Growth Kinetics of the (110) Faces of Complex Potassium Cobalt–Nickel Sulphate K$_2$Co$_x$Ni$_{1-x}$(SO$_4$)$_2$·6H$_2$O Crystals

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Abstract: The normal growth rate, the steepness of polygonized growth hillocks and the velocity of step movement on the (110) faces of potassium cobalt–nickel sulphate crystals in aqueous solutions with cobalt to nickel ratios of 1:1 and 1:2 were investigated as a function of supersaturation by the geometry of growth hillocks using laser interferometry. It was found that the morphologies of growth hillocks on the (110) faces of the crystals grown from 1:1 and 1:2 solutions are similar and that the growth hillocks are formed by multiple screw dislocation sources. The experimental data on the growth kinetics of the (110) faces of the crystals were analyzed by using the Burton– Cabrera–Frank theory. It was found that (1) there is a critical supersaturation for the growth of the (110) faces, and the value of this supersaturation in the 1:2 solution is higher than that in the 1:1 solution, and (2) the kinetic coefficient of the step movement in the sectors of growth hillocks is highly anisotropic, and the values of this coefficient are larger in 1:2 solution than in 1:1 solution. These results are discussed in the presented work.

Keywords: potassium cobalt–nickel sulphate crystals; screw dislocation growth; growth kinetics; surface morphology

1. Introduction

Study of the properties and growth process of the nickel and cobalt sulphate and complex potassium cobalt–nickel sulphate K$_2$Co$_x$Ni$_{1-x}$(SO$_4$)$_2$·6H$_2$O (KCSH) crystals is very important in connection with their application for the production of ultra-violet filters for modern devices based on the principles of the solar-blind technology [1,2]. The previous studies showed that K$_2$Co(SO$_4$)$_2$·6H$_2$O (KCSH) [3] and K$_2$Ni(SO$_4$)$_2$·6H$_2$O (KNSH) [4] crystals had a higher dehydration temperature than that of nickel sulphate hexahydrate crystals. The main drawback of simple nickel sulphate crystals is the existence of a transmission peak in the visible spectral region, which leads to lower sensitivity of the devices. The application of KCSH crystals can help to solve this problem.

The phase diagram of the K$_2$Ni(SO$_4$)$_2$·6H$_2$O–K$_2$Co(SO$_4$)$_2$·6H$_2$O–H$_2$O ternary system for growing complex KCSH crystals was investigated by Zhokhov et al. [5]. Voloshin et al. [6] described the temperature difference technique with continuous solution feeding for growth of KCSH crystals from solutions of various compositions. The reaction of isomorphous replacement in this multicomponent system leads to the formation of mosaic inhomogeneity in KCSH crystals [7]. This process depends on supersaturation and composition of the solution. The growth behavior of the hillocks formed by screw dislocations on the crystal surface can also be more complicated in KCSH solutions. The phenomena, which take place at the surface, essentially influence the quality of the crystals.
Therefore, successful growth of large complex KCNSH crystals of high optical quality requires knowledge about the growth process of their faces under different conditions, such as supersaturation, ratio of cobalt and nickel in the solution, and purity of raw materials.

The first works on the observation of growing KH$_2$PO$_4$ crystals by the Michelson laser interferometry [8–11] demonstrated that this technique can be suitable for simultaneous study of surface morphology and growth rates of crystals in solutions. This work is aimed to investigate by laser interferometry the morphology, growth kinetics and mechanism of the (110) faces of KCNSH over the supersaturation range in the solutions with the cobalt to nickel ratios equal to 1:1 and 1:2.

2. Materials and Methods

Solutions for the experiments were prepared from commercially available chemicals CoSO$_4$·7H$_2$O, NiSO$_4$·7H$_2$O and K$_2$SO$_4$ of analytical grade, and thrice-distilled water. According to the certificates of analysis, the K$_2$SO$_4$ reagent had $2 \times 10^{-4}$ wt % of Fe, Mg, $20 \times 10^{-4}$ wt % of Ca, and less than $2 \times 10^{-4}$ wt % of heavy metals as Pb, the CoSO$_4$·7H$_2$O and NiSO$_4$·7H$_2$O reagents contained $5 \times 10^{-4}$ wt % traces of Fe, Ca, Mg, Zn, Cu, Cd, and $1 \times 10^{-3}$ wt % of Pb. The used reagents also could have other metal impurities the content of which was not tested by the manufacturer of chemicals.

