CRYSTAL FORMATION AT THE SURFACE OF THE SUBLIMING LAYER IN THE VACUUM SUBLIMATION OF ICE

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It has been established that the temperature or corresponding pressure gradient created by radiant heating is the motive force of the sublimation process. A reduction of temperature at the phase interface causes the crystallization (desublimation) of migrating vapor molecules on the surface. The branchlike growth of the crystals is accompanied by the eventual separation and entrainment of the individual branches, which characterizes the molar–molecular sublimation process.

The investigation of the mechanism of vacuum sublimation of ice began a relatively long time ago. However, comparatively little has been published on this question [1-4].

We have made a study of the physics of the sublimation process in order to establish its mechanism, determine the heat and mass transfer potentials, and establish the nature of the accompanying effects.

For this purpose we designed and built a special experimental high-vacuum apparatus with an adiabatic envelope, which enabled us to control the experimental conditions precisely, make visual and photographic observations of the surface of the ice, and accurately fix all the necessary parameters (temperatures and pressures) of the surrounding medium and the ice.

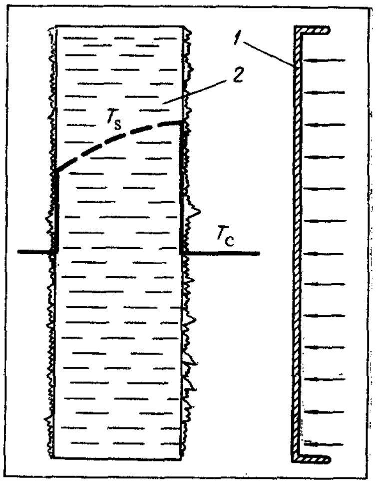

Fig. 1. Temperature variation in the vacuum sublimation of ice: 1) "dark" screen radiator; 2) ice polycrystal.

A special patented automatic vacuum balance was designed for measuring the weight loss of the ice specimen or determining the sublimation rate.

We will examine certain results of an investigation of the process of sublimation of ice to which heat is supplied by thermal radiation.

Temperature and Pressure Gradients. Many investigators have established that ice is an almost absolutely black body ($\varepsilon \sim 0.95$) and in the presence of infrared irradiation is characterized by surface absorption of the heat rays throughout the sublimation process, while the rise in temperature throughout the specimen is the result of phonon heat conduction. A certain fall in temperature over the thickness of the irradiated specimen is attributable to damping of the thermal waves.

We were able to achieve reliable contact and accurate positioning of the thermocouples in the investigated specimen.

The measurements revealed the following pattern of temperature distribution within and at the surface of the ice during sublimation (Fig. 1). The sharp temperature jump at the phase interface (ice surface–ambient medium of the vacuum chamber) is attributable to surface absorption of the infrared rays and marks the region in which the temperature falls abruptly to the saturation (near crystallization)

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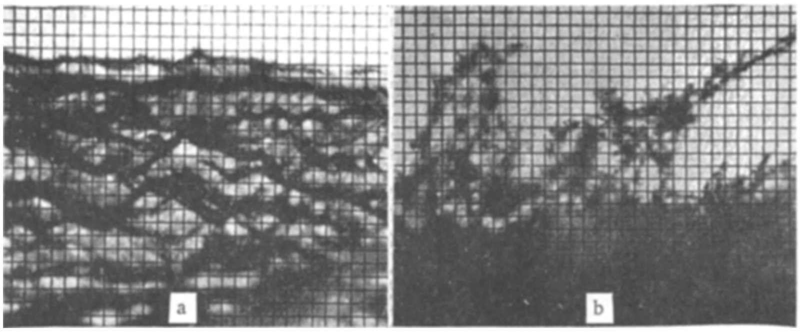

Fig. 2. Crystal growth during the vacuum sublimation of ice (p = 66.6 N/m^2; q = 0.57 W/m^2: a) surface front; b) surface of ice with slip bundles. Side of squares equal to 100 μ.

