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# The Growth of Ice Crystals on Covellite and Lead Iodide Surfaces

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## Abstract

The growth of ice crystals on the basal planes of covellite and lead iodide was studied photomicrographically under low supersaturations and at substrate temperatures to  $-42^{\circ}\text{C}$ . Thermoelectric elements were successfully adapted for cooling the substrates.

Though epitaxial hexagonal ice plates were observed on both substrates, evidence was found to show a fundamental difference between the epitaxy on covellite and that on lead iodide.

On covellite surfaces, the ice crystals grew so thin that they showed vivid interference colours, and they often developed laterally with no discernible increase in thickness. The growth of the ice plates was governed by the migration of  $\text{H}_2\text{O}$  molecules adsorbed on the covellite surfaces, as has been noted by HALLETT (1961) and MASON, BRYANT and VAN DEN HEUVEL (1963), and the ice plates had real contact with the substrate.

At temperatures above  $-20^{\circ}\text{C}$ , ice plates grown on lead iodide had no real contact with the substrate except at the central germ, which appeared along a step or crack on the substrate surface, and the "epitaxy" on the basal plane was considered to result from the epitaxy of the germ on the prism faces of the substrates exposed at the step or the crack. Faintly coloured ice crystals were only observed below  $-20^{\circ}\text{C}$  on the flawless basal surface of lead iodide.

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## I. Introduction

BRYANT, HALLETT and MASON (1959) discovered that ice crystals growing on fresh (0001) covellite cleavage surfaces were often so thin that they gave rise to brilliant interference colours which allowed estimation of their thickness.

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Contribution No. 692 from the Institute of Low Temperature Science.

They found that ice crystals very often grew laterally to  $200\ \mu$  in diameter without discernible change in colour (that is in thickness), when the supersaturation was low. They also observed that, when a thin ice crystal contacted a thicker crystal or an obstacle, successive growth layers spread from the contact point across the surface of the thin ice crystal\*.

From careful analysis of these phenomena, HALLETT (1961) and MASON *et al.* (1963) concluded that both the lateral growth of ice crystals on covellite and the spreading of new layers on the ice surface were produced by the capture of water molecules, migrating on the surface of covellite or ice, at steps and not by the direct diffusion of water molecules from the air.

Covellite is not the only substrate on which ice crystals can grow epitaxially, therefore it is interesting to investigate whether or not the growth mechanism is the same on other substrates\*\*.

Epitaxy of ice crystals on AgI and  $\text{PbI}_2$  has been theoretically treated by FLETCHER (1959) who suggested that nucleation does not in fact easily occur upon basal faces, but only upon small exposed steps of the prism face of the substrates. This was experimentally supported to some extent by BRYANT *et al.* (1959), and HARRIS JR. *et al.* (1963), but the nucleation mechanism and the growth behavior of ice crystals grown "epitaxially" on these substrates have not been clearly explained.

Careful observation is necessary to determine whether or not coloured layer growth of ice crystals actually takes place on lead iodide surfaces, and how ice crystals nucleate and grow on substrates. Lead iodide is very convenient for this purpose, because it easily produces thin crystals with various surface structures and is highly efficient as an ice nucleating agent.

The purpose of this paper is to clarify the difference in "epitaxy" on the basal plane of covellite and lead iodide, and to discover whether or not the remarkable layer growth of ice crystals on covellite is substrate dependent.

## II. Experimental Technique

The apparatus used is shown in Fig. 1. Thermoelectric refrigeration using

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\* ÔNO (1957) reported successive layer growth (or sublimation) on the basal plane of ice crystals growing (or sublimating) on a cold brass rod ( $-20\sim-25^\circ\text{C}$ ) in an atmosphere of reduced pressure (10 mmHg).

\*\* The epitaxial growth of ice crystals on various substrates has been observed by many researchers (WEICKMANN (1951), MONTMORY (1956), FUKUTA (1958), FUKUTA *et al.* (1959) LAYTON *et al.* (1963), HARRIS JR. *et al.* (1963)), primarily in the search for effective ice nucleating agents. There have been no reports of any remarkable colour phenomena on any other substrate than covellite. There have been only uncertain observations as to the "contact" between epitaxial ice crystals and other substrates, such as mica, AgI,  $\text{PbI}_2$  etc.

p and n bismuth-telluride was adapted in a two-stage cascade cooling system composed of a thermoelectric panel, STM-1025 (B) for maintaining sub-zero temperatures, and a thermoelectric junction, STE-1025 (C), for spot-cooling under the microscope. Independent D.C. power was supplied to both (B) and (C) by Silicon rectifiers (1 V, 30 A capacity).

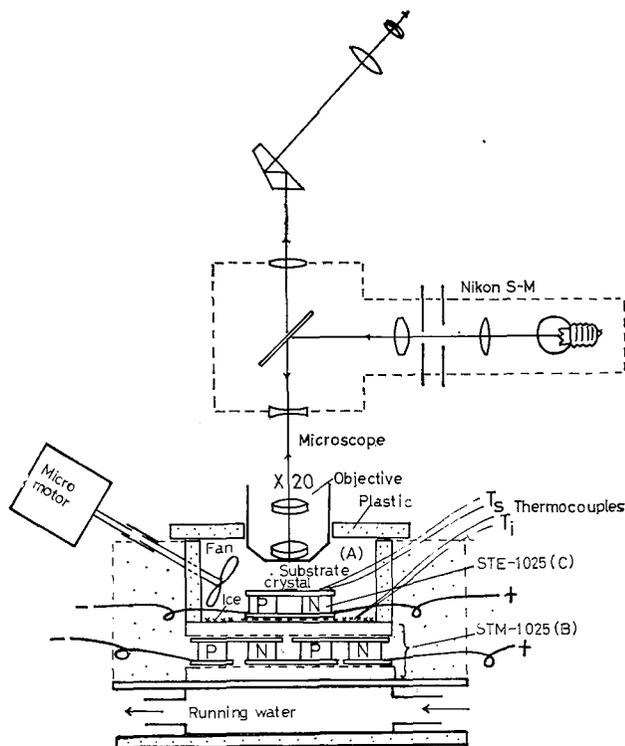


Fig. 1. Experimental apparatus

A small cold box (A),  $32 \times 30 \times 15$  mm, could be cooled to any temperature to  $-35^\circ\text{C}$  by regulating the D.C. current to a STM-1025 (B) in the bottom of the box. A thin ice sheet was placed on the bottom of this box as a vapour source. A small fan inserted through the wall kept the water vapour of the air in equilibrium with the ice at the bottom of the box.

A substrate crystal (lead iodide or covellite) was placed on the copper cold plate of the STE-1025 (C), and cooled to the desired temperature by increasing the current to the STE-1025. The ice crystal growing on the substrate was viewed with the aid of a vertical illuminator, and photographed simultaneously on 35 (still) or 16 mm (cine) colour film.

When the substrate temperature,  $T_s$ , was lower than that of the ice at the bottom,  $T_i$ , the supersaturation,  $s$ , over the substrate was roughly estimated by the temperature difference  $T_i - T_s$ .

*Thermoelectric cooling system :*

With the recent development in thermoelectric material, it is now unnecessary to work in cold rooms or to use compression type refrigeration to study ice-crystal growth under a microscope. The thermoelectric cooling device is recommended for this experiment for the following reasons ;

1. Rapid and simple regulation of and a considerable decrease in the temperature at the cold junction may be obtained, when absorption of a large amount of heat at the junction is unnecessary.
2. Only the area necessary for the microscopic specimen can be cooled, since cold junctions as small as  $8 \times 5$  mm are now available on the commercial market. Also, a refrigerated box may be adapted to the microscope-stage if the proper thermoelectric cooling panel is used.
3. Cooling or heating may be obtained by reversing the direction of the electric current.
4. This cooling system is vibration free, which is essential in using high magnification.

The cooling effect of the STM-1025 is given in Fig. 2.

When this cooling system was used in these experiments, the cooling water was circulated through the radiator of the STM-1025 and through a reservoir of ice and water and the temperature of the cold side could be extended to  $-35^\circ\text{C}$  when the current to the second stage STE-1025 was cut off. The optimum current produced a cold spot of  $-42^\circ\text{C}$  in the box, and a difference of 8 degrees between the hot and cold side of the STE-1025, while heat dissipation in the STE produced a rise of 1 degree in the temperature of the STM.

*Optical system :*

The observation were made with a Nikon STR, tri-ocular microscope with a S-M attachment for metallurgical use. The specimen was illuminated with a tungsten lamp (6 V, 15 W) through the vertical illuminator, viewed primarily with a  $20 \times$  Nikon objective and a  $10 \times$  eyepiece, and simultaneously recorded on 35 mm colour film with the aid of a Nikon SP camera body and a Nikon FMA microscope adaptor. The Nikon  $20 \times$  objective lens (N.A.; 0.40, W.D.; 5.72 mm) was inserted through the upper lid of the box (A), and proved to have no thermal influence upon the specimen. Leitz UM-  $10 \times$ ,  $20 \times$ , and

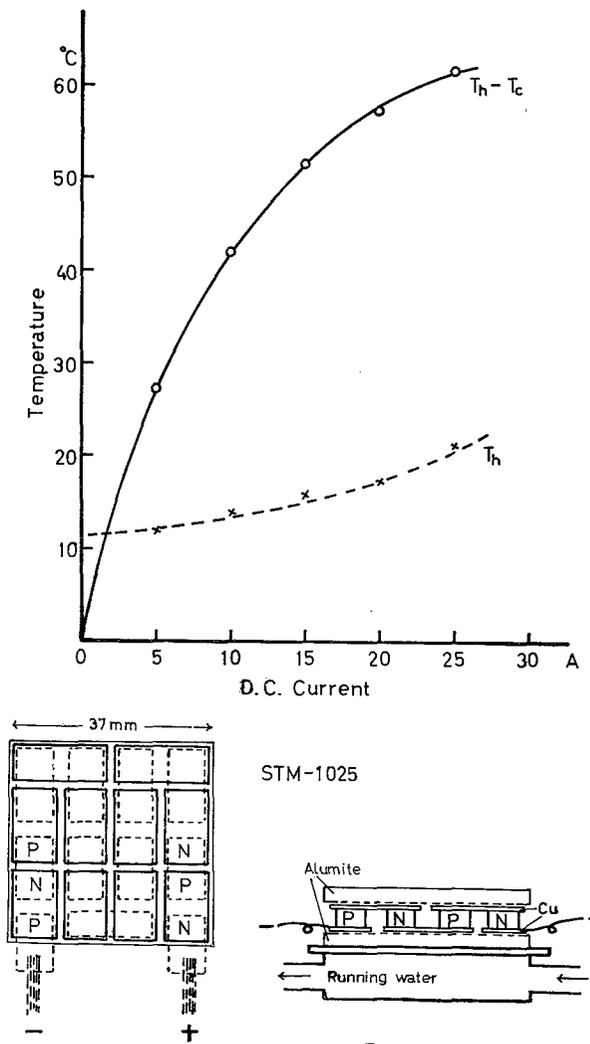


Fig. 2. *Top.* Typical performance data of STM-1025, with no thermal load. The solid line shows the temperature difference between the hot and cold sides, and the broken line the temperature at the hot side  
*Bottom.* Construction of STM-1025, whose properties are;  $\alpha = 3.5 \times 10^{-3}$  V/deg,  $R = 0.034 \Omega$  and  $K = 0.23$  W/deg, where  $\alpha$ : thermoelectric power,  $R$ : electrical resistance and  $K$ : thermal conductance

32x objectives all with working distances of 15.5 mm, allowed observation through an electricity-conducting glass which had been placed on top of the box (A) to prevent condensation of moisture, but all gave rather inferior definition.

