

ELECTRON DIFFRACTION STUDY OF CUPROUS SELENIDE SINGLE CRYSTAL STRUCTURE

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We present the results of electron diffraction investigations on cuprous selenide Cu_{2-x}Se single crystals close to the stoichiometric composition ($x \geq 0$). In the high temperature superionic α - phase, crystalline lattice exhibits cubic symmetry $F\bar{4}3m$, while in the low temperature β - phase, the orientational variants of monoclinic superlattice (Cm symmetry) are present.

The sample of $\text{Cu}_{1.985}\text{Se}$ mounted on heating holder was investigated using the goniometer stage of transmission electron microscope EM 300 ("Philips") by observing selected area electron diffraction patterns (EDPs) subjected to: (i) heating control, so that we could follow the temperature dependence of EDPs and observe the changes at $\beta \rightarrow \alpha$ phase transition; (ii) tilting control, so that the sequence of various zone patterns enable the reconstruction of the reciprocal space.

Upon heating the sample, subsets of weak spots constituting the room temperature EDPs disappeared at ≈ 410 K and only the basic spots characterizing the cubic symmetry remained, Fig 1. Lowering the sample temperature below ≈ 410 K, the sets of superlattice spots appeared again: pairs of weak spots dividing the distances between the basic spots in $\langle \bar{h}h0 \rangle_c^*$ directions in thirds; single weak (or medium) spots halving the distances between the basic spots in $\langle \bar{h}3h\bar{h} \rangle_c^*$ directions; single medium (or strong) spots dividing in halves, and pairs of additional weak spots dividing in quarters the distances between the basic spots parallel with $[hhh]_c^*$, but no new spots except the basic ones along the $[hh\bar{h}]_c^*$ directions.

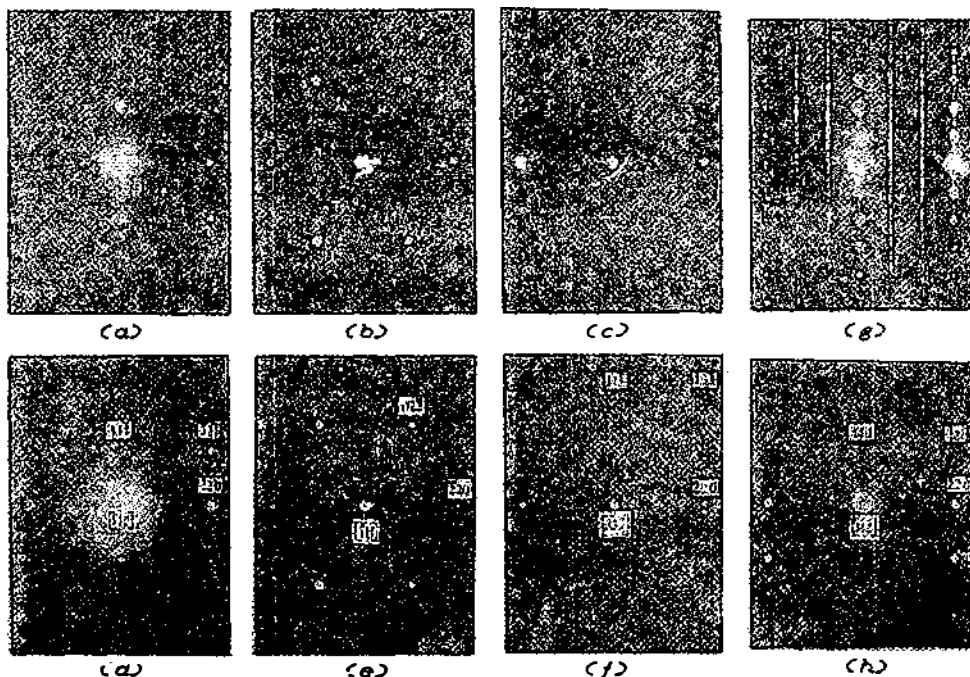


Fig. 1. Electron diffraction patterns of Cu_{2-x}Se single crystal: (a), (b), (c) & (g) - in β phase at ≈ 300 K; (d), (e), (f) & (h) - in α phase at ≈ 423 K. The basic spots and zone axes are indexed in high temperature patterns.

These features are completely consistent with our earlier investigation¹ which revealed the formation of monoclinic superlattice in a slightly distorted cage due to ordering of the cation subsystem in the low temperature β - Cu_2Se phase. The lattice parameters for the monoclinic unit cell, correlated with the cage subcell (unit cell of the α - phase), are such that $d_{001}^\beta \approx 4d_{111}^\alpha$; $d_{020}^\beta \approx 3d_{220}^\alpha$; $d_{200}^\beta \approx d_{111}^\alpha$.

The EDPs in Fig. 1.a, b, c and Fig. 1.d, e, f were recorded from the same single crystal at $T \approx 300$ K $< T_{\alpha \rightarrow \beta}$ and at $T \approx 420$ K $> T_{\alpha \rightarrow \beta}$ respectively, by tilting the crystal around the $[\bar{1}10]_c^*$ axis of the cage sublattice. The tilting angle between the patterns in Fig. 1.a(d) and 1.b(e) was 20° and between the patterns in Fig. 1.b(e) and 1.c(f) it was 10° .

