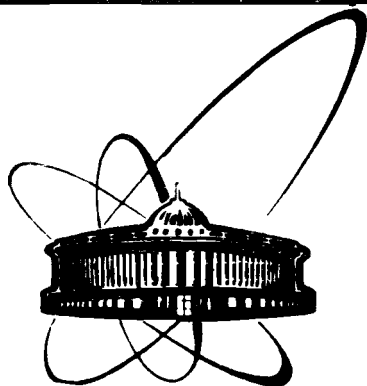


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ДУБНА

B 35

E14-89-795

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NEUTRON DIFFRACTION STUDY
OF THE MODULATED STRUCTURE
OF $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$

Submitted to "Physica C"

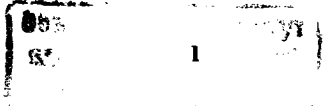
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Introduction

A simplified structural model of the high-temperature superconductor $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_8$ is of a high tetragonal symmetry $F4/mmm$ ($a=5.4 \text{ \AA}$, $c=30.7 \text{ \AA}$). It is built of two alternating blocks, the oxygen - deficient perovskite (P) block and the triple-layer rock-salt block (RS) (See Fig.1). In the centre of the P block there are two conducting CuO_2 planes which sandwich the Ca layer. Because of the mentioned oxygen deficiency, calcium is eight-fold (cube) coordinated instead of the common dodecahedral coordination of large cations in perovskites. The coordination of copper is square-pyramidal in which, however, the apical oxygen is largely displaced leaving copper effectively in the square-planar bonding. The Sr sites are located at the boundary of both blocks and their surroundings is the mixture of the dodecahedral and octahedral coordinations. It involves nine close oxygen atoms.

The Bi cations are in the centre of the rock-salt block and their coordination shown in Fig.1 is octahedral. Such arrangement would be, however, unstable since it brings four oxygen neighbours within the Bi layer to a distance $a/2 = 2.7 \text{ \AA}$ which is out of the region of possible $\text{Bi}^{3+} - \text{O}$ bonds ($2.0 - 2.5 \text{ \AA}$). In fact, the Bi coordination is largely distorted. That is the main reason for a decrease of the $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_8$ symmetry and appearance of a superstructure with period of approximately $5a$.

As it is known from the early work of Subramanian et al.[1] and following single-crystal studies the fundamental structure can be described within the orthorhombic symmetry $Amaa$. There is much less confidence about the nature of the superstructure. The most complete information about the real arrangement of



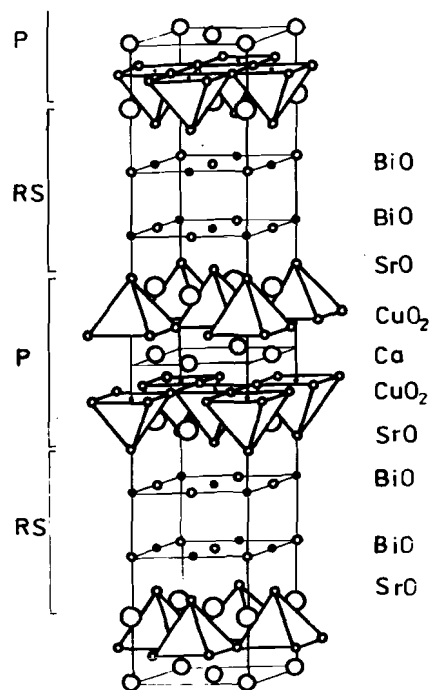


Fig.1 - Scheme of the Bi₂Sr₂CaCu₂O₈ structure.

(P- the perovskite block, RS- the rock-salt block).

atoms comes of Gao et al.[2] who analyzed own single-crystal X-ray data using the approach of incommensurate modulation of the displacive type. They determined the modulation of Bi, Sr and Cu cations and average positions of other atoms. Observed modulation displays components mainly in the a, c plane and amplitudes are as large as 0.5 Å. Independently on their work we have undertaken a single-crystal neutron diffraction study and solved the problem of the superstructure using a different procedure. Here we present our results.

