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Raman signature of polyamorphism in triphenyl phosphite

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The polyamorphism of triphenyl phosphite has been investigated from a low-frequency Raman-scattering study. Interesting features about glaciation processes have been revealed from a study of the boson peak and an analysis of the Raman susceptibility in the glacial and crystalline states. The very close correspondence between the phonon peaks observed in the crystal and the Raman spectrum of the glacial state, as well as some contradictions about the fragility of the glacial state, if it is considered as amorphous, lead us to favor the description of the glacial state in terms of nanocrystallized domains. [S0163-1829(98)01925-0]

Introduction. Triphenylphosphite (TPP) is one component glass-forming material that has recently focused much attention since it is suspected to show a situation of polyamorphism.[1–3] This is due to the possibility for the undercooled liquid to transform, through a first-order transition, into a phase that is believed to be amorphous because x-ray scattering does not show any Bragg reflections.[1] A characteristic of this so-called ''glacial'' state is the Arrhenius temperature dependence of the relaxation, shown both by dielectric and NMR studies.[3] This suggests that this state would be much stronger than the liquid that is considered as very fragile,[3] according to Angell terminology. The structure of the highly viscous glacial state is an important issue since its x-ray diagram appears very similar to that of the liquid.[2] It has been suggested[1] that it could correspond to a mesoscopic array of domains, having a structure locally preferred to that of the observed crystal state, which are prevented to grow by some frustration effect (''defect-ordered crystal''). Raman scattering has both structural and spectroscopic use. It is a very well adapted technique to characterize the fragility of molecular glass-forming liquids, from comparison of vibrational and relaxational contributions. In order to get a better insight into the nature of the glacial state and the origin of the polyamorphism, we have carried out Raman-scattering investigations in the liquid, glacial, and crystalline states of TPP.

Experimental procedure. TPP was purchased at 99% purity from Janssen and used without further purification. The liquid was input in a spherical pyrex cell ($\varnothing = 3$ mm). Stokes Raman spectra were collected on a XY DILOR spectrometer, in backscattering geometry, using the 514.5 nm line of a mixed argon-krypton coherent laser. As usual, the depolarized light scattering $I^{\mathrm{Ram}}(\omega)$ is converted into Raman susceptibility $\chi''(\omega) = I^{\mathrm{Ram}}(\omega)/n(\omega)+1$, where $n(\omega)$ is the Bose occupation number.

The high sensibility of the cooled charge-coupled device multichannel detector allows us to record spectra in the $10-600\ \mathrm{cm}^{-1}$ domain in 100 s with a resolution of about $2\ \mathrm{cm}^{-1}$. Investigations below room temperature were performed using an Oxford nitrogen-flux device that keeps temperature fluctuations within 0.1 K. This device allowed us to perform ramps in temperature with different rates (<6 K/min) as well as a rapid quench.

The undercooled liquid, the glacial state, and the crystal were investigated from an experimental procedure determined from previous studies,[1–4] and described hereafter. The melt is first quenched from room temperature down to 190 K below the glass transition (201.8 K[4]) by shifting the sample into the regulated nitrogen flux. The temperature is then increased up to 215 K where the continuous transformation of the supercooled liquid into the glacial state is investigated during an isothermal aging. The first stage of this aging process provides the spectrum of the undercooled liquid state [Fig. 1(a)]. The glaciation process is observed via a turbiding effect, starting after about 30 min, and a transformation of the Raman spectrum [Fig. 1(b)] in the low-frequency region ($5\ \mathrm{cm}^{-1} < \omega < 200\ \mathrm{cm}^{-1}$). After about 150 min the sample gets clear again and the Raman spectrum remains stable until the end of the analysis, i.e., during 24 h. The stability of the glacial state was not investigated for a longer time at this temperature. However, the temperature dependence of the Raman spectrum of both the undercooled liquid and glacial state were studied on an extended temperature range (100–270 K). On heating the glacial phase (0.25 K/min) the crystallization occurred near 230 K. The crystal was then cooled down to 215 K in order to compare the Raman spectrum of the three states (undercooled liquid, glacial, and crystal) at the same temperature. It is very noticeable that, above $150\ \mathrm{cm}^{-1}$, no Raman feature was found to characterize one of these three states. This observation reveals that no symmetry breaking in the internal mode region occurs in the transformation from liquid to crystal, certainly because of the low crystalline symmetry. Consequently, we focused the study on the analysis of the low-frequency region that shows large modifications.

