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雑誌名	Science reports of the Tohoku University. Ser. 5, Geophysics
巻	6
号	1
ページ	43-61
発行年	1954-08
URL	http://hdl.handle.net/10097/44520

Freezing Mechanism of Supercooled Water

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(Received 30 April 1954)

Abstract

The author builds up a hypothesis about the freezing of supercooled water basing upon three assumptions, namely the assumption on the interfacial free energy between ice and water, the assumption of the shape and direction of the ice bud which forms on the surface of freezing nucleus and the assumption on the epitaxy of the ice bud on the surface of freezing nucleus.

Critical temperatures of the ice particle formation at -41°C , -32°C and others are explained by this hypothesis.

The effects of 17 sorts of freezing nuclei on the freezing temperature of supercooled water droplets are also explained reasonably and systematically by this hypothesis.

1 Introduction

Mechanism of freezing of a supercooled water droplet in the atmosphere is one of the important problems in meteorology which needs to be studied theoretically. Recently, many important experimental results have been reported one after another with respect to the effects of different sorts of nuclei on the freezing temperatures of supercooled water droplets. Yet, there is no systematic theory on the mechanism of freezing of supercooled water. The author gives a hypothesis about this mechanism with three assumptions, namely the assumption on the interfacial free energy between ice and water, the assumption on the shape and direction of the ice bud which forms on the surface of freezing nucleus and the assumption on the epitaxy of the ice bud on the surface of freezing nucleus.

CWILONG and others [1], principally English meteorologists, have reported two special temperatures concerning to the nuclei which form ice particles in the atmosphere. Ice is only formed if the cloud formed by rapid expansion of surface air in small chamber is cooled below a threshold temperature -32°C . Another threshold temperature is -41.2°C which corresponds to a rapid expansion of upper air cleaned of foreign particles. Not only in the case of these two temperatures but also in general case of expansion chamber experiment, relative humidities at which ice particles form are nearly water saturation and far exceed ice saturation. Therefore it is no doubt that in these cases nuclei act as freezing nuclei (see LUDLAM [2], WEIKMANN [3]).

The 41° -nuclei are different from the 32° -nuclei in their behavior. The former shows clear-cut threshold at -41.2°C while the latter shows somewhat vague threshold at -32°C . According to the experiment by FOURNIER DALBÉ (1949) [4], powder nuclei of NaCl, NaNO₃, CdI₂, CsI and the nuclei generated from red-heated platinum wire also show the threshold at -41.2°C . The threshold at -41.2°C seems as if it was the nature of water. The

threshold at -32°C does not appear if the expansion is very slow and also in the case of cooling of fog particles in a cold box. BIGG (1953) [5] observed the freezing temperature of supercooled water droplet against its diameter, which showed remarkable discontinuities at -35°C and at about -31.5°C . This discontinuity at about -31.5°C seems to have some relation to the 32° -nuclei. According to the experiment by FINDEISEN and SCHULZ (1944) [6] which tested surface air with a cloud chamber, a vague threshold for the ice formation at about -30°C in the case of moderate expansion moved to about -29°C as the expansion ratio increased. Though it is not sure that the 32° -nuclei can be identified with Findeisen's 2nd class nuclei, it is sure that one can see somewhat vague threshold temperature between -32°C and -29°C if he expands surface air moderately or rapidly.

Other than the famous threshold at -39°C obtained by SCHAEFER (1949) [7], weak threshold at -35°C was observed by prof. T. ASADA (Osaka University) (1952) [8] who cooled artificial fog in a cold box without any artificial freezing nucleus. This temperature, -35°C , was also observed by BIGG [5] as stated above, but he paid no attention on it.

Many critical temperatures each of which is characteristic to the material of freezing nucleus were obtained by FOURNIER DALBÉ (1949) [4], ASADA (1952) [8], HOSLER (1951) [9], BIRSTEIN (1952) [10] and others in their cold box experiments.

Now, turning to the theories on the freezing of supercooled water, there are many studies by VOLMER (1939) [11], KRASTANOW (1940) [12], OURA (1950) [13], WEIKMANN (1951) [3], MASON (1962) [14] and others.

Almost all of these theoretical studies are founded on the theory of THOMSON-GIBBS which is now applied to the equilibrium between the supercooled water and the small ice particle in it. These theories equally seem to meet great difficulty caused by the theoretical uncertainty of the interfacial free energy between ice and water.

(i) Hence the author studies at first on this energy and sets up an assumption about it.

(1st assumption): *Interfacial free energy between water and ice per one molecule of water contacting with the interface is expressed as $\alpha - kT \log 2$, where*

$$\begin{aligned}\alpha &= \frac{1}{2} \{(\text{inner energy per molecule of water}) \\ &\quad - (\text{inner energy per molecule of ice})\} \\ &= \frac{1}{2} \{(\text{evaporation heat per molecule of ice}) \\ &\quad - (\text{evaporation heat per molecule of water})\}\end{aligned}$$

k = Boltzmann constant

T = absolute temperature

Details of this assumption will be shown in 2.

(ii) Though KRASTANOW's theory contains numerically unknown physical constants, he succeeds in showing that, depending upon the nature and size of the nuclei present, there are three temperature ranges of ice formation: in the first of these only supercooled drops can form; in the second supercooled drops form first but subsequently freeze; and in the third and lowest range primary ice-formation occurs. The third range is generally accepted to be lower than -60°C . Hence, over a large range of temperature, from 0°C

to -60°C , ice particles in the atmosphere may be expected to arise secondarily after the production of water drops. It is natural to assume that there exists a freezing nucleus in a water droplet and that after an ice bud formed at first on a surface of the freezing nucleus freezing propagates from the bud to the other portion of the droplet. The author assumes with respect to the shape and direction of the ice bud as follows.

(second assumption:) Ice bud takes the form of hexagonal prism having its main axis perpendicular to the surface of the freezing nucleus.

The increase in free energy, ΔF , due to the formation of an ice bud which is composed of x number of molecules in the main axis and l number of molecules in the radius, is given by

$$\Delta F = 6 l^2 x (\mu_B - \mu_A) + 6 \{l^2 + (x-1)(2l+1)\} (\alpha - kT \log 2)$$

where μ_B and μ_A represents the free energy per molecule of ice and water respectively.

Freezing temperature or the temperature of initiation of an ice bud of given size is calculated from the condition of equilibrium: $\frac{\partial(\Delta F)}{\partial x} = 0$, $\frac{\partial(\Delta F)}{\partial l} = 0$ for the lengthwise and radial direction of the bud respectively. Results of calculation are shown in Table 1.

