

# The Four-Dimensional, Incommensurately Modulated, Composite Crystal Structure of $(\text{Bi, Sr, Ca})_{10}\text{Cu}_{17}\text{O}_{29}$ at 292 and 20 K Refined Including Satellite Reflections

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The compound  $\text{M}_{10}\text{Cu}_{17}\text{O}_{29}$  with  $\text{M} = \text{Bi}_{0.06}\text{Sr}_{0.39}\text{Ca}_{0.55}$  has been shown to have a composite structure consisting of two interpenetrating, modulated sublattices. One substructure is a sandwich. Adjacent layers are  $\text{Cu}_2\text{O}_3$  sheets extending in the *ac*-plane, and Bi, Sr and Ca atoms, which are statistically distributed over one atomic site. The other substructure is interleaved between the layers of metal atoms and consists of  $\text{CuO}_2$  ribbons extending along the *c*-axis. Both substructures are orthorhombic, with the same *a*- and *b*-axis values, but different and mutually incommensurate *c*-axis values, which accounts for the modulation. First-order satellite reflections are observed. The structure is described and refined in a four-dimensional formalism taking into account measured first-order satellite reflections. All atoms exhibit significant modulation amplitudes in particular along the *b*- and *c*-axes. Atoms in the  $\text{CuO}_2$  ribbons have relatively large mean-square amplitudes along the ribbon axis, which supports a model of modulated ribbons with some phase disorder of the longitudinal modulation waves. Interatomic distances are calculated considering the effect of modulation.

In syntheses aimed at obtaining the superconducting phases of the Bi-Sr-Ca-Cu oxide system a byproduct of dark, shiny, needle-shaped, semiconducting crystals of approximate composition  $(\text{Bi, Sr, Ca})_{10}\text{Cu}_{17}\text{O}_{29}$  formed.  $\text{M}_{10}\text{Cu}_{17}\text{O}_{29}$  (sometimes described by the composition  $\text{M}_{14}\text{Cu}_{24}\text{O}_{41}$ ) is a commonly observed phase in the syntheses of ternary and quaternary copper oxides. A number of structure determinations of this phase have appeared in the literature.<sup>1–3</sup> The structure is a composite consisting of two interpenetrating orthorhombic lattices, which have identical values for their *a*- and *b*-axes, but incommensurate *c*-axes. The two parts both contain copper atoms linked by oxygen atoms in an approximately square planar coordination forming parallel layers. It is a characteristic of this structure that the square planar Cu-coordination polyhedra are connected by edge-sharing. In one sublattice the copper–oxygen squares are joined at neighbouring edges to form ladders with Cu–Cu zig-zag chains, and the fourth oxygen of the copper–oxygen

squares connect these ladders by corner-sharing resulting in two-dimensional sheets of composition  $\text{Cu}_2\text{O}_3$  (Fig. 1a). Layers of statistically disordered Bi, Sr and Ca atoms on one crystallographic site (Fig. 1b) are accommodated on each side of the  $\text{Cu}_2\text{O}_3$  sheet. The metal and the  $\text{Cu}_2\text{O}_3$  layers make up one lattice of the composite structure which at 292 K has cell constants  $a = 11.382(2)$ ,  $b = 12.959(3)$ ,  $c_s = 3.9155(5)$  Å. The other sublattice of the composite structure consists of ribbons of composition  $\text{CuO}_2$ , shown as Fig. 1c. Opposite edges of the copper–oxygen coordination polyhedra are shared forming ribbons extending in the  $[001]$  direction, giving a *c*-axis length,  $c_7 = 2.7522(4)$  Å. Neighbouring ribbons are not interconnected by any bonding contacts, but form a layer of composition  $\text{CuO}_2$  which is sandwiched between the previously mentioned layers of metal atoms in such a way that the *a*- and *b*-axis lengths become identical for the two parts of the composite structure.

The composite character of the crystal structure is apparent on close inspection of diffraction photographs. At first sight, reflections seem to conform to an orthorhombic cell with  $a = 11.38$ ,  $b = 12.96$ , and  $c = 19.4$  Å. This interpretation, however, corresponds to a very peculiar intensity distribution with strong intensities

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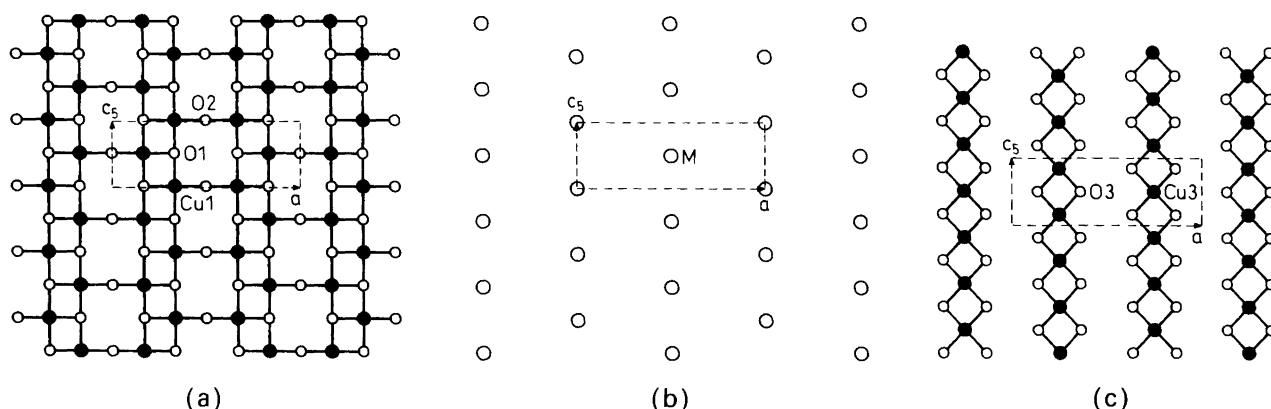


Fig. 1. (a) The  $\text{Cu}_2\text{O}_3$  sheet at  $\gamma=0$  of  $\text{M}_{10}\text{Cu}_{17}\text{O}_{29}$ . The stacking direction of the layers is along the  $b$ -axis perpendicular to the plane. Filled circles are copper atoms, open circles are oxygen atoms. The box in broken lines indicates the unit cell of the  $\text{M}_2\text{Cu}_2\text{O}_3$  sublattice of the composite structure. (b) The layer of metal atoms at  $\gamma=0.13$  of  $\text{M}_{10}\text{Cu}_{17}\text{O}_{29}$ . The box in broken lines indicates the same unit cell as shown in (a). (c) The  $\text{CuO}_2$  ribbons at  $\gamma=1/4$  of  $\text{M}_{10}\text{Cu}_{17}\text{O}_{29}$ . Filled circles are copper atoms, open circles are oxygen atoms. The box in broken lines indicates the same unit cell as shown in (a) and (b).

for  $l=5n$  and a set of weaker intensities for  $l=7n$ , while other intensities—outside these layers in reciprocal space are almost completely missing or at best extremely weak. The two sets of reflections do not have identical  $c$ -axis lengths, but should rather be described by individual and incommensurate  $c$ -axes lengths,  $c_5 = 3.9155(5) \text{ \AA}$  ( $\approx 19.4/5 \text{ \AA}$ ) and  $c_7 = 2.7522(4) \text{ \AA}$  ( $\approx 19.4/7 \text{ \AA}$ ). Each substructure can be solved and refined using only reflections from the respective individual sub-sets of the reflections.  $hk0$  reflections which have contributions from both cells must be excluded from the refinements of the separate substructures.

Kato *et al.*<sup>1</sup> refined the composite structure in a supercell description, i.e. a commensurate approximation, using the combined set of main reflections, i.e. reflections with  $l=5n$  and  $l=7n$ . Later on Kato<sup>4</sup> refined the composite structure in a four-dimensional description according to the formalism of Janner and Janssen<sup>5</sup> still using only the set of main reflections. However, both the supercell and the composite refinements gave unsatisfactory descriptions of the atomic thermal displacements; notably some of the atoms appeared very anisotropic and some had non-positive definite displacement ellipsoids. Electron diffraction studies of this composite structure<sup>6,7</sup> have been interpreted to show initial phase disorder of the  $\text{CuO}_2$  ribbon sublattice, while the  $\text{M}_2\text{Cu}_2\text{O}_3$  sublattice is phase ordered.

