Structural modulation in Bi$_2$Sr$_2$Ca$_{0.4}$Y$_{0.6}$Cu$_2$O$_{8+\delta}$

A I Beskrovnyy$^{1,3}$ and Z Jirák$^2$

$^1$Joint Institute for Nuclear Research, 141980 Dubna, Moscow Region, Russia
$^2$Institute of Physics of ASCR, Cukrovarnická 10, 16200 Prague 6, Czech Republic
$^3$National Research Centre "Kurchatov Institute", 123182 Moscow, Russia

E-mail: jirak@fzu.cz

Abstract. The neutron diffraction study has been performed on a single crystal specimen of yttrium doped compound Bi$_2$Sr$_2$Ca$_{0.4}$Y$_{0.6}$Cu$_2$O$_{8+\delta}$, which is a structural analog of the Bi-2212 superconducting cuprates. The average structure is orthorhombic of Fmmm symmetry ($a$=5.448 Å, $b$=5.439 Å and $c$=30.416 Å). Two kinds of distortion are observed. The first one, manifested by satellite reflections of wavevector [1,0,1] with $\delta$=0.220, is associated with an incorporation of extra oxygen ($\delta$=0.44) into BiO bilayer. The respective modulation consists of a flexing of the bilayer and corrugation of other structural layers with period 4.5$\sigma$. The second distortion is associated with displacements in the BiO planes due to Bi$^{3+}$ bonding and lone pair ordering, which results in common cases in a formation of infinite ribbons of Bi-O-Bi- chains and decrease of average symmetry to Amaa. In the present system, the reflections characteristic for Amaa are absent and, instead, a diffuse scattering along the [001] direction is observed, pointing to a presence of 2-dimensional superstructure with in-plane period 9.0$\sigma$ – twice the one of the regular modulation. Based on these data, we propose a structural model in which bonding chains in the BiO planes of Bi$_2$Sr$_2$Ca$_{0.4}$Y$_{0.6}$Cu$_2$O$_{8+\delta}$ are segmented and rearranged in a tweed pattern.

1. Introduction

The transition metal oxides with layered structures offer many interesting properties with prospects for applications. Among them, the systems based on BiO bilayers are particularly attractive. Two structural classes can be distinguished. The first one is represented by superconducting cuprates of general formula Bi$_2$(Sr, Ca)$_{2n+1}$Cu$_n$O$_{2n+2+\delta}$ (n=1,2,3). These phases consist of [Bi$_2$(Sr, Ca)$_{2n+1}$Cu$_n$O$_{2n+2+\delta}$] rock-salt blocks stacked with oxygen deficient perovskite-like layers [Ca$_{n-1}$Cu$_n$O$_{2n}$]. Conducting parts are the single or multiple CuO$_2$ planar sheets, in which copper ions are arranged in a 2D square lattice. Analogous structures are reported also for other transition metal systems, in particular the n=1 phase Bi$_2$Sr$_2$CoO$_{6+\delta}$ or Bi$_2$Sr$_2$MnO$_{6+\delta}$ [1-3]. The second structural class is represented by so-called misfit cobaltites, where analogous rock-salt blocks alternate with CoO$_2$ layers of hexagonal CdI$_2$ type. In that case the cobalt ions form 2D trigonal lattice sheet and are octahedrally coordinated with oxygen above and below the sheet. Because of lack of an ideal stacking with the rock-salt blocks, the resulting phase is a kind of composite structure. An example is the important thermoelectric system [Bi$_{1.72}$Sr$_2$O$_4$] [CoO$_2$]$_{1.82}$ [4, 5].
Structural complexity is encountered also in the systems of the first structural class, namely in Bi-2212 cuprates (the n=2 phase) schematically depicted in figure 1. The lattice mismatch between the perovskite and rock-salt blocks and character of the Bi-O bond result in a structural modulation – the corrugation of all atomic planes (see figure 2) and large in-plane displacements within the BiO and adjacent SrO planes. The modulation depends on the actual composition of the compound and its period varies between commensurate values 4a and 5a (a~5.40 Å). Important point is the insertion of extra oxygen into the BiO plane after each modulation period, which makes preferable to describe the structure in a multiple cell, sometimes very large, rather than to use the four-dimensional formalism. In such pseudo-commensurate approach we have solved previously the structures of the single crystals of superconducting Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+δ}$ and non-superconducting Bi$_2$Sr$_3$Y$_x$Cu$_2$O$_{8.5}$ with modulation periods of 4.75a and 4.25a, respectively [6, 7]. Both systems are characterized with a formation of ribbons – the Bi-O double chains in the bilayers (see figure 3b, figure 3c). The present study is done on crystals of composition Bi$_2$Sr$_2$Ca$_{0.4}$Y$_{0.6}$Cu$_2$O$_{8+δ}$ where ribbons are apparently absent and a more complex Bi-O bonding is formed.

