

Structure of the Incommensurate Composite Crystal $[\text{Sr}_2\text{Cu}_2\text{O}_3][\text{CuO}_2]_x$ ($x = 1.436$)

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Abstract

$[\text{Sr}_2\text{Cu}_2\text{O}_3][\text{CuO}_2]_x$ ($x = 1.436$), $M_r = 487.5$, orthorhombic, $M_{1s1}^{A2_1mq}; M_{1s1}^{A2_1mq}$, $a = 11.457$ (5), $b = 13.409$ (9), $c_1 = 3.935$ (3), $c_2 = 2.740$ (2) Å, $\mathbf{k}_1 = \mathbf{b}^* + 1.436(2)\mathbf{c}_1^*$, $\mathbf{k}_2 = \mathbf{b}^* + 0.696(1)\mathbf{c}_2^*$, $V_1 = 604.5$, $V_2 = 420.9$ Å³, $Z = 4$, $D_x = 5.36$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 28.9$ mm⁻¹, $F(000) = 890.5$, room temperature, final $R = 0.057$ for 314 unique reflections. The first subsystem $[\text{Sr}_2\text{Cu}_2\text{O}_3]$ is composed of $(\text{Cu}_2\text{O}_3)_\infty$ sheets perpendicular to the b axis and Sr ions coordinated to the sheet. The second subsystem is $(\text{CuO}_2)_\infty$ infinite chains parallel to the c axis, which are located among the Sr ions of the first subsystem. The atomic positions are modulated along the c axis by the interactions between the two subsystems.

Introduction

A composite crystal, which was found to be $\text{Sr}_{1.0}\text{Ca}_{0.5}\text{Cu}_{2.0}\text{O}_x$ by electron-probe microanalysis (EPMA), was obtained during synthesis of Bi–Sr–Ca–Cu–O single crystals. As a result of this we obtained the title compound (Shishido, Ukei & Fukuda, 1992).

After the structure analysis of this compound was completed, the authors were informed of a structural study on this compound (McCarron, Subramanian, Calabrese & Harlow, 1988). The sets of results from both structure analyses are similar. However, in our analysis we used a similar method to the modulated-structure analysis (Yamamoto, 1992; see also Ukei, Yamamoto, Watanabe, Shishido & Fukuda, 1993) and moreover the space group determined by them is incorrect. Therefore, our structure analysis is described here.

Experimental

The crystal was prepared as described elsewhere (Shishido *et al.*, 1992). The chemical composition of the specimen was determined by EPMA as $\text{Sr}_{2.0}\text{Cu}_{3.0}\text{O}_x$ (the chemical composition determined by X-ray measurements is $\text{Sr}_{1.00}\text{Cu}_{1.72}\text{O}_{2.94}$). The sample chosen has dimensions $0.03 \times 0.04 \times 0.68$ mm.

The integrated intensity data were collected on a Rigaku AFC-6A four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation up to $2\theta = 55^\circ$ with the ω - 2θ scan mode [scan speed 2° min^{-1} (ω)]. During data collection, the intensities of three Bragg reflections were monitored after every 100 reflections measured and no significant change in their intensities was observed throughout the experiments. 1133 reflections were measured (within the hemisphere $c^* \geq 0$), 314 unique reflections with $|F_o| > 3\sigma(|F_o|)$ were considered observed, $R_{\text{int}} = 0.110$. Corrections were applied for absorption ($2.17 < A^* < 3.60$) and for Lorentz and polarization effects, but not for extinction. The unit-cell dimensions were determined from 32 sets from the setting angles of four fundamental Bragg reflections ($27 < 2\theta < 30^\circ$). The c^* component of the modulation wavevector \mathbf{k} was determined from five intensity profile data along the c^* direction.

