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The contribution of the Raman spectroscopy to the understanding of the polyamorphism situation in triphenyl phosphite

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Abstract

Raman scattering investigations on triphenyl phosphite, performed in both the low- and high-frequency ranges provide a detailed description of the glacial state. The latter can be described as a two-phase (supercooled liquid/nano or microcrystals) system. Changes of thermal parameters which control the transformation reveal that the glaciation process can be interpreted as an abortive crystallization inherent to a high nucleation rate at temperatures where the crystal growth is very slow. The subsequent high-density nucleation frustrates crystallization leading to an extremely stable sub-microcrystalline (glacial) state. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

First-order structural phase transitions are common in crystalline solids whereas first-order liquid–liquid phase transitions are excessively rare in pure compounds. The existence of liquid polymorphs is beginning to be recognized and a growing interest is devoted to the first-order polyamorphic transitions. These phase transitions are principally observed by applying a high pressure [1–2], and are generally associated with a change of density. The evidence of an apparently amorphous phase in triphenyl phosphite (TPP) at atmospheric pressure [3–4], distinct from the glass, the supercooled liquid and the

normal liquid (and so called glacial phase) was considered as an original manifestation of polyamorphism, and a real opportunity to analyze such a situation. This glacial phase, was obtained via a first-order transition from the supercooled liquid state [3–9], either by slow heating from the glass or by maintaining the temperature isothermally above the calorimetric glass transition in the range 210–235 K. The opportunity to form the intriguing glacial phase of TPP by a mere variation of temperature has given rise to numerous experimental investigations [3–19] leading to controversial descriptions of the glacial state.

Kivelson et al. have suggested that the glacial state was apparently amorphous [3–5], and has determined this phase as a defect-ordered crystal from theoretical

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considerations emanating from the ‘frustration-limited theory’ (FLD) thermodynamic theory of supercooled liquid [20]. The formation of a defect-ordered crystal would be connected to the inability of the system to tile space from the development of a locally preferred structure, i.e. to a topological frustration. Consequently the locally preferred (glacial) and ideal crystal structures should be slightly different. In this context, the glacial state could be the first experimental evidence of topological frustration in supercooled liquids, and the polyamorphism situation in TPP could be considered as an enlightening feature on the understanding of the supercooled liquid state and the subsequent glass formation.

Demirjian et al. [19] have described the glacial state, from RMN experiments interpreted in the frame of the FLD theory, as plastic crystal composed of domains of nanocrystals.

Outside the description of the glacial state as not truly amorphous, Rössler et al. claimed that the glacial state is liquid [8,10,16], and the transformation of the supercooled liquid into the glacial state was interpreted as a change of fragility from dielectric and RMN data, i.e. as a first-order liquid–liquid phase transition. Mizukami et al. [11] have also described the glacial state as a highly correlated liquid from X-ray diffraction, calorimetric and dielectric measurements.

In this paper, direct evidence that the glacial state is composed of nano domains of the crystalline phase is given from the comparison of the low-frequency Raman spectra taken in the different states of TPP. Such an observation leads to the description of the glacial state as an abortive stage of the crystallization process, i.e. as composed of nanocrystallized domains in a matrix of non-transformed supercooled liquid. The influence of thermal parameters which control the formation of the glacial state is analyzed, and a scenario to understand the origin of the glacial state without considerations on structural frustration is proposed from Raman investigations.

2. Experimental

TPP was purchased at 99% purity from Janssen and used without further purification. The liquid was encapsulated in a spherical pyrex cell ($\varnothing = 3$ mm).

The spectra of the different states of TPP covering the frequency range from 3 to 300 cm^{-1} , were taken with a XY Dilor spectrometer equipped with an N_2 -cooled CCD system, using a mixed argon–krypton coherent laser operating at 514.5 nm. Low-temperature investigations were performed using an Oxford nitrogen-flux device that keeps temperature fluctuations within 0.1 K.

The glacial state can be formed either by slow heating of the rapidly undercooled sample or by keeping isothermally the sample at temperatures above the calorimetric glass transition (201.8 K [6]) in the range 210–235 K [8–10]. The latter protocol (displayed in Fig. 1) was mainly used in Raman experiments to investigate the transformation between the supercooled liquid and the glacial state. The liquid was quenched down T_g (201.8 K [6]) at $T_q = 190$ K by shifting the sample into the regulated nitrogen-flux. The sample was then heated ($\dot{T} = 6$ K/min) and the glacial state was prepared by isothermal aging at $210 \text{ K} < T_a < 230 \text{ K}$. Using this experimental procedure the $[3, 300 \text{ cm}^{-1}]$ spectral range was analyzed in the glacial state prepared at $T_a = 214, 216, 218, 220, 222, 224$, and 226 K. Raman spectra were taken during the isothermal transformation of the supercooled liquid into the glacial state (glaciation) corresponding to the procedure 1 of the thermal protocol described in Fig. 1. In a second stage, the glacial state was prepared at $T_a = 224$ K using different heating rates between T_q and T_a . By a further heating above 230 K, TPP crystallizes near 235 K. Raman spectra were taken during this temperature ramp corresponding to the procedure 2 of data acquisition reported in Fig. 1. The crystalline

