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Importance of True Satellite Reflections in the Analysis of Modulated, Composite Crystal Structures. II. The Structure of $[M'_2Cu_2O_3]_7[CuO_2]_{10}$, $M' = Bi_{0.04}Sr_{0.96}$

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Abstract

The structure of the modulated, composite crystal bismuth strontium cuprate $[M'_2Cu_2O_3]_7[CuO_2]_{10}$, with $M' = Bi_{0.04}Sr_{0.96}$, has been determined and refined using a model which allows modulation of the atomic positional parameters for all atoms, as well as modulation of thermal parameters for the M' site. The structure is orthorhombic, with **c** being the misfit direction and $a = 11.4712\,(6)$, $b = 13.3765\,(13)$ Å. Sublattice 1, of composition $(CuO_2)_4$, has $c_1 = 2.7509\,(10)$ Å, while sublattice 2, of composition $(M'_2Cu_2O_3)_4$, has $c_2 = 3.9316\,(3)$ Å. Superspace group $Amma(001+\gamma)ss\bar{1}$; $\mathbf{q} = \gamma\mathbf{c}_1^*$ with $\gamma = 0.6997\,(3)$; $\lambda = 0.6565$ Å, $\mu = 25.4\ \text{mm}^{-1}$. The final residual is $R_{\text{all}} = 0.0474$ for all 1174 reflections, $R_{\text{main}} = 0.0451$ for the 549 main reflections, $R_{1.\text{sat}} = 0.0562$ for the 442 first-order satellite reflections and $R_{2.\text{sat}} = 0.1044$ for the 183 second-order satellite reflections. The satellite reflections have been collected with X-ray synchrotron radiation. It is shown that these reflections help to unambiguously determine the superspace group. The orthorhombic compound has a layered structure, stacked along the b axis. The first sublattice consists of layers of CuO_2 ribbons, with CuO_4 squares sharing edges along the c axis. The second sublattice consists of CuO_4 squares, which are sharing edges in a zigzag pattern. In-between these layers the disordered layers of Bi and Sr atoms are sandwiched. A comparison with structurally and chemically related compounds is made.

1. Introduction

A determination of the four-dimensional incommensurately modulated composite structure $[(Bi_{0.04}Sr_{0.96})_2Cu_2O_3]_7[CuO_2]_{10}$ is presented. The analysis is based on both main reflections and true satellite reflections arising from the interaction of the two sublattices. True satellite reflections are the satellite reflections which are not the main reflections of any of the sublattices. The structure has previously been analyzed in the sublattices (McCarron, Subramanian, Calabrese & Harlow, 1988) and as a composite structure (Ukei, Shishido & Fukuda, 1994) in the noncentrosymmetric superspace group $A2_1ma(001+\gamma)0s0$. Both descriptions were based on main reflections only. The latter description, however, has some less desirable features which will be discussed. We have not been able to obtain a satisfactory fit of our data to Ukei's model. On the contrary, we propose to describe the structure in the centrosymmetric superspace group $Amma(001+\gamma)ss\bar{1}$, which leads to a more stable refinement and a more reasonable coordination chemistry. The structure of the composite compound is, as described by McCarron, Subramanian, Calabrese & Harlow (1988), closely related to that of the calcium-containing $[(Bi,Sr)_{2-x}Ca_xCu_2O_3]_{7+\delta}[CuO_2]_{10}$ compounds with $0.8 \leq x \leq 1.2$ and $0.02 \leq \delta \leq 0.06$. In part I of this paper (Jensen *et al.*, 1997) an improved composite refinement of the $x \simeq 0.96$ compound is described. Here we also give some comparisons between the structures with and without Ca.

The orthorhombic composite structure of $[(Bi_{0.04}Sr_{0.96})_2Cu_2O_3]_7[CuO_2]_{10}$ is a layered structure with two interpenetrating lattices, alternately stacked along the b axis of the unit cell, see Fig. 1 in part I (Jensen *et al.*, 1997).

2. Experimental

The synthesis of the compound has previously been described (McCarron, Subramanian, Calabrese & Harlow, 1988). The same crystal specimen, of size $0.079 \times 0.017 \times 0.240\ \text{mm}^3$ along a, b and c, which was used in the work of McCarron, Subramanian, Calabrese & Harlow (1988), has been used for the present data collections. Main reflections were collected on a Huber four-circle diffractometer using Nb-filtered Mo $K\alpha$ radiation, ω–2θ step scans and a Na(Tl)I-scintillation counter as the detector. The data were reduced with a local program package, as previously described (Jensen *et al.*, 1993). Information about this experiment

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and the data reduction has been deposited.* X-ray synchrotron data were collected at the X3 beamline at the National Synchrotron Light Source, Brookhaven National Laboratory, USA. Experimental information is listed in Table 1, but full details are reported in part I (Jensen *et al.*, 1997). The satellite reflections conform with an orthorhombic *A*-centered Bravais lattice of the composite structure. In total, 1554 first- and second-order satellite reflections were collected, averaging 1167 unique reflections, of which 625 have been considered observed [$I > 3\sigma(I)$]. A merge of synchrotron data and X-ray tube data yielded 707 unique main reflections, of which 549 were considered observed.

Table 1. *Synchrotron data collection of satellite reflections from the compound* $[(Bi_{0.04}Sr_{0.96})_2Cu_2O_3]_7[CuO_2]_{10}$

Scan type	ω
Number of steps	120
Scan speed (° min^{-1})	1.00
Scan width (°)	0.96
No. of reflections measured	1554 satellites, 249 main
No. of unique reflections	1167 satellites, 249 main
No. of observed, unique reflections	625 satellites, 233 main
Internal agreement, $R_{\rm int}$	0.067
Data collection period (d)	3
Standard reflections	$12,\bar{6},0,0$ and $\bar{8},10,1,\bar{1}$
Time between standards (h)	1
Data collection θ range (°)	$0 \le \theta < 25$
Indices	$hk\bar{1}m$, $m = 1, 2, 3, 4$; $hk\bar{2}m$, $m = 2, 3, 4, 5, 6$; $hk\bar{1}m$, $m = 3, 4$; $hk1m$, $m = 1, 2, 3$. $0 \le \theta < 30$ $hkl\bar{1}$, $l = 2, 3, 4$. All satellites $h\ 0 \rightarrow 15, k\ 0 \rightarrow 17$ $15 < \theta < 30°$; $hkl0, h\ 0 \rightarrow 16, k\ 0 \rightarrow 13, l\ 1 \rightarrow 4$.
Wavelength, λ (Å)	0.6565
Absorption coefficient μ (mm^{-1})	25.4
$T_{\rm min}$, $T_{\rm max}$	0.18, 0.65

3. Results

As reported by McCarron, Subramanian, Calabrese & Harlow (1988), the CuO_2 sublattice is described in *Amma*. The $M'_2Cu_2O_3$ sublattice can be described in space group *Fmmm*. The composite structure is a layered structure with edge-sharing CuO_4 squares in ribbons of composition CuO_2 extending along **c** (Fig. 1*a*) and edge-sharing CuO_4 squares in a zigzag pattern extending in the *ac* plane in sheets of composition Cu_2O_3 (Fig. 1*b*). In-between these two types of copper oxide layers, the layers of M' atoms are interleaved (Fig. 1*c*).

