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Author(s)	YOSIDA, Zyungo
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Surface Structure of Ice Crystal and Its Equilibrium Form*

Zyungo YOSIDA
吉 田 順 五
The Institute of Low Temperature Science
Hokkaido University, Sapporo, Japan

Abstract

It is shown theoretically that crystallographic surfaces (0001), (1$\bar{1}$00) and (11$\bar{2}$0) of ice crystal are rough in structure with numerous molecular steps randomly distributed upon them. On surfaces (0001) and (1$\bar{1}$00) the degree of roughness is practically zero at low temperatures and suddenly rises to a large value at a certain temperature T_c, while the degree increases gradually with the rising temperature in the case of a surface of (11$\bar{2}$0).

When crystallographic surfaces are molecularly rough, they do not develop as surfaces of crystal and the resulting equilibrium form becomes round. Ice granules of an old snow cover are not polyhedral but are round. This fact may be explained by the rough structure of the crystallographic surfaces of ice crystal.

I. Introduction

Burton, Cabrera and Frank (1949, 1951) showed, by the use of theories of cooperative phenomena such as ferromagnetism and molecular rearrangement in alloys, that low index crystallographic surfaces of crystal can become suddenly rough in molecular structure when the temperature passes a certain critical temperature T_c in an ascending temperature course. The present author took another theoretical approach to the molecular structure of three crystallographic surfaces (0001), (1$\bar{1}$00) and (11$\bar{2}$0) of ice crystal, and came to the same conclusion as set forth by the above authors for the first two surfaces, in other words, he found critical temperatures for the first two surfaces above which the surfaces are molecularly rough. In opposition the third surface (11$\bar{2}$0) was found to have no critical temperature but nevertheless became gradually rough with the rising temperature.

The ice granules of old snow cover have the appearance of small pebbles in outer shape, which suggests that the equilibrium form of ice crystal is not polyhedral but round. Crystals are usually bounded by plane surfaces of low indices. But it is known that crystals take a round equilibrium form when low index surfaces are molecularly rough (Herring, 1953; Cabrera and Coleman, 1963). The fact that the ice granules in old snow cover are pebble-like may be explained by the above mentioned rough structure of the low index crystallographic surfaces of ice crystal.

II. Basal Surface (0001) and Prismatic Surface (1$\bar{1}$00)

1. MOLECULAR ARRANGEMENT ON THE SURFACES

Figure 1 and Fig. 2(a) show the respective arrangement of molecules on the basal

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surface (0001) and the prismatic surface $(1\bar{1}00)$ of ice crystal. Figure (b) at the bottom of Fig. 2 is the side view of the surface $(1\bar{1}00)$. Circles and triangles, both open and solid, represent molecules of H_2O of ice which are connected to one another by hydrogen bonds shown by straight segments. Triangles represent one of the molecular net planes of crystal lattice which lie perpendicular to the crystallographic c-axis in case of Fig. 1 and to the crystallographic b-axis in case of Fig. 2. Let the net planes of triangles be called "original surfaces" and be used as reference planes for the crystal surfaces. The circles represent fragments of net planes which lie above and next to the original surfaces. ("Above" or "upward" means "on this side of the paper"). Let such fragments of the net plane be called "positive islands", because they form flat elevations on the original surfaces. If a portion of the net plane constituting the original surface is removed, the net plane lying underneath the original surface will become exposed and there will be a flat depression. Let such a depression be called a "negative island". If islands, either positive or negative, come into being on the original surfaces, the structure of the crystal surfaces becomes rough due to the steps that are inevitably formed at

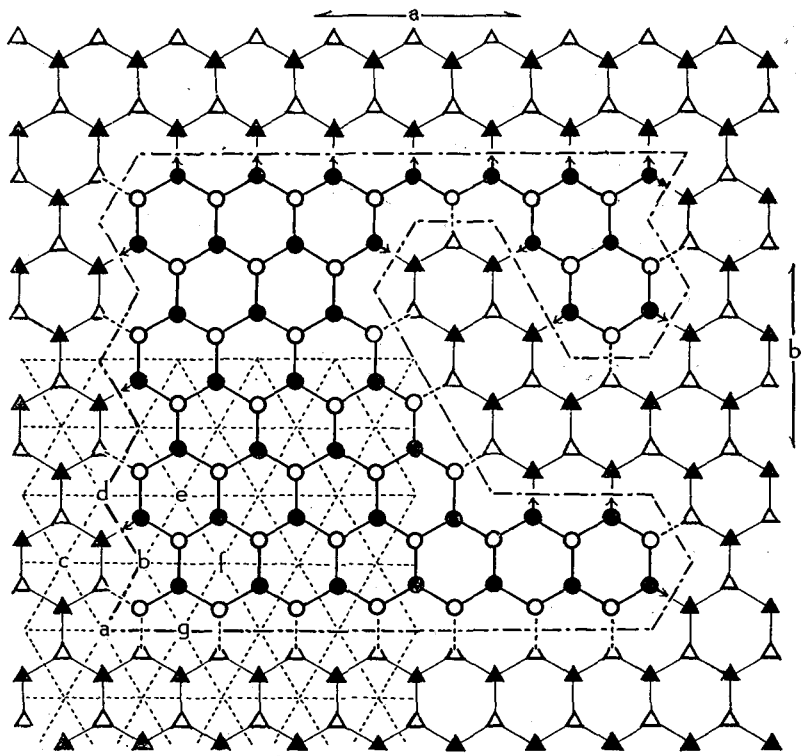

Fig. 1. Arrangement of molecules H_2O on (0001). Molecules are shown by circles and triangles joined by segments representing hydrogen bonds. Triangles, open and solid together, make the original or reference surface. Circles, both open and solid, are the molecules composing a positive island. Molecules of the same shape are assumed to lie evenly to form molecular net planes, although the open ones are actually positioned 0.923 Å above, namely on this side of, the solid ones. The distance between the net planes of circles and triangles measured perpendicular to the plane of paper is 3.694 Å. The two neighbouring molecules of the same shape, for instance open circle and open circle, are 4.524 Å apart