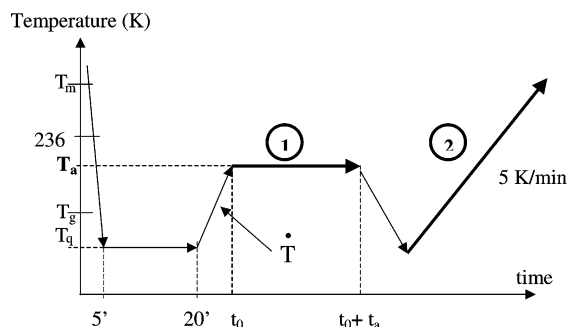


Fig. 1. The temperature profile of the thermal protocol used for experimental investigations are displayed versus time. The thick arrows correspond to the data acquisitions (procedure 1 and 2).

state obtained from this procedure is the ultimately stable phase which was recorded at different temperatures for the comparison of the Raman spectra in the different states at the same temperature. No other crystalline state has been evidenced on the [100, 290 K] temperature range.

3. Results

In a first stage, the glacial state was formed from the protocol described in Fig. 1 using the same heating rate ($\dot{T} = 6$ K/min) at different temperatures T_a . Fig. 2a allows to compare the low- ($5\text{--}200\text{ cm}^{-1}$) frequency Raman spectra of the supercooled liquid, glacial and crystalline states at the same temperature ($T_a = 220$ K). In the inset of Fig. 2a is displayed the time dependence of the low-frequency spectrum during the isothermal transformation at $T_a = 220$ K. The quasi-elastic component, characteristic of the

dynamics of a liquid, transforms progressively into a broad low-frequency band that one can easily recognize as the envelope of the low-frequency phonon peaks of the stable crystalline phase. At higher frequencies is observed the emergence of two Raman bands around 100 and 150 cm^{-1} which correspond to two distinguishing spectral features of the crystal. Fig. 2b clearly demonstrates that the crystal-like features are enhanced when T_a is increased. Consequently experiments carried out during the isothermal transformation of the supercooled liquid are indicative that the glaciation process corresponds to an abortive crystallization in a stage strongly dependent on T_a . If the description of the glacial state as composed of crystallized domains in a matrix of non-transformed liquid is adopted the volume fraction of crystallinity can be determined during a glaciation process and in the glacial state formed at different temperatures, from the determination of the intensity of the crystal-like features

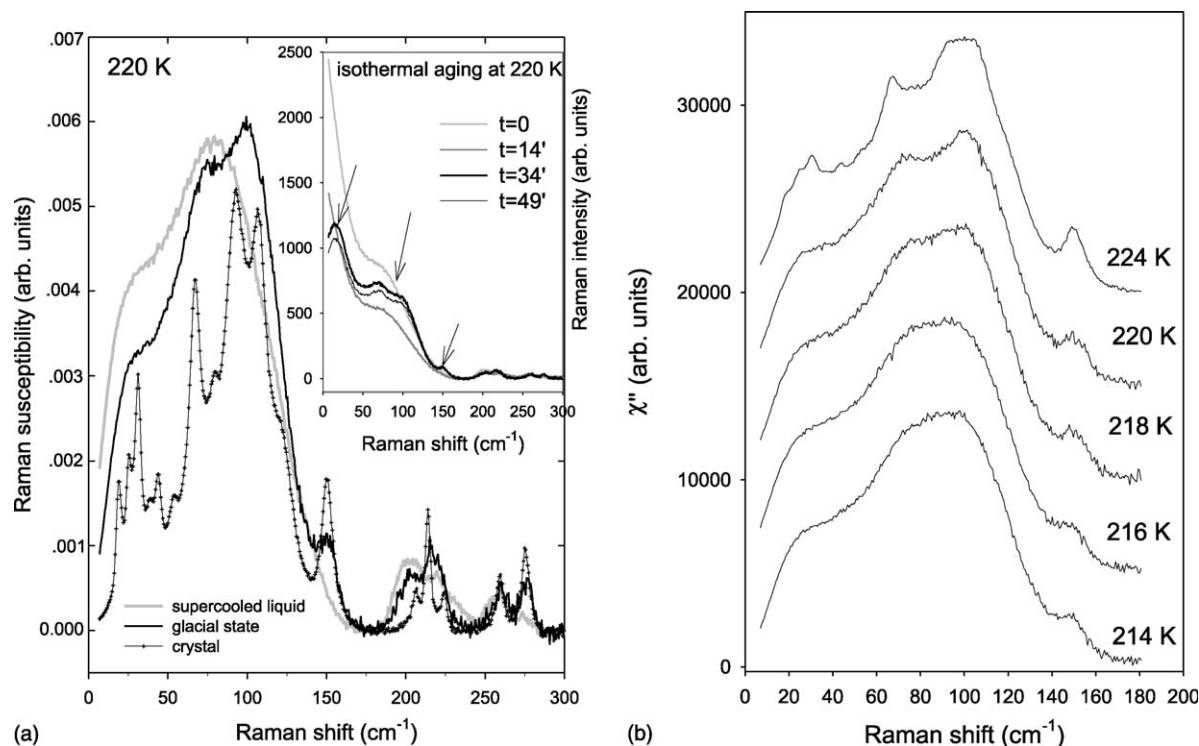


Fig. 2. Low-frequency susceptibilities of the supercooled liquid, glacial state and the crystal. The time dependence of the Raman spectrum of TPP is plotted during an isothermal aging at 220 K in the insert. It is clearly observed that the Raman features of the glacial state appear as the signature of sub-micro particles of the crystal. (b) Low-frequency susceptibility of the glacial state prepared by isothermal aging at different temperature T_a by the procedure 1 of the thermal protocol described in Fig. 1.