The whole unit was fixed to a travelling device on the microscope stage, so that the entire surface of the STE could be scanned.

*Preparation of the substrate crystals :*

1. *Covellite.*

Montana covellite was broken into small pieces and cleaved into 5 mm square, 0.2 mm thick with the thin tip of a forceps or a razor blade. In observing the growth of thin ice layers by successive changes in the interference colours, it is essential to use freshly cleaved specimens.

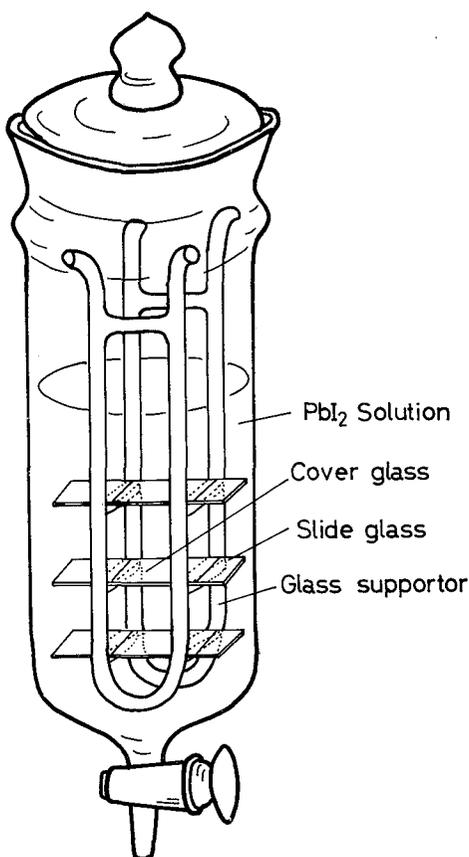


Fig. 3. Apparatus for making very thin  $PbI_2$  crystals

The growing process could be observed and photographed with a microscope and a transparent illuminator. Following desiccation, the cover glass could be easily removed with the  $PbI_2$  crystals adhering to it.

2. *Lead iodide.*

Lead iodide (0.4 g) was dissolved in 1 liter of distilled water at  $100^\circ C$ , and purified by repeated re-crystallization and dissolution.  $PbI_2$  crystals of varying thickness were prepared by various means. Details of the surface structure of these crystals will be given later.

a) *Minute  $PbI_2$  crystals.*

A drop of aqueous solution of  $PbI_2$  (saturated at approximately  $30^\circ C$ ) was placed between a glass slide and a cover glass which had been heated to approximately  $35^\circ C$  on the electricity-conducting glass.

When the solution had cooled, minute crystals began to grow, showing interference colour changes in the initial stages of growth. Since it was difficult to maintain constant, slow cooling rates because of the small heat capacity of the solution and the slides, the crystals finally assumed thick hexagonal shapes with skeleton structures (a few microns thick and  $70 \mu$  in diameter).

b) *Very thin PbI<sub>2</sub> crystals.*

The solution was poured into the glass bottle (Fig. 3) in which three cover glasses (24 × 32 mm, 0.13~0.17 mm thick) were suspended horizontally as is illustrated in Fig. 3. The bottle was kept in a large water bath at a temperature several degrees higher than the saturation temperature of the solution, and then allowed to cool slowly. The temperature and the cooling rate of the bath were regulated by an electronic control. When tiny lead iodide crystals began to glitter in the solution, the cooling rate was reduced to 0.12°C/hr until the crystals precipitated on the cover glasses and grew to the desired size. After the solution and any excess crystals had been removed through a stop-cock at the bottom of the bottle, the crystals which had precipitated on the cover glasses were dried in a desiccator.

The crystals prepared by this method varied in diameter from 0.1 to 5 mm and in thickness from 0.1 to 1  $\mu$ . The crystals deposited with *c*-axes vertical to the glass were so thin that beautiful interference colour patterns could be seen. A portion of the cover glass several millimeters square, containing the desired crystal was cut out and placed on the STE cold stage under the microscope.

c) *Thick PbI<sub>2</sub> crystals.*

A thickness of at least 10  $\mu$  was required to make cleavage surfaces. These crystals were made by continuing the procedure described above for 150 hours without using the cover glasses. The crystals and the solution were allowed to drip on filter paper stretched over a Buchner funnel. When the crystals were desiccated they could be picked up with forceps.

The following technique was used to cleave these crystals. A strip of 2-sided adhesive tape, "Kleen-Stik", was put on a cover glass. The PbI<sub>2</sub> crystals were then placed on the exposed gummed surface and a small piece of Scotch tape was pressed over the crystals so that they were sandwiched between two layers of tape. When the Scotch tape was peeled off the cleaved crystals remained on the cover glass with the cleavage surface uppermost. After they were cut in proper sizes, they were ready to be placed on the STE cold stage for experimental use.

*Evaluation of temperature and supersaturation:*

For detailed analysis of ice-crystal growth on these substrate it is essential to know the surface temperature of the substrate crystal and the water vapour density in the surrounding air. The surrounding air is presumed to be saturated with respect to ice at  $T_i$ , the temperature of the surface of the ice in the

bottom of the box, since the air inside the box (A) is well stirred by the small fan.

$T_i$  was obtained by placing a thin piece of wet paper on the STM cold plate and fixing a thermocouple of 0.1 mm  $\phi$  copper-constantan on its surface.

The surface temperature of the substrate,  $T_s$ , was estimated as follows;

A 0.1 mm  $\phi$  thermocouple was fastened to the surface of the STE cold plate. The measured temperature,  $T'_s$ , was expected to be a little lower than the real surface temperature of the substrate, because of the poor conductivity of the substrate and the cover glass which were located in warmer surroundings. An empirical correction was made from time to time by checking the dew-point on a silvered cover-glass placed close to the substrate crystal, or by observing the temperature at which the surface of the ice on the substrate neither grew nor evaporated. The correction,  $\Delta T$ , proved to be generally less than 0.5°C, with a maximum of 2°C, probably influenced by the nature of the contact between the bottom of the substrate and the STE cold plate.  $T_s$  was then given by  $T'_s + \Delta T$ .

$T_i$ ,  $T'_s$  and other auxiliary temperatures (i.e. the STM cold surface, the air near the substrate, and the water running through the STM radiator) were recorded by a 6-element, automatic balancing recorder, through a D.C. amplifier.

### III. Observations of Ice-crystal Growth on Cleaved Covellite

In this experiment, the threshold temperature for ice-crystal formation on covellite was  $-7^\circ\text{C}$ , two degrees lower than that reported by Bryant *et al.* (1959). This is not the threshold temperature of a flawless basal covellite surface. The first ice crystals usually appeared along steps and cracks.

On several occasions, V-shaped colour fringes were observed to run along a crack before an ice crystal grew from the crack and developed into a thin hexagonal plate over the flat surface of the substrate. These colour fringes appeared to be produced by interference in the wedge of ice formed along the inside of the V-shaped groove, probably by a condensation-freezing process. Unless the supersaturation exceeded 70%, ice crystals seldom grew on flawless cleavage surfaces.

The observations covered the temperature range between  $-7$  and  $-42^\circ\text{C}$ , and were primarily concerned with growth under low ( $<10\%$ ) supersaturation. When necessary, nucleation was facilitated by decreasing the substrate temperature and increasing the supersaturation for a few seconds.

On freshly cleaved covellite surfaces, ice crystals only a few thousand Ångströms thick showed vivid interference colours in the initial stages of growth. In this stage the crystals are not hexagonal but roughly circular. When the

supersaturation was less than 10% with respect to ice, some crystals grew laterally to  $200\ \mu$  in diameter with no discernible change in colour, while others increased in both diameter and thickness. The thicker the crystals, the fainter the hue and the more hexagonal the shape, until they all finally assumed a uniform pink colour. It should be noted that the colour was retained even when the crystals had grown as thick as  $40\ \mu$ .

It was also observed that in the temperature ranges from  $-7$  to  $-10^\circ\text{C}$  and from  $-20$  to  $-42^\circ\text{C}$ , the crystals were more columnar and in the range from  $-10$  to  $-20^\circ\text{C}$  they were thin plates. These observations are similar to observations of snow-crystal growth in air (KOBAYASHI (1961)).

In future experiments the author will analyse successive frames of 16 mm colour film to determine the growth rate of ice layers and the habit change in crystal growth.

The thickness of the ice crystals may be estimated from an analysis of the interference colours. Using the notation given in Fig. 4, the path difference between successive beams is simply  $2n_1d_1 \cos \varphi_1$ , since the phase changes with reflection at the upper and lower surfaces of the ice film are both equal to  $\pi$ , since  $n_0 < n_1$ , and  $n_1 < n_2$ . If  $2n_1d_1 \cos \varphi_1 = m\lambda$ , where  $m$  is an integer, the reflected energy will show a maximum for that wave-length,  $\lambda$ , and the film will possess a characteristic hue. The order,  $m$ , may be estimated by counting the successive changes of colour from the crystal's first appearance. The crystal thickness has been estimated to within  $100\sim 200\ \text{\AA}$  using the ICI chromaticity diagram (EVANS (1948)).

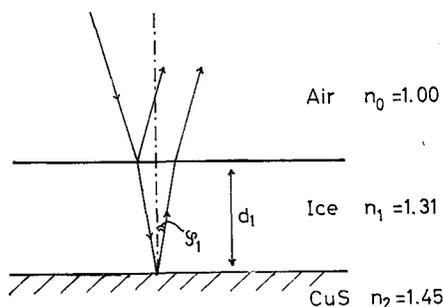


Fig. 4. Interference in an ice layer on a covellite surface

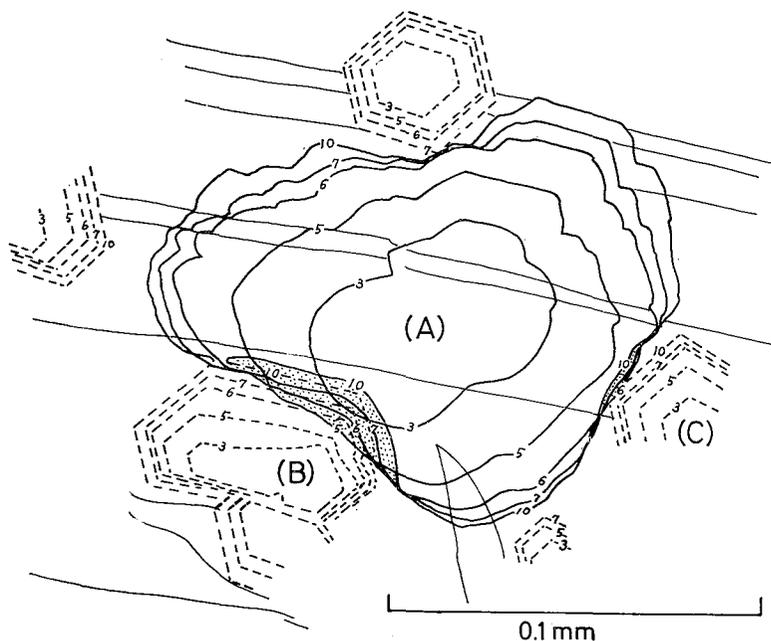
The accompanying colour plates illustrate some of these observations.

