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The vibrational spectra of $v\text{-SiO}_2$ and $\text{SiO}_2\text{-GeO}_2$ glasses

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Abstract. We have calculated the vibrational densities of states for $v\text{-SiO}_2$ and the binary $v\text{-SiO}_2\text{-GeO}_2$ glasses. The results for $v\text{-SiO}_2$ are in agreement with the neutron scattering spectrum and previous theoretical calculation of Bell *et al.* The spectra of $v\text{-SiO}_2\text{-GeO}_2$ glasses which contain only a small fraction of GeO_2 are found to have the general features of $v\text{-SiO}_2$, except for a new peak characteristic of Ge doping and a split TO-like band which agrees with Raman scattering and can be understood simply by the superposition of the local densities of states of SiO_4 and GeO_4 tetrahedra with different weights.

1. Introduction

Although many experiments have been carried out in an effort to study the vibrational and other properties of $v\text{-SiO}_2\text{-GeO}_2$ glasses, including Raman scattering (Xiao 1987), IR spectra (Borrelli 1969), refractive indices (Kolesova and Sher 1973, Kolesova and Kalinina 1975, Huang *et al* 1978), and linear expansion coefficients and viscosities (Riebling 1968), and UV absorption spectra (Schultz 1977), there is little, if any, work concerning theoretical understanding of these experimental results. In this paper, we present our calculations of the vibrational spectra of the binary $v\text{-SiO}_2\text{-GeO}_2$ glasses as well as of $v\text{-SiO}_2$, and compare them with the experimental data.

EXAFS and x-ray scattering (Gregor and Lytle 1987) indicated a substitution model for $v\text{-SiO}_2\text{-GeO}_2$ glasses in which Ge substitutes randomly for Si in the glassy SiO_2 network with little Ge clustering. The coordination number for Ge was found to be $3.9 \pm 20\%$. Vitreous SiO_2 (more generally AX_2) is widely believed to be a continuous random network (CRN) of nearly perfect SiO_4 tetrahedra. Many researchers (Zachariasen 1932, Bell and Dean 1972, Ching 1982, He 1987) proposed their CRN models whose RDFs were all in agreement with the experimental data. The present paper employs two widely accepted models: the hand-built model of Bell and Dean (BD) (1972) and the computer-generated Ching G54 model which was obtained by inserting O atoms between each pair of Si atoms in the periodic model of amorphous Si of Guttman (1977). Compared with the Ching model, the BD model has a larger bond-length distortion $\Delta R/R$, a smaller bridging angle distortion $\Delta\varphi$ and a larger distortion for the tetrahedral angle $\Delta\theta$. The most contrasting property of the BD model is that it contains 19% of four-member rings while the Ching model has no four-member rings.

For $v\text{-SiO}_2\text{-GeO}_2$ glasses of prescribed compositions, random substitution of Ge for Si can be accomplished with a computer by a series of random numbers which distribute

uniformly in the range of $[0, 1]$. In § 2, we outline the method used in our work and the approximations involved. The calculations are presented and discussed in §§ 3 and 4.

2. Calculation method

For non-periodic systems such as amorphous solids, surfaces and interfaces, the \mathbf{K} -space methods are not suitable because there is no translation symmetry. The recursion method, a real-space Green function method, developed by Haydock *et al* (1972, 1975) is quite suitable for this kind of problem.

The vibrational density of states (VDOS) is defined by the following equation:

$$N(\omega) = \sum_n \delta(\omega - \omega_n) = -\frac{1}{\pi} \text{Im} \left(\sum_n \frac{1}{\omega - \omega_n} \right) \quad (1)$$

where ω_n is the normal frequency which satisfies

$$\mathbf{W}u_n = \omega_n^2 u_n. \quad (2)$$

Here \mathbf{W} is the dynamical matrix and u_n the normal vector (Bell 1972). Thus the VDOS can be expressed by (Thorpe 1976)

$$N(\omega) = -(2\omega/\pi) \text{Im}[\text{Tr}(\omega^2 - \mathbf{W})^{-1}] = -(2\omega/\pi) \text{Im}(\text{Tr } G) \quad (3)$$

where G denotes the resolvent operator $(\omega^2 - \mathbf{W})^{-1}$. The trace of G can be written explicitly, and the VDOS then turns into a sum of local densities of states:

$$N(\omega) = -(2\omega/\pi) \text{Im}(G_{00} + G_{11} + G_{22} + \dots). \quad (4)$$

