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Changes in mobility of plastic crystal ethanol during its transformation into the monoclinic crystal state

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Transformation of deuterated ethanol from the plastic crystal phase into the monoclinic one is investigated by means of a singular setup combining simultaneously dielectric spectroscopy with neutron diffraction. We postulate that a dynamic transition from plastic crystal to supercooled liquid-like configuration through a deep reorganization of the hydrogen-bonding network must take place as a previous step of the crystallization process. Once these precursor regions are formed, subsequent crystalline nucleation and growth develop with time. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4863694]

I. INTRODUCTION

The structure and dynamics of hydrogen-bonded systems have attracted the interest of a great number of scientists over the last decades. For instance, it is well established that the peculiar physical properties of water are directly correlated to its strong hydrogen bonding network.[1–4] Hydrogen bonds in monohydroxy alcohols are also characterized by a three-dimensional network that persists in liquid and solid phases.[5–8] This hydrogen bonding network in monohydroxy alcohols fluctuates over time and the molecules continuously get in and out of the network.[8,9] Phase transitions of supercooled liquids into more stable structures are of great interest, for its implications in fundamental science and industry.[10] In supercooled simple alcohols, the configuration of the hydrogen bonds undergoes important modifications across the phase transformations and in order to draw a complete picture of such transitions, not only the structure but also the molecular motions, especially those associated with the mobile hydrogen bonds, must be examined. Ethanol, considered a paradigmatic glass former and extensively studied in the glassy and supercooled regimes, may exist either as a supercooled liquid (SCL, translational and rotational disorder), monoclinic crystalline solid (MC, translational and rotational order), or plastic crystal (PC, translational order but rotational disorder). Several works have been devoted to observe how the state of order of supercooled ethanol affects its dynamics above and below the T_g.[11–16] It has been found that positional order of the ethanol molecules modify the dynamics in a different manner depending on the time scale explored. While the dynamics in the ps regime, as explored by quasielastic neutron scattering (QENS),[17] is faster for the PC phase in comparison to the SCL, on the contrary the relaxational rate studied by dielectric spectroscopy (DS) is faster in the case of SCL ethanol.[11,12,18] This larger rotational mobility in the ps time scale has been considered to play a crucial role on the thermodynamic stabilization of the plastic crystal phase with respect to the supercooled liquid.[16,17] It has also been proposed that in both SCL and PC ethanol, the rotations dominate the structural relaxation process.[12]

Dielectric spectroscopy has been widely used to study the molecular relaxation of monohydroxy alcohols, especially for elucidating the microscopic origin of the main Debye process observed at low frequencies. This strong Debye peak does not possess the main features of the typical structural or α relaxation and different models have been proposed for explaining the origin of this mode but commonly associated with the hydrogen bonding network dynamics.[6,7,9] We aim to remark that the objective of the present work does not focus on getting to the bottom of the microscopic origin of the studied relaxations, although we certainly consider the idea that the Debye peak is associated with the dynamic nature of the hydrogen bonding network in monohydroxy alcohols.[6,7]

We correlate here the dynamic and structural changes occurring in PC ethanol during its phase transition into the monoclinic crystalline phase. We perform a simultaneous monitoring, in real time, of both the crystal development by means of neutron diffraction (ND), and the dynamic changes occurring in the rotational disordered phase by dielectric spectroscopy, providing a complete picture of the ordering process.[19] The dynamics of the plastic crystal or rotator phase becomes faster with increasing of the fraction of monoclinic phase. For intermediate annealing times, the nonlinear relation between the fraction of the remaining plastic crystal phase and the growing monoclinic fraction indicates the existence of an intermediate step as a precursor of the stable monoclinic phase.