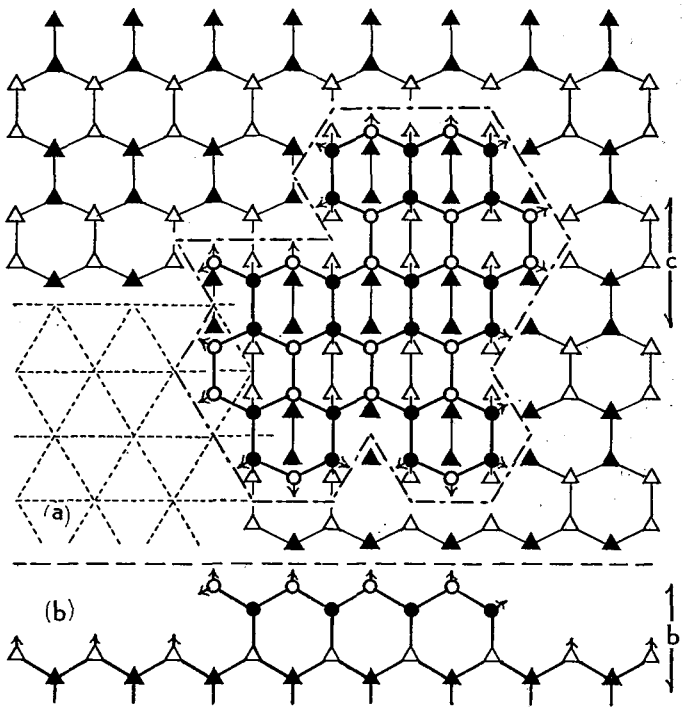

Fig. 2. Arrangement of molecules on $(1\bar{1}00)$. Figure (a) above the horizontal broken line is the plan while Fig. (b) below that line is the elevation in which the arrangement of molecules is the same as that in Fig. 1. Triangles are assumed to make the original net plane and the circles the net plane of a positive island, although open triangles and circles lie actually 1.306 Å above solid triangles and circles respectively

margins of the islands.

Actually the open triangles and circles are located at a slightly displaced upward position with respect to the solid triangles and circles respectively. But our theory is not affected, regardless of whether such displacements are taken into consideration or not. Therefore, for the sake of simplicity, the triangles and circles will be considered to lie on the flat planes as mentioned in the above paragraph.

Though not shown in the figures, a cut hydrogen bond stands upright on each of the open triangles and circles in Fig. 1 and stands slightly inclined on each of the open triangles and circles in Fig. 2 (a). Such cut bonds invariably come into existence if a crystal surface is to be formed at all and are entirely indispensable. The solid circles each have a hydrogen bond directed downward which joins them to the open triangles on the original surface. This results in a diminishing of the indispensable cut bonds by the solid circles which the original surfaces had before the appearance of the islands. But at the same time the open circles bring into existence new cut hydrogen bonds. Therefore the formation of islands does not change the number of the indispensable cut bonds on the crystal surfaces if the open and solid circles composing the islands are, on an average, the same in number. And this is probably the case, because islands form on the crystal surfaces in a considerable number and in variously divergent shapes as

will be described below.

Although the formation of islands brings no change to the number of indispensable cut bonds, it adds to the crystal surface new cut bonds that are produced at the margins of islands almost parallel to the crystal surface. The cut bonds of this type are shown by short arrows or broken segments in Figs. 1 and 2 (a). Let them be briefly called "margin bonds". In Fig. 2 (b) vertical arrows show the indispensable bonds and inclined arrows the margin bonds. Since a cut bond has a larger energy than a joined bond, the energy of a crystal surface increases when islands form upon it. If the excess energy of a cut bond over a joined bond is denoted by ε and total number of margin bonds on the crystal surface by L, the increase E in energy of the surface is given by

$$E = \varepsilon L . \tag{1}$$

Islands can be formed in an exceedingly large number of different ways, in other words, there can be an exceedingly large number of different states for island formation, because their number, position and shape can change over extensively wide range. If the number of different states which the islands can take is denoted by W, the crystal surface is given an excess entropy

$$S = k \ln W , \tag{2}$$

where k is Boltzman's constant. Number W will be found below as a function of L. Excess free energy of the crystal surface due to formation of the islands is given by

$$X = \varepsilon L - kT \ln W , \tag{3}$$

which is function of L with an absolute temperature T. If X has a minimum of negative value at a certain value of L for a temperature, the crystal surface will be more stable with the islands than without, that is to say, the surface will have a rough structure at that temperature.

2. FEATURES OF ROUGH STRUCTURE OF THE CRYSTAL SURFACES

Straight lines connecting centers of the hexagons formed by circles in Figs. 1 and 2 (a) make such lattices as shown by dotted lines near the lower left corners of the figures. These are called dual lattices corresponding to those made by circles. It is convenient to draw margins of the islands on the dual lattices as shown by chain lines in the figures. If the distance a between two adjacent lattice points of the dual lattices is called a "pace", to every pace of the margins one margin bond is assigned. Let a be chosen as the unit of margin length. Then the margin length of an island becomes the same as the number of margin bonds belonging to the island.

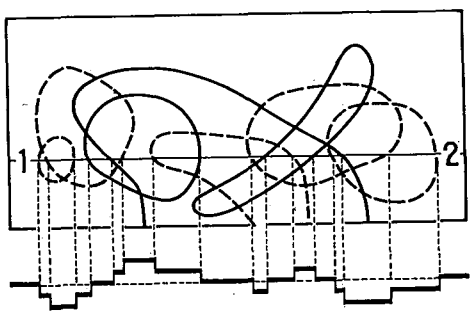

Fig. 3. Closed curves of full line represent positive islands while those of broken line negative islands. The islands overlap one another and give the crystal surface a rough structure. The bottom figure shows the side view of the section made along line 1–2

In Fig. 3, areas enclosed by solid curves represent positive islands while those en-

closed by broken curves represent negative islands. The islands lie one upon another and the spots covered by m positive islands and n negative islands have an $(m-n)\,\delta$ elevation above the original surface. Here δ is the distance between adjacent molecular net planes. It is assumed that islands form on the crystal surface in such a manner and give it the rough structure of which the profile is shown at the bottom of the figure.

3. NUMBER m_i OF DIFFERENT SHAPES OF AN ISLAND

In order to evaluate W, it is necessary to know how many different shapes an island of a definite margin length can take. Let the margin length and the number of different shapes be denoted by l_i and m_i respectively.

(A) Let p denote the coordination number of the dual lattices, namely, the number of lattice points surrounding one of the lattice points. As seen from Figs. 1 and 2 (a), p is equal to 6. If we walk l_i paces on the dual lattices $(p-1)^{l_i}$ paths of different shapes may be traced, because we can take $(p-1)$ different directions at every pace. A small fractions $m_i'=\beta\,(p-1)^{l_i}$ of these paths will come back to the starting point to close; and the closed paths can be margins of the island, for margins are nothing but closed paths on the dual lattices.