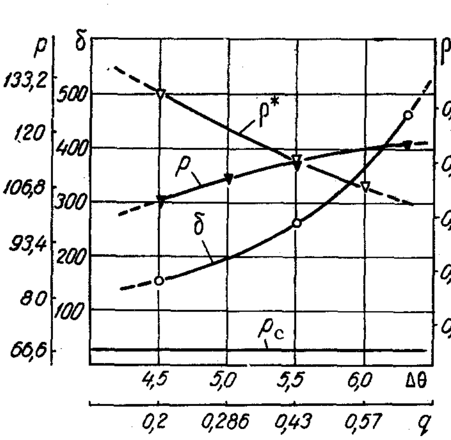

Fig. 3. Effect of heat load q, W/cm^2, on crystal growth.

temperature. The ice sublimes both from the irradiated surface and less intensively from all the other sides of the specimen.

The presence of a temperature gradient also determines the formation of an additional internal anisotropy in the ice crystal. This is why the temperature gradient creates the conditions for a certain volume sublimation process. Depending on the sublimation conditions this volume may vary within wide limits, from zero, when sublimation takes place only at the surface (at atmospheric pressure), to the entire volume of the specimen, when the material is thin or the sublimation process very active. The temperature gradient corresponds to a proportional pressure gradient, which causes the migration of vapor molecules from the interior to the surface. As our subsequent investigations showed, the temperature or pressure gradient (relative to the pressure in the vacuum chamber) is the motive force of the sublimation process even in the presence of a conductive heat supply.

Crystal Growth at Surface of Subliming Layer. By means of a special optical system we filmed the sublimation surface at a magnification of 150 and measured the rate of displacement of the boundary of the subliming layer of ice. This investigation showed that in the presence of radiant heating crystals are formed at the surface of the ice, i. e, "desublimation" is observed.

The characteristics of the vacuum sublimation process are explained by the crystal structure of the ice. Ice crystals belong to the hexagonal system [5, 6]. X-ray analysis of the structure of ice has established that each molecule of water is surrounded by only four nearest molecules 0.76 Å away and located at the vertices of a regular tetrahedron. The structure of ice is determined by the structure of water. Owing to the low coordination number of the water molecules in the ice, namely four, its structure possesses large voids. Ice is a crystal well capable of plastic deformation, which is explained by the layered crystal structure of the water molecules, each molecule being attached by three bonds to molecules belonging to the same layer and by only one bond to the molecules of another layer. Accordingly, sliding along such a layer is relatively easily produced by the action of forces of deformation (for example, pressure gradients, temperature gradients, etc.).

The density and direction of slip form a so-called glide or shear system. Under the action of deformation forces the ice crystal is split into regions between these planes, which are called slip "bundles" (Fig. 2a). These bundles are displaced as a unit whole. As the experiments show, in an ice polycrystal placed in a vacuum under the action of a radiant flux a temperature gradient varying over the thickness (Fig. 1) or a correspondingly pressure gradient is established near the surface or over the entire volume in the course of a certain time. Under the influence of this gradient the initially homogeneous medium (ice) becomes thermodynamically unstable and the polycrystal is plastically deformed, i. e., some molecular planes of the crystal lattice slip over other parallel planes. The glide system of these "bundles" is clearly visible in Fig. 2a.

The slip planes of the crystal bundles are the most convenient regions of vapor migration from the polycrystal and its surface.

It is assumed that the banded structure of the ice surface produced by plastic flow represents the accumulation of various imperfections and defects of the lattice structure. Each imperfection causes a local increase in the free energy of the solid and increases the probability of transformations near these imperfections. Only the formation of a nucleus (crystal) of a new phase at the surface of the ice can reduce the growing free energy.

The sharp expansion of the vapor migrating from the interior of the polycrystal at the surface also increases the probability of a considerable increase in defect concentration at the phase (ice–vapor) interface. The surface itself is bordered by a region of sharp supercooling relative to the temperature of the migrating vapor, which creates all the conditions necessary for crystal growth at the crystallization centers formed. The question of the nature of the crystallization centers – dislocations, surface defects, etc. – is still open. For example, some authors consider that the crystal growth is associated with a screw dislocation built into the polycrystal [7-10]. However, it is clear that the growing ice crystal will acquire a new molecule from the vapor rising from the interior of the ice in the neighborhood of any imperfection, if this tends to minimize the free energy. Both vapor migration to the surface and crystal formation at the surface are associated with the loss of thermodynamic stability.

