

Density of vibrational states in highly disordered systems through Raman scattering and atomic-scale simulation

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ABSTRACT

Raman scattering is used as a probe with regard to the understanding of local structural arrangements and correlated lattice dynamics in highly disordered systems. This investigation is shown to be particularly fruitful if one records the signal over a very wide frequency range (including Stokes, anti-Stokes and multiple-order processes). Results on amorphous semiconductors and vitreous materials are discussed in comparison with those obtained by other techniques (inelastic neutron scattering) or numeric simulations (valence-force-field or molecular dynamics approaches). It is shown that the dynamic response of a disordered material is essentially accounted for by simply considering the lattice dynamics of its crystalline counterpart.

§ 1. INTRODUCTION

Dynamic properties of disordered systems are attracting increasing interest, both theoretically or experimentally. The most marked differences occur at low temperature (i.e. at low frequencies for the dynamic response) where thermodynamic (specific heat and thermal conductivity) anomalies are observed. In particular, low-frequency Raman spectra show features, referred to as light scattering excess (LSE) and the boson peak (BP) in vitreous materials (Fontana *et al.* 1995).

The aim of this study is to examine carefully the Raman spectra of several highly disordered systems. First, we discuss results obtained for a pure covalent amorphous semiconductor material, namely amorphous Si (a-Si). Then, the effects of either homogeneous chemical disorder (amorphous $\text{Si}_{1-x}\text{C}_x$ (a-Si_{1-x}C_x)) or inhomogeneous structural disorder (a-Si including nanovoids) are discussed. These covalent systems allow easy comparison with calculated structural and dynamic properties using a valence-force-field (VFF) model. Finally, Raman scattering in vitreous SiO_2 (v-SiO₂) is presented. Comparison with the preceding systems and other techniques (inelastic neutron scattering and molecular dynamics simulations) is performed in order to get reliable information on these systems. Particular attention is devoted to the low-frequency response (LSE and BP).

§ 2. MULTIPLE-ORDER RAMAN SCATTERING

In highly disordered systems, the lack of translational invariance leads to the activation of all vibrational modes: Raman spectra thus consist of non-intense and broad bands instead of well defined structures as in crystalline materials. It has been shown that the understanding of the dynamic response is improved by recording it over a wide frequency range in order to estimate the multiple-order contribution

(Zwick and Carles 1993). Generally, this contribution is neglected and the structure-less underlying signal is arbitrary subtracted. Then the Stokes first-order signal is written as follows (Shuker and Gammon 1970):

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

where A accounts for the optical properties of the sample, \tilde{n} is the Bose population factor, C is the coupling factor between light and vibrations, and g is the density of the vibrational states (DVS). In fact, in amorphous semiconductors, first-order and multiple-order integrated intensities have been shown to be of the same order of magnitude. The Raman intensity for either Stokes or anti-Stokes processes is then written as follows:

$$I = \sum_n \alpha_{n/1} I^{(n)}, \quad (2)$$

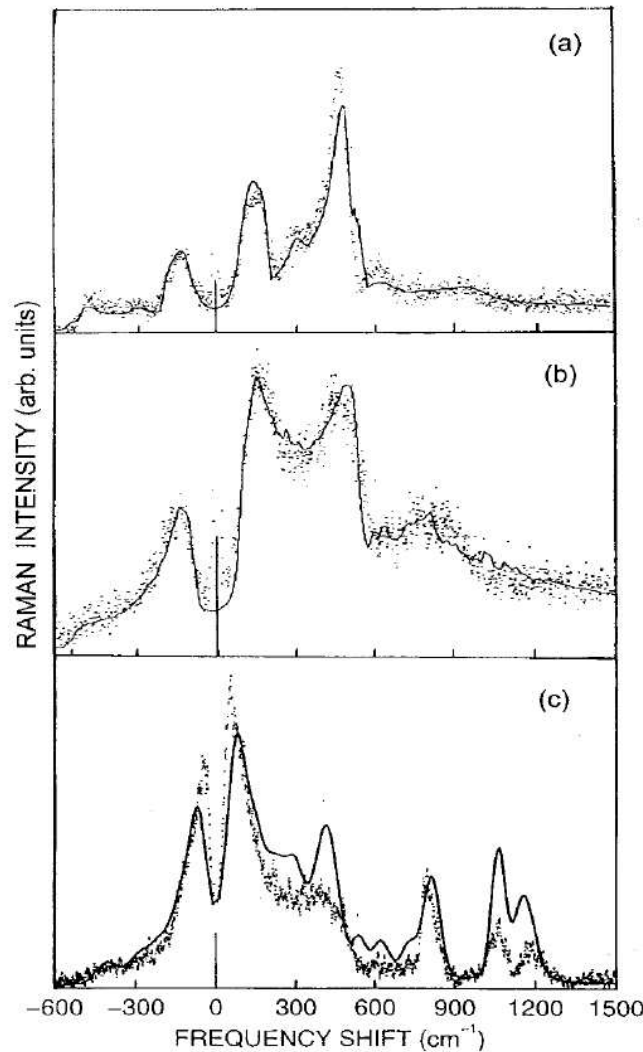
where the coefficient $\alpha_{n/1}$ accounts for the decrease in the scattering efficiency with n . $I^{(n)}$ is the n th order convolution product of the first-order spectrum given by eqn. (1). Taking advantage of the different temperature effects on the $I^{(n)}$ terms provides an original way to obtain the DVS (Chehaidar *et al.* 1994).

