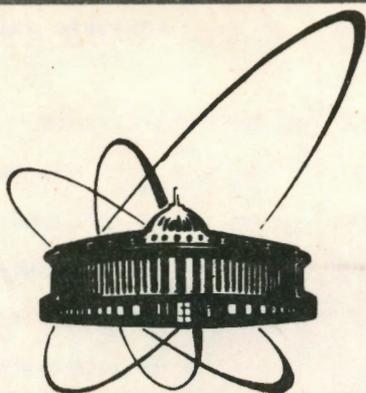


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ОБЪЕДИНЕННЫЙ  
ИНСТИТУТ  
ЯДЕРНЫХ  
ИССЛЕДОВАНИЙ  
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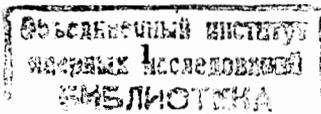
STUDY OF THE MODULATED STRUCTURE  
OF  $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$   
IN THE RANGE 8 - 920 K

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## Introduction

Recent diffraction studies on the 80 K superconductor  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  [1,2] and on the related (semiconducting) compound  $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_{9+\gamma}$  [3] have shown that their structural complexity originates from the peculiarities of the  $\text{Bi}^{3+}$  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 based on a stacking of two structural blocks - the triple rock-salt layer  $\text{Bi}_2\text{SrO}_3$  and the double perovskite-like layer  $(\text{Sr,Ca})_2\text{Cu}_2\text{O}_5$  or  $\text{Sr}_2\text{Fe}_2\text{O}_6$ . It appears that the stable configuration in which each  $\text{Bi}^{3+}$  cation actually acquires three nearly perpendicular Bi-O bonds of 2.0 - 2.2 Å lengths is achieved by two mechanisms - by the ordering of long (non-bonding) and short (bonding) Bi-O distances along one basal axis and by formation of  $\text{Bi}_n\text{O}_{n+1}$  chains along the second basal axis through an ordered insertion of extra oxygen (see [2]). The former mechanism results in an orthorhombic distortion (for the cuprate, of the A<sub>2</sub> symmetry). The latter one is responsible for a superstructure which manifests itself by waving of all atomic layers along the orthorhombic a-axis and by a rearrangement of atoms in the BiO and adjacent layers. Period of this structural modulation, i.e. the spacing with which the extra oxygen rows are incorporated into the BiO planes, amounts for  $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_{9+\gamma}$  [3] to 5a, giving  $\gamma=1/5$ . The data for the cuprate are to some extent controversial. The high-resolution



electron microscopy often reports various sequences of 4a and 5a periods. The X-ray and neutron diffraction on well-crystallized specimens evidence, however, that the insertion of extra oxygen occurs in fact periodically with spacing which equals or very closely approaches 4.75a, independently on the provenance of samples and their actual composition (compare e.g. Ref.[1,2,4]). This indicates that despite of the non-integer period of the modulation the superstructure is commensurate with a cell 19 times enlarged in the a-direction. This  $19a \times b \times c$  supercell comprises four modulation periods of 4.75a. The overall symmetry assigned to  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  [2] is Pnaa and the ideal oxygen stoichiometry  $\gamma=1/4.75 \sim 0.21$ . We note that the structural model derived in Ref.[2] could be realized with a non-commensurate period as well, of course with loss of the symmetry.

Electronic properties of layered cuprates and, particularly, the effect of superconductivity is related to the copper valence state and the Cu-O bonding. In the high-temperature superconductors with hole carriers copper is coordinated by an elongated oxygen octahedron or a square pyramid. In their bases there is approximately square-planar bonding to four oxygens at a distance 1.9 Å, which creates a  $\text{CuO}_2$  net - the main conducting layer in the structure. Remaining two or one (apical) oxygens are displaced to 2.2 Å or even more. A strong correlation between geometry of the copper coordination and the superconducting properties was deduced from data on cuprates of the  $\text{La}_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  types [5]. On the other hand, our recent (room-temperature) data on  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  [2] showed that the interatomic distances and angles in the copper coordination were

