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Structural defects in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ and YBaCuCoO_5

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Résumé. — $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ et YBaCuCoO_5 ont été préparés à 900 °C. Des mailles unitaires tétraogonales ont été déterminées par microscopie électronique et diffraction des rayons X: $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ préparé à l'air, $a = 3,88$, $c = 11,66$ Å et YBaCuCoO_5 , $a = 3,87$ et $c = 7,56$ Å. Une variation de 11,61 à 11,73 Å pour c est causée par la non stoechiométrie de l'oxygène dans $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$. La taille de la maille unitaire de YBaCuCoO_5 restant constante semble confirmer une phase stoechiométrique. Des images et la diffraction électroniques montrent que la triple couche perovskite $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ contient des doubles couches de défauts tandis que la structure en double couche de YBaCuCoO_5 montre des triples couches de défauts. La microanalyse X révèle des défauts avec un rapport Ba/Y décroissant pour $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ et un rapport croissant pour YBaCuCoO_5 . Le rapport Co/Y reste pratiquement constant dans les 2 structures quand les zones fautées ou bien ordonnées sont comparées.

Abstract. — $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ and YBaCuCoO_5 were prepared at 900 °C. Tetragonal unit cells determined by electron and x-ray diffraction: $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ prepared in air, $a = 3.88$, $c = 11.66$ Å and YBaCuCoO_5 , $a = 3.87$, $c = 7.56$ Å. A variation in c of 11.61 to 11.73 Å was caused by the oxygen non-stoichiometry in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$. The unit cell size of YBaCuCoO_5 was constant, indicating a stoichiometric phase. Imaging and electron diffraction reveal that the triple-layer perovskite $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ contains double-layer defects, while the double-layer structure of YBaCuCoO_5 exhibits triple-layer defects. X-ray microanalysis indicated defects with a decreased Ba/Y ratio in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ and an increased Ba/Y ratio in YBaCuCoO_5 . The Co/Y ratios remained fairly constant in both compounds, when defect and well-ordered areas were compared.

1. Introduction.

Since the discovery that $\text{YBa}_2\text{Cu}_3\text{O}_7$ becomes superconducting when cooled in liquid nitrogen [1], a large number of physical and chemical properties of this new material has been studied. Some of this work has been concerned with the performance of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ as a catalyst in a variety of heterogeneous reactions, e.g. the oxidation of methanol [2], methane [3] and carbon monoxide [4]. The reaction $\text{CO} + \text{NO} \rightarrow 1/2 \text{N}_2 + \text{CO}_2$, which is of interest in connection with

catalytic exhaust converters, has also been reported to be catalyzed by $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [5]. We have investigated the catalytic ammoxidation of toluene at 400 °C over this compound and a reversible transition in product selectivity was observed for a catalyst with x close to zero [6, 7]. Benzotrile was selectively formed at low partial pressures of O_2 in the reactant stream, while CO_2 was the dominating product at high O_2 pressures.

A maximum of one copper atom per formula unit can be substituted by cobalt in samples heated at 920 °C in air [8]. The content of lattice oxygen in the crystals varies with temperature and partial pressure of O_2 in the surrounding atmosphere. The observed limits in composition were $0 < x < 1$ in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [9] and $0.7 < x < 1.3$ in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ [8]. The substitution of Co for Cu thus affects the number of oxide ions that becomes mobile at elevated temperatures. The phase YBaCuCoO_5 is probably isostructural with YBaCuFeO_5 [10] and the oxygen content of the former compound is more or less constant, regardless of the oxygen partial pressure in the environment. The crystal structures of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [11] $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ [12] and YBaCuFeO_5 [10] are illustrated in figure 1. All three are superstructures derived from cubic perovskite (ABO_3 , $a_p \approx 3.8 \text{ \AA}$) by ordering of cations and oxygen vacancies along c . $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ are triple-layer perovskites ($c \approx 3 a_p$), while YBaCuFeO_5 is a double-layer structure ($c \approx 2 a_p$).

