SANS and X-Ray Scattering Study of Structure and Phase Transitions in Impurity-Helium Gel Samples and Fine Powders Created on Decay of the Gels

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Abstract

We report here the recent results of the SANS study of structure of nanocluster impurity-helium gel samples in liquid helium and of the X-ray observations of structural and phase transitions in icy fine powders created on decay of the gel samples heated above liquid helium temperatures.

1. Introduction

The impurity gels created by condensation of the ^{4}He gas mixture with impurities of other gases or of vapors of liquids at room temperatures on the surface and in bulk of superfluid He-II cooled below 1.8 K could be assigned to a new class of materials: quantum soft matter [1]. The internal structure and properties of the gels are largely determined by properties of so named van-der-Waals complexes (the impurity nanocluster surrounded by a layer of solidified helium) forming the dispersion system, or backbone of the gel, and by the properties of the dispersion medium of the gel - quantum liquid in nanopores between weakly bounded agglomerates of complexes in bulk of the sample (liquid helium in restricted geometry). Basing on results of our SANS studies of a number of samples: D_2, O_2, CD_4, D_2O and C_2D_5OD gels in liquid helium at D22 and D33 diffractometers [2-6], one could estimate that characteristic dimensions of the impurity clusters (or their aggregates) in gel samples prepared of the gaseous impurities D_2, O_2 and CD_4 at room temperatures are distributed in a wide range of $1 - 150$ nm. And in case of the D_2O and C_2D_5OD gels, prepared from the impurity vapors at room temperatures, the cluster dimensions are distributed mainly in a narrow range of 15 – 30 nm. The total content of the clusters of small diameters d ~ 1 nm in bulk of the sample could be increased by annealing the freshly prepared samples at the raised temperatures (in He-II, at $T \leq T_\lambda$ for D_2 -gel samples, and in normal liquid He-I at $T \leq$ 4.2 K close to the boiling temperature of liquid helium for other impurities).

X-ray studies of the structural and phase transitions in fine powder samples created on decay of the water or ethanol gel samples heated above liquid helium temperatures had shown that at $T \leq 85$ K the inner structure of the icy sample includes grains of amorphous phase, and the amorphous sample could be saved for a long time

(up to two months) at liquid nitrogen temperatures without any visible changes. On heating the powder samples above 100 K one could observe formation of the nanocrystals of the cubic phase and next their transformation to the hcp crystals in case of the H_2O and D_2O ice powder, and formation of the nanocrystals of monoclinic phases in the ethanol C_2H_5OH samples.

2. SANS studies

Some of the most interesting results of SANS experiments at D-22 and D-33 spectrometers are shown below. In Fig. 1 we present the photo of the moment of preparation the methane CD_4 gel sample in He-II. Jelly like layer of CD_4 impurity condensate created in the process of condensation of the ^4He - CD_4 gas flux at the cold vapor – He-II interface inside the filling tube is moving down slowly, detaching from the lower edge of the tube, and next the soft gel clouds are falling down the bottom of the quartz glass cell filled with He-II at T = 1.66 K. The level of superfluid He-II is placed ~1 cm above the edge of the tube.

