

Static Disorder in the Incommensurate Structure of the High T_c Superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

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Abstract

The incommensurate modulated structure of the high T_c superconductor of nominal composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ has been refined using an optimized data set of 1530 reflections (496 main reflections, 753 first-order and 281 second-order satellites) in superspace group $Bbmb(0\beta 1)$ using a Fourier expansion of the modulation functions up to second order. A large improvement of the R (wR) factor [global: 0.056 (0.051); main reflections: 0.049 (0.043); first-order satellites: 0.056 (0.058); second-order satellites: 0.078 (0.079)] is obtained by the introduction of a static modulated disorder on the Bi site without any thermal factor modulation and by considering occupational modulation functions. A detailed comparison with previous studies in modulated structure models or in supercell models is given, in particular for the description of the BiO layers.

1. Introduction

The determination of the modulated structure of the high T_c superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (so-called Bi-2212) is a real challenge which has been taken up by several authors in previous years. The interest in such a structural resolution is always a better understanding of the incommensurate modulation and the eventual relation of these structural features with the electronic structure of the CuO_2 layers responsible for the superconducting properties of the compound. If there is a general agreement in the description of the corresponding average structure ($a \simeq b \simeq 5.4 \text{ \AA}$; b , modulation direction; $c \simeq 30.7 \text{ \AA}$, stacking direction of the BiO–SrO– CuO_2 –Ca layers; space group $Bbmb$), there is still some controversy concerning the structural characteristics of the modulation and its origin.

The reason for such an uncertainty lies in the numerous problems encountered for the structural refinement of these compounds and it is easy to draw up a list of these various difficulties.

The first type of problem is related to the available samples, which are generally small and very anisotropic platelet-like single crystals. The reduced size of the samples does not allow very appropriate single-crystal

neutron diffraction experiments. To our knowledge, there is only one such study (Beskrovnyi, Dlouhá, Jiráček, Vratislav & Pollert, 1990) using only 196 reflections. The particular shape associated with a very high X-ray absorption coefficient requires a very accurate absorption correction of the X-ray diffracted intensities. The crystalline quality is also a very important parameter and numerous studies outline the presence of different defects and disorders for this compound. The first is the frequent observation of twinned domains, which are related to the layered structure and to the pseudo-tetragonal character of the structure (see, for example, Eibl, 1990). The second is the existence of structural disorders in the stacking of the slabs evidenced either by transmission electron microscopy (see, for example, Budin, Eibl, Pongratz & Skalicky, 1993) or by X-ray diffraction experiments (Bdikin, Dorokhova, Lenchenko, Kulakov, Shekhtman & Shmyt'ko, 1992; Wu, Jia, Shi, Zhou, Zang, Qin & Qian, 1993; Johnson, Hatton, Chowdury, Wanklyn, Yan, Zhao & Marshall, 1994; Zhigadlo, 1994). These last studies evidenced the existence of generally diffuse peaks in the diffraction pattern at forbidden nodes of the reciprocal lattice associated with the usual superspace symmetry $Bbmb(0\beta 1)$ in the previous setting. The characteristics of these extra diffusions and their evolution as a function of the temperature seem to be relative to the different samples, even if their appearance seems very frequent. They are generally more diffuse along the stacking direction c and thus have been interpreted on the basis of a shorter correlation length in this direction.

A second type of problem is related to the structural characteristics themselves. The cell volume is rather large and involves at least eight independent atoms. The layered structure is built simultaneously with light (O) and heavy (Bi) atoms with regard to X-ray diffraction. All studies also agree on the existence of a non-stoichiometry for almost all the present species, since from anomalous scattering studies (Lee, Gao, Sheu, Petricek, Restori, Coppens, Darovskikh, Phillips, Sleight & Subramanian, 1989; Roberts, Mayo, Woolsey, Glazer & O'Reilly, 1991), substitution and/or vacancies are expected for Bi, Sr and Ca sites. A particularly difficult problem also concerns the oxygen non-stoichiometry.

Excess oxygen is generally admitted by the insertion of extra O atoms in the BiO layers and different structural studies have tried to locate these extra O atoms (Calestani, Rizzoli, Francesconi & Andreetti, 1989; Yamamoto, Onoda, Takayama-Muromachi, Izumi, Ishigaki & Asano, 1990; Petricek, Gao, Lee & Coppens, 1990; Beskrovnyi, Dlouhá, Jiráček, Vratislav & Pollert, 1990; Jiráček, 1992; Levin, Smolin & Shepelev, 1994). Of course, oxygen location should be preferentially refined using neutron diffraction data. As adequate single crystals are still not available, some studies have used powder (Yamamoto *et al.*, 1990) or combined single crystal and powder diffraction data (Gao, Coppens, Cox & Moodenbaugh, 1993), but in this case the authors had to face another important difficulty: the incommensurate value of the modulation wavevector and the necessity to take into account the real wavevector in the Rietveld-type structural refinements. For single crystal studies, this difficulty is less decisive and a choice is possible between a refinement using the recent formalism for incommensurate modulated structures in the superspace (de Wolff, Janssen & Janner, 1981) or a supercell approximation. In the first case, the main problem is to choose adequate crystallographic parameters to be refined and for these parameters, to find an adequate model to describe the modulation functions. As a matter of fact, from previous studies in this approach (Yamamoto *et al.*, 1990; Petricek *et al.*, 1990; Kan & Moss, 1992; Gao *et al.*, 1993), it appears that the classical Fourier expansion series for the modulation functions are not the best way to describe the particular structural features of the BiO layers and the location of the eventual extra O atom. In the second case, first, one has to remember that the structural description is approximate, which does not take into account the incommensurability of the structure, and second, the structure refinement is achieved in a lower symmetry, which induces a large number of refinement parameters, with associated strong correlations. Such supercell descriptions require a large data collection, which is effectively the case for related previous supercell studies: Levin *et al.* (1994), for the Bi-2212 compound, Gladyshevskii & Flükiger (1996) for a monoclinic variant of the orthorhombic Bi-2212 and Le Page, McKinnon, Tarascon & Barboux (1989) for the isostructural ferrite compound $\text{Bi}_{10}\text{Sr}_{15}\text{Fe}_{10}\text{O}_{46}$. The advantage of these studies in the supercell is their adequateness to try to introduce an extra O atom.

In the present study, the choice has been made to work using high-quality X-ray single crystal diffraction data, in the subcell and in the modulated model using the real modulation wavevector and the best adequate symmetry description of the incommensurate structure. We have first focussed our attention on the accurate determination of the modulation functions for cations as they can be more easily derived from X-ray diffraction data, associated with reasonable values for thermal parameters.

These conditions led us to introduce a static modulated disorder for the Bi atoms, which considerably improved our model. From this basic cationic model, the oxygen location has been refined and, in particular, the existence of an extra oxygen is discussed. Finally, a comparison is made with previously reported studies.

2. Experimental

Single crystals were prepared by the self-flux method from a mixture of oxides and carbonates with the nominal ratio $\text{Bi}_2\text{O}_3:\text{SrCO}_3:\text{CaCO}_3:\text{CuO} = 1.07:1.3:1.3:2$, heated at 1310 K for 24 h, rapidly cooled to 1240 K and then slowly cooled to 1000 K. The detailed description of the preparation is given elsewhere (Ruyter, Simon, Hardy, Hervieu & Maignan, 1994). The atomic composition of different samples measured by EDS (energy dispersive spectroscopy) gave average ratios $\text{Bi}:\text{Sr}:\text{Ca}:\text{Cu} = 2.1(1):1.9(1):1.0(1):2$, where the Cu occupancy is normalized to 2. A monodomain single crystal of good crystalline quality was selected from the melt ($0.500 \times 0.188 \times 0.015 \text{ mm}^3$) and mounted on an Enraf-Nonius CAD-4 four-circle diffractometer.

The experimental data of the collection are summarized in Table 1.* Main and satellite reflections up to second order were measured at room temperature using the SAT program (Doudin, 1985), and are compatible with an orthorhombic symmetry [superspace group $Bbmb(0\beta 1)$]. No significant variation of the intensity of three standard reflections was detected during the measurement. 1530 independent reflections with $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effects. Analytical absorption corrections, based on crystal morphology, were applied using the REMOS program (Yamamoto, 1982, 1990). The relatively large size and good crystalline quality of the sample provided us with numerous reliable data sets compared with other previous X-ray single crystal data collections [between 656 and 1021 independent reflections for the same cuprate phase (Kan & Moss, 1992; Petricek *et al.*, 1990; Levin *et al.*, 1994), 1418 for the related ferrite (Le Page *et al.*, 1989) and 1707 for a monoclinic variant of the cuprate phase (Gladyshevskii & Flükiger, 1996)]. Among these previous studies, the more numerous data collections were generally analysed in a supercell model, which requires more refinement parameters than the modulated structure model. Both a profile analysis and a least-squares refinement on the θ values of selected satellite reflections confirm the irrational value of the y component of the modulation wavevector $[0.210(1)]$.