The crystallizing phase was complex crystals of K$_2$Co$_{x}$Ni$_{1-x}$O$_{y}$·(SO$_4$)$_2$·6H$_2$O belonging to the P2$_1$/a space symmetry group. The Co/Ni ratios in the solutions were 1:1 and 1:2. The dependence of the composition of mixed KCNSH crystals on the composition of the salt part of the solution was studied in the work [5]. The solutions were saturated at temperatures of 41.3–43 °C. The solubility data for KCNSH can be found elsewhere [5]. Prior to the experiments, the solutions were overheated by 15–20 °C above the saturation temperature and filtered through 0.2 µm membranes. The solution supersaturation was calculated as:

$$\sigma = \ln(C/C_e),$$

(1)

where $C$ and $C_e$ are the actual and equilibrium weight concentrations of the complex K$_2$Co$_x$Ni$_{1-x}$O$_y$·(SO$_4$)$_2$·6H$_2$O salt in aqueous solution.

Seed crystals were grown in Petri dishes by spontaneous crystallization in slowly evaporated solutions with the cobalt to nickel ratios 1:1 and 1:2. For further investigations, we selected crystals which had well-developed flat natural (110) faces without visible cracks and inclusions of solution. The size of these crystals was about 3 × 3 × 1 mm$^3$.

The morphology and growth kinetics of the (110) faces of KCNSH crystals were investigated in situ by the Michelson laser interferometry in a flow of solution. The design of the experimental setup and the optical scheme of the interferometer were similar to those described in the previous works [8–11]. The initial beam of a He–Ne laser was split into two beams. The first one, the base beam, passed through an attenuator and was reflected from a base mirror, and the second one, the working beam, was reflected from the observed crystal face. The orientation of this face was intentionally adjusted normally to the working beam. Images with the interference patterns were recorded by a video camera connected to a computer system. A seed crystal was fixed in a special cell with a glass window. The solution was mixed by a stirrer in a thermostated vessel and pumped through the cell. The growth cell had a thermosensor to measure the temperature of the solution in the cell. The temperature of the solution in the cell was 38–43 °C depending on supersaturation. The accuracy of temperature maintenance of the solution in the cell was 0.01 °C. The total amount of the salt deposited from solution on the crystal during the experiment was negligibly small to change the solution composition and to affect the composition of the growing crystal.

The growth units are delivered from the bulk solution to the kinks at the crystal surface by means of diffusion through a boundary liquid layer near the crystal. In terms of hydrodynamics, the thickness of this layer is inversely proportional to the velocity of a flow of ambient solution $u$. Thus, the growth rate of the crystal face asymptotically increases at higher $u$. The value of $u$ in the experiments was about 50 cm/s, and it was set so that
the growth rate approached an asymptotical value. For determining the normal growth rate of the face \( R \), we analyzed the time dependence of the interference pattern intensity at a selected point of the face. The change of the intensity over one period corresponded to growth or dissolution of the crystal face by the value \( h_0 = \lambda/2n \approx 0.226 \, \mu m \), where \( \lambda = 0.6328 \, \mu m \) is the irradiation wavelength of a helium-neon laser, and \( n \approx 1.4 \) is the refractive index of the solution. Thus,

\[
R = \Delta h / \Delta t, \tag{2}
\]

where \( \Delta h \) is the total change of the crystal face height measured over the time \( \Delta t \).

The steepness \( p \) of the surface relative to a singular plane can be found from the formula:

\[
p = \Delta H / \Delta d, \tag{3}
\]

where \( \Delta H \) is the height difference between two selected points of the crystal surface, and \( \Delta d \) is the distance between these points in the interference image plane. \( \Delta H \) is determined by using interference fringes (for example, the two neighboring light or dark fringes correspond to the height difference \( h_0 \)). Wider fringe patterns correspond to the parts of the crystal surface with smaller steepness. Expression (3) is useful for calculation of the average inclination of growth hillocks.

The velocity \( v \) of step movement on the crystal surface is calculated from the relation:

\[
v = R / p, \tag{4}
\]

which is consistent with the relation given by the Burton–Cabrera–Frank (BCF) theory [12], relating the normal growth rate \( R \) of the crystal face growing by the layer-by-layer mechanism with the inclination \( p \) of the plane composed by steps relative to a singular plane, \( v \) being the velocity of movement of these steps.

In every experiment, we measured the normal growth rate \( R \) as a function of supersaturation \( \sigma \) for one selected growth hillock on the surface. Supersaturation was increased by stepwise reduction of the solution temperature. Then, a sequence of interference images was recorded for 5–90 min at fixed supersaturation. We took longer recording times for slow growth rates. The maximum value of supersaturation achieved in the experiments was limited by the solutions stability to spontaneous nucleation.