If, instead of $(p-1)$ directions, all directions were allowed for every pace, the walk would be the same as a so-called random walk. In case of random walk the probability for a path of l_i paces to close is known to be $1/(4l_i)$. The paths mentioned in the above paragraph and those of random walk are not very different. So β, probability that paths l_i long, close on the dual lattices, will not be far different from $1/l_i$, and m_i' can be written as

$$m_i' = (p-1)^{l_i}/l_i\,.$$

(B) In Figs. 4 a, 4 b, 4 c and 4 d, the figures of thick line represent closed paths drawn on the dual lattices with the small circle as the starting point. Although they have the

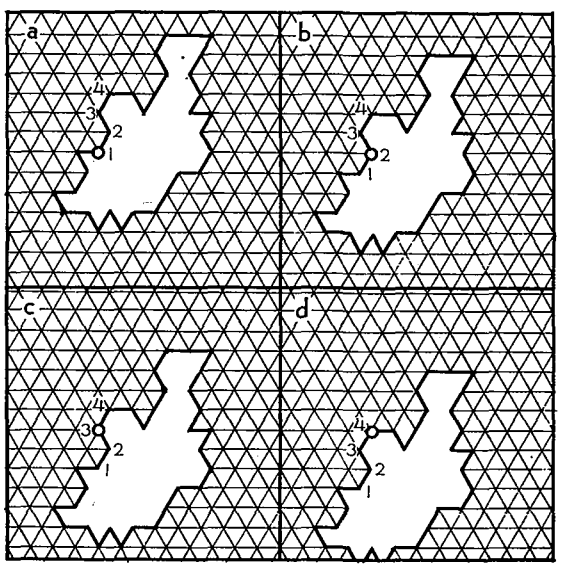

Fig. 4. Islands of the same shape but different in position

same shape they represent different paths, for they differ in position. There are l_i such paths for every shape that can be made by the walk of l_i paces. So number m_i'' of the different shapes that the paths can take is obtained by dividing m_i' by l_i:

$$m_i'' = m_i'/l_i = (p-1)^{l_i}/l_i^2 .$$

For any given shape there are six islands of the same shape tilted against one another by an angle of 60° or its multiples. They are counted as islands of different shapes because generally they cannot be brought into coincidence by parallel displacements.

(C) A closed path can be the margin of an island only when it does not intersect as in the numerical figure 8. The number of the non-intersecting paths must be quite a small part of m_i''. Let it be assumed to be l_i-th part. Then m_i, number of different shapes that an island with margin l_i long, can take, is given by

$$m_i = m_i''/l_i = (p-1)^{l_i}/l_i^3 . \tag{4}$$

In making the above assumption, the present author reasoned as follows. He assumed that the number of paths which intersect j times is a constant, independently of j, namely, it is equal to number m_i of the non-intersecting paths. Let the largest value of j be J. Then we have

$$m_i = m_i''/J ,$$

and the mean value j_0 of j is given by

$$j_0 = J/2 .$$

On an average, path of l_i paces winds around within a circle with a radius nearly equal to $\sqrt{l_i}$. This aspect is roughly similar to that when the path goes and returns $\sqrt{l_i}/2$ times the distance $\sqrt{l_i}$ in one direction and does the same perpendicularly to that direction. In doing so the path intersects $(\sqrt{l_i}/2)^2 = l_i/4$ times. This number $l_i/4$ of intersections gives the mean value j_0, and J turns out to be $l_i/8$. Since small number 8 has no meaning in such a rough reasoning, J can be put equal to l_i itself.

4. EVALUATION OF W

As the basal surface (0001) and the prismatic surface $(1\bar{1}00)$ can be dealt with in the same way because of the similarity in their molecular structures, the evaluation of W will be carried out using the molecular structure of the basal surface only.

Let an original basal surface composed of $2N$ molecules be considered and let it be assumed that a group of islands of total margin length L is formed on the surface. Each island is either positive or negative.

(A) If the group consists of n islands and the margin length of individual island is denoted by l_i, L is given by

$$L = \sum_{i=1}^{n} l_i . \tag{5}$$

There are many different ways in which L can be divided into l_i's. Let the number of those ways be denoted by $q_n(L)$. As seen from Fig. 1, the island composed of circles can be displaced to any position on the original surface if the displacement is made in such a way as to place solid circles on open triangles. This shows that an island can

take N different positions on the original surface. Thus the number of states which the group of islands can take *with respect to position* is found to be

$$q_n(L)N^n . \tag{6}$$

Each of the islands composing the group can have many different shapes. This aspect gives rise to another number of states $\prod_{i=1}^{n} m_i$ which is, by (4) and (5), expressed as

$$\prod_{i=1}^{n} m_i = (p-1)^L \prod_{i=1}^{n} 1/l_i^3 .$$

If l_i is replaced by L/n, the mean value of l_i, this formula turns into

$$\prod_{i=1}^{n} m_i = (p-1)^L (n/L)^{3n} . \tag{7}$$

The number of states *with respect to position and shape* of the group of islands is given by the product of (6) and (7) for fixed value of n. But n, number of islands composing the group, can change. Thus number W_1 of states *with respect to position, shape and number* of the group of islands is given by

$$W_1 = (p-1)^L \sum_{n=1}^{\mu} q_n(L) N^n (n/L)^{3n} . \tag{8}$$

The upper limit μ of the summation in (8) is the mean value of n, that is,

$$\mu = \sum_{n=1}^{L} n q_n(L) \Big/ \sum_{n=1}^{L} q_n(L) . \tag{9}$$

For the statistics mentioned in section 3 to be applicable, the margin of each island must be sufficiently long: the value of n must be kept much less than L. That is the reason why μ is chosen as the upper limit of the summation. By substituting μ for n in $N^n(n/L)^{3n}$ of (8), W_1 is rewritten as

$$W_1 = (p-1)^L N^{\mu} (\mu/L)^{3\mu} \sum_{n=1}^{\mu} q_n(L) .$$

The sum $\sum_{n=1}^{\mu} q_n(L)$ is roughly equal to $(\mu/L)\, q(L)$, where

$$q(L) = \sum_{n=1}^{L} q_n(L) . \tag{10}$$

The final expression for W_1 is thus given by

$$W_1 = (p-1)^L N^{\mu} (\mu/L)^{3\mu} (\mu/L) q(L) . \tag{11}$$

Husimi (1938) derived an approximate formula for μ:

$$\mu = (\sqrt{6L}/\pi)\left[\ln(\sqrt{6L}/\pi) + C\right], \tag{12}$$

where $C=0.577216$ is Euler's constant. For $q(L)$,

$$q(L) = (1/L\sqrt{48})\, \exp\, (\pi\sqrt{2L/3}) \tag{13}$$

is known as Hardy–Ramanujan's formula.

(B) The statement made in section 1 concerning the stability of crystal surface is correct only when the formation of islands brings no change in volume of the crystal. In

evaluating number m_i of different shapes of an island in section 3, we counted each island twice by tracing its margin clockwise and counterclockwise. Let either of the two islands of the same shape traced clockwise and counterclockwise be chosen as positive, then the other becomes negative. Then absolutely no change in the volume of crystal occurs. Another number of states

$$W_2' = \mu!/(\mu/2)!\,(\mu/2)!$$

arises on account of the above choice. But W_2' need not be taken into calculation as its contribution to the entropy of crystal surface is very small.

(C) Molecules of ice crystal are connected to one another exclusively by hydrogen bonds. Therefore each of the cut bonds at the margins of islands does or does not have one hydrogen atom, that is to say, the margin bond is either positively or negatively charged. Due to this situation the group of islands can have still another kind of states. Let the number of these states be denoted by W_3.