Structure refinement

In the composite crystal, prominent reflections define two sets of three-dimensional reciprocal lattices of the two subsystems (Fig. 1). Fig. 2, which shows the intensity profile along the path depicted by the bold line in Fig. 1, indicates the incommensurability of the two subsystems. In the present case, the two subsystems have common periods along the a^* and b^*

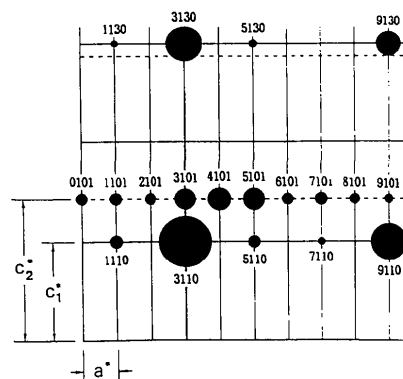


Fig. 1. A schematic view of the diffraction pattern $h1lm$ from $[\text{Sr}_2\text{Cu}_2\text{O}_3][\text{CuO}_2]_x$. The radii of the discs are proportional to $|F_o|$.

directions, and incommensurate periods to each other along the c^* direction. a^* , b^* , c_1^* , c_2^* ($=1.436c_1^*$) were selected as the unit vectors to index reflections ($1.436c_1^*$ was used to index m instead of $b^* + 1.436c_1^*$) and recognized as the projections of the unit vectors in the four-dimensional reciprocal lattice onto the three-dimensional external space (Yamamoto, 1992). In Fig. 3, which shows the intensity profile along another path, two weak first-order satellites are found. These satellites result from the deviation from the average structure because of the interaction between two subsystems.

From the reflection conditions ($k + l + m = 2n$ for $hklm$, $h = 2n$ for $hk00$ and $l, m = 2n$ for $h0lm$), probable space groups for the second subsystem are $A2_1ma$ and $Amma$. $A2_1ma$ was adopted in the later stages of the structure determination because the positional parameters of the Cu ion of the second subsystem conflict with those of the centre of symmetry in the case of $Amma$. The superspace group for the second subsystem was finally determined to be $M^{A2_1ma}_{1s1}$. The superspace group for the first subsystem

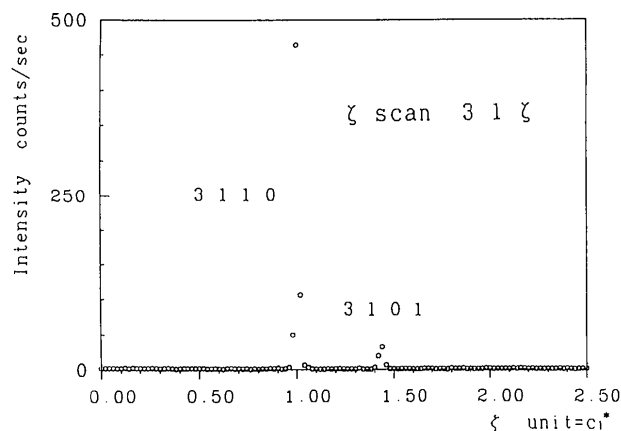


Fig. 2. The intensity profile on ζ scan $3\ 1\ \zeta$.

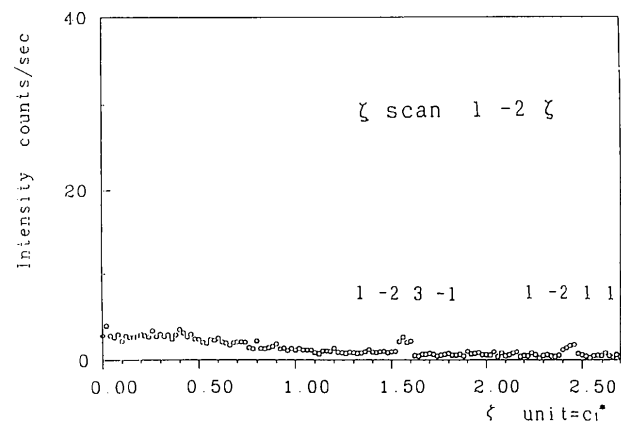


Fig. 3. The intensity profile on ζ scan $1-2\zeta$.

