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Comparative analysis of the fast dynamics in the supercooled nonfragile glass-forming liquid $Na_{0.5}Li_{0.5}PO_3$ observed by coherent neutron scattering

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Experimental results obtained by coherent neutron scattering with a time-of-flight spectrometer on the nonfragile glass-forming liquid $Na_{0.5}Li_{0.5}PO_3$ ($T_g = 515$ K, $T_m = 749$ K) in a wide temperature range (300–773 K) are presented. As predicted by the mode coupling theory (MCT), the resulting dynamical structure factor has a q-independent form in the intermediate β_{fast} regime. Furthermore, it is also found that the q dependence of the dynamical structure factor is the same for the boson peak and the quasielastic region. Thus, a phenomenological model assuming that the quasielastic component is related to the damping of the localized vibrational modes that give rise to the boson peak is discussed. Though the spectra are well described over a wide temperature range, it is shown that the temperature T^* where the boson peak becomes overdamped is significantly above the melting temperature in this system and thus cannot be associated to any onset of metastability as previously suggested. On the other hand, a qualitative discussion of the susceptibility spectra above T_g in the frame of the MCT leads to a possible crossover temperature T_c near 620 K ($\sim 1.2\ T_g$) close to the temperature of the decoupling phenomenon of the relaxation time scales observed by ^{31}P NMR in this system. This T_c value is also compatible with a power-law temperature dependence of the structural relaxation time scale deduced from the viscosity data. [S0163-1829(97)04542-6]

I. INTRODUCTION

During the last decade, the glass transition phenomenon has known a renewed interest triggered in particular by the development of a microscopic theoretical approach, the so-called mode coupling theory (MCT),[1] which offers a fully dynamical picture of the supercooled liquid state. This theory provides an approximation scheme allowing the calculation of the time evolution of the density correlation function from a microscopic equation of motion. In a simplified version, this approach leads to a kinematic instability at a crossover temperature T_c above T_g where the density fluctuation modes arrest with decreasing temperature. In the viscous undercooled liquid above T_c, the correlation function of the density fluctuations is found to decay into two steps which are identified as the α and the β_{fast} relaxation processes and is described by a set of scaling laws whereas under T_c only the β_{fast} process remains, as the structural relaxation or α process is ideally frozen.

In the MCT scheme, the β_{fast} process is thus the short time decay of the density correlation function before the structural relaxation takes place and is ascribed to localized motions associated with the rattling of particles in their cages formed by surrounding particles. This fast process occurs on picosecond time scale and has to be distinguished from the secondary β_{slow} processes[2] that are a typical feature of supercooled liquids. The strict ergodic to nonergodic transition at T_c predicted by the MCT is not observed in real glass-forming liquids due to the existence of temperature activated hopping processes that break the trapping of molecules in cages formed by neighboring molecules and so restore ergodicity below T_c. However, an extended version of the theory, taking these hopping processes into account, replaces this sharp transition by a change in the transport mechanism near T_c from liquidlike to solidlike behavior. Therefore, remnants of the singularity may strongly influence the dynamics around T_c.

Analyzing neutron[3–6] and light[7–10] scattering spectra, some predictions of this mode coupling theory for the liquid glass transition have been verified in particular above T_c for a class of glass-forming liquids which are called fragile.[11] These systems often consist of relatively small, weakly interacting molecules and so are close to the hard-sphere liquids for which the MCT has been developed. In these fragile systems, the crossover seems to be correctly described by the scaling laws of the simplest version of the MCT with a crossover temperature T_c located at about 1.2 T_g. However, it is not clear up to now whether this dynamic instability is also relevant in less fragile systems that are characterized by a smoother temperature dependence of the structural relaxation time scale and thus a stronger influence of the temperature activated hopping processes on the dynamics around T_c. Furthermore, it is now well established that the lowest frequency inelastic feature in the vibrational contribution to the dynamical structure factor $S(q,\omega)$, the so-called boson peak, strongly increases when going from fragile towards strong glass-forming liquids.[12] This inelastic component that has to be regarded as specific to disordered materials[13] is completely neglected in the asymptotic solution of the MCT equations. However, it strongly distorts the dynamical susceptibility above the susceptibility minimum[14–17] between the α and β_{fast} processes in the mesoscopic regime that is just the frequency range concerned by some predicted scaling laws of the MCT. This inelastic contribution could thus be responsible for the departure of the asymptotic exponent from the constraint imposed by the MCT, already slightly observed in fragile liquids and strongly amplified in less fragile systems.[18] So a successful description of the liquid glass transition in less fragile systems has to address the influence of these low-frequency vibrational modes on the relaxation dynamics.

