SO₄-chain formation and ordering in [YSrCa]Sr₂Cu₂.₇₈(SO₄)₀.₂₂O₇₋δ

T. Krekels, O. Milat, G. Van Tendeloo, J. Van Landuyt and S. Amelinckx
EMAT, University of Antwerp (RUCA), Groenenborgerlaan 171, B-2020 Antwerp, Belgium

P.R. Slater and C. Greaves
University of Birmingham, Birmingham B15 2TT, UK

Received 18 February 1993
Revised manuscript received 10 March 1993

YBCO-based materials containing SO₄-tetrahedra centered on the Cu(1)-sites of the CuO-chain plane have been examined by means of electron diffraction and high resolution electron microscopy. An incommensurate modulation is observed and attributed to the ordering of b-oriented SO₄-rich chains in the Cu(1)-S-O-layer, described in terms of an SO₄-concentration wave.

1. Introduction

The concept of block-layers introduced by Tokura and Arima [1] classifies the oxide superconductors from an electronic point of view, with the block-layers determining the carrier density and the electrostatic stability of the compounds. From a structural point of view, the block-layers can be classified as consisting of tetragonal (rock-salt, fluorite, CsCl, perovskite) or orthorhombic layers. The latter are perovskite-layer-based and contain linear chains, of different compositions and configurations.

The best-known LnBa₂Cu₃O₇-compound (Ln: lanthanides or Y) contains an orthorhombic Cu(1)O chain layer, with CuO-chains along the basic perovskite cell b-direction. The efforts of stabilizing the Ba-free compound LnSr₂Cu₂O₇ have led to a variety of cation substitutions of the Cu(1) chain site. Ga- and Co-substitutions in 1212-compounds such as YSr₂GaCuO₇ and YSr₂CoCuO₇ have led to a new type of perovskite-like block with GaO- or CoO-chains in which the metal-atoms are tetrahedrally coordinated by oxygen and which run diagonally with respect to the perovskite cell [2–7]. After the introduction of CO₃-groups in the Sr₂CuO₂CO₃ compound [8,9], creating a new type of orthorhombic layer containing triangular CO₃-groups, substitutions of C for Cu(1) in the YSr₃Cu₄O₇ compound have been reported [10], where the CO₃-triangles align in chains along b. In a recent paper Slater et al. report the substitution of the Cu(1) site by tetrahedral SO₄-groups in compounds with composition [Y₁₋ₓSrₐ]Sr₂Cu₁₋ₓ(PO₄)ₓSO₄O₁₋ₓ and by PO₄-groups in YSr₂Cu₃₋ₓ(PO₄)ₓO₁₋ₓ materials (elements in [ ] brackets are on Y-sites) [11]. In this paper, we report the structural investigation, by means of electron microscopy, of superconducting samples of composition [Y₀.₈₄Sr₀.₁₆]Sr₂Cu₂.₇₈(SO₄)₀.₂₂O₆.₁₂ and [Y₀.₇₄Sr₀.₃Ca₀.₆₆]Sr₂Cu₂.₇₈(SO₄)₀.₂₂O₆.₁₂, the latter with Tc onset between 45 K and 60 K. According to the results of neutron diffraction analysis [11], the material has the orthorhombic tri-perovskite Ln-Ba₂Cu₃O₇ structure with average cell parameters a₀=0.3825 nm, b₀=0.3844 nm and c₀=1.1257 nm (the index 0 is used to refer to this basic tri-perovskite lattice). The S-atoms are located on the Cu(1) positions and the SO₄-groups have a tetrahedral oxygen configuration, with the S-atom at a slightly eccentric position. Relaxation of the atom positions of the adjacent SrO- as well as CuO₂-layers, takes place. Our electron microscopy investigations reveal the formation of SO₄-chains and we will describe an ob-
served modulated structure in terms of the ordering of these chains.

