THE INFLUENCE OF DISLOCATIONS ON THE EVAPORATION OF NaCl SINGLE CRYSTALS IN VACUUM

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In the paper an explanation of the evaporation process of NaCl single crystals in a high vacuum is presented. The evaporation takes place at the faults of the $a/2$ and a high steps mainly. The emergence points of dislocations with the surface appear as sources of the step system. The surface diffusion of ions plays an important role in the formation of the step systems.

ВЛИЯНИЕ ДИСЛОКАЦИЙ НА ИСПАРЕНИЕ МОНОКРИСТАЛЛОВ NaCl В ВАКУУМЕ

В работе дано объяснение процесса испарения монокристаллов NaCl, помещённых в условия высокого вакуума. Испарение имеет место главным образом при дефектах порядка $a/2$ и высокой ступенчатости. Случайные точки дислокаций на поверхности являются источниками ступенчатых систем. В образовании этих ступенчатых систем играет важную роль поверхностная диффузия ионов.

I. INTRODUCTION

Dislocations, as a part of real single crystals, play the substantial role at the evaporation process. In the NaCl single crystals there exist dislocations with Burgers vectors $a/2\langle110\rangle$ $\{110\}$ and $a/2\langle110\rangle$ $\{100\}$ as well as purely screw $a\langle100\rangle$ $\{100\}$ ones. These dislocations become at evaporation sources of the step systems formation on the surface, thus directly influencing the evaporation process.

There are many papers devoted to the evaporation process and, more generally, to the detachment of building elements and the crystal growth. These works may be divided into three groups: a) Papers dealing with binding forces on the surface, surface diffusion, composition of crystal leaving vapour, and the influence of various defects in the crystal lattice on the evaporation process. b) Experimental observation of the shape of pits at certain specific conditions (chemical, thermal, etc.), description and explanation of their origin. c) Theoretical explanation of the

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step motion mechanism (from the source to their annihilation), distances between steps, and multiple steps formation.

After a crystal is cleaved, there remain at its cleavage faces some macroscopically high steps as well as some microscopical ones, one or two lattice spacings high. When placing the crystal in an environment favourable to detachment, the building particles will depart from the crystal surface. It follows from paper by Berkovitz and Chupka [1] that during the NaCl evaporation the dominant reaction is

$$NaCl \text{ (solid)} \rightarrow (1-x)\, NaCl \text{ (vapour)} + \left(\frac{x}{2}\right) Na_2Cl_2 \text{ (vapour)}.$$

The evaporation of the NaCl crystals process in high vacuum at a temperature range 450 °C to 600 °C was described by Lester and Somorjai [2]. These authors measured the evaporation rate by a micro-weighing system and the vapour composition by a mass spectrograph. The following ionic peaks were found in the mass spectrum of NaCl vapour:

$$m/e = 23(Na^+);\quad 58,60(NaCl^+);\quad 81,83(Na_2Cl^+).$$

In the mentioned paper [1] also the presence of $Na_2Cl_2^+$ molecules was confirmed, however, in 1 % concentration only. From the measurements by Pitzer and Snelson [3] it follows that no remarkable concentration of Na_2Cl molecules occurs in the vapour but the NaCl and Na_2Cl_2 molecules predominate.

The evaporation of the crystal surface with steps is caused by several processes such as interchange of molecules between the surface and vapour, diffusion of molecules from a step to free surface and vice versa. When considering diffusion processes on the surface it is important to introduce the mean path which is defined by the Einstein relation $\bar{x}_i^2 = D_i\tau_i$, where D_i is the diffusion coefficient and τ_i is the mean lifetime of a molecule on the free surface before evaporation into vapour. For simple molecules one can write

$$\bar{x}_i = a \exp\{(W_i' - U_i)/2kT\},$$

where U_i denotes the activation energy for the diffusion between two neighbouring equilibrium locations on the surface, a is the distance between these locations, and W_i' is the activation energy for the evaporation of a molecule on the surface into vapour.

The experiments concerned with the investigation of the etch pits shape can be divided into two groups. It is the evaporation at normal pressure and in high vacuum $p < 10^{-2}$ Pa. The evaporation at normal pressure that obviously appears at higher temperatures was studied by Patel, Bahl, and Wagh [4]. The etch pits are of a spiral shape. The authors ascribe these spirals to screw dislocations. Further, there are concentric steps and pits similar to the Frank-Read sources. The steps are

several lattice spacings high and consists of several microsteps. The experimental works dealing with the evaporation in high vacuum in order to study the shape of the etch pits can be divided into two parts : evaporation at temperatures $T>500\,°C$ and that for $T<500\,°C$. Budke [5, 6] studied NaCl evaporation in the temperature range $450\,°C$ to $600\,°C$. He noticed that three types of etch pits appear: a) extremally shallow pits with a slope of 20 min off the (001) plane ; b) medium pits shape with slopes of 30 min at $454\,°C$ and of 50 min to $1°$ at $593\,°C$; c) square-shaped pits with slopes of up to $5°$.

The author declares that various pits shape cannot be explained by using the classical evaporation theory based on the surface diffusion controlled step motion mechanism, nor by the theory. of chemical etching, but they can be explained by using the assumption that the evaporation rate is determined by surface energy. The shape of pits is a function of surface energy anisotropy. The formation of pits is ascribed to surface contamination, thus denying their origin at dislocations (since the number of pits decreases with the evaporation duration).

Bethge [7] described evaporated surfaces of pure as well as doped NaCl single crystals prepared in high vacuum. By evaporation a step structure with the steps $a/2$ and a high is formed. The steps form concentric circular systems and spirals. The author ascribes spirals to screw dislocations and concentric circular systems to edge dislocations. However, they can be also formed around precipitates and at contaminated crystal surfaces.

The presence of step systems on the surface both during growth and depletion evoked the theoretical investigation of step kinetics. Cabrera [8] and Amelinckx et al. [9] studied the evolution of macroscopical steps as a consequence of the surface energy decrease, Mulins and Hirth [11] constructed a set of differential equations for step motion and discussed the case of step binding. Černov [10] studied macroscopic steps as shock waves of steps using the continual theory. Some authors claim that even some inhomogenities on the surface as well as some impurities can slow down the step motion so that the next steps will reach them and form a macroscopic step.

In all these papers it was assumed that atoms (ions) on the surface are detached from the steps or connected to the steps with unit probability. The steps are considered to be ideal sources or absorbers. Erlich and Hudda [12] showed that steps are neither ideal sources nor absorbers, thus yielding probabilities smaller than 1. On this basis Schwoebel and Sipsey [13] and Schwoebel [14] investigated dynamical processes of steps. Surek and Pound [15] investigated the step motion on the surface by computer simulation.

