Comment on "Incommensurate composite structure of the superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$"

D. Grebille, H. Leligny, and O. Pérez
Laboratoire CRISMAT (UMR CNRS 6508), ISMRA, Boulevard du Maréchal Juin, 14050 Caen Cedex, France
(Received 12 September 2000; published 22 August 2001)

J. Etrillard, P. Bourges, and C.T. Lin [Phys. Rev. B **62**, 150 (2000)] compared the structural description of the aperiodic structure of the so-called high-T_C superconductor Bi-2212 in the incommensurate modulated structure model and in the composite model. According to neutron diffraction data, they disqualified the first one. Another calculation proves that this conclusion is not justified. The structural equivalence between both descriptions is demonstrated, using previous structural results, and using the 4D formalism for aperiodic crystals.

DOI: 10.1103/PhysRevB.64.106501 PACS number(s): 74.72.Hs, 61.44.Fw, 61.10.−i, 61.66.Fn

In their recent report,[1] Etrillard and co-workers investigated the nature of the incommensurate structure of the high-T_c superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$. According to elastic neutron scattering experiments and considering the observed neutron diffraction intensities of selected reflections along specific directions of the reciprocal space in the ($\mathbf{b}^*$,$\mathbf{c}^*$) scattering plane, they tried to calculate the corresponding structure factors, using the usual four-dimensional model for modulated structures[2] and the structural refinement parameters given by Miles *et al.*[3] They apparently found an obvious disagreement with their experimental data. When considering the usual modulation vector $\mathbf{q}_s = 0.21\mathbf{b}^* + \mathbf{c}^*$, their calculation gave similar intensities for satellite reflections $(h,k,l,+m)$ and $(h,k,l,-m)$, when the observed intensities $(h,k,l,-m)$ appeared much weaker. An explanation is proposed, based on the composite structural model of Walker and Que.[4] In this case, satellite reflections of higher intensity could correspond to the main reflections of the second sublattice of the composite structure. Unfortunately, it seems not possible for the moment to validate this hypothesis by other calculations.

It is clear that diffraction results strongly depend on the nature of the beam. Particularly with this kind of structure where oxygen atoms coexist with bismuth ones, it would be of primary importance to get valuable measurements using neutron diffraction. Unfortunately, until the work of Miles *et al.*,[3] the size of the samples did not allow reliable neutron diffraction data collections. Moreover, Etrillard *et al.*[1] impute to oxygen the predominant contribution to the modulated structure and so all the previous x-ray diffraction studies should be cautiously considered when describing the oxygen configuration. Indeed, these studies are numerous[5–9] and except the results of Kan *et al.*[7] are in relative good agreement with each other. The differences can only be found in the models used to describe disorders or oxygen position within the BiO layer. This is directly the consequence of the weak sensitiveness of x ray to oxygen. When considering these different results, and even if oxygen is deeply involved in the modulated scheme, in a relatively hidden way, one cannot only attribute to oxygen the main features of the modulated structure. The proof has been given by the last study of Miles and co-workers.[3] They have reported a structure refinement carried out from neutron diffraction data using a large single crystal and have compared their results to the previous ones. The agreement concerning the displacive modulation amplitudes is outlined mainly concerning the cationic description of the structure, and particularly with the results of Petricek and co-workers.[6] The comparison is not made with our own previous study,[8] but in this case too, there is a very good agreement, even concerning the oxygen modulation parameters, except the hypothetical extra oxygen atom in the BiO layers. For the other oxygen atoms, occupation modulations have also been introduced which are quite analogous to the refined ones in our study. Such large similarities cannot be a pure coincidence, and the proposed structural model cannot be completely wrong. Thus the description using the composite model cannot be considered as the only valid description of the structure.