dissimilar to the 93 K superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  despite of the relative closeness of critical temperatures. Namely, copper in the bismuth compound occurs nearly in the plane of its four oxygen neighbors in the  $\text{CuO}_2$  layer whereas in the yttrium compound (see e.g. [6]) it is displaced to 0.3 Å from that plane. The distance to apical oxygen in the  $\text{CuO}_2$  pyramid amounts to 2.5 Å (the average value - actual range over the modulation period 2.38-2.58 Å) and 2.3 Å, respectively. It is, therefore, of primary interest to investigate whether such differences persist to low temperatures where the superconductivity begins. This was why we have continued with a rather tedious neutron diffraction study on our single crystal at temperatures just above and below  $T_c$ . In addition, we performed powder measurements on a ceramics at elevated temperatures up to 650°C.

#### Samples and the instrumentation

Diffraction measurements were performed by the time-of-flight method on the diffractometer DN-2 situated at the pulsed reactor IBR-2 of Joint Institute for Nuclear Research, Dubna (USSR). The apparatus, quality of the  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  crystal and the experimental procedure were described in our previous room-temperature study [2]. We note that dimensions of the single-crystal block investigated were  $1.5 \times 1.0 \times 0.03 \text{ mm}^3$  and its actual composition was established as  $\text{Bi}_2\text{Sr}_{2.14}\text{Ca}_{0.72}\text{Cu}_2\text{O}_{8.21}$  corresponding to formal copper valence 2.35. This formula reflects a mixed occupation 72% Ca + 28% Sr of the cube-coordinated site in the middle of the perovskite block and some

cation vacancies in the Sr site situated at the boundary of the perovskite and the rock-salt blocks. The subcell parameters amounted to  $a=5.397(1)$ ,  $b=5.401(1)$ ,  $c=30.716(3)$  Å and the period of modulation was refined with improved accuracy to  $4.73(2)a$  (in Ref.[2] the value  $4.69(7)a$  was reported). For the present low-temperature study the same crystal was fixed on the cold finger of a closed-cycle He-flow refrigerator which itself was mounted on a goniometric head allowing final adjustment. The investigation was performed at temperatures 90, 55 and 8 K. At the first two temperatures the study comprised three principal reciprocal planes  $hk0$ ,  $h0l$  and  $0kl$ . This is a somewhat smaller extent than at the room-temperature study which included in addition a scanning of the  $hhl$  plane and some individual superstructure reflections. A still more limited study was undertaken at the lowest temperature 8 K.

For the powder diffraction at elevated temperatures we used a ceramics prepared for other purposes from a mixture of oxides and carbonates with some excess of CuO, which corresponded to a stoichiometry  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Cu}_{2.2}\text{O}_x$ . After the calcination and repeated firing the product displayed no signs of the 110 K superconductor  $\text{Bi}_2(\text{Sr,Ca})_4\text{Cu}_3\text{O}_{10+\gamma}$  ( $c=37$  Å) both in the magnetic susceptibility and the X-ray diffraction. The powder neutron diffraction taken at the room temperature revealed presence of the 80 K superconductor  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$ , some amount of tenorite CuO and weak traces of  $\text{Bi}_2(\text{Sr,Ca})_2\text{CuO}_{\sigma+\gamma}$  ( $c=24.3$  Å). Subcell parameters of the main phase were established as  $a \sim b \sim 5.40$  Å and  $c \sim 30.80$  Å. Period of the modulation was estimated from the position of the strongest well-resolved superstructure

line (0 1 2.21) to  $4.80a$ . The ceramics was placed into a small furnace with "diffraction-free" vanadium walls and measured for 2 hours at selected temperatures up to  $650^\circ\text{C}$ . The scanning was taken simultaneously at a high and low Bragg angles,  $\theta = 75^\circ$  and  $10^\circ$ , and covered a range of interplanar spacing  $d=1-20$  Å.

