Structure of Heavy Ice Formed by Rapid Cooling of Heavy Water to a Temperature of 77 or 15 K

By

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(Received June 29, 1981)

Abstract

High-resolution measurements of a cold-neutron total cross-section in heavy ice were carried out by the combined use of a time-of-flight technique with a solid-mesitylene moderator for cold-neutron production. A careful study of several sharp peaks on the cross-section data reveals the presence of a high-degree of structural order in a direction parallel to, say, the *c*-axis for a hexagonal ice crystal. An attempt is made to estimate coherent elastic structure factors for heavy ice at 77 and 15 K on the basis of the observed cross-section data. It turns out that the structure factors thus obtained consist of a family of sharp peaks having both a monotonous rise with an increasing momentum transfer, and an abrupt fall at a certain value of the momentum transfer. The results of the present study suggest that information about the degree of structural ordering in the heavy ice may be obtained directly from the slope of the cold-neutron total cross-section curve.

1. Introduction

The importance of ice in meteorology, biology and other fields is well recognized, but ice also shows somewhat unusual structural and physical properties, owing to the presence of hydrogen bonding. Therefore, the structure of ice has been studied with great interest, not only for its own sake, but also because it provides a useful route of approach to the understanding of the physical and chemical properties of ice. The present paper is concerned with an experimental study of neutron scattering on the structure of heavy(D_2O) ice, prepared by a rapid cooling of heavy water.

By analogy with the liquid structure of light and heavy water, it is interesting to study the structure of such a heavy-ice specimen in terms of correlation in both a molecular orientation and a molecular position. However, this means, as Powles points out[1], the necessity of a differential measurement with great accuracy in order to ex-

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tract some structural information with meaningful accuracy. An alternative approach to this is to make explicit use of the fact that in many cases the atomic structure of D_2O molecules and the crystal structure of heavy ice have been already precisely known. With the assistance of this knowledge, the structure of the present specimen will be determined with a fair degree of reliability even from an integral measurement, if accurate information about the ordering in the disposition of D_2O molecules can be derived from the measurements.

In the present experiments, the total cross-sections for neutron energies ranging from 1 to 30 meV are determined with an accuracy of better than $\pm 3\%$ in the magnitude and $\pm 6\%$ in the energy resolutions. The accuracy obtained is due largely to the use of a cold-neutron source of a solid-mesitylene moderator with an optimized design for the time-of-flight experiment with an electron linac by Utsuro and Sugimoto[2]. It results in the discovery of several sharp peaks and new structures, which are utilized as a useful indicator for the existence of a strong short-range order closely related to the hexagonal form of ice. Previously, the total cross-section measurements on heavy ice have been performed by Whittemore and McReynolds[3] and by Gissler[4]. Their results will be compared with the present ones.

In view of the observed values of an effective Debye temperature for heavy ice by Leadbetter[5], it follows that the cross-section results of the present experiments, especially at lower energies, consist largely of an elastic scattering cross section, both coherent and incoherent. This affords a basis for the interpretation of the total cross-section results in terms of an elastic coherent structure factor for the heavy-ice specimen. In the present paper, the structure factor is calculated from the cross-section curves obtained from statistically weighted least-squares fits of the data points. On the basis of the results of these calculations, the degree of the structural ordering in the rapidly cooled heavy ice will be discussed in detail.

2. Experimental method

The total neutron cross-section was measured by the transmission-ratio method, using the time-of-flight technique to determine neutron energies. The experimental arrangement used is shown schematically in Fig. 1. The Kyoto University 46 MeV electron linear-accelerator was employed to provide a pulsed source of fast neutrons. The width of the neutron burst was about 3 μsec and the repetition rate was 50 pps. The pulsed neutrons were thermalized in a slab-type moderator of solid mesitylene ($C_6H_3(CH_3)_3$) adjacent to the neutron-producing target of tantalum. The moderator had been optimized for the time-of-flight experiment with an electron linac by Utsuro and Sugimoto[2]. At the sample position, boron-carbide (B_4C) collimators defined a rectangular neutron beam, 3.0 cm wide and 3.0 cm high.

