

X-ray investigation of the incommensurate modulated structure of $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 10003

(<http://iopscience.iop.org/0953-8984/7/50/030>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 22:47

Please note that [terms and conditions apply](#).

X-ray investigation of the incommensurate modulated structure of $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$

O Pérez, H Leligny, D Grebille, Ph Labbé, D Groult and B Raveau

Laboratoire CRISMAT (URA CNRS 1318), ISMRA, Boulevard du Maréchal Juin, 14050 Caen Cédex, France

Received 28 June 1995, in final form 19 September 1995.

Abstract. A single crystal of the Bi 2212 iron oxide $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$, exhibiting an incommensurate modulation, was characterized. The modulated structure was refined from x-ray diffraction data including satellite reflections up to the second order and using the four-dimensional formalism. A substitutional modulation (Bi for Sr) occurs over the Sr sites neighbouring the BiO layers whereas the other Sr sites, between the FeO_2 layers, are only occupied by strontium atoms. This leads to a bismuth-rich ferrite of chemical formula $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9+\delta}$. Different types of coordination are observed both for the iron atoms and for the strontium atoms on the substituted sites. Evidence for anomalies in the Bi positions was found; these anomalies were located in the BiO layers, suggesting a possible static disorder of bismuth atoms. Moreover, this effect would be closely related to the variation of the iron coordination. Finally, a comparison with the related superconductor compound $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ is given.

1. Introduction

It is well known that the Bi-based superconducting copper oxides $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ exhibit incommensurate modulations.

As a result the structure of the 80 K superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ ($n = 2$), characterized by the modulation wave vector $q^* = q_2^*b^* + c^*$ with q_2^* close to 0.21, has been particularly thoroughly studied: several models of the modulated structure have been proposed (Levin *et al* 1994, Yamamoto *et al* 1990, Beskrovnyi *et al* 1990, Petricek *et al* 1990). Large atomic displacements from the average positions were observed in the (100) plane. At present, no clear correlation between superconducting properties and structural characterizations of the modulation has been established, although the oxygen ratio seems to be a critical parameter.

In these compounds, the substitution of Fe^{III} for Cu^{II} implies the existence of additional oxygen atoms which are between the two iron layers, leading to the replacement of the double-pyramidal copper layers by double-octahedral iron layers (figure 1). In spite of this major difference, it has been shown that the iron compound $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_9$ is also characterized by a modulation very similar to that described for its copper counterpart.

Single crystals of the so-called 2212 bismuth-iron oxide have in fact been previously investigated by x-ray diffraction, using classical methods (Lepage *et al* 1989) and via Raman scattering and transmission electron microscopy studies (Hadjimitov *et al* 1993). Unlike in the homologous Bi 2212 cuprate, the modulation wave was found to be commensurate ($q^* = 0.2b^* + c^*$), but with atomic displacements comparable to those observed in the copper compound.

