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

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We have performed elastic neutron scattering experiments, using a high-quality single crystal of the high-T_c superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$. By a systematic comparison of intensities between superlattice reflections, we show that the one-dimensional incommensurate modulated model, usually used to interpret the structural characteristics, exhibits important failures. In contrast, in accordance with theoretical predictions [M. B. Walker and W. Que, Phys. Rev. B **45**, 8085 (1992)], a composite structure made of two interpenetrating subsystems can alternatively describe the incommensurate structure and account for the hierarchy of the observed intensities.

Since the discovery of superconductivity in the layered Bi-Sr-Ca-Cu-O systems,[1] there has been a large number of structural studies on Bi-based high-T_c superconductors. If the average structure is readily identified, the real structure seems to be more complicated than expected, including displacive and substitutional modulations. The presence of both heavy (metal) and light (oxygen) atoms makes it difficult to refine the x-ray diffraction data, whereas the lack of high-quality crystals makes it difficult to distinguish what it is due to the intrinsic properties of the stacking faults, dislocations, and intergrowths. A one-dimensional incommensurate modulated model from an average orthorhombic structure is generally proposed to describe the incommensurate structure[2–10] and accounts for the gross features of the real structure. However, the detailed superlattice intensities are actually not well described and the introduction of additional structural features as a standard sinusoidal modulation function has ruled out simple interpretations since the early days.[2] Another class of incommensurate models was then proposed[11] where the crystal structure is described as a composite system in which there are two interpenetrating periodic sublattices whose cell parameters are mutually incommensurate. The main difference from the modulated structure case is that the full system does not have a single basic Bravais lattice. Using a large single crystal of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) of high quality, we have performed detailed neutron diffraction scans in order to confirm the more adequate description.

The average structure of the compound Bi-2212 has been reported by several authors in centrosymmetric space group $Bbmb$ (or the noncentrosymmetric one $Bb2b$) with the unit-cell parameters $a \simeq 5.41$ Å, $b \simeq 5.41$ Å, and $c \simeq 30.9$ Å. Numerous refinements using the superspace formalism have been modeled using an one-dimensional incommensurate modulation with the wave vector $\mathbf{q}_s = 0.21\mathbf{b}^* + \mathbf{c}^*$.[4–9] Despite the discrepancies in these structure refinements, the characteristic feature of the layered structure is the existence of strong displacive modulations. In particular, atoms in the BiO layers move largely in the **b** direction (about 0.4 Å) while those in the CuO_2 and Ca layers are much less displaced and parallel to the **c** axis. SrO layers, which are influenced by the neighboring BiO and CuO_2 layers, are slightly distorted along both the longitudinal and transverse directions. The origin of the displacive modulation is generally attributed to the mismatch between the BiO (rocksalt-type) and CuO_2 (perovskite-type) layers: the latter yields an average orthorhombic structure as in many other high-T_c cuprates with typical Cu^{2+}-O distance of $\simeq 1.9$ Å . Because the typical Bi^{3+}-O bond lengths $\simeq 2.0$–2.5 Å are not compatible with that distance, BiO layers form an incommensurate structure. The main difficulty in structural refinements then concerns the BiO layers. A consensus has been established that the usual sinusoidal modulation is not adequate.[2–8] Additional structural features must be included such as the eventual insertion of extra O atoms (whose number actually varies from 0.2 to 1 depending on the authors),[4,6,8] a linear modulation function (''sawtooth-like''),[5] or a static disorder on the Bi site.[7] To interpret the unrealistic Bi-O distance of 2.7 Å , the BiO layers are generally understood as compressed and ordered-expanded and disordered regions occurring alternatively along the **b** axis. Some commensurate supercell descriptions within the three-dimensional space group symmetry have also been applied, allowing the inclusion of more naturally the additional oxygen atoms into BiO planes.[12,13] However, none of these approaches are really satisfying and no consensus has been reached so far. Because of the lack of an accurate description of atomic positions and occupancies, the relationship between the structural and superconducting properties has not been clarified.