As already pointed out, there are some experimental indications for a possible common physical origin between the boson peak and the quasielastic component (the MCT β_{fast} process). For most glasses, it is well known that the depolarization ratio $[\rho(\omega)=I_{VH}(\omega)/I_{VV}(\omega)]$ observed in low-frequency Raman spectra is similar for both contributions and independent of temperature. Recently, coherent neutron-scattering experiments have shown[19] that the q dependence of the dynamical structure factor was the same for the boson peak and the quasielastic region. These results can be taken into account if it is assumed that the quasielastic part comes from the damping of the vibrational modes that give rise to the boson peak as for example in the approach proposed by Gochiyaev *et al.*[20] Using this model, a good description of the low-frequency Raman spectra has been achieved in fragile liquids as well as in stronger ones.[20–23] Furthermore, an interesting result can be related to this phenomenological approach. It has been found that the boson peak becomes overdamped at a temperature T^* close to the crossover temperature T_c of the MCT deduced from scaling analysis of the susceptibility spectra in the different glass-forming liquids that were investigated.[23] According to these authors, it means that in this temperature range, two independent explanations support the idea of a nonmonotonous change of the dynamics in supercooled liquids.

In the present paper, we report a coherent neutron-scattering experiment on $Na_{0.5}Li_{0.5}PO_3$ initiated in order to study the fast dynamics near the liquid glass transition in a nonfragile glass-forming liquid. The remainder of the paper is organized as follows: after mentioning some experimental details (Sec. II), we present a detailed analysis and discussion of the data. The first part of Sec. III is concerned with the factorization problem of the q and ω dependences of the dynamical structure factor $S(q,\omega)$ in the mesoscopic frequency range in connection with the MCT β_{fast} regime and a possible relation between this β_{fast} process and the boson peak. Then a phenomenological approach, the convolution model first proposed by Gochiyaev *et al.*, which associates these two low-energy processes is used. The spectra are analyzed within this approach in order to determine whether or not the temperature T^*, where the boson peak becomes overdamped in this system, can be connected with a crossover temperature between solidlike and liquidlike dynamics as previously suggested. In the last part of Sec. III, a short qualitative discussion of the dynamical susceptibilities in the framework of the MCT is presented. Our summary and conclusions are given in Sec. IV.

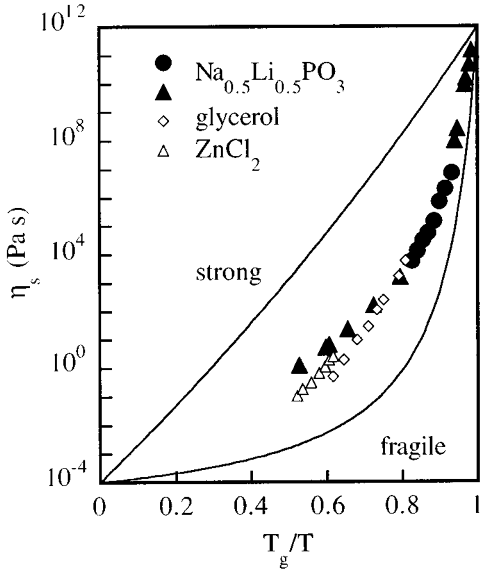

FIG. 1. Viscosity data of $Na_{0.5}Li_{0.5}PO_3$ as compared to those of glycerol and $ZnCl_2$ in an Angell plot.[11] ● are from Ref. 26 and ▲ from Ref. 27.

II. EXPERIMENT

$Na_{0.5}Li_{0.5}PO_3$ is the eutectic composition ($T_g=515$ K, $T_m=749$ K) based on the two alkali phosphate compounds $NaPO_3$ and $LiPO_3$. The structure consists of covalent twisted chains of phosphate tetrahedra PO_4 linked through ionic bonds between nonbridging oxygen and alkali ions. In the crystalline state, $NaPO_3$ (Ref. 24) and $LiPO_3$ (Ref. 25) are characterized by a very different conformational state of the phosphate chain. As the cations are supposed to be randomly distributed in the mixed structure, it results in a random microstructure which prevents the supercooled liquid from crystallizing in the whole temperature range between T_g and T_m, thus over more than 200 K. As it is clearly shown in Fig. 1, the temperature dependence of the viscosity for this glass-forming liquid has an intermediate behavior between fragile liquids and strong ones in the Angell classification like two other systems currently under study, glycerol and $ZnCl_2$, although the high-temperature limit could be noticeably different due to the polymeric structure.

As the liquid glass transition phenomenon seems to be mainly concerned with the phosphate chain dynamics in this system, special care has been taken during the synthesis of the sample used for this neutron-scattering experiment. First, pure ^7Li starting materials have been chosen due to the huge absorption cross section of the ^6Li isotope (7.5% natural abundance). Second, phosphate glasses being slightly hygroscopic,[28] deuterated compounds have been used for the synthesis in order to avoid contamination of the scattered intensity by the incoherent scattering from the residual water. In this condition $Na_{0.5}Li_{0.5}PO_3$ is a coherent scatterer (93.4%) and furthermore, 87.2% of the total scattering cross section is due to the coherent scattering from the phosphate chains. Thus neutron scattering is a suitable probe to analyze the collective dynamics of the liquid glass transition phenomenon in this system.

