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**Determination of hydrogen position in cubic ice by electron diffraction.** By GORO HONJO and KOHJI SHIMAOKA, *Tokyo Institute of Technology, Oh-okayama, Meguroku, Tokyo, Japan*

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At an earlier date in the development of the electron-diffraction method Laschkarew & Usyskin (1933) pointed out the fact that the contribution of hydrogen atoms is relatively larger in electron diffraction than in X-ray diffraction. Taking advantage of this fact, many workers have recently succeeded in determining hydrogen positions in crystal by the electron-diffraction method. (Cf. Vajnsštejn, 1956; Cowley, 1953).

The present authors reported previously an observation that the electron-diffraction intensities from cubic ice and hexagonal ice were appreciably influenced by the presence of hydrogen atoms (Honjo, Kitamura, Shimaoka & Mihama, 1956).

The cubic form is a modification which is formed when water vapour condenses at temperatures lower than about  $-80^{\circ}\text{C}$ . (König, 1942, 1943; Honjo *et al.*, 1956; Lisgarten & Blackman, 1956; Blackman & Lisgarten, 1957). Oxygen atoms in it are arranged in a diamond-type structure with a lattice constant  $a = 6.36 \text{ \AA}$  (O-O distance =  $2.75 \text{ \AA}$ , the same as in the ordinary hexagonal ice). The present authors have already pointed out that Pauling's half hydrogen model (Pauling, 1935) is highly probable for cubic ice (Honjo *et al.*, 1956). Results of further studies are reported briefly below.

A polycrystalline specimen of cubic ice was prepared by condensing water vapour very slowly on a thin colloidal film at  $-150^{\circ}\text{C}$ . The specimen was composed of crystallites of size about  $100 \text{ \AA}$  and showed neither preferred orientation nor traces of hexagonal ice. Debye-Scherrer patterns of it were photographed by means of a  $s^1$ -sector camera (Takagi, 1957) and the intensities of the rings, up to  $s = 4\pi \sin \theta/\lambda = 10 \text{ \AA}^{-1}$ , were measured by photometry according to Karle & Karle's method (1949, 1950) and by visual estimation.

The observed intensities and those calculated for

various models are compared in Fig. 1. All the intensities are normalized so that that of the (220) reflexion is equal to unity, and are plotted on logarithmic scales. The plots for the calculated intensities are displaced vertically on the figure for clarity. Crosses in the figure show the intensities  $I_0$  of the Debye rings at  $-190^{\circ}\text{C}$ . The Debye temperature of the crystal was determined to be  $200 \pm 15^{\circ}\text{K}$ . by comparing the intensities at  $-120^{\circ}\text{C}$ . and  $-190^{\circ}\text{C}$ . The intensities  $I_0^t$  corrected for the temperature effect are shown by plain circles. Dotted circles, black circles and triangles in the figure represent, respectively, (i) the calculated intensities due to Barnes' model assuming a hydrogen atom at the centre of each O-O bond (Barnes, 1929), (ii) the calculated intensities due to Pauling's half hydrogen model assuming a hydrogen atom statistically distributed at two positions along each O-O bond with an O-H distance of about  $1 \text{ \AA}$ , and (iii) the calculated intensities disregarding hydrogen scattering.

The overall trend of the observed intensities and the appearance of (222) and (442) reflexions show that the model of Pauling is the most probable one.

Bernal & Fowler (1933) and Owston (1953) proposed structure models of hexagonal ice having symmetry lower than that of Pauling's model. Analogous models of cubic ice may be conceived. No superlattice reflexion expected from such models was, however, observed.

Fourier maps were calculated by using the structure amplitudes given by the square roots of the temperature-corrected observed intensities  $I_0^t$ . In the calculation, it was assumed that a centre of symmetry exists at the mid-point of the O-O bond. The intensities of the composite Debye rings, such as the ring of (660) and (822) reflexions, were divided into components with ratios determined by Pauling's model. Fortunately, the intensities of such composite rings were so weak that the result was not sensitively influenced by the choice of the dividing ratios. Divisions in other ratios, such as in a ratio of the calculated intensities disregarding hydrogen scattering and in the ratio of multiplicities of reflexions, gave nearly identical results.

Fig. 2(a) shows the potential Fourier map of the crystal projected on (001). The scale of the contours was so determined that the height of oxygen peaks in this map is equal to the height of oxygen peaks calculated for the neutral oxygen framework. The values of mean inner potential needed in the normalization were calculated by the method of Tull (1951). Fig. 2(b) shows the difference Fourier map obtained by subtracting the oxygen contribution from Fig. 2(a).

In these Fourier maps we can clearly find double peaks on each O-O bond corresponding to hydrogen positions. This proves that Pauling's model is appropriate for cubic ice. The O-H distance in Fig. 2(b) is  $0.97 \text{ \AA}$ . This is slightly shorter than the O-H distance of  $1.01 \text{ \AA}$  in hexagonal heavy ice found by the neutron diffraction study of Peterson & Levy (1957). It is premature, however, to stress too much the difference at the present stage of our study.

