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# The Raman coupling function in disordered solids: a light and neutron scattering study on glasses of different fragility

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## Abstract

We report new inelastic Raman and neutron scattering spectra for glasses with different degrees of fragility, v-SiO<sub>2</sub>, v-GeO<sub>2</sub>, (AgI)<sub>0.5</sub>(Ag<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>)<sub>0.5</sub>, (AgI)<sub>x</sub>(AgPO<sub>3</sub>)<sub>1-x</sub>. The data are compared for each sample to obtain the Raman coupling function  $C(\omega)$ . The study indicates a general linear behaviour of  $C(\omega)$  near the boson peak maximum, and evidences a correlation between vibrational and relaxational properties, confirming the results of recent publications.

## 1. Introduction

The evaluation of the vibrational density of states  $g(\omega)$  is crucial for the study of the vibrational anomalies present in disordered solids, among which we may mention the boson peak (BP) [1–3] and quasi-elastic scattering (QES) [4, 5]. In spite of much experimental and theoretical work in recent years [6–8] many questions about the origin of these universal features are still unanswered.

From Raman spectra alone it is not possible to directly obtain the density of states, because the expression of the Raman intensity,  $I_R$ , besides  $g(\omega)$  contains a frequency-dependent, and a priori unknown, function  $C(\omega)$  [9].  $C(\omega)$  measures the average scattering efficiency of the vibrational modes with frequency lying between  $\omega$  and  $\omega + d\omega$ . For Stokes scattering we have

$$I_R(\omega, T) \propto \frac{n(\omega, T) + 1}{\omega} g(\omega) C(\omega) \quad (1)$$

where  $n(\omega, T)$  is the Bose–Einstein population factor.

In principle, not even neutron scattering supplies the true  $g(\omega)$  because of the different scattering amplitudes of the atomic components; however, it has been demonstrated that in glasses [10, 11], using the incoherent approximation, the inelastic neutron scattering intensity,  $I_N$ , is connected to the vibrational density of states by an equation similar to equation (1), but which does not contain any unknown quantity such as  $C(\omega)$ :

$$I_N(\omega, T) \propto \frac{n(\omega, T) + 1}{\omega} g(\omega). \quad (2)$$

Hence, using equations (1) and (2) it is possible to evaluate the most reliable  $C(\omega)$  and assess the validity of the proposed models.

Actually, different models have been proposed for the frequency dependence of  $C(\omega)$ . In particular, for slightly distorted plane-wave modes,  $C(\omega)$  has an  $\omega^2$  low-frequency dependence [12–14]; within the framework of the soft potential model [15, 16]  $C(\omega)$  has a constant value; finally, in the fracton-like model and at low frequency,  $C(\omega)$  follows a power law, whose exponent depends both on the model system under investigation and on the mechanism of polarizability modulation [17–19]. Though experimental efforts have been devoted to this problem [20, 21], a definite conclusion as to the shape of  $C(\omega)$  has not been reached, mainly due to the presence of a luminescence background and QES.

The aim of the present work is to determine the spectral shape of  $C(\omega)$  by combined Raman and neutron scattering experiments, in several kinds of glasses exhibiting different degrees of fragility, i.e. v-SiO<sub>2</sub>, v-GeO<sub>2</sub> and phosphate and borate glasses.

## 2. Experimental details

### 2.1. Sample preparation

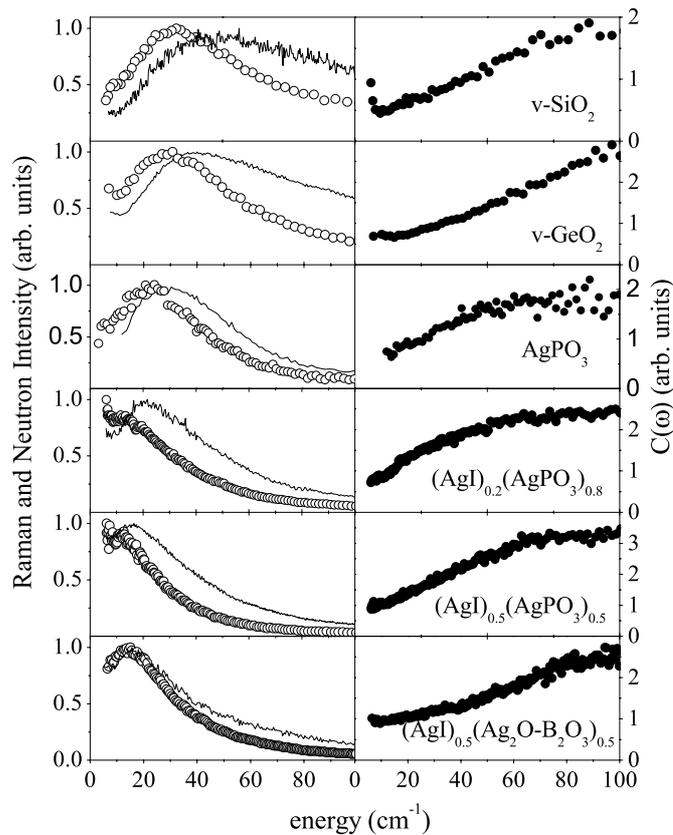
The v-SiO<sub>2</sub> sample was a commercial-grade Spectrosil sample, purchased from SILO (Florence). It had a disc shape with a diameter of about 50 mm and a thickness of 4.8 mm.