One sublattice of the composite structure is influenced by the other. This may result in a modulation of the atomic positions giving satellite reflections in the diffraction pattern. The very faint intensities with  $l \neq 5n$  and  $l \neq 7n$  as expressed in the super-cell description, which were observed in photographs of long exposure, should be explained as such satellite reflections. In this study selected first-order satellite intensities were measured on a diffractometer using counting times of 75 min per reflection, as opposed to 2–4 min per reflection for main reflections, and the former were included with the main reflection

intensities in a refinement of the incommensurately modulated structure of  $(\text{Bi,Sr,Ca})_{10}\text{Cu}_{17}\text{O}_{29}$ . Intensities were collected at both 292 and 20 K in order to get a basis for assessing if displacement parameters have major contributions from sources other than atomic thermal motion.

## Experimental

Needle-shaped crystals were obtained by heat treatment at 920–950°C of a precalcined powder based on  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  in the molar ratios 1:1:1:2. The crystal used for data collection is bounded by  $\{100\}$ ,  $\{010\}$  and  $\{001\}$  planes and has the dimensions 0.044, 0.027 and 0.24 mm along  $[100]$ ,  $[010]$  and  $[001]$ . X-Ray fluorescence measurements showed a Bi and Sr content in the approximate atomic ratio 1:7. The structure solution indicates that Bi, Sr and Ca are statistically distributed over the same site and refinement of occupation parameters gives the formula  $\text{M}_{10}\text{Cu}_{17}\text{O}_{29}$  with  $\text{M} = \text{Bi}_{0.06}\text{Sr}_{0.39}\text{Ca}_{0.55}$ . The absorption coefficient,  $\mu = 245 \text{ cm}^{-1}$ , was calculated according to this formula. A HUBER four-circle diffractometer, Eulerian cradle, type 512, was used for data collection with graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). In the low-temperature data collection the crystal was cooled in a two-stage closed-cycle helium cryostat, a modified Displex CS201 (manufactured by Intermagnetics General Corp.) mounted on the Huber four-circle diffractometer.<sup>8</sup> Experimental information is given in Table 1.

The intensities were corrected for absorption, polarization and Lorentz effects. The structure of each part of the composite cell was determined from Patterson syntheses disregarding the common layer of reflections with  $l=0$ . Refining the structures of the sublattices according to  $Fm\bar{3}m$  symmetry and using atomic scattering factors from Ref. 9 the results conformed closely with those of

Table 1. Crystallographic data for sub-structures of  $\text{Bi}_{0.6}\text{Sr}_{3.9}\text{Ca}_{5.5}\text{Cu}_{17}\text{O}_{29}$ .

Temperature/K	20	20	292	292
Composition	$\text{M}_2\text{Cu}_2\text{O}_3$	$\text{CuO}_2$	$\text{M}_2\text{Cu}_2\text{O}_3$	$\text{CuO}_2$
Space group	<i>Fmmm</i>	<i>F222</i>	<i>Fmmm</i>	<i>F222</i>
<i>a</i> /Å	11.3687(8)	11.3773(10)	11.3819(15)	11.3788(13)
<i>b</i> /Å	12.9135(9)	12.919(3)	12.959(3)	12.961(2)
<i>c</i> /Å	3.9101(4)	2.7483(4)	3.9155(5)	2.7522(4)
Approximate supercell	$5 \times c$	$7 \times c$	$5 \times c$	$7 \times c$
<i>c<sub>s</sub></i> /Å	19.55	19.24	19.58	19.27
Volume/Å <sup>3</sup>	574.04(14)	403.95(19)	577.5(3)	405.90(17)
No. of centered reflections, in range	32, $2\theta > 40^\circ$	24, $2\theta > 35^\circ$	29, $2\theta > 38^\circ$	38, $2\theta > 30^\circ$
Steps/scan, time/step(s)	50, 2	50, 4	75, 2	75, 4
Scan mode	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
$\theta$ range scanned/ $^\circ$	1-60	1-60	1-60	1-40
Scan width ( $\Delta\omega$ )	$1.05 + 0.4 \tan \theta$	$1.05 + 0.4 \tan \theta$	$1.05 + 0.4 \tan \theta$	$1.05 + 0.4 \tan \theta$
Range of indices	<i>h</i> : 0 → 26 <i>k</i> : 0 → 29 <i>l</i> : 0 → 3 and 6 → 8	<i>h</i> : 0 → 25 <i>k</i> : 0 → 29 <i>l</i> : 1 → 5	<i>h</i> : 0 → 27 <i>k</i> : 0 → 31 <i>l</i> : 0 → 7	<i>h</i> : 0 → 19 <i>k</i> : 0 → 21 <i>l</i> : 1 → 4
Standard reflections (every 50 measurements)	(6 0 0) (0 4 0)	(6 0 0) (0 4 0)	(6 0 0) (0 4 0) (0 0 2)	(6 0 0) (0 4 0) (0 0 2)
Transmission factors				
Min.	0.23	0.29	0.30	0.29
Max.	0.51	0.53	0.54	0.51
Unique reflections	753	596	1090	282
No. of reflections with $I > 3\sigma(I)$	308	230	349	154
No. of variables	16	12	16	12
Agreement factors (%),				
$R_F = \Sigma( F_o  -  F_c ) / \Sigma  F_o $	6.2	11.2	7.0	10.0
$wR = \{ \Sigma [w( F_o  -  F_c )^2] / \Sigma w  F_o ^2 \}^{1/2}$ (%)	7.6	12.2	8.0	11.3
$S = [ \Sigma w ( F_o  -  F_c )^2 / (N_o - N_v) ]^{1/2}$	1.932	2.930	1.831	2.684
Max. (shift/ $\sigma$ ) in final cycle	$2.4 \times 10^{-3}$	$3.7 \times 10^{-4}$	$3.3 \times 10^{-3}$	$3.6 \times 10^{-4}$

$N_o$  = no. of observations,  $N_v$  = no. of variables,  $w = \text{weight}$ ,  $w = \sigma(F)^{-2}$ ,  $\sigma(F) = [\sigma(F^2)_{\text{cts}} + 1.03 \cdot F_o^2]^{1/2} - |F_o|$ .

Table 2. Parameters from refinement of substructures.

Atom:	$\text{M}_2\text{Cu}_2\text{O}_3$ sublattice, <i>Fmmm</i>				$\text{CuO}_2$ sublattice, <i>F222</i>		
	Cu1	O1	O2	M	Cu3	O3	M'
292 K							
Occupation	1/4	1/4	1/8	1/4	1/4	1/2	0.036(4)
<i>x</i>	0.33406(8)	0.1678(8)	0	0	1/4	0.6362(14)	0.482(3)
<i>y</i>	0	0	0	0.13013(15)	1/4	1/4	0.368(3)
<i>z</i>	0	0	1/2	0	1/4	1/4	1/4
<i>u</i> <sub>11</sub>	0.0035(5)	0.007(3)	0.002(4)	0.0131(8)	0.0071(12)	0.016(7)	0.013(0)
<i>u</i> <sub>22</sub>	0.0236(10)	0.020(5)	0.036(10)	0.0137(7)	0.0165(16)	0.10(3)	0.013(0)
<i>u</i> <sub>33</sub>	0.0020(7)	0.006(4)	0.009(6)	0.0100(6)	0.033(2)	0.034(9)	0.013(0)
20 K							
Occupation	1/4	1/4	1/8	1/4	1/4	1/2	0.041(4)
<i>x</i>	0.33403(12)	0.1680(7)	0	0	1/4	0.6368(11)	0.482(2)
<i>y</i>	0	0	0	0.13022(14)	1/4	1/4	0.372(2)
<i>z</i>	0	0	1/2	0	1/4	1/4	1/4
<i>u</i> <sub>11</sub>	0.0021(6)	0.003(3)	0.004(4)	0.0078(6)	0.0015(7)	0.011(5)	0.011(0)
<i>u</i> <sub>22</sub>	0.0251(9)	0.033(6)	0.033(8)	0.0154(7)	0.0086(10)	0.074(17)	0.011(0)
<i>u</i> <sub>33</sub>	0.0025(7)	-0.001(4)	0.003(5)	0.0108(6)	0.0350(19)	0.035(7)	0.011(0)

The M' entry in the  $\text{CuO}_2$  sublattice is a metal contribution which was necessary for the refinement. Obviously it is an influence from the M content of the  $\text{M}_2\text{Cu}_2\text{O}_3$  sublattice.  $M = M' = \text{Bi}_{0.06}\text{Sr}_{0.39}\text{Ca}_{0.55}$ .

