

HEXAGONAL AND CUBIC ICE AT LOW TEMPERATURES

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ABSTRACT. The formation of hexagonal and cubic forms of ice was studied by the use of a cold stage in an electron microscope within the temperature range -90° to -180°C . Ice crystal specimens were made on cold substrates, i.e. a collodion film, gold foil, or copper grid on the specimen holder of the cold stage. The hexagonal form of ice formed on the cold substrates at temperatures from -90° to -100°C . At -100° to -130°C , both hexagonal and cubic forms of ice were detected. From -130° to -160°C only cubic ice was found. At temperatures below -160°C , minute crystals of cubic ice were detected. No transformation of the structural form of ice from hexagonal to cubic or from cubic to hexagonal occurred when the temperature of the specimens was varied in the range -90° to -160°C . The lattice constants of hexagonal and cubic ice, and the coefficient of thermal expansion of ice were calculated from the experimental results.

RÉSUMÉ. *Glace hexagonale et cubique aux basses températures.* L'étude de la formation de cristaux de glace cubiques et hexagonaux a été réalisée grâce à l'utilisation d'une enceinte froide placée dans un microscope électronique dans un domaine de température allant de -90 à -180°C . Les spécimens de cristaux de glace furent produits sur des substrats refroidis constitués de couches de collodion, de feuilles d'or ou de grilles de cuivre placés sur le support d'échantillons de l'enceinte froide. Des cristaux hexagonaux de glace furent formés sur les substrats à des températures allant de -90° à -100°C . De -100°C à -130°C , on a pu observer des glaces à formes cubiques et hexagonales. De -130° à -160°C , des cristaux cubiques seuls furent observés. A des températures inférieures à -160°C , on a pu observer de minuscules cristaux de glace cubiques. Aucune transformation de la forme structurelle de la glace, de forme hexagonale en forme cubique ou inversement, ne furent observée lorsque l'on fit varier la température de -90° à -160°C . Les constantes de réseau de la glace cubique et de la glace hexagonale, ainsi que les coefficients d'expansion thermique de la glace, ont été calculés à partir des résultats expérimentaux.

ZUSAMMENFASSUNG. *Hexagonales und kubisches Eis bei tiefen Temperaturen.* Die Bildung von hexagonalen und kubischen Eisformen wurde unter Verwendung einer Kältestufe in einem Elektronenmikroskop im Temperaturbereich von -90°C bis -180°C untersucht. Eiskristalle wurden auf kalten Substraten, d.h. Kollodiumfilm, Goldfolie oder Kupfergitter auf dem Objekttisch in der Kältestufe gebildet. Die hexagonale Eisform bildete sich auf den kalten Substraten bei Temperaturen von -90°C bis -100°C . Bei -100°C bis -130°C wurden sowohl hexagonale als auch kubische Eisformen entdeckt. Zwischen -130°C und -160°C wurde nur kubisches Eis festgestellt. Bei Temperaturen unter -160°C wurden winzige kubische Eiskristalle entdeckt. Bei Variierung der Temperatur der Objekte im Bereich zwischen -90°C und -160°C trat keine Umwandlung der Eisstruktur von der hexagonalen in die kubische oder von der kubischen in die hexagonale Form ein. Die Gitterkonstanten des hexagonalen und des kubischen Eises sowie die Wärmeausdehnungskoeffizienten des Eises wurden aus den Untersuchungsergebnissen errechnet.

INTRODUCTION

Investigations of the structural form of ice sublimed from water vapor onto a cold substrate have been carried out by many investigators using different methods, i.e. X-ray diffraction, electron diffraction, calorimetry, and electron microscopy using the selected-area diffraction method.

When water vapor sublimed on a base at a temperature above -85°C , the X-ray pattern of the ice was found to be normal hexagonal by Burton and Oliver (1935). At temperatures below -110°C , the pattern consisted of two diffuse lines; ice demonstrating such characteristics was described as vitreous ice.

A determination of the lattice constants of hexagonal ice at -66°C was made using the X-ray diffraction method by Megaw (1934) with the results:

$$a = 4.5085 \text{ X. U. } (4.5176 \pm 0.0001 \text{ \AA})$$

$$c = 7.338 \text{ X. U. } (7.3528 \pm 0.0002 \text{ \AA}).$$

From these measurements the ratio c/a is 1.628, which does not agree with the value for close packing (1.633).

An investigation of the cubic and hexagonal forms of ice was carried out by König (1943) using the electron diffraction method. Ice specimens were formed on a thin collodion film

in a low-temperature unit designed for transmission experiments with an electron-diffraction camera. The temperature of the specimen was controlled by a heater in the apparatus. The ice specimen formed at -170°C gave a diffraction pattern of diffused rings. When the specimen was heated to about -140°C , ring patterns characteristic of the diamond-type cubic structure were obtained. The specimen formed at about -80°C produced the electron diffraction ring pattern of hexagonal ice. The lattice constant of the cubic ice was calculated to be $6.36 \pm 0.01 \text{ \AA}$.

Honjo and others (1956) designed a cold stage for electron diffraction analysis of the structure of ice formed at temperatures from -70° to -170°C . The ice specimens were formed on a cooled collodion film on a grid in the cold stage by injecting water vapor from a glass tube containing moisture-laden silica gel. The transmission diffraction patterns of hexagonal ice were obtained above -80°C . Ice specimens formed at -150°C showed the ring patterns of cubic structure. Ice formed below -160°C was found to give diffuse halo patterns. The (222) ring from cubic ice and the corresponding (0004) ring from hexagonal ice were observed. It is suggested that when the scattering by hydrogen atoms in Pauling's position is taken into account, the observed intensity of the rings agrees well with the calculated value.

