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# Low-energy excitations in glass-forming aqueous lithium–chloride

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Low frequency Raman and inelastic neutron scattering from glass-forming aqueous lithium chloride ( $\text{LiCl}, 4\text{H}_2\text{O}$ ;  $\text{LiCl}, 6\text{H}_2\text{O}$ ) are compared. The measurements were carried out from the vitreous to liquid states. The scattering from anharmonic oscillations (light scattering excess), which was separated from the one from harmonic vibrations, is zero in the vitreous state, and increases rapidly in the supercooled state. The frequency dependence of light-vibration coupling coefficient is linear for low-energy harmonic vibrations. It is different for anharmonic oscillations. From the frequency dependence of the density of vibrational states and the absence of light scattering excess in the glassy state, it is deduced that the structure is compact in the glassy state. © 1995 American Institute of Physics.

## I. INTRODUCTION

The vibrational and relaxational dynamics of glass-forming materials, is nowadays extensively studied to access the nanoscale structure and mechanism of the glass-transition. In the glass-forming aqueous electrolyte  $\text{LiCl}, \text{RH}_2\text{O}$ , the compositions  $\text{LiCl}, 4\text{H}_2\text{O}$  and  $\text{LiCl}, 6\text{H}_2\text{O}$  crystallize with difficulty, so that these systems are easily undercooled from the liquid to the glassy-state.<sup>1</sup> The glass-transition occurs between 130 K and 145 K for  $\text{LiCl}, 6\text{H}_2\text{O}$ . The different thermodynamic states, liquid, supercooled liquid, and glass, are well characterized; in particular their local structure and dynamics have been studied by neutron scattering.<sup>2</sup> A further step in the understanding of their dynamics, is obtained by comparing inelastic neutron scattering (INS) and low-frequency Raman scattering (LFR) results.

At frequencies lower than 5 THz the dynamics in the glassy state and partially in the supercooled and liquid states, is described by harmonic acoustical vibrations, and anharmonic oscillations. In the spectral range, above about 0.1 THz, the acoustical vibrations do not propagate because of the disorder, and consequently can be observed by Raman scattering. The principal characteristic of the non propagating modes in most of the glasses is an excess of density of states observed by inelastic neutron scattering,<sup>3,4</sup> responsible for the so-called boson peak observed in Raman scattering at a frequency not higher than 1 THz,<sup>4,5</sup> and for the excess of the low-temperature specific heat.<sup>6</sup> The anharmonic oscillations are responsible for the Raman light scattering excess (LSE) observed at very low-frequency.<sup>7,8</sup> Some authors think that they are related to double-well potentials.<sup>9</sup> They probably concern the free volume and play an essential role in the relaxation and glass-transition.

The intensity  $I(\omega)$  of LFR, as a function of the frequency  $\omega$ , is given by the following expression for Stokes scattering:<sup>10,11</sup>

$$I(\omega) = C(\omega)g(\omega) \frac{[n(\omega) + 1]}{\omega}, \quad (1)$$

where  $C(\omega)$  is the light-vibration coupling coefficient,  $g(\omega)$  is the vibrational density of states (VDOS), and  $n(\omega)$  is the Bose factor. The VDOS can be determined by INS, so that the coefficient  $C(\omega)$  will be deduced from the comparison of LFR with INS. It has been shown that the frequency dependence of  $C(\omega)$  is related to the correlations in the glass.<sup>12</sup> On the other hand, the VDOS gives informations on the nanoscale structure. Several authors suggest that the boson peak or the excess of VDOS is due to the glass nanostructure, and that the position of the peak is inversely proportional to the size of cohesive domains.<sup>5</sup>

In this paper, the vibrational density of states of  $\text{LiCl}, 4\text{H}_2\text{O}$  will be compared to the intensity of low frequency Raman scattering to deduce the frequency dependence of  $C(\omega)$ . The Raman scattering from anharmonic oscillations, i.e., due to structural relaxation, will be separated from the scattering from harmonic vibrations, and determined as a function of temperature. The different thermodynamic states, will be investigated and discussed.

