Dielectric constant of disordered phases of the smallest monoalcohols: evidence for the hindered plastic crystal phase.

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With gradual temperature increase in premelting regions of solid phase of methanol and high pressure phase of ethanol, and using novel procedure of separation of electrode polarization effects, we are able to register the contribution of relaxation process to low-frequency dielectric constant. This contribution is about half the liquid’s dielectric constant near temperature of solidification, and is almost an order of magnitude higher than reported earlier for ambient pressure phase of methanol. As opposed to dielectric constant of water at ambient pressure, which does not change much during crystallization, our finding indicates the hindrance of molecule rotation in orientationally disordered phases of monoalcohols. Similar dielectric responses of ambient pressure methanol and high-pressure phase of ethanol imply existence of hindered plastic crystal phase of ethanol (not observed at low pressures). We also have found some dynamic disorder in nominally fully ordered phase of these monoalcohols (α-phase of methanol and low-pressure phase of ethanol), the contribution of this disorder being dependent on external conditions (e.g., temperature), and increasing at approaching the order-disorder transition. On the other hand, the amplitude of dielectric response in hindered plastic crystal phases is almost independent of temperature.

I. INTRODUCTION

The concept of plastic crystal was first introduced by Timmermans almost hundred years ago1. It was based on observation, that some molecular crystals with almost globular molecular structure have melting entropy lower than 5 cal/K mole (20.92 J/K mole). This implies that some thermodynamic degrees of freedom (predominantly rotational ones) are already activated in solid phase, thus leading to reduced value of fusion entropy. It was postulated, that high-temperature solid phases of these substances just below the melting curve consist of orientationally disordered molecules, which can freely rotate around translationally ordered positions. Translationaly ordered, but orientationally disordered crystal phase was named plastic crystal. Thermodynamic criterion of plastic crystals was chosen slightly arbitrary, thus, for example, ordinary ice with fusion entropy of 21.97 J/K mole, with hydrogen bonds disorder, does not belong to them. However, thermodynamic notion clearly discerns between molecular substances in which orientational disorder at increase of temperature precedes the onset of translational one (melting).

Crystallographic investigations are more definite and can discern between various types of disorder. While orientational disorder in hexagonal ice persists from 273 K down to helium temperature, orientationally disordered methanol (β-phase) exists in quite limited temperature range – from 175.5 K to 160 K. Moreover, the model predicts different types of disorder in ice and methanol. In ice, hydrogen bonds can switch between four positions in tetrahedrally bonded hexagonal crystal4,5, while, in β-phase of methanol, hydrogen bonds have linear structure (plastic crystal of methanol has anisotropic orthorhombic structure with Cnmc space group6–9 in contrast to highly symmetric hexagonal ice) and can be switched between two positions only. It implies different degrees of hindrance of molecules’ free rotation in the phase of plastic crystal. Crystallographic studies reveal disorder of hydrogen atoms in β-phase of solid methanol, while C-O axis direction being fixed6–9. The remnant of this linear ordering in monoalcohols persists even in the liquid phase which results in difference between characteristic time of dielectric response and structural relaxation10,11. In ordinary ice, on the contrary, only oxygen position is fixed, and the pair of protons can freely select between four bonds with nearby oxygen atoms (so called Bjerrum fault)4,5. Previous dielectric spectroscopy studies have shown that disordered phase of methanol exists till very high pressures (P < 6 GPa, see Fig. 2 a)2, while in ice the pressure increase results in exceptionally rich phase diagram which includes crystallographically different proton ordered and disordered phases. In case of methanol theoretical studies (classical molecular dynamics12 and ab-initio crystal structure prediction13) are of little help, because although they describe more or less precisely the stability region of ordered methanol phases (α and γ), but both unanimously predict metastability of orientationally disordered β-phase, which contradicts experimental observations.