In order to clarify this point, we have calculated the squared structure factors using neutron diffusion factors, in the usual incommensurate modulated model with the two sets of refined structural parameters already published[3,8] using the refinement program JANA98.[10] The agreement between both calculations is rather good and the corresponding results are drawn in Fig. 1 using Miles' parameters. These results do not agree with the calculated structure factors in Ref. 1. They are to be compared with the experimental data given in Fig. 1 of Ref. 1. One clearly observes bigger intensities for $k = 2.21$ or $k = 4.42$ then for $k = 1.79$ or $k = 3.58$. Moreover, at least qualitatively, the agreement between the relative observed and calculated intensities is rather good. This calculation clearly shows that the standard usual modulation model cannot be discarded in favor of only the composite model.

Reference is also made to a previous analysis of the 2201 cuprate phase by the composite model, using x-ray and neutron powder diffraction data.[11] This study can be directly compared with the structure refinement of the same 2201 phase using the 4D model for incommensurate modulated structures and single crystal x-ray diffraction data.[12] The composite aspect of the structure mainly concerns the BiO layers, because they are simultaneously built with the Bi atoms belonging to the main sublattice ($b_1 \simeq 5.4$ Å) and with the O atoms belonging to the second sublattice ($b_2 \simeq b_1/2.21$). These BiO layers are schematically drawn in Fig. 2 in both descriptions, with their relative interatomic BiO distances. We can see that both studies, very different in their experimental conditions as in their refinement procedures,

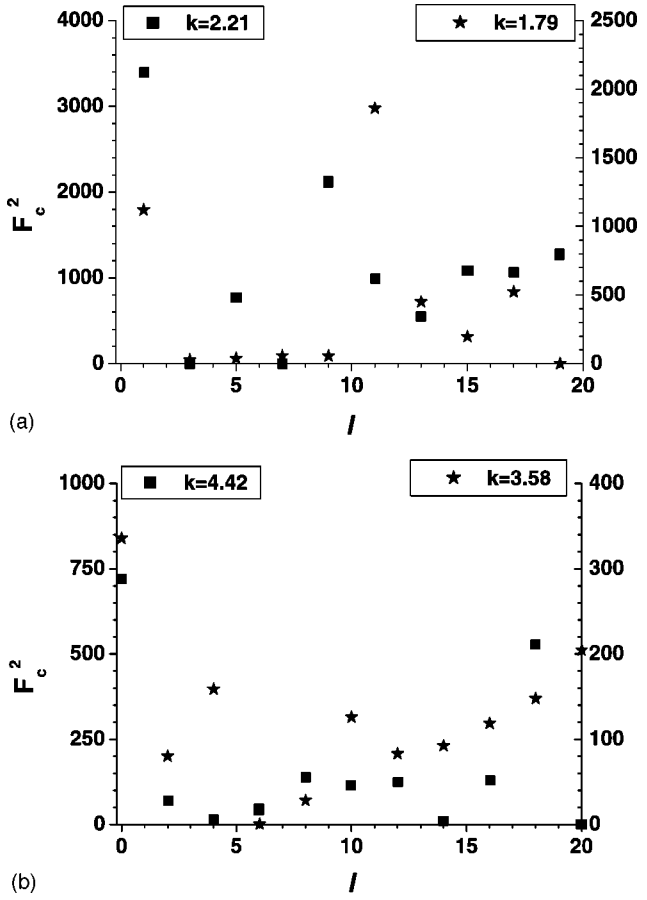

FIG. 1. Calculated squared structure factors in the modulated incommensurate description for first order ($k=2\pm0.21$) and second order ($k=4\pm0.42$).