## II. EXPERIMENTAL TECHNIQUES

The preparation of samples and the neutron scattering technique are described in Ref. 13. To observe the Raman scattering at low-temperature, the aqueous  $\text{LiCl}$  electrolyte was introduced in a glass tube with narrow walls, and placed in a cryostat where it was cooled with a flow of cold helium gas. The Raman scattered light was observed at  $\pi/2$  from the laser beam. The green line at 514.5 nm of the argon laser was used. The scattered light was analyzed with a high resolution quintuple monochromator constructed by Dilor, with a focal

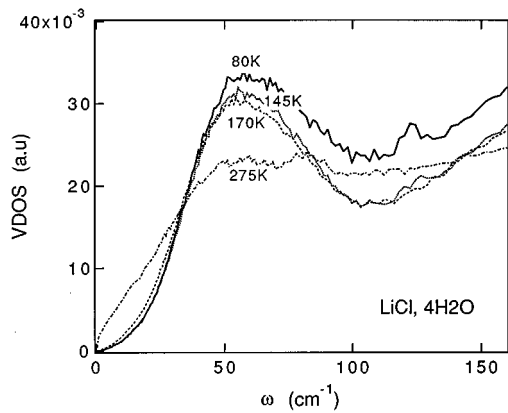


FIG. 1. Vibrational density of states of LiCl·4H<sub>2</sub>O deduced from incoherent neutron scattering.

length equal to 4 m. The temperature of the sample was determined by comparing Stokes and anti-Stokes Raman intensities.

### III. EXPERIMENTAL RESULTS

We give the experimental results for LiCl·4H<sub>2</sub>O. The ones of LiCl·6H<sub>2</sub>O are very similar. In Fig. 1 are represented the VDOS of LiCl·4H<sub>2</sub>O deduced from incoherent neutron scattering after correction of multiple scattering, at various temperatures from the glassy state to the liquid one. The VDOS are normalized to the total number of vibrational states from zero to 250 cm<sup>-1</sup>.<sup>13</sup> For comparison the reduced LFR intensities  $[I(\omega)/n(\omega) + 1]$  for the same system at different temperatures are shown in Fig. 2. The relative intensities  $[I(\omega)/n(\omega) + 1]$  at different temperatures, are determined by taking the same thermal variation of the band at 50 cm<sup>-1</sup> as for the VDOS.<sup>2</sup> From both Figs. 1 and 2, one observes, when the temperature increases a shift, towards the low frequencies, of the band maximum (40–60 cm<sup>-1</sup>) (corresponding to the bending modes related to the O–O–O intermolecular units),<sup>14–16</sup> the decrease of the relative amplitude of this band is also noted.

The thermal evolution of the VDOS (Fig. 1) and of the LFR at very small wave numbers, up to 40 cm<sup>-1</sup>, is remark-

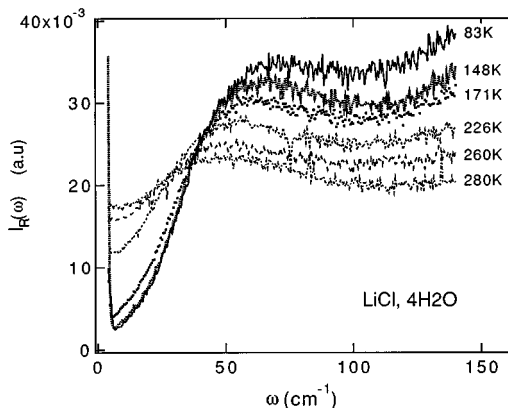


FIG. 2. Low-frequency Raman scattering reduced intensities,  $I_R(\omega) = [I(\omega)/n(\omega) + 1]$ , of LiCl·4H<sub>2</sub>O.