A four-indices description of the reflections, necessary for the analysis of the modulated structure in a four-dimensional formalism, was introduced according to Janner & Janssen (1980) and has been described in part I (Jensen *et al.*, 1997). The *A*-centered CuO_2 sublattice is described by *hkl*0, while the *F*-centered $M'_2Cu_2O_3$ sublattice is described by *hk*0*m*. Systematic extinctions were: *hklm*, present only for $k + l + m = 2n$, *hkl*0, $k + l = 2n$, *hk*0*m*, $h + k = 2n$, $k + m = 2n$ (and $h + m = 2n$), *h*000, $h = 2n$, and *h*0*lm* $l = 2n$, $m = 2n$. These give the Bravais class as $mmmA(001 + \gamma)$ (*International Tables for Crystallography*, 1992, Vol. C). We have found the atomic positions to conform with the origin-shifted centrosymmetric superspace group $Amma(001 + \gamma)ss\bar{1}$. The symmetry operations which have been used are

$$\begin{array}{lllll}
(1) & x_1 & x_2 & x_3 & x_4 \\
(2) & \frac{1}{2} - x_1 & x_2 & x_3 & \frac{1}{2} + x_4 \\
(3) & x_1 & -x_2 & x_3 & \frac{1}{2} + x_4 \\
(4) & \frac{1}{2} + x_1 & x_2 & -x_3 & -x_4 \\
(5) & -x_1 & -x_2 & -x_3 & -x_4 \\
(6) & \frac{1}{2} + x_1 & -x_2 & -x_3 & \frac{1}{2} - x_4 \\
(7) & -x_1 & x_2 & -x_3 & \frac{1}{2} - x_4 \\
(8) & \frac{1}{2} - x_1 & -x_2 & x_3 & x_4
\end{array}$$

and centering translations (0,0,0,0) and (0,1/2,1/2,1/2), which conform with the *A*-centering. With these symmetry operations it is readily seen that the superspace group is a subgroup of $Fmmm(001 + \gamma)ss1$ (origin-shifted) with general positions (1)–(8) and centering translations (0,0,0,0), (0,0,1/2,1/2), (1/2,0,1/2,1/2) and (0,1/2,1/2,1/2).

Within standard deviations, the structure is commensurate with $10c_1 = 7c_2$. However, it has been shown (McCarron, Subramanian, Calabrese & Harlow, 1988) that the structure $[(Bi,Sr)_{2-x}Ca_xCu_2O_3]_{7+\delta}[CuO_2]_{10}$ exists in a solid solution range ($0 \le x \le 1.3$) of the M' layer composition. The c_2-axis length for sublattice 2 decreases with increasing x and thus different modulation vectors ($\mathbf{q}_1 = \mathbf{c}_2^*$) occur in the series of compounds. The $x = 0$ compound is therefore also to be considered incommensurate and has been analyzed as such. Overlap of main reflections from different sublattices or overlap of main and satellite reflections has not been taken into account. $h_lk_l10_l0$ and *hk*07 are overlapping main reflections of sublattices 1 and 2, respectively, but because the scattering from sublattice 1 (the CuO_2 sublattice) is weak, the $h_lk_l10_l0$ reflections must be weak and in reality no overlap occurs. In cases where satellite reflections may overlap, the reciprocal lattice point has been assigned the lowest possible index *l* and as such has become first- or second-order satellites for the $M'_2Cu_2O_3$ sublattice, *hklm*, $1 \le |l| \le 2$. No second-order satellite reflections for CuO_2 were observed, *i.e.* reflections with *hkl*2, $|l| > 2$.

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* Lists of structure factors and experimental details, and a difference-Fourier map have been deposited with the IUCr (Reference: SH0079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3.1. *Refinements*

The superspace group was determined on the basis of the sublattice space groups, given by McCarron, Subramanian, Calabrese & Harlow (1988) as *Amma* and *Fmmm* for sublattices 1 and 2, respectively, and taking into account a necessary origin shift of 1/4 along *y* of one sublattice.

The refinements were carried out with the program *JANA*94 (Petříček, 1994) using 1174 observed $[I > 3\sigma(I)]$ reflections comprising 549 main reflections, 442 first-order and 183 second-order satellite reflections. The atomic parameters from this refinement are listed in Table 2(*a*). Final values of atomic coordinates of the sublattices are given, together with modulation amplitudes. For the definition of the parameters for the description of