Table 1. Freezing temperatures of ice buds ($^{\circ}\text{C}$)

on the right of stair-shaped full line: Freezing temperatures in the radial direction
 on the left of stair-shaped full line: Freezing temperatures in the lengthwise direction

$l \backslash x$	1	2	3	4	5	6
1	-40.3	(ice buds do not exist)					
2	-40.3						
3	-34.8	-31.6	-28.1	-24.9	-24.9	-24.1
4	-28.3	-28.3	-26.0	-22.1	-22.1	-21.2
5	-23.7	-23.7	-23.7	-20.4	-20.4	-19.3
6	-20.5	-20.5	-20.5	-20.5	-19.3	-18.0
⋮	⋮	⋮	⋮	⋮	⋮		

The critical temperature at -41°C is explained to be the freezing temperature, -40.3°C , of the ice buds whose size are given by $x=1$, $l=1$, and 2.

The critical temperature at -35°C is explained to be the freezing temperature, -34.8°C , in the lengthwise direction of the ice bud whose size is given by $l=3$, $x=1$.

The critical temperature at about -32°C is explained to be caused by the formation of the ice bud sized $l=3$, $x=2$, at -31.6°C .

(iii) In many cases, freezing nuclei are solid crystalline particales which have plane surface lattices of equilateral triangular or regular square or rectangular type. The (0, 0, 0, 1)-plane of ice is an equilateral triangular lattice whose lattice constant is 4.53 Å while it is a double rectangular lattice too. Hence, one can so put a lattice of (0, 0, 0, 1)-plane of ice upon a surface lattice of a nucleus that axes of both plane lattices are parallel to each other. In this case, a molecule of the ice lattice can adhere to an atom of nuclear

surface lattice if the transverse displacement between them along the nuclear surface is less than some limit. According to ROYER (1928) [15] the limit of this adhereable displacement is 12% of the lattice constant of ice. Then, many adherent ice molecules will distribute within some domain on the nuclear surface around the point at which the transverse displacement is zero or minimum.

(3rd assumption :) *The author assumes that the ice bud forms on this adhesion domain and the diameter of the domain gives one of the critical diameters of the ice bud on the nuclear surface.*

Moreover, considering that many adhesion domains on a nuclear surface should be placed at equal distance with one another because of the periodicity of both lattices, *the author assumes that the ice bud whose base diameter spans two neighbouring adhesion domains and the one whose base diameter stretches over three neighbouring adhesion domains also are allowed to form on the nuclear surface.*

In this way, from the lattice structure and lattice constant of nuclear surface, one can calculate the critical values of base diameters of the ice buds which can be formed on the surface. These critical diameters give, as shown in (ii), the higher limits of the freezing temperatures in the lengthwise direction of the ice buds, which are nothing other than the critical freezing temperatures characteristic to the nucleus. The results of calculation agree well with the critical freezing temperatures due to many sorts of nuclear substance, (AgI, PbI₂, CdI₂, NaNO₃, CuI, NH₄I, KI, NaCl, MgO, NaF, CdO, I₂, CsI) which were obtained in the experiments by many persons above mentioned. Especially, according to the author's theory, two or more critical temperatures may exist for one sort of nuclear substance, which proved to be true for AgI (-3°C, -12°C), CdI₂ (-9.5°C, -15°C, -41°C) and NaCl (-15°C, -41°C).

In short, the author explains systematically, upon the basis of his three assumptions, many critical temperatures concerning to the freezing of supercooled water that were obtained hitherto experimentally.

2 The interfacial free energy between ice and water

Freezing is in no way a phenomenon in equilibrium. Hence, one can not define precisely in usual thermodynamical sense the interfacial free energy between ice and water which is prevailing in the process of freezing, especially in the beginning process of freezing. A reason for the author's assumption on the interfacial free energy is given in the sense of usual thermodynamics in the following which is of course not very adequate.

The plane interface between ice and water can be regarded as a molecular layer composed of equal number of ice and water molecules. Mean inner energy per molecule of this layer is

$$\frac{1}{2} (2\alpha_w + 2\alpha_i) = \alpha_w + \alpha_i = \alpha + 2\alpha_i,$$

where, $2\alpha_w$ = inner energy per molecule of water

$2\alpha_i$ = inner energy per molecule of ice

$$\alpha = \alpha_w - \alpha_i$$

Hence, this is higher than the inner energy of ice per molecule by α . On the other hand,

there must be the entropy due to the mixing of these two sorts of molecules in this layer. Mixing of $n/2$ ice molecules and $n/2$ water molecules produces the entropy

$$k \log \frac{n!}{\left(\frac{n}{2}\right)! \left(\frac{n}{2}\right)!}$$

which leads to

$$k \log \frac{n^n}{\left(\frac{n}{2}\right)^{n/2} \left(\frac{n}{2}\right)^{n/2}} = nk \log 2$$

when n becomes large. Therefore increase in entropy due to the mixing in this layer is $k \log 2$ per molecule.

In general, free energy is defined as

$$(\text{free energy}) = (\text{inner energy}) - (\text{entropy}) \times (\text{temperature}).$$

Hence, free energy per molecule of this layer is higher than that of ice molecule by $\alpha - kT \log 2$. The author considers the interfacial free energy per molecule to be

$$\begin{aligned} & (\text{free energy of the interfacial layer per molecule}) \\ & - (\text{free energy of ice per molecule}) \end{aligned}$$

which is equal to $\alpha - kT \log 2$.

Though the ratio of mixing may not strictly be 1 : 1, it is sure that the ratio is nearly 1 : 1. In this case, if, for example, we assume the ratio were $\rho_i^{2/3} : \rho_w^{2/3}$ where ρ_i means the density of ice and ρ_w means that of water, this ratio is very near to 1 : 1 and hence the interfacial free energy calculated in the same way as above is not much different from $\alpha - kT \log 2$.

The interfacial free energy or in other words, the increase in free energy at the interface is caused by the irregular motion of the water molecules contacting closely with the interface. Hence, the interfacial free energy shall be counted on each of these water molecules.

Now, let σ , N , V denote interfacial free energy per unit area of plane interface, AVOGADO'S number, volume of one gram molecule of ice respectively, then

$$\sigma = \frac{\alpha - kT \log 2}{\left(\frac{V}{N}\right)^{2/3}} \quad (1)$$

Though, to-day, precise configuration of molecules on the interface and the mean of the area occupied by each molecule are unknown, the above expression of σ will hit at least the essential part of the matter. Values of σ calculated from (1) are given in Table 2.

Table 2. Values of $\sigma = \left(\frac{V}{N}\right)^{-2/3} (\alpha - kT \log 2)$

T°C	0.0	-10	-20	-30	-40	-50	-60
σ erg/cm ²	23.4	20.9	18.4	15.9	13.4	10.9	8.4

Among these values, the value 18.4 erg/cm² at -20°C coincides with the value 18.5 erg/cm² at -20°C which was evaluated in other way by OURA (1950) [13]. The VOLMER's method

(see WEIKMANN (1951) [3])for the estimation of σ gives the following.