Blackman and Lisgarten (1957), using both transmission and reflection electron diffraction, observed three types of diffraction patterns, the type depending on the temperature of the substrate, a cooled collodion film or silver film. Below -140°C diffused rings were obtained. Between -140° and -120°C a sharp ring pattern characteristic of the diamond-type cubic pattern was observed. Between -120° and -100°C a sharp ring pattern of both the hexagonal and cubic ice types was found, and above -100°C only the hexagonal pattern was produced. The lattice constants of the hexagonal ice were calculated to be

$$a = 4.493 \pm 0.004 \text{ \AA} \text{ and } c = 7.337 \pm 0.006 \text{ \AA}, \text{ at } -110^{\circ}\text{C}$$

and those of the cubic ice were

$$a = 6.350 \pm 0.008 \text{ \AA}, \text{ at } -130^{\circ}\text{C}.$$

Bertie, Calvert and Whalley (1963), examined the transformation of cubic ice to hexagonal ice using X-ray diffraction. When a fresh sample of cubic ice was kept at -103°C , no change was observed within 2 h, but hexagonal ice was observed on the following day. When the cubic ice was kept at -140°C , no change was observed for 6 d, but hexagonal ice was detectable at -120°C in 2 or 3 d. When the sample temperature was increased to -103°C , a great amount of hexagonal ice was detected in 15 min, and was completely changed to hexagonal ice in 75 min. The difference in rate of transformation at -103°C in the above experiments is very striking, and shows that the rate depends on the thermal history and probably on the nucleation of hexagonal ice at the sample temperature.

Defrain and Nguyen Trong Linh (1966) obtained diffused rings from X-ray diffraction of ice at temperatures below -140°C , diffraction rings of cubic ice at temperatures between -140°C and -80°C , and rings of hexagonal ice at temperatures warmer than -80°C . McMillan and Los (1965) observed exothermic reactions of ice crystallization in a vacuum chamber at low temperatures, and discussed the recrystallization from cubic to hexagonal at a temperature of -87°C .

Ice crystals of sub-micron diameter were first observed by Hall (1950) using the replica method, and then by Hibi and Yada (1959) using an electron microscope. The first direct observation of ice crystals formed on a cooled Formvar film at temperatures from -70° to -120°C was made by Fernández-Morán (1960), who was also the first to obtain the Moiré pattern exhibited by hexagonal ice crystals grown on a single-crystal film of mica at -80°C . Vertsner and Zhdanov (1965) also made direct observations of ice crystals and the electron diffraction ring pattern of hexagonal, cubic and amorphous forms of ice at temperatures from -70° to -160°C .

This paper presents the results of measurements of the lattice constants and coefficients of thermal expansion of ice crystals, and reports on the temperature dependence and the transformation of the structural form of ice.

EXPERIMENTAL PROCEDURE AND SPECIMEN PREPARATION

The heat exchange for the cooling system was built into the specimen chamber of the electron microscope. The specimen was cooled to -170°C by the use of liquid nitrogen. Intermediate specimen temperatures were provided by the cold-stage heater. The temperature was measured at the specimen by means of a ring-shaped thermocouple consisting of a copper-stainless steel junction formed during construction of the bi-metal specimen holder. The specimen rested against the thermal junction. A microvolt meter, calibrated at 0°C and at -196°C , the boiling point of liquid nitrogen at 1 bar pressure, was used to measure the temperature. The vacuum of the electron microscope was measured by an ionization gauge.

The ice crystal specimens were formed on the surface of a collodion film, a thin foil of gold, a thin cleavage surface of mica, or a grid of copper on the specimen holder of the cold stage. The surface to be used for ice crystal formation was cooled to the desired temperature of less than -90°C in pure nitrogen gas at atmospheric pressure. A steep temperature gradient existed on the surface of the specimen holder. A small amount of water vapor was introduced into the specimen holder, causing minute droplets to form above its surface. The ice crystal specimens grew on the surface of the cold substrates by sublimation of water vapor from the minute droplets. Ice crystal photomicrographs and their electron diffraction patterns were obtained with the electron microscope in the temperature range -90° to -180°C with a vacuum of 10^{-4} to 10^{-5} mm Hg.

MEASUREMENT OF LATTICE CONSTANTS

The lattice constants of the hexagonal and cubic ice crystals were determined by comparing their patterns with those from a standard substance, sodium chloride or gold, which was shadowed in a vacuum chamber on one part of a thin collodion film on the electron microscope grid. At room temperature the electron-diffraction pattern of this substance was recorded on a photographic plate. Ice crystals were then formed on the filmed grid at temperatures from -90° to -180°C . An ice pattern and a combined pattern of ice and standard substance were made on photographic plates by a slight shift of the grid.

The camera constant λL can be obtained for the standard substance by the relation of a Bragg reflection,

$$\lambda L = rd$$

where d is the spacing of the (h, k, l) plane, r is the radius of the ring pattern from the (h, k, l) plane, λ is the electron wave-length, and L is the camera length.

The d -spacings can be obtained from the accurately known value of the lattice constant of sodium chloride, $a = 5.601 \pm 0.003 \text{ \AA}$ at -130°C (Blackman and Lisgarten, 1957). This value was in good agreement with that obtained by estimation based on thermal data using the Grüneisen formula.

Once λL is determined for the standard ring pattern, the d -spacing of the specimen can be obtained by dividing λL by the measured radius r of the ring patterns for the specimen. The radius values are based on eight determinations of each ring diameter, each being taken twice at 45° intervals. The observed value of λL for the standard substance, the average measured values of $2r$ for each ring pattern from the ice, and the calculated values of the lattice constants for hexagonal and cubic ice are tabulated in Table I.

TABLE I. DETERMINATION OF LATTICE CONSTANTS

Hexagonal ice at -110°C $\lambda L = 4.2931$ (\AA cm)				Cubic ice at -130°C $\lambda L = 4.5129$ (\AA cm)		
Ring index	$2r$ cm	a \AA	c \AA	Ring Index	$2r$ cm	a \AA
{10.0}	2.203	4.499	—	{111}	2.456	6.365
{00.2}	2.340	—	7.338	{220}	4.023	6.346
{10.1}	2.492	(4.504)	(7.371)	{311}	4.716	6.348
{10.2}	3.207	(4.513)	(7.365)	{331}	6.181	6.366
{11.0}	3.811	4.505	—	{422}	6.965	6.349
{10.3}	4.139	(4.506)	(7.351)			
{11.2}	4.474	(4.500)	(7.347)			
{12.0}	5.831	4.499	—			
{30.0}	6.612	4.498	—			
{30.2}, {00.6}	7.003	4.505	7.357			
Average $a = 4.501 \pm 0.004$ \AA $c = 7.348 \pm 0.009$ \AA $c/a = 1.633$				Average $a = 6.355 \pm 0.01$ \AA		

The values of the lattice constants were:

$$a = 6.35 \text{ \AA} \text{ at } -130^{\circ}\text{C} \text{ for cubic ice,}$$

$$a = 4.501 \text{ \AA} \text{ at } -110^{\circ}\text{C} \text{ for hexagonal ice,}$$

$$c = 7.348 \text{ \AA} \text{ at } -110^{\circ}\text{C} \text{ for hexagonal ice,}$$

$$c/a = 1.633 \text{ at } -110^{\circ}\text{C} \text{ for hexagonal ice.}$$

In the case of the hexagonal ice crystals, the a spacing was measured from four patterns of {10.0}, {11.0}, {12.0} and {30.0} rings which did not involve the c spacing. The c spacing was determined from the measurement of the combined patterns of the {00.6} and {30.2} rings, and the {00.2} ring (Table I). The temperature of the specimens was measured within an error of about 5 deg by the calibrated copper–stainless steel thermo-couple.