We prepared v-GeO<sub>2</sub> using reagent-grade GeO<sub>2</sub> powder (Aldrich 99.99%). The powder was melted in ceramic crucibles for about 5 h at about 1600 °C. The homogeneous and bubble-free melt was subsequently quenched in air. The containers were cut and peeled from the samples, leaving a cylinder-shaped bulk (15 mm diameter and 5 mm thickness) of clear and transparent glass.

Phosphate glasses (AgI)<sub>x</sub>(AgPO<sub>3</sub>)<sub>1-x</sub> (from  $x = 0$  to 0.55) were prepared following the standard procedure [22]. The powders were heated up to 500 °C, the melted solution was quenched and finally pressed onto a steel mask kept at room temperature, in order to obtain disc-shaped samples with a diameter of about 50 mm and a thickness of 2 mm.

Also the borate glass (AgI)<sub>0.4</sub>-(Ag<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>)<sub>0.6</sub> was prepared following a standard procedure [23] using special grade AgI and AgNO<sub>3</sub> from Erba. For the B<sub>2</sub>O<sub>3</sub> component, the <sup>11</sup>B-enriched material was supplied by Centronic Limited and certified 97% in <sup>11</sup>B. In order to allow for a complete reduction of AgNO<sub>3</sub> to Ag<sub>2</sub>O, the powders were first heated in a quartz crucible at 400 °C for 2 h. Melting was achieved by further heating at 500 °C for 5 h. Quenching was obtained by rapidly pouring and pressing the melted compound into a circular steel mould kept at 100 °C. The samples were then annealed at  $T < T_g$  in order to minimize thermal stresses; they have a disc shape characterized by a diameter of 50 mm and a thickness of 2 mm.

The vitreous nature of the melt quenched samples was verified by means of x-ray diffraction measurements. The samples were subsequently polished in order to obtain good optical surfaces. The fragility of silica and germania is  $m = 20$ , for phosphate and borate glasses  $m = 28$  and for polybutadiene  $m = 60$ .



**Figure 1.** Left panels: low-frequency HV Raman (continuous lines) and neutron scattering (open circles) spectra for the melt quenched systems. Right panels: proportional to  $C(\omega)$ , calculated as the ratio between the Raman and neutron intensities. For borate glasses  $T = 150$  K, for all other systems  $T = 50$  K. Data for  $v\text{-SiO}_2$  and  $v\text{-GeO}_2$  are taken from [20] and [25] respectively.

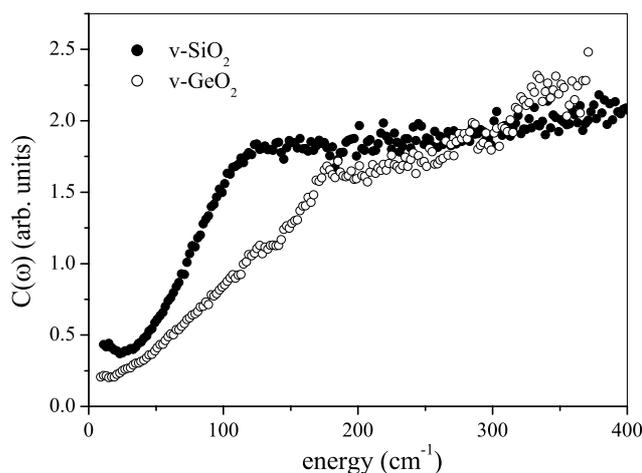
## 2.2. Neutron experiments

The inelastic neutron scattering data were collected by using different time-of-flight spectrometers at the Institut Laue-Langevin (Grenoble, France). In particular, the IN6 spectrometer was used for phosphate and borate glasses, while IN4 was used for  $v\text{-SiO}_2$  and  $v\text{-GeO}_2$ . The incident neutron wavelength employed was different according to the instrument used.

