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# Crystallization and vitrification of ethanol at high pressures

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We present the high pressure (up to 3 GPa) dielectric spectroscopy study of ethanol in supercooled liquid and solid states. It was found that ethanol can be obtained in the glassy form by relatively slow cooling in the pressure range below 1.5 GPa. Glassy dynamics of ethanol is dominated by hydrogen bonds which cause rise of fragility index with pressure rising and relatively slow increase of glassification temperature. The termination of ethanol glassification at 1.5 GPa is related to the phase transition of ethanol in this pressure range to the disordered crystal structure which allows easy crystallization of ethanol at high pressures. Dielectric spectroscopy of solid phases of ethanol reveals the presence of molecular motion in both of them in the temperature range close to the melting curve but demonstrates different molecular dynamics in the two solid phases of ethanol.

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## I. INTRODUCTION

Ethanol is a very interesting object for study of its phase transformations at high pressures because it is quite simple organic substance with only one hydrogen bond per molecule. Its structural properties can be regarded as intermediate of ones of its two neighbors in homological sequence – model glassformer *n*-propanol on the one hand and methanol on the other which can be obtained in glassy form only in the limited pressure range but has a quite rich phase diagram. Structure determination of material composed of light atoms by direct diffraction methods is very technically complicated especially at high pressures<sup>1,2</sup>. So indirect methods for location of possible phase boundaries (which lately could be refined by the structural studies) are very important in this case.

At ambient pressure ethanol has two crystal modifications. The stable one (with  $T_m=156$  K) has monoclinic structure with *Pc* space group with 4 molecules ( $Z=4$ ) per unit cell<sup>3</sup>. However by combination of fast enough cooling and subsequent annealing at temperatures below 115 K<sup>4,5</sup> leads to formation of disordered metastable crystal phase with *bcc* structure<sup>6</sup> which at further cooling transforms into orientational glass structure. Also moderate cooling rate allows one to obtain ethanol in the form of standard (translationally disordered) glass with  $T_g \approx 95$  K. Interesting to note that the orientational and translational glass has almost the same  $T_g$ . The transformation between these two glasses was extensively studied before<sup>6-9</sup>.

The melting curve of ethanol on P-T phase diagram is quite smooth in the pressure range up to 3.5 GPa which would suggest existence of only one crystal phase in its neighbourhood. However it was found that the high pressure crystal phase at room temperature in the pressure range 1.9-3 GPa is different from the

low-temperature phase stable at ambient pressure. This phase is disordered and was indexed in the  $P2_1/c$  space group with  $Z=4$ <sup>10,11</sup>. The disorder mainly concern the positions of hydroxyl hydrogen and orientation of hydrogen bonds although in both phases hydrogen bonds forms infinite linear chains. The ethanol molecule is non-rigid and it is present in the high-pressure (as well as in ambient pressure phase in two conformations – *trans*- and *gauche*-forms. In the ordered ambient pressure phase these two molecules occupies two crystallographically independent positions in the unit cell, while the crystal analysis of high-pressure phase demonstrates that the single molecular position is statistically occupied by two of this conformations in ratio 3:7 (*trans*-conformation being more stable and more probable). Nothing is known about vitrification of ethanol at high pressures.

The dielectric spectroscopy technique is widely used as supplementary method for phase boundaries determination as well as studying of vitrification in polar substances at ambient pressure, e.g. ethanol<sup>5,12</sup>. However at higher pressures due to the limitations imposed by high-pressure conditions and relative scarcity of other methods, the importance of this method rises significantly. The most striking example is the discovery of ice-IX<sup>13</sup> by means of this technique. However, due to the characteristics of standard cylinder-piston setup, the DS applicability was limited to pressures  $P < 1.8$  GPa. Only recently this range was significantly extended<sup>14-16</sup> by introduction of toroid-type high-pressure device<sup>17</sup>. In this paper we for the first time report the results of vitrification of ethanol at high pressure in the range  $P = 0 - 3$  GPa and discuss how these data are connected with the phase transformations of ethanol in this pressure range.

