IMAGING OF THE SUPERSTRUCTURE IN THE Cu-SUBLATTICE OF THE $Cu_{2-x}Se$ CRYSTAL

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Introduction

In high resolution electron microscopy of complex crystals, the substructure 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(1). A method, termed "the oblique zone imaging"(2) is applied here to image the superstructure arrangement of Cu atoms in the Cu-sublattice of the $Cu_{2-x}Se$ room temperature (RT) phase.

Superlattice and sublattices of the RT-$Cu_{2-x}Se$ structure

The RT-$Cu_{2-x}Se$ monoclinic superstructure for $x \approx 0$(3) is a kind of layered structure, as shown in Fig. 1., in which an additional ordering mainly takes place in one type of layers (the Cu_{1-x}-layers) thus inducing the monoclinic superlattice, while the atomic arrangement in the remaining set of Cu-Se layers retains the symmetry of the high temperature cubic HT-$Cu_{2-x}Se$ structure(4).
This 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).

Principles of the "oblique" zone imaging

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 only the rows of basic sublattice spots at such a large reciprocal distance that the corresponding sublattice spacing is below the point resolution of the microscope, Fig. 2(c), then the image reveals mainly the structural features due to the superlattice; the partial structure in the set of layers of the basic sublattice is being imaged 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 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 RT-$Cu_{2-x}Se$ superstructure: the displacement of 1/3 of the Cu-atoms out of each Cu_{1-x}-layers along the $[111]_c$ direction of the basic cubic lattice.

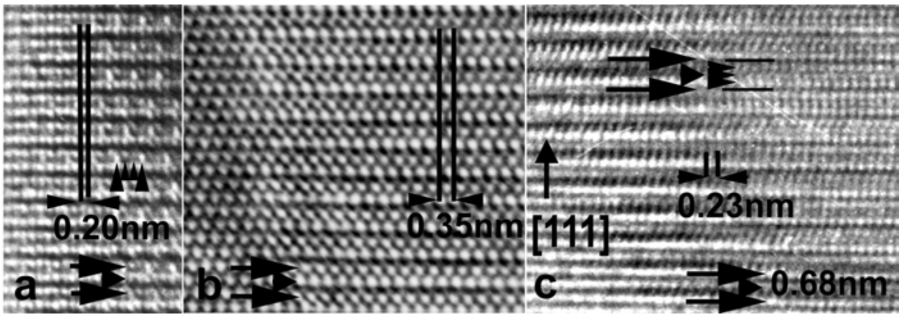

Fig.1.HREM images of the RT-$Cu_{2-x}Se$ superstructure along cubic sublattice axis: (a) - $[112]_c$; (b) - $[011]_c$; (c) - the “oblique” zone $[145]_c$. In (a) lamellar periodicity of 0.68 nm (marked by pair of arrows) is imaged as vertical stacking of pair of horizontal dot rows revealing the double-layer superstructure along $[111]_c$. Intra-layer bright dot spacing of 0.20 nm corresponds to the basic separation of the Cu-Se columns in each layer; one brighter out of two less bright dots in the upper right region disclose the 0.62 nm spacing of superlattice motives. In (b) only the bi-layers of CuSeCu columns are revealed as staggering stacking of pairs of bright and less-bright dot rows. In (c) the stacks of three horizontal rows with dot spacing of 0.23 nm disclose positions of those Cu columns that are responsible for the superstructure.

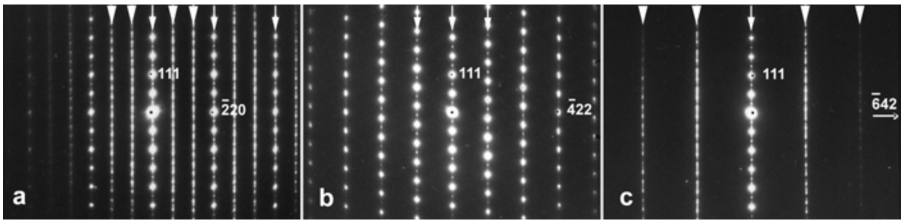

Fig. 2. Electron diffraction patterns of RT-$Cu_{2-x}Se$ along three cubic sublattice zones that corresponds to three imaging directions for Fig.1(a), (b) and (c), respectively. Rows which contain basic reflections are marked with arrows, and arrowheads at the top indicate reciprocal rows that consist exclusively of the superlattice spots. While both types of spots are present in (a), and no superlattice spots out of basic rows in (b), only the superlattice spots are observed along two pairs of reciprocal rows out of the central one in (c). Lateral reciprocal distance between the basic spot rows in (c) is out of range ($1/0.08\ nm^{-1}$) corresponding to unresolvable basic lattice periodicity in Fig. 1(c).

Acknowledgements

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References

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