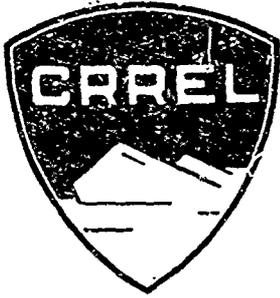


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ON CENTERS OR NUCLEI OF WATER CRYSTALLIZATION

V.IA. Al'tberg

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On the Centers or Nuclei of Water Crystallization

V. Ja. Al'tberg (Leningrad)

Hundreds and thousands of works have been devoted to the study of the nature of water. According to the bibliographic index in E. K. Fritzmann's book The Nature of Water (1935), 699 papers have been devoted to just one physico-chemical side of the problem. But, nevertheless, several sides of the problem remain poorly elucidated. This relates, first of all, to the question of the transition of liquid water into a hard phase, despite the fact that the phenomenon of the formation of crystals was first studied in water. In 1721, Fahrenheit first discovered the phenomenon of the supercooling of water [1]. He was able to cool water to -9.4°C in a sealed tube. When he broke the tip of the tube, all the water filled up with ice splinters (Eissplittern).

I will give two more examples from the same time period. Musschenbroeck [2], on a night with freezing weather, set out a well-stoppered bottle of water and, when he took off the cork the next day, he saw the bottle fill with countless ice splinters at that very moment. Mairan [3] saw the very same splinters when he compared the speed of propagation of the opacity of water (due to the presence of splinters in it) from the surface to the bottom "mit einer Entzündung des Schiesspulvers" (to a gunpowder explosion).

Since then, similar experiments with different variations but with the same results have been done hundreds of times and therefore one need not speak of them. One might, however, mention the latest one which was done, besides, by the very

creator of the theory on the centers of crystallization, Tamman. He noted in his work, together with Böhmer [4], that "the centers of ice crystallization, which are formed in supercooled water, even with an insignificant supercooling, gain so great a speed of crystallization, that very quickly the entire vessel fills with thin ice needles, as a consequence of which one cannot, as is done in other liquids, determine the capability of water crystallization by the number of centers of crystallization formed in a fixed time with a fixed supercooling." (italics mine)

They consider -3.5° a negligible supercooling; a temperature below which they did not get. Further on they write: "Up until now experiments were conducted on substances with a small speed of crystallization. Water has still not been studied in terms of its characteristic great speed of crystallization" (italics mine).

Such is the contemporary position on the matter of centers of water crystallization in the statement of the greatest authority in the field of the onset of crystallization.

Comparing the results of the authors' experiment with the eighteenth century experiments noted above, one must state that it seems there has been only the very slightest movement forward in the last two centuries in the direction indicated above.

However, as we will see below, this does not correspond to reality. The reason is due to Tamman and Böhmer's disregard for many important events which have gradually been revealed in the course of a long period of time. It is necessary therefore to stop here at this important stage in the development

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of knowledge. Blauden [5] (1798), repeating the experiments of Fahrenheit, studied the laws of supercooling of water. He found that well water froze at -4° , distilled at -5° , boiled at -6° , turbid river water at 0° . The turbidity of water turned out to be a steady obstacle for preserving the supercooling of water.

Deluc [6] showed that in strong frosts at -17° and more, droplets of fog in the atmosphere remain liquid, concluding from this, that "for the formation of ice, besides cold, some other thing is needed." Dalton [7] showed that for the supercooling of water its greatest purity is needed (including degasification) for, "in turbid water hard particles contributed to the beginning of crystallization."

Gay-Lussac [8] showed that the access of air to supersaturated solutions causes their crystallization. Ziz [9] noted that, in the presence of air, crystallization always begins at the surface of the liquid, which also indicates the crystallizing action of air.

Forty years later the matter began to be cleared up. Löwel [10] found that when one filters air or allows it to settle for a long period of time, it loses its crystallizing activity. Here Löwel closely approached the heart of the phenomenon since the conclusion from these experiments was self-evident: the whole matter has not to do with air itself, but with particles suspended in it.