2. Experiments

Single phase materials with nominal compositions \( \text{YSr}_2\text{Cu}_{2.78}\text{(SO}_4\text{)}\text{O}_{6.12} \) and \( \text{YSr}_2\text{Cu}_{2.78}\text{(SO}_4\text{)}\text{O}_{0.23}\text{O}_{6.12} \) were obtained from high purity powders by conventional ceramic processing as described in ref. [11]. Tri-perovskite structures could be obtained for \( 0.2 < x < 0.32 \), if partial occupancies of the Y sites by Sr-ions were accounted for. Crushed ceramic powder grains were glued onto copper grids for transmission electron microscopy (TEM) studies. High resolution images were recorded on a high resolution electron microscope operating at 400 kV, with a resolution limit of 0.17 nm; diffraction studies were performed at 100 kV.

3. Observations

The materials \( \text{YSr}_2\text{Cu}_{2.78}\text{(SO}_4\text{)}\text{O}_{0.23}\text{O}_{6.12} \) and \( \text{YSr}_2\text{Cu}_{2.78}\text{(SO}_4\text{)}\text{O}_{6.12} \) cannot be distinguished in the electron microscope, neither from their electron diffraction patterns, nor from the high resolution images. The images shown throughout this paper were observed on the former material, but the proposed model will be valid for both.

In both compounds investigated, satellites are present, associated with every Bragg-spot. A [010]-zone diffraction pattern is shown in fig. 1(a) and shows equally spaced bright first order satellites and weaker second order satellites, aligned along rows inclined at an angle \( \alpha \) of about 30°, with respect to the [100]-direction. The positions of first and second order satellites of a Bragg spot at \( (h,0,l) \) are \( (h \pm q_x, 0, l \pm \frac{1}{2}) \) and \( (h \pm 2q_x, 0, l \pm 1) \) with \( q_x \approx \frac{1}{10} \). The planar mm2 symmetry of the [010]-zone pattern is thus not altered by the appearance of the satellites, and the inclination of the rows of satellites can equivalently be regarded as \( -\alpha \). The length of the satellite-\( q \)-vector is 1 nm\(^{-1}\).

The [001]-zone diffraction pattern of fig. 1(b) shows that satellite spots are present in the (010)*-planes only. The two second order satellites at positions \( h \pm 2q_x \) appear in between every two basic spots, along the \( a^* \)-direction. No spots are observed between the basic spots, along the perpendicular direction \( b^* \).

According to these observations, the structure can be considered to be modulated by a modulation with wavevector in the (010)-plane, inclined over \( \alpha \) with respect to the [100]-direction and with a wavelength \( \lambda = 1 \) nm. Alternatively, the structure can be considered as being modulated by an equivalent modulation with a wavevector of the same length and symmetric inclination over \( -\alpha \).

The angle \( \alpha \) is not constant; a range of angles \( \alpha \) has been observed between 27° and 32°, as well as a range of satellite separations, in different grains of the same batch of material, suggesting the incommensurability of the superstructure. This effect can be noted by comparing the separation between two
nearby second order satellites at positions $h + 2q_s$ and $h + 1 - 2q_s$, observed in the [010]-zone pattern of fig. 1(a) and in the [001]-zone pattern of fig. 1(b).

Although the observed modulation is orthorhombic, most [001] diffraction patterns are tetragonal with superstructure spots along $a^*$ as well as along $b^*$ (fig. 2(a)). This is due to the presence of two orthorhombic variants, related by the usual $(110)$ twin law common in LnBa$_2$Cu$_3$O$_{7-δ}$. The low orthorhombicity $(b_o - a_o)/a_o = 0.005$ [11] (versus 0.016 in YBa$_2$Cu$_3$O$_{7-δ}$) results in a fragmentation of the material in small domains of the two orthorhombic variants, exhibiting a texture known as “tweed” (fig. 2(b)) [12]. In diffraction patterns, the presence of tweed can be recognized by a cross shape of the Bragg spots.