McCarron *et al.*<sup>2</sup> However, an origin shift of (1/4,1/4,1/4) for sublattice 1 (the CuO<sub>2</sub> ribbons) was indicated by residual peaks of Cu atoms from the other sublattice in the difference Fourier synthesis and this shows the true space group to be *F222*, rather than *Fmmm*. Information on the final refinements is given in Table 1. Atomic fractional coordinates and displacement parameters are given in Table 2. A small amount of M was found to contribute to the scattering of sublattice 1, and was included in the refinement. Apparently a small fraction of the M atoms have a periodicity related to that of sublattice 1. The position and occupancies of this site are listed in Table 2 under M'. The agreement factors for sublattice 1 are noticeably higher than for the second sublattice. A difference Fourier synthesis for sublattice 1 showed a residual density of 0.72 e Å<sup>-3</sup> close to the position of Cu 1 from sublattice 2. A difference synthesis for sublattice 2 showed the largest residual of 0.54 e Å<sup>-3</sup> in the neighbourhood of Cu 3 of sublattice 1. All remaining residual densities were less than 0.2 e Å<sup>-3</sup> for both sublattices. Since the main reflections of one sublattice are satellite reflections of the other sublattice, they contain a scattering contribution from both sublattices. However, no attempt was made to refine these residuals as atoms, since such interactions are better explained in the composite, modulated structure. The reason for the poorer agreement factors for sublattice 1 is presumably in part due to the larger residual and in part due to an initial phase disorder evident in electron microscopy studies of this sublattice. The layers of the M<sub>2</sub>Cu<sub>2</sub>O<sub>3</sub> sublattice (from  $l=5n$  reflections) are represented in Figs. 1a and 1b, while the layer of the CuO<sub>2</sub> sublattice (from  $l=7n$  reflections) is shown in Fig. 1c. In the composite structure these layers are stacked along *b* in the sequence a b c b a b c b a, which means that the formula of the structure may be written (M<sub>2</sub>Cu<sub>2</sub>O<sub>3</sub>)<sub>5</sub>(CuO<sub>2</sub>)<sub>7+δ</sub>.

## Theory

*Four-dimensional formalism.* (M<sub>2</sub>Cu<sub>2</sub>O<sub>3</sub>)<sub>5</sub>(CuO<sub>2</sub>)<sub>7+δ</sub> is a composite structure of two lattices with a common *hk0* reciprocal plane, i.e.  $\mathbf{a}_5^* = \mathbf{a}_7^*$  and  $\mathbf{b}_5^* = \mathbf{b}_7^*$  while  $\mathbf{c}_5^* \neq \mathbf{c}_7^*$ . Lattice points in this case may be described by four indices. The CuO<sub>2</sub> sublattice is represented by the indices *HKL0*, while the indices of the M<sub>2</sub>Cu<sub>2</sub>O<sub>3</sub> sublattice are given by *HK0M*. The reciprocal plane with indices *HK00* is common for the two sublattices. Reflections with all indices non-zero are the pure satellite reflections.

The symmetry operations of a modulated, composite crystal are described in a superspace group, which can be determined from systematic absences.<sup>10</sup> In order to re-establish periodicity for the description, a superspace<sup>5</sup> is defined, which is spanned by physical space,  $\mathbf{R}_3$  and a so-called internal (non-physical) space, which here is one-dimensional and spanned by  $\mathbf{e}_4$ . The internal space is perpendicular to  $\mathbf{R}_3$ . The crystal structure is then solved in superspace. The basis vectors in four-dimensional reciprocal superspace are given by expression (1),

$$(\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}_7^*, \mathbf{c}_5^* + \mathbf{e}_4^*) \quad (1)$$

where  $\mathbf{e}_4^*$  is a unit vector reciprocal to  $\mathbf{e}_4$ . The direct superspace is spanned by basis (2), where  $\gamma = c_7/c_5 = 0.7029$ .

$$(\mathbf{a}, \mathbf{b}, \mathbf{c}_7 - \gamma\mathbf{e}_4, \mathbf{e}_4) \quad (2)$$

The extinction conditions observed for all reflections (*HKLM*) are  $H + K = 2n$ ,  $H + L + M = 2n$ ,  $K + L + M = 2n$ , which means an F-centered, orthorhombic basic lattice. This, combined with the choice of modulation vector, leads to a primitive superspace group of Bravais class  $\mathbf{P}_{111}^{Fmmm}$  and, according to Ref. 10, leaves the choice between superspace groups  $\mathbf{P}_{111}^{Fmmm}$ ,  $\mathbf{P}_{111}^{Fmm2}$  or  $\mathbf{P}_{111}^{F222}$  and various derivatives with different translations in internal space. By trial and error it is found that  $\mathbf{P}_{111}^{F222}$  is the only superspace group which is able to describe the relative positions of the atoms in the two subcells correctly.

The atomic position of atom *v* in the cell at  $\mathbf{n}^i$  in sublattice *i* in a modulated composite crystal is described<sup>11</sup> by eqn. (3), where  $\mathbf{r}_{vi}^0$  is the position of the atom in the

$$\mathbf{r}_{nvi} = \mathbf{r}_{vi}^0 + \mathbf{n}^i + \sum_{j=1}^k \mathbf{u}_{jvi} [j\mathbf{q}_i \cdot (\mathbf{n}^i + \mathbf{g}_i)] \quad (3)$$

average structure (sublattice),  $\mathbf{u}_{jvi}$  are modulation functions with periodicity 1,  $\mathbf{q}_i$  is the modulation vector for sublattice *i* and  $\mathbf{g}_i$  is a phase reference point, which in the atomic displacement model is equal to  $\mathbf{r}_{vi}^0$  and *k* is the order of modulation. The atomic positions of one sublattice is modulated by the *c*-axis periodicity of the other sublattice, i.e. choosing ( $\mathbf{a}, \mathbf{b}, \mathbf{c}_7$ ) as the first sublattice,  $i=1$ ,  $\mathbf{q}_1 = \mathbf{c}_5^*$  and the periodicity of the modulation in sublattice 1 is  $c_5 = 3.92$  Å. Similarly, the modulation period of sublattice 2 is  $c_7 = 2.75$  Å. In eqn. (3) each sublattice is described in its own 3D basis. The symmetry operations in the superspace group are defined on basis (2), where the atoms have coordinates ( $x_1, x_2, x_3, x_4$ ). For an atom in sublattice 1, ( $x_1, x_2, x_3$ ) corresponds to ( $x, y, z$ ) in the sublattice, while  $x_4$  is given by eqn. (4).

$$\begin{aligned} x_4 &= \mathbf{q}_1 \cdot (\mathbf{r}_{v1}^0 + \mathbf{n}^1) = \mathbf{c}_5^* \cdot \mathbf{r}_{v1}^0 + \mathbf{c}_5^* \cdot \mathbf{n}^1 \\ &= \gamma\mathbf{c}_7^* \cdot x_3\mathbf{c}_7 + \gamma\mathbf{c}_7^* \cdot (n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}_7) \\ &= \gamma x_3 + \gamma n_3 = \gamma x_3 + t. \end{aligned} \quad (4)$$

$\gamma x_3$  is the *z*-coordinate defined on sublattice 2, while *t* expresses the non-integer part of the unit cell number  $\mathbf{n}^1$  of sublattice 1 along  $\mathbf{c}_5$ . It is also the coordinate in internal space,  $t\mathbf{e}_4$ . Like ( $x, y, z$ ) in  $\mathbf{R}_3$ , *t* is a number between 0 and 1.