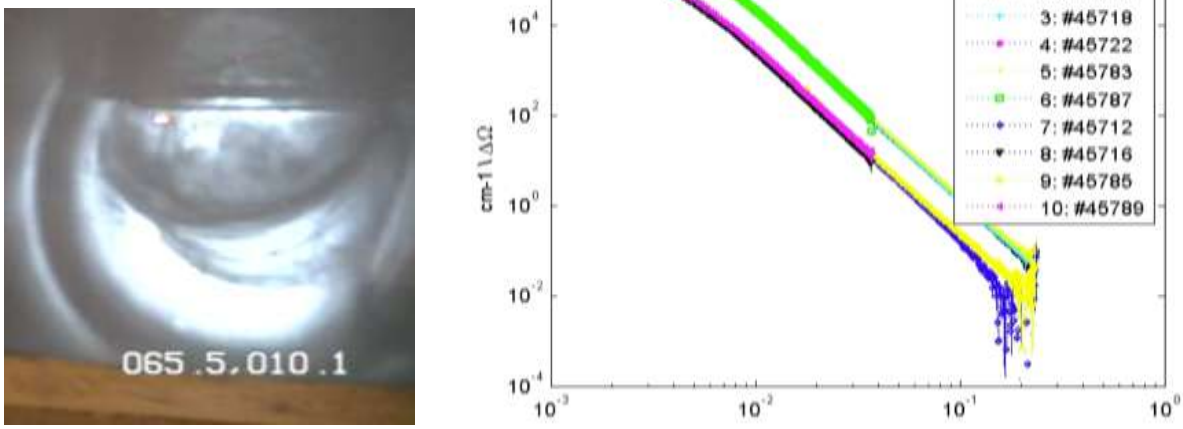


Fig.1. Preparation of the methane CD_4 gel (*left frame*). The r*ight picture* presents the angle dependence of the intensity of the cold neutron scattering I(q) at the gel sample in liquid helium. Results of preliminary measurements at D-33 set-up in two positions – near the bottom of the cell (*the upper set of points*) and 2 cm higher (*the lower set of points).* Points of different lines at the same set correspond to temperatures T=1.66 K and T=4.2 K. It appeared, that at the range q =$3\cdot10^{-3}$ -10^{-1} $Å^{-1}$ the intensity I(q) poorly depends on temperature.

Below are shown the results of the SANS study of the other gel samples. In Fig.2 we present results of investigations of the temperature dependence of the cold neutron scattering on the D_2 gel samples in He-II [3]. It was observed that heating of the deuterium gel sample from 1.66 to 2.15 K resulted in strong increase of the intensity of scattering I(q) at large $q \geq 0.1Å^{-1}$. This should be associated with significant increase of the content of small particles with dimensions $d \leq 10Å$. Significant increase in the fraction of nanoclusters with small sizes of ~1 nm in the gel backbone at temperatures below the critical point T_λ = 2.17 K should be related to drastic changes in properties of the dispersion system (liquid helium in nanopores connected with each other by

narrow channels) - transition from superfluid He-II with extremely high heat conductivity to BEC droplets localized in nanopores, and connected with this sharp falling of heat conductivity in bulk of the gel sample surrounded by He-II, and instability of the cluster aggregates of middle sizes in the backbone of the D_2 gel even at temperatures $T \leq T_\lambda$ [3,4].

