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Neutron Diffraction Studies of Structural Phase Transformations for Water-Ice in Confined Geometry

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Abstract

Neutron diffraction measurements have been made for D_2O water in the confined geometry of various mesoporous silicas over a wide temperature range. The data have been taken for cooling and heating runs incorporating the nucleation and melting of the crystalline phases and the super-cooled liquid phase. The crystaline forms and the temperatures at which they change are shown to be strongly dependent on the pore size and type of silica used as the confining medium and relate to the phase relationship between hexagonal ice $[I_h]$ and cubic ice $[I_c]$.

Key words: water, ice, mesoporous silica, MCM-silica, phase transformation, neutron diffraction
PACS:

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1 Introduction

The phase diagram for ice exhibits many different crystal forms based on local molecular correlations that influence the ordered arrangement of hydrogen-bonded configurations. In addition to these stable structures there are also a number of metastable states, which are dependent on less-ordered hydrogen-bond arrangements. The most obvious examples are super-cooled water, which exists at temperatures below the normal nucleation point for the liquid phase

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and two forms of amorphous ice, formed by vapour deposition or pressure melting of ice I$_c$. The inter-relation of these various structures has been a source of fascination for more than a decade. The essential aspects of hydrogen-bond connectivity and network structure for water were outlined in a pioneering paper of Stanley and Teixeira [1] in 1980. Since that time the puzzling features of the water-ice relationship have continued to generate many further publications which have been summarised in a general review paper [2] of 2000.

A further set of questions was generated by the strange behaviour of water in the confined geometry of sol-gel silicas which exhibited deep-super-cooling with the eventual nucleation to a defective form of cubic ice I$_c$ instead of the normal hexagonal ice I$_h$. Subsequent investigation has shown that the ice structure is dependent on the pore size, pore filling and possibly the pore shape; a review of neutron scattering studies was published in 2000 by Dore [3] and some more recent work [4] reported in 2001. These studies have emphasised the complex behaviour of the nucleation process and the inter-relationship of the solid and liquid phases. In order to make a more detailed investigation, some further neutron diffraction measurements have now been made and a presentation of the initial findings is given in the following sections.

2 Theoretical Framework

Neutron diffraction by liquid D_2O is primarily defined by OD and DD correlations [3] and is therefore sensitive to the local orientational correlations between molecules. The molecular structure factor can be written in terms of intra- and inter-molecular parts as:-

$$S_M(Q) \;=\; f_1(Q) \;+\; D_M(Q)$$

The temperature difference function for a reference temperature T_0, then becomes:-

$$\Delta D_m(Q\;;\;T,T_0) \;=\; S_M(Q\;;\;T) \;-\; S_M(Q\;;\;T_0),$$

and gives a direct measurement of the change in the structural arrangement of the molecules over the temperature range $\Delta T = T - T_0$ through the transform relationship :-

$$\Delta d_L(r,\;\Delta T) \;=\; \frac{2}{\pi}\int_0^\infty Q\,\Delta D_m(Q\;;\;T,T_0)\;\sin Qr\;dQ.$$

This technique is particularly useful when the material under investigation is contained in a porous substrate that does not change with temperature. The difference function eliminates many of the experimental corrections to the raw datasets and provides a convenient and sensitive method for studying structural changes in both the liquid phase and across a phase transformation.

3 Experimental Procedure

a) Sample preparation

Several different silica samples were used and are detailed below:-

Sample A) sol-gel silica; Unilever [5] ; pore size 500Å [f=0.3 and 0.9]

Sample B) sol-gel silica; Unilever [5] ; pore size 100Å [f=1.0]

Sample C) MCM48 silica; Hartl [6] pore size 35Å [f$\sim$0.25]

The samples were dried by heating at 110^{o}C for 24 hrs and the correct quantity of D_2O was added directly to weighed quantities of the powdered samples to provide the filling factors given above; the samples were left for at least 12 hrs to equilibriate.