If an ice crystal is nucleated astride a step, it shows different colours on each side of the step. When the crystal grows over a parallel stepped surface, it exhibits parallel stripes, each stripe a different colour and thickness (Plate I-1, a and b). These ice crystals must have flat upper surfaces. This assumption is justified from the fact, that if a new layer expands from a point on a thin ice crystal, it grows across successive step lines without any discontinuity (Plate I-1, b). An ice crystal growing on a stepped surface often assumes a clam-shell outline, as is shown in the photograph, which suggests that the lateral growth velocity of an ice crystal is inversely proportional to its thickness.

This is additional evidence that the crystal growth is governed primarily by a migration of water molecules adsorbed on the substrate.

Generally, the colour of thin ice plates changes uniformly, either at a constant rate or intermittently. If the rate of change is constant, it may be assumed that the thickness of the crystal is increasing at a constant rate, and if intermittent, then at a varying rate, but in either case, the increase in thickness is accomplished by successive two-dimensional nucleation and lateral nuclear growth in the unit layer.

Occasionally, the colour change was observed to start from one point and spread rapidly over the ice plate. This may be considered evidence of lateral growth of a new layer on the surface of the ice crystal. The thickness of



**Fig. 5.** Crystal boundaries in successive growth stages (see Plate I-1, a and b). The numbers on the different crystal boundaries refer to the frame number of the photographs from which the figure was drawn: 3 is from the third successive photograph, 5 from the fifth, etc.

each layer ranged from 200 to 1800 Å. The layer usually started from a contact point, either where two crystals of different thickness grew together, or where a crystal growing laterally contacted an obstacle on the substrate (a foreign particle or the side of a step). These growth processes are very well illustrated in Plate II-4, a~d.

The crystals shown in Plate I-1 were grown at  $-12^{\circ}\text{C}$  and slightly above ice saturation. The boundaries of these crystals at each stage in their growth are shown in Fig. 5. **A** is a thin ( $2000 \text{ \AA}$ ) plate and **B** and **C** are much thicker ( $5$  and  $20 \mu$ ). When the thin crystal, **A**, approaches within  $3 \mu$  of the thicker crystals, **B** and **C**, the area of **A** closest to **B** and **C** is clearly observed to shrink and **A** is actually invaded by **B** and **C**, although all three crystals continue to grow as separate entities. In the figure, the shaded areas of **A** are the portions which evaporated. Occasionally a thin crystal was completely evaporated by the approach of a thicker crystal. In these cases the environmental supersaturation although low, was sufficient to grow the individual crystals as long as they remained far enough apart.

This phenomenon may be analogous with the well known three dimensional phenomenon observed when a small ice sphere (or water droplet) closely approaches a larger sphere (or droplet) (KUROIWA (1955)). Even though the environmental supersaturation is sufficient to grow individual ice spheres or water droplets, the smaller one will first evaporate and then condense on the larger. The vapour pressure of a thin ice crystal must be considerably higher than that of ordinary flat ice, so that the thin crystal evaporates from the portion closest to the neighbouring thicker crystal, when it grows into the diffusion field around the thicker crystal. Migration of adsorbed  $\text{H}_2\text{O}$  molecules on the substrate should be taken into consideration in modifying the three-dimensional diffusion field.

In addition, some elastic strain results from the misfit between the ice and the covellite surfaces, which may increase the ice-covellite interface energy and may become a contributing factor in the free energy when the ice plate is very thin.

With the aid of an X-ray diffraction photograph (Plate III-5), the author

TABLE 1

Substance	Symmetry	Lattice constant		Substrate plane	Percentage misfit ( $\Delta$ ) in direction		
		$a$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )		$[11\bar{2}0]$	$[0\bar{1}\bar{1}0]$	$[0001]$
Ice	Hex.	4.52	7.36	(0001)			
Covellite (CuS)	Hex.	3.80	16.43	(0001)	-2.8 (3:2)	-2.8 (1:2)	+11.5 (2:1)
AgI	Hex.	4.58	7.49	(0001)	+1.3 (1:1)	+1.3 (1:1)	+1.8 (1:1)
$\text{PbI}_2$	Hex.	4.54	6.86	(0001)	+0.4 (1:1)	+0.4 (1:1)	+6.8 (1:1)

$$\Delta = ((\delta_s - \delta_i)/\delta_i) \times 100 \quad (\text{after BRYANT, HALLETT and MASON (1959)})$$

has confirmed the observation of BRYANT *et al.* (1959) that ice crystals appeared with their  $a$ -axes at  $30^\circ$  to the  $a$ -axes of covellite (CuS), this relative orientation giving a much closer atomic fit between the deposit and the substrate, as is shown in Plate III-6. Table 1 gives the percentage of misfit,  $\Delta = ((\delta_s - \delta_i)/\delta_i) \times 100$ , where  $\delta_i$  and  $\delta_s$  are the atomic spacings of the ice and the substrates. On (0001), three atomic spacings of H<sub>2</sub>O molecules in the ice in the  $[11\bar{2}0]$  direction are matched with two spacings of Cu atoms in CuS in the  $[01\bar{1}0]$  direction, and one spacing in ice in the  $[01\bar{1}0]$  direction is matched with two spacings in the substrate in the  $[\bar{1}\bar{1}20]$  direction, with the closest coincidence,  $\Delta = -2.8\%$ . When the ice crystals grow in this way, one third of the H<sub>2</sub>O molecules in the (0001) plane are bonded to Cu atoms, and two thirds of the H<sub>2</sub>O molecules are located very near the centre of three adjacent Cu atoms on the interfacial plane.

A detailed discussion is given by N. H. Fletcher in the note which follows this paper.

#### IV. Observations of Ice-crystal Growth on Lead Iodide Crystals

Although there have been many experiments on the nucleation ability of lead iodide particles and on the epitaxial growth of ice on the lead iodide single crystals, very little is known about the nucleation and growth processes, or about the nature of the molecular binding between ice and the substrate surfaces. The present experiments clarify the so-called "epitaxial" growth of ice crystals on lead iodide.

##### 1. *Micro-topography of the lead iodide crystals.*

The surface topography of the very thin PbI<sub>2</sub> crystals produced by the method described above was examined by the following techniques.

Very thin PbI<sub>2</sub> crystals were observed with a microscope, using simultaneous oblique (tungsten) and vertical reflected illumination (Na D-line). The oblique illumination clearly showed the surface topography, e. g. trigonal spiral steps, parallel stepped terraces, and circular conical protrusions. The vertical reflected illumination gave Fizeau fringes at intervals of 2945 Å in height, which were formed by the internal reflection of the substrate. Either can be emphasized by regulating the brightness of the tungsten lamp in the oblique illuminator (Plate V-11, a and b).

Plate IV-7~9 illustrate typical PbI<sub>2</sub> crystal surfaces with trigonal growth terraces, separated by spiral or parallel steps. The steps are not usually parallel to the edges of the crystal.

The rate at which the segregating crystals were cooled greatly affected their surface topography. Slow cooling (0.1°C/hr) produced large flat surfaces and isolated high plateaus formed by screw dislocations (Plate IV-10). Occasionally, fine conical protrusions were observed as is shown in Plate V-11. When the cooling rate was increased, the surface patterns were more complex with many overlapping spiral steps (Plate V-12). The density of the spirals reached a maximum of  $10^4/\text{cm}^2$ .

An Olympus, T-O type interference microscope with Leitz UM series objectives was used to measure the height of the growth steps. The specimen was illuminated by a tungsten lamp with a red filter ( $\lambda/2 = \text{ca. } 3300 \text{ \AA}$ ) or by a Na lamp. Plate V-13 shows Fizeau fringes over trigonal spiral steps on a  $\text{PbI}_2$  surface. Using Verma's method (VERMA (1953)), the average step-height in these specimens was found to be from 300 to 600  $\text{\AA}$ .

### 2. *Ice crystal nucleation along cracks and the sides of steps.*

When  $\text{PbI}_2$  substrate crystals are cooled gradually at temperatures lower than  $-5^\circ\text{C}$  in atmospheres supersaturated only with respect to ice, the first ice crystals invariably appear along cracks or along steps not less than  $0.1 \mu$  in height. As FLETCHER (1960) has suggested, ice crystals do not nucleate at the cores of the spiral steps, from which screw dislocations emerge (Plate VI-14~17).

Between  $-10$  and  $-20^\circ\text{C}$ , ice crystals grow laterally in thin hexagonal plates with  $a$ -axes parallel to those of the lead iodide. Often they develop from the small round spot, which seems to have been formed by the freezing of a condensed droplet, and then grow rapidly into a sector form, or, if the degree of supersaturation is high, into a six-leafed form. As they grow, they transform into simple hexagonal plates, and the central spot becomes larger (Plate VII-18, a and b). The vivid colour changes characteristic of ice growth on covellite have never been observed in ice growing on  $\text{PbI}_2$ .

### 3. *Ice nucleation on a smooth, flawless surface.*

In the temperature range above  $-20^\circ\text{C}$ , ice crystals sometimes appear on what seems to be a smooth, flawless substrate surface as is shown in Plate VII-19, a and b. Usually, however, after the ice crystal has evaporated, a minute crack can be found and nucleation can be repeated at nearly the same spot along the crack or step. With repetition, nucleation becomes less likely at these spots.

It is difficult to ascertain whether or not ice crystals actually form on "flawless", (0001) surface of  $\text{PbI}_2$  crystals, since such surfaces may contain minute

cracks or steps which are too small to be seen, however, Plate VIII-20, a~d does reveal that ice crystals do not form on "flawless" surfaces at temperatures above  $-21^{\circ}\text{C}$ . When the substrate crystal was cooled, keeping  $T_i = -11.5^{\circ}\text{C}$ , dew condensed on the surface at  $T_s = -13.0^{\circ}\text{C}$ , which corresponds to 114% saturation with respect to ice (101% saturation with respect to supercooled water at  $-13.0^{\circ}\text{C}$ ) (Plate VIII-20, b). The dew suddenly vanished at  $T_s = -15.5^{\circ}\text{C}$  (142% saturation), probably by diffusing through the air to the ice crystals which had grown along the cracks or higher steps (Plate VIII-20, c). Finally, at  $T_s = -21.5^{\circ}\text{C}$  (240% saturation) ice crystals formed on the "flawless" basal surface (Plate VIII-20, d). These crystals grew in thick hexagonal plates and in the centre of many of them there was a round black spot which was probably hollow (Plate VIII-20, a). About half of the ice crystals were growing in the places where the dew droplets had previously condensed, while the location of the other half appeared to have no relation to those sites.

