Causes of modulation and hole conductivity of the high-T_c superconductor $Bi_2Sr_2CaCu_2O_{8+x}$ according to X-ray single-crystal data

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Abstract. The one-dimensionally modulated structure of the high-T_c superconductor $Bi_2Sr_2CaCu_2O_{8+x}$ with $a_0 = 5.407(2)$, $b_0 = 5.412(3)$, $c_0 = 30.771(8)$ Å, $q = 0.210(2)b_0^*$ has been analysed in the commensurate approximation using the conventional three-dimensional space group $Pnnn$ and utilizing single-crystal x-ray diffraction data. A reliable model ($R = 0.07$, $R_w = 0.079$ for 1011 unique reflections) has been obtained. The extra oxygen atoms have been found inside and between the Bi–O–Bi chains of the BiO layer. The modulation displacement functions of the atoms have been obtained by means of harmonic analysis of the modulation displacements. It has been shown that the topology of Bi–O–Bi chains, the modulation of the structure and the form of the modulation displacement functions can be explained by the shifts of the oxygen atoms in the BiO layer correlated according to the antiferroelectrical law. The cationic vacancies in the Sr sites provide the hole conductivity in the copper–oxygen plane and lead to the formation of the percolation picture in this plane.

1. Introduction

The high-T_c superconductor $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212) was discovered by Maeda *et al* [1]. As shown by x-ray single-crystal studies (see, for example, [2]) this compound is characterized by complex layered perovskite-like structure. It contains the copper–oxygen CuO_3 layers with usual square-pyramidal oxygen coordination of the Cu cations and double $(BiO)_2$ layers. The Ca atoms are located between two neighbouring CuO_3 layers. There are no oxygen atoms in the layer of Ca cations. The Sr atoms lie between the CuO_3 and $(BiO)_2$ layers. The polyhedra of the Cu and Bi atoms are connected by common apical oxygen atoms located in the same layer as the Sr atoms. The fundamental unit cell of Bi-2212 can be fairly well described within the symmetry of the orthorhombic space group $Amaa$ (or $Bbmb$ in the other set of crystal axes) [2].

The one-dimensionally modulated structures of Bi-2212 and related isomorphous compounds have been studied by x-ray single-crystal and neutron diffraction [3–10]. The incommensurate modulated structures of Bi-2212 with wavevector $q \simeq 0.21a^*$ (or $0.21b^*$ in the other set of axes) have been determined using the superspace formalism [3–5]. Bescrovnyi *et al* [6,7] have analysed their data from the modulated crystal of Bi-2212 with approximately the same incommensurate wavevector $q \simeq 0.21a^*$ using the commensurate supercell approach with the unit-cell parameters $a = 19a_0$, $b = b_0$, $c = c_0$ where a_0, b_0, c_0 are the parameters of the fundamental unit cell. Calestani *et al* [8] have performed a full refinement of the structure of the commensurate modulated (with $q = 0.20a^*$)

crystal Bi-2212 on the basis of a commensurate superstructure with the unit-cell parameters $a = 5a_0$, $b = b_0$, $c = c_0$ in a three-dimensional space group. The isomorphous compound $Bi_2Sr_3Fe_2O_{9.2}$ with the same wavevector $q = 0.20a^*$ has been studied on the basis of the same approach by Le Page *et al* [9].

According to [3, 4, 6–10], the type of Bi-2212 modulation is a displacive one. Yamamoto *et al* [5] have found that the modulation has not only a displacive component but also an occupational one. As has been shown, the bonds in the single BiO layers form characteristic chains Bi–O–Bi running along the axis of modulation. Petricek *et al* [4], Bescrovnyi *et al* [5,6] and Le Page *et al* [9] have found extra oxygen atoms inserted into these Bi–O–Bi chains. Yamamoto *et al* [5] have localized not only one additional oxygen atom inserted into a Bi–O–Bi chain but four extra oxygen atoms between these chains for observed modulation period $4.72a$. The conclusion has been drawn that insertion of the extra oxygen atoms causes the modulation of the Bi-2212 structure [5–7,9]. However, Calestani *et al* [8] have not found any extra oxygen atoms in Bi-2212 and supposed that the modulation is produced by the structural mismatch between the perovskite blocks and the BiO layers. Moreover, Calestani *et al* [11] have described the synthesis and the single-crystal x-ray determination of the structure of the modulation-free compounds $(Bi,Pb)_2Sr_2(Ca,Y)Cu_2O_{8+x}$, which are isomorphous with Bi-2212.

Thus, the details of the modulated Bi-2212 structure and the origin of this modulation remain a subject for discussion. This paper presents the results of an x-ray single-crystal study of $Bi_2Sr_2CaCu_2O_{8+x}$ modulated structure.

2. Experimental details

2.1. Preliminary study and techniques

Single crystals of $Bi_2Sr_2CaCu_2O_{8+x}$ were grown from the melt by the CuO flux method. The crystals were confirmed to have a single superconducting transition at the onset $T_c = 80$ K, with the width of the transition being about 5 K. More detailed data on the synthesis and characterization of the crystals will be published elsewhere [12]. A fairly good crystal with dimensions $1.50 \times 0.25 \times 0.014$ mm^3 was selected for the intensity measurements.