T°C	0	-10	-20	-30	-40	-50	-60
σ erg/cm ²	10.0	10.2	10.4	10.6	10.8	11.0	11.2

This method is based upon the idea that

$$\frac{\sigma}{\text{surface tension of water}} = \frac{\text{latent heat of fusion}}{\text{latent heat of vaporisation}}$$

However, this idea has no theoretical nor experimental foundation. MASON (1952) [14] estimated σ at -40°C to be 22 erg/cm² which differs from the author's estimation. MASON seems to have weak reason for his estimation because σ has never been observed directly and hence his assertion that

$$\sigma + \text{surface tension of water} = \text{surface tension of ice}$$

has not yet been proved theoretically nor experimentally.

3 The ice bud and the temperature at which it forms

As stated in 1, it is assumed that the ice bud formed on a surface of the freezing nucleus is a single crystal of hexagonal prism having its main axis perpendicular to the nuclear surface. Let the ice bud be composed of x number of molecules in the main axis and l number of molecules in the radius, then the ice bud is made of $6l^2x$ molecules. The effective number of water molecules which directly surround the ice bud and have effects on the interfacial free energy will be

$$6l^2 + 6(x-1)(2l+1).$$

Hence, the increase ΔF in free energy due to the formation of the ice bud will be given by

$$\begin{aligned} \Delta F &= 6l^2x(\mu_B - \mu_A) \\ &+ 6\{l^2 + (x-1)(2l+1)\}(\alpha - kT \log 2) \end{aligned}$$

The ice bud suffers bombardment of water molecules from the surroundings and hence it can not keep its solid form if the number of the molecules composing it were less than that of the water directly surrounding it.

Therefore, a condition for the existence of the ice bud may be

$$6l^2x \geq 6\{l^2 + (x-1)(2l+1)\}$$

which reduces to

$$(x-1)(l^2 - 2l - 1) \geq 0$$

This gives the condition :

$$x \geq 1 \quad \text{and} \quad l \geq 2.41$$

On the other hand, both x and l must be positive integer. Thus, the ice bud whose radius l is less than 3 can not exist except when $x=1$. If $\frac{\partial(\Delta F)}{\partial x} < 0$ or $\frac{\partial(\Delta F)}{\partial l} < 0$, the ice bud grows and the freezing advances. If $\frac{\partial(\Delta F)}{\partial x} > 0$ or $\frac{\partial(\Delta F)}{\partial l} > 0$, the ice bud con-

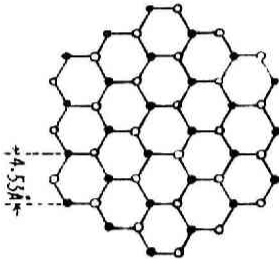
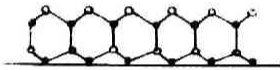


Fig. 1. an ice bud
 $l=3 \quad x=2$

tracts and the freezing does not begin.

The conditions for the equilibrium of the ice bud in l - and x -direction are $\frac{\partial(\Delta F)}{\partial l} = 0$, and $\frac{\partial(\Delta F)}{\partial x} = 0$, respectively. These give also the temperature at which the ice bud begins to grow in respective direction.

One obtains from $\frac{\partial(\Delta F)}{\partial x} = 0$,

$$\frac{l^2}{2l+1} = - \frac{\alpha - kT \log 2}{\mu_B - \mu_A} \dots\dots\dots \text{(in the } x\text{-direction),} \quad (2)$$

and from $\frac{\partial(\Delta F)}{\partial l} = 0$,

$$\frac{l x}{l+x-1} = - \frac{\alpha - kT \log 2}{\mu_B - \mu_A} \dots\dots\dots \text{(in the } l\text{-direction).} \quad (3)$$

The equation (2) and (3) may be put together in one equation as follows :

$$-\frac{q}{2} (\mu_B - \mu_A) + \alpha - kT \log 2 = 0 \quad (4)$$

where $\frac{q}{2} = \frac{l^2}{2l+1} \dots\dots\dots \text{(in the lengthwise direction)}$

$$\frac{q}{2} = \frac{l x}{l+x-1} \dots\dots\dots \text{(in the radial direction)}$$

If $x \geq l-1$, then $\frac{l x}{l+x-1} > \frac{l^2}{2l+1}$.

If $x < l-1$, then $\frac{l x}{l+x-1} < \frac{l^2}{2l+1}$.

The temperature which satisfies the equation (4) is high or low according as q is large or small.

Hence, if $x \geq l-1$, the freezing begins in the direction of main axis at lower temperature than in the direction of radial axis, that is to say, these rather long ice buds begin to grow at first in the direction of radial axis in the course of cooling. And, if $x < l-1$, these rather short ice buds begin to grow at first in the direction of main axis in the course of cooling. The freezing temperatures of the ice buds of various sizes are thus calculated from the equation (4) which are tabulated in Table 1. Hitherto, the author has dealt only with the perfect single crystal of ice bud. Non-perfect single crystals may form in reality. If an ice bud is of slightly deformed form or is in excess or short of some few ice molecules compared with the perfect single crystal, ΔF of the former will be higher than that of the latter. The latter is physically more stable than the former. The latter freezes at higher temperature than the former. Hence, the latter, the perfect single crystal gives critical freezing temperature.

4 Critical freezing temperatures below -20°C due to the freezing nuclei in the atmosphere

(A) -41°C

The ice buds are apt to form on those localities of nuclear surface whose plane lattice

structures are akin to that of the base of the ice bud. In this case, the configuration of atoms on the nuclear surface shall be called to account.

The ice bud indicated by $x=1$, $l=1$, and $T=-40.3^{\circ}\text{C}$, is composed of 6 molecules among which 3 molecules are apt to adhere to the nuclear surface because of their near situations to it. The 3 atoms on the nuclear surface to which these 3 molecules adhere may, in considerable probability and independently of the sorts of nuclear substance, be situated near the each apex of a regular triangle whose side length is 4.53 Å (the lattice constant of ice), because the number of them is only three. The result of FOURNIER DALBE's experiment [4] shows that many sorts of nuclear substance have the critical freezing temperature at -41.2°C . This fact suggests that the above explanation is reasonable.

It is easily accepted that the larger the base of the ice bud the less probable is the configuration of atoms on the nuclear surface which conforms to the ice bud. It is no doubt that the suitable positions on the nuclear surface for the generation of an ice bud having the radius $l=1$ and the sorts of nuclear substance which have those suitable positions on their surface are both far numerous compared with the case of the larger radius of ice buds. This is the reason why apparently clean air in the upper atmosphere shows marked critical temperature at -41°C for the ice formation.

The author considers the critical temperature at -41°C to be the freezing temperature of an ice bud indicated by $x=1$, $l=1$ or 2, $T=-40.3^{\circ}\text{C}$.

(B) -35°C

According to the experiment by ASADA (1952) [8] a critical freezing temperature at -35°C has been shown. BIGG (1953) [5] gave his result of experiment in a graph of freezing temperature of droplets against their diameter which shows two knick points at -35°C and -31.5°C . The author considers this temperature to be the freezing temperature due to the formation of an ice bud indicated by $x=1$, $l=3$, $T=-34.8^{\circ}\text{C}$.

