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X-ray Investigation of the Incommensurate Modulated Structure of $Bi_{2.08}Sr_{1.84}CuO_{6-\delta}$

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Abstract

At room temperature the bismuth strontium cuprate $Bi_{2.08}Sr_{1.84}CuO_6$ [$a = 5.3791$ (6), $b = 5.3811$ (9), $c = 24.589$ (3) Å, $\beta = 89.93$ (1)°, basic space group $A2/a$, superspace group $P^{A2/a}_{\bar{1}1}$, $M_r = 755.44$, $D_x = 7.05$ g cm^{-3}, $V = 711.7$ Å^3, $Z = 4$, Cu $K\alpha$ radiation, $\lambda = 1.541838$ Å, $\mu = 1203$ cm^{-1}, $F(000) = 1278.24$, $T = 294$ K] exhibits a one-dimensional incommensurate modulated structure with a modulation wavevector $\mathbf{q}^*$ having components 0.2030 (2), 0, 0.467 (2). Both a displacive modulation wave, acting on all atoms and a density modulation wave, governing the occupancy probabilities of the Bi, Sr and apical O(2) sites are involved in the crystal. 1117 unique *hklm* reflections with $I \geq 3\sigma(I)$ were used to refine the modulated structure. The final R factors (based on F) of main reflections (292), and first- and second-order satellite reflections (563 and 262) are 0.061, 0.061 and 0.086 respectively. The modulation is anharmonic for all atoms. Evolution of the Bi, Sr and apical O(2) site occupancies throughout the crystal is correlated in a spectacular way and shows the existence of Bi and O(2) vacant sites in some unit cells; moreover, some Sr sites are occupied by Bi atoms. These features give rise to various coordinations *i.e.* square planar, pyramidal, octahedral for copper and from six to nine for strontium. The most likely coordination for bismuth in strontium sites is ninefold coordination; owing to the displacive modulation, both dilute and Bi-condensed regions are found in the crystal. Within the condensed regions, bismuth achieves a classical fourfold coordination. To satisfy the Bi coordination in the Bi-dilute regions it is proposed that extra O atoms have to be introduced either within the Bi—O layers or between two adjacent Bi—O layers.

Introduction

A great number of structural studies have been performed on bismuth cuprates since the discovery of superconductivity in the system Bi–Sr–Cu–O (Michel, Hervieu, Borel, Grandin, Deslandes, Provost & Raveau, 1987). In spite of this intense exploration, the structure of the 2201 oxide $Bi_2Sr_2CuO_{6+\delta}$ is still not really understood.

The oxide of nominal composition $Bi_2Sr_2CuO_{6+\delta}$ called Bi-2201 crystallizes in a pseudotetragonal subcell with basic parameters close to $a \simeq 5.4$, $b \simeq 5.4$ and $c \simeq 24.5$ Å. The diffraction spectrum of all the crystals studied reveals, besides main reflections, the existence of satellite reflections. The main reflections

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are distributed, on cursory examination, according to orthorhombic symmetry and the space group *Amaa*, and the value of *b* then appears slightly greater than *a*. However, the distribution of satellite reflections in reciprocal space leads unambiguously to monoclinic symmetry. The position of these satellite reflections, always in the (a^*c^*) plane, is defined by a single modulation wavevector $\mathbf{q}^*$ with a component q_1^* along a^*, which is close to 0.20 for all the crystals, and a component q_3^* and along c^* which varies from one crystal to another, taking particular values close to 0.33, 0.40, 0.50 and 0.62.

Three solutions of the structure have been attempted using only the main reflections (Torardi, Subramanian, Calabrese, Gopalakrishnan, McCarron, Morrissey, Askew, Flippen, Chowdhry & Sleight, 1988; Von Schnering, Walz, Schwarz, Becker, Hartweg, Popp, Hettich, Müller & Kämpf, 1988; Imai, Nakai, Kawashima, Sueno & Ono, 1988). In the last study, 0.4 Ca was substituted for Sr without noticeable structural changes except for a slight decrease in the *c* parameter. The reliability factors calculated for these average structures were rather high (0.11–0.13); the thermal parameters were large and the oxygen positions of poor precision. However, the results lead to the Bi-2201 structural type, which has also been described for $Tl_2Ba_2CuO_6$. The mean structure consists of single perovskite layers intergrown with double $[BiO]_\infty$ layers. It is shown that the CuO_6 octahedra are axially elongated, whereas bismuth has a strongly distorted octahedral environment.

Three other studies take the existence of satellite reflections into account. A high-resolution electron microscopy examination of a crystal with q_3^* close to 0.5 (Matsui, Takekawa, Horiuchi & Umezono, 1988) indicates fluctuation of the Bi positions which suggests the formation of Bi-concentrated and Bi-deficient bands in the Bi_2O_2 layers. From an X-ray single-crystal analysis (Onoda & Sato, 1988), considering satellites as superstructure reflections with $q_3^* = 0.40$, the structure was solved and refined using classical methods. Although the large number of refined parameters limits the precision of the results, the established model shows that a long-period commensurate modulation wave causes harmonic swelling of the atomic layers. Another incommensurate modulation has been analysed by X-ray diffraction (Gao, Lee, Ye, Bush, Petricek & Coppens, 1989) from a sample of composition $Bi_{2.28}(Sr,Ca)_{1.72}CuO_{6+\delta}$ containing an excess of Bi and displaying a component $q_3^* = 0.61$ of the wave modulation vector. Though the crystal was twinned, this work, using four-dimensional symmetry theory, provides for the first time the modulated displacement of the heavy atoms in successive layers of the actual crystal.

Three other results concerning crystals of the same structural type have recently been published, which relate to cationic substitution of Cu or Bi sites. In $Bi_2Sr_2CoO_{6.25}$ (Tarascon, Miceli, Barboux, Hwang, Hull, Giroud, Greene, Le Page, McKinnon, Tselepis, Pleizier, Eibschutz, Neumann & Rhyne, 1989) and in $Bi_2Sr_2MnO_{6.37}$ (Tarascon, Le Page & McKinnon, 1990), both orthorhombic, the structural modulation is strictly commensurate but along a^* with $q_1^* = 0.25$ and $q_3^* = 0$; this allows the full crystal structure to be solved by classical treatments, demonstrating the existence of extra oxygen in the Bi—O layers. In contrast, the compound $BiPbSr_2MnO_6$ (Tarascon, Le Page, McKinnon, Ramesh, Eibschutz, Tselepis, Wang & Hull, 1990) shows no modulation.

Until now, no single-crystal X-ray analysis including satellite reflections has been carried out for a crystal of approximate composition $Bi_2Sr_2CuO_6$ with $q_1^* \simeq 0.20$ and $q_3^* \simeq 0.50$ as mentioned in the papers quoted previously (Von Schnering *et al.*, 1988; Matsui *et al.*, 1988). This article presents the results of a study based on a four-dimensional treatment using all the information provided by the first- and second-order satellites. In addition to the modulation of atomic displacements, we discuss the evolution of the environment of the metallic sites in the whole crystal.

Growth and characterization of the crystals

Single crystals were grown by a self-flux method, *i.e.* using one of the starting materials as a flux, in our case CuO. High-purity Bi_2O_3, $SrCO_3$ and CuO (all Prolabo 99%) were mixed in an agate mortar in the molar ratio $1Bi_2O_3$:$1.7SrCO_3$:2CuO. The mixture (total weight 20 g) was melted in an alumina crucible and soaked at 1313 K for 24 h, step-cooled to 1223 K and then slowly cooled (2 K h^{-1}) down to 1093 K before reaching room temperature by switching off the furnace. Black shiny crystals were separated mechanically from the frozen melt and carefully cleaved in the direction of the *ab* plane to

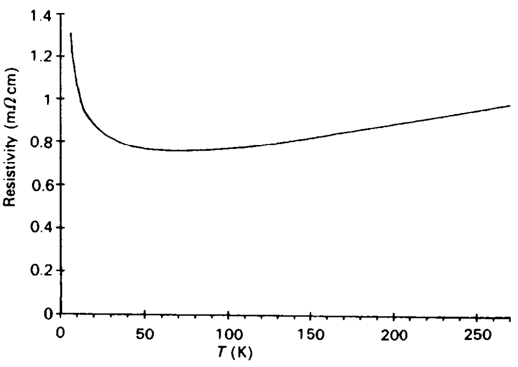

Fig. 1. Variation of resistivity with absolute temperature.

form rectangular platelets of typical size 1 × 1 × (3–10 × 10^{-3}) mm.

