Structural model for the incommensurate bismuth high-T_c superconductors

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This paper demonstrates that the incommensurate high-T_c superconductors $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+\delta}$ can be viewed as being made up of two interpenetrating periodic crystals, each of which modulates the other. The periods of the two crystals are incommensurable along one of the crystallographic axes.

This paper proposes a structural model for the high-temperature superconducting compounds $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+\delta}$. These materials are known to have incommensurate structures, and the incommensurateness is believed to be associated with the presence of additional (i.e., $\delta > 0$ in the above chemical formula) oxygen in the BiO layers.[1,2] The determination of the structure of the BiO layers has been a difficult problem, partly because of the intrinsic difficulty of determining incommensurate structures, and partly because of the difficulty of determining with x-ray data the positions of oxygen ions in the presence of heavy ions such as bismuth. A brief review of efforts to determine the structure of the BiO layers has been given by Hewat.[3]

The bismuth superconductors $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+\delta}$ have three different phases, with $n = 1$, 2, and 3, respectively. Since the $n = 2$ phase $Bi_2Sr_2CaCu_2O_{8+\delta}$ has been the most extensively studied, we will confine our attention to this compound, and note that the proposed model can be extended to other members of the series. Electron microscopy studies of systematic absences by Li et al.,[4] Onoda et al.,[5] and Withers et al.[6] have identified the superspace group symmetry of the incommensurate $Bi_2Sr_2CaCu_2O_{8+\delta}$ structure as being either $M:A2aa:111$ or $M:Amaa:\bar{1}11$. There is, however, still some uncertainty about this assignment since diffraction images have been published showing spots which violate the above assignments.[7,8] Petricek et al.,[9] Gao et al.,[10] and Yamamoto et al.,[11] have recently carried out structural refinements for $Bi_2Sr_2CaCu_2O_{8+\delta}$. Their analyses assumed a modulated structure in which the ions were given average-lattice positions (based on an average-lattice orthorhombic unit cell of dimensions $a \approx b \approx 5.4$ Å and $c \approx 30.7$ Å) plus a modulation whose fundamental period was determined by the incommensurate wave vector $q = \tau a^* = 0.21a^*$; each refinement was carried out for a particular superspace-group symmetry. Our model, developed explicitly below, is similar in that information on the superspace-group symmetry plays an essential role in its development, but not similar in its assumptions concerning the average lattice of the oxygen ions in the bismuth layers.

There are qualitative indications that a simple model in which all ions have a weak sinusoidal modulation of wave vector $q = \tau a^*$ cannot be correct. For example, Fischer et al.[12] have remarked that such a model would give approximately equal intensities for the neutron-diffraction peaks at wave vectors $(2+\tau, 0, \pm 1)$ and $(2-\tau, 0, \pm 1)$ whereas the results of their neutron experiments are that the $(2+\tau, 0, \pm 1)$ peaks are at least an order of magnitude more intense than the $(2-\tau, 0, \pm 1)$ peaks. Beskrovnyi et al.[13] make similar remarks about the observed neutron-diffraction intensities and go on to determine the structure in terms of a model described by a commensurate supercell of dimension $19a \times b \times c$, of symmetry $Pnaa$, and in which the oxygen ions in the BiO layers have an average spacing of $19a/42$ rather than $a/2$ in the a direction. The structure of the BiO layers obtained by Beskrovnyi et al.[13] is strongly reminiscent of that obtained by LePage et al[1] in their refinement of the isomorphous compound $Bi_{10}Sr_{15}Fe_{10}O_{46}$, which has a commensurate $5a \times b \times c$ structure, and an average spacing of oxygen ions in the BiO layers of $5a/11$. The assumption by Petricek et al.[9] of a linear (rather than a sinusoidal) modulation function, with some regions of double valuedness to allow the insertion of extra oxygen ions into the crystal also results in an average a-axis spacing of oxygen ions smaller than $a/2$. The model proposed below allows an average a-axis spacing of oxygen ions in the BiO layer less than $a/2$, and at the same time allows in a natural way the exploitation of the ideas of superspace symmetry. A detailed interpretation of the structure of $Bi_{10}Sr_{15}Fe_{10}O_{46}$ in terms of our model is given in the Appendix.

