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Classification

Physics Abstracts

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Ordering principles for tetrahedral chains in Ga- and Co-substituted YBCO intergrowths

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Abstract. — A model for superstructure ordering in the « chain » layers of Ga (Co) substituted YBCO intergrowths with general formula $(\text{REO}_2)_n\text{Sr}_2\text{MCu}_2\text{O}_5$ ($\text{M} = \text{Co}, \text{Ga}$; $n = 1, 2, \dots$) is proposed. By Ga or Co substitution for Cu, the structure of the « chain » layer changes : instead of the CuO_4 planar squares, the chains consist of MO_4 tetrahedra ($\text{M} = \text{Ga}, \text{Co}$) running along the [110] perovskite direction. The existing model for the Ga substituted « 123 » implies that all the chains are the same.

Our new model is based on the results of Electron diffraction and High-resolution electron microscopy investigations. The model reveals the occurrence of two types of chains as a consequence of « opposite » ordering between neighbouring tetrahedra. The corner linked tetrahedra in each chain appear as alternately rotated in opposite sense, and a chain itself, as being displaced with respect to the underlying structure in one of two senses ; either forth (right) or back (left) along the chain direction. The regular alternation of chains of opposite type doubles the periodicity within a layer and induces the possibility for intrinsic disorder in the chain layer stacking sequence. The planar superstructure and a staggered stacking of the tetrahedral chain layers is found irrespective of the rest of the intergrowth structure. Superstructure ordering in the case of Co substitution is more perfect than for the Ga substitution.

1. Introduction.

The tri-perovskite structure of the prototype « 123 » compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ contains copper in two different layers. A consensus exists that although superconductivity has to be associated with the two-dimensional CuO_2 layers in the structure, the carrier concentration and the T_c value strongly depend on the composition and on the oxygen order in the $\text{CuO}_{1-\delta}$ layers. To optimize the superconducting properties, a large effort has therefore been devoted to the study of the behaviour of this layer under different doping conditions and for different isomorphous substitutions by aliovalent ions. It is quite remarkable to what extent the topology of the structure remains unchanged for a number of such substitutions [1, 2], even though the superconducting properties are strongly influenced ; this is for instance the case for iron and

zinc doping. Substitutions by ions which tend to form a tetrahedral coordination with oxygen ions lead to a change in the geometry of the $\text{CuO}_{1-\delta}$ layer, maintaining the integrity of the rest of the structure ; this is for instance the case for gallium and cobalt.

Superconductivity was recently reported with T_c up to 50 K in the Ca doped Ga-substituted compounds : $\text{RE}_{1-x}\text{Ca}_x\text{Sr}_2\text{GaCu}_2\text{O}_7$ [3].

As a result of the substitutions of Ga or Co for Cu in the CuO layer, chains of corner-sharing MO_4 ($M = \text{Co}, \text{Ga}$) tetrahedra are formed parallel to the $[110]_p$ or $[1\bar{1}0]_p$ directions. The lattice parameters of the unit mesh in the layer plane become : $a_0 \approx a_p \sqrt{2}$; $b_0 \approx a_p \sqrt{2}$ ($a_p \approx 0.38 \text{ nm}$; P : perovskite lattice ; O : orthorhombic lattice).

The structure of the tetrahedral chain layer, proposed in this paper, is based on the previous results [4, 5, 6] and on our electron microscopy study of the $\text{YSr}_2\text{CoCu}_2\text{O}_7$ and $\text{Nd}_{17}\text{Ce}_{05}\text{Sr}_{18}\text{GaCu}_2\text{O}_9$ compounds [7]. In comparison with YBCO, the CuO layer was replaced by a CoO layer in the former compound, while in the latter compound the CuO layer was replaced by a GaO layer and the Y layers were replaced by the $(\text{Nd/Ce})\text{-}[\text{O}_2\text{-}(\text{Nd/Ce})]_m$ lamellae of variable thickness. All studied phases belong to the homologous series of intergrowth structures : $(\text{REO}_2)_n\text{Sr}_2\text{MCu}_2\text{O}_5$ where $M = \text{Co}$ or Ga ; $n = 1, 2, \dots$

2. Structural consideration.

The structure of the compound $\text{RE}_1\text{Sr}_2\text{GaCu}_2\text{O}_7$, noted here as Ga-1212 (according to Adachi's notation [8] and in order to emphasize the Ga- substitution), was found by means of X-ray and neutron diffraction to be orthorhombic with lattice parameters $a_0 = 0.55 \text{ nm} \approx a_p \sqrt{2}$; $b_0 = 0.54 \text{ nm} \approx a_p \sqrt{2}$; $c_0 = 2.28 \text{ nm} \approx 2 c_p$ [5, 6] ; it is closely related to that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The perovskite block has the same topology as in the prototype 123 compound, but the CuO chains along $[010]_p$ are replaced by chains of GaO corner sharing tetrahedra along the $[110]_p$ or $[1\bar{1}0]_p$ direction.

Substitutions are also possible at the level of the Y-layers. Not only can other rare earth ions be substituted for Y, but the Y-layer can be replaced [9] by a lamella of $\text{RE-(O}_2\text{-...-RE)}$ which has the fluorite structure [10-14]. This substitution affects the size and the geometry of the block units as well as their stacking mode [15]. If the number of RE planes is even, the two structure blocks on either side of the $\text{RE-O}_2\text{-...-RE}$ lamella are shifted over $1/2 [110]_p$ leading to a body centred unit cell. If the number of layers is odd, the blocks are stacked vertically. The blocks unshifted with respect to the CuO_2 layer are designated by Tokura [16, 17] as α -block layers (α -BL), whereas the shifted blocks are called β -block layers (β -BL). Very recently an alternative classification of block layers was suggested : the « connecting » layer and the « separating » layer types [18]. We will term here « α' -BL » or « β' -BL » a block layer as opposed to the « CuO-chain »-layers i.e. with respect to the GaO or CoO planes ; α' -type causes no shift (Fig. 1a) while β' -type induces a relative shift between the « chain »-layers above and below the corresponding block layer (Fig. 1b). In the case of the Co- or Ga-1212 structure the α' -BL consists of the sequence of planes $[(\text{SrO})\text{-(CuO}_2\text{)-RE-(CuO}_2\text{)-}(\text{SrO})]$ and the corresponding c -parameter is $c_1 = 2.28 \text{ nm}$. In the case of the Ga-2212, structure the β' -BL contains the sequence of planes $[(\text{SrO})\text{-(CuO}_2\text{)-RE-O}_2\text{-RE-(CuO}_2\text{)-}(\text{SrO})]$ and the corresponding c -parameter is $c_2 = 2.82 \text{ nm}$.

