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The origin of the first sharp diffraction peak in the structure factor of covalent glasses and liquids

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Abstract. It is proposed that the first sharp diffraction peak (FSDP) in the structure factor of network glasses and liquids is a pre-peak in the concentration-concentration structure factor due to the chemical ordering of interstitial voids around cation-centred clusters in the structure. This model can predict quantitatively the positions of the FSDP for a wide range of oxide and chalcogenide glasses and liquids, and can also successfully rationalize the anomalous temperature and pressure behaviour of the FSDP intensity, as well as the effect of the incorporation of network modifiers.

1. Introduction

Medium-range order (MRO) is currently a very controversial topic in the area of structure of amorphous solids [1]. Part of the problem stems from an imprecise understanding of what is meant by MRO, although for the case of covalently bonded materials a definition based on 'structural hierarchy' has proved useful [2]. In this, MRO is regarded as the next highest level of structural organization beyond that of short-range order (SRO), which is characterized by well-defined coordination polyhedra defined by nearest-neighbour bond lengths, coordination numbers and bond angles. Thus, in this picture, MRO is associated with non-random correlations between neighbouring coordination polyhedra, for example characterized by preferred values of dihedral angles.

There is one celebrated feature widely observed in the diffraction pattern of covalent non-crystalline materials that has been regarded as a signature of MRO; this is the so-called 'first sharp diffraction peak' (FSDP). However, the precise structural origin of this feature has, until now, remained as obscure and controversial as MRO in general. The aim of this paper is to propose the first detailed explanation of the origin of this ubiquitous feature, and to give a comprehensive discussion of the effects on the FSDP of temperature, pressure and composition. A preliminary account of this approach has appeared elsewhere [3].

2. Characteristics of the FSDP

The FSDP occurs at a value of scattering vector Q in the range $1\text{--}2\text{ \AA}^{-1}$, and is observed in very many different types of non-metallic, non-crystalline materials including the oxy-chalcogenide glasses [4] AX_2 or B_2X_3 ($A = \text{Si, Ge}$; $B = \text{P, As}$; $X =$

O, S, Se), amorphous pnictogens [4] (P, As) and tetrahedrally coordinated molecular liquids such as P_4 and VCu_4 [5] and zinc halides [6].

The FSDP exhibits anomalous behaviour in a number of ways [7]. It usually has a considerably narrower width than the other peaks in the structure factor, $S(Q)$ —hence its name. There is, in general, no apparent difference in the radial distribution function (RDF) obtained by Fourier transformation of the scattering data whether or not the FSDP is included in the Fourier transform, indicating that the peak results from rather subtle medium-range correlations which are not easily discernible in the RDF [8].

Furthermore, the FSDP exhibits anomalous behaviour as a function of temperature and pressure in comparison with the other peaks in $S(Q)$. The intensity of the FSDP in the glassy state generally increases with increasing temperature [9], unlike the other peaks in $S(Q)$ which decrease in intensity according to the normal Debye–Waller behaviour. The FSDP even persists, essentially unchanged in intensity, into the liquid state [5, 6, 10–12]. As a function of increasing pressure, the FSDP of chalcogenide glasses [13, 14] and of silica [15] rapidly decreases in intensity and shifts to higher values of Q unlike the other peaks in $S(Q)$.

Although the position of the FSDP occurs at rather widely varying values of scattering vector for different materials, in the range $0.8 < Q_1 < 2 \text{ \AA}^{-1}$, it has been found [16, 17] that the FSDPs for a variety of glasses occur at approximately the same positions when the structure factor for each material is plotted against the reduced coordinate Qr_1 , where r_1 is the nearest-neighbour bond length; this common value is $Qr_1 \simeq 2.5$.