The margin bond cannot choose positive or negative charge quite freely, because every oxygen atom in an ice crystal must keep always two and only two hydrogen atoms attached to it. Suzuki (1966, 1967) showed that, on account of such a restriction, each of the margin bonds contributes an amount of a little less than

$$(k/2)\ln 2$$

to the entropy of the group of islands. Therefore W_3 is nearly equal to

$$W_3 = 2^{(L/2)}. \tag{14}$$

Any of the states dealt with in article (A) and any of those mentioned just above can occur simultaneously. Thus number W of states which the group of islands with total margin length L can take is given by the product of W_1 and W_3 which are functions of L.

5. FREE ENERGY OF THE CRYSTAL SURFACES

By the use of (11), (12), (13) and (14), W can be expressed as

$$\begin{aligned} W &= W_1 W_3 = W_a W_b, \\ W_a &= (p-1)^L 2^{(L/2)}, \\ W_b &= N^{\mu}(\mu/L)^{3\mu+1}(1/L\sqrt{48})\ \exp\left(\pi\sqrt{2L/3}\right), \\ \mu &= (\sqrt{6L}/\pi)\left[\ln\left(\sqrt{6L}/\pi\right)+C\right]. \end{aligned} \tag{15}$$

As the energy of the group of islands is equal to εL, free energy X of the group is given by

$$X = \varepsilon L - kT(\ln W_a + \ln W_b),$$

and this can be rewritten as

$$X/kT = \left[(\varepsilon/kT)-\alpha\right]L - \ln W_b \tag{16}$$

with

$$\alpha = \ln(p-1)+(1/2)\ln 2, \tag{17}$$

because $\ln W_a = \alpha L$. Let temperature T_c defined by

$$T_c = \varepsilon/k\alpha \qquad (18)$$

be called "critical temperature" and let t defined by

$$t = (T - T_c)/T_c \qquad (19)$$

be introduced. Then (16) is transformed into

$$X/kT = \alpha\left[-t/(1+t)\right]L - \ln W_b\,. \qquad (20)$$

For $p=6$, α is 1.9560.

The thick curve of Fig. 5 gives the relationship between $\ln W_b$ and $\log L$ for $2N=10^{15}$. There are 1.129×10^{15} molecules on 1 cm² of the basal surface and 1.197×10^{15} molecules on 1 cm² of the prismatic surface $(1\bar{1}00)$ at 0°C. Thin curves 1, 2, 3 and 4 in the same figure are curves of $\alpha[-t/(1+t)]L$, the first term on the right side of (20), drawn for different negative values of t: 1, 2, 3, 4 for $t=-10^{-3}$, -10^{-4}, -10^{-5}, -10^{-6} respectively. It will be seen from Fig. 5 that X should have a minimum of negative value when t is negative, that is, when T is less than T_c.

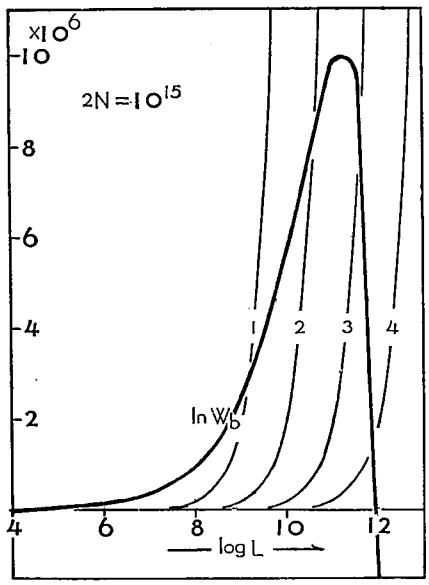

Fig. 5. Curves 1, 2, 3 and 4 stand for $[(\varepsilon/kT)-\alpha]L$ for different values of T less than T_c. From this figure it is seen that $X/kT=[(\varepsilon/kT)-\alpha]L-\ln W_b$ has a minimum of negative value at a given temperature lower than the critical temperature T_c

Let the minimum value of X and the value of L at which X becomes minimum be denoted by F and L_m respectively. If the right hand side of (20) is represented by $f(L)$, L_m is obtained by solving the equation $df(L)/dL=0$ and F is given by $f(L_m)$. In Figs. 6 a and 6 b, L_m and F/kT thus found are plotted against t, for interval $10^{-2}\sim0$ of t in Fig. 6 a and for interval $-10^{-5}\sim+10^{-5}$ of t in Fig. 6 b. As seen from Fig. 6 a, L_m increases and F/kT decreases extremely rapidly as $-t$ approaches zero, that is, as T approaches the critical temperature T_c from below. At $t=0$, $L_m=1.6\times10^{11}$ and $F/kT=-9.9\times10^6$. Practically L_m and F/kT can be considered to be kept at zero as long as the temperature is lower than T_c and to increase or decrease suddenly at the moment when temperature reaches T_c. Clearly the greater L_m is, the more rough crystal surface is. So it may be said that surfaces (0001) and $(1\bar{1}00)$ of ice crystal are smooth at temperatures below T_c and become rough when temperature attains T_c.

If t goes over zero and becomes positive, F continues decreasing until t reaches t_M which is about 0.85×10^{-5} in value as shown in Fig. 6 b. Let L_m and F at t_M be denoted by L_M and F_M respectively. Their values are approximately 10^{12} and -1.5×10^7kT_c. At t_M, curves of L_m and F/kT begin to rise steeply as shown by broken lines in Fig. 6 b and F ceases to be minimum and turns into maximum of $f(L)$. Therefore L_M is the greatest value that L_m is allowed physically to have. Let the state of islands at t_M be called "critical state". Of course the crystal surfaces are more stable with the islands of this state than the original surfaces. Value 10^{12} of L_M is one thousandth of $2N=10^{15}$, the number of molecules on the crystal surfaces in question. The mean margin length

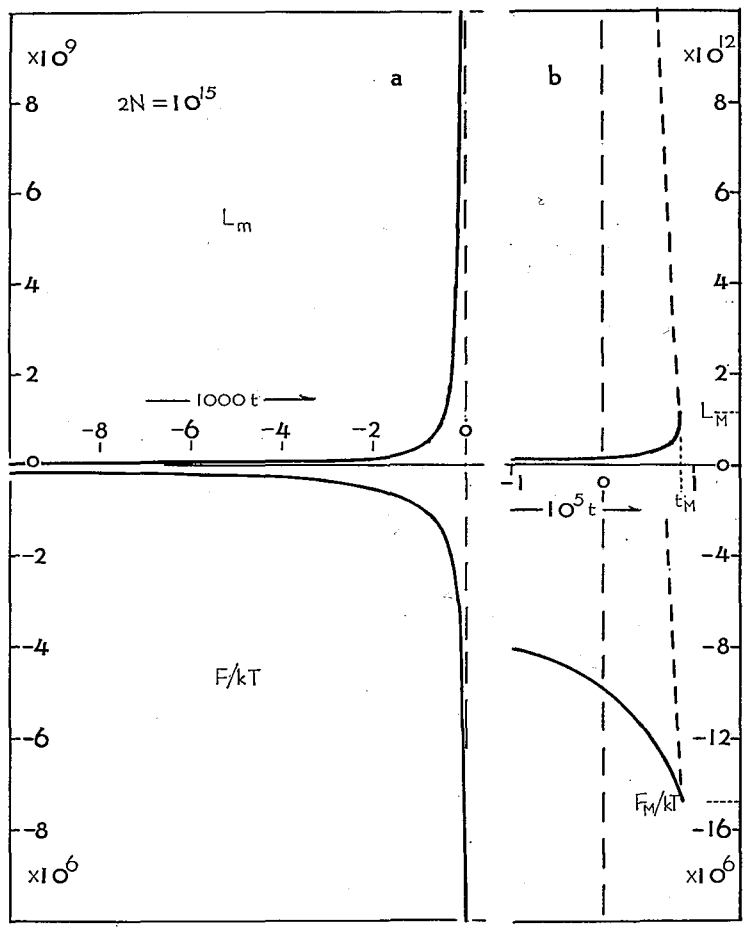

Fig. 6. L_m: total margin length of the group of islands
F: free energy of the group. $t=(T-T_c)/T_c$