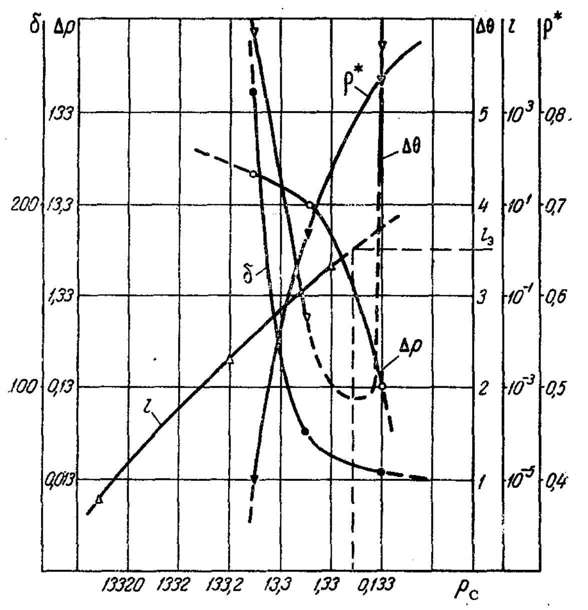

Fig. 4. Effect of pressure in sublimation chamber on crystal growth (l_s is the distance to the screen).

The crystals growing at the surface of the ice have a sharply expressed dendritic form (Fig. 2b). The formation of a dendritic structure may be explained as follows. Because of the presence of a zone a thermal supercooling of the molecules, if a so-called "whisker" (see Fig. 2b) is formed at the crystallization front, its tip will already be located in a region of greater supercooling as compared with neighboring parts of the crystallization front; and this whisker will tend to go on growing.

The corresponding heat of crystallization reduces the supercooling at the crystallization front. Therefore, as the growing crystals advance into the supercooling zone, the crystal is increasingly converted into a needle. In this case the rate of growth of the crystals on adjacent portions of the surface may be reduced.

One of the interesting points observed in connection with crystallization was the fact that the axis of the dendrite and its branches tend to grow in definite directions – laterally relative to the heat flux. These directions also correspond to the direction of the crystallographic axis (Fig. 2b) [9, 10]. The rate of growth of the crystals depends on the relative orientation of the optic axis of the crystals and their plane of growth. As our numerous experiments show (Fig. 2b), each needle of the dendrite is an individual dislocation-free, almost perfect crystal of close-packed structure with a strength considerably exceeding that of the monolithic ice itself. According to statistical calculations, the density of this close-packed ice structure is no longer 0.92 g/cm^3 but of the order of 1.8 g/cm^3. Precisely for this reason, as our experiments showed, in the course of time instead of being melted by the radiant flux the dendrites break off and are carried away.

As many investigators have stated [9-11], for crystal growth it is necessary that the number of molecules joining the solid phase be greater than the number escaping it; therefore the local temperature of the surface must be somewhat lower than the temperature of the migrating molecular flux.

The rate of growth of the crystal during sublimation is thermodynamically determined either by the temperature difference

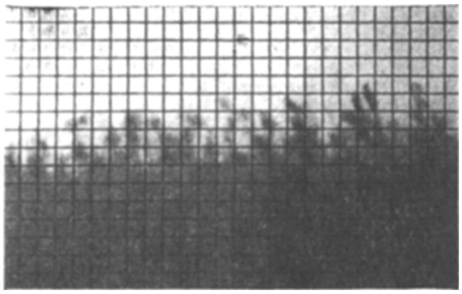

Fig. 5. Effect of vibration of crystal growth in a vacuum ($p = 66.6\ N/m^2$; $q = 0.57\ W/cm^2$). Side of squares equal to 100 μ.

$$\Delta\theta = T_s - T_c, \tag{1}$$

or by the supersaturation

$$\beta = p/p_c. \tag{2}$$

It can be stated that the process of sublimation of ice and all the accompanying phenomena can be explained in terms of its plastic deformation under the influence of a temperature or pressure gradient.

