COMMENTS ON THE ICE Ic STRUCTURE AND Ic TO Ih PHASE TRANSFORMATION MECHANISM : A NEUTRON SCATTERING INVESTIGATION OF ICE PRECIPITATES IN GLASSY LiCl.D2O

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COMMENTS ON THE ICE I_c STRUCTURE AND I_c TO I_h PHASE TRANSFORMATION MECHANISM : A NEUTRON SCATTERING INVESTIGATION OF ICE PRECIPITATES IN GLASSY $LiCl.D_2O$

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Résumé - Nous avons étudié par diffusion de neutrons, les étapes intermédiaires de la transformation de la glace I_c en I_h, telles qu'elles peuvent être observées dans les cristallites de glace précipitant dans le verre $LiC\ell.D_2O$. L'introduction de profils de Warren caractéristiques des structures bidimensionnelles nous a permis de décrire avec précision le profil des raies de Bragg observées et de comprendre la naissance de la série de raies 10ℓ de la glace I_h. Ceci peut s'expliquer par le développement et l'arrangement progressif de défauts d'empilement bidimensionnels de structure I_h dans I_c jusqu'à formation totale de la structure I_h. Une explication est ainsi donnée aux déformations du pic 111 de la glace I_c. Enfin l'analyse du bruit de fond indique qu'une glace amorphe de faible densité pourrait coexister avec la transformation cubique hexagonale.

Abstract - Intermediate steps of the ice $I_c \rightarrow I_h$ Transformation have been observed by neutron scattering in the ice crystallites precipitated from a glassy $LiC\ell.D_2O$ matrix. An accurate description of the observed scattering patterns has been obtained by introducing Warren peak profiles such as obtained by bidimensional structures. This, as well as the progressive appearance of the 10ℓ (I_h) series of lines, could be explained by the formation of ice I_h sheets (such as obtained from stacking faults in ice I_c) and progressive piling up of these sheets until completion of the I_h structure. This might also explain the distortions of the (I_c) 111 peak. Comments are given on a possible low density amorphous ice coexisting with the $I_c \rightarrow I_h$ transformation.

I - INTRODUCTION

Concentrated aqueous electrolytes are very interesting systems for the study of some fundamental physics problems such as glass formation and stability. In some cases such as for $LiC\ell.H_2O$ a very detailed knowledge of their non-equilibrium phase diagrams has been obtained /1/. At concentrations greater than $LiC\ell.12\ H_2O$ (or 8 mole %), glasses are formed by a simple quench of the solutions to liquid N_2. A systematic temperature treatment of the samples (quench to liquid N_2 at a rate of $\sim 100°K/mn$ followed by a warming of $2°K/mn$) has allowed us to obtain the glass transition (T_g) line, the various crystallization (T_c) lines and to determine the strong undercooling displayed at some concentrations by the liquidus line. The various crystallization products obtained on warming the glasses have been identified from their neutron scattering pattern. In particular at concentrations between $LiC\ell.12\ H_2O$ (8 moles %) and $LiC\ell.6\ H_2O$ (14 moles %) ice crystallizes out of the sample for temperatures $140\ K < T < 180\ K$ ($T_g \simeq 139\ K$). When ice crystallization occurs, the remaining glass matrix progressively increases its concentration towards the undercooled ice branch of the liquidus line, i.e. to about $LiC\ell.6\ H_2O$. Depending

on annealing at temperatures a few degrees below T_g it is possible to fully control the size of the ice crystallites. It has been shown /2/ by a combination of small angle neutron scattering and neutron diffraction experiments that a nearly complete crystallization in the cubic ice (I_c) structure could be achieved if the crystallites remained smaller than about 200 Å. Following further warming, the I_c transformed to I_h ice (for T $\gtrsim$ 160 K if annealed samples, and T $\gtrsim$ 150 K if non annealed samples, and a concomitant growth of the crystallite sizes up to a micron or more was observed.

Considering the amount of information which we had accumulated on the correlation between the sample thermal history and its structure we thought that this system was really appropriate for a detailed investigation of the ice I_c to I_h transformation mechanism. Within the electrolytic glassy matrix the ice I_c to I_h transformation can be made slow enough (hours) to be followed by standard diffraction methods and intermediate steps can easily be quenched if necessary. Moreover by varying the electrolyte we have the possibility to study the effect of the medium on the crystallization and phase transformation processes. We shall present below and discuss some typical neutron scattering spectra and briefly outline how they have been analyzed. This will also throw some light on the peculiarities of the I_c pattern itself.