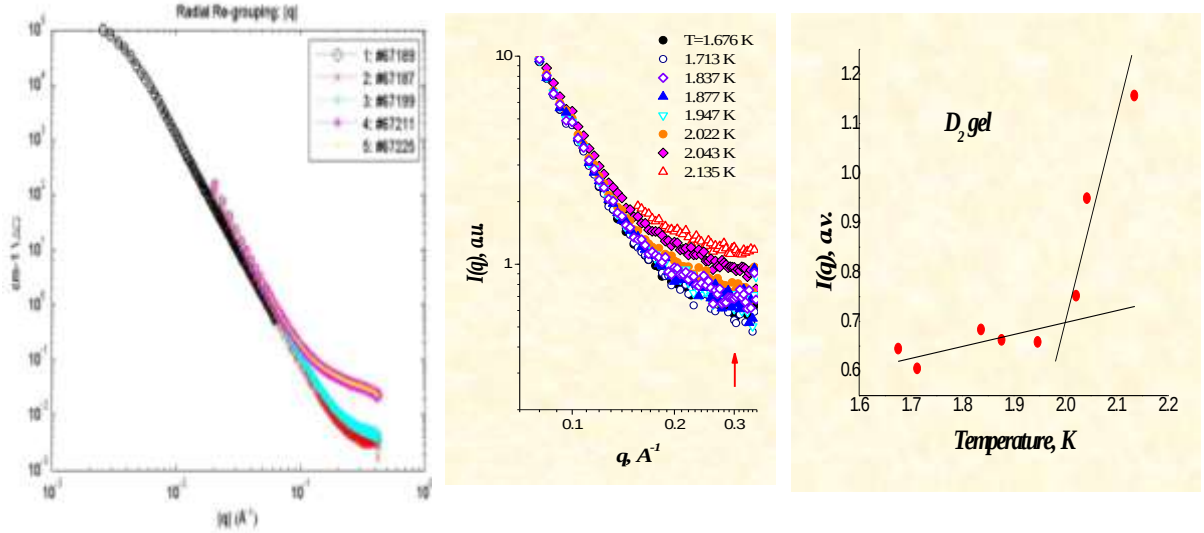


Fig.2. Angle dependence of the neutron scattering I(q) at the D_2 sample in He-II. Shown are evolution of the I(q) curves with heating the as-prepared sample to 2.135 K and dependence of the I(q) at q=0.3Å^{-1} on temperature.

For comparison in Fig. 3 we present the temperature dependence of I(q) observed in the ethanol C_2D_5OD gel sample with heating the sample up to 4.2 K.

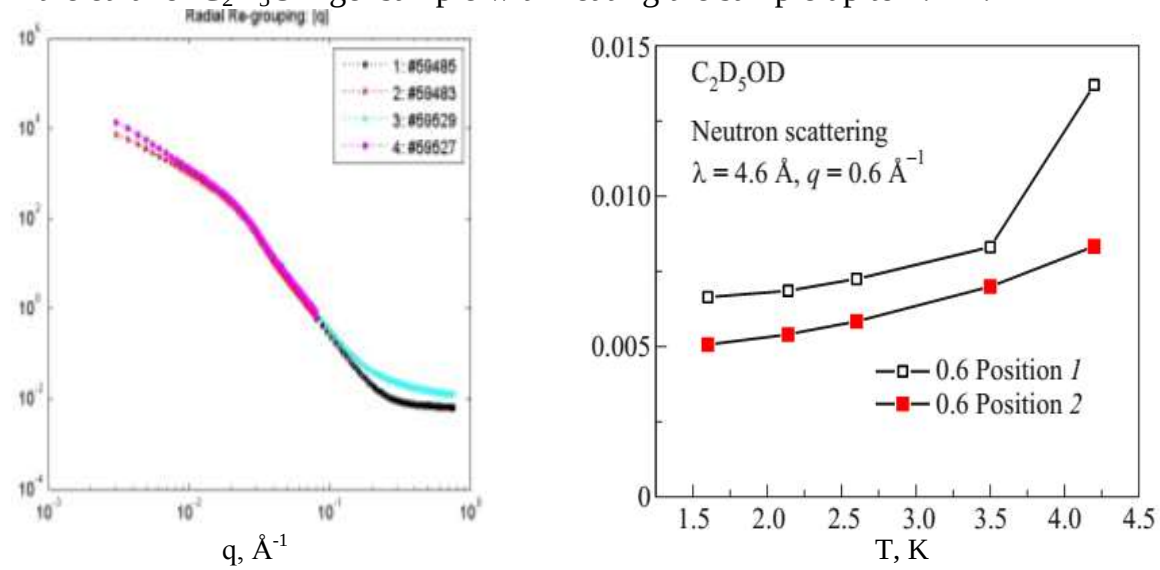


Fig.3. SANS study of the ethanol C_2D_5OD gel sample. *Left frame*: I(q) measured at T= 1.66 K -lower set of points, dark rhombs ♦ and crests x (618 and 616). Upper set T= 2.65 and 3.09 K, crests x, and open circles o (643,646). *Right* - the temperature dependence of I(q) at q= 0.6Å^{-1} measured in two positions along the sample: *1* -near the bottom of the cell, and *2*- 1.5 cm above the bottom.

It is seen that at q > 0.1 Å^{-1} the value of I(q) increases gradually with growing the temperature. In contrast to the D_2 gel sample all the other gel samples were more stable in liquid helium. It was confirmed by the results of measurements of the direct propagation of the neutron beam through the C_2D_5OD gel sample shown in Fig. 4.