The time-of-flight data underwent the usual corrections, such as subtraction of the empty cell and normalization to a vanadium measurement. The density of states  $g(\omega)$  was obtained by an iterative procedure described in the literature [24] and corrected for the Debye–Waller factor and multiphonon contributions, although at 50 K, where we compute the Raman to neutron scattering ratio, the multiphonon correction does not affect the data significantly. More details about the procedure for the treatment of data are reported elsewhere [25, 26].

## 2.3. Raman experiments

Raman scattering experiments in HV geometry were performed using a standard experimental set-up over a wide range of frequencies ( $-300$  to  $5000$   $\text{cm}^{-1}$ ). Such a wide range was



**Figure 2.** Room temperature  $C(\omega)$  for v-SiO<sub>2</sub> and v-GeO<sub>2</sub> in an extended frequency range.

necessary in order to take properly into account the shape and temperature dependence of the luminescence background, which is weak at room temperature but becomes important for a quantitative determination of the coupling function at low frequency ( $<20\text{ cm}^{-1}$ ) and low temperature ( $<70\text{ K}$ ). Details of the data analysis are reported elsewhere [25].

In addition, the low-frequency Raman spectra also contain the QES. Luminescence and (especially) QES cause a great uncertainty in the determination of the  $C(\omega)g(\omega)$  term in (1) from experimental data, and it is necessary to minimize their effect. Accordingly, the experiments were performed at low temperature (50 or 77 K for strong glasses), where the QES intensity is negligible.

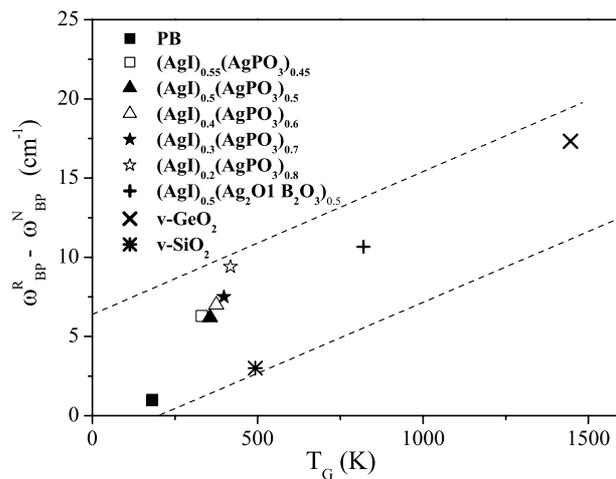
### 3. Results and discussion

In the left panels of figure 1, we report the (arbitrarily normalized) low-frequency Raman and neutron scattering spectra for the melt-quenched samples at the temperatures indicated in the caption, while in the right panels of the same figure we report a quantity proportional to  $C(\omega)$  of the same samples as calculated by the ratio between Raman and neutron data. For all samples, Raman and neutron spectra have a qualitatively similar shape, at all investigated temperatures.

All coupling functions  $C(\omega)$  tend to a constant value at frequencies higher than the BP, as evidenced in figure 2 where we report, as examples, the cases of SiO<sub>2</sub> and GeO<sub>2</sub> in a more extended frequency range; in particular, SiO<sub>2</sub> exhibits a linear behaviour of  $C(\omega)$  in the BP frequency range, followed by a nearly constant plateau up to high frequency where the molecular modes begin to appear [25, 27].

From figure 1 it appears that the maxima of the BP as observed in Raman spectra are at higher energies with respect to neutron spectra, an effect which is reflected in (or is a consequence of) the linear behaviour of  $C(\omega)$  in the corresponding right panels. This blue shift is larger in v-SiO<sub>2</sub> and v-GeO<sub>2</sub> than in the other systems; in general, the blue shift is found to depend on the glass-transition temperature  $T_g$  of the system, as shown in figure 3 for several systems. Even if the scattering of data is large, the trend appears to be significant.

At first sight, the existence of such a correlation appears surprising, because the shift is determined by vibrational properties (the density of vibrational states and the Raman coupling function) which, in turn, depend on the properties of the potential energy surface in the minima,



**Figure 3.** Energy difference between the maximum of the BP measured by Raman and neutron scattering, as a function of the glass-transition temperature  $T_g$  of several glasses. Data on PB from [32].

while  $T_g$  is set by the distribution of barrier heights separating adjacent minima (or basins of minima) and by the geometry of the energy landscape in the neighbourhood of saddle points. However, correlations between vibrational and relaxational characteristics have already been observed and reported in recent papers [28–30], and their origin is far from clear. The present data, together with previously published ones [20, 21, 31], seem to indicate that this behaviour is more common than might be expected.

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