Instrumentation and samples

Diffraction measurements were performed by the time-of-flight method on the neutron diffractometer DN-2 which is equipped with

the linear position-sensitive detector. The diffractometer is placed at the mirror-guide tube of the pulsed reactor IBR-2 at the Joint Institute of Nuclear Research in Dubna. The great advantage of the apparatus is the scanning of the whole angular sector (~10°) of the reciprocal plane at once and the high counting rate which is necessary for the investigation of extremely small crystals.

The integrated intensity of the Bragg reflection (intensity of a Laue spot) is given [3] by

$$I_{obs} = \frac{F_{hkl}^2 \lambda^4}{\sin^2 \theta} N(\lambda),$$

where $N(\lambda)$ is the spectrum of the white neutron beam incident the sample. With the use of the mirror guide the spectrum has a cut-off at $\lambda \sim 1$ Å, maximum at $\lambda \sim 2$ Å and falls down in the long-wavelength side approximately as λ^{-4} . From that it follows that the experimental sensitivity to the structure factor F_{hkl}^2 is nearly uniform in the region $\lambda > 2$ Å (practical limit is 8 Å), but it decreases quickly in the short-wavelength side. With the detector in positions $2\theta = 20^\circ - 120^\circ$ the range $\lambda = 2 - 8$ Å corresponds (Bragg law $\lambda = 2d \cdot \sin \theta$) to the interplanar spacing $d = 1.1 - 25$ Å which was the actual extent of our investigation.

Samples Bi₂(Sr,Ca)₂Cu₂O₈ used in our study were grown by a pseudo-flux method from melts with excess of copper [4]. The samples were of the plate or wedge shape with maximum face 2x2 mm² and width up to 0.8 mm. Some samples displayed facets apparently at right angles, giving the impression of a single crystal. However, the neutron diffraction has shown that each specimen contained several single-crystal blocks, sometimes slightly misoriented, sometimes disposed nearly perpendicularly. Comparison with diffraction on a very thin mica-like platelet revealed that even in bulk samples the width of blocks (the dimension along the c-axis) was microscopic.

In all investigated blocks the $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_8$ phase ($c=30.7 \text{ \AA}$) was found to be interleaved with layers of the $\text{Bi}_2(\text{Sr,Ca})\text{CuO}_6$ phase ($c=24.3 \text{ \AA}$) the amount of which was estimated on the basis of diffracted intensity to 5%. On the other hand, no signs of the $\text{Bi}_2(\text{Sr,Ca})_4\text{Cu}_3\text{O}_{10}$ phase ($c=37 \text{ \AA}$) were detected in our samples.

Extensive diffraction study was performed on a specimen which contained only two relatively large single-crystal blocks, quite misoriented. Investigation on one chosen block included measurements of four reciprocal planes $hk0$, $h0l$, $0kl$, hh' and number of individual reflections associated mostly with the superstructure. Each measurement, which generally comprised detection of one or few reflections (sometimes with their higher orders), took 3 hours. Because of this long exposure the study was confined to one octant only and the h, k, l symmetry was checked on selected reflections.

Measurements by the time-of-flight method are generally strongly influenced by the secondary extinction because of long wavelengths used. To investigate its role, strong reflections were measured at different azimuthal angles, varying thus the mean diffraction path \bar{T} . Such experiments with the strongest reflection 220 allowed us to estimate the width of the investigated block from dimensions of its face (the a, b plane) seen on the surface of the sample. The size of the block was established as $1.5 \times 1.0 \times 0.03 \text{ mm}^3$. Thanks to the very small width, nearly all strong and medium reflections could be measured practically extinction free. Few exceptions were corrected (max. to 20%) using the factor

$$y = (1 + k \frac{F^2 \lambda^3}{\sin 2\theta \bar{T}})^{-1/2}$$

Results

Neutron diffraction experiments showed the same diffraction picture as the previous X-ray study of Gao et al. [2] -

fundamental reflections characteristic for the A_{221} space group (observed lattice parameters $a=5.397(1)$, $b=5.401(1)$, $c=30.716(3) \text{ \AA}$) and satellites of the first and second order in position given by the modulation vector $2\pi[\tau, 0, 1]$ with the observed value $\tau=0.213(3)$ (modulation period $4.69(7)a$). In the investigated part of the reciprocal space the observable intensities were detected for nearly all fundamental reflections allowed by the A_{221} symmetry and for about a half of satellites of the first order. Satellites of the second order were observed only in few cases.

