

# Investigation of dynamic glass transitions and structure transformations in cryovacuum condensates of ethanol

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Received January 23, 2009

IR spectrometric investigation of dynamic glass transition from the rotationally disordered crystal into orientationally disordered crystal of ethanol was carried out. The examples considered are thin films formed from the gas phase at a substrate temperature of  $T = 16$  K. The measurements were performed using the experimental apparatus which has been described in detail in our recent work. The thickness of the sample was  $d = 2$   $\mu\text{m}$ , the typical rate of annealing was approximately 10 K/min. The obtained results are compared with the phase diagram of solid ethanol proposed by M.A. Ramos *et al.* We observe a good agreement between the temperature intervals of existence of amorphous and crystalline states. The low-temperature amorphous phase (12–70 K) is described by the present authors as amorphous solid ethanol by analogy with the amorphous solid water.

PACS: **61.50.-f** Structure of bulk crystals;  
**78.30.-j** Infrared and Raman spectra;  
**78.30.Hv** Other nonmetallic inorganics.

Keywords: IR spectrometric investigation, glass transition, crystal of ethanol.

## I. Introduction

The solid phase of alcohols provides a unique benchmark to discriminate between the roles played by translation, orientation and rotation disorder in solids [1,2]. In particular, ethanol is known to exhibit a very interesting polyamorphism and polymorphism, exhibiting different types of solid state at low temperatures [3–5]. A structural glass (SG) is formed by quenching the supercooled liquid (SCL) below the glass-transition temperature  $T_g$  (Fig. 1). This amorphous state can be achieved using cooling rates higher than  $\approx 6$  K/min. Heating the SG above  $T_g$  (for ethanol  $T_g = 97$  K) leads to the formation of a supercooled liquid and, next, a plastic crystal (PC) or rotator phase (RP), body-centered-cubic, lattice constant  $a = 5.37$   $\text{\AA}$ . The exact temperature for the conversion of SG to PC depends on the warming rate and the initial cooling rate into the glass-state. Once this is formed, cooling below  $T_g \approx 97$  K leads to an orientational glass (OG), or orientationally-disordered crystal (ODC), which preserves the crystal symmetry of the PC, but with freezing of molecular rotations. Especially interesting is the fact that both the ordinary glass transition and the dynamical freezing of PC into OG occur at the same temperature. The fully-

ordered monoclinic crystal (MC) has been obtained by heating the plastic crystal above  $T \approx 116$ –120 K; also, it is possible to obtain it directly by slow cooling of the

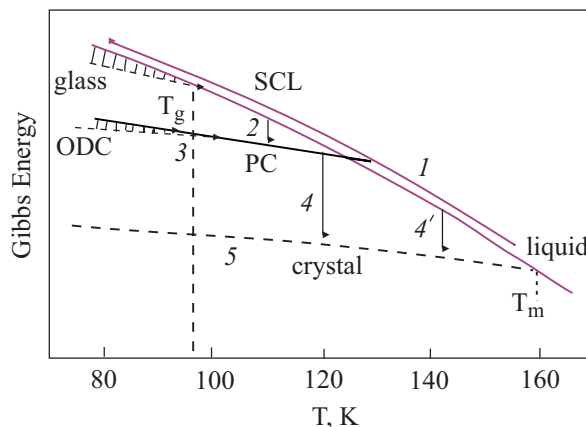


Fig. 1. Schematic phase diagram and thermal routes followed in the experiments. The data and the denotations of states of solid ethanol according to [1,2] are presented: SCL — supercooled liquid; glass — structural glass; PC — plastic crystal (or RP — rotator phase); ODC — orientationally disordered crystal (or OG — orientational glass); crystal — monoclinic crystal (MC);  $T_g$  — glass transition temperature.

supercooled liquid phase. In addition, M. Ramos and coworkers [3] have identified up to four different varieties of the monoclinic crystalline phases depending on the thermal history —  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -modifications.

