

Bi³⁺ Electronic Lone Pair Configuration in the Modulated Bi-2212 Type Oxides

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The Bi³⁺ ion is characterized by the electronic configuration [Xe]4f¹⁴5d¹⁰6s², and its 6s² lone pair plays an important role in the environment of the ion. A program of localization of the lone pair was successively applied to several bismuth oxides. Different Bi environments were then evidenced and a comparison between simple Bi oxides and more complex phases (modulated and collapsed phases in the family of the so-called Bi-2212 oxides or related compounds) was carried out. All these environments are characterized by Bi–Lp distances ranging from 0.5 to 1 Å and O–Lp distances above 2.4 Å. They can always be described as a more or less important distortion of an ideal BiO₃Lp tetrahedron. The possible role of this lone pair in the accommodation of the modulation in some phases is outlined. © 1998 Academic Press

I. INTRODUCTION

High-*T*_c superconducting bismuth copper oxides, as well as the related iron and cobalt compounds, are characterized by very similar layered crystal structures involving the alternation of “NaCl”-type layers ([BiO] and [SrO]) and perovskite-type layers ([CaO] or [SrO] and [MO₂], with *M* = Cu, Fe, or Co). The lattice mismatch between these layers is responsible for both disorder phenomena and the appearance of incommensurate or commensurate modulations. Studies (1–10) using either the superspace formalism or the “supercell” approximation have provided an accurate description of the atomic structure of these modulated phases. The corresponding atomic displacements within each layer have also been characterized and have been found to be maximum within the [BiO] layers. This observation implies that the origin of these modulations is probably located within the [BiO] layers. A frequent explanation involves the insertion of extra oxygen, which should also be responsible for the doping of the [CuO₂] layers and for the nonstoichiometry of these phases (2).

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Various authors (2–5, 7) have attempted to characterize this supplementary oxygen in the [BiO] layers of the so-called 2212 oxides. The corresponding models roughly agree on the periodic insertion of oxygen every four or five cells, but the structural configurations deduced from these models are rather different. More recently, Grebille *et al.* (9) and Pérez *et al.* (10) have shown that within these [BiO] layers static disorder occurs in some regions of crystals, concerning both Bi and O atoms.

The main disorder is observed for the Bi atoms, which occupy split sites along the modulation direction: this phenomenon occurs approximately every five cells and allows for an atomic site to be partially occupied by one supplementary oxygen atom. The proposed models involve different configurations for the Bi atoms, but it is not always possible to discern which provides the most adequate structural description. Moreover, in any given model, it appears that the oxygen environment of the Bi atoms, in the [BiO] layer is likely to change along the modulation direction, particularly in the disordered regions. Thus, it is important to find new criteria to discriminate between the different structural propositions.

The Bi³⁺ ion is characterized by an electronic configuration, [Xe]4f¹⁴5d¹⁰6s², having a 6s² lone pair (*Lp*). This lone pair is responsible for the high value of the dielectric polarizability and as a result is expected to display an important stereoactivity within the previously encountered environments. A realistic description of the lone pair configuration can help to give an explanation for the accommodation of the modulated displacements along the [BiO] chains.

Pb²⁺ is also well known for analogous behavior and the stereochemical part of its electronic lone pair has already been discussed in the case of the lead oxides. In particular, the influence of the Pb lone pair on the existence and stabilization of the modulated structure of α - PbO at low temperature has been clarified (12). In the same study, a first approach to the localization of the Bi³⁺ lone pair in a Bi-2212 superconducting oxide was given, but on the basis of partial and unreliable structural results.

In the present paper the position of the Bi lone pair is first calculated in some simple bismuth oxides to obtain reference environments. This calculation is subsequently carried out for the iron and copper 2212 compounds (modulated and collapsed phases), allowing for comparisons between the different Bi environments to be made. Finally, the role of the Bi lone pair in the modulated structure is outlined.