b) Neutron measurements

The experiment was conducted on the high intensity diffractometer, D20, at the Institut Laue Langevin. The silica samples were put in a thin-walled vanadium container of 5 mm diameter and mounted in a standard helium cryostat. The incident neutron wavelength was 1.3Å and measurements were taken with the 153.6^o position-sensitive linear detector (with 0.1^o cells) using a cryostat control system operating on a temperature ramp protocol with a cooling or warming rate of between 0.2^{o}C and 2^{o}C per minute (ramping rates were reduced near expected phase transitions). The complete diffraction pattern was recorded at one-minute intervals during the temperature scanning sequence. This procedure is preferred over the stable temperature method as it ensures that any temperature gradients remain constant during the runs; the disadvantage is that the actual temperature of the sample is not precisely defined due to the temperature lag but this is similar to thermal measurements made by DSC. The D20 diffractometer has one of the highest neutron fluxes in the world (giving in Fig. 2 around 10^4 counts per minute for the peaks from the small amount of ice in the porous silica) and is ideally suited for this type of time and temperature dependent measurement.

4 Results

It is convenient to use the temperature difference function method [Sec.2] to investigate the structural changes. A preliminary analysis of the transition region is presented below to emphasise the different behaviour in two of the three silicas used in this study.

4.1 Ice I_h pre-melting

The stacked diffraction patterns for the melting of ice I_h in 500 Å pores [Sample A] are shown as a contour plot in Fig 1, covering the temperature range 282-286 K. The sharp Bragg peaks of the crystalline phase are seen to change to the disordered pattern of the liquid phase at a recorded temperature of 284.5 K and there is a corresponding change in the intensity in the lower-Q region indicating a variation of the compressibility. The broad diffraction peak of the water is also seen to shift significantly to higher Q-values as the temperature is increased. Another interesting feature is the apparent reduction in relative intensity of the central peak of the ice triplet in the pre-melting region. This change is presumably indicative of the way the periodicity of the ice lattice is modified by molecular motion [rotational and translational] prior to the breakdown of the lattice structure and the creation of the liquid state. There is much further information to be extracted from these datasets and also from the corresponding information available over a wider Q-range and larger temperature range. It would be impossible to make similar measurements on bulk ice samples due to re-crystallization processes so that these results probably represent the first direct observation of ice melting under controlled conditions.

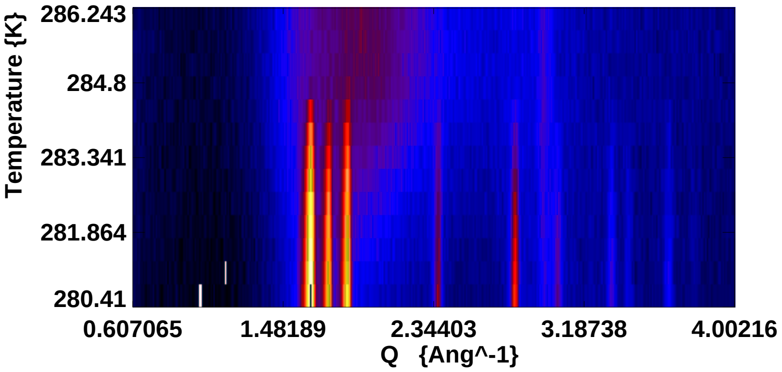

Fig. 1. The variation of the intensity profile for neutrons scattered from D_2O in 500Å pores in the melting region, showing the dissapearence of the hexagonal peaks. [Time runs vertically upwards.]

If the temperature difference functions are evaluated with a recorded reference temperature [T_0] of 286K the $\Delta D_m(Q\ ;\ T, T_0)$plots shown in Fig.2 indicate the sequential disappearance of the crystal peaks and the emergence of the diffuse scattering contribution from the water.