The FSDP is also particularly sensitive to compositional variations, notably when a network modifier is incorporated into the glass. In general, the intensity of the FSDP decreases markedly upon the addition of modifier atoms: this behaviour has been observed in alkali silicate glasses [18] upon the addition of sodium (but not lithium, which has the *opposite* effect—see section 8), in Ag–Ge–Se [19] and Ag_2S – GeS_2 glasses [20], and also Ag_2O – B_2O_3 glasses [21] (but it is to be noted that the addition of appreciable amounts of the doping salt AgI to this binary borate glass causes the appearance of an intense FSDP at a significantly smaller value of Q than that characteristic of pure glassy B_2O_3 [21]).

Finally, a correlation has been observed between the position of the FSDP, Q_1 , and the wavevector, Ω , corresponding to the maximum frequency, ω_m , of the ‘boson’ peak observed ubiquitously in the low-frequency Raman scattering of many glasses ($\Omega \propto \omega_m/\bar{v}$, where \bar{v} is the average sound velocity). This correlation has recently been explained quantitatively on the basis of the approach described in this paper [22].

3. Previous explanations for the FSDP

Many suggestions for the structural origin of the FSDP have been put forward in the past (see e.g. [2, 3]). These proposals can essentially be divided into two categories: the structural correlations responsible have been assumed to be associated either with quasi-crystalline structural configurations or with clusters. In the former case, it is assumed that the FSDP is a distinct feature and represents a single Fourier component in reciprocal space, corresponding to a (quasi-) periodic arrangement of atoms in real space which extends over a given coherence length. In the latter case, it is assumed that the FSDP is either simply the first (i.e. lowest- Q), and most intense,

peak of a rapidly decaying inter-cluster structure factor or else is simply an artefact resulting from the addition of a rapidly decreasing intra-molecular form factor and the increasing inter-cluster structure factor at small Q .

Since the crystal structures of many chalcogenides, whose glassy forms exhibit FSDPs in their diffraction patterns, are layer-like, it has been natural in the past to identify the FSDP with a Bragg-like peak in the scattering factor. Thus, it has been assumed that quasi-crystalline layer-like structural arrangements are present in the glass [9, 23, 24, 26]; the inverse of the correlation length over which such layer motifs exist determines the width of the FSDP. In this picture, the FSDP is taken to be an isolated peak in reciprocal space at Q_1 , arising from the diffraction from a quasi-periodic array of atoms in real space with spatial repeat distance, d ; the FSDP position is then given approximately by the relation $Q_1 \sim 2\pi/d$. More recently, the role of correlations between locally 2D structural arrangements in the glass [27] (not necessarily the same configuration as in a crystalline arrangement) or between ordered (e.g. parallel) ribbon-like configurations [28] in causing the FSDP has also been stressed.

However, this quasi-crystalline model is inconsistent with a number of experimental observations. For instance, the FSDP has been observed to exist, with undiminished intensity, in the liquid state of a number of chalcogenide and other materials [5, 6, 10–12]; it is extremely unlikely that quasi-crystalline structural arrangements, for example layers, having correlation lengths of 20–30 Å, should survive in the liquid state. Furthermore, and perhaps more tellingly, a layer-like interpretation cannot be a general explanation for the occurrence of the FSDP since such a feature is observed even in glasses (e.g. SiO_2) where the crystalline polymorphs are not layer-like. Moreover, x-ray scattering experiments [29] on very thin films of a-GeSe₂ have revealed that $S(Q)$ (in particular the FSDP) is independent of film thickness, indicating that preferential layer-like correlations probably do not exist.