In spite of the fact that during the last twenty years the alcohols received particular attention, there is a number of peculiarities left unclear. In particular, there is lacking investigation of the solid ethanol obtained during the low-temperature gas phase condensation on the cooled substrate. This method of cryocondensation leads to the formation of different structural modifications of condensed state, both amorphous and crystalline. The question which arises is: what is the extent of similarity between the properties of samples of solid ethanol obtained from the liquid phase and obtained as the result of cryocondensation from the gas phase? What is the glass transition for the samples with the thermal history without the liquid phase? These and other questions had stimulated the studies leading to the results described in the following sections.

## 2. Experiment

As it is well known, IR spectrometric studies of structural and phase transitions in the condensed state are based on the substantial shift of characteristic absorption lines following the transition of the substance from one state to another. In order to demonstrate this, IR spectra of ethanol in the gas, liquid, and solid states are shown in Fig. 2 [6]. The main difference between the spectra is the absence, in the gas phase, of the line ( $3000\text{--}3500\text{ cm}^{-1}$ ) corresponding to the hydrogen bond of the OH bond, the absence (in the liquid phase) of the line in the region  $3680\text{ cm}^{-1}$  corresponding to non-bonded valence O–H vibration, and the presence (in the liquid phase) of the absorption line at  $1680\text{ cm}^{-1}$  corresponding to the deformational vibration of the OH bond.

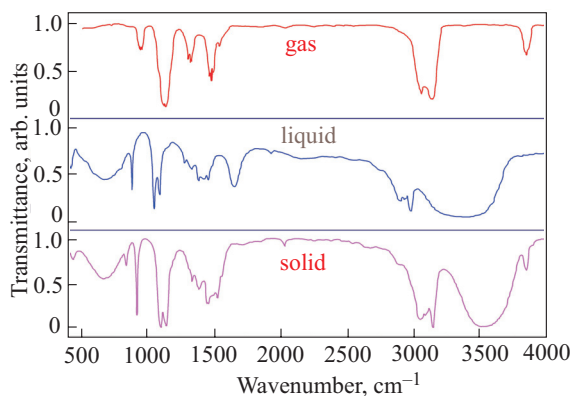


Fig. 2. IR spectra of ethanol in the gas, liquid and solid states [6].

The main absorption lines correspond to the following intramolecular and intermolecular interactions:  $3000\text{--}3500\text{ cm}^{-1}$  — OH bond;  $2700\text{--}3000\text{ cm}^{-1}$  — valent CH bond;  $1400\text{--}1000\text{ cm}^{-1}$  — skeleton vibrations of the C–O–H group, and CH bond;  $700\text{--}1000\text{ cm}^{-1}$  — deformational vibrations of the CH bond. As can be seen from the Fig. 2, the character of the lines strongly depends on the phase state of the sample.

We present here the results of the experimental investigation of thermally stimulated transformations in cryovacuum-condensed films of ethanol ices, formed from the gas phase (we have used pure and dried ethanol with concentration of  $\text{H}_2\text{O}$  0.02%) on the metal substrate at the temperature  $T = 16\text{ K}$ . This state of the solid ethanol enables us to call it amorphous solid ethanol (ASE). The explored temperature interval was  $16\text{--}160\text{ K}$ , which covers the range of both glass phases, as well as the crystal phases. The investigations were performed in the frequency interval  $4200\text{--}400\text{ cm}^{-1}$  using a cryovacuum IR spectrophotometer. A method developed by authors for observing the transformation of the cryoprecipitates at a fixed frequency of the IR spectrometer in combination with thermal desorption was used.

The measurements were performed in an experimental apparatus which has been described in detail in a previous work [7], so that we shall proceed to the description of the measurements themselves (Fig. 3). After the vacuum chamber was evacuated to  $10^{-7}$  Torr, a microcryogenic system was switched on and the substrate (copper mirror, silver-coated surface) was cooled. At the same time, a special slide gate KBr separated the substrate from the main volume of the chamber. This prevented any possible uncontrollable condensation processes. When the substrate temperature reached  $16\text{ K}$ , the working gas pressure of ethanol ( $10^{-6}\text{--}10^{-5}$  Torr) was established in the chamber with the aid of an admitting system. Next, evacuation of the vacuum chamber was stopped, the protective slide gate was moved aside with the aid of a magnetic coupling,

