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(Ba/Sr)O-BI-LAYER ORDERING IN THE $RE_2(Ba/Sr)_2GaCu_2O_9$ SUPERCONDUCTING CUPRATE[1]

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This paper is dedicated to Professor A. Bonefačić on the occasion of his 70th birthday

Ordering in the (Ba/Sr/Nd)O bi-layers (of "Rock-Salt" type structure) of the $RE_2(Ba_{0.65}Sr_{0.20}Nd_{0.15})_2GaCu_2O_9$ high-T_c superconducting cuprate was investigated by electron microscopy and diffraction. Besides the average layered structure based on the tetragonal perovskite cell $a_p \times a_p \times c_p$ and the meandering chain superstructure based on the orthorhombic $4a_p \times 2a_p \times c_p$ cell in the GaO-layers, an additional ordering was found in the pairs of (Ba/Sr/Nd)O-...-(Ba/Sr/Nd)O layers. We propose a model for ordering of 3Ba and 1Sr cations on a two-dimensional $2a_p \times 2a_p$ lattice cell in each (Ba/Sr/Nd)O layer. This compositional intra-layer ordering is accompanied by the inter-layer plane stacking disorder. The 4-fold symmetry of the average tetragonal structure is preserved, while the translation parameters in the (a,b) plane are doubled. This local ordering in the RS-type bi-layers hardly affects the symmetry of the basic structure; however, it may act as a source of weak anisotropy in the CuO_2-layers.

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1. Introduction

Layered structure of high-T_c superconducting cuprates (HTCSC) is anisotropic "per se"; it induces anisotropy of all physical properties such as electrical superconductivity or magnetic susceptibility. The average structure is tetragonal, while the basic structure of the prototype $YBa_2Cu_3O_{7-x}$ compound (noted also "YBCO" or "Cu-1212C" [1]) is orthorhombic. The Cu atoms in the CuO-chain layers of the Cu-1212C structure can be completely replaced [2] by the M = Ni, Ta, Ga, Co, Al, Hg, ... atoms [3-6], and even by the non-metallic C, S, P, N [7-10] atoms. These replacements hardly affect the average tetragonal structure. Various MO-chain arrangements were found to induce structural anisotropy in the form of orthorhombic superstructures with larger superlattice cells [11-14], however, with no profound effect on the anisotropy of physical properties.

In this paper, we present the results of an investigation of ordering in the (Sr/Ba/Nd)O layers of the $(Nd_{0.75}Ce_{0.25})_2(Sr_{0.20}Ba_{0.65}Nd_{0.15})_2GaCu_2O_{9+\delta}$ compound using electron microscopy and diffraction. Although the material is of a particular composition, this ordering is of general interest because the RS-type layers are present in all HTCSC structures; these layers are adjacent to both the MO-chain layers and the CuO_2-plane layers. Ordering in the RS-type layers has not been recognized so far as a significant effect in the most of HTCSC structures.

2. Structural consideration

The basic structure of the $(RE)_2(Sr_{0.20}Ba_{0.65}Nd_{0.15})_2GaCu_2O_{9+\delta}$ compound, termed here the Ga-1222C structure [15], can be represented by the layer stacking sequence in the unit slab, Fig. 1a:

$$\ldots\text{–GaO–}(Sr_{0.20}Ba_{0.65}Nd_{0.15})O\text{–}CuO_2\text{–RE–}O_2\text{–RE–}CuO_2\text{–}(Sr_{0.20}Ba_{0.65}Nd_{0.15})O\text{–}\ldots$$

The thickness of this unit slab is 1.41 nm, while the repeat distances within a slab are determined by the basic perovskite square lattice with parameters: $a_p^{(1)} \times a_p^{(2)}$ ($a_p^{(1,2)} =$ 0.39 nm). The presence of the RE-O_2-RE fluorite-like lamella causes a lateral shift over $1/2[110]_p$ of the two parts of unit slab on either side of the lamella, Fig. 1a. The repeat distance along the normal to the layers contains two unit slabs ($c_p = 2 \times 1.41$ nm), and the resulting basic lattice has a body centred tetragonal cell: $a_p^{(1)} \times a_p^{(2)} \times c_p$.