II. EXPERIMENTAL

The hydrogen-bonded system under investigation is fully deuterated ethanol (CD_3CD_2OD). Deuterated and anhydrous ethanol (ethanol-d6) was purchased from Sigma-Aldrich with a degree of deuteration of 99.5%. Following the

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experimental details described in Ref. 20, ethanol-d6 is rapidly cooled down (cooling > 6 K/min) to 70 K (structural glass) from room temperature inside of a standard ILL orange cryostat and heating it up above the ethanol T_g afterwards (SCL). If the SCL ethanol is annealed between 105 and 110 K, the PC phase is generated. Finally, PC ethanol-d6 is subjected to isothermal annealing at 115 K to induce its transformation into the stable monoclinic phase. In order to monitor the transformation of ethanol-d6 from the plastic crystal into the monoclinic phase, we have used an experimental setup which allowed us to perform simultaneous measurements of time resolved neutron diffraction with dielectric spectroscopy.[19] The ND-DS sample holder was designed to place the liquid in a container made of anodized aluminum between two aluminum electrodes that make possible the application of an alternating electric field of angular frequency ω. The ND-DS sample container is then connected to a Stanford lock-in amplifier SR830 with a dielectric interface and control unit from Novocontrol. Since neutrons are highly penetrable, it is possible to take parallel neutron diffraction patterns. These simultaneous ND and DS experiments have been carried out at the D1B diffractometer of the Institute Laue Langevin (ILL, Grenoble, France) at a fixed wavelength of $\lambda = 2.52$ Å. The ND intensities are given as a function of the scattering vector Q, which is defined as $Q = 4\pi \sin(\theta)/\lambda$, where λ is the neutron wavelength and 2θ is the scattering angle. With the purpose of following in real time the phase transition of plastic crystal ethanol, the ND patterns were taken with 10 min acquisition time. A measurement of the empty container was also performed to be subtracted from the whole sample series in order to get rid of the aluminum Bragg peaks contamination. On the other hand, the dielectric spectroscopy measures the complex dielectric permittivity $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ at different frequencies, where $\epsilon'(\omega)$ is the real part of the dielectric permittivity and $\epsilon''(\omega)$ is the dielectric loss. The utility of dielectric spectroscopy techniques for the evaluation of the molecular dynamics in glass forming systems lies on the dipolar reorientations at a molecular level that are manifested by a maximum in $\epsilon''(\omega)$ at a characteristic frequency ω.[21]

III. RESULTS AND DISCUSSION

The plastic crystal phase of ethanol-d6 is formed by applying the procedure described in Sec. II. The formation of the plastic crystalline state is confirmed by the initial ND patterns displayed at the bottom of Fig. 1 which shows the characteristic and most intense (110) peak of the cubic lattice.[22] At a fixed temperature of 115 K, plastic crystal ethanol-d6 transforms into the stable monoclinic phase. The dependence of the neutron diffraction patterns at selected annealing times is shown in Fig. 1. The starting rotator phase gradually transforms to the monoclinic state, in which neutron diffraction pattern is mainly characterized by those peaks located at 1.56, 1.80, and 2.58 Å^{-1}. After approximately 7 h, the phase transformation is completed and no traces of the plastic crystal phase are found. With the purpose of calculating the volume fraction corresponding to each phase, the diffraction patterns have been analyzed considering a linear combination of the
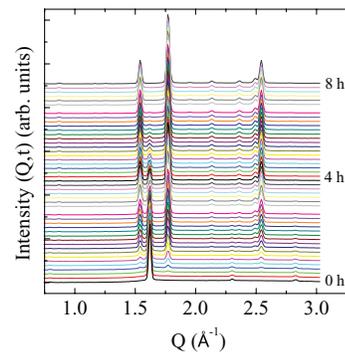

FIG. 1. Neutron diffraction patterns during isothermal annealing at 115 K. ND patterns for every time are represented as a function of the scattering vector Q. Every pattern was recorded with an acquisition time of 10 min. Annealing time is indicated in hours.

ND intensity from the plastic crystal (I_{PC}) and monoclinic (I_{MC}) phases as follows:

$$I(Q, t) = N_{MC}(t)I_{MC}(Q) + [1 - N_{MC}(t)]I_{PC}(Q), \quad (1)$$

where $N_{MC}(t)$ is the volume fraction of the growing monoclinic phase, I_{MC} corresponds to its ND intensity, and I_{PC} is the ND intensity due to the remaining plastic crystal phase. This procedure for calculating volume fractions in real time studies of phase transitions has been extensively used in the literature.[23–25] To show the goodness of fits of the two-phase model described above, in Fig. 2 we present three selected snapshots of the neutron diffraction patterns during crystallization.