In Fig. 2 the  $\mathbf{c}^*$  values of the approximate super-cell description are compared with those of the more reasonable composite structure description. Satellite reflections appear at positions  $\mathbf{c}^* = L\mathbf{c}_7^* + M\mathbf{c}_5^*$ . Four

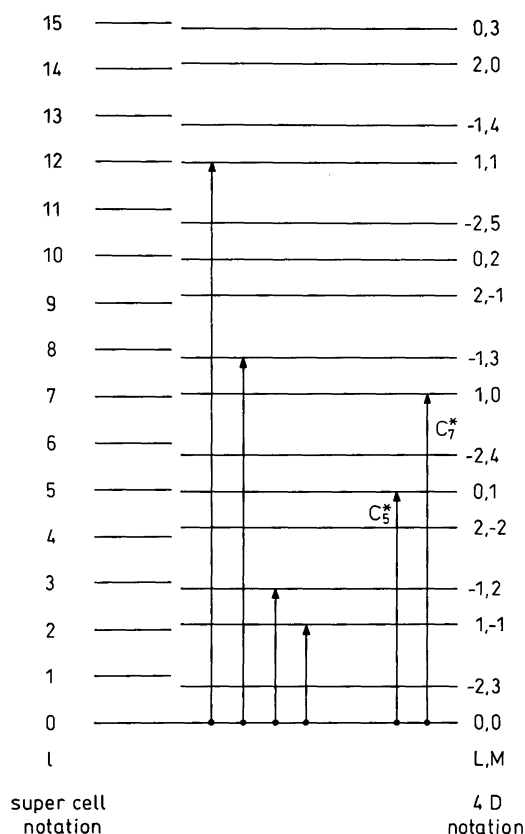


Fig. 2. Stacking of the reciprocal  $a^*b^*$ -layers of the composite cell. The equidistant layer lines of the super cell approximation are shown to the left in the figure for comparison. Four layers of first-order satellite reflections were measured and are indicated by arrows as are the two basic vectors  $c_5^*$  and  $c_7^*$  for the sublattices.

layers of first-order satellite reflections ( $L = \pm 1$ ) for the strong reflections of the  $M_2Cu_2O_3$  sublattice are indicated by arrows. The intensities of these layers were measured as shown in Table 3. 67 of the reflections showed a small but significant intensity of the order of 1–10% relative to the main reflection intensity and peaked at exactly the predicted first-order satellite posi-

tions. Second-order satellites ( $H, K, 2, -2$ ) were also tested for, and only one significant intensity (0,0,2, -2) was found; data collection of second-order satellites was therefore not attempted.

*Composite refinement.* Scattering expressions for incommensurately modulated structures have been given by Petricek and Coppens.<sup>11</sup> The formalism has been extended to composite structures and applied in a new least-squares refinement computer program COMPREF<sup>12</sup> which allows a description of composite crystals in four dimensions, e.g. crystals consisting of two interpenetrating lattices which are incommensurate in one direction. It is restricted to composite structures with a common plane of main reflections for the two lattices and allows refinement of substitutional or displacive modulation. COMPREF has been used for the present refinements of  $(M_2Cu_2O_3)_5(CuO_2)_{7+6}$ .

The modulation of atom  $v$  in unit cell  $n^i$  for modulation vector  $q_i$  is written as a sum of sine and cosine components.<sup>11</sup> For the case of one-dimensional modulation they are written as eqn. (5), where  $j$  is the order of the harmonic and  $U_v^s$  and  $U_v^c$  are three-dimensional vectors

$$u_{jvi} = U_v^s \sin[2\pi j q_i \cdot (r_{vi}^0 + n^i)] + U_v^c \cos[2\pi j q_i \cdot (r_{vi}^0 + n^i)] \quad (5)$$

describing the modulation amplitudes, which are refined in the program together with  $r_{vi}^0$  and thermal parameters.  $U_v^s$  and  $U_v^c$  have to obey symmetry restrictions for atoms on special positions.<sup>13</sup>

Each reflection contains information about both sublattices. A main reflection ( $HKL0$ ), ( $HK0M$ ) is both a main reflection of one sublattice and a satellite reflection of the other sublattice, while a reflection ( $HKLM$ ) with all indices non-zero is a pure satellite,  $M$ th order of sublattice 1 and  $L$ th order of sublattice 2. Therefore, the structure factor expression contains contributions from two scattering processes,<sup>12</sup> and is more than a superposition of the scattering of the component lattices. The structure factor expression is listed in Ref. 12.

Table 3. Satellites, experimental.

$a/\text{\AA}$			11.380(3)	
$b/\text{\AA}$			12.959(5)	
$c/\text{\AA}$	9.2678(9)	6.7822(14)	2.4823(1)	1.6163(9)
$c^*$ satellite	$c_7^* - c_5^*$	$2c_5^* - c_7^*$	$3c_5^* - c_7^*$	$c_5^* + c_7^*$
Four-dimensional space indices	( $HK1-1$ )	( $HK-12$ )	( $HK-13$ )	( $HK11$ )
Supercell indices	( $hk2$ )	( $hk3$ )	( $hk8$ )	( $hk12$ )
$\theta$ range scanned/ $^\circ$	0–30	0–25	0–25	0–25
Temperature/K			292 K	
No. of steps/scan, time/step			75,1 min	
Measured reflections	All	$H+K=2n$	$H+K=2n$	$H+K=2n$
No. of reflections	243	88	79	51
No. of observed reflections	25	21	11	10
Range of indices	$H: 0-15$ $K: 0-18$	$H: 0-13$ $K: 0-14$	$H: 0-12$ $K: 0-14$	$H: 0-11$ $K: 0-12$

## Results and discussion

The composite refinements were carried out in super space group  $P^F_{111}^{222}$ , and different models were tried out. Refinements with only first-order harmonic modulation functions included resulted in a set of plausible thermal vibration parameters, but accounted poorly for the satellite intensities. A model with both first- and second-order harmonics converged towards parameters reported by Kato<sup>4</sup> for a compound of almost the same composition as the presently investigated. Third-order harmonic coefficients were not significant. Finally, a model with first- and second-order harmonic modulation functions was deemed most satisfactory. Refinement results based on this model are given for 292 K in Tables 4 and 5 and for 20 K in Table 6. No phase transitions were observed in the temperature range 292–20 K.

**Thermal parameters.** The conventional least-squares refinements showed M atoms to have nearly isotropic mean-square thermal vibration amplitudes at both room temperature and at low temperature. The values are in line with values found for sandwich layers in high- $T_c$  cuprates, e.g. the Ca layer between  $\text{CuO}_2$  layers in the 2212 Bi-Sr-Ca-Cu-O superconductor.<sup>14</sup>

Copper and oxygen atoms of the  $\text{Cu}_2\text{O}_3$  sheets and the  $\text{CuO}_2$  ribbons appear to have much less isotropic thermal vibration even for the 20 K case. However, for oxygen atoms standard deviations of the mean-square apparent

thermal parameters are so large that general conclusions can hardly be drawn from the conventional refinements. A composite refinement also resulted in significantly anisotropic apparent thermal vibrations for the copper and oxygen atoms. For the  $\text{Cu}_2\text{O}_3$  sheets  $u_{11}$  and  $u_{33}$  for both copper and oxygen are very small and practically identical for all atoms,  $\approx 0.002 \text{ \AA}^2$  (292 K) and  $\approx 0.001 \text{ \AA}^2$  (20 K). These values are comparable in size to mean-square thermal parameters for Cu and O observed in compounds with similar copper oxide layers.<sup>15</sup> For copper and oxygen in the  $\text{CuO}_2$  ribbon  $u_{11} \approx 0.008 \text{ \AA}^2$  (292 K) and  $\approx 0.005 \text{ \AA}^2$  (20 K). The 20 K thermal vibrations are expected to be small and nearly isotropic. The small values of  $u_{11}$  for atoms in the  $\text{CuO}_2$  ribbons and in the  $\text{Cu}_2\text{O}_3$  sheets are therefore interpreted as due to proper atomic thermal vibrations, while the large  $u_{ii}$  values for Cu and O suggests that the modulation model is not entirely capable of accounting for the atomic displacement, which is extraneous to proper atomic thermal vibrations. The magnitude of those  $u_{ii}$ , i.e.  $u_{22}$  for the  $\text{Cu}_2\text{O}_3$  sheet and  $u_{22}$  and  $u_{33}$  for the  $\text{CuO}_2$  ribbon, might be partly attributed to a stacking disorder similar to that of the related superconducting compounds, the Bi-Sr-Ca-Cu oxides, which from electron microscopy studies are known to possess stacking faults. For example, the 2:2:2:3 compound<sup>16</sup> has intergrowth of  $\text{CuO}_2$  layers, giving different repeat periods along the stacking axis.