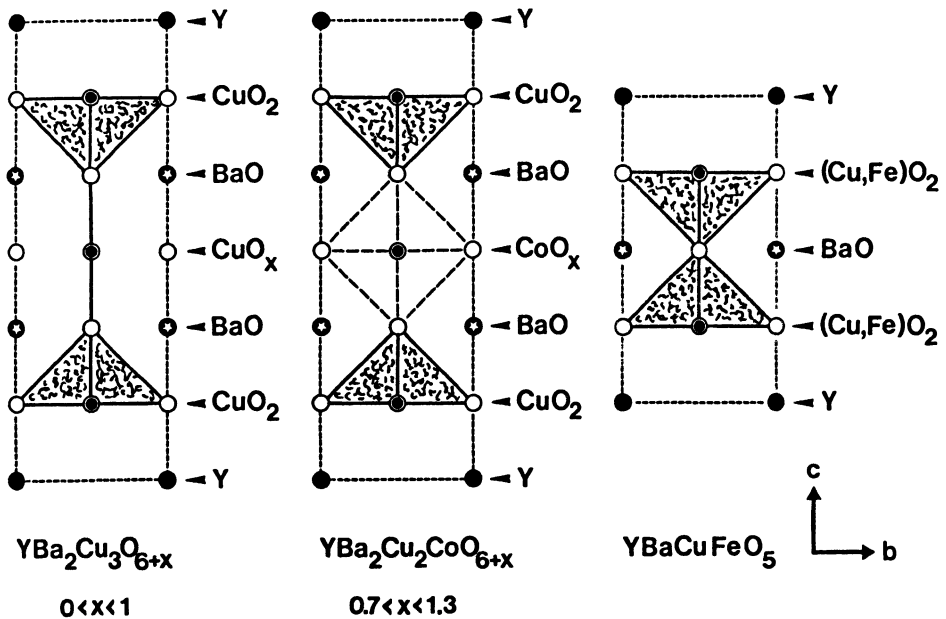


Fig. 1. — Idealized crystal structures of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ and YBaCuFeO_5 . Oxygen atoms are designated by rings.

We have recently investigated the ammoxidation of toluene, as a function of partial pressure of O_2 , over the perovskite phases $\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$, $\text{YBa}_2\text{Cu}_2\text{CoO}_{6.7}$ and $\text{YBaCuCoO}_{4.9}$ [13]. Systematic differences in the rate of formation of products were observed and these were related to the varying content of Cu and Co in the three phases. In this context, a preliminar characterization of the extended defects in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ and YBaCuCoO_5 was carried out.

2. Experimental.

2.1 SYNTHESIS. — Stoichiometric amounts of Y_2O_3 (Ventron, 99.99 %), BaCO_3 (Merck, > 99 %), CuO (> 99 %), Fe_2O_3 (Merck, > 99 %) and Co_3O_4 (Merck, p.a.) were ground with acetone in a mortar of porcelain. After drying, the mixture was ground a second time in an agate mortar. The powder was pressed into tablets under a pressure of 1 GPa and the tablets were placed in alumina boats, which were heated in air at 900 °C using a tube furnace. After a period of 17 to 18 hours the tablets were reground and new tablets were prepared. The second heating (17 - 18 h, 900 °C) was performed in a flow of O_2 , air or N_2 (Aga). The furnace was finally allowed to cool for a few hours until the temperature was below 200 °C. The gas was then turned off and the tablets were removed from the oven.

2.2 POWDER X-RAY DIFFRACTION. — The ceramic powders were ground together with silicon and Guinier patterns were recorded with a camera using $\text{CuK}_{\alpha 1}$ radiation. The camera constant was determined for each film and the cell parameters of the perovskite-type phase were obtained by least-squares refinement, see table I for results.

