ISINN-23

Structure and Phase Transitions in Nanocluster Impurity-Helium Gel Samples and in Fine Powders Created on Decay of the Gels. *SANS and X-rays Scattering Studies*.

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The Short Content

The impurity gels prepared by condensation of the ^4He gas with any impurities of 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 The dispersion system, or backbone, of the gel is formed by agglomerates of van-der-Waals complexes (the impurity nanoclusters surrounded by a layer of solidified helium), and liquid helium impregnating the nanopores between weakly bounded agglomerates (quantum liquid in restricted geometry) serves as the dispersion medium of the gel [1].

Basing on results of our SANS studies of D_2, O_2, CD_4, D_2O, C_2D_5OD and CD_4 gel samples in liquid helium [2,3] one could estimate that characteristic dimensions of the impurity clusters in D_2, O_2, CD_4 gel samples in He-II are distributed in a wide range of d ~1 -150 nm, and in gel samples prepared of vapors of liquids at room temperatures D_2O and C_2D_5OD the cluster dimensions are d ~ 15 – 30 nm.

From results of X-ray observations of the structural and phase transitions in icy samples created on decay of the water or ethanol gel samples heated above liquid helium temperatures it follows that at T ≤ 85 K the powder samples containing amorphous and nanocrystalline phases could be saved for a long time (up to two-three months) at liquid nitrogen temperatures without any visible changes.

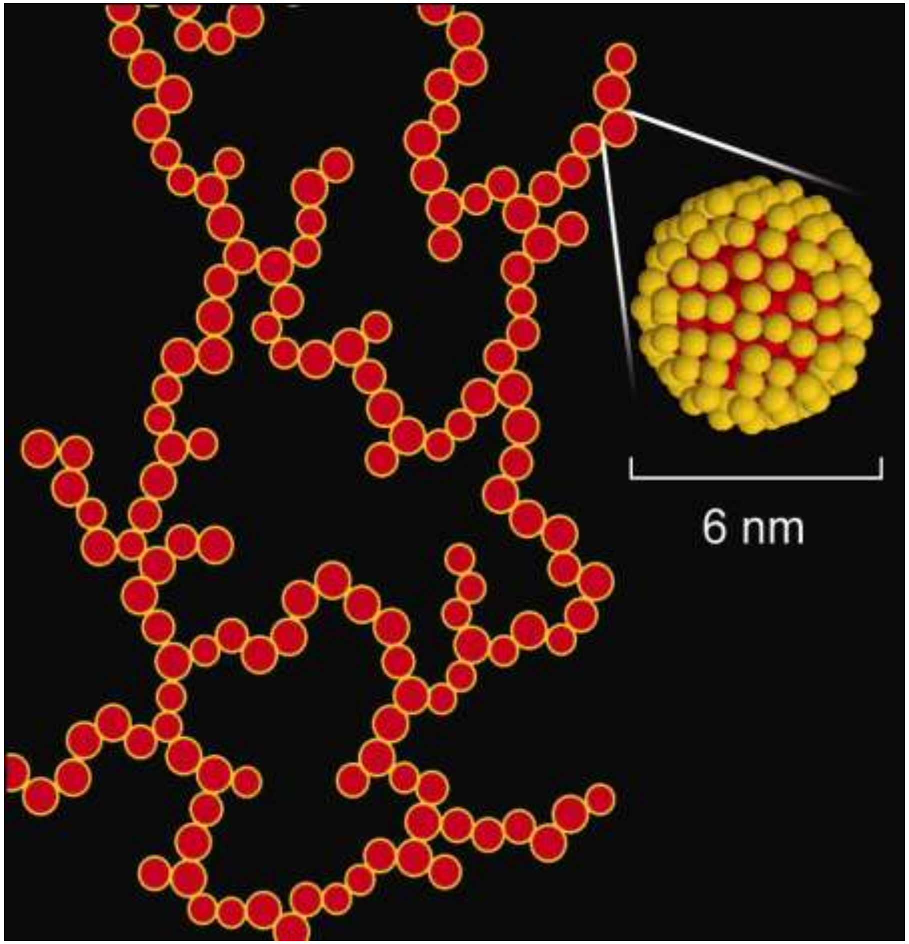
The intensive scattering of slow enough neutrons on nanoparticles in bulk of the impurity gels made of low capture neutrons materials might provide us a powerful tool for VCN reflectors, VCN storage in traps, “quasi specular” CN reflectors, and for cooling VCN to the UCN energy range [4].

[1]. L.P. Mezhov-Deglin, Impurity nanocluster structures in liquid helium, Phys. Usp. 48 (10), 1061 (2005).

[2]. 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. Advances in High Energy Physics, Volume 2015 (2015), Article ID 808212, 4 pages.

[3]. V. Efimov, A. Izotov , L.Mezhov-Deglin, V. Nesvizhevskii, O. Rybchenko, and A.Zimin, Structural and phase transitions in nanocluster ethanol samples at low temperatures. Low Temperature Physics, 2015, v. 4 1, No. 6, pp. 603–607 .

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



Impurity gel samples in liquid helium are assemblages of nanocrystalites of impurity molecules (**red**), each separated by a thin layer of solidified helium (**yellow**).

***Applications*:**

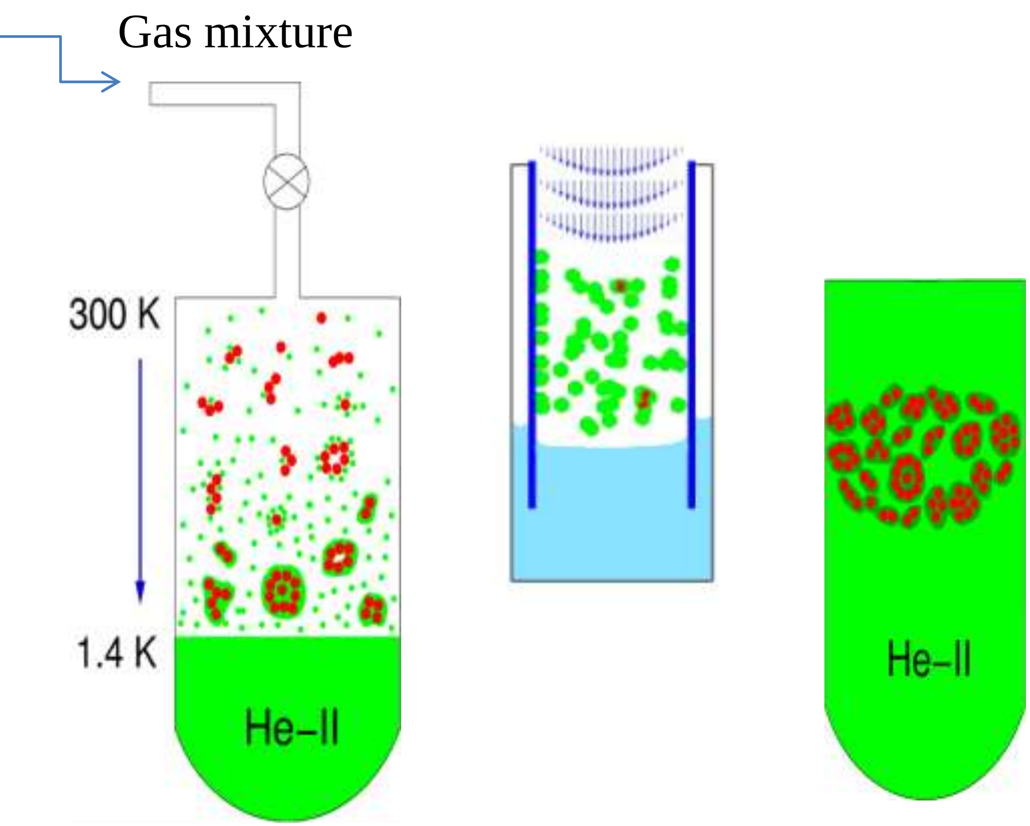
Study of the formation of the nanoclusters within impurity gel samples could lead to a better understanding of the formation of catalysts, which possess a similar structure but are made of precious metals.

Impurity-Helium Condensates (IHCs or impurity gels) can host low temperature chemical reactions at much higher concentrations than materials. Large amounts of chemical energy can be stored in unpaired atoms trapped in IHCs.

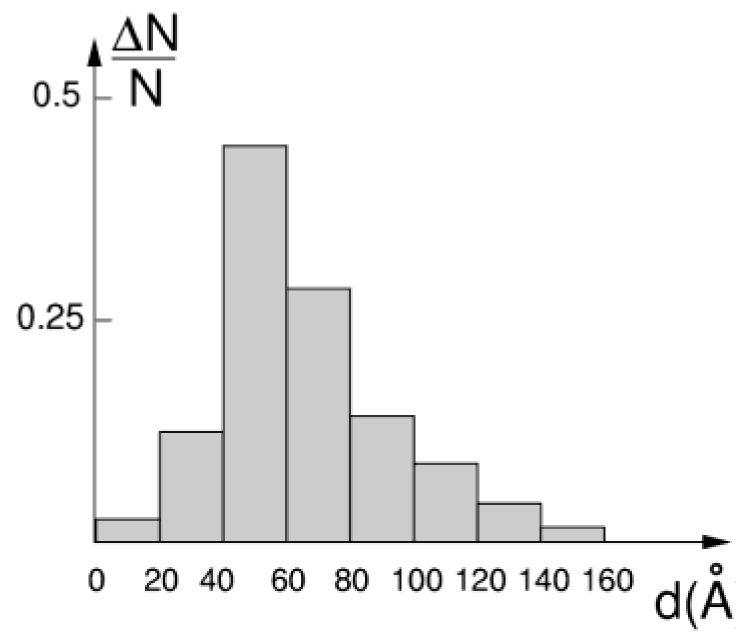
IHCs made of deuterium and heavy water in superfliud He-II and cooled to a few mK might be used for cooling very cold neutrons down to very low temperatures.

From: David M. Lee, Cornell University

Scheme for preparation an impurity-helium gel sample in superfluid He-II.



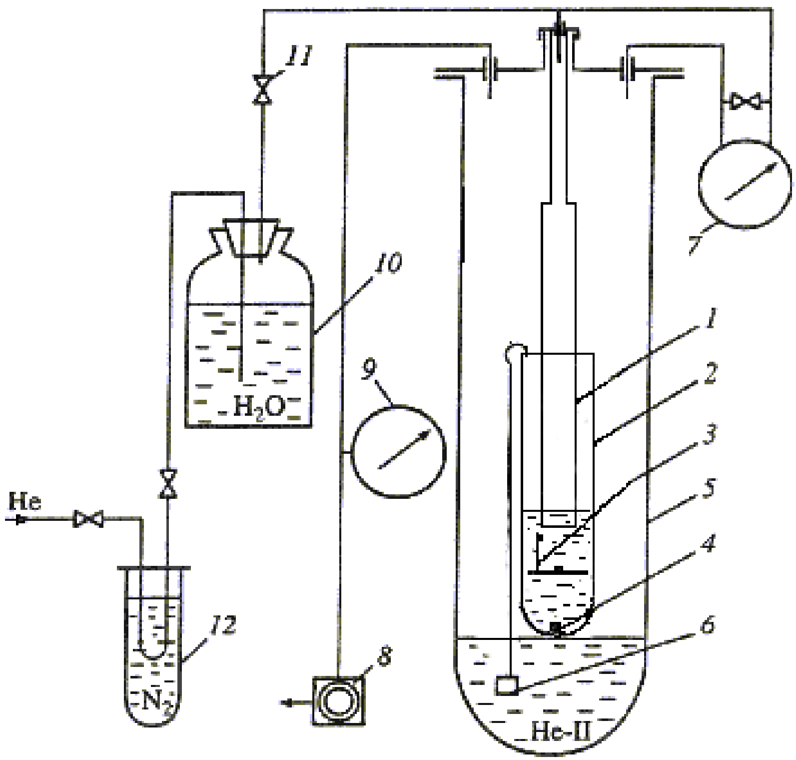
Dimension distribution of metallic particles formed by evaporation of a metal target in a dense vapor of liquid ^{4}He: **d_{mean} ~ 6 nm**.

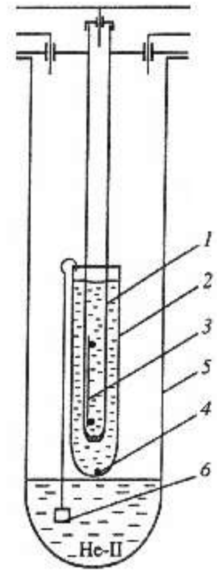


In accordance with estimations based on X-rays and ultrasound attenuation studies the mean dimensions of impurity clusters, covered by a layer of solidified He at the vapor-He-II interface are **$d_{clusters}$ ~ 5 - 10 nm,** and the pores diameters in bulk of a gel sample are distributed in a wide range **d_{pores} ~ 8 - 800 nm**.

L.Ya.Vinnikov, and A.O. Golubok “Methods of direct observations of magnetic structures at the surface of superconductors”. Preprint ISSP RAN, Chernogolovka, Moscow region, 1984.