Cabrera and Levine [16] applied the spiral theory to the case of crystal evaporation and formation of etch pits around the emergence point of screw dislocations with surface. The deformation energy around dislocation represents the dominating factor determining evaporation.

The normal velocity v of a step element with a local curvature ϱ at a distance r from the emergence point is given as $v = v_\infty[1-(\varrho_c/\varrho)-(r_0\varrho_c/r^2)]$, where v_∞ is the velocity of the direct step far from a dislocation, $\varrho_c = \gamma\Omega/\Delta\mu_0$ is the radius of the critical nucleus for the 2–dimensional nucleation on the surface, γ is the surface energy, Ω the volume of a molecule in the crystal, $\Delta\mu_0$ is the difference between chemical potentials above and inside the crystal, $r_0 = Gb^2/(8\pi\gamma)$ describes the deformation energy around a dislocation, G is a shear modulus, and b is the Burgers vector of dislocation.

Generally, the spiral equation is given as $\Theta = f(r) - \omega t$.

Its solution for evaporation yields the existence of a cavity around the dislocation line with the radius

$$r' = 1/2|\varrho_c|\{1-[1-4(r_0/|\varrho_c|)]^{1/2}\}.$$

The radius of cavity during evaporation is constant and given by the minimum of free energy. For $|\varrho_c|<4r_0$ there exists no real solution and, therefore, no static spiral. This yields the existence of the critical value $\Delta\mu_{0c}$. At the critical value the nucleus cavity radius becomes $r'_c = 2r_0$ and the critical value is $|\Delta\mu_c| = 2\pi^2\gamma\Omega/Gb$. When $|\Delta\mu_0| = kT \ln(p_0/p)$, where p_0 is saturated vapour pressure and p is the real pressure of vapour above the crystal, one obtains

$$p_{0c}/p_0 = \exp\{-2\pi^2\gamma^2\Omega/kTGb^2\}.$$

It follows that the formation of a dislocation with a large Burgers vector requires low pre-saturation while the formation of a dislocation with a small Burgers vector requires high pre-saturation.

II. EXPERIMENT

The evaporation of NaCl single crystals in high vacuum as well as the preparation of replicas for electron microscopy observations were performed with a for-this--purpose-built apparatus a the Institute of Physics, Slovak Academy of Sciences. All supporting facilities were included, such as crystal temperature measurement, air pressure in recipient measuring, and sources for evaporation. A modified vacuum system VS-35 was employed. A rotary pump was selected and placed alongside in order to avoid vibration in the place of work. The vacuum was measured with thermal gauges in high- and low-vacuum ranges. The original Pening was replaced by an ionization gauge. A vacuum of 10^{-3} Pa was obtainable in the working part at a rim connected by a pipe with the vacuum system. In the upper rim there are also pipes for crystal heating, gold and carbon evaporation, and gauge connection. A schematical sketch of the heating furnace for crystal evaporation is given in Fig. 1. It is constructed in such a way that a low thermal capacity, a good heat radiation to the surrounding parts, and a sufficiently fast variation of the sample temperature

are provided. The temperature was measured by a PtRh-Pt thermocouple. The gold is evaporated from a wolfram boat. Spectral carbon was evaporated. All these facilities are located in the lower part of the place of work under heating, and are covered by an enclosure. The enclosure prevents condensation of vapours of the
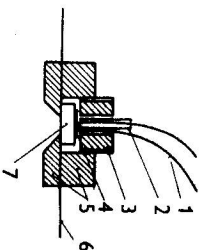
Fig. 1. Schematic sketch of the furnace for evaporation 1 — thermocouple, 2 — quartz ampoule, 3 — hollow screw, 4 — Pt-tin, 5 — Cu-blocks, 6 — wolfram heating strips, 7 — the sample.

material evaporated from the boat and of the carbon which could evaporate and damage the decorated evaporation structure. The mobile part of the enclosure can be moved without affecting the vacuum.

The process of preparation of the evaporated surfaces on the sample, the decoration of the sample, and preparation of replicas, run in the following way: From an NaCl single crystal mechanically and thermally pretreated some samples of the size $0.3 \times 0.3 \times y$ cm^3 were cleaved. Such samples was put on a heated Al block. At a temperature of about 200 °C a sample $0.3 \times 0.3 \times 0.1$ cm^3 was cleaved and put immediately into the evaporation furnace preheated to 100 °C. The sample was put into the furnace in such a way that the fresh cleavage face could evaporate. Then the place was evacuated. At a vacuum of about 10^{-2} Pa the crystal was heated up to the required temperature. The evaporation experiments took place at a temperature of 350—500 °C. The duration of heating in order to reach the working temperature was 30 min. In most cases the heating rate did not exceed 15 °C/min., because it was found that at higher rates some motion of the dislocations appears. The sample was heat-treated at the working temperature for a time related to the experimental requirement. Then it was cooled to a temperature of 200 °C. The cooling rate obeys the same rule as the heating one. At this temperature gold decoration was performed. The amount of gold depends on the arrangement of the experiment, e. g. at distance between boat and heated crystal being 10 cm it is 1.2×10^{-5} cm^3. Evaporation time was 1 min. Then the carbon was evaporated on the sample. The thickness of the carbon layer must be such as to provide a good transfer of electrons and a good contrast between the golden particles and carbon. A thickness of 50 to 100×10^{-8} cm is desirable. The carbon replica was taken from the sample in redistilled water and placed into a microscopic network. After drying it was observed by an electron microscope. The single
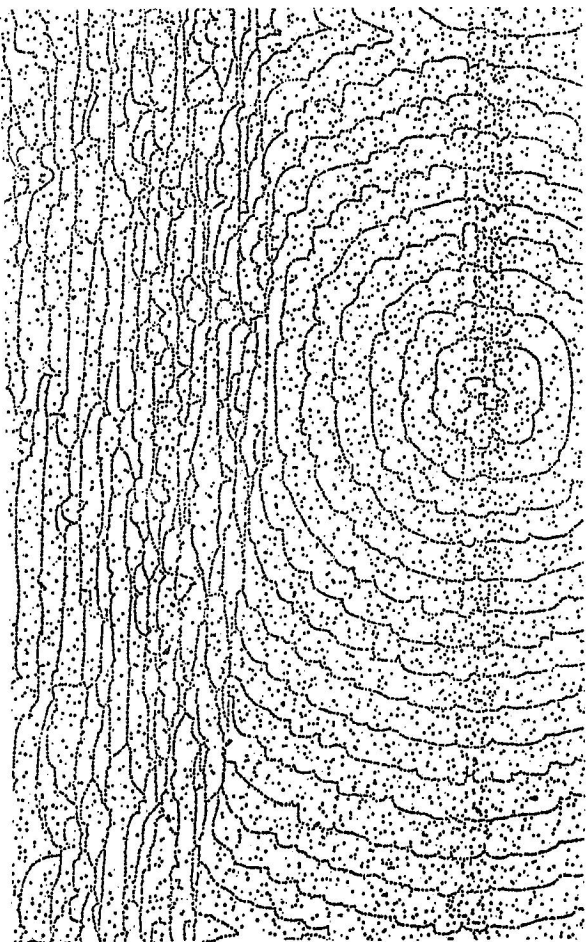
Fig. 2. Remainder of the parallel step system (Au decoration, C replica, magnification 40.000 x).

crystals used in our experiments were grown by using the Kyropolus and Stockbarger method from a specially purified raw material.