Since hydrogen bond has large dipole moment, the difference in crystal structures (and accompanying disorder) would greatly influence the value of dielectric constant4. Static dielectric constant is sensitive to fluctuations of molecular dipole moment, so with the switches of molecular dipoles its value would be large, while in frozen molecules only induced polarization (an order of magnitude weaker) can contribute to dielectric response (thus leading to low values of dielectric permittivity). In liquid water at 273 K dielectric constant is equal to 81 and slightly increases in solid phase14,15. This implies that almost free rotation of molecular dipoles is practically
Dielectric spectroscopy measurements of ethanol and methanol at ultra-high pressures were carried out in Toroid chamber\textsuperscript{18} according to routine, reported earlier\textsuperscript{19–21}. Experimentally accessible frequency window (10 Hz – 2 MHz) and precision of dielectric susceptibility measurements ($\Delta \varepsilon \approx 0.1$) were determined using QuadTech-7600\textsuperscript{22} device. The values of capacitance were measured twice before an experiment, in empty and filled capacitor, and subsequently used for calculation of dielectric susceptibility at high pressure. “Empty” capacitance readings were about 10 pF. During high-pressure experiments, 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 capacitors. The pressure values during experiments were estimated by the readings of manganin gauge in 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. Typical cooling rate was about $-0.5$ K/min, but heating rate could vary in the range $0.5 – 1$ K/min by application of external manual heating. The temperature of the measurement cell was controlled by alumel-chromel thermocouple with precision of 0.01 K. The results presented were obtained in several high-pressure experiments with different measurement cells. Ambient pressure measurement was carried out using controlled heating/cooling setup and was effectuated with the rate $\pm 0.01$ K/s. The data exported were collected during heating of previously cooled samples.

Complex dielectric response of a substance at frequency $\nu$ can be obtained from specific capacitance $C(\nu)$ and conductivity $\sigma(\nu)$ using the formula:

$$\varepsilon(\nu) = \varepsilon' - i\varepsilon'' = \frac{C(\nu)}{\varepsilon_0} + \frac{\sigma(\nu)}{i2\pi\varepsilon_0 \nu}$$  \hspace{1cm} (1)$$

Physical contribution to this response at low frequencies consists of several inputs, including static ionic conductivity and intrinsic dielectric permittivity of the sample with characteristic relaxation frequency $\nu_0$ and additional constant dielectric permittivity at “infinite” frequency. They are usually described by the respective terms:

$$\varepsilon(\nu) = \frac{\sigma_0}{\nu} + \Delta \varepsilon R(\nu/\nu_0) + \varepsilon_\infty$$  \hspace{1cm} (2)$$

The contact polarization term\textsuperscript{23} is usually modeled with constant phase element with impedance:

$$Z_p \propto (i\nu)^{-n}$$  \hspace{1cm} (3)$$

(where $0 < n < 1$) connected in series with the sample. However, this approximation should not be taken too se-

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FIG. 1. a) Phase diagram of methanol according to Kondrin et al.\textsuperscript{2}. $\beta$-phase corresponds to orientationally disordered methanol phase. b) Phase diagram of ethanol according to Kondrin et al.\textsuperscript{3}. In insets the respective molecules of monoalcohols are shown.

retained in solid phase. On the other hand, dielectric constant of liquid methanol phase is equal to $\approx 75$ near the melting point, but strongly decreases during crystallization (down to 4-6)\textsuperscript{2,16,17}. This implies strong hindrance of free rotation in plastic crystal phase of solid methanol, which is not compatible with crystallographic evidence of almost free rotation of methanol molecules around C-O bond\textsuperscript{6–9}. We argue, that static dielectric constant of methanol in the disordered $\beta$ phase is significantly larger, but corresponds to the low frequency relaxation process, so it almost merges with effects caused by contact polarization processes. Still, in premelting region, we are able to separate these two types of processes. Comparison of obtained dielectric spectroscopy data for methanol with high pressure data obtained for another small-molecule monoaolcohol, ethanol, enables us to suggest the existence of orientationally disordered crystal phase in ethanol at high pressures.

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II. METHODS
viously, because beside strong deviation of dielectric permittivity from constant at low frequency region (which is indeed observed in practice), it also results in unphysical decrease of capacitance in high frequency region. So, one has to provide for a certain cutoff function, able to describe faster fall off of dielectric response at higher frequencies (which is yet to be accomplished). Moreover, this approach is usually applied to liquid samples, and it is not clear if it can describe polarization of the sample in the solid form. This significantly undermines separation of the terms, related to contact polarization, from intrinsic sample relaxation and makes impossible direct fitting of experimental data with the formula proposed. However, since intrinsic relaxation can be described by purely Debye function in monoalcohols at low pressures:

\[ R(\nu/\nu_0) = \frac{1}{(1 + i\nu/\nu_0)} \]  