II - EXPERIMENTAL

The neutron scattering experiments were performed at the ILL (Grenoble) on various spectrometers with different resolutions and data acquisition rates (D1A, D1B, D2). The solutions were prepared from weighted amounts of analytical reagent anhydrous LiCℓ (Merck) and 99.7 % enriched D_2O. Deuterated samples were always used because of their low neutron incoherent scattering background. Sample containers were usually tight vanadium cells (Ø 8 mm diameter, 0.1 mm wall thickness, 60 mm height). Samples were quenched in situ, to liquid N_2 in the cryostat tail (standard ILL orange cryostat, with Vanadium tail). After liquid N_2 boil off various annealings or temperature changes could easily be made, the temperature being controlled and read to 0.1°K.

III - RESULTS AND DISCUSSION

A. The ice I_c and I_h "pure" structures

We see in figure 1 various examples of the ice I_c structure which we have obtained. The intense and broad background due to the glassy electrolyte matrix is well noticeable. A pure glassy pattern exempt of Bragg peaks is always obtained aft quench to liquid N_2 and as soon as ice precipitates on warming, it slightly shifts to higher angles following the concentration change which can therefore be quantified. The intense 111 line of the cubic pattern is always broadened by the small crystallite size which accompanies this structure. A shoulder always appears on the low angle and a tail on the high angle side of this peak /3/. The detail of the 111 peak shape depends therefore on sample preparation (crystallite size and shoulder intensity) and also, of course, on instrumental resolution. The effect of the instrumental resolution is shown in the figure 1 where similar samples have been run on the D2 (λ = 1.22 Å) and D1A (λ = 1.39 and 1.909 Å) spectrometers. Of course for too small crystallite sizes the side shoulder could never be resolved. In order to quantify the amount of side shoulder perturbation in the peak and to see what minimum value it takes we would like to have an appropriate model. However, contamination by ice I_h, which has generally been invoked does not allow us to fit the data (the side shoulders of the 111 I_c peak cannot be fitted by the 100 and 101 peaks of I_h, whatever peak broadening or resolution effect is considered).

If we consider the I_h pattern, it is characterized by the 100, 002, 101 triplet and also unambiguously by the 102 peak (see figure 2). As long as the transformation to I_h is not fully achieved the relative intensity of the triplet peaks might slightly vary and there seems to be some background underlying the triplet (this is especially apparent on high resolution spectrometers).

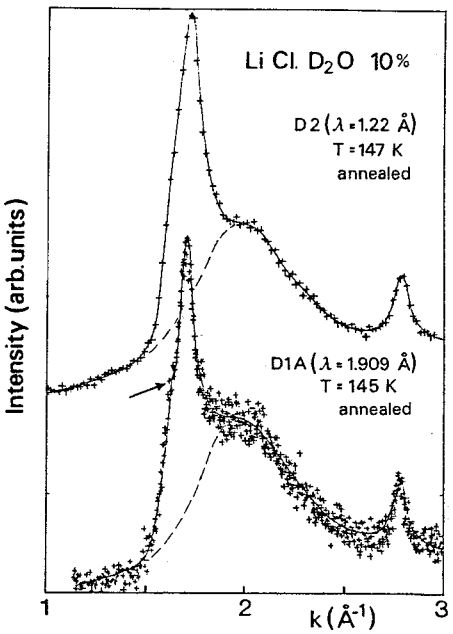

Figure 1
Examples of ice I_c structure showing the effect of instrumental resolution and crystallite size on the detailed shape of the 111 peak. (The broad background peak due to the vitreous matrix is marked with a dashed line).