The compound $(\text{Nd}, \text{Ce})\text{Sr}_2\text{GaCu}_2\text{O}_7$ is the first member of the homologous series of Ga- n -212 phases : ($n = 1$) in $(\text{REO}_2)_n\text{Sr}_2\text{GaCu}_2\text{O}_5$. The $(\text{Nd}, \text{Ce})_2\text{Sr}_2\text{GaCu}_2\text{O}_9$ would be the second ($n = 2$), while the compound $\text{YSr}_2\text{CoCu}_2\text{O}_7$ could be considered as the first member ($n = 1$) of the corresponding Co- n -212 series.

According to the structure determinations of $\text{YSr}_2\text{GaCu}_2\text{O}_7$ by powder diffraction [5], all parallel chains of GaO_4 tetrahedra are equivalent and related by translations $[110]_p$ or

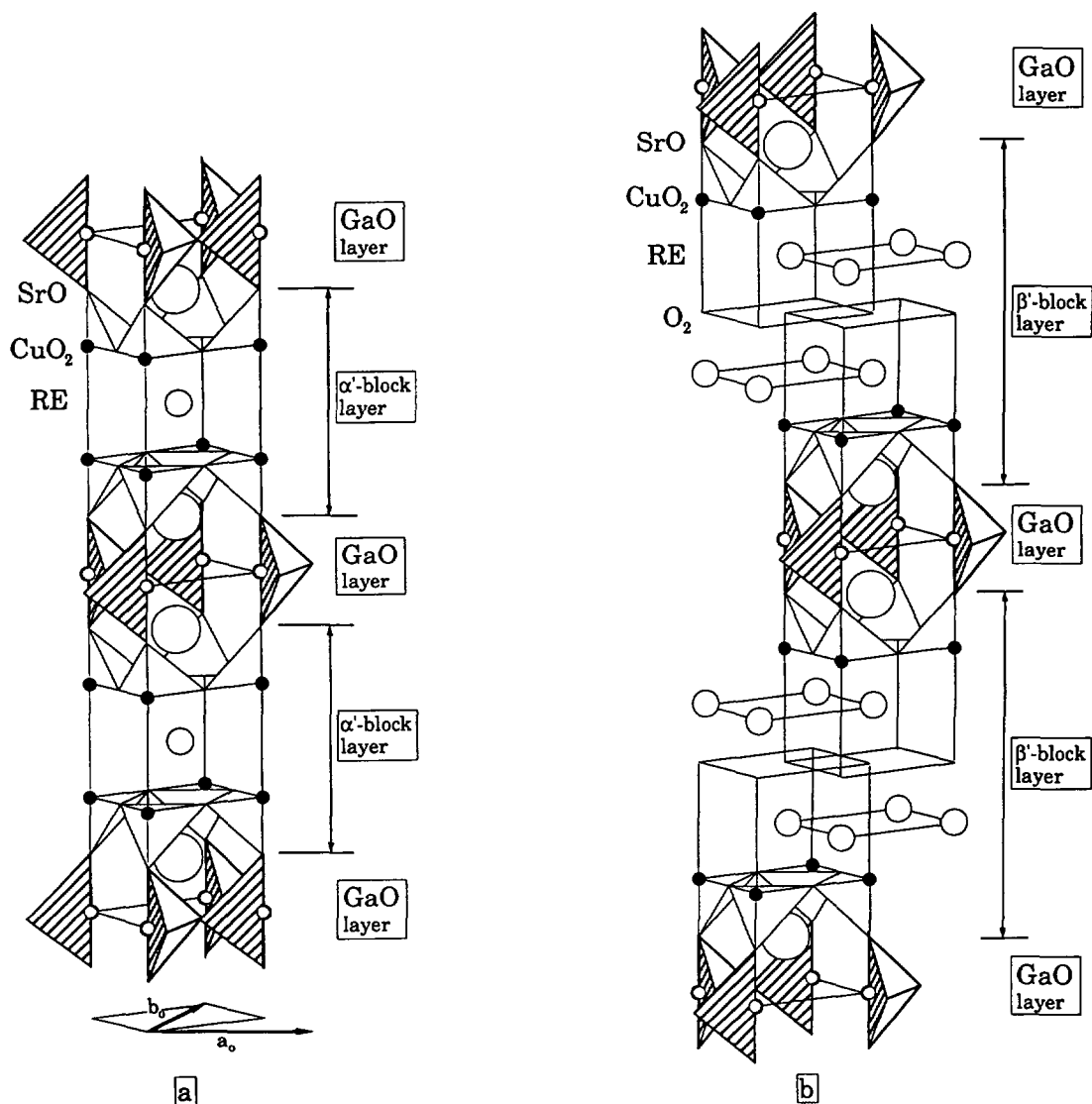


Fig. 1. — Schematic representation of the Ga-1212 and Ga-2212 structures as composed of two partial structures : « GaO » layers, and « block layers » ; the block layers consisting of [SrO-CuO₂-RE-CuO₂-SrO] planes are indicated as α'-BL in (a) while the β'-BL in (b) consists of sequences of planes [SrO-CuO₂-RE-O₂-RE-CuO₂-SrO] which induces a shift of the upper GaO layer with respect to the GaO layer below the β'-BL.

[1 $\bar{1}$ 0]_p. The corresponding cobalt compound YSr₂CoCu₂O₇ (Co-1212) is isostructural with the 1212-gallium compound [6] due to the tendency of cobalt and gallium to be tetrahedrally coordinated by oxygen. The tetrahedral chain layer in these compounds has the same planar structure including the splitting of metal and oxygen atom positions in the CoO or GaO plane [6].

Electron diffraction of these compounds, in particular along the [001]₀ zone (Fig. 2), and along [2 $\bar{1}$ 0]₀ zone (Fig. 3), has revealed that the structure is in actual fact more complicated

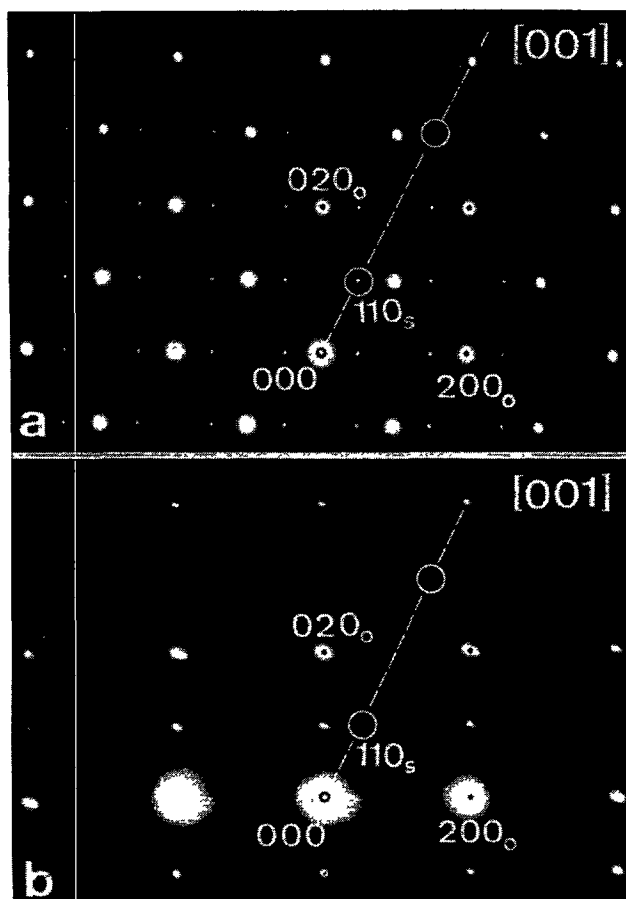


Fig. 2. — Electron diffraction patterns along $[001]$ zone of : (a) Co-1212 ; (b) Ga-2212. The strong spots, marked by black dots, are compatible with Roth's orthorhombic lattice. The dashed line, with circles marking the superlattice spots, are the traces of the $(1\bar{1}0)_s^*$ sections shown in the diffraction patterns in figure 3.