The Raman spectrum of the undercooled liquid and glacial state. The Raman susceptibility of the *undercooled liquid* [Fig. 1(a)] is characterized by a broad vibrational band covering the low-frequency region below $150\ \mathrm{cm}^{-1}$ with a maximum near $80\ \mathrm{cm}^{-1}$ corresponding to microscopic excitations, and a pronounced shoulder at about $30\ \mathrm{cm}^{-1}$ in a frequency range where the boson peak is usually found.[5–11]

The low-frequency Raman susceptibility of the *glacial state* [Fig. 1(b)] shows noticeable evolutions that can be summarized as follows:

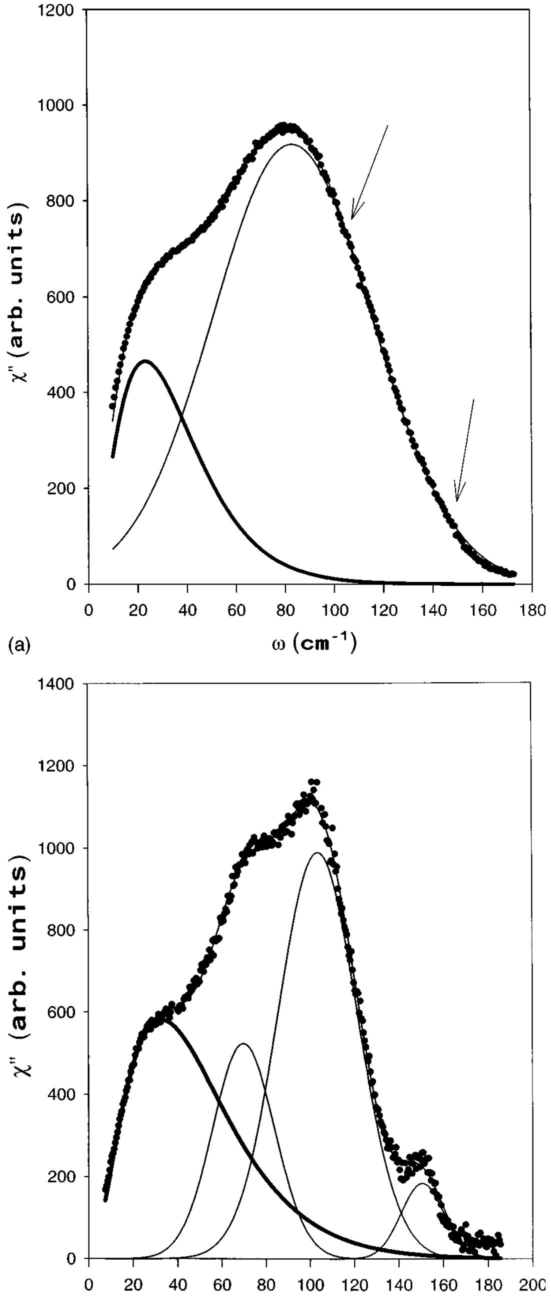

FIG. 1. Representation of the fitting procedure of Raman susceptibilities recorded at 215 K. (a) in the supercooled liquid: the arrows localize the shoulders corresponding to the merging of bands during the glaciation, (b) in the glacial state. Full circles correspond to experimental data, and the lines correspond to the constituent peaks and the result of the fitting procedure. BP is represented by a thick line.

(a) Below 50 cm^{-1} the line shape of the spectrum is very similar to that of the liquid. However, one can notice a decrease in the intensity of the shoulder relative to that measured at the maximum of the band; also the minimum on the susceptibility curve between the central relaxation peak and the microscopic band is seen to shift to higher frequencies (inset of Fig. 3).

(b) The broad microscopic-excitation band becomes structured. This is due to the merging of a peak at about 100 cm^{-1}. The top of the band of the liquid spectrum near 80 cm^{-1} remains as a less intense shoulder on the low-frequency side of the merging peak. Decreasing the temperature of the glacial state shows an amplification of the shape structuration in the 80–100 cm^{-1} range.

(c) The merging of a peak on the high-frequency side around 150 cm^{-1}. Looking at the liquid spectrum very closely, some delicate precursors of the specific features of the glacial spectrum can already been noticed in very gentle shoulders that coincide with the two merging peaks.