Beside the sharp standard main and satellite reflections corresponding to the superspace group $Bbmb(0\beta 1)$, more diffuse satellite reflections were observed at forbid-

* A list of structure factors has been deposited with the IUCr (Reference: DU0408). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental data*

Crystal size (mm)	$0.500 \times 0.188 \times 0.015$
Cell parameters (Å)	$a = 5.401(1), b = 5.403(1), c = 30.713(5)$
T (K)	294
Modulation wavevector	$q^* [0, 0.210(1), 1]$
Superspace group	$Bbmb(0\beta 1)$
D_x (g cm^{-3}), Z , V (Å^3)	6.58, 4, 896.3
Data collection	Enraf-Nonius CAD-4 diffractometer
Scan mode	ω - θ
Wavelength (Å)	$\lambda(\text{MoK}\alpha) = 0.71069$
Registered space	$0 \leq h \leq 8, 0 \leq k \leq 9, 0 \leq l \leq 46, -2 \leq m \leq 2$
Control of intensities	Three reflections every 3000 s; no significant fluctuation observed
No. of measured reflections	10 700
No. of reflections with $I \geq 3\sigma(I)$	$hkl0:496; hkl \pm 1:753; hkl \pm 2:281$
Absorption correction	Analytical based on the crystal morphology
Absorption coefficient (cm^{-1})	$\mu(\text{MoK}\alpha) = 560$
Transmission factor range	0.085–0.648
No. of refinement parameters	97
R, wR ($hklm$)	0.056, 0.051
R, wR ($hkl0$)	0.049, 0.043
R, wR ($hkl \pm 1$)	0.056, 0.058
R, wR ($hkl \pm 2$)	0.078, 0.079

den nodes of the reciprocal lattice. The larger profile of these reflections along the c^* direction can be clearly interpreted by a partly coherent stacking disorder of the modulated corrugated layers of the modulated structure. Such forbidden lines have already been reported by different authors in different crystals (see, for example, Johnson *et al.*, 1994). These reflections were not taken into account in the following structure refinements.

For the refinements, atomic scattering factors and anomalous dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

3. Structure refinements

The refinement was carried out in the four-dimensional formalism for modulated structures (de Wolff *et al.*, 1981), with the F magnitudes, using the *REMOS* program. According to the data collection, the Bravais class $Bmmm(0\beta 1)$ (number 14) was assumed and the centrosymmetric and non-centrosymmetric hypotheses were respectively considered in the space groups $Bbmb(0\beta 1)$ (number 66.3) and $Bb2b(0\beta 1)$ (number 37.3), compatible with the extinction conditions of the diffraction pattern. Both displacive and occupational or substitutional modulations were taken into account. The modulated displacement U^μ of the μ th atom is expressed as a function of the internal coordinate $\bar{x}_4^\mu = \mathbf{q}^* \cdot \mathbf{r}_0^\mu + t$, where \mathbf{r}_0^μ is the average position of the considered atom and t is the so-called phase factor, by Fourier series up to second-order harmonic of its components

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

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

In the same way, the occupancy probability of the site μ is expanded in its Fourier series

$$P^\mu(\bar{x}_4^\mu) = \sum_{n=0}^2 (A_n^\mu \cos 2\pi n \bar{x}_4^\mu + B_n^\mu \sin 2\pi n \bar{x}_4^\mu).$$

The occupation probabilities were constrained by a penalty function to keep reasonable ranges. The minimized quantity was $\chi^2 = (wR)^2 + (pf)^2$, where wR is the usual weighted R factor on the F values and (pf) is the occupation penalty function. Unit weights were used.

Refinement was first carried out in the centrosymmetric hypothesis $Bbmb$ and the atoms were located according to the well known average structure of the so-called 2212 bismuth cuprate. All atoms are on special positions: Bi, Sr, Cu, O3 and O4 on site 8(l), Ca on site 4(e), O1, O2 and O5 on site 8(g). O4 is the O atom of the rocksalt-type structure in the BiO layers and O5 is a bridging O atom between two Bi atoms, introduced in order to try to account for an eventual extra oxygen in the BiO layers, as postulated by all the previous studies. Another bridging position has also been considered at $(\frac{1}{2}, \frac{1}{4}, z)$, but all attempts to locate an O atom on this site failed.

Temperature factors were considered anisotropic for Bi, Sr, Cu and Ca, and isotropic for O. Occupation modulation was introduced for Bi, Sr, O3, O4 and O5 atoms; a modulated substitution of Ca for Bi on Ca sites was also considered.

The first refinement in the previous conditions led, for 91 refinement parameters, to a global agreement factor $wR = 0.080$ (main reflections: 0.054, first-order satellites: 0.084, second-order satellites: 0.190), characterized by poor agreement on second-order satellites.

In such a modulated structure, thermal displacements are expected to be modulated. In a new refinement, modulation of the thermal parameters of Bi atoms was considered and described with 12 new refinement parameters. The agreement is much better (global: 0.055, main reflections: 0.047, first-order satellites: 0.057, second-order satellites: 0.10). The amplitudes of the occupation modulation on Bi and Sr sites was lowered, but the average value and amplitudes of the modulation of the B_{22} thermal parameter became very large, involving non-definite or excessive values as a function of the phase variable. Previous studies in this four-dimensional model (Petricek *et al.*, 1990; Kan & Moss, 1992) have also concluded on very large variations for the thermal parameters of Bi atoms. Even in the previous refinements in the supercell model (Le Page *et al.*, 1989; Levin *et al.*, 1994), the different Bi atoms exhibit very different values of thermal parameters, either isotropic from 1 to 2.7 Å^2 or anisotropic, particularly along the modulation direction. A similar anomaly is also present in the refinement of the monoclinic variant (Gladyshevskii & Flükiger, 1996). To explain this anomaly a static disorder has already been suggested (Petricek *et al.*, 1990).

Therefore, it appears that the refinement of Fourier terms for the modulation function of thermal parameters introduces many supplementary refinement parameters, which generally can take high values and are difficult to justify or to interpret. Because of their excessive sensitivity and their frequent strong correlation with other terms, they can artificially improve the refinement agreement without any proved physical meaning and so can prevent a better understanding and determination of other structural parameters, such as modulated displacements or site occupancies.

Introduction of higher-order terms for modulation functions was also attempted to describe an eventual anharmonicity, but led to a poor improvement of the refinement.

For these reasons, thermal modulation and Fourier terms of third and higher order were not considered in the present study, but rather a static disorder of the Bi atoms. For this purpose, the Bi atom was displaced from its special position $8(l)$ on the mirror plane m_y to a general position, without any constrain for the Fourier terms. In the centrosymmetric hypothesis ($Bbmb$), this results in two symmetry-equivalent positions. Site occupancy of these sites was considered modulated. In the non-centrosymmetric hypothesis which was also tested ($Bb2b$), the first refinement with a unique site gave the same types of problems concerning thermal parameters; so, two independent sites with partial and modulated occupation were introduced, leading to a generalization of the previous centrosymmetric disordered model.

4. Results

4.1. Centrosymmetric case

Starting from the values of the previous standard refinement, the Bi-atom y coordinate was now allowed to vary, involving seven new positional refinement parameters, two thermal parameters and two occupational parameters. After some refinement cycles, some Fourier terms with values smaller than their e.s.d. were fixed to zero, so that the final number of refinement parameters was 97. The final general agreement factor was 0.051 (main reflections: 0.043, first-order satellites: 0.058, second-order satellites: 0.079), leading to a significant improvement of the refinement. Results are summarized in Tables 2 and 3. Refinement of the thermal parameters leads to reasonable values for all atoms, which do not justify any supplementary modulation terms. We can just outline a relatively large thermal parameter for the Sr atom along z and a high value of the isotropic B factor for the supplementary O5 atom.

The amplitudes of the displacive modulation waves are schematically drawn in Figs. 1 and 2 as a function of the phase variable t for all the atoms of the structure. The modulation amplitudes along x are negligible and are not represented. The relative amplitudes of the transverse modulation along z are scaled to the average position

Table 2. *Positional and occupational Fourier parameters*

Parameters with * are fixed by symmetry. Parameters with † were fixed during the refinement due to their large e.s.d.

