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X-ray diffraction study of the incommensurate structure in $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+x}$ single crystals

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Abstract. High-resolution x-ray diffraction measurements have been performed on single-crystal samples of $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+x}$ at 300 K. It was shown that the symmetry of crystals is lower than orthorhombic. In the vicinity of the odd $00l$ ($l = 2n+1$) reciprocal-lattice points, incommensurate satellites corresponding to a modulation wavevector $q = -0.021b^* + 0.01c^*$ with strong asymmetry of superlattice intensities were observed. Asymmetrical arrangements of incommensurate S peaks with the modulation wavevectors $q_1 = -0.225b^* + 0.061c^*$ and $q_2 = 0.193b^* + 0.078c^*$ were also observed. The results obtained are discussed.

1. Introduction

Since superconductivity with a high critical temperature T_c was found in the Bi–Sr–Ca–Cu–O system, this system has been extensively investigated. Bi-based high-temperature superconducting phases, represented by $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, $n = 1$, 2, 3 and written as 2:2:0:1, 2:2:1:2 and 2:2:2:3, are the first three members of the structural series [1–3]. The 'middle' member of this family, $Bi_2Sr_2CaCu_2O_{8+x}$ (the 2:2:1:2 phase), is the most familiar. $Bi_2Sr_2CuO_6$ attracts less interest because of its low critical temperature and $Bi_2Sr_2Ca_2Cu_3O_{10}$ cannot be prepared so easily as a single-phase sample. These superconducting phases are characterized by complex layered structures which differ in the stacking sequence of perovskite and rocksalt layers along the crystallographic c axis. The high critical temperature T_c of these three phases increases with increasing n. It is believed that all these phases have orthorhombic unit cells with parameters $a = 5.41$ Å, $b = 5.43$ Å and $c \simeq 24$ Å, 30 Å and 36 Å, respectively. These phases are modulated structures.

Several electron diffraction, x-ray and high-resolution electron microscopy (HREM) studies have shown that incommensurate modulation in the 2:2:1:2 phase can be described by the wavevector $q = 0.21b^* + c^*$ [4–9]. The point group of the average structure is mmm [10]. Its Bravais class is $L_{11\bar{1}}^{Cmmm}$ (No 1–14) [11, 12] and superspace group is $N_{1\bar{1}1}^{Bbmb}$ (No 66a) [10, 12, 13]. The superstructure appears to be predominantly localized to the Bi–O planes, in which significant atomic displacements have been observed, as well as a buckling of the Cu–O planes [9]. Such results suggest that the incommensurate structure may be of relevance to the superconducting properties of these materials. Several models for the modulation have been proposed [9]. However, the origin of the incommensurate structure is still unclear. There are experimental data which cannot be explained by the proposed models. For example, Kang *et al* [14, 15] found in their experiments that the 2:2:1:2 phase in the [001] and [100] poles presents several types of electron diffraction pattern. It is difficult

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to say whether these modulations belong to a modification of this phase or correspond to various modifications of the 2:2:1:2 phase. Because of the presence of a large amount of false spots and also non-clear-cut indexing the solving of the above-mentioned problem is quite difficult. X-ray diffraction has the advantage over electron techniques, allowing much more detailed (i.e. a higher θ–2θ resolution) study of the incommensurate satellites including information about their relative intensities. In this paper the results of high-resolution x-ray diffraction studies on the $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+x}$ single crystals are presented.

2. Experimental details

Single crystals were grown by heating mixtures of the Bi, Sr, Ca and Cu oxides and carbonates in appropriate ratios to 880 °C over 7 h, holding at 880 °C for 1.5 h, cooling to 860 °C and holding for 24 h. Then the furnace was cooled to room temperature. The selected single crystals were found to be superconductors with $T_c = 85$ K. Such crystals were investigated by x-ray spectral microanalysis which indicated the composition $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+x}$. Least-squares refinement gave lattice parameters of $a \simeq b = 5.40$ Å and $c = 30, 87$ Å at room temperature, in good agreement with previous results [4, 7, 8, 16].

X-ray diffraction studies were performed on DRON-4-07 and Siemens (D-500) diffractometers using Cu Kα radiation, a flat quartz $(10\bar{1}1)$ monochromator and 0.05 and 0.1 mm entrance slits. The scanning step was 0.001°. The beam spread in the scattering plane was 0.05° or less of the full width at half-maximum (FWHM). The single-crystal samples used had the dimensions 1.5 mm × 1.3 mm × 0.3 mm and (001) as the normal face. The sample was aligned with the diffractometer with its b^* and c^* directions in the horizontal scattering plane. All measurements were performed in the Bragg reflection geometry. The experimental data were processed by means of the SURFER program [17].