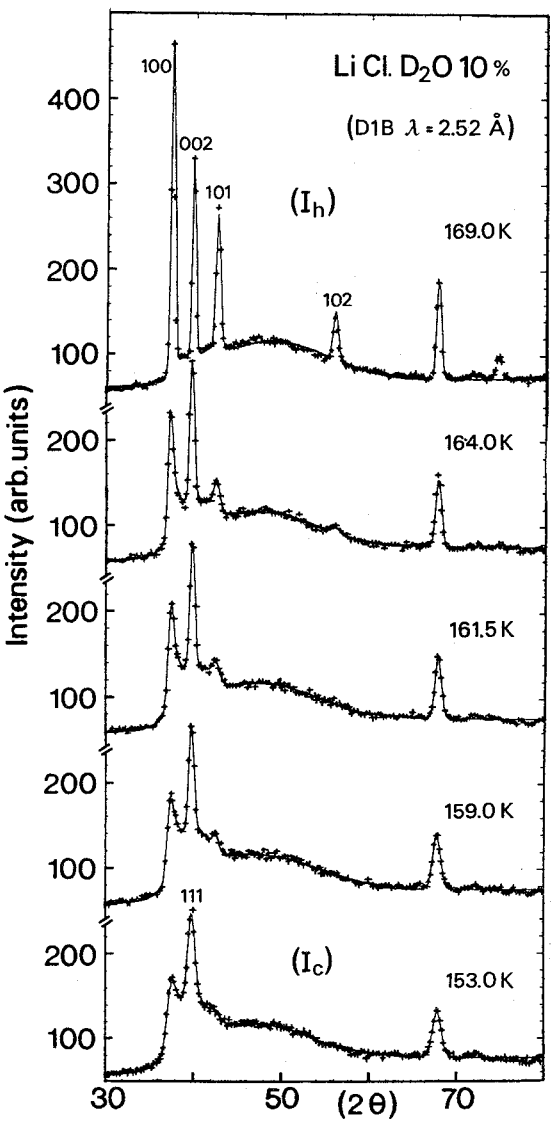

Figure 2
Intermediate steps of the ice $I_c \rightarrow I_h$ transformation. The continuous line has been obtained by a fitting procedure explained in the text.

B. Intermediate structures during the $I_c \rightarrow I_h$ transformation

We see in figure 2 some typical patterns obtained on D1B (λ = 2.52 Å) during the $I_c \rightarrow I_h$ transformation. In this case the $LiCl.D_2O$ sample was directly warmed up from the quench temperature (∿ 77K) to 153K and a series of spectra were taken between 153 K and 170 K. No effort was made to control the particle size neither to insure that complete precipitation of ice was achieved at 153K. Further precipitation and crystallite growth will occur on warming. The interest of these patterns lies in the detail of the appearance of the (I_h) 10ℓ series of lines. On warming, the 100 peak appears first, then 101, then 102 and the strong asymmetry (tail at high angles) of the 100 peak vanishes progressively as the series builds up. This asymmetric peak profile is typically obtained for bidimensional structure (or sheets) randomly oriented in the beam and has been described by Warren /5/. A 100 peak with Warren-profile could, for example, be due to randomly oriented ice I_h sheets such as produced by stacking faults in the I_c crystals. As long as no correlation between sheets exists along the direction perpendicular to the sheet plane, only the 100 peak would be detectable; on the other hand with the piling up of sheets, oscillations will develop at the 10ℓ peak positions and finally will give place to well developed Bragg peaks.

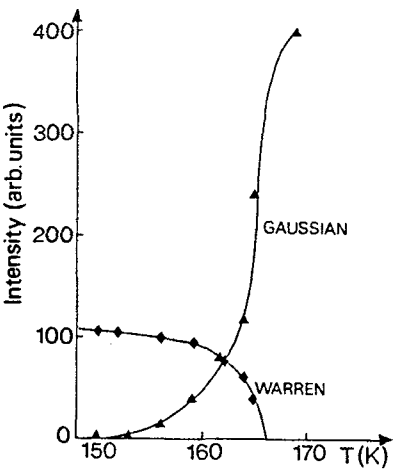

Figure 3
Intensities of the Gaussian and Warren peak profiles used to fit the 100 peak (I_h) as a function of temperature.

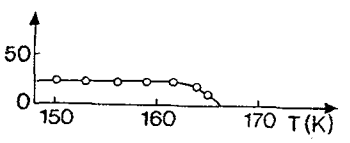

Figure 3 bis
Temperature dependence of the 1.7 $Å^{-1}$ background.

As a first and crude approximation to the data analysis we have therefore proceeded as follows (see also figure 4). The broad background due to the electrolytic vitreous matrix has been fitted by a Gaussian drawn on a linearly angular dependent background; then all Bragg peaks except for the 100 have been fitted by gaussians. The 100 line itself has been fitted by a Warren profile or by a combination of Warren plus Gaussian profile as a function of temperature. The relative intensity of these two profiles gives then a simplified but significative information on the advancement of the $I_c \rightarrow I_h$ transformation (see fig.3) which terminates quite rapidly between 162 and 168 K. (Previous experiments have shown that for T $\gtrsim$ 150 K the size of the crystallites increases. In the present run also the width of the gaussians decreases on warming and progressively reaches the instrumental resolution). Of course, a more elaborated treatment could be pursued by fitting at once the asymmetry of the 100 line and the appearance of the 10ℓ series with a very reduced amount of parameters. This type of data treatment could also be extended to high angle peaks such as around the I_c 222 peak (depending on measurement our data extend up to 3.5 $Å^{-1}$ or 7 $Å^{-1}$). However it is clear that the quality of the fit to the experimental pattern (see fig. 2) is already remarkable and is much better than any combination of pure I_c and I_h

ice structure which cannot represent the detail of the triplet pattern during the intermediate stages of the transformation.

