

On the phase diagram of polymorphic ethanol: Thermodynamic and structural studies

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Abstract

It is well known that ethanol exhibits a very interesting polymorphism presenting different solid phases: a fully-ordered (monoclinic) crystal, a (bcc) plastic crystal, which by quenching becomes an orientationally-disordered crystal with glassy properties (hence sometimes named '*glassy crystal*'), and the ordinary amorphous glass. We have carried out calorimetric, X-ray diffraction, and Brillouin-scattering experiments above liquid-nitrogen temperatures and have found several new features that shed more light on the rich and interesting phase diagram of ethanol. Firstly, we have identified up to four different varieties of the monoclinic crystalline phase depending on the thermal history. We also present new specific-heat data of these glassy and crystalline phases below the glass transition temperature up to the melting temperature. Furthermore, we have unexpectedly found that the amorphous phase can also be obtained by the unusual route of a very slow cooling of the liquid in some particular experimental set-ups, evidencing the heterogeneous character of the crystallization kinetics of these molecular glass-formers.

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1. Introduction

The complex behavior of viscous liquids and the dramatic slowdown in their relaxational processes when approaching the glassy state, as well as the very nature of the glass transition itself, have been recognized as probably the deepest and most interesting unsolved problem in condensed matter physics to be addressed in this new century [1]. One of the central issues to be solved is the so-called Kauzmann paradox [2], which emphasized the existence

of a conflictive temperature (the Kauzmann temperature), where the excess entropy of the supercooled liquid relative to the crystalline one would extrapolate to negative values, had not intervened the kinetic glass transition.

Molecular liquids (organic substances that are liquid at room temperature) are very interesting systems to study, since they often present accessible temperature–time ranges to obtain them in both crystalline and glassy phases. In several cases, they also offer the existence of plastic-crystalline (PC) phases [3] (i.e., crystals with rotational disorder in the molecules and low enthalpy of melting) which can become orientationally-disordered crystals (ODC, often also named *glassy crystals* [4]) when cooled below a dynamical freezing transition temperature.

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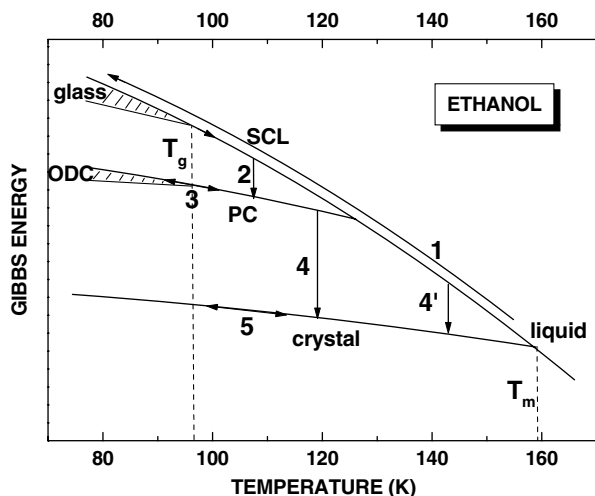


Fig. 1. Schematic phase diagram of ethanol and thermal routes followed in the experiments. SCL: supercooled liquid; PC: plastic crystal; ODC: orientationally-disordered crystal.

In particular, ethanol is a unique case [5], since it is feasible to obtain it in several different solid phases [5–9] depending on the thermal history (Fig. 1 and Ref. [10]): as fully-ordered (monoclinic [11]) crystal; as conventional (amorphous) glass below $T_g \approx 97$ K by quenching the supercooled liquid faster than -30 K/min [5]; as (bcc [6]) plastic crystal by cooling the liquid at an intermediate rate (a few K/min); an ODC or *glassy crystal* is obtained by quenching this plastic crystal also below $T_g \approx 97$ K [5]. Hence, this well-known substance provides a unique benchmark to discriminate between the roles played by translational, orientational and rotational disorder in solids [6–9]. Indeed, ethanol is one of the six glass-formers which appeared in the famous Kauzmann's work [2]. Very interestingly, the 'glass transition' of ethanol presented by Kauzmann in 1948 – using the earlier, available data by Parks et al. [12] – corresponded to the dynamical freezing from the plastic crystal of ethanol into the orientationally-disordered crystal, instead of the true liquid-glass transition, without anybody could notice the unintentional 'fraud'. This proves how similar are – even quantitatively – both transitions, the dynamic departure from ergodicity seemingly being the common key factor. Moreover, ODC of ethanol (and of other substances) exhibits [7–10] the universal behavior found in low-temperature properties and low-frequency dynamics of glasses, hence the nickname *glassy crystals*.