Another starting point to model the structure has then been proposed within a simple picture in terms of a composite structure.[11] The compound Bi-2212 (and also Bi-2201) is

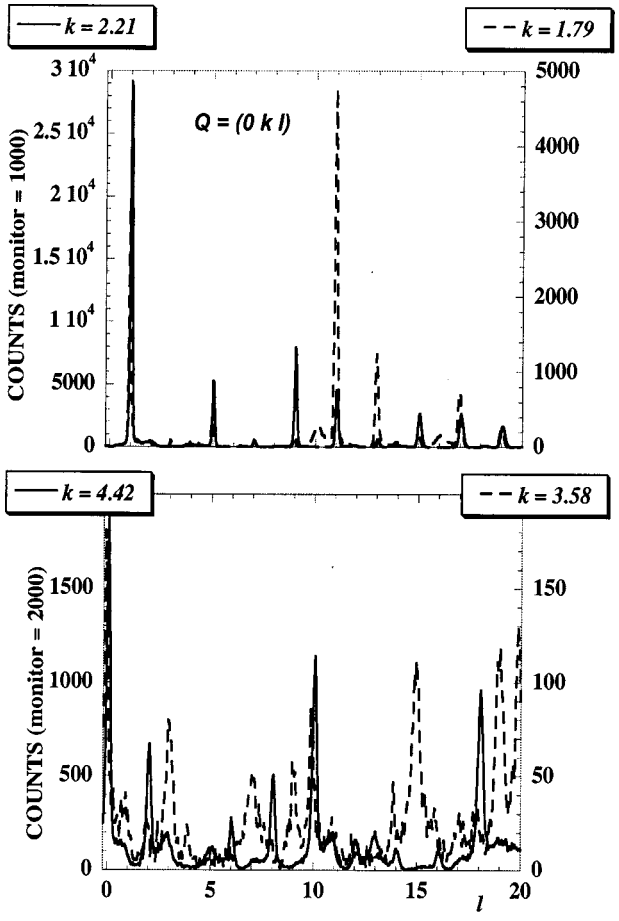

FIG. 1. Neutron diffraction scans $(0kl)$ up to $l=20$. Defining the orthorhombic basic structure, the peaks for $k=2.21$, 1.79, 4.42, and 3.58 correspond, respectively, to $(00l1)$, $(04\bar{l}1)$, $(00l2)$, and $(08\bar{l}2)$ composite reflections. Note the different right and left scales.

assumed to be built of two interpenetrated periodic lattices. The first sublattice, labeled *A*, consists of all the atoms excluding oxygens in the BiO layers while the second one, labeled *B*, is composed only of these O atoms. Such an analysis using the Rietveld method has been already employed to refine the powder diffraction patterns of the Bi-2201 compound.[10] The subsystem *A* is therefore described by the usual orthorhombic unit-cell parameters (a,b,c) while the second one is by the lattice constants $(a,b'=0.452b,c)$. Due to the mutual interactions in the crystal, each subsystem is modulated with the modulation wave vector given by the periodicity of the other subsystem. A complete characterization of the symmetry properties requires the use of the superspace group formalism.[14] Defining the subsystem *A* as the basic structure, each reflection of the diffraction pattern can be identified with the reciprocal vector $\mathbf{q}_{hklm}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\mathbf{b}'^*=h\mathbf{a}^*+(k+2.21m)\mathbf{b}^*+l\mathbf{c}^*$. In this paper, we have performed a neutron scattering study within the $(\mathbf{b}^*,\mathbf{c}^*)$ scattering plane in order to test on a qualitative level these two structural approaches. Our data show clear inconsistencies of the modulated description for the incommensurate structure which are naturally explained within the composite model. Following the model of Walker and Que,[11] the composite model would correspond to the (3+1)-dimensional group $Bbmb\ (0\beta 0)$ [or $Bb2b\ (0\beta 0)$]

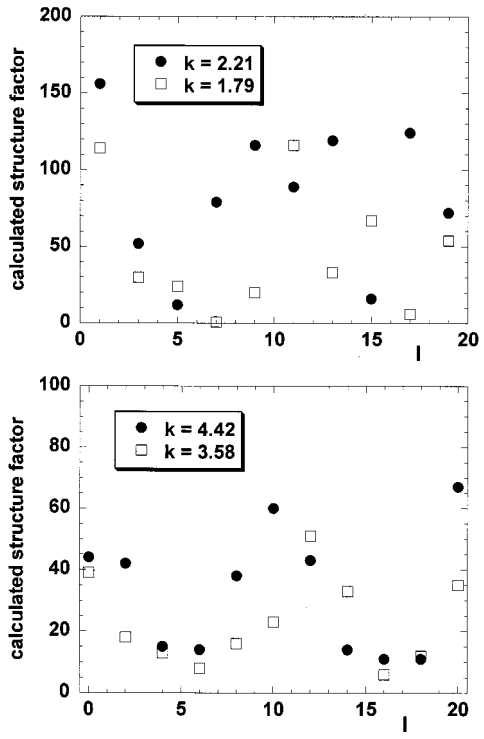

FIG. 2. Structure factors calculated in the modulated incommensurate description for first-order $(k=2\pm0.21\ l\pm1)$ and second-order $(k=4\pm0.42\ l\pm2)$ satellite reflections.