## II. EXPERIMENTAL DETAILS

In experiments we use pure ethanol dehydrated by the copper sulfate to the concentration 99.3 %. Comparison of DS data collected at ambient pressure (see Fig. 1) with the one reported earlier<sup>8,18-20</sup> reveals no difference of ob-

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tained ethanol with the pure (99.9 %) one. In general we follow the same experimental routine as it was outlined earlier<sup>14–16</sup>. Experimentally accessible frequency window (10 Hz – 2 MHz) and the precision of dielectric susceptibility measurements ( $\Delta\epsilon \approx 0.1$ ) was determined by the device used – QuadTech-7600<sup>21</sup>. The capacitance values were measured before experiment twice in empty and filled with ethanol capacitor, and subsequently these values were used for calculation of dielectric susceptibility at high pressure. “Empty” capacitance readings were about 10 pF. During the high-pressure experiments the variation of thermodynamic parameters in crystal phase was possible only along isobars (with typical rate  $\pm 0.5$  K/min), because otherwise the pressure change would lead to the breakage of the measurement capacitor, so the presented data were exclusively isobaric ones. However the small deformation of measurement capacitor can be expected even in this “mild” regime but the checks of capacitance values after pressure release demonstrated that such deformations were negligible. It was found that the final values of “empty” capacitance are within 5% range of the starting ones. The pressure values during experiments was estimated by the readings of manganin gauge in the liquid phase just prior to the crystallization onset, with typical accuracy of  $\pm 0.05$  GPa. The rate of temperature variation was not strictly controlled, mostly it was determined by the thermal inertia (quite large) of our setup. The typical cooling rate was about  $-0.5$  K/min but the heating rate can be varied in the range  $0.5 - 1$  K/min by the application of external manual heating. The temperature of the measurement cell was controlled by the alumel-chromel thermocouple with precision of 0.01 K. Though we weren’t able to repeat exactly cooling/heating cycle at the same P-T conditions several times in a row, but subsequent measurements in similar P-T conditions produced similar results. Because the heating rate was quite small (in comparison, for example, to the “standard” value of 10 K/min adopted for measurements of glass transitions in DTA/DSC experiments) we didn’t observe significant difference of phase transitions temperatures (from the values reported below) depending on the temperature scan rates. Of course some hysteresis were present in the melting temperatures registered in the cooling/heating cycles (even in the high pressure region) but it didn’t typically exceeds 20 K (it is significantly lower than in the case of high-pressure phases of methanol reported in Ref.<sup>22</sup>). Presented results were collected in the process of several high-pressure experiments on different measurement cells.

### III. VITRIFICATION OF ETHANOL

At ambient pressure dielectric response of ethanol (shown in Fig. 1) in the frequency range 10 Hz – 2 MHz consists of two distinct relaxation processes. Each of the

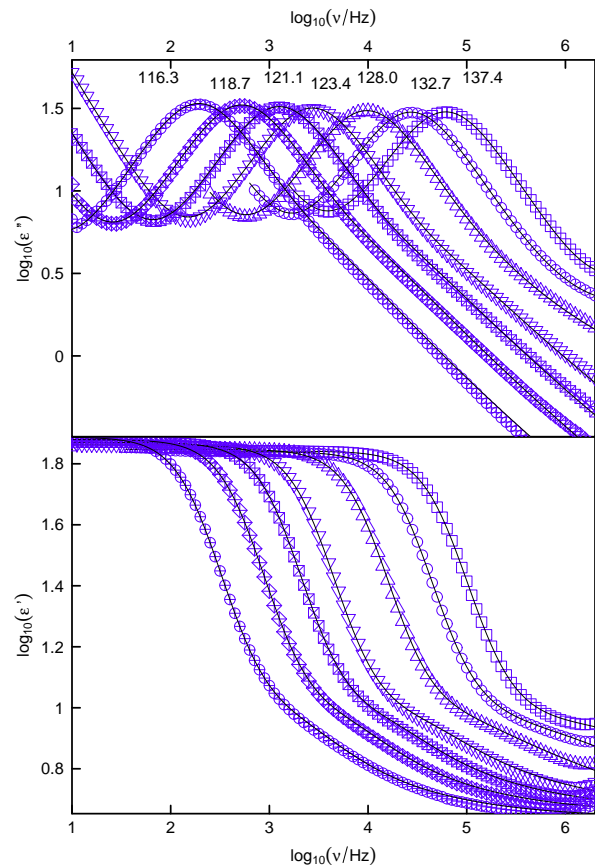


FIG. 1. Structural relaxation in supercooled ethanol at ambient pressure. Temperature values in Kelvins are shown near respective curves. Thin lines are fits based on Eq. (1) (see text).