since weak superstructure reflections show that the unit cell size is twice that proposed in [4, 5, 6], i.e. the lattice parameters of the superstructure (subscript « s ») are $a_s = 2a_0$; $b_s = b_0$; $c_s = c_0$. Since the superstructure reflections are weak, the deviation of the real structure from that proposed previously must be small.

High resolution electron microscopy, as described in more detail below, has allowed us to conclude that the period doubling along a_0 is localized in the GaO (CoO) layer of the structure. This information is obtained by imaging the structure along a zone such as $[1\bar{1}0]_s$ (i.e. along the reciprocal lattice sections shown in Fig. 3), for which the only resolved spacing is that due to the superstructure. Well separated dots, i.e. images of atomic columns, with a spacing of 0.48 nm and 0.24 nm are only obtained for the GaO layers, figure 4a; the other layers being imaged as almost continuous lines because the spacing between the atomic columns is too small : 0.12 nm. This is confirmed by imaging the same area along the $[1\bar{2}0]_s \equiv [1\bar{1}0]_0$ zone, shown in figure 4b, in which the GaO layers as well as the structure of the block layers are

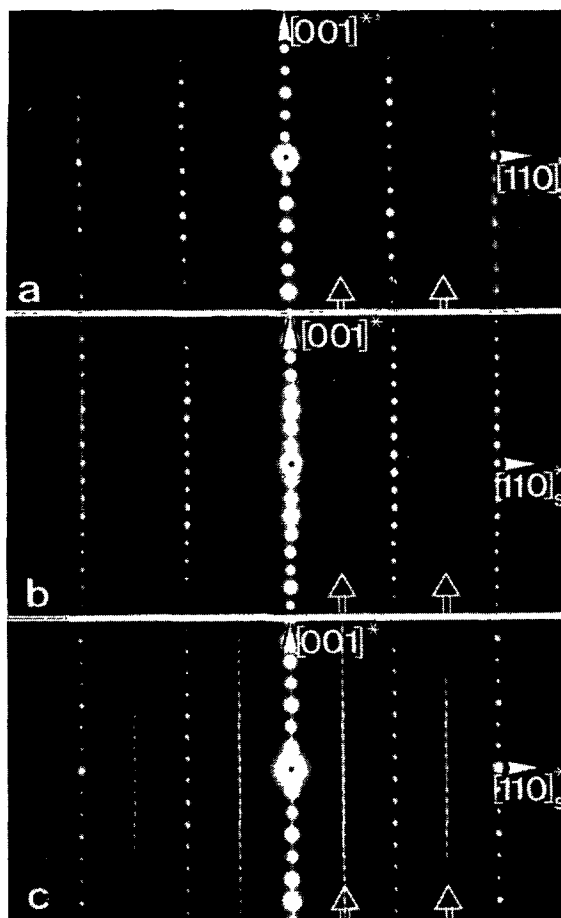


Fig. 3. — $[1\bar{1}0]_s$ zone diffraction pattern of : (a) Ga-1212 and, (b) Ga-2212, (c) Co-1212. Open arrows indicate rows of diffuse streaking $[hh\ell]_s^*$ for $h = \text{odd}$ due to the $2a_0 \times b_0$ superlattice ; sharp spots in the $[22\ell]_s^*$ row can be referred to the $a_0 \times b_0$ orthorhombic cell and indexed as the $12\ell_0$, while the strong spots in the $[44\ell]_s^*$ row can also be referred to the perovskite $a_p \times b_p$ cell as the $13\ell_p$ spots.

revealed. The discussion of ordering can thus largely be restricted to considerations concerning the arrangement of chains on the GaO (CoO) chain sublattice.

The electron diffraction patterns along zones such as $[1\bar{1}0]_s$ in figure 3 reveal rows of continuous diffuse scattering $[hh\ell]_s^*$ for $h = \text{odd}$ (indicated by open arrows in Fig. 3a, b), for the gallium compounds Ga-1212 and Ga-2212, respectively, and streaking through the superlattice spots for the Co-1212 compound (Fig. 3c). These rows cannot be labelled by integer indices considering the unit cell proposed by Roth *et al.* [5]. The diffuse features in the diffraction pattern depend neither on the block layer type : α' - or β' -, nor on their internal structure, but reflect the state of order in the GaO and CoO layers. In the cobalt compound, Co-1212, relatively sharp superlattice maxima, are superimposed on the diffuse streaks, indicated in figure 3c. The streaks are furthermore widened in the a_0^* direction, especially in the Ga-compounds (Fig. 2b), and thus form narrow ribbons parallel to c_s^* rather than lines of diffuse scattering in reciprocal space.

