Diffraction analysis of incommensurate modulation in “chain-ladder” composite crystal $(Sr/Ca)_{14}Cu_{24}O_{41}$

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The “chain-ladder” compounds with formula $(Sr/La/Ca)_{14}Cu_{24}O_{41}$ exhibit a rather complex crystallographic structure due to their composite character. These materials consist of an alternating stacking of two distinct types of layers forming interpenetrated subsystems [1]. One subsystem is formed of $(Sr/La/Ca)_2Cu_2O_3$ layers with a ladder-like structure and orthorhombic unit cell (*Fmmm*), while the other contains layers of CuO_2 chains with orthorhombic unit cell (*Amma*) [2]. All lattice parameters slightly vary with La/Ca for Sr substitution, but the one dimensional incommensurate modulation results from the misfit between the ***c*** lattice parameters of these layer elements. In pure Sr compound: $\boldsymbol{c_{Ch}}$ = 0.273nm, $\boldsymbol{c_{Ld}}$ = 0.393 nm ≈ $\sqrt{2}\cdot\boldsymbol{c_{Ch}}$; the ***a*** parameter (≈ 1.147 nm) is the same in both lattices, as well as ***b*** (≈ 1.341 nm) pointing along stacking direction. For high Ca for Sr substitution in $Sr_3Ca_{11}Cu_{24}O_{41}$: $\boldsymbol{c_{Ch}}$ = 0.276 nm, $\boldsymbol{c_{Ld}}$ = 0.391 nm, so that the ratio of these parameters is always close to $\sqrt{2}$. The $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ ratio also varies from 1.416 for pure undoped $Sr_{14}Cu_{24}O_{41}$, to 1.445 for highly doped $Sr_xCa_{14-x}Cu_{24}O_{41}$[3].

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 emerged recently about charge carriers ordering into a Wigner “hole crystal” on a $5\boldsymbol{c_{Ld}}$ or $3\boldsymbol{c_{Ld}}$ superlattice, found by Resonant X-ray Scattering [4][5]. The “hole crystal” carrying charge and spin, was allocated onto “spin-ladder” subsystem based on a superficial argument of being commensurate to “ladder” lattice, while not commensurate to “chain” lattice.

This modulated structure has been analysed by X-ray diffraction using 4-dim approach, in case of $M_{14}Cu_{24}O_{41}$ (M= $Bi_{0.04}Sr_{0.96}$) [6].

Here, we present the results of detailed electron diffraction study of complete reciprocal space. As shown in Figure 1, all spots of all relevant zones indicated in Figure 2, 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 ***c**** revealing disorder of the phase of modulation in the “chain” lattice [1]. Extinctions in the [1000]* and [0100]* zones of Figure 1 (a)&(e), reveal the superspace symmetry. Each spot along ***c**** reciprocal axis shifts in position depending on the $\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ ratio [3], and in particular those assigned as $00\underline{4}6$ and $005\underline{7}$, at $\boldsymbol{q_{00\underline{4}6}} = 0.333\boldsymbol{c_{Ld}}^*$, and at $\boldsymbol{q_{005\underline{7}}} = 0.08\boldsymbol{c_{Ld}}^*$ in Figure 3, respectively. The RXS intensities observed at these positions [4] were probably misinterpreted as an evidence of “non-structural” satellite reflections revealing “hole crystal” superlattice: $\Lambda_3=3\boldsymbol{c_{Ld}}=1/\boldsymbol{q_{00\underline{4}6}}$ for $Sr_3Ca_{11}Cu_{24}O_{41}$; $\Lambda_5=5\boldsymbol{c_{Ld}}=1/\boldsymbol{q_{005\underline{7}}}$ for $Sr_{14}Cu_{24}O_{41}$ ($\boldsymbol{c_{Ld}}/\boldsymbol{c_{Ch}}$ = 1.441).

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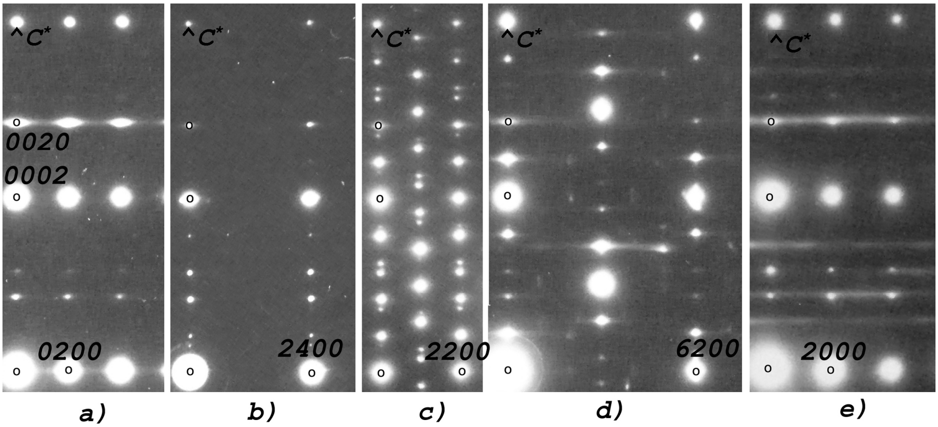

Figure 1. Tilting series of diffraction zones around c-axis for $Sr_3Ca_{11}Cu_{24}O_{41}$, assigned by 4 index notation: (a) - (*0, 2k, 2l, 2m*); (b) – (*2h, 4h, 2l, 2m*); (c) – (*h, h, l, m*); (d) – (*3k, k, l, m*); (e) – (*2h, 0, 2l, 2m*). Traces of corresponding sections of reciprocal space are indicated in diffraction pattern along the common ***c***-axis of Figure 2.

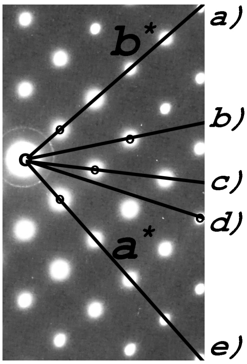

Figure 2. (a* b*) reciprocal plane; marked lines indicate zones in Fig. 1., correspondingly.

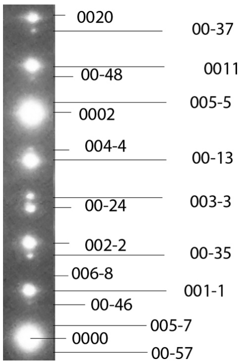

Figure 3. reciprocal lattice raw of (*0, 0, l, m*) reflections from EDP of Fig. 1(c) indicating spots: $00\underline{4}6$ at $\boldsymbol{q^*} = 0.333\boldsymbol{c^*}_{Ld}$, and $005\underline{7}$ at $\boldsymbol{q^*} = 0.08\boldsymbol{c^*}_{Ld}$, which could be incorrectly assigned to $3\boldsymbol{c}_{Ld}$, and $12.5\boldsymbol{c}_{Ld}$ superlattice cell.