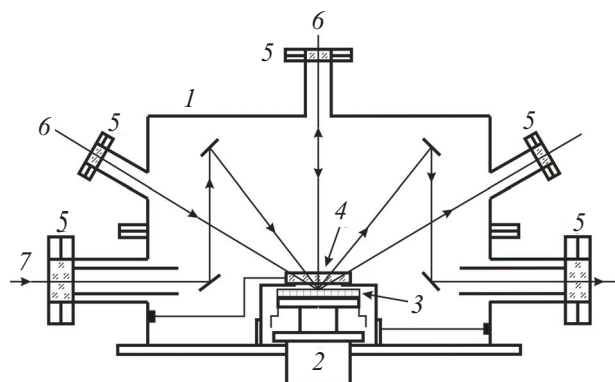


Fig. 3. The experimental setup. The explanations are presented in the text: 1 — case of vacuum chamber, 2 — McMahon microrefrigerator, 3 — protective cowl, 4 — KBr shielding slab, 5 — optical window, 6, 7 — optical guide.

and a double beam laser interferometer was used to measure the refractive index, growth rate and thickness of the film formed from the gas phase.

When the prescribed sample thickness was attained, the admission of gas into the chamber was stopped, a valve was opened, and the vacuum chamber was evacuated once again to the highest possible vacuum. A typical interference pattern of a growing film is displayed in Fig. 4.

### 3. Results

In the majority of previous studies of the structural transformations in solid ethanol the samples were formed from the liquid phase by cooling at very high rates. It were these samples which the diagram corresponds to in Fig. 1. In addition, the authors paid particular attention to the dependence of the final states of the solid phase on the cooling rate. It is obvious that such techniques are limited when applied to massive samples, where the local temperature and the actual cooling rate is left undetermined. In our opinion, this contradiction and limitation is eliminated when we consider thin films with very small condensation rates. This enables us to reach the lowest temperatures of cooling and to be in control of temperature of sedimentation and further thermal variations. Besides the proposed formulation of the experiment it poses the question of thermodynamic correspondence of samples obtained using different routes. In particular, if the glass is the instantaneous thermodynamic snapshot of the supercooled liquid, then what does the glass-state transition of samples obtained from the gas phase correspond to? It was this question that we were trying to answer in this work. The results we obtained are presented in the following paragraphs.

The Figure 5 shows the IR spectra of ethanol cryovacuum condensates of ethanol with film thickness  $d = 0.75 \mu\text{m}$ ,

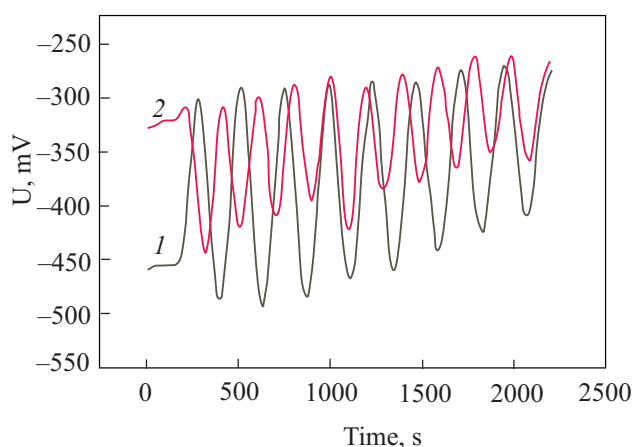


Fig. 4. A typical interference pattern of a growing condensate film.  $T_c = 16 \text{ K}$ ,  $d = 2 \mu\text{m}$ ,  $\alpha$  — the angle of incidence of the rays of the laser interferometer:  $45^\circ$  (1),  $0^\circ$  (2).