¹ O. Milat, Z. Vucic and B. Ruscic, Solid State Ionics 23 (1987), 37

in accordance with the inclination of the corresponding zone axes in the cubic sublattice:

$$\varphi([11\bar{2}]_c, [\bar{1}\bar{1}\bar{1}]_c) = 19.45^\circ; \quad \varphi([\bar{1}\bar{1}\bar{1}]_c, [\bar{3}\bar{3}\bar{2}]_c) = 10.02^\circ.$$

The superlattice reflections are permanently present in the patterns for any intermediate tilting angle in the form of diffuse streaks, as shown in the EDP in Fig. 1.g. These nearly continuous superlattice streaks in between the rows of sharp basic (and superlattice) spots are a consequence of particular type of planar disorder.

The superlattice is composed of planar $\sqrt{3}$ networks in the layers of close packed cage planes. Due to the third - neighbour coordination in the sublattice, $\sqrt{3}$ nets are fixed only in the second - neighbouring $(111)_c$ planes resulting in a double - layer superstructure. For a $\sqrt{3}$ net in the bottom plane there are three sets of sublattice sites for arranging the $\sqrt{3}$ net in the upper plane, Fig. 2. The choice among them leads to three various orientations of the monocli-

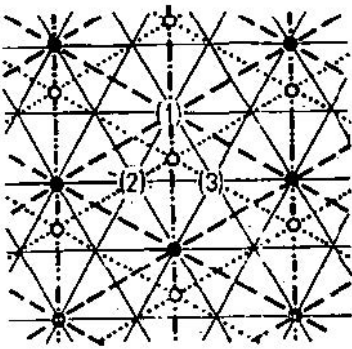


Fig. 2. The superlattice nodes forming the $\sqrt{3}$ net in the starting plane (open symbols and dotted lines) and one choice of net in the second plane above (full symbols and dashed lines). Light lines denote the net of sublattice sites in the upper plane and (1), (2), (3) indicate possible choice of sites for $\sqrt{3}$ network. (See caption of Fig. 3. for shaded triangle.)

nic superlattice in the cage sublattice as is shown in Fig. 3. Regarding the reduction of symmetry from face centred cubic $F\bar{4}3m$ in α phase, to base centred monoclinic Cm in β phase, twelve orientational variances are possible². For the interpretation of EDPs in Fig. 1. only a subgroup of these three variances, shown in Fig. 3. (which transform to each other by rotation round the threefold axis $[111]_c$), has to be considered. In this case, the orientation of superlattice throughout the crystal could be interpreted in

²J. Gladic, O. Milat, to be published

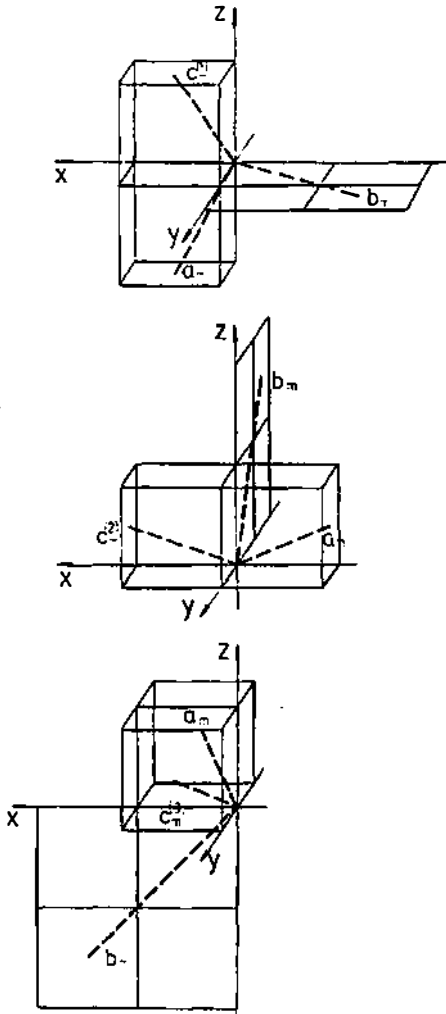


Fig. 3. Edges of monoclinic unit cell (heavy dashed lines) in the three various orientations within the cubic cage sublattice (partially drawn by light lines). The triangle at the end of c_m axis is shaded for comparison with Fig. 2.

terms of unique stacking of $\sqrt{3}$ nets in consecutive double layers of $(111)_c$ planes. Generally, there are three particular types of stacking sequences: $\dots(A)(A)(A)\dots$; $\dots(A)(B)(A)(B)\dots$; $\dots(A)(B)(C)\dots$ where A, B, C correspond to any of (1), (2), (3) sites in Fig. 2. Since we have not observed neither single domain regions, nor single domain EDPs, we presume that planar disorder originates from miscellaneous stacking of superlattice's $\sqrt{3}$ nets, such that the coherence length for a single orientation variance is of the order of a few double layers.