2. LONE PAIR LOCALIZATION METHOD

Assuming the knowledge of the electronic polarizability coefficient, α_p , of the Bi³⁺ ion, a method was proposed by Verbaere (11) to determine the displacement of the electronic lone pair from the Bi³⁺ ion. This method has recently been developed into a computer program by Le Bellac (12). Under the influence of the local electric field, E_p^{loc} , at the Bi atomic position p , the lone pair is displaced by an amount ζ_p , which can be deduced from the relation

$$\vec{\mu}_p = q\vec{\zeta}_p = \alpha_p \vec{E}_p^{\text{loc}},$$

where $\vec{\mu}_p$ is the dipolar momentum of the ion p and q is the electric charge distribution for the electronic lone pair.

The local field is estimated by choosing a model for the charge distribution in the crystal and by assuming that q can be modeled as a point charge. The corresponding displacement induces a change of the local electric field, which can be determined from the new charge distribution in the neighborhood of the studied ion. Thus, a new displacement is calculated, and by successive iterations final values are obtained for the equilibrium positions in terms of relative components of the displacement vector of the lone pair from the ionic position in the crystal cell.

It is important to note that α_p values are not accurately known and that the literature values vary widely according to the method used to derive this polarizability. In the present study, we shall use values obtained from the refraction indices of different compounds containing Bi³⁺, assuming that the Clausius–Mosotti formula (13) can be applied in these cases ($\alpha_p = 3.5 \text{ \AA}^3$). As our purpose is to compare different bismuth oxides, the exact α_p value is not necessary to achieve this goal, as long as we are careful in making conclusions.

In the following, a comparison is proposed between the different environments of the Bi³⁺ ion, including both oxygen atoms and the electronic lone pair Lp , in different bismuth oxide structures.

Owing to their weak participation in the overall bonding scheme, Bi–O bonds having distances longer than 2.6 Å will not be taken into account in the description of the Bi environments. Therefore, the different Bi–O distances will be classified as follows: short distances which are below 2.3 Å and middle distances ranging from 2.3 to 2.6 Å.

3. SIMPLE BISMUTH OXIDES

Results concerning some simple and well-known bismuth oxides are proposed in this section. The Bi₂O₃, BaBiO_{2.5}, Bi₁₂MnO₂₀, Cs₃BiO₃, and Bi₄Ti₃O₁₂ compounds have been previously investigated (14–18). From atomic positions given in the literature, the locations of the lone pairs of the bismuth atoms have been determined by using the calculation method described above in Section 2 and the oxygen environments of Bi are discussed. Cell parameters, symmetry, and relative Lp displacements from the original bismuth atom positions of the previously reported compounds are summarized in Table 1.

The different Bi environments found in these compounds can be described in a similar way. The bismuth atom is located approximately at the center of a distorted tetrahedron. The apexes of the tetrahedron are occupied by three oxygen atoms having short Bi–O distances and by the lone pair. The O–Bi–O angles are close to 90°. A supplementary oxygen atom can be located at a position opposite of one of the three oxygen atoms. In this case, the coordination polyhedron can be described as a distorted triangular bipyramid, with a base constituted of two oxygen atoms and the lone pair. This supplementary oxygen atom adopts a longer Bi–O distance and thereby distorts the polyhedron, inclining the lone pair (Fig. 1a). Ideal angles concerning this polyhedron are summarized in Table 6. The Bi environment in BaBiO_{2.5} (15) (Table 2) exactly corresponds to this ideal polyhedron.

In this description, the Bi environment observed for Cs₃BiO₃ (18) represents a borderline case. The coordination of the bismuth is clearly tetrahedral without any supplementary neighboring oxygen, and the lone pair is directed along the trigonal symmetry axis of the polyhedron. However, the bismuth atom tends to be drawn toward the plane defined by the three oxygen atoms. The resulting O–Bi–O angles increase from their ideal values and the Bi lone pair moves away from Bi ($d_{\text{Bi-Lp}} \simeq 1 \text{ \AA}$; see Table 5). A slightly distorted polyhedron is observed for both Bi₁₂MnO₂₀ (16) and Bi₂O₃ (14), resulting in even more dispersed angular values (Tables 4 and 3).

