Experimental Report

Proposal: **5-24-523** **Council:** 10/2012

Title: Characterisation of glassy NaCl:D2O by neutron diffraction

This proposal is a new proposal

Researh Area: Physics

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Samples: NaCl:D2O

Instrument	Req. Days	All. Days	From	To
D20	3	3	22/03/2013	26/03/2013

Abstract:

In this proposal we intend to characterize samples of glassy salt solutions, NaCl:11D2O, which were produced in our laboratory by hyperquenching the liquid from 300 K to 77 K. As far as we know, such disordered compounds are not known to up to present. We intend to investigate the degree of amorphisation as well as the transitions occurring during warm-up. The results would allow a comparison with the well studied case of LiCl:D2O glass and give insight into the properties and behavior of aqueous solutions in general. Given the omnipresence of salt water, the results might have wider implications beyond physico-chemistry.

Experimental report on “Characterisation of glassy NaCl•D_2O by neutron diffraction” (prop. nr. 5-24-523)

Main Proposer: S. Klotz
Experimental team: S. Klotz, L.E. Bove, A. Ludl, Th. Hansen

The purpose of the experiment was to obtain the first neutron diffraction data of hyper-quenched NaCl aqueous solutions and characterize their transitions as a function of temperature. These investigations fall in our general interest in structural properties of aqueous solutions, including under high pressure [1,2]. The experiments were very successful and the data are currently analyzed.

Several samples were prepared in our laboratory by high-speed projection of micrometer-size droplets on a metal surface kept at 80 K. The samples had a molar concentration close to the eutectic point, i.e. NaCl•RD_2O with R=9.6-10.2. Out of the 5 samples which were transferred at 77 K from a cryo-container to a vanadium can and inserted into an orange cryostat, 2 samples (nr. 3 and 5 with R=10.2) revealed to be highly amorphous with only a small amount of ice Ih contaminant (Fig. 1). The mechanism of formation of this contaminant is still under investigation, the refined lattice parameters appear normal for this temperature compared to literature values [3]. From the integrated intensity we estimate it to be less than 5% in volume.

This sample was subsequently warmed to 280 K, Figure 2 shows the observed transition sequence: We find that glassy NaCl•$10.2D_2O$ is stable up to ~150 K where cubic ice Ic starts to form. This transformation leads to an increasing salt concentration in the remaining material which is visible by a shift of the maximum of the amorphous feature to higher Q (Fig. 3). At ~180 K the salt concentration in this glass is high enough to form a hydrate, without doubt the dehydrate NaCl•$2D_2O$ [4]. When the sample is further heated the cubic ice Ic transforms at 200-230 K into hexagonal ice Ih, leaving a sample of ice Ih and NaCl•$2D_2O$ at 250 K (Fig. 4). From the peak positions and the transformation temperature we conclude that the observed ice Ic is pure and does not include substantial amounts of salt.

A complete analysis of the data including a comparison with molecular simulations is on the way.

References

[1] S. Klotz, L.E. Bove, Th. Strässle, J. Philippe, Th. Hansen, Nature Materials 8, 405 (2009)
[2] L.E. Bove, S. Klotz, J. Philippe, A.M. Saitta, Phys. Rev. Lett. 106, 125701 (2011)
[3]. K. Röttger et al, Acta Cryst. B50, 644 (1994)
[3] B. Klewe & B. Pedersen, Acta Cryst. B30, 2363 (1974)

