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Abstract. The effect of structural disorder on the first-order Raman scattering in glasses is studied by perturbation series approximations to the averaged Green function of an appropriately chosen model system. The proposed theoretical approach is applied to calculating the Raman spectra of Na_2O–SiO_2 glass systems on the basis of the disorder-modified spectrum of a Si_2O_7 dimer.

1. Introduction

Raman spectroscopy has been widely used for studying the structure of both crystalline materials and glasses. While in the former case well developed theoretical methods for treating the Raman spectra exist, the latter are much more difficult to investigate owing to the absence of translational symmetry. Most papers on the Raman spectroscopy of glasses published so far have reported more or less empirical studies in which the strategy is to vary systematically the glass composition in order to follow the corresponding tendencies in the structure variation. At the same time, there is a considerable necessity in materials science and geology for even semiquantitative methods to analyse Raman spectra of glasses.

The theoretical methods used for calculating the Raman spectra of glasses are usually different in the various spectral ranges. In the low-frequency range (below 100 cm^{-1}) the so-called mode-coupling theory [1,2] provides excellent fits to experimental data for a large variety of glasses. However, this approximation, which is continuous in character, is not suitable for modelling the spectra at higher frequencies originating from optical modes.

All theoretical approaches developed so far for studying the Raman spectra of glasses in the intermediate and high-frequency ranges (200–1500 cm^{-1}) are based on their relation to the Green function of the system and to the vibrational density of states (VDOS) [3–5]. The approximations usually employed such as the central force interactions between nearest neighbours only [6,7], Bethe lattice boundary conditions [8,9] or light scattering by individual bonds [10,11], although simplifying considerably the treatment, still either remain rather complicated or do not provide satisfactory results in many cases.

The aim of the present paper is to consider the effect of structural disorder on the first-order Raman scattering of glasses in the intermediate- and high-frequency spectral ranges. For this purpose, self-consistent perturbation approximations for the complex self-energy part of the averaged Green function of previously specified structural units are proposed. These approximations, being computationally much simpler than those used so far, can be easily modified for semiquantitative analysis of the Raman spectra of a large variety of

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glasses. Disorder-modified Raman spectra of Si_2O_7 dimers are also discussed as an example since this structural unit is known to be suitable for modelling the $M_2O–SiO_2$ glass systems extensively studied by Raman spectroscopy.

2. Calculation of the Raman spectra

The intensity of the Raman spectrum of a glass can be presented [3, 4, 12] in the form

$$I_a(\omega) \propto (2\omega)^{-1}(\omega + Y)^4 n(\omega) \sum_p C_a^p(\omega) D_p(\omega) \tag{1}$$

where ω is the anti-Stokes Raman shift, a is the scattered-light polarization index, $C_a^p(\omega)$ is a coupling constant, Y is the frequency of the incident light, $n(\omega) = [\exp(\beta\omega) - 1]^{-1}$ is the averaged number of phonons with frequency ω, and $D_p(\omega)$ is the VDOS in the band p, which contains modes with similar atom vibrations. The coupling constants $C_a^p(\omega)$ for an anisotropic Raman spectrum as well as for parallel (HH) and transverse (HV) polarizations of the scattered light are given by [11]

$$C_{isotr}^p(\omega) = A_p^2(\omega) \qquad C_{HH}^p(\omega) = 7E_p^2(\omega) + 45A_p^2(\omega) \qquad C_{HV}^p(\omega) = 6E_p^2(\omega) \tag{2}$$

where $A_p(\omega)$ and $E_p^2(\omega)$ are the polarizability tensor invariants:

$$A_p(\omega) = \tfrac{1}{3}(\rho_{11}^p + \rho_{22}^p + \rho_{33}^p)$$
$$E_p^2(\omega) = \tfrac{1}{2}[(\rho_{11}^p - \rho_{22}^p)^2 + (\rho_{11}^p - \rho_{33}^p)^2 + (\rho_{22}^p - \rho_{33}^p)^2] + 3[(\rho_{12}^p)^2 + (\rho_{13}^p)^2 + (\rho_{29}^p)^2]. \tag{3}$$

In equation (3) the frequency-dependent polarizability tensor of the pth band is

$$\rho_{ij}^p(\omega) = \sum_l \pi_{i,j,l} \mathcal{U}_l^p(\omega) \tag{4}$$

where $\pi_{i,j,l}$ is the first derivative of the ijth component of the dielectric tensor π with respect to the lth component of the frequency-dependent eigenvector $\mathcal{U}^p(\omega)$ of the pth band [4]. Equation (4) implicitly states that there is no correlation between the mechanical and the electrical disorder in the glass system.