## Results

The single-crystal study at 90, 55 and 8 K has shown that the metrics of the  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_8$  lattice remained orthorhombic down to the lowest temperature ( $\alpha=\beta=\gamma=90.00(4)^\circ$ ). The period of modulation displayed no temperature trend and amounted within the experimental uncertainty to  $4.75(2)a$ . Intensities of both the fundamental and the superstructure reflections exhibited only small changes with respect to the room temperature.

A more complete structural refinement was undertaken with data at 90 and 55 K. They yielded practically identical results which are given together with the room-temperature data in table I. It summarizes average fractional coordinates (related to the A<sub>aaa</sub> substructure) and amplitudes of the sinusoidal c-axis waving of atomic layers. The parameters which define atomic displacements within the layers were fixed on their (more accurate) room-temperature values. We note that they should not vary unless the modulation period is changed. For a full description of the structure we refer to [2].

The investigation of the  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_8$  ceramics by powder method demonstrated that neither at elevated temperatures any dramatic changes occurred. The only significant observation was a

gradual broadening of the main superstructure line ( $0\ 1\ 2.21$ ) above  $\sim 500^\circ\text{C}$ , while the width of the fundamental lines remained apparently unchanged. At the same temperature, the thermal expansion starts to increase anomalously. This is seen in Fig.1 which depicts observed values of cell parameters and the modulation period in all the temperature region investigated. Finally, at  $650^\circ\text{C}$  some increase of the  $\text{Bi}_2(\text{Sr,Ca})_2\text{CuO}_6$  impurity was evidenced which might be a first sign of the transition from metastable  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  to the stable  $\text{Bi}_2(\text{Sr,Ca})_2\text{CuO}_6$ .

#### Discussion

Our experimental effort was directed mainly to the elucidation of two questions related to the  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  structure - the onset of modulation at high temperatures and possibility of phase transitions at low temperatures. As to the formation of the compound itself, we can refer to a complex study of sintering in the Bi-Sr-Ca-Cu-O system by the real-time neutron diffractometry, which is in progress also at Joint Institute for Nuclear Research in Dubna. It appears that  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_8$  ceramics forms via a precursor  $\text{Bi}_2(\text{Sr,Ca})_2\text{CuO}_6$  at  $T > 810^\circ\text{C}$  and melts incongruently at about  $860^\circ\text{C}$ . Below  $810^\circ\text{C}$  the compound is metastable and tends to transform back to  $\text{Bi}_2(\text{Sr,Ca})_2\text{CuO}_6$ . The onset of the 4.75a modulation is still not well documented. It seems to arise in well-grown grains only.

Present powder diffraction measurements showed that the superstructure persisted at least to  $650^\circ\text{C}$  without any marked change of integral intensity of the main superstructure line.

This shows that excess of oxygen in  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  ( $\gamma > 0$ ) is essentially retained and, consequently, the formal copper valence remains greater than 2 even at such relatively high temperature. On the other hand, some indication of disordering and partial release of oxygen do exist. We mean the observed broadening of the superstructure line and the anomalous course of cell parameters in Fig.1. Namely, such course reminds the beginning of the S-shaped temperature dependence of cell dimensions in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [7] which is unambiguously associated with a continuous change of oxygen stoichiometry from  $\delta \sim 0$  towards  $\delta=1$  occurring above  $400^\circ\text{C}$ .

The single-crystal investigation resulted in a detailed determination of the  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  structure at room and low temperatures. Cation coordinations were found remarkably uniform throughout the modulation periods. The room-temperature results show that each bismuth cation possesses a coordination of six oxygen atoms in the form of highly distorted octahedron, characteristic for  $\text{Bi}^{3+}$ . In average, three atoms are at a bonding distance 2.0-2.2 Å and three others at 2.7-3.4 Å. The  $\text{Sr}^{2+}$  cations occur in a capped square antiprism of nine oxygens. Eight of them are in a bonding distance of 2.6 Å, the ninth (one of four neighbors in the SrO plane) is displaced to about 3.0 Å. The mixed alkali-ion site between the  $\text{CuO}_2$  planes is coordinated via 2.5 Å bonds to eight oxygens at the corners of an elongated cube. The copper cations occur in a pyramid formed by a square of oxygen atoms in the  $\text{CuO}_2$  plane in a bonding distance 1.9 Å and one (apical) oxygen which is displaced to about 2.5 Å.