After describing some experimental details of our calorimetric, X-ray diffraction, and Brillouin-scattering techniques concurrently employed above liquid-nitrogen temperatures, we will present and discuss in this work new experimental findings on the phase diagram of ethanol. On the one hand, the existence of four different phases of the stable (monoclinic) crystalline state. On the other hand, we will show how strongly the critical cooling rate to obtain glassy ethanol depends on the experimental environment used, briefly discussing both its fundamental and practical implications.

2. Experimental techniques and materials

We have used pure and dried ethanol (max. 0.02% H_2O) without further purification. All experiments reported in the present work employed ethanol taken from the same bottle.

Calorimetric experiments above 77 K were conducted in the same experimental set-up earlier developed and used to measure the specific heat of ethanol at low temperatures [8,9]. A silicon diode was used as thermometer in the whole temperature range, and a 1 k Ω resistor as electrical heater. The temperature of the internal vacuum chamber was controlled automatically. In addition to a small copper cell #1 (similar to those used in [8,9], around 3 g of addenda and 1.5 cm³ of liquid volume, with a thin copper mesh fitted inside to facilitate thermal equilibrium), we also employed another kind of copper cell #2: a larger and rigid, cylindrical cell, vacuum-sealed using an indium ring and without any internal attachments, that amounted to 14 g of addenda and 3 cm³ of liquid volume [13]. Calorimetric measurements with both cells were performed using the continuous, dual-slope method [14], as well as the adiabatic method [15]. The heat capacities of cell #1 and cell #2, after being emptied, were measured separately and thus subtracted from the total measured values. Agreement between the two methods, and among different experimental runs using both kinds of cells, was always better than 6% in absolute values.

X-ray scattering experiments were performed with a standard diffractometer, using Cu-K α radiation and transmission geometry. The sample holder used was a disk-like cell with its annular section made of brass and the walls made of beryllium. The thickness of the disk, i.e., the distance between the Be windows, was 1.0 mm, and the diameter was about 20 mm. The ethanol was injected into this holder and the cell was sealed with epoxy.

For temperature-dependent Brillouin-scattering experiments, ethanol samples were contained in squared, optical-transparent silicate glass cuvettes with an ethanol free-path of 0.5 mm. The temperature changes were achieved by means of a continuous-flow liquid helium cryostat and a temperature controller. The Brillouin experiments were performed using a light source of Ar⁺ ion laser, provided with an intracavity temperature stabilized single-mode and single-frequency z-lok etalon ($\lambda_0 = 514.5$ nm). The scattered light was analyzed using a Sandercoc-type 3 + 3 tandem Fabry-Pérot interferometer [16]. The typical values for finesse and contrast were 150 and 10⁹, respectively. Backscattering geometry was used.

3. Results

3.1. Different crystalline phases of ethanol

The typical procedure followed by us and other authors to prepare, measure, and characterize the different solid phases of ethanol can be understood through the schematic

phase diagram shown in Fig. 1. We start with liquid ethanol in thermal equilibrium slightly above its melting point. Then, the calorimetric cell containing the ethanol is supercooled fast enough down to below $T_g \approx 97$ K (see route (1) in Fig. 1), so that any kind of crystallization is avoided and the supercooled liquid (SCL) enters into the glass state. What is exactly the necessary (critical) cooling rate to quench liquid ethanol into glass will be discussed in Section 4.2. After conducting the corresponding measurements on the glass phase, ethanol is heated above T_g until a first-order phase transition into the plastic crystal (2) irreversibly occurs around 105–110 K. By cooling this phase after the transition has been completed, one obtains (3) the ODC (*glassy crystal*) phase, that can be measured. When the previous procedure is repeated, the dynamic *glassy crystal* \leftrightarrow plastic crystal transition is observed, also at around 97 K, with a discontinuity in specific heat about 80% of that of the glass-SCL transition (Fig. 2), in agreement with the previous measurements by the Osaka group [5]. When the (bcc) PC is further heated up to about 120 K, another first-order transition (4) into the (monoclinic) stable crystal phase takes place, following Ostwald's rule of stages [17]. Once again, the new phase is cooled down (5), and its specific heat or any other property of interest is measured.