The other type of explanation advanced in the past for the FSDP has involved correlations between (ill-defined) clusters comprising the structure of glasses [7, 30]. It is well known [5] that $S(Q)$ of (tetrahedral) molecular liquids, e.g. CCl_4 , also exhibit sharp, well-defined FSDPs. For such systems, the total structure factor, $S(Q)$, can be regarded as comprising the sum of two distinct terms [5, 31], one arising from inter-molecular correlations and given by an inter-molecular interference function, $D_m(Q)$, and the other resulting from intra-molecular correlations and given by a molecular form factor, $f_m(Q)$, namely

$$S(Q) = D_m(Q) + f_m(Q). \quad (1)$$

The inter-molecular correlations (corresponding to Van der Waals separations) are not very well defined, and consequently peaks in $D_m(Q)$ are rapidly damped with increasing Q . However, the first, and most prominent, peak in $D_m(Q)$ can form the first peak in $S(Q)$, i.e. the FSDP, or the first peak may arise from the combination of the rapid decrease of $f_m(Q)$ and the increase of $D_m(Q)$ at small Q . In either case, the FSDP by itself has minimal structural significance in this picture.

Although the role of correlations between clusters in producing the FSDP in chalcogenide, oxide and other glasses has been stressed [4, 7, 30], in general the structural identity of such clusters in the structure of glasses remains obscure. In some cases, however, the structural identification of the clusters involved is quite clear: in as-deposited evaporated amorphous arsenic [32] or arsenic sulphide [16] films, for example, comprising aggregates of quasi-spherical As_4 or As_4S_4 molecules,

respectively, the very intense FSDP observed results from scattering associated with these molecular species, as in molecular liquids.

For well-annealed films, or bulk glasses, it is significant that many experimental and theoretical studies have shown that the FSDP for, say, an AX_2 material is determined primarily by cation-centred (and primarily cation-cation, i.e. A-A) correlations. For instance, differential anomalous x-ray scattering measurements [29, 33] on a-GeSe₂, x-ray scattering measurements [34] on a series of GeSe₂-GeTe₂ glasses, isotopic substitution neutron diffraction studies [12, 35] of liquid GeSe₂, and molecular dynamics and other computer simulations [36-38] of the structure of glassy and liquid GeSe₂ all lead to this conclusion.

Finally, it has also been proposed [2, 30, 39, 40] that the FSDP arises, not from inter-cluster correlations themselves, but instead from the presence of zones of low atomic occupancy. In this paper we shall adopt this picture, and emphasize the role played by the ordering of interstitial voids in the structure of covalent glasses (or liquids) in giving rise to the FSDP. In so doing, we shall present the first quantitative treatment of the FSDP.

4. A new interpretation of the FSDP in covalent non-crystalline materials

Previously, we have suggested [2, 40], together with others [30, 39], that it is the presence of low-density or void regions in the structure of covalently bonded non-crystalline materials which gives rise to the FSDP in the overall structure factor. This void-based interpretation has the merit of complete generality, i.e. it is not restricted to a particular type, or structure, of non-crystalline material. The glassy (and liquid) systems which exhibit pronounced FSDPs are generally oxide and chalcogenide materials; for these, the packing density is rather low (i.e. they are not close packed) and so interstitial voids are an inherent feature of the structure. Furthermore, such materials (and also the pnictogens, P and As) are characterized by having lone-pair, non-bonding orbitals on the chalcogen (or pnictogen atoms), and the repulsive interactions between these lone pairs contribute to the production of the open network character of the structure. The question at issue is: how do such voids give rise to the FSDP?

Our interpretation [3] of the FSDP is that it is a pre-peak in the concentration-concentration partial structure factor, $S_{cc}(Q)$ (in the Bhatia-Thornton formalism [41]), due to the chemical short-range ordering of interstitial voids around cation-centred 'clusters' in the structure of the glass (or liquid). Our picture of the structure, of say an AX_2 -type glass, for this purpose is thus an aggregate of cation-centred quasi-spherical clusters ($AX_{4/2}$ tetrahedra), separated by the average cation-cation distance, $d = r_{AA}$, with each cluster surrounded by (quasi-spherical) voids at an average distance D from the cation. This simplified density fluctuation model obviously makes no reference to the positions of the anions located in each cluster, and therefore is incapable of describing the total structure of the glass. However, for the present purpose, this deficiency is immaterial since we are only concerned with a consideration of the gross atomic packing and its role in producing the FSDP.