Two different arrangements were found in the GaO-chain layers of the $(RE)_2(Sr_{0.85-x}Ba_xNd_{0.15})_2GaCu_2O_{9+\delta}$ basic structure depending on x, the level of Ba-doping. For $x = 0$, the GaO-chains run diagonally along one of the two $[110]_p$ (or $[1\bar{1}0]_p$) directions [3-5,11,12]. For $x = 0.65$, the GaO-chains meander along the principal directions $[100]_p$ (or $[010]_p$) [13,14,16]. The corresponding superstructures are based either on the $2\sqrt{2}a_p^{(1)} \times \sqrt{2}a_p^{(2)} \times c_p$, or on the $4a_p^{(1)} \times 2a_p^{(2)} \times c_p$ superlattice cell, respectively. Each GaO-chain-layer is ensandwiched by a pair of $(Sr_{0.20}Ba_{0.65}Nd_{0.15})O$ layers, Fig. 1b. The $(Sr_{0.20}Ba_{0.65}Nd_{0.15})O$ plane spacing within this bi-layer is $C = 0.43$ nm, while the separation between the bi-layers is much larger, 0.98 nm.

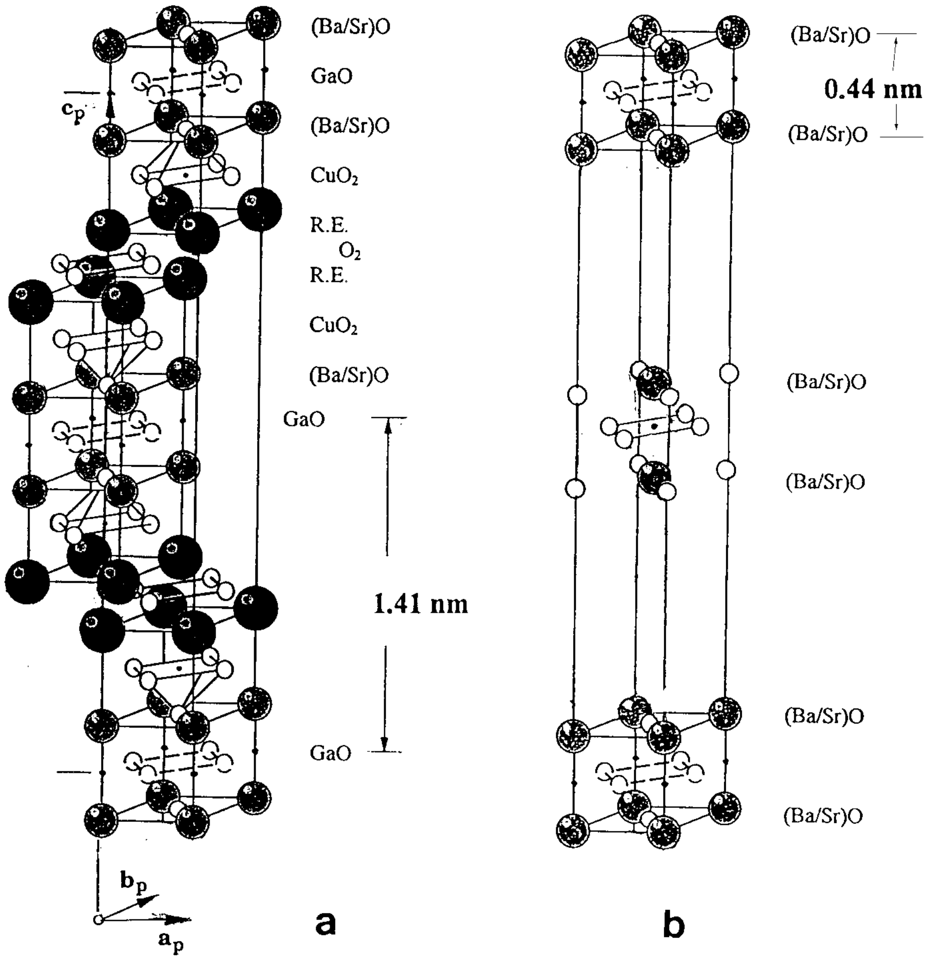

Fig. 1. Schematic representation of layered structure of $RE_2(Ba/Sr/Nd)_2GaCu_2O_9$ *compound: (a) front view of the complete structure; (b) view of the partial* (Sr/Ba/Nd)O *bi-layer structure.*

3. Electron diffraction patterns

The diffraction pattern along the [001] zone of this Ga-1222C structure is shown in Fig. 2. The series of diffraction patterns taken in the course of tilting experiment around the [001] axis are reproduced in Fig. 3. These reciprocal lattice sections provide an unambiguous reconstruction of the complete Ga-1222C structure, the GaO-chain-layer partial structure, as well as the partial structure of the RS-bi-layers.

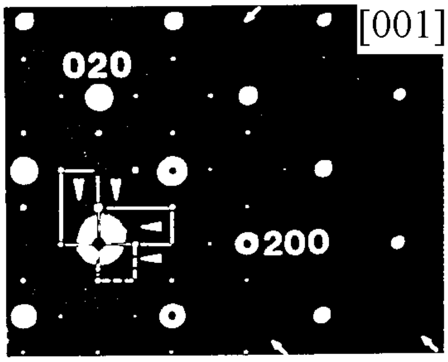

Fig. 2. EDP of the $RE_2(Sr_{0.20}Ba_{0.65}Nd_{0.15})_2GaCu_2O_9$ *compound along the* [001] *zone; four strong basic spots are marked with dots; the broken square marks the unit mesh of the* $2a_p \times 2a_p$ *lattice. The full line rectangles mark the C-centred meshes of two variants of the* $4a_p \times 2a_p$ *superlattice. Arrows at top and bottom indicate the extinctions. Arrowheads mark the spots at the points of intersections of diffuse streaks of Fig. 3.*