We now turn to a more pictorial description of the BiO layers. These layers lie perpendicular to the c axis, and when examined using a high-resolution electron microscope,[7,14-16] can be seen to be modulated with a period of approximately $4.76a$ in the a-axis direction; this is shown schematically in Fig. 1(a). Figure 1(b) shows the positions of the bismuth ions in a unit cell of the average structure of one of the four layers shown in Fig. 1(a), say layer 1. The oxygen positions in this unit cell will vary from cell to cell but should fall approximately on the wavy line. (The figure is only schematic, and no quantitative accuracy is intended.)

An important development was the use of neutron scattering by Bordet et al.[17] to determine the average structure of the BiO layers shown in Figs. 1(c) and 1(d). The different positions of the oxygens in the two figures will be said to represent two distinct but equivalent domains of an "ideal" commensurate structure and are
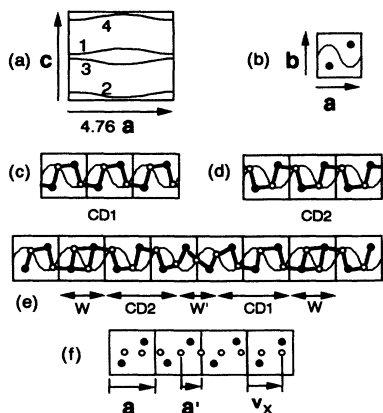
FIG. 1. (a) Schematic high-resolution electron microscope image taken normal to the b axis of $Bi_2Sr_2CaCu_2O_{8+\delta}$. (b) The positions of bismuth ions (black dots) in a given BiO layer in a unit cell of the average structure. The oxygen ions fall on the wavy line. (c) The average structure of a BiO layer determined by Bordet *et al.* (Ref. 17). The open circles are oxygen ions. (d) A structure equivalent to that of (c) but a different domain (the two types of commensurate domains are labeled CD1 and CD2). (e) The structure of a BiO layer in $Bi_{10}Sr_{15}Fe_{10}O_{46}$ determined by LePage *et al.* (Ref. 1). The walls between the commensurate domains are labeled W and W'. (f) Two interpenetrating periodic crystals of bismuth and oxygen ions.

called commensurate domains 1 and 2 (or CD1 and CD2), respectively. Another key advance in the problem of the structure of the BiO layer was the work of LePage *et al.*,[1] who determined the structure of the compound $Bi_{10}Sr_{15}Fe_{10}O_{46}$, which is isomorphous to $Bi_2Sr_2CaCu_2O_{8+\delta}$ but which has a commensurate structure of period $5a$ in the **a** direction. The oxygen-ion positions determined in this study are shown schematically in Fig. 1(e). This structure can roughly be described as being made up of alternating domains CD1 and CD2 (this description has a certain qualitative validity even if the regions called walls have a thickness comparable to the thickness of the domains themselves).

In Fig. 1(e) the walls W are separated by the distance $5a$ and the structure is hence commensurate. The objective of this article is to give a detailed structural model describing the incommensurate structure of $Bi_2Sr_2CaCu_2O_{8+\delta}$ and to develop the model in such a way that the structure of BiO layers reduces to that of Fig. 1(e) in the appropriate limit of the incommensurate structure becoming commensurate. In order to accomplish this, the average structure which forms the starting point of the analysis is assumed to be that of two interpenetrating periodic crystals; as shown in Fig. 1(f), the bismuth ions are part of a crystal which has period a in the **a** direction, while the oxygen ions are part of a periodic crystal having period a' ($\neq a$) in the **a** direction. The modulation function of oxygen ions is represented by wavy lines in Figs. 1(b)–1(e) and has the periodicity of the average bismuth lattice. The bismuth ions on the other hand are modulated by a function which has the periodicity of the average oxygen lattice. This picture is

thus one in which $Bi_2Sr_2CaCu_2O_{8+\delta}$ is viewed as an intergrowth compound[18,19] analogous to $Hg_{3-\delta}AsF_6$ rather than as a modulated structure whose average structure has a normal three-dimensional space-group symmetry.