3. Basic Theoretical Equations

According to the BCF theory [12], the normal growth rate \( R \) of the singular face of crystal growing by the layer-by-layer mechanism on a screw dislocation in the form of a growth hillock is given by:

\[
R = pv, \tag{5}
\]

where \( p \) is the steepness of the growth hillock relative to the plane, and \( v \) is the velocity of step movement on the hillock. When a group of equally-spaced screw dislocations arranged along a line of length \( L \) participate in growth, the steepness \( p \) of the hillock is given by [12]:

\[
p(\sigma) = \frac{mh}{y_0 + 2L} = \frac{mh}{19r_{cr}(\sigma) + 2L}, \tag{6}
\]

where the term in the denominator of the right-hand side denotes the new inter-step distance, \( 2L \) is the perimeter of the contour around a multiple screw dislocation source, \( mh \) is the total Burgers vector of the cooperating dislocation source, \( m \) is the number of steps of elementary height \( h \) on the surface, and \( y_0 = 19r_{cr} \) is the inter-step distance due to an isolated screw dislocation. Budevski, et al. [13] have shown that the ratios \( y_0 / r_{cr} \) for a circular and polygonized spirals are very near to each other. The critical radius \( r_{cr} \) is given by:

\[
r_{cr}(\sigma) = \frac{\omega A}{k_B T \sigma}, \tag{7}
\]
where $\omega$ is the volume of the building unit of the crystal, $\alpha$ is the step free energy per unit step length per unit step height at crystal-solution interface, $k_B$ is the Boltzmann constant, and $T$ is absolute temperature at crystal-solution interface.

The steepness of a growth hillock as a function of supersaturation can be written using Equation (6) as:

$$p^{-1} = \frac{A}{\sigma - \sigma_d} + B,$$

where $\sigma_d$ is the value of threshold supersaturation for growth taken from the data for $p$, $\sigma - \sigma_d$ is the effective supersaturation. At high $\sigma$, all $p^{-1}$ converge to $B > 0$.

Note that Equation (6) gives the supersaturation dependence of $p$ for a multiple dislocation source consisting of a group of screw dislocations spaced apart by a distance less than $9.5r_c$. The dislocation source of this type can form a multiple-thread spiral. If the structure of a multiple source does not change with supersaturation, it is easy to see from Equation (6) that with increasing $\sigma$ the steepness $p$ of all sectors of the growth hillock will tend to the same constant $p \rightarrow mh/2L$ independent of $\alpha$. When a growth hillock is formed by a single screw dislocation source, i.e., $L = 0$ in Equation (6), the steepness $p$ will become linear in $\sigma$ throughout the supersaturation range.

The velocity of steps on a growth hillock is [14]:

$$v = \beta \omega C_e \sigma$$

where $\beta$ is the kinetic coefficient of the steps, $\omega$ is the volume of the building unit of the crystal, and $C_e$ is the equilibrium concentration of the solution in $(m^{-3})$ units. The kinetic coefficient of step $\beta$ is given by the following expression [14]:

$$\beta = a f \exp\left(-\frac{E_a}{k_B T}\right)$$

Here, $a$ is the growth unit (molecule, ion) size perpendicular to the step edge, $f$ is the vibration frequency of the growth units incorporating from a solution into a crystal, and $E_a$ is the activation energy of the incorporation of the growth units into kinks at step edges.

4. Results and Discussion

4.1. Surface Morphology

After the seed KCNSH crystals had been put into a supersaturated solution, many polygonized growth hillocks appeared on the (110) face (Figure 1a). Some parts of the surface were covered with rough macrosteps (the right lower part of the face in Figure 1a). At the beginning of the experiment, the (110) face was regenerated at a small constant supersaturation for $10^{-15}$ h. As a result, the face became flatter, and only one to three well-developed growth hillocks usually remained on the surface (Figures 1b and 2). The centers of the hillocks were frequently located close to the edges or corners of the face. Therefore, some slopes of the hillocks were not clearly visible in the experiments.

A typical growth hillock on the (110) face of a KCNSH crystal grown in 1:1 or 1:2 solution was polygonized and it had four sectors with different steepness (the sectors are numbered in Figures 1b and 2c). Sectors 1 and 3 were less steep, and sector 4 was the steepest.