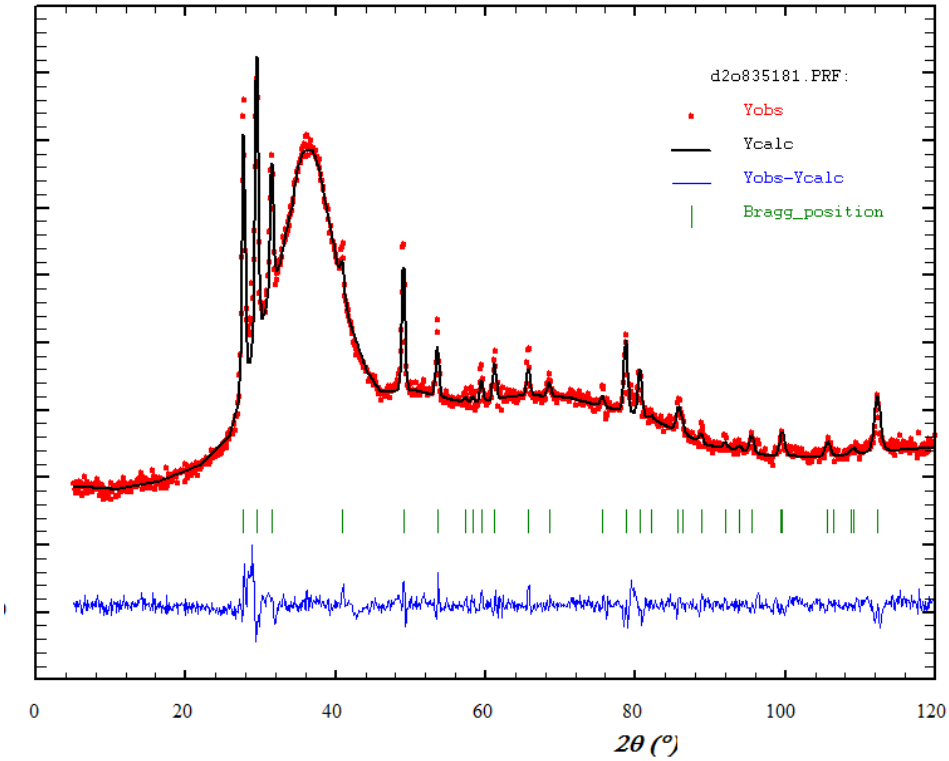

Figure 1: Diffraction pattern of hyper-quenched NaCl•10.2D_2O at 90 K. Peaks are from a small quantity of crystalline D_2O ice Ih. The line though the data is a Rietveld fit (pattern matching).

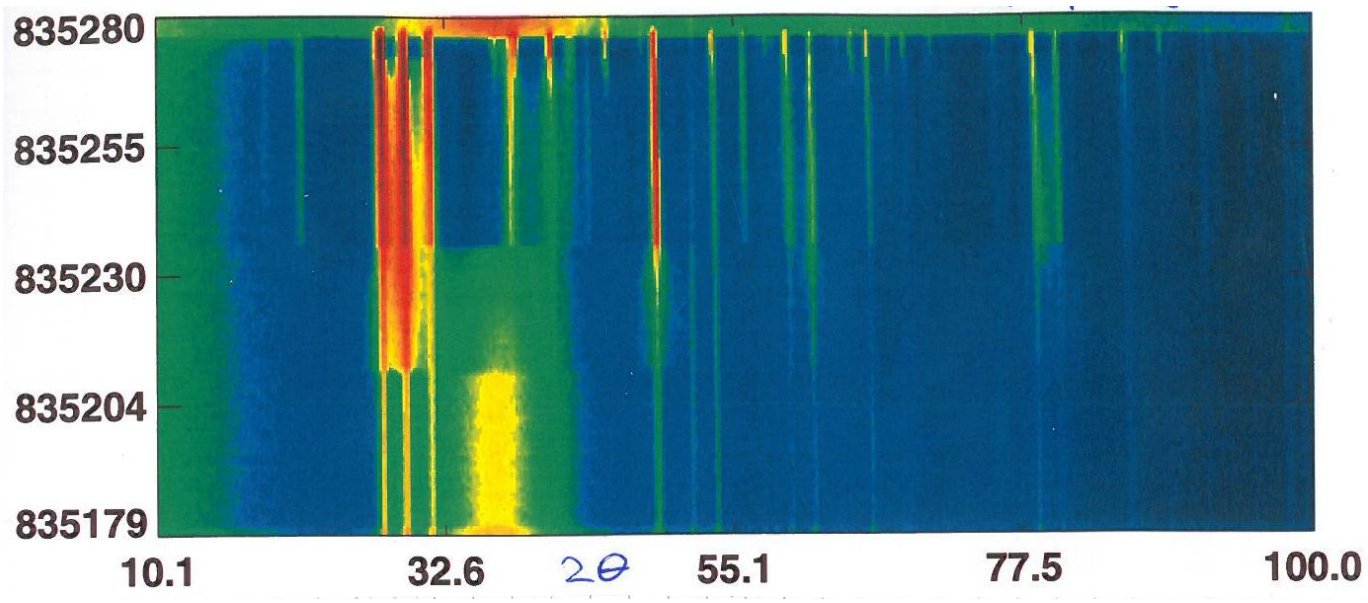

Figure 2: Map of diffraction patterns as a function of temperature: No. 835179-210: 90-150 K; no. 835211-234: 160-180 K; no. 835235-280: 185-280 K. Note the broad amorphous feature at ~ 35 deg. which disappears at ~ 150 K.