More precisely, the positions of the bismuth and oxygen ions in the BiO layer 1 [see Fig. 1(a)] will be written

$$\mathbf{r}^{Bi}_{nmp}(v_x) = \mathbf{a}\left\{\frac{n}{2} + \frac{1}{4} + B_x\left[\left(\frac{n}{2} + \frac{1}{4}\right)a - v_x\right]\right\}$$

$$+ \mathbf{b}\left\{m + (-1)^n B_y\left[\left(\frac{n}{2} + \frac{1}{4}\right)a - v_x\right]\right\}$$

$$+ \mathbf{c}\left\{p + B_z\left[\left(\frac{n}{2} + \frac{1}{4}\right)a - v_x\right]\right\}, \quad (1)$$

$$\mathbf{r}^{O}_{n'mp}(v_x) = \mathbf{a}'[n' + O^B_x(n'a' + v_x)] + \mathbf{v}_x$$

$$+ \mathbf{b}[m + O^B_y(n'a' + v_x)]$$

$$+ \mathbf{c}[p + O^B_z(n'a' + v_x)], \quad (2)$$

where

$$B_\alpha(x + a') = B_\alpha(x), \quad O^B_\alpha(x + a) = O^B_\alpha(x). \quad (3)$$

The quantity $\mathbf{v}_x$ gives the displacement in the **a** direction of the oxygen lattice relative to the bismuth lattice. The inclusion of v_x in the bismuth modulation function is essential to give that modulation the appropriate phase. The ion density associated with BiO layer 1 is

$$\rho^{(1)}_s(R) = \sum_{n,m,p} M_{Bi}\delta(\mathbf{r} - \mathbf{r}^{Bi}_{nmp}(v_x))$$

$$+ \sum_{n',m,p} M_O\delta(\mathbf{r} - \mathbf{r}^{O}_{n'mp}(v_x)).$$

This superspace density depends on the four-dimensional vector $R = (x,y,z,v_z) = (\mathbf{r},v_x)$. The physical density is obtained by evaluating the superspace density at a particular value of v_x, say $v_x = 0$. The superspace density is invariant with respect to translations by the Bravais lattice vectors

$$A_1 = \begin{bmatrix} a \\ 0 \\ 0 \\ a \end{bmatrix}, \quad A_2 = \begin{bmatrix} 0 \\ b \\ 0 \\ 0 \end{bmatrix},$$

$$A_3 = \begin{bmatrix} 0 \\ 0 \\ c \\ 0 \end{bmatrix}, \quad A_4 = \begin{bmatrix} 0 \\ 0 \\ 0 \\ a' \end{bmatrix}, \quad (4)$$

and the corresponding reciprocal lattice vectors are

$$A_1^* = \begin{bmatrix} a^* \\ 0 \\ 0 \\ 0 \end{bmatrix} , \quad A_2^* = \begin{bmatrix} 0 \\ b^* \\ 0 \\ 0 \end{bmatrix} ,$$

$$A_3^* = \begin{bmatrix} 0 \\ 0 \\ c^* \\ 0 \end{bmatrix} , \quad A_4^* = \begin{bmatrix} -a'^* \\ 0 \\ 0 \\ a'^* \end{bmatrix} , \tag{5}$$

where $a^* = 2\pi/a$, $a'^* = 2\pi/a'$, etc. Scattering will thus be observed from this structure at wave vectors $\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* - m\mathbf{a}'^*$. For $Bi_2Sr_2CaCu_2O_{8+\delta}$, $a' = 0.452a$, giving $\mathbf{a}'^* = 2.21\mathbf{a}^* = 2\mathbf{a}^* + \mathbf{q}$, where $\mathbf{q} = 0.21\mathbf{a}^*$. Thus the possible scattering wave vectors can also be written $\mathbf{k} = (h - 2m)\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* - m\mathbf{q}$. Treating $\mathbf{a}'^*$ as the fundamental wave vector is in agreement with the Fischer et al. intensity arguments[12] that the $(2+\tau, 0, \pm1)$ peaks observed with neutrons are at least an order of magnitude stronger than the $(2-\tau, 0, \pm1)$ peaks.