What makes the study of the phase transitions, in which the plastic crystal ethanol is involved, of special interest is that its bcc lattice is dynamically active in the frequency window provided by dielectric spectroscopy. Above the T_g, the center of masses of the molecules of ethanol remain fixed occupying the characteristic sites of the bcc structure, but at the same time they are free to rotate. As a result of this rotational freedom the dielectric spectrum of plastic crystal ethanol shows a strong dispersion with a maximum of dielectric loss (ϵ'') located approximately at 5 Hz for a temperature of 115 K.[11,12] As it was indicated above, successive dielectric measurements were run in parallel to the neutron diffraction experiments
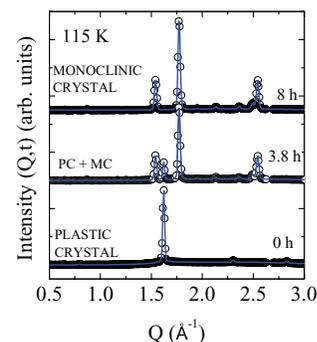

FIG. 2. Selected snapshots of the ND patterns (○) during the transformation of PC ethanol into a monoclinic phase at 115 K. The selected annealing times and the corresponding structural state are indicated. Blue solid lines represent a fit of the total diffraction patterns to a linear combination of the measured diffraction data at the initial (PC) and final (monoclinic phase) times.
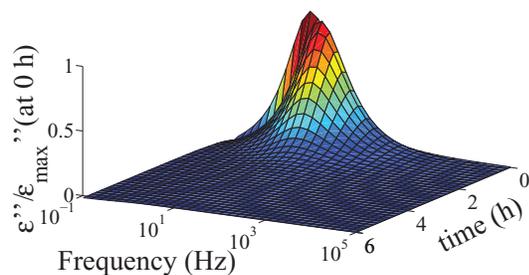
FIG. 3. Time and frequency dependence of the dielectric loss ϵ'' of PC ethanol during its transformation into a monoclinic crystalline phase. Dielectric loss data are normalized to the value at the maximum loss for the data at time 0 h. Every dielectric spectrum was collected with an acquisition time of 10 min.

using a particular ND-DS cell designed for that purpose.[19] Since the area of the dielectric relaxation is proportional to the fraction of mobile dipoles involved in the relaxation process, the growing of the static monoclinic lattice is traduced in a progressive drop in dielectric dispersion as shown in Fig. 3. The intensity of the dielectric loss associated with the mobile rotator phase of ethanol-d6 practically vanishes after 6 h of annealing at 115 K. The raw data have been analyzed in terms of the empirical Cole-Davidson (CD) function.[21, 26, 27] Monohydroxy alcohols in the supercooled regime have been widely investigated by using dielectric spectroscopy with special attention to unravel the molecular origin of the most intense peak located at the low frequency side of the spectrum. These relaxations are characterized by an extremely high dielectric strength and show a Debye type shape (exponential decay). Another peculiar feature of monohydroxy alcohols is the presence of an increase of dispersion at the high frequency side of the Debye peak that in general develops in a better defined shoulder for higher temperatures. The microscopic origin of this shoulder has been intensively debated. Basically, two approaches have been followed to interpret the dielectric response of monohydroxy alcohols. By one side, the Debye type relaxation has been associated with the structural or α relaxation (fingerprint of the glass transition) and the low intensity shoulder would correspond to the secondary or β relaxation, besides it shows an unusual non-Arrhenius behaviour.[14, 28] But the most generally accepted view considers that the genuine α relaxation in monohydroxy alcohols is the excess dispersion detected at the high frequency side of the Debye relaxation.[6, 7, 11, 29] Under this framework, the most intense Debye peak is commonly related to the dynamic features of the hydrogen bonding network of alcohols with a single OH group.

