SHORT RANGE OXYGEN ORDERING IN $YBa_2Cu_3O_{6+x}$

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Dependence of superconducting transition temperature on the oxygen concentration in $YBa_2Cu_3O_{6+x}$ is rather complicated. Numerous electron diffraction experiments on microcrystals with different oxygen contents have revealed a variety of superstructures caused by short range ordering of the oxygen vacancies in plane $Cu1$–$O4$. It is evident that a detailed investigation of $YBa_2Cu_3O_{6+x}$ structure is very important for understanding the phenomenon of superconductivity. As to the averaged structure of $YBa_2Cu_3O_{6+x}$, it was fairly well established in the whole range $0 < x < 1$ in numerous X-ray and neutron diffraction investigations. At $x \simeq 0$ there is no oxygen atoms within the base plane, the compound is in the thetragonal phase and does not display the superconductivity down to lowest temperatures.

Starting $x \simeq 0.4$ the superconducting transition is observed with lowering temperature. At $x \simeq 1$ oxygen atoms form the chains $Cu1$–O4–$Cu1$ along axis b, the unit cell is of orthorombic symmetry and compound has the highest temperature of the superconducting transition equal to 92 K.

It is generally recognized that the superconducting properties of $YBa_2Cu_3O_{6+x}$ are caused by the type and extent of the oxygen ordering in the base plane rather than oxygen concentration. Nevertheless the structure of $YBa_2Cu_3O_{6+x}$ for intermediate values $0 < x < 1$ is insufficiently studied yet, since it is revealed in the diffraction experiment as the weak diffuse superstructure peaks. Besides our publications there are only 3–4 ones in which the fine structure of the compound is determined for some particular and distinguished in different theories values $x = 0.25$, 0.33 and 0.5. The most theories suppose the coexistence of different phases, the types of the oxygen ordering, at given x. The goal of our investigations is the very determination of the structure of $YBa_2Cu_3O_{6+x}$ for intermediate values of x and the setting out phase diagram.

Systematic study of the superstructure in $YBa_2Cu_3O_{6+x}$ has resulted in obtaining the phase diagram in the range $0.4 < x < 0.73$.It was established that ortho-II phase accompanied by doubling of the unit cell along axis a takes place in the limits $0.40(3) < x < 0.63(3)$ and ortho-III phase with tripled unit cell along axis a exists in the range $0.63(3) < x < 0.73(3)$, both caused by short range ordering of the chains $Cu(1)$–O–$Cu(1)$ and $Cu(1)$–vacancy–$Cu(1)$. We have established this fact for the first time. It corroborates a theory which shows that formation of the chains along axis b is energetically much preferable than creating the sequence of atoms $Cu1$–O4–$Cu1$–vacancy–$Cu1$ along axis b and multiplying the unit cell in the same direction. The bounds within the chains $Cu1$–O4–$Cu1$ involve the missing electrons from "reservoir" of the planes $Cu2$–O_2 and create the hole charges. In the second case, the interatomic bounds are formed by electrons of $Cu1$. We have not observed the coexistence of ortho-II and ortho-III phases, at least within the limit of 0.03, that was a minimum change of the oxygen concentration in our investigations.

Structure of ortho-II ($x = 0.40$, 0.46 and 0.58) and ortho-III ($x = 0.70$) phases was refined by the profile analysis of the superstructure peak scans. Some scans along axis c at fixed Miller indices h and k are shown for $x = 0.70$ in Fig.1.

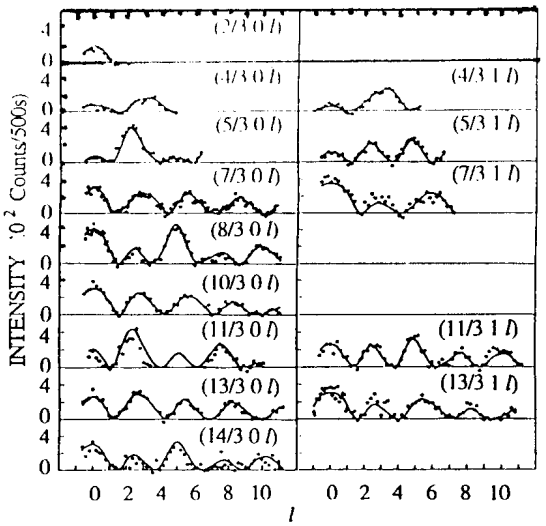

Fig.1. Scans along axis c through the superstructure peaks for sample with $x = 0.70$ Background is subtracted

We have developed the profile analysis method specially for the case of the strongly overlapping peaks of the Lorenzian shape. Such shape of a peak means that the short range superstructure ordering of the oxygen atoms takes place in a crystal. The correlation length of atoms within the chains defines the diffuse peak width along axis b, the correlation length of the chains within the base plane defines that along axis a and the correlation length of the chains belonging to the neighbor base planes does it along c.