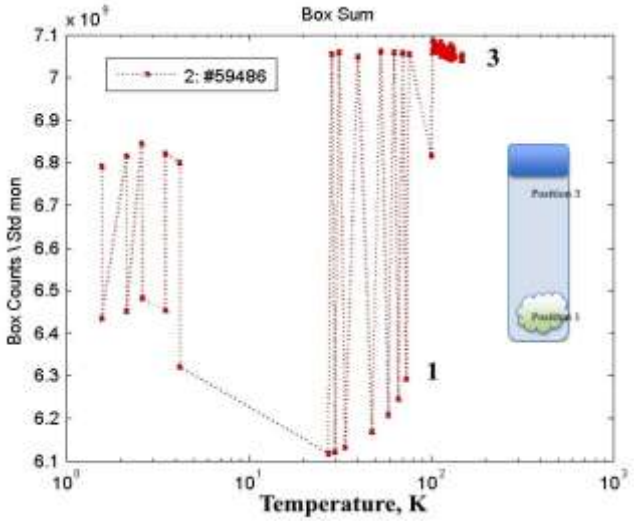


Fig. 4. The neutron beam transmission through the ethanol gel sample.

Basing on measurements of beam transmission and scattering in the gel samples at temperatures near to and above 4.2 K one could conclude on observations of the decay of the gel samples when heating them in atmosphere of He gas at the pressure of P = 1 atm (at temperatures of T ~ 4.5 K for D_2 gel and at of T~ 20 K for D_2O gel).

In Fig. 5 we presented results of the SANS measurements at different gel samples at T=1.66 K, and of the mean dimensions d of the impurity clusters in frames of the gels, estimated from the known value of q shown by arrows.

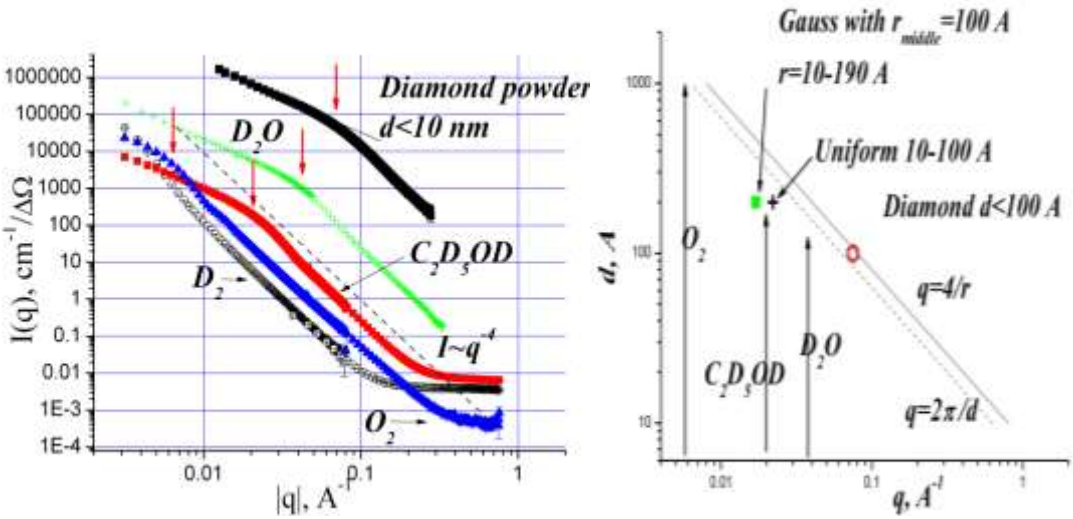
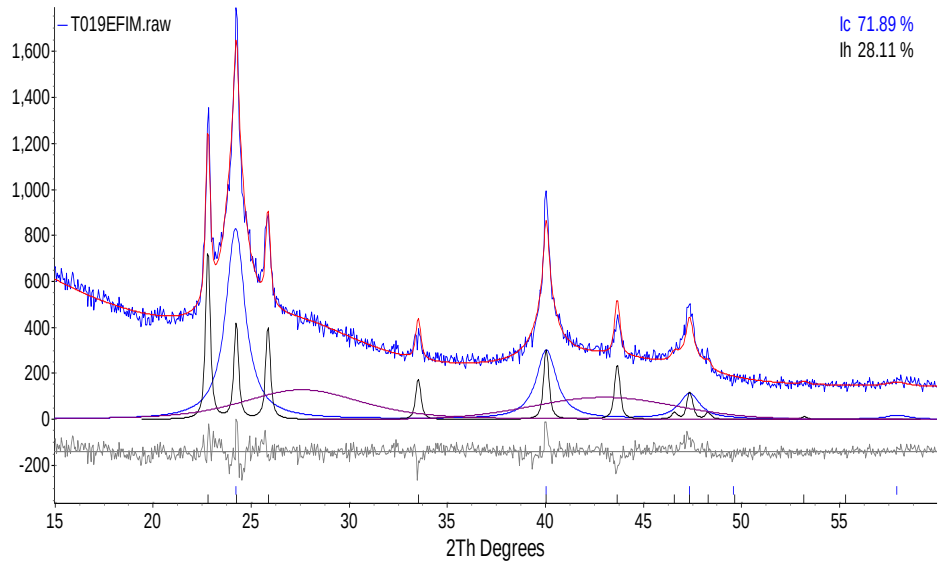


