

A 4D Composite Description for $\text{Ca}_{0.82}(\text{Cu}_{0.65}\text{Co}_{0.35}\text{O}_2)$

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A misfit layer compound has been isolated in the Ca–Cu–Co–O system. It is constituted of two interpenetrating orthorhombic F sublattices exhibiting incommensurate periods along the [100] direction. The structure, determined by single-crystal X-ray diffraction using the 4D superspace formalism, is closely related to other oxide structures already depicted in the literature and corresponds to an alternate stacking along [001] of one-dimensional $[\text{MO}_2]$ chains ($\text{M} = \text{Cu}$ or Co) and of Ca layers. A displacive modulation allows a satisfying bonding scheme for the Ca–O intersystem distances.

Introduction

In recent years, constant attention has been focused onto mixed transition metal oxides involving copper in low-dimensional structural environments. This was already the case for the large and famous family of bi-dimensional high- T_c superconducting cuprate oxides¹ in which transport properties are directly related to the existence of CuO_2 planar sheets with copper in a corner sharing square-planar configuration. The related parent structure is the infinite-layer structure with planar CuO_2 sheets separated by Ca or Sr atoms.^{2,3} Another family closely related to the previous ones concerns the so-called spin-ladder misfit compounds,⁴ where the interpenetration of two sublattices is observed; the first one consists of zigzag chains of edge-sharing CuO_4 units, joined together by bridging O atoms to build ladders; the second one is built with independent edge-sharing CuO_4 chains. The same type of chains has also been observed in other systems: $\text{Ca}_{0.85}\text{CuO}_2$, NaCuO_2 , $\text{Sr}_{0.73}\text{CuO}_2$, and $\text{Ba}_2\text{Cu}_3\text{O}_5$.^{5–10} Another analogy can be found to layered cobalt oxides such as Na_xCoO_2 ^{11,12} or $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$.^{13–15}

In these different systems, structural incommensurabilities are often encountered: modulated Bi-based high- T_c superconductors, misfit spin-ladder compounds, and misfit lamellar calcium–cobalt oxides. The misfit character of these last structures is particularly interesting, since it allows mixed valence for the Cu or Co atoms, even without change in the oxygen stoichiometry. In the case of alkali earth copper oxides, such incommensurabilities are also observed from electron or X-ray diffraction,^{5,10,16–18} implying likely mixed valences in such compounds.

In the present paper, synthesis and characterization of the mixed cobalt–copper oxide $\text{Ca}_{0.82}(\text{Cu}_{0.65}\text{Co}_{0.35}\text{O}_2)$ are presented and the refinement of the actual composite structure is described using the 4D formalism for incommensurate structures. Very recently, a 4D structural description of the $\text{Ca}_{0.825}\text{CuO}_2$ was given,⁶ using powder diffraction data. The present study confirms the adequateness of the description for a new mixed Cu–Co compound in a new orthorhombic space group.

Experimental Section

Synthesis. $\text{Ca}_{0.82}(\text{Cu}_{0.65}\text{Co}_{0.35}\text{O}_2)$ single crystals were prepared in two stages. A precursor was first synthesized using CaO , Co_3O_4 , and CuO . The reactants were weighted according to the above formula. The mixture was pressed into bars and heated at 1000 °C for 24 h. A powder was obtained with the chemical formula $\text{Ca}_{0.82}(\text{Cu}_{0.65}\text{Co}_{0.35}\text{O}_2)$. Second, K_2CO_3 was added in the ratio K:Ca = 3. The mixture was then mingled in 100 mL of deionized water to increase the homogeneity. The obtained blend was placed in a crucible and heated at 150 °C for 24 h. The preparation was then heated to 1000 °C, using a 100 °C/h gradient, kept at this temperature for 100 h, and then slowly cooled at 10 °C/h. Single crystals, platelike shaped, were mechanically isolated.