The relative magnitudes of atomic mean-square thermal vibrations may be understood qualitatively from

Table 4. 292 K parameters from the composite refinement.<sup>a</sup>

Atom:	Cu1 <sup>b</sup>	O1 <sup>b</sup>	O2 <sup>b</sup>	M	Cu3	O3
Occupation	1	1	1/2	1	1/2	1
$x$	0.33409(10)	0.1681(7)	0	0	1/4	0.6363(5)
$y$	0	0	0	0.13005(10)	1/4	1/4
$z$	0	0	1/2	0	1/4	1/4
$u_{11}$	0.0026(4)	0.001(4)	0.002(3)	0.0093(5)	0.0070(5)	0.003(3)
$u_{22}$	0.0204(8)	0.004(8)	0.028(6)	0.0129(5)	0.0190(7)	0.010(4)
$u_{33}$	-0.0010(9)	-0.032(7)	-0.006(10)	0.0088(6)	0.0276(14)	0.024(7)
$u_{12}$	0	0	0	0	0	0
$u_{13}$	0	0	0	0.0(0) <sup>c</sup>	0	0
$u_{23}$	0.0042(17)	-0.009(5)	0	0	0	-0.004(7)
$U_x^s(q)$	0	0	0	0.0601(18)	0	0.11(2)
$U_y^s(q)$	-0.074(2)	-0.050(11)	0	0	0	0
$U_z^s(q)$	-0.045(8)	0.156(10)	0.10(4)	0.003(9)	0	0
$U_x^c(q)$	-0.022(5)	0.084(19)	0	0	0	0
$U_y^c(q)$	0	0	0	-0.035(6)	0	-0.342(11)
$U_z^c(q)$	0	0	0	0	-0.147(13)	0.21(6)
$U_x^s(2q)$	0	0	0	0.00(2)	0	0
$U_y^s(2q)$	0.02(2)	0.18(3)	0	0	0	0.05(2)
$U_z^s(2q)$	0.00(6)	0.05(3)	0.00(2)	0.021(2)	0.019(8)	0.08(3)
$U_x^c(2q)$	0.013(7)	0.07(4)	0	0	0	-0.034(12)
$U_y^c(2q)$	0	0	0	-0.003(5)	0	0
$U_z^c(2q)$	0	0	0	0	0	0

<sup>a</sup>Refinement on main reflections and satellites.  $x$ ,  $y$ ,  $z$  are fractional atomic coordinates. Displacement parameters  $u_{ij}$  are given in  $\text{Å}^2$ .  $U^s$  is the modulation amplitude of the sine-wave and  $U^c$  is the amplitude of the cosine-wave. Modulation amplitudes are given in  $\text{Å}$ . Goodness-of-fit = 1.555. Weight =  $(\sigma_{\text{obs}}^2 + 0.0009F^2)^{-1}$ .  $R(F)$ ,  $R_w(F)$  = 6.27%, 7.23% for 665 reflections.  $R(F)$ ,  $R_w(F)$  = 6.15%, 6.99% for 598 main reflections.  $R(F)$ ,  $R_w(F)$  = 10.0%, 10.4% for 67 satellite reflections. Max shift/esd = 0.0013. <sup>b</sup>Cu1, O1 and O2 have non-positive definite thermal parameters. <sup>c</sup> $Mu_{13}$  fixed to 0.0 in the refinement because of oscillations.

Table 5. 292 K parameters from the composite refinement.<sup>a</sup>

Atom:	Cu1 <sup>b</sup>	O1 <sup>b</sup>	O2 <sup>b</sup>	M	Cu3	O3
Occupation	1	1	1/2	1	1/2	1
x	0.33415(10)	0.1678(7)	0	0	1/4	0.6360(6)
y	0	0	0	0.13010(10)	1/4	1/4
z	0	0	1/2	0	1/4	1/4
u <sub>11</sub>	0.0028(4)	-0.003(4)	0.002(2)	0.0100(5)	0.0065(5)	0.010(5)
u <sub>22</sub>	0.0215(17)	-0.003(10)	0.028(5)	0.0132(8)	0.0186(7)	0.030(8)
u <sub>33</sub>	-0.001(3)	-0.026(8)	-0.018(18)	0.0083(11)	0.0319(17)	-0.008(12)
u <sub>12</sub>	0	0	0	0	0	0
u <sub>13</sub>	0	0	0	0.000(2)	0	0
u <sub>23</sub>	0.003(2)	0.007(5)	0	0	0	-0.005(6)
U <sub>x</sub> <sup>s</sup> (q)	0	0	0	0.049(4)	0	-0.03(6)
U <sub>y</sub> <sup>s</sup> (q)	-0.025(9)	-0.20(3)	0	0	0	0
U <sub>z</sub> <sup>s</sup> (q)	-0.04(3)	0.147(13)	0.14(4)	0.02(2)	0	0
U <sub>x</sub> <sup>c</sup> (q)	-0.01(2)	0.12(2)	0	0	0	0
U <sub>y</sub> <sup>c</sup> (q)	0	0	0	-0.03(2)	0	-0.30(2)
U <sub>z</sub> <sup>c</sup> (q)	0	0	0	0	-0.06(4)	0.38(5)
U <sub>x</sub> <sup>s</sup> (2q)	0	0	0	-0.00(3)	0	0
U <sub>y</sub> <sup>s</sup> (2q)	0.04(4)	0.09(5)	0	0	0	0.09(5)
U <sub>z</sub> <sup>s</sup> (2q)	0.016(9)	-0.03(3)	0.02(3)	0.022(3)	0.035(9)	-0.01(4)
U <sub>x</sub> <sup>c</sup> (2q)	-0.011(9)	-0.05(4)	0	0	0	-0.07(3)
U <sub>y</sub> <sup>c</sup> (2q)	0	0	0	-0.006(6)	0	0
U <sub>z</sub> <sup>c</sup> (2q)	0	0	0	0	0	0

<sup>a</sup>Refinement on main reflections only. Unless otherwise stated, the refinement is as in Table 4. Goodness-of-fit = 1.480.  $R(F)$ ,  $R_w(F)$  = 5.99%, 6.68% for 598 main reflections. Max sift/e.s.d. = 0.0008. <sup>b</sup>Cu1, O1, O2 and O3 have non-positive definite thermal parameters.