l_M of individual islands is given by L_M/μ_M, if μ_M is the μ corresponding to L_M (*cf.* eqs. (9) and (12)). The value of l_M is found to be 1.1×10^5.

As t_M is almost equal to zero, the critical state can be said to occur at the critical temperature T_c itself. Above T_c, $\alpha[-t/(1+t)]L$, the first term on the right side of (20), is negative and decreases as L increases. As seen from Fig. 5, $\ln W_b$ is positive for $L<10^{12}$ and becomes negative when L exceeds 10^{12} to decrease rapidly with increasing L. But the rate at which $\ln W_b$ decreases is less than the decreasing rate of $\alpha[-t/(1+t)]L$. Therefore the presence of islands on the crystal surfaces reduces their free energy at temperatures higher than T_c as well. The free energy becomes increasingly negative as L increases, but L will take some value between L_M and N, as L cannot exceed N. Thus it is shown that the basal surface (0001) and prismatic surface ($1\bar{1}00$) of ice crystal, which are smooth at low temperatures, acquire suddenly at T_c a rough structure and maintain it to the melting point of ice.

Critical temperature T_c given by (18) does not depend on N, the number of molecules on the crystal surfaces. But F_M, L_M and l_M change with N not in proportion to it.

Table 1. Characteristics of the critical state

$2N$	10^7	10^{11}	10^{15}
Area of crystal surface	10 μ^2	0.01 mm^2	1 cm^2
t_M	3.5×10^{-3}	1.7×10^{-4}	8.5×10^{-6}
L_M	2.5×10^{6}	1.8×10^{9}	1.3×10^{12}
μ_M	9.3×10^{3}	3.6×10^{5}	1.2×10^{7}
l_M	2.7×10^{2}	5.0×10^{3}	1.1×10^{5}
F_M/kT_c	-9×10^{3}	-4×10^{5}	-1.5×10^{7}

Their values are listed in Table 1 for three different values of $2N$.

III. Prismatic Surface (11$\bar{2}$0)

1. FEATURES OF ROUGH STRUCTURE OF THE CRYSTAL SURFACE

Figure 7 shows the arrangement of molecules on the prismatic surface (11$\bar{2}$0) of ice crystal; Fig. 7 (a) above the dotted line 1 is the plan and Fig. 7 (b) below that line the elevation. Molecules represented by open circles and triangles form the original or reference surface as seen near the right edge of the figure. Open circles are arranged

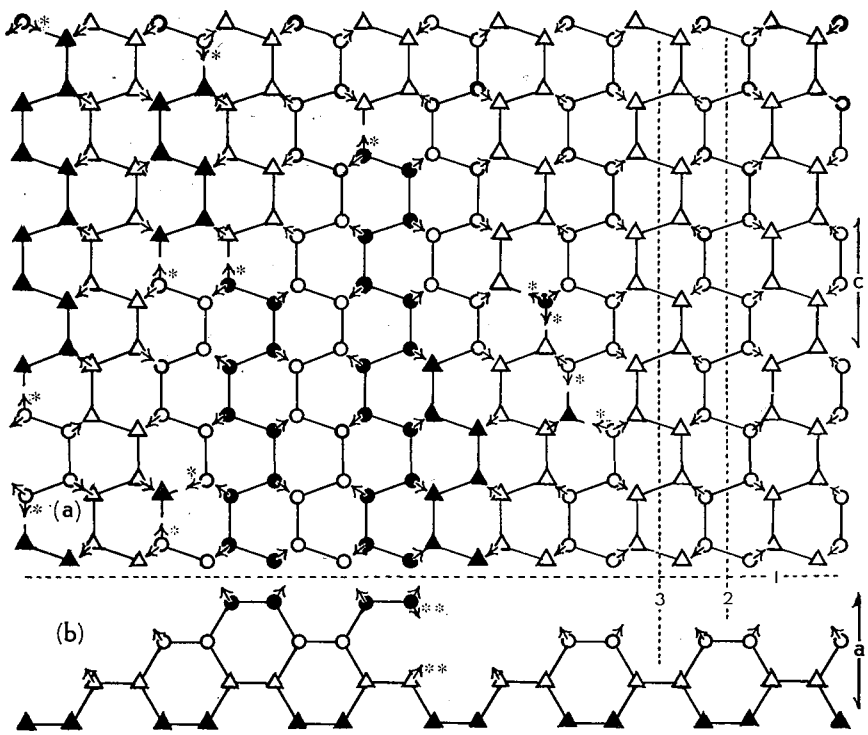

Fig. 7. Molecular arrangement of (11$\bar{2}$0). Open circles and triangles form the original surface. Solid circles and triangles make repsectively positive and negative islands. Distance between dotted lines 2 and 3, central lines of ridge and groove respectively, is 3.9178 Å. Figure (b), the bottom figure, shows the side view of the surface. In this figure molecules are arranged in such a way as to form net plane of (0001)

in such a way as to make ridges running parallel to the crystallographic c-axis while open triangles lie in the grooves between the ridges. The original surface of $(11\bar{2}0)$ is thus wavy in marked contrast to the flat original surfaces of (0001) and $(1\bar{1}00)$.

Trains of solid circles and triangles in Fig. 7 (a) make long islands on the original surface. The island of solid circles is "positive", because they lie above the level of open circles as seen from Fig. 7 (b). The island of solid triangles is "negative" because it is a trench made in the original surface by removing a train of open circles from it. Solid triangles make a molecular net plane lying below that made by open triangles. It is assumed that the prismatic surface $(11\bar{2}0)$ becomes rough when such islands as above are formed upon it.

