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SHAPE RELAXATION DURING EQUILIBRIUM-LIKE GROWTH OF SPHERICAL CUPROUS SELENIDE SINGLE CRYSTALS

ZLATKO VUČIĆ[1] and JADRANKO GLADIĆ

Institute of Physics, Bijenička c. 46, P.O.Box 304, HR-10000, Zagreb, Croatia
E-mail addresses: vucic@ifs.hr, gladic@ifs.hr

Dedicated to Professor Boran Leontić on the occasion of his 70$^{\text{th}}$ birthday

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The spherical equilibrium-like shaped single crystals of nonstoichiometric cuprous selenide have been grown using the modified Ohachi's method at about 30 K below its roughening temperature, $T_R(111) \approx$ 830 K. The growth has been performed under conditions of a constant volume growth rate. During the growth of partly faceted ((111) facets) and partly rounded crystal, the sphere diameter, the diameters of the facets and the heights of the facets were measured in situ, using a CCD camera. Two growth features have been observed. First, there is the exponential-like shape relaxation toward its equilibrium form with a single relaxation time constant of about 1200 minutes, and second, there are facet size oscillations with the period of about 100 minutes, superimposed on the shape relaxation. The facet size oscillations accompanied by facet height time stepping appear to be the basic feature of the growth of faceted crystals of a nearly equilibrium shape. The oscillations feature, being probably the consequence of the facet pinning potential, seems to have certain similarity with the recently reported stepping-like growth mode of ^{4}He solid/liquid interface at 2 mK.

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1. *Introduction*

There are very few single-crystal materials known to exhibit the equilibrium form [1]. The silver chalcogenide compounds, as a new class of crystals suitable for studying equilibrium crystal shape (ECS) properties, as well as the kinetics

[1]Corresponding author, Tel.:+385-1-4680-211; fax:+385-1-4680-399

of crystal growth, have been introduced by Ohachi and co-workers [2,3]. The sub-centimetre size of these crystals, apparently of the ECS form, has been a fascinating achievement, because previously solid ^{4}He crystals have been the only ones known as cm-size ECS single crystals. Namely, being in equilibrium with the superfluid liquid, ^{4}He crystals (due to the high diffusivity and high thermal conductivity of He atoms) rapidly equilibrate their surface (within less than a minute) [4,5]. Other materials investigated as ECS crystals, like small metal particles of Pb, Au and In (on graphite substrate) or NaCl are limited to the micrometer size in order to achieve ECS on a practical time scale (of several days) [1].

ECS of any crystal which is in a stable coexistence with its surrounding liquid/vapour phase will be realised as soon as it is allowed to shape its interface so as to minimise its surface free energy [1]. The ECS can be achieved only in a limited temperature range. The upper limit is the melting temperature, while the lower one is the temperature at which the equilibration takes impractically long time. At certain temperature and pressure (within that range) and for fixed volume of material, ECS is formed by transport of material over crystal-size distances. The time necessary to achieve the equilibrium shape is characteristic of the redistribution processes of atoms or molecules of the material over macroscopic distances. Typically, those are fluid phase transport and/or surface diffusion. For metallic crystals, the dominant mechanism of transport is surface diffusion, causing their long relaxation times, even when they are of the micron size. In the case of ^{4}He crystals, atoms are transported through surrounding superfluid ^{4}He liquid, which makes the relaxation process very fast.

Cuprous and silver chalcogenides are materials known as mixed superionic conductors with a specific physical property of having high bulk ambipolar (metal ions and electrons) diffusion coefficient while still in solid-state phase ($\sigma_h = 10^5$ S/m; $\sigma_i = 10^{-3} \times \sigma_h$) [6,7]. The high Cu atom bulk diffusivity of cuprous selenide is the characteristic of its α phase which exists between the melting temperature T_m and the phase transition to the β non-superionic phase, $T_{\alpha\beta}$. T_m and $T_{\alpha\beta}$ are concentration dependent, for Cu_2Se $T_m = 1430$ K and $T_{\alpha\beta} = 410$ K, while for $Cu_{1.7}Se$, $T_m = 1390$ K and $T_{\alpha\beta} = 320$ K [8]. The bulk diffusivity of Cu atoms in nonstoichiometric cuprous selenide is temperature and concentration dependent. For $Cu_{1.75}Se$ at 800 K (temperature of the growth described here), the bulk diffusivity is found to be 6.2×10^{-7} m^2 s^{-1} [9]. This is about two orders of magnitude higher than the surface diffusion coefficient which dominates the lead-on-graphite spherical crystallite equilibration process [10]. Thus, in the case of $Cu_{2-\delta}Se$, the material transport (Cu atoms), which dominantly controls an interface equilibration, is therefore expected to take place through the bulk. The transport of the non-metallic component is provided via the surrounding vapour. The equilibrium vapour pressure of chalcogenide above its liquid in a closed volume, further away from the growth site, provides the equilibrium vapour pressure for the growing compound and, consequently, fixes its concentration.

The characteristic time (τ) for the relaxation of excess metal atoms for a crystal at 800 K ($Cu_{1.75}Se$) has been calculated to be between 1.6 and 160 seconds for the mm-size and cm-size crystals, respectively [9]. If the bulk diffusion were the only process which controls the interface relaxation, the cuprous selenide equilibration time would have been at most two orders of magnitude longer than the one declared for ^{4}He crystals [4,5].

The heat of crystallisation may also influence the surface relaxation time. Therefore, the heat conduction process, as well as the magnitude of heat of fusion, should be considered as well.

It has been accepted [1] that at $T = 0$ K, the ECS is fully faceted polyhedron with sharp edges and corners at which the atomically smooth facets meet. This shape is the consequence of the high symmetry crystal potential. The macroscopic facets at the surface are oriented in compliance with the inherent symmetry requirements regarding the particular crystal. Although there is an infinite number of regular crystal planes, only the lowest Miller index facets (i.e. of the lowest energy) appear on the interface.

Fully faceted shape of the cuprous selenide single crystal is expected to be a cuboctahedron with eight (111) facets and six (100) facets.

Upon heating the crystal, the rounded parts begin to appear. First the corners, and afterwards the edges become more and more rounded, separating the facets. The facets shrink and finally disappear. Each type of facets disappear at its own roughening temperature T_R. Above the highest T_R, the crystal is completely rounded. Its shape still resembles its original faceted form. Our preliminary measurements show that in the case of $Cu_{1.75}Se$, the roughening temperatures are $T_R(111) \approx 830$ K and $T_R(100) \approx 710$ K.