In Fig. 4 the dependence of the dielectric loss (ϵ'') on frequency at three selected annealing times is displayed. In agreement with previous reports, the dielectric loss data have been described by two contributions. Both relaxations, from now on, will be labeled as primary (Debye type) and secondary relaxations (truly α process). As it was indicated above, two CD functions are used to fit our experimental data as follows:

$$\epsilon^*(\omega) = \epsilon_\infty + \left[\frac{\Delta\epsilon_1}{1 + (i\omega\tau_1)^{c_1}} \right] + \left[\frac{\Delta\epsilon_2}{1 + (i\omega\tau_2)^{c_2}} \right]. \quad (2)$$
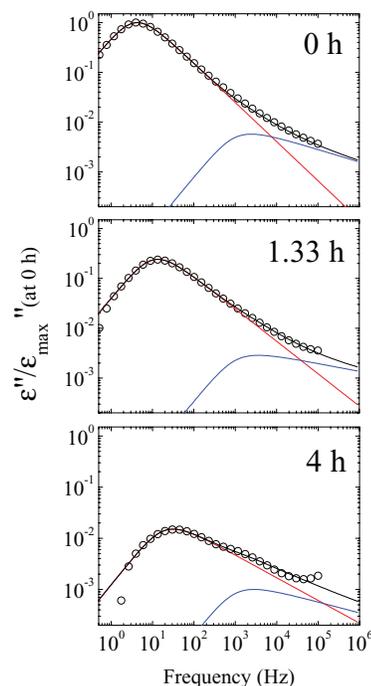

FIG. 4. Dielectric relaxation of PC ethanol during annealing at 115 K at three selected annealing times. Experimental dielectric data ($\bigcirc$) are described by a combination of two CD functions. Black solid lines correspond to the total fit, red solid lines represent the primary or Debye relaxation, and blue solid lines stand for the α process. Dielectric loss data are normalized to the value at the maximum loss for the data at time 0 h.

The subscripts 1 and 2 stand for the primary and secondary relaxations, respectively. In Eq. (2), $\Delta\epsilon$ is related to the amplitude of the dielectric dispersion, normally called dielectric strength, τ is the most probable relaxation time, c determines the asymmetric broadening of the spectrum, and ϵ_∞ is the unrelaxed dielectric permittivity.[21, 26, 27] Since the primary relaxation dominates the spectrum and the secondary one is not totally resolved, the fitting procedure was carried out by keeping slight constrains on the shape (c) and relaxation time (τ) parameters of the secondary process. More precisely, the values of the relaxation time for the secondary process were kept fixed during the fitting procedure. This strategy was chosen in order to control the validity and physical reliability of the resulting fits, keeping in mind the extremely low amplitude and overlapped character of the secondary relaxation. On the contrary, it was possible to let vary its amplitude and shape parameter c, which oscillated between 0.25 and 0.5, obtaining satisfactory fits. In this way, we were able to control the consistency of Eq. (2) for the description of the experimental data. In Fig. 4, the best fit of the dielectric data to Eq. (2) is included, together with the separate contribution from the Debye and secondary relaxations. Interestingly, apart from the clear decrease in amplitude when the annealing time increases, the location of the main peak shifts towards higher frequencies as the crystallization proceeds. In a first approach, this finding suggests speeding up of the hydrogen bonding dynamics of the plastic crystal phase when it progressively transforms into the monoclinic lattice. Modifications on the relaxation of the remaining plastic crystal ethanol can be
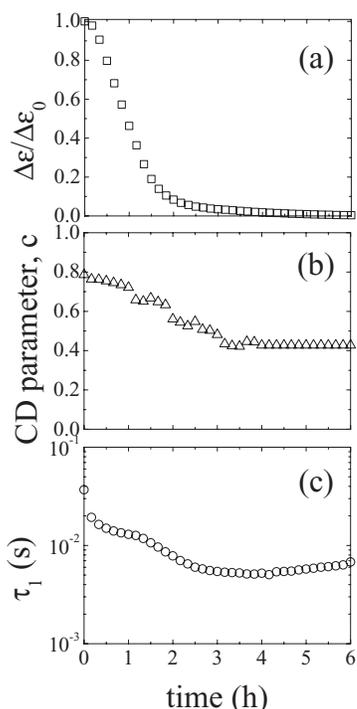
FIG. 5. Temporal evolution of the fitting parameters of the CD function for the primary relaxation during the transformation of plastic crystalline ethanol into its monoclinic phase. (a) Normalized values of the dielectric strength. (b) Shape parameter of the CD function that describes the asymmetric broadening of the dielectric spectrum. (c) Characteristic relaxation time (average of the relaxation time distribution) of the primary or Debye process with annealing time. $\Delta\epsilon_0$ stands for the value of $\Delta\epsilon$ at annealing time 0 h.

