Helical Whiskers of Ice

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Abstract

We have observed the formation of ice whiskers in cold solutions of formvar in ethylene dichloride, usually used as an etchant of ice crystals. Whiskers are supposed to form through a process of freezing of small amounts of water contained in the etchant. They are 1–3 μ in diameter and a few microns up to about 1 mm in length.

The formation of helical and spiral whiskers has been specially noted. Helices usually show quite regular pitches. Changes in direction and kinks are evident in both helix and straight whiskers. The kink angles generally correspond to the hexagonal symmetry. These features indicate that whiskers grow in most cases in the basal plane. The mechanism of growth is related to that of similar whiskers of other substances, the operating dislocation possibly being in the present case in $\langle 11\bar{2}0 \rangle$ directions.

In a special case also straight whiskers were formed parallel to the c-axis of the ice substrate. Their formation is related to probably screw $\langle 0001 \rangle$ dislocations.

I. Introduction

The crystal habit of ice grown from the vapour and from the melt has been studied in a wide range of different conditions of temperature and supercooling and tentative interpretations have been proposed of the features observed. On the other hand, whiskers may be considered as a special case of dendritical formation, so that the study of their morphology and orientation may give useful information about the general process of growth of these crystals.

It is known that ice needles possibly formed from the melt are sometimes observed in nature. Ice whiskers have also been grown from the vapour in the laboratory, using different substrates, such as frozen droplets (Zawidski and Papee, 1962) and freezing nuclei (Serpolay and Toye, 1962); these authors have observed the formation of some helix and spiral whiskers which they relate to defects of the substrate (particles of iron ferrosoferric).

In the present work we investigate the features of ice whiskers grown in cold solutions of formvar in ethylene dichloride, containing small amounts of water. The results are discussed taking into account the possible Burgers vector and dislocations of the lattice.

II. Results and Discussion

Whisker formation

It is known that solutions of formvar in ethylene dichloride are a good etchant of

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ice. However, their etching ability is reduced when they contain small amounts of water, which at $t<0°C$ precipitates forming small crystals or dendrites (Kobayashi, 1955; Bryant and Mason, 1960).

During recent studies of dislocation behaviour in ice we observed in some plastic films showing a poor attack, the formation of spirals, helices and more complex lines. We interpret these as replicas of ice whiskers formed during the process of etching and solvent evaporation. To confirm this hypothesis, either ice samples or microscope slides were coated with a thin layer of formvar solution and exposed for a few seconds to supersaturated water vapour. Immediately after, they were studied under a microscope placed in a cold chamber (at $-15°C$). In these conditions we observed whiskers floating in the liquid solution shaped as needles, spirals and kinked lines. Only exceptionally these whiskers were fixed to the substrate. In some cases they appeared to grow away from frozen droplets; more frequently, their starting and ending points were similar and therefore their growth direction could not be determined. Sometimes if agitation of the formvar solution occurred, the curvature of the whiskers could be observed to change slightly.

Most of the whiskers considered here were obtained by coating ice with formvar solution. We consider that the substrate only plays a secondary role in the process, which probably consists of a certain controlling of the water content of the solution.

Morphology

The observations were made on photographs of replicas. We give in Figs. 1 and 2 some examples of helical whiskers. In Fig. 1 a the axis is straight and in Fig. 1 b slightly curved. In Fig. 2 (a and b) each whisker is formed by two similar branches subtending angles corresponding to the hexagonal symmetry (90° and 150°, respectively). Figure 2 c