observed in the low-frequency Raman spectrum of TPP during the transformation. In this context, the Raman intensity of the supercooled liquid at the earliest stage of the isothermal transformation [$I_{\text{Ram}}(t = 0)$] was subtracted from the Raman intensity recorded during the isothermal aging [$I_{\text{Ram}}(t)$],

leading to the time dependence of the Raman spectrum of crystal-like features. Each spectrum was normalized according to

$$\int_{\omega_0}^{\omega_c} I_{\text{Ram}}(\omega) d\omega = 1$$

where $\omega_0 = 3 \text{ cm}^{-1}$ and $\omega_c = 300 \text{ cm}^{-1}$, and the contribution $I_{\text{Ram}}(t) - I_{\text{Ram}}(t = 0)$ was then calculated.

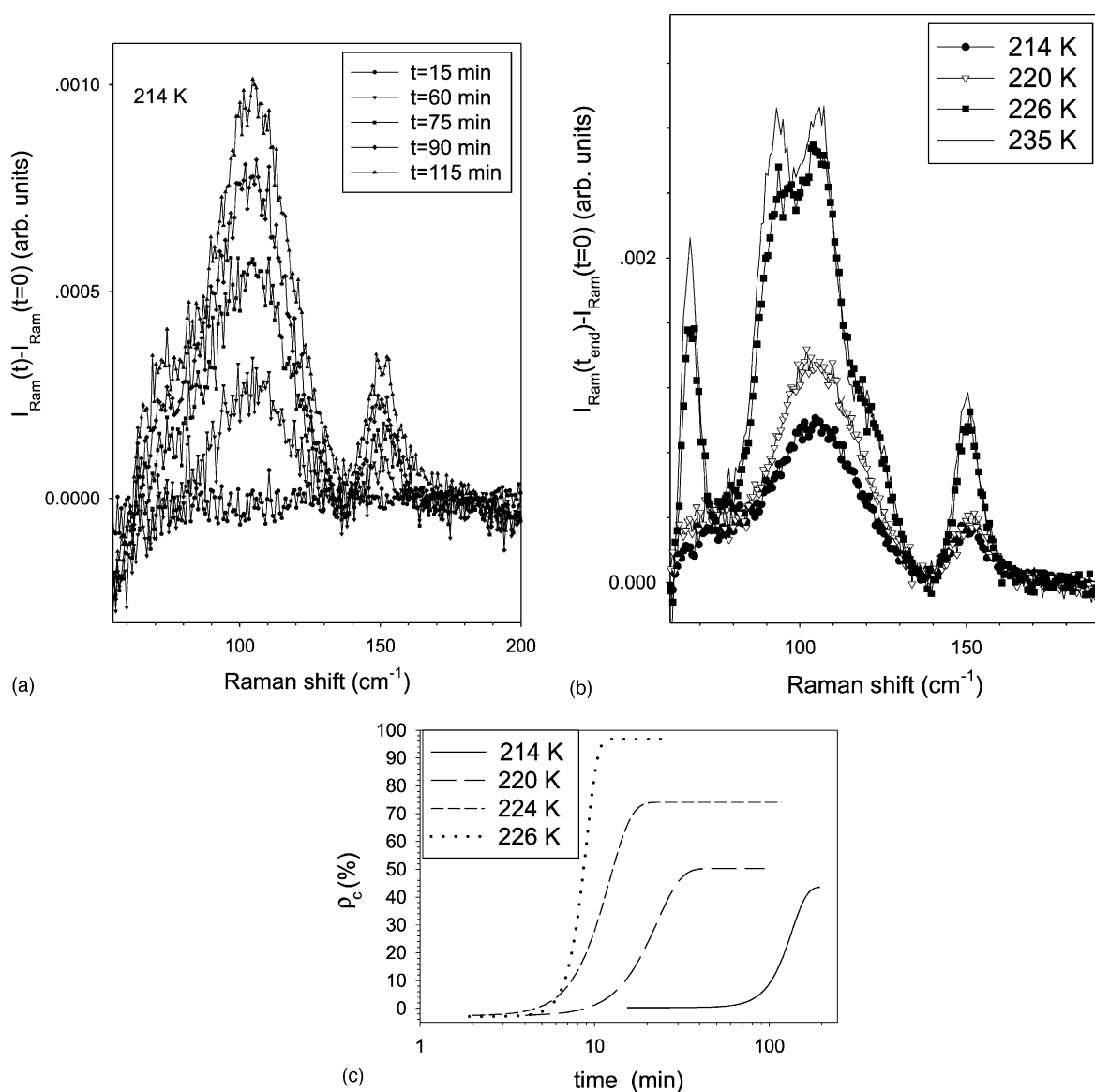


Fig. 3. (a) The difference between normalized Raman intensities $I_{\text{Ram}}(t_{\text{end}}) - I_{\text{Ram}}(t = 0)$ is plotted during a glaciation process at $T_a = 214 \text{ K}$. (b) The same difference is plotted at the end of isothermal transformations ($t = t_{\text{end}}$) performed at different temperatures $T_a = 214, 220, 226$, and 235 K . The isothermal transformation at 235 K is assumed to be the true crystallization. (c) Fitted time dependence of the volume fraction crystallinity ρ_c , during glaciation process at $T_a = 214, 220, 224$ and 226 K , obtained by the use of an Avrami law. Fits are plotted in a t -logarithm scale to highlight the influence of T_a upon the time of transformation.