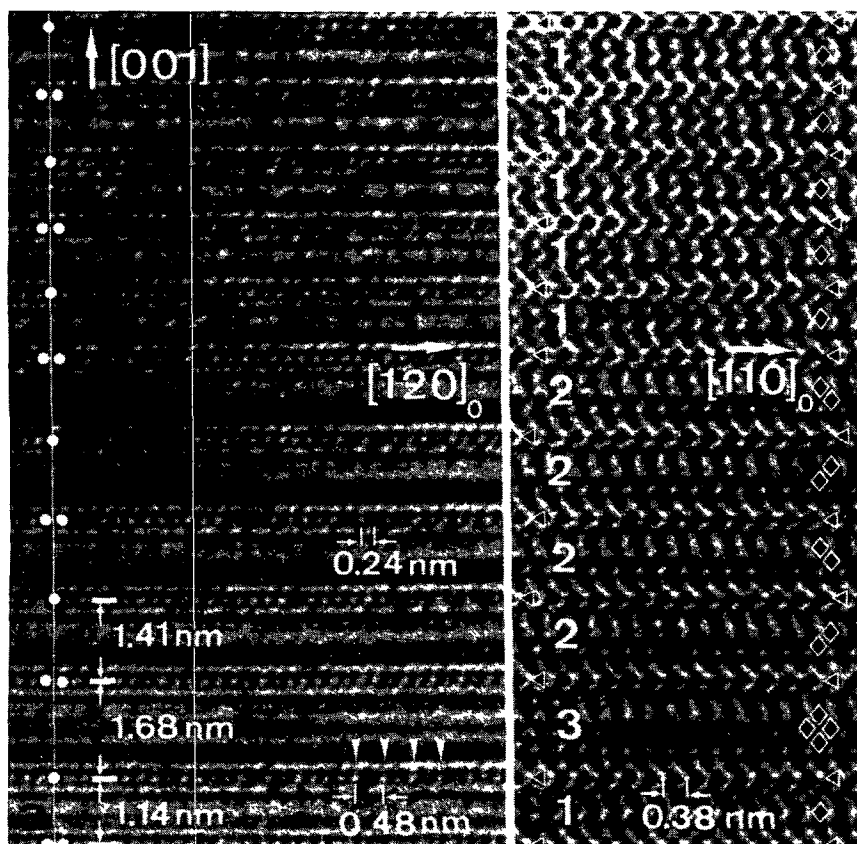


Fig. 4. — HREM images of the same area of Ga-*n*-212 : (a) along $[1\bar{1}0]_s \equiv [2\bar{1}0]_0$ zone ; (b) along $[1\bar{1}0]_0 \equiv [1\bar{2}0]_s$ zone. In (a) the GaO layers are revealed as dotted lines with spacing 0.24 nm ; arrowheads indicate the sequence of dots revealing the superlattice spacing 0.48 nm. The stacking of GaO layers $[001]$ is indicated in the left of (a) ; it is staggered irrespective of the type of intergrown block layer, containing 1, 2, or 3 fluorite like-layers (as indicated in (b)). In (b) the basic intergrowth structure of Ga-substituted perovskite layers (indicated by triangles), and the fluorite-like layers (indicated by rhombs) of various thickness are revealed, figures on the left indicate the numbers of RE layers in fluorite-like lamellae.

3. Model for the superstructure.

A model for the superstructure is suggested by the following structural considerations. The GaO (CoO) chains can adopt two different configurations with respect to the surrounding perovskite blocks along each one of the two possible mutually perpendicular $[110]_p$ and $[1\bar{1}0]_p$ directions. These configurations depend on how the corner sharing tetrahedra are assumed to be rotated. Assuming the oxygen atoms in the two SrO layers adjacent to the GaO (CoO) layer to be undisplaced, successive perovskite blocks remain vertically stacked, figure 1. The rotation of the corner-sharing tetrahedra then takes place about an axis normal to the layer plane, connecting the two oxygen atoms in these SrO layers. The coupled rotations of the tetrahedra, which are necessary to adjust the Ga-O (Co-O) interatomic bond length (and which are accompanied by a tendency of the Ga (Co) atoms to occupy the centres of these

tetrahedra), then result in shifts of the Ga (Co) atoms, as well as of the intralayer oxygens, with respect to the atom positions in the adjacent perovskite blocks on either side of the GaO (CoO) layer (Fig. 5). In particular the shifts of the gallium atoms in a given chain have components, all in the same sense, along the chain direction i.e., along b_0 , but have components in alternating senses along the direction perpendicular to the chains i.e. along a_0 .

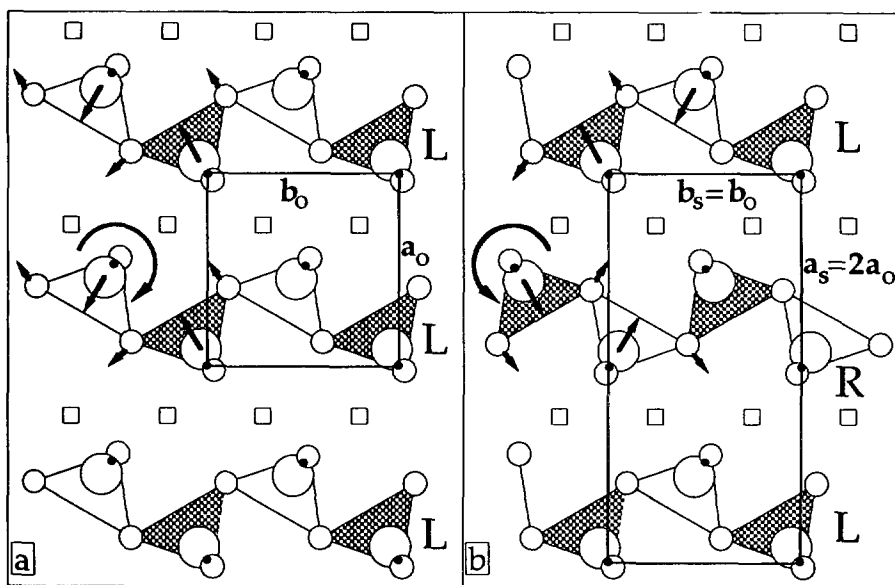


Fig. 5. — Schematic representation of two different planar structures of the tetrahedral chains in the GaO (CoO) layer (plain and hatched triangles represent tetrahedra rotated clockwise and counter-clockwise, respectively): (a) all chains are of the same type- « L »; (a_0 , b_0 lattice cell in agreement with [5] is indicated); (b) left « L » and right « R » chains alternate (the superlattice cell $a_s = 2a_0$, b_0 is indicated). Two possibilities for the rotation of the same tetrahedron resulting in left and right chain shifts are indicated by circular arrows, while the net shifts of Ga (Co) and O atoms with respect to the rest of the structure are indicated by arrows in the upper left part of (a) and (b).

This hypothetical formation process thus results in a net shift of the chains of Ga atoms in the b_0 direction with respect to the surrounding matrix. Such a shift is likely to perturb the electrostatic and/or elastic equilibrium creating hereby a dipole associated with each chain.

The two possible rotation senses of the coupled tetrahedra lead to two types of chains (Fig. 5), arbitrarily called left : « L »-, and right : « R »- chains, and cause shifts of the GaO chains in opposite sense along b_0 and no net shifts in the a_0 direction. The dipoles associated with the two types of chains have opposite signs.

The L and R chains are related by a mirror operation with respect to the $(010)_s$ (i.e. a $(110)_p$ or $(\bar{1}\bar{1}0)_p$) plane normal to the chain axis, or by a 180° rotation about an axis normal to the c -plane. Since both these operations are symmetry operations for the « perovskite » blocks of α' -type and β' -type, the configurational energy of a set of parallel L or R chains sandwiched between two block layers must be the same. Both types of chains thus have equal probability of being formed; as a result they are likely to occur both in the crystal structure in equal numbers.

Assuming a model in which all chains would be of the same type in a given layer (Fig. 5a), clearly leads to a shift in the same sense of all Ga- atom-chains with respect to the rest of the

structure. That would give rise to a net dipole moment associated with the layer, and hence with the orthorhombic cell according to Roth *et al.* [5], where all tetrahedral layers are of the same type.