It has been determined from studies of systematic absences[4-6] that the superspace group of $Bi_2Sr_2CaCu_2O_{8+\delta}$ is either $M:A2aa:111$ or $M:Amaa:\bar{1}11$. Thus the superspace density should be invariant with respect to the substitution

$$R \rightarrow \{\sigma_y | \tfrac{1}{2} A_1\} R = (\sigma_y \mathbf{r}, \sigma_y v_x) + \tfrac{1}{2} \mathbf{A}_1 .$$

As a result, the two Bi ions in the unit cell have the same modulation function, a fact which has already been incorporated in writing Eq. (1). Furthermore,

$$O_{x,z}^B(x - \tfrac{1}{2}a) = O_{x,z}^B(x) , \quad O_y^B(x - \tfrac{1}{2}a) = -O_y^B(x) . \tag{6}$$

If the correct superspace group is $M:A2aa:111$, then the modulation functions are defined by Eqs. (3) and (6) only. If the correct superspace group is $M:Amaa:\bar{1}11$, then the following restrictions must be added:

$$B_x(x) = -B_x(-x) , \quad B_{y,z}(x) = B_{y,z}(-x) , \tag{7}$$

$$O_{x,y}^B(x) = -O_{x,y}^B(-x) , \quad O_z^B(x) = O_z^B(-x) . \tag{8}$$

The A centering of the unit cells means that the ion density $\rho_s^{(2)}(R)$ associated with the BiO layer labeled 2 in Fig. 1(a) is derived from that of layer 1 by

$$\rho_s^{(2)}(R) = \rho_s^{(1)}(R + \tfrac{1}{2}A_2 + \tfrac{1}{2}A_3 + \tfrac{1}{2}A_4) . \tag{9}$$

The invariance of the total density with respect to the translation $\tfrac{1}{2}(A_2 + A_3 + A_4)$ leads to the result that the reflections $k + l + m = 2n + 1$ (n integer) are systematically absent, as required by experiment. Finally, the densities $\rho_s^{(3)}$ and $\rho_s^{(4)}$ associated with BiO layers 3 and 4, respectively, are given by

$$\rho_s^{(3)}(R) = \rho_s^{(1)}(\{C_{2x}|0\}R) , \tag{10}$$

$$\rho_s^{(4)}(R) = \rho_s^{(2)}(\{C_{2x}|0\}R) . \tag{11}$$

It can be seen that Eqs. (10) and (11) give a phasing of the modulation waves on neighboring BiO layers that is in agreement with the results of high-resolution electron mi-

croscopy imaging[7,14-16] and that is indicated schematically in Fig. 1(a).

The superspace density associated with all of the BiO layers is

$$\rho_s(R) = \rho_s^{(1)}(R) + \rho_s^{(2)}(R) + \rho_s^{(3)}(R) + \rho_s^{(4)}(R) .$$

This density is invariant with respect to the transformations $\{E|\tfrac{1}{2}(A_2 + A_3 + A_4)\}$, $\{\sigma_y|\tfrac{1}{2}A_1\}$, and $\{\sigma_z|\tfrac{1}{2}A_1\}$. The corresponding conditions for the existence of nonzero diffraction peaks are $k + l + m = 2n$ for $(hklm)$, and $h = 2n$ for $(h0lm)$ and $(hk0m)$. The resulting diffraction pattern is shown in Fig. 2.

The above analysis has assumed that the correct superspace symmetry for $Bi_2Sr_2CaCu_2O_{8+\delta}$ is either $M:A2aa:111$ or $M:Amaa:\bar{1}11$. Only the ions in the BiO layers have been treated explicitly, but parametrizations of the positions of the other ions in the crystal are similar to those for the Bi ions; the average lattice for these ions has period a in the a-axis direction, and the modulation functions have period a'. The above analysis can also be easily modified to apply to other symmetries should the assignments $M:A2aa:111$ or $M:Amaa:\bar{1}11$ be found to be incorrect. For example, if the structure is found not to be A centered (as suggested by Eibl[7]) the ion positions in layers 1 and 2 would be independent, and Eq. (9) would not apply.