The short arrows without the star mark in Fig. 7 are the cut bonds which come into being indispensably when the surface is formed. These cut bonds neither increase nor decrease if islands appear on the surface. The arrows marked with a single star in Fig. 7 (a) show the cut bonds newly produced by the formation of islands. Let them be called "margin bonds", to use the same nomenclature as in Part II although "end bonds" might suit better. As every island, either positive or negative, has two margin bonds at both ends, the appearance of one island on the surface adds an amount 2ε to its energy. But such is only true when two islands of opposite signs do not lie contiguously as shown at the lower middle part of Fig. 7 (a). If islands form contiguously such cut bonds as indicated by double stars in Fig. 7 (b) come out along the border line between the two islands. Generally those cut bonds appear in large number and increase the energy of the crystal surface much. So contiguity of islands is unlikely to occur. On that account let it be assumed that islands never form contiguously on the crystal surface and let this assumption be called "prohibition of contiguity".

If H islands, positive and negative together, form on the crystal surface, its free energy increases by the amount

$$Y = 2H\varepsilon - kT(\ln W_{\mathrm{I}} + \ln W_{\mathrm{II}}), \tag{21}$$

where W_{I} is the number of different states of the H islands, that is, the number of different ways in which the H islands can be placed on the crystal surface under the restriction of "prohibition of contiguity", while W_{II} gives the number of different states created due to the fact that the margin bonds can be either positive or negative. By the same reason as mentioned in Part II, W_{II} is given by

$$W_{\mathrm{II}} = 2^{H}, \tag{22}$$

because there are $2H$ margin bonds.

2. EVALUATION OF W_{I}

Figure 8 is drawn for the purpose of showing more clearly the distribution of islands on the crystal surface $(11\bar{2}0)$. Dots represent molecules on the original surface while circles are those composing islands. The group of circles connected by thick segments forms one island. Actually, as shown in Fig. 7 (a), the molecules are arranged in a zigzag fashion in the direction of the c-axis, but here in Fig. 8 they are, for the sake of clearness, put on vertical straight columns which represent alternately ridge and groove. The horizontal lines upon which dots and circles are placed will be called "rows". Since

positive islands always form over the grooves and negative islands are made where ridges were, the islands in Fig. 8 are either positive or negative on every other column, although they are represented by the identical circles. Distinction of islands by their signs is needless, because the relationship of positive islands to grooves is the same as that of negative islands to ridges, and by virtue of that, formation of islands causes no change in the volume of the crystal.

The following symbols will be used:

- M for number of columns,
- K for number of rows which is the same as the number of positions for molecules on each of the columns,
- l for number of circles on each of the columns,
- n for number of islands on each of the columns.

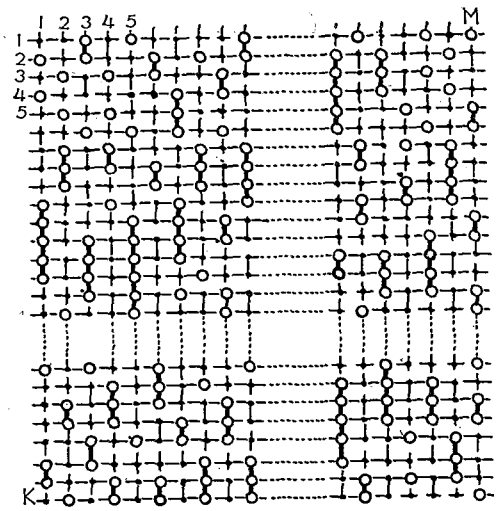

Fig. 8. The circles are the molecules composing islands while dots are those on the original surface. Columns composed of dots and circles represent alternately ridge and groove on $(11\bar{2}0)$. The group of circles connected by thick segments forms an island

As the columns are the equivalent of one another, they have the same l and n in common. It is obvious that $nM=H$ and that KM gives the number of all the molecules on the original surface.

(A) W_A: *number of ways in which islands can be formed on the crystal surface for fixed l and arbitrary n.* As there are l circles on each column in Fig. 8, there are $Q=l(M/K)$ circles on each of the rows. It is required by "prohibition of contiguity" that on each of the rows any given circle must be separated from the next circle with one or more dots in between. The number of ways to place Q circles on a row as required by the prohibition is given by

$$w_M = {}_{M-Q}\mathrm{C}_Q\,, \tag{23}$$

and W_A is obtained as

$$W_A = (w_M)^K\,. \tag{24}$$

Certainly W_A gives the number of different states that islands can take under the restriction of "prohibition of contiguity". But W_A is much larger than W_I, because among W_A states there are many of those that are made by islands not equal to H in number.

(B) w_K: *number of ways in which l circles can form islands on a column.* If n islands should form on a column, it can be carried out in

$$g(K,l,n) = {}_l\mathrm{C}_n \cdot {}_{K-n}\mathrm{C}_n \tag{25}$$

different ways, and w_K is given by

$$w_K = \sum_{n=0}^{l} g(K,l,n) = {}_K\mathrm{C}_l\,. \tag{26}$$

(C) *Another expression for* W_A. Let each of the w_K different distributions of islands on a column be called "substate" of islands. Figure 9 differs from Fig. 8 in that circles here do not represent molecules but the substates of islands on each of the columns. Number j of a column, that is, of ridge and groove, runs up to M while number i of a circle runs up to w_K. Since all columns are equivalent in character, all circles of the same i on different columns correspond to the same substate of islands.

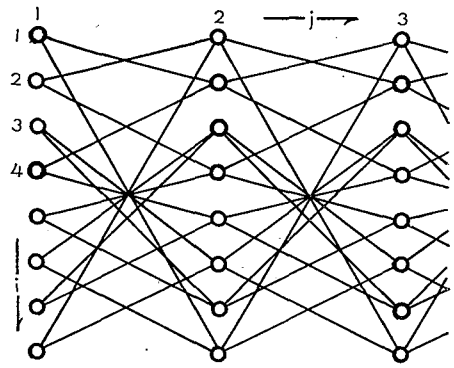

Fig. 9. Each circle represents a "substate" of islands realizable on a column, that is, ridge or groove. The two circles located on adjacent columns and joined by a straight line are two substates which do not conflict with "prohibition of contiguity"

The straight lines crossing the intervals between two neighbouring columns mean that the two circles at their ends do not conflict with "prohibition of contiguity". As all the columns are equivalent, the straight lines cross every interval in quite the same manner as shown in the figure. Any group of M circles that are each located on M columns and are connected by the straight lines represents a combination of substates, namely a distribution of islands, realizable on the whole crystal surface. If v straight lines start, on an average, from a circle on one column toward the next column, there can be $w_K \cdot v^{M-1}$ such groups. And this number must be equal to W_A:

$$W_A = w_K \cdot v^{M-1} . \tag{27}$$

The combination of eqs. (24) and (27) gives the value of v in terms of K, M and l.