where nonzero diffraction peaks occur for $h+l+m=2n$ for $(hklm)$ and $k=2n$ for $(0klm)$ and $(hk0m)$. As far as our measurements are concerned, these selection rules are followed. However, the actual determination of the superspace group and the calculations of structure factors are another step which would require a complete neutron data collection.

The plateletlike crystal Bi-2212 which has been prepared using the floating zone method[3] has dimensions $10.0\times4.0\times0.1$ mm^3. The mosaic spread, by means of neutron diffraction, is about 15′. The elastic coherent neutron scattering experiments were made on a thermal-neutron-source triple-axis spectrometer 2T1 at Laboratoire Léon Brillouin at Saclay (France). As there is no major change in the structure with temperature, all data have been collected at ambient temperature on the chosen scattering plane $(\mathbf{b}^*,\mathbf{c}^*)$. A graphite filter was used in the diffracted beam to avoid $\lambda/2$ contamination. The elastic scans along the $\mathbf{c}^*$ direction at fixed values of *k* were performed with two different incident wave vectors: $k_I=2.662$ Å^{-1} for $k\leqslant3$ and $k_I=3.85$ Å^{-1} for $k\geqslant3$. Note that the sharp profile of the main reflections (Fig. 1), the relatively weak background (about 3 counts for a monitor of 1000), and the absence of parasitic peaks illustrates the high quality of this single crystal.

As is known,[14,15] in the one-dimensionally incommensurate modulated structure, all reflections can be indexed using four indices by defining the diffraction vector $\mathbf{q}_{hklm}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\mathbf{q}_s$ where $\mathbf{q}_s$ is the incommensurate modulation vector and *m* is the satellite order. The symmetry of such a structure is described by a superspace group, corresponding to $Bbmb\ (0\beta1)$ [or $Bb2b\ (0\beta1)$] for the studied compound Bi-2212 ($\mathbf{q}_s=0.21\mathbf{b}^*+\mathbf{c}^*$).[4–9] In the scattering plane $(\mathbf{b}^*,\mathbf{c}^*)$, the existence of $(0klm)$ reflections is determined by the condition $k=2n(l=2n)$. The above analysis allows

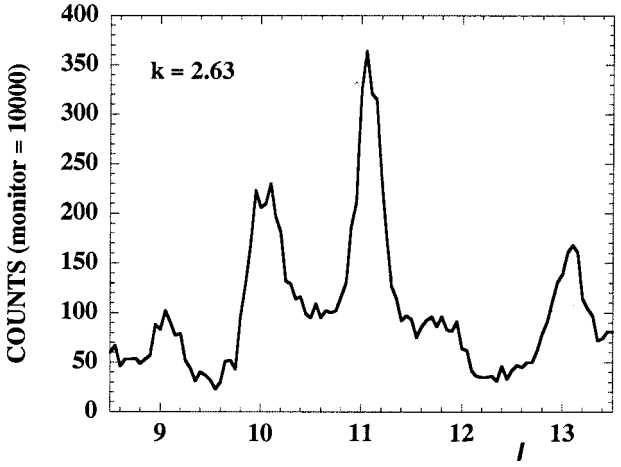

FIG. 3. Neutron diffraction scans ($0\,2.63\,l$). The peaks for l odd correspond to third order satellite reflections. The peaks for l even illustrate the diffuse scattering (see Fig. 4).

