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Thermal expansion of ice.*

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Introduction

In a recent compilation of published data on the lattice expansion of hexagonal ice between −180 and 0 °C., as determined by diffraction methods, there are included measurements made at only five different temperatures in this range. These are shown in Table 1. Four investigations are represented; in one (Blackman & Lisgarten, 1957) electron diffraction techniques were used. The others used X-rays.

Table 1. *Crystal data for ice*

Temp. (°C.)	a_0 (Å)	c_0 (Å)	c/a	Ref.
0	4·5227 ± 0·0014	7·3671 ± 0·0012	1·629	(1)
−46	4·5163 ± 0·005	7·3477 ± 0·0009	1·627	(2)
−66	4·5177 ± 0·002	7·353 ± 0·0035	1·628	(1)
−110	4·493 ± 0·004	7·337 ± 0·006	1·633	(3)
−185	4·476 ± 0·003	7·306 ± 0·012	1·632	(4)

(1) Megaw (1934).
(2) Truby (1955).
(3) Blackman & Lisgarten (1957).
(4) Vegard & Hillesund (1942).

The inadequacy and inconsistency of the data in Table 1 have been noted by Lonsdale (1958) who, nevertheless, subjected these measurements to a detailed analysis which led her to conclude that: 'the trend is clear, the coefficient of cubical expansion is at least 50% greater at −180 than at 0 °C., and the expansion is greater along the a than along the c direction.'

These conclusions conflict with the results of several dilatometric measurements of the thermal expansion of ice. Measurements on bulk ice, orientation unspecified, by Jakob & Erk (1929), are summarized in Table 2.

Table 2. *Coefficient of linear expansion of ice*

T (°C.)	Coeff. of linear expansion × 10^{-6}
0	52·7
−100	33·9
−200	0·8
−250	−6·1

The negative coefficient reported for −250 °C. need not surprise us. Blackman (1958), apparently unaware of Jakob & Erk's results, has predicted that negative coefficients of volume expansion may be expected at low temperatures in certain substances with the open zincblende structure. The similarity between the ice and zincblende structures is well known. More recently Gibbons (1958) determined, dilatometrically, that Si and InSb also have negative coefficients of volume expansion at low temperatures.

Additional dilatometric measurements on bulk ice, between 0 and −195 °C., have been made by Hamblin and reported by Powell (1958). These are in generally good agreement with the results of Jakob & Erk, as are the still more recent bulk ice measurements from 0 to −30 °C. by Butkovich (1959). Both Hamblin and Butkovich worked with large, oriented single crystals; the former found only a small anisotropy in the expansion ($\alpha_c > \alpha_a$) while Butkovich found no significant anisotropy.

It is clear that serious discrepancies exist between these bulk ice measurements and the data listed in Table 1, as well as the conclusions drawn by Dr Lonsdale. These led Butkovich to state that there 'seems to be a systematic difference between X-ray and dilatometric measurements of thermal expansion'. The present work was undertaken to determine whether such a systematic difference really exists, at least in the case of ice.

Experimental

Measurements were made on a diffractometer adapted for work at low temperatures (Miksic, Segerman & Post, 1959). Nitrogen gas, cooled by passage through copper coils immersed in liquid nitrogen, was blown over the specimen. Gas temperatures were varied by mixing dry, room temperature air, with the cold nitrogen. Filtered Cu K radiation was used for all measurements; the detector was a thallium activated sodium iodide scintillation crystal.

Patterns were run at a scanning speed of $\frac{1}{4}°$ (2θ) per minute. Temperatures were measured using calibrated thermocouples in contact with the specimens.