		A_0	A_1	B_1	A_2	B_2
Bi	U_1	0.2243 (3)	-0.00014 (4)	0.0097 (8)	0.0†	0.0†
	U_2	0.5195 (10)	0.0220 (11)	0.0761 (12)	0.0113 (10)	0.0150 (13)
	U_3	0.0514 (1)	-0.00589 (12)	0.00115 (30)	0.0005 (2)	0.0†
	P	0.492 (4)	-0.036 (2)	0.291 (12)	0.0†	-0.302 (8)
	P	0.492 (4)	-0.036 (2)	0.291 (12)	0.0†	-0.302 (8)
Sr	U_1	0.2526 (3)	0.0011 (6)	0.0*	0.0†	0.0*
	U_2	0.0*	0.0*	0.0499 (5)	0.0*	0.0184 (6)
	U_3	0.14035 (6)	-0.00844 (12)	0.0*	-0.0089 (16)	0.0*
	P	0.943 (10)	-0.046 (9)	0.0*	-0.029 (16)	0.0*
	P	0.943 (10)	-0.046 (9)	0.0*	-0.029 (16)	0.0*
Cu	U_1	0.2500 (3)	0.0†	0.0*	0.0†	0.0*
	U_2	0.5*	0.0*	0.0154 (5)	0.0*	0.0†
	U_3	0.19664 (7)	-0.01063 (11)	0.0*	-0.00181 (16)	0.0*
	P	1.0†				
	P	1.0†				
Ca	U_1	0.25*	0.0†	0.0*	0.0*	0.0*
	U_2	0.0*	0.0*	0.0*	0.0*	-0.0037 (11)
	U_3	0.25*	-0.0108 (2)	0.0*	0.0*	0.0*
	P	0.932 (5)	0.0*	0.0*	0.0*	0.013 (9)
	P	0.932 (5)	0.0*	0.0*	0.0*	0.013 (9)
O1	U_1	0.0*	0.0*	0.0†	0.0*	0.0†
	U_2	0.25*	0.0*	0.014 (3)	0.0*	0.014 (6)
	U_3	0.1982 (5)	-0.0103 (8)	0.0*	0.0024 (10)	0.0*
	P	1.0				
	P	1.0				
O2	U_1	0.5*	0.0*	0.0†	0.0*	0.0†
	U_2	0.25*	0.0*	0.016 (4)	0.0*	-0.011 (6)
	U_3	0.1993 (6)	-0.0088 (10)	0.0*	-0.0086 (10)	0.0*
	P	1.0				
	P	1.0				
O3	U_1	0.278 (3)	0.012 (6)	0.0*	0.0†	0.0*
	U_2	0.5*	0.0*	0.088 (4)	0.0*	0.034 (5)
	U_3	0.1173 (6)	-0.0061 (10)	0.0*	0.0†	0.0*
	P	0.81 (3)	-0.24 (4)	0.0*	-0.15 (3)	0.0*
	P	0.81 (3)	-0.24 (4)	0.0*	-0.15 (3)	0.0*
O4	U_1	0.157 (5)	-0.012 (8)	0.0*	0.0†	0.0*
	U_2	0.0*	0.0*	0.164 (5)	0.0*	0.037 (6)
	U_3	0.0540 (12)	-0.006 (2)	0.0*	0.0†	0.0*
	P	0.65 (3)	-0.51 (5)	0.0*	-0.25 (3)	0.0*
	P	0.65 (3)	-0.51 (5)	0.0*	-0.25 (3)	0.0*
O5	U_1	0.0*	0.0*	0.0†	0.0*	0.163 (14)
	U_2	0.25*	0.0*	0.0†	0.0*	-0.042 (15)
	U_3	0.048 (2)	0.0†	0.0*	0.028 (3)	0.0*
	P	0.50 (6)	0.42 (8)	0.0*	0.09 (8)	0.0*
	P	0.50 (6)	0.42 (8)	0.0*	0.09 (8)	0.0*

Table 3. *Thermal parameters B_{eq} or B_{iso} (Å^2) and B_{ij} ($\times 10^4 \text{Å}^2$)*

Parameters with * are fixed to 0 by symmetry.

	B_{eq}/B_{iso}	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Bi	0.98 (3)	73 (2)	70 (7)	3.4 (0)	-2 (1)	0 (4)	-18 (3)
Sr	1.04 (4)	50 (4)	46 (5)	5.2 (2)	0*	4 (1)	0*
Cu	0.80 (4)	22 (5)	41 (5)	4.4 (2)	0*	0 (1)	0*
Ca	0.82 (8)	25 (8)	58 (8)	3.9 (4)	0*	3 (2)	0*
O1	0.52 (12)						
O2	0.53 (12)						
O3	0.94 (13)						
O4	0.65 (17)						
O5	2.4 (5)						

of each atom in this direction and the amplitudes of the longitudinal modulation (along y) are plotted with the same absolute scale beneath the first ones, so the two displacive types of modulation are directly comparable. It can be seen, for example, that the longitudinal displacement of the Bi atoms are much larger than their transverse displacements; for the Sr atoms, they are equivalent and become negligible for the Cu and Ca atoms.

Displacements are very large along y for the Bi atoms (maximum displacements around 0.5 Å) and decrease

regularly from the Bi layers to the Ca layers. In contrast, the transverse displacements along z increase from the Bi layers to the Ca layers. In a real centrosymmetric model and with only the first order of the Fourier expansion, the consequence of the symmetry constrains is that the modulation waves along these two directions should present a phase difference of $\pi/2$. This result is modified here because of the general position of the disordered Bi atoms, which no longer constrains the phase of the Fourier term for this species, and by the addition of second-order terms in the Fourier expansion for all the species. However, the general feature of this centrosymmetric model is still valid and involves a transverse waving of the slabs, which induces a periodic longitudinal expansion and compression of the BiO layers along y , while the CuO_2 -Ca- CuO_2 layers are less distorted with only a periodic moving along z .

The new main results essentially concern the presence of a disorder in the BiO layers and an occupancy modulation of the Bi, Sr, Ca, O3, O4 and O5 sites.

The splitting of the bismuth site, which corresponds to an average value of $0.0195(10)b$, must be considered with the corresponding modulated displacements. These displacements of the two disordered sites are plotted in Fig. 1 and are related by symmetry to each other. The

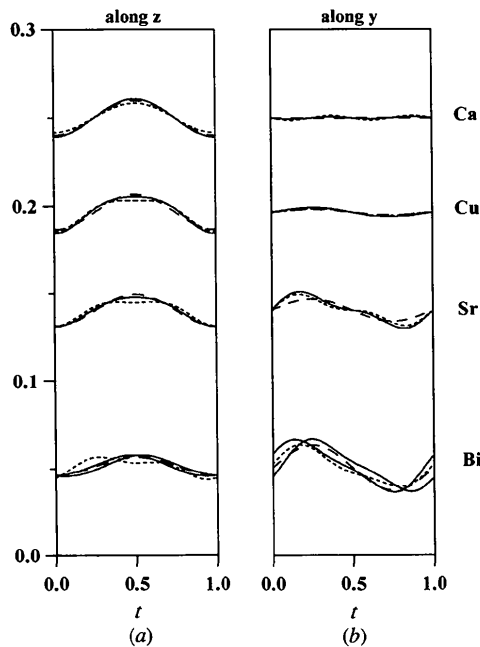


Fig. 1. Relative displacive modulation functions versus the phase variable t for Bi, Sr, Cu and Ca. Solid lines: this study; dashed lines: study I (Yamamoto *et al.*, 1990); dotted lines: study II (Petricek *et al.*, 1990). The two solid lines for Bi atoms are relative to the two disordered sites. The average positions and modulation amplitudes along z are plotted with the same scale. Modulation amplitudes along y are plotted at the same level and with the same absolute scale, so that the absolute displacements along the two directions are directly comparable: (a) along z ; (b) along y .

disorder appears here as a difference in phase between the two modulation functions, which is $\sim 0.18\pi$ and 0.12π for the longitudinal and transversal displacive modulation waves, respectively.

The distance between the two symmetry-related sites is given in Fig. 3 as a function of the phase variable t . Two types of regions can be evidenced in the crystal and described as ordered regions (O regions) for $0.2 < t < 0.8$, and disordered (D regions) around $t = 0[\text{mod}(1)]$. Indeed, in the first regions the two sites are not clearly separated; the corresponding interatomic distance is less than 0.1 \AA , *i.e.* of the order of magnitude of the e.s.d. for this distance ($\approx 0.04 \text{ \AA}$) and of the mean thermal quadratic displacement; as a result, a single Bi site is considered in these O regions. In the second regions, on the contrary,

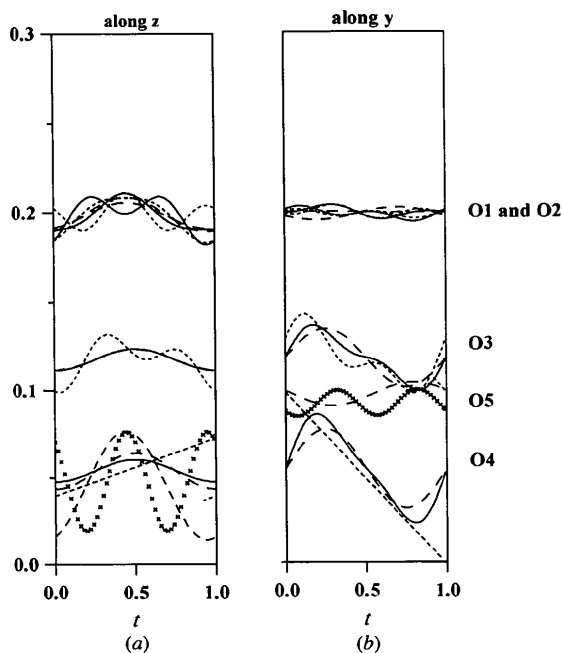


Fig. 2. Relative displacive modulation functions versus the phase variable t for O atoms. The symbols and scaling are as in Fig. 1, except for the O5 atom in the present study (crosses): (a) along z ; (b) along y .

