Selective Imaging of the Cu_x-sublattice Structure in the $Cu_{2-x}Se$ Crystal

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The $Cu_{2-x}Se$ crystal exhibits superionic conductivity in the high temperature (HT) phase (T > 415K; 0 <x< 0.2). The structure is cubic, but complex as being composed of two subsystems: (i) "Se-Cu immobile cage" (ZnS-type structure; a = 0.581 nm), and (ii) "Cu-mobile subsystem" consisting of Cu cations distributed along the open "mobility paths" that connect tetragonal, via trigonal to octahedral interstitial sites in the F43m cell [1]. In the room temperature (RT) phase the superionic conductivity disappears due to closing of these "mobility paths" and subsequent condensation of Cu cations at displaced sites. The ordering of this partial subsystem is revealed as pairing of overall layer stacking, rhombohedral distortion of the cage, superstructure formation on monoclinic lattice [2]. The RT-$Cu_{2-x}Se$ monoclinic phase has a kind of layered structure, as shown in FIG. 1; by selective HREM imaging [3] one can disclose that the Cu-cation ordering mainly takes place in one subset of Cu-layers in a form of commensurate displacement modulation of the average Cu_{1-x}-sublattice sites.

In high resolution electron microscopy of complex crystals, the partial lattices of crystal structure can be selectively imaged in different ways either by changing the microscope observation parameters such as aperture and defocus, or by varying the crystal thickness or orientation [4]. A method of "oblique zone imaging" [3] is applied here to resolve the partial superstructure arrangement of Cu atoms on the Cu-sublattice sites of the $Cu_{2-x}Se$ room temperature (RT) superlattice; it is especially suitable for selective imaging of subsystems in a layered structure. The layer feature of the RT-$Cu_{2-x}Se$ monoclinic phase is revealed as tripling of the basic spacing in one out of two set of layers that constitutes each double-layer stacking unit, imaged as pair of horizontal bright dot rows in FIG. 1(a).

In the basic sections of the reciprocal space the superlattice spots are present together with the sublattice ones (the so called "basic" reflections) as it is shown for the electron diffraction patterns (EDP) in FIG. 2(a)&(b). In an other section (along the "oblique" zone [hkl] – with at least two indices different and non equal zero), the separated superlattice spots appear in one or more additional rows between the sublattice spot rows, FIG. 2(a)&(c). When imaging along such "oblique" reciprocal section which contains one or more rows of exclusively superlattice spots corresponding to resolvable spacing, and which more over contains the rows of basic sublattice spots only at such a large reciprocal distance that the corresponding sublattice spacing is below the point resolution of the microscope, FIG. 2(c), then the corresponding HREM image reveals mainly the structural features due to the superlattice; the partial structure in the set of layers of the basic average cubic sublattice is being present as unresolved fringes in the background, FIG. 1(c).

This method is especially applicable to the HREM study of lamellar superstructures built on two (or more) layers for which the superlattice is due to alternating displacements of subset of atoms constituting one out of the two partial structures. In such a case, imaging along principal zone axis, as in FIG. 1(a)&(b), is heavily affected by the pattern of bright and dark dots representing the average structure; a slight brightness variation, which becomes more prominent in area corresponding to higher crystal thickness reveals mainly the geometry of superlattice nodes while the structural details have to be resolved by image simulation. In the other hand, imaging along the "oblique" zone axis, FIG.1(c), reveals the main feature of the Cu subsystem ordering that generates the RT-$Cu_{2-x}Se$ superstructure: the displacement modulation of 1/3 of the Cu-atoms out of each Cu_{1-x}-layers along the $[111]_c$ direction of the basic cubic lattice.

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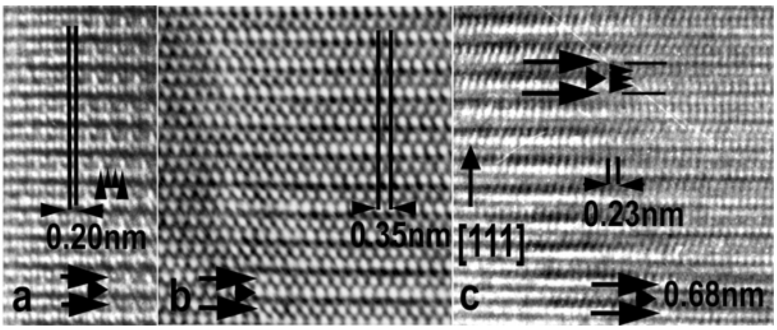

Fig.1. Images of RT-$Cu_{2-x}Se$ structure along cubic sublattice axis: (a) $[112]_c$; (b) $[011]_c$; (c) $[145]_c$. In (a) lamellar periodicity of 0.68 nm is marked by pair of arrows. Intra-layer dot spacing of 0.20 nm corresponds to basic separation of Cu-Se columns; one brighter out of two less bright dots discloses the 0.6 nm spacing of superlattice motives. In (b) average positions of CuSeCu columns are revealed as bright and less-bright dot rows. In the oblique zone (c) stacks of three horizontal rows of dots with spacing of 0.23 nm disclose positions of Cu columns responsible for the superstructure.

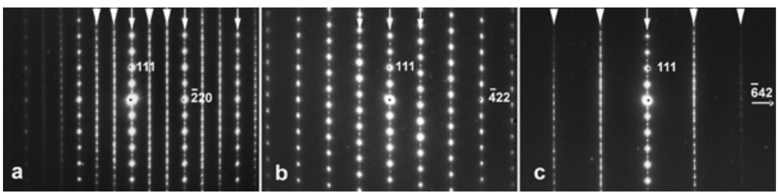

Fig.2. EDPs of RT-$Cu_{2-x}Se$ along three cubic sublattice zones that corresponds to three imaging directions for Fig.1(a), (b) and (c), respectively. Rows which contain basic reflections are marked with arrows, and arrowheads at the top indicate reciprocal rows that consist exclusively of the superlattice spots. Only the superlattice spots are observed along two pairs of reciprocal rows in (c).