In the extension to the $n = 1$ phase $Bi_2Sr_2CuO_{6+\delta}$, the superspace Bravais lattice vectors are

$$\begin{bmatrix} a \\ 0 \\ 0 \\ a \end{bmatrix} , \begin{bmatrix} 0 \\ b \\ 0 \\ 0 \end{bmatrix} , \begin{bmatrix} 0 \\ 0 \\ c \\ \epsilon a' \end{bmatrix} , \begin{bmatrix} 0 \\ 0 \\ 0 \\ a' \end{bmatrix} .$$

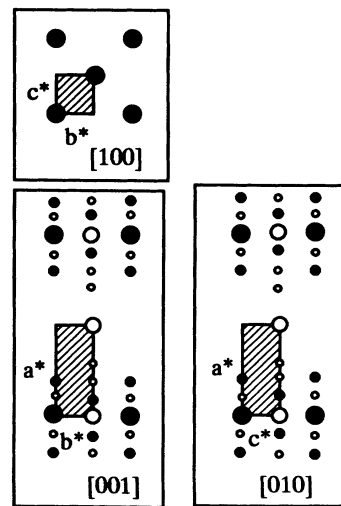This gives possible diffraction peaks at wave vectors

FIG. 2. Schematic electron diffraction pattern. The solid symbols are in the plane of the page, and the open symbols are above the plane by one unit. The larger symbols correspond to diffraction spots of the average lattice defined by the metal ions, and the smaller symbols are satellites. Only satellites corresponding to $m = 1$ and 2 are shown.

$k = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* - m(\mathbf{a}'^* + \epsilon\mathbf{c}^*)$. The superspace group of $Bi_2Sr_2CuO_{6+\delta}$ has been determined by Li et al.[4] to be either $P:B2/b:\bar{1}1$ or $P:Bb:1$. Detailed structural models consistent with these space groups can be developed in the same way as was done for $Bi_2Sr_2CaCu_2O_{8+\delta}$ above.

In conclusion, the model proposed for the structure of the incommensurate bismuth superconductors is one in which there are two interpenetrating periodic crystals. The oxygen ions in the BiO layers form a crystal with lattice constant a' in the a-axis direction, and the remaining ions form a crystal with lattice constant a. Each of these crystals is modulated as a result of its interaction with the other.

Note added in proof. Structural determinations of $Bi_2Sr_2CaCu_2O_{8+\delta}$ have also been carried out in Refs. 20 and 21.

ACKNOWLEDGMENTS

APPENDIX: MODULATION FUNCTIONS FOR $Bi_{10}Sr_{15}Fe_{10}O_{46}$

Table II of LePage et al.[1] gives the atomic positions of the atoms in the $Bi_{10}Sr_{15}Fe_{10}O_{46}$ compound. Our model,
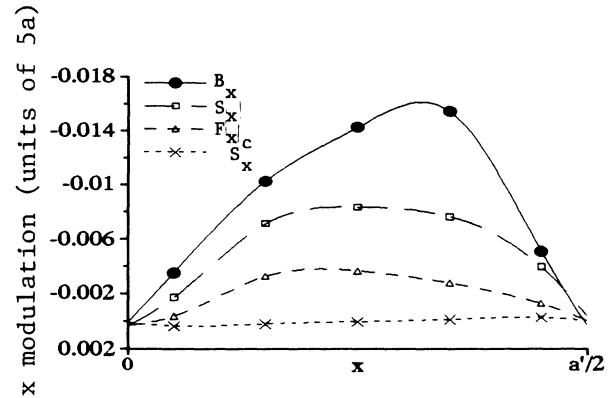

FIG. 3. Modulation functions B_x, S_x, F_x, and S_x^C, in units of $5a$, where $5a = 27.245$ Å. Because the structure considered in the Appendix is commensurate, the modulation functions can be determined only at discrete values of their arguments. The values of the modulation functions, which can be determined are indicated by triangles, crosses, etc. The lines connecting the discrete data points have been added by hand to help guide the eye between the data points associated with a given modulation function.

when specialized to the case of a commensurate structure with period $5a$ in the a direction and with $B222$ space-group symmetry, is exactly equivalent to that of LePage et al.[1] Both models have exactly the same number of un-

TABLE I. Coefficients appearing in the modulation functions. Coefficients in the x direction are in units of $a = 5.449$ Å, which is $\frac{1}{5}$ of the a value in Ref. 1. In the y and z directions the coefficients are in units of $b = 5.4617$ Å and $c = 31.696$ Å, respectively. An absent entry indicates a coefficient that is required to be zero by symmetry.