The ECS crystal interface is regarded as a 2-D two-phase system of facets (atomically smooth) and rounded parts (atomically rough) which meet at phase boundaries, i.e. at facet edges [1].

Our work has been motivated by the comprehensive investigations by Ohachi and co-workers on silver sulphide compounds [2,3,11] that comprised main aspects of ECS features of silver sulphide. Among metal chalcogenide superionic conductors, silver sulphide is the most appropriate for ECS investigation due to its highest metal-atom bulk diffusivity. Another compound from metal chalcogenide group, cuprous selenide, although having a bit lower metal-atom diffusivity, appears to be exceptionally useful for ECS investigation. Its main advantage, in comparison to other chalcogenides, is that it exists in the widest nonstoichiometric range (from Cu_2Se even to $Cu_{1.7}Se$) with the lattice symmetry ($F\overline{4}3m$) remaining unchanged. Thus the possibility to change the Cu concentration by as much as 15% offers a new degree of freedom in this 2-D 2-phase problem. Namely, it should be rewarding to investigate changes of the specific surface free energy, α, within such a wide interval of Cu concentration, δ. In order to achieve this goal, it is of the utmost importance first to perform the ECS characterisation of the cuprous selenide single crystal. There are four well-known criteria [12] which the crystal shape has to fulfil to be regarded as the ECS. Besides the macroscopic crystal symmetry being in compliance with the lattice point group symmetry, the ECS must be time, history and size independent (except for the part truncated by the substrate).

Prior to any ECS testing, the crystal has to be grown to a certain size. Under conditions of meticulous control of growth temperature and of the growth rate, the growth process itself appears exceptionally interesting. The aim of our investigations is to characterise the time development of the growth shape under conditions of constant but very low volume growth rate. Since under these conditions the radial growth rate decreases as the surface area increases, the growth shape is expected to tend in the course of time to its equilibrium shape. In this way, the dynamical aspects of size-scaling criterion will also be tested [1,12]. We had the possibility of tracing the relevant ECS parameters in situ, so we have investigated particularly the extension of deviations from true equilibrium of the crystal during its the growth.

Moreover, some new results on ^{4}He regarding facet height growth have been published recently [13]. Under the conditions of the imposed volume growth rate and at the constant temperature, the irregular alternation of non-growth and fast growth periods has been observed. This mode of growth, called the burst-like mode, is found to be a characteristic of the growth of the ^{4}He facet free of screw dislocations.

In our experiments, we have also observed some features of growth dynamics resembling the stepping-like mechanism of facet growth detected in ^{4}He ECS crystals.

2. *Experimental*

In the present experiments, we have performed the growth of the spherical non-stoichiometric single crystals of cuprous selenide of a few millimetres in diameter, and their growth shapes have been continuously monitored in time. It has been a free-space growth under the conditions of a constant supply of growth material, and at constant temperature and constant Se vapour pressure. The crystals grown at the temperature of 30 K below $T_R \approx 830$ K have revealed spherical, partly faceted (111) shapes, strongly resembling the ECS form. Since the crystals have been grown under the low constant volume growth rate (0.19 mm^3/h), their radial growth rate has decreased from 150 nm/s to almost 1 nm/s as radius has increased from 0.25 mm to 1.7 mm. The scheme of the experimental setup is shown in Fig. 1. A vertical transparent three-zone furnace was constructed by winding a Kanthal (A) wire of 0.75 mm diameter helicoidally, with a constant winding pitch of 3 mm, around a silica tube with the diameter of 30 mm. Constant temperature in each zone was maintained by independent temperature controllers. For the upper (T_U) and lower (T_{Se}) zone we used Haake TP 24 controllers, with platinum Pt100 resistance thermometers as feedback sensors, mechanically fixed to the heating wire. The temperature (T_{G}) of the central growth zone was controlled by programmable a Eurotherm (818P15) controller with Pt-Pt13%Rh thermocouple as a feedback sensor. For the purpose of our experiments, we have used the furnace as a two-zone furnace by keeping the upper two zones at the same temperature ($T_U = T_{\mathrm{G}}$).

The growth process was performed in an evacuated (pressure less than 10^{-8} Pa (10^{-6} torr)) and sealed transparent silica ampoule placed coaxially inside the furnace. The ampoule consists of two belly parts, 6 cm long and of a 17 mm (outer) diameter, connected with a tube of 7 mm in (outer) diameter. On top of the upper belly, a narrow tube (outer diameter being 6 mm) with a capillary ending was inserted and sealed so that the capillary tip coincided with the centre of the upper belly. The capillaries used in these growth experiments had orifice diameters between about 60 and 200 μm. The quasi-conical capillary ending contained an appropriately shaped polycrystalline $Cu_{2-\delta}Se$ specimen tightly fitting in the capillary interior. On the flat top of the polycrystalline sample, there was a pure copper metal disc ($\approx$ 0.1 g, 99.999; Metal Crystals and Oxides) which served as the source of Cu atoms necessary for the crystal growth. The lower belly part, sealed at the bottom, contains coarse Se powder (Fluka AG; 99.999) which melts at $\approx$ 218 °C and serves as the source of Se vapour to complete the chemical reaction at the surface of the growing crystal. The temperature of the vessel containing Se was measured by Pt-Pt13%Rh thermocouple attached to its bottom on the outer side. The temperature of the centre of the upper belly, which we expect to truly represent the temperature of the capillary tip where the spherical single crystal is growing, was measured by a Pt-Pt13%Rh thermocouple (0.1 mm in diameter) attached to the outer wall of the belly. The third thermocouple of the same kind was used to measure temperature of the centre of the furnace top zone.

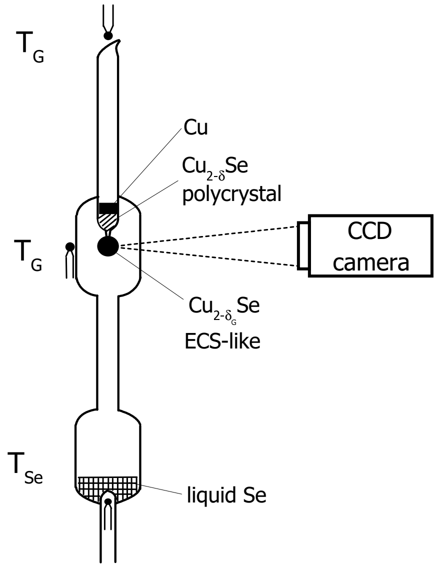

Fig. 1. Schematic diagram of the experimental arrangement used for the growth of equilibrium-like shaped crystals. The transparent evacuated silica ampoule with the area of growth separated enough from the source of selenium vapour. The vertical transparent three-zone furnace is not shown for clarity.