Using atomic polarizabilities defined as in [13] we shall express the polarizability tensor elements $\rho_{ij}^p(\omega)$, according to the model for Raman scattering by independent bonds [5], through

$$\rho_{ij}^p(\omega) = \frac{1}{V} \sum_m \frac{1}{r_m} [A_b^m Q_i^m Q_j^m \Delta b_p^m Q^m + \tfrac{1}{4}(A_b^m + A_n^m - A_{tr}^m)(\Delta b_{i,p}^m Q_j^m$$
$$+ \Delta b_{j,p}^m Q_i^m - 2Q_i^m Q_j^m \Delta b_p^m Q^m)]. \tag{5}$$

In equation (5), V is the volume of the system, (i, j) and p are the Cartesian and band indices, respectively, $\Delta b_p^m(\omega) = \mathcal{U}_l^p(\omega) - \mathcal{U}_k^p(\omega)$ (l, k number the atoms forming the mth bond), Q^m is a unit vector parallel to the mth bond, A_n^m and A_b^m are the bond polarizabilities caused by the non-bonding and bonding electrons, respectively, of the atoms in the bond and the summation is over all bonds in the system. It should be noted that A_n^m and the transverse polarizability A_{tr}^m in equation (5) do not depend on the bond length r^m, while A_b^m is proportional to $(r^m)^4$.

3. Modelling of the Raman spectra

To obtain the Raman intensity from equation (1) we shall propose models below for calculating $C_a^p(\omega)$ and $D_p(\omega)$ based on the so-called corresponding system (CS) approximation.

3.1. Corresponding system approximation

We assume that *for each glass system there exists a CS such that there is one-to-one correspondence between the CS vibrational modes and the glass bands with similar atom vibrations.* Thus, the investigation of a glass of unknown structure is replaced by the study of the effects of disorder on the vibrational spectra of the CS with known structure. The CS for a particular material can be defined in different ways, but, as the short-range order dominates the Raman spectra of silicate glasses [8], the most suitable CS in such materials would be the predominant structural units representing best on this scale the glass atomic configuration [14, 15].

3.2. Effects of disorder

In this section a method based on the lowest-order self-consistent perturbation theory is proposed to evaluate the shift and the broadening of phonon energy levels due to the structural disorder. The broadening of Raman lines of glasses originates from disorder-induced fluctuations both in the photoelastic coefficients and in the glass structure.

In the U^l-representation (U^l are the CS eigenvectors and l numbers the CS vibrational modes), the diagonal elements of the averaged Green function of the glass can be presented as a perturbation series [16]:

$$\mathcal{G}_l = g_l + g_l \langle V_{ll} \rangle g_l + g_l \sum_k \langle V_{lk} g_k V_{kl} \rangle g_l + \cdots \qquad (6)$$

where V_{lk} are the disorder-induced perturbations to the CS dynamical matrix in the U^l representation and $\langle \ldots \rangle$ denotes averaging over all possible atom configurations. In equation (6),

$$g_l(\omega) = (\omega_l^2 - \omega^2 - i\omega_l \gamma_l)^{-1} \qquad (7)$$

is the diagonal element of the CS Green function in quasi-phonon approximation [16], and ω_l and γ_l are the eigenfrequency and the linewidth, respectively, of the lth CS mode.

To calculate the Green function matrix elements in equation (6) we assume the following.

(i) The statistical distribution of V_{lk} is symmetric and zero centred; thus, all averaged terms in the series containing odd numbers of V_{lk} are equal to zero.

(ii) Following the second-order self-consistent perturbation theory the averaged terms can be presented as products of averaged pairs of V_{lk}.

(iii) The $\langle V_{pk} V_{kn} \rangle$ terms with $p = n$ are non-zero (i.e. the interaction between the modes p and k is not correlated with that between the modes k and $n \neq p$).