Neutron-scattering experiments have been done on the time-of-flight (TOF) spectrometer MIBEMOL at the reactor Orphée of the Laboratoire Léon Brillouin (Saclay, France). Using cold neutrons with an incident wavelength set to 6.2 Å, a resolution of 84 μeV (full width at half height) has been achieved at detector angles 2θ ranging from 36° to 141°. Thus, scattering vectors up to 1.9 Å^{-1} at zero energy transfer were allowed. As MIBEMOL is characterized by a resolution function of triangular shape, inelastic and broad quasielastic scattering as low as 0.1 meV can be observed. In order to study the dynamics in $Na_{0.5}Li_{0.5}PO_3$ from well below the calorimetric glass transition temperature T_g up to the melting temperature T_m (about 500 °C), a hollow niobium cell has been especially conceived for this experiment. It consists roughly of two thin rolled up niobium sheets (0.1 mm) forming two cylinders of, respectively, 11 and 15 mm in diameter, leaving an empty space of 2 mm width. This value has been calculated in order to achieve a transmission of 90% that allows us to neglect multiple scattering corrections whereas the cylindrical geometry ensures an as isotropic scattering as possible. During the experiment, care has been taken to guarantee absolute intensity calibration so all runs have been measured in an uninterrupted series without removing the sample from the oven. Furthermore, since the scattering cell is filled at room temperature with glass beads, the experiment has been started from the highest temperature in the stable liquid phase down to room temperature in order to ensure that the same number of scattering nuclei are in the neutron beam during the whole experiment. The detector efficiencies have been determined from a scan with a hollow vanadium cylinder of the same size. The slightly temperature-dependent background of the empty can has been derived from two scans, one at room temperature and the other at 500 °C. After these usual corrections, the TOF spectra $S(2\theta,t,T)$ have been converted in dynamical structure factor spectra $S(q,\omega,T)$ with q dependent energy ranges by interpolation with a wave vector step of 0.2 Å^{-1} ensuring a rather good signal-to-noise ratio (23 spectra from 0.6 up to 5.0 Å^{-1}).

III. RESULTS AND DISCUSSION

In Fig. 2 is shown a representative set of the coherent neutron-scattering spectra obtained from below T_g up to above T_m for the wavevector 1.6 Å^{-1}. In order to remove the trivial temperature dependence of the scattered intensity, these spectra have been plotted in reduced intensity $S_{\text{red}}(q,\omega,T)=S(q,\omega,T)/[\omega n(\omega,T)]$ where $n(\omega,T)$ is the Bose factor. At low temperatures, the inelastic scattered intensity is mainly due to low-energy vibrational excitations that give rise to a broad asymmetric band, the so-called boson peak with a maximum located around 6 meV at 461 K just below T_g. On varying temperature, the scattered intensity follows the Bose factor distribution for the energy above 6 meV whereas at lower energy an excess scattering appears particularly above T_g. This broad quasielastic contribution grows in intensity faster than the Bose factor revealing anharmonic processes and is interpreted in the MCT frames as the β_{fast} relaxation though alternative phenomenological approaches are also used attempting to connect it to the damping of the low-energy vibrational modes.[20,29] In $Na_{0.5}Li_{0.5}PO_3$, the spectrum is not completely quasielastic at the highest temperature studied just above T_m in good agreement with the intermediate fragility of this system.[12] According to the viscosity data shown in Fig. 1, the structural relaxation should give a strictly elastic component on the whole temperature range investigated. Indeed, it is inferred from Fig. 1 that at 773 K the width of the α process remains below 1 μeV that has to be compared to the resolution width of 84 μeV. It means that the broad quasielastic component in $Na_{0.5}Li_{0.5}PO_3$ can be safely studied over a wide temperature range in the whole supercooled liquid phase. In particular, MCT predictions in this mesoscopic β_{fast} regime can be tested.

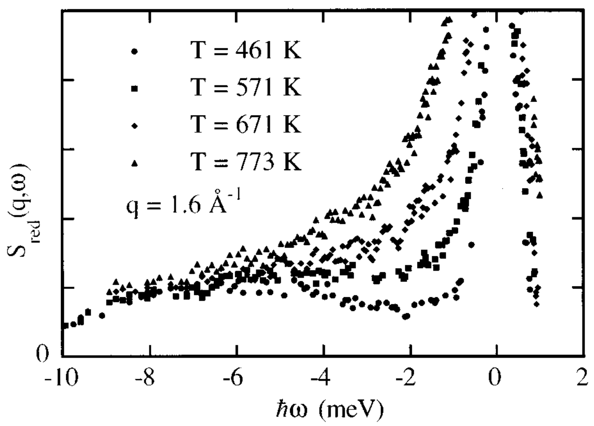

FIG. 2. Coherent neutron-scattering spectra of $Na_{0.5}Li_{0.5}PO_3$ in reduced intensity obtained on the TOF spectrometer MIBEMOL for a momentum transfer $q=1.6$ Å^{-1} at selected temperatures from below T_g up to above T_m. Note the coincidence of all spectra for energy transfers above 6 meV, the energy of the boson peak maximum at 461 K.