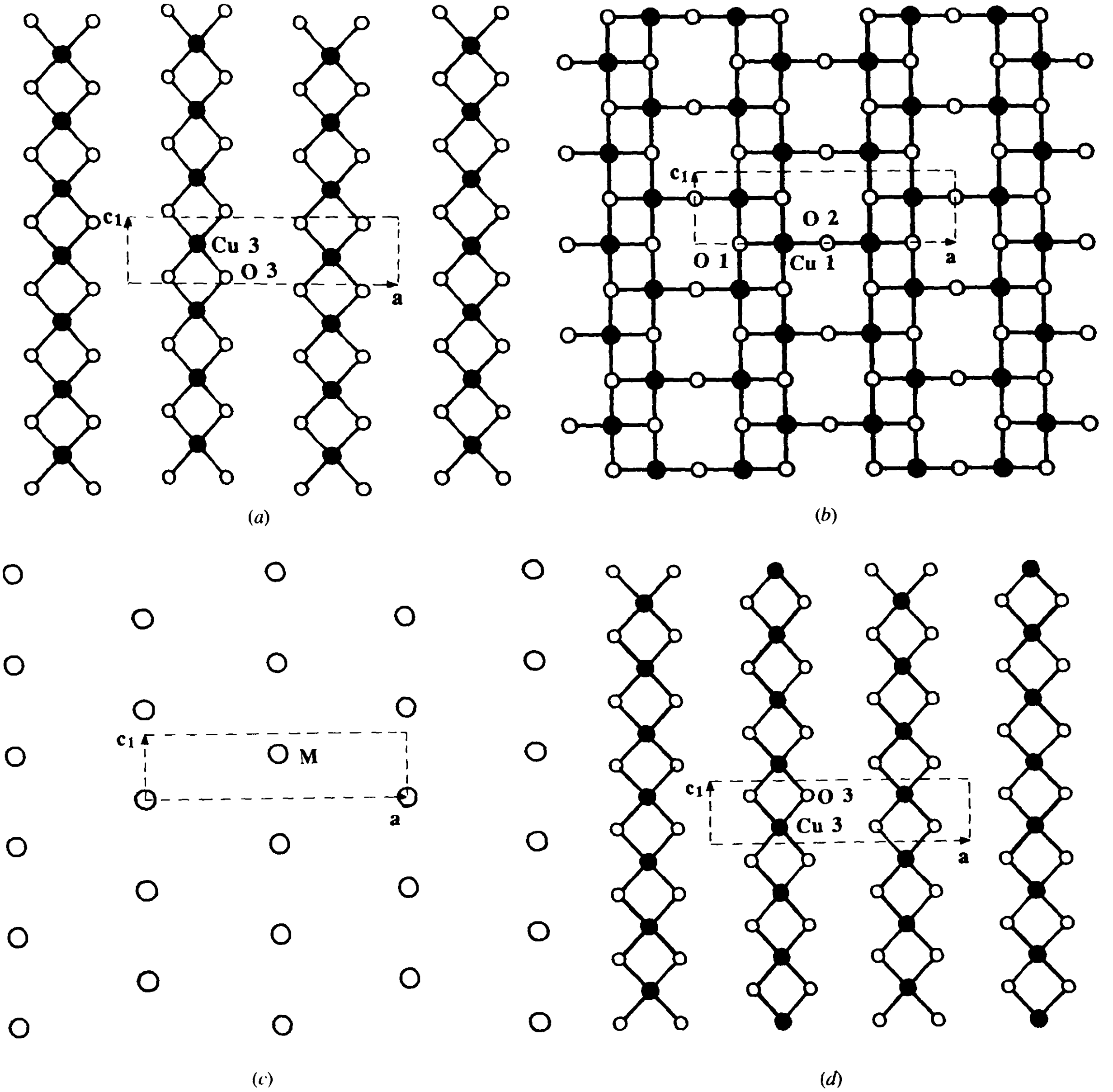
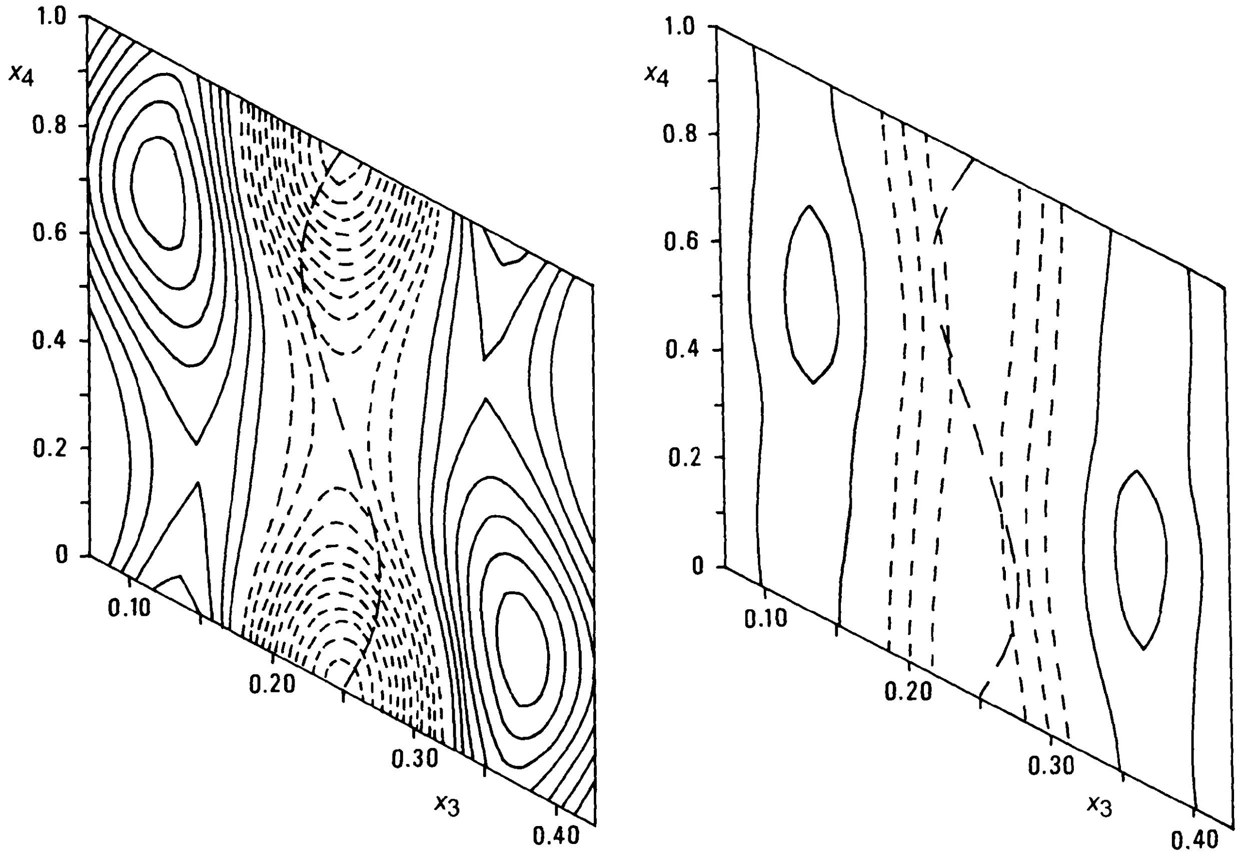


Fig. 1. (*a*) The CuO_2 sublattice of $[M'_2Cu_2O_3]_7[CuO_2]_{10}$, $M' = Bi_{0.04}Sr_{0.96}$. In neighboring ribbons the O atoms (open circles) are close to facing each other. The Cu atoms are filled cirles. The unit cell in the sublattice has been drawn. The layer is in the *ac* plane. (*b*) The Cu_2O_3 layer in the $M'_2Cu_2O_3$ sublattice. The unit cell of the CuO_2 sublattice has been drawn. The layer is in the *ac* plane. (*c*) The M' layer in the $M'_2Cu_2O_3$ sublattice. This layer is interleaved between the CuO_2 layer and the Cu_2O_3 layer. The unit cell of the CuO_2 sublattice has been drawn. The layer is in the *ac* plane. (*d*) The CuO_2 sublattice of $[M_2Cu_2O_3]_{7+\delta}[CuO_2]_{10}$, $M = Bi_{0.06}Sr_{0.46}Ca_{0.48}$. In neighboring ribbons the O atoms are staggered such as to make a zipper-like pattern, *cf.* Fig. 1(*a*). The unit cell of the sublattice has been drawn. The layer is in the *ac* plane.