Small atomic shifts observed at low temperatures are schema-

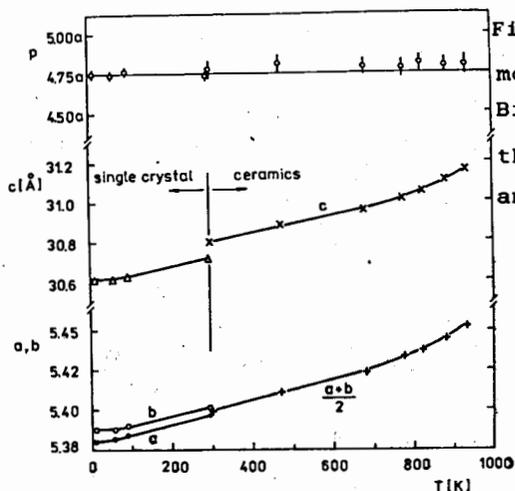


Fig.1 Cell parameters and the modulation period in  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  observed on the single crystal ( $T \leq 290$ ) and ceramic sample ( $T \geq 290$ ).

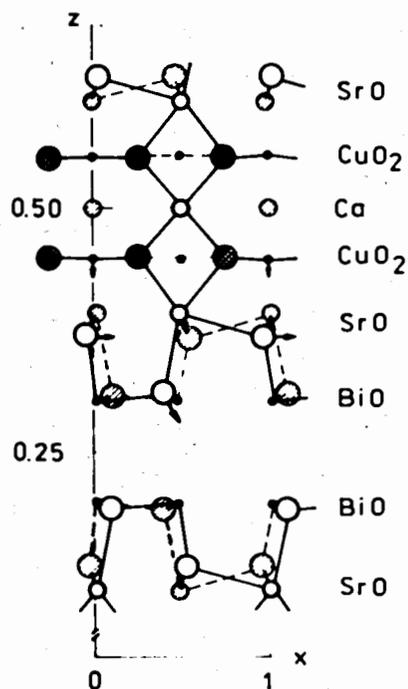


Fig.2 The  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  structure in the  $ac$  plane. The arrows show atomic shifts at low temperatures. (Atoms at  $y \sim 0.5$  are hatched, oxygens at  $y = \pm 0.25$  are cross-hatched)

Table.I

Average coordinates of the modulated  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8.21}$  (related to the Aaaa substructure) and the  $c$ -axis amplitudes of modulation (in Å)

atom	T=290 K (Ref[2])				T=90 K and 55 K		
	x	y	z	$2c_m$	y	z	$2c_m$
Ca,Sr	0.	.5	.5	.64(5)	.5	.5	.86(6)
Cu	0.	-.007(3)	.4474(2)	.57(2)	-.007(3)	.4462(3)	.62(3)
Sr	0.	.494(2)	.3916(4)	.44(4)	.500(2)	.3902(5)	.51(4)
Bi	0.	.023(3)	.3018(2)	.48(4)	.021(2)	.3018(7)	.47(5)
O1	.25	.25	.4488(4)	.53(2)	.25	.4485(9)	.54(2)
O2	.25	.75	.4486(4)	.53(2)	.75	.4488(9)	.54(2)
O3	0.	-.033(3)	.3668(3)	.37(5)	-.026(4)	.3668(5)	.49(5)
O4	0.	.392(5)	.3097(7)	.05(7)	.420(3)	.3067(16)	.09(15)

average distances in cation polyhedra

Bi-O4(a-axis)	2.22 + 2.73	2.19 + 2.72
Bi-O4(b-axis)	2.12 + 3.33	2.13 + 3.29
Bi-O3,4(c-axis)	2.02 + 3.39	2.01 + 3.29
Sr-O1	2 x 2.58	2 x 2.61
Sr-O2	2 x 2.63	2 x 2.62
Sr-O3	3 x 2.64 + 1 x 2.96	3 x 2.63 + 1 x 2.93
Sr-O4	1 x 2.65	1 x 2.71
Ca-O1	4 x 2.47	4 x 2.47
Ca-O2	4 x 2.48	4 x 2.47
Cu-O1	2 x 1.93	2 x 1.93
Cu-O2	2 x 1.88	2 x 1.88
Cu-O3	1 x 2.52	1 x 2.47