At temperatures between  $-21$  and  $-35^{\circ}\text{C}$ , ice crystals in the initial stage of growth on flat surfaces were occasionally observed to show faint colour changes or Fizeau fringes (Plate I-2). These crystals may have had "real contact" with the substrate.

#### 4. *Ice crystal nucleation on $\text{PbI}_2$ cleavage surfaces.*

In the experiments described above, the crude surfaces of  $\text{PbI}_2$  crystals which had precipitated from solution were used as substrates. The surface of these precipitated crystals may be contaminated by impurities however, and therefore it is more desirable to use cleavage surfaces as substrates.

A cleavage surface of  $\text{PbI}_2$  was placed on the STE cold plate and slowly cooled from approximately  $0^{\circ}\text{C}$ , with  $T_i$  maintained at just below  $0^{\circ}\text{C}$ . With this procedure, dew droplets appeared very quickly. These droplets were lower in density ( $1\sim 3.5 \times 10^3/\text{mm}^2$ ) and grew larger ( $5\sim 10 \mu$  in diameter) than those observed on the crude surfaces. The droplets on the "flawless" portions of the surface were then observed to evaporate rapidly while other droplets on the cracks and sides of the steps, froze (Plate IX-21 and 22). The highest temperature at which freezing took place was  $-3^{\circ}\text{C}$ . This suggests that at temperatures below  $-3^{\circ}\text{C}$ , the exposed prism face along the cracks or the sides of the steps may act as an effective nucleating agent.

The substrates were cooled to  $-42^{\circ}\text{C}$ , but no difference was observed between the cleavage and the crude surfaces, except that there seemed to be less tendency for ice crystals to form on the flawless portions of the cleavage surface. Careful observation revealed that some ice crystals in the initial stage of growth on the cleavage surfaces also assume faint colouration (Plate I-3).

### 5. The "epitaxial growth" of ice crystals on $\text{PbI}_2$ basal surfaces.

The most profound problem in epitaxy is the "contact" between the host and the guest crystal. When ice crystals grew epitaxially on the cleavage surfaces of covellite, real contact may exist over the entire crystal interface, but the present experiments showed that real contact only occurs at temperatures below  $-21^\circ\text{C}$  on the (0001) surfaces of  $\text{PbI}_2$  crystals. When ice crystals grow epitaxially on the basal planes of  $\text{PbI}_2$  at temperatures higher than  $-21^\circ\text{C}$ , "cohesion" of the participants in the contact plane seems to be limited to a very small domain, as Royer has suggested (see, SEIFERT (1953)).

A possible explanation of the so-called "epitaxial growth" of ice crystals on  $\text{PbI}_2$  basal planes at temperatures higher than  $-21^\circ\text{C}$  may be as follows:

Above  $-21^\circ\text{C}$ , only the  $\text{H}_2\text{O}$  molecules which are adsorbed along cracks or the sides of the steps may form ice crystals, which are epitaxially related to the prism face of the  $\text{PbI}_2$ . As the supersaturation which is necessary to form ice germs along the cracks usually exceeds the saturation with respect to planar surface of ice, these ice crystals are then able to grow over the basal plane from the cracks. In the temperature range between  $-10$  and  $-20^\circ\text{C}$  these crystals grow into hexagonal plates or sectors with  $a$ -axes parallel to those of the substrate crystal. Epitaxy does not require real contact between these ice crystals and the basal surface of the substrate. Observations show that the only attachment is at the centre germ and that from that the ice crystal spreads *over* the substrate in thin plates.

Plate VII-19 shows a hexagonal plate developing from a frozen droplet and growing *over* an adjacent spiral step on the  $\text{PbI}_2$  surface which is several thousand  $\text{\AA}$  high. If the ice crystal grew *on* the substrate, there would be some discontinuity when it grew across the spiral step. The radius of the frozen droplet in the figure is  $5\ \mu$ . Assuming the semi spherical shape of the frozen droplet as the ice germ, the ice plate may easily develop over the spiral step.

If the ice plate grows into the air above the substrate, a certain thickness is required to withstand the ambient low supersaturation. This may be the reason why ice plates epitaxed "on" the  $\text{PbI}_2$  basal surfaces do not show such vivid interference colours as those on covellite surfaces.

Plate X-23 shows several thin overlapping  $\text{PbI}_2$  single crystals with different  $a$ -axes orientations. Plate X-23, b clearly shows what happens when a thin ice plate nucleated at the edge of a single crystal continues to grow over other  $\text{PbI}_2$  crystals with different orientations. The ice crystal grows in the original orientation, without being influenced by the other substrate crystals. If every  $\text{H}_2\text{O}$  molecule was bound to a corresponding iodide ion, as would be the case

in true epitaxy, the development and orientation of the growing ice plate would be interrupted when it crossed the neighbouring substrate crystal.

The objection may be raised that the ice crystal may have started to grow from the uppermost surface of the overlapping  $\text{PbI}_2$  crystals. Plate X-24 shows that "window hoar"\* , developing from a minute  $\text{PbI}_2$  crystal, creeps up upon another  $\text{PbI}_2$  flat basal surface. The shape of the "window hoar" crystal differs slightly from the familiar window hoar, probably because of the definite orientation produced in its nucleation stage, but it still has the irregular crystal form associated with ice-glass interactions at the interface. When the tip of the window hoar has crept up upon another  $\text{PbI}_2$  crystal, it begins to assume a crystalline face, perceptively decreasing its rate of growth. The tip of the window hoar develops a parallel orientation to the original  $\text{PbI}_2$  crystal, but not to the second one.

This is additional evidence that epitaxy of ice does not require real contact on the  $\text{PbI}_2$  basal surface. It may also suggest that window hoar nucleated with a definite orientation, *c*-axis vertical to the glass surface, grows as a single crystal even though it may assume an irregular crystalline shape (KNIGHT (1962)).

A piece of cover glass on which minute, but thick (a few  $\mu$ )  $\text{PbI}_2$  crystals with some skeleton structure had been precipitated was cooled to form "window hoar". As may be seen in Plate X-25, when the tip of the window hoar came into contact with the prism face of a  $\text{PbI}_2$  crystal, ice grew very rapidly around the sides of the  $\text{PbI}_2$  crystal. Occasionally this rapid freezing was observed to skip along the side of the  $\text{PbI}_2$  crystal which suggests that a great deal of water had been adsorbed or had condensed on the prism face prior to inoculation.

## V. Discussion

The difference in epitaxial growth of ice crystal on covellite and on lead iodide is illustrated in Fig. 6:

On covellite surface (Fig. 6, a and b), ice-crystal nucleation may be facilitated by steps or cracks. Ice crystals grow *on* the substrate with direct contact between the crystal and the covellite, mainly by migration of  $\text{H}_2\text{O}$  molecules adsorbed on the basal surface of the substrate. There may be "cohesion"\*\*

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\* "Window hoar" means crystals of ice growing on glass, primarily by diffusion of water molecules on the glass surface. Window hoar crystals are always in direct contact with the glass.

\*\* The word "cohesion" is used here in its broadest sense, indicating that the ice lattice, which is elastically deformed because of a small misfit, is "coherent" with the lattice of the substrate.

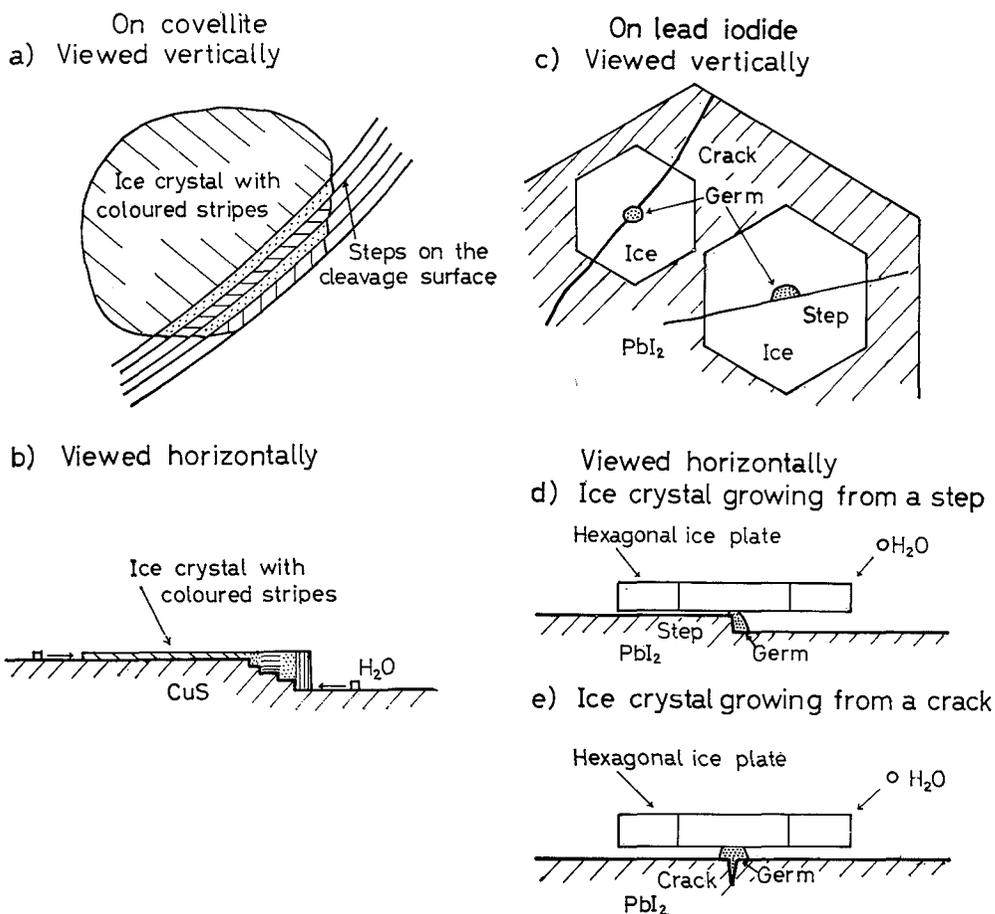


Fig. 6. Epitaxial growth of ice crystal on covellite and on lead iodide

between ice and covellite over the entire interface, and ice crystals, may therefore be so thin that they often show vivid interference colours in the initial stages of growth.

On lead iodide (Fig. 6, c, d and e), most of the ice crystals are observed to nucleate along cracks or steps on the substrate where it is probable that the prism faces are exposed. The edges of the growing hexagonal ice crystals are not always parallel to the cracks or steps, but they are parallel to the *a*-axis orientation of the substrate crystal. This may lead to the false assumption that ice crystals grow *on* the substrate with "cohesion" between the ice and the lead iodide basal surface.