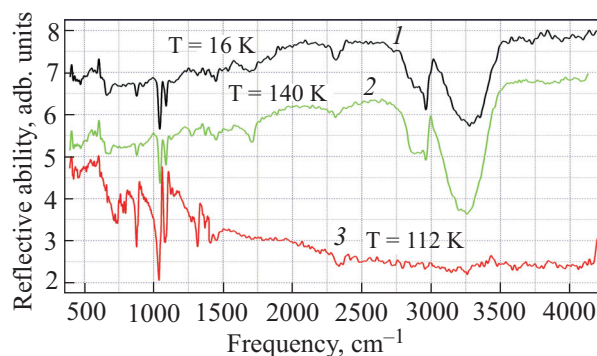


Fig. 5. IR spectra of a  $d = 0.75 \mu\text{m}$  thick film, formed at  $16 \text{ K}$  (ASE), heated to  $T = 112 \text{ K}$  (PC) and  $140 \text{ K}$  (MC).

obtained at the temperature  $T = 16 \text{ K}$  (1), followed by heating to  $T = 112 \text{ K}$  (3) and  $T = 140 \text{ K}$  (2). The pressure of the gas phase during the condensation was  $P = 5 \cdot 10^{-6}$  Torr and the condensation rate no higher than  $1 \text{ nm/s}$ . The main absorption lines correspond to the following intramolecular and intermolecular interactions:  $3000\text{--}3500 \text{ cm}^{-1}$  — OH bond;  $2700\text{--}3000 \text{ cm}^{-1}$  — valent CH bond;  $1400\text{--}1000 \text{ cm}^{-1}$  — skeleton vibrations of the C–O–H group, and CH bond;  $700\text{--}1000 \text{ cm}^{-1}$  — deformational vibrations of the CH bond.

As can be seen from the Figure, the character of the lines strongly depends on the phase state of the sample. This dependence is most expressive for the sample in the state of plastic crystal (3), which is related with the absence of its optical transparency.

The more detailed information about the transformation of the O–H absorption line and C–H valent absorption line in the broad interval is provided by the results shown in Fig. 6. These results were obtained using the following technique. The sample of solid ethanol with the thickness  $d = 0.75 \mu\text{m}$  was condensed under the temperature of  $T = 16 \text{ K}$  at the condensation rate not higher than  $1 \text{ nm/s}$ . This stage was followed by IR spectroscopic measurement in the interval of characteristic frequencies

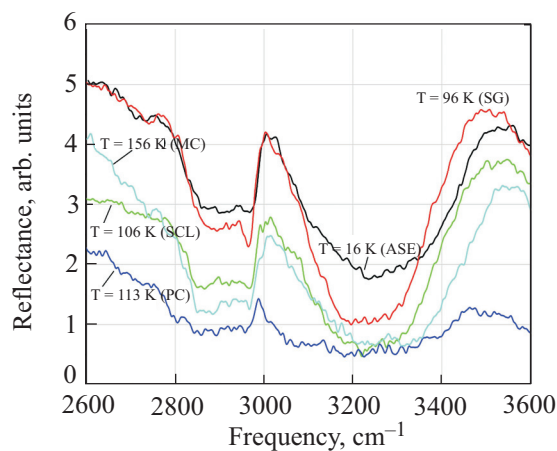


Fig. 6. Vibrational spectra of ethanol films, formed at  $T = 16 \text{ K}$  and in the process of annealing to the temperatures corresponding to the structural and phase states shown in Fig. 1.

of valence CH bond and hydrogen bond, i.e. in the interval from 2600 to 3600  $\text{cm}^{-1}$ . After this, the substrate was slowly heated, with the rate not higher than 1 K/min, accompanied by IR spectroscopic measurement at temperatures depicted in Fig. 5. The annealing process was carried out in order not to introduce additional perturbations in the natural character of thermostimulated transformations in the film. Taking into account the fact that the time spent on measuring the spectra did not exceed 2 min, the temperature change also did not exceed 2 min. The choice of temperatures was governed by the existing knowledge about the structural and phase transformations in solid ethanol [1–4].

Thus, at the condensation temperature  $T = 16$  K the sample is in the amorphous solid state (ASE), which differs from the glass state [5,8]. During the annealing process the amorphous phase transforms into the state of SG. Figure 6 shows the spectra of this state measured at  $T = 96$  K, just before the glass transition.

The transition from the SCL begins at  $T = 98$  K, this state existing up to  $T \approx 108$  K. We think that the measured IR spectrum at  $T = 106$  K corresponds to the sample being in the SCL state. The further annealing leads to the transition from the SCL state to the PC state, corresponding to the spectra measured at  $T = 113$  K. At the temperature  $T = 156$  K, the sample is in the state of MC.