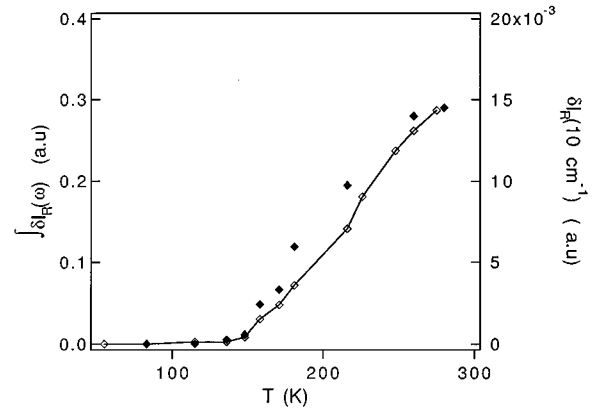


FIG. 3. Comparison between the excess  $\delta I_R$  of Raman scattering at 10 cm<sup>-1</sup> (◇), and the integral  $\int \delta I_R(\omega)$  in the spectral range 6–40 cm<sup>-1</sup> (◆).  $\delta I_R = (I_R)_T - (I_R)_{T=80 \text{ K}}$ .

able. From LFR, there is no variation of the intensity, at wave numbers lower than 40 cm<sup>-1</sup>, from the lowest temperature up to 140 K, in the glassy state. The reduced LFR intensity, in this very low spectral range, begins to increase above 150 K, a temperature which is very close to the glass to supercooled liquid transition. This evolution is illustrated in Fig. 3 where  $\delta I_R$ , the reduced Raman intensity minus the one at 80 K, is represented against the temperature. The excess  $\delta I_R$  was measured at 10 cm<sup>-1</sup>; it is compared to the integral of  $\delta I_R$  between 6 and 40 cm<sup>-1</sup>. The excess  $\delta I_R$  and its integral have a not very different thermal behavior. This means that the nature of the excitations in the excess does not change between 6 and 40 cm<sup>-1</sup>. In Fig. 4,  $\delta I_R$  is also compared to the corresponding  $\delta(\text{VDOS})$  obtained from INS. The thermal variations of both are very close. It was verified that  $\delta(\text{VDOS})$  is a true density of states and does not correspond to quasielastic scattering due to diffusional motion.

In Fig. 5, the reduced LFR intensity is compared with the neutron VDOS at 80 K. It is observed that there is a good coincidence up to 40 cm<sup>-1</sup>. From Eq. (1), we conclude that the light-vibration coefficient  $C(\omega)$  is proportional to the frequency as for most of the glasses.<sup>6,17</sup> The coincidence disappears at higher temperatures in the supercooled or liquid states. This indicates that the additional low-frequency oscil-

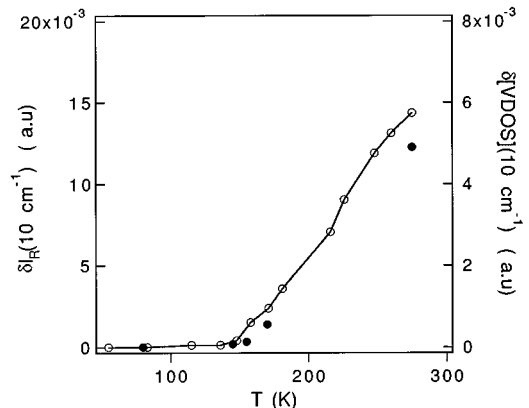


FIG. 4. Comparison between the excess  $\delta(\text{VDOS})$  (●), and  $\delta I_R$  at 10 cm<sup>-1</sup> (○).