Figure 2a–d demonstrate the competition of growth hillocks on the (110) face with increasing supersaturation. At the beginning, there were seven hillocks (marked by the symbol $\times$ in Figure 2a) on the face. Since hillock $O$ was the steepest one, it had the highest normal growth rate. As a result, the steps generated by this dislocation source gradually covered the growth layers produced by other hillocks with smaller steepness (Figure 2a–c). Finally, hillock $O$ occupied most of the face and became a leading growth center (Figure 2c). Then, at a higher supersaturation of 0.029, a new dislocation source $O'$ appeared at the right edge of the crystal face (Figure 2d).
Figure 1. Fringe patterns (interferograms) of the (110) faces of different seed crystals in 1:1 solution: (a) regeneration stage, $\sigma = 0.009$; (b) regular surface growing at $\sigma = 0.013$.

Figure 2. Morphology of the (110) face in 1:2 solution at supersaturations $\sigma$ (a) 0.017; (b) 0.021; (c) 0.025; (d) 0.029.

The relief of the surface is mainly formed by the sectors of polygonized growth hillocks and macrosteps. The morphologies of the (110) faces growing in 1:1 and 1:2 solutions look similar, nevertheless the edges between the adjacent sectors of growth hillocks are rounded and smooth in 1:1 solution (Figure 1b) and sharp in 1:2 solutions (Figure 2c).
The morphology of the (110) faces changes with supersaturation and duration of growth. Long exposure of the crystals at fixed supersaturation leads to a decrease in the total number of growth hillocks on the (110) surface because of their competition (Figure 2a–d). According to Equation (5), a hillock with a higher steepness $p$ gives a higher normal growth rate. The steps of a steep hillock overlap the growth layers from the less active (steep) one and, finally, occupy a larger area on the surface.

4.2. Normal Growth Rate

Normal growth rates of the hillocks on the (110) faces of KCNSH crystals were measured at different supersaturations in 1:1 and 1:2 solutions. The examples of the growth rate curves shown in Figure 3 correspond to the hillocks observed in 1:1 and 1:2 solutions. The points of every $R(\sigma)$ curve were obtained for an individual growth hillock. In 1:1 solutions, the growth rate was close to zero at low supersaturations $\sigma < 0.009$. The growth of the (110) face was unstable under these conditions. In 1:2 solutions with the excess of nickel ions, we could not detect any growth of the (110) face at $\sigma < 0.009−0.01$. When supersaturation exceeded a critical value $\sigma_d$, the growth rate nonlinearly increased with $\sigma$.

![Figure 3](image-url)

**Figure 3.** Normal growth rate of growth hillocks on the (110) face in 1:1 and 1:2 solutions as a function of supersaturation. The data for $R$ in 1:1 and 1:2 solutions are fitted by Equations (12) and (13), respectively (the values of fitting parameters are given in Section 4.5. Instrumental error of the $R$ measurements is within the size of the experimental points.

The narrow range of supersaturation $0 < \sigma < \sigma_d$ where the normal growth rate is suppressed (Figure 3) occurs for the following reasons. The first one is related to the possible influence of the traces of other chemical elements (metals) in raw materials used for the preparation of KCNSH solutions. These impurities are adsorbed on the (110) faces and prevent them from growth. A similar inhibition effect was described for the prismatic faces of KH$_2$PO$_4$ crystals grown in the solutions with trivalent metal ions [15,16]. Critical supersaturation $\sigma_d$ is about two times higher in the KCNSH solutions containing an excess of nickel ions. The origin of $\sigma_d$ in our KCNSH solutions may be connected with the purity of NiSO$_4$·7H$_2$O because a larger amount of this reagent is required to prepare 1:2 solutions. The second, more likely reason for the appearance of $\sigma_d$ is related to the reaction of isomorphic replacement that takes place in a multicomponent system when the crystal composition is not in equilibrium with the composition of the solution. Under
these conditions, if the supercooling of the solution is insufficiently high, local dissolution of the seed crystal and local growth of crystalline islands of a different composition on its surface occur simultaneously [7]. When \( \sigma < \sigma_d \), the growth-dissolution phenomena at the crystal interface are not related to spiral growth. The isomorphous replacement can be stopped by increasing the supersaturation above some critical value \( \sigma_d \). At \( \sigma > \sigma_d \), the growth rates of the (110) faces are approximately equal both in 1:1 and 1:2 solutions. The scattering of the \( R \) values for different seed crystals at high supersaturations is explained by the variation of the structure of screw dislocation sources.