TABLE 1
Cell Parameters, Symmetry Group (SG), and Relative Lp Displacement from the Bismuth Atom for Some Simple Bismuth Oxides

	a (Å)	b (Å)	c (Å)	β (deg)	SG	Δx	Δy	Δz
BaBiO _{2.5}	7.341	7.579	6.072	99.19	$P2_1/c$	+0.816	+0.301	+0.605
Bi ₂ O ₃	7.741		5.634		$P\bar{4}2_1c$	−0.121	−0.444	−0.558
Bi ₁₂ MnO ₂₀	10.206				$I23$	−0.639	+0.046	−0.264
Cs ₃ BiO ₃	9.209				$P2_13$	+0.587	+0.587	+0.587
Bi ₄ Ti ₃ O ₁₂	5.450	5.406	32.832	$\simeq 90$	$B1a1$	+0.188	+0.199	−0.589

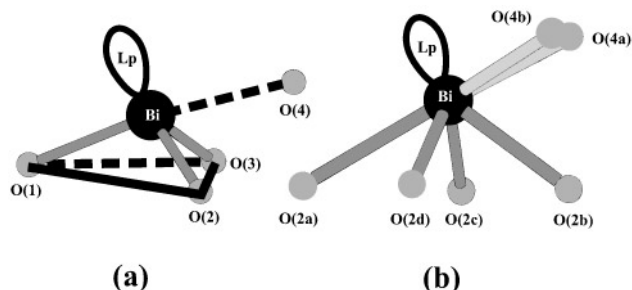


FIG. 1. Different types of Bi environments: (a) schematic representation of the ideal Bi environment; (b) Bi environment in the Aurivillius phase.

The Bi coordination in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (17) Aurivillius phase (Table 7 and Fig. 1b) is also well known and appears to be different from the previous ones. The Bi atom is located at the apex of a square pyramid with a base of four nearest neighboring oxygen atoms. Two supplementary oxygen atoms realize middle Bi–O distances on the other side of the pyramid. These two oxygen atoms and the lone pair build an opposite triangular pyramid. However, considering the previous description of the BiO_3Lp tetrahedron, it is possible to describe a similar tetrahedron in the Aurivillius phase including the three short Bi–O distances ($< 2.3 \text{ \AA}$) and the Bi– Lp distance. The remaining Bi–O bonds have middle distances ($2.45 < d < 2.6 \text{ \AA}$) and are responsible for the pronounced distortion of the basic BiO_3Lp tetrahedron.

In conclusion, some general features can be outlined in simple bismuth oxides: the Bi–O distances are never less than 2 \AA , the Bi– Lp distances vary between 0.5 and 1 \AA , and the O– Lp distances are always longer than 2.4 \AA . Moreover, three short Bi–O distances, with angular values in the range $90 \pm 10^\circ$, are always adopted. The three nearest neighboring oxygen atoms and the Bi lone pair form a more or less distorted tetrahedron. Two limiting cases are observed: the trigonal case of Cs_3BiO_3 (three very short Bi–O distances, a long Bi– Lp distance, and O–Bi–O angles of 117°) and the highly distorted case of the Aurivillius phase. Some more symmetrical environments also seem possible (Bi(1) in $\text{Bi}_2\text{Te}_2\text{O}_8$ (19)), resulting in shorter Bi– Lp distances.

TABLE 2
Main Interatomic Bi–O Distances (\AA) and O–Bi–O Angles (Deg) in $\text{BaBiO}_{2.5}$

Bi	O(2a)	O(3a)	O(1a)	O(3b)	Lp
O(2a)	2.064	2.968	3.105	3.018	2.834
O(3a)	91.6	2.075	3.068	3.036	2.832
O(1a)	92.2	90.5	2.241	3.836	2.596
O(3b)	82.5	82.9	171.4	2.489	2.655
Lp	133.7	132.3	99.9	88.7	0.982

TABLE 3
Main Interatomic Bi–O Distances (\AA) and O–Bi–O Angles (Deg) in Bi_2O_3

Bi	O(2a)	O(1a)	O(1b)	O(1c)	Lp
O(2a)	2.096	2.781	2.944	3.376	2.748
O(1a)	82.4	2.128	3.094	3.035	2.624
O(1b)	85.1	89.8	2.253	4.705	2.485
O(1c)	95.2	82.4	172.1	2.463	2.486
Lp	150.2	126.6	100.2	83.4	0.723