(4)

it is possible to determine inflexion point on the dependence:

\[ \frac{1}{2\pi\nu} = \frac{1}{2\pi\nu(Z_p + 1/(\varepsilon\varepsilon_0\nu))} = \frac{\sigma_{eff}(\nu)}{2\pi\nu} + i\varepsilon_{eff}(\nu) \]  

(5)

which means that the response of sample and electrode polarization terms, connected in series, is approximated by effective leaky capacitor with frequency dependent conductivity \( \sigma_{eff} \) and dielectric function \( \varepsilon_{eff} \). This inflexion point marks transition from diverging region, induced by electrode polarization effects at very low frequencies, to constant term at somewhat higher frequencies, caused by the sample dielectric relaxation and conductivity. Typical dielectric response, obtained by Equation (5) is depicted in Fig. 2.

Although it is very interesting to separate the frequency input of bulk solid sample from polarization effects, it is well beyond the scope of present paper. Still, gradual application of temperature with simultaneous collection of dielectric permittivity data, applied in our experiments, helped us to successfully separate these two inputs in premelting temperatures range. This topic will be thoroughly discussed later on in Section IV. However, we should stress once more, that our “continuous heating” approach is very different from previous works on methanol and ethanol, where frequency scans at fixed temperature were used.

III. DIELECTRIC SPECTROSCOPY OF METHANOL

Dielectric relaxation of methanol at ambient pressure at scans with constant rate along temperature and frequency is presented in Fig. 3 (the scans were collected at heating of previously crystallized sample). Another presentation of the same data, as slices at fixed frequencies, is shown in Fig. 4. The main conclusion that can be drawn from these data is, that freezing of methanol (at 180 K) leads to significant drop of dielectric constant \( (\varepsilon') \). Still, in solid phase of methanol, dielectric response is frequency dependent, so the notion of dielectric constant in this case needs some clarification. Large increase of dielectric constant at frequencies below 1 kHz is due to contact polarization and can be regarded as parasitic effect. This effect is also temperature dependent, and the onset of contact polarization frequency is increased to 10 kHz near the melting temperature. Still the dispersion observed in the frequency range 10 kHz-2 MHz can be considered as intrinsic and connected to relaxation of the solid, orientationally disordered methanol (\( \beta \)-phase). The presence of disordered beta phase in methanol persists till very high pressures (at least up to 6 GPa).

FIG. 2. Effective dielectric function, caused by polarization effects. Downward and upward arrows mark inflexion points due to the onset of deviations, caused by electrode polarization effects in low frequency and high-frequency region respectively. The sample was modeled, as element with constant conductivity and capacitance (equal to 1). Polarization impedance was approximated as constant phase element with exponent 0.7. Dashed horizontal line marks position of “apparent” static dielectric constant of the sample (it is slightly less than the true one).
FIG. 3. Dielectric response of methanol at ambient pressure at specified temperatures.

temperature α-phase of methanol, which is accompanied by the drop of high frequency $\varepsilon'$ from 7.7 to 3.9. This is in $\approx 1.5$ margin corresponds to the results of Denney and Cole\textsuperscript{16} (they report dielectric response in the disordered phase of methanol in the range 4-6 at 5 K below the melting temperature and fast increase of dielectric permittivity at approaching the melting temperature). Nonetheless, in the intermediate temperature region corresponding to the β-phase, dispersion of dielectric response is observed, which can not be attributed to contact polarization. It manifests itself as distinct step on the frequency dependent response of $\varepsilon'$ (see Fig. 3). This step shifts to lower frequencies with the decrease of temperature (Fig. 3). Extrapolating this frequency dependent response to low frequency region, we would get static dielectric permittivity, approximately equal to $\varepsilon_S = 38.9$. Further lowering of temperature results in transition to fully ordered phase, where amplitude of low-frequency relaxation process drops to zero. It should be noted that the similar behavior in methanol below the melting temperature was observed in the work of Denney and Cole\textsuperscript{16}. They carried out experiments in setup with significantly larger separation of electrodes ($\approx 1$ mm vs. 0.1 mm in our case) so in their setup influence of electrode polarization effects should be lower and restricted to lower frequencies. Still, they report observation of dielectric dispersion in the range below $10^5$ Hz which they attributed to the intrinsic dielectric response of the sample. They also report significant deviation of the dielectric response depending of the thermal history, which can be due to the anisotropic character of the solid phase (which the authors of Ref.\textsuperscript{16} seems to support) but as well to electrode polarization in the solid phase.

