Neutron-Diffraction Study of H_2O Ice at 77 K

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A single-crystal neutron diffraction study of H_2O ice, lightly doped with HF, at 77 K shows that the Pauling statistical structure still gives excellent fit to the data at this temperature. It is concluded that the widely discussed "transition" near 100 K does not lead to any substantial proton ordering at lower temperatures.

1. Introduction

The report by Dengel et al.[1] in 1964 of electrical polarization phenomena in ice near 100 K, which suggested a ferroelectric transition near that temperature, has excited considerable attention, and independent studies have shown small anomalies in specific heat[2,3] and in elastic moduli.[4] Although our own studies of electrical polarization phenomena at low temperatures[5] have convinced us that some, at least, of the electrical anomalies can be explained without invoking a ferroelectric transition, it appeared to us to be important to make a direct structural study at a temperature below the reported anomaly.

The first neutron-diffraction study of ice was carried out by Wollan et al.[6] in 1949, using a powdered D_2O specimen, at 183 K. More recently Peterson and Levy[7] performed a single crystal study on D_2O at 123 and 223 K. Least-squares refinement gave clear support to the Pauling statistical structure[8] in all cases and Peterson and Levy achieved weighted R factors of 5.4% at 223 K and 4.6% at 123 K. The polar model proposed by Rundle,[9] which represents the most likely alternative, was ruled out by the experimental results.

While these studies have provided a great deal of our present knowledge of details of the crystal structure of ice, they are of little help in the present problem. Not only is the lowest temperature at which the structure was determined substantially above the reported transition temperature, but also all the studies were made with D_2O ice and it is known that the substitution of deuterons for protons has a considerable effect on the Curie temperature of hydrogen-bonded ferroelectrics like KH_2PO_4 (although in this case the Curie temperature is raised from 123 K to 213 K by deuteration).

2. Experimental Procedure

Previous workers have reported that the 100 K "transition" is aided by the presence of impurities, and by HF in particular, as seems reasonable if it involves proton ordering. Single crystals of ice were therefore grown from water containing an HF concentration of 10^{23} m^{-3}, using the first method of Jona and Scherrer.[10] The diffraction specimens were then machined from these crystals as cylinders about 6 mm in diameter and 6 mm long, the crystal c axis being approximately parallel to the cylinder axis.

The neutron-diffraction facility of the Australian Institute of Nuclear Science and Engineering was used for the experiment, in conjunction with the HIFAR reactor of the Australian Atomic Energy Commission Research Establishment. This provided a monochromatic flux of about 10^6 neutrons cm^{-2} s^{-1} at the specimen with a wavelength of 0.981 Å. A four-circle computer-controlled diffractometer was used and specimen temperature was maintained at 77 K by using nitrogen gas in a Joule–Thomson valve refrigerator.[11] Because of limited time and some difficulties with the Joule–Thomson valve, only 83 individual reflections were measured out of the 88 which should have been observable, but this proved adequate for a least-squares refinement.

3. Analysis of Results

The particular difficulties with a neutron-diffraction experiment on H_2O ice, as opposed to D_2O ice, arise mainly from the extremely large incoherent scattering cross section of hydrogen. The sophistication of a computer-controlled diffractometer, the use of good single crystals and cadmium counter slits overcame the problem of data collection against the incoherent background, while modern computer techniques, including correction for anisotropic extinction in the crystal[12] and for anisotropic temperature factors, allowed interpretation of the collected data. The mosaic-block ellipsoids required for the anisotropic extinction correction had principal radii (2.1, 2.8, 5.7) $\times$ 10^{-5} cm, indicating a high degree of crystal perfection.

An attempt to refine the collected data on the basis

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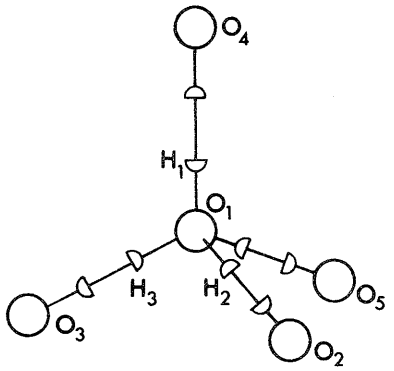

FIG. 1. Nearest-neighbor environment in ice at 77 K. Bond lengths (Å): O_3—O_1 = 2.741 ± 0.001, O_1—O_4 = 2.744 ± 0.002, O_1—H_3 = 1.006 ± 0.005 = 1.023 ± 0.005*, O_1—H_1 = 0.999 ± 0.009 = 1.018 ± 0.009* (the values indicated by asterisks have been corrected for thermal motion). Bond angles: O_3—O_1—O_2 = 109° 33′ ± 11′, O_3—O_1—O_4 = 109° 20′ ± 6′, H_3—O_1—H_2 = 109° 50′ ± 20′, H_1—O_1—H_3 = 109° 9′ ± 28′.

of the Rundle model for ice proved unsuccessful and led to unreal values for some of the parameters if refinement was to proceed past 15%. On this basis, therefore, this model was eliminated.

The Pauling model, on the other hand, refined successfully with anisotropic extinction correction. A refinement on $|F|$ led to a weighted R of 4.4%. The structural data yielded by the refinement are shown in Fig. 1. The O—H bond lengths are given both in their raw form and after correction for thermal motion, as discussed by Peterson and Levy.

The bond lengths and bond angles shown in Fig. 1 are in excellent agreement with those deduced by Peterson and Levy for D_2O ice at 123 K and confirm that there is no significant difference in structure between D_2O and H_2O and no detectable structural modification on passing through 100 K.

Analysis of the thermal ellipsoids for proton motion relative to the oxygen nuclei provides data which can be checked both against that of Peterson and Levy and against known infrared stretching and librational frequencies. The r.m.s. vibrational amplitudes along the bond directions for O_1—H_1 and O_2—H_2 are 0.06 ± 0.03 Å and 0.07 ± 0.04 Å respectively. Assuming these amplitudes to be due to zero-point motion of the protons gives approximate bond-stretching frequencies of 4700 cm^{-1} and 3400 cm^{-1} respectively, each with an uncertainty of ±50%, in approximate correspondence with the observed infrared band in the range 3150–3380 cm^{-1}. Similarly the axes of the thermal ellipsoids transverse to the bonds correspond to r.m.s. amplitudes of about 0.20 ± 0.03 Å. The oblateness of the ellipsoids is thus similar to that found by Peterson and Levy, while the associated frequency of 400 cm^{-1} corresponds reasonably with the observed infrared librational band in the range 500–1050 cm^{-1}.

4. Conclusions

The neutron-diffraction results confirm that the Pauling statistical model remains applicable to the structure of ice at 77 K and therefore suggest that no very significant change in proton ordering occurs across the reported "transition" near 100 K.

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