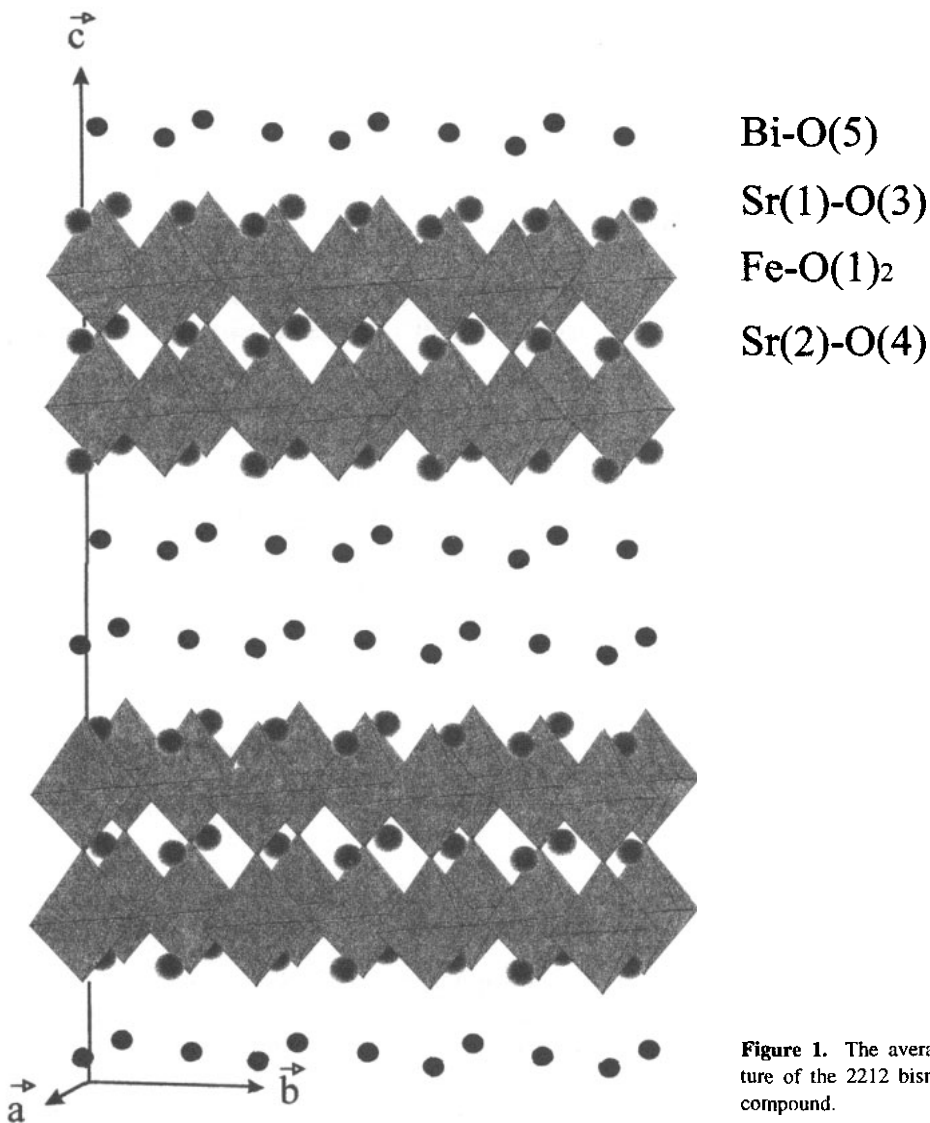


Figure 1. The average structure of the 2212 bismuth-iron compound.

In all preceding structural investigations concerned with either the copper or the iron compounds, the structure was described using either the supercell approach or the 4D formalism for modulated structures. In all cases, these studies were focused on the localization of the oxygen atoms in the BiO layers, which controls the global oxygen ratio. They indicated the presence of extra oxygen atoms in these layers. Another general feature of these studies is large thermal displacements of some bismuth atoms, which are not explained. This anomaly suggests a possible difficulty in locating oxygen in the BiO layers when the Bi-atom positions are not themselves clearly defined.

A bismuth-rich ferrite $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9+\delta}$ with an incommensurate modulation ($q^* = q_2^*b^* + c^*$) is synthesized in the Bi-Sr-Fe-O system. We report in this paper on the single-crystal characterization at room temperature of the modulated structure based on the four-dimensional formalism, using x-ray diffraction data.

2. Experimental details

Single crystals were grown by a self-flux method, with an excess of Bi_2O_3 added as a flux.

A charge composed of 53% Bi_2O_3 , 33% SrCO_3 and 14% Fe_2O_3 by weight was mixed in an agate mortar. It was then heated in an alumina crucible at 850 °C for 2 h, held at constant temperature for 24 h, then heated to 1050 °C for 1 h, held at constant temperature for 5 h and slowly cooled to 900 °C at a rate of 1 °C h⁻¹. The charge was finally cooled to room temperature.

Crystals grew as black plates. They were extracted from the crucible and cleaved along the *ab*-plane. A single crystal, of size 0.116 × 0.051 × 0.006 mm³, showing sharp diffraction spots, no noticeable diffuse streak and a small proportion (10%) of twinned domains was chosen for the data collection.

High-purity powder of the ferrite 2212 has been also synthesized from the starting materials Bi_2O_3 (Prolabo, 99%), SrCO_3 (Prolabo, 99%) and $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (Aldrich, 98%) mixed thoroughly before being heated at 1000 °C for 72 h. The powder was characterized by XRD and analysed by atomic absorption spectroscopy. An average Bi:Sr:Fe cation ratio of 33.2(8):38.1(6):28.7(5) led to the composition $\text{Bi}_{2.31}\text{Sr}_{2.66}\text{Fe}_2\text{O}_{9+\delta}$. We used this formula as the starting composition in the refinement.

Table 1. Crystallographic parameters.

Molecular weight	986.27
Colour	Black
Crystal size	0.116 × 0.051 × 0.006 mm ³
Crystal system	Orthorhombic
Lattice parameters	$a = 5.488(1) \text{ \AA}$, $b = 5.475(1) \text{ \AA}$, $c = 31.509(5) \text{ \AA}$
Chemical formula	$\text{Bi}_{2.41}\text{Sr}_{2.59}\text{Fe}_2\text{O}_{9+\delta}$
Modulation wave vector	$q^* = (0, 0.212(1), 1)$
Super-space group	$N:Fmmm:11s$
Z	4
Data collection technique	CAD4 Enraf-Nonius diffractometer
Temperature	Ambient
Scan mode	ω, θ
Scan speed	Variable, depending on $\sigma(I)/I$
Wavelength	$\lambda_{\text{Cu K}\alpha} = 1.54184 \text{ \AA}$
$((\sin \theta)/\lambda)_{\text{max}}$	0.627 Å ⁻¹
Registered space	$0 \leq h \leq 6, 0 \leq k \leq 6, 0 \leq l \leq 39, -2 \leq m \leq +2$
Number of independent reflections with $I \leq 3\sigma(I)$	$hkl0$: 187 $hkl\pm 1$: 320 $hkl\pm 1$: 125
Absorption correction	Based on the crystal morphology
Absorption coefficient (cm ⁻¹)	$\mu(\text{Cu K}\alpha) = 1250$

The x-ray data collection and refinement are summarized in table 1. The data set was corrected for the Lorentz polarization effect.