III. RESULTS AND DISCUSSION

III.1. Morphology of evaporated surface

Under the conditions described in the experimental part it has been observed that on the evaporated surface some steps with the heights $a/2$, a, and multiples, are formed. Here, a denotes the lattice constant. It follows that the evaporation has a step character as supposed in the theoretical works. The steps move from the source to the annihilator gradually, the distance between the steps being almost equal. There appears an exception: the multiple steps do not keep equal distance. There are formed various step systems according to the properties of the step source.

On the evaporated surface of a clean NaCl single crystal the following step systems have been observed: Parallel step systems (Fig. 2) that proceed from the higher cleaved steps or from crystal edges. These step systems occur mainly in the first stages of evaporation. Further, there are simple spirals (Fig. 3), double spirals (Fig. 4) and square-shaped spirals (Fig. 5). Besides, there exist some concentric
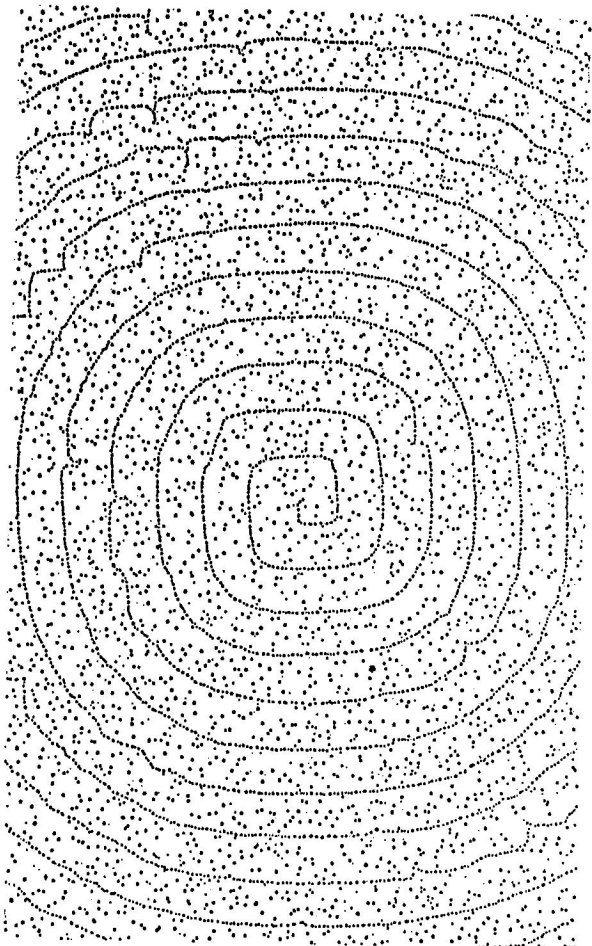
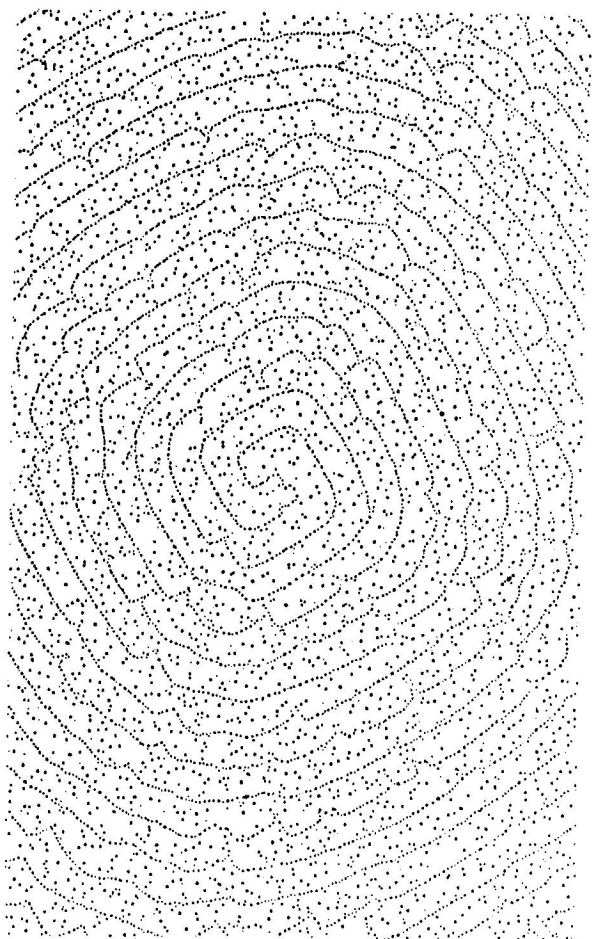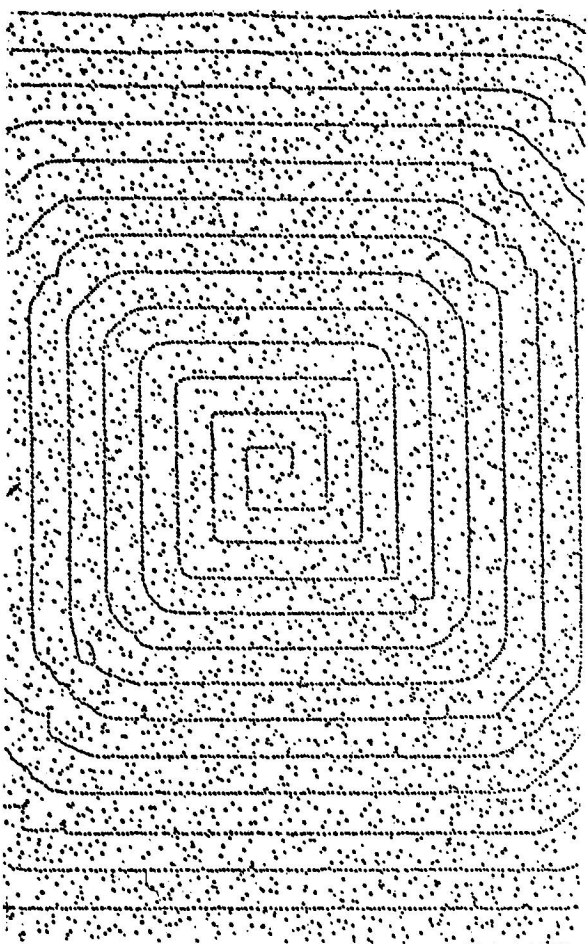Fig. 4. Double circular spiral (Au decoration, C replica, magnification 40.000 x).