The experiments reported here have proven, however, that ice crystals develop *over* the planar basal surface of lead iodide without "cohesion" in the contact plane. They assume an epitaxial relation to the basal surface, but "epitaxy" on the basal surface is in fact a result of the epitaxy on the prism faces. Ice crystals probably nucleate at kinks along the steps where the prism faces are exposed (Fig. 6, d), or are formed by the freezing of water condensed in the narrow grooves (Fig. 6, e). They grow *over* the basal surface primarily by direct diffusion of H<sub>2</sub>O molecules through the air but not by migration on the substrate surface, so an ice plate growing in air must, according to Thomson's formula, have a certain thickness which inhibits interference colours.

It is possible that the basal surface of PbI<sub>2</sub> does not adsorb water molecules, but these experiments showed that a great deal of water could be adsorbed or condensed on the prism faces of PbI<sub>2</sub>. This may be the reason why the prism faces\* are more effective in nucleation than the basal faces are. The height of the steps may also govern the germ size which is related to the threshold temperature of supercooling as has been noted by WEICKMANN (1951).

As is described above, the layer growth was observed on the surface of thin ice plates grown on covellite. HALLETT (1961) measured the spreading rate of the layers,  $U$ , and found a remarkable variation in this rate with temperature. MASON *et al.* (1963) directly determined  $x_s$ , the mean displacement of an adsorbed molecule on the basal surface of ice plates and obtained results similar to Hallett's on the temperature dependence of  $x_s$ . Mason *et al.* proposed a possible explanation of the mechanism of the habit changes of ice crystals, assuming  $x_s$  on the prism faces and relative rates of surface diffusion on the basal and prism faces.

The results of the experiments reported here however, suggest that ice-covellite interface may affect the surface of the thin ice crystals growing on the covellite cleavage surfaces.

Ice crystals with vivid interference colours assume a uniformly pink colour as they thicken, and this colour is retained even after they have grown to thicknesses of more than 40  $\mu$ . This so far unexplainable phenomenon has only been observed in ice crystals grown on covellite.

Sometimes patches of water, also tinted pink, have been observed on very freshly cleaved covellite surfaces. When the ambient supersaturation is raised,

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\* "Prism face" as used here does not imply crystallographic perfection. Real prism faces of PbI<sub>2</sub> crystals may have many cracks or gaps, since the crystals are composed of thin sheets piled up in the  $c$ -axis direction, giving excellent basal cleavage. It is possible that the difference in observed behavior between the prism and basal faces of PbI<sub>2</sub> may in part be due to a different degree of perfection.

these patches of water become larger and increase in thickness (Plate XI-26, a and b). They shrink and become thinner when the ambient supersaturation is lowered. Surprisingly, some of these patches of water retain their pink hue even when heated to temperatures as high as 20°C in the well-stirred atmosphere of the box ( $T_i = -15^\circ\text{C}$ ).

It was also observed that these layers of bound water could be easily super-cooled until they were nucleated, either by another ice crystal or by some obstacle acting as a freezing nucleus. Once inoculated, a dendritic crystal rapidly spread over most of the layer (Plate XI-26, c and 27). The growth rate then decreased and a small portion of the water layer remained unfrozen.

These observations illustrate the importance of tightly bound water on covellite cleavage surfaces, a fact which should be remembered when analysing thin layer growth of the ice crystals grown on these surfaces.

FLETCHER (1959) approached the nucleation problems theoretically, concluding that for substrates such as AgI or  $\text{PbI}_2$ , a basal surface is a poor nucleating agent and nucleating activity should be primarily confined to the prism faces. According to Fletcher, the threshold temperatures of  $\text{PbI}_2$  on the prism and basal faces are as follows:

	Freezing	Sublimation
Prism	- 6°C	- 6°C
Basal	- 18 to -27°C	- 35°C

The experiments reported in this paper lend considerable support to his theory, and lead to the following conclusions:

Large steps and cracks are effective nucleating agents for water droplets, which freeze below  $-3 \sim -5^\circ\text{C}$ . When the temperature is below approximately  $-5^\circ\text{C}$  and the saturation exceeds ice saturation by only a small percentage, ice crystals may form in those places along the larger steps and cracks where prism faces are exposed and it may therefore be concluded that nucleation on  $\text{PbI}_2$  surfaces usually proceeds by a condensation-freezing process along the steps and cracks.

At temperatures as low as  $-15^\circ\text{C}$ , dew droplets may condense on a flawless basal surface, and, if any ice crystal appears along steps or cracks, these droplets will evaporate before they freeze. This means that at temperatures above  $-15^\circ\text{C}$ , a flawless basal surface is inactive as a freezing nucleus. The threshold temperature for the basal surface cannot be determined unless a perfectly flawless surface can be produced.

At temperatures between  $-21$  and  $-35^\circ\text{C}$ , faintly coloured ice crystals appeared on a flawless basal surface, which suggests that the crystals were nucleated by sublimation and grow with real contact with the substrate.

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### Note on Conditions for the Growth of Epitaxial Crystals

In the accompanying paper Kobayashi reports that, when a thin crystal of ice growing epitaxially upon a covellite surface comes close to a very much thicker ice crystal, the thin crystal is caused to evaporate by growth of the thick crystal. He suggests that this phenomenon may be caused by elastic strain and similar influences in the thin crystal due to its epitaxial condition. It is the purpose of the present note to discuss this suggestion in greater detail.

The state of elastic strain in epitaxial crystals has been investigated by VAN DER MERWE (1963) and by FLETCHER (1964). For a crystal whose lattice parameter is  $a$  and whose misfit upon the substrate is  $\delta$ , most of the strain energy is localized within a distance  $a/\delta$  of the interface. For ice growing on covellite this distance is of the order of  $10^{-6}$  cm which is small compared with even the thinnest crystals considered. The strain energy can thus be conveniently considered as part of the ice-covellite interface energy.

Consider an ice crystal of thickness  $d$  growing epitaxially and without change of thickness on a covellite surface. If the ice advances then a small amount of covellite-vapour interface is replaced by an equal area of covellite-ice interface together with the same area of ice-vapour interface. Let us denote the energy involved per unit area by  $E$ . At the same time a number of water molecules whose free energy in the vapour near the surface is  $g_v$  are transferred to the solid ice state where their free energy is  $g_i$ . If  $n$  is the number of molecules per unit volume in the ice, then this process will only occur if

$$ndg_v \geq ndg_i + E$$

or, since

$$g_v - g_i = kT \ln(1+s) \approx kTs$$

where  $s$  is the supersaturation of the vapour with respect to ice, if

$$s \geq E/ndkT.$$

This is the analogue of Kelvin's equation for this case.

Consider now a large thick disc-shaped crystal of radius  $R$  and thickness  $D$  growing in an environment which, at a large distance from the crystal, has a supersaturation  $S$ . For such a crystal growth will usually take place normal as well as parallel to the substrate and it is a reasonable approximation to suppose that the vapour supersaturation is zero at the surface of the crystal itself. By considering solution of the diffusion equation for vapour near such a crystal it can be shown that, at a small distance  $x$  from the edge of such a crystal, along the substrate, the supersaturation has the approximate value  $xSD/R^2$ .

Thus the thin crystal will begin to evaporate if its edge comes closer than about

$$x \approx ER^2/ndkTSD$$

to the large crystal.

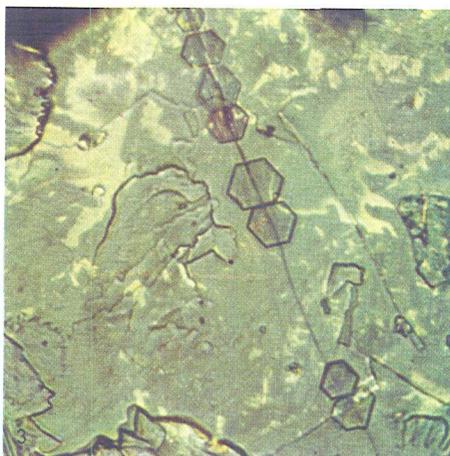
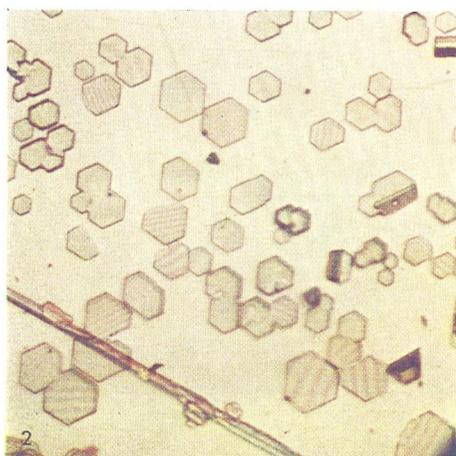
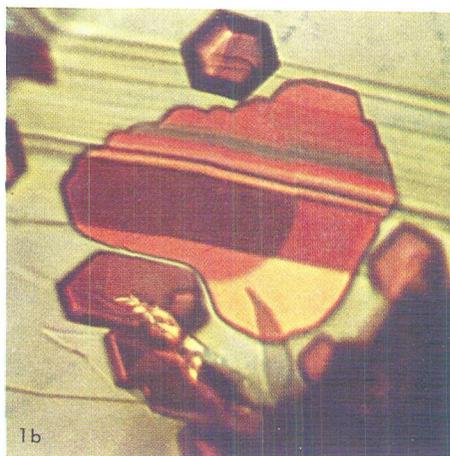
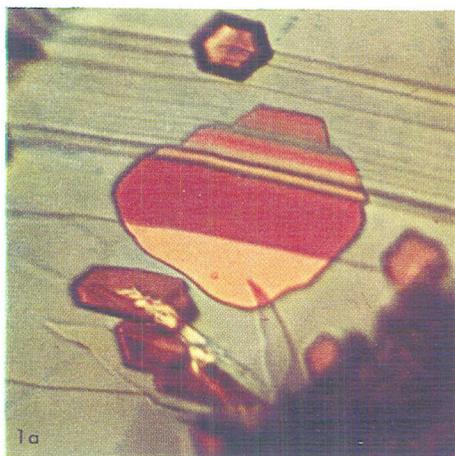
For ice on covellite FLETCHER (1964) indicated a value of the order of  $10 \text{ erg cm}^{-2}$  for  $E$ , which must in any case lie between 0 and about  $200 \text{ erg cm}^{-2}$ . Thus, for  $d \approx 0.2 \mu$ ,  $D \approx 10 \mu$ ,  $R \approx 50 \mu$  and  $S$  a few percent, the separation  $x$  at which evaporation begins is a few microns, in agreement with experiment.