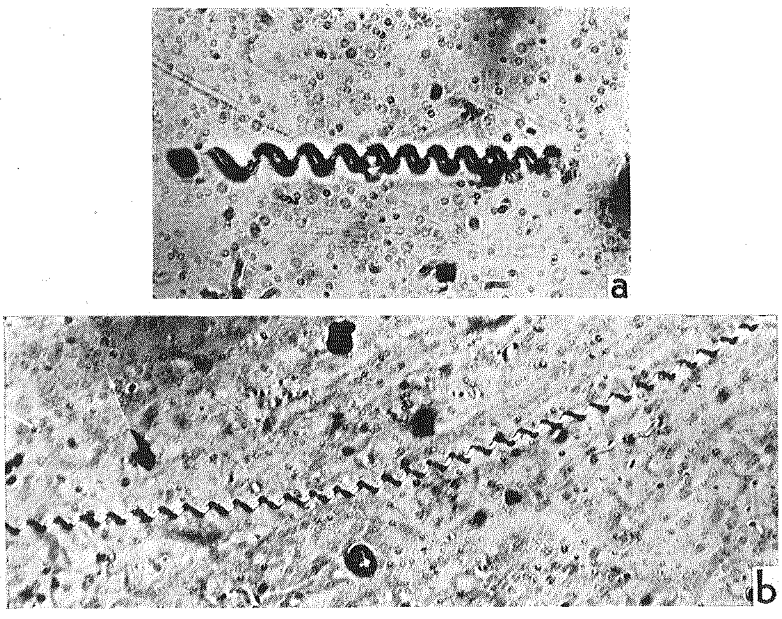

Fig. 1. Helical whiskers with straight and curved axis (a, $\times 500$; b, $\times 200$)

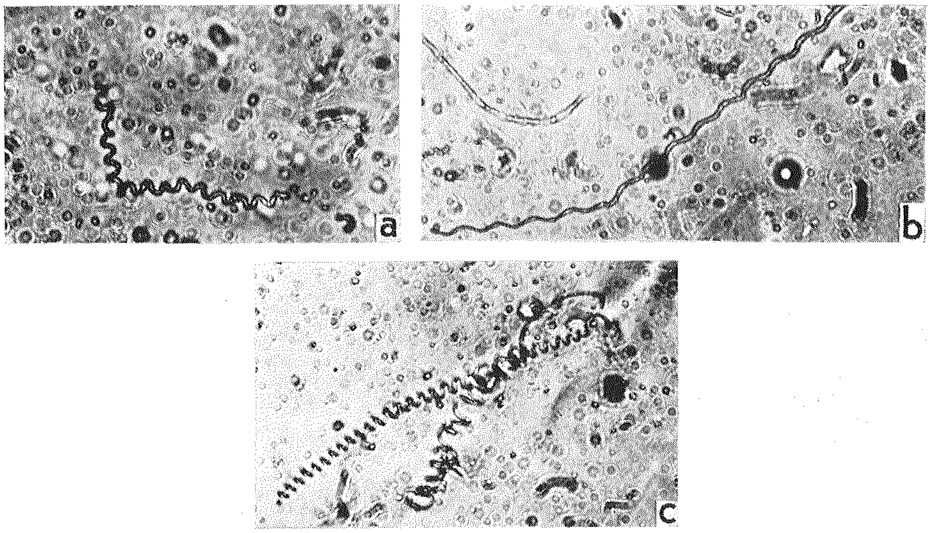

Fig. 2. Helical whiskers formed by branches at different angles (a, $\times 1000$; b, $\times 500$; c, $\times 750$)

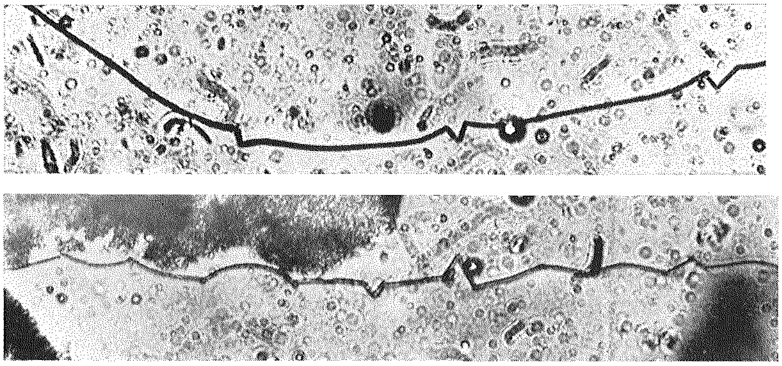

Fig. 3. Kinked whiskers ($\times 500$)

shows a whisker formed by two branches of different morphology. In some cases the helices seem to be reduced to nearly plane sinusoidal lines; an example is given in Fig. 2 b.