Figure 1. A simplified model of the Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+δ}$ structure (space group F41/mmm; typical cell dimensions a=b~5.40 Å, c~30.5Å).

Figure 2. Schematic picture of the (x, z) plane of Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+δ}$ (cations shown by dots and circles, oxygen atoms by the dashed lines). The modulation of atomic planes along x is due to insertion of extra oxygen atoms into the BiO bilayers with period ~4.5a (locations shown by the arrows).

2. Experimental
The Bi$_2$Sr$_2$Ca$_{0.4}$Y$_{0.6}$Cu$_2$O$_{8+δ}$ crystals were grown by the travelling solvent floating zone technique as described elsewhere [8]. For determination of the structural modulation, a small specimen with dimensions 2 x 2 x 0.2 mm$^3$ consisting of a single domain was selected. The neutron diffraction investigation was performed on the DN-2 time-of-flight neutron diffractometer at the Joint Institute of Nuclear Research in Dubna (Russia) [9]. The use of a two-dimensional position sensitive detector
allowed us to record the fundamental and satellite reflections practically in the whole octant of the reciprocal space.

3. Results and discussion
The fundamental reflections \( (hkl) \) measured by single crystal neutron diffractometry show systematic extinctions characteristic for the face centered orthorhombic cell of average \( Fmmm \) symmetry \((a=5.448 \text{ Å}, b=5.439 \text{ Å} \text{ and } c=30.416 \text{ Å})\). In addition, there are sharp satellites \((h \pm \tau k \pm 1)\) with \( \tau=0.220(1) \) that evidence a pseudo-commensurate modulation of 4.5\( a \) period. Some satellites of the second order \((h \pm 2\tau k \pm 2)\) are also observable. In spite of closeness of \( a \) and \( b \) parameters, no twinning is detected. This may suggest that the structural modulation, in particular the incorporation of extra oxygen, is inherent to the phase formation (see also the high-temperature study of the Bi-2212 cuprate in [10]).

In contrast to previously studied systems of the average \( Amaa \) symmetry, the diffraction peaks \((h0l)\) with \( h,l =2n+1 \), which occur due to Bi-O ribbons, are completely missing in the present sample \( \text{Bi}_2\text{Sr}_2\text{Ca}_0.4\text{Y}_{0.6}\text{Cu}_2\text{O}_{8+\delta} \). Instead, new diffuse satellites corresponding to the doubled modulation period 9.0\( a \) are detected in other parts of reciprocal space. These satellites form streaks (diffraction ridges) along the \([001]\) directions. Similar behavior was observed earlier on \( \text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta} \) by electron microscopy [11]. There are, however, some important differences. Both the 4.5\( a \) and 9.0\( a \) periodicities occur for the present sample within one phase and no reflections violating the \( Fmmm \) symmetry are observed.