### 4.3. Steepness of Growth Hillocks

The steepness \( p \) of the growth hillocks was calculated in the four sectors defined by the directions of movement of the adjacent steps of the hillock on the (110) face. Figure 4a,b present plots of the experimentally obtained steepness \( p_i \) for the sector \( i \) \((i = 1.4)\) of hillocks as a function of \( \sigma \) of the 1:1 and 1:2 solutions.

| Sector | Co:Ni = 1:1 | Co:Ni = 1:2 |
|--------|--------------|--------------|
| \( \sigma_{d,i} \) (−) | \( A_i \) (−) | \( B_i \) (−) | \( \sigma_{d,i} \) (−) | \( A_i \) (−) | \( B_i \) (−) |
| 1 | 0 ± 0.002 | 3.1 ± 2.3 | 249 ± 53 | 0 ± 0.002 | 18.2 ± 4 | 154 ± 98 |
| 2 | 0.004 ± 0.002 | 1.7 ± 0.6 | 115 ± 18 | 0.004 ± 0.002 | 11.0 ± 1.3 | 158 ± 41 |
| 3 | 0 ± 0.002 | 5.6 ± 1.1 | 160 ± 39 | 0 ± 0.002 | 23.8 ± 2.9 | 155 ± 72 |
| 4 | 0.005 ± 0.002 | 2.8 ± 0.5 | 19.3 ± 24 | 0.010 ± 0.002 | 1.8 ± 0.2 | 120 ± 17 |

We distinguish three different supersaturation regions in the \( p_i(\sigma) \) plots as follows:

1. Region \( 0 < \sigma < \sigma_d \). In this region growth is suppressed due to the reaction of isomorphous replacement at the crystal surface in complex KCNSH solutions, and possibly due to the inhibition effect of impurities.

2. Region \( \sigma_d < \sigma < \sigma' \), with \( \sigma' \) between 0.037 and 0.05. Here \( p_i \) exhibits nonmonotonous behavior, which is not described by Equation (6), and it may be explained by the morphological modification of the surface. At these supersaturations, the velocities of steps exhibit a nonlinear kinetics (Figure 5). We assume that elementary steps are pinned by traces of impurities, and only macrosteps grow at supersaturations near \( \sigma_d \). Then, with increasing supersaturation, macrosteps gradually decay and elementary steps become mobile, resulting in the local change of the surface steepness. A similar process was studied for growth of the (100) faces of KH2PO4 crystals in solutions with trivalent metal ion impurities [16,17]. We consider that the sharp increase in \( p_4 \) at \( \sigma = 0.017 \) in Figure 4b is related to the formation of macrosteps. In the work [18], it was found that a regular system of macrosteps was formed on the crystal surface in the supercooling interval of 2–4 °C. When supercooling went beyond the boundaries of this interval, these macrosteps disappeared. The measured point corresponds to the specified supercooling interval.

3. Region \( \sigma > \sigma' \). Here steepness \( p_i \) increases with increasing \( \sigma \) in accordance with Equation (6) given by the model for the layer-by-layer growth on a multiple dislocation source. Note that step kinetics becomes linear at \( \sigma > \sigma' \).

In contrast to \( p_1 \cdots p_3 \), the steepness \( p_4 \) begins to tend to the asymptotic values at smaller supersaturations \( \sigma \sim 0.04–0.06 \) in the solutions of both compositions due to lower step free energy \( \alpha_d \). From Equation (8) the steepness is inversely proportional to the step free energy. We expect that with an increase in supersaturation the steepness \( p_1 \cdots p_3 \) will tend to the same asymptotic value as for sector 4. It should be mentioned that the real curves \( p_i(\sigma) \) can reach an asymptotic value at quite high supersaturation, which is difficult to attain in experiments due to limited stability of supersaturated solutions to spontaneous nucleation.
Figure 4. Steepness of the sectors of growth hillocks on the (110) face as a function of supersaturation in solutions: (a,c) 1:1; and (b,d) 1:2, (morphology of the hillock is shown in Figure 2). Panels (c,d) present fitting curves plotted according to Expression (8) (the values of fitting parameters are given in Table 1). Panels (e,f) show plots $1/p_i$ against $1/(\sigma - \sigma_d)$ drawn for the $p_i(r)$ dependences in panels (c,d). Instrumental error of the $p_i$ measurements is within the size of the experimental points.
In the case of spiral dislocation growth, the interstep distance \( y_0 \) in the \( i \)-th sector of a hillock is determined by a critically-sized two-dimensional nucleus as \( y_0 = 19r_{cr,i} \), where \( r_{cr,i} \) depends on the step free energy \( \alpha_i \). The value of \( \alpha_i \) is related to the density of kinks at the step edge. Since \( y_0 \) for different sectors of a growth hillock on the (110) face is due to the anisotropy in \( \alpha \), the density of kinks in the elementary steps in the four sectors is also expected to be different. Consequently, the velocity of propagation of steps in different sectors is also different. When immobile impurities are adsorbed on the growing surface, the values of critical supersaturation \( \sigma_{d,i} \) for the steps moving in sector \( i \) should also be different because \( \sigma_{d,i} \) is determined by the average distance between the adsorbed impurity species. This mechanism is well-known as the Cabrera–Vermilyea mechanism. If the role of the reaction of isomorphous replacement is important in the process, we suppose that \( \sigma_{d,i} \) will be different for the four sectors of the hillock due to various values of \( \alpha_i \).