Near the melting temperature the amplitude of this relaxation rapidly increases (up to values $\varepsilon_L \approx 70.8$) which is also accompanied by rapid increase of frequency of corresponding relaxation process. Thus, relaxation process rapidly moves out of the experimental frequency window and dielectric response of the liquid methanol is characterized by constant, but very high dielectric permittivity caused by fast free fluctuation of molecular dipoles\textsuperscript{16,17,24}. It is interesting to note, that the amplitude of dielectric process is increased by the value approximately equal to $2 \left( \varepsilon_L - \varepsilon_\infty \right) / \left( \varepsilon_S - \varepsilon_\infty \right) = 2.02$. We argue, that this increase is connected to increased hindrance on the molecules’ free rotation in liquid and the solid β-phase of methanol.

In the following we will need some model of dielectric relaxation in monoalcohols. It is known to consist of two processes –the larger effect observed at low frequencies
is Debye relaxation (at ambient pressure relaxation can be well approximated by the Debye relaxation law) and the weaker, high frequency one, called structural or \( \alpha \)-relaxation. It is interesting to note, that in more complex (in comparison to methanol) monoalcohols, the frequency of this weak relaxation usually corresponds to processes, which govern thermodynamic and structural properties observed at e.g. vitrification of monoalcohols\(^{31,25} \). Thus, despite its weakness in thermodynamic response, it is more important in description of molecular dynamics of monoalcohols. Although in application to methanol, exact P-T evolution of the Debye- and \( \alpha \)-relaxations is not well known (which is mostly due to the fact, that methanol vitrifies only at high pressures\(^{2,20} \) where precise spectroscopic techniques are not possible), but our findings suggest that, separation into these two process exists in methanol too. It can be concluded also from the experimental data of Barthel et al. and Fukusawa et al.\(^{27,28} \) where at room temperature the separation between the Debye relaxation process and the next in frequency (presumably \( \alpha \) one) reaches almost one decade (3.09 Ghz and 22.4 Ghz respectively).

To make this model more tractable, we propose simpli-
As it follows from Equations (2,3,4) in the low-frequency region (where the input of this two contributions is approximately equal) the relaxation part and constant current conductivity can be described as leaky capacitor with frequency independent dielectric constant \( \varepsilon \) and conductivity \( \sigma \). The impedance of such element is given by the formula:

\[
Z(\nu) = \frac{1/\varepsilon}{\sigma/\varepsilon + i2\pi\nu} = \frac{A}{B + i\omega}
\]

(6)

I maginary part of this formula has distinct peak-like shape. The peak maximum is located at \( \omega = B \) and its maximum reaches the value \( \frac{A}{2\pi} \). It turns out (as it will be demonstrated below) that the value of this maximum (in the vicinity of the maximum) is significantly higher than the impedance caused by electrode polarization effects given by the Eq. (3) by almost order of magnitude. So, determination of the value and position of this maximum would allow us to determine the static conductivity and the low-frequency dielectric constant of the sample itself.

The experimental dielectric response of methanol converted into impedance values at several fixed temperatures in vicinity of the melting region and \( \alpha - \beta \) phase transition is depicted in the main panel of Fig. 6. Aforementioned maximum on frequency dependency of impedance is evident in all these curves. Moreover, in the high temperature limit (in the liquid state and just below liquid-\( \beta \) phase transition) it is possible to separate the input to overall dielectric response from the sample itself and the electrode polarization effects. In the liquid state this enables us to fully deconvolve the dielectric response into these two inputs. This yields the exponent \( n \) of electrode polarization of methanol in the liquid state which has the value \( n = 0.81 \). Variation of temperature influences both electrode polarization and the sample dielectric response but from position of local maximum we can extract data on the temperature dependence of static dielectric constant near the melting temperature. This data is depicted in inset in Fig. 6.