The most intense spots in all patterns are those generated by the basic perovskite sublattice. Due to the extinction condition, $h_p + k_p + l_p =$ odd, the basic spots can be indexed by a tetragonal face-centred reciprocal cell: $a_p^\star \approx (1/0.39)$ nm^{-1}, $c_p^\star \approx (1/2.82)$ nm^{-1}. This is in agreement with the body-centred cell of the basic Ga-1222C structure, Fig. 1a.

Besides the $d_{110p}^\star \times d_{1\bar{1}0p}^\star$ square mesh of basic spots, marked by black dots in Fig. 2, two meshes of weak spots represent two superlattices: the square mesh of sharp spots (with reciprocal cell indicated by the dashed lines) reveals a $2a_p^{(1)} \times 2a_p^{(2)}$ plane superlattice, and two rectangular meshes (with cells marked by the full lines) indicate the $4a_p^{(1)} \times 2a_p^{(2)}$ (and $4a_p^{(2)} \times 2a_p^{(1)}$) plane superlattices which are due to the meandering GaO-chain arrangements discussed in earlier papers [13,14,16].

Besides the basic spots, the patterns in Fig. 3 consist of two different types of diffuse streaks (based on the two above mentioned plane superlattice cells):

(') the streaks marked by double arrowheads in Figs. 3a,b and d exhibit clear intensity modulation along the $c^\star$-axis. These streaks intersect the $(hk0)^\star$ reciprocal lattice section of Fig. 2 at the vertices of the $1/2d_{100p}^\star \times 1/2d_{010p}^\star$ square mesh which corresponds to the $2a_p^{(1)} \times 2a_p^{(2)}$ superlattice cell;

('') the streaks of very weak intensity marked by single arrowheads in Fig. 3d which intersects the $(hk0)^\star$ section of Fig. 2 at the centres of the $1/4d_{100p}^\star \times 1/2d_{010p}^\star$ rectangular mesh. These streaks are based on the centred $4a_p^{(1)} \times 2a_p^{(2)}$ plane lattice cell.