X-ray Diffraction. A preliminary study, to check crystal quality and to characterize the symmetry, was carried out using a Weissenberg camera, showing the composite character of the crystals. They exhibit two orthorhombic sublattices of different parameters along the *a* axis ($a_1 = 2.80 \text{ \AA}$ and $a_2 = 3.39 \text{ \AA}$) and the same parameters along the *b* and *c* axes ($b_1 =$

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Table 1. Details of Data Collection

chemical formula	$\text{Ca}_{0.82}(\text{Cu}_{0.65}\text{Co}_{0.35}\text{O}_2)$
crystal size (mm)	$0.0250 \times 0.0875 \times 0.3125$
crystal system	orthorhombic
cell parameters (Å) ($T = 294$ K)	
first subsystem	$a_1 = 2.801(1)$ $b_1 = 6.290(3)$ $c_1 = 10.573(5)$
second subsystem	$a_2 = 3.391(1)$ $b_2 = 6.290(3)$ $c_2 = 10.573(5)$
superspace group	
first sublattice	$Fmmmm(\alpha 11)0ss$
second sublattice	$Fmmmm(\alpha^{-1}11)0ss$ $0.8260(4)$
$\alpha = a_1/a_2$	4
Z	4
ρ (g·cm ⁻³), μ (mm ⁻¹)	4.541, 12.752
wavelength (Å)	0.71073
$\theta_{\max}(\circ)$, ($\sin(\theta/\lambda)_{\max}$)	45, 0.995
internal consistency factor R_{int}	
subsystem 1 (main reflctns)	1.15
subsystem 2 (main reflctns)	2.36
extremal transmission factors	
T_{\min}	0.3577
T_{\max}	0.7284
no. of params to be refined	34
no. of params actually refined	26
weighting scheme	$1/\sigma^2$
residual	
$\Delta\rho_{\min}$ (e/Å ³)	-1.85
$\Delta\rho_{\max}$ (e/Å ³)	2.43
no. of reflections (obsd/measd)	
$HKLM$	479/591
corresponding reliability factor R/R_w (%)	2.36/2.98
$HKLM$ (H and/or $M = 0$)	442/468
corresponding reliability factor R/R_w (%)	2.15/2.61
$HKLM$ (H or $M = \pm 1$)	19/60
corresponding reliability factor R/R_w (%)	5.51/4.98
$HKLM$ (H or $M = \pm 2$)	18/63
corresponding reliability factor R/R_w (%)	14.21/16.05

$b_2 = 6.29$ Å, $c_1 = c_2 = 10.57$ Å). Moreover, the diffraction pattern displays some weak reflections along the [100]* direction, indexed as satellite reflections. The chemical formula $\text{Ca}_{0.82}(\text{Cu}_{0.65}\text{Co}_{0.35}\text{O}_2)$ of these crystals was established from EDS analysis with Ca as reference (Ca, 1; Cu, 0.80(2); Co, 0.42-(2)). The corresponding [Ca]/([Cu] + [Co]) ratio is equal to the $\alpha = a_1/a_2$ ratio, within the experimental uncertainties.

The diffracted intensities were collected on an Enraf-Nonius CAD-4 diffractometer, using monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). The cell parameters of each subsystem were refined from 25 independent reflections, and the main reflections of each sublattice were measured separately. A data collection of satellite reflections of both subsystems (first and second orders) was also performed, but, owing to their weak intensities, few of them could be detected and measured. Corrections for Lorentz and polarization effects were applied to the data sets. No significant intensity variation was observed during the acquisition for the three standard reflections chosen for each recording. An absorption correction, based on crystal morphology and using a Gaussian integration method, was applied to reflection intensities with the program Jana2000.¹⁹ Crystal data and experimental conditions are given in Table 1.