High resolution images were recorded along the [010]- and [001]-zones. The image of fig. 3, taken along the [010]-zone, shows the presence of a modulation corresponding to the satellites in the corresponding diffraction pattern of fig. 1(a). The image shows, on the average, the same dot configuration as in undoped LnBa$_2$Cu$_3$O$_{7-δ}$ material with the Cu(I)-O-layer imaged as a dot row, slightly more intense than the rest of the matrix. However, one aspect of these [010] images, that did not occur in the undoped compounds, is rather striking: every three or four repeat distances along the $a$-direction, centered on the Cu(I)-O-layer, more intense squares of dots are formed. The observed contrast is similar to that observed in CO$_2$-containing samples [10] and, in analogy, it is associated to the presence of SO$_4$-groups in this layer. The bright squares will be associated with $b$-oriented columns with a high SO$_4$-content. This interpretation is supported by observations along the [001]-zone as discussed below, and it will be substantiated by image simulations that are under way but that require a detailed knowledge of atom positions in the new material that cannot be derived on the basis of electron microscopy observations. The stacking in the $c$-direction of these columns or “chains” also follows from this image. Typically, SO$_4$-“chains” are staggered along $c$ in such a fashion that their configurations in every second Cu(I)-S-O-plane coincide vertically. The alternation in a single Cu(I)-S-O-plane is roughly $-4a_o - 3a_o - 3a_o -$. An idealized model with a commensurate, centered unit cell $(10a_o \times b_o \times 2c_o)$ is schematically represented in fig. 4.

Looking under a grazing angle at the [010]-zone image along the direction indicated by heavy lines in fig. 3(b), planes containing a high density of SO$_4$-clusters are revealed by a modulation in dot intensity. These planes, separated by about 1 nm, can be considered as the maxima of a planar concentration wave. The normal to this concentration wave makes an angle $α$ of about $30°$ with the [100]-direction, and the length of the wavevector is about 1 nm. The equivalent modulation, making an angle of $-α$ with the [100]-direction, is present in fig. 3 and indicated by a second set of lines in fig. 3(b).

High resolution images along the [001]-zone (fig.
Fig. 3. High resolution image along the [010]-zone showing S-rich columns as brighter squares of four dots centered on the Cu(1)–S–O-layers. (a) Low magnification image showing a modulated domain. The maxima of the modulating wave, easily seen under grazing angles, are stressed by two sets of heavy lines in image (b) with normals inclined over $\alpha$ and $\sim \alpha$ with respect to the [100]-direction. The brighter dot configurations are indicated in part of image (b) by small crosses. The separation between these crosses along the $a$-direction is $3a_0$ or $4a_0$. The stacking mode along $c$ is such that, in a projection along the $c$-direction, bright crosses are generally superimposed vertically every second Cu(1)–S–O-layer.

![High resolution image](image)

Fig. 4. Drawing of a commensurate model for the modulation. Circles represent S-rich chains and squares Cu(1)-columns. The supercell ($10a_0 \times b_0 \times 2c_0$) as well as the basic unit cell is indicated. Vertical dashed lines draw the attention to the $5a_0$ periodicity of the projection along $c$.

5) of a single variant of the structure, corresponding to the diffraction pattern of fig. 1 (b), shows a disordered array of bright and less bright $b$-oriented dot row segments, with a separation between two bright dot rows of $a_0$ or $2a_0$.

4. Model

All of the above observations can be explained by a simple model of SO$_4$-chain formation and ordering. The [001] high resolution image suggests the presence of chains oriented along the $b$-direction, the
nature of which must differ from that of CuO chains by their S content.

A rule for the stacking of the SO$_4$-rich chains can be derived from the observation of a concentration wave of which the characteristics follow directly from the satellite geometry. The wavevector is inclined by $\alpha \approx 30^\circ$ with respect to [100] and has a magnitude $q \approx 1$ nm$^{-1}$. We note the following two features:

1. The SO$_4$-chains substitute the sites of the Cu(1)-sublattice that are closest to the maxima of the concentration waves.
2. The integer $l$-coordinates of the second order satellites as well as direct observations in high resolution images suggest that the SO$_4$-chain-stacking coincides vertically in every second plane along the [001]-direction.