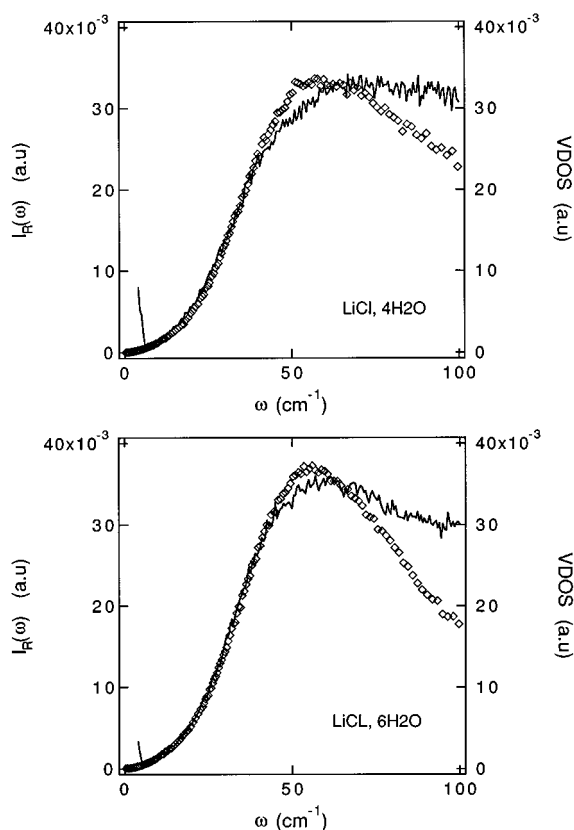


FIG. 5. Comparison between reduced LFR intensity,  $I_R(\omega)$  (continuous line) and VDOS ( $\diamond$ ).

lations, which occur in the supercooled and liquid states have a different nature. The thermal variation of the corresponding scattering shows that they are due to anharmonic modes or structural relaxation. In Fig. 6 the excesses  $\delta I_R$ , defined above, at 170 K and 280 K, respectively, are compared to the corresponding  $\delta(\text{VDOS})$ . A good coincidence is obtained if  $\delta I_R$  is multiplied by  $\omega^{0.5}$ . From Eq. (1), it is deduced that for very low-energy excitations the coupling coefficient  $C(\omega)$  is proportional to  $\omega^{0.5}$ . However the exponent is not considered

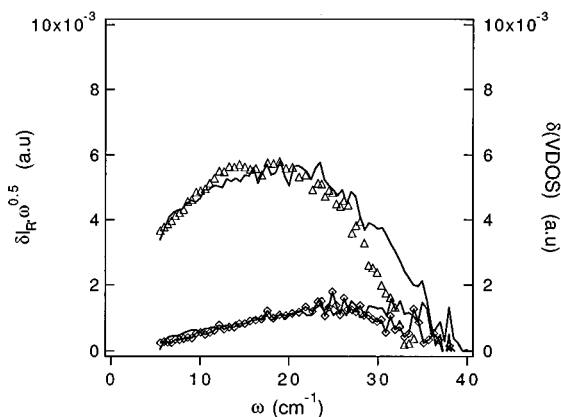


FIG. 6. Comparison between the excess of Raman scattering multiplied by the square-root of the frequency  $\delta I_R \omega^{0.5}$  (continuous line), at  $T=170$  K and  $T=280$  K, with the corresponding excesses  $\delta(\text{VDOS})$ , respectively, at  $T=170$  K ( $\diamond$ ) and  $T=280$  K ( $\triangle$ ).

as rigorously exact. We simply conclude that the frequency variation of  $C(\omega)$  is slower for the excess  $\delta I_R$  than for the LFR from harmonic vibrations.

#### IV. DISCUSSION

The LFR of glasses is often characterized by an excess called boson peak. In the model of Martin and Brenig<sup>18</sup> where the vibrations are described as plane-wave phonons in a nonperiodic medium the excess of scattering is originating from the light-vibration coupling coefficient  $C(\omega)$ . Recently it was shown that the boson peak is simply related to the excess of VDOS.<sup>4,5</sup> The excesses of VDOS, LFR, and specific heat have the same origin. On the other hand the coefficient  $C(\omega)$  in the spectral range around the boson peak was found proportional to  $\omega$  in several glasses.<sup>6,17</sup> It was suggested that the cause of the excess or boson peak is a non-continuous structure of the glass in the nanoscale range;<sup>5</sup> more cohesive domains would be separated by narrow less cohesive ones. The position of the boson peak is, in this model, inversely proportional to the size of the cohesive ones. This interpretation is confirmed by the computer simulation of Nagel *et al.*,<sup>19</sup> and by structural relaxation.<sup>20,21</sup> In other words the boson peak is due to the noncompactness of glasses.