This latter is plotted in Fig. 3a for a glaciation at 214 K in the 50–200 cm⁻¹ frequency range. This plot highlights the spectral changes observed during the glaciation, i.e. a progressive increase of the intensity of crystal-like features around 100 and 150 cm⁻¹, corresponding to the Raman signatures of a transformation of the supercooled liquid into sub-microscopic grains of the ultimately stable state. Each glacial state prepared between 210 and 230 K appears as an aborted and indefinitely stable stage of the crystallization. In this context, the contribution $I_{\text{Ram}}(t) - I_{\text{Ram}}(t = 0)$ is compared at the end of the isothermal transformation ($t = t_{\text{end}}$) for $T_a = 214, 220$ and 226 K, and these three contributions are compared to the same contribution at 235 K (Fig. 3b), where the crystallization is generally observed [13]. Taking account the effect of temperature upon low-frequency Raman intensities, Raman spectra recorded at $T_a > 214$ K were replotted using

$$\frac{I_{\text{Ram}}(\omega, T_a)}{[n(\omega) + 1]_{T_a}} [n(\omega) + 1]_{214 \text{ K}}$$

before the normalization procedure. It can be easily observed in Fig. 3b that the intensity of crystal-like features of the glacial state increases as the aging temperature T_a is increased, and remains lower than the intensity calculated at 235 K. Consequently, if the description of the glacial state in terms of domains of the stable crystalline phase is adopted, the intensity $I_{\text{Ram}}(t_{\text{end}}) - I_{\text{Ram}}(t = 0)$ of crystal-like features between 60 and 190 cm⁻¹ can be considered as proportional to the rate of transformed matter. The isothermal transformation of the supercooled liquid at 235 K is considered to correspond to the true crystallization, and it has been assumed that the intensity of $I_{\text{Ram}}(t) - I_{\text{Ram}}(t = 0)$ between 60 and 190 cm⁻¹ is representative of 100% of volume fraction of crystallinity (ρ_c). From this reference, the transformation rate in the stable phase, i.e. the volume fraction of crystallinity is calculated, and reported Table 1, in the glacial states prepared by isothermal aging in the [214, 226 K] temperature range. The time dependence of ρ_c can be fitted using a sigmoidal shape which is usually suggestive of a nucleation and growth process or merely a growth of incipient nuclei. The time of half transformation t_0 is determined by the fitting procedure using an Avrami law, and the fit of the time

Table 1

Crystalline volume fraction ρ_c determined from the low-frequency investigations in glacial states prepared at T_a

Glacial state prepared at T_a (K)	ρ_c (%)
214	43.6
218	50.2
220	53.7
222	63.9
224	74.1
226	96.8

dependence of ρ_c is plotted in a log-scale in Fig. 3c in the [214, 226 K] temperature range. Fig. 3c reveals a strong influence of the temperature T_a , where the glacial state is prepared, on the time of transformation and the transformation rate. This latter interpreted in terms of volume fraction of crystallinity (ρ_c), is determined to be lower than 50% for the lowest temperatures of glaciation.

In a second stage, the glacial state is formed using the protocol described in Fig. 1 at $T_a = 226$ K, with different heating rates ($\dot{T} = 0.3, 0.5, 1.0$ and 6.0 K/min). The low-frequency Raman spectra of the glacial state formed by isothermal aging at 224 K after different heating procedures from $T_q = 190$ K are plotted in Fig. 4a. It is clearly observed that high heating rate from $T_q = 190$ K up to $T_a = 224$ K favours the crystallization since the Raman spectrum of the glacial state formed at 224 K after heating at 6 K/min is close to the crystal's one. The contribution $I_{\text{Ram}}(t_{\text{end}}) - I_{\text{Ram}}(t = 0)$ is determined for the glacial state corresponding to each \dot{T} value, and plotted in Fig. 4b. The volume fraction of crystallinity corresponding to each glacial state is reported in Table 2.

The Raman investigations in the low-frequency range give an enlightening picture of the glacial state as composed of sub-micro domains of the stable crystalline state. Investigations in the C–H stretching region (3000–3100 cm⁻¹ range) could give additional information since crystallographic data suggest the possible existence of unusual C–H...O hydrogen-bonding networks in the crystal [21]. The temperature dependence of the Raman spectrum in the [3000, 3100 cm⁻¹] frequency range in the crystalline phase reveals (Fig. 5a) a positive frequency shift ($d\omega/dT > 0$) of two Raman bands which are not detectable in the glassy and liquid states (Fig. 5b).