Symmetry

The two orthorhombic sublattices of the composite structure are F centered. The a parameters of both sublattices exhibit an incommensurate α ratio ($\alpha = a_1/a_2 = 0.8260(4)$). The use of the four-dimensional formalism (4D) for aperiodic crystals²⁰ allows us to index all the reflections and to obtain a global symmetry for the two sublattices. Considering the main reflections of the second sublattice as satellite reflections of the M th order of the $0kl$ reflections of the first subsystem,²¹ the diffraction vector can be written as $\mathbf{s}^* = h\mathbf{a}_1^* + k\mathbf{b}_1^* + l\mathbf{c}_1^* + M\mathbf{q}_1^*$, where $\mathbf{q}_1^* = a_2^* + b_2^* + c_2^* = \alpha\mathbf{a}_1^* + b_1^* + c_1^*$ is the modulation vector associated with the first subsystem. This can also be written as $\mathbf{s}^* = H\mathbf{a}_1^* + K\mathbf{b}_1^* + L\mathbf{c}_1^* + M\mathbf{q}_1^{*\text{irr}}$ where $\mathbf{q}_1^{*\text{irr}} = \alpha\mathbf{a}_1^*$ with $H = h$, $K = k + M$, and $L = l + M$. The reflections $HKLM$, $M = 0$ (respectively, $H = 0$), are then considered as main reflections of the first subsystem (respective of the second one). The other reflections $HKLM$, H and $M \neq 0$, are satellite reflections and are the consequence of the modulated interaction between the two sublattices. Different reflection conditions are observed: $HKLM$, $H + K + M = 2n$, $H + L + M = 2n$, and $K + L = 2n$, involving $(\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2})$, and $(0, \frac{1}{2}, \frac{1}{2}, 0)$ centering in 4D space. Moreover, only the reflections $M = 2n$ can be observed for the reflections $(H0LM)$ and $(HK0M)$, suggesting two glide mirrors (\mathbf{g}). The superspace group (SSG), associated with these conditions, is $Fmmmm(\alpha 11)0ss$ or $F2mm(\alpha 11)0ss$ for the subsystem $\nu = 1$ and $Fmmmm(\alpha^{-1}11)0ss$ or $F2mm(\alpha^{-1}11)0ss$ for the subsystem $\nu = 2$.

Refinement

The refinement was carried out with the structure factors, using the four-dimensional formalism²⁰ and the program JANA2000.¹⁹ Patterson maps were calculated without the $0KL0$ main reflections, to determine a structural model for each subsystem. For the first subsystem, the Fourier maps are compatible with an occupation of a cationic site at the cell origin by both copper and cobalt elements. The use of X-ray diffraction does not allow us to distinguish between the copper and cobalt atoms. A mixed occupation was fixed with a ratio corresponding to the EDS results. The relative position of the two component structures was determined using the $(0KL0)$ common reflections. Anisotropic atomic displacement parameters (ADPs)²² were used for each atom.

A displacive modulation was assumed and refined for each atom. The components of the displacement vector \mathbf{U}_ν^μ of the μ th atom in the subsystem ν were written as Fourier series limited to the first and second harmonics.

$$U_{\nu,i}^\mu(\bar{x}_{4,\nu}^\mu) = \sum_{n=1}^2 A_{\nu,i,n}^\mu \sin 2\pi n \bar{x}_{4,\nu}^\mu + B_{\nu,i,n}^\mu \cos 2\pi n \bar{x}_{4,\nu}^\mu$$

$$\nu = 1, 2 \quad i = 1, 2, 3$$

$$\bar{x}_{4,\nu}^\mu = q_\nu^{*\text{irr}} \cdot (r_{0,\nu}^\mu + \mathbf{p}_\nu) = q_\nu^{*\text{irr}} \cdot r_{0,\nu}^\mu + t_\nu$$

where $r_{0,\nu}^\mu$ is the average position of the atom μ in the origin of the unit cell ($a_{0,\nu}$, $b_{0,\nu}$, $c_{0,\nu}$) and \mathbf{p}_ν a lattice vector of the subsystem ν . All terms not fixed by the 4D

