Structural and phase transitions in nanocluster ethanol samples at low temperatures

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Results of neutron (SANS study) and x-ray diffraction experiments with nanocluster samples of deutero-ethanol (C_2D_5OD) or ordinary pure ethanol (C_2H_5OH) are presented. A deuterated ethanol sample, formed via quick cooling of ethanol–helium mixture down to 1.6 K, had clusters with the size of $d \sim 20$–30 nm at liquid helium temperatures. After warming up to liquid nitrogen temperatures the gel decays into an amorphous white powder. It was observed that these powder samples remained in the amorphous state even after keeping at $T \leq 90$ K for a long time (a few months). The neutron studies were supported by further x-ray investigations of the structure and the phase transitions in the highly dispersed powder samples, which were created via the decay of the gel samples of ordinary ethanol at temperatures above liquid nitrogen up to 150 K at saturated nitrogen gas pressure. Annealing of the "gel" sample during half an hour at a temperature of $T \sim 110$ K resulted in a phase transition to a monoclinic phase with the crystallite sizes ~30–40 nm. For comparison we studied the structure and phase transitions in "bulk" samples, prepared via quick freezing of liquid ethanol down to liquid nitrogen temperature. The "bulk" sample had a similar transition at $T \sim 125$ K, which is by 15 K higher than the temperature of the intensive phase transition in the "gel" sample. The mean grain size in the bulk material was $d \geq 60$ nm.

PACS: *61.05.fg* Neutron scattering (including small-angle scattering);
61.46.–w Structure of nanoscale materials;
64.70.K– Solid-solid transitions.

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Introduction

Ethanol is an extremely interesting material for investigating crystalline and orientational transitions. It has been known that ethanol exhibits an interesting phase polymorphism. The fully disordered supercooled liquid transforms into a structural glass upon quick cooling. The orientationally disordered crystalline phase transforms from a rotator phase to an orientational glass upon cooling at a moderate rate. The stable orientational ordered crystal of monoclinic phase was produced via very slow growth of the sample at a temperature close to the melting point. There are a lot of measurements of different type with ethanol samples: x-ray diffraction [1–4], Raman spectroscopy [2], specific heat [3,5–10], complex dielectric susceptibility [11], neutron scattering [3,5,12], thermal conductivity [13], light and infrared reflection [14,15]. In fact, the most evident experimental result is the existence of the stable monoclinic crystalline phase at the temperature close to melting [1] (fully ordered structure) and the amorphous state (glass like state, supercooled liquid and so on) in a completely disordered phase, which was formed by quenching faster than 30 K/min [16]. All other rotational and structural order–disorder transitions are very sensitive to cooling and annealing procedures.

In this work we studied the processes of crystallization of amorphous ethanol with different size of clusters. We produced nanocluster samples of ethanol in the cryomatrix

of helium via quick cooling of a mixture of ethanol vapor with helium gas. For comparison, we measured the time of transition to the monoclinic phase for a "bulk" ethanol sample, produced via quick freezing of liquid ethanol. Our investigation indicated that the temperature of intensive transition depends drastically on the size of the nanoparticles in the sample and the sample preparation procedure.

Experimental results

Preparation of ethanol–helium "gel" samples

The methods for the impurity gel preparations was described earlier [17]. The gel was prepared via condensation of a gas mixture of ethanol vapor and ^{4}He on the surface of superfluid helium He II cooled below 1.8 K. The samples were prepared *in situ* for subsequent studies by small-angle neutron scattering (SANS) at liquid helium temperatures in a special cryostat [18]. Initially the sample of the deuterated ethanol gel was prepared in the cell installed in the middle part of the cryostat [19], where we placed a pair of windows for visual control of the sample formation inside the quartz cell. The process of sample preparation continued for one hour and we got a spongy soft matter filling the whole cell (Fig. 1). The concentration of ethanol molecules in the gel could be estimated from the volume of liquid ethanol at the bottom of experimental cell measured at the ambient temperature after posterior gel sample decay; the volume was $V_{eth} \sim 0.5$ cm^3. Thus, the relative volume concentration was $c = V_{eth}/V_G \sim 2\%$, where V_G is the volume of the experimental cell ($D = 2.5$ cm, $h \sim 5$ cm).