tically shown in Fig.2. As demonstrated in table I, the bond lengths are essentially unchanged while some non-bonding distances are shortened. The only exception is an increase of one Sr bond, concretely the bond to oxygen O4 in the BiO plane. Even if this distance is subjected to relatively high uncertainty the increase seems to be real and is possibly associated with

tilting of much more rigid Bi bond configuration. Copper ions exhibit at low temperatures a non-substantial displacement (0.03 Å) and assume a position 0.07 Å out of the plane of basal oxygens. Distance to the apical oxygen is correspondingly shortened.

#### Conclusion

The essential feature of the superstructure in  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  is the incorporation of extra oxygen ( $\gamma \sim 0.21$ ) which enables more advantageous bonding within the  $\text{Bi}^{3+}\text{O}$  planes. The extra oxygen causes considerable local distortions which interact cooperatively via elastic forces. This results in a regular spacing of inserted oxygen atoms and, consequently, in a large periodic modulation of all atomic layers in the structure.

Excess of oxygen and presence of some cation vacancies (also linked to the superstructure) set the copper valence on a non-integer value exceeding 2, which is common in the superconducting cuprates with hole carriers. As suggested by a remarkable stability of the modulation, the highly-oxidized copper state persists apparently up to high temperatures, which is in distinction to the behaviour of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . This conclusion raises naturally a question how such formal state is realized.

Analogously to the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  superconductor the  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  structure contains the double layer of corner-shared  $\text{CuO}_5$  square pyramids, essential for the high-temperature superconductivity. However, this building part differs for both compounds in details. This suggests that the  $\text{CuO}_5$  geometry alone does not control the superconducting properties.

#### Acknowledgement

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Исследование модулированной структуры  $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$   
в диапазоне температур 8 — 920 К

Исследование структуры 80 К сверхпроводника  $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  проведено при комнатной и низкой температурах методом дифракции нейтронов на монокристалле и при высоких температурах на порошке. Модуляция с периодом 4,75а и избыток кислорода ( $\gamma = 0,21$  в идеальном случае) сохраняются во всем диапазоне температур без заметных изменений. Структуру можно описать в сверхъячейке  $19a \times b \times c$  и ромбической симметрией  $Pnaa$ . При уточнении структуры при 90 К и 55 К обнаружены лишь малые смещения атомов по сравнению со структурой при комнатной температуре, опубликованной ранее (Physica C166 (1990) 79). В основном, длины связей катион-кислород сохраняются. Связи атомов меди в слоях  $\text{CuO}_2$  остаются почти компланарными в отличие от 93 К сверхпроводника  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , в котором катионы меди находятся вне плоскости кислородов.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1990

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Study of the Modulated Structure of  $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$   
in the Range 8 — 920 K

The 80 K superconductor  $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\gamma}$  was investigated at room and low temperatures by the single-crystal neutron diffraction and at elevated temperatures by the powder diffraction. The 4.75a modulation and excess of oxygen ( $\gamma = 0.21$  in the ideal case) persist over all the temperature range without marked changes. The structure can be described within the supercell  $19a \times b \times c$  and the orthorhombic symmetry  $Pnaa$ . Complete structural refinement at 90 K and 55 K revealed only small changes with respect to the room-temperature structure published previously (Physica C166 (1990) 79-86). Essentially, the cation-oxygen distances which are considered as bonding are retained while some non-bonding ones decrease. The bonding of copper within the  $\text{CuO}_2$  layer remains nearly planar in distinction to the related 93 K superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in which the copper cations are substantially shifted out of the oxygen plane.

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

Preprint of the Joint Institute for Nuclear Research. Dubna 1990