To our knowledge, all published works in the literature (with the only exception of the crystallographic studies by Jönsson [11], who was able to grow single crystals at around 156 K) obtained the stable crystal phase of ethanol following above mentioned route (4) by heating the plastic crystal. This is probably the most rapid and convenient way. In principle, everyone would agree that slowly cooling the liquid (route (4') in Fig. 1) also must produce the same stable crystalline phase of ethanol.

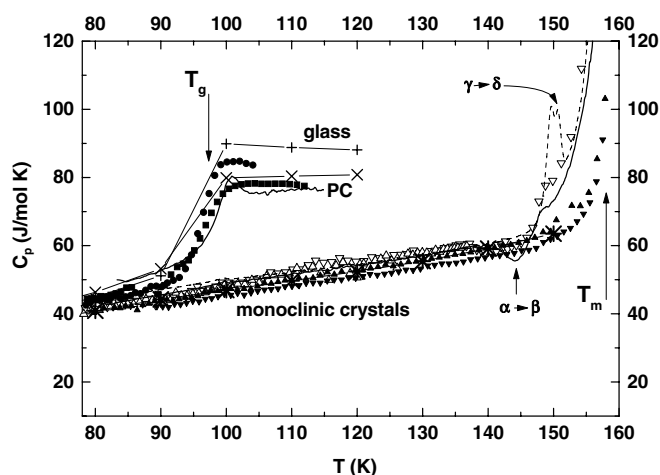


Fig. 2. Specific heat data of ethanol. Solid symbols always refer to adiabatic measurements with cell #2 and open symbols to adiabatic measurements with cell #1. Curves are measurements performed with the continuous method with cell #1. Arrows indicate the crystal $\alpha \rightarrow \beta$ and the crystal $\gamma \rightarrow \delta$ transitions as explained in the text. Down triangles are for crystal α and up triangles for crystal γ . Cross symbols (*, x, +) are published data for crystal, glassy/plastic crystal, and glass phases, respectively, by Haida et al. [5].

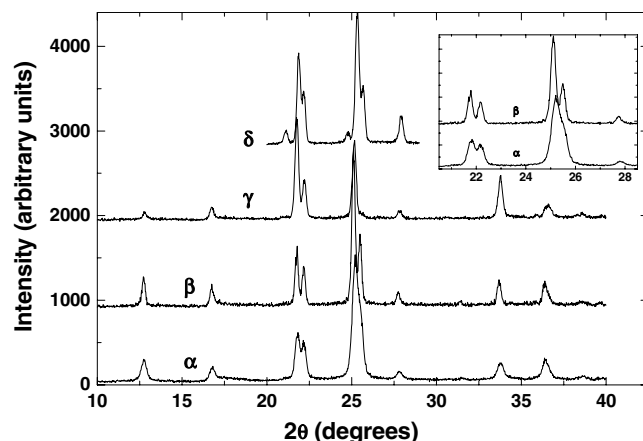


Fig. 3. X-ray diffraction patterns for differently prepared crystalline phases, vertically shifted for clarity. Crystal α was measured at 125 K, after heating the plastic crystal from 110 K. Then, this crystal is further heated, exhibiting a transformation into a β phase, that is measured at 147 K. Crystalline phase γ was obtained by cooling the liquid from 160 K down to 145 K at -0.7 K/min, and it was measured at 135 K. When heated above 145 K, a new transition $\gamma \rightarrow \delta$ occurs. Inset amplifies the main peaks for the $\alpha \rightarrow \beta$ transition.