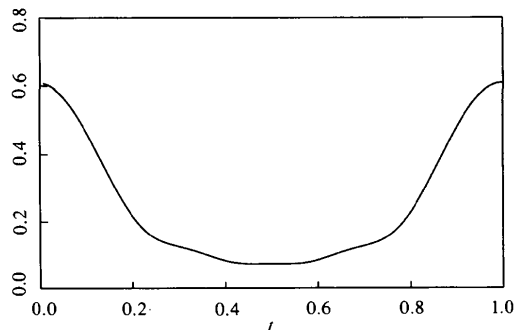


Fig. 3. Interatomic distance between the two disordered sites of the Bi atoms as a function of the phase variable t (e.s.d. $\approx 0.04 \text{ \AA}$).

the two sites are significantly separated ($d \simeq 0.6 \text{ \AA}$), involving a local modulated static disorder. The refined occupancy modulation of the two disordered sites is plotted in Fig. 4. It must be interpreted in relation to Fig. 3. It is characterized by a very large second-order component, which results in a very important fluctuation of the site occupancy in the range where the two sites are not clearly separated. So, if we make the assumption of one unique site in the O domains, these fluctuations are meaningless and are the consequence of the chosen Fourier expansion model for the modulation functions. The corresponding terms are probably refined in such a way that they allow a better description of the occupancy in the D domains. In these domains, the occupancy is closer to a reasonable value of 0.5, characteristic of disorder.

Concerning the occupational parameters, the refinement in the disordered model gave much more satisfactory results for the average occupancy of the different sites, leading to an average composition Bi:Sr:Ca:Cu = 2.06 (1): 1.89 (2): 0.94 (1):2 [rather than 1.85 (2): 1.38 (2): 1.56 (5):2 for the non-disordered model], in close agreement with the results of the EDS measurements previously reported on equivalent samples. A partial occupation of the Ca site by heavier species is confirmed, but it is not possible to distinguish a Sr from a Bi substitution in the structural refinement. Except for the Ca site, which presents an almost constant occupation, the Fourier terms for the occupation modulations confirm the existence of two types of domains with vacancies on Sr, O3 and O4 sites in the D domains (Figs. 4 and 5); in these domains, the oxygen location seems to be better described by the O5 position, which is fully occupied, even if this atom is characterized by very large and probably partially unrealistic Fourier terms. The occupation of the O5 site must probably be considered as zero in the O domains,

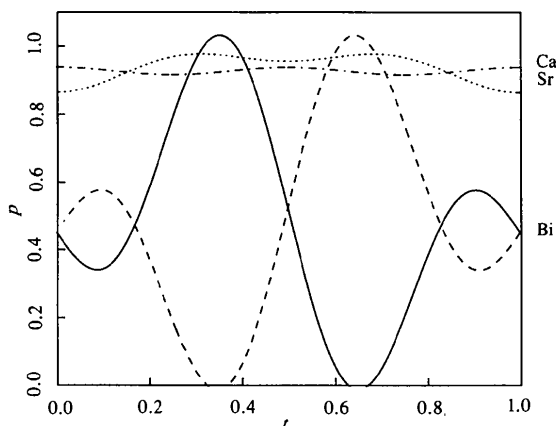


Fig. 4. Occupation probability as a function of the phase variable t . Solid and dashed lines: occupation of the Bi site; dotted line: occupation of the Sr site; mixed line: occupation of the Ca site (substituted by Bi).

in spite of a refined value around 0.2, for it has no physical meaning in these well defined regions. The harmonic model for the description of these Fourier terms is not the most adequate; nevertheless, this approximation allows us to give coherent results.

4.2. Non-centrosymmetric case

A similar refinement was also tested in the non-centrosymmetric hypothesis, with two independent positions for the Bi atom. After some cycles, only Bi, Sr, O4 and O5 atoms were characterized by new significant refined Fourier terms greater than their e.s.d., so that only these parameters were refined together with the preceding refinement parameters for the centrosymmetric hypothesis, leading to 143 refinement parameters and to an improved agreement factor of 0.0424 (main reflections: 0.041; first-order satellites: 0.048; second-order satellites: 0.064). The perovskite-type slabs of the structure keep the same structural characteristics as in the previous centrosymmetric results. Displacive parameters for the O4 and O5 atoms of the BiO layers remain comparable and the corresponding occupational parameters are only characterized by larger modulation amplitudes. The main difference concerns the Bi atoms, which are described by more complex modulations, which have as a consequence more erratic interatomic Bi—Bi and Bi—O distances. The corresponding results were not considered as physically meaningful and the main structural characteristics of the compound are already described in the centrosymmetric model, which will only be considered in the discussion.

5. Discussion

5.1. Structural description

The main characteristics of the layered structure of the high T_c cuprate superconductors are well known

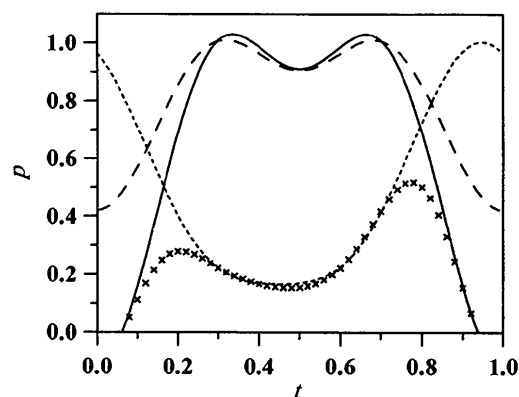


Fig. 5. Occupation probability for the oxygen sites as a function of the phase variable t . Solid line: O4; dashed line: O3; dotted line: O5; crosses: $p(\text{O4}) \times p(\text{O5})$.

and are confirmed by the present study. The structure is built with the stacking of ondulated slabs along the z direction. The slabs are constituted by cationic Bi—Sr—Cu—Ca—Cu—Sr—Bi columns, clearly visible by microscopy, which are schematically drawn in Fig. 6. The medium layer of each slab is a Ca layer with only a modulated displacement along z . The ondulation of the medium Ca layer is accompanied by a flexion of the slabs and a bending of the cationic columns, so that the longitudinal displacements are increasing from the medium to the peripheric layers of the slabs, resulting in high y displacements of the Sr and Bi atoms. Considering only the harmonic approximation, the symmetry imposes opposite phases between the ondulations of two neighbouring slabs, resulting in alternate shorter and longer interlayer distances (Figs. 7c and d). The shorter distances between the slabs occur in the D regions, where the maximum splitting of the Bi site is observed (Fig. 6).

In the description of these structures, one usually distinguishes rocksalt-type BiO and SrO layers from perovskite-type CuO_2 and Ca layers and we shall now describe the structure layer by layer.

5.1.1. BiO layers. The description of the BiO layers has been the subject of numerous discussions on the positions of O atoms and particularly on the existence and location of an extra oxygen. We have first focussed our attention on the Bi-atom location, which is decisive in the refinement from X-ray diffraction data.

The interpretation of the Bi—Bi interatomic distances is complex due to the existence of the static disorder for the Bi site. Nevertheless, when considering the intralayer Bi—Bi distances (Figs. 7a and b), pairs of 'parallel' curves are evidenced, with a relative difference of around

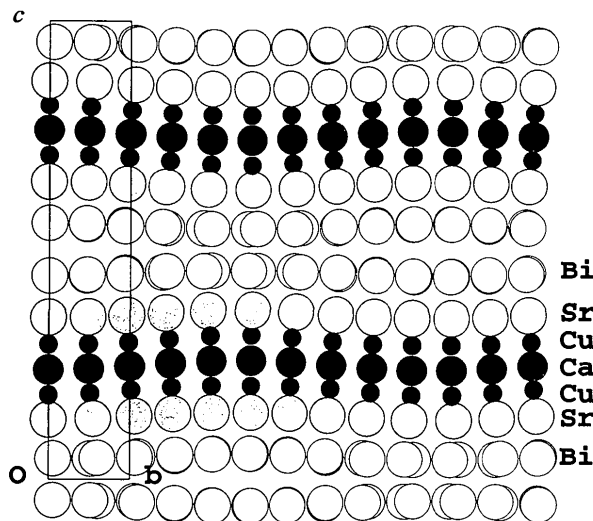


Fig. 6. Schematic representation of the Bi, Sr, Cu and Ca atomic positions in the bc plane. The two disordered Bi sites are clearly visible.