3. Preliminary studies

The q_2^* -component of the modulation wave vector was refined via a least-squares fit using the θ -measurement for 12 first-order satellite reflections. An irrational value of 0.212(1) was found for q_2^* revealing the incommensurate character of the modulation; a similar study

carried out starting from x-ray powder diffraction led to a same result for q_2^* within the experimental error.

Taking account of previous results (Levin *et al* 1994, Yamamoto *et al* 1990, Beskrovnyi *et al* 1990, Petricek *et al* 1990) obtained for the superconductor Bi 2212, it should be mentioned here that ferrite 2212 and cuprate 2212 exhibit the same irrational component for the q^* wave vector and the same modulation periods along b . As a result, the two compounds are directly comparable.

Separating the irrational q_2^* -component of q^* from the rational one, the diffraction vector $s^* = ha^* + kb^* + lc^* + mq^*$ (m is the satellite order) can be rewritten as $s^* = Ha^* + Kb^* + Lc^* + mq_i^*$ with $q_i^* = q_2^* b^*$ and $H = h, K = k, L = l + m$.

The following conditions hold for the $HKLM$ reflections: $H + L + m = 2n, H + K = 2n$ ($K + L + m = 2n$) supporting assignment of the Bravais class N: $Fmmm:1\bar{1}1$ (De Wolff *et al* 1981) to the crystal. It should be noted that the Bravais class of the iron crystals is different from that of copper crystals, N: $Bmmm:1\bar{1}1$ although their structures are related.

The supplementary condition $m = 2n$ observed for the $HK0m$ reflections reveals the existence of a super-glide mirror (σ_z^m) leading to three possible super-space groups (SSG) N: $Fmmm:1\bar{1}s$, N: $Fm2m:1ss$, N: $F2mm:1\bar{1}s$ (De Wolff *et al* 1981).

4. The modulated structure

The $U_i(\bar{x}_4)$ -components of the atomic displacements $U(\bar{x}_4)$ and the modulated part $P'(\bar{x}_4)$ of the occupancy probabilities $P(\bar{x}_4) = \langle P \rangle + P'(\bar{x}_4)$ are expanded in Fourier series in the internal parameter \bar{x}_4 , including the first and second harmonics as the satellite reflections are observed up to the second order. $\bar{x}_4 = q_i^* \cdot \langle r_0 \rangle + \alpha$ is the internal parameter, $\langle r_0 \rangle$ defines the average position of a given atom in the unit cell and α is (modulo 1) a dense set of real numbers on the $[0, 1]$ interval (the incommensurate case). The functions used to describe the displacement, the occupancy and the thermal modulations are

$$U_i(\bar{x}_4) = \sum_{n=1}^2 [A_{i,n} \cos(2\pi n\bar{x}_4) + B_{i,n} \sin(2\pi n\bar{x}_4)]$$

$$P'(\bar{x}_4) = \sum_{n=1}^2 [A_n \cos(2\pi n\bar{x}_4) + B_n \sin(2\pi n\bar{x}_4)]$$

$$\beta_{i,j}(\bar{x}_4) = \sum_{n=1}^2 [\gamma_{i,j,n} \cos(2\pi n\bar{x}_4) + \delta_{i,j,n} \sin(2\pi n\bar{x}_4)].$$

A model of the modulation, assuming the N: $Fmmm:1\bar{1}s$ SSG, was tested via a trial-and-error method and then refined with the F -magnitudes using the REMOS program (Yamamoto 1990).

Refinements using a non-centrosymmetric SSG were tested, revealing convergence problems. Otherwise the lowering of the global R_w was not significant.

The refinement of the average structure has led, for the Sr(1) site, to an occupancy larger than one. It can be interpreted in terms of a substitution of Bi for Sr atoms on this site. This feature is in agreement with the EDS analysis of Hadjimitov *et al* (1993) and with our atomic absorption spectroscopy analysis, but in disagreement with the result of Lepage *et al*. In fact, in this latter study, occupancy of all atom sites was fixed as that of the stoichiometric chemical formula, and not refined.

Then, both a displacive modulation and a density modulation as regards the Sr sites (anticipating a substitution with bismuth atoms, without vacancies) and the Bi sites

Table 2. Refinement results. $\langle x \rangle$, $\langle y \rangle$, $\langle z \rangle$ are the average atomic coordinates ($\times 10^4$); $\langle P \rangle$ the average occupancies ($\times 10^4$); and A_1, B_1 and A_2, B_2 the Fourier terms ($\times 10^4$) of the first and second harmonics respectively of the modulation functions $U_i(\bar{x}_4)$ and $P(\bar{x}_4)$. The e.s.d.s are in parentheses.