![Figure 3. Scheme of the BiO plane in the simplified model (a), \( \text{Bi}_2\text{Sr}_{3.3}\text{Ca}_0\text{Cu}_2\text{O}_{8.2} \) (b), \( \text{Bi}_2\text{Sr}_{3.3}\text{Y}_0.6\text{Cu}_2\text{O}_{8.8} \) (c) and the arrangement found for the present compound \( \text{Bi}_2\text{Sr}_{2.4}\text{Ca}_{0.4}\text{Y}_{0.6}\text{Cu}_2\text{O}_{8.4+4} \) (d). The Bi and O positions are shown are by the dots and circles, respectively; extra oxygen atoms are marked by crosses, the arrows show the modulation periods.](image3)

![Figure 4. The intensity variation along the diffraction ridge \((0.11 3 l)\). Data for \((1.11 2 l)\) and \((2.11 1 l)\), obtained in a limited \( l \) range, are also included.](image4)
The intensities of sharp reflections \((hkl), (h\pm\tau k \pm l \pm 1)\) and \((h\pm2\tau k \pm l \pm 2)\) observed on Bi\(_2\)Sr\(_2\)Ca\(_{1-x}\)Y\(_x\)Cu\(_{2}\)O\(_{8+\delta}\) were analysed within a structural model with supercell nine-times enlarged in the \(a\)-direction. The refinement based on 105 fundamental reflections and 135 satellites showed that actual oxygen amount in Bi\(_2\)Sr\(_2\)Ca\(_{1-x}\)Y\(_x\)Cu\(_{2}\)O\(_{8+\delta}\) is close or equal to the ideal value \(\delta=0.44\) (experimental uncertainty \(\pm0.10\)), which corresponds to two extra oxygen atoms incorporated into BiO layers after each 4.5\(a\) period. The insertion of two oxygen atoms instead of one is a situation similar to what we observed earlier for the related compound Bi\(_2\)Sr\(_3\)Y\(_x\)Cu\(_{2}\)O\(_{8+\delta}\) [7]. Also the extent of the corrugation of atomic planes (the \(c\)-axis modulation sketched in figure 2) is comparable.

The main issue is the absence of ribbons and origin of 9.0\(a\) modulation in the present sample. Relevant information can be deduced from diffuse satellites forming streaks of slowly variable intensity along the [001] direction (see figure 4). This is indicative for a 2-dimensional superstructure, most likely associated with ordering in the BiO bilayer and adjacent SrO planes. The streaks are narrow (resolution limited) in the [010] direction but broadened in the [100] direction, which means that the planar ordering is of a short range in the \(a\)-direction (the estimated coherence length is below 1000 Å). In order to substantiate the 2-dimensional superstructure, let us inspect the diffraction intensities in figure 4 in more detail. The most significant data are obtained along the \((\tau/2 3 l)\) diffraction ridge. The scan shown in figure 4 exhibits a very broad maximum around \(l=0\) and other two maxima spreading over \(l=7 – 11\) and \(l=16 – 21\). As the first maximum is concerned, the diffraction intensity at the middle is rather low while it is stronger on shoulders at \(l=3\) (and \(-3\)). Similar strong diffraction at \(l=3\) is evidenced also in the \((1+\tau/2 2 l)\) and \((2+\tau/2 1 l)\) scans (their \(l\) range was unfortunately limited due to experimental reasons – see figure 4). We presume that the shoulders might occur due to \(a\)-axis shifts in the SrO planes in which the strontium and oxygen atoms adjust to the inserted extra oxygen in adjacent BiO plane. On the other hand, the \((\tau/2 3 l)\) diffraction centred at \(l=0, 9\) and 18 is associated most likely with the \(b\)-axis displacements of bismuth and oxygen atoms in the bilayer and the maxima can be understood as an interference effect of BiO planes, located at \(z\sim0.25\pm0.06\) levels (see figure 2). Based on an analogy with displacements that form ribbons in the \(Amaa\) systems, we propose for Bi\(_2\)Sr\(_2\)Ca\(_{0.4}\)Y\(_{0.6}\)Cu\(_{2}\)O\(_{8+\delta}\) a model with segmented Bi-O double chains, schematically depicted in figure 3d.

The complete structure determination is out of the scope of present study. It might be noted that the actual system could be described as a composite structure (see e. g. [12, 13]).