Scheme of the experimental set-up used for preparation of the gel samples in glass dewars





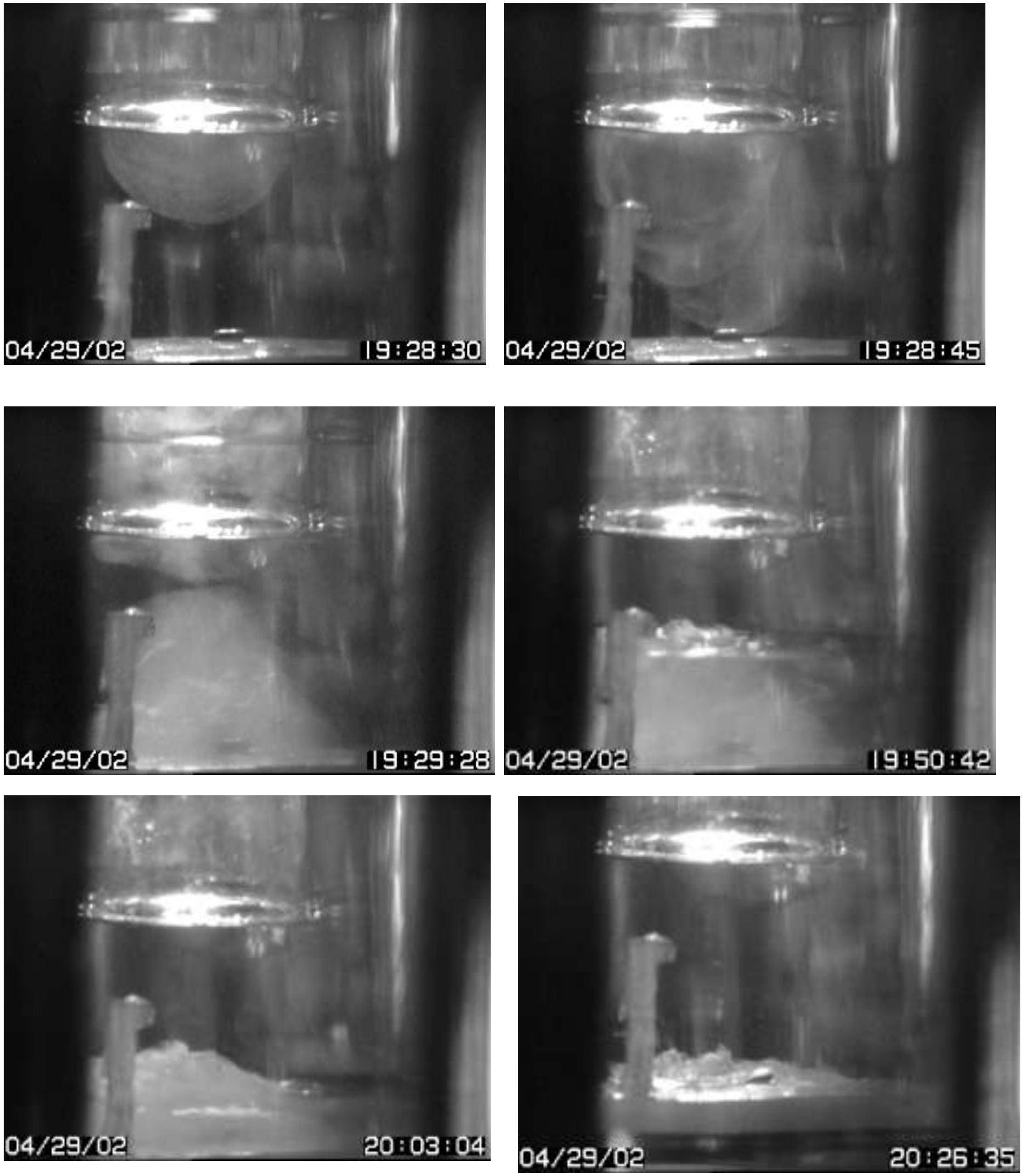
Shown are wide (left, inner diameter d=3 cm) and narrow (right d=0.9cm) glass cells placed inside the glass dewar: 1-filling tube, 2-experimental cell, 3,4-resistive thermometers, 5-the dewar, 6-thermomechanical pump, 7,9-manometers, 8-mechanical pump, 10-glass bottle, 11-discharge cock, 12-charcoal trap cooled by liquid nitrogen.

Formation of the D_2 gel in He-II at T=1.4 K and decay of the protruding part of the sample in He vapor with lowering the level of He-II

Level of He-II

T_{supp} =2.2 K
He-II is placed at the cell bottom

Formation and decay of the H_2O gel in the wide d=28 mm glass cell



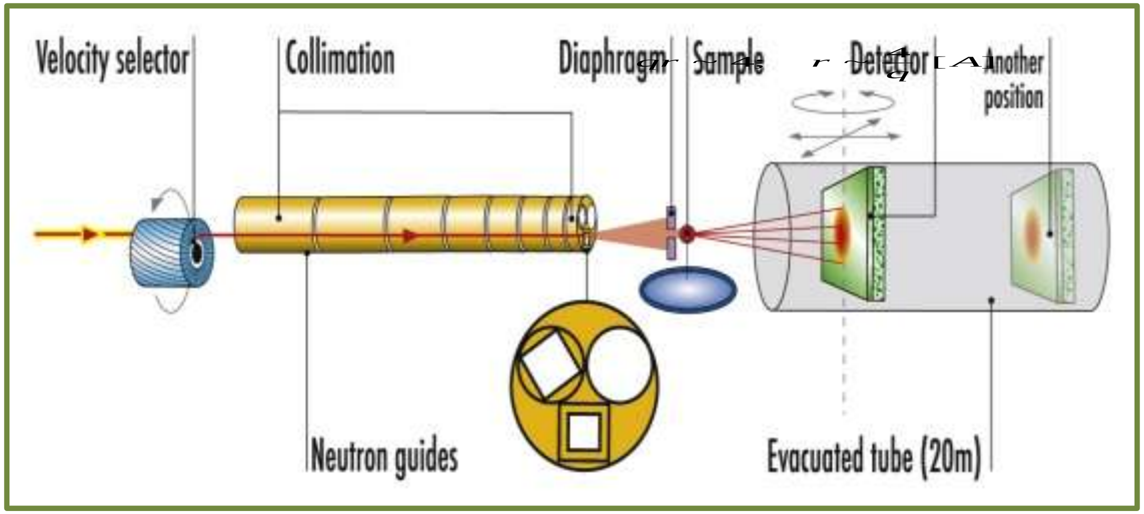
Upper raw **– formation of the sample in He-II at constant T=1.4 K. The level of liquid He-II is placed above the end of the filling tube.**

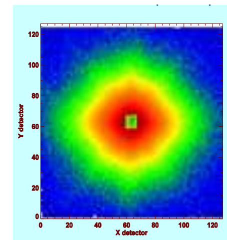
Diameter of the Teflon plate at the bottom of the cell is ~25 mm, and the height of the column supporting the resistive thermometer placed above the plate is ~10 mm.

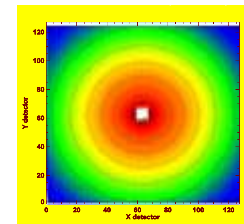
Middle raw – the sample evolution with lowering the liquid level at T=1.4K.

Bottom raw - the sample decay in cold helium vapor above He-II; the vapor pressure is P~2.2 Torr; the temperature of the teflon support T_{supp} = 2.2 K, and of superfluid He-II at the bottom of the cell T~ 1.4 K

Small-angle neutron scattering at the gel samples in liquid helium at D22



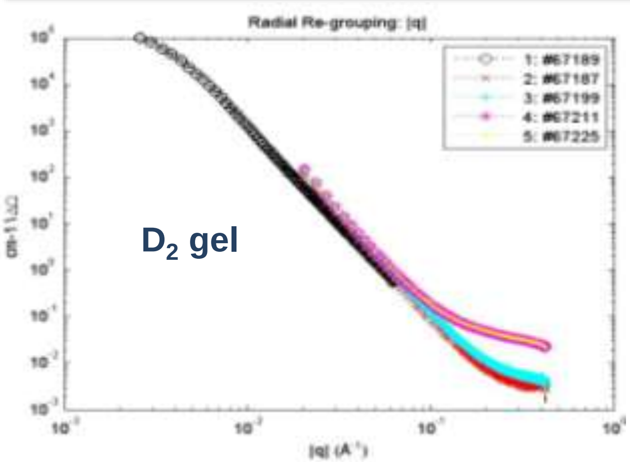


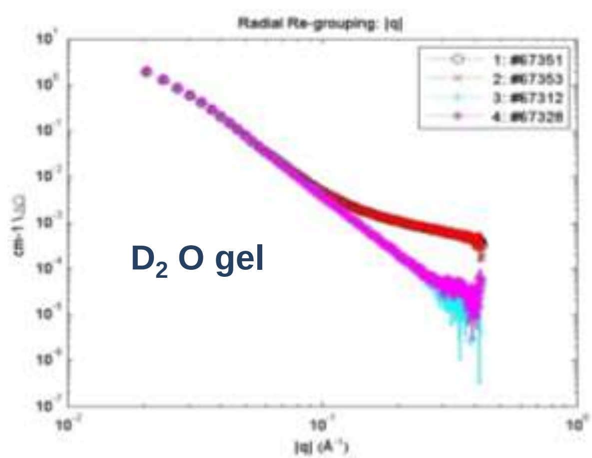


$q = (4\pi/\lambda_n) \cos(\Theta/2) = 2q_n \cos(\Theta/2)$; $\lambda = 4.5 - 24$ A $\rightarrow$ $q = 4*10^{-4} - 0.44$ A^{-1}

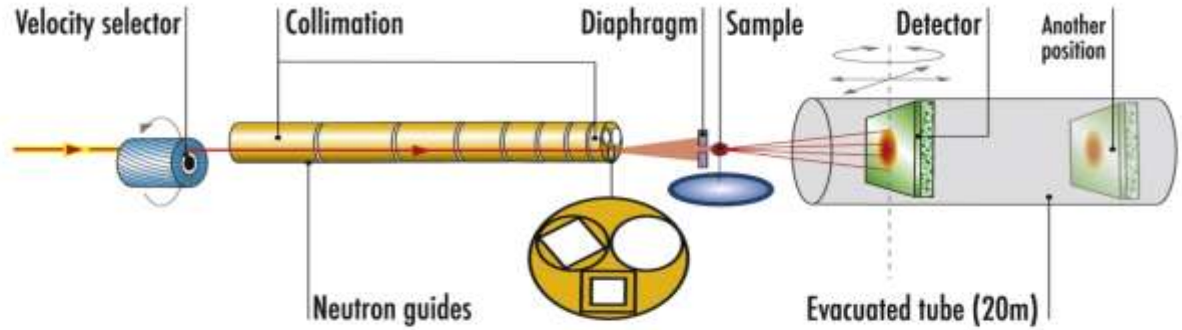
Left frame-cell without the gel sample (BCG): right-watergel D_2O in superfluid He-II

Evolution of the *I (q)* curves with heating the samples in liquid helium:
The left frame – D_2 gel sample: heating the bath from 1.67 to 2.135K and cooling back to 1.67 K.
The right frame –the watergel D_2O sample: heating from T=1.67 K to T=4.2 K