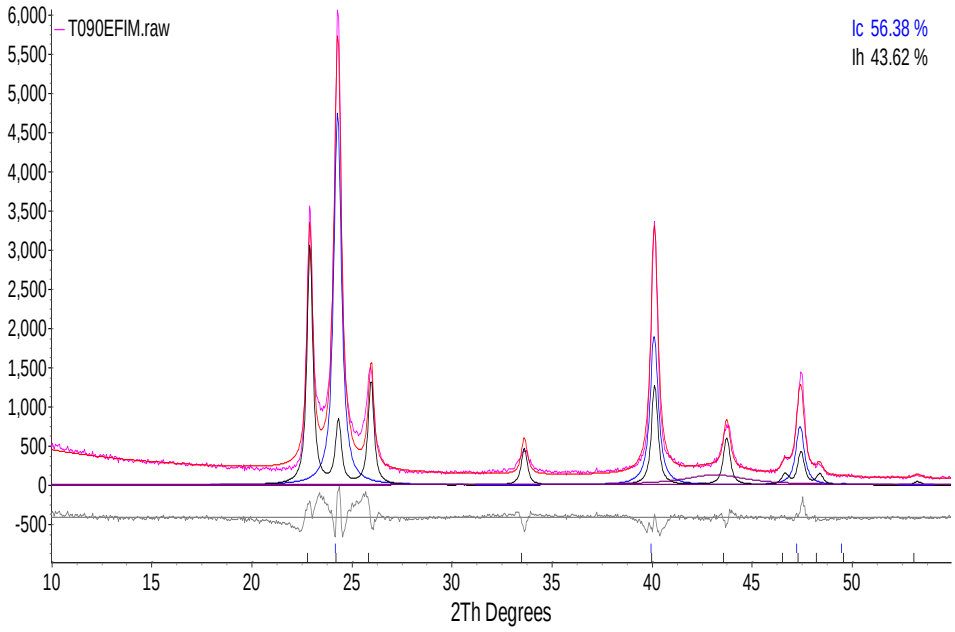
Fig.5. I(q) dependences measured at freshly prepared samples at T=1.66 K, and the mean dimensions of the impurity clusters (aggregates of clusters) estimated from the positions of the excesses on the I(q) curves shown by arrows above the proper curves.

3. X-ray study of the structure and phase transitions in icy samples of water and ethanol produced on decay of gel samples

In short, in X-ray experiments we observed transitions from amorphous water ice at T ≤ 85 K to BCC nanocrystalline structure with the mean size of the grains of ~ 6-8 nm at the temperature T~120 K and then from BCC to conventional HCP ice nanocrystals with the mean sizes of crystallites equal to ~ 80 nm at the temperatures of ~150 K and ~200 nm at the temperature of 200 K.