C. Comments on the background

As a matter of fact a careful analysis shows that it is impossible to describe the experimental patterns simply with a broad background (due to the glassy electrolyte matrix) plus any combination of Bragg or Warren peaks (see insert of figure 4 for such a trial). Some extra background in the region around 1.7 $Å^{-1}$ as shown by the hatched area in figure 4 is necessary. This extra background was used for all fits of figure 2 and the temperature dependence of its intensity is displayed in figure 3 bis, it disappears when ice I_h is fully formed. Further work is being undertaken to characterize more precisely this 1.7 $Å^{-1}$ extra background, however it is already interesting to note that it occurs at the peak position of low density amorphous ice. This raises the question of a disordered ice structure accompanying the I_c to I_h transformation.

IV - CONCLUSION

Since it is possible to fully control and characterize the crystallisation of ice in a glassy electrolytic matrix we have chosen this system to investigate the detail of the ice I_c to I_h transformation. Intermediate steps of this transformation show the progressive appearance of the series of the 10ℓ lines of ice I_h. An appropriate description of the phenomenon as well as of the strong asymmetric profile of the 100 line has been given by considering randomly oriented sheets of I_h structure (such as might be produced by stacking faults in I_c) which progressively develop and

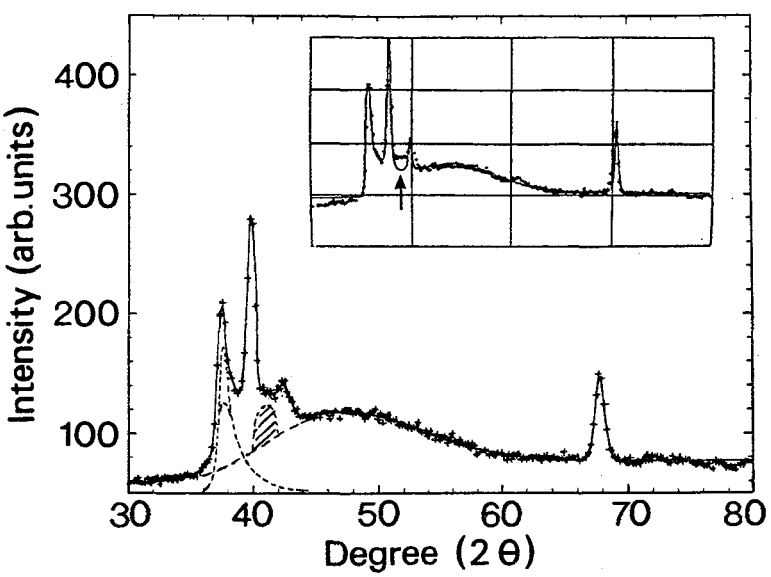

Figure 4
Detail of the fitting procedure showing the Warren peak profile used for the 100 peak, the broad vitreous matrix profile and the extra background at 1.7 $Å^{-1}$. The insert shows the importance of the supplementary background at 1.7 $Å^{-1}$.

pile up. Some low density amorphous ice seems to coexist with $I_c \rightarrow I_h$ transformation and its role should be further elucidated (careful studies of the temperature dependence of the whole background are in progress). The above description of the ice I_h formation is also appropriate to describe the pure I_c ice peak distortions. The role of the ions on the ice formation in these systems is certainly important and is further investigated. For example, $BeCl_2.D_2O$ glasses of equivalent concentration than $LiCl.D_2O$ and under identical thermal treatment will even at the earlier stages of crystallizarion predominantly display the I_h pattern.

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COMMENTS

Remark of W.F. KUHS :

Stacking-faults producing the Warren-type profile are different from stacking faults of the deformation type. Both types may occur at the same time. You have evidence for first type of faults. We have evidence for the second type. The extra intensity on the high-angle side of the 111 cubic peak (ascribed to some amorphous phase in this work ?) may originate in deformation faults (May comment ?)

Answer :

In our profile analysis (Warren type) we only say that the first perturbation which appears in the I_c structure (and seems to always be there since no pure I_c pattern has never been seen) is produced by sheets (bidimensional) of I_h faults, not matter what is the detail mechanism which produces these faults. Then these I_h sheets do progressively correlate and built up the I_h crystals.
Further work is in progress in order to study the background at 1.7 $Å^{-1}$. However for the time being we do not see how stacking or deformation faults can explain this background, which seems always much stronger than any computation based on faults.

P. BOUTRON

At what warming rates have you observed the transition from cubic into hexagonal ice in your LiCl solution ? Have you compared the kinetics of this transition in your solution and in pure water ?

Answer :

1. We have not compared with pure water.
2. The warming rate is choose as a function of the precision we need on the neutron pattern diffraction. It can be change and of course change the kinetics of the transformation. But this problem is secondary compared to the role of the ion, and secondary compared to the condition of "forced crystallization" of the glass.