Specimens were prepared initially by spraying distilled water, in the form of a fine mist, onto a cooled glass specimen holder. It was found that the randomly oriented specimens obtained in this way generally did not yield

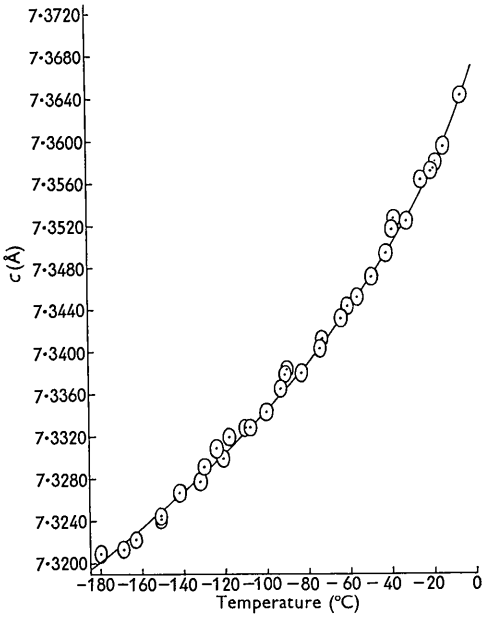

Fig. 1

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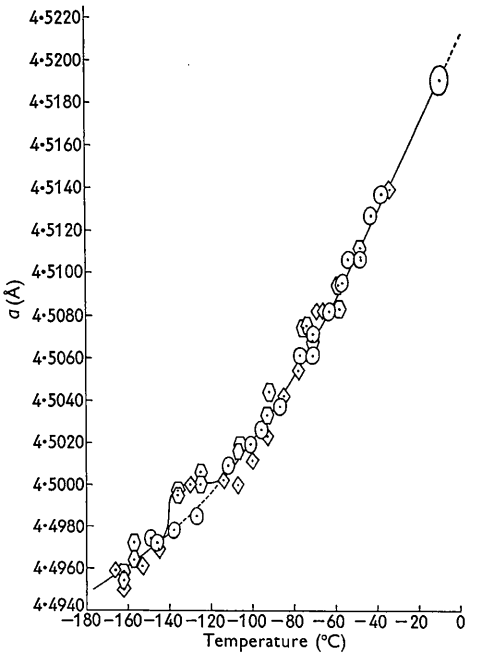

Fig. 2

diffraction patterns suitable for precision measurements of lattice constants. Peaks at angles greater than 50 or 60° (2θ) were too weak to be useful. However, by repeatedly warming the specimens to just below melting point and then cooling slowly, it was possible to obtain specimens showing high degrees of preferred orientation. Patterns of these specimens generally had strong, sharp reflections at relatively high Bragg angles ($2\theta = 100$ to 120°) with $l \gg h$; in other instances other types of orientation were obtained in which reflections with the h index $\gg l$ predominated. In this way all necessary measurements could be made in sensitive, high angle regions.

Table 3. *Thermal expansion of ice*

				Coefficient of thermal expansion $\times 10^{-6}$	
T (°C.)	a (Å)	c (Å)	c/a	$\perp c$	$\parallel c$
−10	4·5190	7·3616	1·6291		
				46	63
−20	4·5169	7·3570	1·6288		
				45	48
−40	4·5128	7·3500	1·6287		
				44	41
−60	4·5088	7·3440	1·6289		
				40	35
−80	4·5052	7·3388	1·6290		
				34	30
−100	4·5021	7·3344	1·6291		
				22	27
−120	4·5001	7·3304	1·6289		
				12	25
−140	4·4990	7·3267	1·6285		
				32	23
−160	4·4961	7·3233	1·6288		
				14	22
−180	4·4948	7·3201	1·6286		

Peak locations were determined several times at each temperature. Repeated runs between 0 and −180 °C. were made over a period of several months; each run involved measurements at small temperature intervals (generally $< 10°$) in that range. Composite plots of the results are shown in Figs. 1 and 2. In Table 3 we list values of c and a taken from the smoothed curves in Figs. 1 and 2, together with values of c/a, and expansion coefficients computed from these lattice constants.

Individual determinations of c or a are estimated to involve relative errors of $\pm 1 \times 10^{-4}$. Absolute values are somewhat less exact and appear to be limited primarily by uncertainties in the temperatures, whose absolute values were probably known only to within about 5 °C. Changes in temperature, in which we were primarily interested, could be measured with much greater precision.