The resistivity in the *ab* plane was measured by a standard four-probe DC technique in a flowing-He cryostat using currents of ± 0.1 mA. Electrical contacts were made using silver paint and fired for 30 min at 673 K. The dependence of the resistivity on temperature (Fig. 1) shows a linear decrease from room temperature down to about 100 K where a semiconducting-like behavior starts to be observed.

Preliminary study

X-ray diffraction photographs, recorded at room temperature using a Weissenberg camera, show both main reflections and satellite reflections with rather high intensities defined by a single modulation wavevector $\mathbf{q}^*$. The distribution of these satellite reflections through reciprocal space points to monoclinic symmetry although the basic unit cell defined from the main reflections is an almost perfectly orthorhombic unit cell. As regards these main reflections, the departure from *mmm* Laue symmetry was found to be both actual and significant; indeed, calculation of the internal *R* factors based on intensities for the two relevant cases $2/m$ and *mmm* led to 0.038 and 0.160 respectively.

The $\mathbf{q}^*$ vector lies in the mirror plane of the $2/m$ Laue symmetry (planar monoclinic case) and consequently its two components are expected to be irrational. It is actually observed by different authors that the q_1^* and q_3^* components, within the axis setting where y is parallel to the twofold axis, deviate from the rational values of $\frac{1}{5}$ and $\frac{1}{2}$. To specify the departure from these values, the following process was used: first, the parameters of the monoclinic cell were refined by least squares from the θ measurement of 20 main reflections ($12 < \theta < 31°$) collected on an Enraf–Nonius CAD-4 diffractometer. No significant difference was found between the a and b parameters; a small departure from the value of 90° was observed for the β angle [89.93 (1)°]. Afterwards, the θ_s angles of 20 independent first-order satellite reflections with $k = 0$ were carefully measured and centred, then compared with the calculated values assuming for the time being that the satellites were superstructure reflections. Significant and systematic discrepancies were then observed between these measured and calculated θ_s values demonstrating irrational components for $\mathbf{q}^*$ and consequently stressing the incommensurate character of the modulation. A least-squares refinement was then carried out leading to the results: $q_1^* = 2030\ (2)$ and $q_3^* = 0.467\ (2)$. All the reflections could then be indexed using the four integers h, k, l, m by defining the diffraction vector: $\mathbf{s}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}^*$ where m is the satellite order.

Table 1. *Experimental data for* $Bi_{2.08}Sr_{1.84}CuO_6$

Crystal size (μm)	5 × 23 × 82
Lattice parameters (Å, °) ($T = 294$ K)	$a = 5.3791\ (6)$, $b = 5.3811\ (9)$, $c = 24.589\ (3)$, $\beta = 89.93\ (1)$
Modulation wavevector	$\mathbf{q}^*$ [0.2030 (2), 0, 0.467 (2)]
Modulation period (Å)	$\lambda = 1/q^* = 23.7$
Superspace group	$P^{A2/a}_{\bar{1}1}$
D_x (g cm^{-3}), Z, M_r, V (Å^3)	7.05, 4, 755.44, 711.7
$F(000)$	1278.24
Data-collection technique	Enraf–Nonius CAD-4 diffractometer
Scan mode	ω–θ
Wavelength (Å)	λ(Cu $K\alpha$) = 1.541838
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0.629
Registered space	$0 \le h \le 6$, $0 \le k \le 6$, $-30 \le l \le 30$, $-2 \le m \le 2$
Control of intensities	3 reflections (008, 028, 228) every 3000 s; no significant fluctuation observed
Number of measured reflections	4556
Number of reflections with $I \ge 3\sigma(I)$	$hkl0$ 292 $hkl \pm 1$ 563 $hkl \pm 2$ 262
Absorption correction	Based on the crystal morphology
Absorption coefficient (cm^{-1})	μ(Cu $K\alpha$) = 1203
Extremal transmission factors	0.123, 0.602
No. of divisions used in the integral calculation of the structure factors by the Gaussian method	12
Atomic scattering factors and f', f'' values	*International Tables for X-ray Crystallography* (1974, Vol. IV)

For such crystals, characterized by a one-dimensionally incommensurate modulated structure, the periodicity can be recovered and the symmetry extended in four-dimensional space owing to the concept of superspace groups (de Wolff, Janssen & Janner, 1981). In agreement with the observed reflection conditions: $k + l = 2n$ for h, k, l, m, and $h = 2n$ ($l = 2n$) for h, 0, l, m; two superspace groups are possible for the crystal, $P^{A2/a}_{\bar{1}1}$ or P^{Aa}_{1}.

A plate-shaped crystal displaying no twinning, giving rather well resolved spots and showing no noticeable streaking effect was selected for collection of the reflection intensities. In spite of the drastic absorption, $K\bar{\alpha}$ radiation from copper rather than that from molybdenum was used because of its higher efficiency.

As some of the first-order satellite reflections showed rather high intensities, involving strong modulation, the second-order satellite reflections were also registered; indeed, in this case, their intensities are expected to be noticeable even if the modulation is harmonic. The diffractometer was controlled by the *SAT* program (Doudin, 1985) which generates a file including the *hklm* and the $Rh = h + mq_1^*$, $Rk = k$, $Rl = 1 + mq_3^*$ reflection indices. The intensities of 1117 unique *hklm* reflections with $I \ge 3\sigma(I)$ were corrected for Lorentz and polarization effects and used to refine the modulated structure. Absorption corrections based on the crystal morphology were applied within the program *REMOS* (Yamamoto, 1982). The main features of the data collection are summarized in Table 1.

The average structure

For a crystal displaying strong displacive modulation, resolution of the average structure using the main reflections entails some difficulty if only classical methods are used. Indeed, the structure factors of the main reflections depend on both the average atomic positions and on the Fourier coefficients of the atomic displacement components (van Aalst, den Hollander, Peterse & de Wolff, 1976). So, if these Fourier coefficients are large, a departure from the true average coordinates is to be expected if classical refinement methods are used. Otherwise, within this classical study, it is necessary to split the atomic sites, in order to take into account the large spread of the electronic density around the average positions.

The average structure was determined assuming the centrosymmetric space group *A*2/*a* which is a subgroup of *Amaa*, the space group which most authors consider describes the average structure of the '2201' phase.

The average structure was refined using the internal *SDP* programs (B. A. Frenz & Associates Inc., 1982); the starting values of the atomic positions, except those of the O atoms lying in the Bi—O layers, were those determined in previous works by Torardi *et al.* (1988) and Von Schnering *et al.* (1988).

To accommodate the actual symmetry *A*2/*a*, the trial positions of the atoms were slightly modified. The first refinements, carried out without splitting the atomic sites, with anisotropic temperature factors for the heavy atoms and isotropic ones for the O atoms led to the agreement factors: $R = 0.14$ and $wR = 0.15$. The third oxygen atom O(3) belonging to the Bi—O layers was then located from Fourier difference maps. However, a large spread of electronic density mainly along the **a** axis was observed involving strong displacement from the average positions inside the actual crystal.