Such a conclusion was made only ten years later by Violette [11] and, independently from him, by Gernez [12]. The methodology of sterile cultures, worked out by Pasteur, served as a stimulus for their work. It was not difficult

for them to carry out the analogy between the contamination of a nutrient substratum by air-borne bacteria and crystallization of the supersaturated solution under the action of dust particles. It is no wonder that the method of contamination of solutions eventually found a great application.

Violette as well as Gernez proved that the crystallization of supersaturated solutions of sodium sulfate is caused exclusively by the entry into them of the finest crystal particles of a dehydrate of this salt suspended in the air.

With little supersaturation, these solutions, kept in sealed vessels, did not crystallize for years. But with a great supersaturation, these same solutions crystallized even under conditions which exclude the possibility of the entry of seeds from without.

Le Coq de Boisbaudran [13] showed that crystal particles of substances isomorphic with the material dissolved can serve as seedings, provided only that the supersaturation not be too small.

De Coppet [14], after detailed investigations, came to the conclusion that, for solutions of each substance, there exists a certain critical supersaturation, higher than which they crystallize spontaneously, that is, without any external influence. Due to a strong discrepancy between the results of the experiment, the maximum supersaturation could not be determined.

In their time, de Coppet's experiments and conclusions served as a starting point for Tamman's building of his theory.

The repeated filtration of solutions (Jaffe's experiments [15]) and of supercooled liquids (Flüchtbauer's experi-

ments [16]) raises the stability of both, that is increases the crystalline supersaturation (supercooling) and proves that the "spontaneous" crystallization of de Copet and others actually arose under the action of some kind of hard particles, suspended in the liquid, which serve as nuclei.

The work of Hinshelwood and Hartley is very interesting. They put a great number of small sealed ampules of p-toluidine in a thermostat and noted the number of specimens which had crystallized within a defined time interval, while plotting the time in minutes along the abscissa and the percent of crystallized specimens at different temperatures along the ordinate. The melting temperature of p-toluidine is 48.3° . These results correct Tamman's statement on the constant growth of the number of seeds with time. Indeed it turns out that the common number of seeds is limited, proving by this that crystallization is caused by some kind of particles suspended in the liquid.

Especially convincing were the experiments of Billmann and Klitt [187], who used centrifugation for purifying liquid of dust and, finally, the experiments of Meyer and Pfaff [19], who filtered liquid through a finely porous Schott filter with an average pore measurement of 1.5μ . It is interesting that if there were still finer dust particles in the liquid which would pass through the filter, then the liquid retained its capability of crystallizing. However, it was always possible to deprive the liquid of this capability if, after filtration, one would supercool it. In that case there begin to form crystal particles on the smallest dust particles still in the liquid which, with repeated filtration, would get stuck in

the filter and the liquid would turn out completely free of dust. Such a liquid turned out to be completely deprived of the capability to crystallize even at the temperature of liquid air.

The last-mentioned authors did a very interesting experiment. They "contaminated" a filtered liquid with crystal particles of the same substance which were absolutely free of foreign particles. After melting the crystallized mass, liquid was once again obtained which was not capable of spontaneous crystallization. The resultant important conclusion is this: suspended particles, which enable crystallization, cannot be microscopic crystal particles of the same substance freely floating in the liquid.

A series of Russian authors (Shubnikov, Kuznetzov, Dankov, Frenkel' and others) also sceptically treat the stability of nuclei which are formed from a small number of molecules of liquid. They show that the formation of nuclei is facilitated by foreign bodies, around which a distinct orientation of molecules takes place, thus facilitating the process of crystallization.

Valmer and Weber [20] studied the contact action of different minerals on supersaturated solutions filtered through an ultrafilter. It turned out that on the surface of all the minerals studied, crystallization begins at a considerably lesser supersaturation than inside the solution; the action of different minerals and even of different facets of one and the same mineral being very specific. The points and edges of the crystals are especially active.