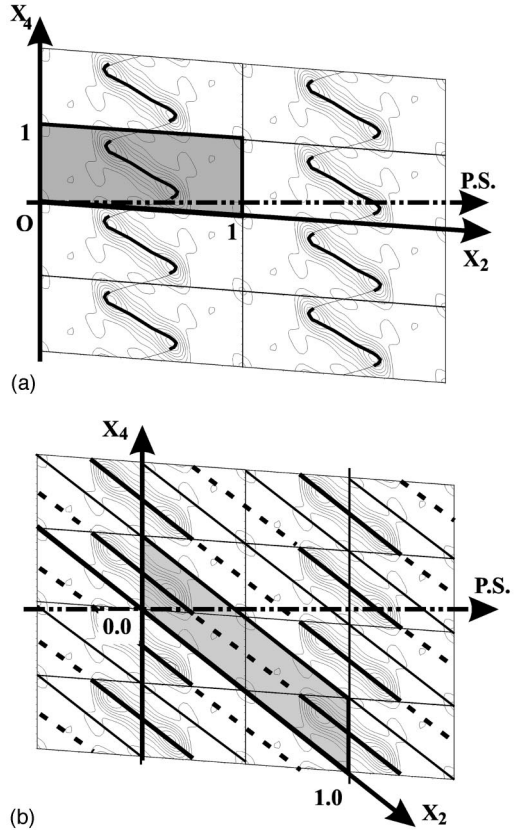

FIG. 3. x_2-x_4 four-dimensional Fourier maps for $x_1=0.157$ and $x_3=0.054$ around the oxygen site. P.S.=physical space. (a) Modulated incommensurate description; bold curves: refined modulated functions with significant site occupation (Ref. 8); (b) composite description.

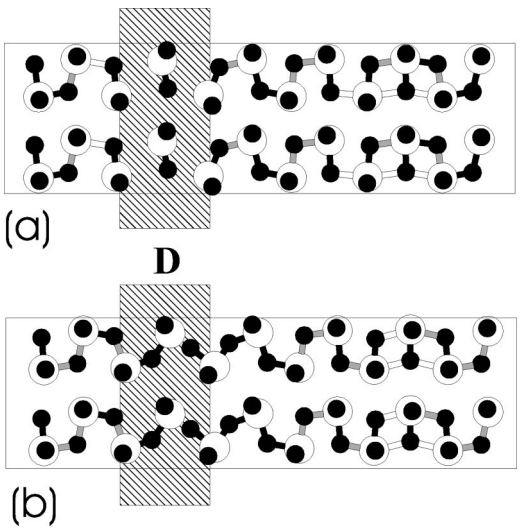

FIG. 2. Schematic representation of the BiO layer of the 2201 cuprate phase projected along **c**. Large opened circles=Bi; small black circles=O; interatomic distances *d*: black: $d<2.2$ Å; grey: 2.2 Å$<d<$2.4 Å; white: 2.4 Å$<d<$2.6 Å. (a) Modulated incommensurate description (Ref. 12); (b) composite description (Ref. 11).

result in quite identical BiO configurations except in a rather limited region, labeled D in Fig. 2. In fact, these D regions correspond to statistical disorders of both the Bi and the O atoms in the BiO layers. This disorder cannot be easily taken into account in standard modulated or composite models and can be neglected in a first approach in this comparison. They have been more properly described in the similar modulated structure refinement of the 2212 phase[8] and still gave equivalent bridging oxygen positions as in the composite description.

We can try to understand the equivalence of both models in the case of the so-called Bi-2212 structure. Let us consider, for example, the 4D Fourier synthesis map corresponding to the atomic position of the oxygen atom within the BiO layer, belonging to the second sublattice defined in the composite description of the structure [Fig. 3(a)]. This figure has been drawn in the 4D superspace with the cell corresponding to the modulated model, i.e., with the modulation vector $\mathbf{q}=0.21\mathbf{b}^*+\mathbf{c}^*$. The 4D unit cell is represented by a gray area. The refined longitudinal modulation function has been drawn and describes very well the electron density except in a limited interval for $x_4\simeq0$ corresponding to the D region previously mentioned. In fact, in this interval, the modulated occupation of the site is very weak[3,8] and this site is replaced by another site,[8] corresponding to the bridging position