In the next refinement cycles, the Bi, Sr, Cu and O(3) sites were split onto two pseudo sites based on the results of Fourier difference synthesis. As regards the mean occupancies of the Bi and Sr sites, the refined values are in agreement with those found using the program *REMOS* (96% Bi over Bi sites, 92% Sr and 8% Bi over Sr sites). The final reliability factors R and wR were 0.079 and 0.091 respectively for the 292 unique reflections used and corrected for absorption.

Structure determination of the modulated crystal

Two kinds of modulation wave, displaying the same period, have to be considered in this crystal: a displacive modulation wave acting on all atoms and a density modulation wave governing the occupancy of atomic sites.

So, in the unit cell defined by $\mathbf{p} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$, where n_1, n_2, n_3 are integers, the displacement of the μth atom from its average position $\mathbf{r}_0^\mu + \mathbf{p}$ is $\mathbf{U}^\mu[\mathbf{q}^*.(\mathbf{r}_0^\mu + \mathbf{p})]$ where $\mathbf{U}^\mu$ is a periodic vector field of the internal parameter $\overline{x}_4^\mu = \mathbf{q}^*.\mathbf{r}_0^\mu + t$; t is the so-called phase factor.

The occupancy probability of a site μ by only one type of atom can be described by the scalar function $P'^\mu(\overline{x}_4^\mu) = P_0^\mu + P^\mu(\overline{x}_4^\mu)$ with $P_0^\mu = \langle P'^\mu \rangle$. If, for instance, two types of atoms are distributed over a same site ν and if no vacancies are involved, the relevant functions to introduce are the complementary occupancy probabilities $P'^\nu(\overline{x}_4^\nu)$ and $1 - P'^\nu(\overline{x}_4^\nu)$.

Owing to the periodicity of the modulation, $P'^\mu(\overline{x}_4^\mu)$ and the $\mathbf{U}^\mu(\overline{x}_4^\mu)$ components are expanded in a Fourier series; the second harmonic was included in so far as the second-order satellite reflections were observed and may involve a departure from the harmonicity for the modulation.

$$P^\mu(\overline{x}_4^\mu) = \sum_{n=1}^{2} (A_n^\mu \cos 2\pi n \overline{x}_4^\mu + B_n^\mu \sin 2\pi n \overline{x}_4^\mu)$$

$$U_i^\mu(\overline{x}_4^\mu) = \sum_{n=0}^{2} (A_{i,n}^\mu \cos 2\pi n \overline{x}_4^\mu + B_{i,n}^\mu \sin 2\pi n \overline{x}_4^\mu)$$

where $i = 1, 2, 3$ and n is the harmonic order.

The zero-order Fourier terms $A_{i,0}^\mu$ allow determination of the true average position $\mathbf{r}_0^\mu$ of the μth atom in the origin unit cell through

$$\mathbf{r}_0^\mu = \mathbf{r}_b^\mu + \sum_{i=1}^{3} A_{i,0}^\mu \mathbf{a}_i \qquad (1)$$

where $\{\mathbf{a}_i\}$ are the basis vectors **a**, **b**, **c**, and $\mathbf{r}_b^\mu$ the approximate average position found from the classical study of the average structure.

Refinement of the modulated structure was carried out with the F magnitudes using the *REMOS* program. The quantity minimized was $\chi^2 = (wR)^2 + (\mathrm{pf})^2$ where wR is the weighted R factor and pf a penalty function which constrains the occupation probabilities P'^μ within reasonable ranges. The superspace group $P^{A2/a}_{\bar{1}\,1}$ was assumed. In the basic crystal, only the copper atom is located on a special position ($\bar{1}$); as a result, restrictions occur on the Fourier terms of P^μ ($B_n^\mu = 0$) and $\mathbf{U}^\mu$ components ($A_{i,n}^\mu = 0$ for $i = 1, 2, 3$) of this atom (de Wolff, 1977; de Wolff *et al.*, 1981).

A model of harmonic modulation was first researched through a trial and error method; the amplitudes of the **U** components and their relative phases, approximated to 0 or π, were refined using only the main reflections and assuming, for the time being, full occupancy of the atomic sites. Then, using the first-order satellite reflections, several models of displacive modulation were tested introducing in turn bismuth, strontium and then copper atoms; within these trials, the values of the absolute phases φ of the

U components were varied with a constant step, leaving the previous amplitudes and relative phases invariant.

The model giving the best agreement factor $R_{h,k,l,\pm 1}$ was refined successfully; the Fourier terms of the O atoms were then determined easily even giving arbitrary starting values to the φ phases.

Afterwards, a refinement of second-order Fourier terms was carried out including the second-order satellite reflections, which led to noticeable values of $A_{i,2}$ and $B_{i,2}$ for the Bi, Sr, Cu atoms, and large values for the O atoms.

The problems arising from the distribution of the atoms over the cation sites were carefully scrutinized. At first, the Bi, Sr, Cu sites were supposed to be occupied only by the Bi, Sr and Cu atoms respectively, and their mean occupancies refined, leading to the following results:

(*a*) The mean occupancy of the Cu sites is one within experimental error ruling out a substitutional phenomenon.

(*b*) The mean occupancy of the Sr sites is significantly larger than one [1.11 (1)] and as a result a few Sr sites are necessarily occupied by Bi atoms.

(*c*) The mean occupancy of the Bi sites is less than one [0.96 (1)] suggesting either Bi vacant sites or an eventual substitution of a few sites by copper or strontium atoms.

Within experimental error, the refined values of the O(1) and O(3) site occupancies were found to be equal to one and in contrast the mean occupancy of the O(2) sites less than one [0.74 (4)].

In the last steps, the Fourier terms of the relevant occupancy probabilities were refined successfully assuming that the Bi sites were occupied by Bi atoms only. A phase fluctuation of the modulation wave (Yamamoto, Nakazawa, Kitamura & Morimoto, 1984) was considered which significantly improved the $R_{h,k,l,\pm 2}$ agreement factor. Temperature factors were assumed to be anisotropic for the Bi, Sr, Cu atoms, isotropic for the O atoms. The eventual modulation of these factors was neglected in order to reduce the number of parameters. The temperature factors, the Fourier terms of the displacive modulation and those of the density modulation were refined alternately, using the weighting scheme: $w = 100/|F_o|^2$ for $|F_o| > |F_{\min}|$ and $w = 100/|F_{\min}|^2$ for $|F_o| < |F_{\min}|$ with $|F_{\min}| = 180$.

Table 2. *Refinement results*

$\langle x\rangle$, $\langle y\rangle$, $\langle z\rangle$ are the average atomic coordinates ($\times 10^4$) deduced from equation (1), P_o the average occupancies ($\times 10^4$), A_1, B_1, A_2, B_2 the Fourier terms ($\times 10^4$) of the modulation functions $U(\bar{x}_4)$ and $P(\bar{x}_4)$, β_{ij} (or $B_{\rm iso}$) and B_{44} the thermal parameters and phason terms respectively ($\times 10^4$); the e.s.d.'s are given in parentheses. The anisotropic thermal parameters are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The occupancy probability of the Sr sites by the Bi atoms is given by $1 - [P_o + P(\bar{x}_4)]_{\rm Sr}$.