modulated atomic positions and thermal vibrations, see part I (Jensen *et al.*, 1997). In Table 2(*b*) the coefficients for the M' site for modulation of thermal vibration parameters have been listed. Only this site showed thermal vibration parameter modulation. A refinement of thermal modulation was attempted for the Cu1 and Cu3 sites, however, it was not a suitable description for Cu1. For Cu3, the values of the extra parameters were all less than four standard deviations and give only a very marginal decrease in the R factor, thus this model was abandoned. In Figs. 2(*a*) and (*b*), the difference Fourier section of the M' site in the x_3x_4 plane is shown before and after inclusion of thermal vibration modulation. It is seen that the inclusion of these parameters gives a much smaller remaining electron density, the maximum peak decreasing from 7.0 to 2.0 e Å^{-3}. The corresponding decreases in R factors on introduction of these parameters were 0.8% for main reflections, 5.3% for first-order and 4.4% for second-order satellite reflections. R factors for different classes of reflections are given in Table 3. There were no correlation coefficients above 0.7 and all atoms have positive definite thermal vibration ellipsoids. The composition for the mixed cation site has been refined to $M' = \mathrm{Bi}_{0.04}\mathrm{Sr}_{0.96}$. Occupational (substitutional) modulation of the second-order for the M' site was attempted according to the formula

$$A = A_o + \sum_{k=1}^{2} A_k^s \sin(2\pi k\mathbf{q}_i.\mathbf{r}_{\nu i}^o) + A_k^c \cos(2\pi k\mathbf{q}_i.\mathbf{r}_{\nu i}^o),$$

where A_o is the total occupation of one species on the site. The largest refined coefficient was only four standard deviations large and A was not significantly different from A_o. The decrease in the R factor was less than 0.05%. A systematic variation of M'—O interatomic distances with the occupational modulation, indicating preferential occupation of Bi, was not observed. For these reasons the model of occupational modulation



(*a*) (*b*)

Fig. 2. (a) Difference-Fourier map, showing the trace (long dashed line) in the (x_3,x_4) plane of the M' site before inclusion of thermal parameter modulation in the refined model. Large peaks of remaining positive electron density are observed, as well as negative density holes. The positive electron density is represented by full lines, negative density by short dashed lines. The contour level is 1.0 e Å^{-3}. (*b*) Difference-Fourier map, showing the trace in the (x_3,x_4) plane of the M' site after inclusion of thermal parameter modulation in the refined model. The remaining electron density lobes from Fig. 2(*a*) are seen to have diminished considerably and the negative holes have been eliminated. Contours as for Fig. 2(*a*).

Table 2. *Parameters from the composite refinement*

(*a*) x, y, z are fractional atomic coordinates. Displacement parameters u_{ij} are given in Å^2. U_i^s is the modulation amplitude of the sine wave and U_i^c is that of the cosine wave. Modulation amplitudes are given in Å. Cu3 and O3 belong to sublattice 1, Cu1, O1, O2 and *M'* to sublattice 2.

Atom	Cu1	O1	O2	*M'**	Cu3	O3
Occupation	1/2	1/2	1/4	1/2	1/4	1/2
x	0.33450 (13)	0.1694 (9)	1/2	1/2	1/4	0.1380 (2)
y	1/4	1/4	1/4	0.37938 (7)	1/2	1/2
z	0.7510 (8)	0.747 (6)	3/4	1/4	0.4118 (3)	0.9115 (11)
u_{11}	0.0012 (7)	0.002 (5)	0.002 (4)	0.0049 (4)	0.0034 (3)	0.0055 (10)
u_{22}	0.0104 (8)	0.020 (6)	0.015 (3)	0.0058 (5)	0.0147 (5)	0.0230 (14)
u_{33}	0.0025 (9)	0.0026 (0)	0.002 (4)	0.0072 (5)	0.0379 (4)	0.0403 (14)
u_{12}	0	0	0	0	0	0
u_{13}	0.0013 (10)	0.0 (0)	0.000 (3)	0.0004 (3)	0	0
u_{23}	0	0	0	0	0	−0.0001 (7)
U_x^s (q)	0	0	0	−0.0158 (3)	0	0
U_y^s (q)	−0.0234 (6)	−0.034 (4)	0	0	0	−0.244 (4)
U_z^s (q)	0	0	0	0.1084 (8)	0	0
U_x^c (q)	0	0	0	0	0	0
U_y^c (q)	−0.0550 (7)	0.032 (4)	−0.154 (7)	−0.0316 (4)	0	0.013 (3)
U_z^c (q)	0	0	0	0	0	0
U_x^s (2q)	0.0099 (4)	0.007 (3)	0.007 (3)	−0.0139 (3)	0	0.006 (3)
U_y^s (2q)	0	0	0	0	0	0
U_z^s (2q)	−0.0027 (5)	0.001 (3)	−0.007 (4)	0.0205 (4)	−0.0138 (13)	−0.027 (5)
U_x^c (2q)	0.0063 (5)	0.006 (3)	0	0	0	0.015 (2)
U_y^c (2q)	0	0	0	0.0049 (4)	0	0
U_z^c (2q)	−0.0012 (7)	0.001 (4)	0	0	−0.0037 (14)	0.025 (6)

(*b*) Parameters from refinement *A* for the modulation of thermal vibration parameters for the Sr/Bi atoms in Å^2.

ij	11	22	33	12	13	23
$u^s_{ij,1}$				0.00044 (9)		0.0 (0)
$u^c_{ij,1}$	0.00052 (10)	−0.00005 (15)	0.0047 (2)		−0.00106 (13)	
$u^s_{ij,2}$				0.00010 (13)		0.00028 (13)
$u^c_{ij,2}$	0.00037 (13)	0.00006 (17)	0.0023 (2)		−0.00033 (11)	

The parameters are defined as: $u_{ij} = u^0_{ij} + \Sigma^2_{k=1}\, u^s_{ij,k} \sin(2\pi k\mathbf{q}_i.\mathbf{r}^0_{\nu i}) + u^c_{ij,k}\cos(2\pi k\mathbf{q}_i.\mathbf{r}^o_{\nu i})$, where u_{ij} is the resulting thermal vibration.
* Occupancy of Bi: 0.044 (6), occupancy of Sr: 0.956 (6).