One of the MCT predictions[1] concerning the β_{fast} relaxation region is a decoupling property of the dynamical structure factor $S(q,\omega,T)$ between a purely frequency-dependent and a purely wavevector-dependent term: $S^{\beta}(q,\omega,T) =G(\omega,T)\ H(q)$. According to this expression, the shape of the dynamical structure factor or the susceptibility spectra $\chi''(q,\omega,T)=S(q,\omega,T)/n(\omega,T)$ is predicted to be independent of the wavevector in the β_{fast} regime. This factorization property has been tested on the susceptibility spectra obtained in $Na_{0.5}Li_{0.5}PO_3$ and reported in Fig. 3 for $T=631$ K. The data for $0.6\ \text{Å}^{-1}\leqslant q\leqslant 5.0\ \text{Å}^{-1}$ are shown to overlap within experimental error over a wide energy range. Therefore, it is found that this factorization property is verified in the whole temperature range (300–773 K) not only in the β_{fast} relaxation region as predicted by the MCT but also for the boson peak whatever the relative intensities of these two processes. Although the verification of this factorization property is a prerequisite condition for any mode coupling analysis in the β_{fast} regime, it does not exclude other interpretations of the data. In particular, the observed similar q dependence of the dynamical structure factor for the boson peak and the quasielastic region does not preclude a vibrational origin for the latter.

Following an idea first proposed by Gochiyaev *et al.*,[20] these observations can be taken into account if it is assumed that each vibrational eigenmode with a frequency Ω is

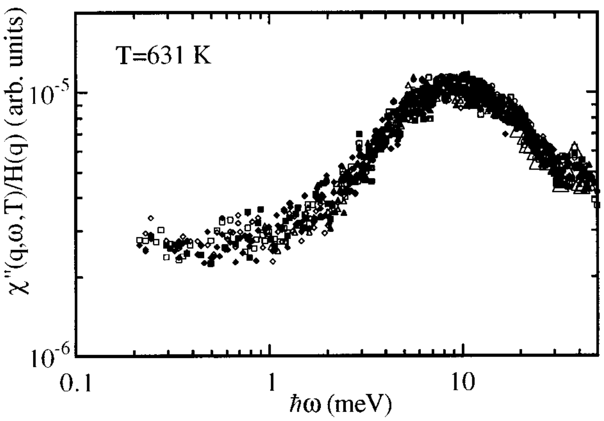

FIG. 3. Test of the factorization property predicted by the MCT for the β_{fast} relaxation region. The 23 susceptibility spectra at 631 K interpolated to constant q between 0.6 and 5.0 Å^{-1} are represented with different symbols. Note that the boson peak at higher energy also verifies the factorization property with the same q dependence.

damped via a relaxation memory function $m(\omega,T)$,

$$m(\omega,T)=\frac{\delta^2(T)}{1-i\omega\tau(T)},\tag{1}$$

resulting in the following susceptibility for each vibrational mode:

$$\chi(\omega,\Omega,T)=[\Omega^2-\omega^2-m(\omega,T)]^{-1}.\tag{2}$$

Then, the scattered intensity is simply given by the sum of the contributions of all the vibrational excitations. Replacing the summation by integration, the vibrational density of states $g(\Omega)$ is introduced:

$$I(\omega,T)=n(\omega,T)\int g(\Omega)\chi''(\omega,\Omega,T)d\Omega.\tag{3}$$

The frequency dependence of the vibrational density of states $g(\omega)$ can then be obtained from the shape of the scattered spectra at sufficiently low temperature when there is no relaxation

$$\frac{I(\omega,T\ll T_g)}{\omega n(\omega,T\ll T_g)}=I_0(\omega,T\ll T_g)=\frac{g(\omega)}{\omega^2},\tag{4}$$

where I_0 is the reduced intensity scattered spectra at this low temperature. Next, the vibrational density of states or I_0 is characterized by $\omega_{\mathrm{bp}}(T)$, the slightly temperature-dependent frequency of the boson peak maximum included in the model in order to take into account the commonly observed softening of the boson peak with increasing temperature. Thus it is assumed that the spectral shape of the boson peak is not temperature dependent. This leads to the following expression for the scattered intensity that has been used to fit the experimental data:

$$I(\omega,T)=n(\omega,T)\int \Omega^2 I_0[\Omega,\omega_{\mathrm{bp}}(T)]\chi''(\omega,\Omega,T)d\Omega.\tag{5}$$

In the Debye memory function of Eq. (1), $\delta(T)$ is the homogeneous temperature-dependent coupling strength between the vibrational and relaxational modes whereas $\tau(T)$ is the relaxation time of the latter. For $T\to 0$, $\delta\to 0$ and Eq. (5) becomes an identity giving an inelastic spectra. On increasing temperature, $\delta(T)$ increases towards $\omega_{\mathrm{bp}}(T)$ giving rise to a broad quasielastic component until $\omega_{\mathrm{bp}}^2=\delta^2$ at $T=T^*$ where the boson peak merges completely into the quasielastic component. By analogy with the soft mode formalism,[30] the renormalized frequency of the boson peak maximum $\omega_0^2=\omega_{\mathrm{bp}}^2-\delta^2$ is expected to follow a critical power-law temperature dependence just below T^*: $\omega_0^2\propto(T^*-T)$. It corresponds to a transition of the excitations that give rise to the boson peak from vibrational to relaxational type of collective motions.