4. MORE COMPLEX BISMUTH OXIDES

Recently, more complex Bi oxides have been extensively investigated because of their interesting physical properties, particularly the so-called 2212-Cu layered structure, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. In the Bi–Sr–Ca–Cu–O or Bi–Sr–Fe–O systems, structural studies of related compounds have provided complementary information about this layered structure type, particularly concerning the structural features of the $[\text{BiO}]$ layers. The majority of these phases have incommensurately modulated structures. The others include the so-called collapsed phases (20–25), which are not modulated but show some common structural features with the modulated structures. In the following, calculations of the Bi lone pair positions for both the 2212-modulated and the collapsed phases are presented.

4.1. Superconductor Phases

Concerning the 2212-Cu phase, different structural models have been proposed using either the superspace description (3, 6, 9) or the supercell approach (7). Owing to the incommensurate character of the modulation, an infinite number of Bi environments are involved. However, to calculate the Lp positions of the Bi atoms inside the crystal, a superstructure approach is necessary; as the irrational component of \vec{q}^* ($\simeq 0.21$) slightly deviates from the ideal value (0.2), a fivefold superstructure (along \vec{b}) was estimated as a sufficient approximation of the actual structure, limiting then the study to only five independent Bi environments. Moreover, disorder can be easily taken into account in the

TABLE 4
Main Interatomic Bi–O Distances (\AA) and O–Bi–O Angles (Deg) in $\text{Bi}_{12}\text{MnO}_{20}$

Bi	O(1a)	O(1b)	O(2a)	O(1c)	Lp
O(1a)	2.067	3.084	2.778	3.158	2.664
O(1b)	92.7	2.192	3.061	2.753	2.578
O(2a)	80.8	88.0	2.214	4.678	2.602
O(1c)	84.3	69.5	152.3	2.603	2.674
Lp	144.9	116.6	116.9	88.3	0.693

TABLE 5
Main Interatomic Bi–O Distances (Å) and O–Bi–O Angles (Deg) in Cs₃BiO₃

Bi	O(a)	O(b)	O(c)	<i>Lp</i>
O(a)	2.035	3.136	3.136	2.658
O(b)	100.8	2.035	3.136	2.658
O(c)	100.8	100.8	2.035	2.658
<i>Lp</i>	117.2	117.2	117.2	1.017

calculation process using the commensurate approximation, keeping only atoms of the supercell with occupation greater than 0.4. The differences between these models lie only in the description of the [BiO] layers in the disordered zones, where the insertion of oxygen is thought to be possible.

The model of Kan and Moss (6) leads, in these disordered regions, to unrealistically short Bi–O distances (1.13 Å). As a consequence, the calculation of the lone pair positions results in very long Bi–*Lp* distances (up to 2.39 Å). In these same regions, long Bi–*Lp* distances (up to 1.54 Å) have resulted from the model of Levin *et al.* (7). Since these values are out of the range of those obtained in the simple bismuth oxides, the description of the disordered regions is not deemed to be physically valid in these two models.

In the model of Petříček *et al.* (3), the Bi–*Lp* distances seem quite reasonable, ranging from 0.56 to 0.93 Å. The introduction of an extra oxygen atom in the disordered zones is achieved by the overlapping of two regular sawtooth functions for the modulated displacements, which also leads to unrealistically short Bi–O distances. In this study, a linear modulated displacement along *z* was imposed for both the regular and extra oxygen atoms; this constraint is probably the reason for the bad agreement with a satisfactory Bi environment.

A structural refinement of this phase was also realized by Yamamoto *et al.* (5) using combined neutron and X-ray powder data sets. In this model, the standard O(4) atom of the [BiO] layer is periodically replaced by the supplementary O(5) and O(6) atoms. The Bi environment resulting from O(3) and O(4) is in agreement with the tetrahedral BiO₃*Lp* model, but when introducing O(5) and O(6) sites, one can observe either too short O–O distances ($2 < d < 2.5$ Å) or three very short Bi–O distances (≈ 2 Å). This last

TABLE 6
Angles Expected (Deg) for the Ideal Polyhedron (Fig. 1a)