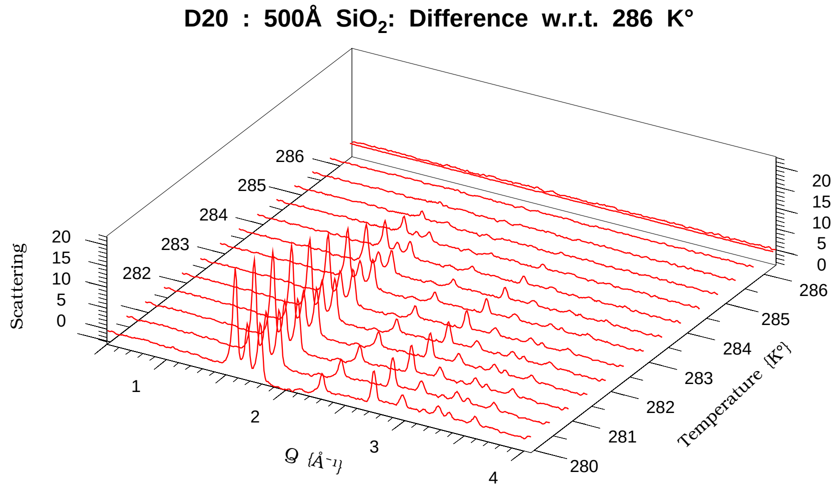

Fig. 2. Selected temperature difference functions for D_2O in 500Å silica [from Fig.1]

4.2 Nucleation and melting of water/ice in MCM silicas

A cooling sequence at 1K/min followed by a heating sequence of 2K/min for water/ice in MCM68 silica [Sample C] is shown in Fig 3. The broad peak arising from the defective cubic ice is seen at low temperatures and appears to grow with increasing intensity as the peak of the super-cooled water becomes displaced to lower Q-values as the temperature is reduced. This effect is similar to that seen in the earlier studies at several fixed temperatures. The heating run confirms the earlier conjecture that the transformation is reversible. The overall sequence indicates that there are also some changes to the ice diffraction pattern in the region below the main nucleation temperature. Some typical temperature variation plots are shown in Fig 4.

The present datasets provide a preliminary insight into the complexity of the structural changes occurring in the water-ice transformation. There are many other gradual changes to the intensity profile which occur over a wider temperature range that can be further studied by a quantitative treatment of the datasets. The technique is able to probe super-cooling and pre-melting phenomena and to 'watch' the structural changes during nucleation and melting.

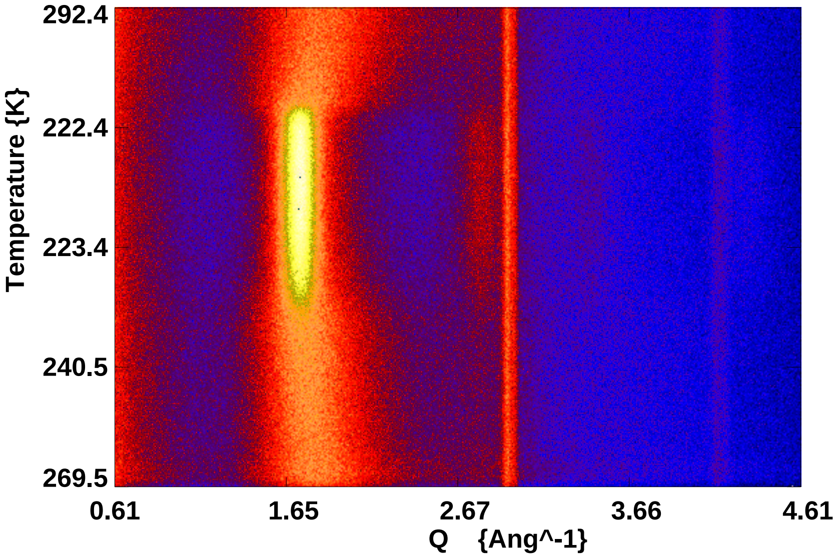

Fig. 3. Intensity profiles for D_2O in MCM68-type silica showing a cooling and heating sequence. [Time runs vertically upwards.]