In our method, we calculate the local densities of states for several atoms near the centre of the chosen cluster and average them to obtain a density of states characteristic of the amorphous solid. The finite size of the cluster is relatively unimportant because the local environment is found to be sufficiently well defined for the central atoms of clusters containing about 200 or more atoms for our purposes (Meek 1976). In our calculation for $v\text{-SiO}_2$ we found that averaging over 30 atoms of a BD CRN gave effectively an identical spectrum to that obtained by averaging over 22 atoms, and averaging over 50 atoms of a Ching CRN yielded almost the same result as averaging over 30 atoms. This is because the amorphous solid is approximately uniform on the scale of several atoms, although the local environment varies from atom to atom. However, this uniformity is destroyed by the substitution of Ge for Si in the binary glasses. A small fraction of Ge in $v\text{-SiO}_2$ can be treated as defects, which makes the uniformity only possible on a larger scale dependent on the GeO_2 concentration.

The local density of states can be obtained through the use of recursion method which defined a new basis of orthonormal vectors $|n\rangle$ out of the displacement vectors $|n\rangle$ according to the recursive relation

$$b_{n+1}|n+1\rangle = (\mathbf{W} - a_n)|n\rangle - b_n^*|n-1\rangle \quad (5)$$

with the initial conditions $|0\rangle = |0\rangle$, $|-1\rangle = 0$, $b_{-1} = 0$, $b_0 = 1$. As \mathbf{W} is a tri-diagonal matrix in the new basis, it is easy to invert $\omega^2 - \mathbf{W}$ analytically to obtain the continued-fraction expansion of $G_{00}(\omega^2)$:

$$G_{00}(\omega^2) = 1/[\omega^2 - a_0 - |b_1|^2/(\omega^2 - a_1 - |b_2|^2/\dots)]$$

where the (a_n, b_n) are evaluated from the orthonormality property of the new basis.

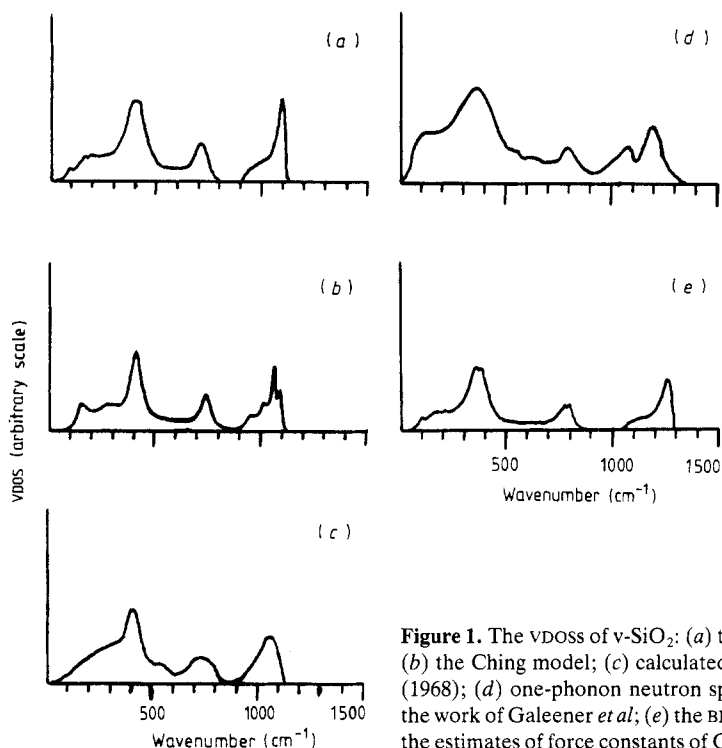


Figure 1. The vDOS of $v\text{-SiO}_2$: (a) the BD model; (b) the Ching model; (c) calculated by Bell *et al* (1968); (d) one-phonon neutron spectrum from the work of Galeener *et al*; (e) the BD model using the estimates of force constants of Galeener *et al*.