accounted by looking at the temporal evolution of the main peak dielectric strength, relaxation time, and c parameter, which are shown in Fig. 5. In this graph, $\Delta\epsilon$ data are normalized by its initial value at 0 h, and the relaxation time τ_1 corresponds to the average of the relaxation time distribution.[21, 24]

Dynamic features of the plastic crystal ethanol might be unequivocally correlated to the fraction of monoclinic phase ($N_{MC}(t)$) as calculated by fitting the ND patterns to Eq. (1). The volume fraction of monoclinic phase as a function of time is presented in Fig. 6. The evolution of $N_{MC}(t)$ with time is nearly sigmoidal and it can be described by a nucleation and growth model, such as the one behind the Johnson-Mehl-
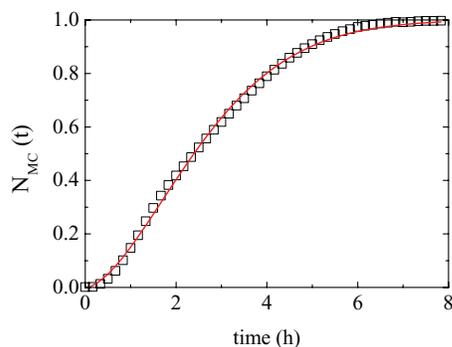

FIG. 6. Volume fraction of monoclinic phase as a function of time for isothermal crystallization of PC ethanol at 115 K. Red solid line corresponds to the best fit of the experimental data to the Avrami equation (Eq. (3)).

Avrami-Kolmogorov equation which reads

$$N_{MC}(t) \propto 1 - \exp\left[-\left(\frac{t - t_0}{\tau_{cryst}}\right)^{AE}\right], \qquad (3)$$

where τ_{cryst} is the characteristic time of the transition, t_0 is the induction period, and AE is the Avrami exponent that determines the nature of the nucleation phenomenon and finally the dimensionality of the ordering process.[30, 31] By describing the experimental values of the volume fraction of the monoclinic phase by Eq. (3), the Avrami exponent AE is estimated to be 1.6 ± 0.1. Values of $AE \leq 2$ are normally compatible with a heterogeneous nucleation process followed by a low dimensional crystallization growth.[30, 32] The use of Eq. (3) also yielded values of 3 and 0.015 h for τ_{cryst} and t_0, respectively.

In relation to the dynamics of the plastic crystal ethanol, Fig. 5(a) shows how the dielectric strength of the Debye peak is drastically reduced during the crystallization at 115 K, especially for low annealing times. As indicated in Fig. 5(b), the broadening parameter c becomes lower during the phase transformation as a consequence of a more heterogeneous dynamic environment. Finally, the evolution of the mean relaxation time of the primary relaxation is shown in Fig. 5(c). It is clearly manifested that the values of τ_1 decrease with the crystallization time up to approximately 3 h, then remaining almost constant for intermediate times or slightly higher. Fig. 5 reflects that the main modifications of the dynamics of the Debye peak occur during the initial stages of the crystallization process.