Table I. — *Tetragonal lattice parameters (Å) of phases prepared in various atmospheres.*

gas	YBaCuCoO_5		$\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$	
	<i>a</i>	<i>c</i>	<i>a</i>	<i>c</i>
O_2	3.8701(3)	7.554(1)	3.8873(3)	11.605(2)
air	3.8671(4)	7.557(1)	3.8827(5)	11.661(1)
N_2	3.8699(6)	7.555(2)	3.8842(3)	11.696(3)
pure N_2^*	3.8699(5)	7.558(2)	3.8835(3)	11.728(1)

* Aga plus, < 5 ppm O_2 and < 5 ppm H_2O . These samples were used in the ammoxidation of toluene [13].

2.3 IODOMETRIC TITRATION. — About 0.1 g of pulverized sample was weighed and then dissolved in a solution, consisting of 15 ml 10 % $\text{KI}(\text{aq.})$ and 10 ml $3.5 \text{ mol l}^{-1} \text{HCl}(\text{aq.})$, which was diluted by 15 ml of water before titrating with $0.05 \text{ mol l}^{-1} \text{Na}_2\text{S}_2\text{O}_3(\text{aq.})$. When the colour of I_2 started to fade, a few milliliters of freshly prepared starch solution was added in order to indicate the end-point of the titration. Titrations on the sample sintered in N_2 gave a composition of $\text{YBaCuCoO}_{4.9}$.

2.4 ELECTRON MICROSCOPY. — The phase purity of the prepared samples was checked by means of powder x-ray diffraction as well as scanning electron microscopy using a JSM-840A microscope, operated at 20 kV, and interfaced to a Link AN10000 system for energy dispersive analysis of X-rays. A phase of composition YBaCuCoO_x was observed as an impurity during a

series of experiments, which confirmed that up to 1/3 of the Cu atoms in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ can be substituted by Co.

Specimens for transmission electron microscopy were prepared by gently grinding samples of $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ and YBaCuCoO_5 in methanol and transferring the suspension to copper grids covered with holey carbon film. These grids were then investigated in a side-entry, high-resolution version of the JEM-2000FX microscope equipped with a high-angle x-ray detector (elevation 70°) connected to a Link AN10000 analysis system.

All work was performed using a double-tilt holder, which allowed the alignment of thin crystal edges with respect to the electron beam. Selected area diffraction patterns are shown in figure 2. Images were usually recorded at a magnification of 600 000 or 800 000 times, see figures 3 and 4.

2.5 MICROANALYSIS. — Chemical analysis of thin crystal edges, with or without planar defects, was undertaken with the help of an electron beam with an approximate diameter of 300 Å. Due to stray radiation from the grids only YL, BaL and CoK peaks could be quantified using the RTS2/FLS software routine. The $\text{CuK}\alpha$ peak was utilized for calibration of the energy scale. Spectra were typically collected during a life time of 300 s. Some microanalysis results are presented in table II.