Equations (1) and (2) show that the calculation of the Raman signal requires knowledge of the DVS in the disordered phase, the coupling factor C and the amount $\alpha_{n/1}$ of multiple-order events. At first sight, since short-range order and short-range interactions are thought to be preserved in these compounds, the DVS in the disordered state will not substantially differ from the crystalline DVS. Indeed, using eqn. (1), this assumption is verified in an amorphous semiconductor DVS which mirrors the broadened image of its crystalline counterpart rather well. Much effort has been devoted to the experimental or theoretical estimation of the coupling factor (Achibat *et al.* 1993, Sokolov *et al.* 1993). It is now well established that it follows a quasilinear frequency dependence over the major part of the spectrum. The multiple-order contribution is estimated from the Raman signal beyond the DVS cut-off.

Figure 1 shows depolarized Raman spectra of three highly disordered systems recorded over a wide frequency range. Results already reported for the amorphous semiconductors a-Si (Zwick and Carles 1993) or a-Si_{1-x}C_x (Chehaidar *et al.* 1994) are here compared with those obtained for v-SiO₂ (Tetrasil) (figs. 1(a), (b) and (c) respectively). In the latter, the DVS is simply taken as a smoothed version of α -quartz DVS (Lee and Gonze 1995) $C(\omega) = \omega$ and $\alpha_{2/1} = 0.1$ (higher-order processes have been neglected). The value of the scaling factor $\alpha_{1/1}$ is determined to account for the recorded integrated intensity between -250 and 250 cm⁻¹. In spite of the crudeness of the approximations, the experimental data (dots) are remarkably well described by the model (full curve).

Whatever the disordered system, two general trends must be emphasized. First, several features (the underlying signal, high-frequency bands are quasielastic scattering) cannot be accounted for if one neglects the multiple-order scattering. Second, the prominent features originate from disorder-activated first-order Raman scattering. In particular, one notes the close correspondence between the so-called BP in the vitreous material and the disorder-activated transverse acoustic band in amorphous semiconductors. However, more detail consideration of this comparison shows that

Fig. 1



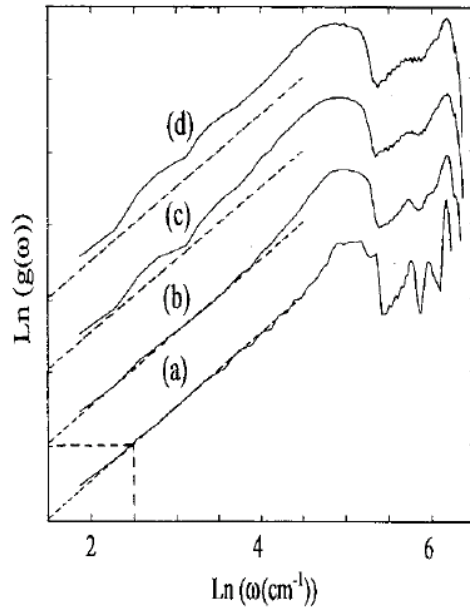
Depolarized Raman spectra of (a) a-Si, (b) a-Si_{1-x}C_x and (c) v-SiO₂: (·), experiment; (—), theoretical calculations.

simply removing all the symmetries of the periodic lattice is not sufficient to describe the lattice dynamics of a disordered material (Chehaidar *et al.* 1995).