0.4 Å. This confirms the cationic configuration in double chains along the y direction (Fig. 8a). When comparing the intra- with the interlayer distances (Figs. 7c and d), one can observe that shorter interlayer distances coincide with longer intralayer ones and with D domains. They lead to expanded zones resulting from the flexing of the

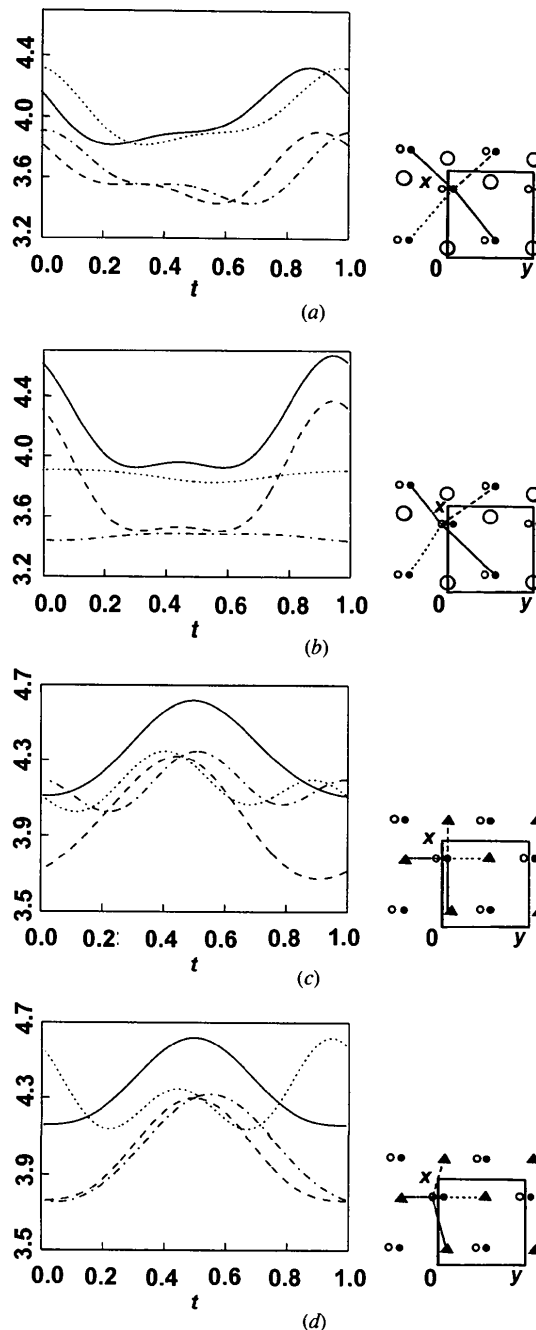


Fig. 7. Interatomic Bi—Bi distances as a function of the phase variable t . (a) and (b) in the BiO layer; (c) and (d) between two adjacent BiO layers. (a) and (c) with the origin at the first Bi site. (b) and (d) with the origin at the second Bi site.

slab (Le Page *et al.*, 1989), which are in correspondence on the other side of the slab with compressed zones in the O domains. In the expanded D domains one can observe that the Bi—Bi interatomic distances, taking into account the double position of the Bi atom (Fig. 7*b*), lead to two different and characteristic behaviours: on one side of the Bi atom, the existence of the two sites allows the possibility of a constant Bi—Bi distance in continuity with the O domains; on the other side, on the contrary, it allows a larger interatomic distance than in the classical model (a single site, similar to that shown in Fig. 7*a*). This characteristic feature reinforces the assumption of an extra O atom (O5) in the D domains.

The BiO layers are also built with two types of O atoms, O4 and O5, following previously reported investigations, and corresponding to a classical rocksalt position and a bridging position, respectively (Le Page *et al.*, 1989). The layers are characterized by very large amplitudes of displacive modulation along *y* for O4 and both along *x* and *z* for O5. The displacements of O4 along *y* and *z* are closely related to the equivalent displacements of the Bi atom; the longitudinal displacement is described by a modulation function which is close to a linear function in the interval corresponding to the O domains and to a full occupancy of the corresponding site. It is similar in profile and phase to the corresponding Bi displacement, but with a larger amplitude. The transverse displacements of O4 and Bi are also very similar with equivalent amplitudes.

Although the occupancies of O4 and O5 sites have not been constrained to each other, the result is an alternation of full occupation of the O4 site in the O domains and of the O5 site in D. This is illustrated by the schematic representation in Fig. 8, where the two zones and their corresponding occupation by rocksalt and bridging O atoms are clearly visible. The O5 atom presents a large isotropic thermal parameter, which is to be related to the corresponding disorder of Bi atoms and is probably the consequence of a similar disorder in oxygen location. It could also be the consequence of the limits of the harmonic model and the difficulty in describing the small electronic density using X-ray diffraction data. Even if the average atomic sites of these two O atoms are quite different, the amplitudes and phases of their modulations give them neighbouring *x* and *y* locations in the D domains, so it can be concluded that the refinement of the O5 atom is a good way to describe the behaviour of the O atom of the BiO layer where the modulation functions of the O4 atom, in continuity with their behaviour in the O domains, are inappropriate. Two original points can be outlined concerning the O5 atom: its *z* coordinate seems to be different from O4, indicating it is closer to the SrO layer in the D regions (see Fig. 8*b*); it allows a partial recovering of their occupation, making possible an excess of oxygen in the BiO layers. To validate this last hypothesis, the coexistence of the two atoms has to be consistent with acceptable O4—O5 and

O3—O5 interatomic distances. As a matter of fact, in the small intervals of coexistence of the O4 and O5 atoms (Fig. 5), the corresponding interatomic distance is either longer than 2.7 Å ($t \approx 0.8$) or very short ($t \approx 0.2$) and then rather compatible with only one atomic site. In the D domains where the O5 atom is present, the O3—O5 distance also takes reasonable values. Therefore, even if the present O5 location is still questionable because of its very small weight in the refinement process, it is not incompatible with the corresponding environment of the D domains and can explain the corresponding modification of the Cu—O3 distance (see below).

In previous studies another O atom was introduced in the BiO layer between two double BiO chains (Yamamoto *et al.*, 1990; Levin *et al.*, 1994). From our results, no evidence could be given for such an introduction and our configuration (Fig. 8) is still compatible with independent double chains, with a projection along the *c* direction (Fig. 8), which is similar to those of Le Page *et al.* (1989), Jiráček (1992) and Beskrovnyi *et al.* (1990).

Interatomic Bi—O4 and Bi—O5 distances are shown in Fig. 9. The curves clearly outline the existence of double BiO chains in the BiO layers (Fig. 8): two

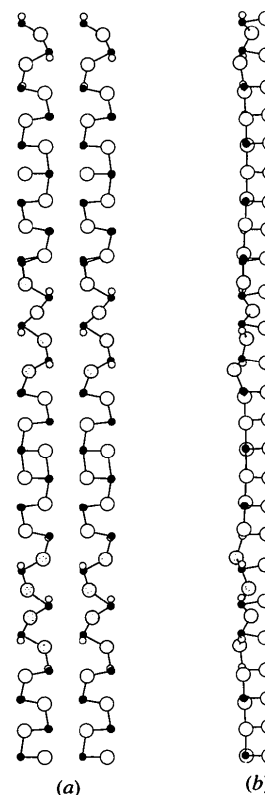


Fig. 8. Schematic representation of the BiO layer: (a) projection along *c*; (b) projection along *a*; small circles: Bi sites; large open circles: O4 atom with $p > 0.5$; large grey circles: O5 atom with $p > 0.5$. BiO interatomic distances < 2.5 Å are represented by solid lines.

intralayer Bi—O distances along x remain almost constant: one long between 3.25 and 3.49 Å and one short between 2.02 and 2.16 Å. The intralayer distances along the modulation direction present large variations. They are shorter and close to 2.0 Å in the O domains and become longer in D. However, in these D regions the O4 site is replaced by O5, with Bi—O5 distances also close

to 2.0 Å (Fig. 9). The Bi—O3 distance is also short and almost constant (2.00–2.12 Å). Therefore, considering all the Bi—O distances and their variations as a function of t , one can observe most of the time a threefold coordination of the Bi atom with three short distances around 2.0–2.1 Å.

In order to illustrate this coordination, and considering that the interatomic distances vary continuously along the modulation direction, a plot of the probability of occurrence of a given Bi—O distance, taking into account all oxygen neighbours of the Bi atom, is given in Fig. 10. In this computation the occupancy of the oxygen sites was not taken into account and we can remark that the unrealistic distances, shorter than 1.9 Å, correspond to Bi—O5 distances in the range where the occupation of the O5 site is minimum and probably null. This plot is to be compared with the results of

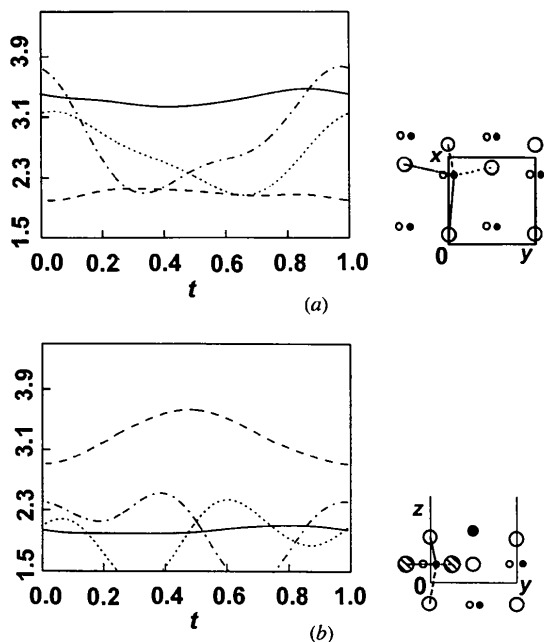


Fig. 9. Interatomic Bi—O distances as a function of the phase variable t . (a) Bi—O4 in the BiO layer from the first Bi site; (b) solid line: Bi—O3 distance; dashed line: Bi—O4 with the apical O4 atom of the adjacent BiO layer; dotted and mixed lines: Bi—O5 distances (to be considered only in the D domains, see text).