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Table 2. Structural Parameters

atom	<i>P</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cu	0.65 ^a	0	0	0						
Co	0.35 ^a	0	0	0	0.0047(1)	0.0091(2)	0.0043(1)	0 ^b	0 ^b	0 ^b
O	1	1/2	0	-0.1198(2)	0.0110(7)	0.028(2)	0.0043(5)	0 ^b	0 ^b	0 ^b
					Subsystem 1					
Ca	1	0	1/4	1/4	0.0231(6)	0.0060(2)	0.0070(2)	0 ^b	0 ^b	0 ^b
					Subsystem 2					

^a Fixed from (EDS) result. ^b Fixed by symmetry.**Table 3. Fourier Terms of the Displacive and (ADPs) Modulations**

atoms	harmonic	<i>x</i>	<i>y</i>	<i>z</i>
Cu/Co	sin(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	cos(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	sin(4 π \bar{x}_4)	0.0020(3)	0 ^a	0 ^a
	cos(4 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
O	sin(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	cos(2 π \bar{x}_4)	0 ^a	0.0670(6)	0 ^a
	sin(4 π \bar{x}_4)	-0.030(1)	0 ^a	0 ^a
	cos(4 π \bar{x}_4)	0 ^a	0 ^a	-0.0032(3)
Ca	sin(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	cos(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	sin(4 π \bar{x}_4)	-0.013(1)	0 ^a	0 ^a
	cos(4 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
atoms	harmonic	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃
Cu/Co	sin(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	cos(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	sin(4 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	cos(4 π \bar{x}_4)	-0.010(2)	0 ^b	0 ^a
O	sin(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	cos(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	sin(4 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	cos(4 π \bar{x}_4)	-0.009(2)	-0.026(2)	0 ^b
Ca	sin(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	cos(2 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	sin(4 π \bar{x}_4)	0 ^a	0 ^a	0 ^a
	cos(4 π \bar{x}_4)	-0.014(2)	0 ^b	0 ^a
atoms	harmonic	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃

^a Fixed by symmetry. ^b Fixed because not significant within their standard deviations.

symmetry (Table 3) were refined. Only the significant values, larger than 3 times the standard deviations, were considered again in a second refinement. The modulation improved significantly the reliability *R* factors, which decreased from 6.51% to 2.15%. The Cu and Co atomic positions, modulation functions and ADP parameters were constrained to be the same.

As α is irrational, all the t_v values in the [0,1] interval are physically significant.

The centro- and noncentrosymmetric SSG were both considered in the refinement, but the use of the $F2mm(\alpha 11)0ss$ SSG does not lead to any convincing improvement. The refinement parameters are given in Table 2 and Table 3.

Discussion

Nonmodulated Composite Structure. The nonmodulated composite structure is obtained by neglecting the modulation scheme. This structure, refined from the main reflections, is related to a structural model first proposed by Babu and Greaves.⁵ The first subsystem ($a_1 = 2.80$ Å) consists of [100] chains of edge-sharing MO_4 ($M = Cu$ or Co) square units and the second ($a_2 = 3.39$ Å) is formed from (001) Ca planes (Figure 1). Such a rare square coplanar coordination for the Co atom was already described.^{23,24} The composition $Ca_{0.82}MO_2$, established from the EDS analysis, can be explained from