Table 3. *Characteristics of the refined model*

	Model
Second-order displacive modulation	Yes
Temperature factor modulation	Yes
No. of nonpositive definite displacement ellipsoids	0
No. of $\rho_{ij} > 0.7$	0
Max shift/e.s.d.	0.002
No. of main reflections	549
Number of first-order satellite reflections	442
Number of second-order satellite reflections	183
Goodness-of-fit	2.45
Number of parameters	71
R, wR, all reflections	0.0474, 0.065
R, wR, main reflections	0.0451, 0.051
R, wR, first-order satellite reflections	0.0562, 0.0758
R, wR, second-order satellite reflections	0.1044, 0.1066

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = [\Sigma w(F_o^2 - F_c^2)]^{1/2}/[\Sigma wF_o^2]^{1/2}$; weight $=$ $w = (\sigma^2_{\rm cts} + 0.0001F^2)^{-1}$.

was abandoned. No significant parameter changes were observed between the model with occupational modulation and the model without. Inclusion in the least-squares refinement of true satellite reflections collected with an X-ray synchrotron source with an incident photon energy close to the Bi $L_{\rm III}$ absorption edge would help decide whether occupational modulation is actually present in the compound.

It should be noted that the success of this model depends on the inclusion of true satellite reflections in the refinement. A refinement was performed on the 549 main reflections only, using isotropic thermal displacement for O atoms, second-order modulation displacement for all atoms, but no modulation of thermal vibration parameters. This resulted in large correlation coefficients ($\rho_{ij} > 0.8$) between modulation amplitudes for the atoms *M'*, Cu1, O1, O3 and also between some thermal parameters and modulation parameters. The reflection-to-parameter ratio was larger than 10. It is evident that the information on modulation in the main reflections is not sufficient to make a stable refinement. In this refined model the interatomic distances were also distributed over very large ranges, implicating a nonphysical model.

Interatomic distances have been calculated with the program *TDIST* (Císařová, 1991) and mapped as a function of t (defined in part I) in Figs. 3(*a*)–(*d*) for one period of the modulation. Minimum, maximum and average values are listed in Table 4.

4. Discussion

4.1. *Structural chemistry*

4.1.1. *Comparison with the* $[M_2Cu_2O_3]_{7.03}$-$[CuO_2]_{10}$ *compound,* $M = Bi_{0.06}Sr_{0.46}Ca_{0.48}$. The structure of $[(Bi_{0.04}Sr_{0.96})_2Cu_2O_3]_7[CuO_2]_{10}$ (1) is very similar to that of $[(Bi_{0.06}Sr_{0.46}Ca_{0.48})_2Cu_2O_3]_{7.03}[CuO_2]_{10}$ (2), described in part I. The latter compound is described in superspace group $F222(001+\gamma)001$, while the former is described in superspace group $Amma(001+\gamma)ss\bar{1}$. Both superspace groups are subgroups of the origin-displaced centrosymmetric superspace group $Fmmm(001+\gamma)ss\bar{1}$. The only chemical difference between the two structures is the presence of Ca in the layer of Bi and Sr atoms in (2). As described by McCarron, Subramanian, Calabrese & Harlow (1988) this leads to a lowering of the symmetry of the CuO_2 sublattice. The neighboring ribbons along **a**, which match as two halves of a zipper in (2), are relatively displaced along **c** in (1) (Figs. 1*d* and *a*). The structure of the second sublattice is the same for both structures. McCarron, Subramanian, Calabrese & Harlow (1988) made a detailed investigation of unit-cell size as a function Ca content in the compounds