A number of experiments were carried out in order to achieve continuous control over the state of the sample during the process of annealing (Fig. 7). The annealing process was accompanied by the measurements of the intensity of IR absorption at a fixed wavelength ( $\nu = 3150 \text{ cm}^{-1}$ ). The changes of the signal of spectrometer corresponded to the shift of the absorption line of the OH bond due to the structural transformation in the sample in the process of temperature change. It can be seen from Fig. 7 that such method of analysis of thermostimulated transformations in cryocondensates of gases enables one to determine the transformation temperatures to high accuracy. In accordance with the data shown in Fig. 7 and taking into account the existing literature data, we came to the following conclusions on the structural and phase transformations in ethanol films.

The peculiarity within the interval of temperature from 16 to 40 K. Such a peculiar character of the annealing curve is inherent to all experiments. We believe that this temperature interval corresponds to the existence of the highly dense state of amorphous ethanol and the transition to a less dense state at  $T \approx 30\text{--}40$  K. This proposition is based on the analogy with the behavior of low-temperature forms of amorphous solid water [7,9,10].

The increase of the temperature from 40 K to 70 K is accompanied by the processes taking place in the amorphous phase, which can also be interpreted using the analogy with the amorphous solid water. The transition

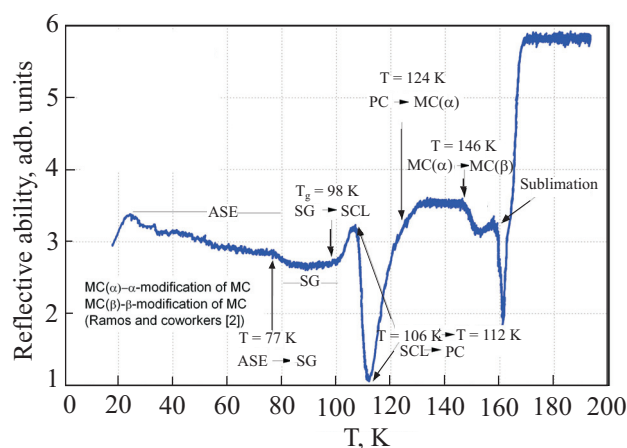


Fig. 7. Changes in the signal coming from the spectrometer at  $\nu = 3150 \text{ cm}^{-1}$  (shift of the absorption line corresponding to OH bond), due to the structural transformations in the samples of ethanol films during the temperature change. Condensation temperature of the sample  $T = 16$  K, film thickness  $d = 2 \text{ }\mu\text{m}$ , temperature change rate  $V = 2 \text{ K/min}$ . MC( $\alpha$ ) —  $\alpha$ -modification of MC; MC( $\beta$ ) —  $\beta$ -modification of MC [3].

encountered at  $T = 77$  K is interpreted by us as a transformation of amorphous ethanol into structural glass. This assumption is based on the fact that the further annealing of the film leads to the transitions which are in good correspondence with [1–5]. These authors used the samples, obtained from liquid phase by fast cooling. In fact, our data beginning at the temperature of glass transition practically coincide with the data coming from the samples obtained from the liquid, which enables us to claim that the peculiarity at the temperature  $T = 77$  K corresponds to the transition of the amorphous ethanol to the structural glass.

In correspondence with the Fig. 7, the structural glass SG transforms into the SCL state at  $T_g = 98$  K followed by the transition to the PC at  $T > 106$  K, which is the intermediate state between the SCL and the state of monoclinic crystal.

The interval of temperatures between  $T = 112$  K and 124 K corresponds to the phase transition between plastic crystal state and monoclinic crystal. In addition, we assume that in accordance with the data from [3], the  $\beta$ -modification of the MC is the initial form, while the peculiarity at  $T = 146$  K corresponds to the transition into the  $\beta$ -modification monoclinic crystal. The sublimation of the sample starts at the temperature about  $T = 159$  K.