3. Results

We present here the spectra of $v\text{-SiO}_2$ using the BD and Ching models, and the vDOS of the binary glasses $v\text{-SiO}_2\text{-GeO}_2$ by the BD model with two different sets of force constants.

The Born potential (Wearie 1981) of the nearest-neighbour interaction was used to obtain the dynamical matrix. For a given set of atomic displacements \mathbf{u}_i of atoms with equilibrium positions \mathbf{r}_i , each bond contributes to the potential a term

$$[(\alpha - \beta)/2][(\mathbf{u}_i - \mathbf{u}_j) \cdot \hat{\mathbf{r}}_{ij}]^2 + (\beta/2)|\mathbf{u}_i - \mathbf{u}_j|^2$$

where $\hat{\mathbf{r}}_{ij}$ is a unit vector parallel to $\mathbf{r}_i - \mathbf{r}_j$. For the central force constants, we adopted Zarzycki and Naudin's estimates as did Bell *et al* (1968), i.e. $\alpha = 4.0 \times 10^5 \text{ dyn cm}^{-1}$ and $\alpha = 3.3 \times 10^5 \text{ dyn cm}^{-1}$ for $v\text{-SiO}_2$ and $v\text{-GeO}_2$, respectively. The non-central force constants were taken to be 3/17 times the central force constants in each case. Such force constants were also applied to the Ching model in order to compare the two different CRNS effectively.

3.1. $v\text{-SiO}_2$

Figure 1(a) illustrates the vDOS of $v\text{-SiO}_2$ calculated from the BD model with fixed-end boundary condition. Figure 1(b) shows the results for the Ching model.

The positions of the peaks are 400, 710 and 1090 cm^{-1} for the BD model and 410, 740 and 1060 cm^{-1} for the Ching model which correspond quite well to those observed at

Table 1. Comparison of the positions of the peaks for different cases in figure 1. The split in the neutron-scattering value for bond stretching is due to Coulomb forces.

	Peak position (cm ⁻¹)				
	Our results			Results of Bell <i>et al.</i> , figure 1(c)	Neutron scattering, figure 1(d)
	BD, figure 1(a)	Ching, figure 1(b)	BD-G, figure 1(e)		
Bond rocking	400	410	370	410	370
Bond bending	710	740	780	730	790
Bond stretching	1090	1060	1260	1040	1070 1090

465, 800 and 1100 cm⁻¹ in the experimental infrared spectrum (Bell *et al* 1968). Our result with the BD model is also in agreement with the result calculated by Bell *et al* (1968) which is shown in figure 1(c). The difference between figure 1(a) and figure 1(c) is that our highest-frequency peak is relatively stronger. Bell *et al* (1968, 1971) and Bell and Hibbins-Butler (1975) have identified the normal modes of these three peaks as bond rocking (400 cm⁻¹), bond bending (710 cm⁻¹) and bond stretching (1090 cm⁻¹).

Good experimental measurements of the vibrational density of states for v -SiO₂ are given by the neutron scattering carried out by Galeener *et al* (1983). The neutron spectrum is shown in figure 1(d). Agreement between experiment and our calculations is encouraging when one realises that the theory omits the Coulomb forces which split the highest-frequency band into an observed TO-LO pair. However, discrepancies exist also. So Galeener *et al* (1983) suggested a repeated large-cluster calculation with their estimates of force constants. Repeated calculation with the BD model and the force constants of Galeener *et al* leads to the result shown in figure 1(e). Agreement between figure 1(d) and figure 1(e) is quite good.

Detailed comparison of the various cases is presented in table 1.

3.2. v -SiO₂-GeO₂ glasses

Being assured of the results for v -SiO₂, we continued to apply the method to the binary glasses using BD CRN model with two sets of force constants; one was adopted from Bell *et al*, and the other from Galeener *et al*. The calculations are shown in figures 2(a) and 2(b), respectively. Here the concentration is taken to be the ratio of the number of Ge atoms to the total number of Si and Ge atoms. The concentrations of the two binary glasses used by Gregor and Lytle (1987) are 5.72% and 15.3% in our notation. In the present work, we ignored the distortions made by the substitution of Ge for Si as the fraction of Ge atoms in our calculations was relatively small.