The arising of the short range ordering in the alternation of the full and vacant chains is accompanied by the shifting of the unit cell atoms from their position in the averaged structure as shown in Fig.2.

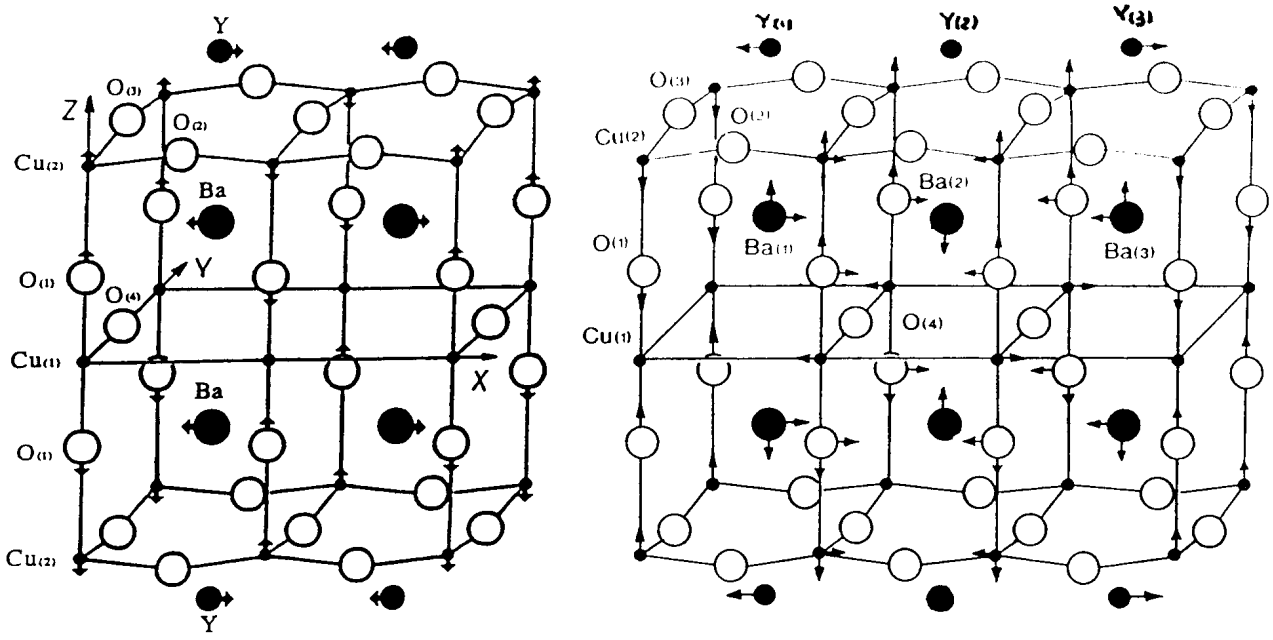

Fig.2. Structure of ortho-II and ortho-III phases. Antiparallel components of atomic displacements are shown by arrows

The values of the atom shifts and the correlation lengths (in angstroms) along the crystal axes are given in Table.

Table

Atom	Axis	x =0.40(3)	0.46(3)	0.58(3)	0.70(3)
Y	a	0.022(6)	0.010(3)	0.011(1)	−0.010(1)
Ba	a	−0.029(2)	−0.038(2)	−0.039(1)	0.059(2)
Ba	c	–	–	–	0.040(2)
$Cu1$	a	–	–	–	−0.034(2)
$Cu2$	a	–	–	–	0.007(1)
$Cu2$	c	0.007(7)	0.012(2)	0.018(2)	−0.009(2)
$O1$	a	–	–	–	0.014(8)
$O1$	c	0.03(1)	0.038(2)	0.049(6)	−0.066(8)
$O4$	a	–	–	–	−0.030(9)
ξ	a	∼4	15(1)	8.9(6)	12(1)
ξ	b	∼8	>55	45(3)	>30
ξ	c	∼3	6.8(3)	7.6(8)	–

Besides X-ray experiment [1, 3], the similar measurements were carried out on a large enough single crystal $YBa_2Cu_3O_{6+x}$ by neutron diffraction [2] which allowed to obtain the fairly precise values of the oxygen shifts.

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