# Commensurate superstructures in the $[(Ca/Sr)_2Cu_2O_3][CuO_2]_{x\approx\sqrt{2}}$ composite crystal

**O. Milat**, **K. Salamon, S. Tomić, T. Vuletić, T. Ivek**

Institute of Physics, Zagreb, Bijenicka 46, Croatia

milat@ifs.hr

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Here, we present an electron microscopy and diffraction study of the nominal $(Sr/Ca)_{14}Cu_{24}O_{41}$ compound. We propose an alternative formula: $[(Ca/Sr)_2Cu_2O_3][CuO_2]_{x\approx\sqrt{2}}$ that better represents this incommensurate composite crystal structure. Namely, composite crystals are a class of long range ordered solids that are composed of two or more subsystems, each one with its own lattice and cell symmetry. For a series of compounds with widely used formula $(Sr/Ca)_{14}Cu_{24}O_{41}$ (Ca for Sr isostructural substitution), the constituting subsystems are: (i) $(Sr/Ca)_2Cu_2O_3$ -"ladders", and; (ii) $CuO_2$ -"chains"[1][2], as schematized in Figure 1a. The lattices of these subsystems have common ***a*** and ***b*** parameters while being incommensurate along *c*-axis. The building unit of the *ladders* is a pair of zigzag edge-sharing $CuO_4$-squares that are connected along "rungs", so that the $c_{Ld}$ period is defined by the $CuO_4$-square diagonal, Fig. 1c. For the *chains*, the $CuO_4$ building units share opposite edges and the $c_{Ch}$ period is equal to the $CuO_4$-square edge, Fig. 1b. Therefore, the $c_{Ld}/c_{Ch}$ ratio is close to $\sqrt{2}$, so that the $[(Ca/Sr)_2Cu_2O_3][CuO_2]_x$ ($x\approx\sqrt{2}$) formula correctly displays compound`s composite structure. With increasing Ca-substitution the $c_{Ld}/c_{Ch}$ ratio varies from 1.44 for pure $Sr_{14}Cu_{24}O_{41}$, to 1.416 for highly substituted $Sr_{0.6}Ca_{13.4}Cu_{24}O_{41}$[3]. This is accompanied by charge (hole) redistribution between the $CuO_2$-chains and the $Cu_2O_3$-ladders. More holes reside in the $CuO_2$-chains for higher $c_{Ld}/c_{Ch}$ ratio [4].

HREM imaging of Fig. 2a. displays structure modulation with a period of 0.92 nm which is not commensurate either with *ladders*, or with *chains* basic periods. The modulation vector $\mathbf{q}_{(00\underline{1}1)} = (0.92\ \text{nm})^{-1}$ is assigned in EDP of Fig. 2b, by 4-dim crystallographic notation. It is very sensitive to the sublattices mismatch. The satellites at $\pm m\mathbf{q}_{(00\underline{1}1)}$ fail to coincide with basic spots indicating absence of commensuration; the weak spots marked as $006\underline{4}$ and $00\underline{7}5$ close the 0000 center, divide $\mathbf{q}_{(00\underline{1}1)}$ in small integer fractions only for some specific values of $c_{Ld}/c_{Ch}$ ratio, as indicated in Fig. 3. The commensurate superstructures should be possible and observable only for those particular values of $c_{Ld}/c_{Ch}$ that belong to the set of integer number ratios (13/9, 10/7, 27/19, 17/12, ...), as marked by vertical lines in Fig. 3. The most prominent hypothetical commensurate superstructure should appear for the case of $c_{Ld}/c_{Ch}$ = 7/5, corresponding to the compound`s nominal formula $(Sr/Ca)_{10}Cu_{17}O_{29}$[5]. The widely accepted notation $(Sr/Ca)_{14}Cu_{24}O_{41}$ rather masks substantial incommensurability of this composite crystal by implying the commensurate superstructure and formula $[(Sr/Ca)_2Cu_2O_3\ ]*[CuO_2]_{x=10/7}$, with the unique $c_{Ld}/c_{Ch}$ ratio fixed to 10/7= 1.428571, in disagreement with the most of observations, so far. Amount of fractional charge transfer from *chains* to *ladders* strongly depends on $c_{Ld}/c_{Ch}$ ratio (Ca/Sr substitution) [4].