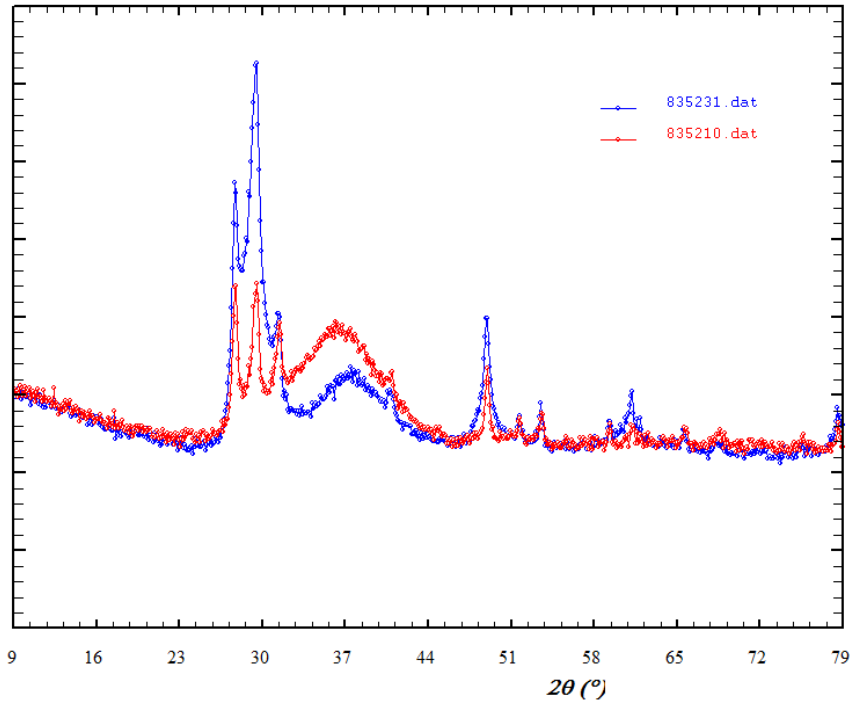

Figure 3: Transition of glassy NaCl•10.2D_2O at 150 K (red, with a contaminant of ice Ih) into ice Ic plus a remaining amorphous solid with higher salt concentration (blue). Note the shift of the peak position of the main amorphous feature.

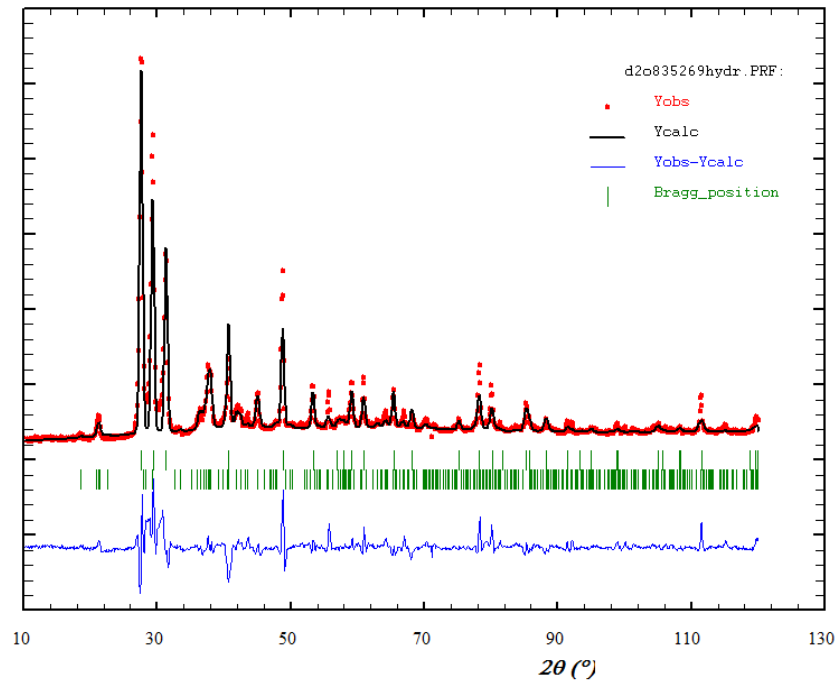

Figure 4: Diffraction pattern of glassy NaCl•10.2D_2O after recrystallisation, at 250 K. The line through the data is a Rietveld fit assuming ice Ih and the dehydrate NaCl•2D_2O [4] (lower tickmarks). Scale factors Ice Ih/hydrate: 114/4.8 ~24.