Small-angle neutron scattering

After the cell was filled we moved it to the bottom part (tail) of the cryostat, which was made of aluminum and thus was transparent for neutrons. The measurements were

Fig. 1. Process of sample preparation. The sample fills the whole cell. A filling tube can be seen in the upper part of the window.
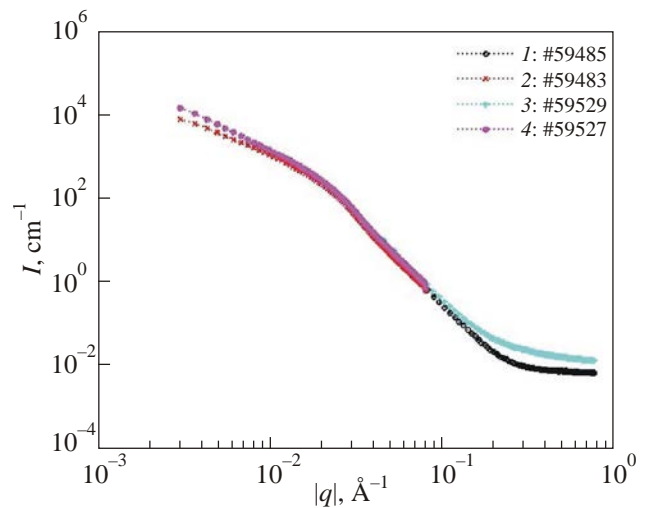

Fig. 2. (Color online) Neutron scattering on C_2D_5OD gel near the cell bottom. The temperature of He II in the cell is 1.6 K (curves *1* and *2*). Curves *3* and *4* are results of measurements at 4.2 K.

performed at ILL using D22 instrument with at neutron wavelengths of 4.8 and 6.1 Å. The angular distribution of the intensity of neutron scattering $I(q)$ allow estimating the maximum size (diameter) of reflecting particles d. The transition from "Porod scattering" ($I(q) \sim q^{-4}$) [20] at large angles ($qd \gg 1$) to a less sharp angular dependences $I(q)$ (Guinier region [21]) took place at angles $qR_g < 1$ (Fig. 2). Here, $R_g = (3/5)^{1/2}R$ for spherical particles, and the particle diameter is $< 2.6/$.

From these experiments we could estimate that the maximum diameter of the deuteroethanol particles in the gel was $d \sim 20$–30 nm. The right part of the $I(q)$ curve in Fig. 2 corresponds to "large-angle" neutron scattering (scattering on small particles). It is seen that the content of particles of small sizes in the sample increased with heating from 1.6 to 4.2 K. A more detailed temperature dependence of the neutron scattering at $q = 0.6$ Å^{-1} is shown in Fig. 3. A simi-
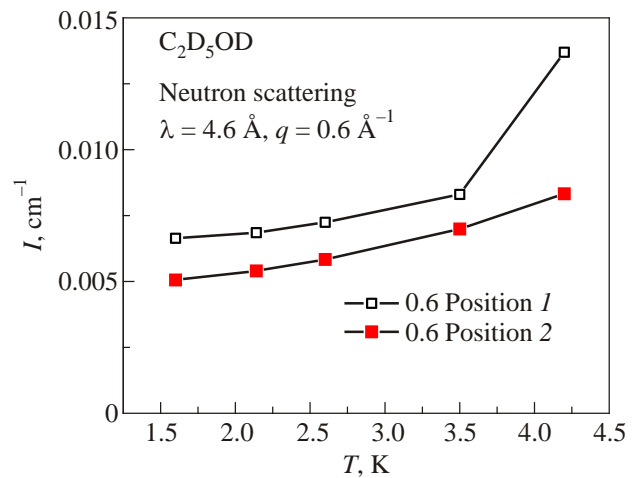

Fig. 3. Temperature dependence of neutron scattering at large angles ($q = 0.6$ Å^{-1}) from the sample of deuteron–ethanol–helium gel in during heating of liquid helium.

lar influence of temperature to "large-angle" neutron scattering was observed earlier for a deuterium-helium gel [22].

