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Competition between composite and modulated configurations in $Bi_2Sr_2CaCu_2O_{8+\delta}$ and its relation to oxygen stoichiometry

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The possible interpretation of the compound $Bi_2Sr_2CaCu_2O_{8+\delta}$ as a composite or a single modulated incommensurate structure is deeply interconnected with the existence of discontinuous atomic domains in the superspace description of the structure. Single-crystal neutron diffraction data have been used to obtain Fourier maps within the superspace description, which show that some atomic domains are indeed either discontinuous, like that of the atoms in the BiO layers, or strongly anharmonic. This contrasts with the structural models of this material, which usually consider a single modulated incommensurate structure with continuous modulations containing a few harmonics. The results demonstrate that these models are bound to yield unrealistic configurations for the so-called *bridging* zones in the BiO layers. The intrinsic discontinuous features of the atomic modulations, especially the longitudinal sawtooth modulations of the oxygens in the Bi_2O_2 slabs, are shown to be the signature of two competing length scales corresponding to the Bi_2O_2 slabs and the perovskite blocks $Sr_2CaCu_2O_6$. In principle, this feature can be naturally included in a modulated composite description with occupational steplike modulations. An ideal composite configuration can be also proposed as a reference structure for describing the effects of the strong coupling between the Bi_2O_2 slabs and the perovskite blocks $Sr_2CaCu_2O_6$, including its effect on the compound stoichiometry, in particular its oxygen content.

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I. INTRODUCTION

The structures of Bi-based high-T_c superconductors are incommensurate and have been the subject of intensive research during the last decade. In particular, several quantitative studies of the structure of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) have been reported.[1–12] In principle, a basic reference structure can readily be identified for the idealized stoichiometric composition ($\delta=0$). This structure can be considered as a stacking sequence along the **c** direction of perovskite-type layers (SrO-CuO_2-Ca-CuO_2-SrO) separated by double BiO layers. Qualitatively, the perovskite slabs, including the neighboring BiO layers on each side, modulate along the **b** direction, perpendicular to the stacking direction, with large transversal displacements along the **c** direction, in opposite phase with the neighboring slab. The distortion includes a large longitudinal modulation along the **b** direction, for some atoms even stronger than the transversal one, in particular for the BiO layers. The modulation direction **b** corresponds to a diagonal direction of the perovskite reference cell ($b=\sqrt{2}a_{\text{perovs}}$). As a result of this longitudinal modulation, a strong deviation of the BiO layers from their idealized configuration is observed, with the alternation in the Bi-O chains of contracted zones of rocksalt type and expanded *bridging* regions with a more irregular configuration.[8] The Bi-O distances in the former zones are of the order of 2.0–2.3 Å, while they can be greater than 3 Å in the bridging zones. These bridging regions occur quasiperiodically, along the **b** direction of the buckled BiO layers, every five or four average cells, in accordance with the wavelength associated with the incommensurate wave vector of the modulation, $\mathbf{q}=q\mathbf{b}^*$ ($q\approx0.21$). The sites of the extra nonstoichiometric oxygen atoms, typical of this compound, are believed to be located in these bridging regions.[8] These zones of the BiO layers would load or unload oxygen quite easily, resulting in considerable variations of the oxygen content [$\delta=0.10$–0.29 (Ref. 13)] and simultaneously significant changes of the superconducting properties.[14,15] There are even reports of oxygen-deficient crystals with $\delta<0$.[7] Usually, however, the oxygen excess δ seems to fall around an "optimal" value of 0.21, related to the modulation wave vector and the maximal loading of the bridging regions.[13] The modulation wave vector is not altered during oxygen loading or unloading, but it is possible to follow the oxygen doping through the decrease of the cell parameter **c** for increasing oxygen content.[14]

As mentioned above, there are quite a number of quantitative structural analyses of Bi-2212, mostly based on x-ray diffraction experiments, either using a conventional commensurate approximation or more rigorously, a superspace $(3+1)$-dimensional approach. Practically all these studies[1–12] describe the structure of Bi-2212 as an incommensurately modulated structure with a single average commensurate structure. This is also the approach taken to describe other members of the family $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+\delta}$ [abbreviated as $Bi22(n-1)n$].[16] The modulation is then given by displacive and occupational modulation functions of all atoms with respect to a single

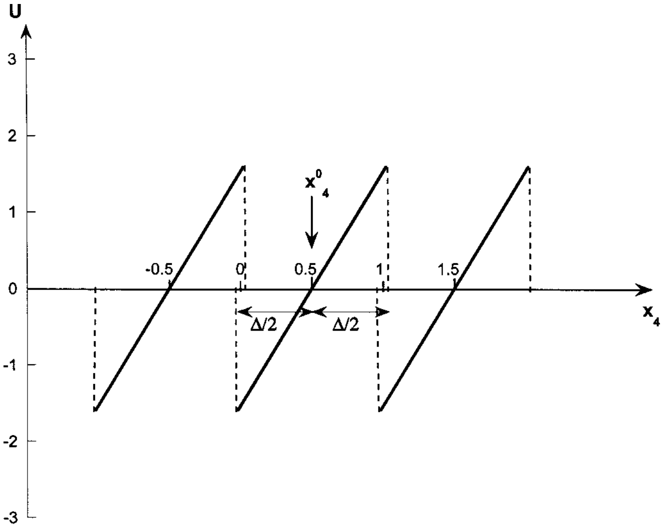

FIG. 1. Sawtooth modulation of oxygen O4 in the BiO layers of Bi-2212, as proposed by Petricek *et al.* (Ref. 2). The amplitude U (vertical axis) along the y direction is expressed in Å.

reference average periodic structure. Most studies include strong occupational modulations for many cationic sites, but few have included modulations of the thermal displacement parameters in the refinement procedure.

Although the symmetry assignment is not trivial and several different symmetries have been attributed to the structure, all proposed structural models essentially coincide, except in two important features: the occupational modulations associated with the cations and the description of the modulated BiO layers. These two features of the structure can vary significantly among the different proposed models. In particular, the important bridging zones of the BiO layers have been given quite different descriptions. The modulations of the oxygen (labeled O4) and Bi atoms in the BiO layers are highly anharmonic in all models. In particular, the O4 modulation has been proposed by Petricek *et al.*[2] to be discontinuous, forming a linear sawtooth function with overlapping regions located in the bridging regions, where the overlap makes the modulation function double-valued and therefore it describes some extra oxygen atoms (see Fig. 1). Despite these early indications that the O4 modulation functions could be unconventional (discontinuous and partially double-valued), most of the studies, including the most recent and most complete ones, have considered for all atoms conventional continuous modulation functions described by truncated Fourier series.[6,7] Forcing the continuity of the O4 modulation leads to configurations of the bridging zones in the BiO layers that are very different from the configuration resulting from a discontinuous sawtooth function, as proposed in Ref. 2. In the bridging zones the continuity of the functions usually forces unphysical distances, which are kept physically acceptable through strong occupational modulations of the corresponding atoms. Some intrinsic disorder of the Bi atoms in the bridging zones has also been proposed.[6] In addition, the extra oxygen atoms, if included in a continuous model, require additional average sites and modulation functions,[6] in contrast with the sawtooth model.

Another type of incommensurate structure, namely an incommensurately modulated composite, was earlier proposed for Bi-2201.[17] This means the structure was described as a system in which there are two interpenetrating modulated substructures whose average cell parameters are mutually incommensurate. One subsystem was thought to consist of the oxygens in the BiO layers, and the other by all the other atoms. The main difference from the pure modulated structure picture is that the full system does not have a single average structure, but two, one associated to each subsystem.[18] This structural model follows the early proposal of Walker and Que[19] and connects with the widespread belief that the origin of the incommensurate modulation in Bi superconductors is the lattice mismatch between the more rigid perovskite slabs (typical CuO distance 1.9 Å) and the BiO layers.[4,9] However, as stressed above, both in Refs. 19 and 17, the second subsystem in the composite description was limited to the oxygen atoms O4 instead of the whole BiO layer. The composite description introduces in natural way a nonstoichiometry between the two subsystems, explaining the systematic excess of oxygen. But a composite picture with one of the substructures formed by only the oxygen atoms within the BiO layers seems quite extraordinary, since the oxygen atoms should be strongly correlated with the Bi atoms in the same layers. In addition, this description does not yield a model fully consistent with a conventional composite,[18] where the two subsystems become perfectly periodic (with different periodicities) if their coupling is virtually ‘‘switched off’’ and the amplitudes of the modulations are set to zero.[6] In any case, all subsequent structural investigations of compounds of the family did not follow this approach any further and have been done considering a conventional modulated structure with an assumed single average structure.