Fig. 3 Simple circular spirals (Au decoration, C replica, magnification 40.000 x).
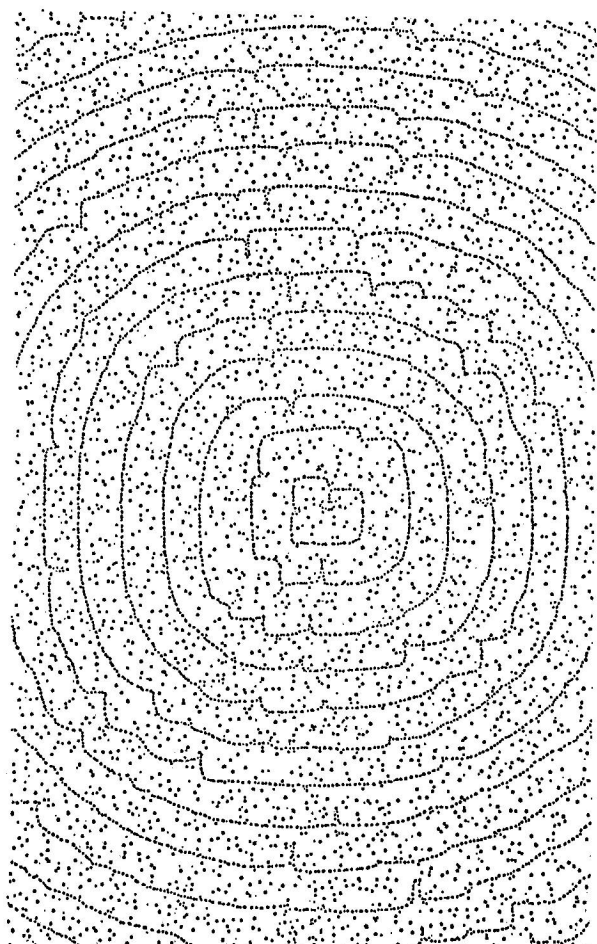
Fig. 6. Concentric circular step system (Au decoration, C replica, magnification 40.000 x).

Fig. 5. Square spiral (Au decoration, C replica, magnification 40.000 x).

step systems (Fig. 6) and square pits with a nonuniform step height (Fig. 7). In the vicinity of single and double spirals, as well as concentric systems, the steps exhibit the tendency to remain in the $\langle 100 \rangle$ direction. With the gradual increase of the distance from the source they become circular. In square spirals the steps remain in the $\langle 100 \rangle$ direction. However, at a sufficient distance from the source the spiral edges are rounded and parts of a step in the $\langle 110 \rangle$ direction are formed. The steps of square pits preserve approximately the $\langle 100 \rangle$ direction. However, they are mutually connected by intersteps.

III.2. The influence of pressure and temperature on the formation of step systems

The morphology of the evaporated surface of NaCl single crystals and the evaporation rate are strongly dependent on air pressure above the crystal and the temperature at which evaporation proceeds. The results of our evaporation experiments at temperatures ranging from 350 °C to 500 °C and various pressures show that no observable evaporation occurs at pressure over 10^{-1} Pa. However, when evaporation occurs, the step systems characteristic for the given temperature are preserved, e. g. at 500 °C (see Table 1).

Fig. 7. Square pit (Au decoration, C replica, magnification 40.000 x).

Table 1

Pressure influence on evaporation process.

p [Pa]	1.33×10^{-3}	1.33×10^{-2}	1.33×10^{-1}	1.013×10^{5}
character of picture	square pits	square pits	square pits	none or weakly evaporated

The temperature of the sample has a decisive influence on the appearance of the selected step systems. The results of these observations at an air pressure 10^{-3} Pa above the crystal in the temperature range from 400 °C to 500 °C are summarized in Table 2. Consequently, the air pressure above the crystal and its temperature are the factors that determine the evaporation rate and the appearance of step systems, i. e. they select the possible action of each step source.

The decision whether on the crystal surface growth or evaporation will occur is given by the difference between the chemical potentials of the particles in the atmosphere surrounding the crystal and those on the crystal surface. In the simplest case of crystal evaporation from a vapour one can write $|\Delta\mu_0| = kT \ln (p_0/p)$. At an equilibrium between solid material and vapour in a one-compound system the dependence of the saturated vapour pressure (sublimation pressure) on temperature can be expressed by the Clausius-Clapeyron equation $d(\ln p)/dT = \Delta H_{subl}/RT^2$. ΔH_{subl} is the molar sublimation heat given according to the Hess law as $\Delta H_{subl} = \Delta H_{melt.} + \Delta H_{evap.}$. The mean activation energy for the evaporation of NaCl crystals in vacuum is 55 kcal/mol [2]. This value also determines the pressure of the saturated vapour above the single crystal. Fig. 8 shows the course of the saturated vapour above the NaCl pressure. The values of saturated vapour pressures above a melt are taken from [17]. The pressure of the vapour above the crystal was calculated using the above written equations. From the dependence of the saturated vapour pressure above the crystal one can see that at the temperature range 350 °C to 500 °C the pressure values are between 10^{-6} to 3×10^{-3} Pa. From the difference between the chemical potentials at evaporation it follows that the

Table 2

Occurrence of step systems as a function of temperature.
+ normal occurrence, − none occurrence

Temperature [K]	673	698	723	758	773
single, double, and square spirals concentric circles	+	+	seldom	very seldom	very
square pits	−	+	+	very seldom	+