Atom			A_1	B_1	A_2	B_2
Bi	$\langle x \rangle$	221(6)	U_1	0	0	0
	$\langle y \rangle$	0	U_2	764(5)	0	-105(7)
	$\langle z \rangle$	2028(0)†	U_3	0	-45(0)†	-6(1)
	$\langle P \rangle$	5000	P'	0	0	0
Sr(1)	$\langle x \rangle$	5000	U_1	0	0	0
	$\langle y \rangle$	0	U_2	383(10)	0	13(13)
	$\langle z \rangle$	1176(1)	U_3	0	-98(2)	-22(2)
	$\langle P \rangle$	7955(120)	P'	0	-433(154)	-788(224)
Sr(2)	$\langle x \rangle$	5000	U_1	0	0	0
	$\langle y \rangle$	0	U_2	0	0	-5(19)
	$\langle z \rangle$	0	U_3	0	-121(3)	0
	$\langle P \rangle$	10 000	P'			
Fe	$\langle x \rangle$	0	U_1	0	0	0
	$\langle y \rangle$	0	U_2	176(19)	0	26(24)
	$\langle z \rangle$	607(2)	U_3	0	-134(3)	-8(4)
	$\langle P \rangle$	10 000	P'			
O(1)	$\langle x \rangle$	2500	U_1	0	0	0
	$\langle y \rangle$	2500	U_2	154(60)	0	0(71)
	$\langle z \rangle$	668(6)	U_3	0	-101(9)	-35(13)
	$\langle P \rangle$	10 000	P'			
O(3)	$\langle x \rangle$	0	U_1	0	0	0
	$\langle y \rangle$	0	U_2	815(116)	0	-455(139)
	$\langle z \rangle$	1389(10)	U_3	0	-27(15)	23(25)
	$\langle P \rangle$	10 000	P'			
O(4)	$\langle x \rangle$	0	U_1	0	0	0
	$\langle y \rangle$	0	U_2	0	0	0
	$\langle z \rangle$	0	U_3	0	-79(20)	0
	$\langle P \rangle$	10 000	P'			
O(5)	$\langle x \rangle$	6917(101)	U_1	0	-772(171)	218(173)
	$\langle y \rangle$	0	U_2	2791(133)	0	-994(120)
	$\langle z \rangle$	1973(11)	U_3	0	21(18)	26(21)
	$\langle P \rangle$	10 000	P'			

† $\sigma < 10^{-4}$.

(anticipating some vacancies) were considered. Refinement of the occupancy was not introduced in previous studies; here it gives a significant improvement of the refinement.

Within the model considered, which takes into account the density modulation, the thermal mean square displacement of Bi atoms along α was found to be abnormally high in comparison with the other displacements. As a result the average position of the Bi was split along α , and the modulated displacement along this direction (constrained to be zero in the previous stage of the refinement) was allowed to vary.

Finally, a modulation of the thermal parameters was attempted for Bi and Sr atoms; this significantly improved mainly the R -factor related to the second-order satellite reflections.

Table 3. Further refinement results. β_{ij}^0 are the average thermal parameters ($\times 10^4$); and $\gamma_1, \delta_2, \gamma_2, \delta_2$ are the Fourier terms ($\times 10^4$) of the modulated parts $\beta_{ij}(\bar{x}_4)$. The e.s.d.s are in parentheses.

Atom			γ_1	δ_1	γ_2	δ_2	
Bi	β_{11}^0	105(8)	β_{11}	0	-12(18)	-27(31)	0
	β_{22}^0	128(9)	β_{22}	0	-106(13)	-48(17)	0
	β_{33}^0	2(0)†	β_{33}	0	-1(0)†	-1(0)†	0
	β_{23}^0	0	β_{23}	-2(1)	0	0	2(1)
	β_{13}^0	-2(1)	β_{13}	0	7(3)	-3(4)	0
	β_{12}^0	0	β_{12}	41(18)	0	0	-16(28)
	Sr(1)	β_{11}^0	106	β_{11}	0	4(11)	8(24)
β_{22}^0		32(7)	β_{22}	0	6(10)	11(11)	0
β_{33}^0		8(0)†	β_{33}	0	-3(0)†	-2(0)†	0
β_{23}^0		0	β_{23}	5(1)	0	0	0(1)
β_{13}^0		0	β_{13}	0	0	0	0
β_{12}^0		0	β_{12}	0	0	0	0
Sr(2)		β_{11}^0	130(8)				
	β_{22}^0	30(9)					
	β_{33}^0	5(0)†					
	β_{23}^0	0					
	β_{13}^0	0					
	β_{12}^0	0					
	Fe	β_{11}^0	80(9)				
β_{22}^0		50(8)					
β_{33}^0		2(0)†					
β_{23}^0		0					
β_{13}^0		0					
β_{12}^0		0					
O(1)		B_{iso} (Å^2)	1.35(1)				
O(3)	B_{iso} (Å^2)	2.0(3)					
O(4)	B_{iso} (Å^2)	2.19(4)					
O(5)	B_{iso} (Å^2)	5.49(26)					

† $\sigma < 10^{-4}$.

The final agreement factors are

$$\begin{aligned} R/R_w &= 0.068/0.083 & R_0/R_{0w} &= 0.064/0.088 \\ R_1/R_{1w} &= 0.063/0.070 & R_2/R_{2w} &= 0.096/0.096. \end{aligned}$$

The indices 0, 1, 2 refer to the main reflections, to the first-order satellites and to the second-order satellites respectively.