We have carried out X-ray diffraction experiments (Fig. 3) which show that the situation is different and much more complex. First, the liquid was quenched (at approximately -10 K/min) from above 160 K to 77 K, and then heated up to 110 K: a diffraction pattern identical to that previously reported [6] for the PC was observed. Employing the usual route (4), this plastic (rotationally-disordered) crystal was transformed into a fully-ordered, monoclinic crystal (let us call it crystal α), that was measured at 125 K. However, when this crystal α is further heated, a small but clear transformation into a β phase is observed in the range 143–147 K (Fig. 3). On the other hand, we also explored the route (4') of Fig. 1 by cooling the liquid from 160 K down to 145 K at -0.7 K/min, where the crystallization began. The diffraction pattern of this crystal (γ), measured at 135 K, was similar to the former ones, but exhibiting clear differences in the relative intensities of the main peaks. When heated above 145 K, a new transition $\gamma \rightarrow \delta$ occurs.

In order to confirm that the observed variations on the monoclinic structure of the fully-ordered crystal indeed correspond to different crystalline phases, we have conducted calorimetric studies. In Figs. 4 and 5, we summarize the most significant and reproducible results, only concerning the crystalline phases, observed after a big amount of experimental runs, and employing both cell #1 and cell #2. Following different thermal histories and cooling rates of the liquid, the observed onset of crystallization ranged $T_x = 125$ –146 K. In Fig. 4, we show the measured variation of temperature as a function of time dT/dt , by applying a constant heating power, for differently prepared crystalline states. First, crystal α was obtained from the PC at around 120 K, taking care that the sample temperature did not exceed the limit of 140 K. When this (metastable) crystal

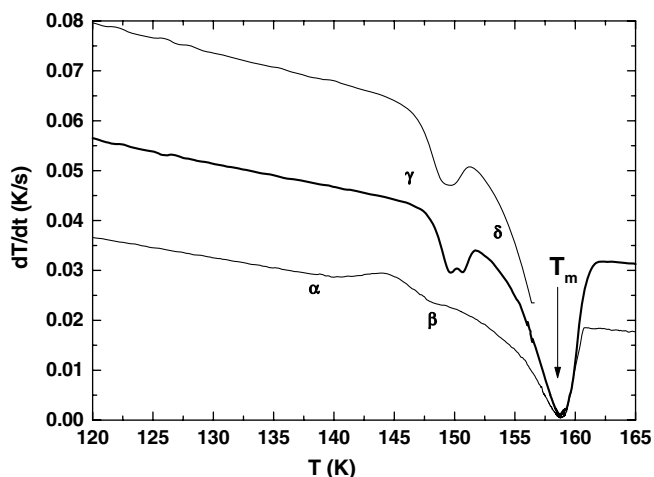


Fig. 4. Directly measured variation of temperature as a function of time, when applying a constant heating power, for differently prepared crystalline states. Crystal α was obtained by heating and controlling the plastic crystal around 120 K; when this crystal is further heated, it exhibits an exothermic process into a β phase (lower curve). Crystalline phase γ was obtained by supercooling the liquid below the melting temperature T_m , crystallization starting for the shown cases (for two different heating rates) at $T_x = 133$ K and finishing above 150 K (where the endothermic transition $\gamma \rightarrow \delta$ occurs), due to self-heating.

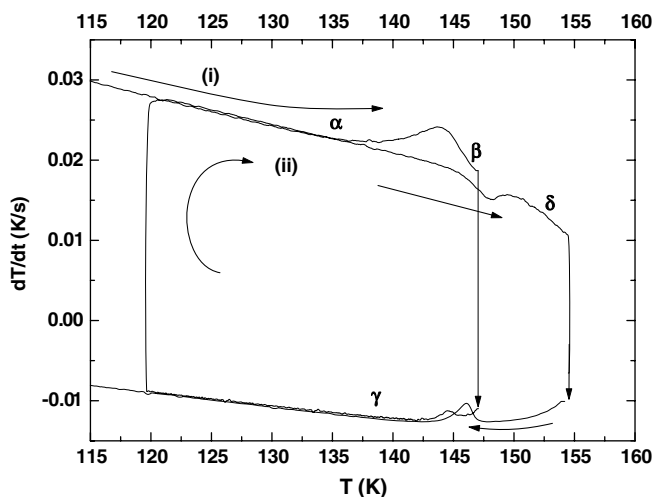


Fig. 5. Thermal cycles below the melting temperature. (i) Metastable crystal α is heated as in Fig. 4, but now the heating process is stopped just after the $\alpha \rightarrow \beta$ transition. When cooled, a small exothermic process into the low-temperature, stable γ phase is observed around 145 K. (ii) When the γ phase is then heated, no exothermic transition occurs, but an endothermic one instead into a high-temperature δ phase, that reverts to the γ phase when cooled. Further thermal cyclings reproduce the $\gamma \leftrightarrow \delta$ transitions.