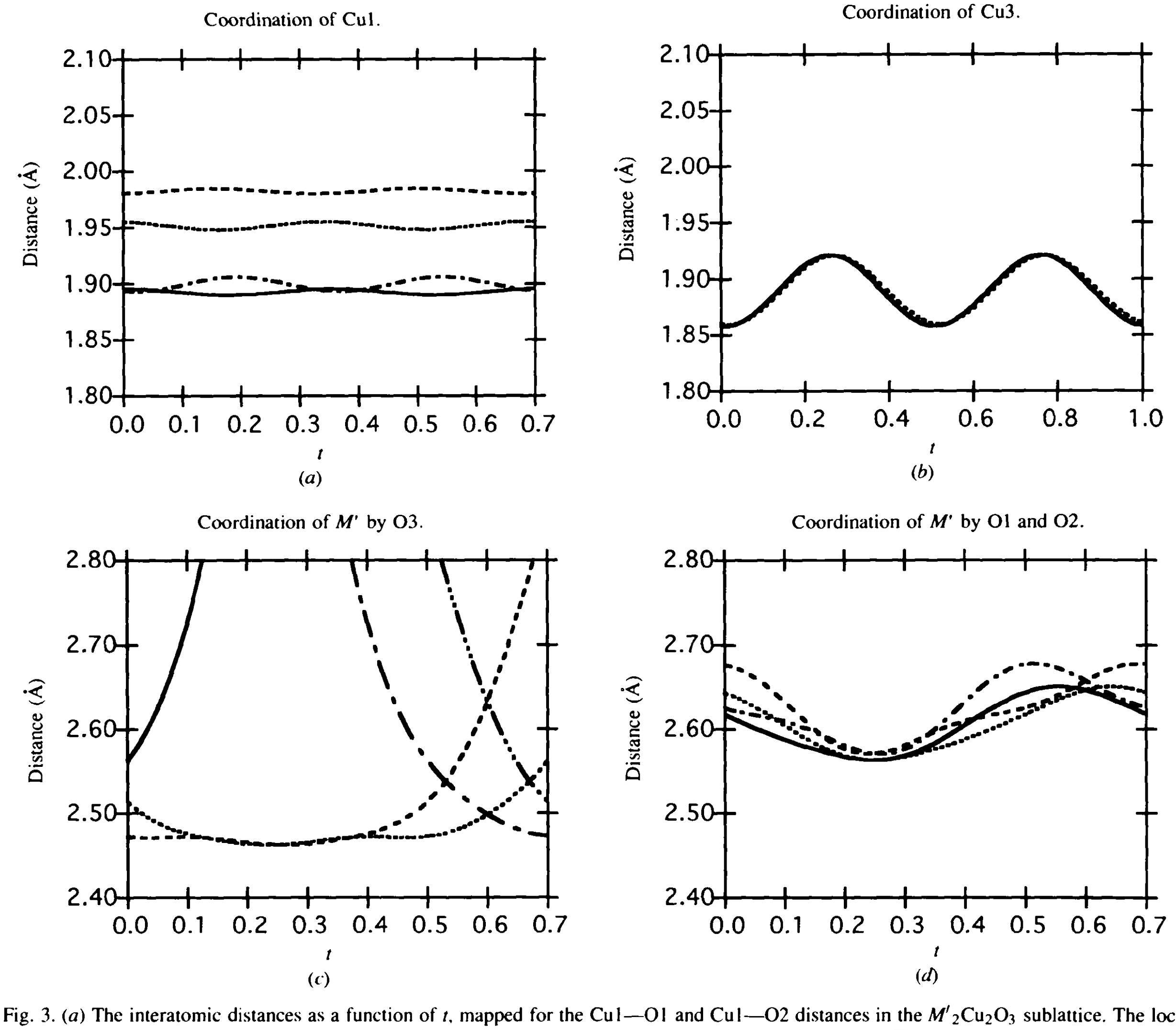


Fig. 3. (*a*) The interatomic distances as a function of *t*, mapped for the Cu1—O1 and Cu1—O2 distances in the $M'_2Cu_2O_3$ sublattice. The local coordination is obtained for one given value of *t*. The two upper curves correspond to bonds along **c**. These distances are not statistically significantly different. The two lower curves correspond to bonds along **a**. *t* is defined by the equation $x_4 = \mathbf{q}_1.\mathbf{r}_o = \gamma x_3 + t$ (see part I). (*b*) The interatomic distances as a function of *t*, mapped for the Cu3—O3 distances in the CuO_2 sublattice. Two distances (to O3 atoms with the same x_3 coordinate) have the same value at any *t*. In total, four Cu3—O3 bonds exist. (*c*) The interatomic distances as a function of *t*, mapped to the *M'*—O3 interlattice distances, *cf.* Fig. 3(*d*). It is seen that when intralattice oxygen is further away ($t = 0.6$), there are four interlattice O atoms in close proximity, while only two when intralattice O atoms are close to *M'*. (*d*) The interatomic distances as a function of *t*, mapped for the *M'*—O1 and *M'*—O2 intralattice bonds in the $M'_2Cu_2O_3$ sublattice, *cf.* Fig. 3(*c*).

Table 4. *Interatomic distances (Å)*

	Minimum	Maximum	Average
Cu1$^{\mathrm{i}}$—O1$^{\mathrm{i}}$	1.892 (11)	1.897 (11)	1.8947 (13)
Cu1$^{\mathrm{i}}$—O1$^{\mathrm{ii}}$	1.95 (3)	1.96 (3)	1.953 (3)
Cu1$^{\mathrm{i}}$—O1$^{\mathrm{iii}}$	1.98 (3)	1.99 (3)	1.981 (3)
Cu1$^{\mathrm{i}}$—O2$^{\mathrm{i}}$	1.894 (3)	1.906 (3)	1.8998 (4)
Cu3$^{\mathrm{i}}$—O3$^{\mathrm{i}}$	1.858 (3)	1.922 (5)	1.8893 (5)
Cy3$^{\mathrm{i}}$—O3$^{\mathrm{iv}}$	1.858 (3)	1.922 (5)	1.8893 (5)
Cu3$^{\mathrm{i}}$—O3$^{\mathrm{v}}$	1.860 (5)	1.921 (5)	1.8903 (5)
Cu3$^{\mathrm{i}}$—O3$^{\mathrm{vi}}$	1.860 (5)	1.921 (5)	1.8903 (5)
M'^{i}—O1$^{\mathrm{vii}}$	2.562 (9)	2.650 (9)	2.6042 (10)
M'^{i}—O1$^{\mathrm{viii}}$	2.562 (9)	2.650 (9)	2.6042 (10)
M'^{i}—O2$^{\mathrm{i}}$	2.5711 (12)	2.678 (5)	2.6230 (5)
M'^{i}—O2$^{\mathrm{ix}}$	2.5711 (12)	2.678 (5)	2.6230 (5)
M'^{i}—O3$^{\mathrm{iv}}$	2.562 (5)	4.858 (6)*	
M'^{i}—O3$^{\mathrm{vi}}$	2.463 (4)	2.563 (5)*	
M'^{i}—O3$^{\mathrm{x}}$	2.462 (4)	2.862 (5)*	
M'^{i}—O3$^{\mathrm{xi}}$	2.473 (4)	4.250 (6)*	
M'^{i}—O3$^{\mathrm{xii}}$	2.514 (4)	4.734 (6)*	

* Maximum value in the interval $0 < t < 0.70$, the distance goes towards infinity outside this interval in t. Symmetry codes: (i) x_1, x_2, x_3, x_4; (ii) $\frac{1}{2}-x_1, \frac{1}{2}-x_2, \frac{1}{2}+x_3, \frac{1}{2}+x_4$; (iii) $\frac{1}{2}-x_1, \frac{1}{2}-x_2, x_3-\frac{1}{2}, x_4-\frac{1}{2}$; (iv) $\frac{1}{2}-x_1, x_2, x_3, \frac{1}{2}+x_4$; (v) x_1, x_2, x_3-1, x_4; (vi) $\frac{1}{2}-x_1, x_2, x_3-1, \frac{1}{2}+x_4$; (vii) $\frac{1}{2}+x_1, x_2, -x_3, 1-x_4$; (viii) $\frac{1}{2}-x_1, x_2, x_3, \frac{1}{2}+x_4$; (ix) x_1, x_2, x_3, x_4-1; (x) $\frac{1}{2}+x_1, x_2, 1-x_3, -x_4$; (xi) $\frac{1}{2}+x_1, x_2, -x_3, -x_4$; (xii) $\frac{1}{2}-x_1, x_2, x_3-2, \frac{1}{2}+x_4$.

$[(\mathrm{Bi,Sr})_{2-x}\mathrm{Ca}_x\mathrm{Cu_2O_3}]_{7+\delta}[\mathrm{CuO_2}]_{10}$, varying x from 0 to ~1.3. They found the b-axis length to systematically increase with decreasing x, ~0.4 Å (3%), over the full range, while c_2 decreased, ~0.025 Å (0.6%). They also found that Bi is not an essential element for the formation of the structure and that the system decomposes in the Ca-rich end. That investigation was based on powder samples. It is likely to assume that it is the presence of Ca which makes the $\mathrm{CuO_2}$ sublattice F-centered, since all the compounds analyzed having $x \simeq 0.86$ (McCarron, Subramanian, Calabrese & Harlow, 1988), $x \simeq 0.96$, described in part I, and $x \simeq 1.13$ (Kato, 1990) have an F-centered $\mathrm{CuO_2}$ sublattice.

On reducing the superspace-group symmetry from F- to A-centered, the z coordinates of Cu3, O3, Cu1 and O1 are released from special positions (1/4 or 3/4) to general positions. For (1) this is particularly evident for Cu1 and O1 of the $\mathrm{Cu_2O_3}$ sheet, see Fig. 1(b), where the z coordinates have e.s.d.'s an order of magnitude larger than the x coordinate. It is notable that in the composite refinement of both structures, u_{33} of Cu1 and O1 tended to refine to very small values. For (1) it was necessary to fix u_{33} of O1 to the same value as u_{33} of O2.