Preliminary study performed at room temperature using a diffractometer showed both the main reflections defining the orthorhombic cell with parameters $a_0 = 5.407(3)$, $b_0 = 5.412(3)$, $c_0 = 30.771(8)$ Å and the satellite reflections of first and second order defined by an incommensurate modulation vector $q = qb_0^*$ where $q = 0.210(2)$. As is known [13], all the reflections can be indexed for such one-dimensionally incommensurately modulated crystals using the four indices by defining the diffraction vector $H = ha_0^* + kb_0^* + lc_0^* + mq$, where m is the satellite order and a_0^*, b_0^*, c_0^* are the reciprocal-lattice unit vectors of the orthorhombic fundamental cell. The integrated intensities were measured on a three-circle automated diffractometer controlled by the original program, which generates the $hklm$ and $Rh = h$, $Rk = k + mq$, $Rl = l$ reflection indices. Graphite-monochromatized Ag K$_\alpha$ radiation ($\lambda = 0.56083$ Å) and a perpendicular-inclination measurement technique were used. The a axis of the crystal was oriented along the ω axis of the diffractometer. The 1021 unique observed reflections with $I > 3\sigma(I)$ were collected in an octant of reciprocal space up to $\sin\theta/\lambda = 0.982$ Å^{-1} utilizing ω-scan with scanning speed 1.2 Å^{-1}. To avoid overlap of some reflections, four counter-apertures of $2\theta = 0.2$–$1.5°$ were used. The profile analysis was performed with the modified Oatley and French procedure [14]. The intensities were corrected for Lorentz and polarization factors. Absorption corrections based on crystal morphology were applied ($\mu = 301$ cm^{-1}).

2.2. Refinement of the average structure

First, the average structure of Bi-2212 was refined using the crystallographic program AREN-90 [15] and modified least-squares program ORFLS [16]. The blocked full-matrix method of least-squares refinements was used. The atomic scattering factors for neutral atoms with dispersion correction [17] and Cruickshank's weighting scheme [18] were used.

The average structure was refined using only 336 unique main reflections with $I > 4\sigma(I)$. The starting values of the coordinates of atoms of the fundamental unit cell were taken from a previous work [5]. The populations of the cationic positions were determined from the minima of the curves of the agreement factors $R(P)$ and $R_w(P)$ obtained by the step-like change of the occupancy probabilities P of positions and refinement of the other structural parameters. Site populations obtained in such a way were refined using the low-angle reflections with $\sin\theta/\lambda < 0.35$ Å^{-1} to avoid a great correlation between the thermal and population parameters. In the final cycles, the refinement of the populations was carried out using all 336 $F(hkl)$.

Two possible orthorhombic space groups $Bbmb$ and $Bb2b$ were tested. The refinement results allowed one to choose the centrosymmetric space group $Bbmb$ to describe the average structure of Bi-2212. The first refinements, carried out without splitting of the atomic positions, with anisotropic temperature factors for all atoms, led to the reliability factors $R = 0.098$ and $R_w = 0.146$. The temperature factors of atom Bi and oxygen atoms coordinating it (O3 and O4 in table 1) were large ($B_{eq} = 7.4$, 15.0 and 18.9 Å^2 for atoms Bi, O3 and O4, respectively), mainly because of components of the thermal factors along the modulation axis b. At the next refinement stage, the positions of Bi cation and O3 and O4 atoms were split onto two close sites with the half-populations based on the results of Fourier difference synthesis. It allowed one to take into account the large spread of the electronic density around the average positions of these atoms. The agreement factors lowered finally to $R = 0.063$ and $R_w = 0.076$. The results of the final refined model are summarized in table 1†.

Table 1. Multiplicities (m) and Wyckoff letters of the sites, occupational, positional and equivalent isotropic thermal parameters ($B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}a_ia_j$) for the atoms of the fundamental cell of Bi-2212. Space group $Bbmb$, $a_0 = 5.407(3)$, $b_0 = 5.412(3)$, $c_0 = 30.771(8)$ Å, $R = 0.063$, $R_w = 0.076$, 336 $F(hkl)$ with $I > 4\sigma(I)$. The numbers in parentheses following refined parameters are the estimated standard deviations.

Atom	m	P	x/a_0	y/b_0	z/c_0	B_{eq} (Å^2)
Bi	16m	0.488(3)	0.2247(4)	0.5530(3)	0.05199(4)	5.13(6)
Sr	8l	0.92(1)	0.2541(10)	0.00	0.14124(14)	5.9(1)
Cu	8l	0.93(1)	0.2496(13)	0.50	0.19694(16)	5.0(1)
Ca	4e	1.23(2)	0.25	0.00	0.25	4.6(2)
O1	8g	1.0	0.00	0.75	0.1969(8)	5.6(10)
O2	8g	1.0	0.50	0.25	0.1991(8)	5.9(10)
O3	16m	0.5	0.287(8)	0.572(7)	0.1193(9)	7.7(15)
O4	16m	0.5	0.159(7)	0.150(8)	0.0547(8)	7.0(12)

† Lists of structure factors for basic and modulated cells, anisotropic thermal parameters of atoms in the base cell, interatomic distances and results of harmonic analysis of displacements of atoms from the average positions in the structure of the supercell (17 pp) have been deposited with British Library Lending Division, Boston Spa, West Yorkshire LS23 7BQ, UK, reference No SUP70 050. Copy may be obtained from this source.