A number of experiments were carried out, when the annealing process was accompanied by the measurements of the intensity of IR absorption at a fixed wavelength ( $\nu = 3150 \text{ cm}^{-1}$ ) and measurements of pressure in the vacuum chamber, which was related to the thermodesorption of the residual gases from the samples (nitrogen). These data are shown in Fig. 8. The upper curve characterizes the change of the position of the absorption line

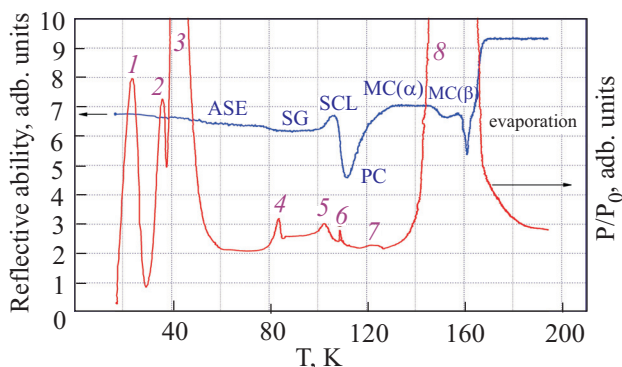


Fig. 8. Variation of the IR spectrometer signal (upper curve) and of the desorption curve (bottom curve) during the heating of the ethanol film. The warming rate was 1 K/min.

corresponding to the OH bond during the process of structural transformation in the samples, and the lower curve corresponds to the reflection of the same processes in the form of the increase of pressure in the chamber as a result of nitrogen desorption.

The peaks 1 and 3 of the desorption curve are related to the evaporation of polylayers and monolayers of nitrogen from the surface of the cryostat, respectively. The peak 8 corresponds to the desorption of the sample itself. The other peaks, probably, are related to the transformations in the film of the solid ethanol. In particular, the appearance of the second peak may be a sign of the existence of the ASE highly dense amorphous phase (in analogy with water). The fourth peak is related to the beginning, at  $T = 78$  K, of the ASE–SG transition. The fifth peak reflects the glass transition at  $T = 98$  K. The sharp peak 6 is related to the formation of the plastic crystal, with further transition to monoclinic crystal (peak 7).

In order to obtain the additional information we carried out simultaneous measurements of the changes in signal coming from the spectrometer at the frequency of  $3150\text{ cm}^{-1}$  and the signal from the laser interferometer during the process of annealing of the films of ethanol cryocondensates. The heating rate was 2 K/min, the film thickness  $d = 2\text{ }\mu\text{m}$ .

It can be seen at Fig. 9 that the processes taking place after annealing on the surface of the sample (laser) and in the volume (IR spectrometer) are in good correlation. Besides, the character of changes of reflection of laser irradiation in the temperature interval corresponding to glass transition from  $T = 98$  K to 102 K reveals that on the surface this transition has a more complex character.

For a more detailed investigation of processes taking place in the temperature interval of glass transition and transition of SCL into plastic crystal, we carried out preliminary studies of relaxation processes in solid ethanol. To this, the film was slowly heated to a corresponding temperature and after that the temperature was stabilized and the time-dependence of the signal coming from the inter-

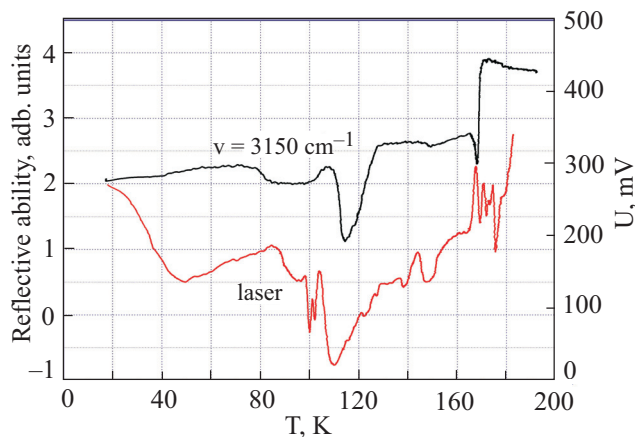


Fig. 9. Changes of the signals obtained from spectrometer at the frequency  $3150\text{ cm}^{-1}$  and the laser interferometer in the process of heating the film of ethanol cryocondensate. The heating rate was 2 K/min, film thickness  $d = 2\text{ }\mu\text{m}$ .

ferometer was measured in vicinity of temperatures corresponding to transformations. These data are shown in Fig. 10. During these measurements, at the temperature  $T = 97$  K, the relaxation process corresponding to a transition from the structural glass to SCL was observed. The total relaxation time was 1840 s. In addition, a new peculiarity was observed at  $\tau = 1480$  s, expressed in the appearance of a local maximum. This peculiarity is in good correspondence with the character of changes in the signals coming from interferometer at  $T = 100$  K.