Recently, the composite viewpoint has been retaken to interpret static and dynamical properties of Bi-2212. The hierarchy of diffraction neutron intensities has been claimed to be more consistent with a composite description,[20] and recent low-frequency inelastic neutron experiments have revealed a phonon signature more appropriate to an incommensurate composite with a branch of low-frequency phason modes.[21] This has immediately provoked some controversy.[22] A discussion about Bi-2212 being composite or purely modulated would have had no meaning if the modulation functions of the purely modulated structural model were continuous or analytic, as presented in the most recent published models. As will be shown in the next section, the distinction between the modulated and composite descriptions only becomes ambiguous when the modulation functions are discontinuous or nonanalytical. In this case, the average positions of the atoms can be defined according to different criteria. Depending on these arbitrary criteria, one may define a single average periodic structure or two distinct periodic average sublattices. In such cases, one can describe the structure mathematically as either purely modulated or composite, as wished, but with discontinuous modulations in both cases. In such situations, the only point to be discussed and decided is which of the two descriptions is more efficient and yields a deeper physical or chemical insight of the material and its measurable properties. Essentially, the composite picture takes as reference a nonstoichiometric structure, while the modulated model takes a stoichiometric one. The composite–modulated *dilemma* is then directly related to the interpretation of the nonstoichiometry of the system. The four-dimensional Fourier maps recently published in the course of the modulated–composite controversy[22] indicate that, contrary to the models proposed in the most recent studies of Bi-2212, the modulation of oxygen O4 is nonanalytic, in accordance with the early proposal of Petricek *et al.*[2] This nonanalytic modulation is the basic cause that the composite–modulated discussion has been again reopened when interpreting new accurate static and dynamical experiments done with neutrons, where oxygen has a much larger contrast than that in x-ray measurements.

The existence of nonanalytical modulations is well known in theoretical studies of incommensurate systems, but has been seldomly reported in experimental investigations, perhaps because of the lack of well-adapted analysis tools. In composite systems, the nonanalytical regime appears at a threshold value of the coupling between the subsystems and is characterized by discontinuous modulation functions in both subsystems.[23] The magnitude of the discontinuities depends on the rigidity of each subsystem but appears in all modulation functions. This suggests that not only O4 but other atomic modulations could be nonanalytical in Bi-2212. One should also consider that, even if the discontinuity is rather small and negligible as such, it may produce a strong signature in the modulation of the thermal displacement factors. Typically, low-frequency phason excitations have very strong amplitudes at the discontinuity points of the modulations, even if these latter are rather ‘‘small.’’[23] Therefore, a strong modulation of the thermal displacement factors, with maxima at these discontinuity points, would be expected in such cases. Such strong modulations of the thermal displacement factors have indeed been detected for Bi ions in some of the early studies.[2–4] But their strong correlation with the occupational modulations has conducted in the most recent studies to believe that they were a spurious effect and/or not to include them in the refinement.[6,7]

All these considerations make it advisable to reconsider the structure of Bi-2212 with a method that abandons in general the *a priori* assumption of continuous atomic domains and conventional modulations described by truncated Fourier series. In addition, the possible existence of strong modulations of the displacement factors should be taken into account and resolved from the occupational modulations. The purpose of this paper is a first step in this direction. Neutron diffraction data have been collected and used to determine a set of Fourier maps of the structure within the superspace formalism. The results will be analyzed considering the two possible descriptions, i.e., as a single modulated or a composite structure. We will show that there are indications that the modulation functions of not only oxygen O4, but also of the atoms Bi, Sr, and O3 (the oxygen in the SrO layers) could be discontinuous, showing a competition of several length scales. A latent ideal composite structure can be clearly proposed, where one of the subsystems is formed by blocks Bi_2O_2 of perfect periodicity. The deviations from this ideal configuration can be understood as a consequence of the strong coupling between the Bi_2O_2 slabs and the rigid perovskite block $(Sr_2CaCu_2O_6)$. This coupling tends to form a single modulated system, not only through displacive modulations, but also through the deficit of atoms, changing the ideal composition of the composite. The single modulated configuration and the composite structure compete through the form taken by the displacive modulations and the gain or loss of extra atoms in the Bi_2O_2 slabs. From these considerations an alternative picture of the stoichiometry flexibility of these compounds arises.

II. COMPOSITE VERSUS MODULATED DESCRIPTION OF AN INCOMMENSURATE STRUCTURE

Before presenting the actual superspace Fourier maps obtained for Bi-2212, we include in this section a general discussion on this type of graphic representations of an incommensurate structure, in particular of its longitudinal modulation. By means of several examples, we discuss the relation between a modulated and a composite description of an incommensurate structure with discontinuous modulations. These general considerations will be useful for analyzing in the next section the actual experimental maps of Bi-2212.

Within the superspace formalism, a real (three-dimensional) incommensurate structure is interpreted as a section of a four-dimensional periodic structure (see Ref. 24 and references therein). The atomic positions distributed aperiodically in real space form dense sets (the so-called atomic domains) in the four-dimensional unit cell of the associated periodic structure in superspace. In the case of conventional incommensurately modulated structures and composites with analytical modulation functions, these domains are continuous along the *internal* subspace (x_4), which in the superspace construction is usually defined orthogonal to the real space. As an example, Fig. 2 depicts a projection on the plane (x_2,x_4) of a hypothetical orthorhombic conventional composite with analytical modulation functions. The system is incommensurate along the y axis and each subsystem is formed by a single atom per average unit cell. The y coordinates of all atomic sites in real space are given by the horizontal section $x_4=0$ of the figure. Thus, the aperiodic y coordinates of all atoms of the first subsystem, say the A atoms, are given by the consecutive points with $x_4=0$ of the continuous atomic domains $\mathcal{A}$, which are equivalent through the superspace lattice translation $\mathbf{e}_2$. The average periodicity of these coordinates is given by b_1, as shown in the figure. By construction, the actual atomic positions are modulated with respect to this average position according to a primary wave vector $\mathbf{q}=q\mathbf{b}_1^*$ $(q\approx1.25)$. Reciprocally, the B atoms of the second subsystem are also located along the y direction according to the points $x_4=0$ of the corresponding translationally equivalent atomic domains $\mathcal{B}$. In this second case, the sites deviate from a set of average positions forming a lattice with parameter $b_2=(1/q)b_1$ $(\approx0.80b_1)$. The modulation with respect to these average positions has a period b_1, or equivalently a primary wave vector $\mathbf{q}_2=(1/q)\mathbf{b}_2^*=\mathbf{b}_1^*$ (by construction $b_1/b_2=q$). The composition of the material is

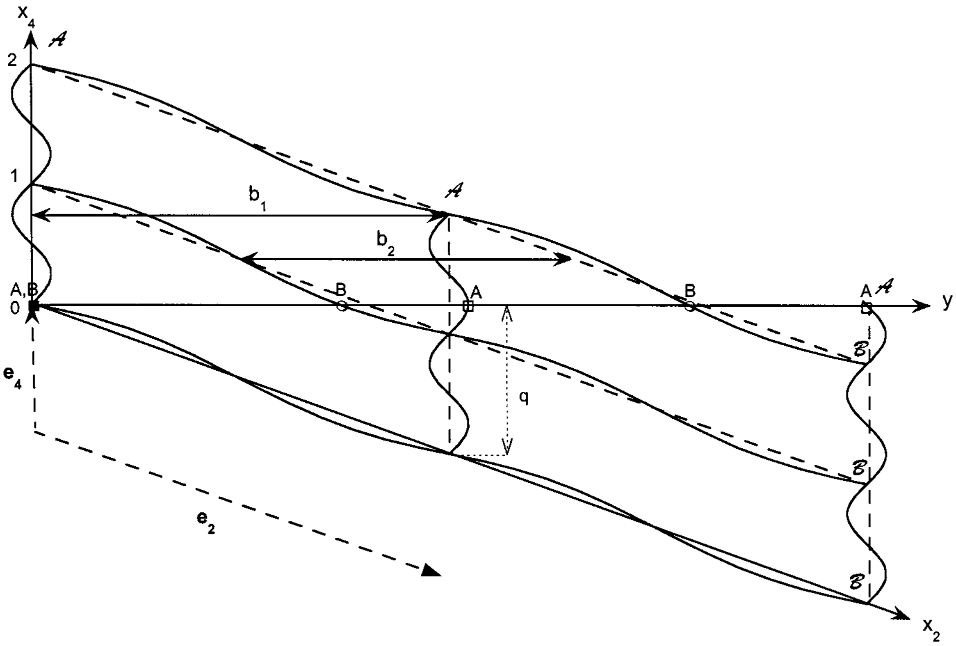

FIG. 2. Example of a conventional composite structure with analytical modulation functions, as seen in a projection on the superspace plane x_2x_4. $q=b_1/b_2 \approx 1.25$.