The summation in the resulting series expansion of $\mathcal{G}_l$ is carried out by the standard diagram technique [17]. The basic diagram used by us is shown in figure 1(a). The solid lines in this diagram represent g_k, and the crosses connecting two lines the matrix elements V_{qn}, while the dashed line connecting two crosses indicates that the corresponding matrix

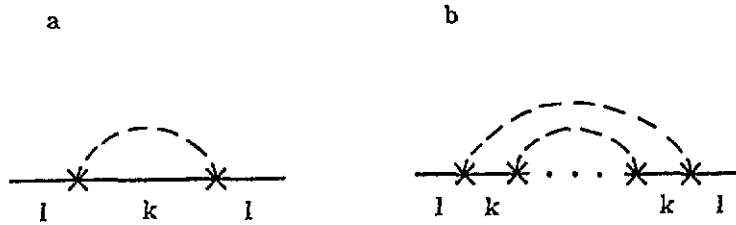a   b

Figure 1. Feynman diagrams used in calculations.

elements are averaged in pairs. As shown in figure 1(b), the sum of all diagrams originating from the basic diagram is

$$G_l(\omega) \simeq g_l(\omega) + g_l^2(\omega) \sum_k \langle V_{lk} V_{kl} \rangle G_k(\omega). \tag{8}$$

The summation of the series expansion of G_l (equation (6)) can be formally performed by introducing the self-energy T_l of the lth mode:

$$G_l(\omega) = g_l(\omega) + g_l(\omega) T_l(\omega) G_l(\omega). \tag{9}$$

In order to write equation (8) in the form (9) the self-energy should be presented by

$$T_l(\omega) = [1 - g_l(\omega) T_l(\omega)] \sum_k \langle V_{lk} V_{kl} \rangle G_k(\omega). \tag{10}$$

On the other hand, the sum of all connected diagrams originating from the basic diagram by replacing the internal g_k-line and one of the external g_l-lines with diagrams such as those shown in figure 1 is given again by (9), but in this case

$$T_l \simeq \sum_k \langle V_{lk} V_{kl} \rangle G_k. \tag{11}$$

In what follows we refer to equations (10) and (11) as approximations A and B, respectively. It is intuitive that approximation B has to be more accurate since in this case more diagrams are taken into account in the perturbation series.

From equations (7), (8) and (10) or (11) the disorder-induced line frequency shifts R_l and broadenings Γ_l of the CS modes can be obtained in a self-consistent manner by keeping in mind, as usual [14], that

$$\mathrm{Re}[T_l(\omega_l)] \simeq R_l = \omega_l^2 - \Omega_l^2 \tag{12}$$

and

$$\mathrm{Im}[T_l(\omega_l)] \simeq \omega_l \Gamma_l = \omega_l(W_l - \gamma_l). \tag{13}$$

In equations (12) and (13), Ω_l is the frequency of the maximum for the lth band of the glass and W_l is its width.

Using equations (9), (12) and (13), one obtains for the lth glass band the following expression:

$$D_l(\omega) = 2\omega \, \mathrm{Im}[G_l(\omega)] \simeq 2\omega \omega_l W_l[(\omega_l^2 - R_l - \omega^2)^2 + \omega_l^2 W_l^2]^{-1}. \tag{14}$$

To use approximations A and B, one must define explicitly the quantities $\langle V_{lk}V_{kl}\rangle$. Assuming that only nearest-neighbour atom interactions are dominant and that the matrix elements of the potential V in coordinate representation are independent of the types of atom (i.e. that $V^{\alpha\beta} = \epsilon$, $\epsilon^{0.5}$ (cm^{-1}) being referred to hereafter as random disorder parameter), one can write $\langle V_{lk}^2\rangle$ in the form

$$\langle V_{ln}V_{nl}\rangle \simeq \epsilon^2 \left(\sum_{\langle \alpha\beta\rangle} U_\alpha^l U_\beta^n \right)^2 \tag{15}$$

where $\langle\alpha\beta\rangle$ denotes summation over nearest-neighbour atoms only.