T=90 K



After annealing at T=150 K

Fig.6. The X–ray spectrum of the H_2O icy powder sample formed on decay of the water gel: T=90 K initial sample; T=150 K – spectrum measured at 90 K after annealing.

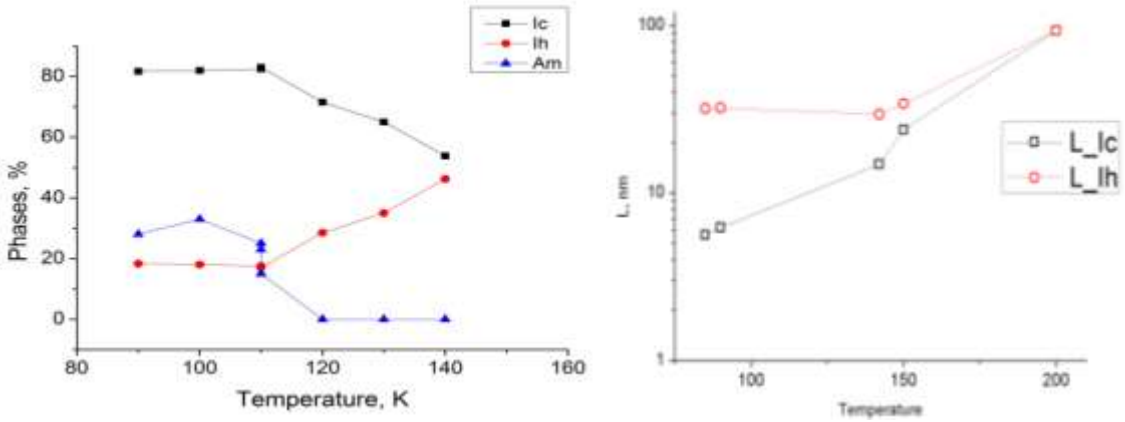


Fig.7. *Left*: the phase transformation with annealing the H_2O icy sample; and *right* growth of the mean dimensions of crystallites of the cubic and hexagonal ice with increasing the temperature.

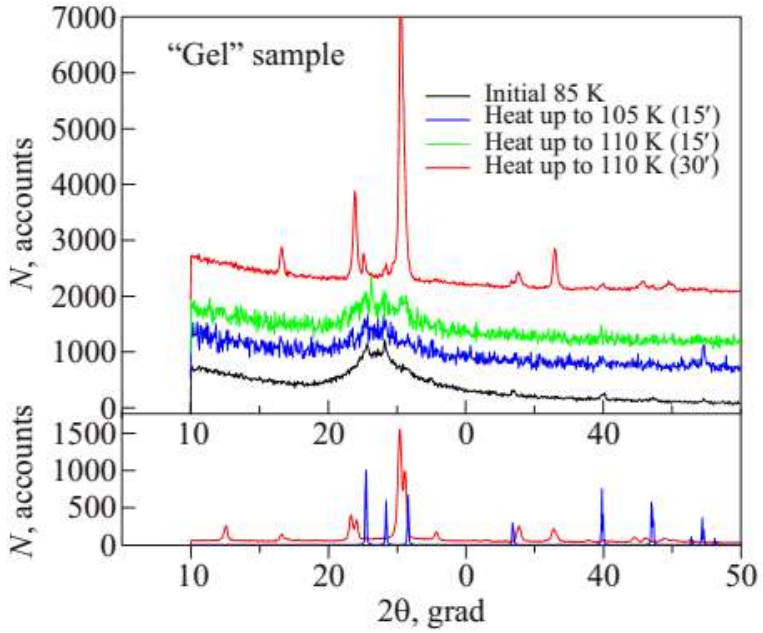


Fig.8. Evolution of the spectrum of the ethanol C_2H_5OH powder sample with annealing at temperatures above 85 K. For clarity the X-ray spectra of the hcp water ice (sharp peaks on a lowest background) and the monoclinic ethanol sample (peaks on a higher background) are shown also.