"nonstoichiometric," namely, AB_q, i.e., it depends on the value of the modulation wave vector q.

A very important and useful property of the superspace description is that the different local coordinations of the atoms taking place along the modulation direction are readily retrieved from the superspace periodic structure by looking at different sections along the x_4 internal axis. In an incommensurate case all local environments seen along x_4 are realized somewhere in real space. Note, for instance, that the y component of the distance between atoms A and B (henceforth the y distance) has no lower bound, and the y coordinates of atoms A and B will coincide at some particular point along the y axis (in the example of Fig. 2 it occurs at the origin). This implies some sterical limitations in a composite with analytical modulations: in our example, A and B atoms should be sufficiently separated on the plane (x,z) to avoid unphysical AB distances over the entire crystal.

The example of Fig. 2 is a typical conventional composite with analytic modulation functions. It contains no ambiguity about the definition of the different average lattices for atoms A and B. The situation is very different in the case shown in Fig. 3, corresponding to a hypothetical material of the same composition (AB_q with $q \approx 1.25$). This figure depicts a projection analogous to that of Fig. 2 of the longitudinal modulations, but for a case where the atomic modulations of the B atoms are nonanalytical and discontinuous atomic domains exist. Note that the discontinuity of the modulation function is such that a minimal nonzero y distance exists between atoms A and B, in contrast to the analytical case of Fig. 2. Hence, a simple sterical or chemical hindrance between the atoms in the two subsystems of the composite can be a sufficient reason for a nonanalytical regime of the atomic modulations.

In the case of Fig. 3, we can still keep the framework of two different average lattices with parameters b_1 and b_2, as done in the example of Fig. 2. The discontinuous modulation functions of the B atoms and the associated average positions separated by a distance b_2 can be clearly seen in Fig. 3(a). The displacements with respect to this composite average positions are indicated by the vectors $\mathbf{u}_c^i$. However, the fact that the modulations are discontinuous allows us to take a different viewpoint. As shown in Fig. 3(b), we can consider the positions of the B atoms as the result of a set of modulation functions describing their deviations, u_m^i, from ideal average positions separated a distance b_1. From this viewpoint the structure is described, not as a composite, but as a modulated structure with a single average period b_1 for all atoms, and a modulation wave vector $\mathbf{q}$, or more conventionally $\mathbf{q}-\mathbf{b}_1^*$ ($\approx 0.25\mathbf{b}_1^*$). In the figure the unit cell corresponding to this equivalent choice of modulation wave vector is also shown. One can see that the modulation functions in this modulated (noncomposite) description are double-valued in an interval along the internal coordinate x_4. This is due to the fact that the width Δ of the occupation domains along x_4 of each discontinuous atomic surface is larger than 1 ($\Delta = q$). The width of the double-valued interval is $\Delta - 1$. It means that in some average unit cells there are two atoms for a single average position. This property goes beyond the conventional definition of a modulated structure and implies a quite drastic extension of the concept of average structure. It allows the paradoxical situation of defining two (or more) average lattices of different periods for the same set of B atoms. In the case of Fig. 3, however, the composite description seems more adequate from a physical viewpoint. If the amplitudes of the modulations with respect to the b_2 average lattice are made zero, a perfect lattice of atoms B separated by a distance b_2 is obtained. On the other hand, if the alternative modulated picture is considered and the displacive modulations of B atoms with respect to the b_1 average positions are made zero, one does not obtain a perfect b_1 lattice of B atoms, but instead, the structure would still be modulated. Some of the unit cells would have pairs of B atoms superposing on a single average y coordinate and

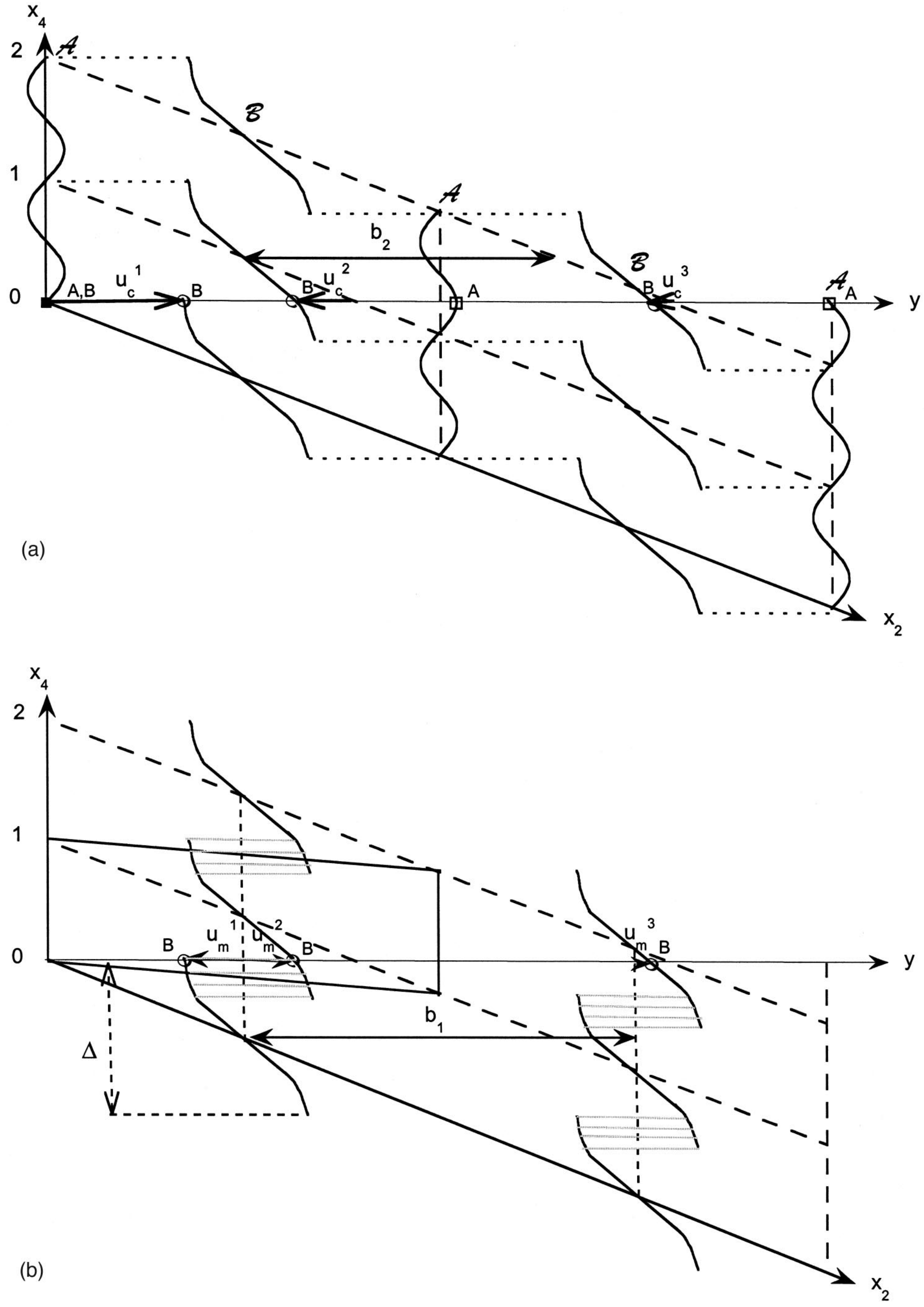

FIG. 3. (a) Projection on the superspace plane x_2x_4 of a hypothetical incommensurate structure with the same wave vector q as in Fig. 2 but with one of the atoms having a discontinuous nonanalytical modulation. The displacements of the B atoms with respect to their b_2 average positions in a composite description are indicated (b) The same example as in (a), highlighting only the subsystem of B atoms and their displacements with respect to their b_1 average positions in a description as a single modulated structure. The conventional unit cell of this description and the double-valued intervals of the modulation functions are indicated. The width of the atomic domains Δ along x_4 is equal to q.

these anomalous cells would occur along the y axis according to the quasiperiodicity associated with the modulation wave vector $\mathbf{q}$.