real pressure of the vapour must be always smaller than the saturated one. At vacuum 10^{-3} Pa the mean free path of molecules is of the order 100 cm. Consequently, most particles leaving the crystal move to the cooler parts of the working room where they condense and therefore the state with the saturated pressure above the crystal cannot occur. Fig. 8 shows that evaporation at lower temperatures requires also lower pressures and, vice versa, at higher temperatures higher pressures in the recipient are allowable.
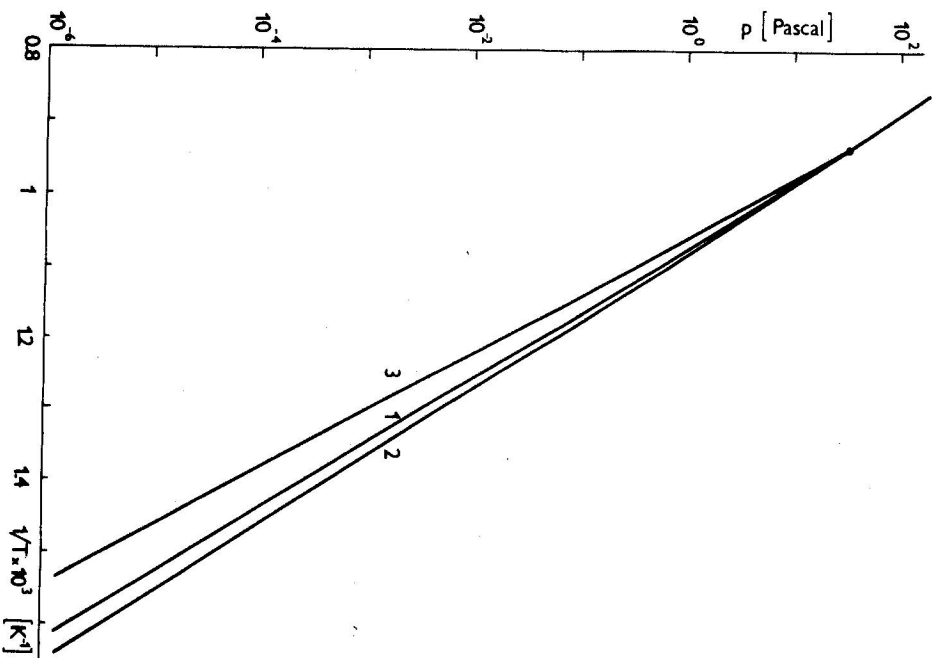

Fig. 8. The course of saturated vapour pressure above the melt and crystal (curve 1 — mean pressure, 2 — M molecules, 3 — D molecules).

III.3. Molecular phenomena on the surface

The step motion on the surface during evaporation is caused by the detachment of the building particles from place where the binding energy is sufficiently low so that ions, ionic groups can be evaporated (due to the added kinetic energy) with an experimentally observable rate. At evaporation on a real surface there occur steps of various heights, step faults, and ions diffusing on the surface (as well as groups of
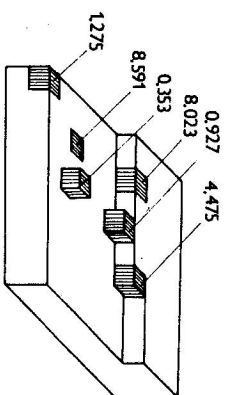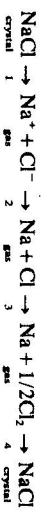

Fig. 9. Binding energies of ions on the surface.

ions detached from the steps.) A summary of the binding energies at various locations on the surface is shown in Fig. 9. Since at evaporation the main part of the vapour consists of monomeric NaCl molecules and dimeric Na_2Cl_2 molecules, we calculate (Fig. 10) the binding energies of couples and four ions in various locations on the steps $a/2$ and a high. The number denotes the binding energy and surface energy of a couple of four ions in eV. The surface energy was calculated using the Schuttleworth approach [18] and in NaCl it possesses the value of 9.687×10^{13} eV-$/cm^2$ of the surface.

Since in the crystal there exist Na and Cl atoms in the form of Na^+ and Cl^- ions and in vapour as molecules, during evaporation some reactions must appear well observable in the so-called Born-Haber cycle [19]. In the cycle the following chain of reactions appears:

$$\underset{\text{crystal}}{NaCl} \underset{1}{\rightarrow} \underset{\text{gas}}{Na^+ + Cl^-} \underset{2}{\rightarrow} \underset{\text{gas}}{Na + Cl} \underset{3}{\rightarrow} \underset{\text{gas}}{Na + 1/2Cl_2} \underset{4}{\rightarrow} \underset{\text{crystal}}{NaCl}.$$

Since during evaporation the reactions 1, 2, and 3 occur, one has to consider their energetic balance. In reaction 1 there are binding energies of ions and groups of ions in several places on the crystal surface. The heat of reaction 2 is given by the ionization energy of Na and the electron affinity of Cl. Since the ionization energy of Na is 119 kcal/mol and the electron affinity of Cl is 90 kcal/mol, the resulting reaction heat will be -29 kcal/mol. In 3 the heat of the $Cl \rightarrow (1/2Cl_2$ reaction equals one half of the Cl_2 dissociation energy. The dissociation energy of Cl_2 is 58 kcal/mol. The above results yield for the activation energy of evaporation of

a monomer molecule $E_M = E_{VM} - 2.5139$ [eV] and a dimer molecule $E_D = E_{VD} - 5.0278$ [eV]. E_{VM} and E_{VD} are the mean values of the binding energies of a couple and four ions on the surface, respectively.
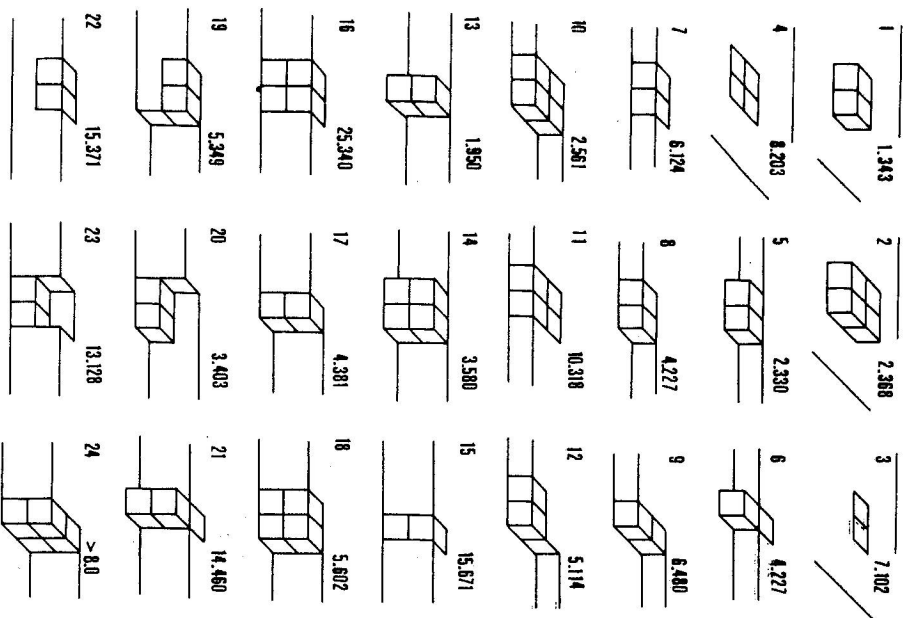

Fig. 10. Binding energies of a couple and four ions on the surface.

