

# (101) and $\bar{1}01$ Extended Defects Accounting for the Non-Stoichiometry of High- $T_c$ Superconducting $M_{2\pm\delta}CuO_{4\pm\delta}$ Phases ( $M_2 = La_{2-x}Sr_x$ )

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## Abstract

Detailed structural interpretation of (101) and  $\bar{1}01$  extended planar defects allows the formulae of the high- $T_c$  superconducting  $M_2CuO_{4+\delta}$ ,  $M_{2+\delta}CuO_{4+\delta}$  and  $M_{2-\delta}CuO_{4-\delta}$  phases ( $M_2 = La_{2-x}Sr_x$ ) to be more exactly expressed. The proposed interpretations comply with all the established crystal-chemistry rules, *i.e.* classical  $CuO_6$  octahedra and mono-, bi- and tricapped triangular prisms,  $MO_7$ ,  $MO_8$  and  $MO_9$  with normal Cu—O, M—O and O—O interatomic distances. They are new alternative explanations of the non-stoichiometry of these  $K_2NiF_4$ -related phases.

## Introduction

The family of superconducting phases  $La_{2-x}Sr_xCuO_4$  of the  $K_2NiF_4$  structural type, as demonstrated by Michel & Raveau (1984), is often formulated with a stoichiometry characterized by an excess or deficiency of oxygen. This is directly related to physical properties which have already been thoroughly investigated. However, these defects affecting the chemical composition have not been systematically described because the aim was to propose a simple relation between structural details and chemical formulae. Too often, structural investigations by X-ray or neutron powder diffraction involve partially occupied crystallographic sites, yielding sets of interatomic distances or polyhedra that do not comply with the rules of crystal chemistry that have long been established for numerous well defined crystal structures.

Based on the defect observed by Alimoussa *et al.* (1992) using high-resolution electron microscopy (HREM) observations of  $La_{1.85}Sr_{0.15}CuO_4$  thin films (Fig. 1) ( $La_{1.85}Sr_{0.15}CuO_4$  is denoted  $M_2CuO_4$  for simplicity;  $M_2 = La_{2-x}Sr_x$ ), detailed structural interpretations of  $M_2CuO_{4+\delta}$  and  $M_{2+\delta}CuO_{4+\delta}$  are proposed and subsequently extended to  $M_{2-\delta}CuO_{4-\delta}$ .

Our proposal, which encompasses extended defects, is in keeping with the proposals of Andersson & Wadsley (1966) for  $ReO_3$ -type networks, Andersson & Galy (1970) for hexagonal close-packed structures and Galy & Carpy (1974) for  $ABO_{3+x}$  perovskites.

## Preliminary remarks on the $M_2CuO_4$ structure

The  $M_2CuO_4$  structure (Fig. 2) has often been described. It consists of  $(CuO_4)_n$  layers of  $CuO_6$  octahedra sharing corners, alternately shifted by  $b/2$  along [001], enclosing the double layer of  $M$  atoms that are themselves ninefold coordinated to O atoms (CN9) at the apices of tricapped triangular prisms (TCTP). These polyhedra and  $CuO_6$  octahedra share faces, edges and/or corners. Note that each  $M$  atom has eight bonds to the same  $(CuO_4)_n$  layer and only one to the next, the oxygen being at the edge of the layer.

Fig. 1 shows an image of the  $La_{2-x}Sr_xCuO_4$  thin film projected along [010]. Clearly the trace of the projection of the  $(CuO_4)_n$  layer to the left of the extended defect [which develops in the plane (101)] is shifted in the [001] direction relative to that in the right part and seems aligned with the first row of  $M$  atoms fixed immediately below the right  $CuO_4$  layer. The estimated shift is approximately 2 Å.