It is interesting that initially (at $T = 1.6$ K) the "large-angle" scattering in the top part of the cell (43 mm from the bottom) was negligible against the background. Warming the sample up to 4.2 K increased drastically the $I(q)$ and was the same as bottom points. This behavior indicates that warming at liquid helium temperatures results in a splitting of large nanoparticles into smaller ones.

Decay of the ethanol–helium gel

In a set of SANS experiments we tried to find the temperature, at which the impurity-helium gel starts to decay. The main interest is related to the problem of interaction between a polar impurity molecule and helium surrounding. One can assume that in He gas atmosphere at saturated vapor pressure the sample keeps its shape until helium atoms in bulk of the sample start "to leave" volume of the sample. Then the gel frame should lose its stability. Unfortunately, SANS measurements assume long neutron counting, and thus this method is poorly compatible with rather fast natural warming of the cryostat towards liquid nitrogen temperatures after liquid helium evaporation (~2 h). Therefore we measured the neutron intensity in the center of direct neutron beam, taking into account that the reduction in number of neutrons, which are passing through the sample directly (neutron transmission), would correspond to certain increase of their scattering. We measured the neutron intensity in two points: near the cell bottom and also at the height of 43 mm above it. The measuring time was only 1 min, so we should be careful with scanning the sample density in different points. The results are shown in Fig. 4.

All changes in the beam intensity in points *1* and *3* were small as long as liquid helium continued staying in the cell.
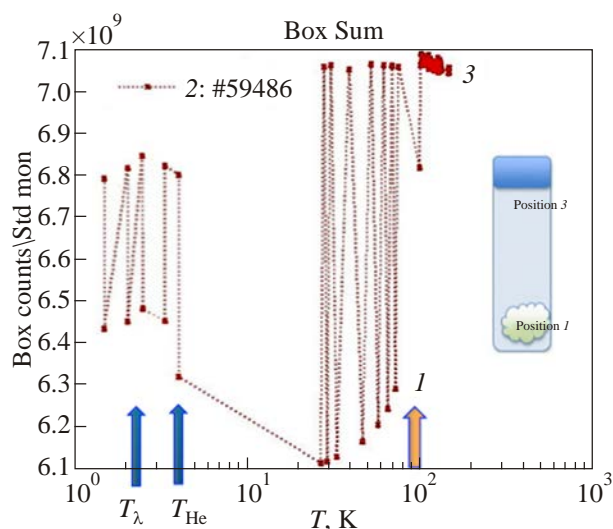

Fig. 4. (Color online) The temperature dependence of neutron intensity in the center of neutron beam in the process of sample warming. A sketch in the right side is an illustration of the beam position. Point *1* is the count near the cell bottom, point *3* is the upper part of the cell.

When the liquid evaporated, the temperature in the cell began raising, and the gel started to release from the upper part of the cell and it became more compact near the bottom. At temperatures ~35 K the sample began to disintegrate and the decay stayed very intensive up to temperatures of 80–100 K. The gel sample transformed to a white powder, collecting at the bottom of the cell. The center of the neutron beam didn't touch the powder, and the intensity in points *1* and *3* stayed very close.

Afterward, we used the powder of pure ethanol produced via similar way for measurements of the phase transitions in the powder by the x-ray diffraction method. It was observed that the ethanol powder could be stored unchanged for a long time (for a few months) in liquid nitrogen for further experiments.

X-ray measurements

The structure of powder samples and the phase transitions under annealing were studied using the method of x-ray powder diffraction. Initial samples were prepared from ethanol in two different ways. One way of preparation of a "gel" sample was described above. We studied "gel" sample powder after helium evaporation. The x-ray diffraction spectra were obtained using Cu-K_{α} irradiation in the nitrogen gas atmosphere.

The structure of as-prepared samples was amorphous. Sometimes we observed a small amount of the water ice. Apparently it formed on the sample surface from the water vapors, which condensed during the cold sample transfer from the container into the measuring cell.

All samples were kept in liquid nitrogen before x-ray investigations, so the question about structure stability at this temperature was important. The x-ray measurements of the "gel" samples made directly after the sample preparation and after half a year holding in liquid nitrogen had demonstrated that there was no difference between diffraction pictures of "virgin" and "conserved" samples.