§ 3. VIBRATIONAL STATES IN HIGHLY DISORDERED SYSTEMS

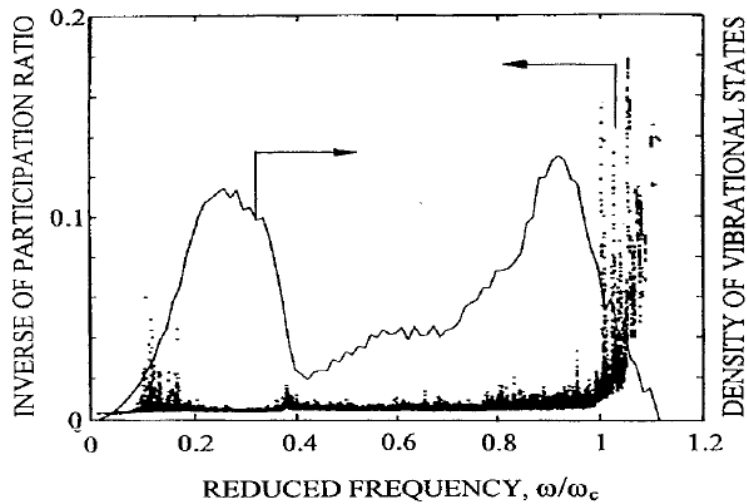
Much effort has been made to obtain accurate description of the structure and its associated dynamics. In covalent semiconductors, the VFF model was particularly successful. We have computed the eigenstates and DVS of both crystalline Si (c-Si) and a-Si. The same set of force constant parameters was used in order to fit both the structure factor and the lattice dynamics (Chehaidar *et al.* 1995). Figure 2 shows the DVS (log-log plot) of the Si crystal (fig. 2(a)) and continuous Si random networks without (fig. 2(b)) or with (figs. 2(c) and (d)) nanovoids. One observes that, the higher the disorder, the more the optical mode broadening increases, and the frequency range of the Debye-like behaviour (ω^2 dependence) reduces. What occurs is particularly shown in fig. 3 where the density (linear scale) and corresponding inverse

Fig. 2



log-log plot of calculated Si DVS against frequency: (a) crystal; (b) fully coordinated a-Si; (c) a-Si with nanovoids created by removing assemblies of 17 atoms; (d) a-Si with nanovoids created by removing assemblies of 47 atoms.

Fig. 3



DVS (—) and inverse participation ratio (·) in a-Si with voids (same as fig. 2(d)).

participating ratio of the vibrational (same system as in fig. 2(d)) are displayed. It demonstrates that extended modes (acoustic like) and localized modes coexist in the same low-frequency range. These calculations show that 'extra states' are directly connected to heterogeneities at medium-range order. In fact, neither structural (a-Si continuous network) nor chemical (a-Si_{1-x}C_x solid solutions) homogeneous disorder generates such modes.

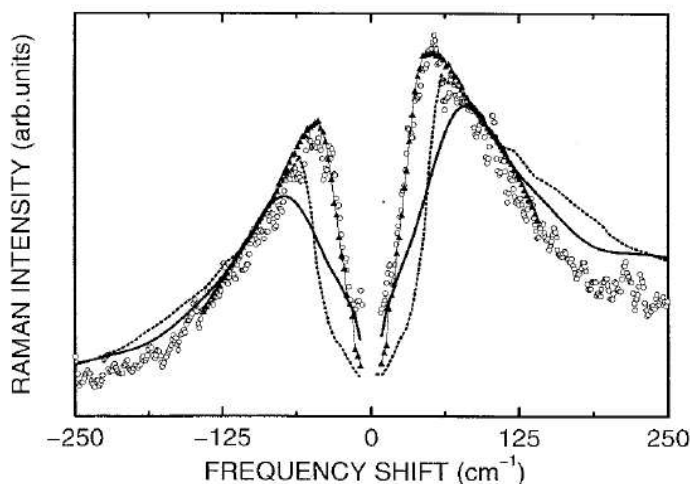
§ 4. RAMAN SCATTERING AND THE DENSITY OF VIBRATIONAL STATES

Short- and medium-range orders are thought to be more affected in vitreous compounds than in tetrahedrally bonded and purely covalent materials. However, the similarities emphasized in fig. 1 show that their dynamics will not substantially differ. The low-frequency range of the depolarized Raman spectrum of $v\text{-SiO}_2$ is reported in fig. 4 (open circles). The full curve resulting from calculations (same as in fig. 1(c)) shows that the major contribution to the BP comes from vibrational states reminiscent of the crystal states.

Nevertheless, the calculated spectrum reaches its maximum at a higher frequency than the experimental value. Coupling factor effects have often been invoked to account for such discrepancy. These effects can be discarded here. Indeed, the quasi-linear frequency dependence of C has been checked by comparing Raman with heat capacity measurements (Sokolov *et al.* 1993) or with inelastic neutron scattering (Achibat *et al.* 1993). Using the neutron data (Buchenau *et al.* 1986), $C(\omega) = \omega$ and $\alpha_{2/1} = 0.1$, we obtain perfect agreement with our Raman data (full triangles and open circles respectively in Fig. 4).