N. H. FLETCHER

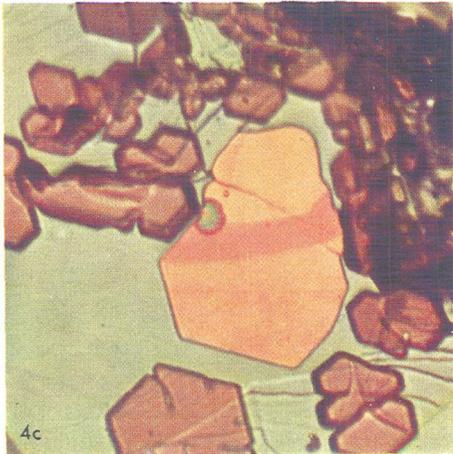
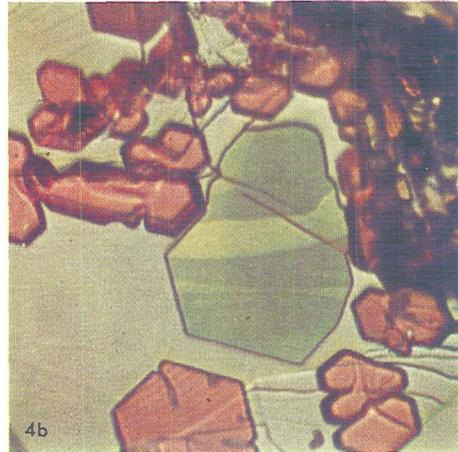
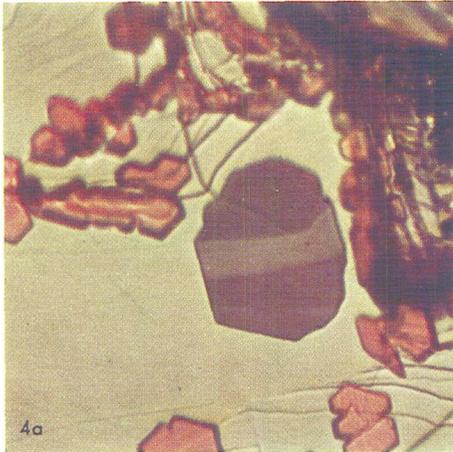
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University of New England  
Armidale N. S. W. Australia

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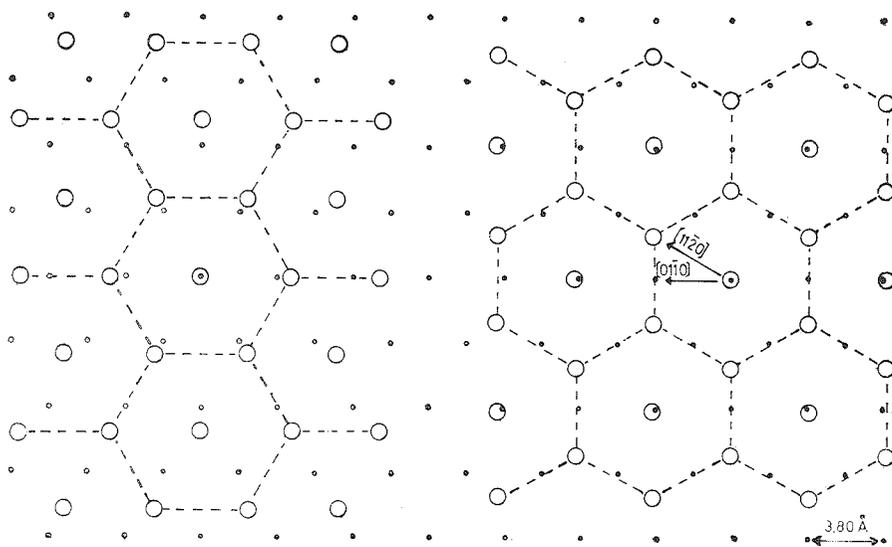
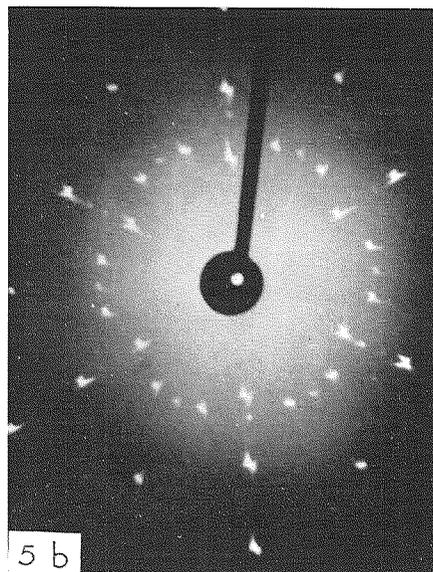
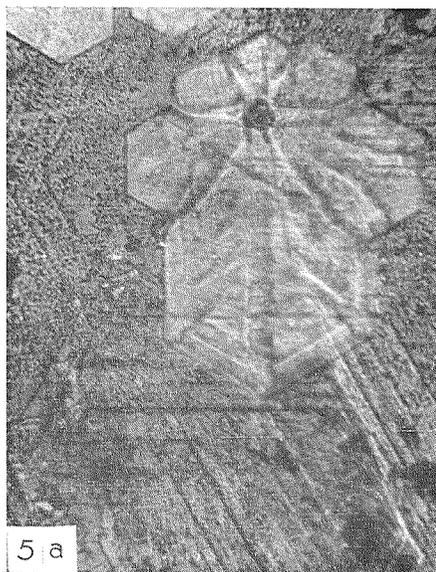
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1. Thin ice plate growing on a stepped covellite cleavage surface, at  $-12.0^{\circ}\text{C}$ , slightly above ice saturation ( $\times 330$ )
  - a) The crystal thickness increases with each step from the lower to upper edge and crystal assumes "clam-shell" out line
  - b) Same field as (a), 5 min 30 sec later; a thin, circular layer develops on the flat ice surface. Note the invasion of the lower portion of the thin ice plate by a much thicker ice crystal
  
2. Faintly coloured ice crystals grown on a flat basal surface of  $\text{PbI}_2$ , at  $-21.5^{\circ}\text{C}$ , slightly above ice saturation. Nucleation was facilitated by cooling the substrate to a considerably lower temperature for a few seconds ( $\times 300$ )
  
3. Faintly coloured ice crystals grown along a crack on a cleavage surface of  $\text{PbI}_2$  at  $-20.8^{\circ}\text{C}$  ( $\times 330$ ). Illuminated by a Xe short arc lamp



4. Successive growth stages of a thin ice crystal on a covellite cleavage surface, at  $-13.1^{\circ}\text{C}$  and 104% ice saturation ( $\times 330$ )
  - a) 48 sec after first viewing the crystal
  - b) 7 min 59 sec after (a). The crystal thickness has increased to  $560 \text{ m}\mu$
  - c) 29 sec after (b). Successive growth layers begin to spread on the flat surface of the thin ice plate, from the point of contact with a much thicker ice crystal
  - d) 49 sec after (c). Between the successive red and blue layers, the step height is approximately  $800 \text{ \AA}$

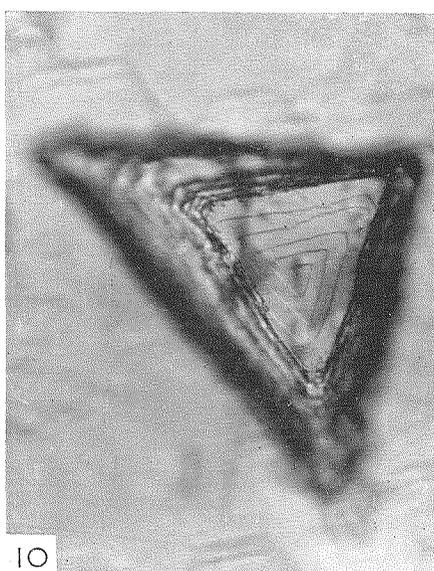
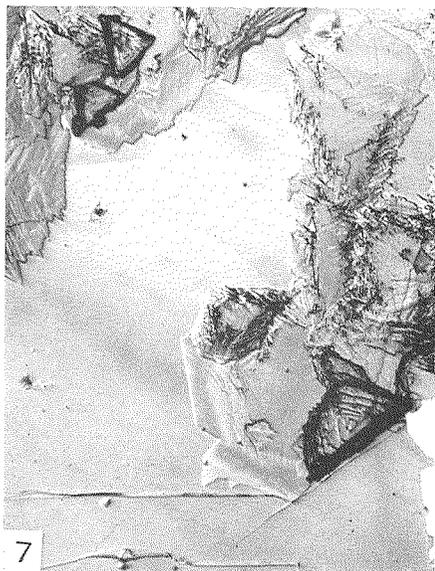


- Cu atoms in the (0001) plane of CuS
- H<sub>2</sub>O molecules in the (0001) plane of ice

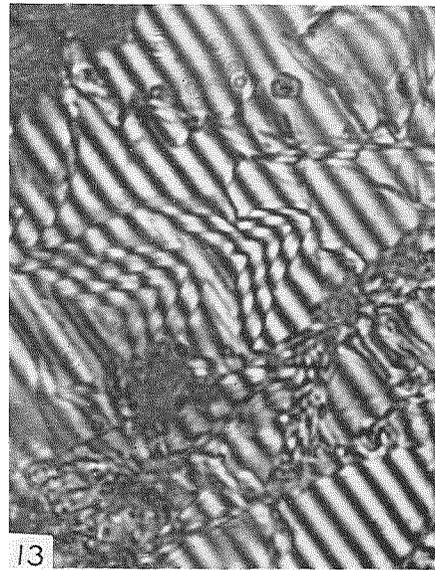
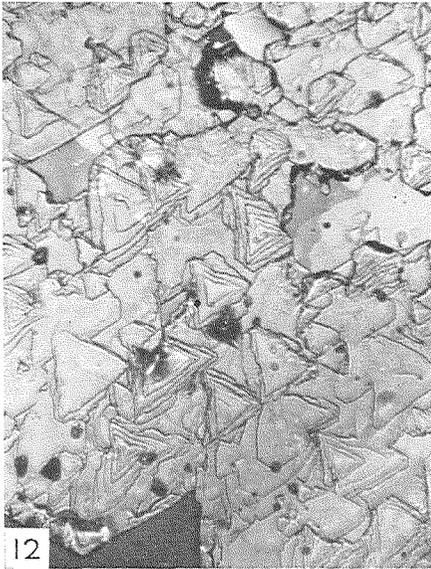
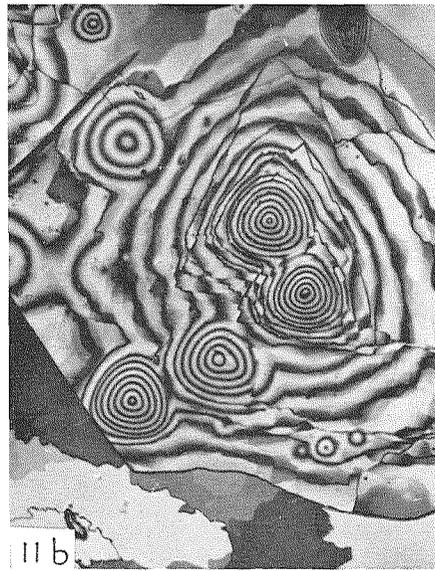
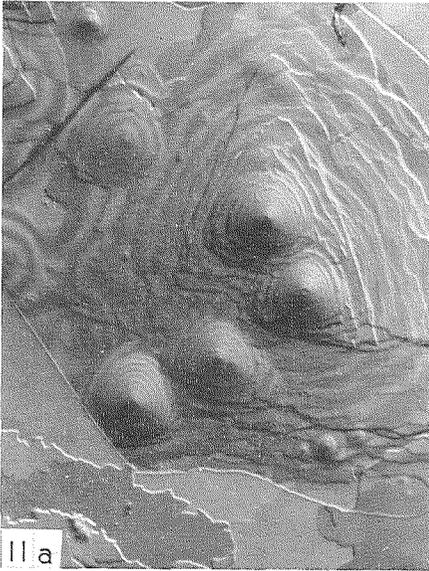
5. a) Ice crystals growing on a covellite cleavage surface ( $\times 160$ )
- b) X-ray diffraction photograph of the same covellite sample and same orientation as (a)
6. Relative atomic positions in the basal planes of CuS and ice (after BRYANT, HALLETT and MASON (1959))