Temperatures of all zones (at the centre of the upper zone, at the growing-crystal position and of the liquid Se) were measured continuously (the sampling interval being 1 minute) using Pt-Pt13%Rh thermocouples connected to Keithley 705 scanner and Keithley 181 nanovolmeter whose output was fed to the computer by an IEEE488 card. During the growth, the temperatures T_{G} and T_{Se} were kept constant to within 2 K.

The ampoule was first filled with ingredients described above, then evacuated, sealed and centred in the furnace tube by the lava spacers which have also served as thermal insulation between zones.

In order to activate the growth process, we have first simultaneously raised the temperature of the bottom zone (Se vessel temperature, T_{Se}) and of two upper zones (the crystal growing temperature, T_{G}). The temperature of the Se vessel determines the equilibrium vapour pressure above the Se liquid, i.e., Se vapour pressure at the position of the growing crystal. The growing crystal has to accommodate its stoichiometry δ until its Se pressure becomes equal to the imposed pressure, which is now the equilibrium Se pressure in $\mathrm{Cu}_{2-\delta}\mathrm{Se}$ as well [14]. The chemical potential of the growing surface is thus fixed, $\mu(\mathrm{Cu}_{2-\delta}\mathrm{Se}$ at the surface$) = \mu_{\mathrm{GROWTH}}$, as well as its composition (Cu concentration). The polycrystalline sample serves as a media of high diffusivity for Cu atom transport. Being in equilibrium with the copper disc on top of it, the upper end of the polycrystalline sample becomes stoichiometric $\mathrm{Cu_2Se}$ having the fixed chemical potential $\mu(\mathrm{Cu_2Se})$.

As soon as the desired temperatures ($T_{\mathrm{G}} = 480\,^{\circ}\mathrm{C} - 530\,^{\circ}\mathrm{C}$, $T_{\mathrm{Se}} = 400\,^{\circ}\mathrm{C} - 480\,^{\circ}\mathrm{C}$) are achieved, the current of Cu atoms begins to flow from the copper metal disc toward the free end of the sample surrounded by a constant Se vapour pressure where chemical reaction takes place. The Cu current is driven by a constant chemical potential difference $\mu(\mathrm{Cu_2Se})$ - $\mu(\mathrm{Cu}_{2-\delta}\mathrm{Se})$ established across the polycrystalline sample. Note that δ is fixed by the constant Se vapour pressure at the growing site and by the copper metal disc at the injecting site. Within an hour or two, a few growing crystal threads appear in the capillary interior at the conical bottom of the polycrystal [9]. They are of different orientations, growing at different rates. The fastest growing thread reaches the capillary orifice first, fills up its interior, and prevents the Se vapour from further feeding the others, thus stopping their growth. The thread that survives grows through the capillary orifice until it reaches the capillary tip. The growth on a tip can be geometrically divided into three regions: i) from the flat front, defined by the orifice entrance, to the hemispherical shape above it, ii) a hemispherical shape extended up to the outer tip diameter and iii) full spherical shape surrounding the tip (see Fig. 2). During the growth, no shift of the sphere centre has been detected.

The role of the capillary in the growth process is essential. First, it is a single crystal seed (thread) selector and the controller of the current of Cu atoms. It is known [2,3] that the high quality spherical single crystal can be obtained only under the growth conditions called the solid-state crystallisation mode. This means that the average growth rate is controlled by the flow of Cu atoms, i.e. that the metal-atom current density is smaller than that of the chalcogenide molecules. The current density of Se_n molecules is defined by T_{Se} (and by the growing spherical surface). Since the chemical potential difference is defined and kept constant during the growth, the Cu current is defined by the actual geometry of the polycrystalline sample. Starting from the basic equations for the ambipolar diffusion in superionic conductors [15], we have calculated in quite some detail [9] the chemical potential, and consequently the excess Cu concentration distribution along the axis of the polycrystalline sample and at the growing sphere. It is shown that less than 5% of the total chemical potential difference arises along the radius of ECS sphere itself. Thus, the Cu atoms current $\mathrm{d}n/\mathrm{d}t$ is independent of the dimension of the growing sphere (within less than 0.2%) and is dominantly determined by the diameter of the capillary orifice [9]. By taking the actual capillary orifice diameter of 76 μm and the parameters given in Table 1 in Ref. [9], the calculation yields the value of the current of 5×10^{15} atoms per second. Note that it is 5 orders of magnitude smaller than the Se current determined by the equilibrium vapour pressure. Therefore, the growth is realised entirely in the solid state crystallisation mode i.e. it is controlled by the flow of Cu atoms.

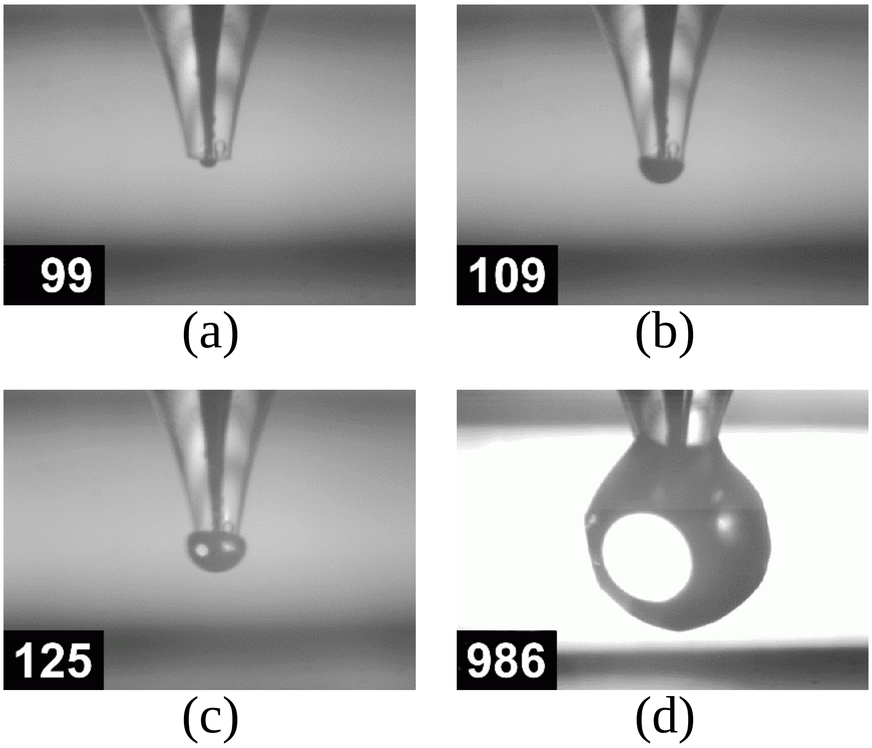

Fig. 2. Hemispherical (after 99 and 109 minutes) and spherical (after 125 and 986 minutes) growth shape in free space on the capillary tip. The growing crystal after 986 minutes (1.82 mm in diameter) is ECS-like with the visible (111) facet.