On the other hand, an arrangement of alternating L- and R-chains in the layer (Fig. 5b), leads to an anti-parallel configuration of the dipoles associated with these chains, doubles the periodicity along the a_0 direction as observed in electron diffraction, and causes compensation of the dipoles within a layer. We therefore believe that the alternating arrangement of chains contributes significantly to the stability of the structure.

When all chains are assumed to be similar in all layers, compensation of the dipoles could be achieved by an alternating arrangement of layers of L-type and layers of R-type chains, like in the Brownmillerite structures [19, 20]. However, such an arrangement would not be in agreement with the period doubling along the a_0 direction in the GaO layers.

The arrangements of the alternating chains in successive layers should not coincide vertically, figure 6c, but be staggered, figures 6a & b. This is required by the observed doubling of the c -parameter : $c_s = 2 c_p$ (we hereby ignore for the moment the possible presence of more than one RE layer in the RE-O₂-RE lamellae, in the gallium compound).

A consistent application of both building principles, i.e. alternation of the two types of chains along a_0 and a staggered arrangement of the chain sublattice along c_0 , leads to two sets of two energetically equivalent but crystallographically different arrangements for the chains in successive layers : two staggered, as represented schematically in figures 6a & b ; and two vertical, figures 6c & d. mainly, the arrangements in figures 6a & b have been observed by high resolution imaging, but occasionally also the arrangement in figure 6d, as discussed below. On the contrary, the stacking represented in figure 6c has never been observed ; if it would occur, the c -parameter would be halved, i.e. : $c_0/2 = c_p$.

An idealized structure for the Ga-2212 intergrowth containing RE-O₂-RE lamellae, would also consist of GaO layers with an alternating arrangement of left and right parallel chains ; the stacking of the successive layers being staggered (and shifted), as represented schematically in figures 7a & b, or vertical (and shifted), as in figures 7c & d.

Since the stacking represented in figure 6a is energetically equivalent with that in figure 6b for the 1212 phase, and the stacking in figure 7a is equivalent with that in figure 7b for the 2212 phase, both stackings, in both phases are equally likely to occur and stacking faults are thus to be expected. The energy of such defects is rather small. This is clearly consistent with the observed streaks of diffuse scattering parallel to c^* , in figure 3.

The results recently presented in [21] on Ca-doped RE-Sr-Ga(Cu-O), indicate possible tripling of the chain periodicity within a GaO layer. This tripling may also be realized by the ordering of the L- and R- chains. When the chain arrangement is of the type.. LLRLLR ... (or .. RLLRLL ..) optimal chain-dipole compensation is achieved by stacking the layers in such a way that a L chain in one layer projects along c_0 midway between two R chains in the adjacent layers or « vice versa ». The lattice of the GaO chains would have the parameters $a_s = 3 a_0$; $b_s = b_0$; $c_s = c_0$, and it would be body-centered (i.e. successive chain layers are related by a translation $1/2 [111]$), as shown schematically in figure 8. The superlattice spots in the (001)* section of reciprocal space would then form a rectangular centered arrangement (i.e. $h + k$ must be even), as seems to be observed in [19]. The presence in reciprocal space of planes of diffuse intensity perpendicular to the chain direction b_s can be understood by noting that intra-chain disorder also leads to disorder in the longitudinal positions of the chains. Such disorder causes planes of diffuse intensity.

The very recently reported tetragonal structure for (Y, Ce)₂Sr₂GaCu₂O₉ [22], with a - parameter $0.38 \text{ nm} \cong a_p$, does not seem to be realistic ; it is probably based on the consideration of only the strong spots (or lines in powder X-ray diffraction patterns) which

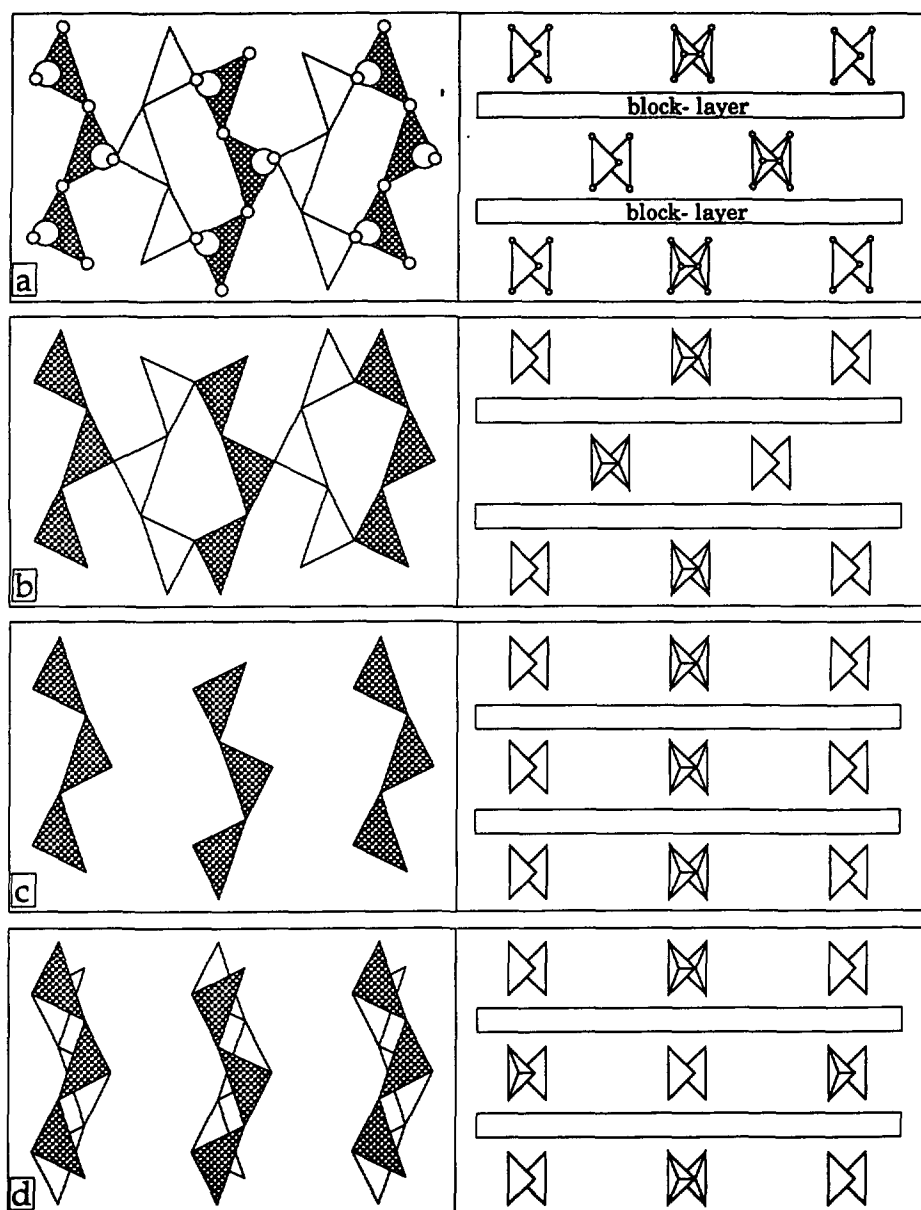


Fig. 6. — Schematic representation of various stacking possibilities for stacking of neighbouring GaO (CoO) layers in the 1212 structure. (a)-(d) left : projection onto the chain-plane ; (a)-(d) right : projection along the chain direction. Block layers are of α' -type. Shaded and plain triangles on the left represent the tetrahedra in the upper and in the middle level, respectively.

belong to the underlying structure of the β' -BL, and its body-centered pseudo-tetragonal lattice cell.