	O(1)	O(2)	O(3)	O(4)
O(2)	90			
O(3)	90	90		
O(4)	180	90	90	
<i>Lp</i>	90	135	135	90

TABLE 7
Main Interatomic Bi–O Distances (Å) and O–Bi–O Angles (Deg) in Bi₄Ti₃O₁₂

Bi	O(2a)	O(2b)	O(2c)	O(2d)	O(4a)	O(4b)	<i>Lp</i>
O(2a)	2.174	2.696	2.726	3.777	2.873	2.712	2.756
O(2b)	75.1	2.247	3.777	2.726	3.165	2.970	2.611
O(2c)	75.2	112.7	2.289	2.696	2.712	2.873	2.656
O(2d)	114.6	70.7	69.5	2.457	2.970	3.165	2.598
O(4a)	75.9	149.1	69.1	132.4	2.484	3.423	2.503
O(4b)	68.6	75.2	139.5	142.9	84.6	2.599	2.656
<i>Lp</i>	150.2	117.5	118.0	95.2	84.2	87.9	0.649

environment leads to a Bi–*Lp* distance around 2.1 Å, which is out of the acceptable range. This structural refinement was limited because only first-order harmonic modulation functions were used and the probable static disorder of the Bi atom was not taken into account.

The structural models obtained by Grebille *et al.* (9) and Pérez *et al.* (10) for 2212-Cu and 2212-Fe, respectively, are very similar concerning the [BiO] layers. The difference ensures from the interpretation of the regular oxygen atom within the [BiO] layer, which was considered to occupy either a single site or two disordered split sites. This slight difference has no significant consequence for the corresponding Bi environment and only the [BiO] model of the 2212-Fe structure will be presented here. Cell parameters, symmetry space group, and lone pair displacements are given in Tables 8 and 9. Some typical corresponding Bi environments are listed in Tables 10 and 11 for ordered and disordered regions, respectively. The corresponding configuration is drawn in Fig. 2. In this model, satisfactory Bi–O and Bi–*Lp* distances are calculated, even in disordered zones.

In the ordered regions, two types of Bi environments are observed. They can be described from the ideal polyhedron drawn in Fig. 1a. The three oxygen atoms defining the base of the tetrahedron are very close to the ideal positions. In the first type (Bi(β)), the fourth distance is greater than 2.6 Å and was not included in the table. In the second type (Bi(α)),

TABLE 8
Cell Parameters and Symmetry Group (SG)
[Superspace Group (SSG) for Modulated Structure]

<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Bi _{2+x} Sr _{3-x} Fe ₂ O _{9+δ} \vec{q}^*	SSG
5.477	5.464	31.685	0.21 \vec{b}^* + \vec{c}^*	<i>Abmm</i> (0 β 1)
<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Bi _{6+x} Sr _{9-x} Fe ₅ O ₂₆ β (deg)	SG
16.491	5.481	30.086	91.39	<i>P2₁/n</i>

TABLE 9
Relative Position of the Bi Lone Pair in the $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$
and $\text{Bi}_{6+x}\text{Sr}_{9-x}\text{Fe}_5\text{O}_{26}$ Compounds

$\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$			$\text{Bi}_{6+x}\text{Sr}_{9-x}\text{Fe}_5\text{O}_{26}$		
Δx	Δy	Δz	Δx	Δy	Δz
-0.367	0.241	0.492	-0.111	-0.312	0.903
-0.391	0.053	0.444	-0.405	0.508	0.623
-0.417	-0.139	0.481	-0.549	-0.384	0.401
-0.523	-0.071	0.572	-0.608	0.464	0.253
-0.483	0.276	0.349	-0.605	-0.380	0.135
			-0.654	0.310	-0.205

the fourth oxygen atom is closer to Bi. This induces a lengthening of one of the short Bi–O distances and leads to two short and two middle Bi–O distances, according to our classification.

In the disordered region, the bismuth environment can be described in the same way but the polyhedron seems to be more distorted (Table 11). This distortion can be due to a limitation of the model, which is compatible both with the existence of an extra oxygen atom and with a Bi environment in agreement with the usual configuration.