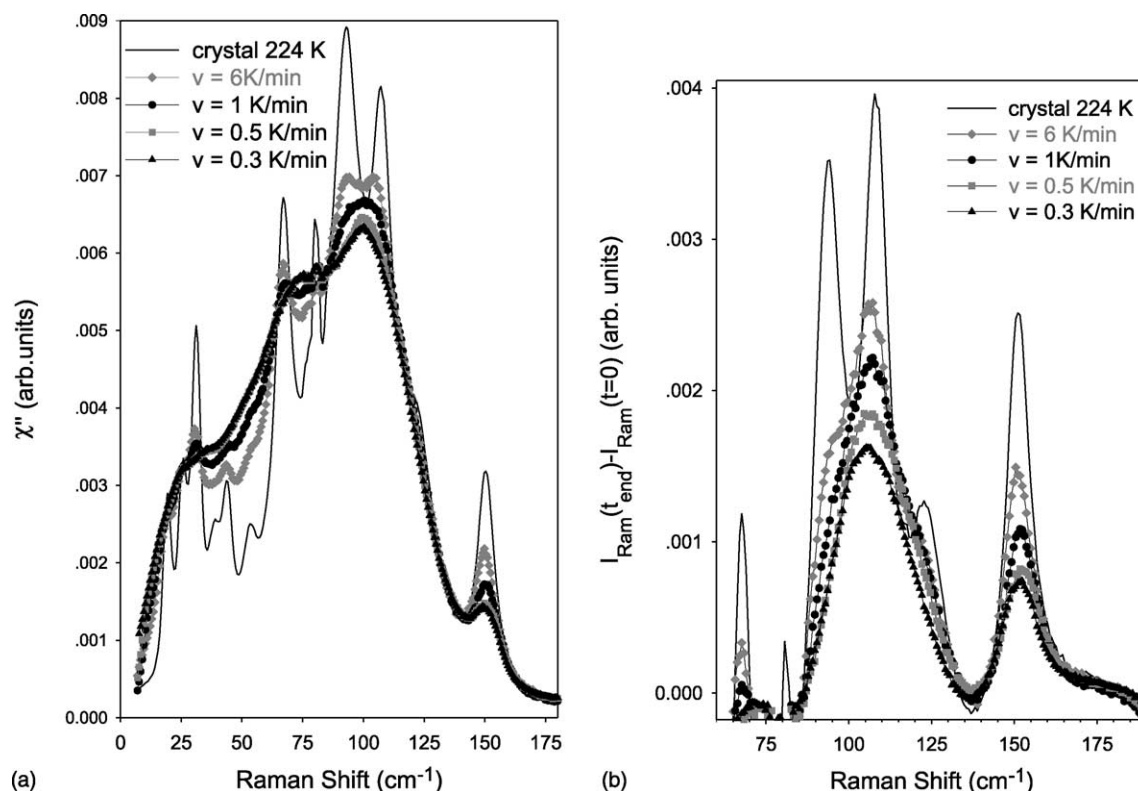


Fig. 4. Influence of the heating rate (\dot{T}), between T_q and T_a , described in the temperature profile of the thermal protocol on the low-frequency Raman spectrum of the glacial state prepared at $T_a = 224$ K on the crystal-like features of the glacial state formed at 224 K determined by spectrum difference between supercooled liquid and glacial state.

The observation of two distinct stretching-mode frequencies that are temperature dependent is suggestive of the existence of two types of molecular associations through two weak intermolecular C–H···O hydrogen bonds characterized by two different H···O distances. Such a type of hydrogen bond can be considered as an additional stabilizing force when short C–H···O–P contacts exist [22]. In Fig. 5b, it is clearly shown that the Raman C–H stretching band associated to the C–H···O hydrogen bond is not observed in the Raman spectrum of the liquid, and glassy states, and thus such hydrogen-bond networks are the signature of the crystalline structure. The same Raman investigations were carried out in glacial state prepared at $T_a = 216$, 222, and 226 K. Each Raman spectrum (Fig. 5c) exhibits these Raman bands which are not resolved at the temperature where the glacial state is formed. It can be seen in Fig. 5c that the Raman intensity of these bands is larger for glacial

state prepared at higher temperatures. This observation confirms the description of the glacial state as corresponding to an abortive crystallization in a stage depending on the temperature T_a . The relative intensity of the two characteristic bands associated to the C–H···O hydrogen-bond networks is reported in Table 3 and converted in volume fraction of crystallinity from the comparison with the intensity of

Table 2

Crystalline volume fraction ρ_c determined from the low-frequency investigations in glacial state prepared by isothermal aging at $T_a = 226$ K after different heating ramps (\dot{T}) between $T_q = 190$ K and $T_a = 226$ K