Table 1. Final Fourier coefficients of the modulation waves; standard deviations are in parentheses, A_0 for u, v, w means the position in the fundamental structure

	A_0	A_1	B_1	A_2	B_2
Subsystem 1					
Sr	u 0.25	0.009 (1)	-0.0019 (9)	0.003 (3)	0.004 (1)
	v 0.1284 (3)	0.0016 (5)	0.001 (1)	-0.003 (3)	-0.001 (3)
	w 0.25	-0.02 (1)	-0.028 (5)	0.02 (1)	-0.028 (6)
	B 0.4 (1)	0.0 (2)	0.9 (4)	0.2 (8)	0.7 (7)
Cu(1)	u -0.0890 (7)	0.0	0.0		
	v 0.0	0.000 (4)	-0.007 (2)		
	w 0.25	0.0	0.0		
	B 0.9 (1)	0.0	0.0		
Cu(2)	u 0.0805 (7)	0.0	0.0		
	v 0.0	0.007 (2)	0.000 (4)		
	w -0.25	0.0	0.0		
	B 0.1 (1)	0.0	0.0		
O(1)	u -0.081 (3)	0.0	0.0		
	v 0.0	0.00 (2)	0.01 (1)		
	w -0.25	0.0	0.0		
	B 1.0	0.0	0.0		
O(2)	u 0.077 (3)	0.0	0.0		
	v 0.0	-0.01 (2)	0.00 (2)		
	w 0.25	0.0	0.0		
	B 1.0	0.0	0.0		
O(3)	u 0.255 (2)	0.0	0.0		
	v 0.0	0.012 (4)	0.01 (1)		
	w -0.25	0.0	0.0		
	B 1.0	0.0	0.0		
Subsystem 2					
Cu(3)	u 0.000 (1)	0.0	0.0		
	v 0.25	0.00 (2)	-0.001 (2)		
	w 0.139 (2)	0.0	0.0		
	B 1.15 (7)	0.0	0.0		
O(4)	u -0.108 (2)	0.0	0.0		
	v 0.25	-0.015 (5)	-0.01 (1)		
	w 0.67 (1)	0.0	0.0		
	B 1.0	0.0	0.0		
O(5)	u 0.113 (3)	0.0	0.0		
	v 0.25	0.03 (6)	-0.01 (8)		
	w 0.60 (2)	0.0	0.0		
	B 1.0	0.0	0.0		

is also $M^{A2_1ma}_{1s1}$ from a consideration of the permutation (Yamamoto, 1992). Symmetry operations are $(0,0,0,0; 0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + x, y, z, t; x, -y, z, \frac{1}{2} + t; \frac{1}{2} + x, y, -z, -t; \frac{1}{2} + x, -y, -z, -t$. Accidentally there exists another reflection condition ($h + l = 2n$ for $hkl0$). Combined with the aforementioned reflection condition ($k + l + m = 2n$ for $hklm$), the first subsystem is deduced to be a face-centred lattice. The symmetry operator ($\bar{3}$) is changed to ($\bar{1}$) by the permutation above and this causes the $\frac{1}{4}$ shift of the origin along the b axis in the case of the space group $A2_1ma$. In the analysis, positional parameters were referred to the origin for the first subsystem.

Approximate coordinates of Sr ions in the average structure were derived from the Patterson function, those of other ions were obtained by trial models. REMOS90 (Yamamoto, 1992), a new version of a

computer program for the refinement of average and modulated structures by the least-squares method (Yamamoto, 1982), was used for the refinement.

In the j th modulated subsystem, the x , y , z components of the displacement (u , v , w) and the isotropic temperature factor B of an atom are described here in terms of Fourier series as follows:

$$c^j(\bar{x}_4^j) = A_0 + \sum_{n=1}^m [A_n \cos(2\pi n \bar{x}_4^j) + B_n \sin(2\pi n \bar{x}_4^j)],$$

where $c^j = u^j, v^j, w^j$ or B^j , $\bar{x}_4^j = \mathbf{d}_4^{*j} \cdot (\mathbf{X}^j + \bar{\mathbf{x}}^j)$ with the fourth unit vector in the four-dimensional reciprocal lattice \mathbf{d}_4^{*j} , \mathbf{X}^j is the lattice vector and $\bar{\mathbf{x}}^j$ the position in the fundamental structure, a bar denotes quantities belonging to the fundamental structure and m is the maximum order of harmonics. In our analysis, m is 2 for Sr and 1 for Cu and O ions. The temperature factors, B , of O ions were fixed to 1.0. Since Cu and O ions are at the special positions with site symmetry (∞), some Fourier coefficients are forbidden: u , w and B for odd n and v for even n . Average z parameters of the ions in the first subsystem are constrained to the fixed value $\pm \frac{1}{4}$ because of the face-centred lattice of the first subsystem and the existence of an a -glide plane. The x parameter of the fundamental structure for Sr is set to $\frac{1}{4}$ in order to fix the origin.