(C) -32°C and -29°C

The critical temperature at -32°C seems to be the freezing temperature due to the freezing in the radial direction of an ice bud indicated by $x=2$, $l=3$, $T=-31.6^{\circ}\text{C}$ so far

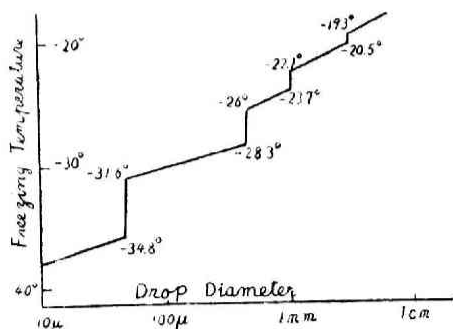


Fig. 2.

as only the temperature apparently concerns. Surely the freezing temperature of a drop is a function of its diameter, but it is also effected by the size of the ice bud which is controlled by the plane lattice structure of nuclear surface. This effect causes the knick points at -35°C and -31.5°C in the graph of BIGG's experiment [5]. The author considers the result of BIGG's experiment should be so expressed by a polygonal line having 8 knick points on it as shown schematically in Fig. 2.

Among these 8 temperatures all of which are quoted from Table 1, 4 temperatures -34.8°C , -28.3°C , -23.7°C , and -20.5°C are due to the freezing in the direction of main axis of the ice bud having the sizes $l=3$, $l=4$, $l=5$, and $l=6$, respectively, and remaining 4 temperatures -31.6°C , -26°C , -22.1°C , and -19.3°C are due to the freezing in

the radial direction of the ice buds having the sizes $l=3, x=2$; $l=4, x=3$; $l=5, x=4$; and $l=6, x=5$ respectively.

The author considers that the temperature of FINDEISEN's 2nd class nuclei, -29°C , is due to the ice bud above mentioned, indicated by $l=4, T=-28.3^{\circ}\text{C}$.

5 Plane lattice structures of (0,0,0,1)-plane of ice and the surfaces of freezing nuclei

The author regards the surface of freezing nucleus as a crystalline plane where atoms are arranged as to make a plane lattice. Almost all of various nuclear substances have a crystalline surface making a regular triangular or a regular square or a rectangular plane lattice. Some of them are listed below, among which (0, 0, 0, 1)-plane of ice — the base of an ice bud — is contained. It attracts ones attention that the base plane of ice bud is a regular triangular lattice on the one hand and a rectangular lattice on the other. This fact enables the ice bud to form on various nuclear substances inspite of their varieties of space lattice structures and constants.

A list of plane lattice structures of various surfaces of nuclear substances.

nuclear substance	crystal system	index of the surface plane	plane lattice type	plane lattice const.		
				a (Å)	b (Å)	
Ice	Hex.	(0,0,0,1)	reg. tri.	4.53	7.846	
"	"	"	rectangular	4.53		
AgI	Hex.	(0,0,0,1)	reg. tri.	4.58	7.846	
CdI ₂	"	"	"	4.24		
PbI ₂	"	"	"	4.54		
NaNO ₃	Hex. (Rhombohed.)	(1,1,1)	"	5.152		
NH ₄ I	Cub.	"	"	5.121		
NaI	"	"	"	4.569		
KI	"	"	"	4.986		
CdO	"	"	"	3.309		
NaF	"	"	"	3.266		
MgO	"	"	"	2.969		
NaCl	"	"	"	3.980		
CuI	"	"	"	4.272		
CsI	"	"	"	6.452		
NaCl	Cub.	(0,0,1)	reg. square	5.628		7.846
"	"	"	"	3.980		
KI	"	"	"	7.052		
NaF	"	"	"	4.62		
MgO	"	"	"	4.20		
CdO	"	"	"	4.68		
NaI	"	"	"	4.569		
NH ₄ I	"	"	"	5.121		
CuI	"	"	"	4.272		
CsI	"	"	"	4.562		
I ₂	Rhombic	(0,0,1)	rectangular	4.795	7.255	
CsI	Cub.	(0,1,1)	"	4.562	6.45	

6 The condition for and the domain of the adhesion of the ice-bud-base to the regular triangular lattice of nuclear surface; The critical freezing temperature and the base-diameter of the ice bud formed on the adhesion domain

The (0, 0, 0, 1)-plane of ice is a regular triangular lattice on one hand and a rectangular lattice on the other. Put this on a nuclear surface of any one of the three

lattice types stated in 5, and let us consider the adhesion which may occur between these two surfaces. One can always put the former so as each axis of it to be parallel to that of the latter. If the distance along the nuclear surface between an atom on the nuclear surface and a molecule at a lattice point of ice surface is less than certain limit, the atom and the ice molecule can adhere to each other. According to the study by ROYER [15] on the epitaxial between two crystals, the limit of the distance along the nuclear surface which admits the mutual adhesion is 12 per cent of the lattice constant of ice in each direction of axes of the surface lattice, that is to say, the limit is $4.53\text{\AA} \times 0.12$ in the direction of each axis.

The transverse distance between the atom and the ice molecule varies periodically as we go along the nuclear surface from one place of it to the farther. Henceforth, let us consider the case where the plane lattice of the nuclear surface is a regular triangular one. In this case, the lattice points where the adhesion occurs distribute in a hexagonal domain on the nuclear surface, at the centre of which the transverse distance between nuclear lattice point and ice lattice point is zero or minimum.

The author assumes that the base of the ice bud which can form on the nuclear surface is limited within this domain of adhesion. This assumption is the same as the ROYER's [15] and also as the WEIKMANN's [3]. From now on, the author calls this domain of adhesion "the central adhesion domain".

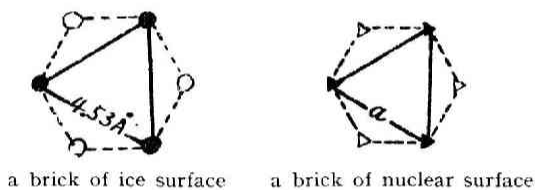


Fig. 3.

After the example of ROYER, one can regard the base of the ice bud to be composed of many hexagonal "bricks" and also similarly as for the nuclear surface. Let m denote the number of ice bricks on the diameter of the central adhesion domain,

then m is given by the integer part of the ratio $(2 \times 0.12 \times 4.53\text{\AA}) : (\text{difference between } a \text{ and } 4.53\text{\AA})$. For example, in the case of (0, 0, 0, 1)-plane of AgI, $a = 4.53\text{\AA}$, and from

$$\frac{2 \times 0.12 \times 4.53 \text{ \AA}}{4.58 \text{ \AA} - 4.53 \text{ \AA}} \approx 21.7$$

we have $m = 21$.