\dot{T} (K/min)	ρ_c (%)
0.3	46
0.5	54
1	63
6	73

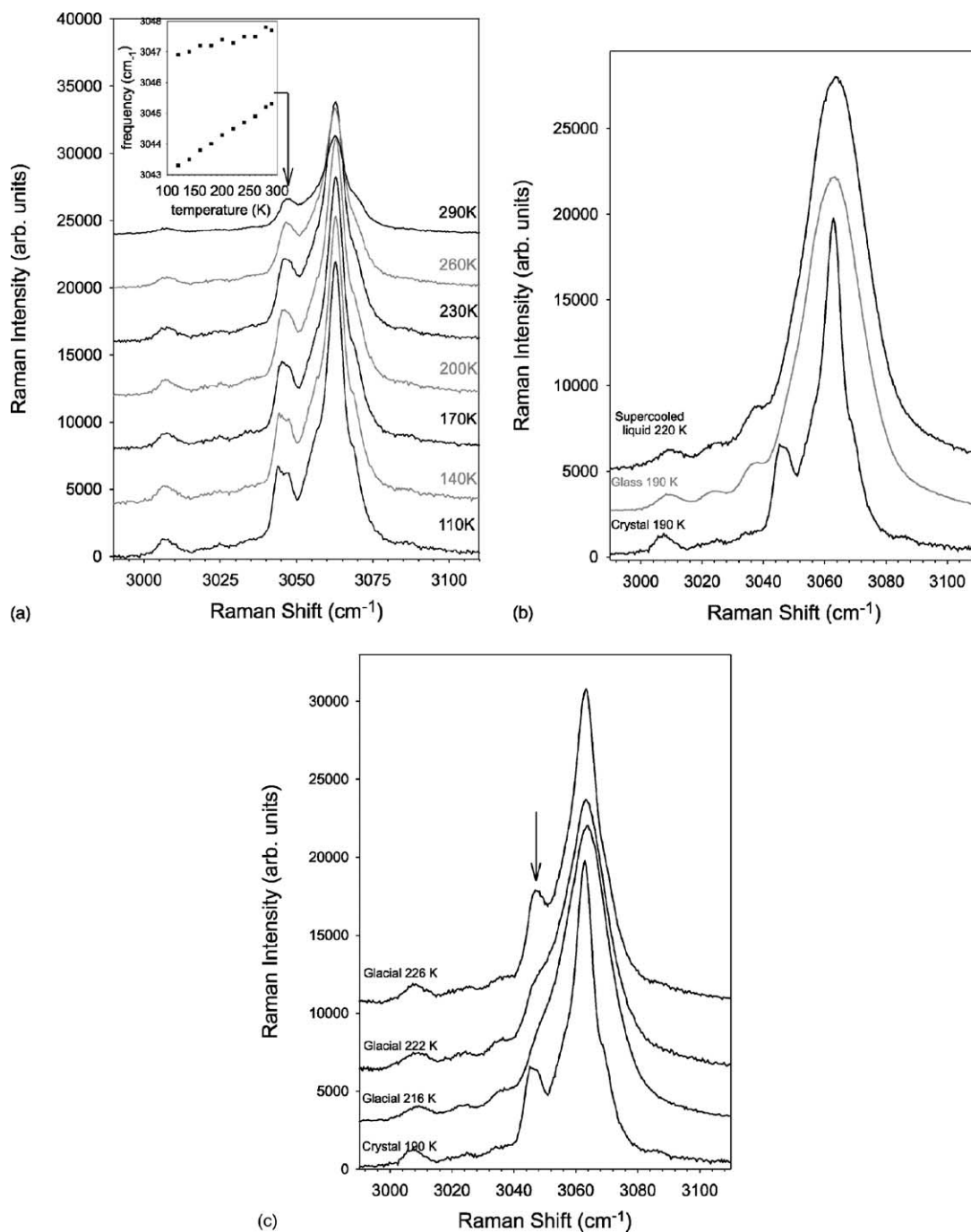


Fig. 5. Raman spectra in the C–H stretching region in the different states of TPP. (a) temperature dependence of the C–H stretching modes in the crystal; the frequency temperature dependence of Raman bands near 3045 cm⁻¹ is plotted in the insert. (b) Evidence of the 3045 cm⁻¹ Raman band only in the spectrum of the crystal. (c) influence of the temperature T_a (where the glacial state was prepared) on the 3045 cm⁻¹ band (localized by the arrow).

Table 3

Crystalline volume fraction ρ_c determined from the intensity of C–H stretching bands associated with hydrogen bonding in glacial state prepared at T_a with respect to that calculated in the Raman spectrum of the crystal. Taking into account that the intensity of these Raman bands in the crystal was observed to be temperature independent temperature effects on the determination of ρ_c were neglected

Glacial state prepared at T_a (K)	ρ_c (%)
216	48
222	60
226	89

the same bands in the crystal. It can be observed from the comparison of Tables 1–3 that the analyzes of the low-frequency and the C–H stretching regions are converging into a similar description of the glacial state as composed of domains of the stable crystal.

The picture of the glacial state as a mixed phase supercooled liquid/crystallized domains is confirmed from the examination of the $1100\text{--}1200\text{ cm}^{-1}$

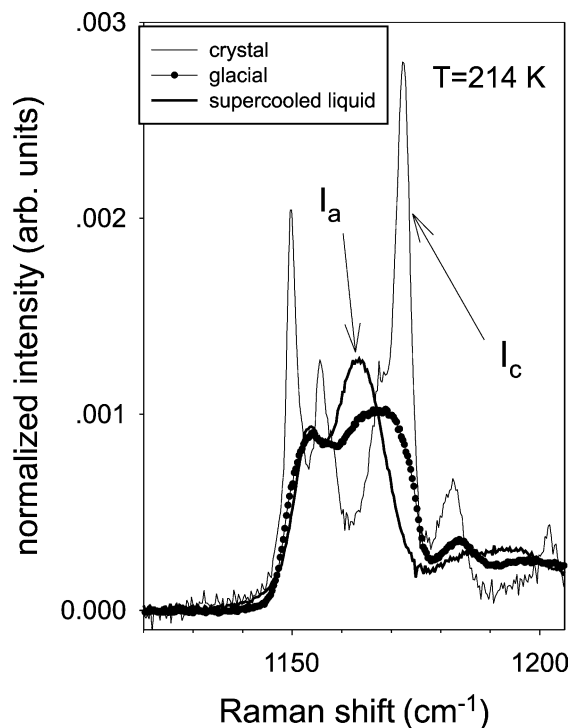


Fig. 6. Evidence, in the $1120\text{--}1200\text{ cm}^{-1}$ frequency range, of a mixing of nanocrystals and supercooled liquid in the glacial state from the observation of Raman band composed of distinguished features of the liquid and the crystal.

frequency range (Fig. 6) where the spectral signatures of the crystal (I_c component) are especially distinctive from that of the liquid (I_a component). In Fig. 6, we can recognize the spectrum of the glacial state as a combination of the spectra of the crystal and the non-transformed supercooled liquid.