In this experiment lattice spacings of hexagonal ice for high indices such as {10.6}, {11.6}, {31.2} and {31.3} were observed for the first time (Table II).

Most of the observed ring patterns of the diamond-type cubic ice coincide within the error of observation with the ring patterns of the hexagonal ice. In the examination of many diffraction patterns, very weak traces of the {400} and {222} ring patterns from cubic ice, and the {00.4} ring pattern from hexagonal ice, were observed.

DIFFRACTION PATTERN AND GRAIN-SIZE OF ICE

A large number of hexagonal crystals with diameters of 0.1 to 2.0 μm , with the most frequently occurring diameter 0.3 μm , were formed on copper grids previously cooled to -100°C . The basal and prismatic planes were revealed upon examination (Fig. 1a). The average height of the hexagonal crystals was about 0.7 of the diameter of the hexagonal base. This is close to the value 0.8 obtained by Krastanov (1943) and Wolff (1957) for an equilibrium form of hexagonal ice when only the interaction between the nearest oxygen neighbors was taken into consideration.

Transmission electron diffraction patterns for ice crystals of known size distribution (Fig. 2) were observed. The width of the diffraction ring depends on the grain size of the ice crystals, the camera length, the diameter of the electron beam, the amount of electron beam absorption by ice, etc. Using a beam diameter of about 20 μm and a selected area of 50 μm^2 , the transmission electron diffraction pattern of hexagonal ice in the diameter range 0.1 to 2.0 μm , with a most frequently occurring diameter of 0.3 μm (Fig. 1a), showed ring patterns with some spots in the ring (Fig. 1b). Ice crystals larger than 1 μm in diameter showed spot

TABLE II. INTERPLANAR DISTANCES FOR HEXAGONAL AND CUBIC ICE*

Hexagonal ice at -110°C				Cubic ice at -130°C			
Plane	d_{calc} (Å)	d_{obs} (Å)	I_{obs}^{\dagger}	Plane	d_{calc} (Å)	d_{obs} (Å)	I_{obs}^{\dagger}
{10.0}	3.898	3.919	v.s.	{111}	3.670	3.690	v.s.
{00.2}	3.674	3.676	v.s.				
{10.1}	3.446	3.450	v.s.				
{10.2}	2.674	2.665	med				
{11.0}	2.251	2.263	v.s.	{220}	2.246	2.249	s.
{10.3}	2.074	2.075	s.				
{20.0}	1.949	1.963	w.				
{11.2}	1.919	1.926	s.	{311}	1.916	1.925	med.
{20.1}	1.884	1.884	w.				
{00.4}	1.837	1.838	v.w.	{222}	1.834	1.840	v.w.
{20.2}	1.722	1.715	w.				
				{400}	1.593	1.591	v.w.
{20.3}	1.525	1.514	med.				
{12.0}	1.473	1.471	med.				
{12.1}	1.445	1.437	med.	{331}	1.458	1.455	med.
{12.2}	1.367	1.362	med.				
{30.0}	1.299	1.299	med.				
{12.3}	1.263	1.261	med.	{422}	1.297	1.304	med.
{30.2}, {00.6}	1.225	1.228	w.	{511}, {333}	1.223	1.217	w.
{10.6}	1.168	1.166	w.				
{22.0}	1.125	1.128	w.				
{11.6}	1.075	1.068	w.				
{31.2}	1.037	1.036	w.				
{31.3}	0.989	0.983	v.w.				

* Calculated value for interplanar distances are based on $a = 4.501 \text{ \AA}$, $c = 7.348 \text{ \AA}$ for hexagonal normal ice at -110°C , and $a = 6.3546 \text{ \AA}$ for cubic ice at -130°C .

$\dagger I_{\text{obs}}$ = observed intensity, v.s. = very strong, s. = strong, med. = medium, w. = weak, v.w. = very weak.

patterns. When the most frequently occurring diameter was larger than $0.3 \mu\text{m}$, the spot pattern was more prominent and the ring patterns became faint (Fig. 3a, b). With further growth of the $0.3 \mu\text{m}$ crystals in the direction of the electron beam, the characteristic needle-like patterns of electron diffraction were observed (Fig. 3c, d). Minute crystals, possibly around 500 \AA in diameter, gave sharp ring patterns, (Fig. 4a) and even more minute crystals less than 100 \AA in diameter gave broad diffraction rings (Fig. 4b) as was observed by Vertsner and Zhdanov (1965).

In an examination of many diffraction plates, faint traces of the {00.4} ring of hexagonal ice were observed in some plates, and very weak traces of {400} and {222} ring patterns from cubic ice were present. The observed lattice spacings of hexagonal ice (Fig. 1a) are shown in Table II.

TEMPERATURE DEPENDENCE OF THE STRUCTURAL FORM OF ICE

A series of experiments was carried out on crystals formed at temperatures from -90° to -180°C to determine the structural forms present at these temperatures. At temperatures above -100°C hexagonal crystals formed (Fig. 1a, b). At -120°C both hexagonal and cubic ice formed on the collodion film. The cubic crystals were detected by their electron diffraction patterns. The hexagonal ice crystals grew to a diameter of 1 to $3 \mu\text{m}$, and the cubic crystals grew to a diameter of less than $0.1 \mu\text{m}$ (Fig. 1c). The rate of growth of the hexagonal crystals was more than 10 times greater than that of the cubic crystals at -120°C . The cubic ring patterns from {111}, {220}, {311} and {331} and the spot patterns from the hexagonal crystals are seen in Figure 1d.