3. Results and discussion

The high quality of the samples and the method applied made it possible to carry out measurements in the 2θ angle range 100–150°. The results of the x-ray diffraction analysis of the $Bi_{2.2}Sr_{1.8}CaCu_2O_{8-x}$ single crystals along the [001] direction showed the existence of even reflections belonging to the 2:2:1:2 phase and two weak 00.33 and 00.35 reflections (figure 1). When determining the cross sections around the odd nodes of the reciprocal lattice with $l = 2n+1$, extra reflections were observed. Figure 2 shows two- and three-dimensional isometric presentations of the 00.35 reflection of the $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+x}$ single crystals. A similar pattern would be found around most of the odd 001 nodes of the reciprocal lattice. The extra reflections labelled F in figure 2 are not on nodes of the reciprocal lattice. It is possible to observe them if the scanning is performed along c_1^*, but not along c^* (figure 3). Therefore they cannot be considered as forbidden reflections. Sometimes odd reflections can be observed simultaneously with the even reflections, if the studies of the even reflections along [001] are carried out without a monochromator, using wide entrance slits and poor alignment of the crystal, which may unavoidably lead to incorrect experimental results and conclusions. The wavevector q is associated with the superlattice peak F:

$$q = \beta b^* + \gamma c^*$$

where $\beta = -0.021 \pm 0.005$ and $\gamma = 0.016 \pm 0.001$. The asymmetrical intensity distribution near the F reflection and its mirror image across the $(010)^*$ plane (figure 2) remain puzzling.

A possible explanation for this 'selective extinction' of the satellites was proposed by Khasanov and Zaretskii [18, 19]. The well known incommensurate satellites S_1 and S_2 were also observed. S peaks are slightly asymmetrical with respect to the [001] direction. In addition, they are displaced from the [0 35 0] line with asymmetry which is more pronounced than in the previous case (figure 4). Similar phenomena for the Bi-based superconductors were observed by other investigators [20, 21] and they were sometimes referred to as 'orientation and spacing anomalies' [20]. The wavevectors q_1 and q_2 are related to these S peaks:

$$q_1 = \beta_1 b^* + \gamma_1 c^* \qquad q_2 = \beta_2 b^* + \gamma_2 c^*$$

where $\beta_1 = (-0.225 \pm 0.005)$, $\gamma_1 = (0.061 \pm 0.001)$, $\beta_2 = (0.193 \pm 0.005)$ and $\gamma_2 = (0.078 \pm 0.001)$. The average modulation vector in the b^* direction amounts to $\beta_1 + \beta_2/2 = 0.209$.

