occ)
<4	0.0345(4)	0.0870(2)	0.0869(2)	0.1435(2)	0.1433(2)	0.1932(1)	0.2329(2)	36(3)	40(3)
17.0	0.0359(2)	0.0867(1)	0.0866(1)	0.1432(1)	0.1432(1)	0.1935(1)	0.2327(1)	38(2)	27(2)
17.5	0.0353(1)	0.0869(1)	0.0865(1)	0.1433(1)	0.1433(1)	0.1935(1)	0.2327(1)	39(2)	29(2)
18.2	0.0352(4)	0.0874(2)	0.0867(2)	0.1435(3)	0.1431(3)	0.1934(3)	0.2326(2)	25(5)	38(5)
22.4	0.0357(2)	0.0869(1)	0.0867(1)	0.1434(1)	0.1431(1)	0.1936(1)	0.2327(1)	43(3)	27(2)
23.8	0.0360(1)	0.0867(1)	0.0866(1)	0.1432(1)	0.1430(1)	0.1935(1)	0.2328(1)	36(1)	30(1)
40.0	0.0362(4)	0.0870(2)	0.0866(2)	0.1433(2)	0.1433(2)	0.1938(2)	0.2326(2)	24(4)	30(4)
24.0	0.0358(2)	0.0863(1)	0.0863(1)	0.1431(1)	0.1431(1)	0.1935(1)	0.2326(1)	40(2)	32(2)
30.6	0.0353(2)	0.0861(1)	0.0859(1)	0.1431(1)	0.1429(1)	0.1934(1)	0.2327(1)	40(2)	31(2)
29.0	0.0358(2)	0.0860(2)	0.0858(2)	0.1434(2)	0.1429(2)	0.1931(1)	0.2328(2)	42(3)	37(3)
29.7	0.0354(2)	0.0861(1)	0.0857(1)	0.1433(1)	0.1431(1)	0.1932(1)	0.2327(1)	33(3)	34(3)
22.9	0.0363(4)	0.0862(2)	0.0858(2)	0.1435(2)	0.1430(2)	0.1931(2)	0.2330(2)	50(5)	42(5)

Note. Variables shown are T_c; lattice constants a, b, c; volume v; orthorhombicity, or $= (b - a)/(b + a) \times 10^3$; R, R_w; Cu1(occ) and O1(occ), refined occupancies of the Cu1 and O1 sites (single-chain 123 unit); Ca(Ba1) and Ca(Y), contents x and y at the Y and Ba1 sites, respectively; Ba1 (z/c), etc., fractional z/c coordinates of the atoms; O8, O9, occupancies of the O8 and O9 positions. Standard deviations are given in parentheses. Structural data for 124 are space group *Ammm*; Ba1 ($\frac{1}{2}$, $\frac{1}{2}$, z); Ba2 ($\frac{1}{2}$, $\frac{1}{2}$, z); Y ($\frac{1}{2}$, $\frac{1}{2}$, z); Cu1 (0, 0, 0); Cu2 (0, 0, z); Cu3 (0, 0, z); Cu4 (0, 0, z); O1 (0, 0, z); O2 ($\frac{1}{2}$, 0, z); O3 (0, $\frac{1}{2}$, z); O3 (0, $\frac{1}{2}$, z); O4 ($\frac{1}{2}$, 0, z); O5 (0; $\frac{1}{2}$, z); O6 (0, 0, z); O7 (0, $\frac{1}{2}$, z); O8 (0, $\frac{1}{2}$, 0); O9 ($\frac{1}{2}$, 0, 0). The oxygen nonstoichiometry z is equal to the sum of the occupancies of O8 and O9.

101% for the Ba site in the double-chain units of 124 and 247, and scatter around 100 ± 1.5% for Ba1 in the 123 unit of 247. This is a hint that even in undoped crystals small amounts of impurity atoms, which prefer a cuboctahedral coordination, accumulate at the Ba1 position. This cuboctahedral coordination is only possible by both