On the other hand, the volume growth rate is given [9] by

$$\frac{\mathrm{d}V}{\mathrm{d}t} = v_0 \frac{\mathrm{d}n}{\mathrm{d}t} = \mathrm{const}\,, \qquad (1)$$

where v_0 is the crystal volume per Cu atom. During the entire growth of the sphere, even up to the diameter of 5 mm, the volume growth rate is constant within the accuracy of 1%.

Note that the volume grown on the capillary tip can be simply related to the radius of the ECS sphere as soon as the volume of the sphere is corrected by the volume of the capillary tip enclosed by the sphere.

The growth process has been monitored in situ by taking images of growing crystals at intervals of one minute or longer (up to 2 hours), depending the on actual radial growth rate. The image acquisition system consisted of a CCD camera (Pulnix TM-765, having 756(H)×581(V) resolution with 256 levels of grey) mounted as an ocular to a microscope (Technival 2000, with 5 enlargement steps, from 1 to 5). The signal from the camera was fed to the computer via an appropriate frame grabber (Matrox PIP-512B) as well as to Sony monitor and a Panasonic videocassette recorder. The camera microscope system was first calibrated using a commercial micrometer scale having the total length of 1 mm with 10 μm divisions. The final resolution of computer images obtained in this way was between 10 μm and 2 μm for the microscope enlargement settings of 1 and 5, respectively. Under the usual working conditions, the microscope objective was at the distance of 8 – 12 cm from the furnace centre.

3. Results and discussion

During approximately first two hours after the appearance of the growing crystal at the capillary orifice, the crystal exhibits a hemispherical shape until its dimension becomes larger than the outer diameter of the capillary. During this first stage of growth, there are no facets on its surface. The growth continues in the way that the sphere overgrows the capillary tip. From that moment on, the shape is spherical, but enclosing the part of the tip which it surrounds. During the growth, the centre of the sphere is located at the capillary orifice centre and its position is independent of the diameter of the sphere. The first appearance of facets is observed after 2 – 3 hours of growth.

The chosen set of growth parameters (T_G and $p_{Se}(T_{Se})$) has determined the stoichiometry of growing spherical single crystals to be $Cu_{1.75\pm0.01}Se$ [9]. Under the stationary growth conditions, the diameter of the sphere was measured as a function of time (see Fig. 3). We have also measured the parameters of the facets which were seen as circles on the spherical surface, but when projected onto the plane of the image appear as ellipses. The long axis (a) provides directly the diameter L of the facet. By using it together with the short axis (b), one can calculate the azimuthal angle between the radius vector of the facet and its orthogonal projection to the image plane. Using the SForm program [16] for the image analysis, it is also possible to determine the position of the centre of each elliptical facet as well as the position of the centre of the sphere, obtaining in this way their relative distance ρ. Simple geometrical considerations give the magnitude of the facet radius vector $Z = \rho/\sqrt{1-(b/a)^2}$ (i.e. the height of the facet measured from the sphere centre) for each facet.

In Fig. 3 we present the results of the measurements of the sphere radius R, the facet radius L and the height of the facet Z as functions of time.

First, we analyse the time dependence of R which is measured as the radius of the maximum circular envelope of the sphere projection to the screen. Note that because of the present way of measurement and of the resolution, R should be taken as a radial size of the crystal in the (101) direction (rough part of the interface between

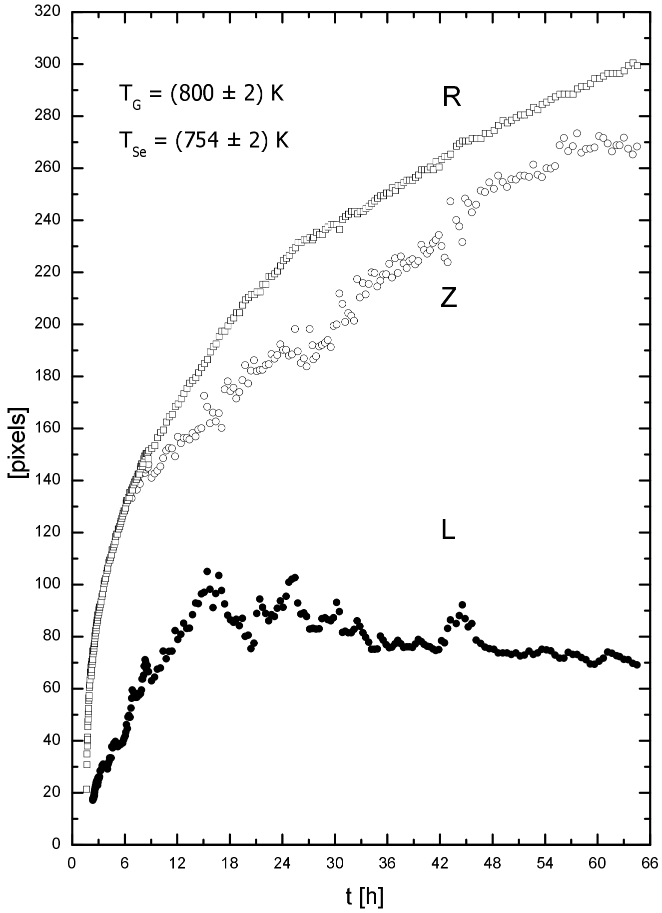

Fig. 3. Horizontal radius R of the sphere, height Z of the (111) facet measured from the centre of the sphere, and radius of the same facet (in pixels; 138 pixels = 1 mm) as a function of time (in hours) at $T_{\rm G} = (800 \pm 2)$ K and $T_{\rm Se} = (754 \pm 2)$ K.