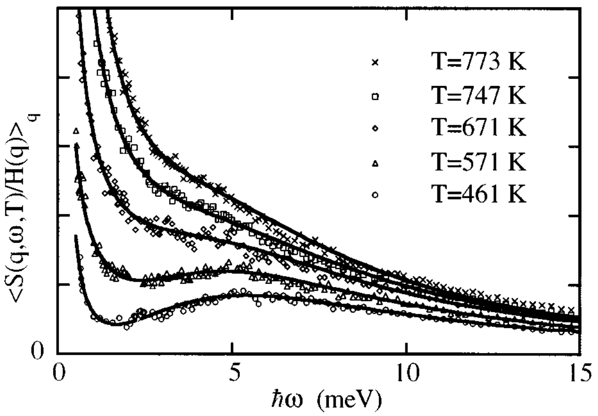

FIG. 4. q-rescaled spectra from below T_g up to above T_m fitted with the convolution model Eq. (5) (Ref. 20) showing a very good agreement over the whole temperature range investigated.

Using this phenomenological approach, Raman spectra obtained on several glass formers have been fitted leading to $\omega_{\mathrm{bp}}^2=\delta^2$ for a temperature T^* close to the crossover temperature T_c of the MCT deduced from scaling analysis of the susceptibility spectra.[23] These results have led the authors to conclude that at this temperature $T^*\sim T_c$ a dynamical crossover occurs in this energy range between a solidlike dynamics for $T<T_c$ characterized by a vibrational spectra towards a liquidlike dynamics for $T>T_c$ characterized by a relaxational spectra. This crossover could thus be observed either by the critical behavior of the relaxational spectrum within the frames of the MCT or by the critical behavior of the boson peak.

As shown in Fig. 4, this phenomenological model with only three free parameters describes very well the coherent neutron-scattering spectra obtained in $\mathrm{Na_{0.5}Li_{0.5}PO_3}$ in the whole temperature range investigated from below T_g up to above T_m. According to Eq. (4), the shape of the vibrational density of states $g(\omega)$ has been deduced from the room temperature reduced intensity spectra where the quasielastic component is strongly reduced. But in this glass, the strong asymmetric shape of the boson peak is very well described by a phenomenological generalized Lorentzian form:

$$I_0(\omega,\omega_{\mathrm{bp}}(T))\propto\frac{\omega^2}{[\omega^2+\omega_{\mathrm{bp}}^2(T)]^2}.\tag{6}$$

So in the fitting procedure, this analytic function characterized by a unique parameter $\omega_{\mathrm{bp}}(T)$ has been used for I_0

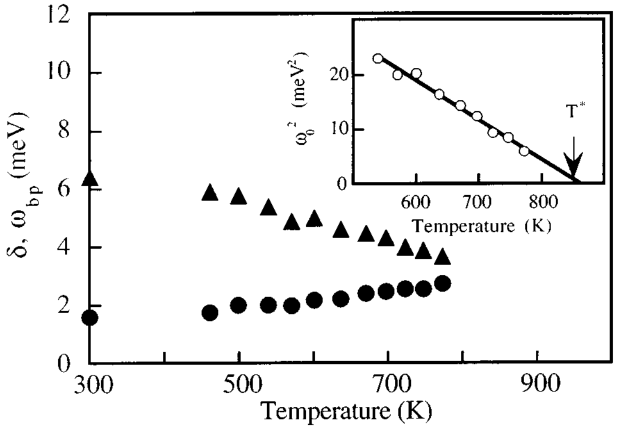

FIG. 5. Temperature dependence of the coupling strength δ (●) and the position of the boson peak maximum ω_{bp} (▲) obtained from the fitted spectra of Fig. 4 with the convolution model. Inset: Critical temperature dependence of the renormalized frequency of the boson peak maximum $\omega_0^2 = \omega_{\mathrm{bp}}^2 - \delta^2$ leading to $T^* = 875$ K well above the melting temperature in this system.

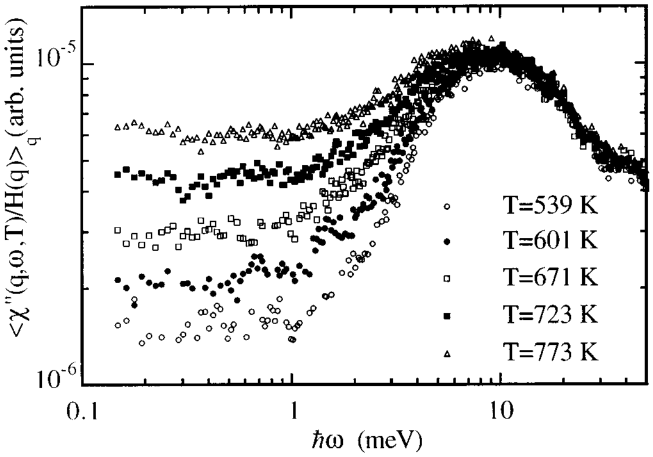

FIG. 6. Temperature dependence of the q-rescaled susceptibility spectra for some temperatures above T_g. At high energy, the boson peak is clearly seen even for temperatures above T_m whereas at lower energy the β_{fast} region remains almost flat with an increasing amplitude with temperature.

rather than the experimental data. It should also be mentioned that no extra intensity parameter has been added in the fitting procedure as the temperature dependence of the boson peak intensity follows the Bose factor which is included in Eq. (5).