processes can be fitted by the Cole-Davidson function:

$$\epsilon(\nu) = \epsilon' + i\epsilon'' = \frac{\Delta\epsilon}{(1 + i\nu/\nu_0)^\beta} \quad (1)$$

with additional direct current ( $i\sigma(\nu)/\nu$ ) and high frequency capacitance ( $\epsilon_\infty$ ) contributions. Real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of susceptibility were fitted simultaneously (the target function to be minimized was the squared sum of residuals in both real and imaginary parts of response).

The temperature dependence of characteristic frequency of the main Debye process (exponent  $\beta \approx 0.95$ ) can be well interpolated with the Waterton-Mauro (WM)<sup>23</sup> relation (see Fig. 2):

$$\log_{10}(\nu_0) - \log_{10}(\nu_\infty) = \frac{A}{T} \exp\left(\frac{E}{T}\right) \quad (2)$$

Thus we obtain glassification temperature  $T_g=100$  K (temperature where characteristic frequency is equal to  $10^{-3}$  Hz) and fragility index

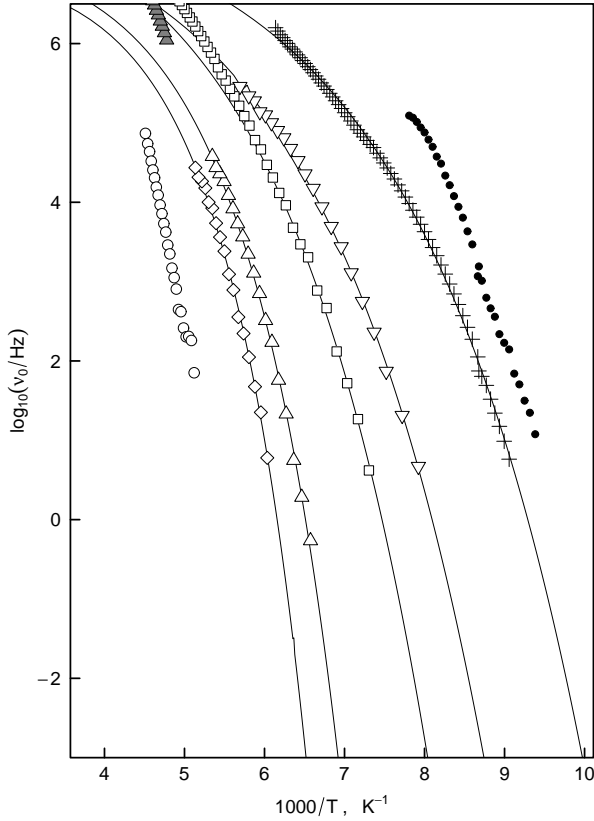


FIG. 2. Temperature dependencies of characteristic frequencies of Structural relaxation in supercooled and solid ethanol at different pressures. Primary  $\alpha$  relaxation:  $+$  - 0 GPa,  $\nabla$  - 0.5 GPa,  $\square$  - 0.8 GPa,  $\triangle$  - 1.2 GPa,  $\diamond$  - 1.5 GPa.  $\bullet$  - secondary  $\beta$  relaxation at 0 GPa,  $\circ$  - structural relaxation in the solid high-pressure phase of ethanol (II) at 2.3 GPa. The grey symbols mark the relaxation frequency of solid phase of ethanol-I at 1.2 GPa. Thin lines are fits according to Eq. (2).