already mentioned. Thus the corresponding part of the displacive modulation function has no physical meaning. The same supercrystal can be equivalently described by another 4D cell, characterized by a different modulation vector $\mathbf{q}_2 = 2.21\mathbf{b}^* + \mathbf{c}^*$, as predicted by Etrillard *et al.*, and schematically represented in Fig. 3(b). Another modulation vector $\mathbf{q}_2 = 1.21\mathbf{b}^* + \mathbf{c}^*$ could be still more appropriate. In any case, the oxygen electron density can then be represented by a linear function $x_4 = 0.5$ (bold lines in the figure), only interrupted for $0.25 < x_2 < 0.75$. Let us recall that for a composite crystal, neglecting intermodulation between both sublattices, the 4D supercrystal can be described by two independent sets of linear atomic strings[14,13] corresponding to both sublattices. In the present case, the linear string corresponding to the oxygen atom is attributed to a second sublattice, and the present supercrystal can easily be described within the composite model. However, the interruption of the string has to be explained. In fact, for $0.25 < x_2 < 0.75$ (respectively $0.75 < x_2 < 1.25$), the oxygen atom within the BiO layer, is characterized by $x_1 \simeq 0.16$ (respectively, -0.16). So, we have to attribute to this oxygen atom a corresponding average position with $x_1 = 0$ and with a large displacive transverse modulation function along x_1 (amplitude ± 0.16). The same type of modulation was already attributed to the corresponding oxygen atom of the BiO layer of the 2201 structure using the composite description;[11] for this compound, the equivalence of both descriptions has been outlined above. In the composite description, the introduction of the additional huge transverse modulation appears rather artificial. It outlines the strong correlation between oxygen and bismuth atoms which belong to the same rocksalt type structural block, and for which it is rather difficult to imagine that Bi and O atoms belong to two different sublattices.

In fact, the displacive modulation associated to the 4D electron density function corresponding to the Bi atom (Fig. 4) can also be described by a sawtooth function. The same type of modulation function was also refined in the case of the BiO layer of the intrinsically modulated composite structure $[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$.[15] In this last case, the sawtooth function had also for consequence a very large discrepancy between diffracted intensities of satellite reflections with $+m\mathbf{q}$ and with $-m\mathbf{q}$ (let us recall that these satellite reflections correspond to the intrinsic modulation of the BiO layer, which is independent from the composite character of the structure). The asymmetry is clearly not a proof for a composite structure but is directly related to the asymmetry of the sawtooth modulation functions.

Another useful comparison can be made with the modulated structure of the bismuth 2212 ferrite.[16] In this study, a new model has been given for the oxygen atom of the BiO layer. Instead of only one site in special position in the mirror plane orthogonal to the *y* direction, two symmetry related sites were introduced in general positions. This description allows us to give to the oxygen atom a reduced longitudinal

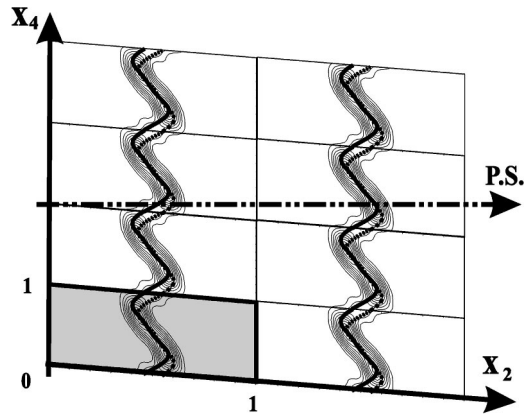

FIG. 4. $x_2 - x_4$ four-dimensional Fourier maps for $x_1 = 0.224$ and $x_3 = 0.0514$ around the bismuth site. Bold and dashed lines: refined displacive modulation functions for the disordered Bi site (Ref. 8); P.S.=physical space.

modulation amplitude (it becomes of the same magnitude as the Bi modulation amplitude) and to explain the corresponding Fourier maps with two distinct maxima. Even if this duplication is less clear in the case of the cuprate compound, we can nevertheless observe also two maxima, and the same description could also be applied. In this case, the composite description appears also to be less adequate. This example shows that it is not possible to describe these structures without taking into account Bi and O disorders, which are intrinsic and systematic in high-T_c superconductor layered compounds.