(D) $W_n(l)$: *number of ways in which islands can be formed for fixed values of* l *and* n. Of w_K circles on each column of Fig. 9, $g(K, l, n)$ are circles of n islands, that is, the circles that represent the substates realized by n islands. On the basis of this fact, let it be assumed that any circle on a column is connected by

$$v_n = v \cdot g(K, l, n)/w_K \tag{28}$$

straight lines to the circles of n islands on the next column. If all circles of n islands are picked out from Fig. 9, they will make a diagram similar to Fig. 9 in which each column is made of $g(K, l, n)$ circles each radiating v_n straight lines. Obviously groups of M circles connected by the straight lines in the diagram thus made give possible distributions of islands on the whole crystal surface with n islands on each ridge and groove. There are $g(K, l, n) \cdot (v_n)^{M-1}$ such groups and this number gives $W_n(l)$. By the use of eqs. (23) to (27), $W_n(l)$ is found to be

$$W_n(l) = g(K, l, n) \cdot (v_n)^{M-1} = [{}_{K-Q}C_Q]^L \cdot [{}_lC_n \cdot {}_{K-l}C_n / {}_KC_l]^K \tag{29}$$

with

$$Q = l(K/L) .$$

(E) W_I *and* $\ln W_I$. Since the increase $H\varepsilon = nM\varepsilon$ in energy of the crystal surface caused by formation of islands does not depend on l, W_I is given by the sum of $W_n(l)$

made for all possible values of l. If l exceeds $K/2$, "prohibition of contiguity" is violated, and l cannot be less than n originally. Therefore W_{I} turns out to be

$$W_{\mathrm{I}}=\sum_{l=n}^{K/2} W_n(l)\,. \tag{30}$$

By the use of Stirling's formula and by introducing new variables

$$\lambda=l/K<1/2 \quad \text{and} \quad \nu=n/K<\lambda\,, \tag{31}$$

$\ln W_n(l)$ can be written as

$$\begin{aligned}\ln W_n(l)&=KM\psi(\lambda,\nu)\\ \psi(\lambda,\nu)&=\lambda\ln\lambda+3(1-\lambda)\ln(1-\lambda)-(1-2\lambda)\ln(1-2\lambda)\\ &\quad-(\lambda-\nu)\ln(\lambda-\nu)-(1-\lambda-\nu)\ln(1-\lambda-\nu)-2\nu\ln\nu\,,\end{aligned} \tag{32}$$

and (30) transforms into

$$W_{\mathrm{I}}=\sum_{l=n}^{K/2} W_n(l)=K\int_{\nu}^{1/2}\left[\exp\psi(\lambda,\nu)\right]^{KM}d\lambda\,. \tag{33}$$

As function $\psi(\lambda,\nu)$ has a maximum at $\lambda=\Lambda$ which is related to ν by the equation

$$\partial\psi(\lambda,\nu)/\partial\lambda=0 \tag{34}$$

or

$$\nu=\Lambda\frac{(1-\Lambda)^3-(1-\Lambda)(1-2\Lambda)^2}{(1-\Lambda)^3-\Lambda(1-2\Lambda)^2}\,, \tag{34'}$$

the final expression for $\ln W_{\mathrm{I}}$ is, by applying the method of saddle point currently used in statistical mechanics, obtained in the following form

$$\ln W_{\mathrm{I}}=KM\psi(\Lambda,\nu)\,. \tag{35}$$

3. FREE ENERGY OF THE CRYSTAL SURFACE

If H, $\ln W_{\mathrm{I}}$ and W_{II} in (21) are replaced by nM, (35) and (22) respectively, the expression for free energy Y of the crystal surface becomes

$$Y=KMkT\left[\left(\frac{2\varepsilon}{kT}-\ln 2\right)\nu-\psi(\Lambda,\nu)\right]\,, \tag{36}$$

which is a function of T and $n=H/M$, number of islands on a ridge or a groove on the crystal surface. By the same reason as mentioned in Part II, the crystal surface is rough with islands upon it if Y has a minimum of negative value for a positive value of n.

By putting

$$T_{\mathrm{b}}=\varepsilon/k\,, \tag{37}$$

and

$$y=Y/(KMkT)\,, \tag{38}$$

(36) is rewritten as

$$y=\left[(2T_{\mathrm{b}}/T)-\ln 2\right]\nu-\psi(\Lambda,\nu)\,. \tag{39}$$

In Fig. 10, A is the straight line for $[(2T_{\mathrm{b}}/T)-\ln 2]\nu$ and curve B represents

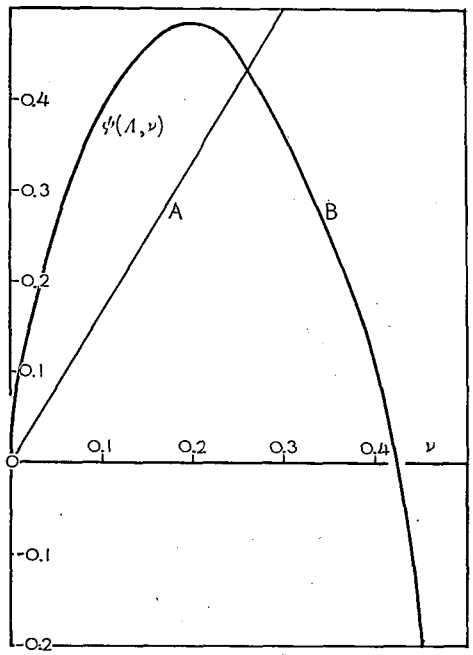

Fig. 10. Straight line A gives $[(2T_b/T)-\ln 2]\nu$. This figure shows that $y=[(2T_b/T)-\ln 2]\nu-\psi(\Lambda,\nu)$ has a minimum of negative value at any temperature T

$\psi(\Lambda,\nu)$. From this figure one sees that y should have a minimum of negative value at a positive value of ν for any temperature T. If the values of ν and Λ that make y minimum are denoted by ν_m and Λ_m respectively, they are the roots of the simultaneous equations

$$\frac{(\Lambda-\nu)(1-\Lambda-\nu)}{\nu}=\exp\left[(2T_b/T)-\ln 2\right] \tag{40}$$

$$\nu=\Lambda\frac{(1-\Lambda)^3-(1-\Lambda)(1-2\Lambda)^2}{(1-\Lambda)^3-\Lambda(1-2\Lambda)^2}\,. \tag{41}$$

Equation (40) is a transformation of $\partial y/\partial\nu=0$ and (41) is the same as (34) or (34′). Those roots are functions of T and formation of $MK\nu_m$ islands on the crystal surface reduces its free energy to make it rough in structure. The negative free energy Φ of the surface is given by

$$\Phi=KMkT\varphi(\Lambda_m,\nu_m)\,, \tag{42}$$

where $\varphi(\Lambda_m,\nu_m)$ is the minimum of y which can be written as

$$\varphi(\Lambda_m,\nu_m)=\left[(2T_b/T)-\ln 2\right]\nu_m-\psi(\Lambda_m,\nu_m)\,. \tag{43}$$

In Fig. 11 $\varphi(\Lambda_m,\nu_m)$, Λ_m and ν_m are plotted against T/T_b. Since $KM\nu_m$ gives the number of islands on the crystal surface, ν_m can be regarded as a measure of its roughness. The gradual increase of ν_m with T/T_b as seen in Fig. 11 shows that the roughness of crystal surface $(11\bar{2}0)$ grows continually as temperature rises whereas surfaces (0001)