The theoretical works of Valmer, who developed a formula

for work on the formation of a stable seed, were a great step forward.

Valmer and Flood [21] were successful in showing that the theory corresponds well to the results of the experiments.

Valmer especially emphasized that the hard sides and boundary surfaces play an important role in the process of forming a new phase since they facilitate the formation of stable seeds. With small supersaturations (supercoolings), the seeds can in general form only on boundary surfaces, on dust particles and so forth.

The experiment, as we saw above, corroborates this theoretical conclusion. Since surfaces of hard bodies are never uniform (they have protuberances, depressions and fissures), then only specific portions are active. This also is corroborated by the experiment.

Of the two kinds of origins of crystals, forced and spontaneous, the first is especially interesting and important. This is due to the variety and multitude of different factors influencing the formation of the seed.

It follows from the many and very successful experiments, that with small supersaturations and, in particular, supercoolings, spontaneous crystallization in general does not take place, since the origin of crystals takes place on dust particles and foreign solid bodies. This is similar to how condensation takes place, as is known, only on dust particles and other particles of impurity.

In view of the fact that the formation of ice in reservoirs takes place with a very insignificant supercooling of water, one can say with complete assuredness, that ice nuclei form

not spontaneously, but by force, under the action of one or another group of factors.

Besides Tamman, Meyer studied spontaneous crystallization in detail. His experiments are in full accord with the newest theory on the pseudocrystalline structure of every liquid, even a superheated one, not to mention a supercooled one. The results of these interesting experiments are in contradiction with Tamman's research.

According to Shubnikov, these contradictions can be eliminated by taking into account two circumstances which neither author paid attention to: 1) "gemination" of the centers of crystallization and 2) contamination of liquids by particles of other substances capable of causing crystallization.

The phenomenon of gemination noted above is well demonstrated, according to Shubnikov, on a salol preparation.

They place a preparation with a supercooled drop on a polarizing microscope and observe with crossed nicols how crystallization of salol will take place if they introduce a seed of hard salol into the supercooled drop on the tip of a needle, touching it to the glass at one point. In this spot a group of crystals begins to grow slowly. However, a few seconds after the beginning of the process, more and more individual crystals which are invisible at the moment of ejection due to their smallness and which grow to significant proportions at the moment of their speed loss, begin to fly out from the surface of the growing crystals with a great speed. The crystals which are ejected are shaped like small boats, their long axis is always oriented perpendicular to the direction of movement, completely analogous to a real



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boat when it, left to itself, tends to turn its side to the wind. This beautiful experiment, which was constantly being shown by the late Prof. Wolfe in his lectures on crystallography, extraordinarily reminds one of artillery fire from a fort. Only instead of seeing growing puffs of smoke after an explosion of shells, we see "little boats" sparkling with their unceasingly changing interference coloration.

"The phenomenon of the ejection of seeds by the growing crystal, together with the earlier-described phenomenon of crystal coalescence, has, in our opinion, a great theoretical significance. They show how much more complicated reality is than those schemes which are so necessary to the scientist for prediction and precalculation of phenomena which are contained in these schemes and which are a great harm to foreseeing really new phenomena not having any relation to the schemes thought up."

The phenomenon of gemination described by Shubnikov throws a new light on the mechanism of the origin of crystallization nuclei and on the process of their reproduction under the action of seeding.

This phenomenon, apart from its beauty, has a very substantial and general meaning, as even Shubnikov himself recognizes.

The process of gemination, of seeding liquid with nuclei (Impfwirkung), must have its place in the case of water crystallization as well.

Before going on to this, it is necessary to note that Meyer and Pfaff did experiments similar to the above-described one, also with water which they tried to purify of impurities

and nuclei. For this they applied all their art and used the most perfect technology for purifying liquid, but nevertheless they still did not succeed in completely purifying water of nuclei. The maximal degree of purity achieved by them can be seen in the fact that their water did not freeze even at -33° .