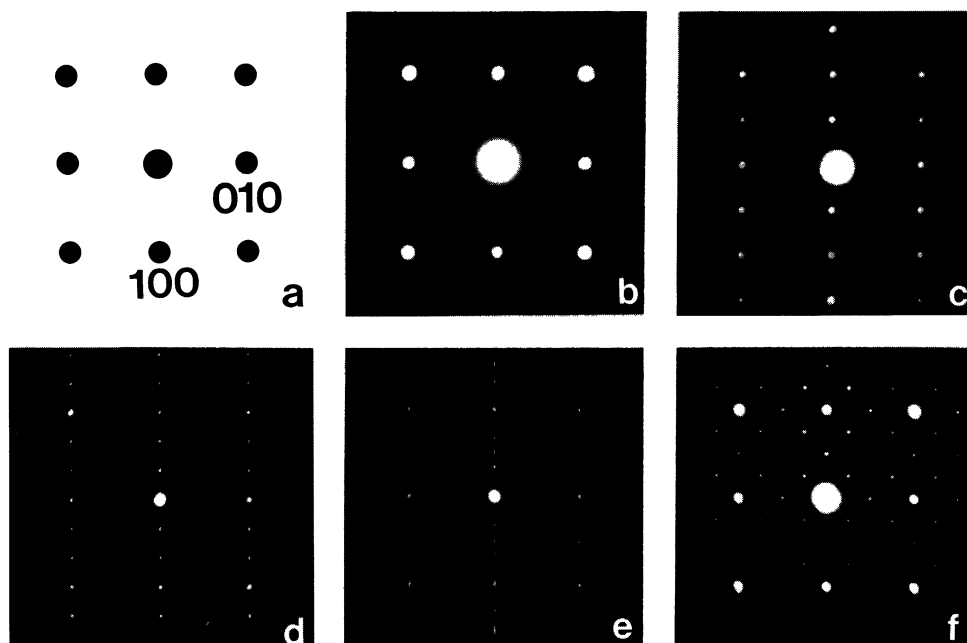


Fig. 2. — Electron diffraction patterns of phases prepared in air. a) Basic perovskite lattice. b) $hk0$ zone, YBaCuCoO_5 . c) $h0l$ zone, YBaCuCoO_5 . d) $h0l$ zone, $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$. e) Defect area, $h0l$ zone, $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$. f) Superlattice, YBaCuCoO_5 .

Table II. — Atomic ratios determined by energy dispersive analysis of X-rays generated with an electron probe of 300 Å diameter and the specimen areas shown in figure 4.

		Ba/Y	Co/Y
$\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$	ordered area	2.07	0.92
	defect area	1.54	1.28
YBaCuCoO_5	ordered area (ac)	1.05	1.05
	ordered area (ab)	1.09	1.08
	defect area	1.40	0.90

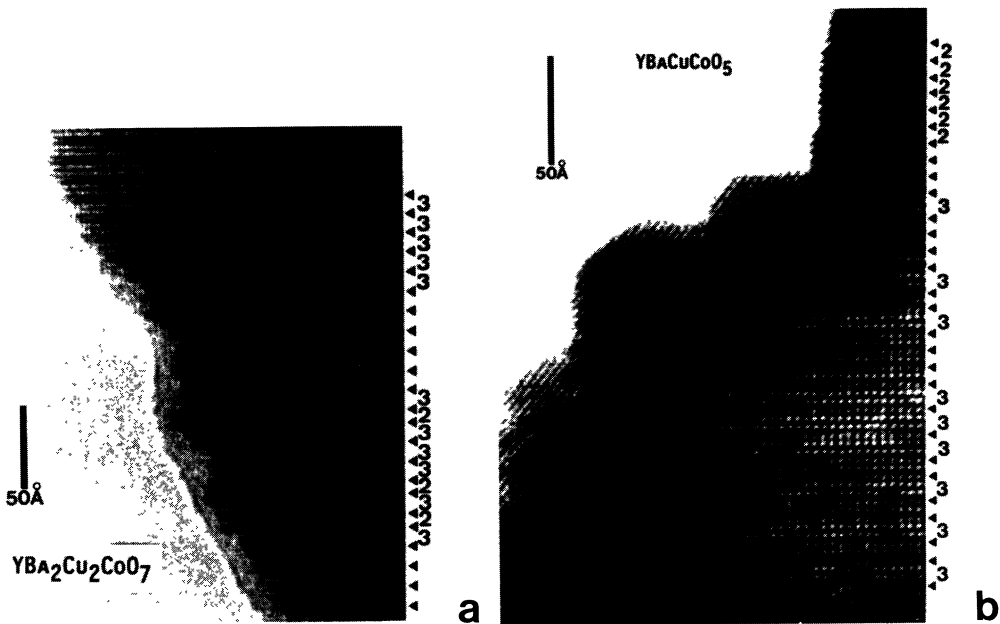


Fig. 3. — Lattice images of phases prepared in air. a) $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$, seen along [110]. b) YBaCuCoO_5 , seen along [010].