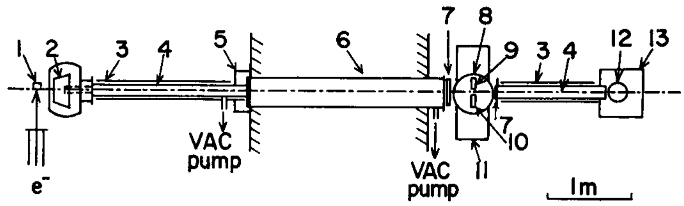

Fig. 1. Schematic representation of the experimental arrangement for measuring total neutron cross-sections of heavy ice: 1-*Ta* target, 2-solid-mesitylene slab-type moderator, 3-*Cd*-cover, 4-flight tube, 5-borated paraffin, 6-concrete shield, 7-B_4C collimator, 8-cryostat, 9-heavy-ice sample, 10-empty cell, 11-movable table (connected to data memory location control), 12-BF_3 counter (10 cm diam.), 13-B_4C shielding box.

The deuterium oxide sample (isotope purity higher than 99.8 mol %) was in an aluminum container providing a 50 mm wide, 60 mm high and 20 mm thick sample, which is approximately the mean-free-path thickness for neutrons with an energy of 10 meV. An empty cell with the same dimensions was also prepared as a dummy in a symmetric position to the sample in an aluminum cryostat. After the sample-dummy set had been tightly connected with an aluminum rod under a refrigerant bottle in the cryostat, the bottle was cooled with liquid N_2 or with liquid N_2, and afterwards with liquid He. In these cases, several hours of waiting time were required until the proper temperature was reached and the measurements started. The sample temperature was measured during the transmission measurements with a chromel-constantan thermocouple, mounted on the surface of the aluminum container. It was observed to be 77 K during the liquid-N_2 cooling, and 15 K during the liquid-N_2 and -He cooling.

To eliminate the effect of time variations in neutron-producing conditions, the heavy-ice sample and the dummy cell were exchanged in and out of the neutron beam with a mechanical oscillator at about 10-minute intervals throughout the measurements. The neutron beam transmitted through the cryostat was detected, using a BF_3 proportional counter with 10 cm diameter and associated electronics. The time spectra for the sample and the dummy position were recorded by a 1024 channel time analyser. 512 channels were used for each of these two positions. The integrated neutron counting in the target room was also synchronized to the motion of the mechanical oscillator, and recorded for monitoring and normalizing purposes during the course of each run. The total flight-path length was 6.60 m and the channel width of the time analyser was 61.59 μsec, yielding an electronic timing resolution of 9.33 μsec/m.

3. Analytical procedures

The total cross-section σ_t was calculated according to

$$\sigma_t(E) = -N^{-1} ln[\phi(E)/\phi_0(E)], \tag{1}$$

where N is the number of D_2O molecules per square centimeter of the transmission area, and $\phi_0(E)$ and $\phi(E)$ are the energy-dependent neutron fluxes transmitted through the empty cell and the sample, respectively. The fluxes were obtained from the observed time spectra with the normalization by the integrated neutron counts of the monitor. The correction for background was not applied to the fluxes, since it was assured to be much smaller than the total counts. The value of N was determined by normalizing the cross-section results to the accepted free-atom cross-section of 10. 5 b per D_2O molecule at the higher neutron energies where the chemical binding effects are taken to be negligible. The present cross-section data lead to values of the sample density of $\rho=0.945$ g/cm^3 for heavy ice at 77 K, and $\rho=1.03$ g/cm^3 at 15 K.

The neutron energy E was determined by the familiar relation

$$E=\frac{1}{2}mv^2=\frac{1}{2}m(L/t)^2, \tag{2}$$

where m is the neutron mass, L is the flight-path length and t is the time-of-flight. The time-of-flight was corrected for the finite source pulse decay by subtracting the mean emission time, which was estimated through the measurements of the total cross-section for graphite with the Bragg cut-off energy of 1. 818 meV. It was determined to be 160±20 μsec for neutron energies up to 10 meV, and smaller in the higher energy region. The corrections applied to the flight-path length for the finite counter thickness were quite small, since the mean absorption depth within the counter for neutron energies of interest is very small compared with the flight-path length. The time channels were grouped non-uniformly to yield a constant analyser timing resolution of 3 %, except where the resolution was already channel-width limited, i. e. at high neutron energies. This was done to reduce statistical errors while allowing a slight loss of energy resolution. After grouping, the total energy resolution was estimated to be equal to ±4, ±4 and ±8 % for neutron energies of 1, 10 and 50 meV, respectively.