The relaxation time τ derived from these fits is found to be weakly temperature dependent and in the range of the picosecond. Thus the strong temperature dependence of the scattered spectra is only due to the variations of the coupling strength δ and the position of the maximum of the boson peak ω_{bp} as shown in Fig. 5. In the framework of this model, the boson peak is not overdamped even at the highest temperature studied just above T_m as the temperature dependence of the coupling strength $\delta^2(T)$ does not cross the $\omega_{\mathrm{bp}}^2(T)$ one. As shown in the inset of Fig. 5, this leads to a renormalized frequency of the boson peak maximum $\omega_0^2 = \omega_{\mathrm{bp}}^2 - \delta^2$ that goes to zero around $T^* = 875$ K, well above the melting temperature. Thus, contrary to the suggestion of some authors,[23] the temperature T^* at which the boson peak merges into the quasielastic scattering cannot be associated with any metastability onset in this system since T^* is found in the stable liquid phase.

Some of the most detailed predictions of the MCT are based on an asymptotic development of the susceptibility spectrum in the β_{fast} region around the minimum that separates the α process on the low-frequency side from vibrational modes at higher frequencies.[1] For T above but close to the crossover temperature T_c, the susceptibility minimum is predicted to exhibit a universal spectral shape characterized by a first power law ω^{-b} at low frequencies in the range that is the high frequency part of the stretched exponential for the α relaxation. For the high-frequency side of the minimum, a second power law ω^a characterizing the β_{fast} regime is predicted. This susceptibility minimum can be then approximated by an interpolation formula between these two power laws leading to the determination of two parameters ω_{min} and χ''_{min}, the frequency and the amplitude of the susceptibility minimum. According to the MCT, these two parameters follow critical temperature dependences: $\omega_{\mathrm{min}} \propto (T-T_c)^{1/2a}$ and $\chi''_{\mathrm{min}} \propto (T-T_c)^{1/2}$.

Note that the critical exponents a and b are not independent but obey a relation involving the gamma function and a parameter λ with the conditions $0<b<1$ and $0<a<0.395$. Furthermore, a critical temperature dependence is also predicted for the structural relaxation time scale $\tau_\alpha \propto (T-T_c)^{-\gamma}$ with a critical exponent γ also related to the previous ones $\gamma = \frac{1}{2}a + \frac{1}{2}b$. So above T_c, all these critical behaviors are determined by the unique parameter λ that could be theoretically calculated from the static structure factor $S(q)$ but is usually left as a free parameter in MCT analysis on real glass formers.

One should keep in mind that these predictions of the idealized MCT in the β_{fast} regime are only asymptotic results derived from the mode coupling equations for frequencies around the susceptibility minima and for temperatures not too far from T_c. Furthermore, it has also been shown that even in very fragile liquids, these predictions break down very close to T_c as hopping processes, neglected in this idealized version, restore ergodicity below T_c.[31] It should also be remembered that in the mode coupling asymptotic results, the lowest-frequency vibrational component, namely, the boson peak, is not properly taken into account. These limitations notwithstanding, several fragile liquids investigated have exhibited these different critical behaviors for the susceptibility spectrum obtained by neutron scattering[32,33] as well as by light scattering.[7–10,34] The scaling laws have been particularly verified above T_c, locating the crossover temperature around 1.2 T_g. For the temperatures below T_c, only one fragile liquid ($[\mathrm{Ca(NO_3)_2}]_{0.4}[\mathrm{K(NO_3)}]_{0.6}$) seems to clearly exhibit up to now the knee in the β_{fast} region of the susceptibility following correctly the MCT predictions.[7] All the other systems investigated show deviations probably due to a stronger boson peak influence resulting in critical exponents a and b that cannot fulfill the MCT constraint.

As shown in Fig. 6, the coherent neutron susceptibility spectra obtained on $\mathrm{Na_{0.5}Li_{0.5}PO_3}$ above T_g are also strongly influenced by the presence of the boson peak around 6 meV. Furthermore, the structural relaxation remains sufficiently slow to not enter the energy window scanned by our experi-

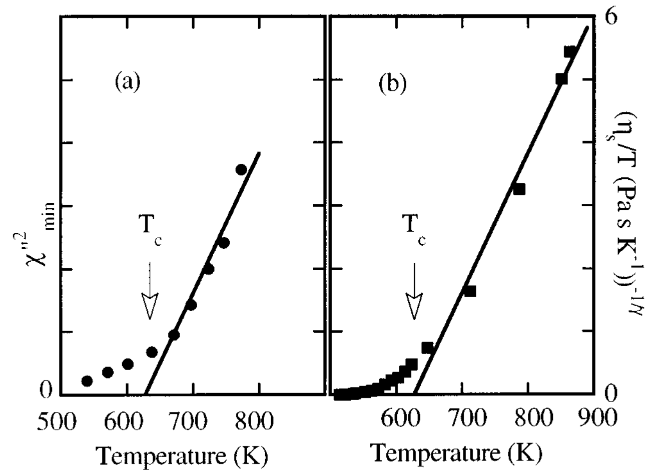

FIG. 7. (a) Temperature dependence of the susceptibility plateau height deduced from the susceptibility spectra of Fig. 6 leading to a possible crossover temperature $T_c \sim 620$ K. (b) Critical scaling of the structural relaxation time scale $\tau_\alpha \propto \eta_s/T$ also leading to the same crossover temperature $T_c \sim 620$ K with $\gamma = 3$.

ment even for the highest temperature studied, 773 K, just above T_m. All these features result in almost flat susceptibility spectra in the $\beta_{\rm fast}$ region without any prominent minimum. The slope at high energies is rather close to $a \approx 1$ as for other nonfragile glass-forming liquids investigated.[14,15,17] So the lack of pronounced susceptibility minima in these spectra do not allow a complete line shape analysis within the framework of the MCT.