At temperatures lower than the glass transition (140 K), the LiCl,4H<sub>2</sub>O electrolyte has a structure typical of a glassy material, as shown by neutron diffraction.<sup>22</sup> The correlations between atoms are observed up to relatively long distances ( $\sim 15$  Å). The glassy behavior is confirmed by the linear variation of  $C(\omega)$  with frequency (Fig. 5), observed for several glasses of different types.<sup>6,17</sup> However no boson peak is observed for LiCl,4H<sub>2</sub>O. The broad band which appears with a maximum near  $50 \text{ cm}^{-1}$  in the neutron VDOS, and the reduced LFR, corresponds to transverse acoustic modes observed in crystalline ice<sup>23</sup> and in liquid or supercooled water.<sup>16</sup> This is related to the hydrogen bonding between H<sub>2</sub>O molecules. The maximum is attributed to the flexing motion of the O–O–O unit<sup>14,15</sup> in the tetrahedron formed by five H<sub>2</sub>O molecules. Conventionally the boson peak is the maximum which appears at low-frequency in the reduced LFR divided by the frequency  $\omega$ ,  $\{I(\omega)/[n(\omega) + 1]\omega\}$ . This quantity has a maximum at  $40 \text{ cm}^{-1}$ , as seen in Fig. 7. This frequency is too close to the maximum of the transverse acoustic modes (O–O–O–bending) to allow us to conclude in favor of a boson peak. Therefore, our conclusion of this absence of boson peak, is then that the glass LiCl,4H<sub>2</sub>O is compact. The compactness was already deduced from neutron scattering, for LiCl,6H<sub>2</sub>O.<sup>24,25</sup>

The integrated light scattering excess (LSE) which is shown in Fig. 3 is related to thermally dependent structural relaxation or motions in anharmonic potentials. The LSE is zero in the glass and appears at the glass to supercooled liquid transition (130–145 K) (Fig. 3). It increases rapidly in the supercooled state and slows down in the liquid, as expected. The slowing down in the liquid state is less clear for the LSE at  $10 \text{ cm}^{-1}$ , probably because, at this energy, there is a contribution due to molecular diffusional motions. In the most tested glasses the LSE exists at temperatures much lower than  $T_g$ .<sup>7,8,26,27</sup> The fact that it is not observed in the

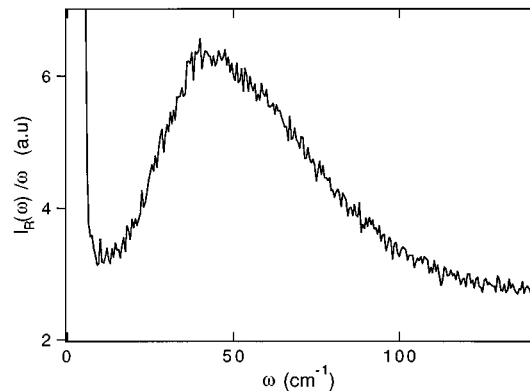


FIG. 7. LFR reduced intensity divided by the frequency  $\omega$ ,  $\{I(\omega)/[n(\omega) + 1]\omega\}$  of  $\text{LiCl} \cdot 4\text{H}_2\text{O}$  at  $T=83$  K.

glassy state of  $\text{LiCl} \cdot 4\text{H}_2\text{O}$ , is due to the compactness which does not allow any structural relaxation. This is in agreement with the absence of a Boson peak which was discussed above.

As shown in Fig. 5, the light-vibration coupling coefficient  $C(\omega)$  for the LSE, has a frequency dependence different from that of harmonic acoustic vibrations,  $C(\omega) \propto \omega^{0.5}$  instead of  $C(\omega) \propto \omega$ . This shows the difference between the scattering by oscillations related to structural changes and the one from harmonic vibrations. If it is possible to interpret the linear frequency dependence of  $C(\omega)$  for harmonic vibrations by a radial correlation in the glass,<sup>12,28</sup> we are not able now to explain the slower frequency dependence of  $C(\omega)$  for the oscillations related to structural changes.

## V. CONCLUSION

The comparison between inelastic neutron and low-frequency Raman scatterings shows that the light-vibration coupling coefficient  $C(\omega)$  is linearly frequency dependent as for most of the glasses.<sup>6,17</sup> The frequency dependence of this coefficient for oscillations related to structural changes is different. The absence of a thermally dependent light scattering excess and of Boson peak in the glassy state of  $\text{LiCl} \cdot 4\text{H}_2\text{O}$  is interpreted by a compactness of the structure, which is contrary to that observed in most of the glasses.

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