Most data concerning the superstructure were obtained from the $h0l$ plane. There were several strong satellites $\tau 0 l$ which indicated large modulation of atomic layers along the c -axis. Remarkably strong were the satellites $2+\tau 0 l$ (the satellite reflection $2.21 0 1$ was very strong even among the fundamental reflections and reached 1/6 intensity of the strongest reflection 220). Relatively strong were also some second-order satellites $4+2\tau 0 l$ (especially $4.42 0 0$). On the other hand, satellites $2-\tau 0 l$ were weak. Such observation indicated that some atoms in the $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_8$ structure were arranged along the a -axis with spacing rather $a/2.21 = 2.44 \text{ \AA}$ than with $a/2 = 2.7 \text{ \AA}$ inherent in the true A_{221} symmetry. We inferred immediately that such property is associated probably with oxygen in the Bi layer and that the misfit is compensated by insertion of extra oxygen after each modulation period.

Search for the satellites was accomplished in the $hk0$ and $0kl$ planes. In the former plane and close to it we observed satellites $2+\tau k l$ ($2.21 1 0$, $2.21 2 1$, $2.21 1 2$, $2.21 3 2$). All satellites of other types (i.e. $1+\tau k 0$, $2-\tau k 0$, $3+\tau k 0$) were unobservable. In the vicinity of the $0kl$ plane we investigated satellites $\tau 1 l$, $\tau 2 l$ and $\tau 3 l$. As observable were found only some satellites $\tau 2 l$. Among them the weak satellite $0.21 2 1$ (disposed in the reciprocal space near the 010 line) evidenced

some b-axis modulation of the structure. Other $\tau/2$ satellites with larger l index were associated rather with the c-axis modulation.

In total, we obtained for the structure refinement data on 114 fundamental reflections (including 14 unobservable), 72 satellites of the first order (28 unobservable) and 10 satellites of the second order (4 unobservable). The unobservable satellites included were those which carried a substantial information about the structure or were measured within a very small absolute uncertainty (concretely those with very large d-spacing). The gross of observable intensities displayed statistical uncertainty 10-20%.

Our structural model involved sinusoidal waving of atomic planes and a redistribution of atoms within the planes due to the insertion of extra oxygen into the Bi layer, both periodic along the a-axis. Longitudinal displacements associated with the redistribution were expressed by two harmonics except for oxygens in the Bi layer which were spaced out nearly equidistantly (including, of course, the extra oxygen). First refinements were carried out in the approximation of a supercell $5a \times b \times c$ (i.e. treating τ as equal to 0.2) within the space groups Pnnn and Pmnn. Both variants (See Fig.2a and b) yielded a satisfactory fit of the fundamental and satellite (properly speaking - superstructure) reflections and confirmed the expected excess of oxygen in the Bi layer. We note that the configuration of the BiO layer in the Pnnn model is the same as found recently in the $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_{p,y}$ of the B222 symmetry [5].

Final refinement was performed within a more realistic model shown in Fig.2c. It corresponds to a supercell $19a \times b \times c$, possesses the Pnaa symmetry and unites to some extent configurations in the previous Pnnn and Pmnn models. The Pnaa model accounts for a modulation with the period $19a/4$ ($=4.75a$) which agrees well with existing observations on

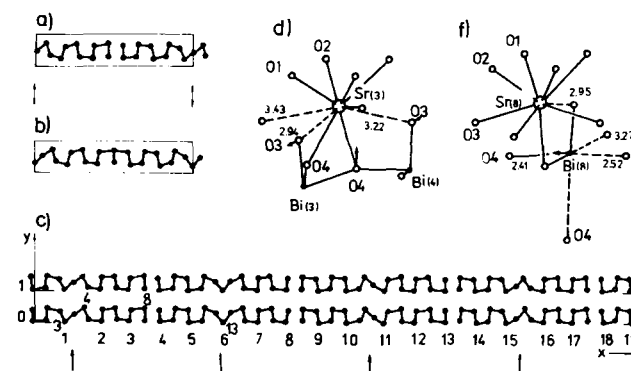


Fig.2 - Bonding in the BiO plane in tentative models Pnnn (a) and Pmnn (b) of the $5a \times b \times c$ superstructure and the conclusive model Pnaa of the $19a \times b \times c$ superstructure (c) (Bi cations shown by full dots; arrows mark the modulation periods, i.e. the places of the inserted oxygen.)