$m_p \equiv d \log_{10} \left( \frac{1}{\nu_0} \right) / d \frac{T_g}{T} |_{T=T_g} = 51$  (measure of “non-Arrheniusness” of glassification process) which is similar to the values reported for the pure ethanol earlier<sup>20,24</sup>. Previously WM equation was applied for interpolation of ethanol data and it is preferable to the more widely used Vogel-Fulcher-Tammann (VFT) law because of non-divergent relaxation times at finite temperatures, more realistic values which approximation of experimental data yields and last but not the least the more robust fitting of experimental data collected in the limited temperature range. For example, the WM equation yields the values  $\nu_\infty$  close to the frequency of dynamic crossover and the values  $E$  (it two-level glassy system this is the energy difference between the energy levels) of several hundreds of kelvins. However if one is interested only in composite parameters of vitrification process – fragility index  $m_p$  and glassifica-

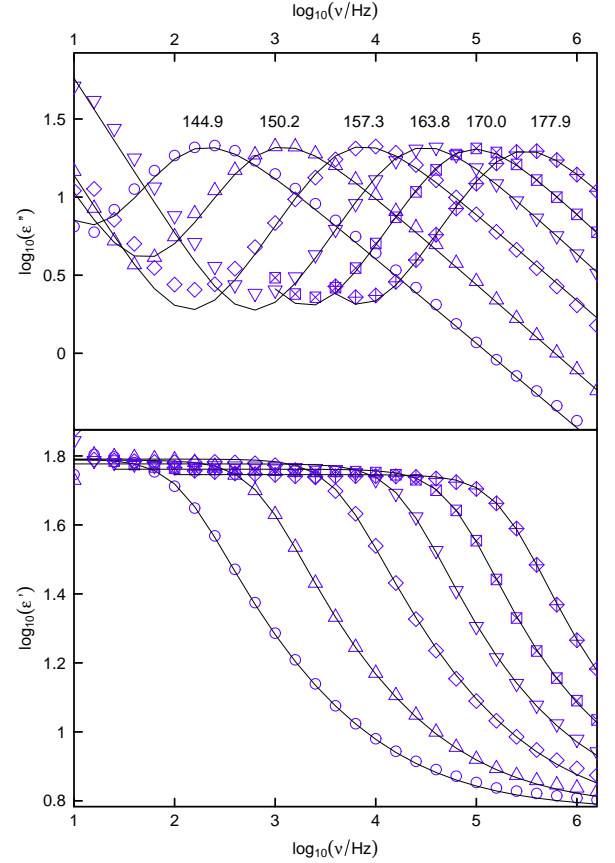


FIG. 3. Structural relaxation in supercooled ethanol at  $P=0.8$  GPa. Temperature values in Kelvins are shown near respective curves. Thin lines are fits based on Eq. (1) (see text).

tion temperature  $T_g$ , then both WM and VFT laws yields approximately similar results. Interesting to note one peculiar feature of ethanol – low characteristic frequency ( $\nu(T_m) \approx 10^6 - 10^7$  Hz) at melting point and consequently the low frequency  $\nu_\infty$  of dynamic crossover – the transition from super-activation dependence to the Arrhenius one at higher temperatures. One practical consequence of that is impossibility to accurately fit all temperature dependence of characteristic frequency of ethanol in the frequency range up to MHz with one formula. So for the fitting procedure the high frequency data above  $10^5$  Hz was left out.

In the pressure range up to 1.5 GPa ethanol can be obtained in the vitreous form by relatively slow cooling. It was also found that ethanol is impossible to glassify by this sort of procedure at pressures above 1.5 GPa and temperature lowering always leads to crystallization of ethanol. However obtained ethanol glass is very unstable and transforms into crystal during heating. The only exception is the pressure range around 0.8 GPa where glass is retained up to the melting point. The crystallization can be detected in our experiment as a large drop (al-