The errors quoted in the results of the measurements correspond to standard deviations calculated by using estimated statistical errors. The following relation was used to calculate the error $\delta\sigma_t$ in the cross-sections:

$$\delta\sigma_t(E)=\pm N^{-1}ln[(1+\epsilon_0)/(1+\epsilon)], \tag{3}$$

where the upper and lower signs refer to positive and negative deviations from σ_t respectively, and ϵ_0 and ϵ are given by

$$\epsilon_0=\sqrt{\phi_0(E)}/\phi_0(E) \quad \text{and} \quad \epsilon=\sqrt{\phi(E)}/\phi(E). \tag{4}$$

4. Results and discussion

4.1. Total cross-section

The total cross-sections for heavy ice at temperatures of 77 and 15 K obtained

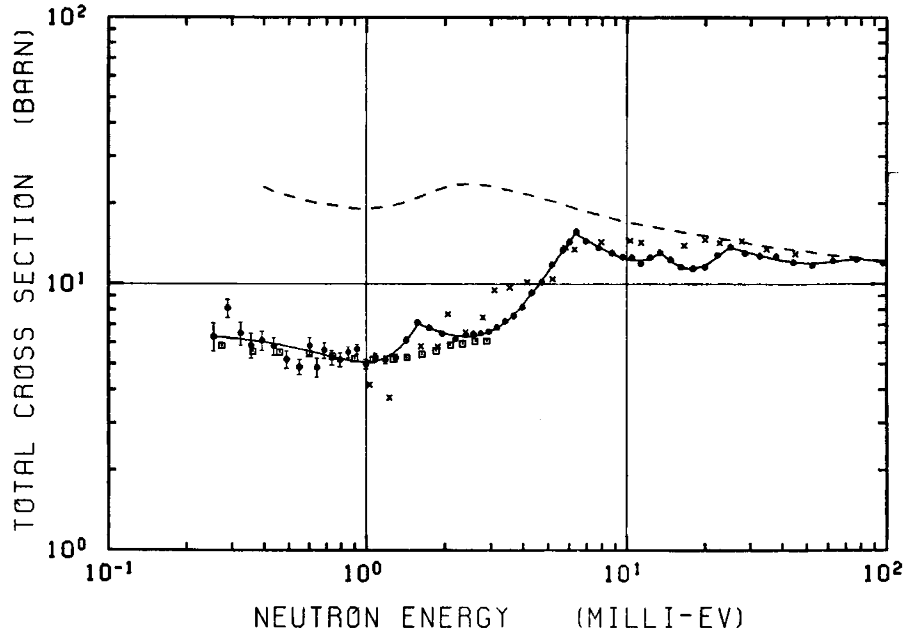

Fig. 2. Total cross-sections of D_2O molecule in heavy ice at 77 K. Solid circles, measured by the present authors; crosses, by Whittemore and McReynolds[3]; square, by Gissler[4]; solid curve, obtained by the method of statistically weighted least-squares fittings to the present data. Also shown by dashed curves are the total cross-sections in heavy water at room temperature, taken from ref. 6.