By these investigations no trace of structural frustration was directly evidenced. However, some calorimetric features observed by heating the glacial state, just before the crystallization [6,11,14,17,19] were considered as a partial melting inherent to topological defects [14,19]. These features were also interpreted as the signature of a glass transition [6,11]. The analysis of the conversion of the glacial phase into the crystal phase appears as a significant contribution in the understanding of the origin and the description of the glacial state. Consequently, a special attention was focused upon the heating of the glacial state prepared at 220 K and cooled down to 190 K. It is worth pointing out that no change in the shape of the Raman spectrum was detected in decreasing temperature down to 190 K. In Fig. 7a and b, are reported the Raman spectra recorded during a heating ramp at 5 K/min. A significant change of the Raman spectrum on heating glacial TPP can be easily observed from 215 K (Fig. 7a). This change seems to result from the emergence of an additional Raman component in the very low-frequency regime, where the quasi-elastic component characteristic of the liquid state was detected. The intensity of the quasi-elastic component increases up to 222 K, whereas the Raman band-shape remains coarsely the same between 50 and 150 cm^{-1} . Above 150 cm^{-1} , Raman spectra are superimposed. No change of local order was detected between 190 K up to 230 K. Above 222 K, the intensity of the quasi-elastic component decreases and Raman bands sharpen until the crystallization. In order to assign indubitably the quasi-elastic component to the presence of supercooled liquid, the Raman intensity of the supercooled liquid recorded at the beginning of the isothermal aging (I_{sqliq}) was subtracted from the Raman intensity of the glacial state (I_{glacial}) recorded on heating at 221.2 and 222.4 K. Fig. 8 shows that $I_{\text{glacial}} - I_{\text{sqliq}}$ corresponds to the broadened spectrum of the crystal, and can be considered as the Raman spectrum of nanocrystals. As a consequence, the glacial state heated around 220 K appears as composed of nanocrystals and the original

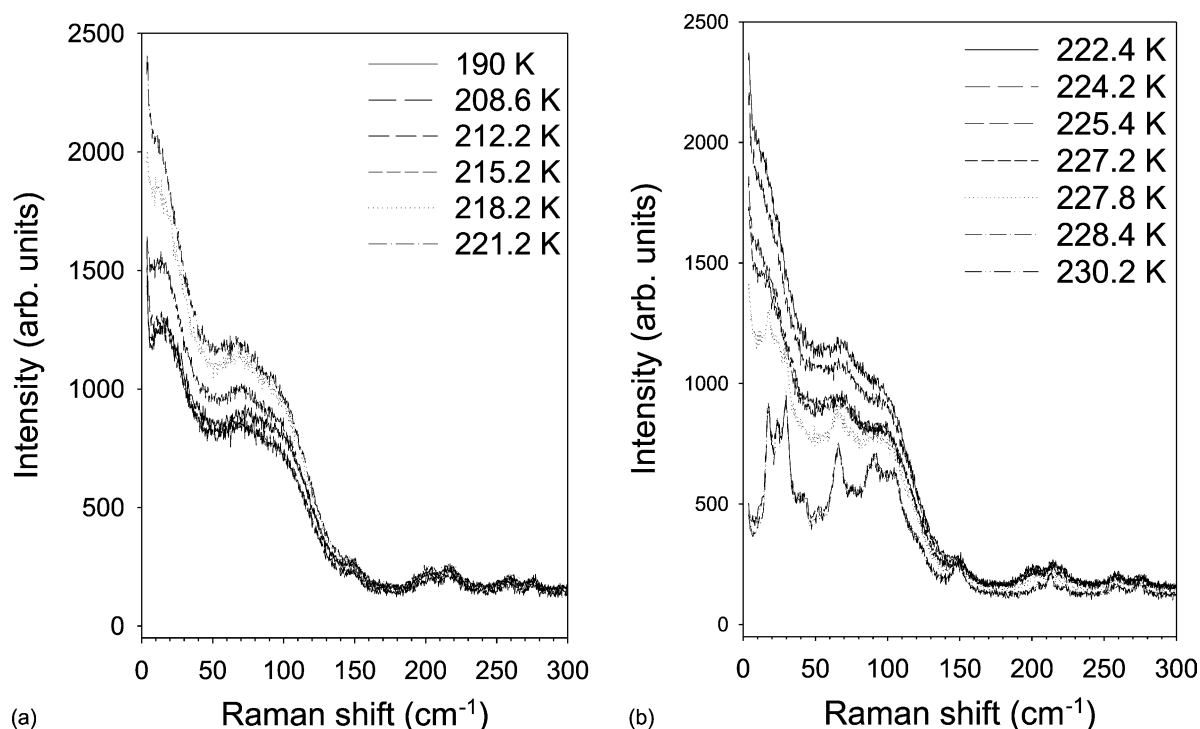


Fig. 7. The temperature dependence of the Raman spectrum of the glacial state prepared at 220 K, recorded on a heating ramp at 5 K/min. The spectra are displayed on two plots to show clearly the evolution of the Raman intensity in the 4–300 cm^{-1} range.

supercooled liquid. The decrease of the intensity of the quasi-elastic component and the sharpness of the Raman bands observed in Fig. 7b above 220 K reveals that the nanocrystals are growing at the depends of the volume of supercooled liquid.

