FIZIKA Volume 21, Supplement 1, 1989.
Proceedings of the XI Yugoslav SYMPOSIUM OF THE PHYSICS OF CONDENSED MATTER.
M. Davidović and M. Lj. Napijalo Editors, Donji Milanovac, October 3–7, 1988.

ORIENTATION VARIANTS IN THE ORDERED β PHASE OF STOICHIOMETRIC CUPROUS SELENIDE

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Having cleared up the origins of previously published contradictory findings about the structure of low temperature β phase of Cu_2Se, Milat et al. /1/ described it in terms of a monoclinic "block cell" superstructure (space group C_s^3(Cm)), spanned by the ordered cation subsystem within a uniaxially distorted cubic cage sublattice. For interpretation of the β phase electron diffraction patterns they had to take into account three simultaneously present monoclinic superlattice orientation variants differing by ±120° rotations round a threefold symmetry axis of the cubic cage sublattice. This distinguished axis was the same one along which the rhombohedral cage distortion occured. After completing the $\beta \rightarrow \alpha \rightarrow \beta$ heating and cooling cycle, three analogous monoclinic orientation variants were observed again, coupled to the cage elongation axis, but now generated along another of the four crystallographically equivalent $\langle 111 \rangle_c$ directions.

The slight uniaxial distortion of the α-Cu_2Se cubic cage lattice along a body cube diagonal at the $\alpha \rightarrow \beta$ phase transition means that besides being an ordering transition for the mobile cation subsystem, it is also characterized by reducing the cage sublattice symmetry from

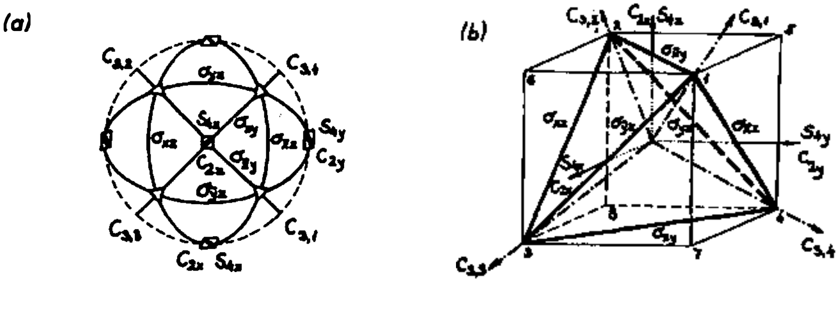

Figure 1. (a) Stereographic projection of point group $G \equiv T_d(\bar{4}3m)$;
(b) Symmetry elements of the group $T_d(\bar{4}3m)$ shown in their exact positions with respect to the regular tetrahedron inscribed in a cube

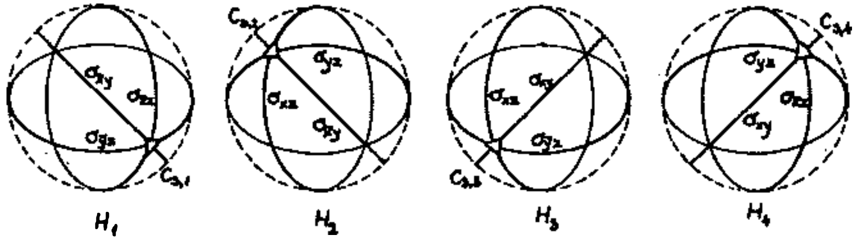

Figure 2. Stereographic projection of the subgroup $H \equiv C_{3v}$(3m) showing exactly the four possible orientations with respect to the G group T_d($\bar{4}$3m) (compare to Fig. 1.)

cubic T_d^2 (F$\bar{4}$3m) to rhombohedral C_{3v}^5 (R3m) /1,5/. In order to examine the orientation variants arising upon the $\alpha \rightarrow \beta$ phase transition in Cu_2Se we turned to group-theoretical considerations.

The point group G of the disordered high-temperature α-Cu_2Se is T_d ($\bar{4}$3m) (Fig.1) which contains 24 elements in 5 classes (see Table 1.).

In the ordered β-Cu_2Se phase, the point group of the cage is $H \equiv C_{3v}$ (3m). The C_{3v} group (Fig. 2) which contains 6 elements in 3 classes can adopt four different orientations within the T_d group, denoted by H_i (i = 1,2,3,4). All four H_i groups are crystallographically equivalent and related by symmetry operations of G. It is easily checked that by performing the transformation $g^{-1}H_ig$ (i = 1,2,3,4; $\forall$ g $\in$ G) one of the four possible H_i groups is obtained (see Table 1.).