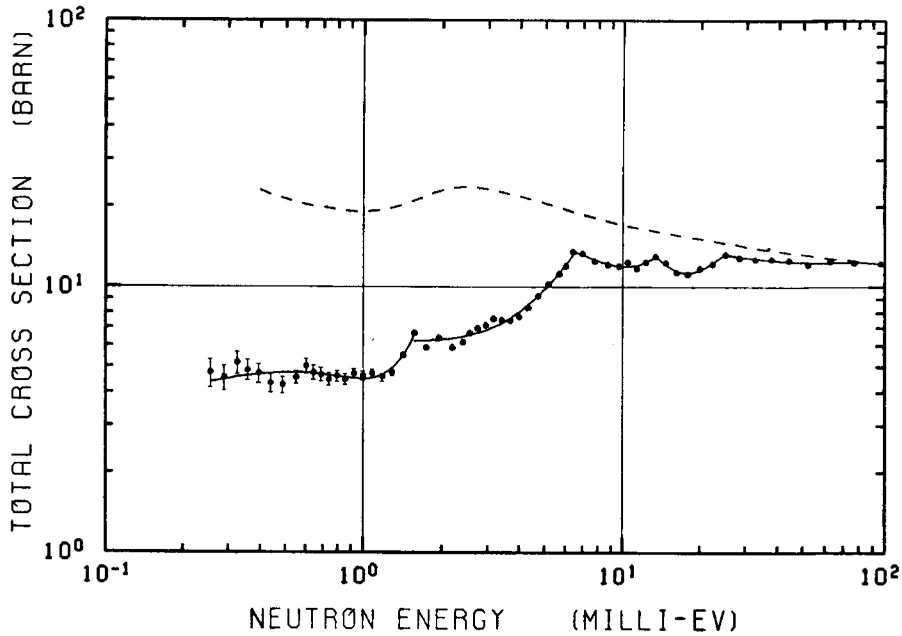

Fig. 3. Total cross-sections of D_2O molecule in heavy ice at 15 K. The meanings of solid circles, solid curve and dashed curve are the same as those in Fig. 2.

from the present experiment are shown by solid circles in Figs. 2 and 3, respectively. The error bars represent only an uncertainty greater than ± 3 %. The dashed curves shown in the figures are the experimental results of ref. 6 for heavy water at normal temperature. The solid curves will be interpreted in the next section.

Also included in Fig. 2 are the total cross-sections for heavy ice at 77 *K* determined by Whittemore and McReynolds[3] and by Gissler[4]. At neutron energies lower than 1.3 meV, the present data agree within the error bars with the results of Gissler. It was Gissler who found that the soft increase in a cross-section with decreasing energy can be reproduced reasonably well by the sum of an incoherent elastic scattering cross-section of 4. 50 *b* and an inelastic scattering cross-section calculated in the Debye approximation at an effective temperature of 228 ± 5 *K*. As for neutron energies higher than 1. 3 meV, the present high-resolution data exibit new several sharp peaks not observed in the previous measurements.

It can be observed in Figs. 2 and 3 that there is a monotonous decrease in the present data for neutron energies below 6. 39 meV. This decrease in cross-section is entirely different from that for a crystalline specimen showing the Bragg cut-off. It may be preferable to compare such a decrease in a cross-section with the shape of the total cross-section for coherent elastic neutron scattering by a liquid, e. g. liquid oxygen and nitrogen. (See e.g. Vertebnii et al. [7].) Except for the presence of a sharp maximum at 6. 39 meV, the present cross-section curves are very similar to those for the liquids, in which a short-range order in the disposition of liquid molecules is found. (See e. g. refs. 1 and 8.)

Another interesting feature of the present data is the presence of sharp maxima, being particularly marked for energies 1. 53 ± 0. 03, 6. 39 ± 0. 20, 13. 4 ± 0. 60 and 25. 1 ± 1. 54 meV. These correspond to the neutron wavelengths of 7. 31 ± 0. 06, 3. 58 ± 0. 05, 2. 47 ± 0. 05 and 1. 81 ± 0. 05 Å, respectively. With the present energy resolution, these values for the peak energy were found to be the same at the temperatures of 77 and 15 *K*. It will be noticed that the first two wavelengths are nearly multiples of the last one, and that the value of 3. 58 Å is equal to approximately one-half the length of the *c*-axis for the hexagonal heavy-ice structure. (See e.g. Fletcher[9].) This result suggests that there is a high possibility of the existence of a fairly strong local ordering made up of a definite family of reflecting crystalline planes with its own plane separation very similar to the hexagonal ice.

It should be noted that the cross-sections of 15 *K* heavy ice for energies below about 30 meV are somewhat smaller than those obtained at 77 *K*, indicating a less local ordering. At lower energies between 0.7 and 1. 2 meV, although the error bars become larger, the little depletion of total cross-sections results in a good agreement with the constant value of the spin-incoherent cross-section for a D_2O molecule, i. e.

4.50 b.