First of all, from this data it follows that the “naive” separation of constant \( \varepsilon \) pertinent to the sample’s bulk by simply ignoring divergent tail pertinent to the electrode polarization effects really works under condition that the dielectric constant of the sample is large enough (like in the liquid and the solid disordered \( \beta \)-phase of methanol). Both approaches yield approximately equal values of dielectric constant: \( \varepsilon \approx 70 \) for liquid state and constant (independent of temperature) \( \varepsilon \approx 35 \) in the disordered \( \beta \)-phase. However, the application of this procedure to the ordered \( \alpha \)-phase produce rather unexpected result. It turns out that the dielectric constant at \( \alpha - \beta \) transition drops to rather large value \( \approx 15 \) but further diminishes at the temperature lowering (and reaches the value of \( \approx 7 \)). This suggests that the dielectric constant in the fully ordered phase of methanol increases when the temperature approaches the order-disorder phase transition in the solid state. So, this means that some amount of dynamic disorder is present even in the nominally fully ordered phase in the vicinity of phase transition and temperature rising increase the amount of this disorder. The similar behavior is observed in the low-pressure solid phase of ethanol in vicinity of melting temperature which will be discussed in the next Section V.
FIG. 7. Experimental dielectric relaxation in liquid and solid low-pressure phases of ethanol at 0.5 GPa.

V. DIELECTRIC SPECTROSCOPY OF ETHANOL AT LOW PressURES

Ambient pressure solid phase of ethanol (marked as I in Fig. 2 b) can by no means be considered as orientationally disordered. Beside crystallographic evidence, it does not by large margin satisfy Timmerman’s criterion (its fusion entropy is equal to 31 J/K mole). Similar conclusions can be derived from dielectric spectroscopy experiments at ambient pressure, where transition from $\varepsilon'$ values equal to 75 at the melting temperature to 4-5 in the fully solidified samples. The last value of dielectric permittivity is compatible with the notion of induced polarization of ethanol molecules with fully arrested molecular motion.

It is worth noticing, that our dielectric spectroscopy experiments suggest presence of slight orientational disorder in the vicinity of the melting temperature at ambient pressure (which resembles the onset of disorder in fully ordered $\alpha$-phase of methanol while approaching $\alpha-\beta$ phase transition). Still the overall behavior of dielectric relaxation is quite different from the methanol case int he premelting region and we can not designate distinct temperature region, in which ethanol transforms into disordered state. Since the ethanol easily vitrifies upon cooling at low pressures, it is easy to register both Debye and $\alpha$-relaxation processes, being in experimentally attainable frequency range. However, glassy state of ethanol is unstable and crystallizes upon heating (the cold crystallization). Upon heating near the premelting region the disordering of ethanol crystal phase takes place, which manifests itself in gradual increase of dielectric permittivity in the low frequency region. The example of such a relaxation is shown in Fig. 7. This dielectric response in this temperature region is also frequency dependent and its extrapolated characteristic frequency slightly below the frequency of the Debye relaxation collected in the glassy/supercooled liquid state (see Fig. 8, where the data observed at elevated pressure $P = 0.5$ GPa are presented). The characteristic frequency of relaxation process in glassy and solid phases of ethanol is obtained by simultaneous fitting of real and imaginary part of dielectric response by simply ignoring polarization effects according to Equation 2 with relaxation part described by Equation 4. This quite matches the model
FIG. 9. Temperature dependence of ethanol dielectric permittivity in the low (P=0.5 GPa, red curves) and high pressure (P=2.5 GPa, blue curves) phases. Various symbols correspond to different frequencies (○–100 Hz, □–1 KHz, ♦–10 kHz, ▽–100 kHz, △–1 MHz). Dashed vertical lines mark onset of melting temperature. Downward arrow marks transition from the high-pressure ordered phase to high-pressure orientationally disordered phase accompanied by the increase of dielectric permittivity.

proposed for description of relaxation in methanol but with very small downshift of characteristic frequency during solidification. Still we would stress once more, that the amplitude of this relaxation process monotonously depends on temperature and one can find no kinks on the temperature dependence of low-frequency dielectric permittivity which could be ascribed to phase transitions to disordered high-temperature phase (see Fig. 9). The amplitude of dielectric response gradually increases with temperature, approaching the melting transition.

However, with crossing the pressure where the phase transition into high-pressure crystal phase takes place, the dielectric response of solid ethanol drastically changes. We consider this change as the evidence, that high pressure phase of ethanol near premelting region is in the state of hindered orientational disorder similarly to β-phase of methanol. However the similarity between these two phases require further investigation which will be carried out in the next Section VI.