Table 6. 20 K parameters from the composite refinement.<sup>a</sup>

Atom:	Cu1	O1 <sup>b</sup>	O2	M	Cu3	O3
Occupation	1	1	1/2	1	1/2	1
x	0.33406(10)	0.1676(5)	0	0	1/4	0.6372(5)
y	0	0	0	0.12997(10)	1/4	1/4
z	0	0	1/2	0	1/4	1/4
u <sub>11</sub>	0.0007(4)	-0.011(4)	0.001(3)	0.0059(4)	0.0038(4)	0.005(2)
u <sub>22</sub>	0.0203(7)	-0.019(3)	0.025(5)	0.0107(9)	0.0155(6)	0.032(8)
u <sub>33</sub>	0.0011(6)	-0.013(6)	0.006(4)	0.0071(16)	0.033(3)	0.042(6)
u <sub>12</sub>	0	0	0	0	0	0
u <sub>13</sub>	0	0	0	0.000(2)	0	0
u <sub>23</sub>	0.0(0) <sup>c</sup>	0.004(2)	0	0	0	-0.030(14)
U <sub>x</sub> <sup>s</sup> (q)	0	0	0	0.049(3)	0	-0.02(6)
U <sub>y</sub> <sup>s</sup> (q)	-0.079(6)	0.08(2)	0	0	0	0
U <sub>z</sub> <sup>s</sup> (q)	-0.011(19)	-0.053(19)	0.0(0) <sup>d</sup>	-0.047(14)	0	0
U <sub>x</sub> <sup>c</sup> (q)	-0.000(15)	-0.058(16)	0	0	0	0
U <sub>y</sub> <sup>c</sup> (q)	0	0	0	0.086(9)	0	-0.28(2)
U <sub>z</sub> <sup>c</sup> (q)	0	0	0	0	-0.13(4)	0.07(9)
U <sub>x</sub> <sup>s</sup> (2q)	0	0	0	-0.001(10)	0	0
U <sub>y</sub> <sup>s</sup> (2q)	-0.001(16)	0.242(8)	0	0	0	0.01(8)
U <sub>z</sub> <sup>s</sup> (2q)	-0.017(4)	0.095(17)	0.000(17)	0.023(3)	0.035(10)	0.05(4)
U <sub>x</sub> <sup>c</sup> (2q)	-0.027(7)	-0.139(19)	0	0	0	-0.00(2)
U <sub>y</sub> <sup>c</sup> (2q)	0	0	0	-0.007(6)	0	0
U <sub>z</sub> <sup>c</sup> (2q)	0	0	0	0	0	0

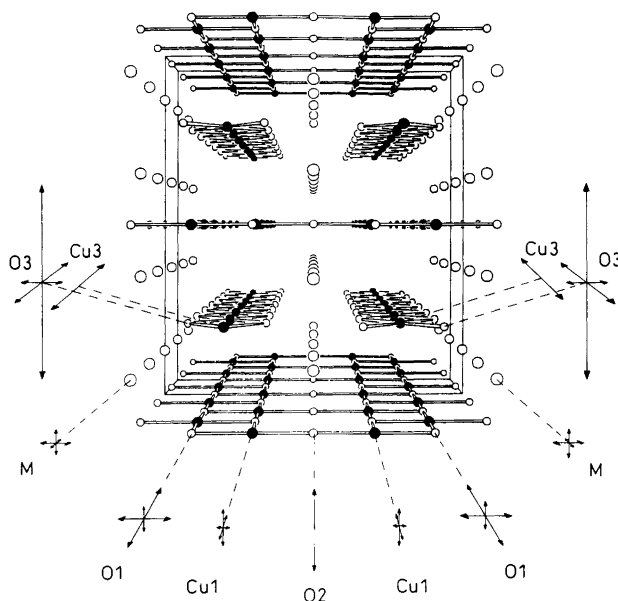
<sup>a</sup>Refinement on main reflections only. Unless otherwise stated, the refinement is as in Table 4. Goodness-of-fit = 1.644.  $R(F)$ ,  $R_w(F)$  = 6.35%, 7.13% for 629 main reflections. Max sift/e.s.d. = 0.0113. <sup>b</sup>O1 has non-positive definite thermal parameters. <sup>c</sup>Cu1  $u_{23}$  fixed to 0.0 because of oscillations in the refinement. <sup>d</sup>O2  $u_z^s$  (1 harm.) fixed to 0.0 because of oscillations in the refinement.

interactions in the structure. The  $\text{Cu}_2\text{O}_3$  sheets have strong interatomic bonding extending in the entire  $ac$ -plane which explains that both  $u_{11}$  and  $u_{33}$  are practically identical and small for Cu 1, O1, and O2. Weaker inter-layer connections allow bigger values for  $u_{22}$ . The  $\text{CuO}_2$  ribbon atoms have relatively larger apparent thermal parameters, particularly in the  $b$ - and  $c$ -directions. The ribbons are potentially easier movable than the sheets because of the lack of short bonding interactions between neighbouring  $\text{CuO}_2$  ribbons. Lateral restrictions of the ribbon movement come from interaction between the ribbon and the sheets of atoms in the  $\text{M}_2\text{Cu}_2\text{O}_3$  part of the structure, in particular the Bi-Sr-Ca atoms.

In the longitudinal direction of the  $\text{CuO}_2$  ribbons there is a mismatch relative to the  $\text{Cu}_2\text{O}_3$  sheet as evidenced in the incommensurability of  $c_5$  and  $c_7$ . Systematic modulations are the result but possibly also some disordered misplacements of the  $\text{CuO}_2$  ribbons relative to the  $\text{M}_2\text{Cu}_2\text{O}_3$  part of the structure. The large values of  $u_{33}$  for Cu3 and O3 indicate that the apparent thermal parameter may include an additional contribution from disorder in the  $c$ -axis direction.

**Modulation parameters.** Satellite reflections were only collected at room temperature. Even so, the modulation parameters determined by refinements based on only the 20 K main reflections have values not significantly different from the 292 K values, which are based on refinements of both main and satellite reflections. This is because main reflections include a contribution from modulation as previously explained. Standard deviations on the 20 K modulation parameters are generally much bigger than those of the 292 K refinement and will not be mentioned further.

The incommensurability of  $c_5$  and  $c_7$  results in sizable (between 0.05 and 0.20 Å) modulations along  $c$  for all atoms. Most atoms also have significant modulation amplitudes along the  $a$ - and  $b$ -directions. The modulation in the  $c$ -direction (Table 4) is largest for sublattice 1, the  $\text{CuO}_2$  ribbons. This is evident from comparing modulations of Cu3 vs. Cu1. The oxygen atoms have the same magnitude of modulation in this direction. Comparing the  $b$ -axis modulation for the oxygens, however, clearly shows that O3 and therefore the ribbons have the largest modulation amplitude. For symmetry reasons, Cu3 is not allowed a modulation amplitude in this direction. The apparent thermal parameter for Cu3  $u_{33}$  and O3  $u_{22}$  are seen to diminish considerably by introduction of modulation from comparison of Tables 2 and 4. By far the largest modulation, however, is that of O3 along the  $b$ -axis direction,  $U_y^c = -0.34(1)$  Å, i.e. the O3 atom may move significantly out of the  $ac$ -plane in order to relieve stress incurred from the modulation in the  $c$ -axis direction. This displacement is much bigger than the amplitude due to atomic 'thermal' displacement,  $u_{22}^{1/2} = 0.10(2)$  Å, while for all other atoms modulation amplitudes are of comparable size to the atomic 'thermal' displacements. The order of magnitude of  $U_y^c$  is comparable with modulations found