α was further heated, it exhibited an exothermic process typically starting at 144–145 K, into a β phase. Then, the crystal melts at $T_m = 158 \pm 1$ K. On the other hand, the liquid can be supercooled below the melting temperature T_m , and a crystalline phase γ is obtained: two different experimental runs are shown in Fig. 4. In both cases, crystallization from the liquid started at $T_x = 133$ K (and fin-

ished above 150 K, due to the self-heating produced by this strong first-order transition). A small maximum embedded in the larger minimum at 150 K was often observed, especially at slow heating rates, presumably because a mixture of phases could have been produced when the crystallization process is not fully controlled below the transition $\gamma \rightarrow \delta$ transition range around 150 K.

In addition, we performed several thermal cycles of these crystalline phases below the melting temperature, some of them are shown in Fig. 5. When the (metastable) crystal α is heated (i) and the heating process is stopped just after the $\alpha \rightarrow \beta$ transition around 145 K, a small exothermic process into a low-temperature phase is observed. When this phase is then heated, no exothermic transition is observed, but rather an endothermic one around 150 K into a high-temperature phase, that reverts again to the previous phase when cooled. Further thermal cyclings reproduce back and forth these endothermic/exothermic transitions, which we interpret as $\gamma \leftrightarrow \delta$ transitions between the stable low-temperature and high-temperature crystalline phases. The lack of the above-mentioned small exothermic peak within the endothermic one supports the interpretation given at the end of the previous paragraph. We also want to mention that preliminary Brillouin-scattering experiments [18] confirm the general trends of phase transitions observed by diffraction and calorimetry.

3.2. Specific heat

In Fig. 2 we plot specific-heat measurements for the different solid phases of ethanol, using the different methods and cells mentioned above. In all cases, the contribution to the heat capacity of the addenda (empty cell plus heater and thermometer) was measured using the same methods, in order to exactly subtract its contribution. The true glass \rightarrow supercooled liquid transition and the dynamical glassy crystal \rightarrow plastic crystal one are observed around 97 K. Specific heat of metastable crystal α and stable crystal γ are the same within our experimental error, indicating that the vibrational entropy of such similar structures cannot differ appreciably. At higher temperatures (145–150 K), but still well below the melting temperature, exothermic $\alpha \rightarrow \beta$ and endothermic $\gamma \rightarrow \delta$ transitions are manifested as a decrease and an increase in the observed heat capacity, respectively. Smoothed published data for crystal (α , β following our notation), glassy/plastic crystal, and glass phases, by Haida et al. [5] can be seen to agree reasonably with our data.

3.3. Critical cooling rates

It is well known and accepted [2,17,19] that whether a supercooled liquid becomes a glass below T_g or crystallizes crucially depends upon the cooling rate R_c . Literature on glasses is plenty of R_c data, above which the corresponding liquid can be vitrified. Therefore, the knowledge of the critical cooling rate for ethanol, which has the merit of a poly-

morphism allowing to access separately different categories of disorder, seems a most interesting issue. As mentioned above, the group in Osaka that discovered in the 70s the difference between the truly (amorphous) glass and that ‘glassy crystal’, claimed [5] that they needed a quench faster than -30 K/min in order to get the glass state. If cooled slower, they obtained, at least partially, the plastic crystalline phase, as deduced from their differential thermal analysis measurements [5]. Nevertheless, there seems to be some confusion in the literature concerning this point. In our previous low-temperature experiments [8,10], we observed and reported a critical cooling rate around -20 K/min, in the light-scattering experiments by Surovtsev et al. [20] a quench of -10 K/min was enough to avoid crystallization, and in other experiments -6 K/min has been reported [6,7,21]. Of course, some discrepancies from one experimental set-up to another, including different thermal arrangements and thermometry for these rapid variations of temperature, could be expected, but the found discrepancies seem excessive. Indeed, although, with our calorimetric cell #1 we needed a cooling rate (evaluated around 125 K) of -20 K/min, with the cylindrical cell #2 only -6 K/min sufficed to obtain a full glassy phase (as evidenced by later calorimetric characterization).