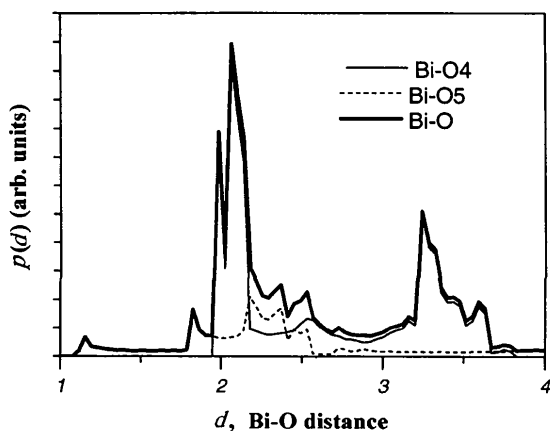


Fig. 10. Probability of occurrence of the Bi—O distances. This curve has been obtained by integrating the different BiO distances around the Bi atom without taking into account the occupation probability of the oxygen site. The shorter distances (<1.95 Å) are due to Bi—O5 distances in the range where the O5 site occupancy is negligible and are not relevant.

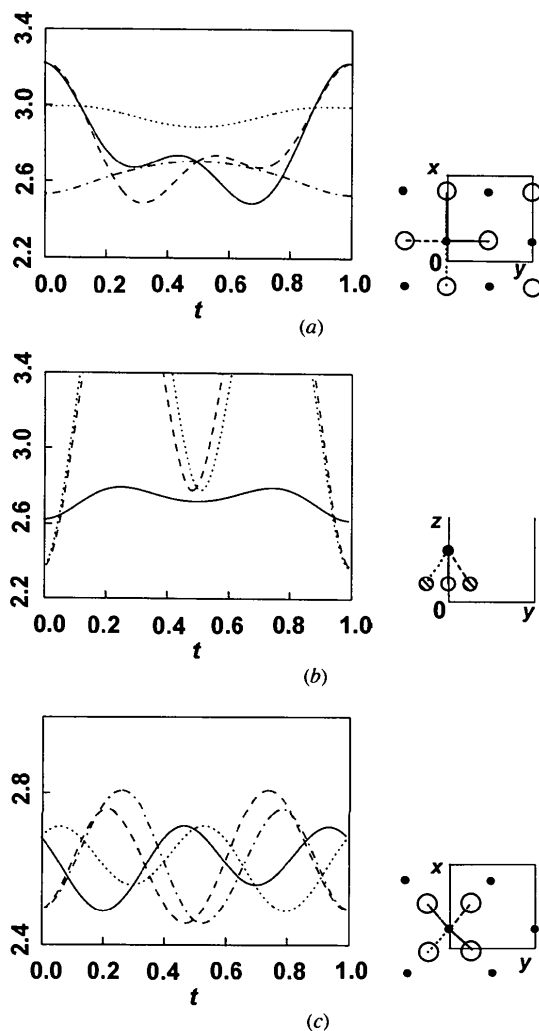


Fig. 11. Interatomic distances Sr—O as a function of the phase variable t : (a) Sr—O3 distances; (b) Sr—O4 (solid line) and Sr—O5 (dashed lines) distances. (c) Sr—O1 and Sr—O2 distances.

the EXAFS studies of Kizler, Su, Majewski & Aldinger (1994) and Akhtar, Akhtar & Catlow (1994). Despite the difficulty in interpreting the EXAFS signal for the coordination number or the determination of the longer interatomic distances for such heavy atoms, and despite their apparent disagreement concerning these two points, they nevertheless agree for the presence of several short distances around 2.0–2.1 Å and with less frequent longer distances between 2.2 and 2.4 Å. Within the accuracy of the method, this is in agreement with the present results. One indeed generally observes three short Bi—O distances, two of them being constant and the third corresponding to different O atoms being variable between 2.0 and 2.4 Å.

5.1.2. *SrO layers.* SrO layers are still largely influenced by the neighbouring BiO layer, as can be seen from the modulation functions (Figs. 1 and 2).

D and O domains are still clearly evidenced. The schematic representation of the different Sr—O distances versus t (Fig. 11) shows a SrO3 configuration comparable to BiO4, with two almost constant transverse distances around 2.6 and 2.9 Å and with the appearance of double SrO chains (Fig. 12). The longitudinal Sr—O3 distances present larger fluctuations with the formation

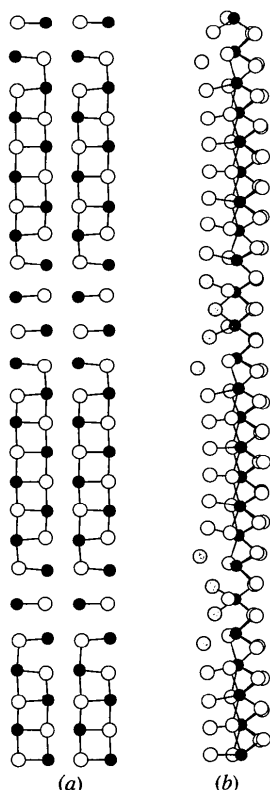


Fig. 12. Schematic representation of the SrO layer. (a) Projection along c ; (b) projection along a ; filled circles: Sr sites; open circles: O3 and O4 atoms; grey circles: O5 atom with $p > 0.5$. Sr—O interatomic distances < 2.8 Å are represented by solid lines.

of an expanded zone corresponding to the D domains. In these domains the displacement of the O5 atom along z allows a new Sr—O5 link in the place of the longer Sr—O3 ones. The poor quality of the refinement of the O5-atom location here is responsible for a relatively short Sr—O5 distance, which varies very quickly with t . The SrO layers are probably still characterized by a residual disorder, which is not taken into account in the present description and which is probably enhanced by the occurrence of vacancies for $t \simeq 0[\text{mod}(1)]$ (Figs. 4 and 5).

5.1.3. *CuO₂ and Ca layers.* The perovskite-type layers are only characterized by a large transverse displacive modulation along z (Fig. 1) and small and negligible longitudinal ones. As a consequence, the interatomic Cu—O and Ca—O distances (Figs. 13 and 14) present smaller fluctuations than Bi—O and Sr—O, which is in agreement with a larger stiffness of the corresponding chemical bonds. In particular, the weak variations of the Cu—O distances in the CuO₂ layers show that the Cu atom is always at the centre of a regular O square. The Cu atom is also linked with a larger distance to the apical O3 atom, giving a global pyramidal fivefold coordination. In the O domains the Cu—O3 distance is practically constant (2.5 Å), and one observes only a noticeable shortening of this distance in the D domains (2.25 Å). This last value is still perhaps overestimated, as the Fourier expansion with two orders

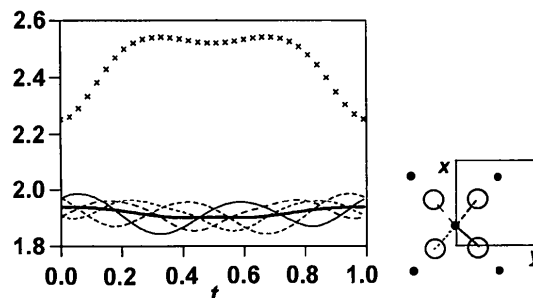


Fig. 13. Interatomic Cu—O distances as a function of the phase variable t . Bottom: Cu—O1 and Cu—O2 in the CuO₂ layer; thick solid line: average in-plane Cu—O distance; top (crosses): Cu—O3.

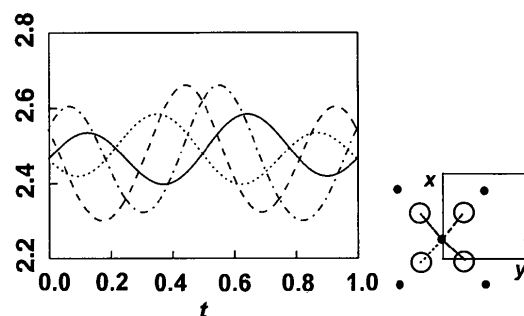


Fig. 14. Interatomic Ca—O1 and Ca—O2 distances.

of harmonics does not allow an accurate description of modulation functions, which are likely to vary with a deep minimum only in a small interval around $t=0$.