4. Conclusions

We have presented here the recent results of the SANS study of structure of a number of impurity-helium gel samples in liquid helium – a new class of "soft matter." The intensive scattering of slow enough neutrons on nanoparticles in bulk of the impurity gels made of low capture neutrons materials might provide us a powerful tool for VCN reflectors, VCN storage in traps, "quasi specular" CN reflectors, and for cooling VCN to the UCN energy range [8,9]. It would open new options for expanding our knowledge on properties of molecular gels in superfluid He-II

(quantum soft matter) and any perspectives of their usage in the area of particle physics.

From the X-ray studies of the water ice powder sample created on decay of the convenient water gel it follows that at $T \geq 150$ K the rate of the cubic-hexagonal phase transition in our water ice powder samples was a few orders of magnitude higher than in massive ice samples in bulk of icy comets or in the cold continental ice in Antarctica judging from the known literature data. In case of the ethanol powder samples the transition from amorphous to crystalline monoclinic structure was observed on annealing them at temperatures above 110 K (see Fig.7).

References

[1] L.P. Mezhov-Deglin, Impurity nanocluster structures in liquid helium. PHYS-USP, 48 (10), 1061–1070 (2005).

[2] L.P. Mezhov-Deglin, V. B. Efimov, A. V. Lokhov, E. V. Lychagin, A. Yu. Muzychko, V.V. Nesvizhevskii, A.V. Strelkov, Scattering of Cold Neutrons on Gel Samples Formed by Impurity Clusters in Superfluid He-II, , J. of LTP, 148, 5/6, 833-838 (2007).

[3] L.P. Mezhov-Deglin, V.B. Efimov, A.V. Lokhov, R. May, V.V. Nesvizhevskii, A.A. Levchenko, G.V. Kolmakov, L.V. Abdurakhimov, M.Yu. Brazhnikov, E.V. Lebedeva, A.V Strelkov, E.V. Lichagin, and A.V. Muzychko, Neutron Studies of Impurity Gels of Heavy Water and Deuterium in Superfluid He-II, J. of LTP, 150, 3/ 4, 206-211 (2008).

[4] N.V. Krainyukova, V.B. Efimov, and L.P. Mezhov-Deglin, Instability of Small Deuterium Clusters in Superfliud Helium near the λ Point. J. Low Temp. Phys. 171, 718 (2013).

[5] V. B. Efimov, A.V. Lokhov, L.P. Mezhov-Deglin, C. Dewhurst, V.V. Nesvizhevsky, G.V. Kolmakov Nanocluster Magnetic Gel in Superfluid He-II. JETP Letters, 2014, Vol. 99, No. 1, 32–36. (2014).

[6] V. Efimov, A. Izotov, L. Mezhov-Deglin, V. Nesvizhevskii, O. Rybchenko, A. Zimin, Structural and Phase Transitions in Nanocluster Ethanol Samples at Low Temperatures. Low Temp. Physics, 41, № 6 (2015).

[7] V.B. Efimov, A. N. Izotov, A. A. Levchenko, L. P. Mezhov-Deglin, and S. S. Khasanov, Structural Transitions in Ice Samples at Low Temperatures and Pressures, JETP Letters, 94, (2011), 621.

[8] E.V.Lychagin, A.Yu.Muzychka, G.V.Nekhaev, V.V.Nesvizhevsky, et al, UCN Source at an External Beam of Thermal Neutrons. Advances in High Energy Physics, Volume 2015 (2015), ID 547620; 7 pages.

[9] V.B. Efimov, L. P. Mezhov-Deglin, C. D. Dewhurst, A. V. Lokhov, and V. V. Nesvizhevsky. Neutron Scattering on Impurity Nanoclusters in Gel Samples, ibid Article ID 808212, 4 pages.