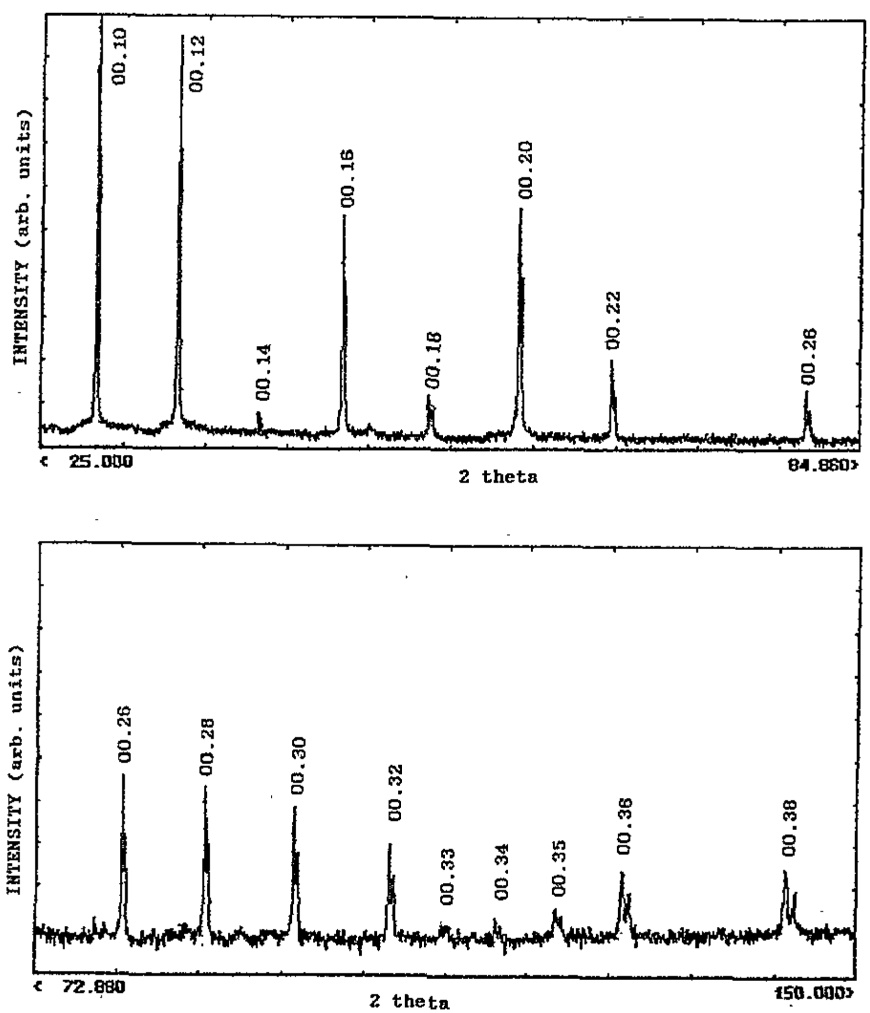

Figure 1. X-ray diffraction pattern of the $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+x}$ single crystal along [001] at room temperature.

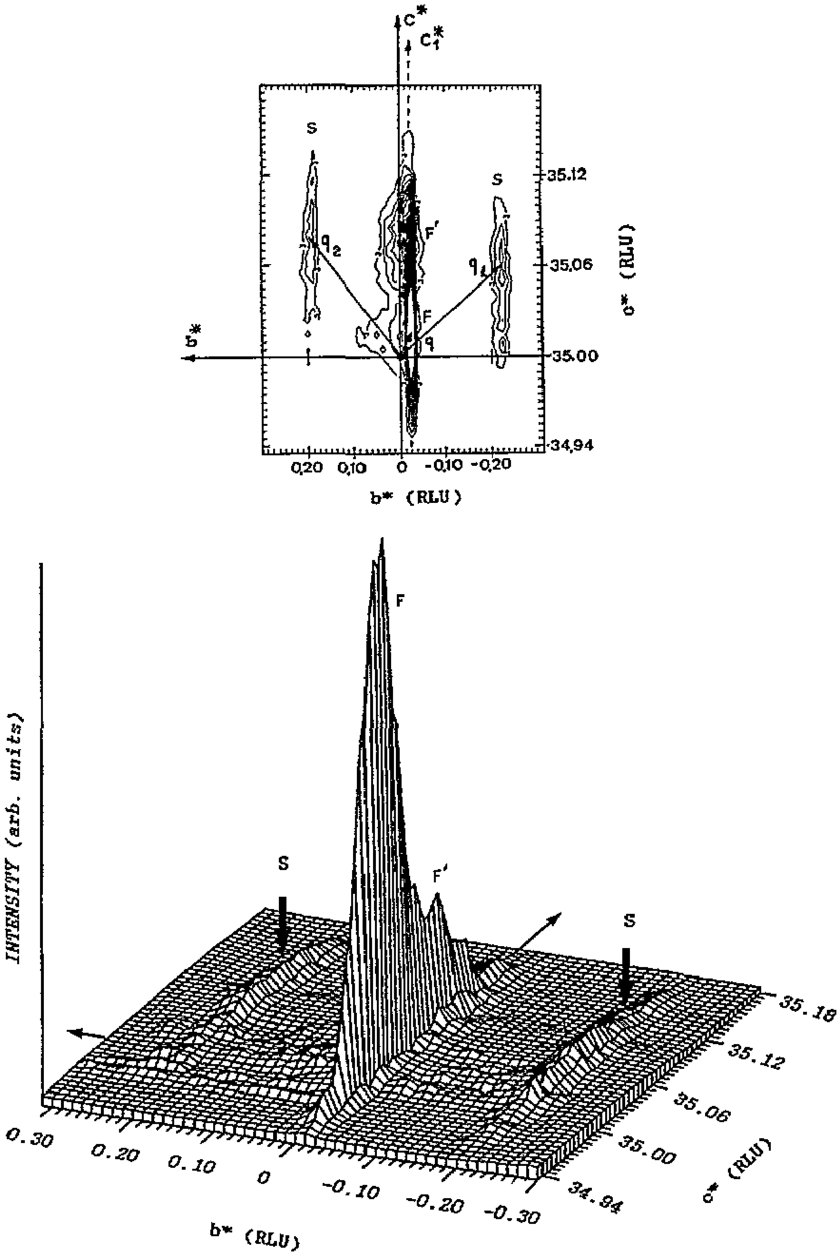

Figure 2. (a) Two- and (b) three-dimensional isometric presentations of the diffracted intensity around the reflection 00.35 of the b^*–c^* plane for the $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+x}$ single crystal. Local peaks labelled F and F′ are supposed to be satellite refections. The satellite reflections S are well known from the literature. RLU is reciprocal-lattice reflections units.