Before invoking 'extra states' to account for the differences observed between the experimental DVS and the calculated DVS, much care has to be taken in the choice of the latter. Indeed, at least eight different allotropic forms of $c\text{-SiO}_2$ have been identified, leading thus to a large set of microscopic structural entities (at medium-range order) that can be involved in building a disordered SiO_2 network. This is well supported by the presence of optical modes at 77 and 116 cm^{-1} in coesite (Serghiou *et al.* 1995) and by the similarities between DVS of $\alpha\text{-cristobalite}$ and $v\text{-SiO}_2$ (Dove *et al.* 1997). Another way to obtain the DVS is by theoretical estimation. The dotted curves in fig. 4 depicts the Raman signal calculated using molecular dynamics simulations data (Jin *et al.* 1993). An improvement in the fit is obtained for the location of the BP, although its low-frequency wing is clearly underestimated (note that one must take account of finite size effects of the supercell).

Fig. 4



Low-frequency Raman spectrum in $v\text{-SiO}_2$: (\circ), experiment; (—) theory using DVS from $\alpha\text{-quartz}$; (\blacktriangle), neutron data; (\cdots), molecular dynamics simulation.

Keeping in mind our preceding results for heterogeneous amorphous semiconductors, one may infer that the difference between the experimental BP and the calculated BP, or the ω dependence of the coupling factor (an ω^2 dependence is expected for extended acoustic modes) originate in the presence and specific coupling of localized states. In fact, vitreous materials are well known to reveal particularities in the low-frequency range. Various explanations have been put forward, such as the occurrence of two-level systems, tunnelling states or soft potential effects (Gil *et al.* 1993, Gurevitch *et al.* 1993). However, concerning the so-called LSE, one should mention that the present work has originally shown that multiple-order processes cannot be discarded. Of particular relevance is the appearance of a band centred at 0 cm^{-1} in the second order spectrum for all the disordered systems, and the fact that its intensity does increase with increasing temperature more rapidly than $\tilde{n} + 1$.

§ 5. CONCLUSION

Raman scattering provides a valuable means of correlating dynamics and short- or medium-range order in highly disordered structures. It has been shown that this probe is particularly efficient if one takes account of the complete data (anti-Stokes and Stokes scattering, and multiple-order effects). General trends have been derived irrespective of the type of material, either amorphous covalent semiconductors or glasses. Some particularities invoked for vitreous compounds (BP, LSE, localized states, medium-range order effects, etc.) are shown to be inherent in disordered phases. Moreover, the coexistence of localized and extended (acoustic-like) states in the same low-frequency range may be the key to a better understanding of thermodynamic anomalies observed at low temperatures. As an example, it would be of particular interest to test either experimentally or by means of dynamic simulations the effect of nanometre-sized voids on vibronic localization.

REFERENCES

- ACHIBAT, T., BOUKENTER, A., and DUVAL, E., 1993, *J. chem. Phys.* **99**, 2046.
 BUCHENAU, U., PRAGER, M., NUCKER, N., DIANOUX, A. J., AHMED, N., and PHILIPS, W. A., 1986, *Phys. Rev. Lett.*, **34**, 5665.
 CHEHAIDAR, A., DJAFARI-ROUHANI, M., and ZWICK, A., 1995, *J. non-crystalline Solids*, **192–193**, 238.
 CHEHAIDAR, A., ZWICK, A., CARLES, R., and BANDET, J., 1994, *Phys. Rev. B*, **50**, 4345.
 DOVE, M. T., HARRIS, M. J., HANNON, A. C., PARKER, M. J., SWAINSON, I. P., and GAMBHIR, M., 1997, *Phys. Rev. Lett.*, **78**, 1070.
 FONTANA, A., CARINI, G., BRODIN, A., TORREL, L. M., BORJESSON, L., and SAUNDERS, G. A., 1995, *Phil. Mag. B*, **71**, 525.
 GIL, L., RAMOS, M. A., BRINGER, A., and BUCHENAU, U., 1993, *Phys. Rev. Lett.*, **70**, 182.
 GUREVITCH, V. L., PARSHIN, D. A., PELOUS, J., and SCHOBER, H. R., 1993, *Phys. Rev. B*, **48**, 16318.
 JIN, W., VASHISHTA, P., KALIA, R. K., and RINO, J. P., 1993, *Phys. Rev. B*, **48**, 9359.
 LEE, C., and GONZE, X., 1995, *Phys. Rev. B*, **51**, 8610.
 SERGHIU, G., ZERR, A., CHUDINOVSKIKH, L., and BOEHLER, R., 1995, *Geophys. Res. Lett.*, **22**, 441.
 SHUKER, R., and GAMMON, R. W., 1970, *Phys. Rev. Lett.*, **26**, 642.
 SOKOLOV, A. P., KISLIUK, A., QUITMANN, D., and DUVAL, E., 1993, *Phys. Rev. B*, **48**, 7692.
 ZWICK, A., and CARLES, R., 1993, *Phys. Rev. B*, **43**, 6024.