				A_1	B_1	A_2	B_2
Bi	$\langle x\rangle$	−6 (2)	U_1	−544 (3)	642 (3)	−182 (4)	102 (4)
	$\langle y\rangle$	2754 (2)	U_2	54 (5)	55 (5)	36 (8)	49 (7)
	$\langle z\rangle$	654 (0)	U_3	−49 (0)	−121 (0)	−3 (0)	−7 (0)
	P_o	9579 (95)	P	−476 (45)	−277 (45)	−237 (60)	−264 (60)
Sr	$\langle x\rangle$	5003 (4)	U_1	−341 (6)	265 (6)	−161 (7)	−29 (8)
	$\langle y\rangle$	2473 (5)	U_2	11 (12)	1 (11)	10 (21)	−12 (21)
	$\langle z\rangle$	1785 (1)	U_3	−23 (1)	−150 (1)	−6 (2)	−14 (1)
	P_o	9200 (90)	P	200 (80)	90 (75)	−435 (120)	684 (95)
Cu	$\langle x\rangle$	0	U_1	0	132 (13)	0	−18 (16)
	$\langle y\rangle$	$\frac{1}{4}$	U_2	0	0 (23)	0	24 (46)
	$\langle z\rangle$	$\frac{1}{4}$	U_3	0	−186 (3)	0	−36 (4)
	P_o	10000	P				
O(1)	$\langle x\rangle$	2526 (50)	U_1	−148 (80)	103 (40)	−52 (90)	−25 (50)
	$\langle y\rangle$	4 (40)	U_2	−8 (100)	26 (50)	−74 (100)	170 (80)
	$\langle z\rangle$	2517 (10)	U_3	2 (25)	−177 (10)	−77 (15)	−22 (15)
	P_o	10000	P				
O(2)	$\langle x\rangle$	147 (40)	U_1	−364 (60)	590 (60)	−326 (70)	130 (70)
	$\langle y\rangle$	2003 (50)	U_2	−40 (90)	−238 (90)	129 (120)	−249 (110)
	$\langle z\rangle$	1499 (8)	U_3	−38 (10)	−161 (10)	24 (15)	−16 (15)
	P_o	7410 (370)	P	−674 (450)	−1428 (600)	1518 (700)	−2025 (600)
O(3)	$\langle x\rangle$	5210 (50)	U_1	−736 (70)	1376 (80)	−403 (85)	561 (80)
	$\langle y\rangle$	3404 (40)	U_2	146 (80)	90 (85)	−3 (100)	143 (95)
	$\langle z\rangle$	698 (9)	U_3	−52 (14)	−125 (10)	24 (15)	9 (15)
	P_o	10000	P				

	β_{11}	β_{22}	β_{33}	β_{23}	β_{31}	β_{12}	B_{44}
Bi	75 (4)	92 (3)	5 (0)	−1 (0)	1 (0)	5 (5)	170 (28)
Sr	53 (7)	72 (8)	10 (0)	−5 (1)	0 (1)	0 (9)	345 (80)
Cu	65 (17)	22 (18)	6 (1)	2 (4)	2 (3)	−16 (20)	270 (200)

	B(Å^2)
O(1)	0.3 (2)
O(2)	0.3 (2)
O(3)	1.0 (4)

The results of the refined model are summarized in Table 2.* The global agreement factor is $R = 0.066$; the partial R factors related to the main reflections, first- and second-order satellite reflections are $R^0 = 0.061$, $R^1 = 0.061$ and $R^2 = 0.086$ respectively; the corresponding weighted factors are $wR = 0.075$, $wR^0 = 0.072$, $wR^1 = 0.071$ and $wR^2 = 0.102$. Although their standard deviations are rather large, the Fourier terms of the O atoms (Table 2) can nevertheless be considered significant; indeed, if these terms are given zero values the partial agreement R factors become 0.098, 0.085 and 0.107. As the R factors have relatively small values and the refinement convergence is well assured [$(\Delta/\sigma)_{\max} = 0.05$], the hypothesis of a centrosymmetric superspace group appears to be reasonable. Concerning this result it should be noted that the superspace group considered by Gao *et al.* (1989) to refine the modulated structure of $Bi_{2.3}Sr_{1.1}Ca_{0.6}CuO_6$ was the noncentrosymmetric one P^{Aa}_{1}.

Discussion

A projection of the basic structure onto the (010) plane is shown in Fig. 2; the atomic sites relevant for

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* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55018 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0333]

the discussion are specified with numbers in parentheses. Let us first point out the main characteristics of the displacive and density modulation wave.

As regards Bi, Sr and Cu atoms, the U_3 component, along **c**, of the displacive modulation wave is almost harmonic while the U_1 component, along **a**, deviates in a noticeable way from harmonicity (Table 2). The anharmonic effect is enhanced for the O atoms. Compared with the other components, the U_2 components are small (less than 0.15 Å), except for the O(2) atom (0.30 Å). These features are illustrated in Fig. 3 taking the Bi and O(3) atoms as examples. To procure an image of the modulated structure, the actual positions of the atoms can be shown in a restricted number of unit cells, five along **a**, two along **c**, since the q_1^* and q_3^* values are rather close to $\frac{1}{5}$ and $\frac{1}{2}$ respectively. This type of image is drawn in Fig. 4 for the Bi, Sr and Cu atoms [projection onto the (010) plane] underlining the waving of the cation (001) sheets and the large amplitude of the displacive modulation wave. The following features are observed:

(*a*) The structure can be described as being built up of blocks of five corrugated layers 'Bi—Sr—Cu—Sr—Bi', labelled *A* in Fig. 4. Within each *A* block the five layers exhibit approximately the same curvature, *i.e.* the different cations of these layers display rather similar displacements along **c**.

(*b*) Two successive blocks along **c**, *A* and *A*′, are inverted with respect to each other. Moreover, the displacements of the cations along **c**, which are nearly harmonic, are about $\pi/2$ out of phase in two adjacent blocks.

(*c*) Correspondingly the two bismuth layers which form the junction between two successive blocks do not exhibit the same waving. The distance along **c** between two adjacent Bi layers varies in a regular and significant way. One indeed observes expanded regions where the interlayer distances are maximal (labelled *E*) and compressed regions where the interlayer distances are much smaller (labelled *C*). This phenomenon is in agreement with high-resolution electron microscopy observations (Matsui *et al.*, 1988).

(*d*) Within the Bi bilayers built up of two nearest Bi sheets, the interlayer Bi—Bi(1) distances and the

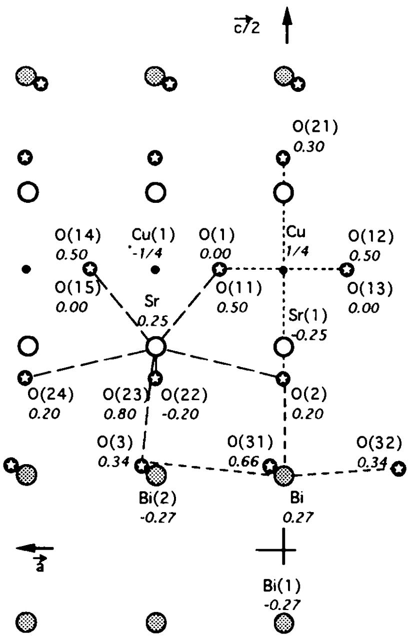
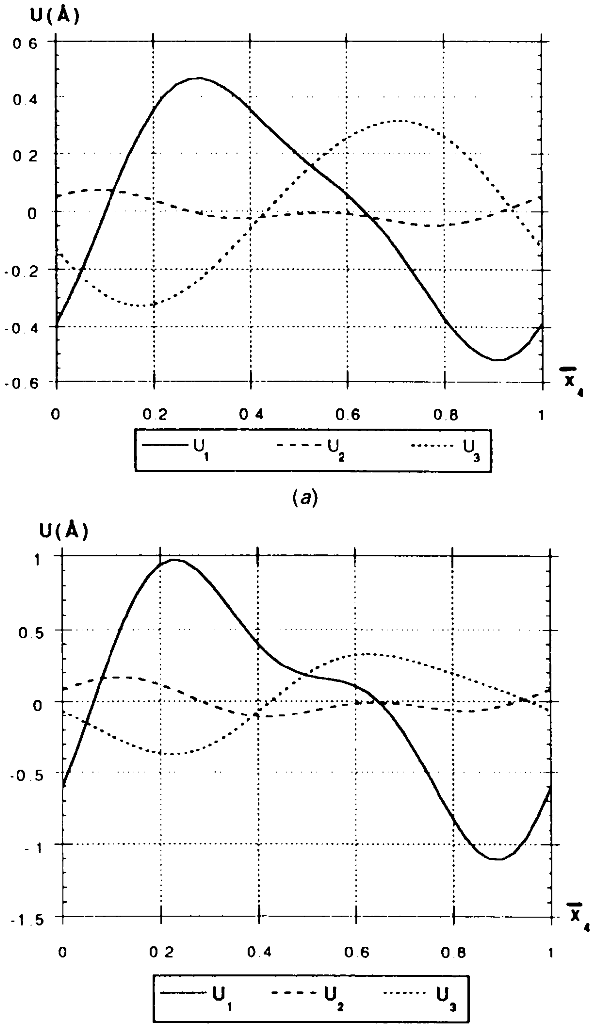


Fig. 2. Basic structure projected onto the (010) plane; space group *A*2/*a*. The atomic sites are specified by the numbers in parentheses and their ⟨*y*⟩ coordinates are also indicated. The main bonds are marked with dotted lines.



