Prominent structure modulation in the Ca_xCuO_2 composite crystal ($x \approx 5/6$); an artifact of imaging conditions

Ognjen Milat, Kresimir Salamon, and Nazif Demoli

Institute of Physics, Bijenička 46, PO Box 304, Zagreb, HR 10000, Croatia.

milat@ifs.hr

Keywords: composite crystal structure, modulation, imaging conditions, tilted illumination

Ca_xCuO_2 crystal may disclose very remarkable features of its composite structure by selective HREM imaging under specific conditions [1]. Its structure consists of two subsystems: "Ca-strings" and "CuO_2-chains" that are interpenetrated, as schematized in Fig. 1(a). Due to non-stoichiometry, two sublattices are mutually incommensurate [2] at least in one dimension; the structure is modulated, and 4-dim crystallographic notation [3] has to be used for its interpretation. In the case of the $Ca_5Cu_6O_{12}$ composition, the structure is nearly commensurate along "string & chain" direction with the modulation period of 5Ca equal to 6Cu sublattice spacing [1]. Due to difference in the Ca and Cu scattering potentials and difference in the Ca-Ca and Cu-Cu inter-columnar separations, these two types of atomic columns can be selectively imaged at different thickness, as indicated in Fig. 1(b); 5 bright dot row and 6 bright dot row marked by arrowheads in thinner and in thicker crystal regions reveal these two column types, respectively. In addition, for imaging along the [0010] zone axis, brightness modulation is displayed more or less prominent, as evidenced in Fig.1 (c&d); this is found to be an artifact of imaging conditions as shown by diffraction pattern calculations presented in Fig. 2., and HREM image simulation presented in Fig.3.

ED patterns of the $Ca_5Cu_6O_{12}$ crystal were calculated (Cerius2 [4] software package) as a function of thickness for illumination direction precisely parallel and/or slightly tilted off the [0010] zone axis. Main beams responsible for imaging formation of either Cu- or Ca-lattice columns, are marked in Fig.2; beams intensities reveal that for t <160A (left panel) the beams corresponding to Ca-sublattice are stronger relative to those corresponding to Cu-sublattice, while this ratio is reversed for t >170A (right panel). This is in agreement with findings in Fig. 1(b), and holds for small illumination tilt corresponding to Laue-circle centre at $|R_{LC}| \approx 0.3\text{-}0.4\text{A}^{-1}$. In the other hand, this off-axis illumination tilt profoundly affects brightness modulation in the simulated HREM images, as is presented in Fig.3. Previous image calculations performed so far for $Ca_5Cu_6O_{12}$ crystal ([5], [6]) with parallel illumination failed to reproduce prominent brightness modulation, regardless of the model structure [5].

In conclusion, imaging of crystal structure generally depends on all instrumental and observational parameters such as: focusing, aperture, crystal tilt, specimen thickness. Contrast of atomic columns is a consequence of dynamical interaction of channeling electron with the crystal potential, so that at constant thickness, columns of different types are imaged with different contrast, while the same type of columns can be imaged differently at different thickness. Imaging of modulation in composite crystals is affected by illumination tilt.

1. O. Milat, G. Van Tendeloo, S. Amelinckx, Ultramicroscopy, 41, (1992), 65.
2. T. Janssen, et al, in *International Table for Crystallography*, *vol.C*, ed. A.J.C. Wilson, Kulwer Academic Publishers Dordrecht/Boston/London (1995) p.p. 797-844
3. O. Milat, et al. Sol. St. Comm., 79, (91), 1059
4. http://accelrys.com/products/materials-studio/
5. O. Milat at all, Journal of solid State Chemistry, 97, (1992), 405
6. O. Milat et al., *5th MCEM Proc.*, ed. L. Dini, M. Catalano, Lecce, Italy, (2001) pdl.5