Discussion

In general, the trends exhibited by our X-ray diffraction measurements resemble those shown by dilatometry, although there are some significant differences. Over most of the temperature range from 0 to −180 °C. both techniques indicate expansion coefficients of approximately the same magnitudes; both also indicate that the coefficients decrease markedly as the temperature is decreased. The X-ray results also show somewhat more anisotropy of expansion than do the dilatometric measurements, but the major differences between the two sets of measurements concern the temperature region between −100 and −130 °C. The X-ray results reveal an anomaly in the thermal expansion normal to c in this temperature range; for almost the entire thirty degrees there is virtually no change in the dimension of a, although c behaves normally. The effect was checked in repeated runs. Determinations of a did show their largest experimental errors in this temperature range, but it was evident that a change in da/dT, much larger than the experimental error, had occurred.

The intensities of (h00) and (hk0) reflections also behaved erratically in this temperature region. They decreased regularly as the temperature was raised from −180 °C. up to about −130 °C.; between that temperature and −100 °C. changes in intensities of these reflections appeared to be almost random and the variation of these intensities with temperature did not resume their normal course until temperatures well above −100 °C. were reached. The effect is not understood, though it should be remembered that the cubic form of ice is reported to form in this range of temperature. It is possible that distortions of the structure in the direction of the cubic form were involved in the anomaly; if this is so, it is not clear why only directions normal to c are affected.

The c/a ratio of the hexagonal ice did not show the relatively large variation indicated by the data in Table 1. All the measurements fall within the range $1{\cdot}6288 \pm 0{\cdot}0003$, and, if the anomalous region between −100 and −130 °C. is not considered, the range of c/a is even narrower.

The general trends of our results are consistent, except for the a axis anomaly, with the findings of Jakob & Erk. It would, therefore, be of great interest to obtain measurements of the lattice dimensions of ice at temperatures well below −180 °C. to investigate the negative expansion coefficient which they reported.

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X-ray data for the phosphides of aluminium, gallium, and indium.

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A comparison of the intensities of the lines in powder photographs of AlP and InP obtained in this laboratory with previously reported values (Passerini, 1928; Iandelli,* 1941) has shown significant differences. We have calculated the intensities, using the relation

$$I_c = p|F|^2(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)$$

(p = multiplicity, θ = Bragg angle of reflection, $|F|$ = structure factor modulus) and atomic scattering factors for neutral atoms (*Internationale Tabellen zur Bestimmung von Kristallstrukturen*, 1935; Thomas & Umeda, 1957) and find a good agreement with the observed values.

* In private correspondence with Prof. Iandelli we learned that his calculated values for InP include an absorption correction with $\mu r = \infty$.

The relevant data and, for completeness, analogous data for GaP, are reported in Table 1.

The calculations of intensities were done on our Bendix Computer, Model G–15–D, by Mr F. W. Kuhlman, whom we wish to thank.

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Table 1. *X-ray data**

	AlP		GaP		InP	
hkl	I_o	$I_c \times 10^{-3}$	I_o	$I_c \times 10^{-3}$	I_o	$I_c \times 10^{-3}$
111	*vvs*	866	*vs*	2,933	*vs*	8,952
200	—	3	*vvw*	399	*ms* to *w*	2,236
220	*vs*	568	*s*	1,688	*s*	4,931
311	*s*	339	*ms*	1,136	*s*	4,040
222	—	53	—	138	*vw*	684
400	*vw*	88	*vvw*	281	*w*	791
331	*ms*	136	*w*	442	*ms*	1,606
420	—	<1	—	104	*w*	778
422	*ms*	250	*w*	604	*ms*	1,694
511+333	*w*	83+28	*vs*	281+94	*ms*	939+313
440	*vvw*	72	*vww*	225	*w*	579
531	*ms*	146	*w*	523	*ms*	1,488
600+442	—	0+44	—	17+111	*w*	98+436
620	*ms*	157	*w*	520	*ms*	1,089
533	*vw*	95	*vw*	351	*w*	777
622	—	64	—	160	*vw*	471
444	*w*	143	*vvw*	425	*vvw*	459
711+551					*ms*	1,081+1,081
640					*vvw*	627
642					*s*	6,040

(*v* = very; *s* = strong; *w* = weak; *m* = moderately).

* The lattice constants are, in the order: AlP $a_0 = 5{\cdot}451 \pm 0{\cdot}004$ Å (present determination. Cf. White & Bushey, 1944); GaP $a_0 = 5{\cdot}4505$ Å and InP $a_0 = 5{\cdot}8687$ Å (Giesecke & Pfister, 1958).