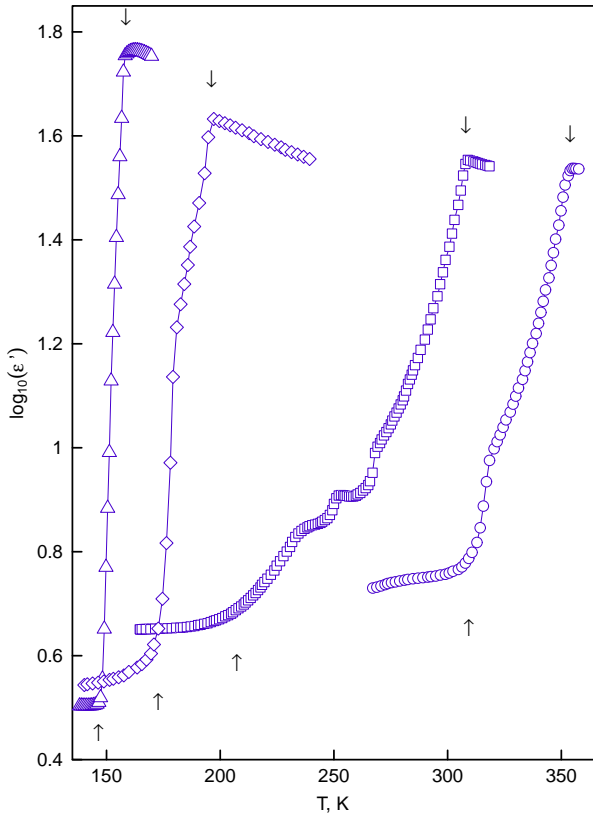


FIG. 4. Dielectric susceptibility of solid and liquid phases of ethanol at different pressures at frequency 300 kHz.  $\triangle$  – 0 GPa,  $\diamond$  – 0.5 GPa,  $\square$  – 2.3 GPa,  $\circ$  – 3.0 GPa. Downward arrows marks melting temperatures, upward – points of crystal lattice “softening”.

most to zero) of relaxation process amplitude  $\Delta\epsilon$ . Similarly the melting temperature also can be registered during subsequent heating as the point where the relaxation process amplitude is restored to the values approximately equal to the ones detected in the supercooled liquid (see Fig. 4). The values of melting temperatures obtained in such a way are shown in Fig. 5. They are quite close to the melting curve taken from Ref. 25.

Pressure rising leads to transformation of the structural relaxation in supercooled ethanol to the single-mode one which can be fitted well by single Cole-Davidson function. This is shown in Fig. 3 where experimental data collected at 0.8 GPa is presented. The similar reduction of relaxation modes is also known for other mono-alcohols for example 2-ethyl-1-hexanol<sup>26</sup> where rising of pressure leads to the decreasing of frequency difference between primary and secondary relaxation so that at pressures above 0.5 GPa relaxation process appears to consist of only one mode. Interesting to note that relaxation in glycerol<sup>14,15</sup> and some other hydrogen-bonded

liquids demonstrate different tendency with pressure rising that is appearance of secondary relaxation at higher pressures. In the case of ethanol we also observed the widening of  $\alpha$ -relaxation and drop of exponent  $\beta$  values from about 1 at ambient pressure to  $\beta = 0.6 \pm 0.05$  at higher pressures. This widening of structural relaxation might indicate that in fact the relaxation consist of more than one mode which we are not able to separate by the fitting procedure. Parameters of vitrification process of ethanol at high pressures are collected in Table I. The pressure rising in the pressure range 0 – 1.5 GPa leads to almost doubling of activation energy  $E$  (from 470 to 985 K) accompanied by a small decrease of dynamic crossover temperature ( $\log_{10}(\nu_{\infty}) \approx 8 \rightarrow 7$ ) and the rise of fragility index to  $m_p = 60 \pm 5$  at  $P=1.5$  GPa. The pressure dependence of fragility index seems to be correlated with the type of bonds present in the studied glassformer: in hydrogen-bonded glassformers (for example glycerol<sup>14,15</sup>) it increases with rising of pressure but in non-hydrogen bonded (like propylene carbonate<sup>16</sup>) it decreases.

From comparison of pressure dependence of glassification and melting temperatures one can conclude that in general the phenomenological ratio  $T_g/T_m \approx 2/3$  is retained (see Fig.5 and Table I). However at pressures below 0.5 GPa where vanishing of secondary relaxation is observed this ratio is violated and the melting curve is significantly steeper than the glassification curve. This means that at this pressure range the characteristic frequency of the relaxation process at the melting temperature rises substantially (from  $\log_{10}(\nu_0/Hz) \approx 5.8$  to 6.2), so viscosity of ethanol according to the Maxwell relation  $\eta = G_{\infty}/\nu_o$  decreases accordingly. One might conclude that lower viscosity prevents vitrification of ethanol at pressures above 1.5 GPa, but it can be shown that (see Table I) the characteristic frequency of the  $\alpha$ -relaxation process at the melting curve remains almost the same ( $\log_{10}(\nu_0/Hz) \approx 6.3$ ) in the pressure range 0.5-1.5 GPa. So this model does not explain abrupt termination of ethanol glassification at pressures above 1.5 GPa.