Blétry has recently shown [42] that the structure of a tetravalent monatomic amorphous material (e.g. a-Si or Ge) can be represented approximately as a mixture of spherical atoms and holes, having the same diameter and concentration, arranged in a packing which maximizes the local chemical short-range order of holes and atoms.

The overall neutron scattering cross section in the Bhatia–Thornton formalism [41] can be written as

$$d\sigma/d\Omega = N \left[\bar{b}^2 S_{NN}(Q) + 2\bar{b}(b_1 - b_2) S_{NC}(Q) + (b_1 - b_2)^2 S_{cc}(Q) \right] \quad (2)$$

where b_i is the neutron scattering length of component i , $\bar{b} = \sum C_i b_i$ is the compositionally weighted average scattering length, and the subscripts N and C for the partial structure factors refer to number density and concentration, respectively. For the particular situation considered by Blétry [42] for the structure of say a-Ge, this general expression reduces to

$$d\sigma/d\Omega = N_a b_a^2 (S_{NN}(Q) + S_{cc}(Q))/2 \quad (3)$$

where N_a and b_a are the number and scattering length, respectively, of the atoms. The simplified form of (3) results because the scattering length, b_v , of a void is zero and also since $S_{NC}(Q) = 0$ for a substitution mixture of equally sized spheres for which $N_a = N_v = N/2$. Equation (3) may also be compared with the equivalent Ashcroft–Langreth relation for the scattering cross section expressed in terms of *atom–atom* partial correlation functions, which reduces in this situation (when $b_v = 0$) to [42]

$$d\sigma/d\Omega = N_a b_a^2 S_{aa}(Q). \quad (4)$$

Thus, it can be seen [42] that the first peak in the measured structure factor, $S_{aa}(Q)$, of this monatomic system, i.e. the FSDP at Q_1 , corresponds to the pre-peak in $S_{cc}(Q)$, indicative of short-range chemical ordering of atoms and holes; the second peak in $S_{aa}(Q)$, at Q_2 , corresponds to the first peak in $S_{NN}(Q)$. In the case where the atoms and voids have the same diameter, $d = D$, Blétry has shown that [42]

$$Q_1'' \simeq 3\pi/2d \quad (5)$$

corresponding to a ‘chemical pseudo-period’ equal to $4d/3$ in the packing of atoms and holes. When there is a size difference between atoms and holes, given by the ratio $\delta = D/d = 1 + \epsilon$, the chemical order pre-peak (FSDP) becomes shifted to the value [42]

$$Q_1'' \simeq 3\pi(1 - \epsilon/2)/2d. \quad (6)$$

In this way, Blétry [42] has interpreted the first peak in the structure factor of a-Ge, appearing at $Q_1 \simeq 2 \text{ \AA}^{-1}$ (and not previously regarded as an example of an FSDP), as a chemical order pre-peak reflecting the ordered packing of atoms and voids.

In the present discussion of the structure of binary oxide and chalcogenide glasses and liquids, we consider the chemically ordered packing of cation-centred ‘clusters’ and interstitial voids, the clusters, in the case of AX_2 -type materials, being the $AX_{4/2}$ tetrahedra themselves [3]. Thus (5) or (6) can be used to obtain estimates for the position of the FSDP of, for example, AX_2 glasses, if values for $d = r(A-A)$, the average nearest-neighbour cation–cation separation, and $D = r(A-V)$, the average cation–void distance, are known.