Two exceptional cases of the Bi(j) and Sr(j) coordination for $j=3$ (d) and 8 (f). (Labelling as in Figs.2c and 3a; expected shifts marked.)

$\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_8$. (The most precise determination of the modulation period [2,6] report a value $4.76(1)a$.) The refined structural parameters are given in Tab.I and characteristic features of the superstructure are illustrated in Figs.2c-f,3 and 4. Some x and y coordinates in Tab.I were fixed on special values corresponding to the higher Amaa symmetry since our data were insensitive to small deviations from them (possible range ± 0.01). For some atoms the modulation parameters a_1 , a_2 were smaller than 0.01 and could not be determined with certainty for the same reason.

Finally, we should note that reflections $00l$ appeared to be ~40% enhanced with respect to other reflections. The excess of

Table 1

Structural parameters of the modulated $\text{Bi}_2(\text{Sr,Ca})\text{Cu}_2\text{O}_8$ space group Pnaa ($a = 19 \times 5.397(1) \text{ \AA}$, $b = 5.401(1) \text{ \AA}$, $c = 30.716(3) \text{ \AA}$, $z = 4x19$)

Atom	Number of positions	Gao et al. ^{a)} x_1^0 y_1^0 z_1^0	Present results x_1^0 y_1^0 z_1^0	z_j^0	$B_{\text{iso}}(\text{Å}^2)$	Modulation amplitudes ^{d)} a_1 a_2 c_1	Splitting ^{e)} ΔC	Occupation ^{f)}
Ca, Sr ($j=1,19$)	4x19	0 .5 .5	0 .5 .5	.5	2.3(9)	-	-	.72(9)Ca+.28Sr
Cu ($j=1,19$)	8x19	0 .0002 .4467	~0 .007(3) .4467(2)	~0	2.1(6)	-	-	.0062(16)
Sr ($j=1,19$)	8x19	0 .5037 .3909	~0 .494(2) .3916(4)	~0	2.1(6)	-	-	.0084(10)
Bi ($j=1,19$)	8x19	0 .0215 .3022	~0 .023(3) .3018(2)	~0	2.0(4)	-.047(4)	-.017(4)	-.0078(6)
O1 ($j=1,19$)	8x19	.25 .25 .445	~.25 .25 .445	~.25	0.9(3)	.070(4)	.058(5)	-.0078(6)
O2 ($j=1,19$)	8x19	.25 .75 .452	~.25 .75 .452	~.25	0.9(3)	-	-	-.0086(3)
O3 ($j=1,19$)	8x19	0 -.03 .372	~0 -.033(3) .372(5)	~0	0.9	-	-	-.0086
O4 ($j=1,21$)	8x21	0 .40 .303	~0 .392(5)g) .303	~0	3.9(8)	-.098(5)	.051(8)	-.0061(8)
					3.4(11)	-	-	-.0008(11) .0115(6)

$B_{\text{iso}}^{\text{Cu}} = 13.2 \text{ \AA}^2$

a) Ref. $2/1$, space group Pnaa with origin shifted to the inversion centre at $(0, 1/4, 1/4)$.

b) $x_j^0 = x_1^0 + (j-1) \cdot 0.5$ (except for O4),

$y_j^0 = (j-1) \cdot 19/42 - 4.75/42$ (for O4),

$z_j^0 = (0.25 - x_1^0) \cdot (-1)^j + 0.25$ (except for O4)

d) a,c modulation

$$x_j = x_j^0 + a_1 \sin(2\pi x_j^0/4.75 - \pi/2) + a_2 \sin[2\pi(x_j^0/4.75 - \pi/2)]$$

$$z_j = z_j^0 + c_1 \cos(2\pi x_j^0/4.75 - \pi/2)$$

b modulation (for O4 only)

$$y_j = 0.25 + A \cdot (-1)^j \sin[0.5\pi(x_j^0/4.75 - \pi/2) + K \sin(2\pi x_j^0/4.75 - \pi/2)]$$

where $A = 0.168(7)$, $K = 1.14(35)$.

e) Each site splitted along the c-axis to $z_{j \pm 4c}$.

f) Neutron scattering length used: $b_{\text{Cu}} = 4.900$, $b_{\text{Sr}} = 7.020$,

$b_{\text{Ca}} = 7.718$, $b_{\text{Bi}} = 8.526$, $b_{\text{O}} = 5.805 [10^{-15} \text{ m}]$.

g) Average value over the b-axis modulation.