The mean activation energy of evaporation of a monomer molecule is 2.28 eV. A comparison of this value with the binding energies of the ions on the surface (Fig. 10) leads to the conclusion that the evaporation of monomeric molecules takes

place preferably on the steps a/2 high and their faults at position 8, 17. The faults are formed on a smooth step by evaporating a couple of ions from position 7. The resulting activation energy is then given as a certain mean value of the binding energies between the positions 7 and 5 (or 15) and 21 and 13, respectively.

According to Lester and Somorjai [2] in NaCl vapour there are about 10 % Na_2Cl_2 molecules with the activation energy of 2.67 eV. The molecules of this type will most probably evaporate from the position 14, 18, and 21. Of course, the activation energy is again given as a certain mean value.

As follows from the values of the activation energies of the ions at the faults of the steps a/2 and a high, the rate of a couple hopping at the faults a/2 high will be greater than that at the steps of height a. Consequently, the speed of a step a/2 high will be greater. Of course, the speed of the step motion influences the rate of formation of new faults in a straight step. However, this depends on the location of the step formation, the shape of the formed step (spiral or square), and surface diffusion. Since on the evaporated surface some square spirals have been observed, it follows that the ratio of speeds of the steps a/2 and a high must be less than 2, otherwise all the steps a high would be annihilated by the a/2 high steps.

In the square spirals the steps a high preserve their height during evaporation. The reason for this is provided again by the binding energies. Looking at the activation energy of evaporation of an ionic couple from the position 19 it is clear that the position 20 is formed where the couple is bound more weakly and thus annihilates fast.

There appears probably no splitting at the position 22 since the evaporation of a couple requires a rather high activation energy.

The surface diffusion of the building particles plays an important role in the formation and motion of the steps on the surface. Prior to a quantitative evaluation of this process one should determine whether reactions 2 and 3 of the Born-Haber cycle take place on the free surface or just above it, i.e. whether there are neutral molecules or groups of ions on the surface, respectively. Since even on the crystal surface the atoms are placed in the field of other ions we assume that there will be ions there, and the reactions take place at a certain distance above the surface. There are various calculations of the diffusion activation energy of molecules on the surface by various authors. They all agree that its value is small compared to the desorption energy. Supposing, however, that the atoms on the surface are in the form of ions, the activation energy of the desorption is given by Fig. 10, positions 1, 2. By diffusion the ions must go through a position where the binding energy equals zero. Thus the activation energies of desorption and diffusion are equal. In such a case there would be no diffusion on the surface. However, taking into account the surface energy one finds out that the difference $E_{des} - E_{diff}$ for a couple of ions is 0.635 eV and for four ions 0.954 eV. The mean paths of the couples and the four ions on the surface are given in Table 3.

Table 3

Mean path of couples X_{xm} and four ions X_{xd} on the surface (d – mean distance between steps, d, X_{xm} and X_{xd} are in units $a/2$).

T [K]	X_{xm} (Na+ + Cl-)	X_{xd} (2Na+ + 2Cl-)	d	X_{xm}/d	X_{xd}/d
638	456.9	8323	1770	0.258	4.703
683	311.5	4683	873	0.357	5.364
703	267.7	3730	660	0.406	5.652
723	232.0	3008	547	0.424	5.449
773	166.3	1824	350	0.475	5.210
823	124.5	1181	250	0.498	4.724

III.4. The formation of step systems around emergence points of dislocations with a surface

A screw dislocation on the crystal surface forms a step of the height of one Burgers vector pinned near the emergence point of dislocation on the surface. Under conditions suitable for evaporation the step evaporates at a sufficient distance from the dislocation $r > r_{cr}$ with a constant rate v_∞. In the range $r < r_{cr}$, due to pinning the step evaporates with some mean angular rate ω, thus forming a spiral. Using this simplification, the distance between steps can be written as $h = 2\pi r_{cr} = 2\pi v_\infty/\omega$.

The shape of the spiral is determined by the evaporation course in the closest vicinity of the dislocation line, i.e. at a distance smaller than r_{cr}. The results of Cabrera and Levine [16] yield the possible formation of a cavity in the dislocation core at evaporation. In NaCl the radius of such a cavity at the $a/2$ $\langle 110 \rangle$ $\{110\}$ dislocation would be $r' < 4 \times 10^{-8}$ cm. A real solution of a spiral exists only at $\varrho_c < 8 \times 10^{-8}$ cm. Thus, a critical situation occurs at $\varrho_c = 4r_0 = 8 \times 10^{-8}$ cm. Since ϱ_c is a function of pressure, this also yields a critical pressure value p_c. The existence of a spiral is then possible in pressure range p_c to p_0. At 450 °C it is $p_c = 0.4 p_0$. The existence of a cavity around the dislocation line has not been proved yet experimentally. Without taking into account its existence, we shall next discuss the evaporation process in the vicinity of the dislocation line of a screw dislocation $a/2 \langle 110 \rangle \{110\}$. The binding energies of ions at a pinned step gradually increase from the position 7 to the position 4. Realizing that the deformation energy of the dislocation core is here 0.15 eV per atomic plane, it is clear that this value cannot cause preferably an evaporation of ions from the core compared to the evaporation of the other ions at the step. The direction of the trailing faults will be toward the dislocation core and not oppositely. The course of the spiral formation will be such as that to be seen in Fig. 11. The distance between the steps will be given by the surface diffusion of the ions-free path. The steps close

to the dislocation line preserve the $\langle 100 \rangle$ direction. By a gradual increase of the distance from the emergence point of dislocation they become rounded. This effect is caused also by the surface diffusion of ions which diffuse into corners and thus slow down evaporation in these places until the step is rounded. The binding energy of ions plays of course an important role in the step corner.
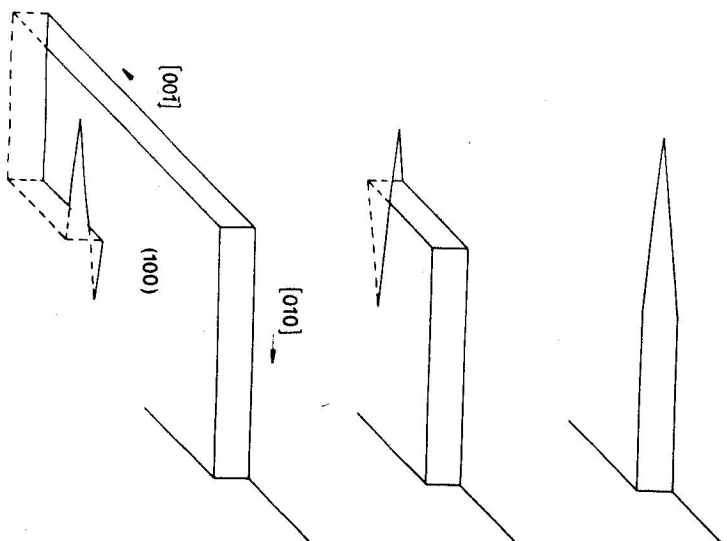

Fig. 11. Formation of a single spiral in the vicinity of the emergence point.