Effect of Heat Load on Crystal Growth. An increase in the heat load q (at constant pressure in the sublimation chamber) increases the temperature gradient in the polycrystal $\Delta\vartheta$, the supersaturation β and the number of crystallization centers at the surface as well as causing a more intense migration of vapor to the surface. The simultaneous increase in all the above-mentioned factors thus leads to an increase in the rate of growth and the height of the crystals δ as well as to a decrease in the density of the surface layer of crystals ρ^*. The results obtained are presented in Fig. 3.

Effect of Vacuum on Crystal Growth. As shown in Fig. 4, the height of the crystals δ and hence the sublimation process itself depend significantly on the degree of vacuum in the sublimation chamber. An increase in the vacuum affects the sublimation process in two ways. Firstly, the temperature of the polycrystal is reduced, which leads to an increase in its strength, improved resistance to plastic deformation and a reduction in surface defects, and this reduces the number of crystallization centers. Secondly, the migration of vapor to the surface is impeded. Moreover, such kinetic factors as the mean free path l begin to play a part. In our case the molecular mean free path is determined by the distance of the first probable collision of migrating vapor molecules above the surface of the polycrystal. As it expands in the vicinity of the surface in the low vacuum, the migrating mass of molecules is in direct contact with the surface defects, on the one hand, and with the supercooling zone, on the other. This causes the deposition of molecules at surface defects and the growth of crystals.

With further increase in the vacuum the mean free path l of the migrating molecules becomes even greater and the first probable collision occurs not at the surface of the single crystal but somewhere in the supercooling zone. This reduces the probability of the deposition of molecules at surface defects.

All this reasoning is confirmed by the calculations of molecular-kinetic theory [12]. Consider the first collision of two molecules with identical velocities $c = c'$ as they leave the ice at the phase interface. According to calculations, for $c/c' = 1$ the velocity conservation coefficient is 0.4, i.e., 40% of the original value. For other ratios $c/c' = 0-\infty$ the value of this coefficient varies from 1/3 to 1/2.

However, if three or more molecules collide, it is to be expected that the coefficient will be much smaller. Thus, the flow of molecules is sharply retarded and their velocity at the surface falls on the mean free path, which inevitably has an important influence on crystal growth and the process of desublimation when the pressure in the sublimation chamber is varied.

Our investigation of the effect of the vacuum on the sublimation kinetics and numerous photographs of the crystal growth convincingly confirm these physical arguments.

The effect of the principal parameters on crystal growth as the vacuum in the sublimation chamber varies is shown in Fig. 4.

In Fig. 4 the $\Delta\theta = f(p_c)$ curve has an extremum, which is attributable to the fact that at a certain vacuum the mean free path of the molecules becomes equal to the distance to the screen l_c. The molecules strike the heat-radiating screen, and then are diffusely reflected from it. Having acquired a new reserve of energy, the molecules bombard the surface of the ice and raise its temperature.

From an analysis of the $\Delta\theta = f(p_c)$ curve it follows that under our conditions the Knudsen number $Kn = l/l_s$.

It should be emphasized that the parameter l_s in the Knudsen number is a factor reflecting the change in the molecular process at the surface of the specimen and the thermodynamic parameters inside it.

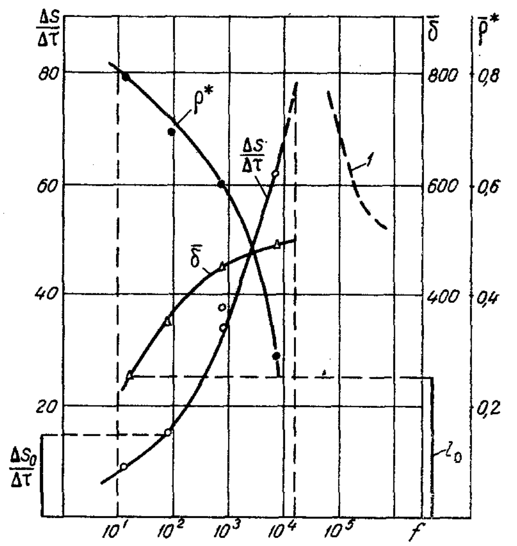

Fig. 6. Effect of audio frequencies on sublimation rate $\Delta S/\Delta\tau$, μ/min, and crystal growth at $p = 66.6$ N/m^2 and $q = 0.57$ W/cm^2 (10^1-10^4 – audio frequency range).