We can conclude that an adequate application of the above formulated building principles, and the presence of defects and disorder discussed below, leads to an interpretation of the

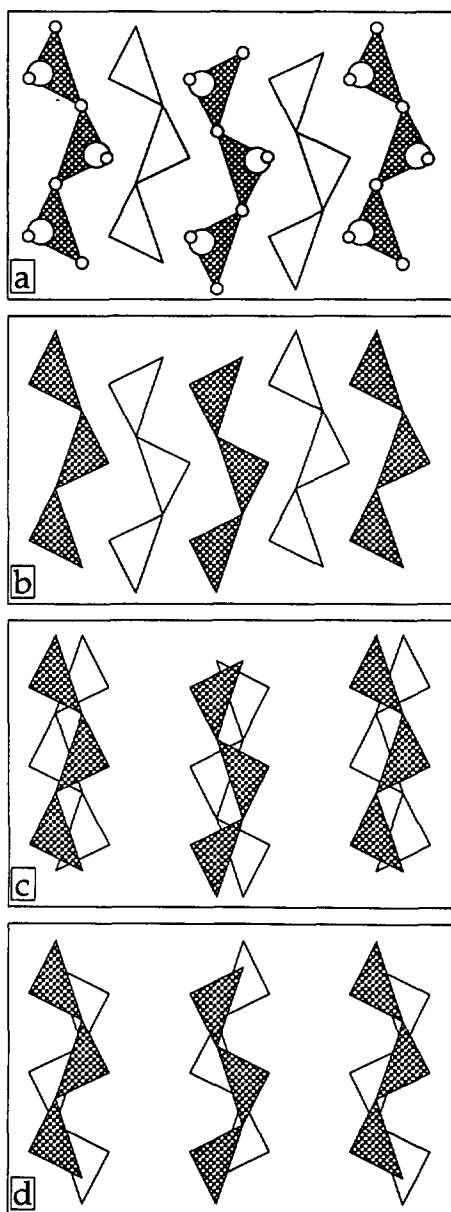


Fig. 7. — Schematic representation of various stacking possibilities for stacking of neighbouring GaO layers in the Ga-2212 structure ; (a)-(d) : projection onto the chain-plane. Block layers are of β' -type. The indications are the same as in the left part of figure 6 ; the projections along the chain direction would correspond to these in the right part of figure 6.

structural features in Ca- doped $\text{YSr}_2\text{GaCu}_2\text{O}_7$, as recently observed in [21] ; the structure claimed for $(\text{Y/Ce})_2\text{Sr}_2\text{GaCu}_2\text{O}_9$ in [22] neglects the tetrahedral chain ordering in the GaO layers.

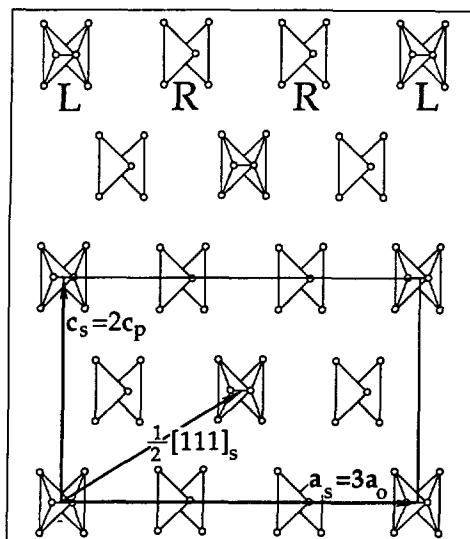


Fig. 8. — Arrangement of chains in the GaO layers (in front view) which generates the $a_s = 3a_o$ superlattice observed in [21]. « L » and « R » indicate two types of chains ; block layers are not indicated.

4. High resolution electron microscopy images.

The ordering model is in agreement with the high resolution images for Ga-n-212 phases shown in figure 3 and for the Co-1212 phase shown in figures 9, 10. Figure 9 is made along the zone parallel to the chain direction ; the spacing of the bright dots in the CoO layers is 0.55 nm ; it corresponds to the spacing between successive parallel chain sites. The dots in

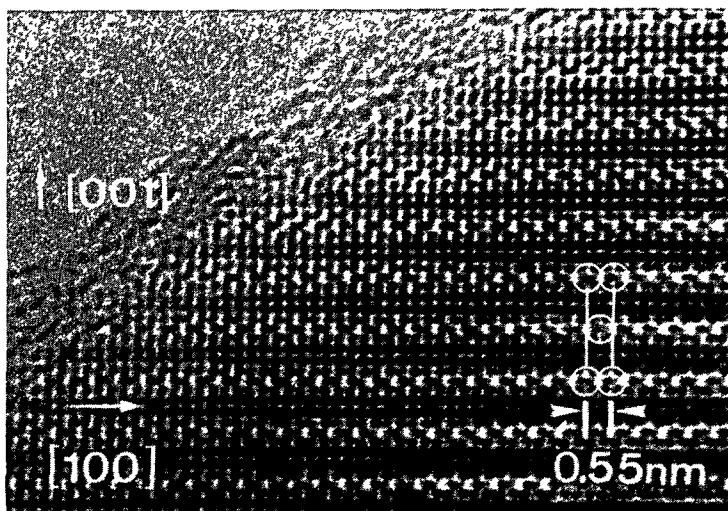


Fig. 9. — HREM image of Co-1212 along the $[010]_s$ zone. The CoO chains are imaged along their length axis revealing no difference between « L » and « R » types of chain. Encircled pairs of dark dots represent double columns of CoO_4 chains at the vertices of the indicated unit cell.