4. Numerical results and discussion

To illustrate the proposed theoretical method we calculated the Raman line positions, widths and intensities for two glasses in the system Na$_2$O–SiO$_2$ which is of great technological and geological importance and which has been intensively studied [18, 19]. In calculating the spectra of both materials (Na$_2$O.SiO$_2$ and Na$_2$O.1.22SiO$_2$ glasses) we used as CS the Si$_2$O$_7$ dimer which is the smallest structural unit suitable for describing the disorder in both the Si–O–Si bridging angle and the dihedral angle in this type of glass. The Si–O$_{br}$ distances were set equal to 1.67 Å, and the Si–O$_{nbr}$ distances to 1.59 Å (O$_{br}$ and O$_{nbr}$ stand here for bridging and non-bridging oxygen atoms, respectively). All tetrahedral angles were set equal to the ideal value of $\Phi_T = 109.2°$, and the Si–O–Si bridging angle to 135°. In calculating the dynamical matrix of the Si$_2$O$_7$ dimer we used the same values of the force constants as those used in [2].

The eigenfrequencies and the eigenvectors of the CS were found by standard normal mode calculations and the Raman line shifts R_l and widths W_l were calculated by the method described in section 3.2.

Table 1. Frequency shifts $\Delta\omega_N = \Omega_N - \omega_N$ and spectral linewidths W_N of the Si$_2$O$_7$ dimer calculated in approximations A and B. N numbers the modes.

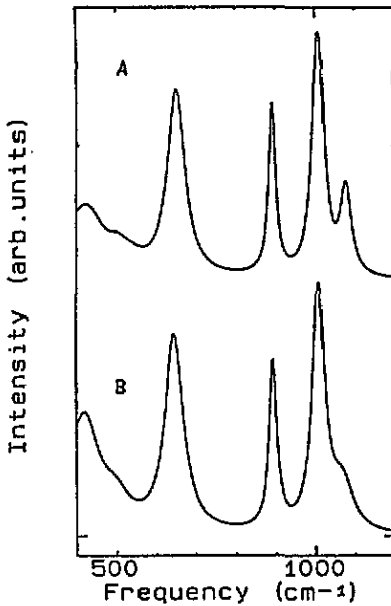| N	ω (cm^{-1})	A ($\epsilon' = 210$ cm^{-1})[a]		B ($\epsilon' = 175$ cm^{-1})[a]	
		W (cm^{-1})	$\Delta\omega$ (cm^{-1})	W (cm^{-1})	$\Delta\omega$ (cm^{-1})
1	1055	36	23	72	13
2	1014	27	1	34	0
3	1011	32	−19	59	−8
4	1007	40	3	41	2
5	1005	27	0	31	0
6	891	22	2	24	3
7	639	56	13	56	8
8	490	73	46	98	15
9	484	59	19	71	12
10	456	97	−53	100	−9
11	415	132	1	89	5
12	414	107	18	86	5
13	412	112	−20	86	−4

[a] $\epsilon' = \epsilon^{0.5}$.

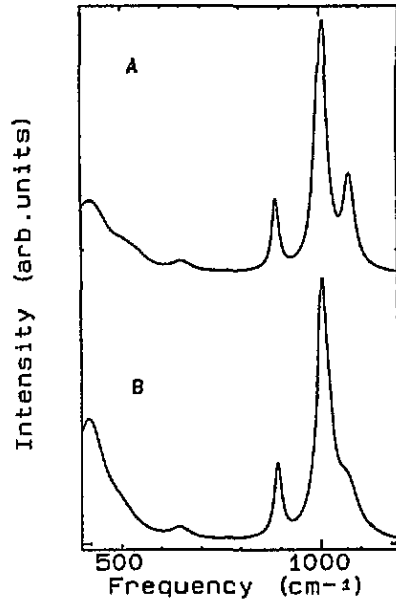Figure 2. HH Raman spectrum of the Si₂O₇ dimer calculated using approximations A and B.

Figure 3. HV Raman spectrum of the Si₂O₇ dimer calculated using approximations A and B.

The calculations were carried out in approximations A and B and the results obtained in the spectral range above 400 cm^{-1} are given in table 1, figure 2 and figure 3. The low-frequency vibrational modes (frequencies below 400 cm^{-1}) cannot be well reproduced through these approximations for the following reasons.

(i) The modes include vibrations between several structural units.

(ii) The model does not account for possible tunnelling between different atomic configurations [21] and for relaxation processes [1].

(iii) The self-energy corrections to these modes are quite large and the lowest-order perturbation theory is not valid in this case. This can be seen if one analyses equations (10) and (11), keeping in mind that, according to equation (15), the quantities $\sum_n \langle V_{ln} V_{nl} \rangle$ are of the same order of magnitude for all modes.