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<tr><th>g^{-1}</th><th>g</th><th>g^{-1}</th><th>g</th><th>g^{-1}</th><th>g</th><th>g^{-1}</th><th>g^{-1}</th></tr>
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<tr><td colspan="2">$g^{-1}H_1g = H_1$</td><td colspan="2">$g^{-1}H_1g = H_2$</td><td colspan="2">$g^{1}H_1g = H_3$</td><td colspan="2">$g^{-1}H_1g = H_4$</td></tr>
<tr><td colspan="2">$g^{-1} \in EH_1$</td><td colspan="2">$g^{-1} \in C_{2z}H_1$
$\in S_{4x}^{-1}H_1$
$\in S_{4y}^{1}H_1$</td><td colspan="2">$g^{-1} \in C_{2x}H_1$
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Table 1. For $g \in G$, $H_j = g^{-1}H_ig$ (e.g. for i=1; j=1-4)

In order to find the variant generating group (V. G. G.), we must look for a subgroup of G of order four (24/6) which has no elements in common with H other than the unit element E. Out of three subgroups of G of given order (D_2 (222), C_2 (mm2), S_4 ($\bar{4}$)), groups D_2 and S_4 qualify for the V. G. G. Using D_2 and the three possible crystallographically equivalent orientations of S_4 ($S_4^{(x)}$; $S_4^{(y)}$, $S_4^{(z)}$) within G, and proceeding from Table 1., we can decompose $G \equiv T_d$ into cosets of e. g. H_1:

$$\begin{aligned} T_d &= EH_1 + C_{2x}H_1 + C_{2y}H_1 + C_{2z}H_1 = D_2 \wedge H_1 \\ &= EH_1 + C_{2x}H_1 + S_{4x}^{1}H_1 + S_{4x}^{-1}H_1 = S_4^{(x)} \cdot H_1 \\ &= EH_1 + S_{4y}^{-1}H_1 + C_{2y}H_1 + S_{4y}^{1}H_1 = S_4^{(y)} \cdot H_1 \\ &= EH_1 + S_{4z}^{1}H_1 + S_{4z}^{-1}H_1 + C_{2z}H_1 = S_4^{(z)} \cdot H_1 \end{aligned}$$

($\wedge$ denotes semi - direct product, $\cdot$ denotes weak direct product).

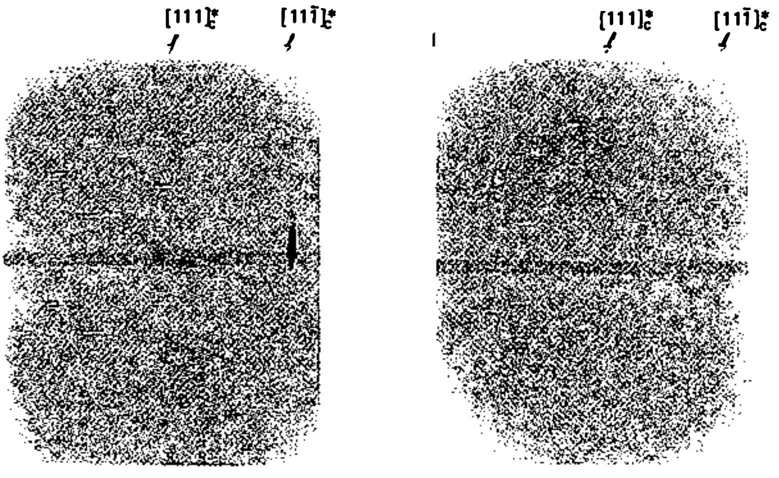
All four V. G. G.'s generate the same set of variants H_i (i = 1,2,3,4). Since all four possible rotation variants of the ordered structure characterized by the point groups H_i are mutually related by symmetry operations not belonging to the point group H of the ordered phase, they can arise with equal probabilities at the ordering transition. These four variants represent the four available choices of one cubic threefold axis as the direction of the uniaxial rhombohedral distortion of the cubic cage sublattice.

In order to check these theoretical predictions, we equipped a standard Weissenberg goniometer with a microfurnace /3/ built following mostly the design by Tuinstra and Fraase Storm /4/.

We followed the structural changes of Cu_2Se macroscopic syngle crystal, taking the zero- and higher-level Weissenberg photographs in the temperature interval from 430 K to 300 K, that is above and bellow the ordering $\alpha \rightarrow \beta$ transition temperature (413 K).

The high temperature α phase photographs displayed the well-known cubic pattern. Upon cooling the samples through the ordering $\alpha \rightarrow \beta$ transition, the superstructural spots appeared, indicating the doubling of periodicity along the $[111]_c$ direction. Some samples showed this feature dominantly along only one of $\langle 111 \rangle_c$ axes, while for the others it was equally well pronounced along the both $\langle 111 \rangle_c$ axes which can be seen within a single Weissenberg photograph of a crystal rotating round the $[1\bar{1}0]$. The results are comprised in Fig. 3.

As already suggested /6/ the choice of any of body cube diagonals as the direction of the rhombohedral deformation upon the $\alpha \rightarrow \beta$ transition would be equally probable if there were no external influences. But, during



(a) (b)

Figure 3. Sections of Weissenberg photographs of Cu_2Se single crystal displaying the $(a_1^*+a_2^*,\ a_3^*)$ plane (cubic notation): (a) in high-temperature α-phase; b) in β-phase with two orientation variants developed along $[111]_c^*$ and $[11\bar{1}]_c^*$.

the phase transition, the real crystals are subject to different anysotropic fields and temperature gradients due to imperfections in crucible shape and nonuniform heating. These most probably result in singling out some preferred orientations for the cage distortion to occur upon the α → β transition.

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