Using only the fundamental reflections ($hk0$ and $hk0m$), the refinement by the full-matrix least-squares method on $|F|$ converged at an R factor of 0.057. R factors for reflection subsets are as follows: 0.042 for 51 reflections with $l = 0, m = 0$; 0.059 for 138 reflec-

tions with $l \neq 0, m = 0$; 0.071 for 125 reflections with $l = 0, m \neq 0$. Final parameters are listed in Table 1.*

In addition to *REMOS90*, the *UNICSIII* program system (Sakurai & Kobayashi, 1979) was used during the analysis. Atomic scattering factors for the O²⁻ ion were taken from Tokonami (1965) and those for other ions from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 79, 81, 149–150).

The projection of the fundamental structure along the c axis is shown in Fig. 4. A perspective view of the modulated structure of the first subsystem and the second subsystem with the surrounding Sr ions are shown in Figs. 5 and 6, respectively. Some interatomic distances and angles of the ions shown in the figures are presented in Table 2.

* A list of observed and calculated structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71455 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

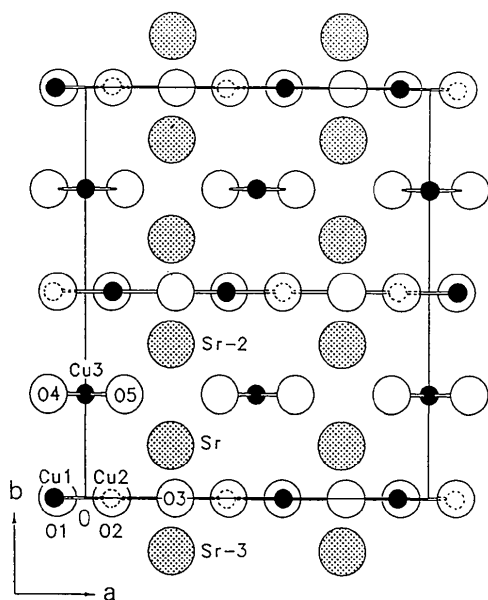


Fig. 4. A view of the fundamental structure along the c axis. Dotted, filled and open circles represent Sr, Cu and O ions, respectively. Atomic nomenclature is abbreviated, for example, Sr-2 means Srⁱⁱ.

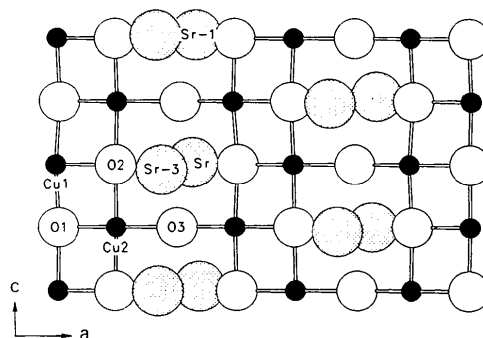


Fig. 5. A perspective view of the modulated structure of the first subsystem. The atom key is the same as in Fig. 4.

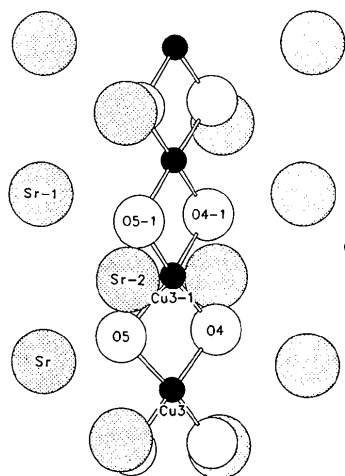


Fig. 6. A part of a $(\text{CuO}_2)_\infty$ column and the surrounding Sr ions. The atom key is the same as in Fig. 4.