Either some remnant of nuclei still remaining in the water or the influence of the walls of the vessel which they did not succeed in eliminating prevented the further lowering of supercooling.

These experiments prove the significant abundance of nuclei in water. Even such experienced researchers as Meyer and Pfaff could not purify water of nuclei. Billmann and Klitt also have the same opinion on the constant presence of nuclei in water.

These facts point out that water has particularly favorable characteristics for experiments on crystallization which were not utilized, however, by Tamman.

For explaining the nature of nuclei of crystallization it is important to take into account the result of an analogous stage in the development of knowledge (already reached in the last century) relating to nuclei of condensation.

Kuhle, Maskar and Aitken [22] already in the last century proved that the formation of fog is stopped if the air is purified beforehand (by means of its filtration through cotton wadding) of dust particles which are, in essence, the same centers on which condensation takes place. This question was studied in more detail, theoretically and experimentally, by Thompson. Here it is appropriate to bring in Aitken's generalizing position. He put much work and time into the study of nuclei.

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"Already long ago I showed (says Aitken), that for the transition of bodies from a liquid state to a gaseous or from a gaseous to liquid or from liquid to solid or, finally, from solid to liquid with corresponding points of boiling, condensation and freezing, it is necessary to have the presence of a nucleus or a free surface (the dividing boundary of two phases) on which the transition from one phase to another can take place."

It is important to note that such a specialist on nuclei like Aitken was convinced of the indispensibility of nuclei as carriers of a free surface (dividing boundary); extraneous particles (dust particles) being the nuclei. This is necessary, according to Aitken, not only for condensation, but also for crystallization.

Thus even in the last century it was firmly established and recognized by all in the field of condensation, that dust particles or impurities are nuclei of condensation and not accumulations of molecules of steam as was formerly thought.

A similar idea on the formation of nuclei not by means of an accidental collision of many molecules of a liquid, but on the already prepared boundary surfaces (with dust particles always being in the liquid) began to take root in science due to the many and ever more convincing experiments.

From Tamman and Büchner's second sentence cited by me at the beginning of the article it follows that substances are divided as it were into two classes: those with a small speed of crystallization and those with a large one (water). However Tamman, as is known, earlier proposed the general

dependence of crystallization speed of all substances on the degree of supercooling; the crystallization speed being practically equal to zero with insignificant supercoolings and very slowly growing with an increase in supercooling.

Tamman and Büchner for some reason make an exception for water, considering that it has only great speeds of crystallization. They did not do experiments with supercooling less than -3.5° . Herein lies their error and incorrect interpretation, as we shall see below, on the question of the crystallization speed of water.

In Tamman and Büchner's second quote cited above it is stated that centers of water crystallization were not studied because of the great speeds of crystallization supposedly characteristic of water and the necessary impossibility of doing experiments on the centers of water crystallization.

There is an evident misunderstanding here. On the one hand, according to Tamman, the speeds of crystallization are very small with insignificant supercoolings.

On the other hand they, by analogy with other substances, considered a supercooling at -3.5° insignificant for water too. They did not get below the indicated limit in their experiments, as a result of which they did not find the optimum conditions for experiments with nuclei.

Just as every substance has its optimum for investigation of nuclei, so water must also have its optimum, lying, apparently, considerably lower than -3.5° ; a temperature at which the speeds of crystallization are still very significant.

These considerations and also the cited experiments of Meyer and Pfaff and those of Shubnikov with germination

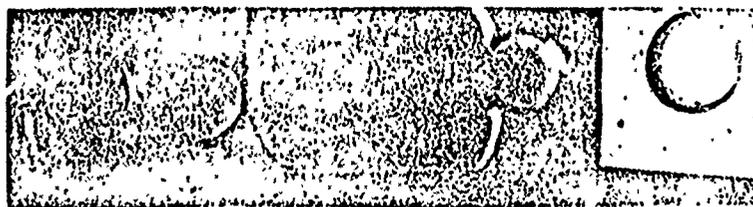
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definitely point, first of all, to the incorrectness of Tamman and Büchner's conclusion on the inaccessibility, as it were, of nuclei of water for investigation and, secondly, to the complete accessibility, as we shall see below, of these nuclei for investigation under optimal conditions.