#### IV. DIELECTRIC RELAXATION IN SOLID PHASES OF ETHANOL

There is certain correlation between vitrification ability of ethanol and its crystal structure. Although the phase boundary between high-pressure and low-pressure modifications is not known, there is experimental evidence<sup>11,27</sup> that it should lay below 1.9 GPa so it is comparable with pressure range 1.5-2.1 GPa where we have detected stopping of ethanol vitrification. Also in this pressure range we observed crossover in dielectric properties of solid ethanol. Although the low-temperature dielectric susceptibility of ethanol is about 4-6 and this value smoothly rises with pressure increasing but in the temperature range close to the melting temperature it increases significantly (see Fig. 4). In Fig. 4 the onset of this increasing which we labeled as “soften-

TABLE I. Parameters of the Mauro-Waterton equation (2) in ethanol at high pressures.

$P$ , GPa	$T_g$ , K	$T_m$ , K	$\log_{10}(\nu_\infty/\text{Hz})$	$m_p$	$E$ , K	$\log_{10}(\nu_0(T_m)/\text{Hz})$
0	100	154	7.85	51	470	5.8
0.5	114	200	7.9	47	495	6.2
0.8	124	213	8.1	49	550	6.4
1.2	144	240	7.25	60	850	6.3
1.5	153	262	7.00	65	985	6.3

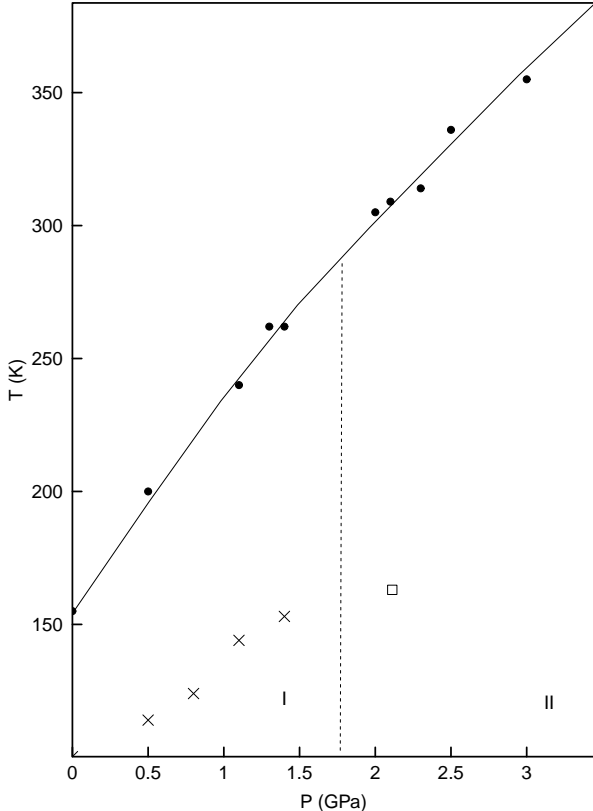


FIG. 5. Phase diagram of ethanol at high pressure.  $\bullet$  – experimental point of ethanol melting,  $\times$  – glassification temperature,  $\square$  – “glassification temperature” of structural relaxation in solid ethanol. Dashed line – the tentative phase boundary between the ambient pressure (I) and the high-pressure (II) solid phases of ethanol. Solid line – melting curve of ethanol according to Ref. 25.

ing” is marked by upward arrows. Another interesting feature of dielectric response of solid phases of ethanol is the presence of strong dispersion and polarization effects in the low-frequency flank of the dielectric spectra especially at high-temperature range close to the melting point (see Figs. 6,7). This means that at high temperatures in the high-pressure and low-pressure phases

there are some disorder in the crystal lattice that lifts the arrest of molecular motion which enables formation of double electrical layer responsible for contact polarization (which manifests itself in  $\varepsilon'(\nu)$  dependence as a low frequency divergence visible in Figs. 6,7). It can be described as a “softening” of ethanol crystal structure due to unfreezing of some molecular degrees of freedom. It can be shown that the relaxation in the solid phase of ethanol-I has the same nature as in the liquid, at least the temperature dependence of characteristic frequency of both follows the same master curve (see relaxation data for  $P=1.2$  GPa in Fig. 2), although the relaxation in the solid phase-I has significantly smaller amplitude than in the liquid.