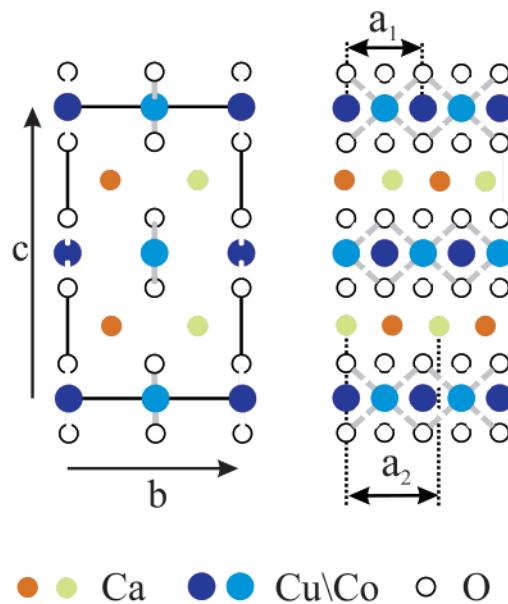


Figure 1. Composite structure of $Ca_{0.82}(Cu_{0.65}Co_{0.35}O_2)$, neglecting the modulation, projected (a) along [100] and (b) along [010] ($-0.10 \leq y \leq 0.35$).

the total occupation of the Ca sites in the second sublattice. The refinement of the Ca occupancy in the second sublattice led to a total occupation of the site and confirmed the EDS analysis. As a matter of fact,

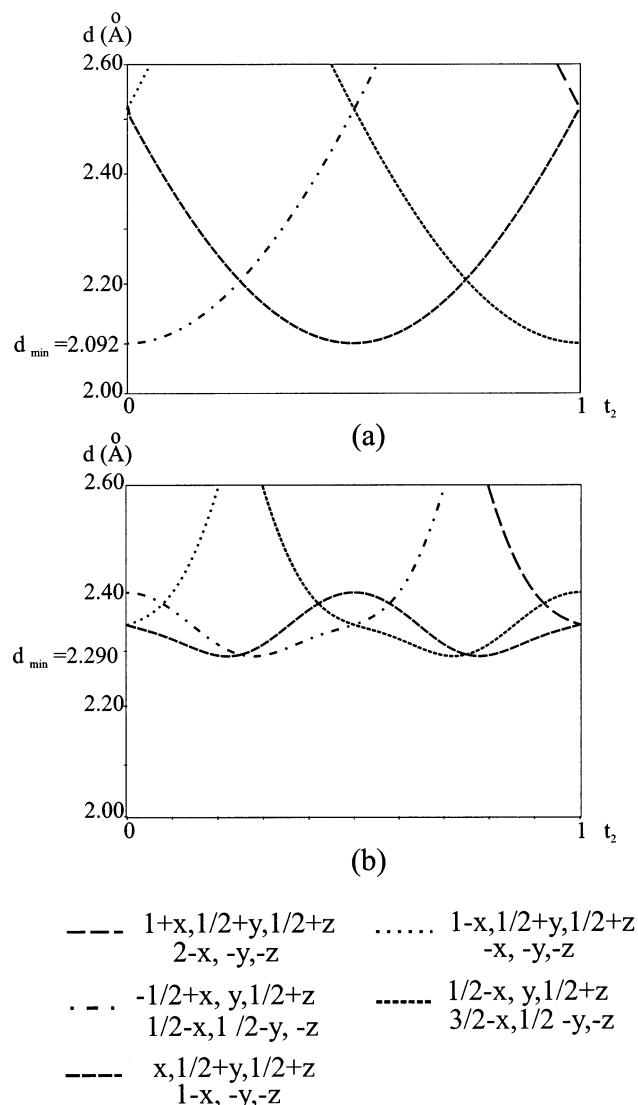


Figure 2. Variations of the intersystem Ca–O distances versus the internal phase parameter t_1 , (a) neglecting modulation and (b) for the modulated structure.

the α composite ratio corresponds to the Ca ratio in the above formula. This gives a new interpretation of the ratio obtained by Babu et al.⁵ in the case of the pure cuprate $\text{Ca}_{0.82}\text{CuO}_2$ ($a = 2.807$ Å, $b = 6.321$ Å, and $c = 10.573$ Å, $Fmmm$ SG). This ratio was only calculated from the refined partial occupation (0.425) of the Ca site. This is also confirmed by the same type of calculation for the $\text{Sr}_{0.73}\text{CuO}_2$ compound.⁹ In fact, the composite description of these pure cuprates clearly explains these nonstoichiometries. The reliability factor R obtained from the average structure is 6.51% with large ADPs for the oxygen atom along the [010] direction. Moreover, the distance Ca–O appears too short ($d_{\min} = 2.092(6)$ Å) (Figure 2a).