Nevertheless, a prediction that can be tested, as it does not require any determination of a critical exponent, is the temperature dependence of the susceptibility plateau height $\chi''_{\rm min}$. Its temperature dependence for $T > T_g$ is reported in Fig. 7(a) showing a steeper increase above about 650 K. These data are compatible with the MCT scenario leading to a possible crossover temperature T_c near 620 K. As shown in Fig. 7(b), the α relaxation time scale that is related to the shear viscosity η_s via the Stokes-Einstein relation $\tau_\alpha \propto \eta_s/T$ can also lead to the same crossover temperature $T_c \sim 620$ K. However, the $\gamma = 3$ value used to obtain the linear dependence in Fig. 7(b) cannot be checked against the MCT constraint as the other critical exponents a and b are unknown in this supercooled liquid and cannot be safely determined from the susceptibility spectra.

It is very interesting to note that the possible crossover temperature $T_c \sim 620$ K found is very close to the temperature where a secondary $\beta_{\rm slow}$ process emerges from the structural relaxation as detected by ^{31}P NMR measurements[35] and mechanical experiments[36] in this glass-forming liquid and shown in Fig. 8. This secondary process has been attributed to local reorientations of the PO_4 tetrahedra forming the phosphate chains. It merges into the structural or α process above 600 K, thus slightly below T_c ($\sim 1.2\ T_g$). In the case of fragile liquids, the temperature where this decoupling phenomenon between the structural relaxation and a secondary $\beta_{\rm slow}$ process observed by NMR or dielectric spectroscopy occurs is also often found just below the crossover temperature T_c deduced from MCT analysis.[37]

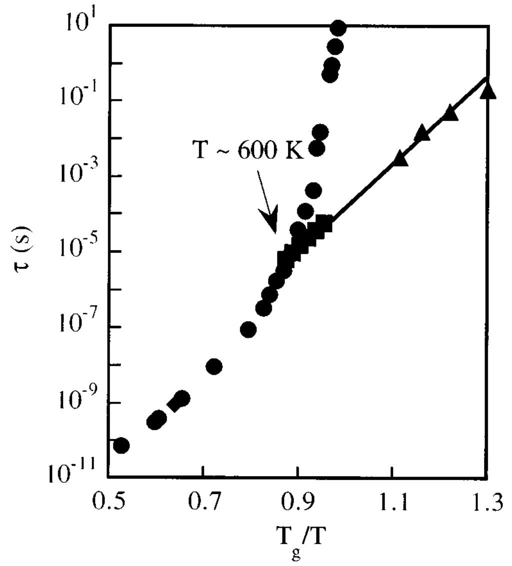

FIG. 8. Temperature dependence of the structural relaxation time scale $\tau_s \propto \eta_s/T$ (●) and relaxation times obtained by ^{31}P NMR (■,◆) (Ref. 35) and DMA (▲) (Ref. 36). Below $T \sim 600$ K occurs a decoupling between the α process and a secondary $\beta_{\rm slow}$ process.

IV. CONCLUSION

In this paper, we have shown that in $Na_{0.5}Li_{0.5}PO_3$, the dynamical structure factor obtained by a coherent neutron-scattering experiment is independent of the wave vector in the whole temperature range investigated from below T_g up to above T_m. This factorization property of $S(q,\omega,T)$ is thus in good agreement with the results given by the MCT for the $\beta_{\rm fast}$ region. Nevertheless, the observed similar q dependence of the dynamical structure factor for the boson peak and the fast relaxational process does not preclude a vibrational origin for the latter. Using an alternative approach that relates these two contributions, a very good agreement has been found between the coherent neutron-scattering spectra and the model in the whole temperature range from below T_g up to above T_m. However, it has been demonstrated that the temperature T^*, where the boson peak becomes overdamped, cannot be associated with any metastability of the liquid as recently suggested. Indeed, in this system T^* has been found above the melting temperature.

On the other hand, the temperature dependence of the fast process intensity can be accounted for by the predictions of the simplest version of the MCT. It leads to a crossover temperature $T_c \sim 620$ K ($\sim 1.2\ T_g$) in the supercooled liquid phase, in good agreement with scaling analysis of the structural relaxation time scale deduced from viscosity data. Furthermore, it is also close to the temperature where a decoupling phenomenon between the structural relaxation and a secondary $\beta_{\rm slow}$ process occurs in this system as already observed by ^{31}P NMR. However, it has not been possible to use the susceptibility spectra for a line-shape analysis and thus a more quantitative comparison with the MCT predictions. In particular, the susceptibility spectra obtained in $Na_{0.5}Li_{0.5}PO_3$ are strongly distorted by low-lying vibrational modes, the boson peak, not really taken into account by the MCT.

These results suggest that in less fragile systems, the fast relaxational intensity could be the result of two nearly equally weighted contributions: one from the structural relaxation as described by the MCT and the other one from the damping of the boson peak of negligible intensity in more fragile liquids.