(*b*)

Fig. 3. Variation of the displacement components U_1, U_2, U_3 along **a**, **b**, **c** respectively, with internal $\bar{x}_4$ parameter. (*a*) For the Bi atom. (*b*) For the O(3) atom.

intralayer Bi—Bi(2) distances (see Fig. 2) vary in opposite ways *versus* the *t* parameter as shown in Fig. 5. Thus, in the expanded *E* regions of the crystal the intralayer Bi—Bi(2) distances are the smallest whereas in the compressed *C* regions the intralayer Bi—Bi(2) distances are the largest giving rise to bismuth condensed and diluted regions respectively.

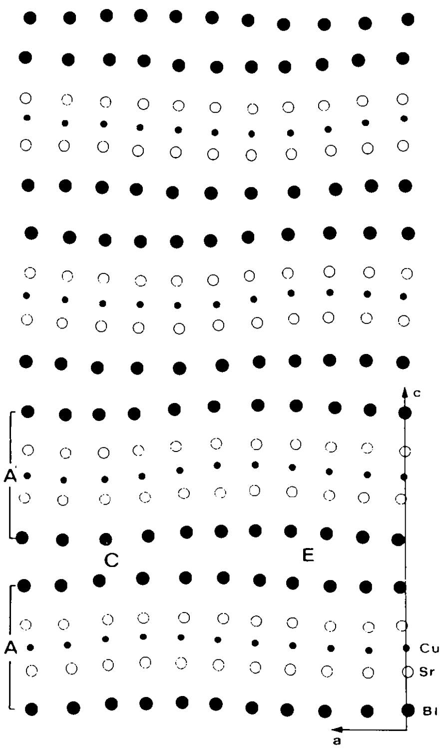


Fig. 4. Waving of the Bi, Sr and Cu sheets in the actual crystal, as viewed projected onto the (010) plane. Atomic displacements from the basic positions are not magnified.

(*e*) The intralayer Sr—Sr(1) distances (see Fig. 2) vary in a similar way as the intralayer Bi—Bi(2) distances *versus t*. In contrast, the intralayer Cu—Cu(1) distance (see Fig. 2) is nearly constant and close to 3.80 Å through the whole crystal, ruling out any large variation of the Cu—O bond lengths inside the CuO_4 square-planar groups.

One of the most unexpected refinement results is the existence of O(2) vacant sites within the Sr—O layers, the mean occupancy of these sites being about 0.75 (4); moreover, a large modulation of this occupancy is observed (Table 2). This phenomenon is closely correlated to the occupancy modulation of the bismuth and strontium sites as shown in Fig. 6. To describe this correlation, the Bi, Sr(1), O(2) and O(21) sites lying almost in the same (100) plane (Fig. 2) inside the basic crystal are chosen as reference sites. The *P′* functions related to these atomic sites are drawn *versus* the *t* parameter which characterizes the **p** unit cells. The standard deviations of the *P′* values are about 0.01, 0.02 and 0.10 for Bi, Sr and O(2) respectively, leading in particular to the conclusion that the O(2) result is significant. Examination of the *P′* curves (Fig. 6) allows the following main features to be evidenced.

(*a*) In some parts of the crystal the Bi sites may be vacant; this phenomenon occurs in unit cells where the Bi layers are compressed along **c** (Fig. 4); as a matter of fact, the smallest Bi—Bi(1) interlayer distances (Fig. 5) and the smallest occupancy probabilities of the Bi sites (Fig. 6) are observed for the same *t* values, which are close to 0.

(*b*) In some parts of the crystal the Sr(1) sites are occupied by Bi atoms; in the corresponding unit cells, the occupancy probabilities of the O(2) and O(21) apical sites are about one.

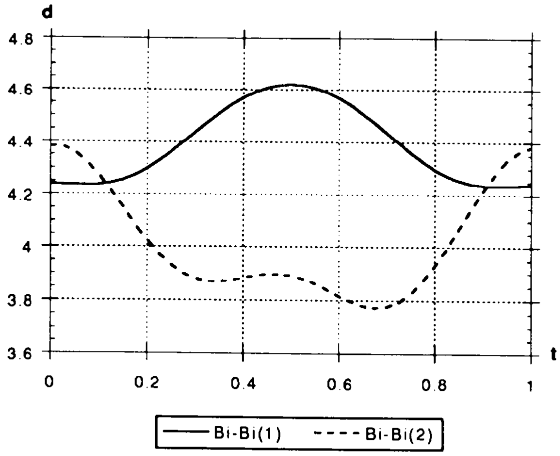


Fig. 5. Comparison of the variation of Bi—Bi(1) interlayer and Bi—Bi(2) intralayer distances (Å) with *t* parameter. $\langle\sigma\rangle \simeq 0.005$ Å.

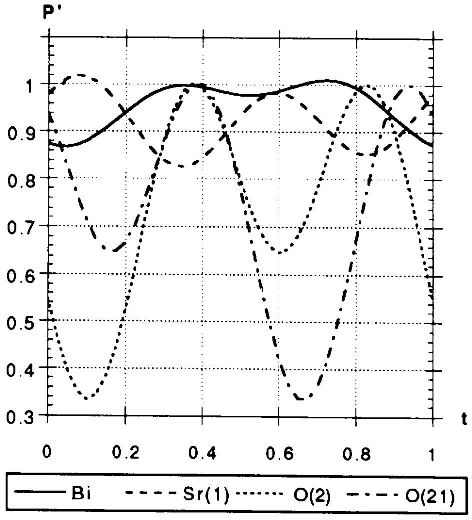


Fig. 6. Occupancy probabilities *P′* of the Bi, Sr(1), O(2) and O(21) sites as a function of *t*; O(2) and O(21) are the apical sites.

(*c*) The O(2) and O(21) apical sites may be vacant in unit cells where Sr(1) sites are likely occupied by only strontium.

These different features lead us to carefully scrutinize the surroundings and coordination of the cations in the actual crystal.

The copper coordination

Variation of the Cu—O bond lengths with t is shown in Fig. 7; the notation used to specify the atom sites is that defined in Fig. 2. Calculated standard deviations on these distances are given in the figure captions. Neglecting temporarily the occupancy variation of the O(2) and O(21) apical sites, the displacive modulation observed within the copper polyhedra appears as a combination of rotations, translation motions and distortion effects; this distortion of the polyhedra, throughout the crystal, is obvious as suggested by the amplitude variation of the Cu—O distances (Fig. 7). The rotations and translations were derived from a least-squares refinement, assuming a rigid-body model. The latter was tested introducing an agreement factor R which corresponds to the averaged value of $(\sum|\mathbf{U}_o - \mathbf{U}_c|^2/\sum|\mathbf{U}_{oi}|^2)^{1/2}$ in several unit cells (Zuñiga, Madariaga, Paciorek, Pérez-Mato, Ezpeleta & Etxebarria, 1989). The $\mathbf{U}_o$ vectors are the atomic displacements observed in the polyhedra and the $\mathbf{U}_c$ vectors those calculated from the model used. Owing to the distortion effect, the R factor is large (0.43) but less than (0.50).