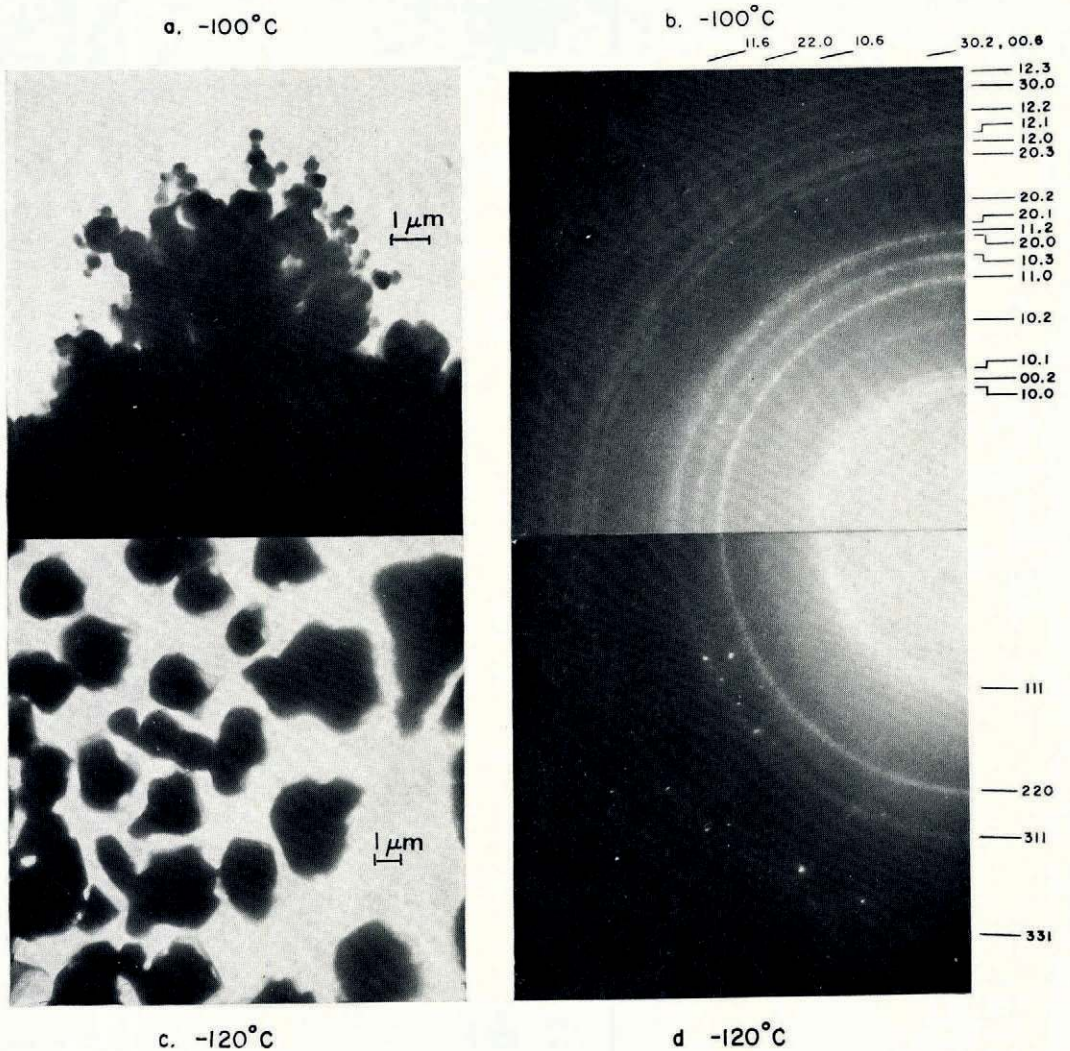


Fig. 1. (a) Hexagonal ice crystals formed on a copper grid at -100°C , (b) their hexagonal ring patterns, (c) hexagonal and cubic ice crystals formed on a collodion film at -120°C , (d) spot patterns from the hexagonal ice and sharp rings from the cubic ice shown in (c)

The ice crystals formed at -140°C from the residual water vapor in the electron microscope showed $\{111\}$, $\{220\}$, $\{311\}$ and $\{331\}$ cubic diffraction rings (Fig. 4a). At -170°C the cubic ring patterns appeared (Fig. 4b), although the rings were more diffuse than those at -140°C . It is concluded that a very minute form of crystalline cubic ice is present at -170°C . These experiments have shown that the structural form of the ice depends on the temperature of the substrate on which it forms.

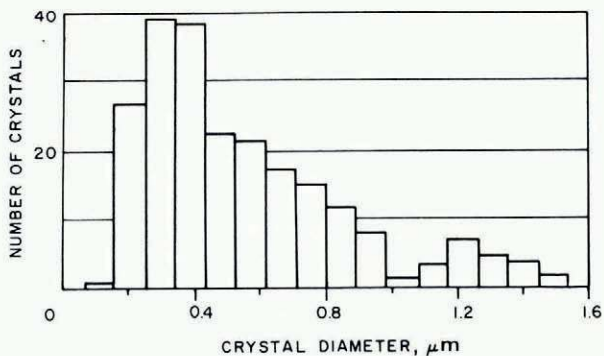
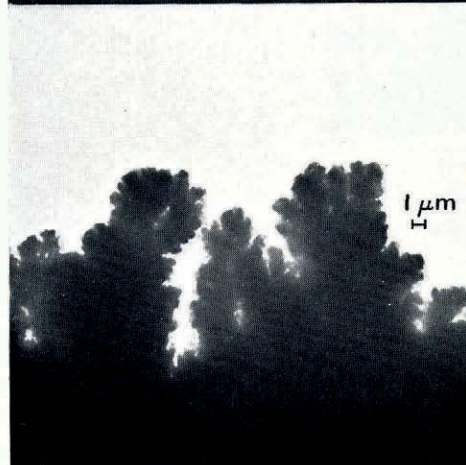
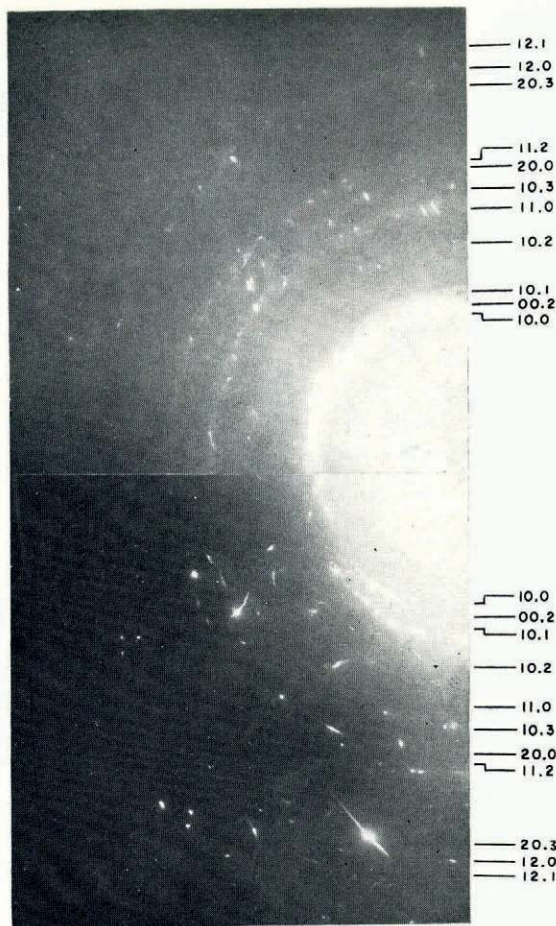
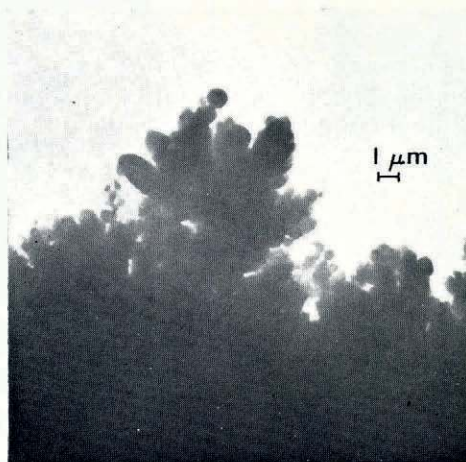