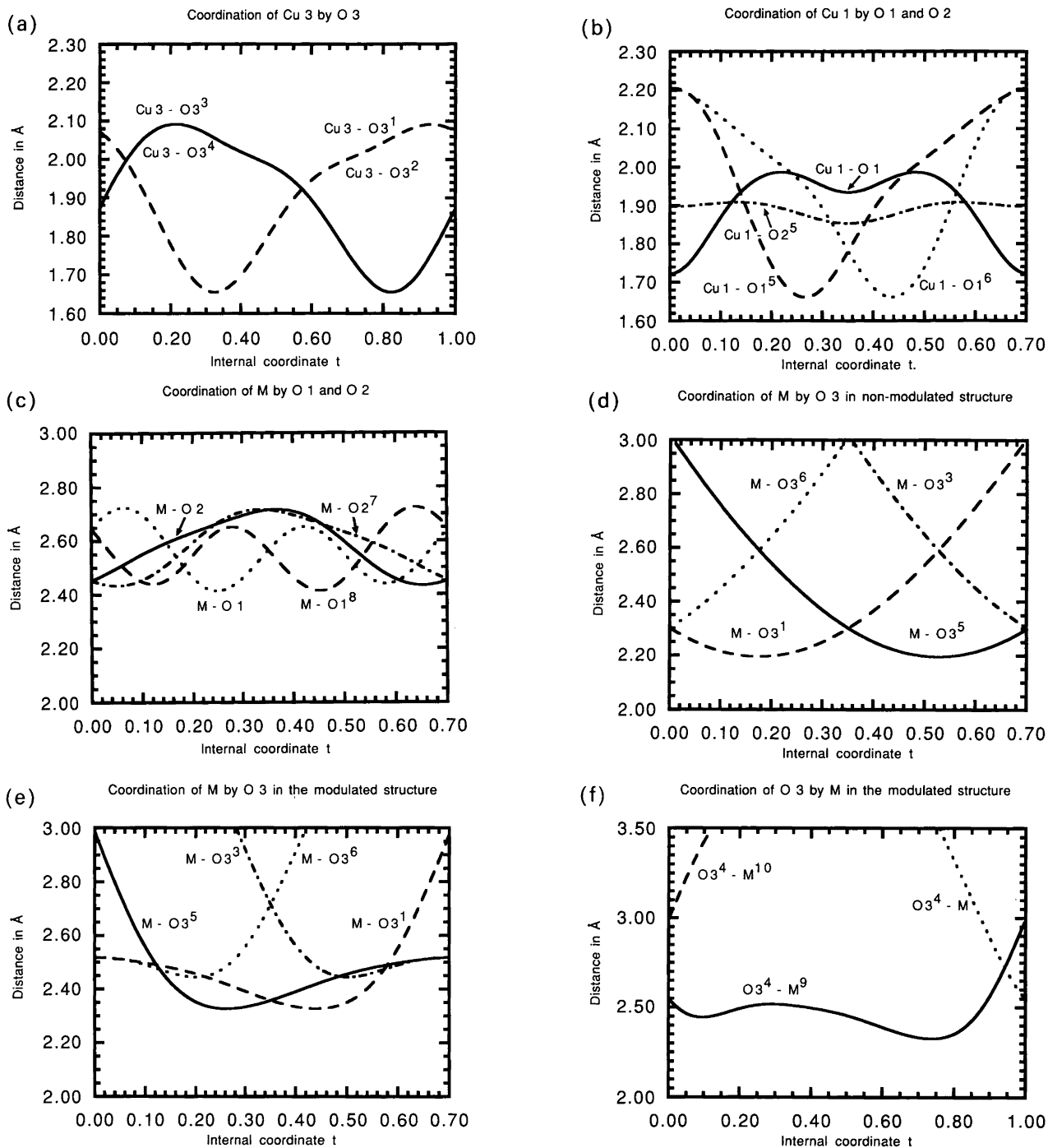
**Fig. 3.** The composite structure of  $\text{M}_{10}\text{Cu}_{17}\text{O}_{29}$  viewed down the  $c$ -axis. The  $b$ -axis is in the vertical direction. Filled circles are copper atoms. Oxygen atoms are denoted by small and M atoms by large open circles. The  $\text{Cu}_2\text{O}_3$  sheets are at  $y=1/2$ . The M atoms are in columns between the  $\text{Cu}_2\text{O}_3$  sheets and the  $\text{CuO}_2$  ribbons at  $y=1/4, 3/4$ . The arrows shown at the periphery of the drawing represent the amplitudes of modulation enlarged by a factor 200 and so indicate the relative sizes of the atomic modulation amplitudes.

in the 2:2:1:2 Bi-Sr-Ca-Cu-O superconductor.<sup>14</sup> Fig. 3 depicts the composite structure viewed down the  $c$ -axis. The significant modulations are indicated as vectors.

Our interpretation of the temperature factors having a contribution from additional disorder is supported by two recent electron diffraction studies<sup>6,7</sup> of  $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ . Both observe that the reflections from the  $\text{CuO}_2$  sublattice are streaked in a direction perpendicular to  $c^*$ . Milat *et al.*<sup>6</sup> also observe that the satellite reflections have the same features. Wu *et al.*<sup>7</sup> interpret this streaking as being due to 'initial phase disorder' in the  $\text{CuO}_2$  ribbons, which means that neighbouring ribbons, considered as rigid bodies, are displaced relative to each other along the  $c$ -axis direction. Milat *et al.*<sup>6</sup> in high-resolution electron diffraction images directly observed that relative positions of atoms in the  $\text{Cu}_2\text{O}_3$  sheets and  $\text{CuO}_2$  ribbons may differ over the image. They interpret the streaks in the electron diffraction patterns as caused by longitudinally modulated ribbons of  $\text{CuO}_2$ , where phases of the longitudinal modulation waves in neighbouring ribbons are disordered. Only small atomic displacements are sufficient to cause an appreciable change in the phase. This disordered longitudinal modulation wave model accounts for both satellite reflections and streaks in the electron diffraction pattern, and is in accordance with our observation of the relatively high value of  $u_{33}$  for atoms in the  $\text{CuO}_2$  ribbon.

A composite refinement based on the room tem-





**Fig. 4.** (a) Cu3 to O3 distances (in Å) over one full modulation period given as a function of the internal coordinate  $t$ . For symmetry reasons, the Cu3 to O3 distances are pairwise identical. O3<sup>*i*</sup> means the atom obtained by symmetry operation  $i$  on the atom O3 from Table 4. The symmetry operations in the composite crystal are four-dimensional, but for simplicity the corresponding three-dimensional ones are listed, since these are sufficient for the present purpose. The symmetry operations used are: (1)  $(x-1/2; y, z-1/2)$ , (2)  $(1-x, y, -z)$ , (3)  $(x-1/2, y, z+1/2)$ , (4)  $(1-x, y, 1-z)$ , (5)  $(1/2-x, y, 1/2-z)$ , (6)  $(1/2-x, y, -1/2-z)$ , (7)  $(x, y, z-1)$ , (8)  $(-x, y, -z)$ , (9)  $(x, y, z+1)$ , (10)  $(x, y, z+2)$ . (b) Distances (in Å) from Cu1 to the surrounding three O1 atoms and the one O2 atom given as a function of the internal coordinate  $t$  for one modulation period. Symmetry operations as for (a). (c) Distances (in Å) from M to bonded oxygen atoms O1 and O2 in sublattice 2 given as a function of the internal coordinate  $t$  for a full modulation period. Symmetry operations as for (a). (d) Distances (in Å) from M (in sublattice 2) to oxygen atoms O3 in sublattice 1 for the composite non-modulated structure given as a function of the internal coordinate  $t$  for a full modulation period. Symmetry operations as for (a). (e) Distances (in Å) from M to oxygen atoms O3 in sublattice 1 for the composite modulated structure given as a function of the internal coordinate  $t$  for a full modulation period. Symmetry operations as for (a). (f) Distance (in Å) from O3 (in sublattice 1) to M given as a function of the internal coordinate  $t$ . Note that the scale is different from (c) and (d). Symmetry operations as for (a).

perature main reflections only gives similar results (Table 5) to the refinement including satellites. This shows that the 20 K results which are based on main reflections only are valid.

**Distances.** Some selected distances are calculated and shown in Table 7. In a regular three-dimensional crystal a particular interatomic distance is the same in all unit cells. For a modulated structure, however, the distances between two atoms will vary as a function of unit cell number  $n$ . This is in particular true for distances between atoms from two different sublattices in a composite structure.<sup>17</sup> By varying the internal coordinate  $t$  of expression (4) in the range 0.0 to 1.0 all possible distances in all unit cells are obtained. For atoms belonging to the same composite part there will be minimum and maximum interatomic distances for each pair of atoms, but for atoms from two different composite parts only minimum interatomic distances can be meaningfully defined. In the present case, the atoms are modulated along the  $c$ -axis ( $c_5, c_7$ ), and all possible interatomic distances can be calculated by considering a large (infinite) number of unit cells stacked along  $z$  or, alternatively, by varying  $t$ . Generally, the distances from a particular central atom in a particular unit cell to all other atoms will correspond to one single value of  $t$ , but neighbouring symmetry-related central atoms may have very different  $t$  values. The periodicity of distance variation is related to the periodicity of modulation. For atoms of sublattice 1 ( $\text{CuO}_2$ ), the modulation period is  $c_5 = 3.91 \text{ \AA}$ , which is the period of  $t$ . For atoms of sublattice 2, the modulation period is  $c_7 = 2.75 \text{ \AA}$ , which is the period of  $\gamma \cdot t$ , with  $\gamma$  defined by eqn. (2) and  $t$  by eqn. (4). Thus the distances in the sublattices (Figs. 4a–4c), will be periodic with  $c_5$  and  $\gamma c_5$  for sublattice 1 and 2, respectively. For a detailed discussion of the significance of distances in a composite structure, see van Smaalen *et al.*<sup>18</sup> In all figures to be presented, exactly one period of variation is shown.