One can imagine the opposite case, as shown in Fig. 4, where $\Delta=1$. In this case, the composition of the compound becomes “stoichiometric,” *AB*. The modulated description now has a perfect b_1 periodic average structure for zero-amplitude modulations. On the other hand, the composite description, still possible, implies a b_2 average structure for zero-amplitude modulations with some average unit cells having no B atom. These vacant cells form a dense set along the x_2 direction in superspace, as shown in the figure. Therefore, the resulting b_2 average structure has B vacancies located quasiperiodically along y according to the incommensurate period b_1. Therefore, in the case of Fig. 4, one cannot take the b_2 average structure as a nonmodulated subsystem, physically relevant for virtual null coupling between the two subsystems, as done in conventional composites.

In a more general case, with $1<\Delta<q$, both the b_1 and the b_2 average structures for the subsystem of B atoms will be unconventional; one would have some extra atoms in some unit cells, and the other one some vacant unit cells, following a modulated pattern. The compound would have in this case a composition AB_Δ, related to the width along x_4 of the occupation domains. In this general situation, there is, in principle, no particular reason to prefer either the modulated or the composite description of the structure, except maybe for a question of mathematical efficiency in the re-

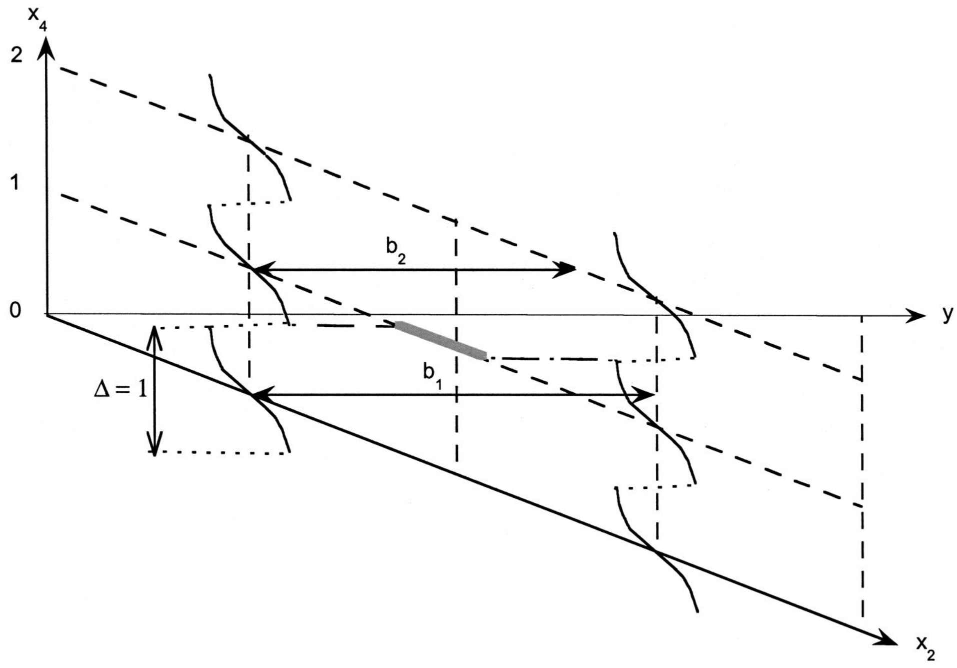

FIG. 4. Similar example as in Fig. 3(b) but with $\Delta=1$, so that no double-valued intervals of the modulation functions along x_4 exist. The figure stresses the dense domains of vacancies along x_2 when the modulation is considered with respect to a b_2 average lattice in a composite description.

finement procedure of the resulting parametrization (magnitude of the displacements with respect to one or the other reference).

Experimental superspace Fourier maps for a real structure yielding information about the type of atomic modulations, through projections or sections of the type discussed above, can be obtained from the measured diffraction intensities. The measured Bragg reflections are indexed with four indices taking a set of four basis vectors. The diffraction vectors are expressed as $\mathbf{q}_{hklm}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\mathbf{q}$, where $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ generate the chosen reference reciprocal lattice, and $\mathbf{q}$ is the chosen incommensurate modulation wave vector. The Fourier series of the corresponding structure factors $F(h,k,l,m)$ represents by definition the periodic four-dimensional superspace scattering density associated with the material:

$$\rho(x_1,x_2,x_3,x_4)=\sum_{h,k,l,m} F(h,k,l,m) \times\exp[-i2\pi(hx_1+kx_2+lx_3+mx_4)]. \tag{1}$$

This four-variable function is represented in superspace, considering that (x_1,x_2,x_3,x_4) represents a vector $r_s=(r_\parallel,t)$ with a component $r_\parallel$ in real space plus a component t along the one-dimensional internal (orthogonal) space.[24] This so-called superspace embedding of the aperiodic structure depends on the chosen indexation basis.[25] In our specific case where $\mathbf{q}$ is parallel to $\mathbf{b}^*$, $\mathbf{q}=q\mathbf{b}^*$, the relation between a generic $\mathbf{r}_s$ and its components (x_1,x_2,x_3,x_4) is $\mathbf{r}_s=\Sigma x_i\mathbf{e}_i$, with $\mathbf{e}_1=(\mathbf{a},0)$, $\mathbf{e}_2=(\mathbf{b},-q)$, $\mathbf{e}_3=(\mathbf{c},0)$, and $\mathbf{e}_4=(0,1)$, where $\{\mathbf{a, b, c}\}$ are the direct real-space unit-cell parameters corresponding to the basis $\{\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*\}$ used in the index. Therefore, the real and internal components of $\mathbf{r}_s$ are $\mathbf{r}_\parallel=x_1\mathbf{a}+x_2\mathbf{b}+x_3\mathbf{c}$ and $t=x_4-qx_2$.

III. THE Bi-O SYSTEM IN THE Bi-2212 COMPOUND

Neutron diffraction experiments have been performed at the Orphée reactor (Laboratoire Léon Brillouin) on the four-circle 6T2 diffractometer (thermal neutron guide, $\lambda=1.54$ Å). The single crystal (volume $10\times4\times0.3\ \mathrm{mm}^3$) was the one used for previous triple-axis spectrometer experiments.[20,21] The measurements were done at ambient temperature and the results were consistent with those obtained with the triple-axis spectrometer.[20] Different scans have been applied to adjust to the diffractometer resolution (ω for $2\theta\leqslant50°$, ω/θ for $50°\leqslant2\theta\leqslant80°$ and $\omega/2\theta$ for $80°\leqslant2\theta\leqslant120°$). Integrated intensities of Bragg reflections were collected following the indexing in accordance with the usual modulated structure description. An orthorhombic average structure with cell parameters $a=5.40(65)$ Å, $b=5.40(13)$ Å and $c=30.71(32)$ Å, and a modulation wave vector $\mathbf{q}=q\mathbf{b}^*$ with $q=0.21$ was employed to express the diffraction vectors in the form $\mathbf{q}_{hklm}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\mathbf{q}$. Main reflections $(m=0)$ and first-order $(m=1)$ and second-order $(m=2)$ satellite reflections were measured. Some third-order reflections were also collected but their intensities with an exposure time per frame of 20 s were too weak to be considered. As superspace symmetry, the superspace group $Nbmb(0q0)$ was assumed, where N stands for the unconventional centering translation $(\frac{1}{2},0,\frac{1}{2},\frac{1}{2})$ in superspace. This group is equivalent to $Bbmb(0q1)$ for the alternative choice of the modulation wave vector as $q\mathbf{b}^*+\mathbf{c}$.[6] It is the one that has been considered in the most recent studies[6,7] and is equivalent to the superspace group No. 66.3 in the list of Ref. 24.