Arising from the indispensable presence of a stage of small crystallization speeds for all substances (including water) with sufficiently small supercoolings, we decided to establish experimentally for water the necessary optimum of supercooling, which allows one to comfortably and easily investigate nuclei of water and, foremost, to ascertain them and to reveal their structure and properties, for which there are no data in the literature as Tamman notes.

In our experiments we went considerably farther than that limit of supercooling which Tamman reached (-3.5°) and took supercooled water to ten, one hundred and even one thousand times less than Tamman.

Under these conditions we, for the first time, obtained centers of water crystallization not with colossal crystallization speeds as Tamman had, but hundreds of times less. These speeds allowed us to investigate them completely freely and even to count them which Tamman could not do. He does not



Ill. 1. Nuclei of water crystallization

even say anything about the form of nuclei and their structure, noting only the fact known to all, that "ice crystallizes usually in the form of feathers." This fact, however, has

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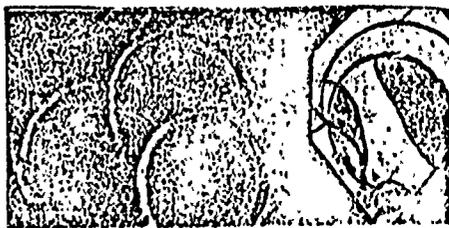
no relationship to nuclei.

If under Tamman's conditions exceptional technical difficulties did not allow him to investigate centers of water crystallization, then under our conditions, just the opposite, there were no difficulties and the experiments could be carried out very easily and simply. For this it was necessary to have, in a series of glass cylinders, water supercooled at -0.02° , -0.05° , -0.1° , -0.3° , -0.5° .

The introduction of a seed (a small piece of ice the size of a pin head) in any of the indicated cylinders caused, after stirring the water, the appearance of many very small ice elements in the shape of thin, transparent, completely round plates (ill. 1, 2 & 3).¹



Ill. 3. Disks of ground ice on a stone extracted from the bottom of a glacial river.



Ill. 2. Nuclei of water crystallization.

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In the vessel with the least supercooling there arose the least number of centers, their speed of growth also being the least (one thousand times less than the speeds indicated by Tamman at 5000 mm/min.). In the subsequent vessels, as the supercooling increased, both the number of centers as well as their speed of growth increased, remaining, however, hundreds and tens of times less than 5000 mm.

¹The photographs were obtained as the result of new experiments at the Hydrological Group of the State Hydrological Institute.

In the last cylinder the number of centers of crystallization and their speed of crystallization increased so much that to calculate them already presented great difficulties. With a further increase in supercooling we get into Tamman's very difficult conditions for the experiment. Therefore supercoolings from -3.5° and higher are not of interest to us. We concentrated all our attention on supercoolings one hundred times less.

In the process of work we did tens of similar experiments with the same results noted above. Later we got involved with investigating the growth of centers of crystallization and for that we worked out a corresponding methodology and apparatus [23].

Here we are reporting only on the final results of these experiments. Watching the growth of disks, we observed how a very small ice disk hardly visible to the eye grew, as it moved through the supercooled water, at first into a disk several millimeters in diameter; then the disk turned into a hexagonal plate which, with further growth, turned into a hexagonal star. This star turned into a more complex formation reminiscent of a snowflake (ill. 4).

The artificially grown formations were very beautiful in their slender structure, but photographing them was extraordinarily difficult. Their maximal measurements could be brought to 2 cm and more, but they were distinguished by extreme fragility which prevented extracting them from water. In the water they were hardly

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Ill. 4. A snowflake growing in a free, floating state in water.

visible and could not be photographed.