Nonetheless, we have found a much more dramatic contrast in our X-ray diffraction and Brillouin-scattering experiments. In the former case, after a long thermal stabilization at 160 K the liquid was supercooled slowly down to 90 K, in steps of -2 K, taking some 30 min for recording each diffraction spectra, which exhibited no sign of crystallization, only a slight continuous shift of the two broadened peaks characteristic of the supercooled liquid or glassy states. We remind that all other phases (including the PC) exhibited very distinct crystalline patterns. Hence, the total period of time elapsed between the diffraction pattern of the liquid at 160 K and that of the glass at 90 K, shown in Fig. 6, was almost 20 h. Therefore, even a cooling rate of about -0.06 K/min has allowed us to obtain the

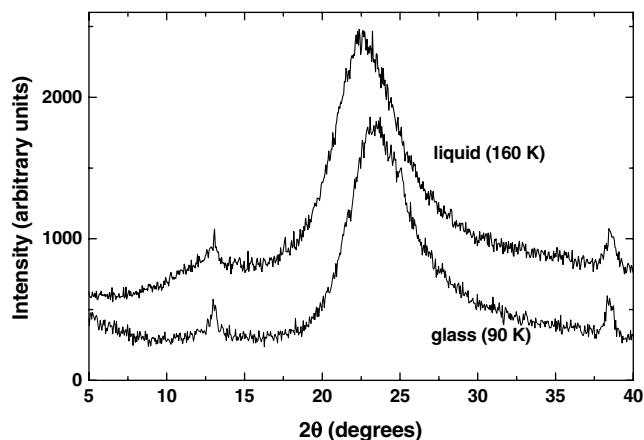


Fig. 6. X-ray diffraction patterns (shifted vertically for clarity) of ethanol in liquid state at 160 K, after being thermally stabilized for 18 h, and in the glass state at 90 K, after very slowly (-4 K/h) cooling of the liquid.

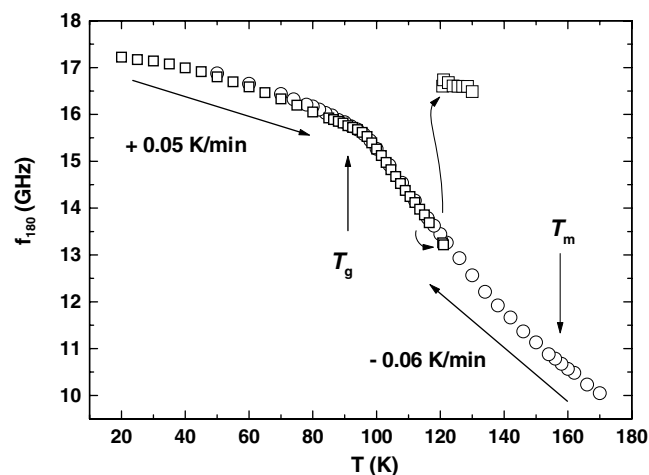


Fig. 7. Brillouin frequency shift in backscattering geometry for ethanol, when cooling from the liquid state at -0.06 K/min (circles) and when heating from a glass (squares), previously prepared by quenching the liquid at about -6 K/min. Curved arrows indicate the jumps observed when the supercooled liquid transforms into the plastic crystal at around 115 K and then the stronger transition into the stable crystal at 120 K. Glass transition (T_g) and melting (T_m) temperatures are also marked.

glass of ethanol. This unexpected finding was confirmed by Brillouin-scattering experiments. First, a glass was made by quenching the liquid at about -6 K/min. The Brillouin frequency shift, proportional to the longitudinal sound velocity, was then measured (square symbols in Fig. 7): a kink was observed at T_g followed in the supercooled liquid state by a temperature jump around 115 K indicative of the transition into the plastic crystal phase, and finally a much stronger change into the stable crystal at 120 K. However, when cooling from the liquid state at -0.06 K/min (circles) a continuous temperature variation was observed, that reproduces the data of glass and supercooled liquid of the heating curve, again with no sign of crystallization.