Modulated Structure. The global reliability factors are clearly improved by the introduction of modulation parameters. The refinement result shows significant displacive and ADP modulation parameters for all

atoms (Table 3). The weight of the satellite reflections ($HKLM$ with $H \neq 0$ $M \neq 0$) is not very important in the refinement process, because of both their very small number and their weak intensity. Despite of this weak intensity, the R factor calculated with these reflections is rather good (Table 1), especially for first-order satellites. The larger displacements are observed for Ca and O atoms. According to the relative position of the Ca atom (second sublattice) along the composite direction, the oxygen atom undergoes displacements along the [010] and [100] directions (Figure 3). These displacements result in a significant increase of the minimum Ca–O intersystem distances ($d_{\min} = 2.290(3)$ Å) (Figure 2b). As a matter of fact, because of the composite scheme, the average positions of the Ca and O atoms are directly facing each other in some particular cells in the crystal. Consequently, our 4D refinement confirms the preliminary model given by Babu et al.⁵ The same behavior was already observed in the case of $\text{Sr}_{0.73}\text{CuO}_2$.⁹ Note that this structure was only refined in a large supercell model ($a = 40.968$ Å, $b = 6.823$ Å, and $c = 11.026$ Å with the $Cmcm$ space group). Nevertheless, for $\text{Sr}_{0.73}\text{CuO}_2$,⁹ two independent orthorhombic sublattices are clearly seen: one is F centered and corresponds to the same CuO_2 chain lattice observed in our case. The second one, defined by the Sr atoms, is given as C centered, whereas our Ca lattice is F centered. This probably corresponds to another superspace symmetry group. Concerning the composite $\text{Ca}_{0.83}\text{CuO}_2$,⁶ the two sublattices are F centered, as in our study, but are characterized by a monoclinic symmetry.

Concerning the MO_2 chain lattice ($M = \text{Cu}$ or Co), a noticeable variation of the M –O distances is observed ($1.838(2)$ Å $\leq d_{M-O} \leq 1.990(2)$ Å) (Figure 4). These values are usual for the Cu or Co atoms in a square-planar configuration^{8,9,16,23} (1.8639 Å $\leq d_{M-O} \leq 1.975$ Å) and for the CuO_2 chains in the spin-ladder compounds ($1.858 \leq d_{\text{Cu}-\text{O}} \leq 1.922$).^{25,26} The M site is weakly modulated (Table 3); Then, the corresponding M–M distances are roughly constant as well for intra-chain ($d = 2.803(1)$ Å) as for interchain ($d = 3.445(1)$ Å) ones. These observations are in agreement with similar distances observed for the pure cuprate.^{5,6,8}

However, the studied crystal displays a noticeable difference with the CuO_2 chains in the $\text{Sr}_{0.73}\text{CuO}_2$ compound. In this last structure, the true mirror plane, orthogonal to the c axis, imposes undulations of the CuO_2 chains (Figure 5a). The O atoms at the same x position are in phase. On the contrary, in the $\text{Ca}_{0.82}(\text{Cu}_{0.65}\text{Co}_{0.35}\text{O}_2)$ structure, the corresponding glide mirror in 4D space implies twisted displacements of the (Cu/Co)–O₄ unit (Figure 5b) resulting from the out-of-phase relation between the atoms connected to O. The same undulation of CuO_2 chains is observed in the pure cuprate $\text{Ca}_{0.83}\text{CuO}_2$ ⁶ (Figure 5c).