As emphasized in Ref. 20, rather strong diffuse scattering was observed between the sharp main and satellite reflections, at nodes forbidden for the assumed space group. The broad profile along the $\mathbf{c}^*$ direction of the peaks is attributed to stacking faults of the layers. In order to minimize the diffuse scattering effects, the sample was aligned with the diffractometer in Bragg reflection geometry with its reciprocal **a*** and **b*** axes in the horizontal scattering plane. Nevertheless, diffuse intensities were similar to the intensity of the second-order satellite reflections, and because of the resolution broadening (full width at half maximum$\geqslant 2°$), many satellite reflections have been spoiled. Many equivalent reflections in different quadrants were measured and averaged. The value of the internal factors ($R_{\rm int}$) was 3.18, 3.96, and 7.63 for main reflections and first-order and second-order satellite reflections, respectively. Finally, the intensities of 429 unique ($hklm$) observed reflections with $I > 3\sigma(I)$ were derived (182 main reflections and 190 and 57 first- and second-order satellite reflections, respectively). They were corrected for Lorentz effect and have been treated using the program package JANA2000.[26]

The number of unique observed reflections is too limited to produce a full derivation of a structural model with a better accuracy than those that already exist. But being a neutron data set, it is large enough for producing Fourier maps where both cations and oxygens have similar contrast. One can then observe the shape of the occupation domains of the different atoms and directly check the generally accepted modulated structural models with continuous modulations and the implications of a composite interpretation of the structure. The phases (signs) of the structure factors in Eq. (1) were first obtained from a model essentially taken from Miles *et al.*,[7] with the simplification that no continuous occupational modulations were included. The Fourier maps were generated and visualized with JANA2000.[26] The first preliminary maps clearly showed that the modulation of O4 follows a discontinuous pattern far from the anharmonic continuous modulation.[6,7] As earlier proposed by Petricek *et al.*[2] (see Fig. 1), it can be nicely described by a sawtooth function $u_y(x_4)$ defined by three parameters, Δ, x_4^0, and u_0 and given by

$$u_y(x_4) = 2u_0[(x_4 - x_4^0)/\Delta], \quad x_4^0 - \Delta/2 < x_4^0 < x_4^0 + \Delta/2. \tag{2}$$

The value of x_4^0 is forced by symmetry to be $\frac{1}{2}$, and the width Δ is of the order of 1. The O4 modulation was therefore changed accordingly in the phasing model, and the corresponding parameter u_0 refined to -0.251 (fractional atomic coordinate). The parameter Δ is in general related to the oxygen stoichiometry of the studied compound $\mathrm{Bi_2Sr_2CaCu_2O_{8+\delta}}$. In the case of full occupancy of the other inequivalent oxygens, the oxygen excess would be $\delta = 2(\Delta - 1)$. The resulting Fourier map of a section (x_2x_4) at $x_1 = 0.193$ and $x_3 = 0.051$ is shown in Fig. 5. The coordinates x_1 and x_3 have been chosen in order to visualize simultaneously the longitudinal modulations of the atoms Bi and O4, which are approximately colinear along the y direction within one layer of BiO. For comparison, the assumed sawtooth function of the O4 atom is also shown in the figure. One can clearly see the discontinuous character of the O4 modulation. For the compound investigated, the overlap region with a double-valued modulation does not seem to be significant. If refined, the width Δ tends even to values slightly smaller than 1, in accordance with the results of Miles *et al.*,[7] who also proposed an oxygen-deficient model. This is also in accordance with the relatively low value of the c parameter of the sample investigated.[7,13] Note, however, that this smaller width of Δ could be a spurious effect of the expected strong modulation of the displacement (Debye-Waller) coefficients with maxima at the discontinuities, and not included in the model (see below). In the following, we therefore kept $\Delta = 1$, corresponding to a case with no extra oxygens in the BiO layer.

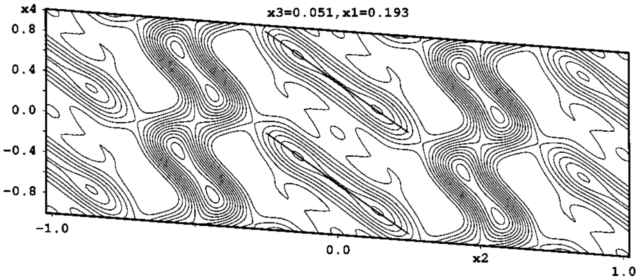

FIG. 5. x_2x_4 section of the calculated four-dimensional Fourier map. The modulation functions of O4 used in the phasing model are also drawn.

In Fig. 5, it is also clear that the modulation of Bi is far from being a typical continuous modulation. It is strongly anharmonic, and shows a clear tendency to produce also a sawtoothlike modulation with the linear parts approximately aligning with the O4 domains. It has strong density minima around $x_4 = 0$. The Fourier map in Fig. 5 suggests the presence of a discontinuity at $x_4 = 0$ of the Bi modulation function. Here the probable nonanalycity of the Bi modulation becomes evident. It is clear that its usual modelization by means of displacive Fourier components up to second order and an occupational modulation with also a few Fourier terms should be quite inefficient to describe the modulation around $x_4 = 0$. The zone around $x_4 = 0$ of the modulation corresponds to the *bridging* zones in the BiO layers. Therefore, deciding whether a discontinuity of the modulation exists is essential to model the actual configuration of the bridging zones.

An accurate analysis of this issue is further complicated by the probable presence of a strong modulation of the atomic displacement (thermal) parameters. The eigenvector of the low-frequency phason branch is expected to have strong amplitudes for the atoms corresponding to the points with maximal slopes in the atomic modulations or closer to the discontinuity points of the atomic modulations, if any.[23] A low-frequency phason branch in Bi-2212 has indeed been recently observed.[21] Therefore, if a continuous modulation model is used, given the form of the Bi modulation, one should expect a strong modulation of the Bi displacement parameter $U_{22}(x_4)$ with a sharp maximum at $x_4 = 0$. Refinement runs including this possibility resulted indeed in clear anharmonic strongly modulated parameters for Bi with the features mentioned above. This characteristic modulation of the Bi atomic displacement parameter was in fact already pointed out in the earlier work of Petricek *et al.*[2] There, it was suggested, however, it could correspond to some Bi de-

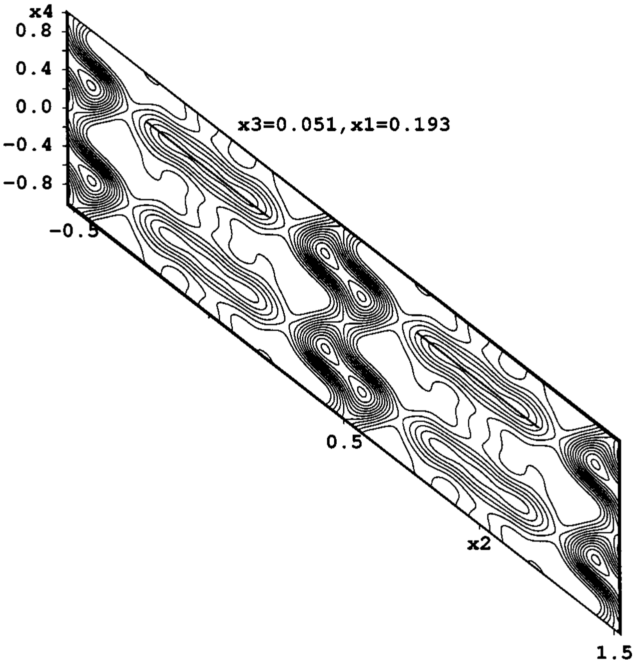

FIG. 6. Same Fourier map section as in Fig. 5 but with a different setting ($\mathbf{q}_c = 2.21\mathbf{b}^*$) corresponding to a possible composite description with the BiO layers as second subsystem with x_2 as the diagonal direction corresponding to its average positions.

ficiency, i.e., some Bi vacancies in regions corresponding to x_4 around zero (the bridging zones). Apparently based on this interpretation, the most recent studies, which include occupational modulations, have not introduced any modulation of the thermal displacement parameters in their models.