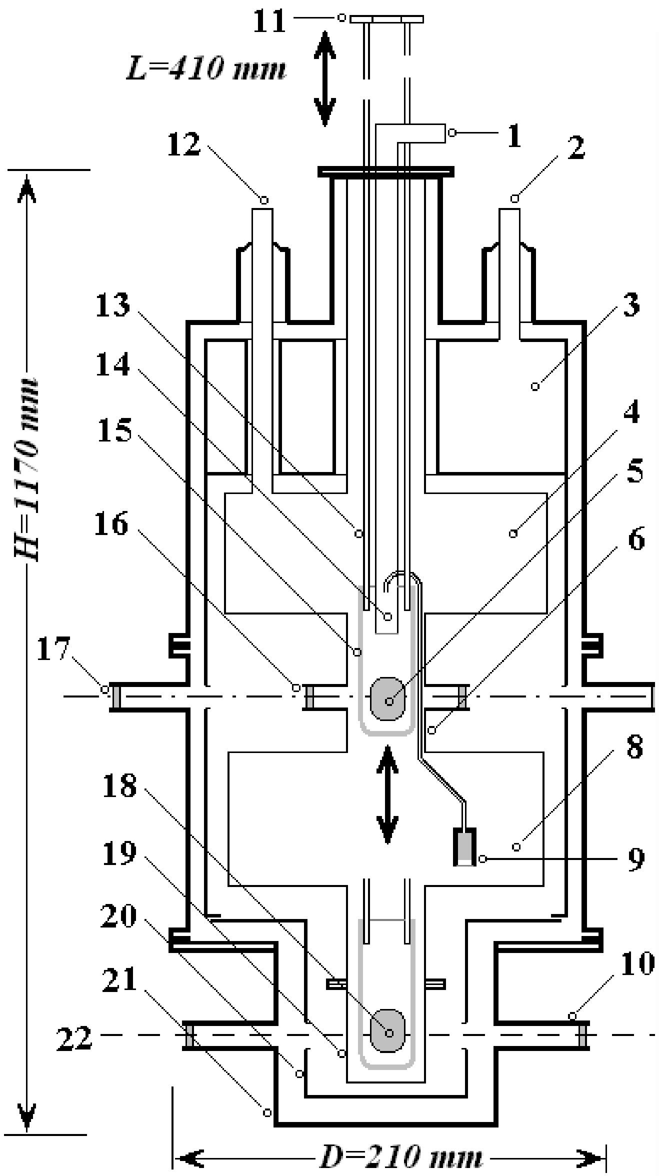


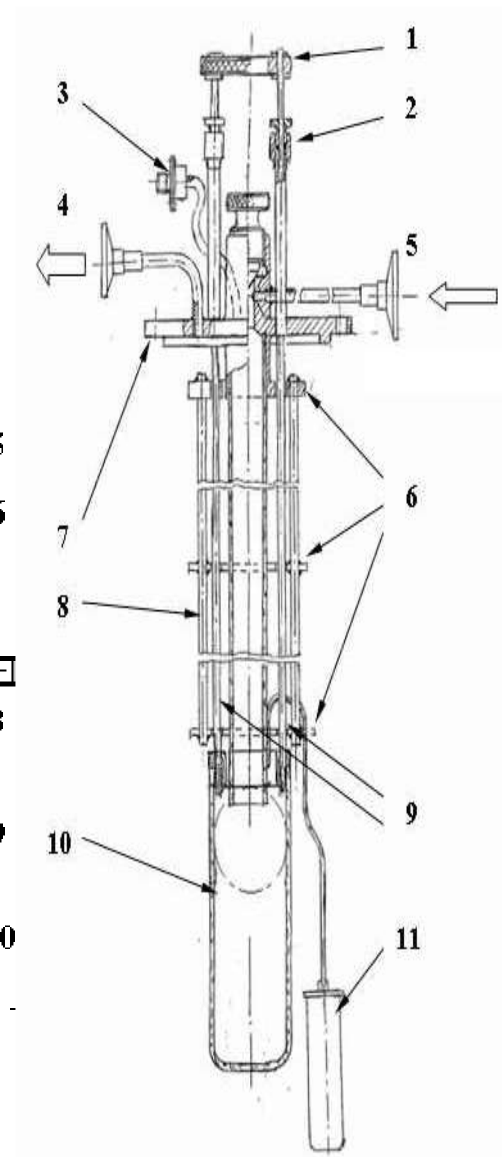


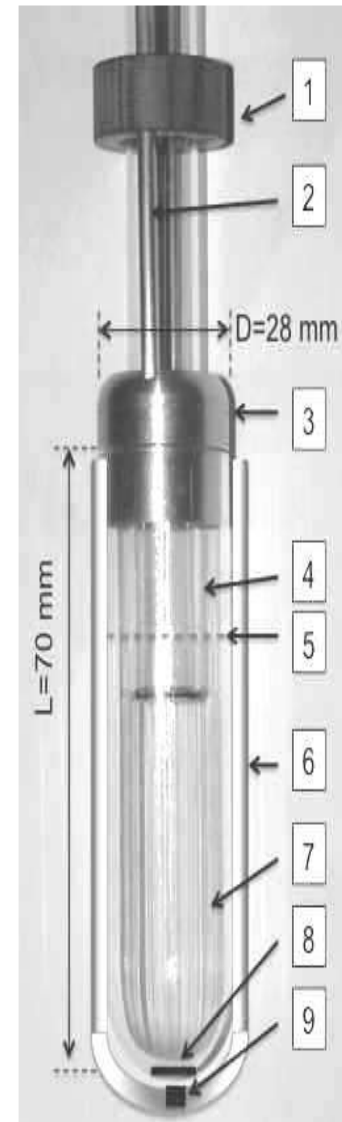
SANS Study at D-22 and D-33 instruments



Metal cryostat for neutron and optical studies



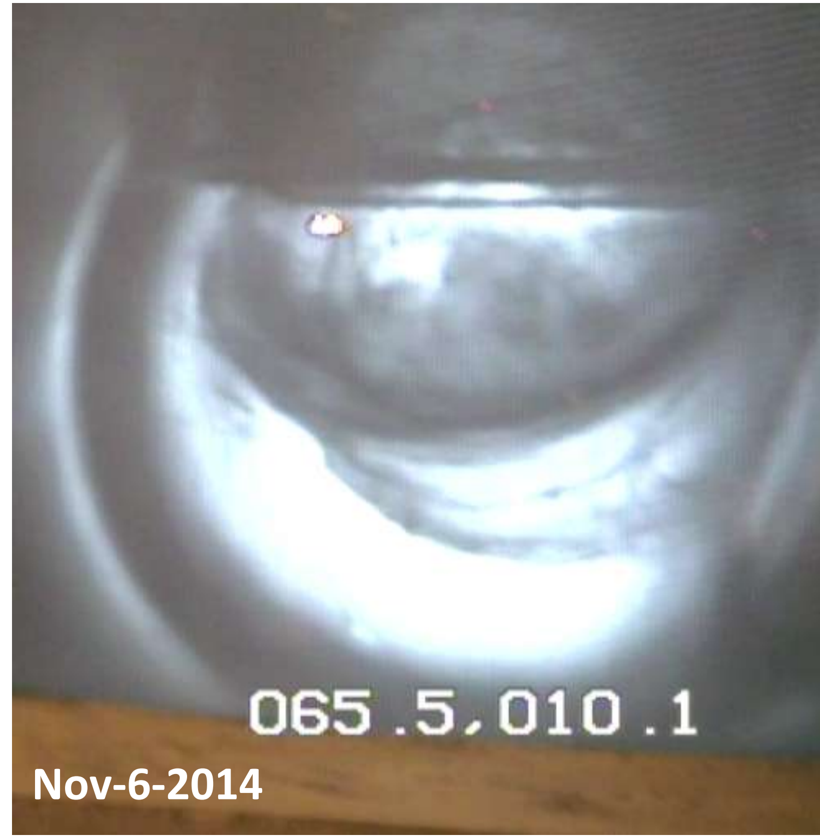




Preparation of the Methane CD_4 Sample for SANS studies

Lower edge of the filling tube

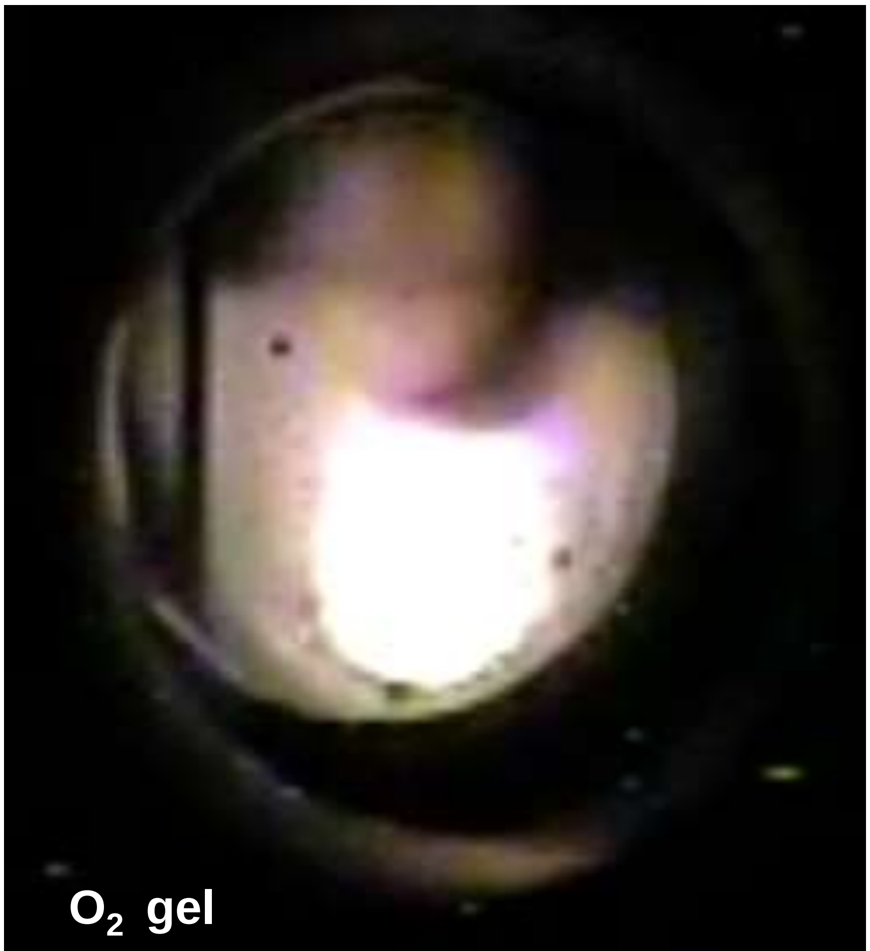
Clouds of the CD_4 gel in He-II;



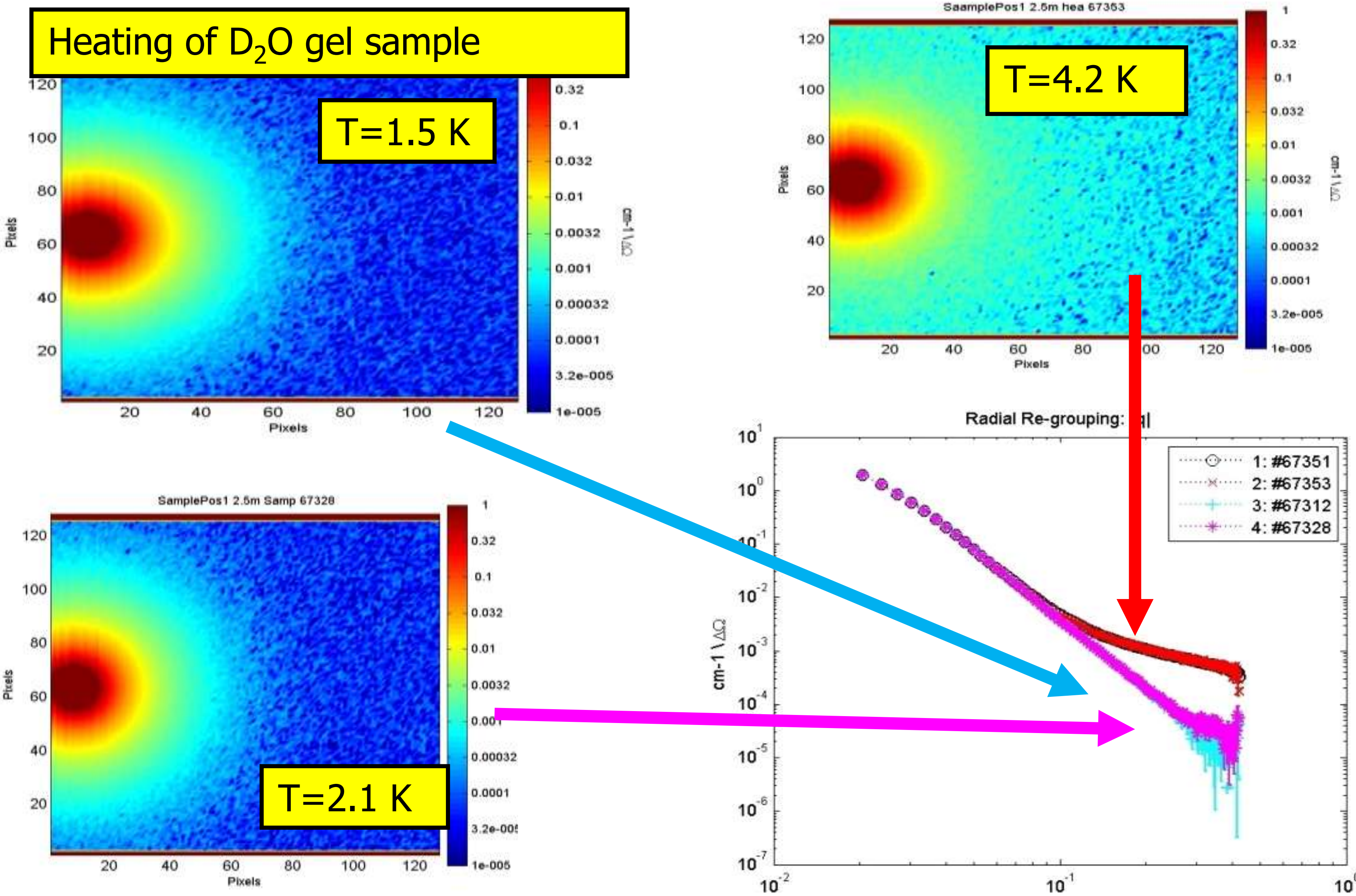
The view through the upper optical window: jelly like layer created at the vapor – He-II interface inside the filling tube was detached from the lower edge of the tube and fall down to the bottom of the quartz glass cell filled with He-II at T = 1.6 K. The level of superfluid He-II is placed ~1 cm above the edge of the tube.

Growth of O_2 (left) and C_2D_5OD (right frames) gel samples

The gel layer was forming on the vapor-He-II interface inside the filling tube and then it was sliding slowly along the walls of the tube and fall down the bottom of the cell with He-II at T = 1.6 K.