The bond valence calculation²⁷ yields an average valence of +2.10 for the calcium atoms, close to the expected value (+2) and of +2.30 for the cationic M site. The same values are calculated for the compound $\text{Ca}_{0.85}$

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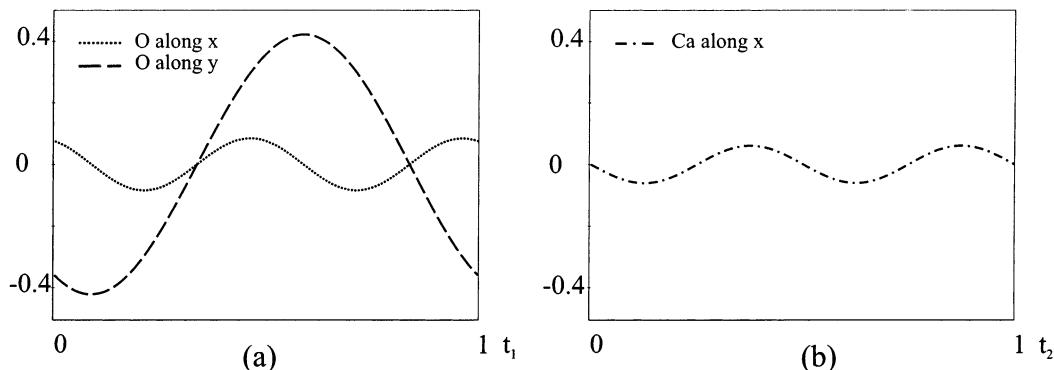


Figure 3. Relative displacements of the O and Ca atoms, versus the internal phase parameters t_1 (a) and t_2 (b).

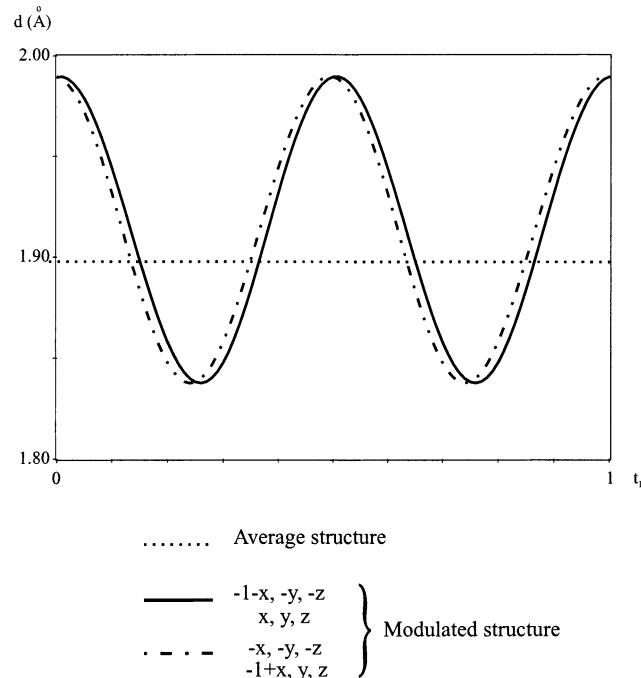


Figure 4. Variations of the (Cu/Co)-O distances versus the internal phase parameter t_1 .

CuO_2 .¹⁶ It can be explained considering a +2 valence state for the Cu atoms and +3 for the Co atoms. Preserving the electroneutrality, a limiting model can be proposed by assuming the ideal cationic composition and a valence of -2 for the oxygen atoms: $\text{Ca}_{0.82}^{+II}(\text{Cu}_{0.65}^{+II}\text{Co}_{0.35}^{+III}\text{O}_2)$.