Kinked whiskers have been observed as well, as it is shown in Fig. 3. The angles correspond to the hexagonal symmetry (30°, 60° and 90°). Examples in Fig. 3 also indicate that an approximate periodicity exists in the formation of kinks.

Spiral whiskers are shown in Fig. 4. The spiral of Fig. 4 a has its center in a dendrite. The grain boundaries of the substrate and a low chemical etching may be observed under the whisker. In Fig. 4 b two similar spirals start at the same origin, probably a frozen droplet. The whisker in Fig. 4 c may be described as a non perfectly plane spiral formed by several turns.

It has been reported previously that helical whiskers of different substances (Edwards and Svager, 1964), sometimes show sudden changes of their morphology. Such changes have also been observed in ice whiskers and are shown in Fig. 5. The whisker of Fig.

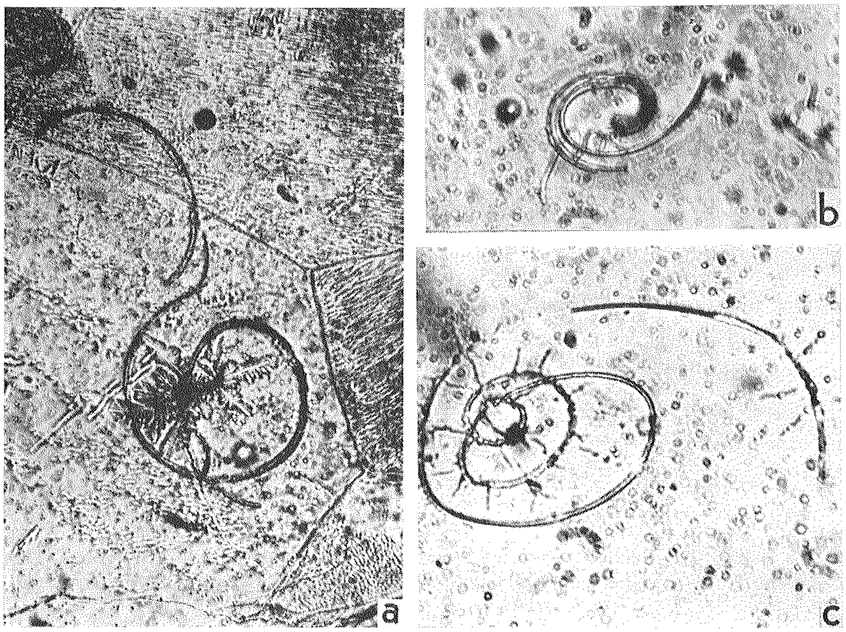

Fig. 4. Spiral whiskers ($\times 500$)