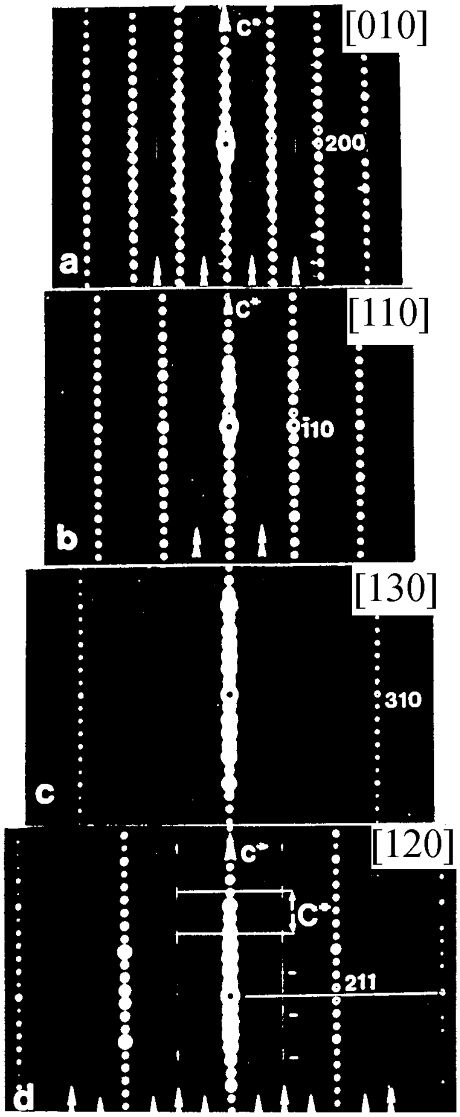

Fig. 3. Series of EDPs of the $RE_2(Sr_{0.20}Ba_{0.65}Nd_{0.15})_2GaCu_2O_9$ *compound: (a) the* $[010]_p$ *zone; (b) the* $[110]_p$ *zone; (c) the* $[\bar{1}30]_p$ *zone; (d) the* $[\bar{1}20]_p$ *zone. Black dots mark the basic spots which are labelled in perovskite notation; double arrowheads in (a) and (d) mark the diffuse streaks which belong to the* $2a_p \times 2a_p$ *mesh; single arrowheads in (d) mark the very weak diffuse streaks which belong to the centred* $4a_p \times 2a_p$ *mesh. Period of streak intensity modulation* $C^\star$ *is indicated in (d), along the intensity maxima positions.*

The family of diffuse streaks based on the $2a_p \times 2a_p$ lattice is of particular interest because of its prominent intensity modulation visible in Figs. 3a and d; the streaks are absent in Fig. 3b due to extinction; the period of this sinusoidal modulation is $C^\star \approx 6.4c_p^\star$. The positions of intensity maxima and minima along $c^\star$ can not be unambiguously determined from Fig. 3a where both families of streaks overlap, but the minima are clearly discerned at $l = 0$ in the $[120]_p$ zone pattern of Fig. 3d, where the two families of streaks appear separated.

4. Model and discussion

The family of streaks with the intensity modulation in reciprocal space is a well known indication [17] of the existing bi-layer configuration within the unit cell in direct space. The investigation of this diffuse intensity allows one to determine:

(i) which of the plane-layer substructures exhibits additional ordering, and

(ii) what are the symmetry restrictions on the ordering scheme in these planes.