On the other hand there is qualitative difference in the temperature dependence of the relaxation amplitude in the low-pressure phase (phase-I, Fig. 6  $P=1.5$  GPa) and the high-pressure phase (phase-II, Fig. 7  $P=2.3$  GPa). In the former case temperature decreasing leads to decreasing of relaxation amplitude to zero at about 200 K. In the latter case the decreasing of amplitude is stopped at some level ( $\Delta\varepsilon \approx 4$ ) and subsequent lowering of temperature leads only to the lowering of characteristic frequency of this relaxation. Due to the presence of polarization effects and small amplitude of this relaxation we couldn’t fit it using Eq. (1), but the temperature dependence of characteristic frequency  $\nu_0$  can be deduced from the temperature dependence of maxima on the imaginary part of dielectric susceptibility. This dependence turns out to be Arrhenius one and is shown in Fig. 2. Glassification temperature obtained from extrapolation of this dependence is also compatible with temperature dependence of  $T_g$  deduced from temperature dependence of  $\alpha$ -relaxation in supercooled liquid ethanol (see Fig. 5) which also corroborate our assumption that this relaxation is the same structural relaxation. The similar type of relaxation was also observed in ethanol at higher pressures although there it was significantly smeared by polarization effects so the data does not allow that easy quantification using positions of relaxation maxima.

The different behavior of relaxation amplitude in high-pressure (II) and low-pressure (I) solid ethanol phases can be explained by the presence of structural disorder in the high-pressure phase of ethanol(II). Indeed at the high-temperature region in both solid phases of ethanol some of the molecules are able to effectuate almost free motion dynamically indiscernible from the molecular motion in

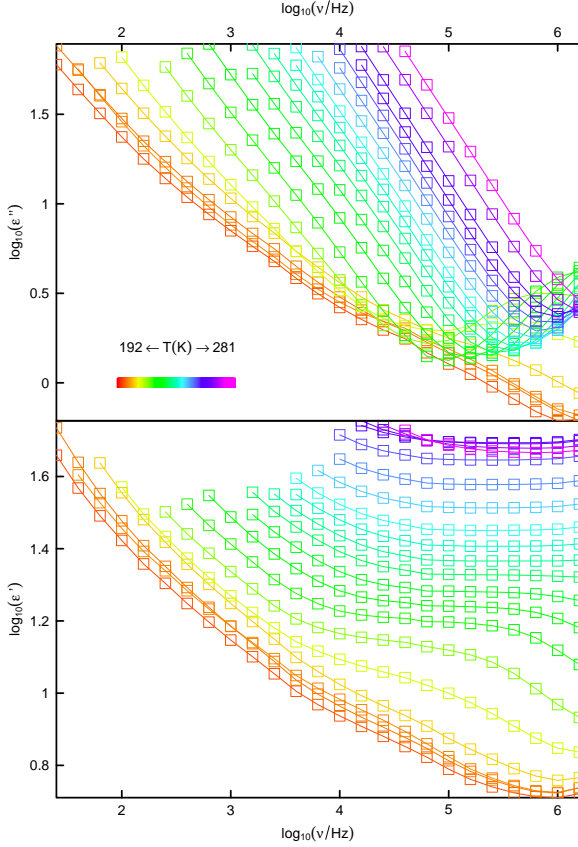


FIG. 6. Dielectric response in high-pressure solid phase of ethanol at  $P=1.5$  GPa in the temperature range 198-281 K.

the liquid. Due to the relatively small number of defects in the solid ethanol-I the amplitude of dielectric response is significantly lower in the solid phase than in the liquid. However in the high-pressure phase of ethanol-II there are another possible type of molecular motion namely the switching between *trans*- and *gauche*-transformation of ethanol at high enough temperature. This type of motion should be frozen in the process of temperature lowering which leads to the formation of *trans-gauche* disorder observed in the solid phase of ethanol-II at room temperature<sup>10,11</sup>.