Fig. 2. The size distribution of ice crystals shown in Figure 1a

a. -110°C

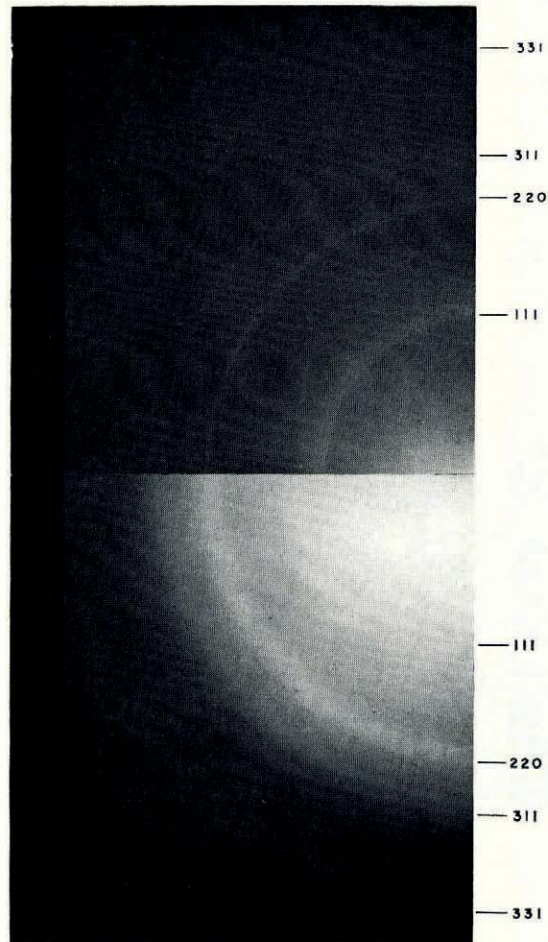
b. -110°C



c. -110°C

d. -110°C

Fig. 3. (a) Hexagonal ice crystals grown on a copper grid at -110°C , (b) electron diffraction pattern of (a) showing prominent spots and faint rings, (c) hexagonal crystals grown further in the direction of the electron beam, (d) the characteristic needle-like patterns of the electron diffraction of (c)

a. At -140°C b. At -170°C Fig. 4. *Electron diffraction patterns of ice crystals*

The four types of electron diffraction patterns produced by ice at temperatures from -100° to -180°C are shown in Table III, and the results of experiments by many workers (as well as those reported here) on the temperature dependence of the structural form of ice at low temperatures are summarized in Table IV.

TABLE III. TYPES OF ELECTRON DIFFRACTION PATTERNS OF ICE CRYSTALS FORMED AT VARIOUS TEMPERATURES

<i>Temperature of base</i> $^{\circ}\text{C}$	<i>Type of pattern</i>
> -100	Sharp rings of hexagonal ice
-100 to -130	Sharp rings of both hexagonal and cubic ice
-130 to -160	Sharp rings of cubic ice
-160 to -180	Diffuse rings of minute cubic ice

TABLE IV. TEMPERATURE DEPENDENCE OF THE STRUCTURAL FORM OF ICE CRYSTALS FORMED AT LOW TEMPERATURES

Experimental method	-180°	-170°	-160°	-150°	-140°	-130°	-120°	-110°	-100°	-90°	-80°	-70°	Reference
X-ray diffraction	amorphous						semi-crystalline			hexagonal			Burton and Oliver (1935)
Electron diffraction	small crystals	cubic									hexagonal	König (1943)	
Calorimetric	amorphous						crystalline						Pryde and Jones (1952)
Electron diffraction	amorphous or minute crystals			cubic						hexagonal	Honjo and others (1956)		
Electron diffraction	amorphous or small crystals				cubic		hexagonal and cubic		hexagonal			Blackman and Lisgarten (1957)	
Electron microscope and electron diffraction					cubic		hexagonal					Fernández-Morán (1960)	
Electron microscope and electron diffraction	amorphous				cubic		hexagonal					Vertsner and Zhdanov (1965)	
Electron microscope and electron diffraction	minute cubic crystals	cubic			hexagonal and cubic			hexagonal				Kumai (this paper)	

TRANSFORMATION OF THE STRUCTURAL FORM

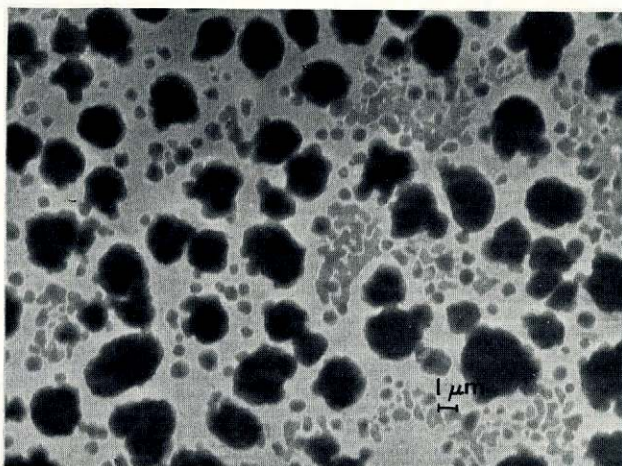
Transformation of the structural form of the ice by temperature change was examined by comparing the electron diffraction patterns of the ice before and after the temperature change.