4. Discussion

4.1. Different crystalline phases of ethanol

As shown in Section 3.1, there is more than one monoclinic crystalline structure of ethanol. At least four different phases have been observed by concurrent use of X-ray diffraction and calorimetry experiments. The diffraction patterns obtained for the crystalline phases denoted as α , β , γ , and δ correspond always to a monoclinic symmetry, but with slight changes in the relative positions of some diffraction peaks and different distributions of their intensities. These are very likely due to relative distortions of the atomic arrangement in the (monoclinic) unit cell, that produce variations in the structure factors of the Bragg peaks.

We want to emphasize that γ phase exhibits additional small peaks at diffraction angles of 21.08° and 24.75° and a more intense peak at 25.68° . It is also important to remark that the structural parameters found by Jönsson

[11] for a single crystal of water-free ethanol grown at 156 K, agree very well with our diffraction pattern for δ phase. It is also apparent in Fig. 3 that the diffraction pattern obtained for the α phase is suggestive of a higher morphological disorder. Indeed, we have calculated that the mosaic-block average size for this sample is three times lower than that in the other phases. In this case therefore, some melting and recrystallization effects could be relevant and the X-ray diffraction experiments alone cannot be used as a sufficient argument to justify the existence of a new phase. However, the strongest evidence supporting that the exothermic process indeed corresponds to a phase transition rather than a recrystallization of smaller crystallites is the high reproducibility of this feature (always occurring at 144 ± 1 K), observed in three very different experimental cells: X-ray disk-like cells, and both cell #1 and cell #2 of copper used in calorimetric experiments.

On the other hand, we have assigned β and δ phases in calorimetric experiments to those higher-temperature phases correspondingly obtained in diffraction experiments. One can observe that both phases behave very similarly and melt at the same temperature. However, X-ray diffraction experiments clearly support the existence of two different phases at these temperatures, following very similar thermal histories. Since, we have not observed any further $\beta \rightarrow \delta$ transition by calorimetry, we assume that they are two different phases, though very similar thermodynamically. We recognize, however, the possibility that for some reason we were obtaining in the calorimetric experiments always one of the two phases (say, δ), in contrast to the case of X-ray experiments, where both phases are more clearly distinct. This can be considered an open question to be confirmed by future experiments.

By a closer inspection of the diffraction patterns, one can note that these structural differences in crystalline phases of ethanol seem to be already present in the literature, although, never noticed by the authors, who might have attributed them to the different experimental temperatures employed. For instance, the X-ray diffraction pattern for the monoclinic crystal published by Bermejo and co-workers in Fig. 1 of Ref. [6] matches exactly with that of our crystal α , as expected, but their neutron data [21] are probably from a crystal β , and earlier data by Jönsson (who indeed reported to get the crystal by stabilizing the liquid at 156 K) match better with our curve for crystal δ , as said above. More exhaustive diffraction experiments and analysis are still necessary to solve these crystallographic details and determine their exact unit-cell parameters.

4.2. Critical cooling rates

We have shown that the critical cooling rate necessary to quench the supercooled liquid of ethanol in the amorphous, glassy state can be much lower (at least 2–3 orders of magnitude) than expected from the literature and from our previous experience. To understand the reason, atten-

tion should be paid to the details of the different sample-holder cells employed in each experimental technique. Our typical calorimetric cells [8,10] as cell #1 of the present work were made of rough, thin walls of copper, where we fitted an internal mesh of fine copper wires to improve thermal equilibrium. As explained in Section 2, cylindrical cell #2 had smoother copper walls, devoid of internal wires. Experimental cells employed in neutron-scattering experiments [7,21] are not very different from the latter. On the contrary, the experimental cells employed for X-ray diffraction and Brillouin-scattering consisted of clean, smooth glassy windows, with rather thin (around 1 mm) layers of liquid. Devoid of artificial nucleation centers, these cells seem to exhibit extremely low critical cooling rates. We believe that these are upper limits for the true critical cooling rates for thermodynamically-driven, homogenous crystallization [17,19]. However, in other typical cells, one is unwisely inducing a different kinetics of heterogeneous crystallization [19]. Indeed, let us note that a moderately fast cooling (-0.7 K/min) of the liquid did produce the crystallization around 145 K, presumably by the thermal strains induced. Further work on all these open questions is in progress.