The parameters \( A_i, B_i \), and \( \sigma_{d,i} \) (Table 1) for the sector \( i \) of a polygonized hillock given by Equations (8) and (9) were found from the plots of \( 1/p_i \) against \( 1/(\sigma - \sigma_{d,i}) \), such that the difference between \( B_i \) for all sectors of the hillock was the least. Figure 4c,d show that the model curves fit the data. The experimental points for the supersaturations \( \sigma_d < \sigma < 0.037 - 0.05 \) were excluded from the calculation because nonmonotonous behavior of \( p_i \) in this range of supersaturations was not taken into account by the theoretical dependence (6). These points deviate from the approximation curves in Figure 4c,d.

Obviously, the normal growth of a polygonized dislocation hillock is possible, when the steps in all segments are mobile. Thus, \( \sigma_d \) obtained from \( R(\sigma) \) data coincides to error accuracy with the largest \( \sigma_{d,i} \) (Table 1).

Parameter \( B_i \) is not equal to zero for all slopes of the hillocks (Table 1). Therefore, the observed growth hillocks were formed by multiple dislocation sources in both 1:1 and 1:2 solutions. In the case of a multiple dislocation source with contour \( 2L \), the steepness \( p_i \) of all sectors of a hillock, according to Expressions (6) and (9), should tend to a constant value \( mh/2L = B^{-1} \) at large \( \sigma \). With an accuracy of approximation error, the values of \( B_i \) can be considered the same for sectors 1−4 of the hillock (Table 1) only in 1:2 solution. Taking the height of the elementary step on the (110) face \( h = 6.8 \times 10^{-10} \) m and \( B = 147 \) averaged for all sectors of the hillock in 1:2 solution (Table 1), we estimate using Equation (9) for \( B \) the perimeter of the multiple dislocation source \( 2L \sim (0.1 \pm 0.04) \) m \( \mu \). In 1:1 solutions, parameter \( B \) is significantly different for various sectors of the hillock. We suppose that this occurred due to possible variation of the structure of the powerful multiple dislocation source with increasing \( \sigma \). At higher supersaturations, the critical radius (7) becomes smaller, and a multiple source can divide into several dislocation sources. Therefore, perimeter \( 2L \) in Expression (8) is no longer constant and changes with \( \sigma \).
Parameters $A_i$ in Table 1 are smaller for the hillock sectors in 1:1 solution than those in 1:2 solution. According to Equation (9), this behavior may be explained by a lower step free energy $a_i$ or a larger Burgers vector $mh$ for the hillocks of crystals growing in 1:1 solution. Here the relative error for $A_i$ is large and it is difficult to establish a definite trend of its variation in different sectors. A possible interpretation of this behavior is that the perimeter $2L$ for the formation of hillocks on the (110) face of the crystals growing from the 1:1 solution is variable at different $\sigma$.

4.4. Step Velocities and Kinetic Coefficient of Step Displacement

The step velocities $v_i$ in sectors 1–4 of the growth hillocks on the (110) faces were determined from formula (4) on the basis of the data for normal growth rates $R$ and sector steepness $p_i$. For simplicity, we plotted in Figure 5a,b only some examples of the obtained experimental dependences $v_i(\sigma)$, which correspond to the sectors with the steepness $p_i$ shown in Figure 4a,b. The step movement was suppressed at $\sigma < \sigma_d$. In the interval of supersaturations $\sigma_d < \sigma < 0.035−0.05$, the step kinetics exhibited nonlinear behavior. Then, $v_i$ increased linearly with increasing supersaturation.