The latter implies that the SO$_4$-concentration wave introduced can equivalently be considered as having a wavevector oriented $-\alpha$ with respect to the [100]-direction. Moreover, the latter rule implies a relation between the angle $\alpha$ and the period $\lambda$ of the modulation:

$$2c_0 \sin \alpha = \lambda.$$  \hspace{1cm} (1)

5. Discussion and conclusions

Figure 6 represents the Cu(1) sublattice only. Dashed lines are the maxima of the concentration waves with angles $\alpha = \pm 30^\circ$ and $\lambda \approx 1$ nm so as to satisfy condition (1). SO$_4$-chains (circles) are positioned at the Cu(1) column sites (dots) that are closest to the wave maxima. Due to the incommensurability of the basic lattice with the modulation represented in this drawing, the ordering along the $a$-direction is essentially aperiodic. This is in agreement with the absence of a periodic superstructure spot configuration along $a^*$ in the [010] diffraction pattern (fig. 1(b)).

Nevertheless, some choices of $\alpha$ and $\lambda$, taking into account condition (1), yield simple commensurate unit cells, as the one represented in fig. 4 for $\alpha = 29.47^\circ$ and which closely resembles the observations at high resolution in fig. 3. The $c$-axis projection of the structure represented in fig. 4, yields the atomic configuration observed in the [001] high resolution image of fig. 5. Since in this projection all SO$_4$-containing sheets are equivalent, a period of $5a_0$ arises, with an $-5a_0 - 2a_0 - 2a_0$ alternation of the separation between S-containing columns. The five-fold periodicity is revealed in restricted areas of the images only (fig. 5), due to the high degree of per-
turbations in the ordering and to the deviation of the exact modulation from the model.

The general model hitherto satisfies the structural observations, but does not fully account for the S-content which was determined to be \( r = 0.22 \) by the composition of the starting reagents before preparation, as well as by gravimetric chemical analysis of the obtained cuprates [11]. The fraction of S-rich chains versus the total number of \( \text{SO}_4 \)-chains and S-free \( \text{Cu}(1) \)-columns is related to the parameters and the angle \( \alpha \) by the formula:

\[
f = \frac{a_0}{2c_0} \cot \alpha.
\]  

For a value \( \alpha = 30^\circ \) this yields a concentration \( f = 0.3 \). Values of \( f \) for angles in the range of the observations are always higher than the overall S-content \( r = 0.22 \), suggesting either the presence of a second less S-rich phase or implying that in the \( \text{SO}_4 \)-chains the substitution of \( \text{Cu}(1) \) sites by S is only partial, with an in-chain S-content of about \( \frac{1}{3} \), this being the ratio of the nominal S-content \( r \) and of the \( \text{SO}_4 \)-chain fraction \( f \). Supposing a fixed \( \text{SO}_4 \)-concentration inside the chains, a slight average concentration change within the material is expected to result in the change of wavevector and the observation of a range of possible \( \alpha \)-values.

It is of some interest to speculate on a physical explanation for the observed \( \text{SO}_4 \)-chain arrangement. The chains occupied by \( \text{SO}_4^2- \) ions cause cylindrically symmetrical stress fields as a consequence of the difference in size of the sulphur-ions and the copper-ions that they replace. Parallel chains thus interact by mutually repulsive elastic forces which depend on the separation \( r \) as \( 1/r \). The equilibrium configuration of such a set of repelling parallel chains, when confined to a finite area, or with a specified concentration, consists of a triangular array. With the restriction that the \( \text{SO}_4 \)-chains can only be located at positions in the \( \text{Cu}(1) \)-column layers, the observed distribution of \( \text{SO}_4 \)-chains is the one that yields the largest average separations between different chains, taking in account the concentration of \( \text{SO}_4 \)-chains.

The restriction on the allowed sites for the \( \text{SO}_4 \)-chains also restricts the possible wavevectors of the concentration waves. The \( q \)-component of the wavevector \( q \) must be a simple fraction of \( c_0 \), which is within broad limits independent of the concentration of \( \text{SO}_4 \)-ions. Since a staggered arrangement of
repelling chains, restricted to c-layers, is energetically more favorable than a vertically aligned one, it can be understood that the c-component is \( \frac{1}{2}c^* \) and not \( c^* \). On the other hand, the \( a^* \) component is \( SO_4^- \) concentration dependent, and leads to a variable vector. The fact that the c-component of \( q \) is \( \frac{1}{2}c^* \), implies further that two wavevectors can be chosen, related by mirror symmetry with respect to the \((001)\)-plane, leading to equivalent occupation waves. It is clear that the proposed model satisfies these conditions.