When hexagonal ice crystals that were produced at -90°C were cooled to -140°C, the temperature of cubic ice formation, no change in structural form was noted even after about an hour at the lower temperature.

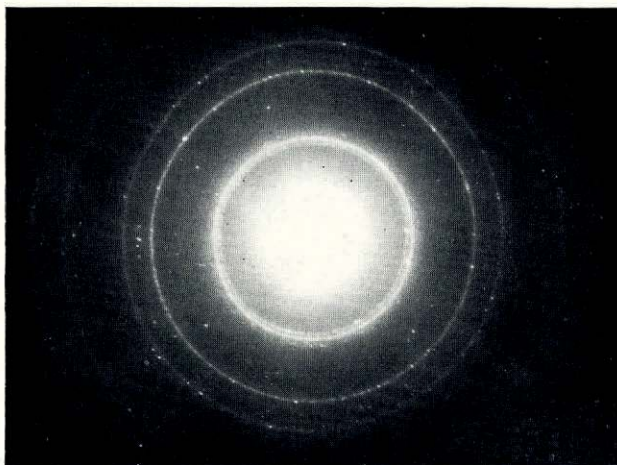
Similarly, the combination of hexagonal and cubic ice which was formed at -120°C did not change structure when cooled to -170°C (Fig. 5a, b).

Ice crystals formed at -170°C on collodion film under a poor water vapor supply condition by residual water vapor in the electron microscope showed diffused ring patterns corresponding to the {111}, {220}, {311} and {331} rings of cubic crystals (Fig. 4b). These were microcrystalline cubic crystals. When these minute crystals were warmed to -140°C the rings appeared sharper because of the growth of the crystals but the same rings were observed, indicating no structural transformation. It was found that cubic ice crystals are formed below -100°C at a lower rate of growth than that of the hexagonal ice; minute cubic ice was detected even at -170°C; and no transformation of the structural form was observed after the specimen temperature was changed.

Cubic ice crystals formed at -140°C were warmed to -100°C. No direct transformation from cubic to hexagonal was observed within two hours during the experiments. However,



a



b

Fig. 5. (a) Ice crystals formed on a collodion film at -120°C , then lowered to -170°C , (b) electron diffraction pattern of (a) at -170°C

the transformation may be possible by the occurrence of hexagonal ice nucleation at temperatures above -130°C .

THERMAL EXPANSION OF ICE

The coefficient of linear expansion of polycrystalline bulk ice was determined by Jakob and Erk (1928) in the temperature range 0° to -240°C . The measurements were made on rod-shaped ice frozen slowly in paper tubes from the outside in. The ice showed no indication of any regular orientation of the crystal axes.

The coefficient of expansion for ice can be calculated from the lattice constants obtained at various temperatures (Table V). The lattice constants of hexagonal ice were measured by

TABLE V. LATTICE CONSTANTS OF HEXAGONAL ICE

Temperature °C	<i>a</i> Å	<i>c</i> Å	<i>c/a</i>	Reference
0	4.5227 ± 0.0014	7.3671 ± 0.0012	1.629	Megaw (1934)
-40.5	4.511 ± 0.001	7.345 ± 0.001	1.628	Camp (1963)
-46	4.5163 ± 0.0005	7.3477 ± 0.0009	1.627	Truby (1955)
-110	4.493 ± 0.004	7.337 ± 0.006	1.633	Blackman and Lisgarten (1957)
-110	4.501 ± 0.004	7.348 ± 0.009	1.633	Kumai (this paper)
-185	4.479	7.308	1.632	Vegard and Hillesund (1942)

several workers by diffraction methods at temperatures between 0° and -180°C. The lattice constants measured in the present experiments and by Blackman and Lisgarten (1957) made use of electron diffraction techniques. Others listed in Table V used the X-ray diffraction method. The discordance of the data in Table V, which may be due to the different forms of the specimens, has been noted by Lonsdale (1958), who desired a new determination with the same kind of specimen varied over a wide range of temperatures.

Comprehensive low-temperature measurements were made by LaPlaca and Post (1960) with a Geiger-counter diffractometer. Specimens were prepared on a cooled glass specimen holder by spraying a fine mist of distilled water. The specimens were warmed up to just below the melting point and then cooled slowly down to a certain temperature to get sharp diffraction for lattice-constant measurements. The *c/a* ratio of the ice formed from a fine mist was smaller than that of the ideal value of 1.633 for close packing. The ice may have unequivalent tetrahedral bonds, i.e. the hydrogen bond along the *c*-axis might be slightly shorter than the centro-symmetric hydrogen bonds or, alternatively, the O-O-O angles may differ slightly from the exact tetrahedral value. However, the *c/a* ratio was 1.633 in this experiment and for the experiments of Blackman and Lisgarten (1957) for ice formed from the vapor at an air temperature of approximately -100°C and a low vapor pressure of about 10⁻⁵ mm Hg.

The density and the coefficient of expansion of ice can be found from the unit-cell parameters obtained at various temperatures from 0° to -180°C (Table VI). The values given in

TABLE VI. THE UNIT-CELL PARAMETERS, THE DENSITIES, AND THE COEFFICIENTS OF EXPANSION OF ICE AT A PRESSURE OF 1 BAR

Temperature °C	Unit cell parameters			Density (calculated) g cm ⁻³	Coefficients of expansion		
	<i>a</i> Å	<i>c</i> Å	<i>c/a</i>		Linear $\alpha_a \times 10^6$ deg ⁻¹	$\alpha_c \times 10^6$ deg ⁻¹	Cubic $\gamma \times 10^6$ deg ⁻¹
0	4.5227	7.3671	1.6289	0.9166			
-30	4.5163	7.3565	1.6288	0.9205	47	48	142
-60	4.5099	7.3461	1.6288	0.9244	47	47	141
-90	4.5044	7.3379	1.6290	0.9277	41	37	117
-120	4.4998	7.3302	1.6290	0.9306	34	35	102
-150	4.4960	7.3240	1.6290	0.9329	28	28	83
-180	4.4930	7.3196	1.6290	0.9348	22	20	63

Table VI were obtained from the curves of unit-cell parameters shown in Figure 6 by taking the molecular weight of ordinary water as 18.016, and Avogadro's number as 6.02486×10^{23} mol⁻¹ (Cohen and DuMond, 1957). The coefficients of cubic and linear expansion of hexagonal ice are shown in Figure 7 along with the results of other workers. The coefficient of linear expansion along *c*-axis is almost the same as that of the *a*-axis. Therefore it is almost the same as that of polycrystalline ice as determined by Jakob and Erk (1928).