A careful analysis of the final Γ_ρ peaks gave evidence of residual electron density in two sites, which were similar to the extra oxygen atom positions in the BiO layer found by Yamamoto *et al* in Bi-2212 [5] and by Torardi *et al* [2] in isomorphous $Bi_2Sr_{2.4}Y_{0.6}Cu_2O_{8+x}$. The assumption of these oxygen positions partly occupied with occupancy probabilities P about 0.10 led to the drop of the R and R_w factors only by 0.01. (The refinement gave the positional parameters $(x/a_0, y/b_0, z/c_0) = (0, 0.25, 0.073(8))$ and isotropic temperature factor $B_{iso} = 5.0(55)$ Å^2 for the first such position, and $(x/a_0, y/b_0, z/c_0) = (0.35(8), 0.80(7), 0.87(9))$ and $B_{iso} = 5.1(62)$ Å^2 for the second one.) Thus, only the determination of the modulated structure could definitely clear up the problem of the existence of extra oxygen atoms in the BiO layer of Bi-2212.

2.3. Determination of the modulated structure

The incommensurately modulated structure should be analysed on the basis of the superspace formalism [13, 19]. According to the four-index scheme [13], the observed 1021 reflections can be divided into 353 main reflections and 502 first- and 166 second-order satellites. Only 10 relatively weak and diffuse reflections violating the extinction rules of the superspace groups $N: Bbmb: 1\bar{1}1$ and $N: Bb2b: 1\bar{1}1$ were detected, thus confirming these possible superspace groups in accordance with [3–5]. The existence of a small number of such weak diffuse reflections was reported by Calestani *et al* [8] and Eibl [20].

As long as the modulated period for our single crystal, $p = 1/q = 4.76(4)$, is close to the commensurate one, $p = 5$, with the period b_0 of the fundamental cell, the structure can be analysed as a superstructure with the unit-cell parameters $a = a_0$, $b = 5b_0$, $c = c_0$ based on a conventional three-dimensional space group. The space group describing the symmetry of the superstructure was determined from systematic absences observed for the conventional indexing of the 1011 reflections on the basis of the supercell with parameters $a = 5.407(3)$, $b = 27.060(15)$, $c = 30.771(8)$ Å. This space group was found as *Pnnn* in accordance with Calestani *et al* [8]. Among the 1011 reflections, there were 353 main reflections, 494 satellite reflections of the first order and 164 of the second order.

The same programs and techniques were used for the determination of the supercell structure as for refinement of the average structure. The starting coordinates of the five Bi cations in the supercell were derived from the position of the Bi atom in the fundamental cell (table 1). One of the Bi atoms was shifted from its position by 0.4 Å along the axes b and c. The sites of the other cations were localized from subsequent Fourier syntheses combined with blocked full-matrix least-squares refinements. The oxygen atom positions were found from the difference electron density maps. If the correlations during the least-squares refinements of the parameters of the superstructure drove out some oxygen atoms (particularly the oxygen atoms of the CuO_3 layer unmodulated in the ab plane) from their real positions, giving unreal interatomic distances, the coordinates of such oxygen atoms were redetermined from the difference syntheses of the electron density.

The populations of the cationic positions were refined by the same technique as those of the average structure using the low-angle reflections with $\sin\theta/\lambda$ up to 0.40 Å^{-1}. Some occupancies P showed only a slight deviation, not more than $0.5\sigma(P)$, from full occupancy. Those for the oxygen atoms were not significant owing to the low scattering power of oxygen. Therefore, these occupancies were fixed to unity in the final refinement cycles. The Bi cations were refined with the anisotropic temperature factors. The isotropic ones were used for the other atoms. First, the thermal parameters of the oxygen atoms were assumed to be equal to each other in layers. In the final cycles, the individual isotropic factors of the oxygen atoms were refined. The final agreement factors R are 0.070, 0.061, 0.072 and 0.091 for all the reflections, the main ones, the first- and the second-order satellites,

respectively. The corresponding values of the agreement weight factors are 0.079, 0.071, 0.079 and 0.099.

The results of the refined model of the Bi-2212 superstructure are summarized in tables 2 and 3. The indices of the oxygen atoms Oij of the superstructure (table 2) related to the oxygen atoms Oi of the fundamental structure (table 1) begin from the corresponding values of indices i ($i = 1$–4). As is clear from table 2, we located two extra oxygen atoms in the BiO layer labelled as O6 and O7. These oxygen atoms were located taking into account stereochemical considerations and the heights of the corresponding residual electron density peaks, which were the strongest ones not counting the peaks related to the termination-of-series effects for the Bi cations.

3. Discussion

3.1. Cation coordinations

The Cu cations occur in pyramids CuO$_5$ formed by four oxygen atoms in the plane of the CuO$_3$ layer labelled below as O(Cu), and one apical oxygen atom located in the same layer as Sr cations and labelled as O(Sr). The mean Cu–O(Cu) distances are 1.91(10), 2.00(10), 1.85(2), 1.95(9) and 1.92(10) Å in the Cu1, Cu2, Cu3, Cu4 and Cu5 oxygen squares respectively (here and below during the description of cation coordination, the values in parentheses are mean deviations). The apical oxygen atom O(Sr) is displaced to the mean distance 2.51(8) Å from the Cu cation in the CuO$_5$ pyramids.