The screw dislocation $a \langle 100 \rangle \{100\}$ forms on the surface either a step of the height a pinned, similarly as before, in the vicinity of the dislocation line, or the two steps $a/2$ high pinned in one point: the emergence point of the dislocation line. By evaporating a square or double spirals are formed at these steps. The reason for the formation of two types of step systems around the emergence point is as follows: when cleaving the crystal, steps of various heights are formed on the surface. Among them there are also steps formed by screw dislocations $a \langle 100 \rangle \{100\}$. At the initial stage of evaporation some smoothing of the surface appears, i.e. these steps are eliminated. The elimination proceeds from the steps and edges of the crystal. At the last stage of surface smoothing two following cases may appear

(Fig.12): In the case a) a step of height a is formed. In the case b) two steps $a/2$ high are formed.

By evaporating the step a high a square spiral is formed. Since at this dislocation a high core energy is assumed, there is a strong electrostatic disturbance and the dislocation is immovable. Therefore, the faults will appear at the emergence point
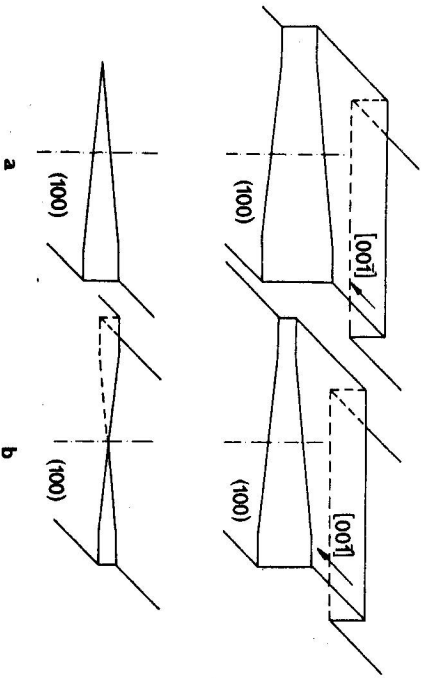

Fig. 12. Formation of steps for square and double spirals.

of the dislocation line (Fig. 13). The further course of the evaporation is similar to the single spiral one. However, the step motion is slower. The steps preserve the directions $\langle 100 \rangle$ ($\langle 110 \rangle$) and do not cleave. The distances between the steps are rather smaller.

At the steps $a/2$ high a double circular spiral is formed by evaporation. The evaporation process in the vicinity of a dislocation line is illustrated in Fig. 14. Here also the nucleus for the evaporation of faults appear at the emergence points. The steps do not remain at the same pinning but they change each half turn. Similarly as in a single spiral, the steps gradually become rounded. The distance between the steps is different from that of a single spiral. Since the motion in the vicinity of the line dislocation is controlled by surface diffusion, the distance between the steps of

a single can be written as $d_1 \sim n_d/b_1$, $n_d \sim n_d/(a/2\sqrt{2})$. Considering one step of the double spiral it is $d_2 \sim 2n_d/b_2$, $b_2 \sim 2n_d/a$, where n_d denotes the diffusion of ions from a step to the emergence point, b_1 and b_2 are the Burgers vectors. A comparison yields that the distance between the steps of a double spiral is $\sqrt{2}$ times greater. This fact agrees with the experimental data. When considering both steps, a distance $\sqrt{2}/2$ times smaller is obtained.

The concentric step systems are formed around the emergence points of the edge dislocations $a/2 \langle 110 \rangle \{110\}$ and $a/2 \langle 110 \rangle \{100\}$ with the surface. This place is strongly disturbed. The core energies of these dislocations are 0.39 and 1.5 eV per atomic plane, respectively. The ions in these places are bound more weakly and,
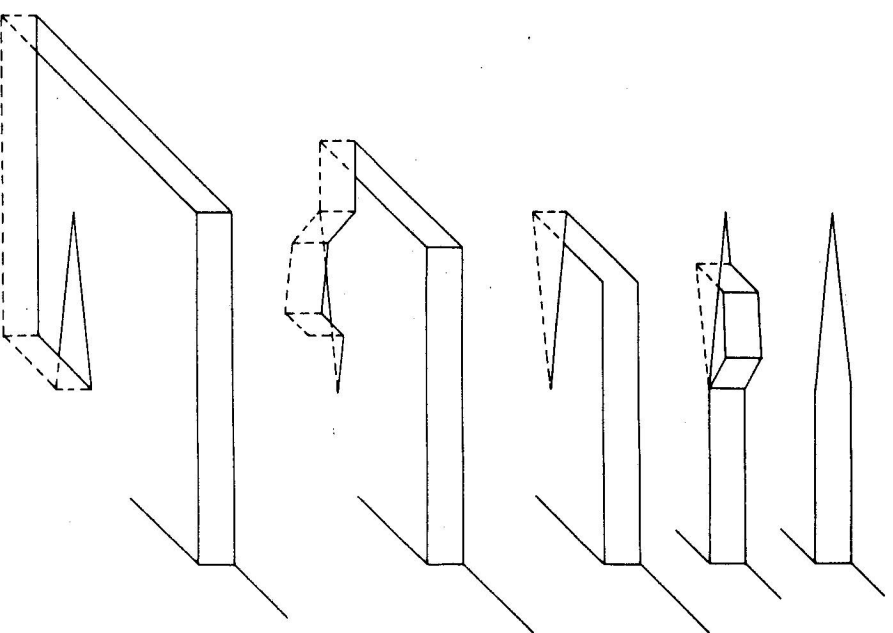
therefore, there are locations favouring the formation of nucleus. In the vicinity of the dislocation line the steps preserve the $\langle 100 \rangle$ direction, with an increasing distance they are gradually rounded. The height of the steps is $a/2$. Since the evaporation of particles is of a statistical nature one may expect no equidistance between the steps. However, the opposite is true. The steps in the core are formed at almost equal time intervals. This fact can be explained on the basis of the surface

Fig. 13. Shaping of a square spiral.