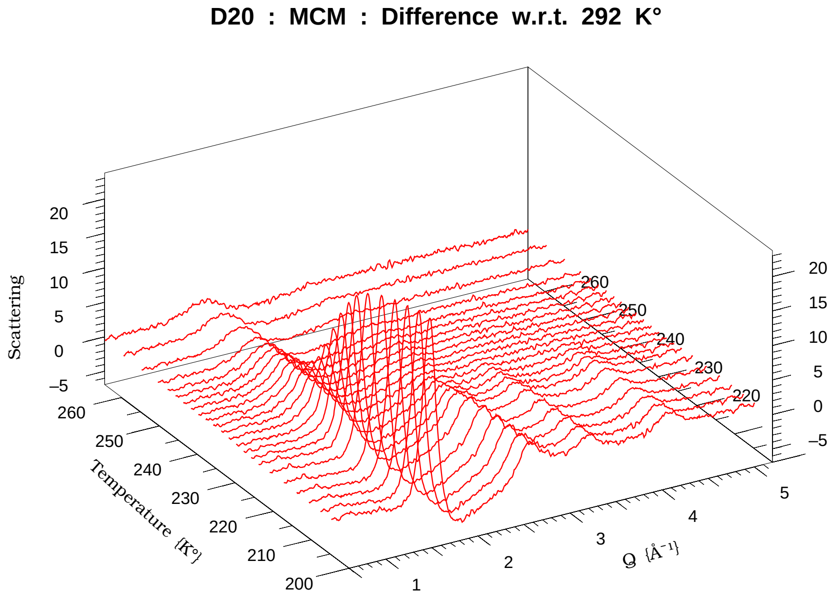

Fig. 4. Selected temperature difference functions for D_2O in MCM silica cooling run [from Fig.3], showing the emergence of the cubic peaks as a function of time and temperature.

5 Interpretation of Results

It is clear from the above treatment that the nucleation behaviour is dependent on several factors and that the ice formed in the pores of the different samples has different characteristics. The reason for this behaviour is unknown and, once again, emphasises the complex features of the correlated hydrogen-bond network. Several conclusions can be made from the preliminary analysis that confirm earlier conjectures:-

the depression of nucleation temperature may be as large as 45K for small diameter pores,

the normal phase of ice I_h is formed in large pores but a defective form of ice I_c is formed in pores of 100Å diameter or less,

modification of the ice structure with temperature occurs below the nucleation point.

6 Conclusions and Future Work

The present results indicate the powerful methods available for the detailed study of structural modification in molecular systems by time/temperature-dependent neutron diffraction. The technique is particularly valuable for nucleation and melting studies. The results described above concern water/ice in confined geometry but similar measurements have also been made for cyclohexane [7] due to its importance in the study of pore distribution functions by NMR cryoporimetry [8], [9]. Furthermore, studies using synchrotron x-rays have been started which are more difficult due to the higher scattering intensity from the silica substrate but should eventually give complementary information on the changes in the oxygen correlation function.

The wider context of the present work is to study the structural features of water and ice in a range of different mesoporous materials and also at interfaces. The wide range of silica samples constitutes a convenient system for investigating the effects of variable pore size and it will be convenient to continue this type of investigation by using surface-modified materials to determine whether the hydrophilic interaction plays a major role in defining the behaviour. However, the eventual aim must be to study the properties of the interfacial water in systems of biological interest. There are considerable problems in extending the work to soft condensed matter where the organic substrate itself undergoes change with temperature and where removal of the water leads to the collapse of the meso-structure. However, these difficulties can hopefully be overcome by a combination of x-ray, neutron and computational techniques that will eventually reveal the subtle ways that Nature uses the remarkable properties of hydrogen-bonded assemblies to create the life sciences from simple physical means. Complexity often results from simple rules of behaviour that we do not fully understand! Water seems to provide us with an excellent example!

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