

the deuterium solid phases exist at higher temperatures.<sup>16</sup> Because of the requirement of full coverage of the neutron beam by the sample, a volume of 10 to 12 ml of powdered ice was needed. Five separate samples of D<sub>2</sub>O ice V were prepared by cooling the

liquid at 5 kbar to -35°C, lowering the pressure to 3 kbar after ice V had formed, and holding the sample at this pressure for 1 h at this temperature. It appears that the rate of transformation must be slow under these conditions for D<sub>2</sub>O since a single ice V phase was indicated by the neutron-diffraction spectrum of the combined samples treated in this fashion.

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### Neutron-Diffraction Study of Ice Polymorphs. III. Ice Ic\*

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Neutron-diffraction spectra have been recorded at 80°K for polycrystalline D<sub>2</sub>O cubic ice (Ic) obtained by the transformation of the high-pressure ices II, V, and IX. Spectral differences were found among these ice Ic preparations, principally in the degree of asymmetry of the (111) cubic reflection and in the extent of line broadening. The cubic (111) peak of greatest symmetry was obtained by the transformation of ice II. The line broadening appears to be associated with the small particle sizes of the ice Ic produced by the transformation of the high-pressure ices under controlled-temperature conditions. Peak centroids for scattering angles between 15° and 62° give a weighted cubic lattice parameter,  $a_0 = 6.353 \pm 0.001$  Å. As revealed by an analysis of neutron-diffraction line intensities, attempts to induce the formation of ice Ic by the quenching of aqueous ferrous chloride or potassium chloride solutions in liquid nitrogen were unsuccessful.

#### INTRODUCTION

Neutron-diffraction studies of cubic ice (Ic) have been made in this work to supplement investigations made on this form of ice by electron-diffraction,<sup>1-4</sup> x-ray,<sup>5,6</sup> and nuclear magnetic resonance methods.<sup>7</sup>

In addition to ordinary hexagonal ice (Ih), ice Ic and vitreous (or amorphous<sup>8</sup>) ice can be prepared by the condensation of water vapor at low temperatures. The particular form which is produced is dependent upon the temperature of deposition. Ice Ic can be prepared between -120° and -140°C, while vitreous ice requires temperatures of -160°C or below.<sup>6</sup> Bertie *et al.*<sup>9</sup> have demonstrated that the high-pressure ice polymorphs first transform to ice Ic as they are warmed at atmospheric pressure from the metastable quenched condition at 77°K. These authors suggest that large

amounts of ice Ic can be conveniently prepared by the conversion of ice IX at 156°K for a minute or two.

Nozik and Kaplan<sup>10</sup> have reported that aqueous solutions of ferrous sulfate and of ferrous chloride which have been quenched in liquid nitrogen induce the formation of ice Ic rather than ice Ih. Their conclusion was based on changes observed in the two-line Mössbauer spectrum characteristic of a nuclear quadrupole hyperfine interaction in <sup>57</sup>Fe. Weltman<sup>11</sup> has reported that ice Ic was prepared along with ice Ih by quenching 0.04*N* and 0.4*N* aqueous KCl solutions in liquid nitrogen. The ices were identified by their x-ray patterns.

The oxygen atoms in ice Ic are arranged in puckered-hexagonal rings identical to those found in ice Ih; however, each layer of oxygens is displaced one-half the diameter of the ring relative to adjacent layers. This arrangement gives rise to a repetitive structure of the type ...ABCA... characteristic of the diamond-cubic system. The infrared<sup>12</sup> and Raman spectra<sup>13</sup> of ices Ih and Ic are identical in the O-H stretching region. Both infrared<sup>12</sup> and electron-diffraction results<sup>3</sup> have been interpreted as indicating a disordered-proton arrangement in ice Ic.

Dowell and Rinfret<sup>6</sup> have obtained the cubic lattice

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