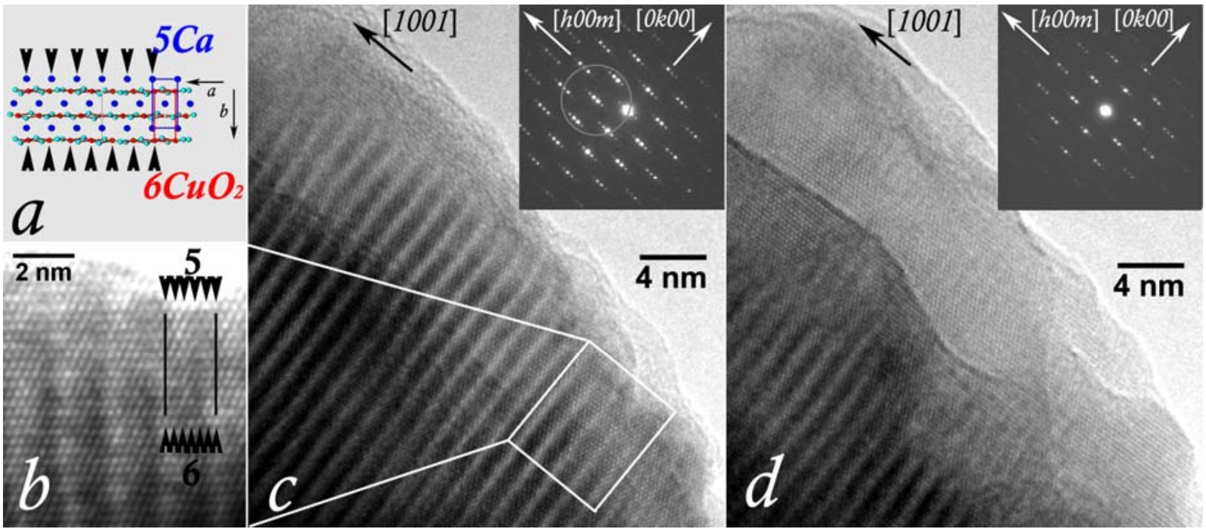

Figure 1. Two lattices model of $Ca_{5/6}CuO_2$ composite crystal (a), and imaging of same area (bcd). Prominence of modulation depends on deviation of imaging direction off the exact [0010] axis; illumination tilt in (c) is revealed in asymmetric EDP, marked by circle in inset; in (d) modulation fades out for 0º-tilt (see inset), particularly in thinner crystal regions.

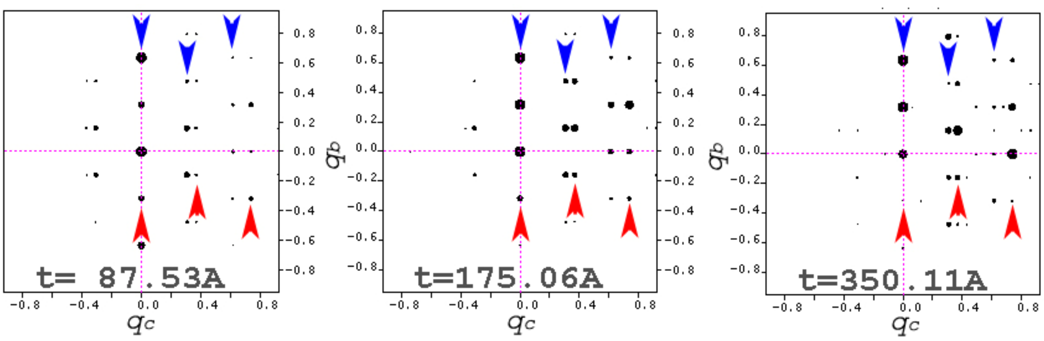

Figure 2. Calculated [0010] zone EDPs of $Ca_{5/6}CuO_2$ at indicated thickness for the off-axis illumination tilt: centre of Laue circle at $(q_c,q_b) = ({}^1/_{2.8}A^{-1},{}^1/_{3.2}A^{-1})$. Image forming beams for Ca and Cu sublattices are marked by downward (blue) and upward (red) arrows, respectively. Weak spots in the right panel reveal satellite beams responsible for modulation imaging; satellites intensities increase with crystal thickness for small illumination tilt.

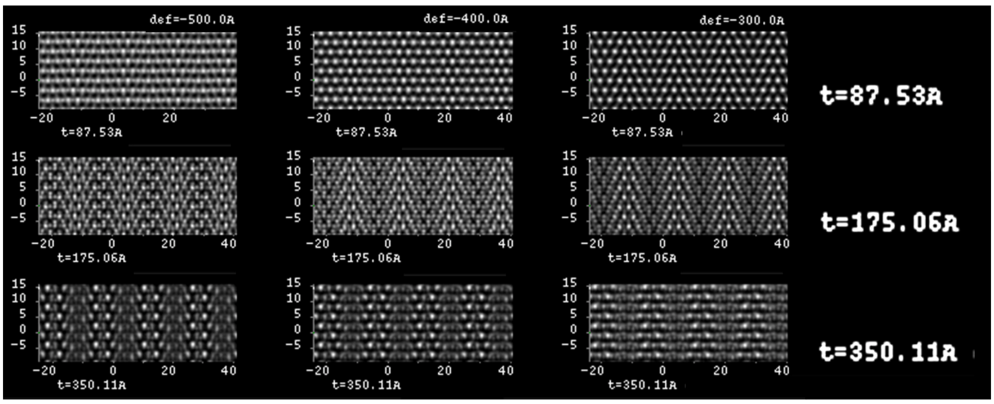

Figure 3. Set of calculated images of the $Ca_{5/6}CuO_2$ modulated structure along [0010] zone, with off axis illumination tilt as in Fig.2. Columns represent defocus: -500A, -400A, -300A. Brightness modulation for all thicknesses is compatible with the observed one in Fig.1(b&c).

G. Kothleitner, M. Leisch (Eds.): MC2009, Vol. 1: Instrumentation and Methodology,
DOI: 10.3217/978-3-85125-062-6-009, © Verlag der TU Graz 2009