The results of the refinement are given in tables 2 and 3.

5. Discussion

A projection of the modulated structure onto the (100) plane is shown in figure 2 underlining the undulation of the (010) and (001) cation layers.

The displacement amplitudes along c increase gradually in going from the Bi layers to the Sr(2) layers while an opposite effect occurs for the displacement along b . These facts

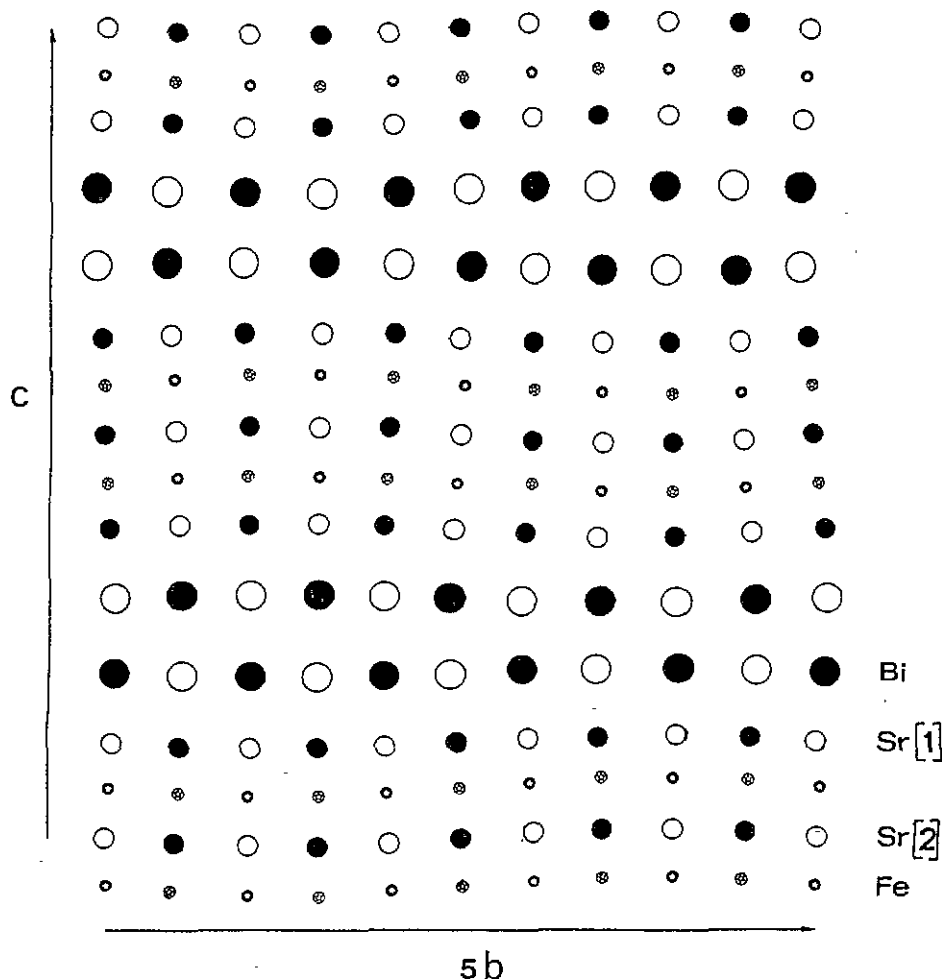


Figure 2. The undulation of the (010) and (001) cation planes.

illustrate the general features already mentioned concerning the modulated structures of all these related compounds.

The interlayer and intralayer Bi-Bi distances vary in an opposite way versus the internal parameter $\alpha = n_2 q_2^*$ (the integer n_2 specifies the unit cell along b) (see figure 3). Within the BiO layers Bi-condensed (C) and Bi-diluted (D) regions are evident. Thus, in the C regions of the crystal the interlayer Bi-Bi distances are the largest whereas in the D regions these distances are the smallest. We can observe that no Bi vacancy is implied inside the BiO layers.

The structure of the ferrite can be described as a stacking of two blocks: the first one formed by FeO_2 and $\text{Sr}(2)\text{O}$ layers (the perovskite layers) and the second one formed by BiO and $\text{Sr}(1)\text{O}$ layers (the rock-salt layers).

5.1. The rock-salt layers

The distances between the bismuth sites on the two sides of the mirror (σ^m) (corresponding to the splitting of the average position of Bi along a) are almost constant throughout the crystal.

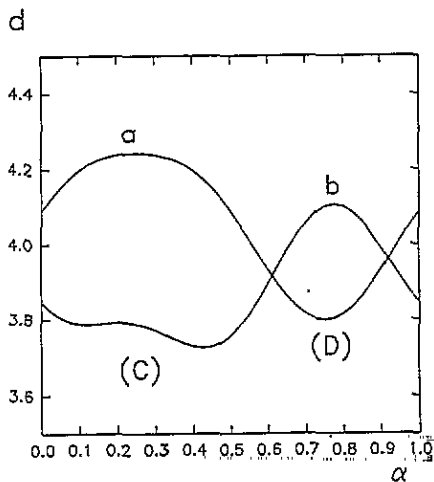


Figure 3. Variations of the interlayer (a) and intralayer (b) Bi-Bi distances (\AA) versus the α -parameter.