For simplicity all the CS linewidths γ_l were set equal to 20 cm^{-1}, a value close to that measured experimentally in meta-silicate crystals [18]. Numerical calculations performed with other values of γ_l do not change the conclusions given below. In both approximations the random disorder parameter $\epsilon^{0.5}$ was specified in such a way that the width of the peak at 639 cm^{-1}, with $N = 7$ in table 1, is close to 56 cm^{-1}, a value corresponding approximately to that observed in the Raman spectra of vitreous $Na_2O.SiO_2$ [18]. This peak is used as a reference because it is well separated from the other bands in the spectrum.

The following general features caused by the disorder are evident from the numerical results.

(i) The linewidth of the vibrational bands increases on decreasing the mode frequency.

(ii) The spectrum of the initial Si₂O₇ dimer broadens as a result of the disorder. This is in accordance with the calculations performed by Mattis [21] in the Debye approximation for the eigenfrequencies.

(iii) The disorder affects in different ways the line positions and widths of the various vibrational modes.

A comparison of the calculated HH and HV spectra with the experimental HH spectrum of $Na_2O.SiO_2$ (figure 4) and the experimental HV spectrum of $Na_2O.1.22SiO_2$ (figure 5) indicates the following:

(i) As expected (see section 3.2), the HH Raman spectrum calculated in approximation B fits the experiment better than that in approximation A.
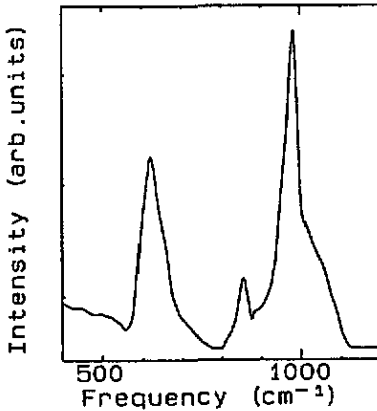

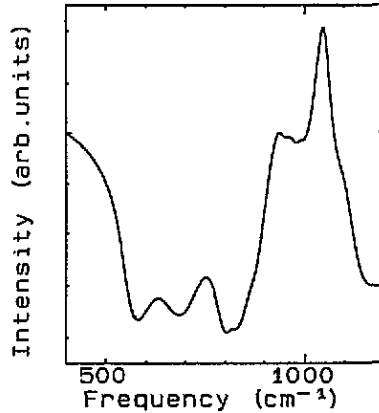**Figure 4.** Experimentally measured HH Raman spectrum of $Na_2O.SiO_2$ [18].

Figure 5. Experimentally measured HV Raman spectrum of $Na_2O.1.22SiO_2$ [19].

(ii) In both approximations the calculated HH Raman spectra are in better agreement with the experiment than the HV spectra are for the following reasons. On the one hand, $\langle V_{ln} V_{nl} \rangle$ should be carefully approximated for each particular glass, and averaged eigenvectors instead of unperturbed values should be used in calculating the polarizability tensor. On the other hand, the HV spectrum is more sensitive to the approximations used than is the HH spectrum. This is seen from equations (3) and (5) as A_p depends only on the components of eigenvectors along the mth bond, while E_p^2 does not and, thus, the latter is more sensitive to the approximations involved.

In the case of strong disorder, i.e. of large differences between the structural units, $\text{Im}(T_l)$ and $\text{Re}(T_l)$ in equation (9) have to be functions of ω and the assumption (iii) in section 3.2 would not be appropriate for extending this method to lower-frequency modes. Such studies are now in progress.

5. Conclusions

A theoretical model for calculating Raman spectra of glasses on the basis of the so-called CS is proposed. The effect of random disorder in the matrix elements of the nearest-neighbour interaction potential on the position and width of the Raman lines is analysed in two different approximations for the self-energy. The model was applied to two sodium silicate glasses modelled through a Si_2O_7 dimer as the CS. It is found that the disorder-induced broadening of the Raman lines depends strongly on this type of atom vibration of the dimer, but, in

general, the spectral line width decreases with increasing frequency in both approximations. In addition, a broadening of the spectrum as a whole is obtained as a result of the disorder, although some intermediate-frequency modes remain approximately unshifted in frequency.

The proposed theoretical method, being much simpler in calculations than others reported in the literature, gives results in good agreement with experimental data. Improved approximations to this method will be employed in future to study various types of glass.

Acknowledgments

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