In order to study dynamics of crystallization of an amorphous phase a few series of annealing were carried out. The temperatures of annealing were from 105 to 150 K, durations were from 15 min up to 7 h. X-ray measurements were carried out after each annealing.

The time of the measurements of one of diffraction scanning is up to some hours. This time is comparable with time of phase transformation into a crystalline state at temperatures above 105 K. Therefore all the diffraction measurements were carried out at the temperature of liquid nitrogen. We annealed a sample at a fixed temperature during certain time, after that cooled it down to 85 K and carried out x-ray measurements.

These x-ray investigations allowed us to find the temperature of intensive crystallization; for the "gel" sample it was about 110 K. The typical process of phase transition of ethanol powder samples, prepared through the gel, is shown in Fig. 5.
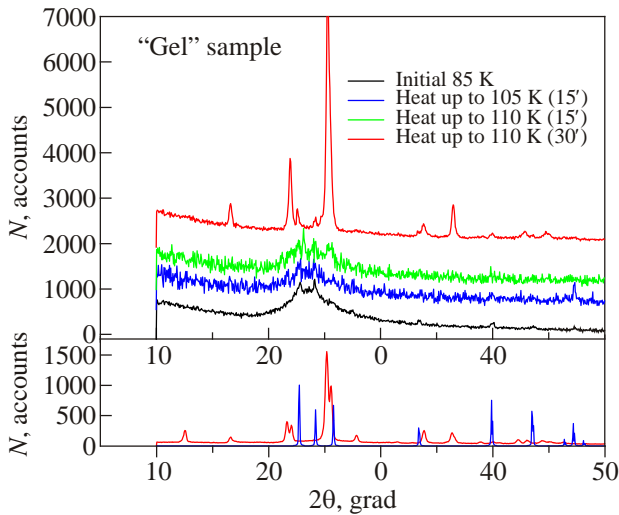
Fig. 5. (Color online) Transformation of amorphous ethanol "gel" sample into monoclinic phase at annealing. In the bottom graphic we plotted diffraction pictures for monoclinic ethanol (red curve, [1]) and hexagonal ice (blue curve).

Fig. 7. (Color online) Transformation of an amorphous ethanol "bulk" sample into monoclinic phase at annealing.

As seen in Fig. 5, annealing at the temperature of 110 K during half an hour results in crystallization of almost the whole sample. The size of crystallites was about 30 nm and didn't depend considerably on annealing duration. Apparently it is related to the size of particles in amorphous ethanol's powder, which is prepared through "gel" procedure.

For comparison we prepared amorphous ethanol samples by rapid quenching of a liquid ("bulk" sample). A quartz substrate with the depth = 0.3 mm was filled with absolute ethanol. Then the sample was cooled down to liquid nitrogen temperatures faster than 20 K/min and put into x-ray diffractometer for studying the phase transformation at annealing. The x-ray diffraction patterns of initial amorphous phases of "bulk" and "gel" samples (Fig. 6) are identical.

The x-ray diffraction patterns of amorphous phases of "bulk" and "gel" samples (Fig. 6) indicated that the distance between ethanol molecules in both samples is close.
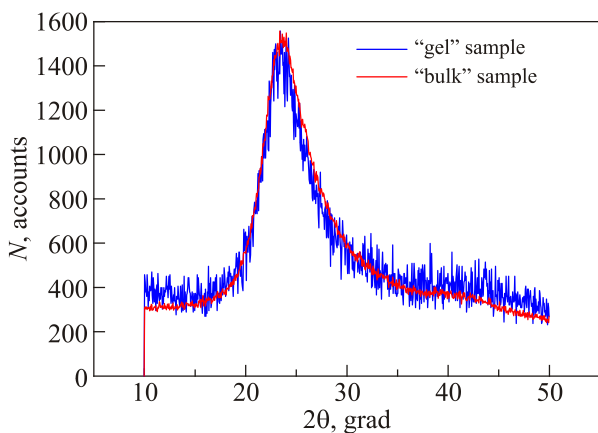