The first-order Stokes Raman spectrum can be described as a reduced intensity by[12]

$$I_r(\omega)=\frac{I^{\mathrm{Ram}}(\omega)\times\omega}{n(\omega)+1}=C(\omega)g(\omega),$$

which is the vibrational state density $g(\omega)$, weighted by the phonon-photon coupling function $C(\omega)$. Considerable attention has been devoted to the low-frequency contributions of the Raman susceptibility.[13–16] It is well known that for many glasses, at low temperatures $I_r(\omega)\approx\omega^4$ in the very low-frequency region, and then develops into the broad so-called boson peak[16,17] (BP) at higher frequencies. Controversial features about the nature of the BP are reported.[17,18] An analysis[17] of several results has revealed that the BP seems to have a universal nature, and would not thus be associated to the chemical composition of glass nor to the structure of the corresponding underlying crystal structure. However, in several molecular glass-forming liquids[18] phonon peaks of the crystal are found in the frequency range of the BP. Generally, the BP is considered to be closely connected with a medium-range order developing in the glass, and the position of the maximum intensity $\omega_{\max}$ is then expressed as[16] $\omega_{\max}\propto v/R_c$, where v is a sound velocity and R_c determines a length scale that may characterize different structural features, such as chemical ordering,[19] or microcrystallinity.[20] The low-frequency region of the shoulder was tentatively identified to the BP both for the liquid and the glacial state. It was fitted using the spectral profile representation of the BP proposed by Martin and Brenig[21] corresponding to $C(\omega)\approx\omega^2\exp(-\omega^2/4\omega_{\mathrm{MB}}^2)$ and also using a damping oscillator with a characteristic frequency ω_0. At frequencies higher than that of the BP, damped oscillators were used to fit the microscopic excitation bands in the 50–200 cm^{-1} region. This fitting procedure specifies our previous observations.

(a) The merging of a phononlike peak at 150 cm^{-1} was clearly observed during the glaciation.

(b) The shape of the most intense microscopic-excitation band is well fitted with only one damped oscillator profile in the supercooled liquid at 215 K, whereas in the glacial state a good agreement between experimental and fitted susceptibilities is obtained from consideration of two oscillators at 70 and 102 cm^{-1}.

(c) For both the supercooled liquid and the glacial state, the region of the shoulder is correctly fitted using either the Martin and Brenig model or a damped oscillator profile for the $C(\omega)$ function. The fitted values of the BP frequency, ω_{MB} and ω_0, respectively, are significantly different, however both fitting procedures lead to a similar profile of the BP and reveal a significant shift of the BP to the higher frequencies during the glaciation ($\omega_{\mathrm{MB}}=11.2\ \mathrm{cm}^{-1}$ in the super-

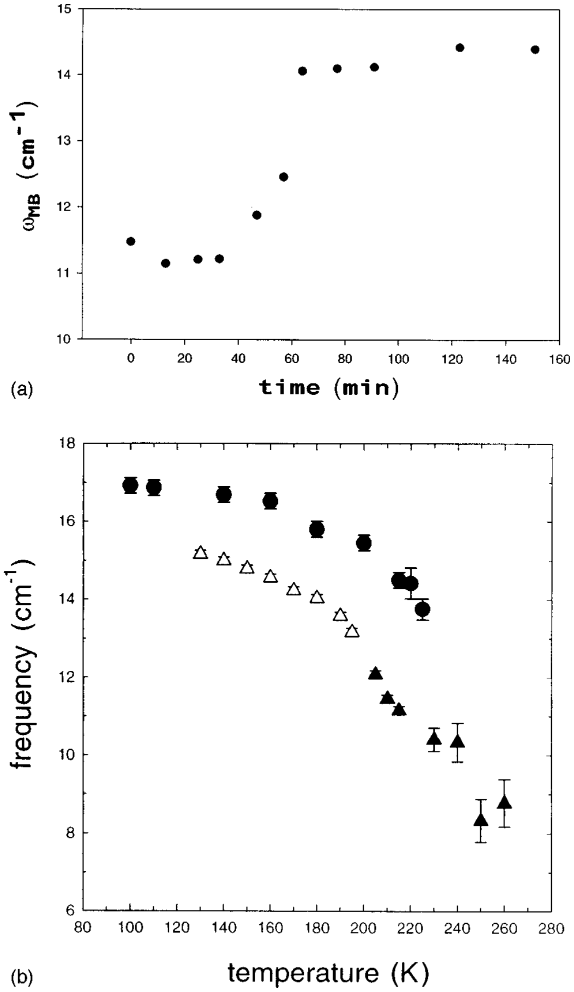

FIG. 2. (a) Isothermal time dependence of the BP frequency during the glaciation at 215 K. (b) Temperature dependence of the BP frequency in the supercooled liquid (full triangles); experimental data were obtained by cooling the melt from room temperature down to 200 K in the glassy state (open triangles) and in the glacial phase (full circles).