(111) facets) rather than the radius of curvature of the same direction. As shown in details in [9], R appears as a good measure of the growing volume. In Fig. 4 we demonstrate the validity of Eq. (1). The linearity in time of the volume $V(t)$, calculated [9] from the measured values of R as described earlier (and corrected for the capillary tip volume incorporated into the sphere), is observed during more than 120 hours. This is contrary to the previously published result [11] of a parabolic growth law ($R^2 \propto t$), which extends during 8 hours, at the average radial growth rate of 1 mm/h.

For the particular growth shown in Fig. 4, the volume growth rate of 0.19 mm^3/h is constant during 120 hours. Due to the spherical shape, the radial growth rate continuously decreases from 350 nm/s to 1.5 nm/s, throughout the interval of the volume linearity.

We have proved on the basis of Eq. (1) and of the demonstrated volume linearity during the growth that the crystal is growing under the conditions of a constant material flow to its surface. Note that the flow is controlled by the Cu atoms current supply through the capillary orifice. Since this current is driven by the constant chemical potential difference, its magnitude is dominantly determined by the size of the capillary orifice.

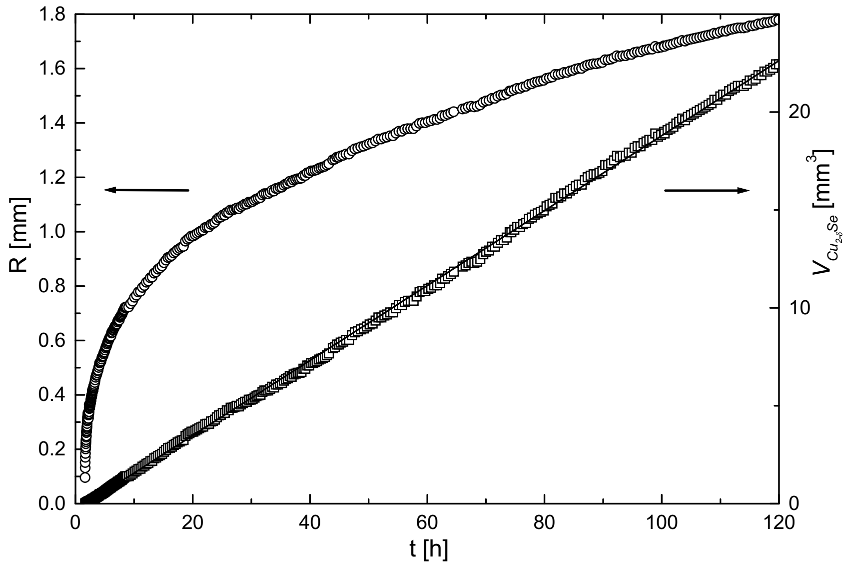

Fig. 4. Radius of the growing sphere and the pure growing volume V (calculated from R and corrected for the capillary tip volume incorporated into the sphere) as a function of time. Straight line is the least-squares linear fit through the measured data points.

We have also tested the behaviour of $R(t)$ in the limit $V \to \infty$ by rescaling $R(t)$ with the cube root of volume (from Fig. 4) using Eq. (1)

$$r(101) \equiv \lim_{V\to\infty} \left[\frac{R(101)}{\widetilde{\lambda}\, V^{1/3}}\right] \tag{2}$$

where $\widetilde{\lambda}$ is dimensionless. The size of $r(101)$ is a measure of the specific surface free energy of the crystal in the (101) direction or, in our case, rather of the specific surface free energy of the rough surface. This rescaling has revealed that after more than about 15 hours of growth, $r(101)$ does not depend on volume, or that $R(101)$ scales linearly as $V^{1/3}$. Therefore, R itself may be taken as a good scaling parameter beyond $t = 15$ h (total growth time has been more than 120 h).

The time dependences shown in Fig. 3 of both $L(t)$ and $Z(t)$ are interesting besides the fact that they reflect the growth shape features. To the best of our knowledge, this is one of the rare records of the facet behaviour during the slow growth of the crystal in a free space in which the growth in both the direction of the facet normal ($Z(t)$) and the direction perpendicular to it ($L(t)$) is monitored simultaneously. Leaving aside the pronounced "noisy" behaviour of the facet radius L, its growth behaviour may be described as follows. During the first 15 h of growth it rapidly increases its absolute size. During the rest of the growth time, it changes its behaviour to a slowly decreasing one. The "noisy" behaviour of L during the growth seems to be the characteristic feature of the facet growth and consequently it deserves special attention. The behaviour of the facet height Z (the distance of the facet from the centre of the sphere) should be related to the smooth R behaviour. In the first 15 hours, there is a size delay compared to the increasing size of R. In terms of the constant volume of the crystal (see Eq. (2)), the reduced height of the facet (Z/R) shown in Fig. 5 is rapidly decreasing, reaching its minimum value after about 15 h (the most flattened sphere in the (111) directions). As the growth continues, the reduced height increases towards (seemingly) equilibrium value for this temperature. Due to the poor resolution in the determination of Z, there is a great uncertainty of its initial as well as its long-time behaviour.

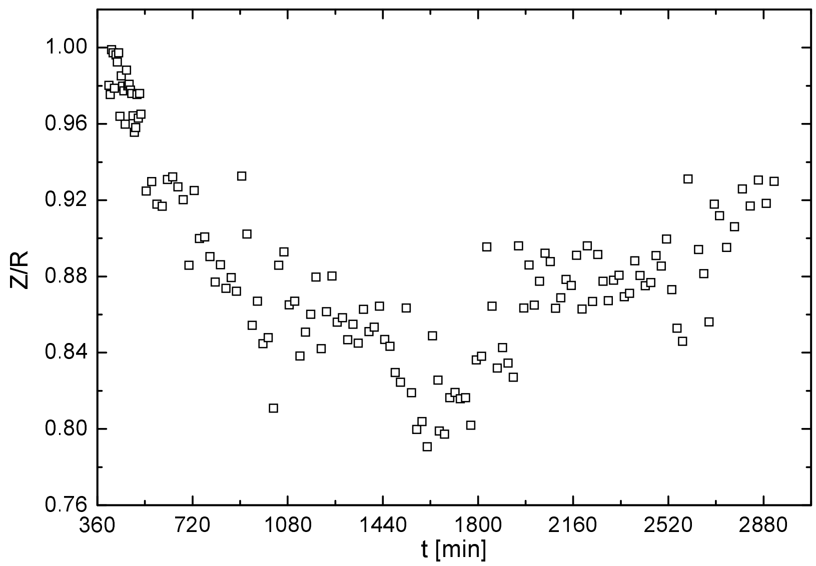

Fig. 5. Reduced height of the (111) facet Z/R as a function of time.