7, 8 and 9. Surface views of thin  $\text{PbI}_2$  crystals ( $\times 160$ )

10. An isolated high ( $6\ \mu$ ) plateau formed by screw dislocations ( $\times 530$ )



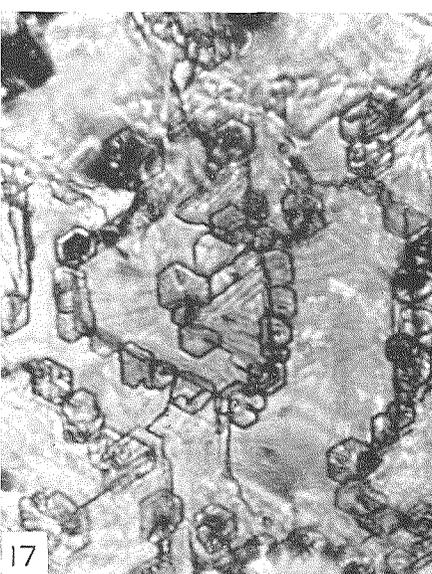
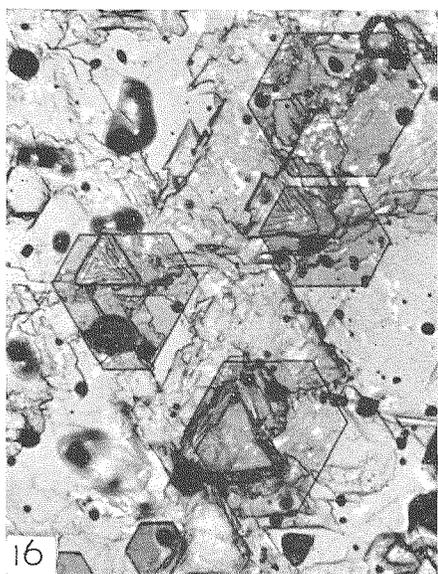
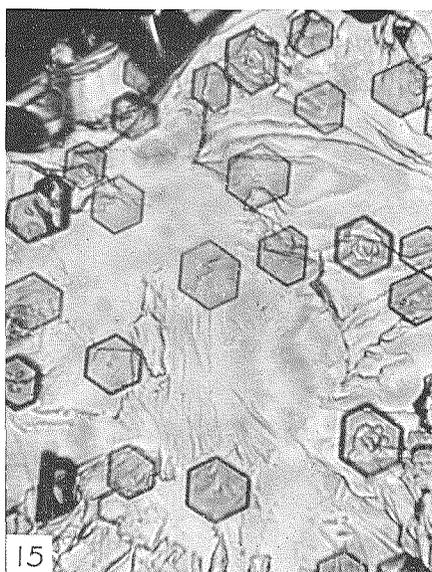
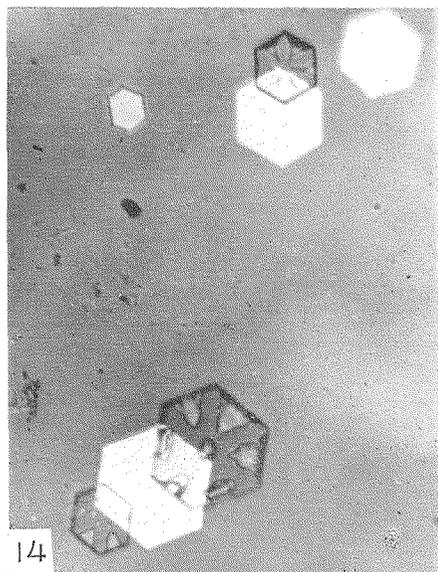
11. Circular conical protrusions on a  $\text{PbI}_2$  crystal ( $\times 160$ )
  - a) With transparent, oblique illumination
  - b) With vertical reflected illumination (Na D-line)
12. Surface pattern produced by many overlapping growth steps ( $\times 110$ )
13. Fizeau fringes over trigonal spiral steps on a  $\text{PbI}_2$  surface  
( $\lambda/2 = \text{ca. } 3300 \text{ \AA}$ ) ( $\times 340$ )



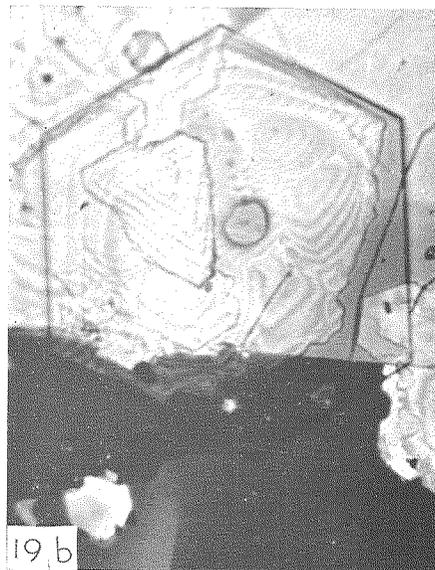
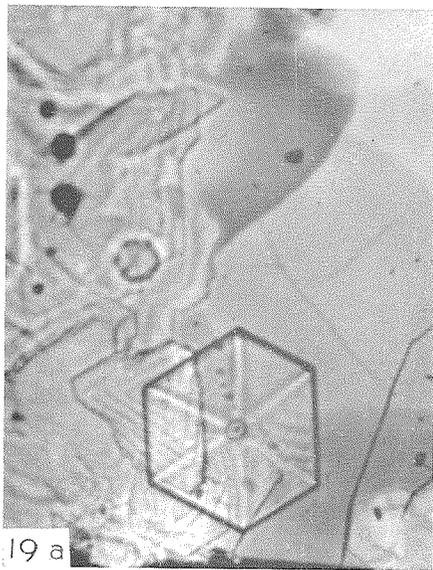
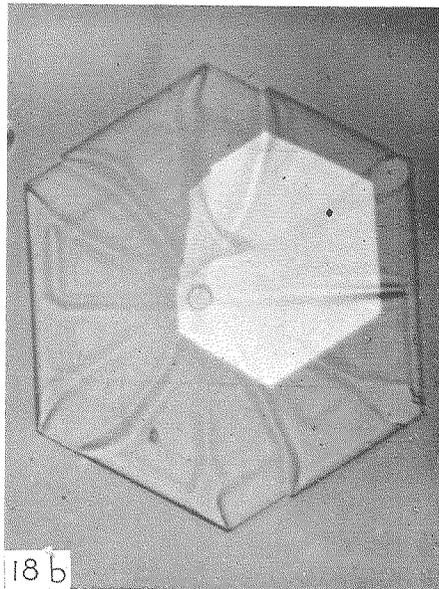
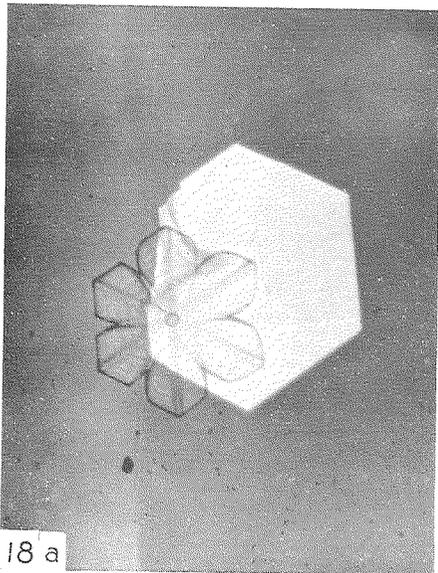
- 14\*. Ice crystal growing on the sides of  $\text{PbI}_2$  crystals, at  $-19.1^\circ\text{C}$  and 103% ice saturation ( $\times 290$ )
- 15\*. Ice crystals growing along cracks and steps on a  $\text{PbI}_2$  cleavage surface, at  $-18.6^\circ\text{C}$  and 111% ice saturation ( $\times 290$ )
16. Ice crystals growing over trigonal spiral steps on a  $\text{PbI}_2$  surface, at  $-17.5^\circ\text{C}$ . Crystals develop from the outer edge of the spiral steps but not from the core ( $\times 150$ )
17. Ice crystals on spiral steps on a  $\text{PbI}_2$  crystal at  $-25^\circ\text{C}$  ( $\times 330$ )  
There are no crystals on the central core where the step height is less than  $0.1 \mu$