The next value of the stabilization temperature was observed at  $T = 99$  K, i.e., in the zone corresponding to existence of supercooled liquid. The aim was to determine the degree of stability of SCL. As can be seen from the Figure, during the next 4500 s the state of the sample did not change.

The sample was further cooled to  $T = 116$  K. As can be seen from the Fig. 10, one can observe the intensive process of crystallization of SCL into plastic crystal, which

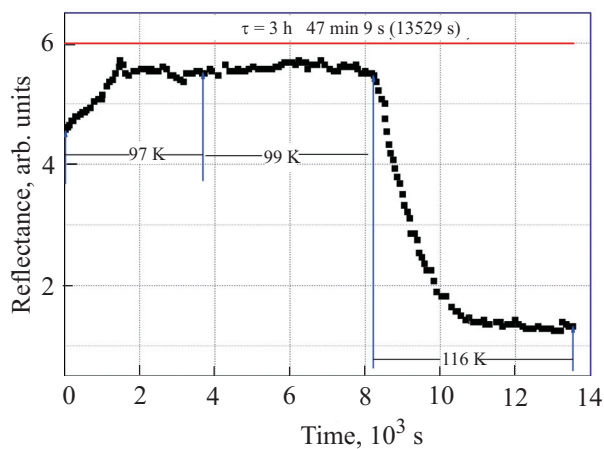


Fig. 10. Relaxational processes in the film of ethanol at fixed temperatures.

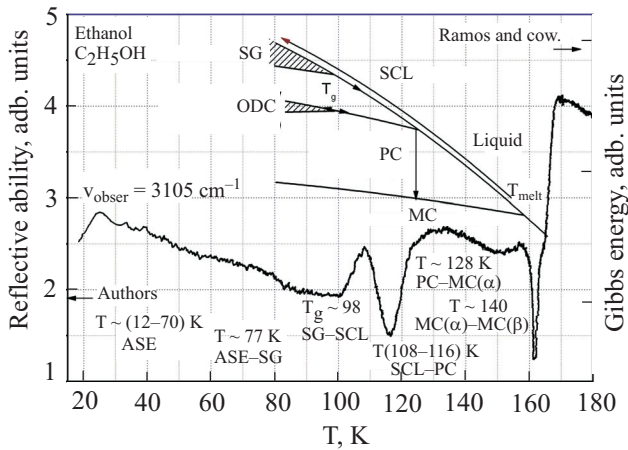


Fig. 11. Characteristic transformations in thin films of cryovacuum condensates of ethanol (lower curve) compared to the results obtained by Ramos et al. [3]

begins after the temperature reaches the point  $T = 116$  K and finishes after  $\sim 2500$  s.

#### 4. Conclusion

1. In general, taking into account the newly observed effects and peculiarities, we come to the conclusion that our results are in good agreement with previously reported data, in particular, the results from [1–5]. For the purpose of illustration and comparison, the phase diagram of solid ethanol obtained from the liquid phase and our data of annealing of samples obtained from the gas phase are shown in Fig. 11.

2. The low temperature condensation of ethanol leads to the formation of amorphous layers. In particular, within an interval of temperatures between 16 and 45 K we

assume that the film of ethanol is in the high density amorphous state (HAD ethanol).

3. At the temperature  $T \approx 78$  K amorphous ethanol transforms into the state of structural glass. From this temperature, followed by further heating, our samples behave similarly to samples obtained from the liquid phase by fast quenching.

4. The combined use of alternative methods of analysis — IR spectrometry, thermodesorption and laser interferometry leads us to conclusion that the transition process of structural glass to supercooled liquid takes place in two stages.

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