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

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Structure

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 1. 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 $\boldsymbol{c_{Ld}}$ period is defined by the CuO_4-square diagonal, Fig. 1c. For the *chains*, the CuO_4 building units share opposite edges and the $\boldsymbol{c_{Ch}}$ period is equal to the CuO_4-square edge, Fig. 1b. Therefore, the $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ ratio is close to $\sqrt{2}$, so that the formula $[(Ca/Sr)_2Cu_2O_3][CuO_2]_x$ ($x\approx\sqrt{2}$) correctly displays compound`s composite structure.
With increasing Ca-substitution the $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ 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 $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ ratio [4].

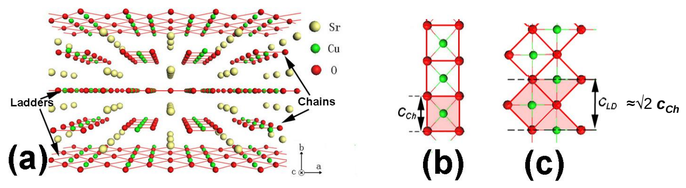

Fig. 1. Schematic representation of the "Chain-ladder" composite crystal structure of $(Sr\text{-}Ca\text{-}La)_{14}Cu_{24}O_{41}$ in top view (up) and front view (down);

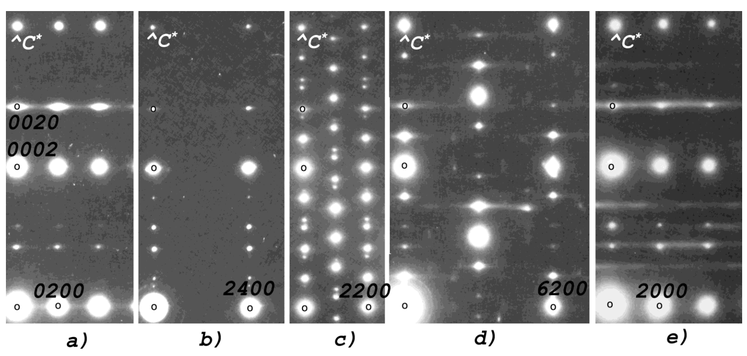

Fig 2. Tilting series of diffraction patterns around c-axis for $[(Ca/Sr)_2Cu_2O_3][CuO_2]_{x\approx\sqrt{2}}$ assigned by 4 index notation: (a) - (*0, 2k, 2l, 2m*); (b) – (*2h, 4h, 2l, 2m*); (c) – (*h, h, l, m*); (d) – (*3k, k, l, m*); (e) – (*2h, 0, 2l, 2m*).

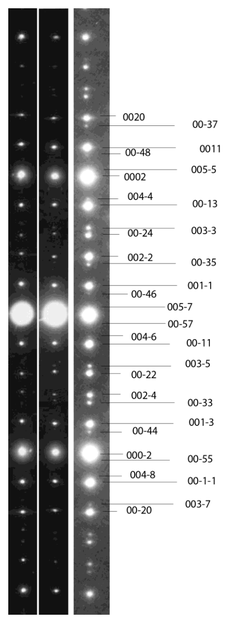

Fig. 3. reciprocal lattice raw of (*0, 0, l, m*) reflections from EDP of Fig. 2(c) indicating shifting of spots: 00$\underline{4}$6 at $\boldsymbol{q^*} = 0.333\boldsymbol{c^*_{Ld}}$, and 00$\underline{5}$7 at $\boldsymbol{q^*} = 0.08\boldsymbol{c^*_{Ld}}$, which could be incorrectly assigned to $3\boldsymbol{c_{Ld}}$, and $12.5\boldsymbol{c_{Ld}}$ superlattice cell.

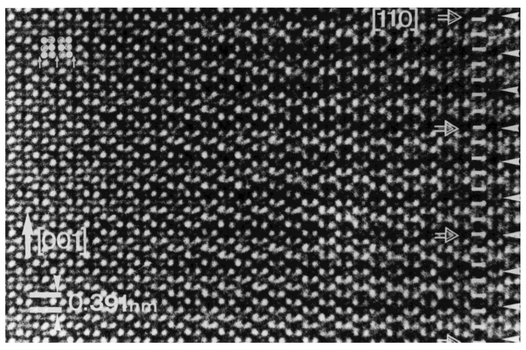

Fig 4. Imaging along the [1100] zone, of the $[(Ca/Sr)_2Cu_2O_3][CuO_2]_{x\approx\sqrt{2}}$ composite crystal structure; top and bottom inset display *ladders* substructure with $\boldsymbol{c_L}$=0.39 nm, while incommensurate modulation with $1/\boldsymbol{q}_{(00\underline{1}1)}$=0.92 nm, is marked by arrows at right margin; no modulation commensurate either with $3\boldsymbol{c_L}$, or $5\boldsymbol{c_L}$, or $7\boldsymbol{c_L}$ is revealed.