The Ca cations are located between two CuO$_3$ layers and surrounded hexahedrally by eight O(Cu) atoms with the mean Ca–O distances of 2.49(22), 2.54(24) and 2.56(14) Å in the Ca1, Ca2 and Ca3 polyhedra, respectively.

The Sr atoms are located on the opposite side of the copper–oxygen plane with respect to the Ca cations and surrounded by four O(Cu) and four O(Sr) atoms. One (or two for the Sr2 cation) of the four O(Sr) oxygen neighbours of the Sr cation is always displaced to a distance greater than 3 Å, considerably exceeding the sum of ionic radii of the Sr and O atoms. In addition, one (or three for the Sr1 atom) oxygen atom O(Bi) of the BiO layer is bonded to the Sr cation. The mean distances are Sr–O(Cu) = 2.63(19) Å, Sr–O(Sr) = 2.16(22) Å and Sr–O(Bi) = 2.75(11) Å, and the coordination numbers of the Sr1, Sr2, Sr3, Sr4 and Sr5 cations are equal to 10, 7, 8, 8 and 8, respectively. The increase of the coordination number of the Sr1 atom is caused by the connection of this atom with the extra oxygen atoms O6 and O7 of the BiO layer.

The Bi cations form with their oxygen neighbours trigonal (Bi2, Bi3, Bi4) or tetragonal (Bi1, Bi5) pyramids in which the Bi atom occupies the apical vertex and the oxygen atoms O(Bi) and O(Sr) are sited in the basal plane of these pyramids. The mean Bi–O(Bi) and Bi–O(Sr) bond lengths are 2.17(11) and 2.05(2) Å, respectively.

3.2. The BiO layer

The oxygen polyhedra of the Bi atoms are connected in the BiO plane by common vertices or edges forming a zigzag chain along the b axis. Without the additional O6 and O7 atoms, the topology of the chain is similar to the one described in [8]. The BiO layer consists of 10-membered chains Bi$_{10}$O$_{10}$. In [8], the chains are connected to each other along the a axis (in the set of axes [8]) by metallic Bi–Bi bonds between the terminal Bi atoms with a bond-length distance Bi–Bi of 3.18 Å. In this work, the O6 atom is a bridging one between 10-membered chains, giving rise to the infinite chain Bi–O–Bi. The

Table 2. Multiplicities (m) and Wyckoff letters of the sites, occupational, positional and equivalent isotropic thermal parameters ($B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i a_j$) for the Bi cations and isotropic thermal parameters for the other atoms of the supercell of Bi–2212. Space group $Pnnn$, $a = 5.407(3)$, $b = 27.060(15)$, $c = 30.771(8)$ Å, $R = 0.070$, $R_w = 0.079$, 1011 $F(hkl)$ with $I > 3(I)$. The numbers in parentheses are the estimated standard deviations.