4.2. Structure factor

Since effective Debye temperatures for heavy ice at 77 and 15 K are estimated to be about 228 and 185 K respectively[5], an elastic neutron scattering, both coherent and incoherent, seems predominant throughout the energy range from 0.5 to 10 meV. The total cross-section thereupon can be directly related to a coherent elastic structure factor $S(\kappa)$ by:

$$\sigma_t(E) = \sigma_{inc} + 8\pi b_{coh}^2 \left(\frac{\lambda}{4\pi}\right)^2 \int_0^{4\pi/\lambda} \kappa S(\kappa)\, d\kappa, \tag{5}$$

where σ_{inc} = total incoherent elastic scattering cross-section for D_2O molecules, i. e. 4.50 b,

$4\pi b_{coh}^2$ = total coherent elastic scattering cross-section for D_2O molecules in the short-wave (incoherent) approximation, i. e. 15.0 b,

λ = de Broglie wavelength of a neutron,

κ = momentum transfer.

This relationship indicates that $S(\kappa)$ can be determined from measurements of the total cross-section $\sigma_t(E)$. In fact, introducing the quantity $\xi = 4\pi/\lambda$, it follows from eq. (5) that

$$S(\xi) = \frac{1}{8\pi b_{coh}^2} \frac{1}{\xi} \frac{d}{d\xi}\{(\sigma_t(\xi) - \sigma_{inc})\xi^2\}. \tag{6}$$

In order to evaluate the structure factor by use of eq. (6), a least-squares analysis was used to express the energy dependence of the cross-section data in terms of a polynomial of neutron energy. For each data point, the deviations of the experimental points from the curve to be fitted are squared, and then weighted with the factor $(\delta\sigma_t)^{-2}$. Statistical weighting was used. The sum of these weighted quantities which yields the total error of fit is taken separately for five different regions of neutron energy: below 1.53, from 1.53 to 6.39, from 6.39 to 13.4, from 13.4 to 25.1 and above 25.1 meV. The order of the polynomial to be fitted was determined in such a way that the total error of fit is equal to approximately 1.0 per one data point. In other words, the average deviation of all data points in an energy region from the fitted curve is of the same order of magnitude of statistical errors in the cross-section data.

The results obtained for the total cross-sections at 77 and 15 K are summarized in Table 1, and shown by solid curves in Figs. 2 and 3. The present least-squares analysis is carried out on a representation of the main features of the cross-section data. Hence, the resulting curves tend to smooth out the fine structures of the data: one of which is seen from Fig. 3 for the energy region from 1.53 to 3.0 meV. On the basis of the results of the least-squares analysis, the structure factors for heavy ice at 77 and 15 K

Table 1. The results obtained by method of statistically weighted least-squares fitting for the cross-section data of heavy ice at temperatures of 77 and 15 K

Temperature (K)	C_n^a and δ^b	Energy region (meV)				
		Below 1.53	From 1.53 to 6.39	From 6.39 to 13.4	From 13.4 to 25.1	Above 25.1
77	C_0	6.68E+0	1.34E+1	3.02E+1	6.26E+1	2.06E+1[c]
	C_1	−5.11E−1	−6.42E+0	−3.26E+0	−7.29E+0	−4.19E−1
	C_2	−3.83E+0	1.68E+0	1.48E−1	3.34E−1	6.55E−3
	C_3	2.75E+0	−9.62E−2	0.0	−4.81E−3	−3.24E−5
	δ	0.638	0.516	0.925	0.443	0.500
15	C_0	3.01E+0	6.91E+0	2.39E+1	6.10E+1	1.59E+1
	C_1	7.99E+0	−8.78E−1	−2.32E+0	−7.08E+0	−1.62E−1
	C_2	−1.15E+1	2.91E−1	1.13E−1	3.25E−1	2.41E−3
	C_3	5.05E+0	0.0	0.0	−4.74E−3	−1.17E−5
	δ	0.405	1.61[d]	0.946	0.484	0.457

a C_n is coefficient for the polynomial $\sum_{n=0}^{3} C_n E^n$ of neutron energy E in meV.

b δ is related with the total error of fit as follows:

$$\delta = \left\{ N^{-1} \sum_{n=1}^{N} \delta\sigma_t(n)^{-2} (\sigma_t^E(n) - \sigma_t^T(n))^2 \right\}^{1/2}$$

where $\sigma_t^E(n)$, $\sigma_t^T(n)$ and $\delta\sigma_t(n)$ are the cross-section data, the value of the polynomial and the statistical error of the data at the nth data point, respectively, and N is the total number of the data points for each energy region.

c 2.06E+1 stands for 2.06×10^1.

d use of third-order polynomial results in an increase in δ value.