We are dealing all the time with the growing shapes of crystals. The radial growth rates continuously decrease inversely proportional to the area of the surface of the crystal. In the range of the volume-time linearity, and for the growth time larger than 15 h, the radial growth rate decreases from 6.5 nm/s (at 15 h) to less than 1.5 nm/s (at 120 h). These growth rates are very slow compared, for example, with the facet growth rate in Ag_2S (30 nm/s) [3]. As the radial growth rate decreases, the relative effectiveness of the surface equilibration processes increases. Therefore, the slowly growing shape will not differ very much from the true equilibrium shape, and the difference will diminish with decreasing radial growth rate. In other words, the redistribution process of new molecules arriving at the surface in order to minimise free surface energy, and thus to equilibrate the shape, becomes more effective, particularly at the facets. It could be, therefore, worthwhile to try to apply the usual description of the equilibrium crystal outline. We recall the well-known [17] Gibbs-Curie-Wulff rule that relates the size of the crystal in the particular direction and the specific surface free energy.

$$\vec{n} \cdot \vec{r} = \frac{2\Omega\alpha(\vec{n})}{\Delta\mu} \tag{3}$$

where $\vec{n}$ is the unit vector normal to the surface element associated with radius vector $\vec{r}$, $\alpha(\vec{n})$ is the specific free energy of the interface (or, shortly, the surface energy) dependent on the orientation of the surface element relative to the facet orientation and $\Delta\mu/2\Omega$ is the chemical potential difference per unit volume or the parameter λ (Lagrange multiplier) that determines the crystal size scale.

In 1+1 dimensions geometry, the dependence of the specific surface free energy $\alpha(\phi)$ on the surface element orientation relative to facet axis (111) is [18]

$$\alpha(\phi) = \alpha_{111}\cos\phi + \frac{\beta}{d}\sin\phi + \frac{\delta}{d^3}\phi^3\cos\phi \tag{4}$$

where ϕ is the angle between $\vec{n}$ and the (111) direction, α_{111} is the specific surface free energy of the smooth (111) facet, β is the step free energy per unit length and d is the step height or the crystal periodicity along the normal to the facet. The third term accounts for step-step interactions.

The three specific directions of $\vec{n}$, along the (111) axis ($\phi = 0$), slightly inclined to the (111) axis ($\phi = \delta\phi$), and along the (101) direction ($\phi = 35.26°$) reveal the meaning of the measured quantities in terms of the specific surface free energy α for these surface orientations

$$\lambda Z = \alpha_{111} \qquad \lambda L = \frac{\beta}{d} \qquad \lambda R = \alpha(101) \tag{5}$$

where $\alpha(101)$ is the specific surface free energy of the rough surface in the (101) direction. In order to eliminate the size of the crystal (i.e. λ) the most appropriate expressions would be the ratios of L and Z to R. Note that R was shown to scale linearly with the cube root of the volume in the range of interest, beyond 15 h. The equilibrium ratios are

$$\left(\frac{Z}{R}\right)_{eq} = \frac{\alpha_{111}}{\alpha(101)} \qquad \left(\frac{L}{R}\right)_{eq} = \frac{\beta}{d\,\alpha(101)} \tag{6}$$

In Fig. 6, we show the growth shape ratio of the facet radius L to the sphere radius R, L/R, vs. time, in order to check how far out of the equilibrium is the crystal during the growth, as well as how the ratio approaches the equilibrium value. Namely, the equilibrium L/R ratio should be a solely temperature-dependent quantity within this model.

As may be seen in Fig. 6, there are two distinct regimes of behaviour of that ratio. The fast increase of the facet radius up to about 15 h turns into a slow decrease. The regime of the size decreasing behaviour resembles a time relaxation process. Indeed, this part of the ratio vs. time dependence can be described as an exponential relaxation, using a single relaxation time constant τ of 1200 $\pm$ 100 minutes. The fitting procedure has offered the values of two other constants, $(L/R)_{t=0} = 0.7$ and $(L/R)_{t=\infty} = 0.215$. Note that the ratio $\overline{L}(111)/\overline{R}$ (where $\overline{L}$ and $\overline{R}$ are effective radii) for the case of the fully faceted cuboctahedral crystal (ECS at $T = 0$ K) has been calculated to be 0.654.

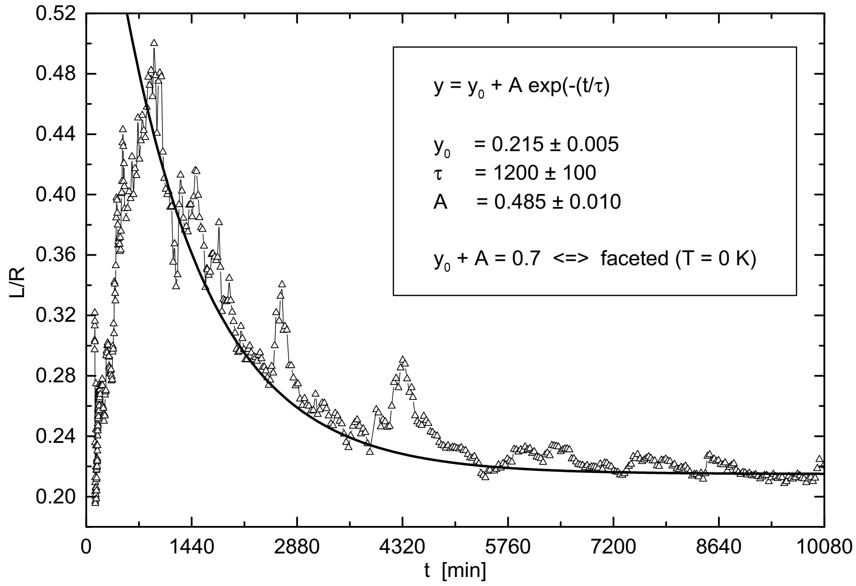

Fig. 6. Ratio of the (111) facet radius L to the sphere radius R as a function of time and the three-parameter exponential fit. The values of the fit parameters are given in the inset.