Atom	m	P	x/a	y/b	z/c	B (Å^2)
Bi1	8m	1.00	0.039(1)	0.3061(1)	0.2046(1)	2.73(10)
Bi2	8m	0.82(1)	0.459(1)	0.4202(1)	0.1999(1)	1.25(9)
Bi3	8m	0.90(1)	−0.009(1)	0.5125(1)	0.1986(1)	1.31(9)
Bi4	8m	0.84(1)	0.432(1)	0.6063(2)	0.1935(1)	1.49(10)
Bi5	8m	1.00	0.003(1)	0.7070(1)	0.1933(1)	1.05(6)
Sr1	8m	0.95(3)	0.478(3)	0.3099(4)	0.1173(4)	2.18(20)
Sr2	8m	0.56(4)	0.970(6)	0.4057(10)	0.1188(9)	3.18(45)
Sr3	8m	1.34(3)	0.513(3)	0.5083(2)	0.1102(2)	1.25(8)
Sr4	8m	0.81(3)	0.964(2)	0.6045(5)	0.1015(3)	0.72(13)
Sr5	8m	0.75(2)	0.464(2)	0.7023(9)	0.1034(3)	0.45(9)
Cu1	8m	0.92(3)	0.977(2)	0.3033(6)	0.0636(3)	1.02(14)
Cu2	8m	0.89(4)	0.457(3)	0.3999(6)	0.0611(5)	1.25(20)
Cu3	8m	1.00	0.981(3)	0.5030(4)	0.0522(3)	0.55(12)
Cu4	8m	1.00	0.464(2)	0.6027(6)	0.0458(4)	0.34(14)
Cu5	8m	0.85(3)	0.966(3)	0.7011(11)	0.0453(4)	1.13(16)
Ca1	8m	1.03(4)	0.536(2)	0.2967(8)	0.0110(3)	0.25(14)
Ca2	8m	1.58(8)	0.031(2)	0.3998(3)	0.0062(3)	0.58(15)
Ca3	4f	0.92(7)	0.50	0.50	0.00	0.36(30)
O11	4k	1.00	0.25	0.25	0.071(4)	2.0(18)
O12	8m	1.00	0.211(14)	0.350(2)	0.059(2)	0.4(9)
O13	8m	1.00	0.194(20)	0.449(3)	0.055(3)	1.1(10)
O14	8m	1.00	0.218(23)	0.550(4)	0.048(3)	1.6(14)
O15	8m	1.00	0.245(40)	0.653(5)	0.048(3)	1.5(13)
O16	4l	1.00	0.25	0.75	0.041(3)	0.4(13)
O21	4l	1.00	0.75	0.25	0.060(7)	2.8(28)
O22	8m	1.00	0.691(16)	0.341(3)	0.062(3)	1.6(13)
O23	8m	1.00	0.748(16)	0.454(2)	0.060(2)	0.4(8)
O24	8m	1.00	0.743(25)	0.553(3)	0.043(3)	0.4(12)
O25	8m	1.00	0.760(33)	0.648(4)	0.045(3)	0.9(14)
O26	4k	1.00	0.75	0.75	0.031(4)	2.8(24)
O31	8m	1.00	0.002(34)	0.323(4)	0.142(4)	3.3(17)
O32	8m	1.00	0.540(37)	0.419(6)	0.135(4)	4.0(24)
O33	8m	1.00	−0.093(14)	0.525(2)	0.132(2)	0.5(8)
O34	8m	1.00	0.521(14)	0.609(4)	0.130(2)	0.5(7)
O35	8m	1.00	0.036(13)	0.704(6)	0.128(2)	1.6(9)
O41	8m	1.00	0.391(21)	0.342(3)	0.206(3)	2.4(14)
O42	8m	1.00	0.095(29)	0.431(4)	0.195(4)	3.6(22)
O43	8m	1.00	0.373(17)	0.533(3)	0.198(3)	1.2(11)
O44	8m	1.00	0.049(15)	0.629(2)	0.184(2)	1.4(10)
O45	8m	1.00	0.412(15)	0.711(2)	0.190(2)	1.7(12)
O6	4k	1.00	0.25	0.25	0.178(3)	1.1(15)
O7	4l	1.00	0.75	0.25	0.174(5)	2.9(25)

Table 3. Anisotropic thermal parameters ($\times 10^5$) of the Bi cations of the supercell of Bi-2212 according to the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bi1	2985(219)	132(7)	22(2)	102(37)	18(19)	30(4)
Bi2	1589(240)	36(4)	22(4)	−13(23)	−48(22)	17(3)
Bi3	1847(210)	25(3)	26(4)	63(40)	−106(26)	−13(3)
Bi4	760(183)	93(7)	22(4)	−17(31)	−37(17)	16(5)
Bi5	963(130)	38(4)	23(2)	−33(35)	99(16)	18(2)

Bi1′–Bi1–Bi2–Bi3–Bi4–Bi5–Bi5′ distances in the chain are 3.796(7), 3.836(7), 3.557(7), 3.484(7), 3.579(6) and 3.544(5) Å, respectively. The O7 atoms join the adjacent infinite chains through every 10 links of the chains. The position of the O7 atom differs from that found by Yamamoto *et al* [5]. Such an interchain oxygen atom and a similar structure of the BiO layer was described in [21] for Bi$_2$Sr$_2$MnO$_{6.5}$, which is isomorphous to the Bi$_2$Sr$_2$CuO$_{6+x}$ superconductor.
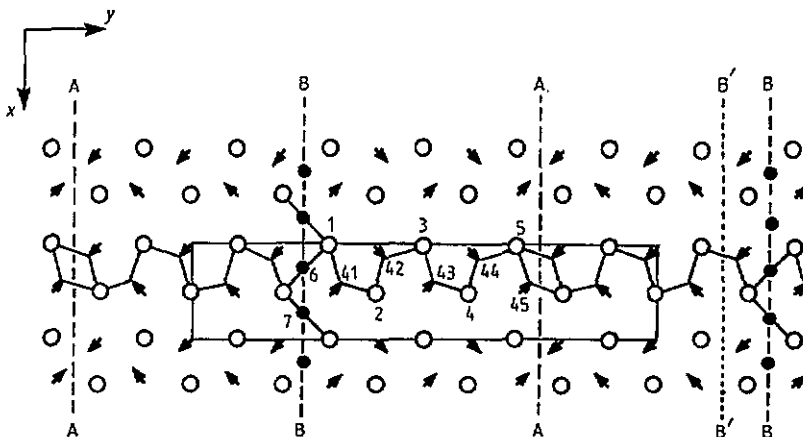

Figure 1. Scheme of the BiO chains forming in the BiO layer. The shifts of the oxygen atoms are marked by arrows. The open circles are Bi atoms. The labelling of the atoms is given according to table 2. the boundaries AA and BB between the bands with opposite sign of atomic shifts are shown (see text).