5. Conclusion

We have found that there exist at least four different monoclinic crystalline phases of ethanol, in addition to the cubic glassy crystal and to the truly amorphous glass. The phase diagram of ethanol is thus more complex and interesting than previously known. On the other hand, we have observed through X-ray diffraction and Brillouin-scattering experiments, that the true critical cooling rate of ethanol can be extremely low (hence it can be a very good glass-former) provided that its container is free enough from impurities, rough surfaces, or any artificial nucleation centers, which lead to heterogeneous nucleation processes. This finding opens therefore the possibility to study the supercooled-liquid state of ethanol in a wider temperature region, without danger of crystallization.

Acknowledgements

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References

- [1] P.W. Anderson, *Science* 267 (1995) 1615.
- [2] W. Kauzmann, *Chem. Rev.* 43 (1948) 219.
- [3] J.N. Sherwood (Ed.), *The Plastically Crystalline State (Orientationally-Disordered Crystals)*, Wiley, New York, 1978.
- [4] H. Suga, S. Seki, *J. Non-Cryst. Solids* 16 (1974) 171.
- [5] O. Haida, H. Suga, S. Seki, *J. Chem. Thermodyn.* 9 (1977) 1133.
- [6] A. Srinivasan, F.J. Bermejo, A. de Andrés, J. Dawidowski, J. Zúñiga, A. Criado, *Phys. Rev. B* 53 (1996) 8172.
- [7] M.A. Ramos, S. Vieira, F.J. Bermejo, J. Dawidowski, H.E. Fisher, H. Schober, M.A. González, C.K. Loong, D.L. Price, *Phys. Rev. Lett.* 78 (1997) 82.

- [8] C. Talón, M.A. Ramos, S. Vieira, G.J. Cuello, F.J. Bermejo, A. Criado, M.L. Senent, S.M. Bennington, H.E. Fischer, H. Schober, *Phys. Rev. B* 58 (1998) 745.
- [9] A. Matic, C. Masciovecchio, D. Engberg, G. Monaco, L. Börjesson, S.C. Santucci, R. Verbeni, *Phys. Rev. Lett.* 93 (2004) 145502.
- [10] M.A. Ramos, C. Talón, R.J. Jiménez-Riobóo, S. Vieira, *J. Phys.: Condens. Matter* 15 (2003) S1007.
- [11] P.G. Jönsson, *Acta Crystallogr. Sect. B* 32 (1976) 232.
- [12] G.E. Gibson, G.S. Parks, W.M. Latimer, *J. Am. Chem. Soc.* 42 (1920) 1542;
G.S. Parks, *J. Am. Chem. Soc.* 47 (1925) 338;
K.K. Kelley, *J. Am. Chem. Soc.* 51 (1929) 779.
- [13] The copper cell #2 was one of those made at the University of Messina, prepared by A. Mandanici and M. Cutroni, in order to perform calorimetric experiments in several other molecular liquids.
- [14] S. Riegel, G. Weber, *J. Phys. E: Sci. Instrum.* 19 (1986) 790.
- [15] T.H.K. Barron, G.K. White, *Heat Capacity and Thermal Expansion at Low Temperatures*, Kluwer, New York, 1999.
- [16] J.R. Sandercock, in: M. Cardona, G. Guntherodt (Eds.), *Light Scattering in Solids III*, Springer, Berlin, 1982.
- [17] I. Gutzow, J. Schmelzer, *The Vitreous State*, Springer, Berlin, 1995.
- [18] R.J. Jiménez-Riobóo, M.A. Ramos, *Philos. Mag.*, in press.
- [19] P.G. Debenedetti, *Metastable Liquids: Concepts and Principles*, Princeton University, Princeton, 1996.
- [20] N.V. Surotsev, S.V. Adichtchev, J. Wiedersich, V.N. Novikov, E.A. Rössler, *J. Chem. Phys.* 119 (2003) 12399.
- [21] F.J. Bermejo, A. Criado, R. Fayos, R. Fernández-Perea, H.E. Fischer, E. Suard, A. Gueylyah, J. Zúñiga, *Phys. Rev. B* 56 (1997) 11536.