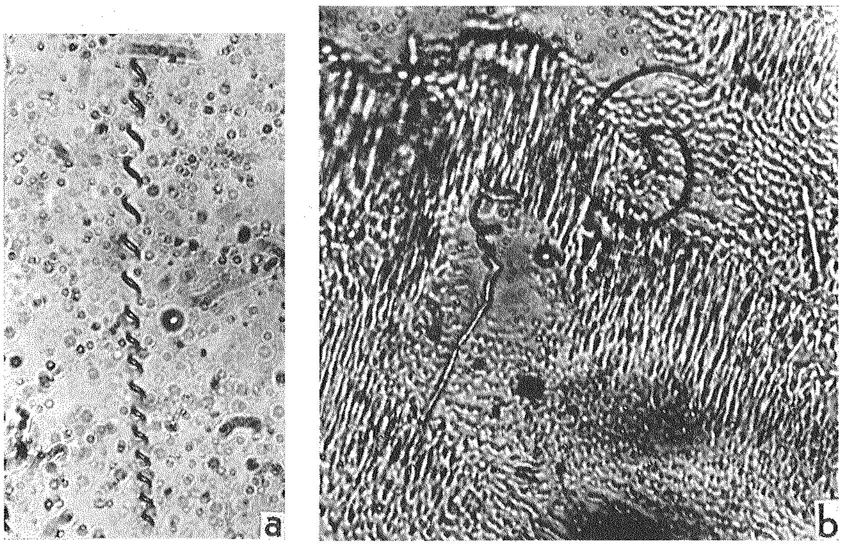

Fig. 5. Whiskers showing changes of morphology

5 a has a nearly straight axis, but the helix changes its diameter and pitch. In Fig. 5 b two whiskers are shown, one of them is a spiral with an helix turn in its center, while the other is a tapered helix which ends in a nearly straight branch.

Whiskers in Fig. 6 were obtained without ice substrate. Straight branches forming angles of 120° may be observed in Fig. 6 b; the whisker marked A (Fig. 6 a) is formed by straight segments, connected by helix turns.

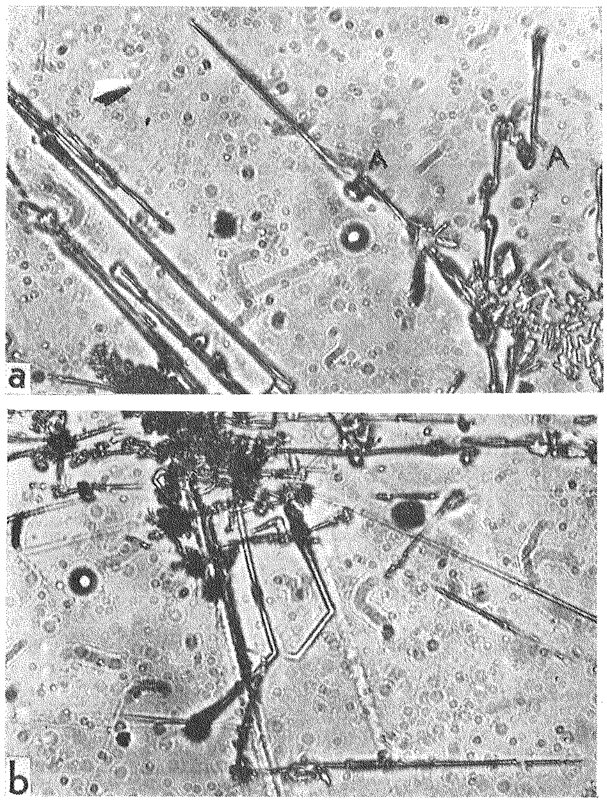

Fig. 6. Whiskers obtained without an ice substrate (×500)

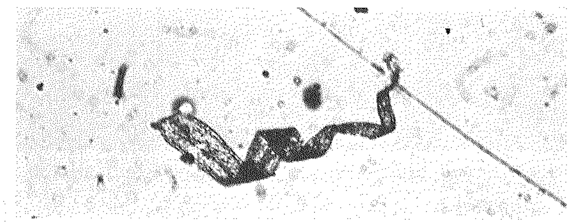

Fig. 7. Helical ribbon (×200)

In Fig. 7 a helical ribbon is shown; a central line is noticed, which might correspond to the original whisker. Ribbons of this type were also observed by De Micheli and Licenblat in experiments of evaporation of ice (unpublished).

Finally, Fig. 8 (a and b) represents one of the rare examples where whiskers have grown from the edges of the ice substrate. They are parallel to the striations produced by chemical etching of the substrate, *i.e.*, to the *c*-axis of the crystals. The sample was a polycrystal and it is seen that both striations and whiskers change their direction in different grains.