Relationships have already been postulated between the superconducting transition temperature T_c and the in-plane and apical Cu—O distances (see, for example, Rao & Ganguli, 1995*a,b*). In the present case the incommensurate modulated structure presents, in the same crystal, variations of the Cu—O distances from 1.84 to 1.98 Å for in-plane and from 2.25 to 2.54 Å for apical distances. These rather large ranges of variations do not allow easy conclusion. Nevertheless, one can observe a correlation between the two types of distances. Indeed, when averaging the four in-plane distances (Fig. 13), one can see that the O regions correspond to a compressed CuO_2 layer (average distance 1.90 Å) and the D regions to a longer in-plane distance (1.94 Å) and so on, to an expanded layer, but to a shortening of the apical distance (2.25 Å). In these latter regions the configuration seems analogous to that in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Following the method developed by Brown & Altermatt (1985) and Brese & O'Keefe (1991), it is also possible to calculate the corresponding formal Cu valence as a function of the phase variable t , taking into account the five previously mentioned Cu—O distances. Despite the uncertainty of the calculation, it appears that the high value obtained (around 2.24) is almost constant. This value is first a consequence of the short in-plane Cu—O distances in the O regions and partially of the shortening of the apical distance in the D regions, when the previous values are longer.

5.2. Comparison with literature

As many different studies have already been published with different approaches and conclusions, it is important to compare these different results. In the following a direct comparison with the previous descriptions in superspace (study I: Yamamoto *et al.*, 1990; study II: Petricek *et al.*, 1990) is first given, then, equivalent discrete atomic positions have been calculated from recent supercell descriptions (study III: Levin *et al.*, 1994; study IV: Gladyshevskii & Flükiger, 1996) and compared with the present refined modulation functions.

5.2.1. Four-dimensional superspace descriptions. Comparison with the first type of description can be directly established from the different results of Fourier terms. The different modulation functions are plotted in Figs. 1 and 2. Let us first recall that in study I the structure was refined from X-ray and neutron powder data using the Rietveld method and this only allows a refinement in the centrosymmetric group and with only one order of harmonics, so this description is expected to give a first approximation of the incommensurate structure up to first order. This is clearly exemplified by the different cation and oxygen modulation functions in Figs. 1 and 2, which show a very good agreement in amplitude and phase for all the atoms. The main

differences lie in the description of the O atoms of the CuO_2 layers and of the extra O atoms of the BiO layers, for which the second-order modulation terms become important. The very small weight of the extra O5 and O6 atoms and their closeness to the heavy Bi atom explain the difficulty in finding reliable positions for oxygen in this very simple model and outline the necessity of a more detailed description of the modulated positions of Bi.

In the single crystal study II, on the contrary, a simple description in the previous model appears to be insufficient and the authors claim for a non-centrosymmetric model, limited for convergence reasons to the BiO layers, for Fourier terms up to second order and for particular linear modulation functions for O atoms in the BiO layers. A thermal modulation for Bi atom was also introduced, but occupancy modulation functions were not considered. Our results are still very close to the corresponding ones for Sr, Ca and Cu atoms. For Bi atoms both results are rather different, since the chosen models are also different; they are characterized by a larger dispersion in study II, which is perhaps due to the smaller reflection data set. Both the splitting of the Bi atoms and the centrosymmetric model in our study seem to be sufficient to achieve a more satisfactory agreement. We have already discussed the sensitivity of the refinement to Bi thermal parameters and the difficulty to interpret their very large variations, which can be either the signature of a disorder or of vacancies. Even after introducing occupation modulations, our study suggests more probably a static disorder, correlated with partial occupations of Sr and O4. The two studies clearly outline the usefulness of second-order Fourier terms, which allow to account for almost linear dependence of the y displacements of Sr and Bi *versus* t , for $0.2 < t < 0.8$.

As far as oxygen in the BiO layer is concerned, although different in their models (a 'sawtooth function' with partial recovering for study II and two independent classical modulation functions in alternation in the present study), our two descriptions are practically equivalent. The linear function with partial recovering in study II is plotted in Figs. 2(a) and (b). One can see that the two different y modulation functions for the O4 atom are equivalent in the domain where this atom is present and around $t=0$ the linear function of the O4 atom is close to the modulation function of the O5 atom of the present study. The model chosen in study II also imposes a sawtooth-type function for the O4 z displacive modulation. This description seems to be less adequate, since from our study the O4 displacement along z seems to be very similar to the corresponding Bi one. Nevertheless, the harmonic and 'sawtooth' functions are rather similar for $t < 0.6$ and $t > 0.9$; the recovering of the two parts of the linear function is close to the two harmonic functions of O4 and O5 in our model (lower part of Fig. 2a). Despite the great insensitivity of the X-ray data refinements to the oxygen location, these

analogous results with quite different models clearly outline a common behaviour of oxygen in these BiO layers.

5.2.2. *Supercell descriptions.* Study III and this study are related to the same orthorhombic incommen-

surate modulated phase. The phases and amplitudes of the displacements of the different atoms of the structure have been recalculated and plotted in Fig. 15 for comparison with our modulation functions. The agreement concerning both the amplitudes and the phases is remarkable, even if the positions refined in the supercell description, independent with each other, introduce far more refinement parameters and, as a consequence, are characterized by a larger dispersion. This dispersion increases from the Ca and Cu layers to the Bi layers. In the latter case it appears that the two curves corresponding to the two disordered Bi sites are sufficient and necessary to account for the different representative points of the Bi-atom position in the supercell description; each of these points can practically and unambiguously be attributed to one of the two modulation functions. Therefore, this hypothesis of disorder seems to be a good interpretation of the dispersion of the calculated points and is in close agreement with this supercell description. A larger dispersion is observed for the points representing the O atoms; however, the overall agreement with the present modulation functions can also be considered as very satisfactory. Two extra O atoms were also introduced in the expanded D zones and differ by their x coordinate. For one, the y and z coordinates coincide with the coordinates of the O5 atom of the present study. The second was located as a possible link between the double BiO chains. No evidence of this second O atom was found in the present study.

Study IV deals with a monoclinic variant of the present orthorhombic phase and its structure was refined within a ninefold supercell model. Except the different Bravais lattice, the main structural characteristics are still available. The lower symmetry is only responsible now for the independence between the so-called A and B layers. Therefore, in order to compare these results, it was necessary to take into account systematically two independent chains of nine atoms for one modulation function of the orthorhombic description. The corresponding points have been represented by circles and crosses, respectively, in Fig. 16, simultaneous with our modulation functions. As a consequence, the lower symmetry is also responsible for a larger number of refinement parameters, which is not completely counterbalanced by the more numerous data collection and it results in a larger dispersion of the points, which are not always distributed on continuous and regular displacement functions, particularly for the O atoms. Nevertheless, agreement between the two results is still very good and enlightens the common features between the orthorhombic and the monoclinic structures. The positions of the cations are well described by our modulation functions. When considering more specifically the Bi atoms, the two independent chains A and B seem to have specific behaviours. The first, represented by circles, is following rather accurately only one of the

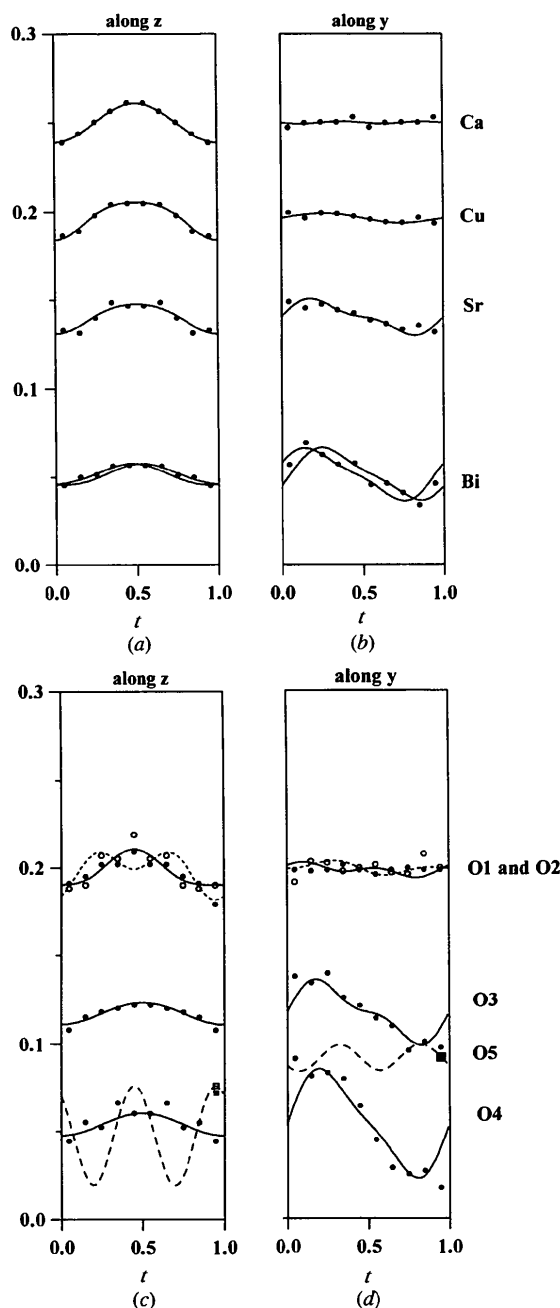


Fig. 15. Comparison between the different relative displacive modulation functions from this study (solid lines; see Figs. 1 and 2) and the corresponding atomic positions as refined in the supercell model of study III (Levin *et al.*, 1994): (a) Bi, Sr, Cu and Ca along z ; (b) Bi, Sr, Cu and Ca along y ; (c) O atoms along z boxes: extra O6 and O7 atoms of study III; (d) O atoms along y boxes: extra O6 and O7 atoms of study III.

two disordered modulation functions, while the other, represented by crosses, is distributed half by half on the two curves.