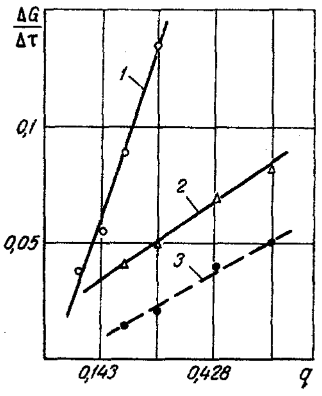

Fig. 7. Molar fraction of mass transfer flux: 1) conductive heating; 2) radiant heating; 3) molar flux.

The establishment of the Knudsen number in this form has important consequences in engineering practice, since it determines the optimal distance between the emitter and the irradiated material. The Knudsen number indicates that for the sublimation process to proceed in the molecular region it is necessary, on the one hand, that the radiating screen be installed at a distance from the material $l_s < l$ and, on the other, that the reflection of molecules from the screen be close to specular, i.e., in molecular sublimation (Kn > 1) a part is played by such factors as interaction of the molecules of vapor migrating from the ice and the radiating screen.

Effect of Vibration on Crystal Growth. Technically, the most promising method of intensifying sublimation process is the use of electrodynamic vibrators.

Vibration of the ice polycrystal leads, on the one hand, to the accelerated migration of vapor to the crystal surface and to an increase in the defects at the surface due to additional dislocation of the crystal lattice and, on the other hand, to an increase in the number of molecular collision events. The increased number of surface defects increases the number of crystallization centers and leads to the formation of a more fine-grained structure.

Whereas without vibration the crystals grow at a certain angle (Fig. 2b) to the surface, in the presence of vibration the crystals grow at right angles to the surface (see Fig. 5). Correspondingly, the optic axes of the crystals are directed, in one case, at an angle and, in the other, normal to the surface. It is known [9, 10] that the more inclined the optic axis of the growing crystal, the more slowly the crystal grows.

We conducted numerous photographic experiments, which are generalized in Fig. 6, to investigate the effect of audio frequencies on the rate of sublimation or the rate of advance of the sublimation front $\Delta S/\Delta\tau$ and the crystal growth $\bar{\delta}$. As may be seen from the figure, the sublimation rate, proportional to $\Delta S/\Delta\tau$, and the mean height of the crystals $\bar{\delta}$ increase with the frequency f, while the density of the surface layer of crystals $\bar{\rho}^*$ decreases. For comparison, Fig. 6 includes the sublimation rate $\Delta S_0/\Delta\tau$ and the height of the crystals l_0 for sublimation processes without vibration.

We noted that the crystal growth $\bar{\delta}$ probably tends to a certain limit (like the growth of the sublimation rate) over the full range of audio frequencies.

In this case, from the mechanical standpoint, the crystal may be regarded as a cantilevered rod, whose growth, though it increases as a result of all the above-mentioned factors (acceleration of vapor migration to the surface, increase in the number of crystallization centers, etc.), must be limited on account of the purely mechanical characteristics of such a model. Undoubtedly, resonance should occur in this system at a particular frequency.

Curve 1 in Fig. 6 is purely hypothetical and is intended to indicate that at a certain frequency outside the audio range a decrease in sublimation rate and crystal growth is possible.

Undoubtedly, the determination of the resonance frequency for the sublimation of ice and other materials is a very important engineering problem.

Molecular and Molar Sublimation. Our comparison of sublimation rates measured with a balance and by the photooptical method from the rate of advance of the boundary of the subliming ice revealed a considerable difference due to the entrainment of crystals.

It remains to enquire what contribution is made to the total mass transfer flux by "spalled" crystals (molar component).