Neutron diffraction experiments show a tetragonal coordination by oxygen for every S-ion. The oxygen-atoms of the SrO-layers, which are the apical oxygens of the \( CuO_2 \)-sheets, have been slightly displaced to form the short \( SO \)-bonds. (This induces the existence of two different oxygen surroundings for \( Cu \)-atoms of the \( CuO_2 \) sheets.) The two other \( O \)-atoms are situated in the \( Cu(1) \)-S-O-plane and cannot be shared by adjacent \( SO_4^- \)-tetrahedra due to the shortness of the \( SO \) bonds. Every S-atom in an \( SO_4^- \) chain thus forms bonds with two \( O \)-atoms of the \( Cu(1) \)-S-O-plane. For a nominal S-content \( y = 0.22, 0.44 \) O-atoms are eliminated to form \( CuO \)-chains. The remaining oxygens in the plane (0.56) can be bound to the remaining \( Cu(1) \)-atoms (0.78) to form \( CuO \)-chains. The oxygen content in the \( CuO \)-ribbons in between \( Cu(1) \)-S-O chains is thus 0.72, high enough to allow for \( CuO \)-chain formation into domains of macroscopic dimensions. The occurrence of tweed, and with it a very low orthorhombicity (as in quenched or low oxygen content materials [12]), instead of the occurrence of macroscopic twin domains, suggests that the \( SO_4^- \)-presence or chain formation has an inhibiting effect on the orthorhombic domain growth.

Appendix

High resolution micrographs seldom exhibit good dislocation images, because the concentration of dislocations is in fact rather small so that the chances to find one in a small crystal fragment are almost negligible. Moreover, the dislocation strain field is only revealed clearly if the dislocation is seen end-on. Such images are nevertheless of importance because they allow one to locate the glide plane with respect to the structure, which is not obvious in complicated crystals. Figures 7 and 8 show a \([010]\) high resolution image and a model of such an undissociated edge dislocation. From the Burgers circuit, the Burgers vector can be deduced: it is \( a [100] \). The slip plane is located between a \( CuO \)-layer and an adjacent SrO-layer. Slip over \( a [100] \) brings the strontium-atom from the centre of one square of oxygen-atoms in the centre of the adjacent oxygen square. It should be noted that the core of the dislocation coincides with the site of a row of \( SO_4^- \)-ions, suggesting strongly that the dislocation has been pinned by

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Fig. 7. \([010]\) high resolution image of an edge dislocation pinned at a row of \( SO_4^- \) groups by elastic interaction between dislocation stress field and stress field due to a line of \( SO_4^- \) ions (indicated by small crosses). The dislocation is viewed end-on. Dashed lines allow one to locate the extra half-plane also indicated by a vertical arrow. Conservative glide takes place as this half-plane moves left or right. Alternative extra half-planes can be seen under grazing angles along the diagonal arrows.
Fig. 8. Schematic representation of the situation of fig. 7. The (conservative) glide plane is situated between the CuO-layer and a SrO-layer. On the right hand side, the SrO- and CuO-layers adjacent to the glide plane are drawn in a [001] view. The Burgers vector \( \mathbf{b} \) is indicated.

Cottrell-interaction with the row of SO\(_4\)-ions [13]. This image is to the best of our knowledge the first pictorial illustration of the Cottrell-interaction.

Acknowledgements

This text presents research results of the Belgian programme on InterUniversity Poles of Attraction initiated by the Belgian State, Prime Minister’s Office of Science Policy Programming. The scientific responsibility is with the authors. The work has been performed with the financial support of the Belgian National Science Foundation (NFWO) and the National Impulse Programme on High-\( T_c \) superconductivity (SU/03/17). OM acknowledges the EC commission for a grant DG XII No. S/C 11*913167.

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