In all the cases studied here, whiskers have diameters of about 1–3 μ. Their length changes from a few microns to about 1 mm. We give in Table 1 the average values of

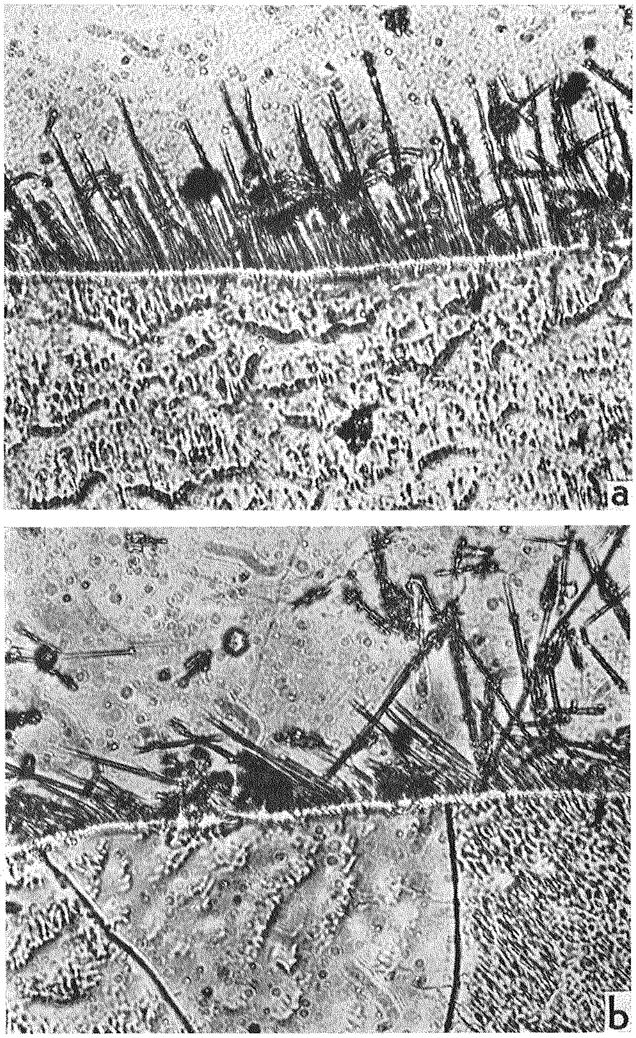

Fig. 8. ⟨0001⟩ whiskers (×500)

Table 1.

l (μ)	$2R$ (μ)	P (μ)	Fig.
1×10^2	8	10	1 a
7 〃	10	17	1 b
0.35 〃	1.5	2.5	2 a
1.6 〃	2.7	2.9	2 c
1.4 〃	3	8.8	2 b

the external diameter $2R$ and pitch P and of the total length l of some helical whiskers. We note that helices are generally open. In most cases the angle between the helix axis and the tangent to the helix turns

$$\beta = \tan^{-1} \frac{2\pi R}{P}\,, \tag{1}$$

was

$$\beta > 60^\circ\,. \tag{2}$$

Only exceptionally, $\beta < 45^\circ$ has been observed.

Discussion

In the present work we have not determined crystallographically the orientation and structure of the observed whiskers. However, we have shown that usually either kinks or different branches of the same whisker form angles of 30°, 60° and 90° (Figs. 2 and 3). Whiskers showing these features must lie in (or very near to) the basal plane probably running in low index directions of both types, $\langle 11\bar{2}0 \rangle$ and $\langle 10\bar{1}0 \rangle$. Then, whiskers show the same preferential growth in the basal plane, as known for ice crystals in a wide range of different conditions. An example was given, however, in which whiskers are formed in a non basal plane (Fig. 8).