3. Discussion.

3.1 LATTICE OXYGEN DEFECTS. — The diffraction patterns in figure 2 illustrate the superlattice relationship between the two phases under investigation and cubic perovskite. The structure of YBaCuCoO_5 is assumed to be similar to that of YBaCuFeO_5 [10], since the composition and the unit cells are analogous. Guinier patterns recorded with the two phases also exhibit similar intensity distributions. The cell dimensions of YBaCuCoO_5 are insensitive to the method of preparation, cf. table I, and this indicates a constant oxygen content in the crystals. The composition was determined to be $\text{YBaCuCoO}_{4.9}$ and this suggests the presence of a somewhat greater number of oxide ion vacancies than in YBaCuFeO_5 , which was found to contain 5.02 oxygen atoms per unit

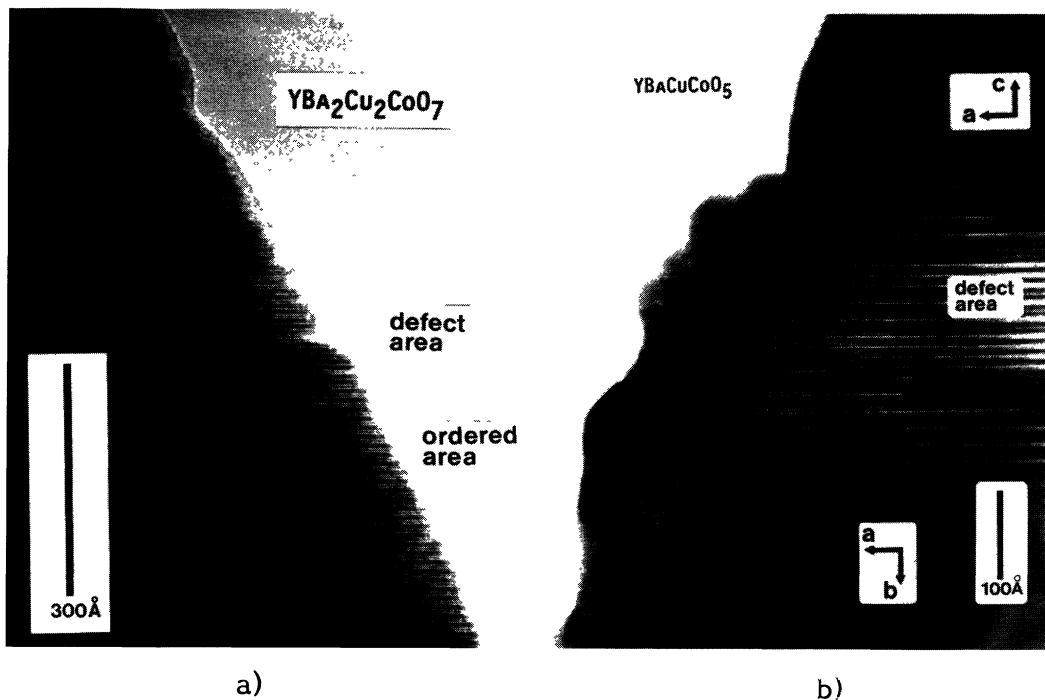


Fig. 4. — Defect areas used for microanalysis. a) $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ prepared in air, seen along $[110]$. b) YBaCuCoO_5 prepared in air, seen along $[010]$.

cell $[10]$. A $2\sqrt{2} a_p \times 2\sqrt{2} a_p$ superlattice has on a few occasions been observed in $\text{YBaCuCoO}_{4.9}$, see figure 2f. The same type of eight-fold supercell has been attributed to long range ordering of oxygen vacancies affecting one of the eight oxygen positions in the CuO_x plane of $\text{YBa}_2\text{Cu}_3\text{O}_{6.875}$ [14]. Further experiments are needed in order to clarify if the same type of argument is applicable to a phase of composition $\text{YBaCuCoO}_{4.875}$.