All diffraction features can be accounted for by a simple scheme of composition ordering of 3Ba and 1Sr atoms on the $2a_p \times 2a_p$ lattice in the $(Sr_{0.25}Ba_{0.75})O$ layers as shown in Fig. 4 (for simplicity, the fraction of Nd atoms is not considered).

Let the contribution to the scattering amplitude of 3Ba+1Sr atoms, arranged on a $2a_p \times 2a_p$ cell in one layer, be written as:

$$F_g^{2\times 2} = f^{(Sr)} \left[1 + \Delta f \left(e^{\pi i \vec{g}\cdot\vec{a}'} + e^{\pi i \vec{g}\cdot\vec{b}'} + e^{\pi i \vec{g}\cdot(\vec{a}'+\vec{b}')} \right) \right]$$

where $\Delta f = f^{(Ba)} - f^{(Sr)}, \vec{a}' = 2\vec{a}_p^{(1)}$ and $\vec{b}' = 2\vec{a}_p^{(2)}$, while $\vec{g}$ is the diffraction vec-

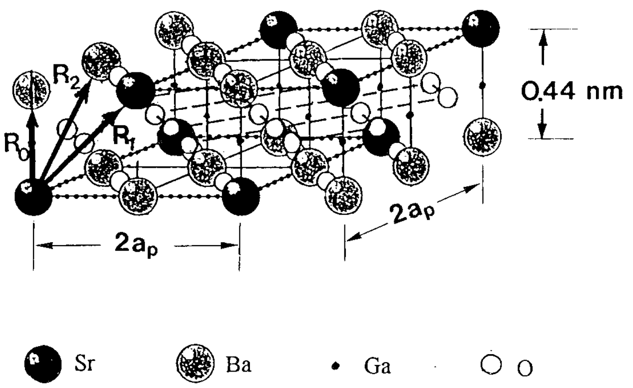

Fig. 4. Scheme of compositional ordering in the $(Sr_{0.25}Ba_{0.75})O$ planes (RS-type layers) of the (Sr/Ba)O-GaO-(Sr/Ba)O lamella in $RE_2(Sr_{0.20}Ba_{0.65}Nd_{0.15})_2GaCu_2O_9$ structure. The broken lines indicate the $2a_p \times 2a_p$ square units in the bottom and top planes. Vectors $\vec{R}_i$ denote the correlation vectors.

tor. The additional scattering amplitude from the whole family of RS-layers is:

$$F_g^{(L)} = F_g^{2\times 2} \sum_{jl} \mathrm{e}^{2\pi\mathrm{i}\vec{g}\cdot\vec{r}'_{jl}},$$

where the summation index j runs over all layers and index l over all (a', b') sites in one layer. In the case when these sites are related by a displacement vector $\vec{R}$ in the pair of adjacent RS-layers, the corresponding structure factor can be written as:

$$F_g^{(BL)} = F_g^{2\times 2} \left(1 + \mathrm{e}^{2\pi\mathrm{i}\vec{g}\cdot\vec{R}}\right) \sum_{j'l} \mathrm{e}^{2\pi\mathrm{i}\vec{g}\cdot\vec{r}'_{j'l}},$$

where the index j' runs now over all bi-layers. The vector $\vec{R}$ relating the two layers in a bi-layer can be decomposed in two components: $\vec{R} = \vec{R}_\perp + \vec{R}_\parallel$, where $\vec{R}_\perp$ $(= \delta\vec{c})$ is perpendicular to the layers (δ denotes fraction of the c-spacing), and the component $\vec{R}_\parallel$ is parallel to the layers. The intensity distribution along the streaks in the corresponding diffraction pattern is given by a sinusoidal modulation with the period $1/\delta$ and phase $\alpha_g = 2\pi\vec{g}_\parallel \cdot \vec{R}_\parallel$:

$$I_g = 2[1 + \cos 2\pi(\delta l + \alpha_g)] \ \ |F_g^{2\times 2} \sum_{j'l} \mathrm{e}^{2\pi\mathrm{i}\vec{g}\cdot\vec{r}'_{j'l}}|^2,$$