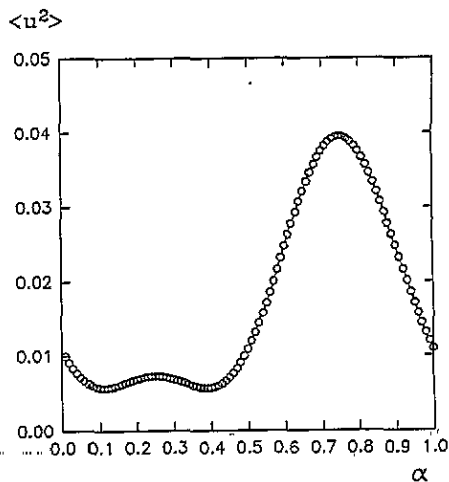


Figure 4. Variations of the thermal mean square displacement ($\langle u_{22}^2 \rangle$) (\AA^2) versus α .

Refinement within the non-centrosymmetric SSG $N:F2mm:\bar{1}1$ s with a unique Bi site leads to a larger anomaly of the thermal mean square displacement of bismuth along a . As a result, we see that this change of SSG does not allow us to avoid the Bi splitting. The observed splitting of Bi along a is probably related to a too high symmetry of lattice translation within the orthorhombic symmetry. Nevertheless, the additional reflections eventually obtained do not appear in the reciprocal lattice for the crystal studied.

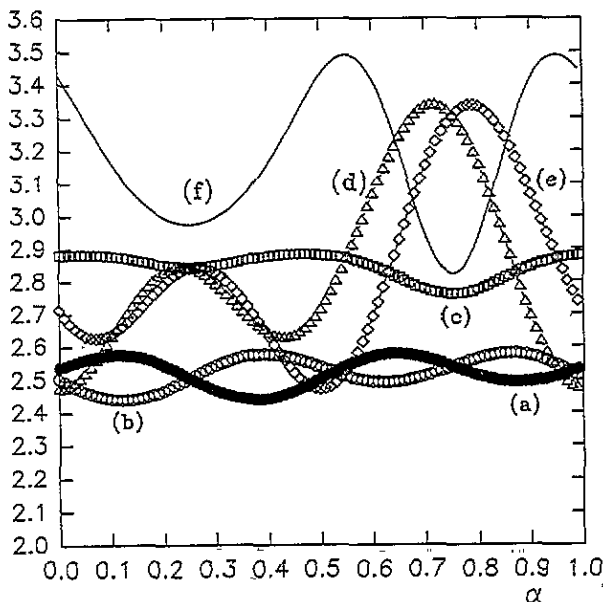


Figure 5. Variations of the Sr(1)-O distances (\AA) versus α . (a) Sr(1)-O(1), (b) Sr(1)-O(1a), (c) Sr(1)-O(3), (d) Sr(1)-O(3a), (e) Sr(1)-O(3b), (f) Sr(1)-O(5).

According to the refinement results for modulation of thermal parameters, it should be assumed that an anomaly is possible within the BiO layers. Indeed, in some unit cells of the crystal, abnormally large values are observed for the thermal mean square displacements of Bi (figure 4) along *b*. Similar features were also observed in the study of Lepage *et al* (1989) for the commensurate oxide $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_{9.2}$. This can be explained either in terms of a lowering of the symmetry leading to the SSG $N:Fm2m:1ss$ or in terms of a static disorder of the bismuth atoms within the layers. The difficulty of locating the atom O(5) of the BiO layers, which exhibits a large thermal parameter (see tables 2 and 3), would be related to the previous anomalies. The chemical formula $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9.2}$ deduced from the charge balance taking into consideration the species Bi(III), Sr(II) and Fe(III) requires an excess oxygen with respect to the ideal formula ' $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_9$ '. It is likely that the insertion of these oxygen atoms within the BiO layers would locally disturb the array of Bi atoms. This hypothesis favours static disorder. Moreover, it is in agreement with the model developed by Lepage *et al* (1989), involving additional oxygen in some areas of the crystal.

The Sr(1) atoms are bound to the oxygen atoms O(1), O(3) and O(5) belonging to the FeO_2 , Sr(1)O and BiO layers respectively (figure 5). The variation of the Sr(1)–O(1) distance remains small, but the distances Sr(1)–O(3a), Sr(1)–O(3b) and Sr(1)–O(5) take large values (≤ 2.9 Å). The O(3) and O(5) atoms are not bound to the strontium atom in all the unit cells. As a result, the coordination of the strontium atom varies in a complex way (figure 6).