4.2. The 2212 Collapsed Phase

The $\text{Bi}_{6+x}\text{Sr}_{9-x}\text{Fe}_5\text{O}_{26}$ collapsed phase is, as the modulated 2212 compounds are, a layered structure but within each layer, a regular alternation of all the cation types is observed. Even though its structure is not modulated and could be unambiguously solved by standard techniques, it presents a strong analogy to the related modulated structures (2–5, 7, 9, 10). In particular, the structural sequence observed inside the [BiO] layers in the ordered regions of the modulated crystal is also observed in the collapsed phases (Fig. 3). Nevertheless, the disordered

TABLE 10
Examples of Bi Environments in Ordered Regions of
 $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$

$\text{Bi}(\alpha)$	$\text{O}(3\alpha)$	$\text{O}(5\alpha_1)$	$\text{O}(5\alpha_2)$	$\text{O}(5\alpha_3)$	$Lp(\alpha)$
$\text{O}(3\alpha)$	2.04	3.67	3.00	3.15	2.47
$\text{O}(5\alpha_1)$	96	2.13	3.05	2.74	2.58
$\text{O}(5\alpha_2)$	87	87	2.32	4.58	2.51
$\text{O}(5\alpha_3)$	93	76	162	2.32	2.41
$Lp(\alpha)$	131	133	92	102	0.59
$\text{Bi}(\beta)$	$\text{O}(3\beta)$	$\text{O}(5\beta_1)$	$\text{O}(5\beta_2)$	$Lp(\beta)$	
$\text{O}(3\beta)$	2.04	3.04	3.07	2.55	
$\text{O}(5\beta_1)$	93	2.15	3.01	2.62	
$\text{O}(5\beta_2)$	93	88	2.17	2.58	
$Lp(\beta)$	129	125	118	0.72	

TABLE 11
Bi Environment in the Disordered Regions of $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$

$\text{Bi}(\gamma)$	$\text{O}(6\gamma)$	$\text{O}(3\gamma)$	$\text{O}(5\gamma)$	$Lp(\gamma)$
$\text{O}(6\gamma)$	2.07	2.51	2.83	2.79
$\text{O}(3\gamma)$	73	2.17	6.75	2.89
$\text{O}(5\gamma)$	79	94	2.35	2.90
$Lp(\gamma)$	136	136	120	0.90

regions found in the modulated phases do not appear in $\text{Bi}_{6+x}\text{Sr}_{9-x}\text{Fe}_5\text{O}_{26}$. The study of this phase is therefore useful to confirm the Bi environments found in the ordered regions of $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$ or $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. In Table 12, three examples of Bi environments observed in the 2212 collapsed phase are summarized. In fact, they can also be described well with slightly distorted versions of the previous ideal polyhedron (Fig. 1a) and they closely correspond to the three Bi environments found in the modulated phases. Even the Bi(e) atom, which is in a very peculiar position at the end of a [BiO] ribbon (between two [SrO] ribbons and connected with an Fe type site on the [FeO₂] ribbon), adopts a configuration entirely compatible with this description. This study allows us to confirm the appropriateness of the model concerning the ordered regions of the modulated phase.

5. CONCLUSION

Very similar Bi environments have been observed in simple as well as in more complex bismuth oxides. They can always be described by a more or less important distortion of an ideal BiO_3Lp tetrahedron (Fig. 1a), with a possible inclusion of a fourth middle Bi–O distance. Even in the case of the Aurivillius phase, the general characteristics of the ideal tetrahedron can still be observed in the Bi environment. In the description of the 2212 modulated or collapsed compounds, the recent structural studies evidence that all

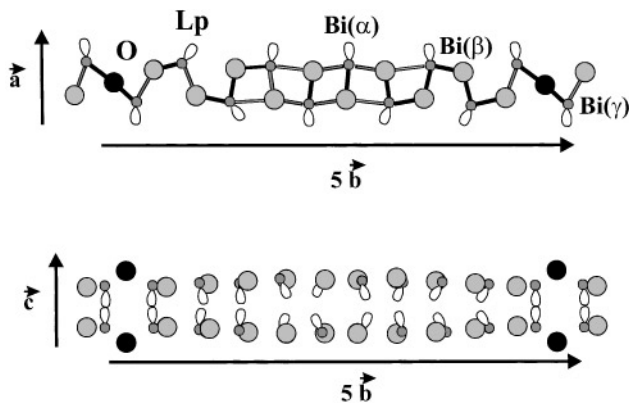


FIG. 2. Configuration of the [BiO] layers for the “2212” modulated compound for the model of Pérez *et al.* (10).