Not many composite structures have been found to exist over a solid solution range. A recent example is $(1-y)\mathrm{Ta_2O_5}.y\mathrm{WO_3}$, $0 \le y \le 0.267$, analyzed by Rae, Schmid, Thompson, Withers & Ishizawa (1995). They have solved the composite structures of the two phases $\mathrm{Ta_{22}W_4O_{67}}$ and $\mathrm{Ta_{74}W_6O_{203}}$ and find that both conform with the superspace group $Cmmm(0\alpha0)s\bar{1}1$. However, when analyzed as three-dimensional superstructures they have different space groups, $C112/m$ and $Pbam$, respectively, which are subgroups of different classes to $Cmmm$. The addition of $\mathrm{WO_3}$ in this chemical system and of Ca in $[(\mathrm{Bi,Sr})_{2-x}\mathrm{Ca}_x\mathrm{Cu_2O_3}]_{7+\delta}[\mathrm{CuO_2}]_{10}$ can be compared with a continuous phase transition and it is therefore not surprising that the (super)space groups of the different phases are related *via* sub-/supergroup classes.

4.2. *Thermal vibrations*

The thermal vibration amplitudes of (1) show the pattern also displayed by (2). The $\mathrm{Cu_2O_3}$ sheet atoms (Cu1, O1 and O2) have very small (~0.002 Å^2) u_{ii} values in the plane of the sheet (u_{11} and u_{33}), while perpendicular to the sheet they are almost an order of magnitude larger. The $\mathrm{CuO_2}$ ribbons also have quite small u_{11} (~0.005 Å^2) values, while vibration along the ribbon, u_{33}, and out-of-plane, u_{22}, is considerable. The large u_{33} may indicate longitudinal shifts of the $\mathrm{CuO_2}$ ribbons along **c**. The thermal vibration ellipsoid of the M' atom, which in both structures is very isotropic, is for (2) significantly larger than for (1). This is also true for subsets of the data, even though a truly quantitative comparison cannot be made because systematic errors in the absorption correction will often affect the thermal vibration description severely. However, it may indicate a more disordered M' layer when Ca is introduced into the structure.

Modulation of the thermal vibration of the M' site has been necessary for both structures and it was much more important in terms of remaining electron density for (1) than for (2). The largest amplitude is for both along **c** and amounts to 65% of u_{33} for (1). The change in coordination environment is particularly large for the M' site, because it is coordinated to O atoms of both sublattices, while the Cu atoms are not. For (1), the modulation in the z direction is much larger than for other directions, while for (2) the thermal vibration amplitude modulation is considerable in all directions. This may be due to a static disorder of the $\mathrm{CuO_2}$ sublattice along z in (1).

4.3. *Displacive modulation*

For both structures the displacive modulation amplitudes for Cu3 are small (0.01–0.02 Å), while O3 has the largest amplitude of all atoms, 0.244 (4) Å for (1) and 0.311 (6) Å for (2), along **b**, illustrating that the ribbons are much less rigid than the sheets. The remaining amplitudes for O3 are small (< 0.03 Å). Also for Cu1, the structures are similar, 0.0547 (7) Å along **b** is the largest amplitude. Amplitudes of O1 along **b** are slightly smaller for (1) than for (2), 0.034 (4) *versus* 0.073 (4) Å. However, a notable difference is for O2, which has an amplitude of 0.153 (7) Å along **b** in (1), while it is only allowed modulation along **c** in (2) and its amplitude is small (< 0.04 Å). The most important difference is for M' in (1), the largest amplitude is along **c**, 0.1084 (8) Å, while along **b** it is only 0.0316 (4) Å and along **a** less than 0.02 Å. For (2) the modulation of *M* along **a** is the largest, 0.0459 (6) Å, while along **c** it is 0.0296 (8) Å and along **b** less than 0.01 Å. The *M*′ site in (1) thus has its largest modulation along **c** and smaller along **b** in (1), while in (2) *M* is mostly modulated along **a**.

4.4. *Interatomic distances*

Cu1 is coordinated to four O atoms, namely three positions of O1 and one of O2. In contrast to (2), there are two crystallographically different bond lengths along **c**, because the symmetry operation (x_1, $1/2-x_2$, $-x_3$, $1/2-x_4$) no longer exists. The distance variations are similar to those for (2) ranging from 1.890 (11) to 1.906 (3) Å in the *a* direction and from 1.95 (3) to 1.99 (3) Å in the *c* direction (Fig. 3*a*). The distances along **c** are not significantly different due to the aforementioned imprecise determination of *z* of Cu1 and O1. Cu3 is coordinated by four O3 atoms, which have pairwise symmetry-related distances, and all distances are very similar, ranging from 1.860 (5) to 1.920 (5) Å, whereas for (2) the equivalent intervals are slightly larger, ranging from 1.826 (10) to 1.979 (11) Å (Fig. 3*b*).

The *M*′—O distances have a larger minimal distance in (1) than in (2) for the interlattice contact, *M*′—O3, namely 2.462 (4) *versus* 2.396 (11) Å (Fig. 3*c*). Due to variations in the interlattice oxygen contacts (O3), the coordination number of *M*′ ranges from 6 to 8, 6 at $t \simeq 0.2$–0.3 and 8 at $t \simeq 0.5$–0.7. The intralattice distances to two O1 and two O2 are, as expected, very similar for the two compounds ranging from 2.563 (9) to 2.677 (5) Å for (1) (Fig. 3*d*) and from 2.519 (15) to 2.620 (9) Å for (2), since these atoms belong to the sublattice which is common to the two structures.

4.5. *Comparison with Ukei's model*

Ukei, Shishido & Fukuda (1994) presented a structural model for $(Sr_2Cu_2O_3)_{7+\delta}(CuO_2)_{10}$ with $\delta = -0.04$ using the noncentrosymmetric superspace group $A2_1ma(001+\gamma)0s0$, a subgroup of the superspace group used in the present work. Their description uses nine independent atoms, three more than our model. This would correspond to our positions Cu1, O1 and O3 splitting into two independent sites. The two Cu1 atoms seem to be very close to being symmetry-related by a twofold axis along **b**, which is also the case for the two O1 atoms. The coordinates of the basic structure have low precision. Presumably due to a limited set of data, all atoms have been refined with isotropic thermal motion and, in addition, for O atoms the thermal displacement ellipsoids were fixed at $B_{\rm iso} = 1.0$. The two chemically equivalent Cu atoms (our Cu1 site) have thermal displacement parameters which differ by an order of magnitude.

Their refinement was based on 314 main reflections, the number of parameters was 46, the refined *R* value was 0.057. They have observed a few true satellite reflections, but not included them in the refinement. For Sr (our *M*′) up to second-order harmonics in the modulation functions were included, while for Cu and O atoms only first-order harmonics were included. In their superspace group this model implies displacive modulation along **b** only for Cu and O. No modulation amplitudes for Cu and O atoms are larger than 4σ, while for Sr one amplitude larger than 5σ has been determined. The O3 atoms have amplitudes of 0.19 (6) and 0.4 (8) Å along **b**. This is to be compared with our value of 0.244 (4) Å.