Reciprocal space in 4-dim notation

Our electron diffraction study of complete reciprocal space is shown in Figure 2. All spots in all relevant zones can be indexed as structural reflections according to:

$$\boldsymbol{H} = h\boldsymbol{a^*} + k\boldsymbol{b^*} + l\boldsymbol{c_{Ld}^*} + m\boldsymbol{c_{Ch}^*},$$

and they need not to be assigned to some additional "exotic" modulation on top of the complex composite structure. All spots with non-zero *m*-index are more or less streaked with diffuse feature perpendicular to $\boldsymbol{c^*}$ revealing disorder of the phase of modulation in the "chain" lattice [2]. Extinctions in the [1000]* and [0100]* zones of Figure 2, reveal the superspace symmetry of this complex composite structure.

Commensurate superstructures

Commensurate superstructure as revealed in HREM imaging of Fig. 4. and schematically represented in Fig. 5 (at right margin) could be revealed only for those particular values of $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ that belong to the set of integer number ratios (13/9, 10/7, 27/19, 17/12, ...), as marked by vertical lines in Fig. 6. The most prominent hypothetical commensurate superstructure should appear for the case of $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ = 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 $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ 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 $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ ratio (Ca/Sr substitution) [4].

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[2] O. Milat et al., Acta. Cryst. **A48** (1992), 618
[3] Z. Hiroi et al, Phys. Rev. **B54** (1996), 15849
[4] C. Ma et al., J. Phys.(Condensed Matter) **21** (2009) 215606
[5] K. Kato et al., Acta Cryst C44 (1988), 1881
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[6] P. Abbamonte, et al. Nature **431** (2004) 1078

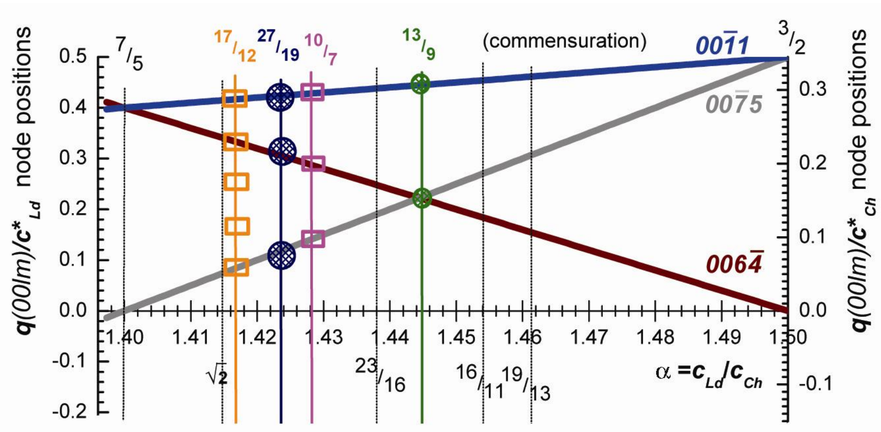
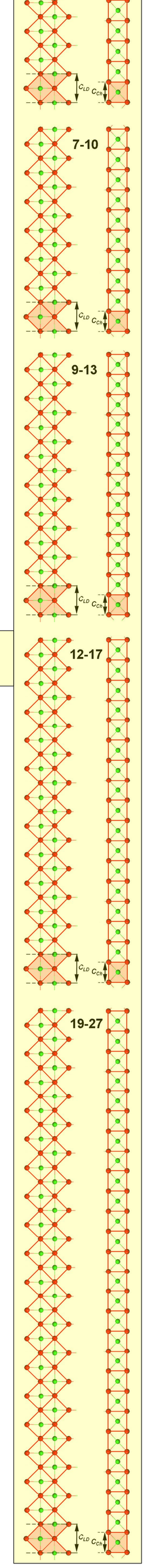