4. Conclusions

Structural modulation is a general property of Bi-2212 cuprates. The reason is in incompatibility of the ideal tetragonal structure of the \(F4mm\) symmetry shown in figure 1 with the bonding character of the Bi\(^{3+}\) cation and its lone electron pair. In particular, the atoms in the ideal BiO plane are regularly spaced with a distance \(a/2\sim2.7\) Å (see figure 3a), which is outside the range of possible Bi\(^{3+}\)-O bonds (2.0–2.5 Å). It appears that an appropriate coordination is achieved by two mechanisms - by the ordering of short (bonding) and long (non-bonding) Bi-O distances along the \(b\)-axis and by a periodic insertion of extra oxygen (typically with 4-5\(a\) spacings) and significant rearrangement of atoms in the BiO and adjacent SrO planes along the \(a\)-axis. The former mechanism results in an orthorhombic distortion, most commonly of the \(Amaa\) symmetry. In these cases, characteristic ribbons in the BiO plane as seen in figure 3b or figure 3c are formed. The insertion of extra oxygen defines the superstructure and is responsible for flexing of BiO bilayers and subsequent corrugation of other atomic planes.

The present Bi\(_2\)Sr\(_2\)Ca\(_{0.4}\)Y\(_{0.6}\)Cu\(_{2}\)O\(_{8+\delta}\) system is characterized by the \(Fm\overline{m}\)m symmetry. Extra oxygen atoms (\(\delta=0.44\)) are inserted into BiO bilayers with period 4.5\(a\). Though the flexing of BiO bilayers and corrugation of other atomic planes is similar to the \(Amaa\) systems, the planar pattern of bismuth and oxygen atoms in bilayers is significantly modified. Instead of the infinite strips of the Bi-O-Bi-
bonds running along the \(a\)-directions, a tweed arrangement of Bi\(_9\)O\(_{11}\) segments is realized (figure 3d). This gives rise to a novel kind of 2-dimensional superstructure with in-plane period \(9a\).

In the conclusion, it is worth mentioning that the present sample is not superconducting. This is most likely related to an underdoping of conducting CuO\(_2\) layers since the formal valence calculated for composition Bi\(_{2}\)Sr\(_{2}\)Ca\(_{0.4}\)Y\(_{0.6}\)Cu\(_2\)O\(_{8.44}\) is Cu\(^{2.14+}\), inferior to Cu\(^{2.20+}\) in the Bi\(_2\)Sr\(_x\)Ca\(_x\)Cu\(_2\)O\(_{8.2}\) superconductors.

**References**

[1] Tarascon J. M. et al. 1989 *Phys. Rev.* B 39 11587
[2] Jakubowicz N, Grebille D, Leligny H and Evain M 1999 *J. Phys.: Condens. Matter* 11 3997
[3] Jirák Z, Pollert E, Sedmidubský D, Dlouhá M and Vratislav S 1992 *Physica* C 196 68
[4] Hervieu M, Maignan A, Michel C, Hardy V, Creon N and Raveau B 2003 *Phys. Rev.* B 67
045112
[5] Leligny H, Grebille D, Perez O, Masset A-Ch, Hervieu M, Michel C and Raveau B 1999 *C. R. Acad. Sci. Paris IIc* 2 409
[6] Beskrovnyi A I, Dlouhá M, Jirák Z, Vratislav S and Pollert E 1990 *Physica* C 166 79
[7] Beskrovnyi A I, Jirák Z, Nevřiva M and Shelkova I G 1993 *Physica* C 206 27
[8] Nevřiva M, Jirák Z, Šíma V, Beskrovnyi A I, Martin C and Raveau B 1997 Book Series: *Electrochemical Society Series* 97-39 pp 480-486
[9] http://flnp.jinr.ru/137/
[10] Beskrovnyi A I, Dlouhá M, Jirák Z and Vratislav S 1990 *Physica* C 171 19
[11] Zhang X F, Van Tandeloo G, Emmen J H P M and Brabers V A M 1993 *Physica* C 215 39
[12] Perez-Mato J M, Etrillard J, Kiat J M, Liang B and Lin C T 2003 *Phys. Rev.* B 67 024504
[13] Etrillard J, Bourges P and Lin C T 2000 *Phys. Rev.* B 62 150