Fig. 6. (Color online) Comparison of x-ray diffraction pictures of amorphous ethanol samples prepared through "gel" procedure and those prepared by freezing of liquid ("bulk" sample).
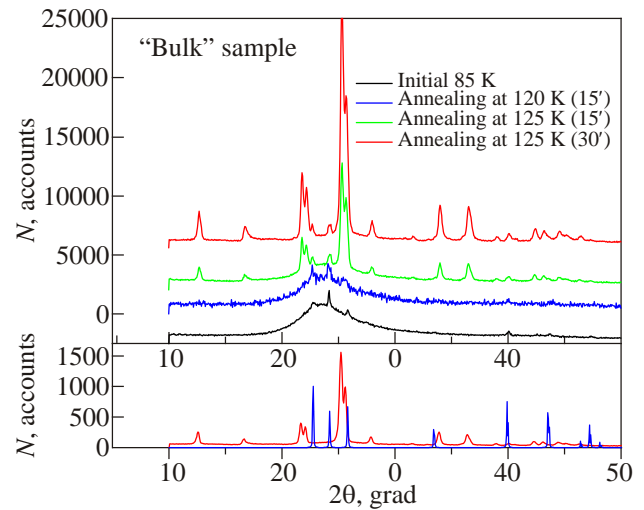
The process of annealing with subsequent x-ray measurements of "bulk samples" was carried out using the same procedure as for "gel" samples. The temperature of annealing, at which phase transformation happened quickly enough, was about 125 K that is higher by 15 degrees than the temperature of intensive phase transition in the "gel" sample.

The phase transition at heating results in formation of the monoclinic phase in both cases. Diffraction spectra of the obtained monoclinic phase are close to that described in [1,4]. They differ a bit for various temperatures of annealing and for samples obtained from "gel" and by direct quick freezing. We believe that it is connected with various ways of packing of ethanol molecules in a crystal cell.

The difference in temperatures of crystallization for "gel" and "bulk" samples might be explained by two factors influencing on the dynamics of transition.

On the one hand, for particles of order of ten nanometers in size, as in "gel" sample, the share of the molecules, which are in surface layer, is rather great, so the role of superficial energy is considerable. It can lead to essential decrease in temperature of phase transition.

On the other hand, explanation is connected with the procedure of "gel" samples preparation. Ethanol molecules in the ethanol–helium mixture are separated by helium atoms, that impedes formation of H bonds, during the quick cooling of this mixture. After removal of helium from a sample, molecules of ethanol in amorphous phase "are frozen" in the positions, but aren't connected by O–H intermolecular bonds. Therefore the formation of the crystalline phase under annealing is just associated to the reorganization of the ethanol molecules and does not require of additional energy for breaking H bonds unlike crystallization of the "bulk" amorphous samples (supercooled liquid). So, it decreases the temperature of phase transition.

Additional research is needed for resolving the structure of various modifications of the monoclinic phase, which are formed at different conditions from "gel" and "bulk" amorphous samples, and for answering the question on nature of so large difference in temperatures of the phase transition.

Conclusions

We studied the phase transition of the ethanol powder samples from amorphous to monoclinic phase. We formed the ethanol samples by two methods: through the ethanol–helium gel decay and by quick freezing of the liquid down to the liquid nitrogen temperatures. Measurements of small-angle neutron scattering (SANS) of deutorated ethanol samples indicated that this procedure provided nanoparticles of ethanol with the size of the order of $d = 20–30$ nm, relevant in particular for reflectors and thermalizers of slow neutrons [23].

The decay of the nanoparticle gel occurs at temperatures below liquid nitrogen temperatures. As a result we got an amorphous powder, which stayed changeless at time at least half a year in liquid nitrogen. The x-ray measurements were done at the liquid nitrogen temperature, so we are sure that the concentration of the crystalline phase didn't changed for the time of angle scanning. The size of the monoclinic crystallines after phase transitions was 30–40 nm that is close to the estimation from the SANS measurements. So we could conclude that the size of nanoparticles via gel preparation of the powder was of the order of some tens nanometers. At the temperature 110 K at least 90% of amorphous nanoparticles transmute into the crystalline phase for one hour.

The "bulk amorphous samples" of ethanol, prepared by quick cooling of the fluid, demonstrated shifting the temperature of quick crystallization to higher values up to $T \sim 125$ K. The mean size of crystalline particles after transition was rather large (> 60 nm).

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