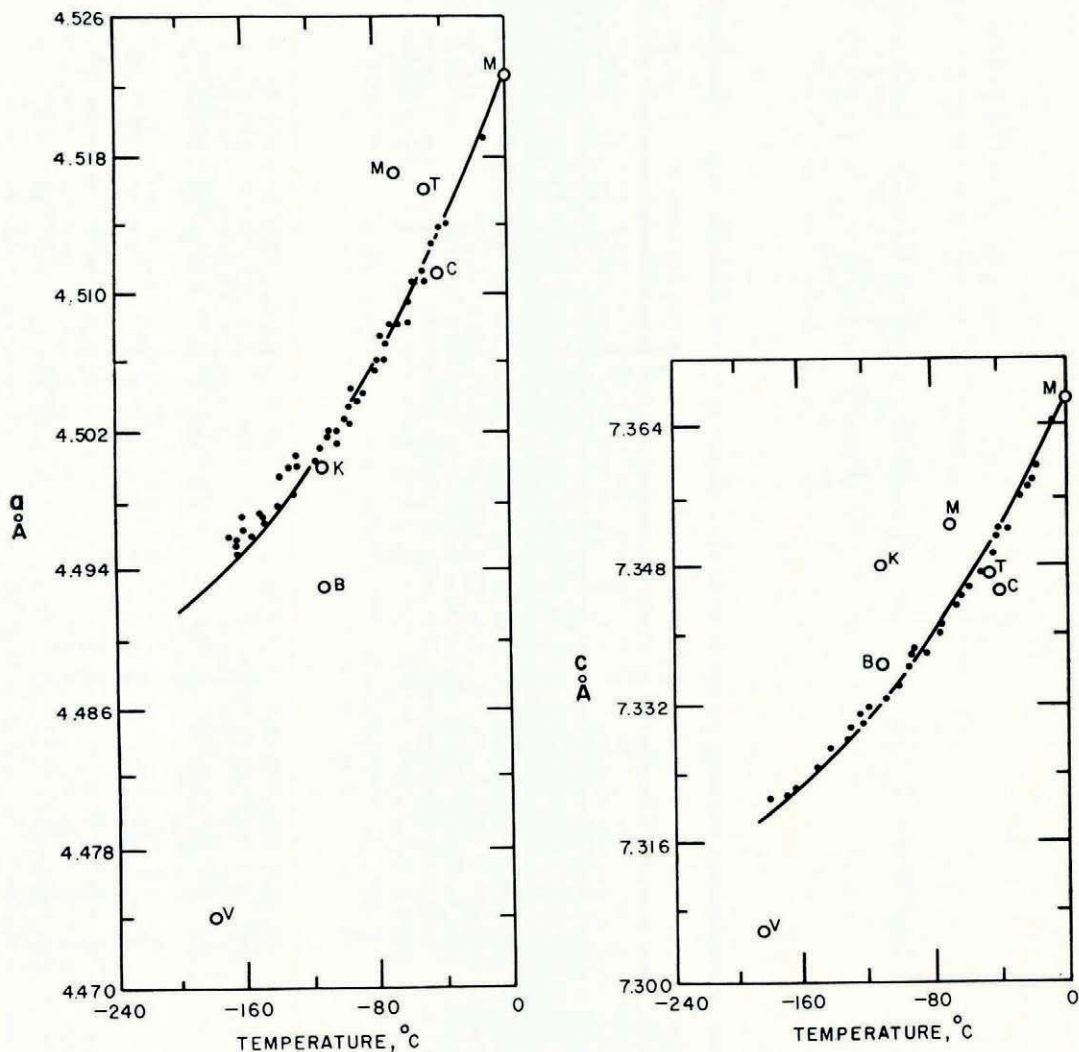


Fig. 6. Unit cell parameter of hexagonal ice determined by Blackman and Lisgarten (B), Camp (C), Kumai (K), LaPlaca and Post (●), Megaw (M), Truby (T), and Vegard and Hillesund (V)

SUMMARY AND CONCLUSIONS

The formation and lattice spacings of the hexagonal and cubic forms of ice crystals were observed by the use of a cold stage in an electron microscope within the temperature range -90° to 180°C .

Hexagonal ice formed on the cold substrates at temperatures above -100°C . At temperatures from -100° to -130°C , both hexagonal and cubic forms of ice were detected. Cubic ice was formed on cold substrates from -130° to -160°C . At temperatures below -160°C , a minute form of cubic crystalline ice was detected. It is concluded that ice crystal formation depends on the temperature and the crystal habit of the substrate.

No transformation of the structural form of ice from hexagonal to cubic or cubic to hexagonal was observed when the temperature of the specimens was varied in the range -90° to

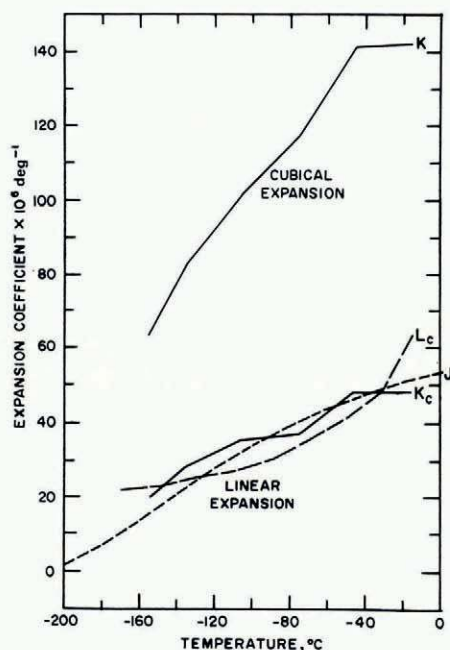


Fig. 7. The coefficient of thermal expansion of hexagonal ice determined by Kumai (K ; K_c , along the c -axis), LaPlaca and Post (L_c , along the c -axis), and Jakob and Erk (J , polycrystalline ice)

-180°C . The minute crystalline cubic ice formed below -160°C grew larger at a temperature between -130° and -150°C , displaying the sharp diffraction patterns of cubic ice.