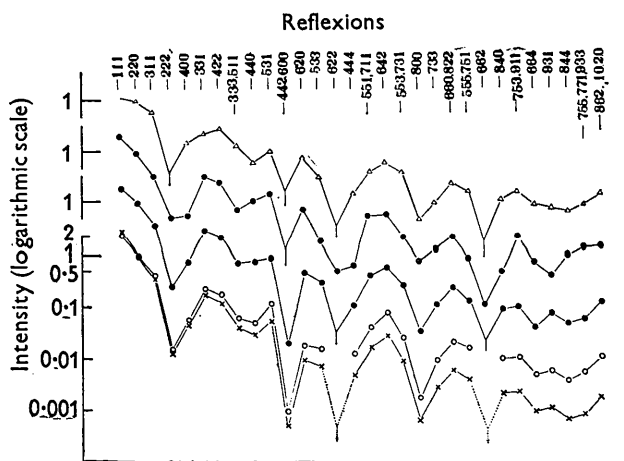


Fig. 1. Comparison of observed and calculated intensities of cubic ice. The arrows directed downward indicate zero intensity. See text for further explanation.

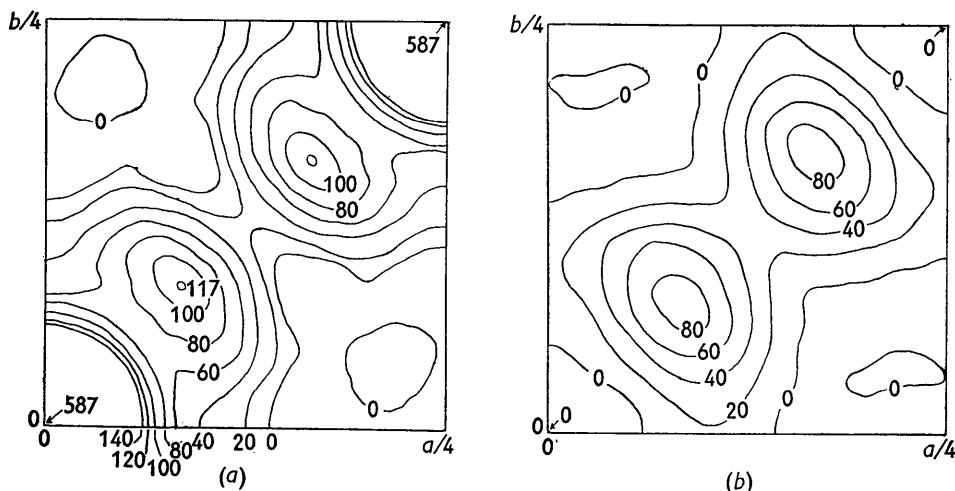


Fig. 2. (a) Potential Fourier map of cubic ice projected on (001). The unit of the contour scale is 0.37 V. Å.  
(b) As (a) with oxygen contributions subtracted.

In conclusion, the authors express their sincere appreciation to Prof. S. Miyake for his kind advice and interest.

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**On the determination of crystallographic directions.** By J. W. DAVISSON and J. PASTERNAK, *U.S. Naval Research Laboratory, Washington, D.C., U.S.A.*

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Relations previously developed using linear transformation equations yield the crystallographic directions of paths uniquely from their angles of inclination  $\theta$  and azimuth  $\varphi$  in any crystal plate of known orientation (Davisson, 1957). The purpose of this note is to modify the transformation equations so that they apply directly to goniometric measurements of crystals. Directions are specified by such measurements in terms of angles from two known reference directions.

The problem we consider is the determination of a specific crystallographic direction  $\mathbf{R}_2$  when we are given the angles  $\theta_{01}$ ,  $\theta_{02}$  and  $\theta_{12}$  between the directions  $\mathbf{R}_0$ ,  $\mathbf{R}_1$ , and  $\mathbf{R}_2$ , where  $\mathbf{R}_0$  and  $\mathbf{R}_1$  are two known reference directions and  $\theta_{01} = \mathbf{R}_0 \wedge \mathbf{R}_1$ , etc. The crystallographic direc-

tion  $\mathbf{R}_2$  can then be computed uniquely for any crystal from equations (8), (9), and (10) given by Davisson (1957) when the following relationships are used:

$$\theta = \theta_{02},$$

$$\varphi = \cos^{-1} \left\{ \frac{\cos \theta_{12} - \cos \theta_{01} \cos \theta_{02}}{\sin \theta_{01} \sin \theta_{02}} \right\},$$

where the angle  $\varphi$  is positive or negative depending upon whether the direction  $\mathbf{R}_2$  lies on the positive or the negative side of the plane defined by the vector  $\mathbf{R}_3 = \mathbf{R}_0 \times \mathbf{R}_1$ .

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