The kinetic coefficients $\beta_i$ were calculated from the slopes of the linear parts of the curves $v_i(\sigma)$ by using formula (10). We took $C_e = 2.34 \times 10^{26}$ m$^{-3}$, $\omega = 3.25 \times 10^{-28}$ m$^3$, and $C_p = 2.24 \times 10^{26}$ m$^{-3}$, $\omega = 3.24 \times 10^{-28}$ m$^3$ for 1:1 and 1:2 solutions, respectively. The saturation temperature was 41.3−43 °C. The data for the kinetic coefficients of the steps averaged over the independent values obtained in two-three experiments are presented in Table 2. Since it was not possible to perform measurements for $v_1$ and $v_2$ in 1:1 solution at supersaturations larger than 0.067 due to the spontaneous crystallization, we had to calculate the kinetic coefficients $\beta_1$ and $\beta_2$ in 1:1 solution under the assumption that the last experimental points for $v_1$ and $v_2$ at high $\sigma$ were roughly the beginning of the linear regions of the $v_1(\sigma)$ and $v_2(\sigma)$ curves because the slopes of these curves sharply decreased here. The extension of the linear part of $v_i(\sigma)$ curves intersects vertical axis at $v_i = 0$ when $\sigma = 0$. Thus, we plot the linear functions for the $v_1(\sigma)$ and $v_2(\sigma)$ curves using two points, and attempted to estimate the kinetic coefficients $\beta_1$ and $\beta_2$ in 1:1 solution.

### Table 2. Kinetic coefficients of steps on the sectors of growth hillocks on the (110) faces.

| Sector | Co:Ni = 1:1 | Co:Ni = 1:2 | $\Delta E_a$ (kJ/mol) |
|--------|-------------|-------------|-----------------------|
|        | $10^{-2} \beta_i$ (m/s) | $10^{-2} \beta_i$ (m/s) |                      |
| 1      | 0.11 ± 0.03 | 0.13 ± 0.03 | 0.49 ± 0.9            |
| 2      | 0.06 ± 0.02 | 0.11 ± 0.02 | 1.6 ± 1               |
| 3      | 0.09 ± 0.02 | 0.17 ± 0.03 | 1.7 ± 0.7             |
| 4      | 0.03 ± 0.01 | 0.05 ± 0.01 | 1.3 ± 1               |

The existence of isomorphous replacement results in the absence of the step propagation at supersaturations below $\sigma_d$. In 1:2 solutions, higher supersaturation $\sigma_d$ is required to suppress the process of isomorphous replacement. From formula (10), the velocity of the steps with atomically rough edges should depend linearly on supersaturation. The nonlinear step kinetics at supersaturations $\sigma_d < \sigma < 0.037−0.05$ (Figure 5) can be explained by the percolation of the steps through the impurity species adsorbed on the surface. Similar shapes of $v(\sigma)$ curves were previously observed in the experiments with the crystals of other compounds grown in the presence of impurities [15,19].

High anisotropy of the kinetic coefficients $\beta_i$ (Table 2) of the steps of the hillocks in different sectors on the (110) faces can be explained from consideration of anisotropy in the density of kinks in the steps and the activation energy $E_a$ for step motion in different sectors (Equation (11)). The kinetic coefficients for the growth of crystals in 1:2 solutions are 1.2−1.9 times higher than those in 1:1 solutions (Table 2). Since the dimensions of elementary cells and growth units of the KCNSH crystals grown in 1:1 and 1:2 solutions are practically the same, it may be concluded that the difference in the kinetic coefficients $\beta_{1,1}$ and $\beta_{1,2}$ for the steps in sector $i$ of the hillocks in 1:1 and 1:2 solutions, respectively, is
mainly due to the change in the activation energy \( \Delta E_a = (E_a)_{1:1} - (E_a)_{1:2} = k_B T \ln(\beta_{1:2}/\beta_{1:1}) \). The calculated values of \( \Delta E_a \) are listed in Table 2. Taking the average growth unit size perpendicular to the steps \( a_{av} = 9.1 \times 10^{-10} \) m the average difference between the activation energies for growth in 1:1 and 1:2 solutions from Equation (11) is \( \approx 1.2 \) kJ/mol. KCNSH has different solubility in 1:1 and 1:2 solutions. The pH of these solutions of the same concentration also slightly differs by a value of 0.1. Thus, we suppose that the excess of nickel modifies the inter-ion interactions in 1:2 solution.

4.5. Analysis of Normal Growth Rates

We analyzed the growth rate data in Figure 3 using the following relations for the normal growth rate derived by Sangwal [20] in the model for the systems containing a certain amount of impurities:

1. The relation for face growth from a multiple dislocation source:

   \[ R = \frac{\sigma(\sigma - \sigma_d)}{A' + B'\sigma} \quad (12) \]

   where

   \[ A' = \frac{19\alpha}{k_B T m h \beta c_e}, \quad B' = \frac{2L}{m h \beta \omega c_e}. \]

2. The power-law relation:

   \[ R = A_p \sigma^{n-1}(\sigma - \sigma_d), \quad (13) \]

   where the parameter \( A_p \) is related to the activation energy for growth, and the values of the exponent are between \( \frac{11}{12} \) and 2. Equation (13) holds when \( L > 0 \).