In order to realize the general principle of formation of such topologically complicated Bi–O–Bi chains, we consider the ideal rock-salt scheme of the BiO layer shown in figure 1. The Bi atoms are located in the vertices of the squares with side of about 3.84 Å and the oxygen atoms occupy the centres of the squares. However, such a scheme results in a rather long Bi–O distance of about 2.7 Å. To obtain the ordinary umbrella-like pyramidal coordination of Bi^{3+}, the oxygen atoms are displaced towards the square edges. If the displacements are not correlated, there will be no special direction in the BiO layer. Such a case takes place in the TlO layer of the Tl superconductors [22] which are isostructural to the Bi$_2$Sr$_2$Ca$_n$Cu$_{n+1}$O$_{6+2n+x}$. If the oxygen shifts are correlated, a special direction emerges in the BiO layer, and the Bi–O–Bi chains are formed. The topology of the chains will depend on the correlation law. In the modulation-free compound Bi$_{2-z}$Pb$_z$Sr$_2$Ca$_{1-y}$Y$_y$Cu$_2$O$_{8+x}$ [11], there is only one displacement direction, as it takes place at ferroelectric transitions.

The unit-cell parameter along the displacement direction does not change and only one kind of infinite zigzag chain is built in the BiO layer. Therefore, these crystals have no modulation.

In the case of pure $Bi_2Sr_2CaCu_2O_{8+x}$ compounds, the law of displacements of the oxygen atoms shows up just as at antiferroelectric transitions. In the band consisting of five rows of O(Bi) atoms, parallel to the a axis, the y component of the displacement has an identical sign, and in the adjacent bands the sign of the y component is the opposite. The displacements of the oxygen atoms of the BiO layer are shown by arrows in figure 1. Such correlated shifts lead to the formation of the 10-membered zigzag chains $Bi_{10}O_{10}$; one of them is marked with open circles (the Bi atoms) and lines (Bi–O–Bi bonds).

The existence of two kinds of bands with antiparallel shifts of the oxygen atoms causes the appearance of two types of boundaries between the bands labelled AA and BB in figure 1. The oxygen atoms are shifted towards the AA boundary, moving away from the BB one. These shifts can be accompanied by shifts of the Bi atoms and of the atoms connected to them, giving rise to atom-concentrated and -diluted regions. The chain $Bi_{10}O_{10}$ is centrosymmetric. The centre of symmetry is situated on the AA boundary. Two parts of the chain are connected by two Bi–O bonds in the concentrated region near this boundary. The extra oxygen atoms O6 and O7 occupy positions on the line BB in the diluted region. Thus, from our consideration, we have obtained the topology of the BiO layer, which is in full coincidence with one found in this work.

The shifts of the oxygen atoms in the BiO layer correlated with respect to the antiferroelectric law give rise to the fivefold increase of the b parameter of the unit cell, and the crystal structure becomes commensurately modulated. The commensurate modulation was observed in $Bi_2Sr_2CaCu_2O_8$ [8] and in the isomorphous $Bi_2Sr_3Fe_2O_{9.2}$ [9].

However, in most cases the sign change of the y component of the displacements occurs not very regularly, every five rows. For example, the line BB in figure 1 can be situated in the site B′B′, and the periodicity along the b axis is changed. In a general case, the modulation period will be

$$pb_0 = b_0 \sum_i n_i p_i$$

where p_i is the probability of the band consisting of n_i rows and b_0 is the period of the fundamental structure. If the band width n_i is 5 or 4 rows with probabilities 0.75 and 0.25, respectively, then the modulation period will be equal to $4.75b_0$. This value is in good agreement with the observed modulation period in our and other [3–7] Bi-2212 crystals. Cationic substitutions can change the relative concentration of the bands with a different width and lead to different modulation periods, $4 < p < 4.75$ [11], $p > 5$ [10, 11]. Direct measurement of the distances between similar boundaries by the high-resolution electron microscopy (HREM) technique and determination of the modulation periods from electron diffraction have shown a close interrelation between the number and the width of the bands, on the one hand, and the modulation period, on the other [22–24].

3.3. Harmonic analysis

Analysis of the modulation of structural parameters as a function of the y coordinate has been carried out using the Fourier technique by calculation of the five harmonics for all parameters of the atoms in the fundamental unit cell. The analysis showed that the deviations from the respective average values of the x coordinates as well as of the thermal and occupational parameters of the atoms are rather random. The wave amplitudes of the y and z coordinates

modulation obtained by us are very close to those found in [3–9]. Figures 2 and 3 show the displacements (Å) of the y and z coordinates of the atoms from their average values versus the y coordinate of the unit cell. The displacive modulation waves calculated using only the first and second harmonics are plotted by the full curves.
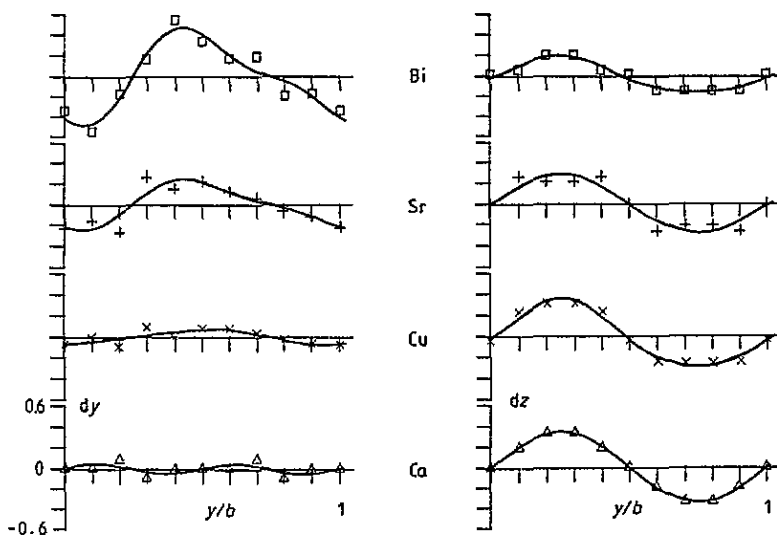