The magnitude of τ is more than 3 orders of magnitude larger than the characteristic bulk Cu atom relaxation time (≈ 10 s). To some extent, τ comprises the information on the surface mobility, but is also influenced by the continuos change of the driving force for the surface transport. (Note that the surface transport in cuprous selenide is absent or negligible. The material transport between two points on the surface is realised exclusively through the bulk.) Namely, the radial growth rate is inversely proportional to the surface area of the sphere and, even more important, it is different for the rough and the smooth/faceted parts of the surface. The more realistic approach should take into account the time dependent material flow caused by the nonequilibrium chemical potential difference between the rough and the smooth part of the surface caused by their different growth rates. However, it is intriguing that the growing crystal should have any "memory" about its own polyhedral shape at $T = 0$ K, since its temperature is kept constant at 800 ± 2 K during the seeding of the crystal, as well as during its entire growth. This is beyond the common knowledge related to the physics of the ECS interface phase diagrams [1] and deserves further investigation.

Even more interesting is the observation of the effect superimposed to the relaxation behaviour, which may be described as facet-size oscillations during the growth. Here we report the first observation of this effect regarding the radius of the facet under the conditions of the constant volume growth rate.

However, the observation of a novel growth mechanism characterised by a modulation of (0001) or c - facet height of solid ^{4}He effective at very low temperatures and in a wide range of average growth rates has been reported recently [13]. Since there are serious indications that the oscillations of the facet radius L and the modulations of facet height Z during the growth of $Cu_{1.75}Se$ crystals are correlated, we believe that these effects could have similar physical background in both systems.

Namely, the growth rate modulation vs. time of c facet of solid hcp ^{4}He containing no screw dislocations, at temperatures between 2 mK and 200 mK has been published by a group from Finland [13]. They recorded the vertical growth of the c facet (with the resolution of 5 nm), by applying the driving pressure to the superfluid liquid above previously prepared crystal that had completely covered the bottom of a 17-mm-diameter cylindrical experimental chamber. The growth mode observed, named the burst-like mode, is essentially irregular alternation of non-growth (or very slow growth - less than 2 atomic layers per second) and fast-growth periods, in a wide range of average velocities of vertical motion of c facet, between 1 nm/s and 50 μm/s. When the overpressure (at constant rate) exceeds the equilibrium pressure, the facet resists increasing its height until the overpressure reaches some (again irregular) threshold level after which the facet bursts upward creating abruptly $200 - 2000$ new atomic layers. During the period of the burst-like growth, the overpressure almost instantaneously drops to the so-called restabilisation value. The effect has been successfully interpreted using 2-D nucleation mechanism with the quantum nucleation rate [19].

In our experiments, the poor resolution of the (111) facet height measurements (up to 2 μm) does not enable us to make any quantitative conclusions on the Z vs. time dependence (see Fig. 3). Although there are certain modulations of Z with time, more accurate data are needed. Nevertheless, even with the present resolution, we are encouraged to search for a time correlation of the facet size L and of the facet height Z in the region where they are more pronounced. In fact, we expect at least to indicate periods in which enhanced rise of L above some smooth relaxation value is correlated with fixed, time independent value of the facet height Z (measured from the centre of the sphere), while the relaxation of L back to the smooth behaviour corresponds to the enhanced rise of Z. Note that we have no information whatsoever on the state of the (111) facet surface, i.e. on the presence or absence of screw dislocations.

In Fig. 7 a, we show four distinctive oscillations of the facet size L during first 10 hours of the growth. In Fig. 7 b, we plot L vs. Z in the same interval of time. We may say that, within the experimental resolution, at least for the two last oscillations, the extra enhancement of the facet diameter of the order of 20% is followed by the constancy of the facet height (within the error not larger than 2%). Duration of the single oscillation/modulation in the presented region is about 100 minutes. Note that the decreasing of the radial growth rate from 150 nm/s to 1.5 nm/s makes the facet size oscillations less and less pronounced.

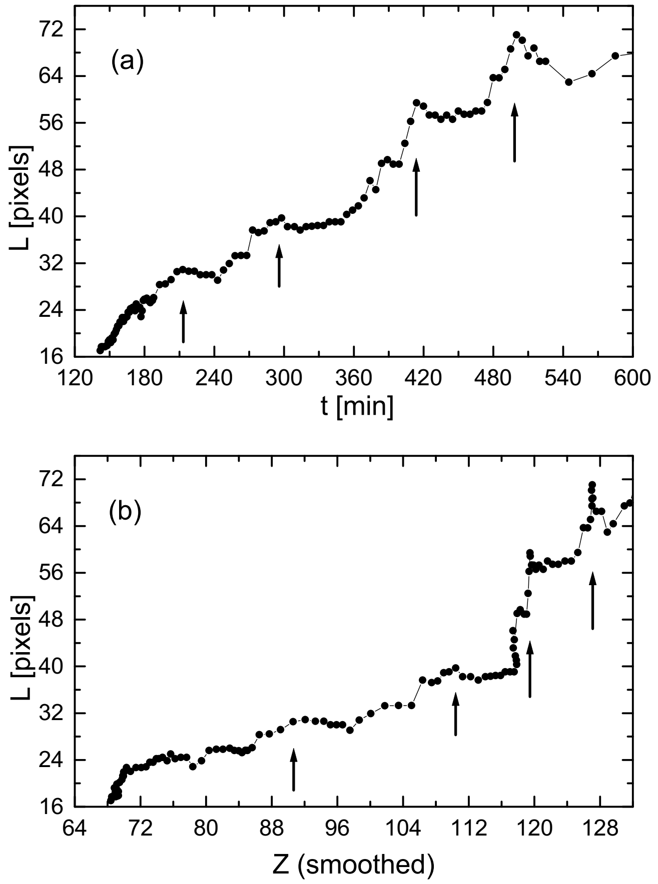

Fig. 7. a) Facet (111) radius L vs. time t in the first ten hours of growth (arrows mark local maxima of facet radius). b) Facet radius L vs. facet height Z (the same maxima as in a) are marked by arrows).

The existence of the L-Z time correlation suggests two conclusions.

First, during the growth, the facet pinning and consequently the facet L and Z oscillations appear to be the essential growth feature of cuprous selenide resembling those found for ^{4}He during the growth at moderate growth rates [13]. There is, of course, the essential difference in the behaviour of the facet height/size relaxation after crossing the threshold level (the chemical potential difference instability) when cuprous selenide is compared to ^{4}He. The burst-like growth is characteristic of helium crystal and it is ascribed to the quantum tunnelling [19]. In the case of cuprous selenide, the growth after threshold is continuos and slow, governed dominantly by the Cu atom current that feeds the surface through the bulk from the inside of the crystal. This current is constant during the entire growth, close to 2×10^{15} atoms/s. The growth temperature of 800 K, compared to $2 - 200$ mK for ^{4}He, has to be emphasised in order to suggest that in the case of cuprous selenide, purely classical description of the observed phenomena, i.e. a thermal nucleation mechanism, can be used.