4. Discussion

The reported Raman analyzes in the different frequency ranges are converging into the description of the glacial state as a two-phase (supercooled liquid/crystallized domains) system. The close relationship between the low-frequency Raman spectra of the glacial and crystalline states, and the detection unusual hydrogen bonding both in the glacial and crystalline states are strong arguments to support the idea that the local structure in crystallized domains in the glacial state is rigorously similar to the structure of the stable crystal. Moreover no trace of change in the local order can be detected during the conversion of the glacial state into the crystal, and

then the partial melting observed by heating the glacial state should not be considered as the melting of topological defects.

Consequently, the remaining fundamental question is to determine the origin of the glacial state, i.e. what is the phenomenon responsible for a failed crystallization in a relative stable state. The results obtained from the preparation of the glacial state at 224 K using different heating ramps suggest that a rapid heating from the glassy state (190 K) up to T_a favours the crystallization. This consideration is in agreement with calorimetric investigations [8,17] in which the glacial state (i.e. the failure of crystallization) is observed only on slow heating runs. Such a phenomenon can be understood from the consideration of a low degree of overlapping of the nucleation rate- and growth rate-curves. A controlled slow heating treatment or isothermal aging around temperatures at which the nucleation rate is very high and the crystal growth is slow (near 210 K [13]) can lead to a high-density sub-microcrystalline structure, with particle dimension in the 30 Å range [12], corresponding to a

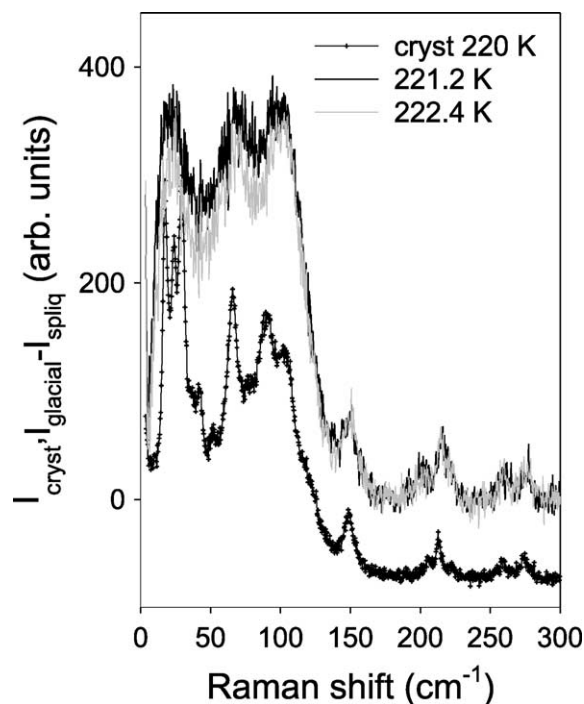


Fig. 8. The contribution $I_{\text{glacial}} - I_{\text{spliq}}$ is plotted at 221.2 and 222.4 K to demonstrate the appearance of supercooled liquid in this temperature range when the glacial state is heated. This contribution is compared to the Raman spectrum of the crystal which is arbitrarily shifted to give a clear illustration that $I_{\text{glacial}} - I_{\text{spliq}}$ corresponds to the Raman spectrum of nanocrystals.

heavily nucleated state. Taking into account the large unit cell of the crystal [21], long-range order may not be fully achieved in the smallest crystallites, and it may be difficult to distinguish structurally between crystallites and local structures in the non-transformed supercooled liquid with similar short-range order. Such a picture of the glacial state is very close to the description of a defect-ordered crystal given by Kivelson et al. [3–5], however, its origin would be fundamentally different from the one emerging from the FLD theory [3–5]. A high-density of very small crystallites subdivides the residual supercooled liquid and could frustrate crystallization because the interstitial volumes of the remaining liquid may not exceed the critical size for crystallization. This can explain the extreme stability of the glacial state. The conversion of the glacial state into the crystal via a (pre)melting described in this paper can also be understood from the description of the glacial state as

a heavily nucleated state. It can be reasonably assumed that the size of the smallest particles nearly corresponds to the critical radius which is dependent on the temperature where nucleation occurs. By increasing temperature these particles become unstable and melt. Consequently Raman data support that a structural change in the short-range order is not necessary to explain this partial melting within the crystallization process. Further crystallization occurs at temperatures where crystal growth is rapid (near 230 K [13]) and high nucleation density is not necessary to completely crystallize the remaining liquid.

5. Conclusion

Raman spectroscopy gives an enlightening picture of the glacial state and its origin. More generally Raman spectroscopy appears as a well-adapted probe to analyze polymorphism and to differentiate a nanostructured state from a really amorphous phase. Raman data have indubitably revealed that the glacial state was described as a mixed phase (supercooled liquid/nanocrystallized domains) where nanocrystals have the same structure that the stable crystal. No trace of structural frustration has been detected from the careful inspection of the Raman spectrum of the glacial state, and from the analysis of this spectrum during the conversion of the glacial state into the crystal by heating. This result should have a significant impact on the consideration that molecular supercooled liquid (and the subsequent glass formation) could result from the structural frustration of a locally preferred structure which prevents crystallization.

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