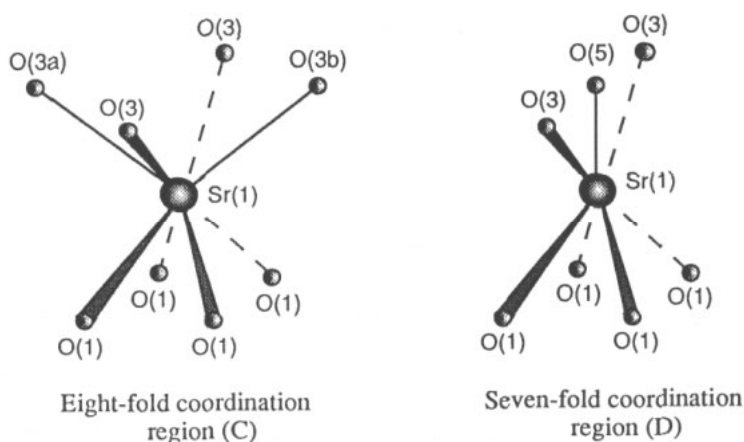


Figure 6. Extreme coordinations of the Sr(1) site.

The probability of occupancy of a Sr(1) site by strontium atoms is found to be maximal in the neighbourhood of the Bi-diluted D regions, while in the other zones of Sr(1)O layers a substitution of Bi for Sr may occur (figure 7). Thus, the bismuth atoms are not uniformly distributed in the crystal.

5.2. The perovskite layers

In these layers no vacancies or substitutions are involved for Fe sites or Sr(2) sites.

The variations of the Sr(2)–O distances versus α do not cause significant variation of the coordination of the Sr(2) site (table 4); the strontium atom exhibits a twelfold coordination throughout the crystal. This result explains the absence of bismuth from the

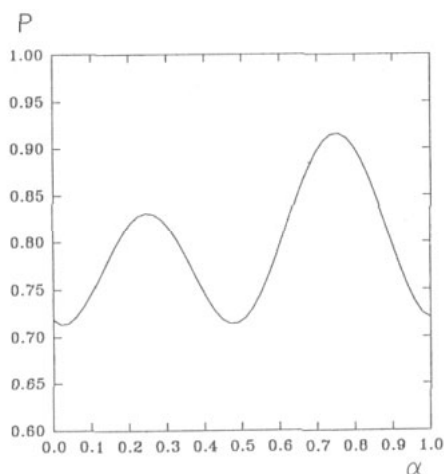


Figure 7. Variations of the occupancy probability P of the Sr(1) site by strontium atoms versus α ($1 - P$ is the probability of occupancy of a Sr(1) site by a bismuth atom).

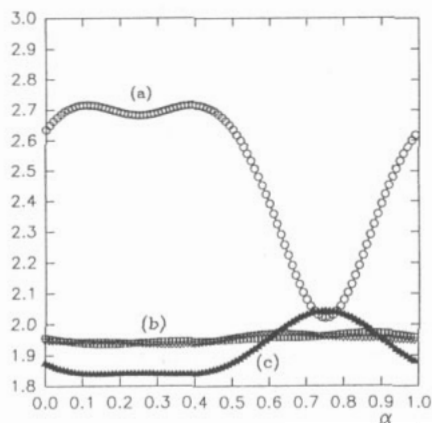


Figure 8. Variations of the Fe-O distances (Å) versus α . (a) Fe-O(3), (b) Fe-O(1) and Fe-O(1a), (c) Fe-O(4).

Table 4.

	d_{min} (Å)	d_{max} (Å)	Average distances (Å)
$8 \times d_{Sr(2)-O(1)}$	2.74(3)	2.98(4)	2.86(3)
$4 \times d_{Sr(2)-O(4)}$	2.745(2)	2.745(2)	2.745(2)

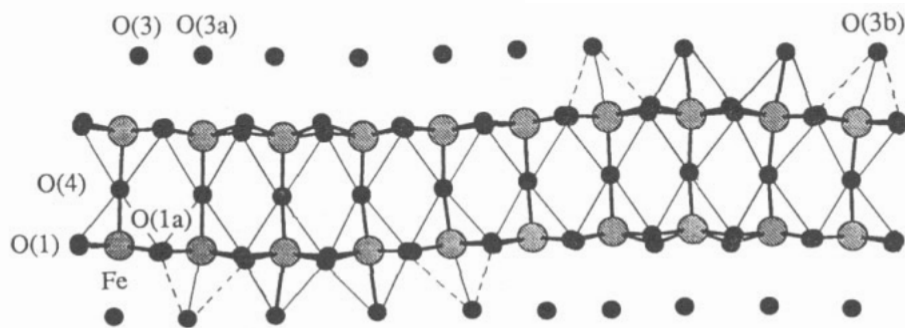


Figure 9. The sequence of iron polyhedra in the double iron layers.

Sr(2) site. Indeed, *a priori*, bismuth atoms cannot achieve a twelfold coordination.

In contrast, we observe that the geometry of the iron polyhedra is rather distorted. The variations of the equatorial Fe-O(1) distances and the apical Fe-O(3) distance are very small. However, the evolution of the apical Fe-O(3) bonds throughout the crystal is complex (figure 8). In the neighbourhood of the D regions the iron displays a regular octahedral coordination while in the other zones it displays instead a fivefold coordination. Figure 9 shows, within the double iron layer, the sequence of the iron polyhedra.