Fig. 3 illustrates various possibilities following  $(CuO_4)_n$  breaking which keep the  $(CuO_4)_n$  layer at the same  $y$  coordinate. In Fig. 3(a), in which the O—O distances and the coordination for Cu, *i.e.* CN6, have been preserved, a new formula is obtained,  $M_2CuO_{4+\delta}$ . As the synthesis of the phase occurs in air, extra oxygen is readily provided. Also, the  $(CuO_4)_n$  layer is slightly displaced in the  $[\bar{1}00]$  direction (by approximately 2 Å). In Fig. 3(b), the layer is only shifted in the [001] direction and, with respect to the O—O distances, this results in a 4 Å displacement. Again, the stoichiometry shift will be expressed by an excess of oxygen,  $M_2CuO_{4+\delta}$ . However, this does not fit in with the experimental result shown in Fig. 1. Fig. 3(c) depicts the same displacement along [001], but with an additional slip in

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the [100] direction; both parts of the  $(\text{CuO}_4)_n$  layer are corner shared by  $\text{CuO}_6$  octahedra. In this case, the layer stoichiometry remains  $(\text{CuO}_4)_n$ . Fig. 3(d) illustrates a shear mechanism; both parts of the  $(\text{CuO}_4)_n$  layer are displaced by  $2 \text{ \AA}$ , but are now associated by edge sharing between two  $\text{CuO}_6$  octahedra. The composition of the copper oxide layers becomes  $(\text{CuO}_{4-\delta})_n$ .

### Over-stoichiometry



This type of compound has already been analysed by Chaillout *et al.* (1989) and by Jorgensen, Dabrowski, Pei, Richards & Hinks (1989), who proposed an interstitial site for oxygen within the  $\text{La}_2\text{CuO}_4$  original network. Our proposal, which attempts to account for the formation of these phases, is illustrated in Figs. 4(a) and 4(b). Fig. 4(a) shows a cut through the  $M_2\text{CuO}_4$  structure along (101). The upper part of the structure remains unchanged, just like the lower part, where the copper

oxide layers are ended by a  $\text{CuO}_5$  square pyramid, the whole being displaced by  $2 \text{ \AA}$  in the [100] and [001] directions, *i.e.* a  $1/6$  slip in the [301] direction. This operation can be expressed by  $1/6 [301] (101)$ . The structure representation clearly exhibits two types of vacancy: one for extra O atoms, denoted by squares, and one for extra  $M$  atoms, denoted by triangles. As the synthesis of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  occurs in air, there is no need for the Cu atoms to maintain CN5 and the proposed model shows that the extra O atoms easily spread through the network. The formula for the resulting structure becomes  $M_2\text{CuO}_{4+\delta}$ .



The shear operation creates an empty oxygen polyhedron. It consists of the conventional bicapped triangular prism (BCTP), which accommodates La or Sr atoms in numerous structures. It is found in the present structure in the same proportion as the extra O atoms. The composition becomes  $M_{2+\delta}\text{CuO}_{4+\delta}$ . As a result, the defect formula is  $(MO)_n$ .