From figure 2, we can see that, when the concentration is high enough, a new peak emerges at about 570 cm⁻¹ whose strength increases with increasing concentration. We can call it a peak characteristic of Ge doping.

Another difference between v -SiO₂-GeO₂ glasses and v -SiO₂ is that, when the GeO₂ concentration attains a certain value, the highest-frequency (TO-like feature) band is split into several sub-bands which are expected to be split further by the Coulomb forces omitted in the calculations. In order to be assured of the results, we repeated the

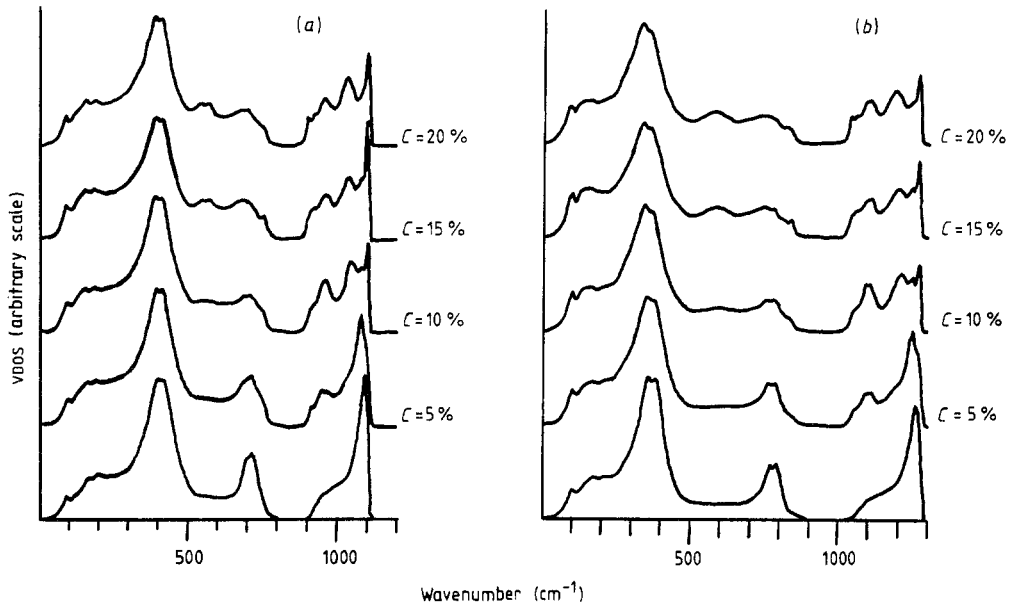


Figure 2. The vDOS of GeO₂-SiO₂ glasses, using the BD model with two sets of force constants which were adopted from (a) Bell *et al* and (b) Galeener *et al*.

calculations several times using different sets of random numbers which represented the random substitution of Ge for Si, and each calculation proved the points mentioned above, except for some slight difference in the positions of the split peaks.

The Raman experiment (Xiao 1987) also showed a peak characteristic of Ge doping and the split of the TO-like band in the Raman spectra of ν -GeO₂-SiO₂ glasses.

4. Discussion

The TO-like features of the spectrum of ν -SiO₂ are constructed from modes involving bond-stretching motions and therefore depend on the arrangement of the bonds around each atom. For the perfect tetrahedral crystal without non-central forces, Weaire and Alben (1972) have shown that the TO-like peak forms a δ -function which is broadened on inclusion of imperfect tetrahedral coordination. The conclusion could be extended to more complex compounds (Weaire 1976, Thorpe and Weaire 1971). In fact, for ν -SiO₂, Galeener *et al* (1983) showed a δ -function at the top of the highest-frequency band from their 'augmented central-force model' in which the central and non-central forces are included simultaneously. The bands and δ -functions from this highly idealised model are spread by disorder. From figures 1(a) and 1(b), we can see that the TO-like peak of the BD model displays a steep high-frequency edge. In contrast, the TO-like peak of the Ching model is broadened more for low frequencies and yet reveals a slightly lower maximum frequency and a gentler high-frequency edge. The TO-like peak of the BD model is more like a δ -function. So we can deduce that the bond angle distortion of the BD model is smaller than that of the Ching model. Although the O-Si-O bond angle distortion $\Delta\theta$ of the BD model is larger than that of the Ching model, the Si-O-Si bond

Table 2. Properties of v-SiO₂ models.