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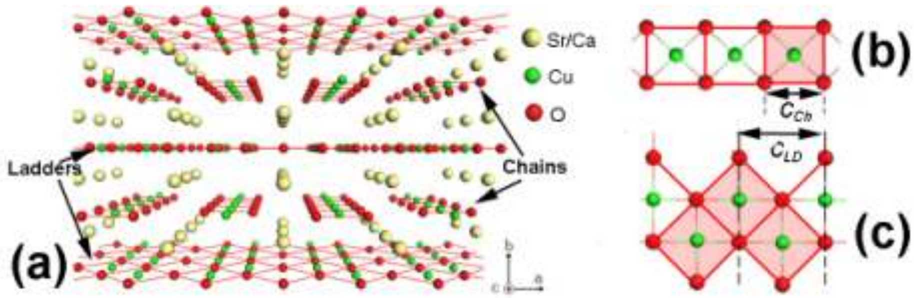


Fig. 1. (a) Perspective view of the $[(Ca/Sr)_2Cu_2O_3][CuO_2]_{x\approx\sqrt{2}}$ composite crystal structure with *ladders* and *chains* subsystems interpenetrated; (b) building unit for *chains*: $\boldsymbol{c}_{Ch}$ ~ square edge; (c) building unit for *ladders:* $\boldsymbol{c}_{Ld}$ ~ square diagonal.

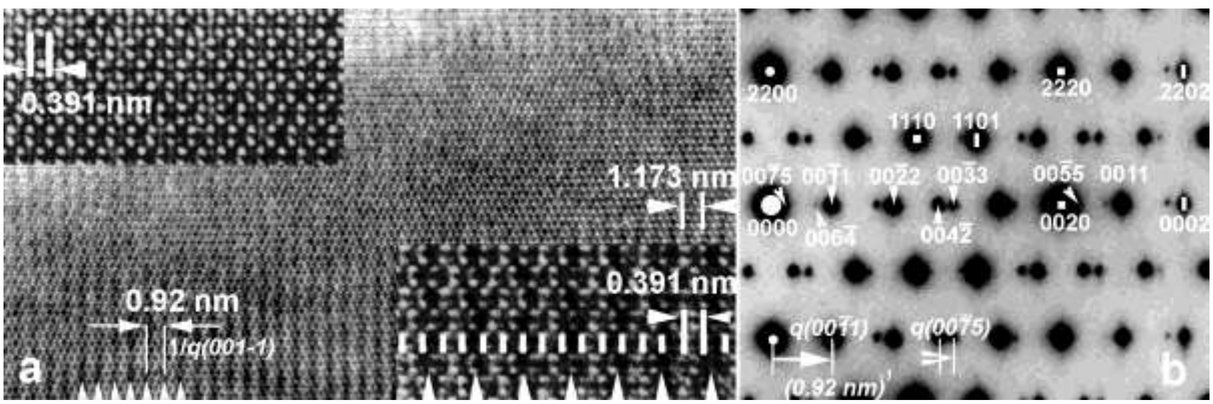


Fig. 2. Imaging -(a), and diffraction -(b) along the [1100] zone, of the $[(Ca/Sr)_2Cu_2O_3][CuO_2]_{x\approx\sqrt{2}}$ composite crystal structure; in (a) top and bottom insets display *ladders* substructure with $\boldsymbol{c}_L$=0.39nm, and incommensurate modulation with $1/\boldsymbol{q}_{(00\underline{1}1)}$=0.92 nm, respectively; no modulation commensurate either with $3\boldsymbol{c}_L$, or $5\boldsymbol{c}_L$, or $7\boldsymbol{c}_L$ is revealed; in (b) all spots and modulation vector can be assigned by four index notation *hklm* with *l* and *m* corresponding to *ladders* and *chains*[2]

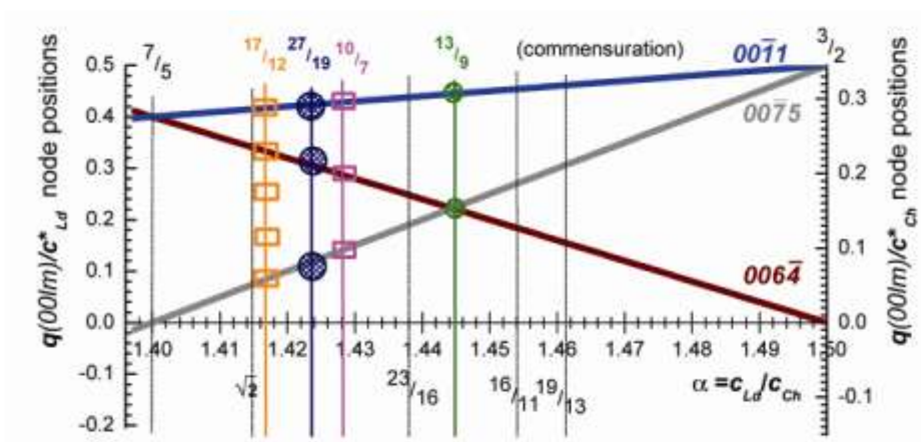


Fig. 3. Relative positions of satellite spots 00$\underline{1}$1, 006$\underline{4}$, 00$\underline{7}$5 (observed and marked close to the 000 center of the EDP in Fig. 2b), as a function of $c_{Ld}/c_{Ch}$ ratio; vertical lines mark the small integer ratios for possible commensurate superstructures at 13/9, 10/7, 27/19, 17/12, in the range $1.41 < c_{Ld}/c_{Ch} < 1.45$.