Single ice crystals larger than $0.3\ \mu\text{m}$ in diameter produced diffraction spot patterns. Many ice crystals less than $0.3\ \mu\text{m}$ in diameter produced uniform sharp ring patterns. Ice crystals less than $50\ \text{\AA}$ in diameter produced halo patterns. The width of the halo pattern increased with the reduction of crystal size.

Cubic ice was formed at temperatures between -130° and -160°C . It is estimated from the width of the diffraction rings that the cubic crystals are from $50\ \text{\AA}$ to $300\ \text{\AA}$ in diameter.

The coefficients of linear expansion along the c -axis of the hexagonal ice ranged from $50 \times 10^{-6}\ \text{deg}^{-1}$ to $20 \times 10^{-6}\ \text{deg}^{-1}$, and were almost the same as that of the a -axis in the temperature range from 0° to -180°C . The coefficients of cubical expansion ranged from $140 \times 10^{-6}\ \text{deg}^{-1}$ to $60 \times 10^{-6}\ \text{deg}^{-1}$ at temperatures from 0° to -180°C . The c/a ratio of hexagonal ice sublimed from vapor at temperatures around -100°C was the ideal value of 1.633 for close packing.

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REFERENCES

- Bertie, J. E., and others. 1963. Transformations of ice II, ice III, and ice V at atmospheric pressure, by J. E. Bertie, L. D. Calvert and E. Whalley. *Journal of Chemical Physics*, Vol. 38, No. 4, p. 840-46.
- Blackman, M., and Lisgarten, N. D. 1957. The cubic and other structural forms of ice at low temperature and pressure. *Proceedings of the Royal Society, Ser. A*, Vol. 239, No. 1216, p. 93-107.
- Burton, E. F., and Oliver, W. F. 1935. The crystal structure of ice at low temperatures. *Proceedings of the Royal Society, Ser. A*, Vol. 153, No. 878, p. 166-72.
- Camp, P. R. 1963. Properties of ice. Part II. *U.S. Cold Regions Research and Engineering Laboratory. Research Report 114*.

- Cohen, R., and DuMond, J. W. M. 1957. The fundamental constants of atomic physics. (In Flüge, S., ed. *Handbuch der Physik*. Berlin, Göttingen, etc., Springer-Verlag, Bd. 35, p. 1-87.)
- Defrain, A., and Nguyen Trong Linh. 1966. Détection par diffraction des rayons X et par analyse thermique différentielle de la glace et du phénol amorphes. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences* (Paris), Sér. C, Tom. 263, No. 22, p. 1336-39.
- Dvoryankin, V. F. 1959. Nizkotemperaturnyy metod v elektronografii [The low-temperature preparation method in electron diffraction analysis]. *Kristallografiya* [*Crystallography*], Tom 4, No. 3, p. 441-59. [English translation in *Soviet Physics—Crystallography*, Vol. 4, No. 3, 1960, p. 415-35.]
- Fernández-Morán, H. 1960. Low-temperature preparation techniques for electron microscopy of biological specimens based on rapid freezing with liquid helium II. *Annals of the New York Academy of Sciences*, Vol. 85, Art. 2, p. 689-713.
- Hall, C. E. 1950. A low temperature replica method for electron microscopy. *Journal of Applied Physics*, Vol. 21, No. 1, p. 61-62. [Letter.]
- Hibi, T., and Yada, K. 1959. Low temperature replica and its application. *Journal of Electron Microscopy* (Tokyo), Vol. 7, p. 21-24.
- Honjo, G., and others. 1956. Low temperature specimen method for electron diffraction and electron microscopy, by G. Honjo, N. Kitamura, K. Shimaoka and K. Mihara. *Journal of the Physical Society of Japan*, Vol. 11, No. 5, p. 527-36.
- Jakob, M., and Erk, S. 1928. Wärmedehnung des Eises zwischen 0 und -253° . *Zeitschrift für die gesamte Kälteindustrie*, Bd. 35, Ht. 7, p. 125-30.
- König, H. 1943. Eine kubische Eismodifikation. *Zeitschrift für Kristallographie*, Bd. 105, Ht. 4, p. 279-86.
- Krastanov, L. 1943. Über die Bildung und das Wachstum der Eiskristalle in der Atmosphäre. *Meteorologische Zeitschrift*, Bd. 60, Ht. 1, p. 15-26.
- LaPlaca, S., and Post, B. 1960. Thermal expansion of ice. *Acta Crystallographica*, Vol. 13, No. 6, p. 503-05.
- Lonsdale, Dame K. 1958. The structure of ice. *Proceedings of the Royal Society*, Ser. A, Vol. 247, No. 1251, p. 424-34.
- McMillan, J. A., and Los, S. C. 1965. Vitreous ice: irreversible transformations during warm-up. *Nature*, Vol. 206, No. 4986, p. 806-07.
- Megaw, H. D. 1934. Cell dimensions of ordinary and "heavy" ice. *Nature*, Vol. 134, No. 3397, p. 900-01.
- Pryde, J. A., and Jones, G. O. 1952. Properties of vitreous water. *Nature*, Vol. 170, No. 4330, p. 685-88.
- Truby, F. K. 1955. Lattice constants of pure and fluoride contaminated ice. *Science*, Vol. 121, No. 3142, p. 404.
- Vegard, L., and Hillesund, S. 1942. Die Strukturen einiger Deuteriumverbindungen und ihr Vergleich mit denjenigen der entsprechenden Wasserstoffbindungen. *Avhandlingar utgitt av den Norske Videnskaps-Akademi i Oslo. Mat.-Naturvid. Klasse*, 1942, Nr. 8.
- Vertsner, V. N., and Zhdanov, G. S. 1965. Elektronno-mikroskopicheskoye issledovaniye nizkotemperaturnykh modifikatsiya l'da. [Electron-microscope study of the low temperature forms of ice]. *Kristallografiya* [*Crystallography*], Tom 10, No. 5, p. 715-22. [English translation in *Soviet Physics—Crystallography*, Vol. 10, No. 5, 1966, p. 597-602.]
- Wolff, G. A. 1957. The growth of ice crystals. (In Weickmann, H., and Smith, W., ed. *Artificial stimulation of rain*. London, Pergamon Press, p. 332-39.)