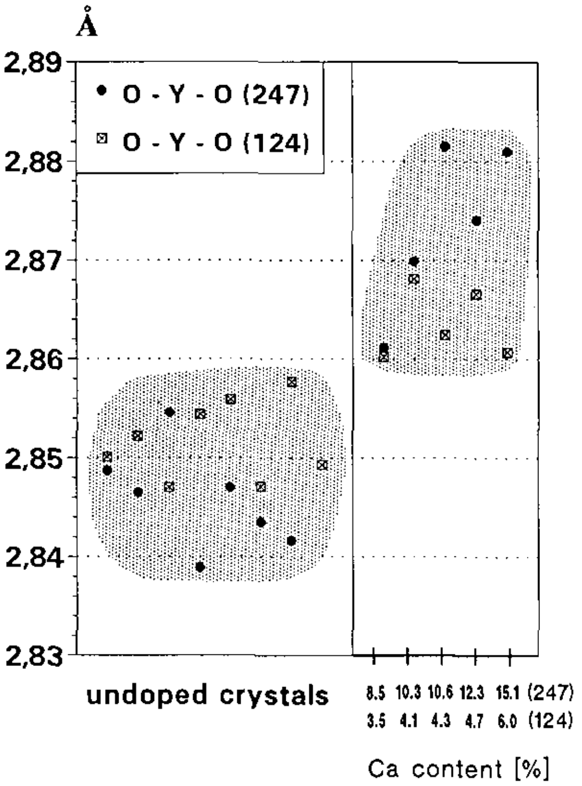

FIG. 4. Distance between oxygen layers adjacent to Y/Ca atoms, which is increased if yttrium is replaced by the larger calcium.

the O8 and the O9 position being occupied in the single-chain 123 unit and cannot be achieved in the 124 unit. The Ca-doped crystals show clearly a reduced electron density at the Y position for 124 and 247. By replacing yttrium in the YBaCuO compounds, Ca has the same eightfold coordination as in the other Ca-containing Tl-, Bi-, and Hg-based HT_c superconductors. Furthermore, Ba1 in the 123 unit of 247 is substituted by Ca. Thus Ca has the same coordination as in the classical perovskite $CaTiO_3$. *On average the Ca content at Ba1 is 50% higher than that* at the Y site. Surprisingly this is not the case in Ca-123, at which only yttrium is substituted (6, 8). The Ba sites in the double-chain units of the Ca-doped crystals have slightly lower electron densities than those in the undoped crystals. Therefore, to a small degree, a substitution of Ba in 124 is probable.

The most distinct effect of substituting yttrium by calcium is the widening of the distance between the adjacent oxygen layers. Figure 4 shows the distance between the average oxygen position of two adjacent CuO_2 planes, which increases by almost 1% in the Ca-doped crystals. This is due to the bigger size of Ca^{2+} (r = 1.12 Å), which replaces Y^{3+} (r = 1.019 Å) and forces the adjacent oxygen layers to separate. Figure 5 shows other effects in the Ba–Y–O sublattice. In 247 the large Ba1 atom in the 123 unit is partially substituted by the smaller Ca atom. Therefore, the distance to the adjacent oxygen layers O2,3 and O8,9 shrinks in the Ca-doped crystals. Ba1(Ca) does not move within its oxygen cage, and the distance to Y remains constant. In contrast, the unsubstituted Ba atom in the double-chain unit in 124 and 247 changes its relative position within the oxygen cage, which does not change its size. This is expressed by decreasing distances from Ba to the plane oxygen atoms and by increasing distances to the chain oxygen atoms. In 124 this effect is mainly due to a shift of Ba toward Y with increasing Ca content. In the double-chain unit of 247 the oxygen cage