The radius l of the largest ice bud which can be formed on given nuclear surface, is determined from m , as

$$\begin{aligned} 2l &= m && \text{when } m \text{ is even,} \\ 2l - 1 &= m && \text{when } m \text{ is odd.} \end{aligned}$$

This maximum radius l determines the critical freezing temperature T for the nuclear surface, that is to say, the critical temperature is equal to the temperature due to the freezing in the direction of main axis of the ice bud having the size l , with the exception that when $l = 1$ or $l = 2$, T is given as the freezing temperature in the direction of radius ($T = -40.3^\circ\text{C}$). Hence, one can easily calculate T with given l from eq. (2).

m	l	T (°C)	m	l	T (°C)
1,2,3,4	1,2	-40.3	12,14	7	-18.0
5,6	3	-34.8	15,16	8	-15.9
7,8	4	-28.3	17,18	9	-14.4
9,10	5	-23.7	19,20	10	-13.3
11,12	6	-20.5	21,22	11	-12.2

For example, AgI-nucleus will show the critical temperature at -12.2°C because of $m=21$ and hence $l=11$. In this manner, the critical temperatures due to the central adhesion domains of several nuclei are calculated and listed below.

Table 3. Critical temperature due to the central adhesion domains of several nuclear surfaces having regular triangular lattice.

nuclear substance	crystal system	index of the surface	m	l	T (°C)
AgI	Hex.	(0,0,0,1)	21	11	-12.2
PbI ₂	"	"	108	54	-2.81
CdI ₂	"	"	3	2	-40.3
NaNO ₃	Hex. (Rhomboh.)	(1,1,1)	1	1	-40.3
CuI	Cub.	(1,1,1)	4	2	-40.3
NH ₄ I	"	"	1	1	-40.3
KI	"	"	2	1	-40.3
NaI	"	"	27	14	-9.35
NaF	"	"	0	0	—
MgO	"	"	0	0	—
CdO	"	"	0	0	—
CsI	"	"	0	0	—

There are many central adhesion domains on a nuclear surface situated at equal distance from one another as shown in Fig. 4.

This distance is nearly equal to $m_1 \times 4.53\text{\AA}$ and also to $m_1' a$, where m_1 and m_1' are both integers and mutually prime.

The author assumes that the ice bud can form on the large hexagonal area

whose diameter spans two neighbouring central adhesion domains. This area is called "the

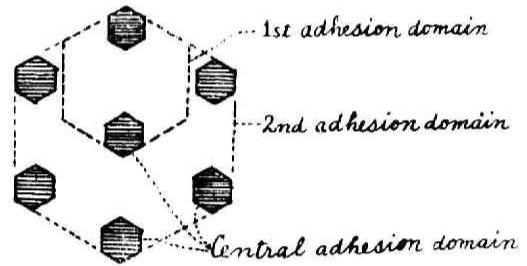


Fig. 4.

Table 4. Freezing temperatures for several nuclei having regular triangular surface lattice.

nuclear substance	index of the surface	centr. ad. d.		1st ad. d.			2nd ad. d.		
		m	T (°C)	m_1	m_1'	$m+m_1$	T (°C)	$m+2m_1-1$	T (°C)
AgI	(0,0,0,1)	21	-12.2	92	91	113	-2.80		
PbI ₂	"	108	-2.81						
CdI ₂	"	3	-40.3	15	16	18	-14.4	32	- 8.7
NaNO ₃	(1,1,1)	1	-40.3	17	15	18	-14.4	34	- 8.3
CuI	"	4	-40.3	16	17	20	-13.3	35	- 8.5
NH ₄ I	"	1	-40.3	17	15	18	-14.4	34	- 8.5
KI	"	2	-40.3	11	10	13	-18.0	25	-11.2
NaI	"	27	- 9.4						
NaCl	"	1	-40.3	7	8	8	-28.3	14	-18.0

1st adhesion domain."

Further, the author assumes also *that the ice bud can form on a more large hexagonal area whose radius spans two neighbouring central adhesion domains*. This area is called "the 2nd adhesion domain." The number of ice bricks on the diameter of the 1st adhesion domain is $m+m_1$, and that of the 2nd adhesion domain is $m+2m_1-1$. The freezing temperatures of the ice buds which form on these two adhesion domains are calculated in the same way as on the central adhesion domain, and the results are listed below.

Now, these results of calculation will be compared with the observed temperatures.

(A) (0, 0, 0, 1)-surface of AgI

The critical temperature of AgI-nucleus was observed at -3°C by HOSLER [9] and at -2.9°C by CwILONG [16] both of which well coincide with the calculated temperature at -2.8°C of the 1st adhesion domain.

Another critical temperature, between -11°C and -12°C , was reported by FOURNIER DALBE [4] which accords well with the calculated one at -12.2°C of the central adhesion domain.

(B) (0, 0, 0, 1)-surface of PbI_2

HOSLER [9] observed the critical temperature at -4°C which accords fairly well with the calculated one at -2.81°C of the central adhesion domain.

(C) (0, 0, 0, 1)-surface of CdI_2

Three critical temperatures are observed, namely, at -41.2°C and -9.5°C by FOURNIER DALBE [4] and at -15°C by HOSLER [9]. The observed temperature at -41.2°C accords with the calculated one at -40.3°C of the central adhesion domain.

The observed temperature at -15°C accords with the calculated one at -14.4°C of the 1st adhesion domain.

The observed temperature at -9.5°C accords with the calculated one at -8.7°C of the 2nd adhesion domain.

(D) (1, 1, 1)-surface of NaNO_3

FOURNIER DALBE [4] observed the critical temperature at -41.2°C which accords with the calculated one at -40.3°C of central adhesion domain. Two calculated temperatures, -14.4°C and -8.3°C have not been ascertained by observation which may be due to the fact that the usual cleavage surface of NaNO_3 is not the (1, 1, 1)-surface but the (2, 1, 1)-surface. Anyhow, further investigation is desirable concerning with this nucleus.

As for the nuclei belonging to the hexagonal system, the assumption that their surfaces are (0, 0, 0, 1)-surface seems appropriate because of these four examples.

As for the nuclei belonging to the cubic system, the assumption that their surfaces are (1, 1, 1)-surface is somewhat doubtful. Nevertheless, the positive evidence that they are any other than (1, 1, 1)-surface has not yet been observed. Though merely through an indirect way, the author will show in the followings that some of them may be regarded as (1, 1, 1)-surface so far as the author's theory and the observed freezing temperature concern.

(E) (1, 1, 1)-surface of CuI

HOSLER [9] observed the critical freezing temperature for CuI-nucleus at -9°C . This accords fairly well with the calculated temperature, -8.0°C , of the 2nd adhesion domain.