We agree with Etrillard *et al.* that the choice of one model for the structural description of these aperiodic compounds can induce different interpretations for lattice dynamics properties. We want to outline that such a choice is not as simple as it seemed to be in their presentation and that the arguments given to disqualify the modulated model are not valid. From a structural point of view, both models result in the same atomic positions for these phases. We agree about the fact that the structure cannot be described as a classical modulated one, but we can hardly support the composite description with an oxygen lattice deeply interwoven with the main bismuth lattice. This last description would impose severe and artificial occupation or displacement rules for the unique O atom of the corresponding sublattice. A crucial problem probably lies in the systematic existence of structural disorders in the present structures, which do not depend on the considered model. Two questions are still open: how two different formal models, which can describe in equivalent ways the same structure, can also explain in equivalent ways the complex lattice dynamic of these phases, and how unavoidable disorder phenomena, as related in the extended zones of the BiO layers, can influence collective modes and have to be taken into account in any dynamic study.

[1] J. Etrillard, P. Bourges, and C.T. Lin, Phys. Rev. B **62**, 150 (2000).
[2] T. Janssen, A. Janner, A. Looijjenga-Vos, and P. De Wolff, *International Tables for Crystallography* (Kluwer Academic, Dordrecht, 1992).
[3] P.A. Miles, S.J. Kennedy, G.J. McIntyre, G.D. Gu, G.J. Russell, and N. Koshizuka, Physica C **280**, 66 (1997).
[4] M.B. Walker and W. Que, Phys. Rev. B **45**, 8085 (1992).
[5] A. Yamamoto, M. Onoda, E. Takayama-Muromachi, F. Izumi, T. Ishigaki, and H. Asano, Phys. Rev. B **42**, 4228 (1990).
[6] V. Petricek, Y. Gao, P. Lee, and P. Coppens, Phys. Rev. B **42**, 387 (1990).
[7] X.B. Kan and S.C. Moss, Acta Crystallogr., Sect. B: Struct. Sci. **B48**, 122 (1992).
[8] D. Grebille, H. Leligny, A. Ruyter, Ph. Labbe, and B. Raveau, Acta Crystallogr., Sect. B: Struct. Sci. **B52**, 628 (1996).
[9] R.E. Gladyshevskii and R. Flukiger, Acta Crystallogr., Sect. B: Struct. Sci. **B52**, 38 (1996).
[10] V. Petricek, *Crystallographic Computing System Jana98* (Institute of Physics, Academy of Sciences of the Czech Republik, Prague, 1998).
[11] A. Yamamoto, E. Takayama-Muromachi, F. Izumi, T. Ishigaki, and H. Asano, Physica C **201**, 137 (1992).
[12] H. Leligny, S. Durčok, Ph. Labbe, M. Ledésert, and B. Raveau, Acta Crystallogr., Sect. B: Struct. Sci. **B48**, 407 (1992).
[13] A. Yamamoto, Acta Crystallogr., Sect. A: Found. Crystallogr. **A48**, 476 (1992).
[14] S. van Smaalen, Phys. Rev. B **43**, 11 330 (1991).
[15] H. Leligny, D. Grebille, O. Pérez, A.C. Masset, M. Hervieu, and B. Raveau, Acta Crystallogr., Sect. B: Struct. Sci. **B56**, 173 (2000).
[16] O. Pérez, H. Leligny, D. Grebille, J.M. Grenêche, Ph. Labbé, D. Groult, and B. Raveau, Phys. Rev. B **55**, 1236 (1997).