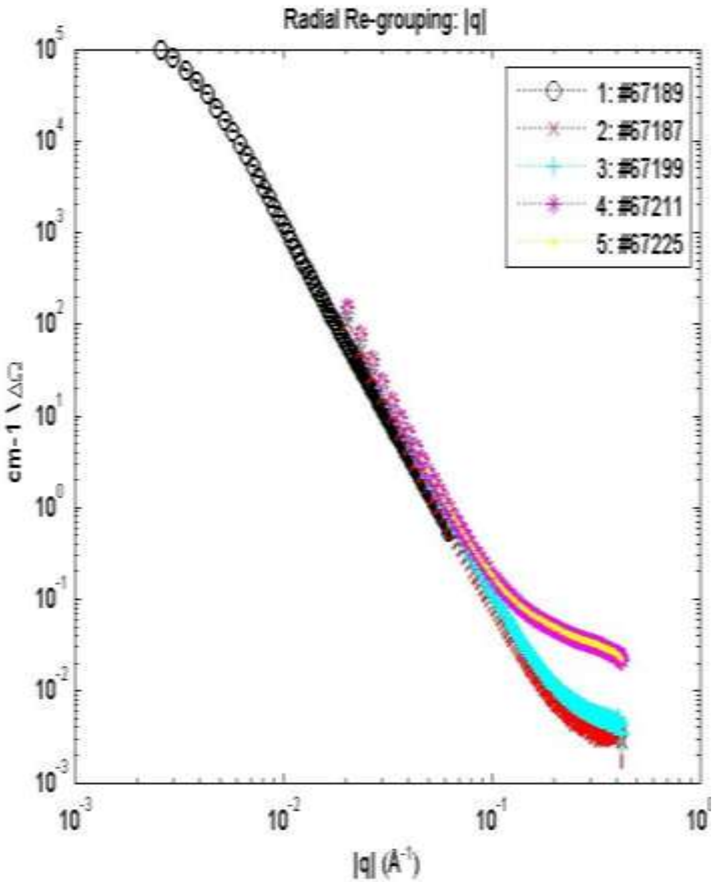


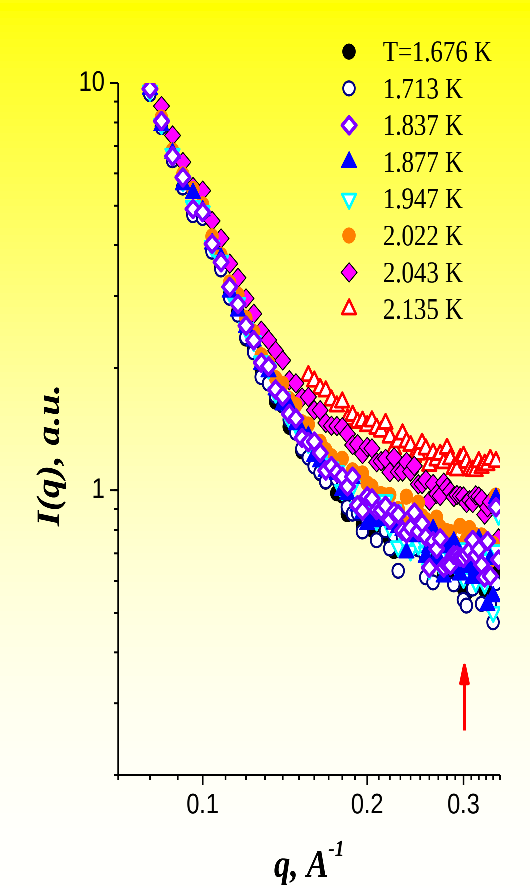
Lower edge of the filling tube

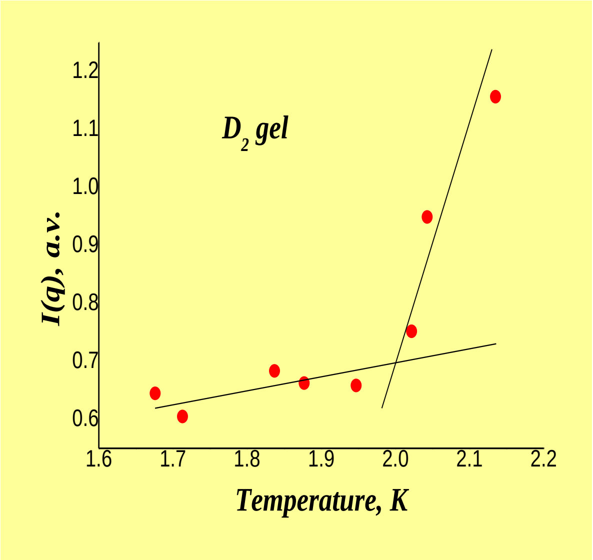


SANS study at D22: **Heating of the of D_2O gel sample in liquid helium from 1.5 to 4.2K results in increasing of the intensity of the neutron scattering I(q) at high q> 10^{-1} $Å^{-1}$, hence in increasing the content of small particles with mean dimensions d ≤ 10 Å.**

Heating of the Deuterium Gel Sample in He-II from 1.66 to 2.15 K.

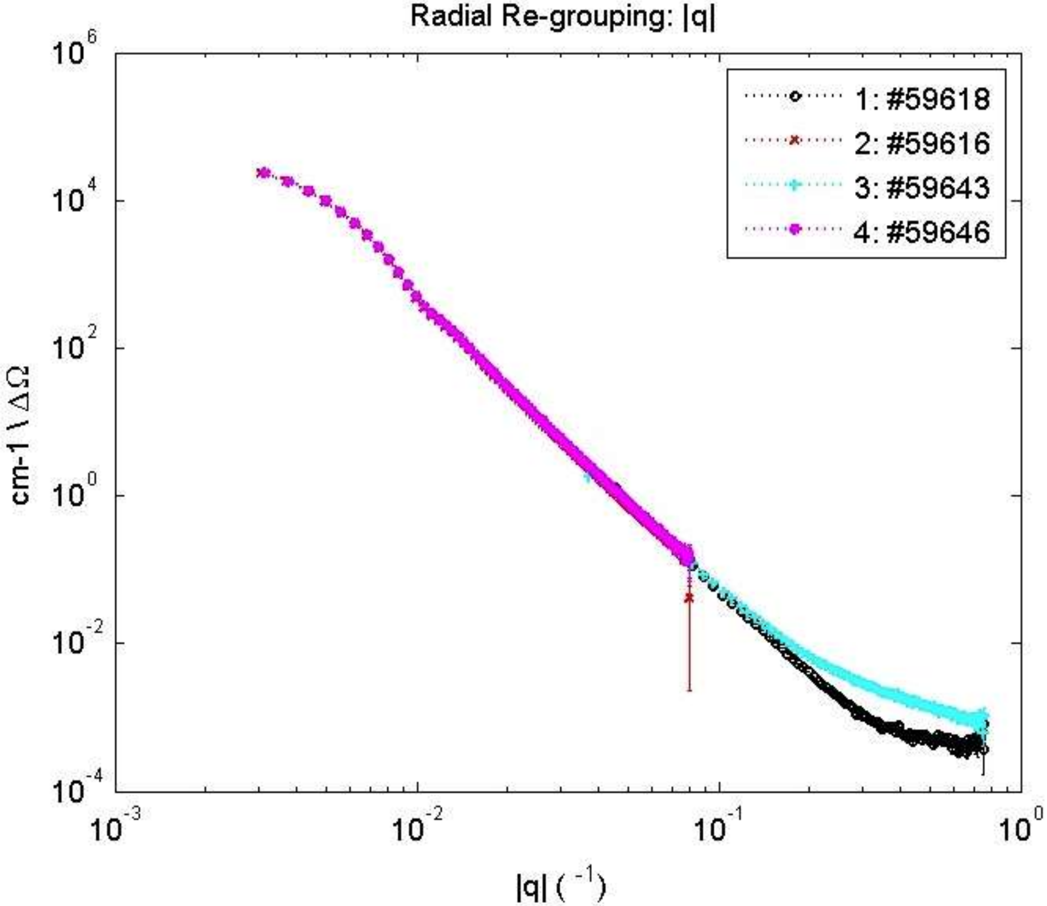




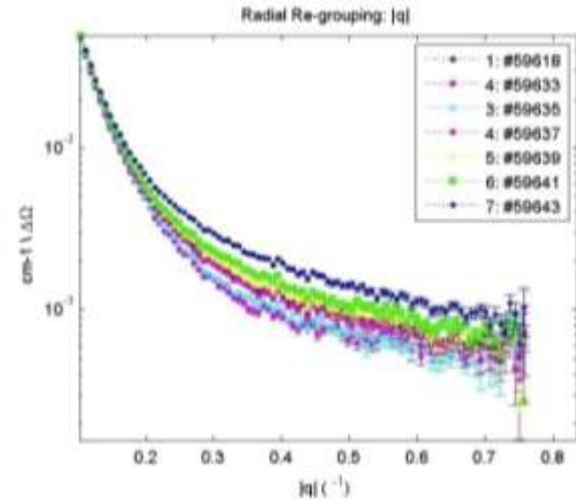


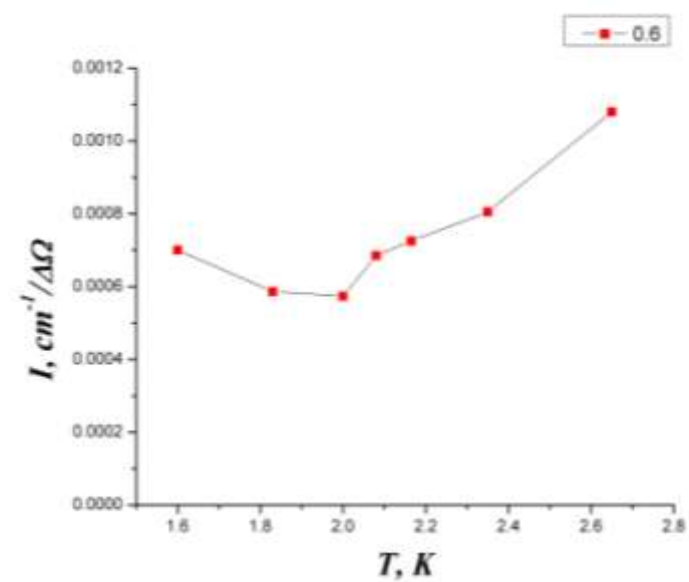
The total content of clusters with small diameters is increasing with heating the sample up to T~ Tλ. Dimensions of the small clusters should be less than d ≤ 2 π/ q_{max} , more strict ≤ 10Å.

Oxygen Gel (Pos.1, different temperatures)



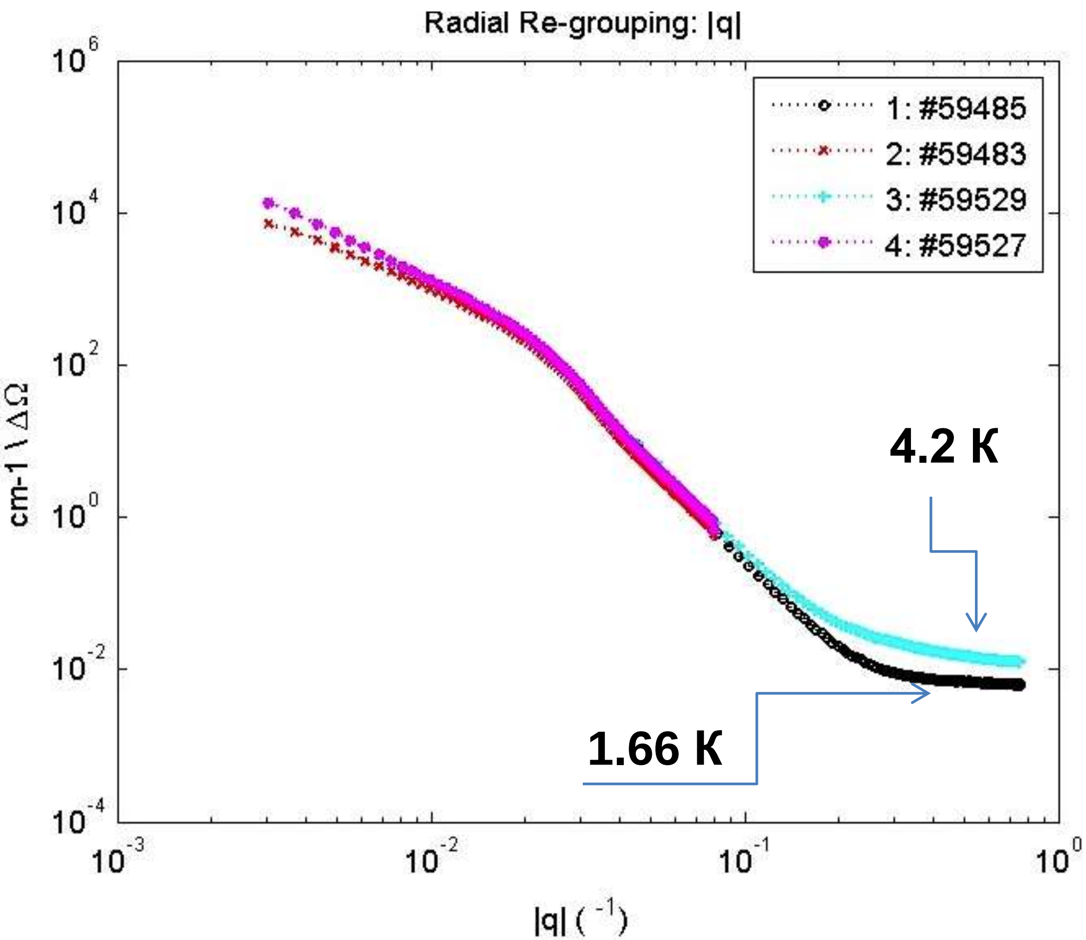
Growth of the content of small particles with increasing the temperature of the helium bath



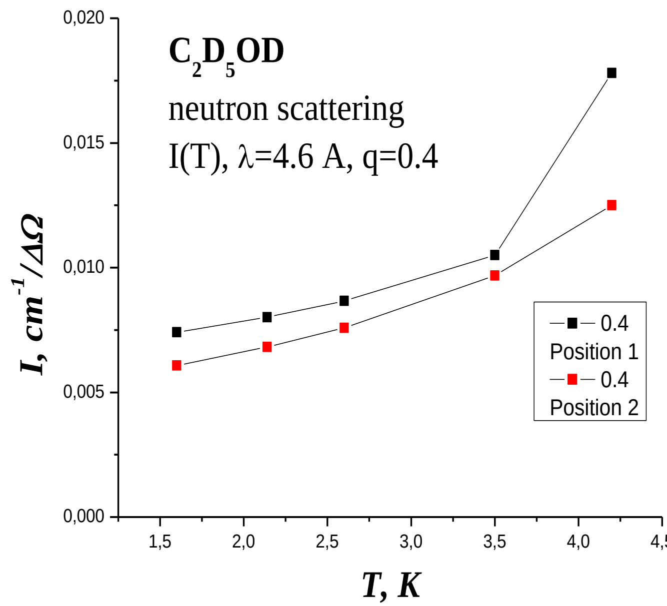


Left frame.
T = 1.66 K, dark rhombs ♦ and red crests x (618 and 616);
T= 2.65 and 3.09 К, blue crests x and violet circles o (643, 646).