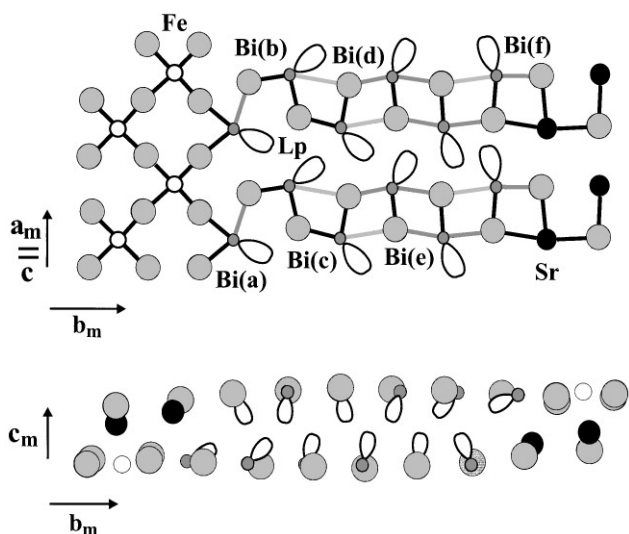


FIG. 3. Configuration of the [BiO] ribbon in the collapsed phase $\text{Bi}_{6+x}\text{Sr}_{9-x}\text{Fe}_5\text{O}_{26}$ (20).

cases between the extreme limits of an ideal tetrahedron or of a distorted bipyramid are encountered: these always have the lone pair at 0.5–1.0 Å from its Bi atom and in the opposite direction to the three shorter Bi–O distances. Both the flexibility of such an environment and the different tilts observed between adjacent BiO_n polyhedra seem to allow for the accommodation of disorder phenomenon resulting from the periodic insertion of an extra oxygen, and this is probably at the origin of the modulation. This study emphasizes the crucial role of the electron lone pair. In spite of its weak participation from the cation–anion bonding point of view, it shows a particular stereoactivity with preferred

standard distances ($\text{Bi–Lp} = 0.5\text{–}1 \text{ \AA}$, $\text{O–Lp} > 2.4 \text{ \AA}$). Its electrostatic dipolar interaction leads to the formation, along \vec{a} and \vec{c} in the 2212 modulated phases or along \vec{a}_m and \vec{c}_m in the collapsed phase, of double [BiO] layers and then to the very well known shape of these layers. The particular arrangement of the lone pair seems to induce the ordering in the [BiO] layers and, therefore, the modulation in $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$ or $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ compounds, in comparison with other nonmodulated, but disordered, Bi-free superconducting oxides.

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TABLE 12
Main Interatomic Bi–O Distances (Å) and O–Bi–O Angles (Deg) in $\text{Bi}_{6+x}\text{Sr}_{9-x}\text{Fe}_5\text{O}_{26}$

Bi(c)	O(3c)	O(5c)	O(5b)	Lp(c)	
O(3c)	2.03	3.07	2.97	2.65	
O(5c)	78	2.11	3.94	2.57	
O(5b)	91	88	2.13	2.60	
Lp(c)	135	107	119	0.79	
Bi(a)	O(1f)	O(3a)	O(2f)	O(5a)	Lp(a)
O(1f)	2.16	3.06	2.75	2.61	3.03
O(3a)	90	2.16	3.26	3.12	2.68
O(2f)	78	97	2.19	3.09	2.73
O(5a)	70	90	147	2.41	2.91
Lp(a)	151	113	115	92	0.96
Bi(e)	O(3e)	O(5e)	O(5f)	O(5d)	Lp(e)
O(3e)	2.08	3.18	3.16	3.02	2.70
O(5e)	94	2.12	3.09	2.85	2.60
O(5f)	88	100	2.42	4.81	2.59
O(5d)	92	78	163	2.45	2.62
Lp(e)	143	125	99	93	0.73