cooled liquid, and $\omega_{\rm MB}=14.5$ cm^{-1} in the glacial state). The frequency shift of the BP $\omega_{\rm BM}(t)$ during the isothermal process at 215 K is plotted in Fig. 2(a). This temporal evolution has a clear sigmoidal shape with an induction period of about 40 min, which must be associated to the lifetime of metastability of the undercooled liquid phase with regard to the glacial state at the investigated temperature. Such a time dependence can be associated with an Avrami law that is suggestive of a nucleation and growth process or simply a growth process of incipient nuclei. It confirms the apparent first-order character of the liquid-glacial transformation. This figure also shows that the transformation associated with the glaciation is certainly completed after 2 h at 215 K. The shift of $\omega_{\rm MB}$ cannot be explained only from the consideration of a variation of the sound velocity evidenced by Brillouin spectroscopy.[3] The frequency shift of the Brillouin line obtained by Wiedersich *et al.*[3] during the glaciation can be expressed as a ratio of frequencies $(\Delta v^{\rm glacial}/\Delta v^{\rm liq}=1.081)$, which is significantly different from the ratio of the $\omega_{\rm MB}$ values $(\omega_{\rm MB}^{\rm glacial}/\omega_{\rm MB}^{\rm liq}=1.295)$ obtained from our Raman experiments. If the frequency of the BP was to be connected to

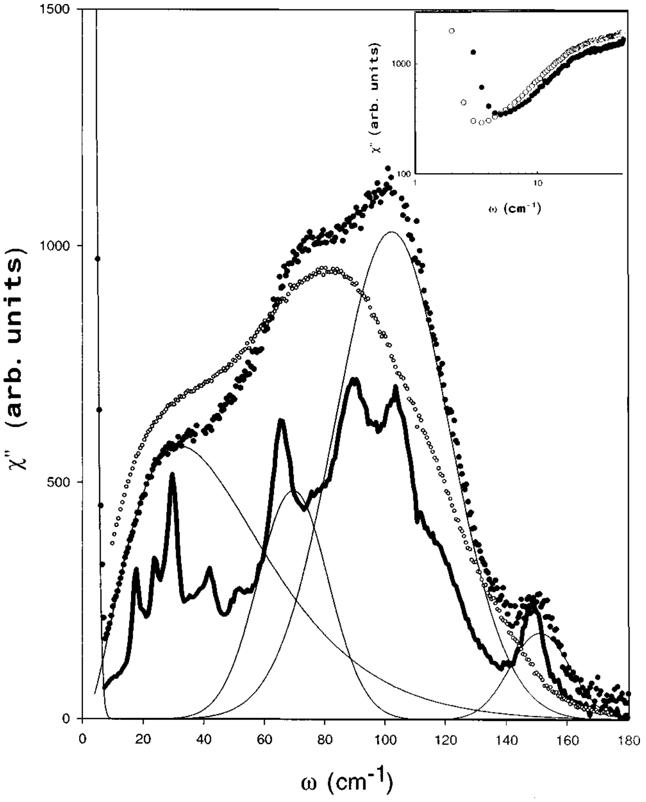

FIG. 3. Low-frequency Raman susceptibilities of the undercooled liquid (open circles), the glacial state (full circles), and the crystal (thick line) at 215 K. The thin lines correspond to the different peak components of the Raman spectrum of the glacial state determined by fitted procedure. This figure illustrates the filiation between the apparent boson peaks of the undercooled liquid state, glacial state, and low-frequency phonon peaks of the crystal. The corresponding Raman susceptibilities in the very low-frequency region of the supercooled liquid and the glacial state are reported in the inset.