Two main and significant rotations of the copper polyhedra are observed. The first rotation, about **b**, which was expected, exhibits a very anharmonic character with different extreme angular values of −4 (1) and + 9 (1)°. The second, about **a**, which was quite unexpected, is harmonic with an amplitude of 4 (1)°; this rotation, related to the noticeable U_2 component of the apical O(2) oxygen, has a periodicity of $\lambda/2$ ($\lambda = 1/q^*$).

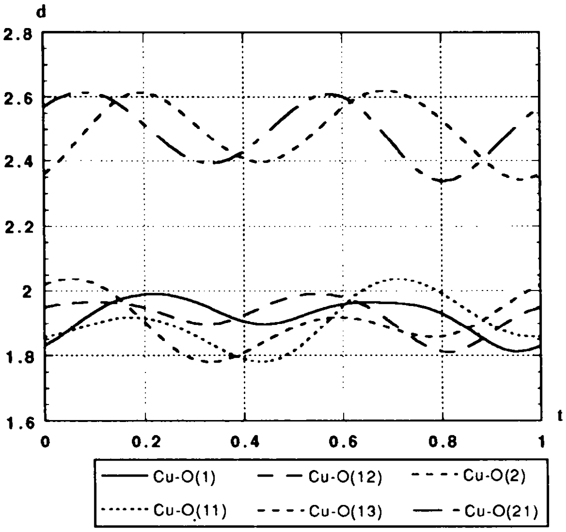


Fig. 7. Variation of the Cu—O bond lengths (Å) with t. $\langle\sigma\rangle$ from 0.05 to 0.06 Å.

From the characteristics of the P' curves (Fig. 6) related to the O(2) and O(21) apical sites, copper atoms can achieve three types of coordination – square, pyramidal or octahedral – throughout the crystal. A similar property is observed in the $La_{8-x}Sr_xCu_8O_{20}$ crystal (Er-Rakho, Michel & Raveau, 1988). The geometry of the copper polyhedra is rather distorted and evolution of the Cu—O bonds throughout the crystal is complex. The square-planar coordination which is most likely to occur for t values close to 0.15 and 0.62 (Fig. 6), *i.e.* in regions where Sr sites are only occupied by strontium, is rather distorted. One indeed observes (Fig. 7) three long distances close to 1.98 Å, *i.e.* longer than the mean distance of 1.92 Å observed for the Cu—O equatorial bonds and one normal distance of 1.92 Å. In contrast, in unit cells where octahedral coordination is highly probable, *i.e.* for t values close to 0.38 and 0.88 (Fig. 6), a different distortion of the basal plane is involved; one observes (Fig. 7) two equatorial Cu—O distances close to the mean value of 1.92 Å and two shorter equatorial Cu—O distances (1.80 Å for $t = 0.38$, 1.85 Å for $t = 0.88$). In these CuO_6 octahedra, the two Cu—O(2) apical distances of 2.40 Å, although significantly larger than the equatorial ones, appear as the smallest apical distances (mean value 2.50 Å) observed throughout the crystal. It is worth pointing out that this type of octahedral coordination occurs in unit cells where the occupancy probability of Sr sites by bismuth is the highest. It must also be emphasized that a rather similar distribution of Cu—O distances has recently been observed for $La_2Cu_2O_5$ (Cava, Siegrist, Hessen, Krajewski, Peck, Batlogg, Takagi, Waszczak, Schneemeyer & Zandbergen, 1991) which exhibits two short Cu—O equatorial distances (1.86–1.89 Å), two longer ones (1.93–1.95 Å) and two similar apical Cu—O distances (2.43 Å).

In the other unit cells, corresponding to intermediate t values, abrupt variation of the O(2) apical site occupancy does not permit determination of what is the predominant coordination, pyramidal or square planar/octahedral; thus it is not realistic to draw conclusions about the geometry of the eventual pyramidal environment of copper.

The strontium sites

Variation of the Sr—O distances corresponding to apical O(2) oxygen sites, which are in fact partly occupied, has been studied (Fig. 8*a*) separately from that of the other Sr—O distances (Fig. 8*b*), which are related to the fully occupied oxygen sites. In order to study the evolution of Sr—O distances as a function of *t* and to specify the coordination of strontium we have considered the site labelled Sr in Fig. 2; the occupancy probabilities of the surrounding O(2) sites have been obtained from the $P'(t)$ curve of O(2) (Fig. 6). The strontium atom (or bismuth atom which may substitute Sr over some sites) achieves bonds with oxygen atoms O(1) and O(3) belonging to the Cu—O and Bi—O layers respectively (Fig. 8*b*). Such phenomena take place throughout the whole crystal. In contrast, the O(2) atoms are not bound to the strontium atom in all their unit cells, either because the Sr—O distances are too large (Fig. 8*a*), or because the occupancy probabilities of the O(2) sites are too small in some parts of the crystal. As a result, the coordination of the strontium atom varies in a complex way. In the unit cells where the occupancy probability of Sr sites by bismuth is the highest, *i.e.* for *t* intervals of 0.20–0.35 and 0.65–0.80, the most likely coordination of Sr (or Bi) is ninefold. It is then observed that the average ⟨Sr—O⟩ distances calculated for each polyhedron are similar and nearly equal to 2.7 Å.

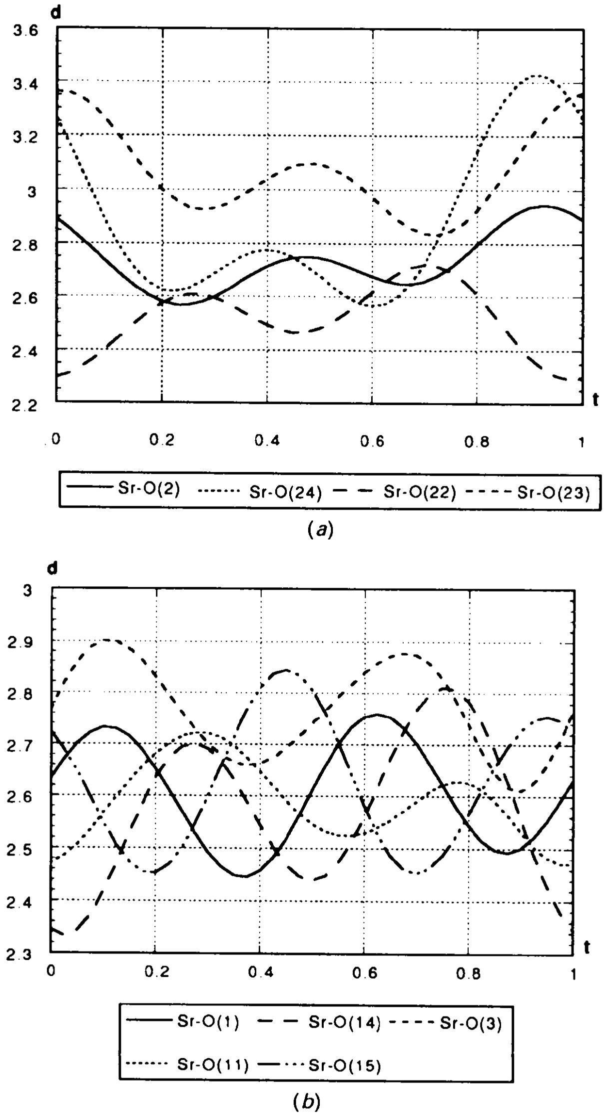


Fig. 8. Variation of the Sr—O bond lengths (Å) with *t*. (*a*) Sr—O(2)-type distances; ⟨σ⟩ from 0.05 to 0.08 Å; some oxygen sites of O(2) type may be vacant. (*b*) Sr—O(1)- and Sr—O(3)-type distances; ⟨σ⟩ from 0.05 to 0.06 Å; these oxygen sites are fully occupied.