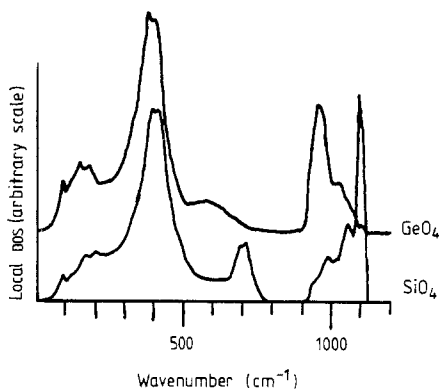
Model	No. of atoms	Type	$\Delta R/R$	$\Delta\theta$ (deg)	$\Delta\varphi$ (deg)
BD	614	Cluster	0.035	6.2	9.6
Ching	162	Periodic	0.007	4.8	13.8

angle distortion $\Delta\varphi$ of the former is smaller than that of the latter; this is shown in table 2 (Ching 1982).

From his calculations, Meek (1976) found that the TO-like feature exhibited a lower maximum frequency for a structure containing a larger proportion of odd-member rings. We can generalise this remark to the present case and conclude that the Ching model contains a larger proportion of odd-member rings. It is consistent with the following argument.

For the BD model, the proportions of n -member rings are 19% ($n = 4$), 28% ($n = 5$) and 53% ($n \geq 6$), and the proportions of rings with $n \geq 7$ are very small (Bell and Dean 1972). Since the Ching model had no four-member rings, it had to contain a larger proportion of five-member rings in order to make the average of the Si–O–Si angle equal to 109.3°, the same value as the corresponding value of the BD model. Ching *et al* (1977) have given the same number of n -member rings per Si atom for v-Si as Guttman which was not changed for the Ching G54 model of v-SiO₂: they are 0.57 ($n = 5$), 0.63 ($n = 6$) and 0.35 ($n = 7$). From the data mentioned above, it is obvious that the Ching model has a larger proportion of odd-member rings.

The split of the TO-like peak of the binary glasses can be understood from figure 3 which shows the local densities of states of SiO₄ and GeO₄ tetrahedra in a v-SiO₂ network. The shift of the highest-frequency peak in figure 3 may account for the split of the TO-like band in the spectra of the binary glasses. When the concentration of GeO₂ increases, the highest-frequency peak of a GeO₄ tetrahedron will have an increasing effect on the spectrum of the binary glass. The difference between the positions of the middle-frequency peaks of the local densities of modes of SiO₄ and GeO₄ can explain the emergence of the new peak characteristic of Ge doping.

**Figure 3.** The local densities of states of SiO₄ and GeO₄ tetrahedra.

5. Conclusion

We have calculated the spectra of $v\text{-SiO}_2$ and $v\text{-SiO}_2\text{-GeO}_2$ glasses. The results are in agreement with experiments. Although the BD and the Ching models differ drastically, they produce similar results. The VDOS of $v\text{-SiO}_2$ using the BD model with the force constants of Galeener *et al* agrees quite well with the experimental neutron scattering spectrum.

Short-range order is very important in determining the VDOS of amorphous solids. In this paper, we consider only nearest-neighbour forces which give the general form of the spectra. Intermediate- and long-range forces will cause some changes in the vibrational densities of states. Apart from the general features of $v\text{-SiO}_2$, the binary glass $v\text{-SiO}_2\text{-GeO}_2$ has a spectrum with a new peak characteristic of Ge doping and a split highest-frequency band which can be understood simply by the local densities of states of SiO_4 and GeO_4 tetrahedra.

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