Experimental Report

30/09/2013

Proposal: **3-15-74** **Council:** 10/2012

Title: Evolution of the structure of nanostructured icy samples in a broad temperature range - SANS study

This proposal is a new proposal

Researh Area: Nuclear and Particle Physics

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Samples: D2O (heavy water), D2 (deuterium), C2D5OD (deuterated ethanol)

Instrument	Req. Days	All. Days	From	To
D22	8	4	25/06/2013	29/06/2013

Abstract:

Slow neutrons (UCN, VCN, CN) are coherently scattered by nanoparticles that provides a powerful tool for VCN reflectors, for VCN storage in traps, for "quasi-specular" CN reflectors and for cooling VCN. Our recent X-rays measurements had shown that on heating a water nanocluster-gel sample above 4 K in He gas atmosphere, one can observe formation of highly-dispersed ice samples consisting of a mixture of amorphous and cubic ice (Ic), where the inner structure of the sample changes from amorphous to cubic Ic and then to commonly observed hexagonal ice Ih with increasing the temperature from 80 to 200 K. This observation opens up unique opportunities for improving reflecting properties of nano-structured reflectors by replacing diamond nanoparticles (with hardly-removable hydrogen contaminations) to nanoparticles from low-absorbing materials like pure D2, or D20, or C2D5OD (deuterated ethanol) at reasonably high temperatures. We propose to perform a set of SANS experiments, using our specialized optical cryostat for in-situ preparation of the gel samples, for studies of nanostructured ice samples in the temperature range up to 25 K for D2 ice) and up to 200 K for D2O and ethanol ices

Experimental report 3-15-74

In the frame of experiment 3-15-74 we measured small angle neutron scattering on impurity-helium gel samples at the D22 instrument. The following points, previewed in our proposal 3-15-74, were studied:

a) Variations in the size distribution of D_2 (deuterium) and a new material C_2D_5OD (deuterated ethanol) impurity nanoclusters in dispersion systems (backbone, or skeleton) of deuterium and deuterated ethanol gel samples in bulk of superfluid helium He-II when heating the samples to temperatures close to the critical temperature in He-II T_λ =2.172 K, and also when heating the samples in bulk of normal helium He-I up to the boiling temperature of T_b= 4.22 K at the normal pressure of P=1 atm.

b) The range of existence of the gels in the bulk of liquid helium and in He gas atmosphere in a wide temperature range below and above T_b up to 30 -100 K .

In addition to the points previewed in our proposal and in contrast to preceding measurements with D_2 gel samples with neutrons with the wavelength of ~6.1 A, now we expand the neutron wavelengths: the neutron transmission and scattering were measured with neutrons with the wavelengths of 4.3 A (the q-range was expanded up to 0.8 A^{-1}). Moreover we measured small angle neutron scattering on a sample of oxygen O_2 gel for the first time. Beam transmission and scattering were measured at three different heights along the gel samples; at the heights of ~ 10, 20 and 30 mm above the bottom of the experimental cell (positions 1, 2 and 3) respectively. Thus we could compare evolution of properties of the samples of different density of impurity nanoparticles when changing external parameters. Treatment of the raw experimental data (more than 500 runs) will demand a lot of time and will continue later in the Institute of Solid State Physics RAS in Chernogolovka.

The main purpose of the experiments was to find dominate sizes of the particles in these gels (remember that the deuterated ethanol and oxygen gel samples were studied for the first time) and to study regimes of the gel stability.

Our preliminary results are the following:

1. We confirmed long-term stability of the structure of the deuterium impurity gel samples cooled below the temperature of 1.8 K, and also the gel samples prepared from pure C_2D_5OD and O_2, see Fig.1. We estimate the dominate sizes of particles in these gels as d>300 nm in D_2 samples, d~30 nm in the deuterated ethanol samples, and d>60 nm in the oxygen sample.

2. Increase in the temperature of surrounding superfluid He-II from 1.8 K to 2.15 K (i.e. 0.02 K below the critical point T_λ for He-II in the bath) resulted in multiple increase of the fraction of the small nanoclusters with sizes of ~1-2 nm in the gel backbone, comparable with the wavelengths of cold neutrons used. One reason for this transformation could be related to the poorer thermal stability of the system due to drastic changes of the heat transport properties of liquid helium restricted in the gel nanopores connected via narrow channels (from superfluid He-II to localized Bose-Einstein droplets accompanied by the strong decrease in the thermal conductivity of the gel dispersion system) at temperatures far smaller than the critical temperature in bulk liquid).

3. Basing on measurements of beam transmission and scattering in the gel samples in liquid helium at temperatures above T_λ and in He gas above T_b, one can conclude on observations of the decay of the gel samples when heating them in He gas at

the pressure of P = 1 bar (at temperatures of T ~ 3 K for D_2 gel, see Fig.2, and at the temperature of T~20-30 K for ethanol and oxygen gels). We are going to compare the results of our recent SANS measurements with results of our X-ray studies of phase transitions in icy samples of conventional and heavy water (H_2O and D_2O), as well as ethanol produced via decay of the gel samples, for which we had observed transitions from amorphous ice to BCC nanocrystalline structure with the mean size of ~6-8 nm at the temperatures T~100-120 K, and then from BCC to conventional HCP ice nanocrystals with the mean size of nanoparticles equal to ~80 nm at the temperature of ~150 K, and ~200 nm at the temperature of 200 K. In principle, small enough deuterium, oxygen and deuteron ethanol nanoparticles of such sizes could form an excellent reflector for VCN and UCN, but we should confirm the time stability of such samples at different temperatures.

As mention in our proposal, our investigation is a part of the broader ILL Program of investigations of nanoparticle reflectors.