As mentioned previously, one of the main advantages of performing simultaneous diffraction and dielectric spectroscopy measurements is the direct and unambiguous correlation between the dynamic properties and the volume fraction of the growing ordered phase.[33, 34] Fig. 7 collects the dependence of the dielectric strength for both primary and
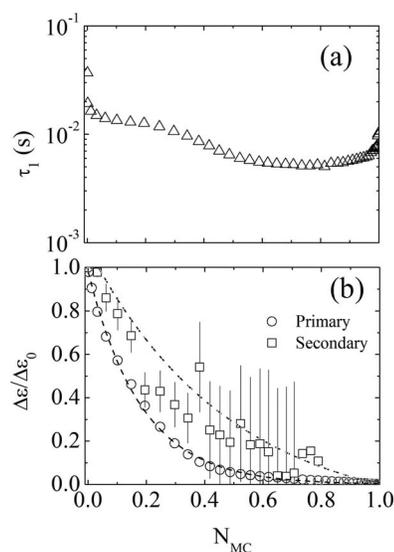

FIG. 7. Dependence of CD parameters on the fraction of monoclinic phase, estimated by neutron diffraction, for isothermal annealing at 115 K. (a) Average relaxation time for the Debye relaxation. (b) Normalized values of the dielectric strength for the primary ($\bigcirc$) and secondary or α ($\square$) relaxations. $\Delta\epsilon_0$ stands for the value of $\Delta\epsilon$ at annealing time 0 h. Dashed lines are guides to the eye.

secondary relaxations, and also the average relaxation time of the primary process as a function of the volume fraction of the monoclinic crystal phase. In Fig. 7(a) we observe a speeding up of the primary relaxation as soon as the MC starts to grow up to volume fractions of 0.8 approximately. Only for large volume fractions of monoclinic phase, the primary relaxation time of the remaining plastic crystal ethanol seems to keep constant or slightly increase. At the bottom, the variation of the normalized dielectric strength for the Debye (○) peak with the MC volume fraction is shown. Data for the secondary relaxation (□) are also included for comparison. A nonlinear behaviour is clearly observed for the prominent Debye peak. Considering that the Debye peak arises from the dynamic character of the hydrogen bonding network that connects the ethanol molecules across the bcc lattice of plastic crystal ethanol, the results shown in Fig. 7(b) reveal that the disruption of the hydrogen bonding network is not directly linked to the total ordering of the molecules into the monoclinic lattice. In the same graph, the values corresponding to the secondary relaxation show a less strong dependence of the dielectric strength with the fraction of monoclinic phase. That is telling us, in a first approach, that the amplitude of the secondary relaxation shows a closer relationship to linearity with the vanishing of the mobile plastic crystal phase. In a similar investigation carried out on fully disordered supercooled isopropanol,[33] we reported that the secondary relaxation showed a nearly linear dependence with the crystalline volume fraction, phenomenon that was explained in terms of the connection of the secondary process with the glass transition and, therefore, being a relaxation mode much less affected by the extension of the hydrogen bonding network. On the contrary, we see here in Fig. 7(b) that the behaviour for the secondary or α relaxation of plastic crystal ethanol during its transformation into the monoclinic phase displays a clear curvature, unlike the purely linear fashion shown by isopropanol. On the basis of that behaviour, it is highly plausible that the geometrical restriction imposed by the bcc lattice that strongly controls the nature of the intermolecular hydrogen bonding forces makes the α relaxation more sensitive to distortions of the hydrogen bonding network. In addition to that, we indirectly give additional support to the model that proposes the secondary relaxation as the truly α mode.[28,29]

As indicated already, the mobility of the plastic crystal ethanol seems to be driven by the rotational freedom of the ethanol molecules. It has also been evidenced that PC ethanol molecules perform whole body rotations at different time scales, from those detected at the ps regime by neutron scattering, to those assessed by dielectric spectroscopy at slower time scales.[11,13,17,35] Very recently, the main dielectric relaxation for supercooled monohydroxy alcohols has been attributed to the formation of supramolecular dipoles that undergo continuous fluctuations via formation and subsequent breakage of hydrogen bonds.[7] In addition to that, by means of molecular dynamics simulations, it has been proposed that, in contrast to previous considerations, the orientation of the ethanol molecules that occupy the bcc lattice in the rotator phase is not completely random.[16] These authors propose that the orientation of the ethanol species is governed by the formation of hydrogen bonds with surrounding molecules. As-