Ethanol C_2D_5OD gel sample.



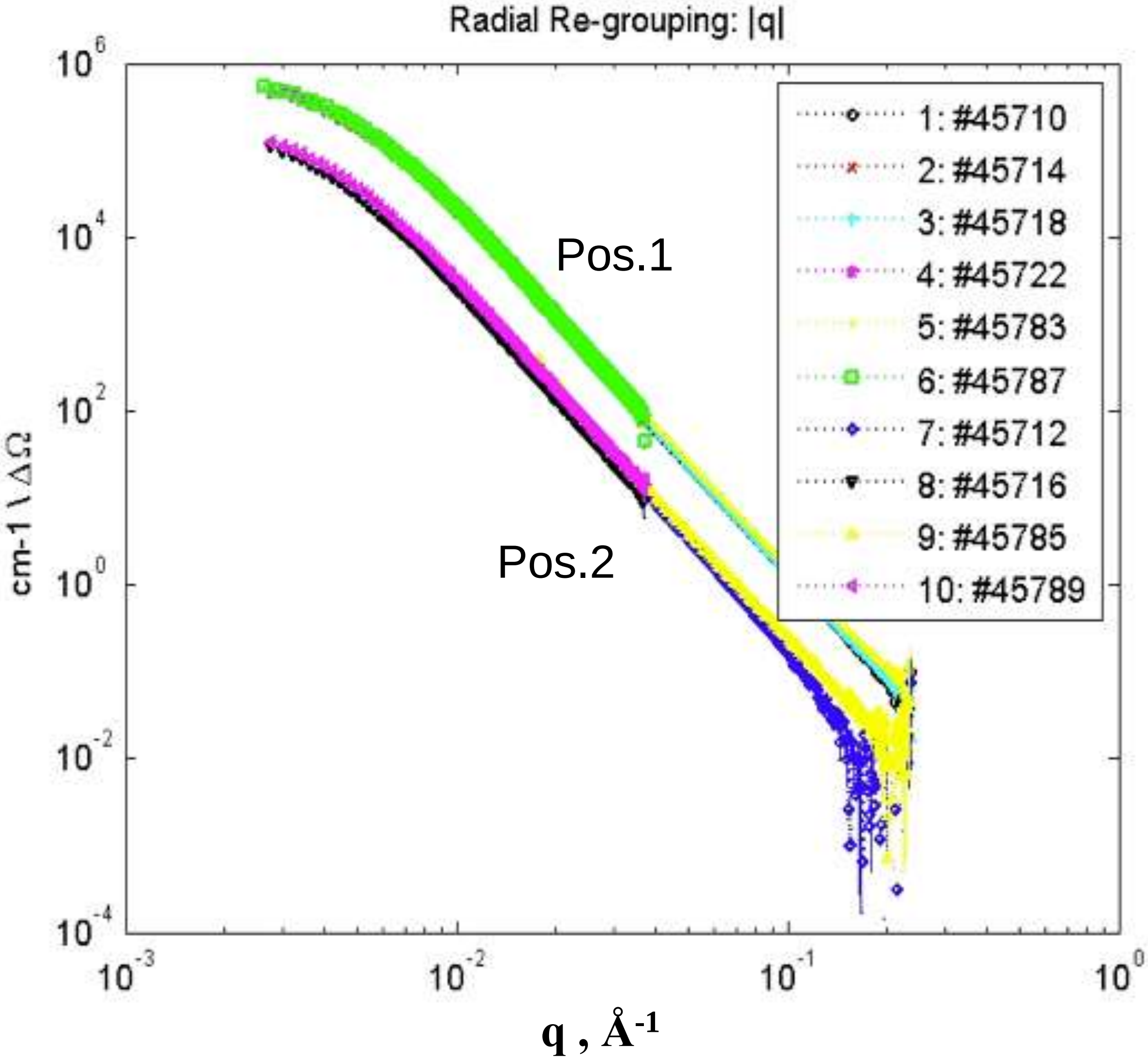
The temperature dependence of I(q) at q = 0.6 Å^{-1} · Mean diameter of the smallest clusters corresponds to d ≤ (2π/q) ≤ 10 Å



Pos.1.T = 1.66K : • 59485; x 59483; and T = 4.2 K : + 59529, o 59527.

The distance sample to detector L=1.5 и 17 m. Dependences I(q) in Pos. 1 and 2 near coincided. BGD was subtracted.

SANS study of the deuterated methane CD_4 gel sample formed in He-II by van der Waals bonded clusters *(Oct.2014)*



Results of the preliminary measurements at D-33 in two positions – near the bottom of the cell in Pos.1 (*the upper set of points*) and 2 cm higher – in Pos.2 (*the lower set of points*).

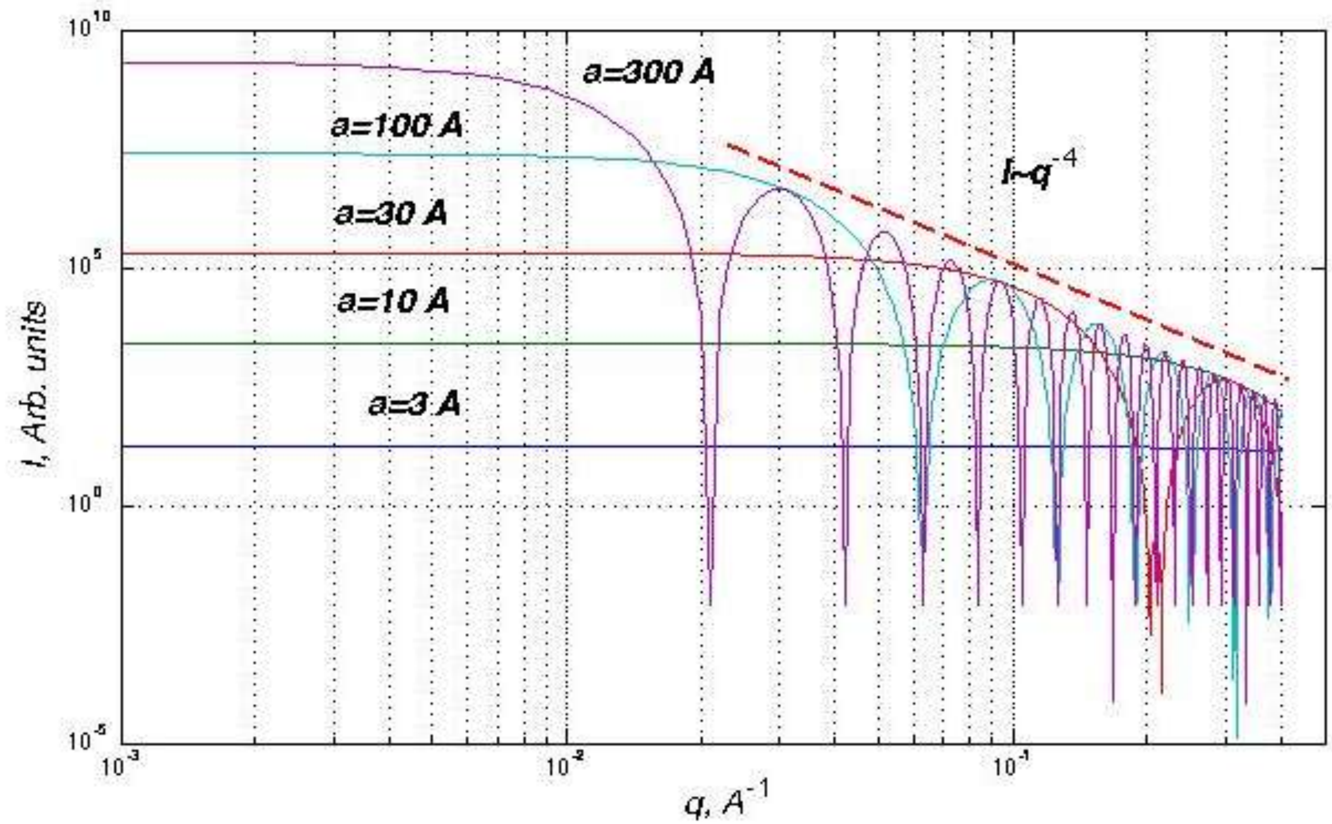
Points of different colors at the same set Pos.1 or 2 correspond to temperatures T=1.66 K and T=4.2 K (weakly depended on T at the range q $=3*10^{-3}$ -10^{-1} $Å^{-1}$) and also to different distances from the sample to detector.

SANS study. Angle dependence of the amplitude of scattering I(q) for particles of different radii a = 3, 10, 30, 100 и 300 Å; in Born approximation

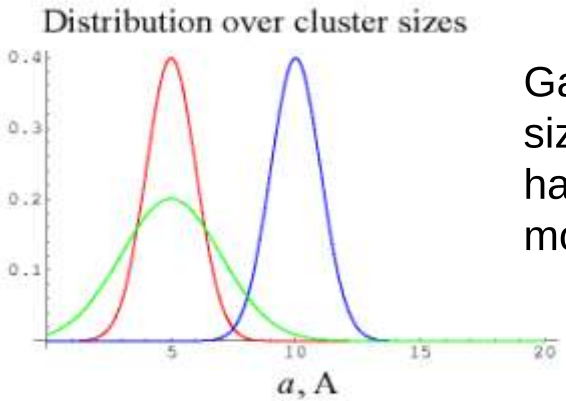
U= - U_0 at r < a, and U= 0 при r > a.

$$I = |f|^2 = \frac{4m^2}{\hbar^4}\left(\int_0^\infty U(r)\frac{\sin qr}{q} r\,dr\right)^2$$

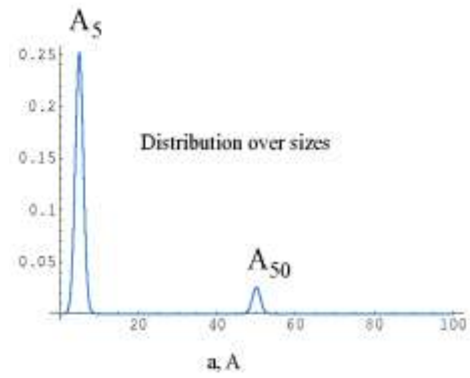
L.D. Landau and E.M. Livshiz, Quantum Mech. , 7, “Born approximation”, task 1

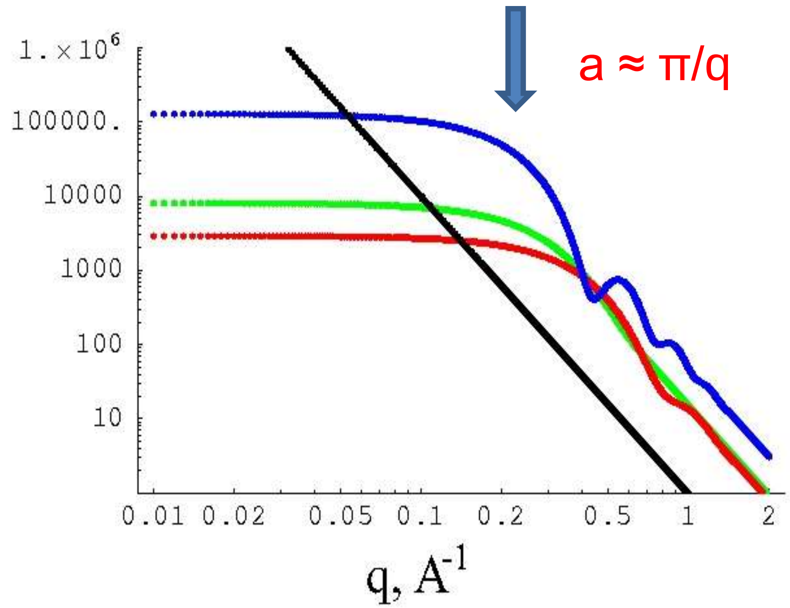


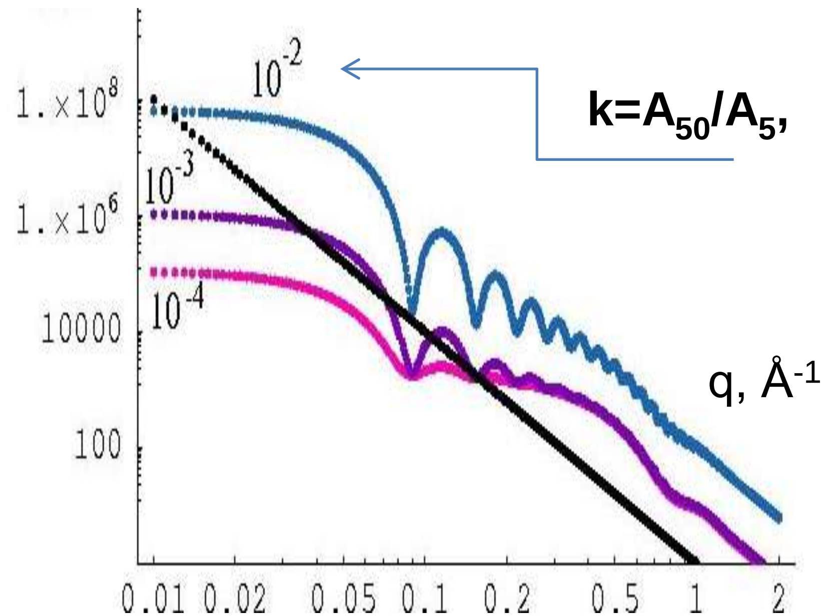
SANS - numerical estimations (G.V. Kolmakov)



Gaussian distributions for the cluster sizes (i.e. the probability for a cluster to have the radius ***a***) proposed in the model.