When \( A' >> B'\sigma \) and \( \sigma_d \to 0 \), the normal growth rate in Equation (12) tends to the classical BCF parabolic law \( R \to \sigma^2/A' \). This corresponds to the cases when supersaturation is very low or/and the perimeter \( 2L \) of the contour around a screw dislocation source is relatively small or equal to zero. At large supersaturations and \( L \), we have \( A' \ll B'\sigma \) and \( R \to (\sigma - \sigma_d)/B' \). The linear relation for \( K(\sigma) \) is typical for atomically rough surfaces. According to Equation (7), the inter-step distance \( y_0 = 19r_c \) in the sector of a growth hillock decreases with increasing \( \sigma \), and the crystal face with high kink density at step edges becomes atomically rough. It was found that in some cases the normal growth rate of crystal faces can be also approximated by the power-law relation (13) [21,22]. Note that the relation (13) becomes parabolic at \( n = 2 \) and linear at \( n = 1 \), respectively.

The values of the best-fit parameters of Equations (12) and (13) for the growth rate curves in Figure 3 are listed in Table 3. Here, \( r^2 \) is the \( r^2 \)-factor of approximation. Fitting of the growth rate curve for 1:1 solution by Equation (12) gave inappropriate values for \( \sigma_d \) and \( B' \). The calculated critical supersaturation \( \sigma_d = 0.014 \) was too large, whereas we could easily observe stable growth at supersaturations down to 0.009. The equality of \( B' \) to zero is possible when a screw dislocation source is single, that is \( L = 0 \). However, this contradicts the experimental data for the hillock steepness in Figure 4a,c, which confirm that the growth hillock is formed by a multiple dislocation source. Perhaps, the structure of a multiple dislocation source in 1:1 solution changed with increasing supersaturation, i.e., the perimeter \( 2L \) was not constant. The power-law relation (13) gives a better fit to the growth rate in 1:1 solution. As regards the growth rate for 1:2 solution, the functions (12) and (13) both provide a good fit to the experimental data. The exponent \( n \) is less than 2 in the relation (13), i.e., the growth has occurred on a multiple dislocation source. This conclusion is also confirmed by the data for the hillock steepness in 1:2 solution (Figure 4b,d).
Table 3. Values of constants of Equations (12) and (13).

| Equation | Co:Ni | $10^6 A'$ (s/m) | $10^6 B'$ (s/m) | $\sigma_d$ (−) | $r^2$     |
|----------|-------|-----------------|----------------|----------------|----------|
| (12)     | 1:1   | 0.15            | 0              | 0.014          | 0.99     |
|          | 1:2   | 0.13            | 0.7            | 0.013          | 60.999   |
| (13)     | Co:Ni | $10^{-6} A_p$ (m/s) | $n$ (−) | $\sigma_d$ (−) | $r^2$     |
| 1:1      | 18.8  | 2.44            | 0.0045         | 0.998          |
| 1:2      | 2.84  | 1.74            | 0.014          | 0.999          |

5. Conclusions

In this work, we have confirmed by the Michelson laser interferometry that the (110) faces of KCNSH crystals grow by the layer-by-layer mechanism on screw dislocations. The growth hillocks on the (110) faces are formed by multiple screw dislocation sources consisting of a group of dislocations. In 1:1 and 1:2 solutions, the growth of the (110) faces is impeded at supersaturations less than the critical value mainly because of the process of isomorphous replacement in a system with complex sulphates.

We have found the previously unknown values of the fundamental parameters determining crystal growth, such as the kinetic coefficients of steps on the hillocks of the (110) faces of KCNSH. The kinetic coefficients of steps in 1:2 solutions are larger than those in 1:1 solutions because of the different activation energy in the solution with nickel excess. The kinetic coefficient of steps is highly anisotropic.

From a practical point of view, the (110) faces of KCNSH crystals can be grown with the same rate from solutions with the cobalt to nickel ratios equal to 1:1 and 1:2. Successful growth of KCNSH crystals is possible at the supersaturations higher than the critical values determined in this work. We expect that the (110) face of KCNSH will have a higher concentration of solution inclusions during growth in 1:1 solutions because the growth hillocks are formed by screw dislocations with larger Burgers vectors and produce steps of larger heights. However, the difference in the morphology of the (110) faces in 1:1 and 1:2 solutions is insignificant, therefore, both solution compositions seem to be suitable for growing single KCNSH crystals.

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