If we assume that the porosity of the "frosting" of crystals removed from the surface $\varepsilon = 0.9$ and consider that the density of these crystals is twice as high as the density of ice at atmospheric pressure, then the total coefficient in the photooptical calculations

$$a = (1 - \varepsilon), \ \rho^*/\rho = 0{,}2.$$

In this case, depending on the heat load, the molar component, as shown in Fig. 7, may be from 20 to 60% of the total loss of mass. Its variation, like the growth of the crystals, also depends on the vacuum and other external influences, whose effects have already been considered. It is merely necessary to note that to each vacuum and each heat load there corresponds a molar component having a maximum or minimum value.

Thus, the vacuum sublimation process may be molecular, molecular–molar, or molar depending on the pressure and the heat load.

The isolation of these components and their mutual influence are of considerable interest, although their exact determination involves serious experimental difficulties.

The practical significance of the desublimation of crystals at the surface of ice deserves consideration. Desublimation does not affect the consumption of heat (the energy expended on the phase transformation of the ice molecules, i. e., on the conversion of ice from the solid to the vapor state, remains constant), since there is no melting of the crystals formed, which are systematically carried away into the vacuum chamber and then into the condenser. This facilitates the operation of the condenser, since instead of molecules being condensed on its surface ice crystals are deposited. The reduction of the condenser load will be the greater, the greater the molar component. In both molecular and molar sublimation a "frosting" is formed on the condenser surface.

Our calculations showed that even at large molar components the molecular volume of vapor creates in the chamber velocities greater than the entrainment velocity of the measured crystalline particles carried out of the sublimation chamber.

In conclusion, we note the importance of the results obtained in relation to the freeze-drying process.

Kessler [6] investigated the one-sided radiant sublimation drying of capillary-porous materials placed in a rectangular plastic box.

As these experiments showed, there is a continuous depression of the surface of the sublimation zone because the ice-filled capillaries do not ensure a supply of moisture to the irradiated surface. In the sublimation zone a certain temperature, higher than the temperature in the sublimation chamber, is established. This temperature gradient or the corresponding pressure gradient is also the mass transfer potential. It should be noted that the hydraulic resistance of the dried layer of material did not have much effect on the sublimation rate and the variation of the parameters of the process, which changed only when the residual moisture, which was more strongly bound to the material, began to be removed. This process was a slow one. In this case the presence of temperature or pressure gradients, even though small, probably also led to plastic deformation of the ice polycrystals and the migration of vapor molecules in accordance with the model we have described.

In a high-frequency current field, as in our process of vibration drying, sublimation drying is considerably intensified. There have been a number of studies along these lines, the most comprehensive being those of E. I. Guigo [13].

Our results make it possible to supplement Guigo's description of the sublimation mechanism as follows. Excitation of the ice molecules produces thermal effects and creates considerable pressure gradients, which cause total sublimation, i.e., plastic deformation of the ice crystals over the entire volume of the frozen body and intense migration of vapor molecules to the surface of the material. In this case, however, some depression of the sublimation zone is unavoidable and internal desublimation of vapor molecules at the phase interface is possible. The rate of sublimation will also be reduced in connection with the removal of sorption-bound moisture and the moisture in microcapillaries. These questions require further study.

NOTATION

T_s	is the sublimation temperature;
T_c	is the vapor saturation temperature (in sublimation chamber);
$\Delta\theta$	is the temperature difference between temperatures inside specimen and in sublimation chamber, °C;
p	is the vapor pressure in ice specimen (equal to pressure in sublimation chamber), N/m^2;
t_c	is the saturation pressure (in sublimation chamber), N/m^2;
$\Delta p = p - p_c$;	
l	is the mean free path of water vapor molecules, cm;
l_s	is the distance to heater screen;
δ	is the height of crystals, μ;
δ_0	is the height of crystals without vibration, μ;
$\bar{\delta}$	is the mean height of crystals, μ;
f	is the frequency, Hz;
ρ^*	is the density of surface layer of crystals;
$\Delta S_0/\Delta\tau$	is the sublimation rate without vibration, μ/min;
$\Delta G/\Delta\tau$	is the total sublimation rate, g/min.

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