Fig. 5. Series of superstuctures can be generated by apperiodic stacking of "small integer" commensurate units: $2c_{Ladd}\cap 3c_{Ch}$; $3c_{Ladd}\cap 4c_{Ch;}$ $5c_{Ladd}\cap 7c_{Ch}$

Fig. 6. 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 7/5, 13/9, 10/7, 27/19, 17/12, in the range $1.41< c_{Ld}/c_{Ch}<1.45$



Appendix

Wigner Crystal by Resonant Sof X-ray Scattering (RSXS)

As La for Sr substitution reduces intrinsic hole-doping (six hole per formula unit in pure $Sr_{14}Cu_{24}O_{41}$), a lot of doubt has recently emerged about charge carriers ordering into a Wigner "hole crystal" on a $5\boldsymbol{c_{Ld}}$ or $3\boldsymbol{c_{Ld}}$ superlattice, as found by Resonant X-ray Scattering The "hole crystal" carrying charge and spin, was allocated onto "spin-ladder" subsystem based on an argument of being commensurate to "ladder" lattice, while not commensurate to "chain" lattice [5][6]. .

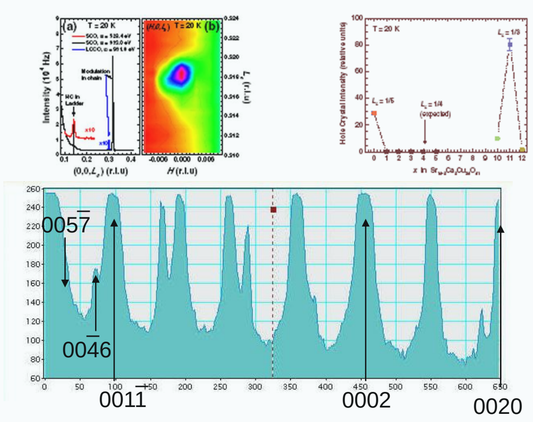


Fig. 7. SXRS scans and ($h0l_{Ld}$) map of Intensity from refs. [5] and [6],which were interpreted as revealing the "hole crystal" structurewith superperiodicities $5\boldsymbol{c_{Ld}}$ and $3\boldsymbol{c_{Ld}}$, respectively.

Fig. 8. ED Intensity profile along the c* reciprocal lattice direction *(00lm)* from Fig. 3., indicating detectable intensity at the locations found in SXRS experiment [6]

Interpretation of the RSXS findings in therms of composite structure modulation

Each spot along $\boldsymbol{c^*}$ reciprocal axis shifts in position depending on the $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ ratio [3], and in particular the one assigned as 00$\underline{4}$6 at $\boldsymbol{q}(00\underline{4}6) = 0.333\boldsymbol{c_{Ld}^*}$, for $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$=1.416 in Figure 3. The SRXS intensities observed at this positions for $Sr_2Ca_{12}Cu_{24}O_{41}$ ($\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ = 1.416) [5], was probably misinterpreted as an evidence "hole crystal" superlattice formation with triple ladder lattice periodicity: $\Lambda_3=3\boldsymbol{c_{Ld}}$, failing to correlate it with $1/\boldsymbol{q}(00\underline{4}6)$.
Analogously, the SXRS intensity observed at position q=(0.200 0.009) $\boldsymbol{c_{Ld}^*}$ in pure $Sr_{14}Cu_{24}O_{41}$, and interpreted as an evidence of Hole Crystal (HC) formation in the ladder-subsystem due to apparently commensurate spacing $\Lambda 5=5\boldsymbol{c_{Ld}}$ ($=1/0.2\boldsymbol{c_{Ld}^*}$), could be assigned as a modulation satellite emerging in reciprocal lattice point 00$\underline{4}$6, or 00$\underline{5}$7 (see Fig). Namely, for the case of: $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ = 1.445 these two spots coincide at: $\boldsymbol{q}(00\underline{4}6) = \boldsymbol{q}(00\underline{5}7) = 0.222\boldsymbol{c_{Ld}^*}$, while for $\boldsymbol{c_{Ld}^*}/\boldsymbol{c_{Ch}^*}$= 1.449 position for the *00$\underline{4}$6* spot coincides to $= 0.2\boldsymbol{c_{Ld}^*}$.