| p	0	1	2	3	4	5
$B_{xp;s}$		−0.075 59	0.011 603	−0.001 33	−0.003 044	−0.002 81
$B_{yp;c}$	−0.232 04	0.001 878	−0.000 71	−0.004 57	−0.001 57	
$B_{zp;c}$	0.547 656	0.004 496	−0.000 259	0.001 096	−0.000 055	
$S_{xp;s}$		−0.044 28	0.003 545	−0.001 74	0.003 695	0.000 69
$S_{yp;c}$	0.251 2	0.001 656	0.000 076	−0.001 658	−0.006 024	
$S_{zp;c}$	0.632 032	0.008 81	−0.001 708	0.000 445	0.000 29	
$F_{xp;s}$		−0.018 32	0.000 105	0.000 88	0.002 3	0.000 7
$F_{yp;c}$	−0.250 06	−0.000 043	0.007 756	0.002 707	−0.012 184	
$F_{zp;c}$	0.689 64	0.011 643	−0.000 148	0.000 046	−0.000 388	
$O^S_{xp;s}$		−0.070 395	0.029 94	−0.015 695	−0.000 89	0.010 2
$O^S_{yp;c}$	−0.2654	−0.001 03	−0.015 16	0.002 518	0.010 24	
$O^S_{zp;c}$	0.614 98	0.002 629	0.001 568	−0.003 317	−0.001 612	
$S^C_{xp;s}$			0.001 315		0.000 765	
$S^C_{yp;c}$	−0.251 44		0.004 427		−0.000 133	
$S^C_{zp;c}$	$\frac{1}{4}$	0.011 203		−0.000 331		
$O^C_{xp;s}$			−0.003 36		−0.010 54	
$O^C_{yp;c}$	0.264 2		−0.033 885		−0.051 085	
$O^C_{zp;c}$	$\frac{1}{4}$	0.012 648		−0.007 535		
$O^{FA}_{xp;s}$		0.019 165	0.000 075	0.011 025	0.000 31	
$O^{FA}_{yp;s}$		0.003 535	−0.014 221	−0.005 339	−0.009 315	
$O^{FA}_{zp;c}$	0.681 7	−0.011 173	0.001 561	0.001 393	−0.002 061	−0.005 62
$O^{FB}_{xp;s}$		0.014 585	0.005 59	−0.010 855	−0.005 22	
$O^{FB}_{yp;s}$		0.011 08	0.004 343	0.002 616	−0.003 625	
$O^{FB}_{zp;c}$	0.683 36	−0.009 622	−0.000 291	−0.000 498	−0.000 469	0.003 52
$O^{B}_{xp;s}$		−0.001 732	−0.014 763	−0.017 915	0.010 948	0.001 473
$O^{B}_{yp;s}$		0.201 154	−0.039 126	0.042 522	0.040 529	−0.003 126
$O^{B}_{zp;c}$	0.549 564	−0.003 393	−0.003 421	−0.000 349	0.002 151	0.000 448
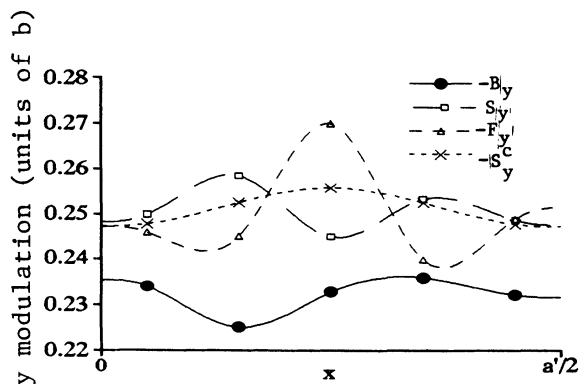
FIG. 4. Modulation functions B_y, S_y, F_y, and S_y^C, in units of $b = 5.4617$ Å. For B_y, F_y, and S_y^C, a minus sign has been dropped.
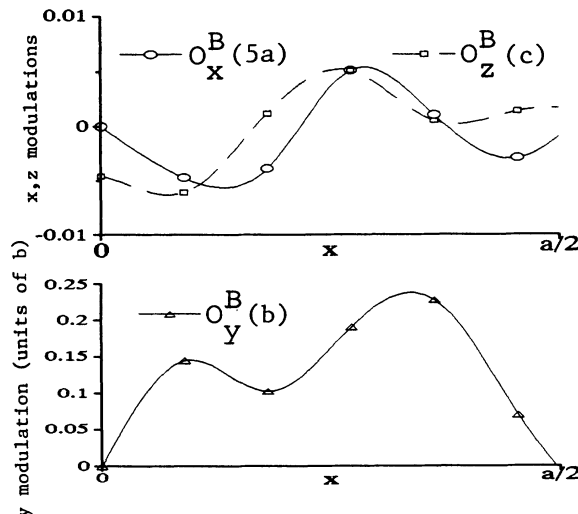