Cu3 is coordinated by four O3 atoms in sublattice 1. Fig. 4a shows the Cu3 to O3 distances around the Cu3 in  $(1/4, 1/4, 1/4)$ . The coordination polyhedron is a square planar unit in the unmodulated structure. The modulation causes a distortion of the Cu3 to O3 distances so that they split into two sets, one set involving O3 atoms at  $z = -1/4$  and the other involving O3 atoms at  $z = 3/4$ . The distances are symmetry-related, mirror-reflected

Table 7. Ranges of interatomic distances (in  $\text{\AA}$ ) in  $\text{M}_{10}\text{Cu}_{17}\text{O}_{29}$ .

Distance	Minimum	Maximum	Average	Comment
Cu1–O1 <sub>c</sub>	1.66(3)	2.21(4)	1.966(3)	Bond along $c$
Cu1–O1 <sub>a</sub>	1.72(4)	1.99(3)	1.903(3)	Bond along $a$
Cu1–O2	1.853(9)	1.908(6)	1.899(6)	
Cu3–O3	1.66(3)	2.09(3)	1.907(2)	
M–O1	2.41(3)	2.72(3)	2.557(3)	
M–O2	2.43(4)	2.72(4)	2.583(3)	
M–O3	2.33(4)	No maximum distance exists		

around  $t = 0.58$ . When the oxygen atoms at  $z = -1/4$  have a minimal distance to Cu3, the oxygen atoms at  $z = 3/4$  have maximum distance and *vice versa*, in accordance with chemical intuition. The bond is in the  $ac$ -plane, and since both atoms have large modulations along  $c$  and O3 along  $a$  as well, the resulting distances span a range of  $0.5 \text{ \AA}$ .

Cu1 is coordinated by three O1 and one O2 atoms in sublattice 2. Fig. 4b shows the Cu1 to O distances around Cu1 in  $(0.33, 0, 0)$ . The distorted square involves two O1 atoms bonded to Cu1 along  $c$  at  $z = 1/2$  and  $z = -1/2$  and one O1 bonded along  $a$  at  $x = 0.17$  and an O2 atom bonded along  $a$ , at  $x = 1/2$ . It is evident from the figure that when the oxygens along  $c$  are close, the oxygens along  $a$  are farthest away and *vice versa*. The oxygens along  $c$  also show a symmetry-related countervariation of the distances for  $t$ -values in the range 0.20–0.50. Beyond this range, the Cu1 distances to the oxygen atoms along  $z$  are in phase. Since both Cu1 and O1 have large modulations along  $c$ , the distance variation is  $0.5 \text{ \AA}$ , while it is smaller,  $0.3 \text{ \AA}$ , in the  $a$  direction because the Cu1 modulation in this direction is negligible. Similarly the Cu1 to O2 distance is also roughly constant, since O2 by symmetry is not allowed a modulation in the  $a$ -direction.

The values for the cation to oxygen distances are well in line with corresponding ones observed for the high- $T_c$  superconductors, to which this compound is structurally related. The values to be referred to here is from the study of the 2:2:1:2 Bi-Sr-Ca-Cu oxide superconductor based on X-ray and neutron powder diffraction data by Yamamoto *et al.*<sup>19</sup> Distances in that compound are influenced by a substitutional modulation of Ca and Bi on the Sr site, and the Ca site contains an amount of randomly distributed Sr. However, the M site in the present compound is also a random mixture of Bi, Sr and Ca.

The coordination polyhedron of Cu in Bi-2212 is a pyramid with four short distances, ranging  $1.80$ – $2.00 \text{ \AA}$ , in the Cu–O layer and one longer distance (ranging  $2.35$ – $2.55 \text{ \AA}$ ) to the apex oxygen. This coordination is very similar to the present compound. However, we have not included the apex oxygen in our calculation, since the smallest modulated distance between Cu1 and O3 is  $2.83(2) \text{ \AA}$ , which we considered too long for a bonding distance. The in-layer Cu–O distances are seen to show more variation in our compound.

Figs. 4c–4e show M–O distances for the coordination polyhedron around M in  $(0, 0.13, 0)$ . In Fig. 4c the distances of M to oxygens in sublattice 2 are seen to vary between  $2.41$  and  $2.72 \text{ \AA}$ . The variation is periodic in  $\gamma c_5$  for reasons explained above. It is seen that the distances to O1 in the  $ab$ -plane are in antiphase with respect to each other. On the other hand, the distances to O2, in the  $bc$ -plane, are in-phase. The pseudo period of  $\gamma c_5/2$  for the M to O1 distances is probably due to the large second-order harmonic of the O1 modulation in the  $b$ -direction.

Fig. 4d for comparison shows the distance between M of sublattice 2 and O3 of sublattice 1 in the (physically non-existing) unmodulated composite structure. Because

the central atom is M and we let the O3 atoms vary over symmetry equivalents, the periodicity of these distances is that of sublattice 2,  $0.7c_s$ . Noteworthy is the presence of at least one O3 atom at very short distance, 2.2–2.3 Å, at all  $t$ -values and the presence of at least one other O3 atom less than 2.6 Å away. The corresponding distances for modulation included are shown in Fig. 4e. The very short distance of 2.196(3) Å disappears, the minimum now being 2.33(4) Å, but at the same time the longer distances have been shortened, so that there are now in total two O3 atoms less than 2.5 Å away for all  $t$ . For most  $t$ -values, there is an additional O3 at a distance shorter than 2.72 Å, which was the upper limit for coordination of M to O1 and O2. It is also noteworthy that the minimum in the M to O3 distances occurs when the M to O2 distances are at maximum ( $t = 0.35$ ).

As previously mentioned, the definition of a maximum distance between two atoms from different composite parts (sublattices) is not possible on mathematical grounds because of the incommensurate nature of the composite crystal. However, from a chemical point of view, we can define a maximum M–O coordination distance of O3 by M. In Fig. 4f is shown the O3 to M distance from the O3 atom at (0.13, 1/4, 3/4) to the M atoms at (0, 0.13, 0) at (0, 0.13, 1) and at (0, 0.13, 2) for the modulated structure. It is noted that the periodicity is now  $c_s$ , because the central atom is now O3 of sublattice 1. At a distance of 2.72 Å there is a crossover point where the shortest distance changes from M at  $z = 1$  for M at  $z = 0$ , and below that distance the O3 atoms are coordinated by exactly one M atom for all  $t$ . This is of course the same crossover point which is observed in Fig. 4e at  $t = 0.35$ . This is also the maximum coordination distance to M for the oxygens of sublattice 2. Therefore this limit seems to be a chemically reasonable one for a coordination distance. With this in mind, Figs. 4c–4e can be interpreted as showing an average coordination of M by seven atoms in the range 2.33–2.72 Å. Only for very limited regions of  $t$  is the coordination number less, (6 at  $t = 0$ ), or more (8 at  $t = 0.35$ ). It is evident that the role of the modulation is to make the coordination environment of the atoms more homogeneous, to avoid very short and very long distances to nearest neighbours, and thereby also to bring the inter-sublattice distances more in line with those within the sublattices.

Ca in Bi-2212 is coordinated by a distorted cube of oxygen atoms which is similar to the coordination polyhedron of M. Ca–O distances vary between 2.40 and 2.65 Å, which are comparable to M–O distances. The Sr atom in Bi-2212 is coordinated by 12 oxygen atoms belonging to the Sr–O layer, the Cu–O layer and the Bi–O layer. The latter is heavily modulated, and the Sr distances to oxygens in this layer therefore vary much, from 2.30 Å to more than 3.30 Å, while the distances from Sr to oxygens in the same layer as Sr are between 2.40 Å and 2.70 Å and the distances to the oxygens in the Cu–O layer are in the range 2.35–3.15 Å. In this light, the M–O distances obtained for the present compound seem very

reasonable, since they span a much narrower range, 2.33–2.72 Å, considering the mentioned chemical definition of maximum coordination distance.

The modulation is an effective means for relieving stress in a composite structure, and therefore satellite reflections are to be expected in a diffraction pattern of a composite structure.

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