suming that whole body reorientation is the main contribution to the dielectric response of supercooled ethanol, the dynamics for the SCL and PC is essentially the same, only differing in the time scale which is slightly slower for the rotator phase due to the spatial restrictions imposed by the positional order.[11,12] During the phase transition from the PC into the monoclinic crystal phase, the mobility of the former experiences dramatic changes, especially important are those occurring at the initial stages of the ordering process. In contrast to other low molecular weight glass formers where the location and broadening of the main dielectric process remain nearly unchanged during crystallization,[36,37] here the shape and location of the maximum dielectric loss of the main dielectric dispersion is deeply modified with the crystallization progress as shown in Figs. 5 and 7. The Debye relaxation becomes broader as the ethanol molecules leave the nodes of the bcc lattice and incorporate into the monoclinic crystals. That broadening evidences a strong disruption of the relaxation mechanism upon crystallization, suggesting a more extended relaxation time distribution. At the same time, the acceleration of the main peak of the rotator phase of ethanol, getting closer to that exhibited by the fully disordered SCL, indicates how new ethanol molecules abandon progressively the rotator phase and become free to rotate without their initial spatial restrictions. On the contrary, similar to what usually happens in polymeric materials, a slowing down of the relaxation dynamics of some low molecular weight glass formers during crystallization has been reported.[38–40] However, in the same line as reported here, some examples in which the main relaxation process undergoes a speeding up upon crystallization can be found in the literature,[41,42] albeit a physical insight of this accelerating dynamics was not proposed.

In this work, we evidence that prior to the formation of the monoclinic structure of ethanol-d6, a rapid disruption of the dipolar reorientations that originate the Debye peak must take place. In this context, Wang *et al.*[6] have proposed that a minimum content of monohydroxy alcohol molecules is required to originate the long range interactions for the triggering of the Debye relaxation. Under the same angle, these authors consider that a complete disappearance of the Debye process does not necessarily imply that the hydrogen bonding network is totally destroyed. Following that same line of reasoning, we may deduce that the dramatic decreasing of the Debye peak amplitude for low volume fractions of the monoclinic phase observed in our Fig. 7 is the consequence of a progressive approaching of the ethanol molecules content to the minimum percolation threshold proposed by Wang *et al.*[6] In Fig. 7(b), the secondary process shows a different behaviour and the depletion of the dielectric strength is directly proportional to the monoclinic volume fraction to a greater extent than the Debye relaxation, as one would expect for a genuine α relaxation.

All things considered, we postulate that a dynamic transition from PC to SCL-like configuration through a deep reorganization of the hydrogen bonding network must take place along the pathway followed by the ethanol molecules on their way to the monoclinic crystals. Similar results were obtained for the ordinary crystallization of supercooled isopropanol.[33]

IV. CONCLUSIONS

To summarize, the aim of our work was to investigate the structure-dynamics interrelationships during the phase transformation of plastic crystal ethanol into the more stable monoclinic phase. With that purpose, real time and simultaneous measurements of neutron diffraction with dielectric spectroscopy on fully deuterated ethanol were carried out. In this way, a direct correlation between the dynamic magnitudes and the volume fraction of the monoclinic phase was established. The most significant results derived from our work are listed as follows:

- The dielectric spectrum is dominated by a prominent Debye relaxation.
- A dramatic decrease of the amplitude of the Debye relaxation takes place during the early stages of the crystallization process, together with a significant broadening of the curve.
- There is clear departure from a linear relation between the area of the Debye relaxation of the rotator phase with the monoclinic volume fraction. On the contrary, that relation is closer to linearity for the secondary process detected at higher frequencies.
- The later results give additional support to those models that associate the Debye and secondary relaxations with the dynamics of the hydrogen bonding network and with the truly α relaxation, respectively.
- We propose that a deep reorganization of the hydrogen bonding network must take place along the pathway followed by the ethanol molecules on their way to the monoclinic crystals.
- We cannot discard that the dramatic decrease of the Debye peak amplitude for low volume fractions of the monoclinic phase is the consequence of a progressive approaching of the ethanol molecules content to the minimum percolation threshold proposed by Wang *et al.*[6]

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