Two calculated temperatures, -40.3°C and -13.3°C have not been ascertained by observation. The crystal of CuI is composed of two equal sized face centred cubic lattices one of which is made of I-atoms only and the other of which is made of Cu-atoms only. The relative displacement of each I-atom from each Cu-atom is $(a_0/4, a_0/4, a_0/4)$, where a_0 is the lattice constant. Hence, the plane perpendicular to this displacement, that is to say the (1, 1, 1)-plane is apt to become the surface of cleavage.

(F) (1, 1, 1)-surface of NH_4I

HOSLER [9] observed the critical temperature of NH_4I -freezing-nucleus at -9°C . This accords well with the calculated freezing temperature at -8.3°C due to the 2nd adhesion domain. It is not certain whether the NH_4I -nucleus has usually a (1, 1, 1)-plane as its surface or not. However, according to the author's theory, the (0, 0, 1)-surface of NH_4I , the regular square lattice, has no place for the adhesion of one brick of ice.

(G) (1, 1, 1)-surface of KI

HOSLER [9] observed the critical temperature of KI-freezing-nucleus at -13°C , which does not accord with the calculated one, -11.2°C , of the 2nd adhesion domain on the (1, 1, 1)-surface.

(H) (1, 1, 1)-surface of NaI

HOSLER [9] observed the critical temperature for NaI-freezing-nucleus at -13°C , which does not accord with the calculated temperature, -9.35°C , of central adhesion domain on the (1, 1, 1)-surface. Hence, NaI-nucleus seems to have no surface of (1, 1, 1)-plane. Moreover, according to the authors theory, the regular square lattice of (0, 0, 1)-surface nor the rectangular lattice of (1, 1, 0)-surface of NaI-nucleus has no place for the adhesion of only one brick of ice. According to Mellor (A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. II, p. 596 ~ 621) solution of NaI has a transition point of stable hydrates from $\text{NaI}\cdot 2\text{H}_2\text{O}$ to $\text{NaI}\cdot 5\text{H}_2\text{O}$ at -13.5°C above which $\text{NaI}\cdot 2\text{H}_2\text{O}$ is stable and below which $\text{NaI}\cdot 5\text{H}_2\text{O}$ is stable. The critical temperature obtained by Hosler seems to be concerned with this transition point, because both of his experiments, in the case of very small droplets of NaI-solution and in the case of vapour (small powder) nuclei of NaI, gave the same result, -13°C . In the latter case of his experiments, vapour nuclei of NaI must have dissolved in the water droplets as soon as they touched them and have made up the droplet of NaI-solution which must have frozen at -13.5°C as the small crystal of $\text{NaI}\cdot 5\text{H}_2\text{O}$ appeared.

(I) (1, 1, 1)-surface of NaCl

Two critical temperatures are obtained by FOURNIER DALBE [4] at -41.2°C and by BIRSTEIN [10] at -15°C . The former accords well with the calculated temperature of central adhesion domain, -40.3°C , while the latter can not be explained by the regular triangular lattice of (1, 1, 1)-surface. The author will discuss the case of regular square lattice of (0, 0, 1)-surface of NaCl in the following paragraph.

(J) (1, 1, 1)-surfaces of NaF, CdO, MgO, and CsI

These surfaces cannot cause the formation of ice buds because as seen in Table 3, all m 's of these surfaces are zero.

7 The base diameters and the freezing temperatures of the ice buds formed on the regular square surface lattices of freezing nuclei

To deal with this problem, the (0, 0, 0, 1)-surface of ice must be regarded as a rectangular lattice having the longitudinal constant $\bar{a}=4.53 \text{ \AA}$ and the lateral constant $\bar{b}=7.846 \text{ \AA}$.

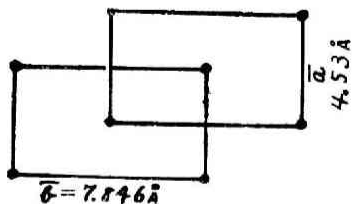


Fig. 5. the rectangular double lattice of (0,0,0,1)-surface of ice.

The maximum of the transversal displacement along b -axis from an atom of nuclear surface to a molecule of base surface of ice, which allows them to adhere to each other, must be taken as $0.12 \times 4.53 \text{ \AA}$, and not as $0.12 \times 7.846 \text{ \AA}$.

The adhesion domain on which the ice bud can form must be considered from two conditions of \bar{a} -axis and \bar{b} -axis of the ice base at a time. After the examples of the central, 1st and 2nd adhesion

domains in the preceding paragraph, the author considers now the central, 1st and 2nd ranges on each of longitudinal and lateral axis,.

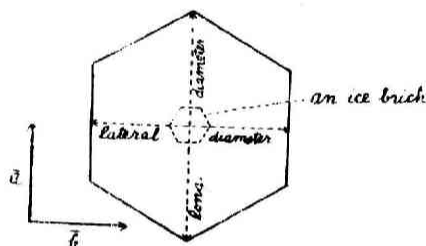


Fig. 6. longitudinal and lateral diameter of an ice bud.

The author assumes that each of the central, 1st and 2nd adhesion ranges on the lateral axis can afford the ice buds having the lateral diameter (see Fig. 6) less than or equal to respective each of them, provided there is a central adhesion range on the longitudinal axis capable of at least one ice brick.

(A) (0, 0, 1)-surface of NaCl

The (0, 0, 1)-surface of NaCl is a twofold regular square lattice of $a = a_0/\sqrt{2} = 3.98 \text{ \AA}$. Adhesion on the longitudinal axis :

$$4.53 \text{ \AA} - 3.98 \text{ \AA} = 0.55 \text{ \AA} \quad \dots\dots\dots \text{ difference of lattice constants}$$

$$\frac{2 \times 0.5436 \text{ \AA}}{0.55 \text{ \AA}} \approx 1.9 \quad \dots\dots\dots \text{ the longitudinal condition is satisfied}$$

Adhesion on the lateral axis :

$$2 \times 3.98 \text{ \AA} - 7.846 \text{ \AA} = 0.114 \text{ \AA} \quad \dots\dots \text{ difference of lattice constants}$$

$$\frac{2 \times 0.5436 \text{ \AA}}{0.114 \text{ \AA}} \approx 9.5 \quad \dots\dots\dots \text{ central adhesion range on the lateral axis,}$$

which reaches to $7.846 \text{ \AA} \times 9$

Hence, the number of ice bricks on the lateral diameter of the ice bud reaches to $9 \times 2 = 18$, and the critical temperature due to the freezing in the direction of main axis of the ice bud is calculated to be -14.4°C . This accords well with the experimental result by BIRSTEIN [10], -15°C .

(B) (0, 0, 1)-surface of KI

The (0, 0, 1)-surface of KI is a regular square lattice of alternately arranged I-atoms and K-atoms having the lattice constant 3.526 \AA .