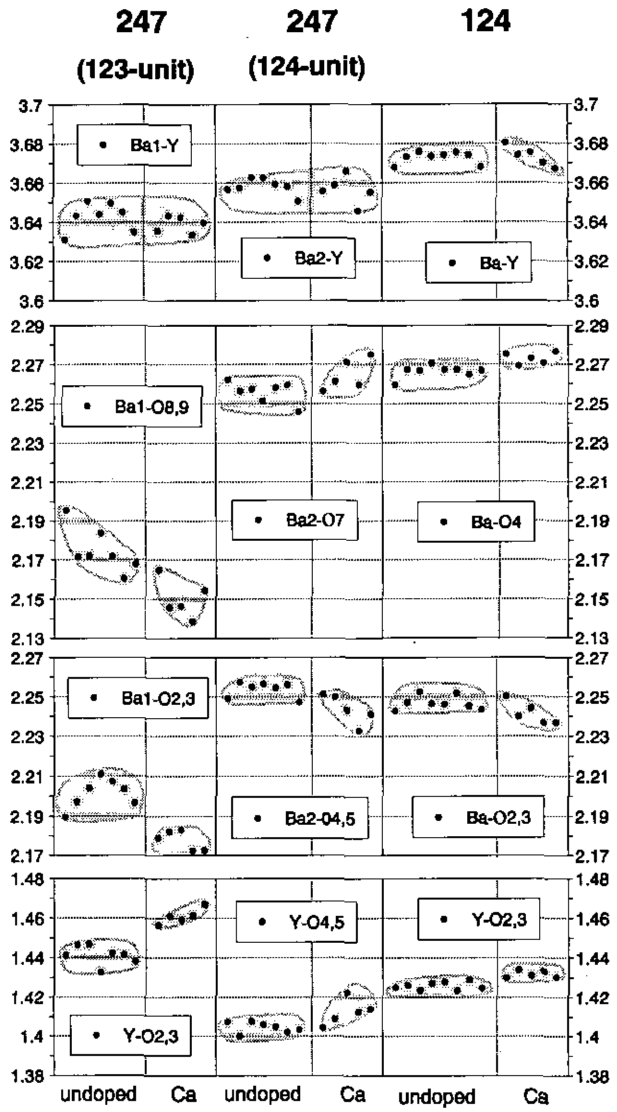

FIG. 5. Distances within the Ba–Y–O sublattice of 247 and 124. Each row shows the corresponding distances in the 123 unit of 247 and in the 124 units of 247 and 124 for the undoped and Ca-doped crystals (cf. Fig. 7). The values for the undoped crystals are plotted with increasing T_c, and those for the Ca-doped crystals with increasing Ca content.

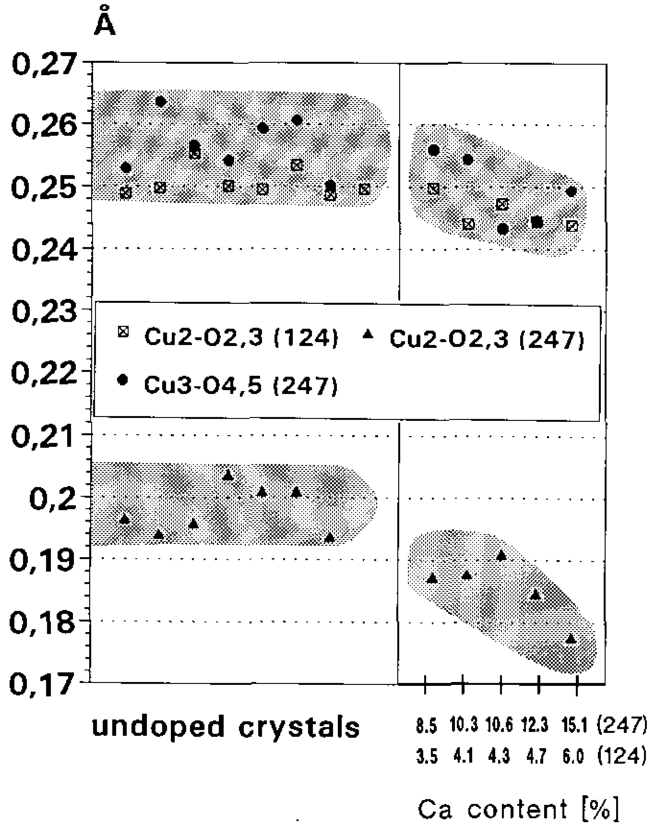

FIG. 6. Buckling of the CuO_2 plane is the distance between copper atoms and the averaged oxygen layer of the CuO_2 planes in the 123 unit (▲) and in the 124 units (☒, ●).

surrounding Ba2 moves away from Y(Ca). Again the distance between Ba and Y remains almost constant in undoped and Ca-doped crystals. The absolute value, however, is about 0.015 Å higher in 124 than in the 124 unit in 247.

The approach of Y and Ba in Ca-124 might be explained by a reduced electrostatic repulsion between the cations, because the charge at the Y^{3+} site is reduced by Ca^{2+} substitution. The electrostatic compensation in Ca-247 is probably done by the shift of the O2,3 layer toward Ba1(Ca). The decreasing charge at the Y site diminishes the attraction between the O2,3 layer and Y(Ca).

A further consequence of the mutual movement of the oxygen plane and the Ba atoms is the reduction of the buckling, i.e., the distance between Cu and the oxygen layer of the CuO_2 planes (Fig. 6). All the changes discussed here due to Ca doping are shown schematically in Fig. 7.

The influence of Ca doping on the lattice constants is only clearly visible in the case of the c parameter in 247. Figure 8 shows the size of the 123 and 124 units, limited by the oxygen layers of the CuO_2 planes. The enormous shrinking of the 123 blocks due to the substitution of Ba1 by the smaller Ca cannot be compensated for by the increasing distance between the 123 and 124 units due to the substitution of Y by the bigger Ca. Therefore, the *c* lattice constant in 247 decreases with Ca doping. The size of the 124 units in 247 and 124 is almost the same.