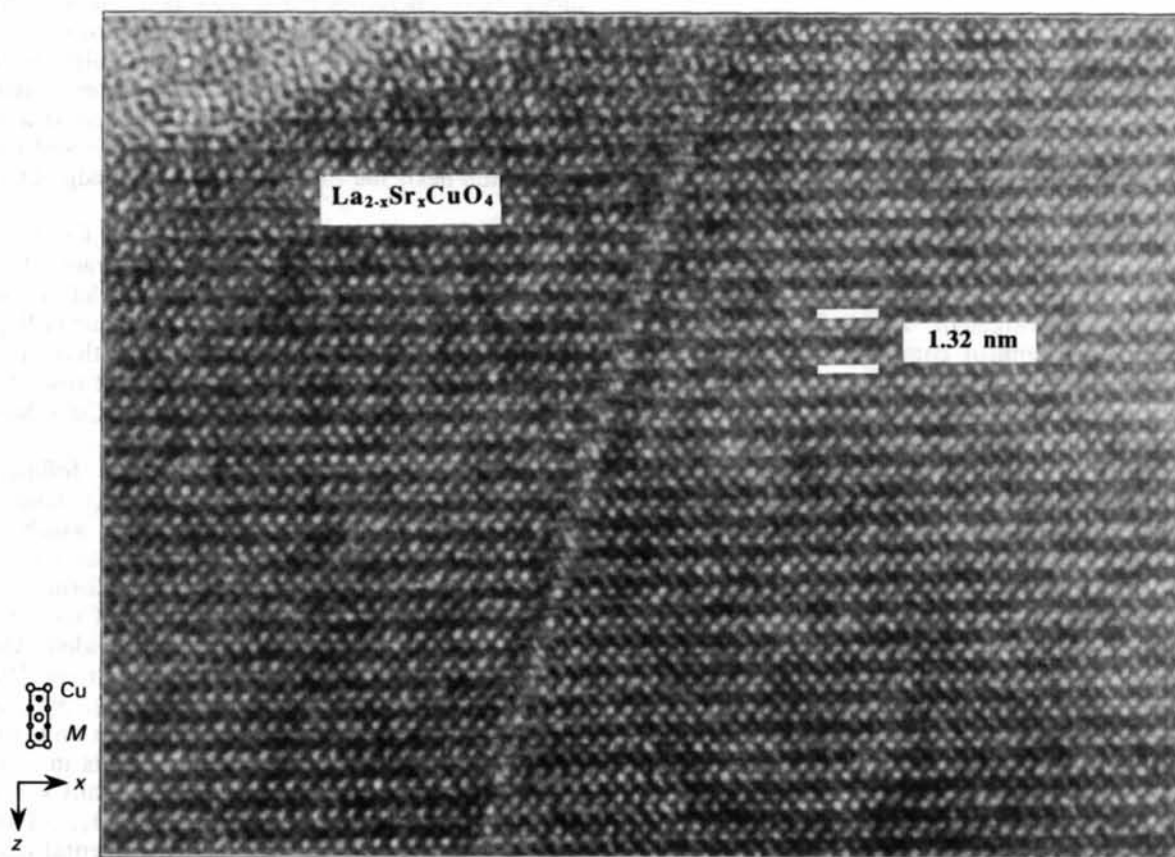


Fig. 1. HREM picture of a (101) extended planar defect in the high- $T_c$  superconducting  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  phase ( $x = 0.15$ ), kindly provided by Alimoussa *et al.* (1992).

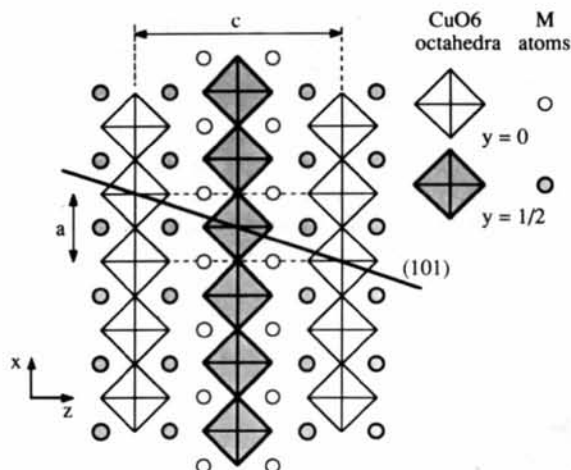


Fig. 2. Ideal representation of the  $M_2CuO_4$  structure projected onto the (010) plane.

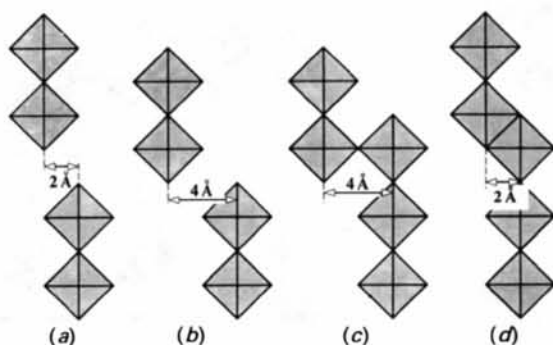


Fig. 3. Various possibilities following  $(CuO_4)_n$  layer breaking: (a), (b) a shift in the [001] direction gives over-stoichiometry,  $(CuO_{4+\delta})_n$ , (c) the same  $(CuO_4)_n$  stoichiometry; (d) shear operation giving  $(CuO_{4-\delta})_n$ .

*Structural details of the  $(MO)_n$  extended defect in  $M_{2+\delta}CuO_{4+\delta}$*

Following the shear operation various polyhedra are found around the  $M$  atoms (La or Sr) within the defect. Our aim now is to describe these polyhedra according to the periodicity of their locations along  $\vec{\tau} = \vec{a} + \vec{c}$ , starting with the  $M1$  polyhedron and ending with the  $M6$  polyhedron (Fig. 4a).