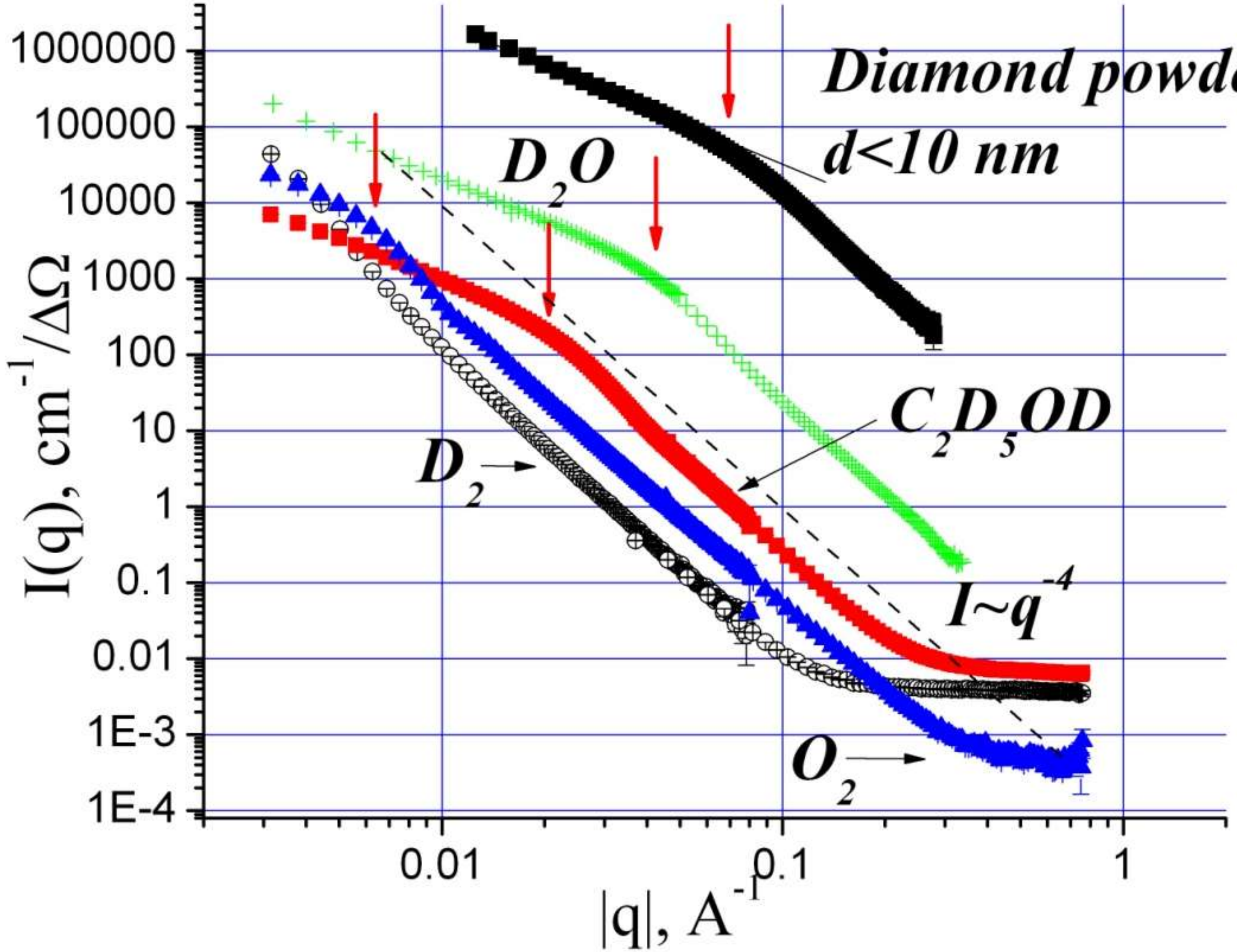






A_5 and A_{50} are the probability for a cluster to have the radius *a* equal to 5 or 50 Å. Evolution of the I(q) curves with changing the relative number of 50 Å clusters. The relative content of 50Å clusters, $k=A_{50}/A_5$, is marked at the curves. Decreasing of the content of 50 Å clusters down to 0.1% results in strong deviation from the I(q)~ q^{-4} law in the region 0.1 Å^{-1} < q < 1 Å^{-1} and appearance of the two plateaus on the I(q) curves.

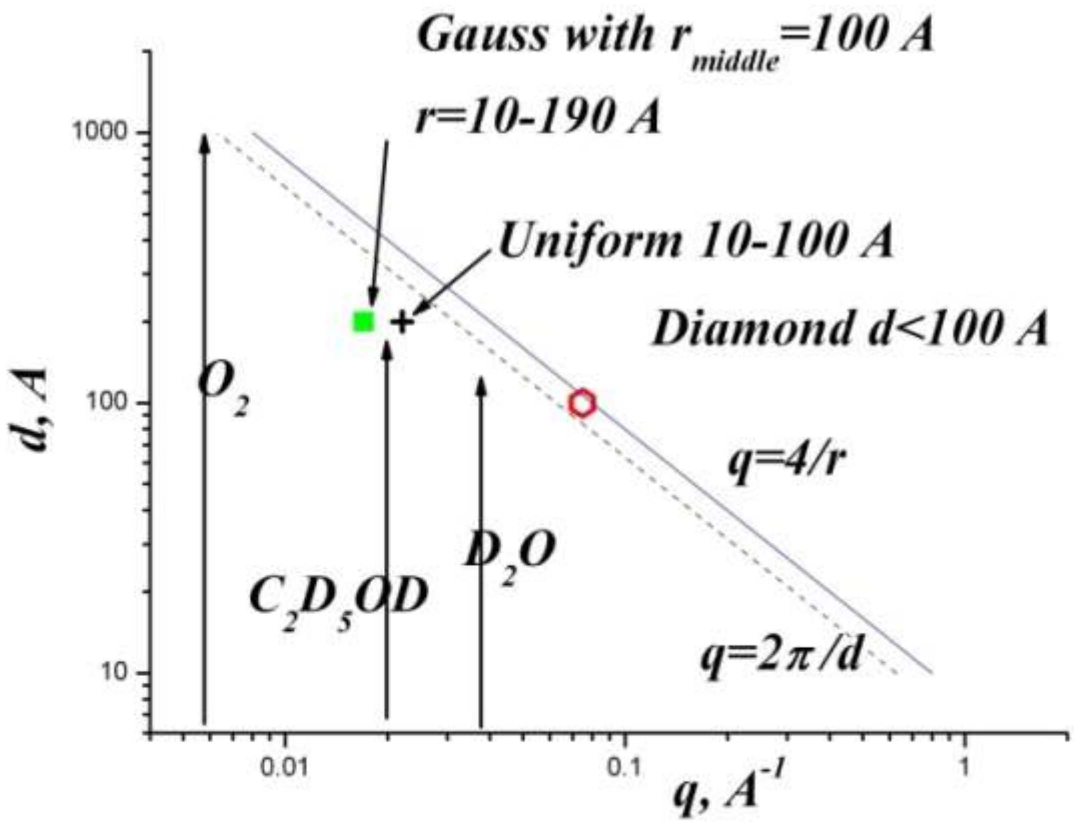
SANS data for the gel samples in He-II at T=1.66 K



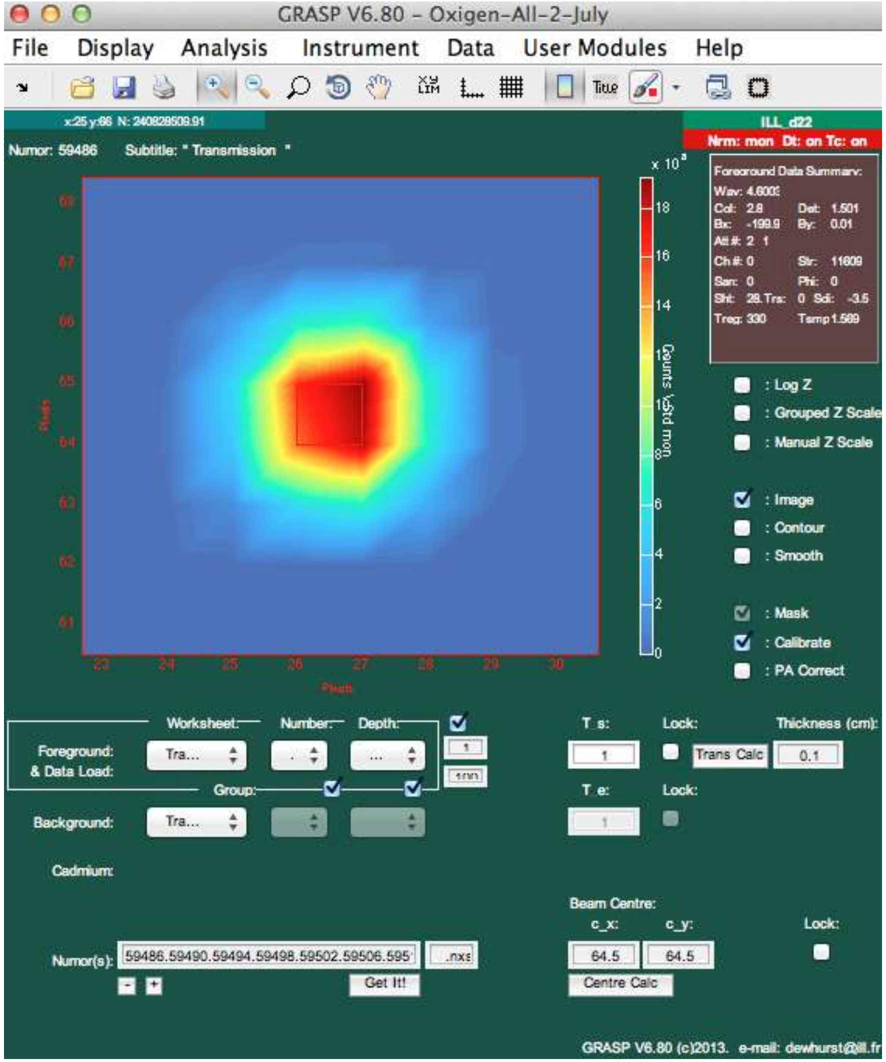
The dashed line corresponds to the Porod law $I \sim q^{-4}$ (for the product q*d>>1) . Transition from Porod to Gunier region (q*d<<1) should took place at q*d ≈2π.