The effect of the structural changes on T_c is not yet completely clear. The flux-grown 247 single crystals have relatively low transition temperatures <40 K (15, 21). As we have shown recently (15), this is caused by the number of defects at the Cu1 position in the single-chain unit. The defects are mainly aluminum from the crucible or carbonate from the air or from the precursor material. The T_c enhancement by Ca doping in 124 is not caused by a higher hole concentration due to the substitution of Y^{3+} by Ca^{2+}. NQR, NMR, and EELS measurements (10–12) did not show evidence for an increase of the hole concentration in the CuO_2 planes of Ca-124. Therefore, it is possible (14) that the structural changes lead to a slightly modified band structure at the Fermi level E_f, and in this way become responsible for the increase of T_c.

CONCLUSIONS

X-ray structure refinements of undoped and Ca-doped $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{14+x}$ single crystals show remarkable differences but also common features:

(1) Calcium replaces partial yttrium in both 124 and 247. Ba1 in the single-chain 123 unit of 247 is substituted as well, whereas Ba in the 124 units is hardly affected.

(2) This substitution is responsible for the widening of oxygen layers adjacent to Y(Ca) and for the shrinking of the 123 unit. These effects are due to the different ion sizes of Y^{3+}, Ba^{2+}, and Ca^{2+}.

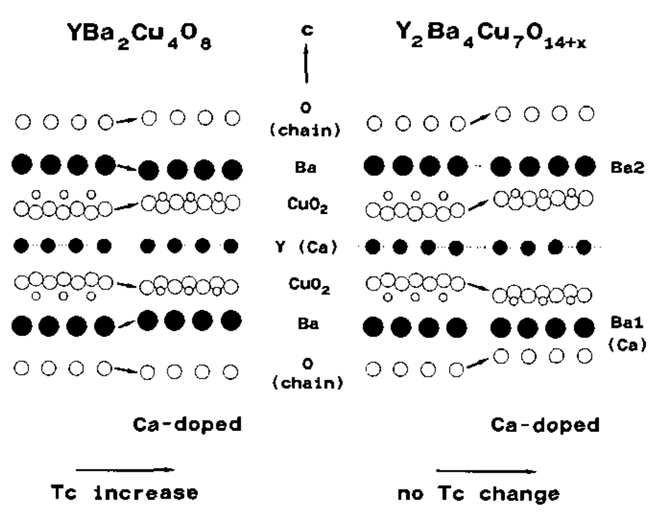

FIG. 7. Schematic view of parts of the crystal structures of undoped and Ca-doped 124 and 247. The shifts due to Ca doping are exaggerated.

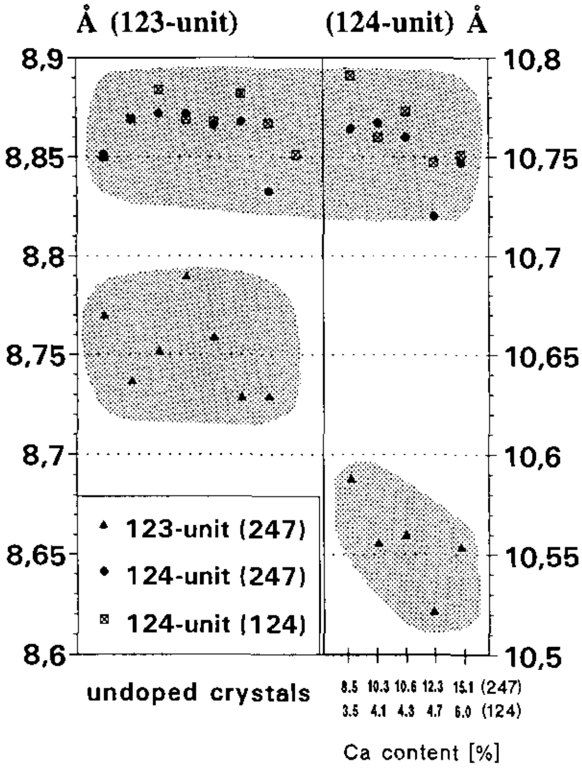

FIG. 8. Size of the 123 and 124 blocks in 247 and 124, limited by the CuO_2 layers. The 123 blocks in 247 are compressed due to the substitution of Ba1 by the smaller Ca.

(3) The different charge distribution in Ca-doped crystals leads to a changed electrostatic equilibrium. This causes an approach of Ba and the oxygen layers of the CuO_2 planes to one another, and, as a consequence, a reduction of the buckling in the CuO_2 planes.

(4) The Ba–O sublattices in the 124 units in 247 and 124 have the same dimensions and change in the same way upon Ca doping. The main differences are observed in the Ba–Y sublattices.

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