The monoclinic structure has been interpreted with a phase difference between the transverse displacements of adjacent BiO layers different from π . The corresponding phase shift is $\pi/9$ and is similar to the difference in phase between the two transverse displacive modulation functions of the present disordered model. As a consequence, it would be possible to interpret the monoclinic variant as a regular ordering from slab to slab of the residual disorder of the orthorhombic phase, even if traces of this disorder are still likely to exist in the *B* chain. This disorder originates in the expanded D domains, which allow two possible Bi sites characterized by such a phase difference.

5.2.3. Composite structure description. Another model has also been proposed for the description of this structure. To account for the regular insertion of an extra O atom in the BiO layers, one can try to describe the structure as the interpenetration of two lattices: one is constituted by the O atom in the BiO layers and the other is constituted by all the other atoms and is characterized by the conventional average cell parameter *b*.

Following the previous model of Walker & Que (1992), one can suppose that the modulated structure of the Bi-based lattice originates in the second periodicity introduced by the O4-based lattice. Considering the irrational component of the modulation wavevector ($0.210b^*$), the different possible values for the average cell parameter of the O4 lattice are $4.76b$, $0.826b$ or $0.452b$. They would be compatible with 10, 2 or 1 O atoms per cell and 0.050, 0.211 or 0.106 extra O atoms per Bi atom, respectively. Only the last value seems to be compatible with all the previous results and with a simple description of the second oxygen lattice. When considering only the average atomic positions of the O atoms along the modulation direction in this second subsystem, one can easily calculate the corresponding modulation function which would be equivalent to describe this lattice as a modulated structure on the Bi-based average structure. This is a linear function which is plotted in Fig. 16 (O4 modulation function along *y*). It is in fairly good agreement with the linear part of our refined modulation function and confirms the relevance of such a description. Nevertheless, what is better described along the modulation direction *y* is more difficult to describe in the transverse direction. As a matter of fact, in such a description with only one O atom per cell in the second subsystem, the average position of the O atom along *x* should now be 0, and it would be necessary to introduce a modulation function along *x* with a very large amplitude (~ 0.20) for its first-order term, to take into account the two symmetry-related O4 sites in the Bi-based cell. Moreover, the practically constant *x* positions of O4 in this description would require a crenel-type modulation function with sharp

variations corresponding to the D domains. In the same way, an adequate description of the *z* location of the O4 atom, which is assumed to follow the corresponding

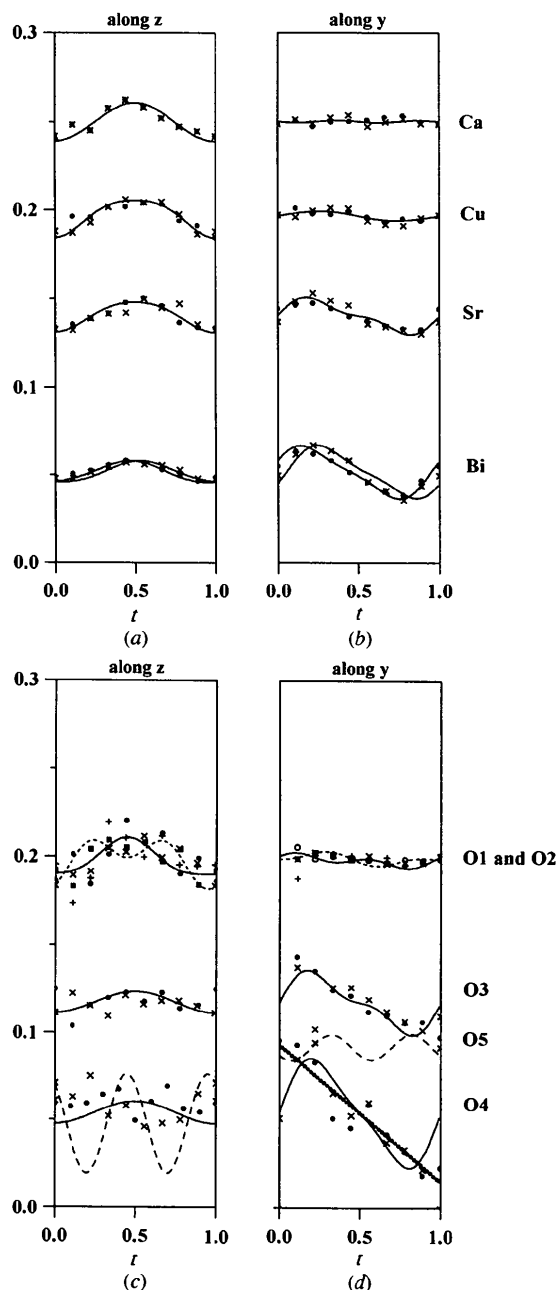


Fig. 16. Comparison between the different relative displacive modulation functions from this study (solid lines; see Figs. 1 and 2) and the corresponding atomic positions as refined in the supercell model of study IV (Gladyshevskii & Flükiger, 1996). Filled circles and boxes: atomic sites of layer of type A; crosses and plus signs: atomic sites of layer of type B. (a) Bi, Sr, Cu and Ca along *z*. (b) Bi, Sr, Cu and Ca along *y*. (c) O atoms along *z*. (d) O atoms along *y*: the linear function ($\bullet\bullet\bullet$) at the O4 level represents the equivalent modulation function for a perfect composite structure with a non-modulated O4 sublattice (see text).

ondulation of the Bi atom, would require a modulation function with predominantly second-order Fourier terms to allow a displacement in-phase of two neighbouring O atoms in this direction.

6. Conclusions

The present structural investigation of the modulated structure of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ compound and comparison with previous different studies already cited in the literature have still confirmed the difficulty in choosing a definitive structural model. Supercell models are the less constrained models, but require very numerous and high-quality data sets and for the moment, the results in these descriptions are still characterized by too high a dispersion for the proper structural parameters. On the other hand, a good structural analysis using the formalism of the modulated structures allows a smaller number of refinement parameters and introduces symmetry restrictions to the atomic site position, occupation and thermal parameters. The main problem here is to choose an adequate model for the modulation functions, in order to fit in the best way the real structure with the minimum of independent refinement parameters.

In this last approach the major part of the structure is well fitted in a classical description using two orders of harmonics for the modulation functions in a centrosymmetrical space group and it has been clearly established here the equivalence and the limits of the different descriptions of the same phase, or even using a variant of this basic structure (monoclinic variant in study IV) or isotopic structures (iron compounds: Le Page *et al.*, 1989; Pérez, Leligny, Grebille, Labbé, Groult & Raveau, 1995); but the main difficulty lies in the description of the BiO layers, in which one must account for the alternation of two types of regions. Almost all studies agree on the description of ordered parts of these layers, corresponding to compressed Bi-rich domains with a structural configuration close to rocksalt. For the intermediate regions, corresponding to expanded Bi-poor domains, common features can be outlined: many studies make the assumption of an additional O atom, but the ways to introduce this new atomic position are various: a new atomic site with occupation modulation (study I and the present one), particular linear modulation functions with a possible overlapping (study II) or a composite crystal hypothesis. Even if each of these models seems to be relevant in a certain way, none of them are completely satisfying. The description of the Bi thermal parameters generally shows important anomalies. An important improvement of the structural refinement has been achieved in the present study, introducing a static disorder for the Bi atoms, allowing a better description of thermal displacements. The corresponding modulation functions have allowed an interpretation of this static disorder as a difference of phase between neighbouring ordered BiO domains. Analogous static Bi disorders

are also probable in the iron-related compounds (Pérez, Leligny, Grebille, Labbé, Groult & Raveau, 1996).

This type of disorder was already suggested from electronic microscopy observations or from the supercell study IV of the monoclinic variant. One can now imagine different local correlations between these phase shifts, resulting in different configurations. It would now be interesting to decide if the diffuse scattering observed on forbidden lines of the *Bbmb*(0 β 1) superspace symmetry is to be related either to this type of disorder or to another correlation such as the trace of a second modulation as it can appear in the Pb-substituted compounds. A study is in progress for the characterization of this second modulation.

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