

TABLE I. Neutron-diffraction centroids, widths, and intensities of peaks in pure and in doped ices.

Sample	Peak	Centroid	Width ^a	Intensity
A. Pure hexagonal ice	(10·0)	16.85°	0.68°	1.00
	(00·2)	17.94	0.65	0.54
	(10·1)	19.11	0.67	0.59
B. Ice doped with 0.47M FeCl ₂	(10·0)	16.86	0.67	1.00
	(00·2)	17.94	0.64	0.54
	(10·1)	19.11	0.69	0.62
C. Ice doped with 0.40M KCl	(10·0)	16.83	0.67	1.00
	(00·2)	17.94	0.65	0.50
	(10·1)	19.10	0.67	0.55

^a Full width at half-maximum.

the presence of even relatively small amounts of cubic ice. As indicated by the results in Table I, the triplet peaks in the hexagonal ice spectrum were obtained for pure ice Ih, for ice doped with 0.47M FeCl₂, and for ice prepared by quenching 0.40N KCl. The doped-ice-peak positions were not significantly altered from those of pure ice and the measured half-widths were in agreement with expected values on the assumption of no line broadening. The relative intensities were referenced on the (10·0) peak and were obtained from the relation $I = 1.064 (\Delta H_{1/2}) Y_m$, where I is the intensity, $\Delta H_{1/2}$ is the full width at half-height, and Y_m is the peak height. Although the intensities of the peaks are not identical in the three ices, the differences in the ratios are small. A significant amount of ice Ic mixed with the hexagonal form would have been revealed by the alteration of the relative intensities of these peaks as well as by a displacement of the peak centroids.

Lattice cell parameters have been obtained for polycrystalline D₂O ice Ih at 80°K from an analysis of the neutron-diffraction spectrum, a portion of which is shown in Fig. 2. The values which have been obtained are $a_0 = 4.500 \pm 0.001$ Å and $c_0 = 7.324 \pm 0.002$ Å. These results are in excellent agreement with the recent precise x-ray measurements of H₂O ice Ih reported by Brill and Tippe.¹⁴ These lattice parameters give densities of 0.932 g cm⁻³ and 0.933 g cm⁻³ for H₂O ice Ih and ice Ic at 80°K, respectively, assuming that there is no difference in cell dimensions for the H₂O and D₂O ices.

DISCUSSION

The line centroids of the peaks in the ice Ic neutron-diffraction spectrum shown in Fig. 1 are in good accord with the calculated line positions based on a cubic cell lattice parameter, $a_0 = 6.353$ Å. Several features of the spectrum require comment, however. The obvious asymmetry of the (111) peak suggests that an impurity is present, and ice Ih would seem to be a likely possibility. The presence of ice Ih as an impurity would not be surprising, since it appears that pure ice Ic has not been prepared previously, and hexagonal ice has been considered to be the contaminant. If the line on the

low-angle side of the (111) cubic reflection is assigned to the (10·0) line in ice Ih (see Fig. 2), its intensity may be used to calculate the intensity to be expected for the (10·2) line. This results in an expected counting rate for the (10·2) peak of about 4×10^3 counts/8 min above background. In fact, as shown in Fig. 1, the observed (10·2) ice Ih line ($2\theta = 24.72^\circ$) has only about one-tenth the calculated intensity, all of which can be attributed to the amount of ice Ih known to be present prior to the transformation. It appears that preferential growth of the crystals, possibly coupled with over-all small particle size and crystal strain, has occurred to limit the intensity of this reflection, and that a greatly broadened line resulted. The calculated position of the centroid of the (111) cubic ice peak coincides (within 0.03° in 2θ) with that of the (00·2) hexagonal peak. It appears that line broadening is responsible for the fact that the lines in the ice Ic-ice Ih mixture are unresolved while the triplet of ice Ih prepared from ice II (which covers the same range of 2θ) is well resolved.

It is well known that crystals smaller than approximately 1000 Å give rise to broadened peaks in the diffraction spectrum.¹⁷ A particle size of about 400 Å was found for ice Ic transformed from vitreous ice.⁶ In Table II, application of the Scherrer formula, $t = C\lambda/B \cos\theta$, has been made in a particle-size analysis of ice Ic prepared from ice II. In this expression, t is the crystal thickness in angstroms, C is a constant, ~ 0.9 , λ is the wavelength in angstroms of the radiation, B^2 is the difference between the square of the observed linewidth (full width at half-height) and the square of the linewidth expected for large particles from the known diffractometer resolution, and θ is the Bragg angle. Although great accuracy is not to be expected in the application of this expression in the present case, because of the possibility of the presence of a range of crystal sizes and the lack of sphericity of the crystals, it nevertheless serves to provide an estimate of the mean crystal size. As shown in Table II, an analysis of the lines in the ice Ic spectrum indicates that

TABLE II. Evaluation of ice Ic particle size from line broadening.^a

(hkl)	2θ	B (deg)	t (Å)
(111)	17.9	0.45	130
(220)	29.5	0.36	170
(222)	36.3	0.49	130
(331)	46.1	0.71	90
(422)	52.3	0.65	100
(333)(511)	55.7	0.67	100
(440)	61.1	0.46	150
(531)	64.3	0.47	150

^a Ice Ic prepared by transformation of ice II, 15 min at -65°C.

¹⁷ C. W. Bunn, *Chemical Crystallography* (Clarendon Press, Oxford, England, 1961), Chap. 11.

in this sample the mean particle size of the crystals as determined by the crystallographic analysis is expected. However, the intensity associated with the (10·2) peak is only qualitatively indicated.

The ice Ic prepared from ice Ih in several experiments for 15 min at -65°C and for 30 min at -65°C was recorded and indicated by the size of ice Ih in the diffraction pattern and finally to the increasing intensity of the (10·2) peak and (10·2) peak occurred at the same time as the exceedingly small intensity of the ice Ih patterns after many days of storage.

The fact that the amount of ice Ic prepared by the quenching of ice Ih with FeCl₂ or Fe nuclei influenced the intensity of the diffraction pattern.

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