In the case of v-SiO₂, these quantities have been found during our recent void analysis [43] of a molecular dynamics structural model [44] of this material. As can be seen from figure 1(a), a remarkably well defined first-neighbour peak in the Si–void partial radial distribution function (RDF) occurs at $D = 3.2 \text{ \AA}$, demonstrating the chemical short-range ordering of the interstitial voids. Furthermore, it is evident from figure 1(a) that there are additional well defined Si–hole correlations at yet larger

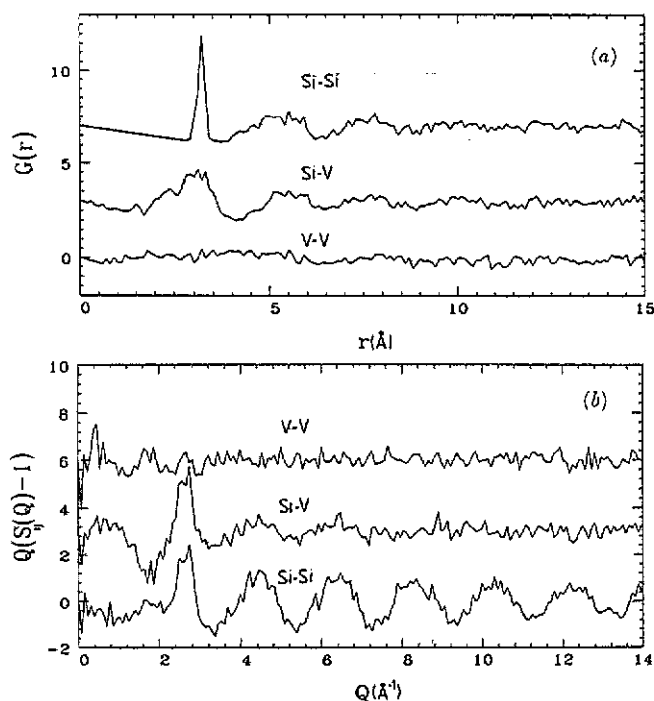


Figure 1. Partial correlation functions involving Si atoms and interstitial void centres for a molecular dynamics model [44] of v-SiO₂; (a) partial reduced RDFs; (b) partial interference functions.

distances, indicating that the interstices in this structure are indeed chemically ordered around SiO_{4/2} tetrahedra, being located on the surfaces of a series of spherical shells centred on the Si atoms.

The value for the average nearest-neighbour Si-hole separation ($D = 3.2$ Å), taken with the value [44, 45] for the Si-Si average separation, $d = 3.12$ Å, yields an estimate for the position of the FSDP, $Q_1'' = 1.51$ \AA^{-1} using (5) (the size difference parameter ϵ is nearly zero in this case). This theoretical estimate is very close to the value observed experimentally [17], $Q_1 = 1.52$ \AA^{-1} .

This interpretation of the FSDP as a chemical order pre-peak in $S_{cc}(Q)$ receives further confirmation if comparison is made with the data for another system in which unambiguous chemical ordering is believed to occur. As an example, we may consider the case of the metallic glass Ni₄₀Ti₆₀. Neutron scattering measurements [46] of the zero-scattering alloy of this glass ($\bar{b} = 0$) provide directly $S_{cc}(Q)$, which has a well defined pre-peak at $Q_1 \approx 1.95$ \AA^{-1} . The Fourier transform of the concentration-concentration partial structure factor, $G_{cc}(r)$, given by

$$G_{cc}(r) \equiv 4\pi r \rho_{cc}(r) = \frac{2}{\pi} \int Q \left[\frac{S_{cc}(Q)}{c_1 c_2} - 1 \right] \sin Qr dQ \quad (7)$$

has a corresponding sharp and negative first *minimum* at $r_1 \approx 2.56$ Å, indicative of strong chemical ordering of Ni-Ti nearest-neighbour pairs [46]. In terms of the partial number density functions, $\rho_{ij}(r)$, $\rho_{cc}(r)$ can be written as [47]

$$\rho_{cc}(r) = c_1 c_2 \{ [\rho_{11}(r)/c_1] + [\rho_{22}(r)/c_2] - 2[\rho_{12}(r)/c_2] \} \quad (8)$$

or the corresponding functions involving $G_{cc}(r)$ and $G_{ij}(r)$.