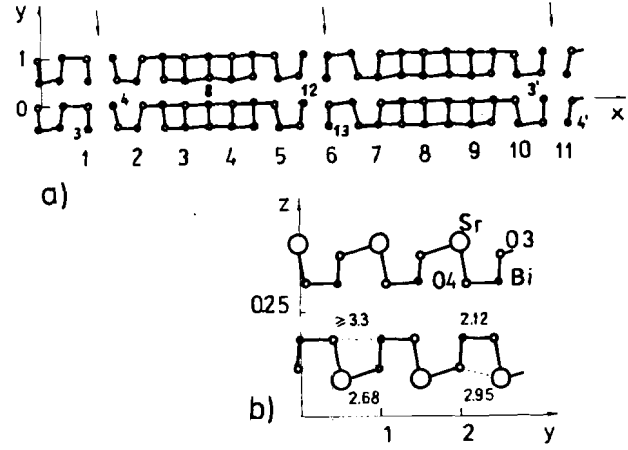


Fig.3 - (a) Bonding in the SrO plane in the Pnaa model (Sr cations shown by full dots) and (b) the Sr-O4-Bi-O3-Sr links along the b-axis.

intensity was related to tiny blocks (some of them evidenced by the diffraction) which were attached to the main block but were misoriented in the a,b plane.

Discussion

Our diffraction experiments have shown that the $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_8$ superconductor, grown by the single-crystal technology, formed lamellar structures consisting of a stacking of microscopically thin blocks misoriented in the basal plane. The $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_8$ blocks were partially interleaved with layers of the related compound $\text{Bi}_2(\text{Sr,Ca})_2\text{CuO}_8$. Exceptionally, thicker blocks of several tens of microns were encountered making the single-crystal study possible. Despite of the pseudocubic metrics of the orthorhombic atomic structure all observed blocks were untwinned.

The essential feature of the modulated structure in $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$ is the insertion of extra oxygen into the BiO

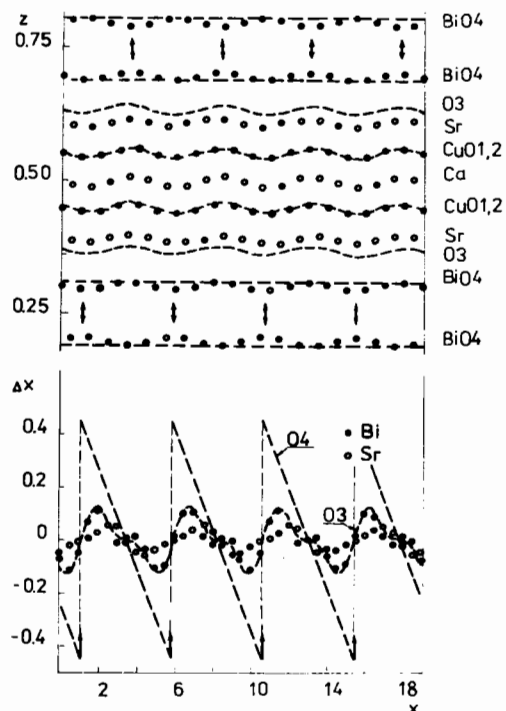


Fig.4 - Waving of atomic planes along the a-axis and the longitudinal displacements observed.

(Cations shown by dots and circles, oxygen atoms by the dashed lines. Note the periodic expansions and contractions of the bismuth bilayers and their opposite phases for $z=0.25$ and $z=0.75$. The arrows mark the location of additional oxygen.)

layers and associated displacive modulation of all layers with the period $4.75a$. This gives rise to a superstructure of the $19a \times b \times c$ type and maximum symmetry $Pnaa$. Structural refinement performed with the use of harmonic analysis resulted in an overall fit of observed and calculated intensities given by the R-factor of 13.2%. Trial refinements going beyond the simplest harmonic analysis indicated, however, that the R-factor could be improved significantly still within the $Pnaa$ space group.