A substantial variation in oxygen stoichiometry was indicated by the variable c axis repeat in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$. It was found to be 11.61 \AA for a sample heated in O_2 and 11.73 \AA for one prepared in N_2 . The composition of the latter was $\text{YBa}_2\text{Cu}_2\text{CoO}_{6.7}$ [13]. Reference [12] reports $c = 11.64\text{ \AA}$ for a sample of composition $\text{YBa}_2\text{Cu}_2\text{CoO}_{7.16}$. The length of the c -axis in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ thus changes with the crystal content of oxygen, in a manner which is well documented [9] in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, where $c = 11.68\text{ \AA}$ when $x = 1$ and $c = 11.83\text{ \AA}$ when $x = 0$.

3.2 PLANAR DEFECTS. — Imaging and electron diffraction results reveal frequent defects on the (001) plane of both phases. The triple layer perovskite $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ contains double-layer defects, see figures 2e, 3a and 4a, while the double-layer structure YBaCuCoO_5 contains triple-layer defects, see figures 3b and 4b. In the lower part of figure 3b, an ordered intergrowth sequence 3, 2, 3, 2, 3 is seen. This raises the question if ordered intergrowth phases exist at intermediate compositions. A sample of nominal composition $\text{YBa}_{1.5}\text{Cu}_{1.5}\text{CoO}_6$ was prepared at 900°C in air, but the powder pattern showed the presence of mixture of $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ and YBaCuCoO_5 .

A comparison of the (001) defects in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ show that they are different. The (001) defects in the former phase corresponds to the extraction of two atomic layers parallel to (001) , see figure 1, while the planar defects in the latter phase correspond to

the intercalation of one or two extra atomic layers into the ordered structure. The layer sequence in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is Y, CuO_2 , BaO, CuO, BaO, CuO_2 and the simplest defect [15] corresponds to the insertion of an extra CuO layer at the central CuO layer in the repeating unit. Planar defects consisting of two extra atomic layers correspond to the insertion of either YO, CuO [16] or CuO, CuO [17], again at the CuO layer. The defect sequence obtained by insertion of a single CuO layer into the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure is also found in the ordered phase $\text{YBa}_2\text{Cu}_4\text{O}_8$. It is interesting to note that crystals of $\text{YBa}_2\text{Cu}_4\text{O}_8$ in their turn have been shown [18] to contain planar defects, which are intergrowing slabs of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure.

The most simple interpretation of the planar defects, observed in the two cobalt-containing phases, is that slabs of the YBaCuCoO_5 structure occur as defects in the $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ crystals and *vice versa*. In order to test this hypothesis we have tried to chemically analyse ordered and faulted areas in the crystals, figure 4 and table II. The results indicate defects with a decreased Ba/Y ratio in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ and an increased Ba/Y ratio in YBaCuCoO_5 . The Co/Y ratios, on the other hand, remain fairly constant when comparing defect and well-ordered areas.

If it is assumed that the cation composition of the double layer units is YBaCuCo and that of the triple layer units is $\text{YBa}_2\text{Cu}_2\text{Co}$, the composition of the analysed crystal area can be calculated from the corresponding lattice image. A square of $300 \times 300 \text{ \AA}$ was used as a first approximation of the area hit by the beam, in reality the electron probe is more or less circular. Inspection of the $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ image in figure 4a shows the defect zone to be composed of about 12 double layers and 18 triple layers, leading to the calculated atomic ratios $\text{Ba/Y} = 1.60$ and $\text{Co/Y} = 1.00$, while the ratios 2.00 and 1.00 are expected for the ordered matrix. The image of YBaCuCoO_5 , figure 4b, exhibits a faulted area with approximately 14 double layers and 16 triple layers giving the calculated ratios $\text{Ba/Y} = 1.53$ and $\text{Co/Y} = 1.00$. In this case, unit ratios are expected for ordered areas.

A comparison of the atomic ratios obtained by x-ray microanalysis and those predicted by the simple defect model shows reasonable agreement between them, though the microanalysis results need to be improved by the inclusion of copper among the quantified elements as well as optimization of experimental parameters. Close inspection of figure 4a reveals one defect of deviating image contrast, which suggests the presence of more than one type of planar defect in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+x}$ and that future work should include transmission electron microscopy at atomic resolution.

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