Second, it appears that the facet-growth rate modulations are more pronounced and thus easier to measure, in facet size vs. time than the height vs. time measurements.

One may regard the longest relaxation time of 1200 minutes either as the series of times of successive facet size oscillations (duration of the order of 100 minutes) or as the complex event parameter influenced by time (size) dependent radial growth rate. The oscillation of the facet size accompanied by the modulation of the facet height emerges as the basic event, which governs a nonequilibrium and probably nearly-equilibrium growth process. Under a constant driving material supply for growth, the oscillation event involves the kinetics of the assembly of mutually interacting steps and of the pinned facet. Both are strongly influenced by the pronounced spatial anisotropy of the surface stiffness at the facet edge. Any further conclusions should rely upon results of more sophisticated experiments in which the height Z of the (111) facet will be measured by interference holography. We are preparing to perform such experiments shortly, hoping to achieve much better insight from the measurements with a considerably improved resolution.

In the process of growth, many of our crystals have revealed facet oscillations which are more pronounced at lower temperatures (but not too low). Therefore, the results obtained on our crystals (which, hopefully, contain no dislocations) offer the possibility to achieve at least some partial new insight in the physics of the facet growth dynamics.

4. *Conclusion*

The ECS-like spherical crystals of the superionic conductor, nonstoichiometric cuprous selenide, have been grown in free space using modified Ohachi's method. The growth is based on the specific property of the high diffusivity of Cu atoms through the bulk cuprous selenide ($D = 6.2 \times 10^{-7}$ m^{2}s^{-1} at 800 K), providing the chalcogen (Se) component as the equilibrium vapour pressure in order to complete the chemical reaction at the growing surface, as well as to fix the composition (the chemical potential) of the growing crystal. The driving force for the growth is related to the chemical potential difference of 0.5 eV, with values fixed at both ends of the sample (polycrystal and spherical single crystal). Using the capillary narrowing, the growth rate of the spherical single crystal is controlled by the the constant current of Cu atoms supplying the surface of the spherical crystal during the growth. Under the constant chemical potential difference, the current of Cu atoms depends solely on the size of the capillary orifice.

Applying Yokota's diffusion theory for superionic conductors to our experimental geometry, we have calculated the volume growth rate. It appears that the volume growth rate is constant during 120 hours of growth, which is in agreement with our calculations. The linear increase of the growing volume in time contradicts the Ohachi's results. The discrepancy was shown to be the consequence of Ohachi's too crude approximation used for the chemical potential difference distribution within the growing sphere [9].

Several experiments of the growth of spherical single crystals have been performed at $T_G = (800 \pm 2)$ K and $\Delta\mu \approx 0.5$ eV (with $T_{Se} = (754 \pm 2)$ K). During the 150 hours of growth, we have measured in situ the time dependence of the sphere diameter R, the facet diameter L and the height of the facet Z relative to the sphere centre. The facet radius, normalised to the sphere radius, has revealed the exponential relaxation behaviour with a single time constant $\tau = (1200 \pm 100)$ minutes. The magnitude of τ is more than 3 orders of magnitude longer than the characteristic bulk relaxation time. Under the present growth conditions ($V(t)$ and $R(t)$ are increasing functions of time), the time is not a good parameter and, therefore, it is difficult to ascribe τ to a single transport process.

The facet size oscillations, superimposed on the time relaxation process, under the conditions of the constant volume growth rate, have been observed. Although they are irregular in time, an average periodicity of about 100 ± 20 minutes may be recognised. Also, we have shown to some extent the correlation between the facet-radius oscillations and facet-height modulations. Considering the time stepping of the facet height accompanied by facet burst-like growth of the solid/liquid ^{4}He interface at $2 - 200$ mK, it seems that the facet size oscillations in $Cu_{2-\delta}Se$ observed at 800 K are also caused by the existence of the facet pinning potential. The essential difference is related to the nucleation mechanism. Instead of the quantum nucleation on ^{4}He pinned c-facet, which manifests itself as a burst-like growth mode, one should probably consider classical thermal nucleation on (111) facet of cuprous selenide. Duration of the oscillation period depends on the magnitude of the supply of Cu atoms and the actual facet size. It seems that the facet-size oscillations accompanied by the facet height modulations dominantly govern the crystal growth, so this effect may be regarded as the basic mode of the ECS surface growth.

Acknowledgements

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URAVNOTEŽENJE OBLIKA SFERNIH $Cu_{2-\delta}Se$ MONOKRISTALA TIJEKOM GOTOVO RAVNOTEŽNOG RASTA

Narastali smo sferne monokristale nestehiometrijskog bakar selenida gotovo ravnotežnog oblika površine uporabom prilagoene Ohachijeve metode na temperaturi 30 K ispod temperature hrapavljenja - isčezavanja ravnih ploha, $T_R(111) \approx 830$ K. Rast se odvijao u uvjetima konstantne volumne brzine rasta. Za vrijeme rasta kristala, površina kojeg je dijelom sadržavala ravne makroskopske plohe tipa (111), a ostatkom bila zaobljena, mjerili smo *in situ* CCD kamerom radijus sfernog kristala, radijus ravnih ploha te udaljenost centra plohe od centra sfere. Opazili smo dvije značajke koje pripisujemo neravnotežnim oblicima odnosno oblicima kristala u rastu. Prvo, opazili smo eksponencijelno uravnoteženje oblika s jedinstvenim karakterističnim vremenom od oko 1200 minuta i drugo, opazili smo oscilacije radijusa plohe perioda oko 100 minuta koje se zbivaju neovisno o eksponencijelnom uravnoteženju za vrijeme rasta. Pokazujemo da su oscilacije radijusa plohe povezane s vremenski moduliranim rastom (period bez rasta - period bržeg rasta) udaljenosti plohe od centra sfere temeljna značajka rasta kristala djelomično prekrivenog plohama za vrijeme gotovo ravnotežnog rasta. Oscilacije radijusa plohe koje su vjerojatno posljedica potencijala zapinjanja plohe, izgledno imaju određenu sličnost s nedavno opaženim moduliranim rastom ploha na površini kristala ^{4}He u dodiru sa supratekućinom na 2 mK.