In unit cells where the Sr sites are likely to be occupied by strontium, *i.e.* for *t* intervals of −0.15–0.10 and 0.40–0.60, various coordinations may occur. Assuming an arbitrary distance limit of about 3.0 Å for a Sr—O bond, the following main features are found:

(*a*) In the first interval (−0.15–0.10), sixfold or sevenfold coordination would be involved for the strontium atoms; since there is only a small probability that the two sites O(2) and O(22) are vacant in the same unit cell, fivefold coordination can be rejected; this conclusion is in agreement with the results of different studies which indicate that the usual coordination of strontium ranges from 6 to 12 (Shannon, 1976).

(*b*) In the second interval of *t* (0.40–0.60), the most likely coordination of Sr is 8.

To sum up, the variation of strontium coordination, from 6 to 9, throughout the crystal is remarkable; in contrast, when bismuth atoms substitute the strontium atoms over Sr sites, only one coordination is involved, ninefold coordination, the bismuth then achieving bonds with all the nearest O atoms surrounding the Sr sites.

The bismuth coordination and oxygen stoichiometry

Variation of the Bi—O bond lengths, with *t* parameter, is illustrated in Fig. 9. One of the most remarkable results concerns the dramatic variation of the Bi—O(3) and Bi—O(32) distances corresponding to O atoms in the Bi—O layer; such variations occur in regions of the crystal where two adjacent bismuth layers are compressed along **c**, *i.e.* in the bismuth-diluted regions labelled *C* in Fig. 4. By contrast, the Bi—O(2) and Bi—O(31) distances, which correspond to apical oxygen and to O atoms located within Bi—O layers, remain approximately constant throughout the whole crystal; moreover, the latter Bi—O distances are rather short, *i.e.* close to 2.1 Å, indicating the existence of strong bonds.

In unit cells where two adjacent Bi layers are expanded along **c**, *i.e.* in the bismuth-condensed regions labelled *E* in Fig. 4 (the *t* interval is 0.25–0.85) the most likely coordination of bismuth is fourfold. In these regions, the bismuth coordination can be described as a trigonal bipyramid in which one corner is occupied by the $6s^2$ lone pair of bismuth. This type of coordination, as shown in Table 3, is to some extent similar to that described in recent work concerning β-Bi_2O_3 (Blower & Greaves, 1988) and $BaBiO_{2.5}$ (Lightfoot, Hriljac, Pei, Zheng, Mitchell, Richards, Dabrowski, Jorgensen & Hinks, 1991). It should be also noted that similar bismuth coordination is observed in the Bi-condensed regions of the superconducting oxide $Bi_2(Sr,Ca)_3Cu_2O_{8+x}$ (Yamamoto, Onoda, Takayama-Muromachi, Izumi, Ishigaki & Asano, 1990).

In other parts of the crystal ($-0.10 < t < 0.20$) a drastic change of bismuth coordination is expected; in these parts one indeed observes that the O(3) and/or O(32) oxygen atoms are too far from the Bi atom to be considered as neighbours (Bi—O distances greater than 3 Å as shown in Fig. 9); moreover, the occupancy probabilities of the O(2) sites are smaller than 0.5 in unit cells defined by $0 < t < 0.20$. Obviously, these features would lead, in some unit cells, to the unlikely bismuth-atom coordination of 1 or 2.

At this stage, we have to consider the chemical formula of the compound deduced from refinement of atomic site occupancies. If the O(2) site was fully occupied, then the formula would be $Bi_{2.08}Sr_{1.84}CuO_6$. As the O(2) site is $\frac{3}{4}$ occupied on average, the formula deduced from this X-ray investigation is in fact $Bi_{2.08}Sr_{1.84}CuO_{5.5}$. The charge balance of cations and anions requires an amount of oxygen equal to 5.96 assuming no mixed valencies for bismuth and copper atoms. Thus, the existence of extra oxygen inside the crystal, not detected by the X-ray investigations, appears to be necessary not only in order to satisfy the charge balance but also to achieve coordination of bismuth in some parts of the crystal. Such extra oxygens are indeed observed in the related compounds $Bi_2Sr_2MnO_{6.37}$ (Tarascon, Le Page & McKinnon, 1990) and $Bi_2Sr_2CoO_{6.25}$ (Tarascon *et al.*, 1989) which exhibit commensurate structures.

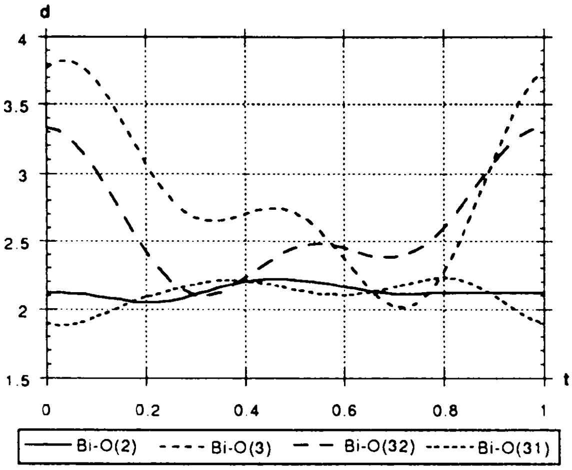


Fig. 9. Variation of the Bi—O bond lengths with t. $\langle\sigma\rangle$ from 0.05 to 0.07 Å.

Table 3. Bi—O *distances* (Å), *and* α *and* β O—Bi—O *valence angles* (°) *in the three crystals* β-Bi_2O_3, $BaBiO_{2.5}$ *and* $Bi_{2.08}Sr_{1.84}CuO_6$

Bi is four-coordinated in a pseudotrigonal bipyramidal environment where the electron lone pair occupies one of the equatorial sites. The Bi—O*e* and Bi—O*a* notations specify the equatorial and axial bond lengths respectively. α and β are the Oe_1—Bi—Oe_2 and Oa_1—Bi—Oa_2 angles respectively. As regards the crystal studied, the Bi—O distances are averaged on the t interval of 0.25–0.85 where the fourfold coordination of Bi occurs.

	β-Bi_2O_3	$BaBiO_{2.5}$	$Bi_{2.08}Sr_{1.84}CuO_6$	
Bi—Oe_1	2.10	2.06	⟨2.15⟩	2.06 to 2.22
Bi—Oe_2	2.13	2.08	⟨2.17⟩	2.10 to 2.23
Bi—Oa_1	2.25	2.24	⟨2.39⟩	2.10 to 2.83
Bi—Oa_2	2.46	2.49	⟨2.50⟩	2.02 to 2.81
α	82	92	~⟨97⟩	93 to 101
β	172	171	~⟨163⟩	161 to 166

First, let us consider the possible existence of extra oxygens within the Bi—O layers of the crystal studied. This type of extra oxygen is expected in the Bi-dilute regions. The local environment of Bi was studied for t values equal to 0, 0.05, 0.10, 0.15, 0.20 and 0.95. The positions of eventual supplementary oxygen atoms, labelled O*s*, were determined constraining the relevant Bi—O*s* and O—O*s* distances to values greater than 1.9 and 2.6 Å respectively. Two of the corresponding configurations are given as examples. The first one related to $t = 0$ (Fig. 10*a*) shows the possible inclusion of O atoms over two sites Os_1 and Os_2; each O*s* is then locally bound to two bismuth atoms. The second configuration (Fig. 10*b*) for $t = 0.10$ allows only one supplementary O atom to be introduced in the Bi—O layer. For $t = 0.20$ no O*s* can be introduced. Within the first two configurations this results in one and one half additional O atoms per bismuth respectively. A formal calculation of the total number of additional oxygen O*s* per bismuth, throughout the unit cells where these configurations are likely to occur, leads to a maximum value of 0.16 ($1 \times 0.10 + 0.5 \times 0.12$), less than the required value of 0.23. Consequently, the existence of extra oxygens between two adjacent Bi—O layers appears necessary.