Parallel to the described experiments we later did the same experiments in a slightly different form which allowed us to see the multiplication of nuclei in a very effective form. A seed, weighed down by a little weight, was introduced into supercooled water (-1.5° , -2.0°). This seed, caused, at that very moment, a fountain of sparks exactly like fireworks in the water. This suddenly blazing cloud of many hundreds of disks and small ice stars, which reflected the light falling on them, was a beautiful sight.

Thus we, for the first time, observed the centers of water crystallization, studied their properties dependent on supercooling of water and, finally, worked out a methodology and arrangement for investigating the growth of elements which we succeeded in preparing separately in a free and floating state (in water) to 2 cm and more.

Tamman's treatment of the supposed impossibility of investigating centers of water crystallization and supposedly "inherent" only to water exceptionally great speeds of crystallization and a lack of a stage of small crystallization speeds for the nuclei turned out to be wrong.

Our research now corrects this interpretation--it is very important because it opens a broad possibility for investigating that area which seemed "inaccessible" even to such authorities like Tamman.

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This field has not only a great scientific significance (it concerns water, the most widespread liquid on earth and its hard phase--ice), but it has an even more practical significance in view of the fact that ground ice and the

suspended stage of ice (slush ice) are nothing other than nuclei and a seed of crystallization--that is just what is being discussed in this article. It was proven by me before. Ill. 5 shows a mass growth of centers of crystallization.

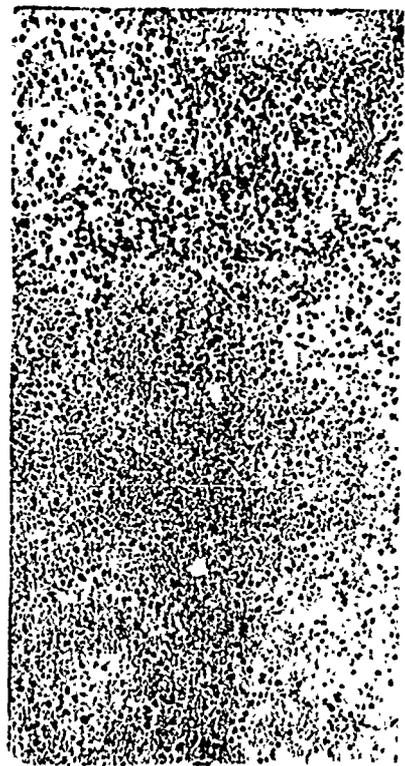
In connection with this it is interesting to bring in the results of the interesting experiments of A.M. Shenrok and D.A. Smirnov who threw small grains from a cooling mixture (salt + ice) into supercooled water. On the path of movement of such a small grain there appeared the finest crystal particles so that one got the impression of a falling meteor with a tail behind. The crystal particles which appeared, moving in the water, in their turn caused in the same way the formation of more and more nuclei.

The process went on much more quickly if the water was stirred as in our experiments.

The nuclei appearing when the water is moved spread, as it were, the contamination throughout the entire liquid and the reproduction of crystals took place at an accelerated tempo, not unlike an avalanche. The turbulent movement of water in a river contributes to the formation of ground ice since it spreads the contamination of crystal formation in the water.

The results of our experiments (just like the observations of Shenrok and Smirnov) which establish for water the fact of reproduction of nuclei of crystallization which was known before only for other substances, have a deep and fundamental significance since they put an end to the false dogma concerning the role of seeding. It had been assumed that the role of

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Ill. 5. Mass forma-
tion of centers of
water crystallization.

seeding consisted only of the growth of the seed itself and that in nature there do not exist processes of contamination of a supercooled liquid by means of nuclei with the help of a seeding and of a process of reproduction of nuclei after the introduction of at least one nucleus or crystal particle into the liquid.

This dogma strives to repudiate that which was long ago accepted in science that is widely used in the chemical industry and even more widely appears in nature (ground ice, the formation of clouds and fog, the accumulation of salts in estuaries and in salt lakes and so forth).