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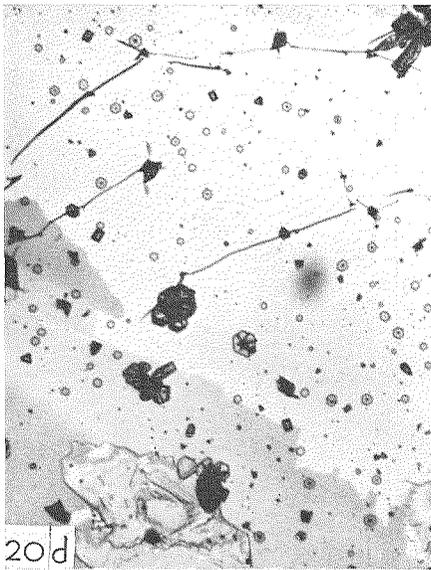
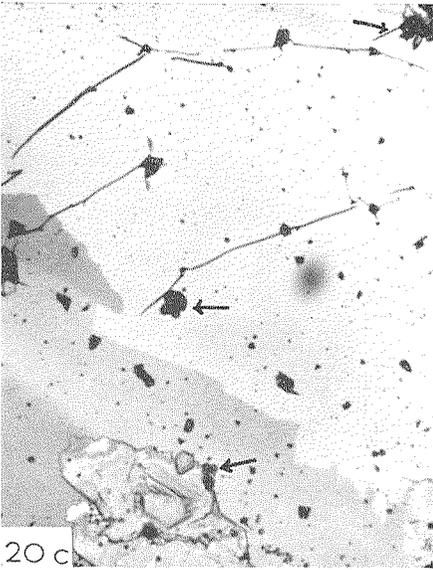
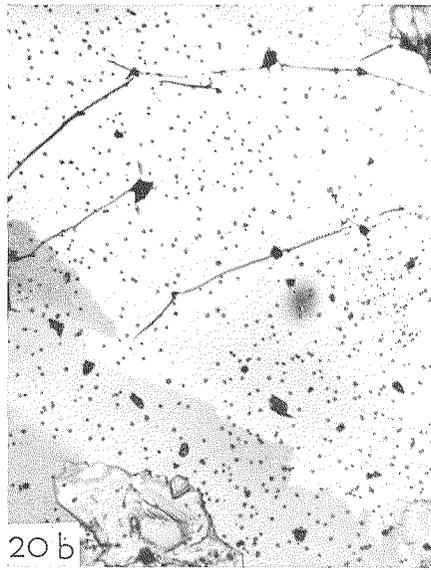
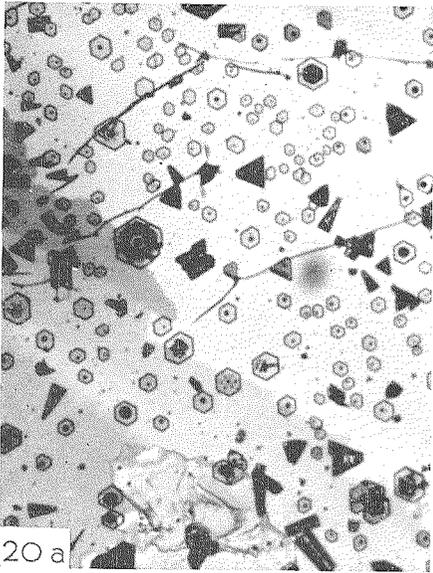
\* Photographs duplicated from colour slides.



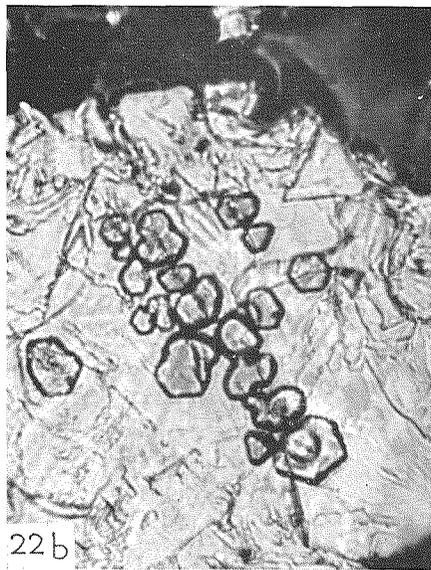
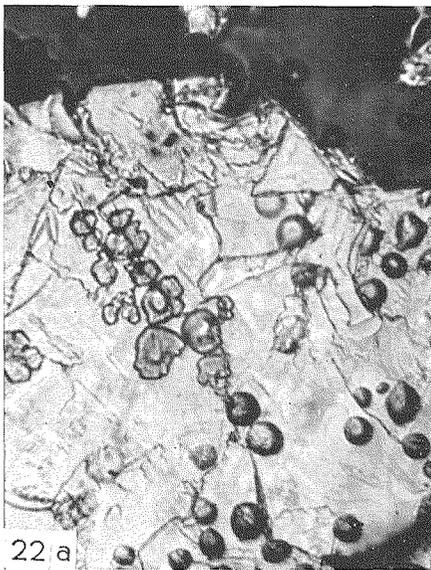
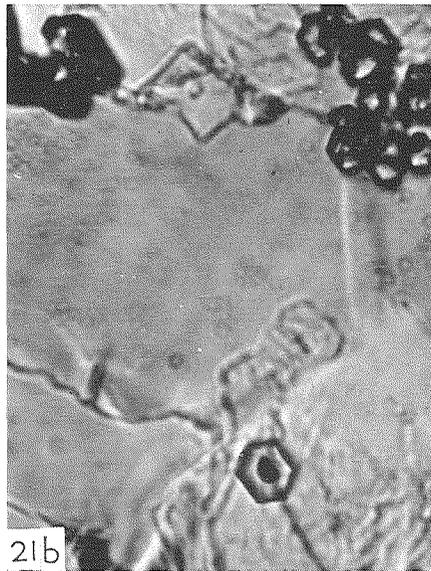
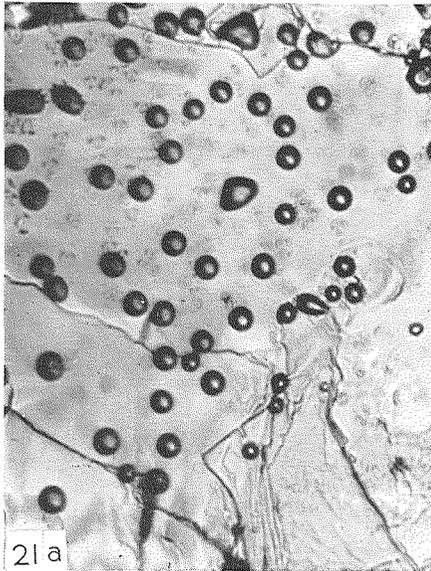
- 18\*. Thin ice plate growing epitaxially over a  $\text{PbI}_2$  crystal ( $\times 290$ )
- a) Initial six-leafed form developed from centre spot, at  $-14.2^\circ\text{C}$  and 110% ice saturation
  - b) Transformation of crystal to thin hexagonal plate. Faint fringe pattern produced by interference of two beams reflected on upper and lower surfaces. Note enlargement of centre spot as plate develops
- 19, a and b\*. Thin hexagonal ice plate growing over a trigonal growth step on a  $\text{PbI}_2$  surface ( $\times 290$ ). Crystal probably produced by freezing of a droplet condensed on a minute crack in the flat surface of the  $\text{PbI}_2$ . The thin plate develops from the frozen droplet (radius,  $5\ \mu$ ), and grows into the air with no direct contact with the  $\text{PbI}_2$  surface



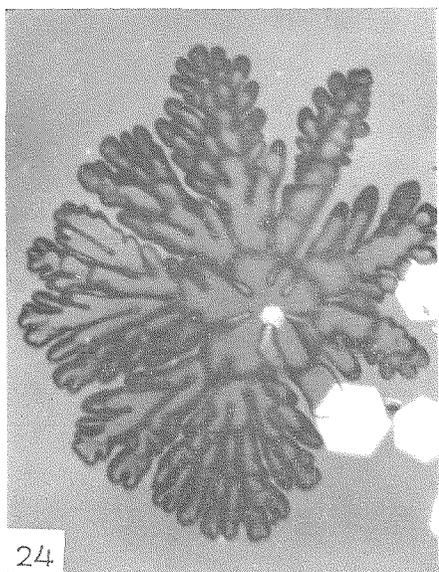
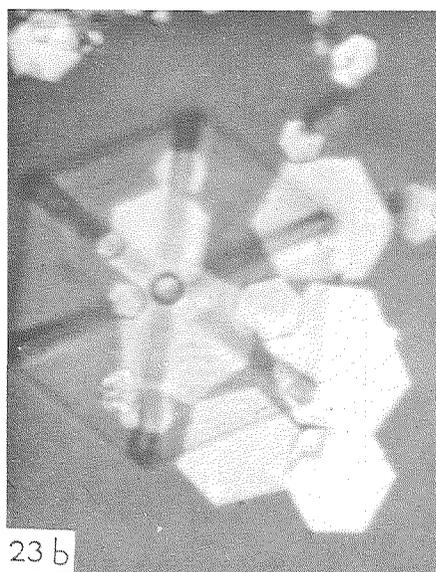
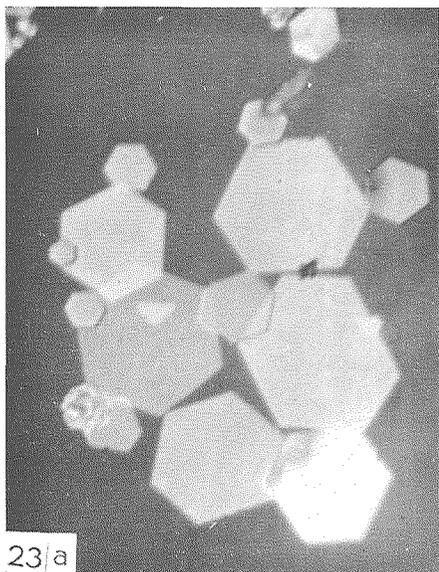
20. Ice crystal formation on a  $\text{PbI}_2$  "flawless" basal surface ( $\times 120$ )
- a) Ice crystals grown at  $-25.8^\circ\text{C}$  and 320% ice saturation
  - b) Substrate warmed to evaporate all of the crystals, and re-cooled.  
Dew droplets condense on the surface at  $-13.0^\circ\text{C}$  and 114% ice saturation
  - c) Dew vanishes at  $-15.5^\circ\text{C}$  and 142% ice saturation, when a few ice crystals (indicated by arrows) appear along the steps etc.
  - d) Ice crystals growing on an apparently "flawless" surface at  $-21.5^\circ\text{C}$  and 240% ice saturation



- 21\*. a) Dew droplets condensed on  $\text{PbI}_2$  cleavage surface ( $\times 290$ )  
b) Same field as (a), 30 sec later; At  $-14.5^\circ\text{C}$  droplets on "flawless" portions of the surface evaporate when ice crystals appear along the steps
- 22\*. a) Droplets freezing along steps or cracks, at  $-3.1^\circ\text{C}$  ( $\times 290$ )  
b) Same field as (a), immediately thereafter; Some droplets have vanished



- 23\*. a) Thin overlapping  $\text{PbI}_2$  single crystals with different  $a$ -axis orientations ( $\times 600$ )
- b) Thin ice plate nucleated at the edge of a single  $\text{PbI}_2$  crystal growing over other  $\text{PbI}_2$  crystals and maintaining original orientation, at  $-15.5^\circ\text{C}$
- 24\*. Tip of a branch of window hoar developing from a minute  $\text{PbI}_2$  crystal, creeps up upon another  $\text{PbI}_2$  crystal. Orientation of this crystalline face is parallel to the original  $\text{PbI}_2$  crystal but not to the second one ( $\times 290$ )
- 25\*. Ice crystal inoculated by tip of window hoar is growing around the sides of  $\text{PbI}_2$  crystal (a few  $\mu$  thick), at  $-18.3^\circ\text{C}$  ( $\times 150$ )



- 26\*. a) Coloured patches on a covellite cleavage surface, at  $+13.7^{\circ}\text{C}$   
( $\times 290$ )  
b) Condensation proceeds when the substrate is cooled to  $-10^{\circ}\text{C}$   
c) Dendritic freezing develops at  $-13^{\circ}\text{C}$
- 27\* Dendritic crystal spreads into water film following inoculation by ice crystals grown along a crack, at  $-16^{\circ}\text{C}$  ( $\times 290$ )