Adhesion on the longitudinal axis :

$$4.53 \text{ \AA} - 3.526 \text{ \AA} = 1.004 \text{ \AA} \quad \dots\dots \text{ difference of lattice constants}$$

$$\frac{2 \times 0.5436 \text{ \AA}}{1.004 \text{ \AA}} \approx 1.07 \quad \dots\dots\dots \text{ the longitudinal condition is satisfied}$$

Adhesion on the lateral axis :

$$7.846 \text{ \AA} - 3.526 \text{ \AA} = 4.320 \text{ \AA} \dots\dots \text{ difference of lattice constants}$$

$$\frac{2 \times 0.5436 \text{ \AA}}{4.320 \text{ \AA}} \approx 0.2 \dots\dots\dots \text{ no central adhesion range}$$

$$\begin{matrix} \text{(ice)} & & \text{(KI)} \\ 9 \times 7.846 \text{ \AA} & - & 20 \times 3.526 \text{ \AA} = 0.094 \text{ \AA} \end{matrix}$$

$$10 \times 7.846 \text{ \AA} - 22 \times 3.526 \text{ \AA} = 0.888 \text{ \AA} < 2 \times 0.5436 \text{ \AA}$$

Hence, the 1st adhesion range on the lateral axis spans $10 \times 7.846 \text{ \AA}$ in length on which the ice bud of radius size $l=10$ can form at $-13.^\circ\text{C}$, the freezing temperature in the direction of its main axis. This temperature corresponds to the critical temperature, -13°C , obtained by HOSLER [9] in his experiment.

(C) (0, 0, 1)-surface of NaF

As for the Na-atoms and also as for the F-atoms, the (0, 0, 1)-surface of NaF is a twofold regular square lattice having the constant, $a=4.62 \text{ \AA}$. It is also a regular square lattice of alternately arranged Na-atoms and F-atoms having the lattice constant $a/2=2.31 \text{ \AA}$. The lateral lattice constant of ice \bar{b} ($=7.846 \text{ \AA}$) contains two brick widths. Therefore, the lateral width of an ice brick is $\bar{b}/2=3.923 \text{ \AA}$ which can, in the present problem, be regarded as the lateral lattice constant of ice.

Adhesion on the longitudinal axis :

$$4.62 \text{ \AA} - 4.53 \text{ \AA} = 0.09 \text{ \AA} \dots\dots\dots \text{ difference of lattice constants}$$

$$\frac{2 \times 0.5436 \text{ \AA}}{0.09 \text{ \AA}} \approx 12.1 \dots\dots\dots \text{ the longitudinal condition is satisfied}$$

Adhesion on the lateral axis :

$$4.62 \text{ \AA} - 3.923 \text{ \AA} = 0.697 \text{ \AA} \dots\dots\dots \text{ difference of lattice constants}$$

$$\frac{2 \times 0.5436 \text{ \AA}}{0.697 \text{ \AA}} \approx 1.5$$

Hence, the central adhesion range on the lateral axis has one brick of ice. ($l=1$, $T=-40.3^\circ\text{C}$)

$$\begin{matrix} \text{(ice)} & & \text{(NaF)} \\ 16 \times 3.923 \text{ \AA} & - & 27 \times 2.31 \text{ \AA} = 0.398 \text{ \AA} \end{matrix}$$

$$17 \times 3.923 \text{ \AA} - 29 \times 2.31 \text{ \AA} = -0.299 \text{ \AA}$$

Hence the 1st adhesion range on the lateral axis spans 17 bricks of ice on which the ice bud of radius size $l=9$ forms at -14.4°C , the freezing temperature in the direction of its main axis. This temperature explains well the critical temperature, -15°C , obtained by ASADA [8] in his experiment.

(D) (0, 0, 1)-surface of MgO

As for the Mg-atoms and also as for the O-atoms, the (0, 0, 1)-surface of MgO is a twofold regular square lattice having the constant, $a=4.20 \text{ \AA}$.

Adhesion on the longitudinal axis :

$$4.53 \text{ \AA} - 4.20 \text{ \AA} = 0.33 \text{ \AA} \dots\dots\dots \text{ difference of lattice constants}$$

$$\frac{2 \times 0.5436 \text{ \AA}}{0.33 \text{ \AA}} \approx 3.3 \dots\dots\dots \text{ the longitudinal condition is satisfied}$$

Adhesion on the lateral axis :

$$4.20 \text{ \AA} - 3.923 \text{ \AA} = 0.277 \text{ \AA} \dots\dots\dots \text{ difference of lattice constants}$$

$$\frac{2 \times 0.5436 \text{ \AA}}{0.277 \text{ \AA}} \approx 3.8$$

Hence, the central adhesion range on the lateral axis is capable of 3 bricks of ice, and can afford the ice bud sized $l=2$ at -40.3°C .

$$\begin{array}{cc} \text{(ice)} & \text{(MgO)} \\ 15 \times 3.923 \text{ \AA} - 14 \times 4.20 \text{ \AA} = 0.045 \text{ \AA} \end{array}$$

Hence, the 1st adhesion range on the lateral axis is capable of $(15+3)$ bricks of ice and produces the ice bud sized $l = \frac{15+3}{2} = 9$ at -14.4°C . This temperature explains well the critical temperature obtained by ASADA [8] in his experiment, -15°C .

(E) $(0, 0, 1)$ -surface of CdO

As for the Cd-atoms and also as for the O-atoms, the $(0, 0, 1)$ -surface of CdO is a twofold regular square lattice having the constant, $a=4.68 \text{ \AA}$. It is also a regular square lattice of alternately arranged Cd-atoms and O-atoms, having the constant $a/2=2.34 \text{ \AA}$.

Adhesion on the longitudinal axis:

$$\begin{array}{l} 4.68 \text{ \AA} - 4.53 \text{ \AA} = 0.15 \text{ \AA} \quad \dots\dots\dots \text{ difference of lattice constants} \\ \frac{2 \times 0.5436 \text{ \AA}}{0.15 \text{ \AA}} \approx 7.2 \quad \dots\dots\dots \text{ the longitudinal condition is satisfied} \end{array}$$

Adhesion on the lateral axis:

$$\begin{array}{l} 4.68 \text{ \AA} - 3.932 \text{ \AA} = 0.777 \text{ \AA} \quad \dots\dots\dots \text{ difference of lattice constants} \\ \frac{2 \times 0.5436 \text{ \AA}}{0.777 \text{ \AA}} \approx 1.5 \end{array}$$

Hence, the central adhesion range on the lateral axis is capable of one ice brick. ($l=1$, $m=1$, $T=-40.3^\circ\text{C}$).

$$\begin{array}{cc} \text{(ice)} & \text{(CdO)} \\ 16 \times 3.923 \text{ \AA} - 27 \times 2.34 \text{ \AA} = -0.412 \text{ \AA} \end{array}$$

Hence, the 1st adhesion range on the lateral axis spans $(16+1)$ bricks of ice and produces the ice bud sized $l=9$ at -14.4°C . This temperature explains well the critical temperature obtained by ASADA [8] in his experiment, -15°C .