A thin layer of the commercial powder of nano-diamond in an Al envelope was studied at the room temperatures. By certificate the size of particles d ≤ 10 nm

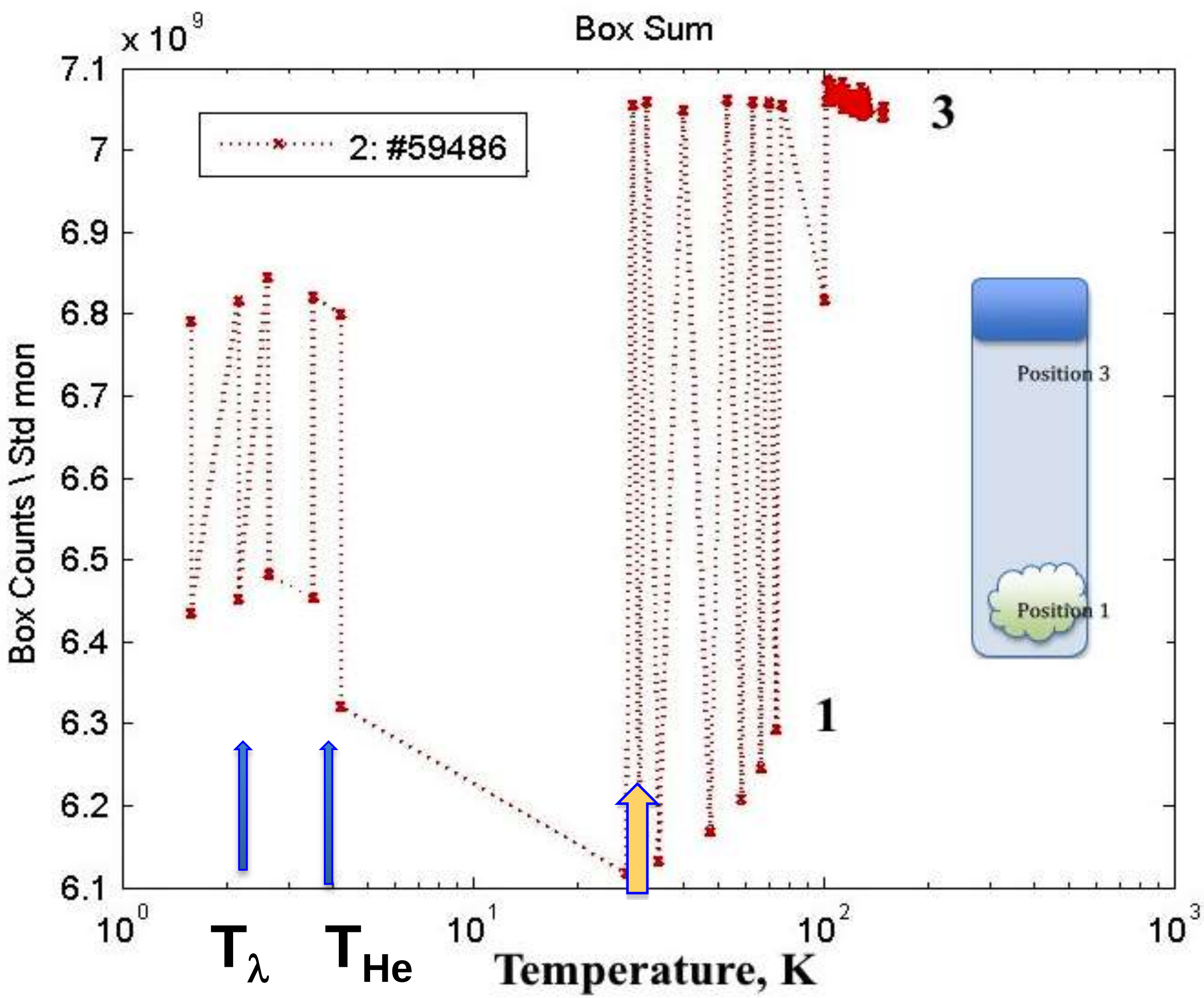
Mean dimensions of the impurity clusters (aggregates of clusters) estimated from the positions of the excesses on the I(q) curves shown by arrows on the curves



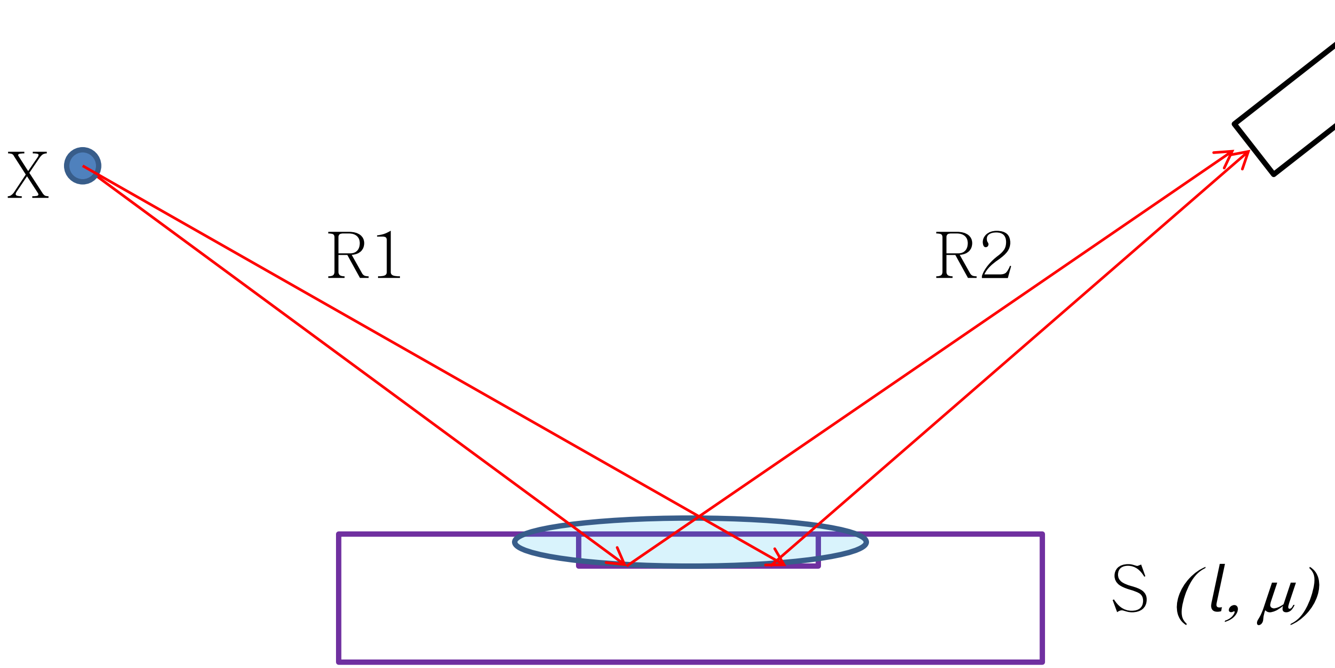
SANS STUDY: direct propagation of the neutron beam through the gel sample



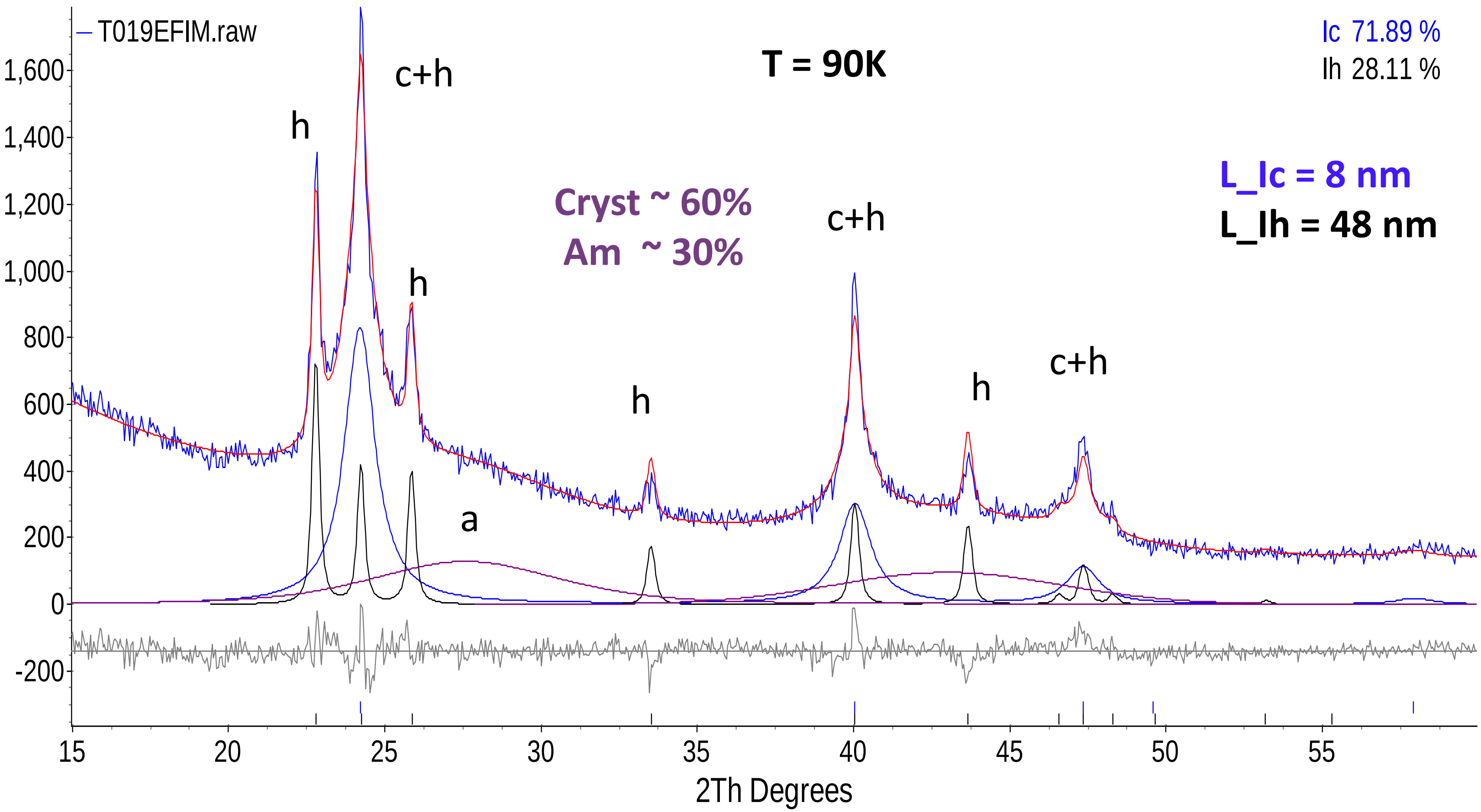
SANS STUDY:
direct propagation of the neutron beam through the C2D5OD gel sample