We saw above that even the contemporaries of Pasteur--Violette and Gernez [11, 12] --adopted his viewpoint on the essence of contamination and transferred this concept to the field of crystallization. Later the method of contamination with the help of a seed got wide application in the works of Tamman and his school as well as in the works of other researchers in the field of crystallization (Müller, Otmer, Nanken and others).

The process of reproduction got, besides the name "contamination", still other designations, namely: inoculation (after Tamman's Impfwirkung), gemination (after Shubnikov)

and others.² On the basis of this phenomenon Tamman perceived a resonance action; others perceived an action, analogous to catalysis, of induction. Wolfe and Shubnikov's experiments lift slightly the curtain which was hiding the mechanism of this ~~phenomenon~~ phenomenon.

Here we approached the very border dividing the investigated area from that not yet investigated which is subject to research in the future. The question about the mechanism of the origin of a nucleus--about the seed of the future crystal is very interesting. It is a question of the future of experimental and theoretical physical chemistry and work goes on in this direction with unflagging intensity.

Ill. 6 shows slush ice artificially reproduced by us.

In conclusion it is necessary to touch on objections made by my opponents which simply consist in that some consider the disks observed by me originating as a result of "melting"; others consider it a result of "rounding off" of ice elements among themselves; a third group considers them "fragments"; a fourth group simply recommends that one not believe one's eyes and that one should not consider the clearly visible disks as disks, but as some other kinds of formations.

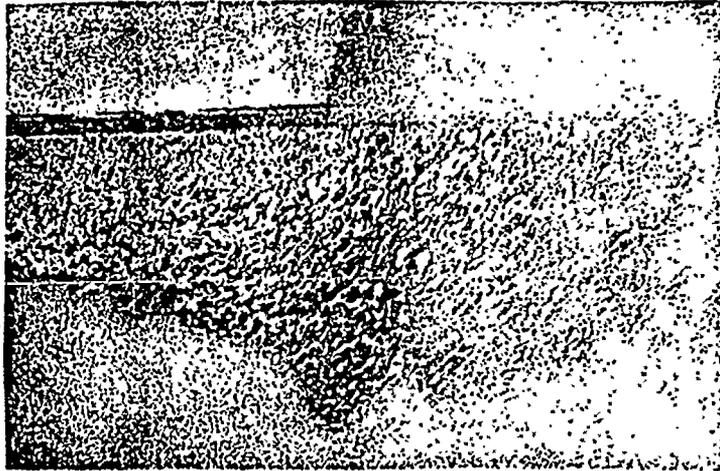
I answer these objections:

1) Only a person little informed in the field of physics can talk about melting at $t < 0$, that is under conditions of supercooling when the nucleus can only grow and not melt.

2) Only a person who does not understand, in essence,

²Even the very names--contamination, inoculation, gemination--indicate that one is discussing reproduction, a fact which, therefore, is not subject to any doubt: it is firmly established experimentally.

what a fragment is and what kind of difference there is between it and a regular body in the form of a completely round disk can call round disks (precisely disks), with mirror surfaces and seemingly polished edges, fragments of a thin structure.



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Ill. 6. Artificially reproduced slush ice.

3) Only a person who does not wish to be considered as having common sense and logic can assert that disks supposedly arise as the result of "rounding off", when indeed the growth and shaping of individual crystals can be observed with one's own eyes even under conditions of absolute impossibility of contact with other disks (due to there not being any).

4) Finally the recommendation of not believing one's eyes I repudiate (as advice) as not deserving any attention.

It is all the more interesting that ^{none} of these opponents consider it necessary to make similar objections in relation to other researchers who have obtained the same kind of disks in other liquids that I obtained in water.

Bibliography numbers 1 to 22 are not in Russian

#23 V. Altberg. Izvestija Glavnoj Geofiz. Observatorii, 1929.

State Hydrological Institute