the classification of the three-dimensional subsets: $(0kl)$ main reflections and first-order $(0\ k\pm0.21\ l\pm1)$ and second-order $(0\ k\pm0.42\ l\pm2)$ satellite reflections. In the scattering plane $(\mathbf{b}^*,\mathbf{c}^*)$, the satellite reflections represent a cross centered on the Bragg peak $[\tau=(0,k,l)]$, with the size defined by the satellite order m. Figure 1 shows clearly that the intensities of reflections of the same satellite order are not similar: typically, the intensities for $\mathbf{q}_{hklm}=\boldsymbol{\tau}+m\mathbf{q}_s$ are surprisingly about one order of magnitude larger than intensities for $\mathbf{q}_{hklm}=\boldsymbol{\tau}-m\mathbf{q}_s$. To emphasize this point, we have calculated the structure factors for the first-order $(0\ 2\pm0.21\ l\pm1)$ as well as the second-order $(0\ 4\pm0.42\ l\pm2)$ satellite reflections. We have applied the crystallographic program package JANA98 (Ref. 16) using the results of previous neutron diffraction studies.[9] Using the four-dimensional analysis for an incommensurate modulated structure, we have chosen the refined parameters (average positions, modulation amplitudes with first- and second-order harmonic terms) deduced from the data labeled ''Present study ILL RT crystal'' of Ref. 9. The results in Fig. 2 clearly show that the intensities of the satellite reflections $m\pm1$ or $m\pm2$ have the same order of magnitude in contrast to our measurements (Fig. 1). Further, we always found the satellite intensities are very similar to those of Fig. 2 whatever the modulation parameters chosen among the published values. Such discrepancies have been already underlined in previous studies[2,3] for the $(0\ 2\ \pm q_s\ 0)$ peaks. We here extend it for all measured first- as well as second-order satellites. These specific differences between the satellite intensities have been neglected in the previous structural refinements. Finally, as the incommensurate structure is predominantly related to the oxygen atoms, the inconsistency of the modulated structure is not that crucial in single-crystal x-ray measurements. Only the use of a high-quality single crystal in neutron diffraction allows one to pin it down.

The composite structure model proposed by Walker and Que[11] then represents a natural alternative to understand the present observed neutron diffraction intensities. As mentioned above, both subsystems, labeled A and B, can be considered as incommensurate intermodulated structures. For the first subsystem, the diffraction pattern will be equivalent

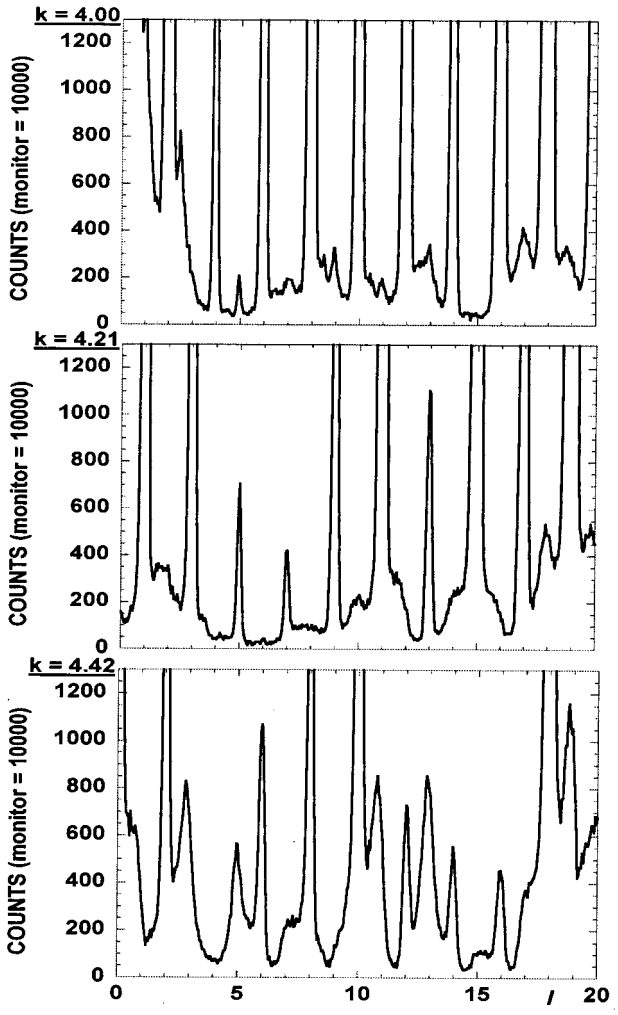

FIG. 4. Neutron diffraction scans across $(04l0)$, $(02l1)$, and $(00l2)$ reflections in composite notation. The diffuse scattering is observed at forbidden nodes, $l+m=2n+1$.

to the one described above. However, the second subsystem gives rise to strong reflections at the positions $(0klm)$ with $k=0$, with weaker satellites at positions with $k\neq0$. In other words, using the composite notation, the $(0\ 2.21\ l)$ and $(0\ 4.42\ l)$ peaks are attributed to the main reflections $(00l1)$ and $(00l2)$ of the subsystem B and the $(0\ 1.79\ l)$ and $(0\ 3.58\ l)$ peaks to the satellite reflections $(04\bar{l}1)$ and $(08\bar{l}2)$. The systematic lower intensities observed at these latter positions are then naturally explained as they correspond to the intermodulation of the two sublattices.