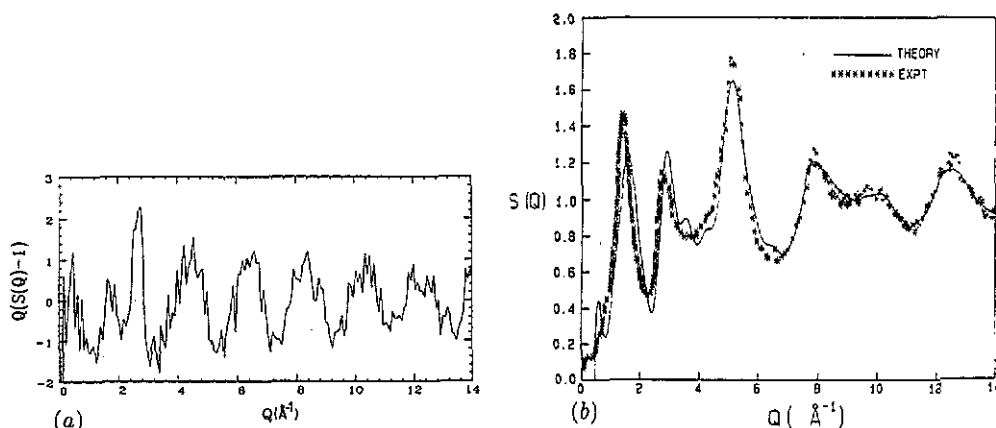


Figure 2. (a) Concentration-concentration correlation function involving Si-atom and interstitial-void positions for a model [44] of v-SiO₂ (calculated from the partial functions shown in figure 1); (b) experimental and calculated total structure factors [44].

Thus, for the case of v-SiO₂, regarding the structure in terms of a packing of Si-centred clusters (species 1) and voids (species 2), the concentration-concentration partial RDF, $G_{cc}(r)$, can be calculated from the corresponding Si-based and hole-based partial RDFs (figure 1(a)); it is found that $G_{cc}(r)$ exhibits a first minimum at $r \approx 3.2$ Å. Thus, an estimate for the FSDP position for v-SiO₂ can be obtained by scaling with respect to the values for glassy Ni₄₀Ti₆₀, namely $Q_1 \approx 1.95 \times 2.56 / 3.2 \approx 1.56$ Å⁻¹; this value is in very good agreement with the experimental value [17] of $Q_1 = 1.52$ Å⁻¹.

Of course, the crucial test of this approach is to see whether there is a pre-peak in $S_{cc}(Q)$ due to the packing of SiO_{4/2} 'clusters' and voids at a value of Q corresponding to the FSDP. The concentration-concentration partial structure factor can be evaluated either by Fourier transformation of $G_{cc}(r)$ (the inverse of (7)), or by using the relation [48, 49]

$$S_{cc}(Q) = c_1 c_2 \{1 + c_1 c_2 [S_{11}(Q) + S_{22}(Q) - 2S_{12}(Q)]\} \quad (9)$$

where, as before, Si-centred clusters are labelled 1 and voids are labelled 2. Figure 2(a) shows $Q[S_{11}(Q) + S_{22}(Q) - 2S_{12}(Q)] \propto Q S_{cc}(Q)$ calculated using (9) in terms of the partial Si- and hole-based interference functions (see figure 1(b)); it can be seen that indeed there is a chemical order pre-peak at $Q \approx 1.6$ Å⁻¹. Although this value for the position of the FSDP is somewhat larger than that observed experimentally [17], nevertheless it is worth noting that the Feuston-Garofalini MD model [44] for v-SiO₂ exhibits an FSDP in $S(Q)$ at $Q_1 = 1.6$ Å⁻¹ (figure 2(b)); the position of the FSDP shown in figure 2(a) is in very good agreement with this model value, as should be the case. Thus, our picture of the origin of the FSDP in loosely packed covalent glassy or liquid structures in terms of a chemical ordering of voids of 'clusters' appears to be borne out. However, it should be stressed that this approach to understanding the FSDP considers only gross packing effects and ignores detailed atom-atom correlations (particularly involving the anions); comparison of figures 2(a) and 2(b) shows that there is a difference in the behaviour at higher Q between theoretical and experimental scattering curves due to the neglect of oxygen-related correlations.