IV. THE COMPOSITE VIEWPOINT

The direction defined by the linear sawtooth modulation of the O4 oxygens, also latent somehow in the Bi modulation, is a very specific one. If the indexing is changed so that the modulation wave vector is taken as $\mathbf{q}_c = 2\mathbf{b}^* + \mathbf{q} \approx 2.21\mathbf{b}^*$, the direction corresponding to the newly defined coordinate x_2 coincides with the direction of the oxygen linear displacive modulation. This is illustrated in Fig. 6, where the Fourier map of Fig. 5 is newly shown using this alternative superspace unit cell (different choice of wave vector). One can clearly see that the atomic domains of O4 and Bi approximately align along the newly defined x_2 direction, defining a virtual line of average positions, similarly as happens in the example of Fig. 3(a). We can then consider a composite description with the BiO layers forming the second subsystem with an average distance $b' = [1/(2+q)]b \approx (1/2.21)b$ along the y direction. The difference with a conventional composite is that two types of atoms along this average line have to be considered, so that in fact this average distance b' corresponds in general to a Bi-O y distance. The O4 does not essentially deviate from these virtual line of average positions along y, while for Bi, its modulation suggests a frustrated configuration with a compromise between a Bi-O average y distance b' and a Bi-Bi average y distance b.

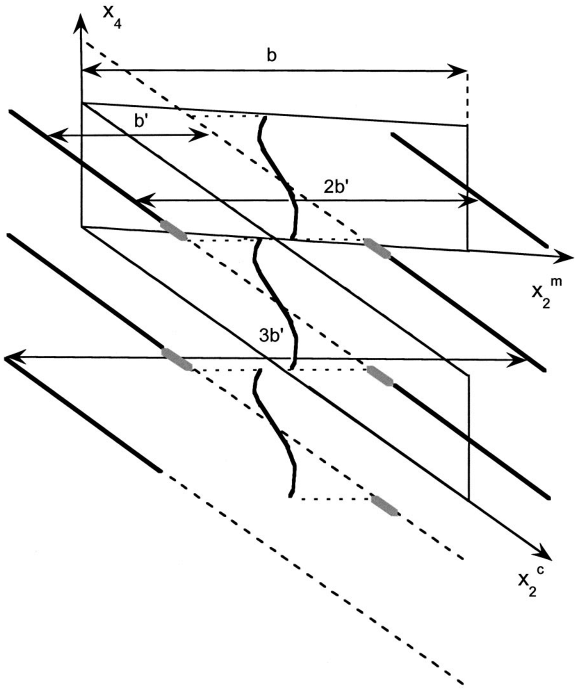

FIG. 7. Idealized scheme of the x_2x_4 projection corresponding to Fig. 6 showing the Bi and O4 modulations and their average distance b' in a composite description. The vacancy domains along x_2 associated with this composite description when $\Delta = 1$ are also shown.

Figure 7 represents schematically the projection on the plane x_2x_4 of the Bi and O4 longitudinal modulations, as proposed from the preceding Fourier maps. The depicted modulations correspond to a row of Bi-O along the y direction. The modulations of the neighboring rows in the Bi_2O_2 slab are obtained by the superspace symmetry operations. The figure outlines the two alternative unit cells corresponding to the usual modulated and "composite" descriptions. The x_4 interval corresponding to the bridging zones is also stressed. The widths of the atomic domains of both atoms have been taken to be unity, corresponding to the idealized stoichiometric composition ($\Delta_{\mathrm{Bi}} = \Delta_{\mathrm{O4}} = 1$). Out of the bridging zones, the atoms O4 are perfectly equidistant along y with a y distance $2b'$, while in the bridging zones their y distance becomes $3b'$. This regularity of the O4 sites along the y direction is remarkable compared with their important modulation along the z direction. The Bi atoms follow a more intermediate pattern. Far from the bridging zones, at the regular rocksalt zones they are close to being y equidistant (b') from the neighboring O4 atoms in the row. In the bridging regions, as one could expect, the Bi modulation curves significantly in order to produce Bi sites, which are more central with respect to the abnormal $3b'$ y distance between the neighboring O4 atoms. The discontinuity of the Bi modulation implies, however, that the Bi atoms in all bridging zones are clearly off center, staying closer to either one or the other neighboring oxygen and breaking one of the two bonds. This is in accordance with the general trend of off-center coordination for underbonded cations.[27] The assumption of a discontinuity in the Bi-modulation allows keeping the y coordination of the Bi atoms in the bridging regions more uniform. One can see that a continuous Bi modulation necessarily passing through zero at $x_4=0$ would force the existence of a significant number of bridging zones with the Bi atoms close to a central position with respect to widely separated O4 atoms. Due to the long distance between the neighboring anions, according to the bond-valence sum rules, center positions would be unstable.[27]

Obviating the transversal modulation (essentially the buckling of the BiO layers along the *z* direction), which is not relevant for the present considerations focused on the incommensurability along the *y* direction, we can broadly describe the BiO subsystem as an ordered configuration of blocks of Bi_2O_2 with a length along the *y* direction of four or five "average" periods $2b'$ separated by *bridging* zones where the system circumvents the misfit between this period $2b'$ and that of the underlying perovskite block, *b*, through a "fault" in the Bi-O4 sequence. In the following block, O4 and Bi atoms interchange the occupation of the ideal sites in the underlying b' lattice, leaving some of the virtual sites of this lattice vacant. The modulation of the Bi with respect to its idealized average position for the "composite" description (aligned with the sawtooth pattern of O4), represents an adaptation to these vacant sites, and also indicates a stronger coupling with the *b* average periodic perovskite block. On the other hand, the O4 atoms show a surprising rigidity with respect to the virtual sites of period b' along the *y* direction. The aperiodic presence of the bridging zones with O4/Bi vacancies and a change in the sequence of the Bi-O rows is a discontinuous occupational modulation of the Bi_2O_2 subsystem due to the coupling with the perovskite slab. Even if we make zero the displacive modulations of Bi with respect to its ideal average line in the composite description, the Bi_2O_2 subsystem is intrinsically modulated with respect to the ideal $2b'$ rocksalt periodic structure through this discontinuous steplike modulation. In this sense, as explained in Sec. II, the setting we are calling a composite description does not correspond to a conventional composite.

The reason for the discontinuous occupational modulation of Bi and O4 is rather clear in Fig. 7. If we imagine a perfect ideal slab of Bi_2O_2, with b' as the periodic *y* distance for Bi-O4 and sandwiched between the quite rigid perovskite block of period *b*, the incommensurate misfit of b' with *b* will result in chemically unacceptable configurations, with the O4 and Bi lying directly below the O and Sr, respectively, of the neighboring SrO layers. The system solves the problem by interchanging the occupation of the O and Bi sites, every four or five unit cells, while keeping in between the favored b' distance. When the O and Bi sites in the regular b' blocks become too far from the corresponding cations and anions in the neighboring perovskite layers, a bridging zone occurs with a "fault" in the Bi-O sequence, the sites of Bi and O4 are interchanged, and a new b' block more or less well adapted to the neighboring perovskite occurs. This is represented in the superspace description of Fig. 7 by the alternation of the atomic domains of O4 and Bi along a single diagonal line corresponding to their average positions.

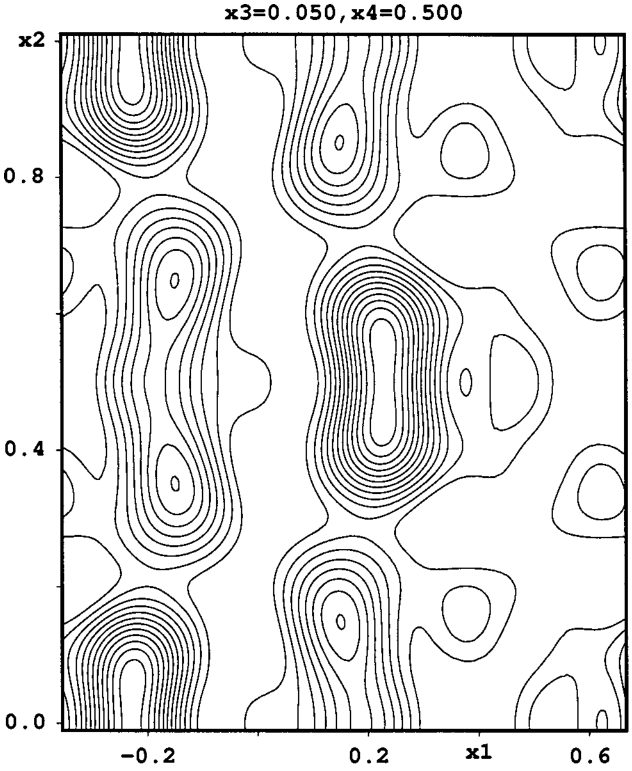

FIG. 8. x_1x_2 section for the composite setting ($q_c=2.21$) of the calculated Bi-2212 Fourier map showing the O4 and Bi domain sections of the two closest neighboring BiO rows in a BiO layer. The less-dense domains correspond to O4. As the O4 domains are practically parallel to x_2, the map shows an essentially undistorted picture of the width of the O4 domain along x_2. The deviation of the Bi domain from the x_2 direction (see Fig. 7) yields in contrast an apparent shorter width.