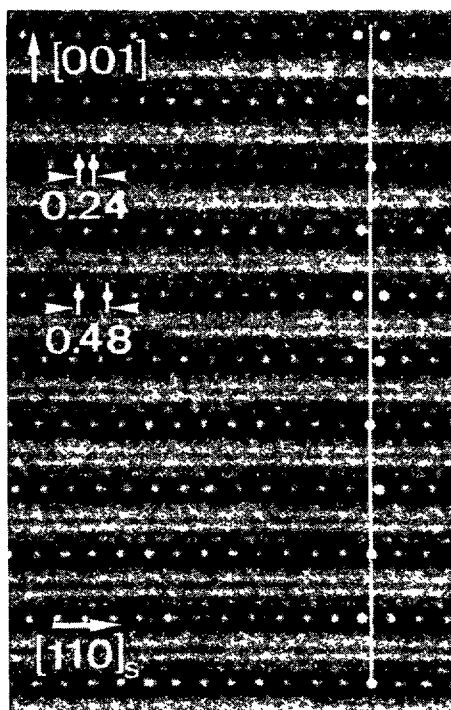


Fig. 10. — HREM image of the Co-1212 along $[110]_s$ zone revealing the superstructure in the CoO layers. The stacking of Co layers is indicated by the dots staggering left and right of the vertical line. A dot spacing of 0.48 nm reveals perfect order of the alternating chains ; a dot spacing of 0.24 nm is due to overlap of the chains in antiphase.

successive CoO layers form a staggered arrangement. Along this zone the two types of chains cannot be distinguished since their projected structures are identical. The dot sequences reveal the sites of the chain sublattice, but do not allow to distinguish between sequences of identical chains (either all LLL, or all RRR) and sequences of alternating chains (LRLR). Images made along the $[1\bar{1}0]_s \equiv [2\bar{1}0]_0$ direction however allow to make this distinction (Fig. 10). Along this zone the chain lattice is not revealed directly, however a sequence of identical chains is revealed as a succession of equivalent dots with a spacing of 0.24 nm = d_{210_0} , whereas an alternating sequence of L and R chains is revealed as a dot sequence with a period of 0.48 nm = d_{110_s} . In order to make this point clear, the relationship between the structure of the CoO layer and the dot-pattern observed in figure 10, is represented schematically in figure 11. The dot-producing columns of heavy atoms are emphasized by shaded bands, parallel to the viewing direction which is $[1\bar{1}0]_s$. If all chains are assumed to be equal the unit cell is orthorhombic (a_0, b_0), the viewing direction is $[2\bar{1}0]_0$ (Fig. 11a), and the column spacing should be 0.24 nm, whereas an alternating sequence of L and R chains generates the $(2a_0, b_0)$ superlattice (Fig. 11b) in which the projected repeat spacing along $[1\bar{1}0]_s$ is 0.48 nm [7]. The dot-pattern of figure 10 thus images indirectly the presence of an alternating chain arrangement, confirming the model proposed above. A staggered stacking of the layers represented in figure 11b, is imaged in figure 10 as a zig-zag arrangement of bright dots along the $[001]$ direction ; successive rows of dots are shifted over one fourth of the interspot

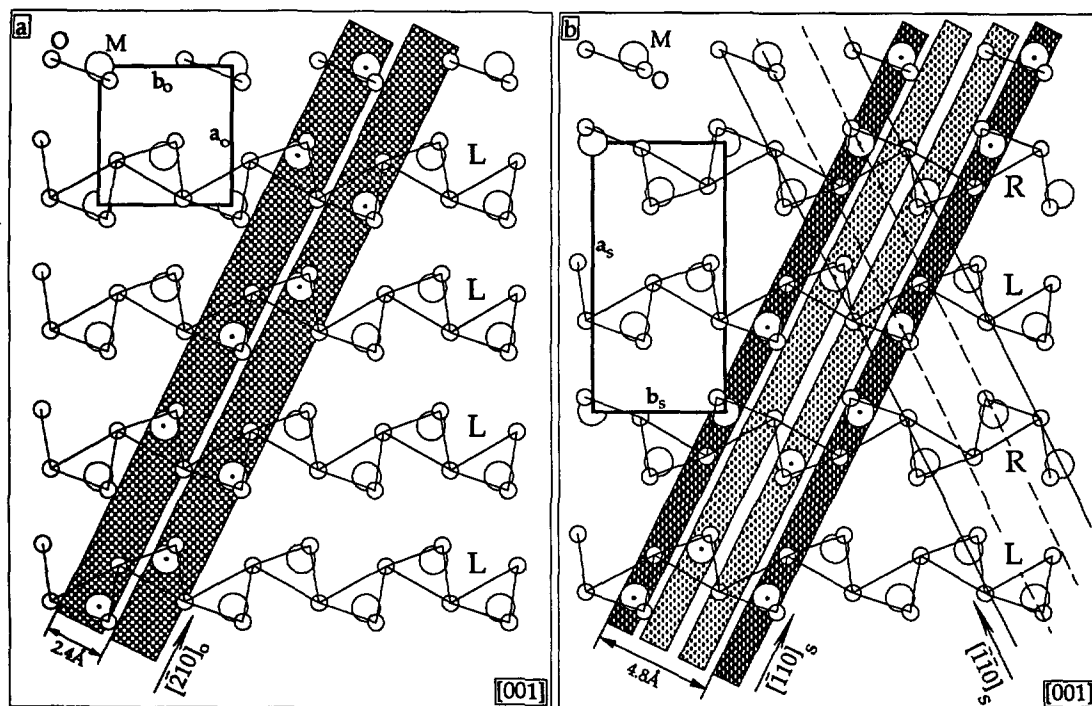


Fig. 11. — Schematic representation of the image formation in the tetrahedral chain layers for figure 10. The viewing direction of figure 10 is parallel to the shaded bands which indicate the heavy atom columns : (a) all chains are of the same type and all columns are equivalent along the $[2\bar{1}0]_0$ zone direction of Roth's cell ; (b) the alternating chain superstructure induces differences between the successive atom columns doubling the repeat spacing (as indicated by two levels of shading) ; the viewing $[2\bar{1}0]_0$ direction corresponds to the $[1\bar{1}0]_s$ direction in the superlattice cell.

distance. The irregularity of the zig-zag arrangement, indicated in figure 10, shows that the stacking of CoO layers is not unique, but is a mixture of the configurations represented in figures 6a & b with the configuration represented in figure 6d. The dot-pattern with a spacing of 0.24 nm, but with dots of unequal brightness in figure 10, reveals that within some of the CoO layers the regular alternation of L and R chains is perturbed. In the Ga-compound most of the GaO layers only exhibit a dot sequence with a 0.24 nm spacing, figure 4a, suggesting that the superstructure image is blurred by the intra- and inter-chain disorder discussed below.

5. The defect structure.

In both compounds defects are found to be present at several levels : within the chains, within the chain layers, and in the layer stacking. Some of the chains may be partly L and partly R, the change of type occurring at a copper atom or at an oxygen vacancy [6, 7]. These point defects, when sufficiently abundant, cause all chains to become mixed ; this is presumably the case in the Ga-compound, since in the $[1\bar{1}0]_s$ zone imaged in figure 4, the superperiod is observed only in small areas as the unequal brightness of the dots. In the Co-compound, chains are rather perfect as can be judged from figure 10 where the superperiod is visible over large areas. However, faults of the type ... L R L L R L R R L R ... may still occur in the alternation of R and L chains, the superspacing and the basic spacing being both present in different parts of the same

layer, i.e. in the same row of the image in figure 10. The presence of defects of this kind in the Ga-compounds is responsible for the widening of the diffuse streaks in the a_s^* direction (Fig. 2b) or for their internal structure as observed in [19]. It was noted that extra spots appear along the direction which we labelled a_0^* , dividing the diffraction vector g [200] in three equal parts [19]. In some samples these extra spots are found to be heavily streaked along a_0^* . All these features follow logically from our model ; within the chain layers regular sequences such as ... LLRLLR .. or .. RRLRRL ... would give rise to the observed periodicity ; a disordered array would lead to streaking and to reciprocal lattice planes perpendicular to b_0^* .