The appearance of such Fe atoms within different local environments occurring due to

the modulated structure can now explain why at least three sites are needed to correctly fit the Mössbauer spectrum of the Bi 2212 iron counterpart $\text{Bi}_2\text{Sr}_2\text{CaFe}_2\text{O}_{9+\delta}$ recently described by Sedykh *et al* (1995). Moreover it should be pointed out that the relative intensities of the three sites denoted D_1 , D_2 and D_3 by the authors are in good agreement with the percentages found here for iron (see figures 8 and 9) in a sixfold coordination corresponding to a regular octahedron ($\sim 20\%$), a fivefold coordination corresponding to a very distorted octahedron with an Fe–O(3) bond longer than 2.6 Å ($\sim 60\%$) and a [5+1]-coordination state corresponding to a less distorted octahedron with a Fe–O(3) bond close to 2.3 Å ($\sim 20\%$).

The modulated structure of the oxide $\text{Bi}_2\text{Sr}_2\text{CaFe}_2\text{O}_{9+\delta}$ (Sedykh *et al* 1995) has not been established in detail. However, the authors have measured—as in the $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9+\delta}$ compound—an irrational component for the modulation wave vector ($q^* = 0.22(3)b^* + c^*$) and have attributed the incommensurateness to the presence of Ca. From our study, we can conclude that the incommensurate character of the modulation does not result from the replacement of Ca for Sr in the perovskite Sr(2)O layers. The origin of the modulation is probably more complex but should be connected with the rock-salt-type layers which do exhibit located disorder phenomena and undulations.

6. Conclusion

As regards the displacive modulation, our results are consistent with those of Lepage *et al*; indeed the types of undulation of the cationic sheets along b and c are quite similar. It is stressed that the 2212 ferrite $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9+\delta}$ differs from the phase previously described by Lepage *et al* only as regards the incommensurate character of its modulation. In fact, we were able to measure different values of the q_2^* -component of the q^* vectors from different preparations using PbO as the flux, and in that case we even obtained a rational value of 0.2, similar to that observed by Lepage *et al*. Nevertheless, all our syntheses without lead led to incommensurate modulation.

In this respect our ferrite is closely related to the Bi 2212 superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, in spite of the fact that it exhibits one additional oxygen per formula unit. Both structures in fact exhibit the same modulation vector, with an incommensurate component close to 0.21. The rational character of the component of the wave vector is not directly related to the Fe or Cu cation since evidence for the existence of both commensurate and incommensurate structures has been provided for both systems. The displacive modulations of the Fe and Cu compounds are very similar. Hence, the same large displacement of the Bi atoms is observed—mainly along b ; in the BiO layers there is evidence for condensed and diluted regions.

For the copper compound, a static disorder of the Bi atoms, in the b direction, would also be involved (Ruyter *et al* 1994)—but this is still not clearly characterized.

Occupation modulations are observed in both structures; in the Fe compound a substitution of Bi for Sr(1) is observed, while in the Cu compound, the Ca atom is partly substituted for with Bi or Sr. This can be explained as being a result of the particular environment of the Ca and Sr(2) sites, in both structures, which can accommodate a Bi atom or not.

The $[\text{FeO}_2]_\infty$ and $[\text{CuO}_2]_\infty$ layers are not very much distorted. An evolution of the Fe coordination has been shown to occur from an octahedral to a pyramidal environment. This reveals also an analogous behaviour of the apical oxygen O(3) for the Fe and Cu compounds.

Nevertheless, we can outline some differences between these two compounds. For example, it is found that the lattice symmetry of the ferrite (F) is different from that of

the cuprate (B)—but this difference apparently has no consequences for the modulation characteristics of the structures. Indeed, only symmetry constraints induce this change of lattice.

Moreover, in the copper oxide additional diffuse satellite reflections are observed in the diffraction pattern. The pattern of the ferrite, where these reflections do not appear, should allow for more accurate study.

References

- Beskrovnyi A I, Dlouhá M, Jirák Z and Vratislav S 1990 *Physica C* **166** 79
De Wolff P M, Janssen T and Janner A 1981 *Acta Crystallogr. A* **37** 625
Hadjimitov V N, Iliev M N, Dimov V, Pissas M and Mitros C 1993 *J. Phys.: Condens. Matter* **5** 907
Lepage Y, McKinnon W R, Tarascon J M and Bardoux P 1989 *Phys. Rev. B* **40** 6810
Levin A A, Smolin Y I and Shepelev Y F 1994 *J. Phys.: Condens. Matter* **6** 3539
Petricek V, Gao Y, Lee P and Coppens P 1990 *Phys. Rev. B* **42** 42387
Ruyter A, Grebille D, Leligny H, Labbé P and Raveau B 1994 *Aperiodic 94 (Les Diablerets, 1994)* (Singapore: World Scientific) p 470
Sedykh V, Smirnova I S, Dubovitskii A V, Narymbetov Zh, Shekhtman V, Suvorov E V, Goncharov V A and Novomlinskii L A 1995 *Appl. Phys. A* **60** 71
Yamamoto A 1990 *The REMOS Program* National Institute for Research in Inorganics, Niichari-gun, Ibaraki, Japan
Yamamoto A, Onoda M, Takayama-Muromachi E and Izumi F 1990 *Phys. Rev. B* **42** 4228