Comparing the refined parameters given in Tab.I with results of previous diffraction studies we find that the cell parameters are smaller than in other single-crystal investigations and are close to the lower limit of values reported for powder samples. This may be a sign of the saturated oxygen content. The average atomic positions are in overall agreement with Ref[2]. A difference occurs for the Sr site which is slightly shifted along the b-axis, increasing thus the bond length to its O3 neighbour to 0.05 \AA , as if our cation was larger. Similar shift, caused perhaps by the $\text{Sr}^{2+} - \text{Cu}^{2+}$ repulsion, is observed for the Cu site. The Cu cation thus occurs slightly off the centre of its square oxygen coordination. In contrary to previous data the average z-coordinates of the O1 and O2 sites are found equal (their modulation is also the same within the e.s.d's). Largely different z-values in Ref [2] and in the powder neutron diffraction work [7] are likely a consequence of omission of the O1, O2 modulation. Extent and the course of the a and c-axis modulation (See Fig.4) is similar to results on the related compound $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_{9+\gamma}$ which exhibits a superstructure of the $5a \times b \times c$ type [5]. Separation of the BiO planes in the bilayer is quite large even in the narrowed place of the inserted oxygen. No additional atoms were detected between them. Total lack of oxygen in the Ca layer was confirmed, as well.

Calculated interatomic distances are summarized in Tab.II. In spite of limitations associated with the harmonic approximation the coordination of cations is highly uniform. All bismuth cations display three nearly perpendicular bonds of $2.0 - 2.2 \text{ \AA}$ length, two of them towards the O4 oxygens in the BiO plane, third to the O3 oxygen in the SrO plane. Other oxygen neighbours are displaced to 3 \AA or more. (Somewhat less advantageous configuration was obtained for Bi(8). Fig.2f shows a shift which would establish a better bonding.) Interconnection of bonds in the BiO plane forms the $\text{Bi}_n\text{O}_{n+1}$ chains ($n = 9$ and

Tab.II Calculated metal-oxygen bonds and close oxygen-oxygen approaches (<2.7 Å) in $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8.21}$

atoms (j=1,19)	number of bonds	range of distances	mean distance
Bi(j) - O3 ^{a)}	1	1.97 - 2.07	2.02
Bi(j) - O4 ^{a)}	1	2.12 - 2.41	2.22
Bi(j) - O4 ^{b)}	1	2.06 - 2.19	2.12
total Bi-O	3		2.12
Sr(j) - O1	2	2.50 - 2.71	2.58
Sr(j) - O2	2	2.53 - 2.74	2.63
Sr(j) - O3 ^{c)}	3	2.45 - 2.81	2.64
Sr(j) - O3 ^{d)}	1	2.66 - 2.70	2.68
Sr(j) - O4 ^{c)}	1	2.52 - 2.80	2.65
Sr(j) - O4 ^{d)}	1-2	2.54 - 2.77	2.63
total Sr-O ^{c)}	8		2.62
total Sr-O ^{d)}	6-7		2.62
Ca(j) - O3	4	2.40 - 2.54	2.47
Ca(j) - O2	4	2.41 - 2.55	2.48
total Ca-O	8		2.48
Cu(j) - O1	2	1.93 - 1.94	
Cu(j) - O2	2	1.88	
total Cu-O	4		1.91
(Cu(j)- O3	1	2.38 - 2.58)	
O4(3)-O4(4) ^{e)}		2.50 (< O4(3)-Bi(3)-O4(4)=72°)	
O4(4)-O4(5)		2.60 (< O4(4)-Bi(4)-O4(5)=74°)	
O4(14)-O4(15)		2.45 (< O4(14)-Bi(3)-O4(15)=71°)	

- a) bonds directed approximately along the a-axis
b) bonds along the b-axis
c) data for atoms out of the region of the inserted O4 oxygen, i.e. except j=3,4,12 and 13
d) data for j=3,4,12 and 13
e) short O-O distances and small O-Bi-O angles are likely artifacts of the sinusoidal approximation of the z-axis modulation (See text and Fig.2d)

10) along the a-axis (See Fig.2c). The excess of oxygen and the configuration of bonds reminds the situation in $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_{9.7}$ [5]. In contrary to it we have found no indications for further segmentation of the $\text{Bi}_n\text{O}_{n+1}$ chains or for the formation of Bi_2O_2 dimers as described in Ref [8].