The correlation of the neighboring Bi-O rows is shown in the calculated Fourier map of Fig. 8, where a section x_1x_2 displaying the O4 and Bi domains is presented, with x_2 corresponding to the composite description ($q_c=2.21$). In this composite description x_2 represents the internal coordinate for the modulations of the Bi-O subsystem. The O4 and Bi domain sections of two neighboring BiO rows in a BiO layer are shown. The less dense domains correspond to O4. As the O4 domains are essentially parallel to x_2, the map shows a clear picture of the width of the O4 domain along x_2. One can see that the O4 atomic domains of neighboring rows (Fig. 6 shows only those of a single row) are close to fulfilling the "closeness" condition, so that along x_2 one O4 domain in one row "begins" when that in the neighboring row "ends." This would exactly happen for $\Delta=1+(q/2)\approx 1.105$ ($\delta=0.21$), which is in fact of the order of the maximal oxygen excess that has been usually reported. For this Δ value one could then consider for the O4 atoms in both rows a single squarelike displacive modulation along x_1 with respect to an *average* intermediate position around $x_1=0$. One could then consider the second subsystem as formed only by the O4 atoms with their average structure given by this intermediate position. This is the approach taken by Yamamoto *et al.*[17] when analyzing Bi-2201. This description implicitly considers the approximate rocksalt structure of the BiO layers or even the alternation of Bi and oxygen atoms along the Bi-O rows as part of the modulation resulting from the coupling between a perfectly periodic subsystem of oxygen atoms O4 (with b' as the distance along the y direction) and the rest. From the practical viewpoint of describing the static structure, this is a perfectly valid procedure. But Fig. 8 shows that in general, one must then describe the necessary squarelike O4 displacive modulation along x_1 with a discontinuous function or even better with discontinuous occupation domains to allow Δ to deviate from the ideal closeness condition value, if necessary. The use of a continuous function with only a couple of Fourier terms for O4 as second subsystem, as done in Ref. 17, is clearly not well adapted to describe such modulations and would necessarily produce rather unrealistic atom sites in the *bridging* regions.

The sudden change in the Bi-O4 sequence necessarily produces sites of the b' lattice "chemically stressed" in the bridging zones. They would correspond to "misplaced" cations or anions in the Bi-O4 row, such as Bi-O4-[O4]-Bi-O4, O4-Bi-[Bi]-O4, etc. The x_4 domains in superspace corresponding to these sites are specially outlined in Fig. 7. Full stoichiometry of the Bi_2O_2 slab with respect to the perovskite block is attained by allowing these stressed positions to be vacant. These vacant sites of the b' average lattice in the bridging zones would be those occupied by additional oxygen atoms when the sample has an oxygen excess. This implies $\Delta_{O4}>1$ and the existence of double-valued regions for the O4 sawtooth modulation along x_4, as proposed by Petricek *et al.*[2] If all these sites were occupied by oxygen, Δ_{O4} would become $1+q$, and the theoretical maximum oxygen load δ would be $2q$ ($\sim$0.42). However, as shown above, for $\Delta=1+(q/2)$ the closeness condition between O4 domains in neighboring Bi-O rows is attained. Above this value, configurations in the bridging zones would become rather problematic as they would have at the same y-level anions in all Bi-O rows. One can then assume that in normal conditions only half of the vacant positions can be occupied by oxygen (half of the vacant atomic domains in Fig. 7) and $\Delta_{O4}^{\max}=1+(q/2)$ with $\delta^{\max}=q$ ($\sim$0.21), which corresponds to the closeness condition mentioned above. Oxygen loading can be, however, chemically enhanced through substitution of calcium by yttrium. In this case, it has been reported that δ attains values as high as 0.5 in the pure Y compound, where on the other hand, the value of q is about 0.247.[13] This suggests that in this case the width of the oxygen sawtooth modulation attains indeed its maximal theoretical value of $1+q$, which would correspond to an oxygen excess of 0.494. In this fully loaded configuration all bridging zones would have pairs of consecutive oxygens at a y distance b'. This unfavorable situation with anions too close to one another without intermediate cations is known to be palliated in other materials through the presence of a global relative shift (antiphase boundary) of the blocks whose interface is formed by the neighboring oxygens. These types of antiphase shifts along the x_1 direction have been in fact observed between the Bi_2O_2 blocks in a Y-substituted compound,[13] supporting the above model for the extra oxygen sites.

From the above considerations it is clear that the Bi_2O_2 slabs exhibit a clear competition between two length scales for their periodicity along the y direction. This confirms the idea that a misfit between the Bi_2O_2 slabs and the rest of the crystal is at the origin of the incommensurate modulation. The oxygens are less coupled to the perovskite neighboring slabs, and their clear sawtooth modulation is a signature of the strong tendency to produce a different y period. The discontinuity of the modulation function is directly related to the tendency of the compound to load extra oxygen atoms, by this means approximating the oxygen stoichiometry associated with the b' period.

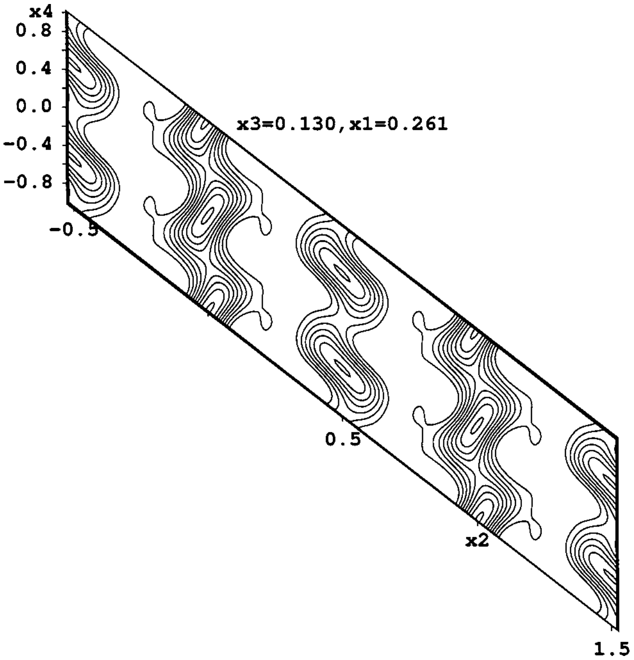

FIG. 9. x_2x_4 section of the Bi-2212 superspace Fourier map showing the modulation of Sr and O3 in the SrO layer.

It is also interesting to observe the behavior of the neighboring SrO layers on both sides of the BiO slabs. Figure 9 shows the Fourier map in the composite setting for one of the Sr-O rows, the other ones being symmetry related. The map suggests that the modulations of both Sr and oxygen (O3) could also be discontinuous or close to having a discontinuity. The modulation of O3 centered around $x_2=0.5$ clearly follows the modulation of the immediate neighboring Bi on the layer below, so that both atoms keep approximately the same y coordinate. Therefore, O3 is quite rigidly attached to the Bi_2O_2 slab and the slope of its distorted sawtooth modulation follows the average diagonal line defined by the O4 modulations corresponding to x_2 in the setting of the map. The bridging zones produce also in O3 an abrupt change in its configuration following the Bi in the block interface. On the other hand, the Sr modulation presents a structure suggesting a sawtoothlike modulation with reverse slope, centered at $x_4=0$. The discontinuity or stronger slope is localized at $x_4=\frac{1}{2}$. Similar to O4, the slope of the Sr sawtooth can be "indexed" as having the direction (0, 1, 0, 4) with respect to the superspace unit cell in the modulated setting. This means that Sr-Sr y distances along the row tend to be expanded at the sites closer to the bridging zones, with an approximate y distance $b/[1-(q/4)]$, while the y distance shrinks with respect to the perovskite reference b at the sites closer to the center of the Bi_2O_2 blocks.