diffusion. Let us consider the crystal surface around the emergence point of the dislocation with the surface. Let n_i denote the number of particles evaporating from this place per time unit, n_p is the number of particles impinging from the vapour on the crystal and diffusing at the emergence point, n_d is the number of
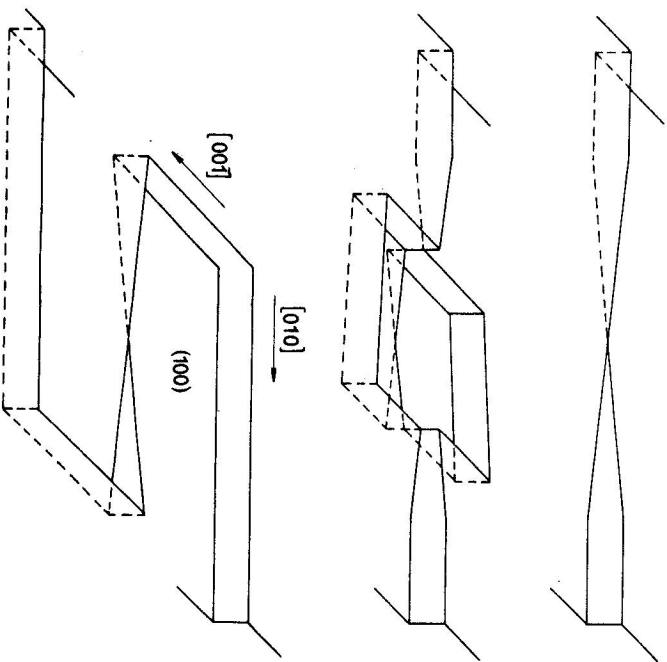

Fig. 14. Formation of a double circular spiral.

particles obtained by diffusion from the first step to the emergence point. Then, if $n_i > n_p + n_d$, a new step is formed. If $n_i < n_p + n_d$, no new step appears.

It is clear that evaporation can proceed only if $n_i < n_j$. The number of particles with a path greater than the mean path decreases until the relation $n_i > n_p + n_d$ is fulfilled. These two conditions define the distance between steps and its regularity. Since both variables are functions of temperature, the distance between the steps will also vary with temperature.

The occurrence of square etch pits is observed at temperatures over 470 °C. Since at these pits the height of the steps is higher than a it follows that the particles in the step sources possess weak bonds. These conditions occur at the emergence points of the edge dislocations $a/2 \langle 110 \rangle \{100\}$. These conditions occur at the emergence points of the edge dislocations $a/2 \langle 110 \rangle \{100\}$. The core energy of these dislocations is up to 1.5 eV per atomic plane. Contrary to the $a/2 \langle 110 \rangle \{110\}$

dislocations, the Burgers vector has a non-zero component perpendicular to the surface.

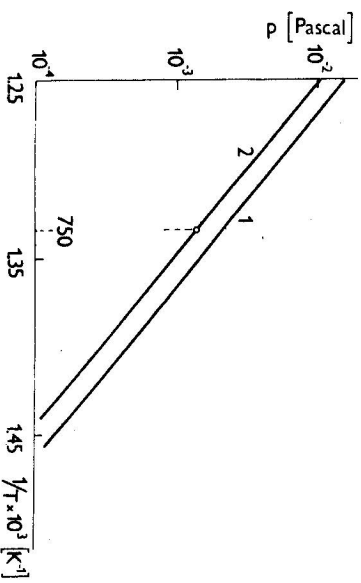We have observed that steps higher than $a/2$ move slower. The distances between the steps are smaller because the steps affect the particles moving on the surface by means of some gravitational field, thus favouring motion along the steps. This effect increases with an increasing height. At a sufficiently high temperature when both n_p and n_d are small, the step formation has a statistical character.

Another possible source of the square pits formation is presented by the screw dislocations $a \langle 100 \rangle \{100\}$. The core energy of these dislocations was not calculated yet, but according to the shape of the defect in the core it will be large. According to Cambera and Levine the spirals can exist only in the pressure range p_c to p_0. At pressures $p < p_c$ some pits in the dislocation core are formed. In Fig. 15 the temperature dependences of the saturated vapour pressure and the critical pressure of monomeric molecules is given. Until the pressure of saturated vapour is lower than the air pressure in the precipient, the real vapour pressure differs little from the saturated one. In this case there is formed a spiral around the emergence point of the screw dislocations. If the pressures of vapour and air become equal, so that the NaCl vapour can be carried into the surrounding atmosphere and condensate at the cooler places of the chamber, the vapour pressure does not increase any more and the course of evaporation is vigorous (an equivalent of the boiling point in liquids). With a further increase of temperature a critical undersaturation appears and square pits are formed at dislocations. During our experiments the pressure in the precipient was 10^{-3} Pa. Fig. 15 shows that the critical undersaturation is at temperature 477 °C. The change in the concentration of the square pits with time is caused by the fact that some sources of the pits formation are more effective and the created pits consequently absorb the others.

Fig. 15. The course of saturated (curve 1) and critical (curve 2) pressure of vapours above the crystal.

III.5. The influence of dislocations on the evaporation rate

As written at the beginning, dislocations are sources of step systems as a consequence of the evaporation process. Lester and Somorjai [2] found that by changing the density of dislocations from $10^6/cm^2$ to $10^7/cm^2$ the evaporation rate increases by a factor of 2. The evaporation activation energy increases as well. We have done a detailed study of this effect which shows that the increase of the rate is not caused by the changes of distance between the steps (if remains constant, the density of steps does not change). Then, a small variation in the speed of the step motion may cause changes in the evaporation rate. In the vicinity of a dislocation due to a greater deformation of the lattice there are formed more faults than at the step, so that both the mean activation energy and the evaporation rate increase. Since the distance between the steps is kept by the surface diffusion, as a consequence the step just annihilated will control the motion of the others in the system. In this way the density of dislocations can influence the evaporation rate. On the basis of observation and measurements the following empirical relation for the evaporation rate has been proposed:

$$I = A\sigma \exp\left[-\frac{4.458 + 10^{-4} \cdot \sigma^{1/2}}{2kT}\right],$$

where A is a constant and σ is the density of dislocations. The activation energy 2.229 eV corresponds to the mean activation energy of a crystal without dislocations.

On the basis of interactions of impurities built into the crystal, at the thermal treatment in the core of edge dislocations nucleation of a mixed or a foreign phase appears, followed by precipitation. The precipitates influence the deformation energy around the core and dislocation and also the evaporation process. Around these precipitates either concentric circular systems or square pits are formed.

IV. CONCLUSION

The evaporation of NaCl single crystals takes place in steps. During evaporation step systems of spirals, double spirals, square spirals, concentric circular step systems, and square pits are formed. The occurrence of selected step systems is a function of crystal temperature. The spirals are formed around emergence points of screw dislocations with the surface, the concentric circular steps are formed around the emergence point of edge dislocations or around precipitated particles, respectively. The square pits appear either around the emergence points of the edge dislocations $a/2 \langle 110 \rangle \{100\}$ or the screw dislocations $a \langle 100 \rangle \{100\}$. Monomer molecules at faults $a/2 \langle 110 \rangle \{100\}$ and a high possess a priority position at

evaporation. The regularity of the steps and the distances between them is controlled by the surface diffusion of the particles.

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