a vitreous structure size R_C, the interpretation of the $\omega_{\rm MB}$ shift would need to consider a decrease of R_C in addition to the increase of the sound velocity. If the glacial state was considered as amorphous, this behavior would then be associated with an apparent decrease of the fragility during the glaciation, which is generally connected to a decreasing of the characteristic cluster size in the liquid. In order to investigate this feature further, a careful analysis of the very low-frequency region of the Raman susceptibility was performed. At lower frequencies than the boson peak, the quasielastic contribution of the spectra is considered as an excess over the vibrational spectrum, and exhibits a stronger temperature dependence than the boson peak.[5] This contribution is assigned to some relaxational processes. The relaxation and the vibrational contributions overlap and are not simply determinable.[5–11] However, Sokolov *et al.*[5] consider that the ratio (R_1) of the intensity at the low-frequency minimum to the intensity of the boson peak maximum can characterize the relative contributions of relaxations and vibrations to the spectrum. It is often observed that the higher the fragility, the smaller is this ratio.[5] This is consistent with the fact that the vibrational contributions are more marked in strong glass formers. The inset in Fig. 3 points out a significant decreasing of R_1 after glaciation. If the glacial state is assumed to be amorphous, it thus exhibits all the usual low-frequency spectroscopic criteria corresponding to a more fragile state than the original undercooled liquid. However, this interpretation is not in agreement with the Arrhenius behavior of the correlation times obtained from dielectric spectroscopy[3] performed in the glacial state, which seems to reveal the strong character of this state.

The temperature evolution of the Raman spectrum of both the supercooled liquid and the glacial state have been analyzed during their lifetime of stability, between 110 and 270 K. The corresponding temperature dependences of the BP frequencies are reported in Fig. 2(b). It shows a similar temperature dependence of ω_{MB} in the glassy and glacial states, which is certainly connected to the temperature dependence of the sound velocity. This behavior validates the fitting procedure used both in the liquid and in the glacial state.

The relationship between the supercooled liquid, the glacial state, and the crystal. The crystallization occured near 230 K after heating the glacial state with a strong structuration of the low-frequency Raman spectrum. Once transformed, no further evolution of the spectrum was observed in the temperature range (110–270 K). The crystalline phase is therefore the ultimately stable state at low temperature. Consequently, the Raman spectrum of the crystal was recorded at 215 K to be compared to the spectra of the supercooled liquid and the glacial state at the same temperature (Fig. 3). The Raman spectrum of the crystal exhibits a large number of lattice modes that confirms certainly the low symmetry of the crystalline phase. These modes are organized in three groups of phonon peaks corresponding clearly to three broad vibrational bands of the glacial state observed at 70, 102, and 150 cm^{-1}. Moreover, the group of sharp phonon peaks observed in the low-frequency region exhibit a very close correspondence with the profile of the low-frequency shoulder, the frequency of the most intense phonon being very close to $\omega_{\max}$. Consequently, Fig. 3 highlights that the spectrum of the glacial state corresponds to the perfect envelope of the phonon peaks observed in the crystal. This characteristic shows that the low-frequency spectrum results from the inhomogeneous broadening of the lattice modes generated by the distribution of molecular surroundings, and so reveals that the local order in the glacial state is a very clear picture of the crystalline symmetry. The very close connection between the crystal and the glacial state suggests that the latter could be described as a mesoscopic array of domains of the crystalline phase. The picture of the glacial state obtained from this study is in agreement with the description given by Ha *et al.*[1] in terms of a defect-ordered phase. However, there is no indication from the Raman spectra that the locally preferred structure inside the domains could differ from the crystalline one. A fundamental question is thus to understand the origin of the frustration that is responsible for the stability of the glacial state over a temperature range corresponding to the domain of stability of the crystal. According to Ha and co-workers[1,2] the glacial state would result from a geometric frustration of the growth of the preferred local structure. However, our Raman data seems to indicate that the latter finally could spread out into the long-range order crystalline phase, when crystallization occurs.

Figure 3 provides additional information that the spectrum of the supercooled liquid can also be seen as constituted by very broadened phonon peaks of the crystal from the observation of discrete shoulders near 100 and 140 cm^{-1}. Moreover, the BP-like shoulder in the supercooled liquid appears also as clearly reminiscent of the phonon peaks in the crystal. Consequently, this study highlights a structural organization in the supercooled liquid that is reminiscent of the structure of the crystal.

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