Recall that all existing  $M$  atoms were in TCTP, CN9, with the threefold axis along [010] before the shear. New possible sites will be denoted  $M^*$ . The  $M1$  polyhedron is transformed to a BCTP, CN8;  $M2$  occupies a monocapped triangular prism MCTP, CN7, with the prism axis directed along [301];  $M^*3$  is in a BCTP, CN8; the  $M4$  polyhedron becomes a BCTP, CN8;  $M5$  is in a MCTP, CN7; and the  $M^*6$  polyhedron is a BCTP, CN8; these last four polyhedra have their prism axes along [010].

The zigzag sequence of the polyhedra along [101] can be schematized, from left to right in Fig. 4(a), as follows:  $M^*6CN8(y = 1/2)/M1CN8(y = 1/2) - M2CN7(y = 0) - M^*3CN8(y = 0)/M4CN7(y = 0) - M5CN7(y = 1/2) - M^*6CN8(y = 1/2)$ . A view of the structure built of  $(La,Sr)O_9$  polyhedra cut along (101) is given in Fig. 5(a) together with the detailed polyhedron packing of the  $(MO)_n$  defect. Fig. 5(b) shows their projection onto the (010) plane and an exploded view is given in Fig. 5(c) for the sake of clarity.

*Structure and solid-state chemistry*

The occurrence of these extended defects giving  $M_2CuO_{4+\delta}$  or  $M_{2+\delta}CuO_{4+\delta}$  is in good agreement with the solid-state chemistry of these phases. When

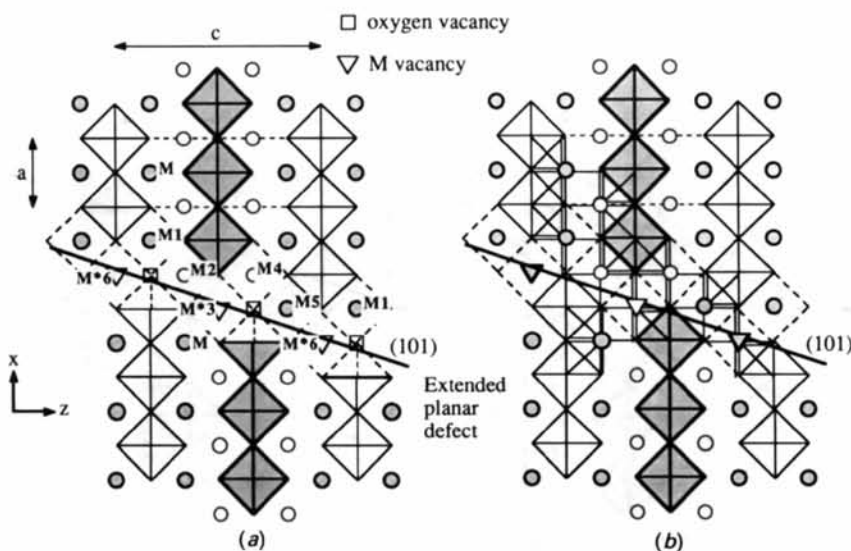
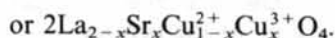
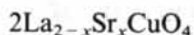
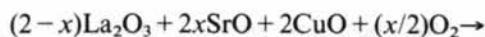


Fig. 4. Detailed drawings of the structure after the occurrence of the defect: (a) O- and M-atom vacancies; (b) coordination polyhedra following oxidation.

synthesizing the  $La_{2-x}Sr_xCuO_4$  phase in air, the formal equation is



Given the aforementioned proposals, with all the ratios of La/Sr/Cu being perfectly maintained, this

phase can be over-oxidized. The proposed structure for the (101) extended defect allows easy cooperative migration of the extra O and M atoms concerned with this phenomenon.

The empty polyhedron resulting from the shear operation supports the assumption that this oxygen over-stoichiometric phase is initiated or combined with an excess of M atoms, yielding the formula  $M_{2+\epsilon}CuO_{4+\delta}$  with  $\epsilon \leq \delta$ . These defects have been