On the other hand, the similarity between whiskers of ice and of other substances, suggests that a similar mechanism may be responsible for their formation. Helical whiskers of Pd have been particularly studied by Webb (1965). According to this author their growth is determined by the operation of an axial dislocation with a screw component, the helix shape being caused by climb of the edge component at the tip of the whiskers. Whiskers of Pd are found to be in $\langle 111 \rangle$ directions forming an angle $\gamma = 35.27^\circ$ with the $\langle 110 \rangle$ Burgers vectors of this f.c.c. structure. Webb points out that helix whiskers may be formed as an equilibrium configuration if the angle between their axis and the tangent to the dislocation line fulfils the condition $\beta > \gamma$.

We have seen that helical whiskers of ice usually have their axis in $\langle 11\bar{2}0 \rangle$ and $\langle 10\bar{1}0 \rangle$ directions. The Burgers vector for basal dislocations of these crystals have been shown by Hayes and Webb (1965) to be of the type $\frac{1}{3}\langle 11\bar{2}0 \rangle$. Then, the following values for the angle γ are geometrically possible:

$\langle 11\bar{2}0 \rangle$ whiskers	$\langle 10\bar{1}0 \rangle$ whiskers
$\gamma = 0^\circ$ or 60°,	$\gamma = 30^\circ$ or 90°.

Of those, we must rule out $\gamma = 90^\circ$, because it would lead to a pure edge dislocation, the other cases being possible. For $\gamma = 60^\circ$ the screw component is relatively low, but we note that according to eq. (2), for the three cases the condition $\beta > \gamma$ is fulfilled.

In particular, the whisker of Fig. 2 a is an example where $\gamma = 60^\circ$ is expected. Actually, if a screw component of the same dislocation is supposed to operate in both branches at 90° to each other, it must be $\gamma = 30^\circ$ for one of them, in a $\langle 10\bar{1}0 \rangle$ direction and consequently $\gamma = 60^\circ$ for the other, in a $\langle 1\bar{2}10 \rangle$ direction.

On the other hand it does not seem very probable that two different dislocations, one of them perfectly screw, would operate in the two branches with the same external morphology.

Finally, it is interesting to note that the growth of $\langle 0001 \rangle$ whiskers of Fig. 8 have been evidently caused by the conditions of the substrate. Their concentration, as determined from the photographs, is about $10^3\,\mathrm{cm}^{-1}$, *i.e.* it coincides with the linear concentration of dislocations, which may be expected to emerge in the basal plane (Achaval *et al.*, 1964). Then it may be supposed that these whiskers have grown by operation of screw dislocations, with ⟨0001⟩ Burgers vectors (Levi *et al.*, 1965).

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References

1) ACHAVAL, E. M., LEVI, L. and SURASKI, E. 1964 Chemical etching in ice crystals. *Physica Status Solidi*, **12**, 61–63.
2) BRYANT, G. W. and MASON, B. J. 1960 Etch pits and dislocations in ice crystals. *Phil. Mag.*, **5**, 1221–1227.
3) EDWARDS, P. L. and SVAGER, A. 1964 Spiral copper whiskers. *J. Appl. Phys.*, **35**, 421–423.
4) KOBAYASHI, T. 1955 Studies of small ice crystals, III. Some remarks on replica methods. *Contr. Inst. Low Temp. Sci.*, **8**, 75–86.
5) LEVI, L., ACHAVAL, E. M. and SURASKI, E. 1965 Experimental study of non basal dislocations in ice crystals. *J. Glaciol.*, **5**, 691–699.
6) SERPOLAY, R. and TOYE, M. J. 1963 Un nouveau processus pour la croissance de la glace sur les noyaux glaçogènes. *J. Recherches Atmospheriques*, **1**, 85–91.
7) WEBB, W. W. 1965 Dislocation mechanism in the growth of palladium whisker crystals. *J. Appl. Phys.*, **36**, 214–221.
8) HAYES, C. E. and WEBB, W. W. 1965 Dislocation in Ice. *Science*, **147**, 44–45.
9) ZAWIDSKI, T. and PAPEE, H. 1962 Pseudo whiskers of ice grown from clouds of supercooled water in an electric field. *Nature*, **196**, 568.