FIG. 5. Modulation functions for the oxygen in the bismuth layer O_x^B in units of $5a$, O_y^B in units of b, and O_z^B in units of $c = 31.696$ Å.

determined parameters, the difference being that the undetermined parameters of LePage et al.[1] represent ion positions, while the undetermined parameters in our case describe the amplitudes of the various harmonics of the modulated functions. The atomic positions given by LePage et al.[1] can therefore be used to obtain the modulation functions in terms of which our model is formulated. This in turn allows us to evaluate the relative importance of the various harmonics occurring in the modulation functions.

Since the bismuth modulation functions are periodic with period a', they can be written

$$B_\alpha(x_n) = \sum_p [B_{\alpha p;c}\cos(pa'^*x_n) + B_{\alpha p;s}\sin(pa'^*x_n)] , \quad (12)$$

where $x_n = (n/2 + \frac{1}{4})a$, $a'^* = 2\pi/a'$, and v_x has been set to zero. The $Bi_{10}Sr_{15}Fe_{10}O_{46}$ structure is a commensurate one with $5a = 11a'$ and hence the only values of p required in the sum in Eq. (12) are $p = 0,1,2,3,4,5$. Also, the fact that the c axis is a twofold axis of symmetry (the space group is $B222$) requires certain coefficients in Eq. (12) to be zero. (For example, all $B_{xp;c}$ are equal to zero.) The modulation functions for the Sr atoms in the layer corresponding to the Ca layer of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductor are denoted S_α^C, whereas the modulation functions for the other Sr atoms in the other Sr layers and for the Fe atoms are denoted S_α and F_α, respectively. The oxygen modulation functions for the oxygens in the layers associated with the B_α, S_α, S_α^C, and F_α functions are denoted by O_α^B, O_α^S, O_α^C, and O_α^{FA} and O_α^{FB}, respectively. (Our notation is similar but not identical to that used in Table II of LePage et al.[1]) The atomic positions for the atoms labeled by B, S, SC, F, OS, and OC are given by formulae identical to Eq. (1), and the corre-

sponding modulation functions can be written as in Eq. (12). The atomic positions for atoms OFA and OFB are also given by Eq. (1), but with $(n/2 + \frac{1}{4})$ replaced by $n/2$. Again Eq. (12) describes the corresponding modulation functions. The modulation function for the atoms OB is parametrized as in Eq. (12), except that a'^* is replaced by a_* and $x_n = na'$. All nonzero coefficients which appear in the expressions for the modulation functions have been determined for $Bi_{10}Sr_{15}Fe_{10}O_{46}$ from the data of LePage et al.[1] and are given in Table I. This is not difficult since, as stated above, there are exactly the same number of undetermined parameters in our description of the structure as there are in the usual description employed by LePage et al.[1]

Some of the modulation functions are shown graphically in Figs. 3–5. Note (from both the figures and Table I) that the x and z components of the modulations functions of the metal ions are reasonably well described in terms of their first nonzero harmonic. However, the y component of the modulation functions of the metal ions requires more than one harmonic for an adequate description, as do many of the modulation functions of the oxygen ions. The estimated errors in the determination of the ion positions have been given by LePate et al.[1] These errors are not sufficiently large to discredit the qualitative conclusions on harmonic content just drawn, except possibly in the case of the OFA and OFB ions, for which the errors in positions are comparable to the modulation amplitude.

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