FIG. 10. Experimental dielectric relaxation in the liquid and solid high pressure phases of ethanol at 2.5 GPa.

VI. DIELECTRIC SPECTROSCOPY OF ETHANOL AT HIGH PRESSURES

Drastic difference between the high pressure and low-pressure crystal phases of ethanol (obviously beside their different crystal structures\(^\text{12}\)) is that by cooling from the liquid we can not obtain glassy state in the pressure region of high pressure phase stability (above 2.1 GPa)\(^3\). Stability region of high pressure phase of ethanol is marked as II in Fig. 2 b). However, we will demonstrate, that beside that, there is also difference in dielectric response of high pressure crystal phase, which is not observed in the low pressure phase but makes the former similar to disordered methanol phase.

In Fig. 10 typical example of dielectric response collected at pressure $P=2.5$ GPa is shown. In solid phase on the panel corresponding to real part of dielectric response the distinct step-like feature is evident. Amplitude of this feature is independent of temperature (while its characteristic frequency is increased with temperature rise). We can evaluate relative amplitude of this feature in respect to dielectric response of liquid ethanol as \(\frac{(\varepsilon_L-\varepsilon_\infty)}{(\varepsilon_S-\varepsilon_\infty)} = (48.9-7.4)/(31.6-7.4) = 1.7\). Still we observe, that the ratio is close to 2 (as in methanol) but substantially lower. In our opinion, this discrepancy
can be connected to the significant hindrance of ethanol rotation in liquid phase, where longer hydrogen bonded threads might be present. There is also a quite different behavior of dielectric permittivity at fixed frequencies in comparison to the data, collected at low pressures (see Fig. 9). At these high-pressure slices a quite distinct kink (marked with arrow) is observed. which demarcates premelting region of high dielectric permittivity from low temperature range, where low values of dielectric constant are observed. So in the premelting region, (which spans \( T = 288 - 335 \) K range) dielectric response of solid ethanol resembles that of \( \beta \)-phase of solid methanol with constant (independent on temperature) value of static dielectric permittivity and high values of high-frequency dielectric constant \( \varepsilon_\infty \). It is possible that these high-pressure phase of ethanol is similar to the orientationally disordered metastable form of ethanol with \( fcc \) structure which is produced by special cooling treatment at ambient pressure.\(^{35-38} \) In this metastable phase it was also found that the dielectric relaxation process is also diminished by two times at temperature lowering during transition to the orientational glass state.\(^ {37,39} \) This might indicate that the orientational disorder in this state also has hindered character.

We argue that the stability region of this partially orientationally high-pressure disordered phase is higher in temperature than the stability region of fully ordered phase II investigated by synchrotron radiation by Allan et al.\(^ {32} \) at 2.75 GPa and room temperature. According to our high-frequency dielectric spectroscopy data the transition to the fully ordered phase takes place at temperatures 288 K at 2.5 GPa (marked by arrow in Fig. 9) and 318 K at 3 GPa.\(^ {3} \) So it is highly likely that measurement of Allan et al.\(^ {32} \) were carried at temperatures just below the transition into fully ordered phase of ethanol, so the lowering of pressure below 2.5 GPa at room temperature (but above 2.1 GPa) would result in transition into hindered plastic crystal phase of ethanol.

VII. DISCUSSION

So far we have demonstrated, that some sort of disorder present in crystal phases of methanol and ethanol leads to significant increase of dielectric constant. Moreover, it was found, that in orientationally disordered phase of methanol and high-pressure-high-temperature phase of ethanol it can lead to the values of dielectric constant as high as several tens of \( \varepsilon \). The value of this constant practically does not depend on temperature, only characteristic frequency of relaxational process giving rise for such a large value of dielectric permittivity decreases with lowering the temperature. However, common feature of all these phases is that the dielectric constant being approximately two times less than that of liquid in the premelting temperature region. We consider this an indication of hindered molecule rotation in orientationally disordered phases in comparison to liquid phase, and of the fact that in disordered crystal phase molecule’s rotation is not free. We proposed to call such phases as hindered plastic crystals.