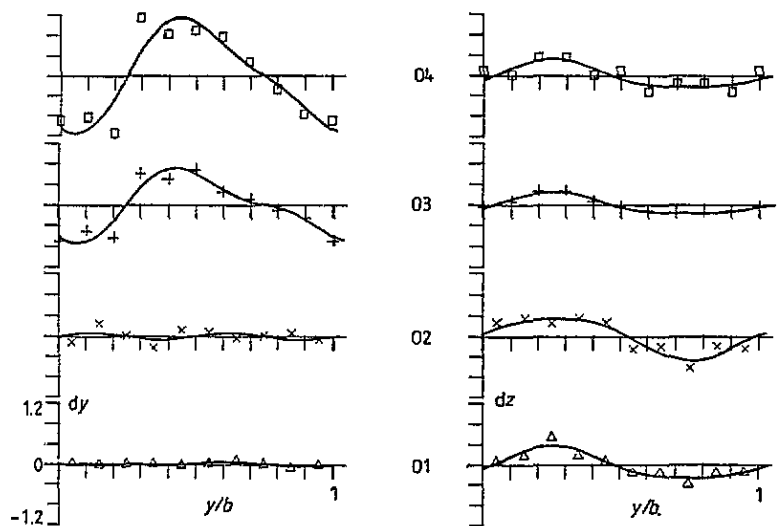**Figure 2.** The y and z components (Å) of the displacive modulation for cations.

Figure 3. The y and z components (Å) of the displacive modulation for oxygen atoms. Labelling of the atoms is given according to table 1.

As can be seen from figures 2 and 3, the y coordinate of the O4 atom of the BiO layer has the maximum shift and its modulation function can be described by a linear saw-like

function. In figures 2 and 3, the boundary AA passes at $y/b = 0.75$ and BB at $y/b = 0.25$. Thus it means that, the closer the atom is to the AA boundary, the smaller its displacement towards AA. The Bi and Sr cations as well as the O3 atoms located in the same layer as the Sr cations have similar but more smoothed modulation functions of the y coordinates. In the copper–oxygen plane and in the Ca layer, the modulations of the y coordinates of atoms are negligible.

The modulation of the z coordinates of all atoms has a wave-like form. The atoms in the copper–oxygen plane and in the Ca layer have the maximum amplitudes of the modulation waves. It seems that the change of distances caused by the shifts along the b and c axes of the Sr and O3 atoms is compensated by the shifts of the z coordinates of the Cu, O1 and O2 atoms only. The Ca atoms sandwiched by the copper–oxygen planes are shifted with the Cu, O1 and O2 atoms of these planes.

The distances between two neighbouring BiO layers vary in accordance with the wave-like function of the z coordinate modulation. In the concentrated region (line AA), the interatomic distances from Bi atoms of the BiO layer to the oxygen atoms of the adjacent BiO layer are longer (Bi4–O44$'$ = 3.82(6) Å, Bi5–O45$'$ = 3.63(6) Å) then those in the diluted region (Bi1–O41$'$ = 2.93(8) Å).

3.4. Occupancy of the cationic positions

As can be seen from table 2, the occupancies of many cationic sites differ from unity. The average values for the Bi, Sr, Ca and Cu cation occupancies of 0.91, 0.88, 1.23 and 0.93 are in good agreement with those obtained for the fundamental structure (table 1). The occupancies of the Sr3, Ca1 and Ca3 sites are greater than unity. It is evident that the heavier atoms are located in these positions. If one assumed that the x-ray scattering power of the atom is proportional to its atomic number, full occupancies of the sites Sr3, Ca1 and Ca2 would be obtained by $0.71Sr + 0.29Bi$, $0.97Ca + 0.03Sr$ and $0.36Ca + 0.64Sr$, respectively.

With the assumption of full occupancies of the oxygen sites and the presence of vacancies in the cationic positions with occupations less than unity, the composition of this crystal is $Bi_{1.94}Sr_{1.78}Ca_{0.72}Cu_{1.86}O_{8.4}$. This composition is in fair agreement with that determined by x-ray spectral microprobe analysis, $Bi/Sr/Ca/Cu = 1.90/1.79/1.00/1.86$.

3.5. Alkaline-earth vacancies

The crystal investigated by us contains intra- and interchain extra oxygen atoms in the BiO layer, and the onset temperature T_c of the superconducting transition of this crystal is equal to 80 K. Close values of T_c are shown by crystals Bi-2212 containing only intrachain oxygen atoms [4, 6, 7] and crystals without extra oxygen atoms [8] and without modulation [11]. Obviously, the extra oxygen content of the BiO layer is not the main factor defining the superconducting properties of the Bi-2212 compound. The same can be said about the displacive modulation of the BiO layer.