We have tried refining the data of our compound in the noncentrosymmetric superspace group of Ukei, Shishido & Fukuda (1994) using their structural model. The isotropic description of thermal parameters, particularly for the Cu3 site, does not give an adequate model for our data. On introduction of anisotropic thermal vibration, high correlation between thermal parameters describing chemically equivalent atoms resulted. Inclusion of true satellite reflections in the refinement maintained correlation coefficients larger than 0.7 between virtually all parameters describing chemically equivalent atoms, and second-order satellite reflections could not be well described. The refinement also suffered from nonphysical values of parameters, such as nonpositive definite thermal displacement ellipsoids and huge modulation amplitudes.

The refinement in the centrosymmetric superspace group allows a much more stable refinement, with only 71 refined parameters *versus* 97 using anisotropic displacement parameters and second-order modulation on all atoms, and no highly correlated parameters occur. As a consequence, more physically reasonable parameter values are obtained than in the refinement in the noncentrosymmetric superspace group.

The structural difference between the present compound and that of Ukei, Shishido & Fukuda (1994) could be due to the small content of Bi in the Sr layer in the former. The modulation vector is also different. Whether this structural difference also justifies choosing a noncentrosymmetric superspace group is not obvious. The coordination chemistry displayed by the present centrosymmetric structural model is more physically pleasing than that reported by Ukei, Shishido & Fukuda (1994). They obtained Sr—O distances in a large range from 2.0 (4) to 2.78 (8) Å, one Sr apparently coordinated to only three O atoms. Their Cu—O distances range from 1.82 (9) to 2.0 (2) Å, which again is a larger range than for the present case. However, none of the mentioned variations are statistically significant due to the imprecise determination of both basic structure coordinates (*x*, *y*, *z*) and modulation amplitudes.

5. Conclusions

The four-dimensional composite modulated structure has been determined for the compound

$[M'_2Cu_2O_3]_7[CuO_2]_{10}$, with $M' = Bi_{0.04}Sr_{0.96}$. Refinements in the centrosymmetric superspace group $Amma(001+\gamma)ss\bar{1}$ have been based on both main reflections and true satellite reflections, measured by synchrotron radiation, which has aided the convergence to physically meaningful parameters.

The obtained coordination chemistry is in good agreement with chemically related compounds, such as the high-T_c superconductor $Bi_2Sr_2CaCu_2O_{8+\epsilon}$ for which a variety of structural models has been presented in the literature. The compound has a modulated crystal structure and is structurally and chemically related to (1) and (2). An ongoing discussion is whether it should be described in a centrosymmetric or noncentrosymmetric superspace group. This has particular importance for the description of the Bi site, which is difficult to model. Most structural models have very similar interatomic distances for Sr—O, Ca—O and Cu—O, respectively (Ruyter, Grebille, Leligny & Labbe, 1995, and references therein). The single crystal studies, except one, all agree that Ca—O distances are slightly shorter than Sr—O distances. The Sr is coordinated to 12 O atoms, while Ca is coordinated to 8 O atoms in a distorted cubic arrangement. However, Sr may be found on Ca sites. The distance ranges are for the centrosymmetric refinement Sr—O from 2.41 to 3.33 Å and for Ca—O from 2.30 to 2.71 Å (Ruyter, Grebille, Leligny & Labbe, 1995), while in the noncentrosymmetric refinement Petříček, Gao, Lee & Coppens (1990) obtain ranges from 2.30 to 3.42 Å for Sr—O and from 2.23 to 2.75 Å for Ca—O. The refinements in centrosymmetric superspace groups generally give shorter ranges of distances, as is the case in the present work as well. In the modulated compound $Bi_{2.08}Sr_{1.84}CuO_{6-\epsilon}$, which is nonsuperconducting and where Bi is four-coordinated, Bi—O distances range from 2.06 to 2.83 Å, which is similar to distances in nonmodulated compounds of 2.10–2.46 Å in β-Bi_2O_3 and 2.06–2.49 Å in $BaBiO_{2.5}$ (Leligny, Durcok, Labbe, Ledesert & Raveau, 1992, and references therein). As with our compound, Bi is found on the Sr sites (8%) in $Bi_{2.08}Sr_{1.84}CuO_{6-\epsilon}$, but with occupational modulation. The Sr—O distances in this compound fall into two groups, six bonds have distances ranging from 2.35 to 2.85 Å, while the remaining two distances range from 2.55 to 3.45 Å. For Sr_2CuO_3 and $SrCuO_2$, where in both compounds Sr is coordinated by seven O atoms, the Sr—O distances range from 2.50 to 2.65 Å. The ranges of distances observed for Sr—O and Bi—O are therefore large, but with Bi—O preferentially shorter. For $[(Bi_{0.04}Sr_{0.96})_2Cu_2O_3]_7[CuO_2]_{10}$ the range of distances, from 2.462 (4) to 2.678 (5) Å for the Sr/Bi site, is much smaller, disregarding the upper limit for the interlattice contact and no clear allocation of Bi-dense and Bi-dilute regions can be made.

The Cu—O distances are in the range 1.860 (5)–1.99 (3) Å. For high-T_c cuprates with nonmodulated crystal structures, such as $YBa_2Cu_4O_8$, which have copper oxide sheets identical to the Cu_2O_3 sheet, the in-layer Cu—O distances are in the range 1.83–1.94 Å, while for the pyramidal coordination of Cu by O, the in-sheet distances are 1.92–1.95 Å and the apical oxygen distances were 2.28 and 2.39 Å (Bordet *et al.*, 1988). For $Bi_2Sr_2CaCu_2O_{8+\delta}$ the Cu is coordinated to four oxygens in the sheet and one apical oxygen. Literature values for the Cu—O distances range from 1.78 to 2.06 Å (except one reference) for the sheet O atoms and longer for the apical oxygen, from 2.21 to 2.86 Å [except two references (Ruyter, Grebille, Leligny & Labbe, 1995, and references therein)]. For Sr_2CuO_3 (with idealized corner-sharing CuO_4 squares) and $SrCuO_2$ (with a double row of edge-sharing CuO_4 squares in a zigzag pattern), the Cu—O distances are in the range 1.89–1.96 Å (Teske & Müller-Buschbaum, 1970).

Note added in proof. A compound in this family, $[Sr_{2-x}Ca_xCu_2O_3]_{7+\delta}[CuO_2]_{10}$, x = 1.94, has recently been reported superconducting under pressures of 3 and 4.5 GPa with transition temperatures of 12 and 9 K, respectively (Maekawa, 1996, and references therein).

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