Further lowering of temperature induces transition of these plastic crystal phases into fully ordered ones. So, the temperature stability region of hindered plastic crystal phases is not large and spans 10-20 K. In fully ordered phases at temperatures far from order-disorder transition the dielectric constant is small (below 10) which indicates full extinguishing of relaxational process of molecules as a whole and is likely to be caused by induced polarization only. Beside low temperature phases of hindered plastic crystal the low pressure phase of ethanol is also fully ordered one. However, near the order-disorder transition we observe the increase of dielectric constant, which indicates thawing of rotational molecular degrees of freedom. So, fully ordered phases of lower-weight monoalcohols differ from hindered plastic crystal phases not only in characteristic frequency of relaxational process, giving rise to large dielectric constant depends on temperature but its amplitude too.

It is interesting to compare dielectric response of hindered plastic crystals of ethanol and methanol to that of classical example of plastic crystal monoalcohol – cyclooctanol (with entropy of fusion as low as 6.98 \( J/(K \text{ mole}) \)). Its dielectric properties were investigated in number of works (see e.g. the works). In contrast to high-pressure phase of ethanol and \( \beta \)-phase of methanol, dielectric constant of cyclooctanol does not decrease, but slightly increases during freezing of liquid phase.\(^ {43} \) This is accompanied with slight decrease (less than one order) of characteristic frequency of relaxational process.\(^ {14} \) So, this indicates that in contrast to methanol and ethanol, rotation of cyclooctanol molecule in plastic crystal phase is practically free. In this respect it resembles ordinary hexagonal ice. However, in our opinion, the cause of absence of hinderance of molecular rotations in cyclooctanol is different and may be due to the presence of large molecular “tail” of cyclooctanol. Interaction of these tails prevents formation of more tightly bound hydrogen-bonded chains in plastic crystal phase of cyclooctanol. So, in crystal phase of cyclooctanol there is no definite direction, along which the hydrogen bonds can align.

There is another similarity between water and cyclooctanol in regard of their transition into fully ordred phase. Hexagonal ice is notorious for difficulty of proton ordering at low temperatures, and it usually requires addition of external components (like ionic salt LiCl) to facilitate it. Similar situation is true for cyclooctanol, where orientation disorder tends to “vitrify” in process of lowering the temperature. It is definitely opposite to ethanol and methanol, where hindered plastic crystal phases exist in very limited temperature range. How it can be connected with the hindrance of molecular rotation, is the question yet to be resolved.
VIII. CONCLUSIONS AND FINAL REMARKS

Our first main conclusion is that static dielectric permittivity of methanol in orientationally disordered $\beta$-phase is significantly higher than supposed before. Our measurements in the premelting region suggest, that in disordered solid phase of methanol, relaxational process typical to reorientation motion of molecules still exists, but significantly shifts to the low frequency region. Due to the hindered motion of molecules in this solid phase in comparison to almost free motion in liquid phase, the amplitude of dielectric relaxation in solid $\beta$-phase of ethanol is almost twice lower, than relaxation amplitude in liquid phase near melting temperature. This is different from ordinary ambient-pressure water, where dielectric relaxation shift to the low-frequency region upon crystallization is not accompanied with lowering of amplitude of dielectric relaxation in solid phase of ethanol relative to one observed in liquid phase is close to two, but substantially lower (approximately equal to 1.7). We believe, that the decrease of this coefficient indicates somehow hindered motion of ethanol molecules in high-pressure liquid phase, compared to methanol.

We should also mention that these results were only possible due to our experimental setup which allows us to collect dielectric response during simultaneous heating and scanning the frequency. Also there was significant breakthrough in data processing procedure that enables us to separate electrode polarization effects from the dielectric relaxation of the sample in the low frequency region and unambiguously establish the value of static dielectric constants in the solid phases of ethanol and methanol.

We argue, that the phase similar to hindered plastic crystal phase of methanol exists at high pressures in another small-molecule monoalcohol - ethanol too. Low pressure phase of ethanol is obviously ordered, but application of high pressure (above 2.1 GPa) and temperatures leads to orientational disordering of its molecules. We have found, that amplitude ratio of relaxational process observed in solid high-pressure high-temperature phase of ethanol relative to one observed in liquid phase is close to two, but substantially lower (approximately equal to 1.7). We believe, that the decrease of this coefficient indicates somehow hindered motion of ethanol molecules in high-pressure liquid phase, compared to methanol.

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