In [8, 22–24], additional reflections with odd l were found with x-ray diffraction. Moschkin *et al* [23] have found that these reflections are not really disposed strictly in the reciprocal-lattice nodes as in our case (the satellite peaks are present in x-ray diffraction patterns near forbidden (001) reflections with $l = 2n + 1$). In their case the position of these

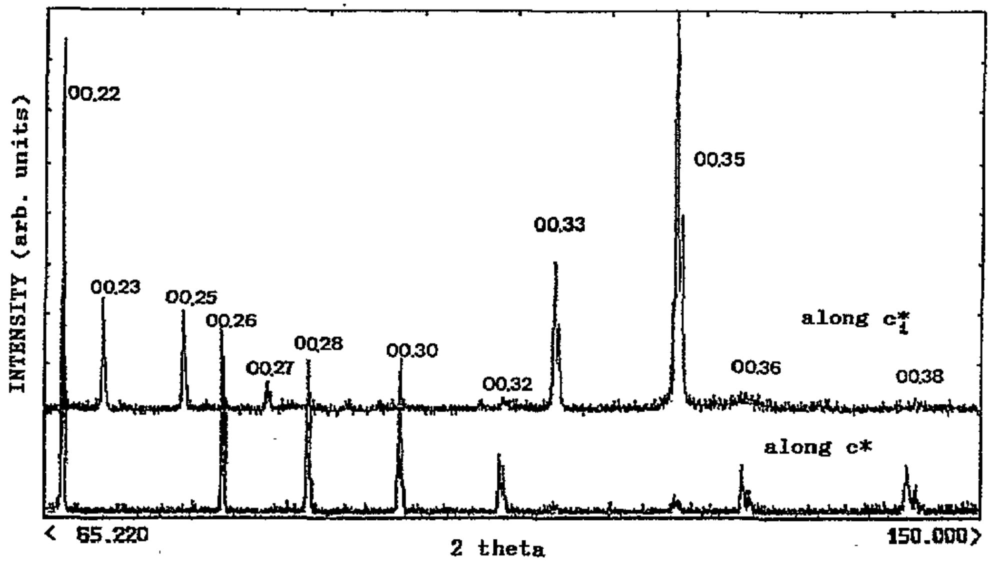

Figure 3. X-ray diffraction pattern of the $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+x}$ single crystal on scattering along c^* and along c_I^* (see figure 2(a)).

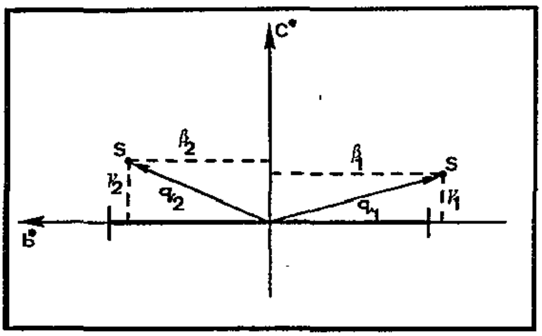

Figure 4. Schematic representation of the reciprocal lattice of the diffraction pattern around the reflection 00.35 of the $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+x}$ single crystal.

peaks varies from crystal to crystal, almost coinciding with the centre of the reciprocal-lattice node. It is known [9, 14] that the basic 2:2:1:2 structure can be described by the *Bbmb* space group. However, as indicated in [25], the presence of odd reflections in the x-ray diffraction patterns of the 2:2:1:2 phase is inconsistent with the above-mentioned space group. On the other hand, the presence of the forbidden reflections $l = 2n + 1$ is quite acceptable, if one assumes that the 2:2:1:2 phase lattice is not B centred but primitive [25]. Thus, it is highly probable that several structural modifications exist for the 2:2:1:2 phase of the Bi-based system which, evidently, are realized depending on the particular synthesis conditions. This result displays more complicated structural processes which take place in the 2:2:1:2 single crystals. To elucidate the nature of these transformations, more detailed investigations should be made. The problem of the formation of these modifications and their identification is highly essential. Note that these modifications differ from each other not only in structure but also in their characteristics (e.g. T_c [24]).

Experimental work [26, 27] and theoretical studies [28, 29] have shown that the crystal structures of superconducting materials used for most applications are indeed not characteristic of structures in thermodynamic equilibrium, but they represent the result of non-equilibrium treatment during the processing of the samples. This unexpected complication for the structural description of high-T_c superconductors is not unwelcome; it creates the possibility of optimizing the material through changes in thermal history in addition to purely chemical changes.

4. Conclusion

High-resolution x-ray diffraction measurements on the $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+x}$ single-crystal samples are presented. It was shown that the symmetry of crystals is lower than orthorhombic. To determine the cross section around odd reciprocal-lattice points, the incommensurate satellites corresponding to a modulation wavevector $q = -0.021b^* + 0.01c^*$ with strong asymmetry of superlattice intensities were observed. Asymmetrical arrangements of the incommensurate S peaks with the modulation wavevectors $q_1 = -0.225b^* + 0.061c^*$ and $q_2 = 0.193b^* + 0.078c^*$ were also observed.

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