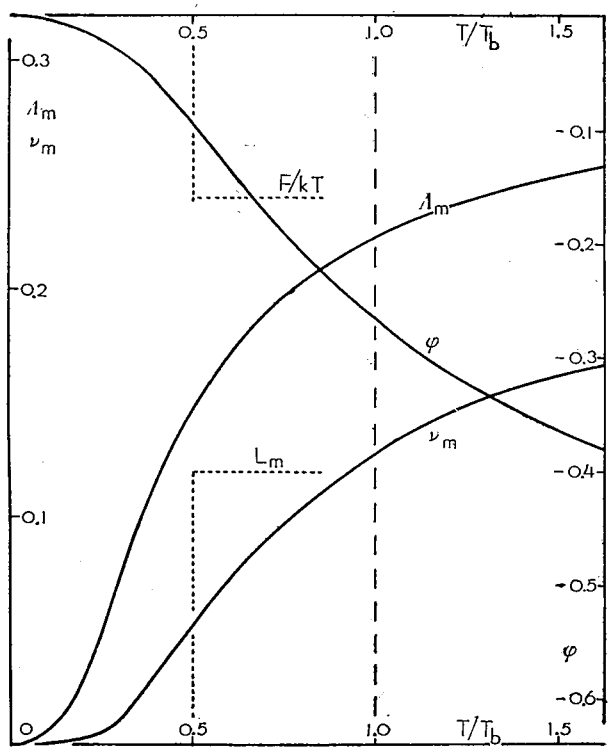

Fig. 11. φ: free energy per molecule on $(11\bar{2}0)$ devided by kT. $\varphi=-0.640$ at $T=\infty$. ν_m: mean number of islands on a column of Fig. 8 per unit length of it, vertical distance between two successive dots and circles on a column, which is 1.847 Å long. $\nu_m=0.240$ at $T=\infty$. Λ_m: mean number of circles of Fig. 8 per unit length of the column. $\Lambda_m=0.304$ at $T=\infty$. Ratio $l_m=\Lambda_m/\nu_m$ gives the mean number of molecules composing an island. Dotted curves F/kT and L_m: schematic curves for the free energy and the roughness of surfaces (0001) and $(1\bar{1}00)$

and $(1\bar{1}00)$ became rough abruptly at T_c. Surface $(11\bar{2}0)$ differs from these surfaces in one more point, namely, in that free energy Φ of surface $(11\bar{2}0)$ is proportional to its area while free energy F of the other surfaces was not. Number of molecules, open circles and triangles together in Fig. 7, on 1 cm^2 of surface $(11\bar{2}0)$ is 1.3820×10^{15}.

IV. Discussion

1. THE CRITICAL TEMPERATURE T_c

As shown above, surface $(11\bar{2}0)$ of ice crystal is rough at any temperature while surfaces (0001) and $(1\bar{1}00)$ can have a rough structure only when their temperature lies above the critical temperature $T_c=\varepsilon/\alpha k$. Therefore, for the surfaces (0001) and $(1\bar{1}00)$ of ice crystal to be rough, T_c must be lower than T_0, the melting point of ice.

The value of ε, the energy needed for cutting a hydrogen bond connecting the molecules in ice crystal, is known to be about 5000 cal/mol. Pauling (1940, p. 304) gave 4500 cal/mol and Nagamiya (1954, p. 30) 5700 cal/mol for ε. When 5300 cal/mol is used for ε, T_c turns out to be 1365°K, a temperature five times as high as $T_0=273$°K. (For

$p=6$, $\alpha=\ln(p-1)+(1/2)\ln 2$ is 1.9560.) The present author measured the amount of air molecules adsorbed on snow crystals on a previous occasion and found that they were covered by a monomolecular layer of air. This fact will show that air molecules reduced ε of the cut hydrogen bonds located on surface of ice crystal by being adsorbed upon it. Although its exact rate cannot be known, the reduction will be great enough to make ε much less than a fifth part of 5300 cal/mol with the result that T_c lies far below T_0.

Free energy of vicinal surfaces, surfaces inclined at small angles θ to the low index surfaces of crystal, changes continually with θ if the latter surfaces have a rough structure. According to the Wulff's theorem, the low index surfaces do not develop in such a case in the equilibrium form of the crystal and it takes a round form (Herring, 1953; Cabrera and Coleman, 1963). As mentioned in the introduction of the present paper, an old snow cover is composed of ice granules with an appearance of small pebbles. As this fact suggests that pebble-like form is the equilibrium form of ice crystal, the same fact may be well considered to render additional evidence for the rough structure of low index surfaces of ice crystal, consequently, for $T_c<T_0$.

The following fact may be taken as one more evidence for $T_c<T_0$. The present author (1954) placed an ice ball (1 cm in diameter) in vacuum at -30°C and found that planes shining like a mirror made their appearance on the ball in a week or so. In vacuum no air could be adsorbed on ice surface and the critical temperature T_c of surfaces (0001) and $(1\bar{1}00)$ rose above 0°C. Those surfaces could not be rough and tended to develop by transforming the ice ball into a polyhedron.

2. FREE ENERGY OF THE THREE CRYSTALLOGRAPHIC SURFACES

As α is equal to 1.9650, $T_b=\varepsilon/k$ is twice as high as the critical temperature $T_c=\varepsilon/\alpha k$. Free energy of the prismatic surface $(11\bar{2}0)$ increases in proportion to its area, that is, free energy per molecule on that surface is determined when its temperature is given. But in cases of the basal surface (0001) and of the prismatic surface $(1\bar{1}00)$, free energy per molecule depends not only on their temperature but also on their area. Actually Table 1 shows that F_M/kT_c, ratio of the free energy at T_c to kT_c, increases at a rate extremely smaller than the increasing rate of the area of those surfaces. The author assumes that a similar aspect will be maintained also at temperatures higher than T_c, although it is not possible to obtain the values of free energy of surfaces (0001) and $(1\bar{1}00)$ for those temperatures by the present theory. The values of free energy per molecule on the three crystallographic surfaces at T_c are listed in Table 2 for three different areas $10\,\mu^2$, 0.01 mm^2 and 1 cm^2. In the first column is given $2N_0$, number of molecules on 1 cm^2 of the three surfaces.

Table 2

$2N_0$	Crystallographic surface	$10\,\mu^2$	0.01 mm^2	1 cm^2
1.129×10^{15}	(0001)	$-9\times10^{-4}kT_c$	$-4\times10^{-6}kT_c$	$-1.5\times10^{-8}kT_c$
1.197×10^{15}	$(1\bar{1}00)$			
1.382×10^{15}	$(11\bar{2}0)$	$-9.5\times10^{-2}kT_c$		

The Wulff's theorem referred to in the previous section is valid when free energy of crystal surfaces is proportioned to their area. As this is not true with surfaces (0001) and $(1\bar{1}00)$ of ice crystal, the theorem cannot be applied to it in the strict form of the theorem. But the equilibrium form of ice crystal can still be round due to the roughness of its crystallographic surfaces.

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