8 The base diameters and the freezing temperatures of the ice buds formed on the rectangular surface lattices of the freezing nuclei

(A) $(0, 0, 1)$ -surface of I_2

The crystal of I_2 belongs to the rhombic system. The $(0, 0, 1)$ -surface of it is a rectangular lattice having the longitudinal constant $a=4.795 \text{ \AA}$ and the lateral constant $b=7.255 \text{ \AA}$.

Adhesion on the longitudinal axis:

$$\begin{array}{l} 4.795 \text{ \AA} - 4.53 \text{ \AA} = 0.265 \text{ \AA} \quad \dots\dots\dots \text{ difference of lattice constants} \\ \frac{2 \times 0.5436 \text{ \AA}}{0.265 \text{ \AA}} \approx 4.4 \quad \dots\dots\dots \text{ the longitudinal condition is satisfied} \end{array}$$

Adhesion on the lateral axis:

$$\begin{array}{l} 7.846 \text{ \AA} - 7.255 \text{ \AA} = 0.591 \text{ \AA} \quad \dots\dots\dots \text{ difference of lattice constants} \\ \frac{2 \times 0.5436 \text{ \AA}}{0.591 \text{ \AA}} = 1.8 \end{array}$$

Though the central adhesion range on the lateral axis spans $1 \times 7.846 \text{ \AA}$ long ($m=2$), it can not attract one brick of ice because the nuclear surface has no configuration of I-atoms to which 3 molecules of an ice brick can adhere.

(ice) (I)

$$12 \times 7.846 \text{ \AA} - 13 \times 7.255 \text{ \AA} = -0.163 \text{ \AA}$$

Hence, the 1st adhesion range on the lateral axis is capable of 12×2 bricks of ice and produces the ice bud sized $l=12$ at -11.2°C . This temperature explains the critical temperature obtained by HOSLER [9] in his experiment, -12°C .

(B) (0, 1, 1)-surface of CsI

The (0, 1, 1)-surface of CsI is a twofold rectangular lattice as shown in Fig. 7.

Adhesion on the longitudinal axis:

$$4.562 \text{ \AA} - 4.53 \text{ \AA} = 0.032 \text{ \AA} \dots\dots$$

difference of lattice constants

$$\frac{2 \times 0.5436 \text{ \AA}}{0.032 \text{ \AA}} = 33.8 \dots\dots \text{the longitudinal condition is satisfied}$$

Adhesion on the lateral axis:

$$3.923 \text{ \AA} - 3.225 \text{ \AA} = 0.698 \text{ \AA} \dots\dots \text{difference of lattice constants}$$

$$\frac{2 \times 0.5436 \text{ \AA}}{0.698 \text{ \AA}} = 1.5$$

Hence, the central adhesion range on the lateral axis is capable of one brick of ice and produces an ice bud sized $l=1$ at -40.3°C . This temperature explains the critical temperature, -41.2°C , obtained by Fournier Dalbe [4] in his experiment.

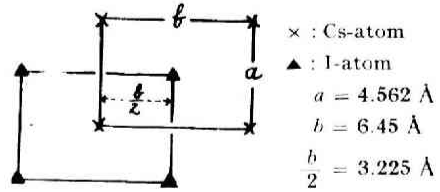


Fig. 7. (0,1,1)-surface of CsI.

9 A table of the author's theoretical results compared with the experiments by several persons on the relation between the critical temperature and the nuclear substance

Table 5. Comparison of the theoretical values with the experimentals.

nuclear substance	nuclear surface	authors theoretical results				experimentals	
		surface lattice	adhesion domain or range	size l	freezing temp. ($^\circ\text{C}$)	critical temp. ($^\circ\text{C}$)	persons
AgI	(0,0,0,1)	triang.	central	11	-12.2	-11~-12	Fournier
"	"	"	1st	57	-2.80	-3	D'albe ⁴⁾
"	"	"	"	"	"	-2.9	Hosler ⁹⁾
PbI ₂	"	"	central	54	-2.81	-4	Cwilong ¹⁰⁾
CdI ₂	"	"	central	2	-40.3	-41.2	Hosler ⁹⁾
"	"	"	1st	9	-14.4	-15	F.D. ⁴⁾
"	"	"	2nd	16	-8.7	-9.5	Hosler ⁹⁾
"	"	"	"	"	"	"	F.D. ⁴⁾
NaNO ₃	Rhomboh	"	central	1	-40.3	-41.2	Fournier
"	(1,1,1)	"	"	"	"	"	D'albe ⁴⁾
CuI	(1,1,1)	"	2nd	18	-8.0	-9	Hosler ⁹⁾
NH ₄ I	"	"	2nd	17	-8.3	-9	Hosler ⁹⁾
NaCl	"	"	central	1	-40.3	-41.2	F.D. ⁴⁾
"	(0,0,1)	square	central	9	-14.4	-15	Birstein ¹⁰⁾
KI	"	"	1st	10	-13.3	-13	Hosler ⁹⁾
MgO	"	"	1st	9	-14.4	-15	Asada ⁸⁾
NaF	"	"	1st	9	-14.4	-15	"
CdO	"	"	1st	9	-14.4	-15	"
I ₂	"	rectang.	1st	12	-11.2	-12	Hosler ⁹⁾
CsI	(0,1,1)	"	central	1	-40.3	-41.2	F.D. ⁴⁾

10 Conclusion

The author draws conclusions briefly as follows.

- (A) The interfacial free energy between ice and water is expressed by $\alpha - kT \log 2$ per molecule of water contacting directly with the interface.
- (B) The ice bud, the hexagonal prism in shape, forms on a crystalline surface of freezing nucleus directing its main axis perpendicular to the surface, at the beginning of freezing.
- (C) The ice buds occur on the adhesion domain of the nuclear surface where the atoms of the domain and the molecules of the ice-bud-base can adhere to each other. The maximum base diameter of the ice bud allowable on a nuclear surface is equal to the diameter of the adhesion domain, which is determined by the relation between the lattice structure of the nuclear surface and that of the base surface of ice. The critical freezing temperature due to a nuclear surface is explained to be the freezing temperature in the direction of main axis of the maximum sized ice bud on that surface.
- (D) The critical temperature, -41°C (Fournier D'albe and others), of the ice particle formation is caused by the formation of the ice bud sized $l=1$ or 2 on a surface of freezing nucleus.

The critical temperature at -35°C is due to the formation of the ice bud sized $l=3$, $x=1$ on a surface of a freezing nucleus.

The critical temperature at about -32°C is due to the formation of the ice bud sized $l=3$, $x=2$ on a surface of a freezing nucleus.

The critical temperature at about -29°C (FINDEISEN) of the ice particle formation in the atmosphere is caused by the formation of the ice bud sized $l=4$ on a surface of a freezing nucleus.

(E) The effects of 17 sorts of freezing nuclei on the freezing temperature of supercooled water are explained reasonably and systematically by author's theory, as shown in Table 5.

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