Interesting to note that the dielectric relaxation in the solid phase of polar compound was observed earlier in acetone<sup>28</sup>. It was also accompanied by the decreasing of characteristic frequency with almost constant amplitude of the relaxation process and was attributed by the authors of Ref. 28 to the presence of defects. However the certain difference should be stressed. In the case of acetone the solid phase is ordered one and consequently the amplitude of relaxation consists of several hundredths of  $\epsilon'$ -unit. In the case of ethanol-II the amplitude of relaxation process is almost equal to that present in the dis-

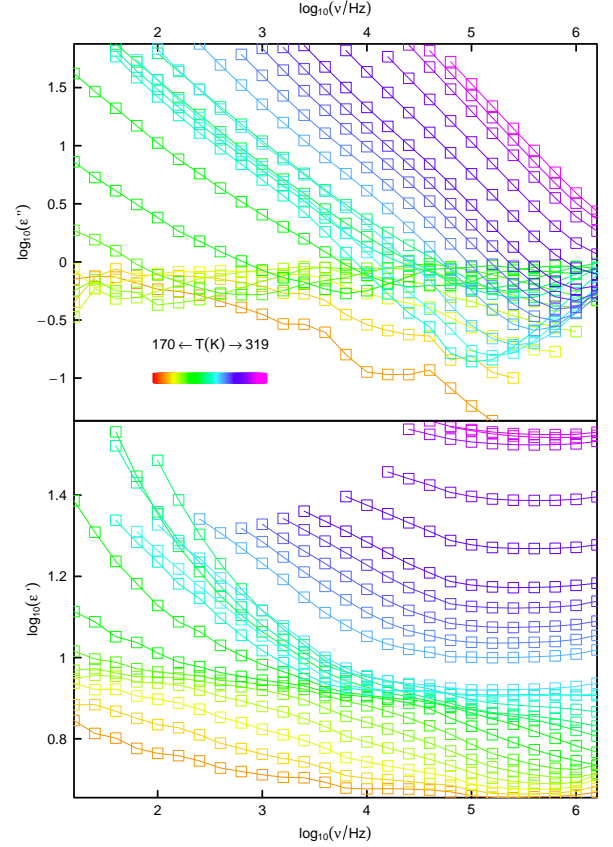


FIG. 7. Dielectric response in high-pressure solid phase of ethanol at  $P=2.3$  GPa in the temperature range 188-317 K.

ordered plastic crystal  $\beta$ -phase of methanol<sup>22,29</sup> with exception that in methanol we deal with true plastic crystal (where the whole molecule rotates) in contrast to ethanol where only part of the molecules moves. Nonetheless both relaxation processes produce approximately similar amplitude of dielectric response. In  $\beta$ -phase of methanol  $\epsilon \approx 4$  (Ref. 29) which is almost the same as in the high-pressure phase of ethanol-II which in our opinion demonstrates the similar type of hydroxyl group motion in both these cases.

## V. CONCLUSIONS

In this work we have determined that under high-pressure conditions ethanol can be obtained in the glassy form. It was found that dynamics of structural relaxation is controlled by the hydrogen bonds which on the one hand causes the increase of fragility index  $m_p$  from about 50 at ambient pressure to about 60 at 1.5 GPa and relatively slow rise of glassification temperature (from 100 to 153 in the same pressure interval). Stopping of ethanol



vitrification at pressures above 1.5 GPa we relate to the phase transition to another crystal form stable at this pressure range which expedites crystallization of liquid ethanol. The difference between ambient-pressure and high-pressure polymorphs of ethanol can also be revealed by dielectric spectroscopy. It was shown that some extent of disorder is present in both phases close to the melting curve but only in the high-pressure form this disorder is retained down to low temperatures. In our opinion dispersion in dielectric response of high-pressure phase is connected with the “switching” of hydrogen bonds in two conformations of ethanol molecules. The absence of ethanol glassification in the high-pressure region can be accounted to the disorder of hydrogen bonds which seems to lower nucleation barrier so nucleation process is significantly faster in the high-pressure phase (II) than in the low-pressure one (I).

## ACKNOWLEDGMENTS

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