The faults occurring in the stacking of the chain layers are revealed along the $[1\bar{1}0]_s$ zone (Figs. 4 and 10) by the occasional deviation from the zig-zag arrangement of the dot-pattern along c ; they are responsible for the streaks along the c^* direction (Fig. 3). Such stacking faults are inevitable if the alternating arrangement within the layer is faulted, but they may occur even if the intra-layer order is perfect [7]. The probability of such a faulted stacking is rather high since the separation of successive chain layers is rather large ($1.14 \text{ nm} = c_1/2$ for the 1212 ; $1.41 \text{ nm} = c_2/2$ for the 2212 phase) and hence their interaction weak ; the energy of such stacking faults is rather small.

The occurrence of polytypoids [19], differing by the stacking of the chain layers, is accounted for in our model of alternating chains which allows for such possibility. Moreover, no polytypism in a staggered stacking is possible if all chains are equal, i.e. if there are no alternating chains in the superstructure of the CoO (GaO) layers. Therefore, with the alternating chain superstructure of the layer the different regular stackings of the CoO layers are possible, leading locally to multiple $c_s (= c_0 ; 2 c_0 ; 4 c_0 \dots)$ parameters, as recently observed in [9].

A further form of disorder follows from the two possible orientations ($[110]_p$ and $[1\bar{1}0]_p$) of the alternating tetrahedra chains with respect to the rest of the structure ; this leads to a domain structure of twins on $(100)_p$ or $(010)_p$ planes [7]. The average domain is found to be of smaller size but of higher perfection in the case of Co-compound than in the Ga-case ; this is presumably related to the larger orthorhombicity of the Ga-compounds compared to that of the Co-compounds

6. Discussion and conclusions.

The model of the superstructure of the tetrahedral chains in the GaO (CoO) layers of the Ga-*n*-212 (Co-1212) intergrowth phases is based on a simple ordering principle : the nearest neighbours are arranged in opposite sense, in all principal lattice directions and on different structural levels, i.e.

- (*) within a chain (along b_s) — the rotation of successive corner sharing GaO_4 tetrahedra are in the opposite sense ; clockwise and counter-clockwise ;
- (*) within a layer (along a_s) — successive GaO_4 chains are shifted in opposite senses ; left and right ;
- (*) between the GaO layers (along c_s) — the stacking is staggered, as opposed to vertical.

Our proposed model meets all of the experimental evidence observed in the electron diffraction patterns :

(i) the unit spacing along a_0^* is halved : this corresponds to a superlattice with : $a_s = 2 a_0$; ($b_s = b_0$) ;

(ii) the superlattice modes are widened along a_0^* for Ga-compounds, i.e. the superstructure ordering is not long range. Within the layers the L-R-L chain stacking can be faulted in such a way that the neighbouring chains may be of the same type ; e.g. R-L-L ;

(iii) the superlattice nodes are streaked (continuous for the Ga-compounds) along c_0^* ; the stacking sequence of the layers is intrinsically disordered because even for perfectly ordered layers, there are at least two staggered stacking configurations of adjacent layers, of equal probability;

(iv) the superstructure of the GaO_4 and CoO_4 tetrahedral chain layers is topologically the same for the α' -type and β' -type of block layers forming the rest of the intergrowth structure, and irrespective of the spacing between the tetrahedra chain layers, i.e. of the block layer thickness. This holds for at least the first and the second member of the homologous series of intergrowth compounds $\text{Ga-}n\text{-}212 : (\text{REO}_2)_n\text{Sr}_2\text{GaCu}_2\text{O}_5$ and also for the Co-1212 compound : $\text{YSr}_2\text{CoCu}_2\text{O}_7$ [7].

An interpretation, consistent with the model proposed here, may also be given for the recently observed tripling of the superlattice parameter $a_s = 3 a_0$ in the corresponding Ga-compound [21], by assuming the formation and alternation of the LRR or/and RLL chain arrangements.

The model is also a basis for the explanation of the previous results of Roth *et al.* [5] on the Ga-1212 compound and of Huang *et al.* [6] on the Co-1212 compound in terms of the « average » structure. The splitting of the Ga and O sites in the GaO layer and also of the Co sites in the CoO layer of the Ga- and Co-1212 compound, as suggested by Huang *et al.* [6], corresponds with the concept of « average » structure and is quite consistent with our model because, a tetrahedron on each node of Roth's orthorhombic lattice has to contain simultaneously L and R features.

The superstructure ordering in the tetrahedral chain layers, and the positional disorder of alternating chains, account for the anisotropy of the Debye-Waller factors which was found by Roth *et al.* [5] and discussed by Huang *et al.* [6]. The largest axis of the thermal ellipsoids for Ga and Co are aligned along the chain direction ($b_0 \equiv c_{\text{Roth}}$); for the O (1) (oxygen atoms in the GaO plane), mainly along directions in the chain plane; and for the O (4) (apical oxygen atoms common to a GaO_4 tetrahedron and a CuO_5 pyramid), along the a_0 axis i.e., perpendicular to the chains.

Very recently, the crystal structure of RESrGaCuO_5 has been determined [23]. It was found to be analogous to that of $\text{RESr}_2\text{GaCu}_2\text{O}_7$ [5]. This phase, with the brown-millerite structure, may be considered as $(\text{RE}_{0.5}\text{Sr}_{0.5})_2\text{GaCuO}_5$, i.e. Ga-0211, the « zeroth »-member of the Ga- n -212 series with perovskite structure [22, 23]. It would not be surprising if the alternating chain ordering, could also be traced in the tetrahedral layers of the end member Ga-0211, as it was indicated previously in the brown-millerite structure of $\text{Sr}_2\text{Fe}_2\text{O}_5$ [19].

Finally, according to the model proposed previously [4, 5, 6], the structure of the Ga-1212 phase, would not be « balanced » in the sense that the atomic (and the charge) distribution in the GaO layer, with respect to the rest of the structure, would lead to a net dipole moment. As far as we known no exotic optical or dielectric properties were found in this material. We can only speculate about the type of anti-ferroelastic, or anti-ferroelectric (or anti-ferromagnetic [24]), interaction which favours anti-parallel ordering between adjacent tetrahedral chains and planes. It seems that the resulting mechanical strain relaxation significantly contributes to the stability of the alternating chain superstructure.

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