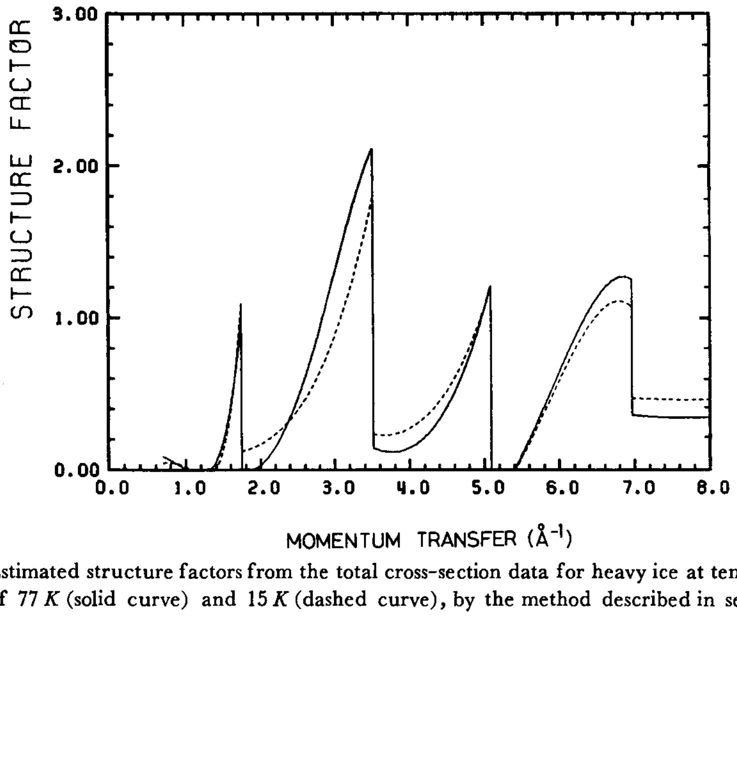

Fig. 4. Estimated structure factors from the total cross-section data for heavy ice at temperatures of 77 K (solid curve) and 15 K (dashed curve), by the method described in section 4.2.

are calculated by eq. (6), and they are shown in Fig. 4. No corrections are made for the reduction in $S(\kappa)$ due to the thermal vibrations of a D_2O molecule and the contribution of inelastic scattering processes to $S(\kappa)$, especially at larger values of κ. Hence, the structure factors obtained are useful only for small values of κ, e. g. below about 4. 0 $Å^{-1}$. For larger values of κ, these suggest the presence of peaks very similar in form to those of the smaller values of κ.

It should be noted that the results of the present fittings do not change significantly when the cross-section data are fitted by another method of fittings with a series of third-order polynomials passing through all data points. The method for interpolation with B-spline functions of the third order was used. (See e. g. Greville[10].) The structure factors resulting from this method represent contamination of many small sharp peaks and valleys. However, it is confirmed that there is a marked tendency to exhibit the results very similar to those shown in Fig. 4.

It can be observed in Fig. 4 that there is a family of sharp peaks having both a monotonous rise with an increasing κ and an abrupt fall at a certain value of κ. The former property is similar to that found in heavy water by Page and Powles[11] and by Matsumoto et al[12]. The latter is the very picture of a crystal. This indicates that the form of the structure factor thus obtained characterizes the strong short-range ordering in heavy ice formed by the rapid cooling of heavy water. In other words, the results of the present study suggest that the information about the degree of structural ordering in the heavy ice may be obtained directly from the slope of the total cross-section curve, e. g. just below the neutron energy of 6. 39 meV.

Acknowledgements

The authors are sincerely grateful to Prof. A. Steyerl of the Technische Universität München for valuable discussions about the measured cross-section results. They also wish to thank Messrs. M. Sugimoto and K. Okumura for their appreciated assistance during the experiments.

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