X-Ray study of an icy powder sample formed on decay of a gel

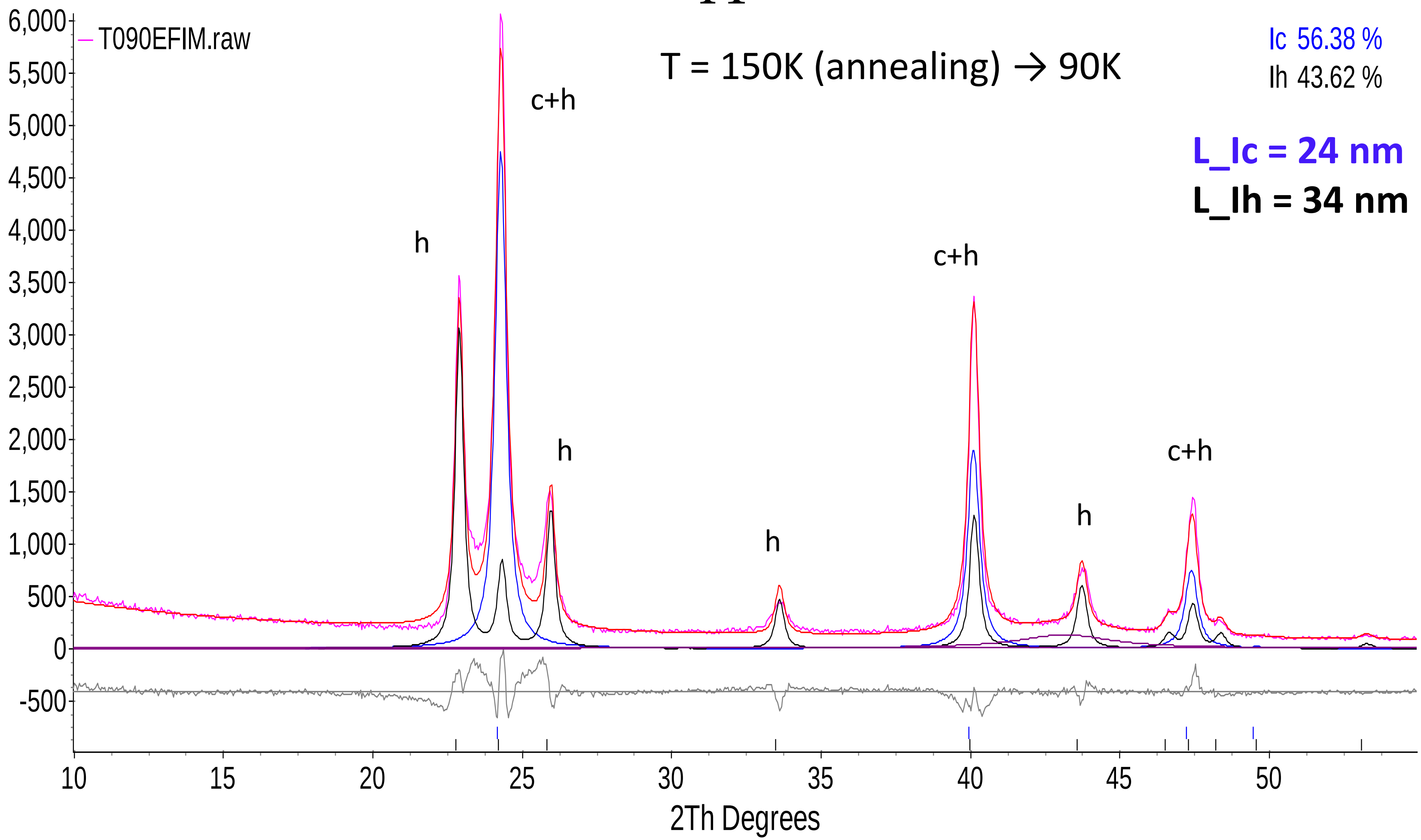


The −ray spectrum of the H2O icy powder sample formed on decay of the water gel

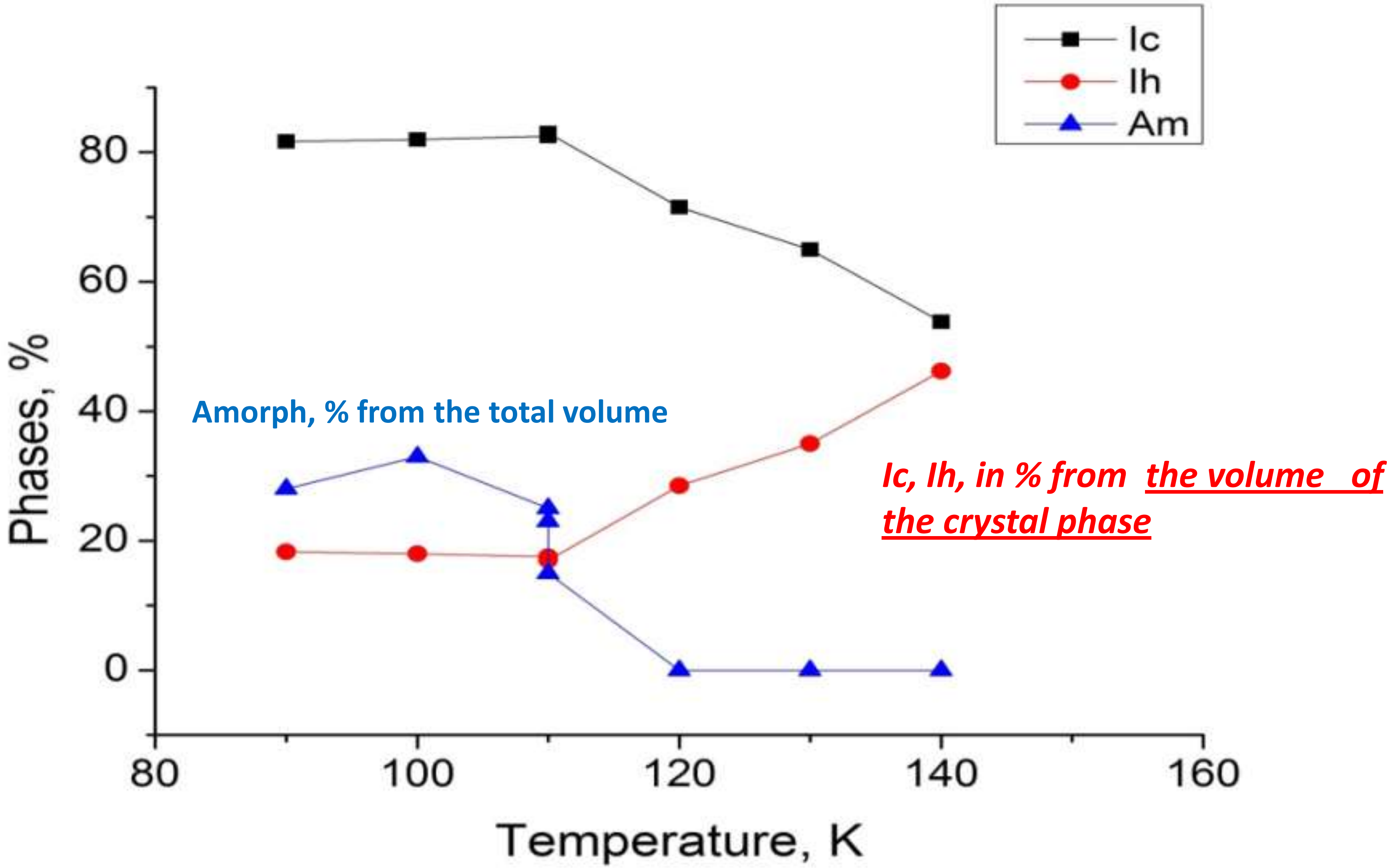


Shown below is the spectrum of the convenient hcp ice

The spectrum after annealing the icy sample at 150 K

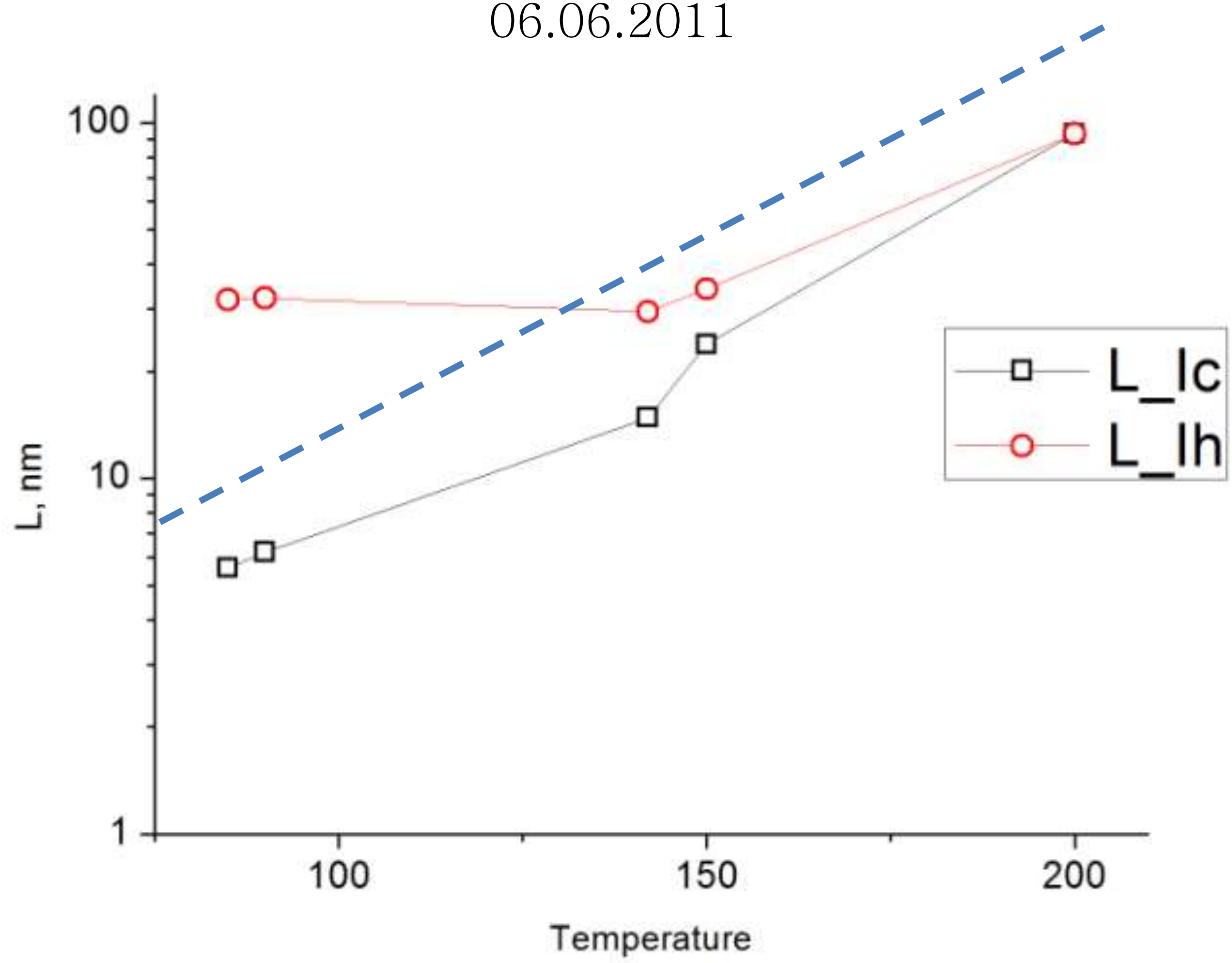


The phase transformation with annealing the H20 icy sample

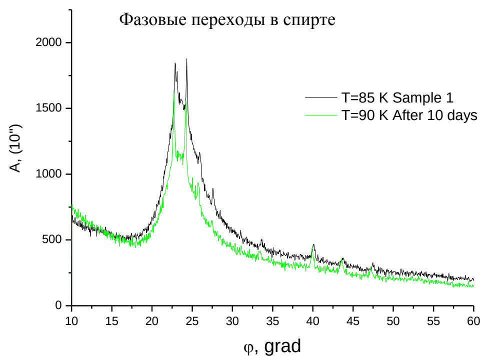


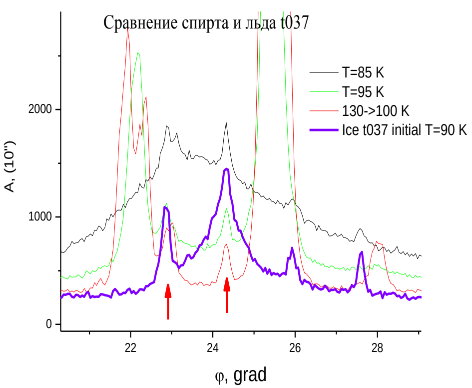
Growth of the dimensions of crystallites of the cubic and hexagonal ice H20 structures with increasing the temperature

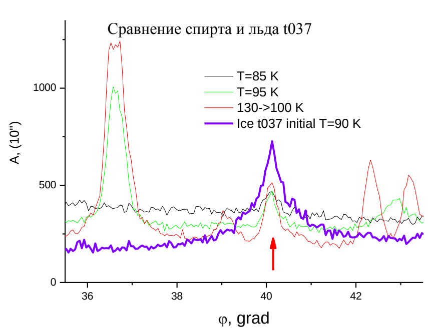
06.06.2011

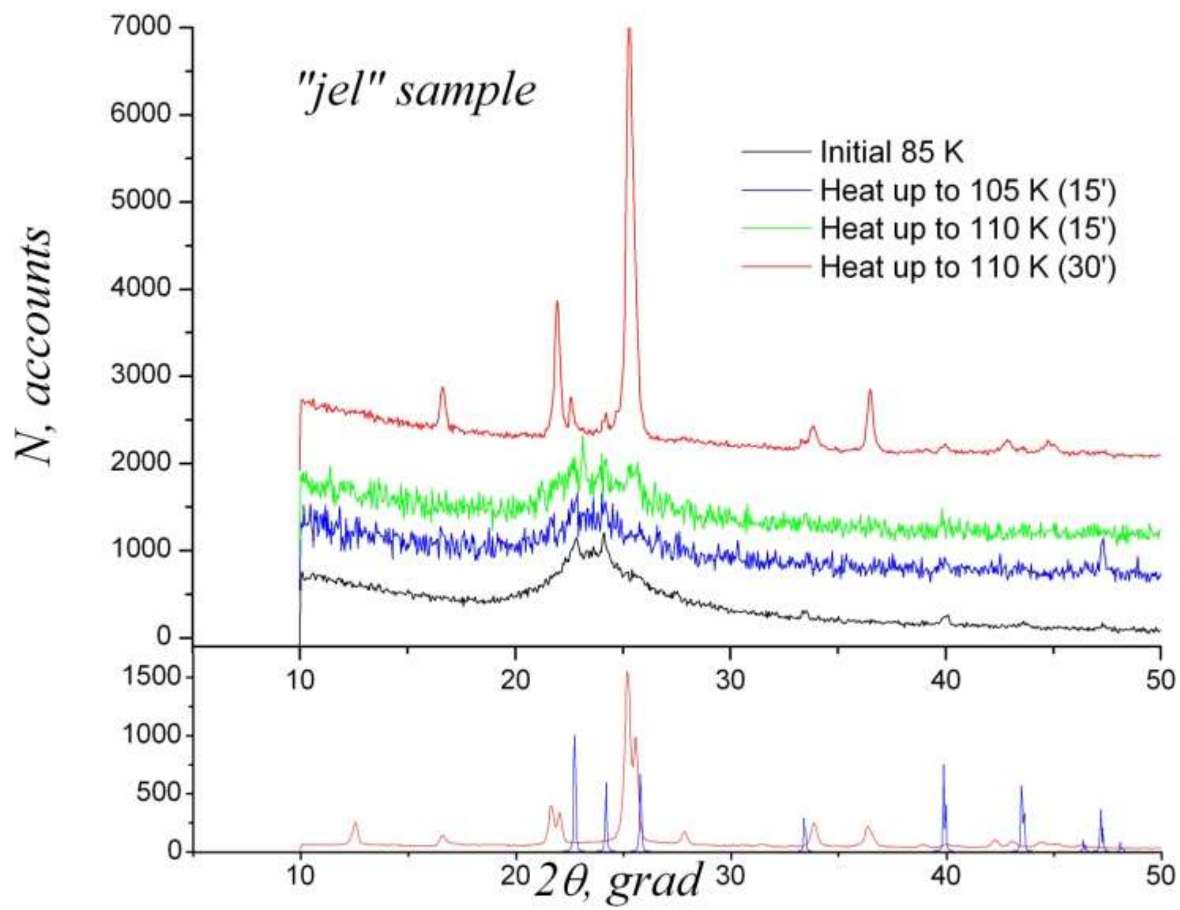


Structure and phase transitions in the ethanol C2H50H icy powder formed on decay of the gel









Amorphous sample transforms into crystalline monoclinic phase. The size of crystallites ~30-40 nm is close to dimensions of the ethanol clusters in the backbone of the D_2H_5OD gel from the SANS measurements

References

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

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