Table 2. *Interatomic distances (Å) and angles (°)*

Sr—Sr ⁱⁱ	3.99 (6)	Sr—Sr ⁱⁱⁱ	3.76 (6)
Sr—Sr ⁱⁱⁱ	3.48 (6)	Sr—Cu(2)	3.25 (4)
Sr—Cu(3)	3.2 (1)	Sr—Cu(3')	3.80 (4)
Sr—O(2)	2.5 (2)	Sr—O(3)	2.78 (8)
Sr—O(5)	2.0 (4)	Sr ⁱ —Sr ⁱⁱ	3.79 (6)
Sr ⁱ —Cu(3')	3.79 (5)	Sr ⁱ —O(5')	2.5 (5)
Sr ⁱⁱ —Cu(3')	3.16 (5)	Sr ⁱⁱ —O(5)	2.8 (5)
Sr ⁱⁱ —O(5')	2.4 (3)	Sr ⁱⁱⁱ —Cu(2)	3.22 (4)
Sr ⁱⁱⁱ —O(2)	2.8 (2)	Sr ⁱⁱⁱ —O(3)	2.39 (8)
Cu(1)—Cu(2)	2.765 (8)	Cu(1)—O(1)	1.970 (3)
Cu(1)—O(2)	1.91 (4)	Cu(2)—O(1)	1.85 (4)
Cu(2)—O(2)	1.97 (1)	Cu(2)—O(3)	2.00 (3)
Cu(3)—Cu(3')	2.739 (8)	Cu(3)—O(4)	1.92 (3)
Cu(3)—O(5)	1.9 (2)	Cu(3')—O(4)	1.79 (3)
Cu(3')—O(4')	1.92 (3)	Cu(3')—O(5)	2.0 (2)
Cu(3')—O(5')	1.82 (9)	O(1)—O(2)	2.68 (4)
O(2)—O(3)	2.84 (4)	O(4)—O(4')	2.76 (4)
O(4)—O(5)	2.6 (2)	O(4')—O(5')	2.6 (1)
O(5)—O(5')	2.8 (2)		
O(1)—Cu(1)—O(2)	87. (1)	O(1)—Cu(2)—O(2)	89. (1)
O(2)—Cu(2)—O(3)	91. (1)	O(4)—Cu(3)—O(5)	87. (3)
O(4)—Cu(3')—O(4')	96. (1)	O(4)—Cu(3')—O(5)	86. (3)
O(4')—Cu(3')—O(5')	87. (3)	O(5)—Cu(3')—O(5')	94. (5)
Cu(1)—O(1)—Cu(2)	93. (1)	Cu(1)—O(2)—Cu(2)	91. (1)
Cu(3)—O(4)—Cu(3')	95. (1)	Cu(3)—O(5)—Cu(3')	90. (9)

Symmetry code: (i) $x, y, z + 1$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $x, -y, z$.

Several structural studies on very closely related materials have been reported: $(\text{Sr}_{14-x}\text{Ca}_x)\text{Cu}_{24}\text{O}_{41}$ ($0 < x \leq 8$) (McCarron *et al.*, 1988); $M_{10}\text{Cu}_{17}\text{O}_{29}$ ($M = \text{Bi}_{0.031}\text{Ca}_{0.564}\text{Sr}_{0.405}$) (Kato, 1990); $(\text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ (Milat, van Tendeloo, Amelinckx, Mehdob & Deltour, 1992). As found by McCarron *et al.* in the Ca-free compound, adjacent $(\text{CuO}_2)_\infty$ chains are staggered along the c axis and a face-centred lattice is not formed in the second subsystem unlike the Ca-

containing compounds. In the TEM study (Milat *et al.*, 1992), diffuse intensity planes perpendicular to the c^* axis were observed in the second subsystem, which indicate the positional disorder in the successive rows of $(\text{CuO}_2)_\infty$ chains. The precession photographs of our samples were taken perpendicular to the b^* axis (Shishido *et al.*, 1992) and none of the aforementioned streaks were visible.

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Experiences with a Structure Determination on the Basis of Powder Data

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Abstract

The result of a crystal structure determination on the basis of Guinier powder data is compared with the structure based on single-crystal data. Both determinations agree roughly regarding the arrangement

of the atoms; however, the powder-data result shows strong deviations with respect to the correct atomic positions.

Introduction

In connection with the problem of characterization of a series of alanates, the authors were confronted

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