where the reciprocal period $1/\delta = C^\star$ (in $c^\star$ units) indicates that the layers exhibiting additional ordering (responsible for this modulation) must be separated by $\delta = C$. The phase α_g indicates a relative shift of two configurations of ordered $2a_p \times 2a_p$ meshes between adjacent layers. Since the intensity of the streaks have a minimum at $l = 0$ in Fig. 3d, vertical stacking of the $2a_p \times 2a_p$ meshes in the $(Sr_{0.25}Ba_{0.75})O$ bi-layers is forbidden. The relative displacement vector $\vec{R}_1$ in Fig. 4 represents one possible bi-layer configuration of 3Ba and 1Sr atoms on the $2a_p \times 2a_p$ lattice in the $(Ba_{0.75}Sr_{0.25})O$ layer below and above the GaO-chain plane. All other configurations with the non-zero component $\vec{R}_\parallel$ of the displacement vector ($\vec{R}_2$ in Fig. 4) are also consistent with the intensity minima at $l = 0$; vertical stacking $\vec{R}_0 = \delta\vec{c}$ would have $\alpha_g = 0$, thus giving a maximum at $l = 0$. The stacking of bi-layer in successive slabs is correlated by one of four vectors: $\vec{S} = \pm 1/2\vec{a}_p^{(1)} \pm 1/2\vec{a}_p^{(2)} + 1/2\vec{c}_p$, thus generating the observed extinction conditions $(h + k = 2/\mathrm{mod}\, 4)$ for the superlattice spots, indicated by small arrows in Fig. 2, and for the streaks indicated by double arrowheads in Fig. 3b. The streaking along the $c^\star$-axis reveals a high degree of plane stacking disorder which is due to four possible vectors $\vec{S}$ correlating the bi-layers in successive slabs.

The HREM imaging of the Ga-1222C structure along the $[100]_p$ and $[210]_p$ zones, in Figs. 5a and b, respectively, supports this model. Namely, the proposed scheme for RS-layer ordering is a rather weak modification of the average basic structure. Therefore, imaging along the $[100]_p$ zone in Fig. 5a represents only the basic Ga-1222C structure with no certain indication of additional $2a_p \times 2a_p$ plane-structure in the RS-bi-layers. This RS-bi-layer ordering is revealed only by the "oblique zone" imaging [18] along the $[210]_p$ zone of fig. 5b, a weak variation of dot brightness in the pair of bright fringes marked by arrows. The fringe separation $C = 0.44$ nm fully agrees with the streak modulation period $C^{\star} = (1/0.44)\ \mathrm{nm}^{-1}$ in the corresponding diffraction pattern of Fig. 3d.