Let us discuss this possibility. These types of oxygens, labelled O*c*, are to be expected in unit cells where the occupancy probabilities of the O(2) sites are the smallest, *i.e.* for $0 \leq t \leq 0.20$ and $0.55 \leq t \leq 0.65$ (see Fig. 6). Two cases have to be considered according to whether extra oxygens can or cannot be introduced within the Bi—O layers. In the first case, let us take as an example the configuration $t = 0.10$. If O(2) is present, the insertion of an O*c* atom is not necessary; Bi then achieves a threefold coordination owing to the presence of O*s* (Fig. 10*b*). On the other hand, if O(2) is absent, the insertion of two O*c* atoms is necessary to satisfy the Bi coordination (Fig. 10*c*); indeed, the insertion of O*c* atoms is incompatible with insertion of an O*s* atom. Bi then has a threefold coordination (Torardi, Parise, Santoro, Rawn, Roth & Burton, 1991). To illustrate the second case, let us take as an example the configuration $t = 0.60$. If O(2) is present, Bi achieves a fourfold coordination; if O(2) is absent, the insertion of one O*c* seems necessary to satisfy the Bi coordination in so far as two Bi—O distances are too large (about 2.4 Å). Such a configuration may occur in several unit cells of the crystal, for t about 0.60 and 0.20. Thus, the insertion of O*s* and O*c* atoms would give sufficient extra oxygens in the crystal. Finally, various orientations of the bismuth lone pair should be involved because of the different environments of this cation.

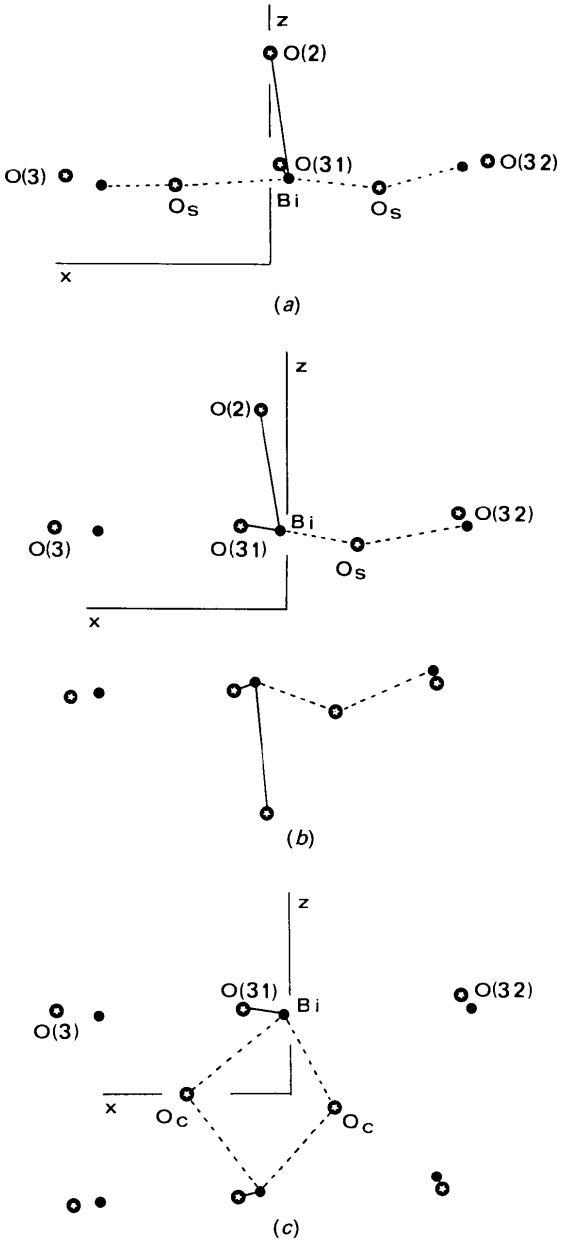


Fig. 10. The bismuth environment in the presence of extra oxygens. (*a*) $t = 0$, (*b*) and (*c*) $t = 0.10$. The bonds achieved between the Bi atom and the apical O(2) atom and oxygen atoms of O(3) type are indicated by full lines. Other bonds with extra oxygens are shown by dotted lines. The y coordinates of the O*s* and O*c* extra oxygens are close to 0. For $t = 0.10$, two different Bi environments have to be considered according to whether the O(2) site is occupied or vacant.

Concluding remarks

This X-ray investigation of the '2201' monoclinic bismuth cuprate, on an untwinned crystal of exceptionally good quality, has allowed the modulated structure of this phase to be determined, taking into account for the first time the displacive modulation of the O atoms.

Significant and remarkable results were obtained. The existence of a strontium deficiency was observed which is compensated for by an excess of bismuth, with a significant partial occupation of strontium sites by bismuth atoms in some parts of the crystal. A second significant and unexpected feature concerns the partial occupation of the apical O(2) sites of the CuO$_6$ octahedra. Throughout the crystal, evolution of the occupancy probabilities of Bi, Sr and apical O(2) sites is correlated in a spectacular way. Within the Bi—O layers, the O(3) oxygen atoms exhibit very large displacements along **a**, up to 1.1 Å from their basic positions.

This accurate structure determination does not allow an excess of oxygen to be detected with respect to the ideal formula Bi$_2$Sr$_2$CuO$_6$, but rather the maximum oxygen content deduced from this X-ray study leads to the formula Bi$_{2.08}$Sr$_{1.84}$CuO$_{5.5}$. This suggests that extra O atoms are probably located both within and between the Bi—O layers giving rise to the complex environment of the bismuth atoms. The small amount of additional oxygen, *i.e.* about 0.4–0.5 per formula, distributed over several sites throughout the crystal, prevents its localization by X-ray techniques.

The rather large cationic disorder, and especially the existence of oxygen vacancies on the apical sites of the CuO$_6$ octahedra may be responsible for the absence of superconductivity. A systematic structural study of other different crystals in which the **q*** vector varies, and especially of a superconducting crystal will be absolutely necessary in order to elucidate the relationships between modulation, oxygen stoichiometry and superconductivity in this phase.

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Structure Refinement of Commensurately Modulated Bismuth Strontium Tantalate, $Bi_2SrTa_2O_9$

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Abstract

The displacive ferroelectric $Bi_2SrTa_2O_9$ [M_r = 1011.47, a = 5.5306 (5), b = 5.5344 (5), c = 24.9839 (24) Å, Z = 4, D_x = 8.785 g cm^{-3}, Mo $K\alpha$, λ = 0.7107 Å, μ = 806.8 cm^{-1}, $F(000)$ = 1687.64], is described at room temperature in space group $A2_1am$ as a commensurate modulation of an idealized $Fmmm$ parent structure derived from an $I4/mmm$ structure. A final value of 0.045 for $R_1 = \sum_{\mathbf{h}}||F_{\rm obs}(\mathbf{h})| - |F_{\rm calc}(\mathbf{h})||/\sum_{\mathbf{h}}|F_{\rm obs}(\mathbf{h})|$ was obtained for 3082 unmerged data with $I(\mathbf{h}) > 3\sigma[I(\mathbf{h})]$. The crystal studied showed both twinning and disorder which were successfully modelled in the refinement. The final structure suggests that these features are almost inevitable. The structure is contrasted with that of Bi_3TiNbO_9 [Thompson, Rae, Withers & Craig (1991), *Acta Cryst.* B47, 174–180] with particular interest in the effects of a Bi^{3+} ion being replaced by an Sr^{2+} ion. The value of anomalous dispersion for detecting false minima, centrosymmetric twinning and disorder is detailed. An apparent valence interpretation of the crystal chemistry is included.

Introduction

In recent years the room-temperature crystal structures of the ferroelectric Aurivillius phases,

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