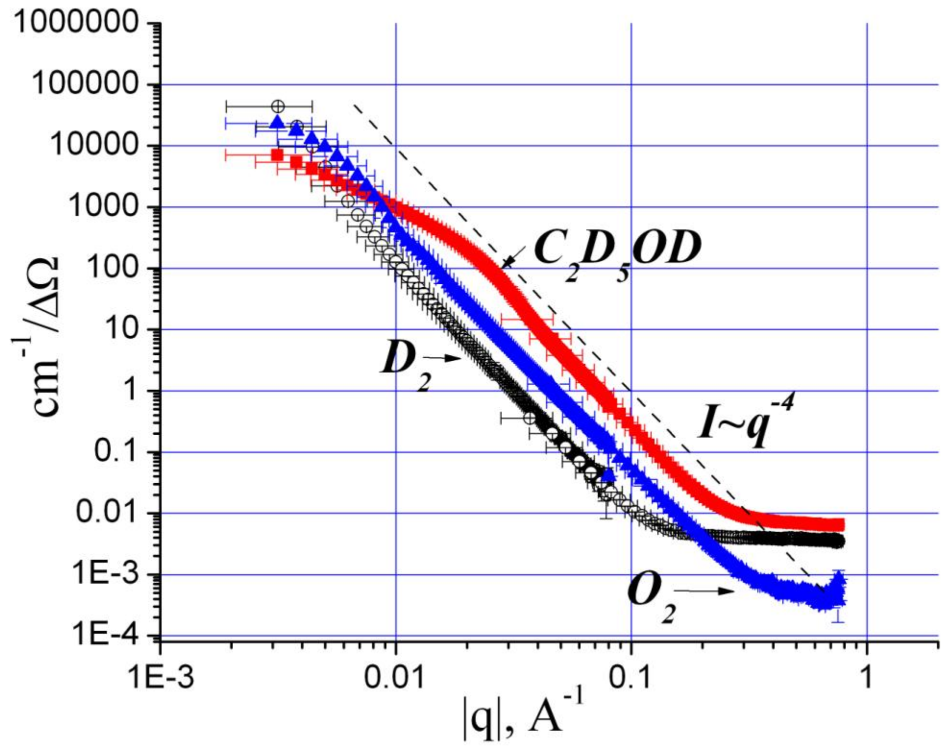

Fig. 1. Small angle neutron scattering on samples of deuterium (D_2), oxygen (O_2) and deuterated ethanol (C_2D_5OD) gels in superfluid helium He-II at the temperature of T= 1.66 K.

We studied also the intensity of the central part of the direct neutron beam as a function of the sample temperature. Decay of the gel should increase the intensity of the direct neutron beam. For comparison we measured the beam transmission in two positions: near the bottom of the cell (position 1, red signs in Fig. 2), and in position 3 at the height of 3 cm above the bottom cell, where the total amount of the impurity clusters was small or negligible. After the sample preparation at the temperature of T=1.66 K, the beam transmission in position 1 is smaller than the transmission in position 3. With increasing the temperature, at T>4.2 K the transmission in both positions increased thus indicating that the deuterium gel sample starts to decay to icy powder. At T>10 K the transmission in positions 1 and 3 was about the same as that corresponding to sublimation of solid deuterium.

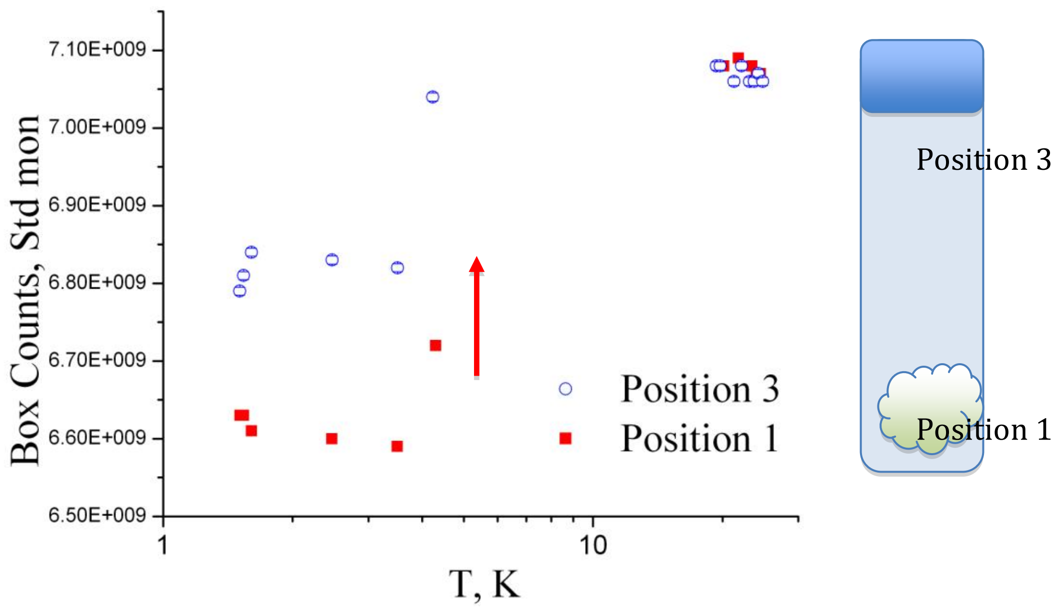

Fig. 2. The neutron beam transmission (λ_n~4.3 A) as a function of temperature; measurements are performed at two different heights in the experimental cell filled in with the deuterium gel sample. Red signs correspond to position 1; blue points stand for position 3 (the total amount of impurity nanoclusters in position 3 is much smaller than that in position 1).