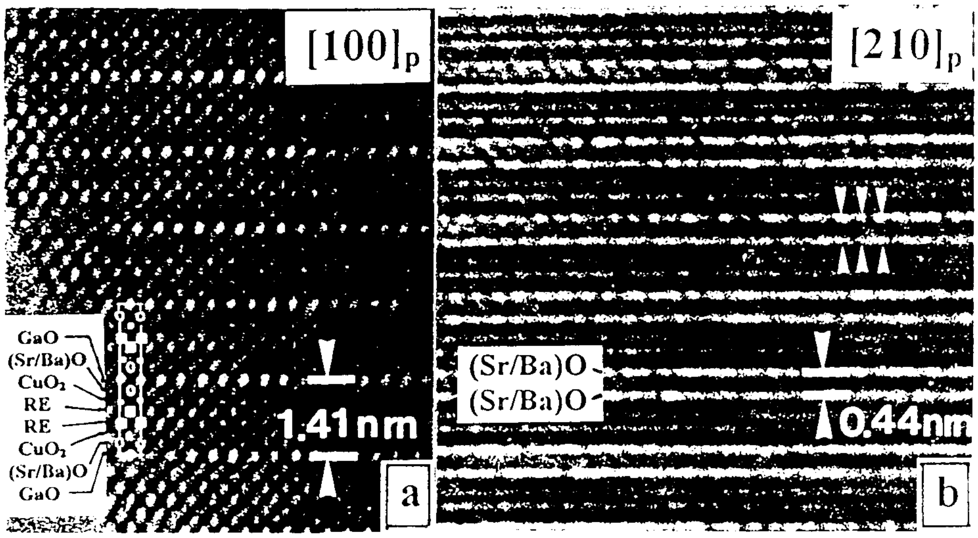

Fig. 5. HREM imaging of the $RE_2(Sr_{0.20}Ba_{0.65}Nd_{0.15})_2GaCu_2O_9$ *structure: (a) along the* $[100]_p$ *zone and; (b) along the* $[210]_p$ *zone. The layers of basic structure are indicated in the legend of (a). The RS-type bi-layers* (Sr/Ba)O. . . (Sr/Ba) *are marked by arrows in (b).*

5. Conclusions

Compositional ordering of Ba and Sr atoms is detected in $(Sr_{0.20}Ba_{0.65}Nd_{0.15})O$ ... $(Sr_{0.20}Ba_{0.65}Nd_{0.15})O$ ... bi-layers of the Ga-1222C basic structure; the bi-layers are of the RS-type with the $2a_p \times 2a_p$ superstructure. This ordering in the RS-bi-layers takes place on top of the meandering chain arrangement in the GaO-layers of the $(RE)_2(Sr_{0.85-x}Ba_xNd_{0.15})_2GaCu_2O_{9+\delta}$ compound for $x = 0.65$. The ordering seems to be only a weak, local modification of the basic Ga-1222C structure. Namely, the absence of vertical stacking of the $2a_p \times 2a_p$ configuration in two (Ba/Sr)O planes of a single bi-layer can locally accommodate for the 4-fold symmetry of the CuO_2-plane layers and the 2-fold symmetry of the meandering chains in the GaO-layers based on the $4a_p \times 2a_p \times c_p$ superlattice. Due to twinning in the GaO-chain layers, and the plane stacking disorder of the adjacent (Ba/Sr)O...(Ba/Sr)O

bi-layers in successive slabs, the symmetry of this structure is apparently enhanced to the tetragonal symmetry of the average Ga-1222 structure.

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UREDJENJE (Ba/Sr)O-DVOSLOJEVA U SUPRAVODLJIVOM KUPRATU $RE_2(Ba/Sr)_2GaCu_2O_9$

Strukturno uređenje (Ba/Sr/Nd)O dvoslojeva u supravodljivom kupratu sastava $RE_2(Ba/Sr)_2GaCu_2O_9$ istraživano je pomoću elektronske mikroskopije i difrakcije. Osim prosječne tetragonske strukture na osnovi slojevite perovskitske tetragonske ćelije $a_p \times a_p \times c_p$, i nadstrukture meandrirajućih lanaca u GaO-ravninama s ortorombskom ćelijom $4a_p \times 2a_p \times c_p$, nađeno je dodatno uređenje u parovima (Ba/Sr/Nd)O-...-(Ba/Sr/Nd)O ravnina. Predložen je model uređenja 3Ba i 1Sr kationa unutar $2a_p \times 2a_p$ dvodimenzijske ćelije u svakoj (Ba/Sr/Nd)O ravnini. Ovo unutar-ravninsko uređenje popraćeno je među-ravninskim neredom u nizu slaganja slojeva. Simetrija 4-reda, koja je svojstvena prosječnoj tetragonskoj strukturi ostaje sačuvana, uz podvostručenje parametara rešetke u (a,b) ravnini. Opaženo uređenje unutar (Ba/Sr/Nd)O dvoslojeva ovog supravodljivog kuprata nema jaki utjecaj na simetriju osnovne strukture, ali može biti izvor lokalne anizotropije u CuO_2-ravninama.