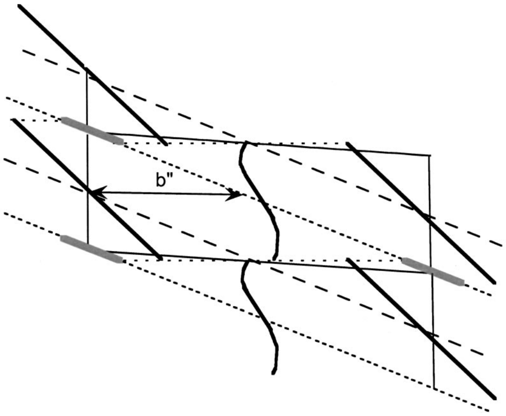

FIG. 10. Scheme of the average lines for Bi and O4 as a second subsystem in a composite description with 1.21**b*** as modulation wave vector. b'' defines the Bi-O distance of the perfect average rocksalt BiO structure. The figure corresponds to an ideal oxygen excess of 0.42 ($\Delta_{O4}=1+q$) for which the O4 domains would fulfill the *closeness* condition. The ''Bi-vacancy'' domains along the average lines of Bi are highlighted.

V. COMPETITION OF MODULATED AND COMPOSITE CONFIGURATIONS

In the above discussion we have stressed that the choice of the modulation wave vector $(2+q)\mathbf{b}^*$ introduces a description of Bi-2212 as unconventional composite with the second subsystem formed by the Bi_2O_2 slabs, but the latter having an intrinsic steplike occupational modulation producing the aperiodic sequence along the y direction of Bi_2O_2 blocks, with interfaces (the *bridging* zones) where the Bi-O sequence is interchanged. One can wonder if, instead, an idealized conventional composite configuration with two perfectly periodic substructures could be defined as basic reference for the real structure. This perfect nonmodulated composite reference can indeed be readily derived from the scheme of Fig. 7 if the width of the O4 sawtooth modulation is expanded to its maximal value $(1+q)$. One can then observe that O4 domains of a single BiO row fulfill then the ''closeness'' condition (now among themselves, not with those of the neighboring row) and an average continuous reference line can be defined, corresponding to a perfect periodic lattice of oxygens O4 along y of period $2b''=b/(1+q)$. The maximal oxygen load of $\delta=2q$ mentioned before corresponds to the full occupation of all the virtual sites of this average periodic lattice. A scheme of the resulting reference average lines is shown in Fig. 10. The conventional composite setting corresponding to this third alternative viewpoint takes as modulation wave vector $(1+q)\mathbf{b}^*$. As shown in Fig. 10, a set of intermediate average lines can also be defined for the Bi atoms as ideal positions in a perfect rocksalt structure for the Bi_2O_2 layers. These ideal positions would also yield $2b''$ and b'' as Bi-Bi and Bi-O4 average distances, respectively. Together with the average lines for O4, they define a conventional composite configuration for the Bi_2O_2 subsystem as a rocksalt structure, which could be used as an alternative reference. The difference with the usual composites is that the coupling with the perovskite subsystem is obviously so strong that the modulations or deviations from this ideal configuration can be hardly interpreted within a perturbative approach. The coupling produces the discontinuity of both the O4 and Bi displacive modulations avoiding positions with respect to the neighboring perovskite slabs of cationic and anionic character, respectively. These discontinuities correspond to the bridging zones. Furthermore, the strong chemical coupling tends to reduce the misfit between both subsystems and these unfavorable atomic sites by adapting the stoichiometry of the Bi_2O_2 subsystem to the perovskite slab. From simulations it is known that atomic sites corresponding to points in the modulation closer to the discontinuities are much looser (this is the reason for their larger displacement factors). Hence, it is there that the atomic domains of both O4 and Bi have vacancies. Bi is so strongly coupled to the perovskite block that it apparently has not much flexibility and attains full stoichiometry with the perovskite slab by reducing its domain width from $1+q$ to 1. The theoretical ''vacancy'' zones in the superspace description of its ideal $2b''$ average lattice are indicated in Fig. 10. By this means, and also through a strong displacive modulation, the Bi atoms adapt themselves to the different period of the perovskite slab so that they virtually belong to it. Only the discontinuity of its modulation is a reminder of the composite viewpoint and the competing periodicity of the Bi_2O_2 slab. One may propose that a stronger coupling with the perovskite block could make even disappear the discontinuity of the Bi modulation, if it exists. We have then a picture quite more complex than that in the usual models for composites: the strong coupling between the two subsystems causes the nonanalycity of the modulations, but eventually may lead through the creation of vacancies and strong displacive modulations to the recovery of analytical modulations with respect to a different average periodicity.

On the other hand, the O4 atoms seem much weaker coupled to the perovskite subsystem, at least concerning the b periodicity. Its linear modulation creates locally an average b periodicity among O4 atoms different from that of the perovskite. The coupling changes this periodicity from b'' to b' and induces the loss of the looser atomic sites at the extremes of the sawtooth modulation (the *bridging* zones). This results in a variable width Δ_{O4} of the atomic domains that would depend directly on the oxygen excess of the sample. The usual nonstoichiometry and variability in the oxygen content of the samples is then directly related to the discontinuity of the O4 modulations and its tendency to form a lattice with different periodicity. One can speculate that, in general, the approximate linearity of the modulations could be a typical feature of atomic domains that have a strong flexibility in their total width or atomic content.

In the above discussion, for the sake of simplicity, we have considered $1+q$ as an intrinsic (constant) value relating the periodicities of the two subsystems if they were isolated one from the other. This is obviously a great oversimplification. In general, the value of q would depend on the coupling of the two subsystems. In fact, as is the case in other, more conventional composite materials with much weaker coupling between the subsystems, such as the inclusion compounds, each subsystem isolated is obviously not stable.

Therefore their average periodicities have no physical meaning without "switching" the coupling between the two subsystems forming the composite. Despite this simplification, a picture emerges where the variable nonstoichiometry of the compound and its description as a composite with discontinuous atomic modulations are deeply connected.

VI. CONCLUSIONS

The present work shows that the longitudinal modulation function of O4 is clearly discontinuous if Bi-2212 is described as a single modulated structure, while those of other atoms, if not discontinuous are close to a nonanalytic regime. Truncated Fourier series, as considered by most of the structural models published up to now, do not correctly describe these features. For O4, a nonanalytical sawtooth shape for the longitudinal modulation, as proposed earlier by Petricek *et al.*,[2] is a more appropriate description. Other atomic modulations also require a strong anharmonic parametrization for their adequate description or even to introduce finite atomic domains in order to allow for possible discontinuities when refined. This implies that the structural models generally accepted for Bi-2212 contain in general unrealistic configurations for the bridging zones in the BiO layers, which correspond to the discontinuities or strong slope regions in the modulation functions.

The approximate sawtooth modulation function of O4 defines an alternative average distance along the y direction between the oxygen sites of the BiO layer and can be considered as the signature of a latent composite character of the material. Two alternative composite descriptions can indeed be proposed that define two ideal reference structures with nonstoichiometric compositions. The system deviates, however, from a conventional composite in the important fact that the modulation of the second subsystem (the Bi_2O_2 slabs) as a result of its strong coupling with the first one, includes steplike occupational modulations with the presence of ordered vacancy domains whose width variation is directly related with the composition flexibility of these materials, in particular with their oxygen content. The Bi atoms are so strongly coupled with the perovskite subsystem that in practice they may be considered part of this first subsystem.

From a static viewpoint, the description of the structure as a composite or as a single modulated structure are mathematically equivalent, as in the end one has to determine "where the atoms are" and this can be done properly with one or the other method. However, the situation changes, if, when using the single modulated structure description, as done generally until now, the usual parameterization with continuous modulations is employed. This approach is bound to produce incorrect configurations for a significant proportion of atomic sites, as it obliterates the discontinuities or strong anharmonicities of the atomic domains, which are intrinsic to the composite features of the compound. It is therefore advisable to reconsider the structure determination of these materials under this viewpoint. This situation is not limited to Bi-2212, but it is also most probably common to other members of the series.

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