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[1] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).

[2] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).

[3] F. Fujara and W. Petry, Europhys. Lett. **4**, 921 (1987).

[4] W. Knaak, F. Mezei, and B. Farago, Europhys. Lett. **7**, 529 (1988).

[5] B. Frick, B. Farago, and D. Richter, Phys. Rev. Lett. **64**, 2921 (1990).

[6] W. Petry, E. Bartsch, F. Fujara, M. Kiebel, H. Sillescu, and B. Farago, Z. Phys. B **83**, 175 (1991).

[7] G. Li, W. M. Du, X. K. Chen, H. Z. Cummins, and N. J. Tao, Phys. Rev. A **45**, 3867 (1992).

[8] W. M. Du, G. Li, H. Z. Cummins, M. Fuchs, J. Toulouse, and L. A. Knauss, Phys. Rev. E **49**, 2192 (1994).

[9] W. Steffen, A. Patkowski, H. Gläser, G. Meier, and E. W. Fischer, Phys. Rev. E **49**, 2992 (1994).

[10] E. Rössler, A. P. Sokolov, A. Kisliuk, and D. Quitmann, Phys. Rev. B **49**, 14 967 (1994).

[11] C. A. Angell, in *Relaxations in Complex Systems*, edited by K. L. Ngai and G. B. Wright (NRL, Washington, 1984), p. 3.

[12] A. P. Sokolov, E. Rössler, A. Kisliuk, and D. Quitmann, Phys. Rev. Lett. **71**, 2062 (1993).

[13] *Amorphous Solids: Low Temperature Properties*, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981).

[14] A. Brodin, L. Börjesson, D. Engberg, L. M. Torell, and A. P. Sokolov, Phys. Rev. B **53**, 11 511 (1996).

[15] M. J. Lebon, C. Dreyfus, G. Li, A. Aouadi, H. Z. Cummins, and R. M. Pick, Phys. Rev. E **51**, 4537 (1995).

[16] A. Patkowski, W. Steffen, G. Meier, and E. W. Fischer, J. Non-Cryst. Solids **172–174**, 52 (1994).

[17] J. Wuttke, J. Hernandez, G. Li, G. Coddens, H. Z. Cummins, F. Fujara, W. Petry, and H. Sillescu, Phys. Rev. Lett. **72**, 3052 (1994).

[18] A. P. Sokolov, W. Steffen, and E. Rössler, Phys. Rev. E **52**, 5105 (1995).

[19] B. Frick and D. Richter, Science **267**, 1939 (1995).

[20] V. Z. Gochiyaev, V. K. Malinovsky, V. N. Novikov, and A. P. Sokolov, Philos. Mag. B **63**, 777 (1991).

[21] M. Krüger, M. Soltwisch, I. Petscherizin, and D. Quitmann, J. Chem. Phys. **96**, 7352 (1992).

[22] M. Krüger, A. Kisliuk, A. P. Sokolov, M. Soltwisch, and D. Quitmann, J. Phys.: Condens. Matter **5**, 127 (1993).

[23] A. P. Sokolov, A. Kisliuk, D. Quitmann, A. Kudlik, and E. Rössler, J. Non-Cryst. Solids **172–174**, 138 (1994).

[24] K. H. Von Jost, Acta Crystallogr. **14**, 844 (1961).

[25] J. C. Guitel and I. Tordjman, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **32**, 2960 (1976).

[26] B. Rufflé, Thesis, University of Rennes I, 1996.

[27] R. Wäsche and R. Brückner, Phys. Chem. Glasses **2**, 80 (1986); **2**, 87 (1986).

[28] B. C. Bunker, G. W. Arnold, and J. A. Wilder, J. Non-Cryst. Solids **64**, 291 (1984).

[29] U. Buchenau, C. Schönfeld, D. Richter, T. Kanaya, K. Kaji, and R. Wehrmann, Phys. Rev. Lett. **73**, 2344 (1994).

[30] V. L. Ginzburg, A. P. Levanyuk, and A. A. Sobyanin, Usp. Fiz. Nauk **130**, 615 (1980).

[31] H. Z. Cummins, W. M. Du, M. Fuchs, W. Götze, S. Hildebrand, A. Latz, G. Li, and N. J. Tao, Phys. Rev. E **47**, 4223 (1993).

[32] M. Kiebel, E. Bartsch, O. Debus, F. Fujara, W. Petry, and H. Sillescu, Phys. Rev. B **45**, 10 301 (1992).

[33] R. Zorn, D. Richter, B. Frick, and B. Farago, Phys. Rev. A **201**, 52 (1993).

[34] G. Li, W. M. Du, A. Sakai, and H. Z. Cummins, Phys. Rev. A **46**, 3343 (1992).

[35] B. Rufflé, S. Beaufils, and J. Gallier, Chem. Phys. **195**, 339 (1995).

[36] P. Green, D. Sidebottom, and R. Brow, J. Non-Cryst. Solids **172–174**, 1353 (1994).

[37] E. Rössler, U. Warschewske, P. Eiermann, A. P. Sokolov, and D. Quitmann, J. Non-Cryst. Solids **172–174**, 113 (1994).