Further, due to high sample quality, we have been able to detect third-order satellite reflections in Bi-2212. Figure 3 shows $(0\bar{4}l3)$ peaks for l odd using the composite notation. Due to their very weak intensities ($\sim10^{-3}$ of first-order satellites), such an observation has not been reported so far.[2–9,12,13]

Beside the sharp main and satellite reflections, diffuse reflections with a broad shape along the $\mathbf{c}^*$ direction are systematically observed at forbidden nodes for the assumed space groups as $(l+m=2n+1)$ in $(\mathbf{b}^*,\mathbf{c}^*)$ reciprocal space. Some diffuse scattering profiles have been fitted by a Lorent-

zian phase-phase correlation function, confirming the correlation length $\xi_z \sim 180$ Å .[8] Although these diffraction phenomena have already been noticed in the literature,[5–9,12,17] they have been systematically excluded in the refinement procedures. Moreover, no direct quantitative analysis or structural models have reproduced them. We have extended their observation at all forbidden wave vectors. Detailed neutron scans using sufficient counting times have been performed and are shown in Fig. 4 around $k=4$: $(04l)$, $(0\ 4.21\ l)$, and $(0\ 4.42\ l)$. Surprisingly, the diffuse intensities are about one order of magnitude larger at $(0\ 4.42\ l)$ than at $(0\ 4.21\ l)$. We here additionally established that they also occur at the main reflection positions as similar contributions are also detected along the $(04l)$ line for l odd although with much weaker intensity. In the incommensurate modulated model, extrinsic features should be invoked to account for the existence of the diffuse scattering. For instance, some x-ray studies have attributed this diffuse scattering to phase defects of the modulation of the BiO layers, subjected to two-dimensional correlations,[8] which would be related to the presence of additional oxygen inside the BiO layers. However, it has been recently shown that this modulation does not simply originate from the intercalation of the extra oxygen.[18] Our observation indicates that this diffuse scattering is related to the whole structure and it makes the above interpretation unlikely. In the composite approach, the diffuse signal is a generic feature which results from the intrinsic disorder induced by the mismatch between the two sublattices. However, unlike other composite systems such as urea inclusion compounds,[19] the diffuse scattering is here significant everywhere, illustrating the strong coupling between the two sublattices. Of course, the larger intensity at the main reflections of the sublattice B proves that the disorder affects primarily the oxygen atoms.[11] In any case, this generic diffuse scattering which locally breaks the selection rule $h+k+l=2n$ of the space group (face-centered B) has to be taken into account in any structural refinement.

Elastic neutron scattering measurements on a high-quality single crystal of superconducting cuprate Bi-2212 have been performed to study the incommensurate structure. They show the inconsistency of the modulated model generally used to describe it. In contrast, they rather exhibit features of an interpenetrating composite system. The oxygen atoms in the BiO layers form a substructure with the cell parameter $b'=0.452b$ and the remaining atoms form another lattice with the cell constant b. Modulation of each substructure by the other gives rise to satellite reflections with weaker intensities in addition to the parent Bragg reflections of each substructure. This composite approach has also the advantage to simply account for the number of oxygen atoms in the BiO layers: the parameter δ in the chemical formula. It directly derives from the ratio between the two cell parameters, $b/b'=2+\delta$, i.e., $\delta=0.21$. In summary, following the classification of quasiperiodic systems[14] as modulated crystal phases, incommensurate composite structures or quasicrystals, our data show that the superconductor Bi-2212 belongs to the second category. Another fundamental difference between the two classes, modulated-composite structures, lies in their different collective lattice dynamics.[20] The actual structure will be especially important in the identification of the collective modes for future inelastic coherent neutron scattering experiments: acoustic phonons emerging from main reflections or phasonlike modes from the satellite ones.

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