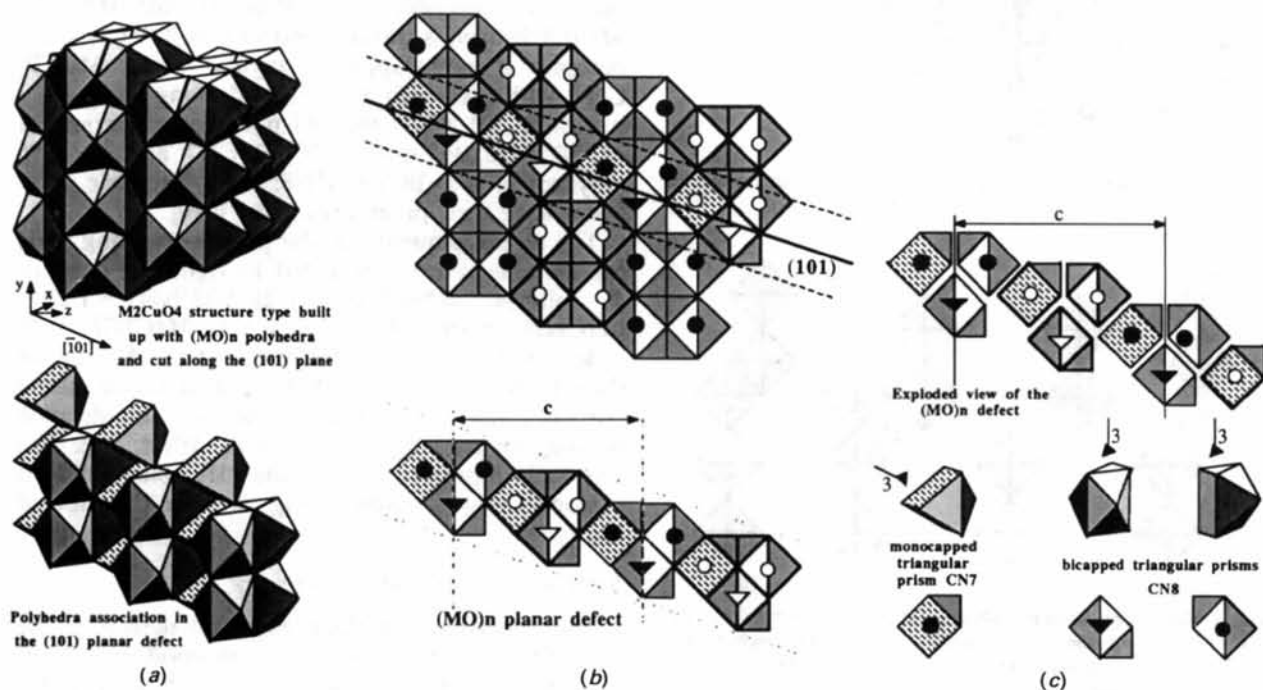


Fig. 5. Detailed drawings of the  $MO_7$ ,  $MO_8$  and  $MO_9$  mono-, bi- and tricapped triangular prisms: (a) their association within the (101) extended planar defect and (b) their schematic representation projected onto the (010) plane; (c) an exploded view of the scheme.

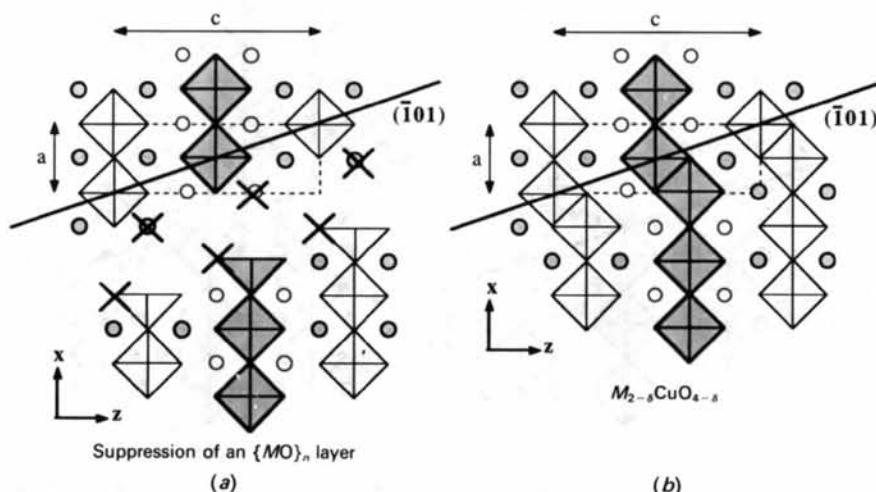
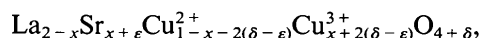


Fig. 6. Formation of an under-stoichiometric phase: (a) removal of an  $(MO)_n$  layer, (b) formation of the  $M_{2-\delta}CuO_{4-\delta}$  phase.

found to be more numerous when  $x$  increases (from 1), that is when the amount of strontium oxide greatly increases, and  $x$  increases by  $\geq 0.15$ . These phases, which are considered fully oxidized ( $\text{CuO}_6$  octahedra), can be reasonably formulated by



with  $0 \leq \varepsilon \leq \delta$ .