The marked peculiarity of the structure of the investigated crystal is a rather great concentration of the vacancies in the Sr positions. The absence of Sr^{2+} (or Ca^{2+}) must be compensated by two holes in the CuO_3 layer. Therefore, the hole conductivity of the CuO_3 layer results from the existence of cationic vacancies in the Sr (and Ca) positions. This assumption is supported by the fact that the compound Bi-2212 without the cation deficiency did not show the superconducting transition, and the sample with a deficiency of Sr was a superconductor with $T_c = 80$ K [25].

3.6. Percolative cluster in the copper–oxygen layer

Previous studies of the $YBa_2Cu_3O_{6+x}$ and $La_{2-x}Sr_xCuO_4$ superconductors showed that the existence of superconducting properties in the compounds is closely connected with the existence in their structures of an infinite percolative cluster (percolative network) from Cu–O bonds with undistorted electronic structure [26–28]. The generation of the percolative picture can be considered in the copper–oxygen layer of the Bi-2212 superconductor, too.

Without vacancies, the bridging oxygen atom of the Cu–O–Cu bond is surrounded by four alkaline-earth cations. The action of the Sr and Ca cations on the Cu–O–Cu bonds is equivalent, because the electronic shells of these atoms are similar. The presence of a vacancy in the coordination of the oxygen atom distorts somewhat the electronic structure of the Cu–O–Cu bond. Therefore, the Cu–O–Cu bonds may be subdivided into two groups, namely one with undistorted and another with distorted electronic structure. According to the percolation theory, the infinite cluster with undistorted Cu–O–Cu bonds will exist if the fraction of these bonds in the copper–oxygen plane exceeds the percolation bond limit P_c, which is equal to 0.50 for the square lattice [29, p 140]. In our case, the position of Ca is fully occupied by alkaline-earth cations and the exceeding of the limit will take place at $P(Sr)^2 > P_c$ or $P(Sr) > 0.71$, where $P(Sr)$ is the occupancy of the Sr position by the Sr (and Ca) cations.

The random distribution of the vacancies over the crystal leads to the appearance of regions in which the concentration of vacancies is increased. The electronic structure of such regions seems to be different from those of the vacancy-diluted regions. The average size of the regions with distorted bonds is equal to the correlation length [29, p 135] of the infinite percolative cluster $L = d/[P(Sr)^2 - P_c]^{1.33}$, where $d = 3.83$ Å is the mean period of the square lattice in which the Cu atoms are situated. We have assumed that for the existence of superconductivity it is necessary that the average size of the vacancy-concentrated regions must be greater than the correlation length of the Cooper pair, which is about 25 Å in Bi-2212 [30, 31]. Using the expression for the correlation length of the cluster, we can obtain the upper limit of the Sr site occupancy equal to 0.86. In the crystal investigated by us, the mean Sr site occupancy is 0.75, and this value is within the mentioned range 0.71–0.86.

The disturbance of electroneutrality caused by the lack of the Sr^{2+} cation is compensated by the appearance of two holes in the conducting copper–oxygen plane. The observed deficiency of Sr^{2+} corresponds to the concentration of holes equal to 4.3×10^{21} cm^{-3}. This concentration estimated from the structural data is very close to the value of 4.6×10^{21} cm^{-3} obtained by Hall's method for the crystal Bi-2212 having parameters $a = 5.409$, $b = 5.414$, $c = 30.81$ Å and $T_c = 77$ K [32], similar to the ones for our crystal.

Of course, the presence of other defects, for example the substitution of alkaline-earth cations by Bi or the deficiency of Cu cations, can somewhat change the above values of the concentration limits, but in general the percolation picture of the copper–oxygen plane will be maintained.

4. Conclusions

The approximation of the commensurate modulated supercell by using the 3D space symmetry group has made it possible to obtain the modulation displacement parameters of all atoms in the structure. The amplitudes of the first and second harmonics are in good agreement with those found in other studies using the 4D space group technique. Harmonic analysis of the atomic displacements showed the remarkable contribution of the third and fourth harmonics to the displacement modulation functions of the Sr and O atoms.

The extra oxygen atoms have been observed both inside and between the Bi–O–Bi chains in the BiO plane. The topology of the Bi–O–Bi chains, the modulation of the structure and the form of the modulation displacement functions can be explained by the shifts of the oxygen atoms in the BiO layer correlated according to the antiferroelectric law. A randomly occurring disturbance of the change of the shift sign results in the incommensuration of the modulation.

The lack of cations in the Sr sites is compensated by the appearance of holes in the copper–oxygen planes and creates the percolation picture in the copper–oxygen square 2D lattice on the Cu–O–Cu bridging bonds with distorted and undistorted electron structure. We believe that superconductivity takes place in the case if in the copper–oxygen plane there is an infinite conducting cluster consisting of Cu–O–Cu bonds with undistorted electron construction and if the correlation length of the cluster is greater than the size of the Cooper pair.

Acknowledgments

Note added in proof. Intra- and interchain extra oxygen atoms in similar sites of the BiO plane have been found by Bescrovnyi *et al* [33] in single-crystal neutron diffraction study of $Bi_2Sr_{2.4}Y_{0.6}Cu_2O_{8+x}$ with the modulation period of $4.25b$.

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