Conclusion

The present study exhibits the composite character of the $\text{Ca}_{0.82}(\text{Cu}_{0.65}\text{Co}_{0.35}\text{O}_2)$ compound. The 4D composite analyses allow us to give an accurate quantitative description of the incommensurate modulated atomic positions in both sublattices. This structure clearly presents very close analogies to the related binary cuprate compounds $\text{Ca}_{0.85}\text{CuO}_2$, $\text{Ca}_{0.83}\text{CuO}_2$, and $\text{Sr}_{0.73}\text{CuO}_2$. The present results about the mixed copper-cobalt compound give new insight to the structures of these pure copper phases.

Nevertheless, some differences are still to be explained. In the case of the Ca compound or of its Y-substituted related compounds,¹⁶ both electron diffraction and powder X-ray diffraction are compatible

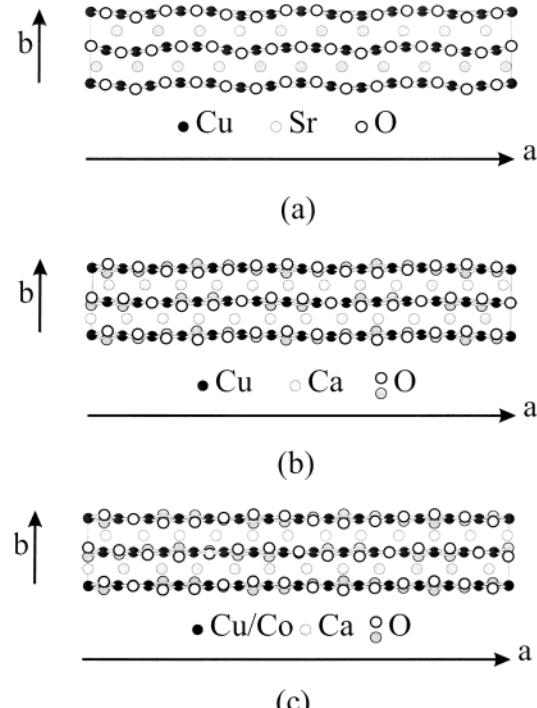


Figure 5. Comparaison of the orientation of MO_2 planar chains between the $\text{Sr}_{0.73}\text{CuO}_2$ structure (Karpinski et al.⁹) (a), the $\text{Ca}_{0.83}\text{CuO}_2$ structure (Miyazaki et al.⁹) (b), and the composite studied $\text{Ca}_{0.82}(\text{Cu}_{0.65}\text{Co}_{0.35}\text{O}_2)$ (c).

with a different symmetry and with two components for the modulation vector in the (a, c) plane. This is only compatible with a monoclinic symmetry, and the structural modulated models were proposed in this global monoclinic symmetry.^{16–18,28} As a matter of fact, our orthorhombic 4D symmetry cannot explain all the diffraction lines observed in the $\text{Ca}_{0.82}\text{CuO}_2$ powder diffraction pattern.^{5,16} This symmetry can simply be explained by the introduction of a difference of phase in the stacking of the different corrugated slabs along the [001] direction. Such shifts between layers were already proved to be responsible for a similar lowering of the symmetry in the misfit layered cobaltites.¹⁵

Moreover, the real symmetry of the Ca sublattice is still to be clarified. Most of the time, the Ca sublattice was described as disordered and partially occupied. In the present study, the stoichiometry is perfectly explained by the composite character of the structure, and

this allows us to rule out any disorder phenomenon. The Ca sublattice is then characterized by an *F*-centered orthorhombic lattice, in agreement with the 4D symmetry of the global structure.

Finally, we have also proved here a possible substitution of Co for Cu in this type of structure, which could be compatible with a charge localization of the type $Cu_{0.65}^{+II} Co_{0.35}^{+III}$. The question of the ordered or disordered distribution of the metal in this site cannot be answered by using standard X-ray techniques and needs either

anomalous X-ray diffraction or neutron diffraction experiments. Moreover, the study of the influence of such a substitution on the physical properties is still in progress.

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