Strontium cations are bonded to eight oxygen atoms in maximum since one of four O3 neighbours in the SrO plane occurs always in a non-bonding distance larger than 2.9 Å. The net of the Sr-O bonds shown in Fig.3a displays the Sr_nO_n chains (n =9 and 10) along the a-axis which are terminated in the vicinity of the inserted oxygen in the Bi layer. There is a link of the Sr_nO_n and $\text{Bi}_n\text{O}_{n+1}$ chains along the b-axis as shown in Fig.3b. The mean Sr-O bonding length amounts to 2.62 Å and slightly exceeds the sum of ionic radii. This suggests that the decreased scattering length, observed in the Sr site, is rather due to a partial occupation (93%) than by some calcium substitution. The most likely location of Sr vacancies are the unfavorably coordinated sites which terminate the Sr_nO_n chains and are labelled 3, 4, 12 and 13 in Fig.3a. These sites (expected occupation -1/2) form zigzag chains along the b-direction. We note also that oxygen O3 (apical in the CuO_5 pyramid) makes a closest approach to copper just at the mentioned sites. In principle the real location of vacancies could be revealed by diffraction. Our data appeared, however, quite insensitive.

Second alkali-ion site located between the CuO_2 planes, is coordinated via 2.48 Å bonds to eight oxygens in corners of an elongated cube. According to the observed scattering length, the site is occupied by 72% Ca and 28% Sr. Total composition is thus given by the formulae $\text{Bi}_2\text{Sr}_{2.14}\text{Ca}_{0.72}\text{Cu}_2\text{O}_{8.21}$. This corresponds to the formal copper valence of 2.35.

Calculated oxygen-oxygen distances involve a couple of approaches of 2.5 Å only (occurring e.g. in the Bi(3) coordination shown in Fig.2d). These very short distances are artifacts of the harmonic analysis which is not able to describe discrete features of the modulation in places of the inserted oxygen. Trial refinements performed with the more symmetrical models within the 5a x b x c approximation did show that atoms O4, instead of lack of any c-axis modulation in Fig.4, in fact

follow to some extent the waving of the Bi layer, except for the inserted oxygens (e.g. O4(4)) which are shifted to a position intermediate between the O4 and O3 levels. The shift of O4(4) is accompanied with solitary shifts of O3(3) and O3(4) as marked in Fig.2d. In this way the oxygen-oxygen distance increases to $\sim 2.7 \text{ \AA}$ and the O-Bi-O angle becomes closer to 90° .

Besides the modulation given by the harmonical amplitudes a_1 , a_2 and c_1 , the structure involves other considerable displacements. They manifest themselves in the anisotropy of the temperature factor. Concretely, large displacements along the c-axis were evidenced for sites O4, O1+O2, Sr, Ca and Cu. (They were characterized in Tab.I within a split-atom model by the amplitude Δc .) On the other hand, the O3 site exhibited somewhat larger displacements in the basal plane. We concluded that the main contribution to the splitting amplitude Δc comes from random displacements arising due to the dissimilar size of atoms in the mixed (Ca,Sr) site and due to vacancies present in the Sr site. Other possibilities like the modulation with period $9.5a$ (inherent in the Pnaa model), the second and higher order harmonical c-axis modulation or a corrugation of atomic planes due to some cooperative ordering may apply only to some of the mentioned sites or can contribute in a limited extent.