With respect to Fig. 1, and assuming the presence of an extended  $(\text{MO})_n$  defect and the same thickness for the examined crystal as corresponds to the coherent HREM image, the real chemical formula can be approximated. The area of the crystal affected by the defect can be roughly estimated at 20 and 60 cells in the [001] and [100] directions, respectively. As there are two  $M_2\text{CuO}_4$  units per cell, the formula can be written as  $M_{2400}\text{Cu}_{1200}\text{O}_{4800}$ . Taking into account the defect, which extends over 20 cells along [001],  $M_{40}\text{O}_{40}$  must be added. The final formula becomes  $M_{2440}\text{Cu}_{1200}\text{O}_{4800}$  or  $M_{2.033}\text{CuO}_{4.033}$ .

Many papers have described chemical analyses revealing a slight excess of oxygen and formulae such as  $M_2\text{CuO}_{4.03}$  have been proposed. Fig. 1 clearly shows that for powder, or even single-crystal, X-ray or neutron diffraction analyses the pattern of  $M_2\text{CuO}_4$  will not really be affected by this enhanced concentration. These techniques turn out to be of little use. In other respects, the insertion of O atoms into such a dense  $M_2\text{CuO}_4$  network is barely acceptable.

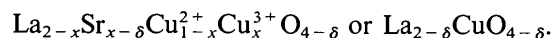
Based on a detailed inspection of the HREM image of the (101) defect in the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  crystal, a qualitative, as well as reasonably quantitative, structure has been achieved for these  $M_{2+\delta}\text{CuO}_{4+\delta}$  phases.

### Under-stoichiometry

It was similarly worth proposing a shear mechanism for a substoichiometric process, with the same 2 Å displacement for the  $(\text{CuO}_4)_n$  layers. Note that Van Tendeloo & Amelinckx (1991) proposed a mechanism associated with the  $\text{La}_2\text{CuO}_{4-\delta}$  formula that is different from ours.

The connection between both parts of the  $(\text{CuO}_4)_n$  layers is assumed to make use of edge sharing by  $\text{CuO}_6$  octahedra in the plane (010). To achieve an under-stoichiometric structure, it appears necessary to remove an  $(\text{MO})_n$  layer parallel to  $(\bar{1}01)$  (Fig. 6a). After the shear, the structure collapses to form a network corresponding to the  $M_{2-\delta}\text{CuO}_{4-\delta}$  formula. The related chemistry should involve the

formula



The lack of  $M$  atoms (for convenience Sr) is compensated for by Cu atoms (equivalent to the Sr deficiency) oxidized to a trivalent state. Even after this removal of  $M$  atoms the  $M$  atoms in the shear plane appear as pairs, necessitating lattice relaxation. The resulting structure, which is once again a mixed-valence copper oxide, is illustrated in Fig. 6(b).

### Concluding remarks

The aim of this paper was to propose simple mechanisms for both the over- and under-stoichiometry of these major  $M_2\text{CuO}_4$  families of high  $T_c$  superconducting phases. The challenge has been successfully taken up in terms of compliance with all of the established crystal-chemistry rules, *i.e.* classical  $\text{CuO}_6$  octahedra and  $\text{MO}_7$ ,  $\text{MO}_8$  and  $\text{MO}_9$  polyhedra (mono-, bi- and tricapped triangular prisms) sharing edges, corners and faces with normal Cu—O, M—O and O—O interatomic distances. It has also been shown that oxygen under-stoichiometry, implying crystallographic shears resulting in edge-sharing  $\text{CuO}_6$  octahedra, must be accompanied by a correlative non-stoichiometry of  $M$  atoms. A crystallographic shear which reflects a condensation of the structure associated with a formula  $M_2\text{CuO}_{4-\delta}$ , as proposed by Van Tendeloo & Amelinckx (1991), is very difficult to handle from the viewpoints of both crystal chemistry and chemistry.

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