Concluding remarks

The complexity of the $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$ structure originates from the peculiarities of the Bi^{3+} bonding. It is known that this cation has a lone pair which leads generally to a distorted coordination. Namely, in the direction of the lone pair the oxygen atoms are largely displaced whereas opposite to it short bonds occur. Such coordination cannot be realized within a simple tetragonal model. It is achieved by two mechanisms - by the ordering of long (non-bonding) and short (bonding) Bi-O distances along the b-axis and by formation of the $\text{Bi}_n\text{O}_{n+1}$

chains along the a-axis through the inserted oxygen. The former mechanism results in an orthorhombic distortion of the Amaa symmetry. The later one is responsible for waving of atomic layers along the a-axis and for considerable longitudinal modulation within some layers. Transversal modulation along the b-axis is certain only for oxygen in the BiO layer. In spite of the non-integer period of the modulations there are strong indications that the superstructure is commensurate with a cell 19 times enlarged in the a-direction. This supercell comprises four modulation periods of $4.75a$. A direct proof of the commensurability would be e.g. an observation of a modulation with double period $9.5a$ which might manifest itself by very weak superstructure reflections.

The $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$ structure involves one rather theoretical aspect. The Bi_2O_2 bilayers are in the Pnaa symmetry formally polar. Realization of a polarized state would be e.g. possible if the cation vacancies present in the Sr layer were distributed in an ordered way over the sites suggested in the present study.

Acknowledgement

The authors thank to Drs. S.Durčok and M.Nevřiva for the preparation of the single crystals.

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Received by Publishing Department
on November 27, 1989.

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E14-89-795

Нейтроннографическое исследование модулированной структуры $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$.

Исследование 80 K сверхпроводника $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$ проводилось в широкой области обратного пространства с помощью времяпролетного нейтронного дифрактометра DH-2 с однокоординатным позиционно-чувствительным детектором. Модуляция структуры была уточнена по набору дифракционных рефлексов, полученных от монодоменного блока размерами $1,5 \times 1,0 \times 0,03 \text{ nm}^3$. Модуляция признака соизмеримой с периодом $4,75 \text{ \AA}$, что дает сверхрешетку $19 \text{ a} \times \text{b} \times \text{c} / \text{a} = 5,397(1), \text{b} = 5,401(1), \text{c} = 30,716(3) \text{ \AA}$ / и симметрию Pnaa . Основной чертой структуры является периодическое внедрение дополнительных рядов атомов кислорода в плоскости BiO , что вызывает большие модуляции всех слоев. Идеальное стехиометрическое соотношение для кислорода составляет $\gamma = 4/19 \approx 0,21$. Связи в плоскостях BiO и SrO создают характерные цепочки вдоль оси a . Окружение катионов Bi^{3+} является однообразным и состоит из трех почти перпендикулярных связей с атомами кислорода длиной $2,0\text{-}2,2 \text{ \AA}$. Катионы Sr^{2+} связаны максимально с восемью атомами кислорода. Часть позиций Sr , находящихся вблизи внедренного кислорода, могут остаться вакантными. Позиция Ca между плоскостями CuO_2 на 30% замещена атомами стронция.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

Preprint Объединенного института ядерных исследований. Дубна 1989

Beskrovnyl A.I. et al.

E14-89-795

Neutron Diffraction Study of the Modulated Structure of $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$

The modulated structure of the 80 K superconductor $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$ is refined from the single-crystal neutron diffraction data on a monodomain block of dimensions $1.5 \times 1.0 \times 0.03 \text{ nm}^3$. The modulation is recognized as commensurate with period 4.75 \AA , resulting in the supercell $19 \text{ a} \times \text{b} \times \text{c}$ ($\text{a} = 5.397(1), \text{b} = 5.401(1), \text{c} = 30.716(3) \text{ \AA}$) and symmetry Pnaa . The essential feature of the structure is the periodic insertion of additional oxygen rows into BiO planes, which in turn causes large displacive modulation in all layers. The ideal oxygen stoichiometry is $\gamma = 4/19 \approx 0.21$. Bonds in the BiO and SrO plane form characteristic chains running along the a -axis. The coordination of the Bi^{3+} cations is uniform and consists of three mutually nearly perpendicular bonds to oxygens of $2.0\text{-}2.2 \text{ \AA}$ lengths. The Sr^{2+} cations are bonded only to eight oxygen atoms in maximum. About 7% of the Sr sites, located in the vicinity of the inserted oxygen, are possibly vacant. The Ca site situated between the CuO_2 planes is substituted to 30% by strontium.

The investigation has been performed at the Laboratory of Neutron Physics, JINR.

Preprint of the Joint Institute for Nuclear Research, Dubna 1989