This approach can be extended to other AX_2 -type glasses. Approximate evaluations made [3] using (6) yield good agreement between theoretical estimates and experimental values of Q_1 , at least to within a margin of 10%. Exact agreement is not expected for a number of reasons: equations (5) and (6) are only approximate and moreover, at least for the case of $v\text{-SiO}_2$ where the appropriate void analysis has been performed [43], the conditions underlying the derivation of (5) and (6) are not satisfied exactly, namely the voids in the structure are more numerous than the clusters and have a relatively wide distribution of sizes.

It is noteworthy that, as the anion bond angle, $\theta(\text{A-X-A})$, decreases in the series $\text{O} \rightarrow \text{S} \rightarrow \text{Se} \rightarrow \text{Te}$, the anion packing fraction progressively increases [50] or, in other words, the cation-centred spheres increasingly overlap. Such sphere overlap can also be regarded in terms of non-additivity of sphere radii, namely $d(\text{A-A}) < 2r(\text{A-X})$, with the parameter $\Delta = (2r/d) - 1$ characterizing the degree of such non-additivity. Blétry has shown [42] that, in such a case, the formula for the FSDP position (equation (6)) becomes modified by the addition of an additional multiplicative factor involving Δ :

$$Q_1'' \approx 3\pi(1 - \epsilon/2)(1 + 1.3\Delta)/4r_1 \quad (10)$$

where the actual sphere diameter $2r_1$ has been used instead of the inter-centre separation d . Values of the FSDP position, Q_1'' , evaluated using (10) (see table 1), are in good agreement with experimental values and are very similar to those obtained previously [3] using (6).

Table 1. Positions of the first sharp diffraction peak for AX_2 glasses. Q_1 are experimental values and Q_1'' are values obtained from (10).

Glass (AX_2)	Q_1 (\AA^{-1})	$r_1(\text{A-X})$ (\AA)	$d(\text{A-A})$ (\AA)	Q_1'' (\AA^{-1})	$Q_1''r_1$
SiO_2	1.52 ^a	1.61 ^b	3.12 ^c	1.52	2.45
GeO_2	1.55 ^d	1.74 ^d	3.18 ^d	1.52	2.64
BeF_2	1.63 ^e	1.54 ^e	3.01 ^f	1.58	2.43
ZnCl_2	1.09 ^f	2.29 ^f	3.7 ^f	1.23	2.82
GeS_2	1.04 ^g	2.23 ^h	3.78 ⁱ	1.22	2.73
GeSe_2	1.01 ^j	2.38 ^j	3.57 ^j	1.19	2.83

^a [60]. ^b [7]. ^c [45]. ^d [65]. ^e [66]. ^f [50]. ^g [67]. ^h [68]. ⁱ [69]. ^j [70].

5. Discussion

The approach outlined in this paper, and described in a preliminary fashion elsewhere [3], is the first to be able to account, in a *quantitative* fashion, for the positions of the FSDP in the structure factor of covalent AX_2 -type glass-forming materials.

In principle, this approach can be extended to other loosely packed covalent solids, for example chalcogenide glasses (e.g. V-VI materials), as well as those elemental amorphous solids (e.g. P, As) which also exhibit prominent FSDPs in their structure factors. It should also be applicable to polymers. For example, for the case of $a\text{-As}_2\text{S}_3$ for which experimentally [7] $Q_1 \approx 1.26 \text{ \AA}^{-1}$, use of (5) (with ϵ assumed to be zero) yields the theoretical estimate $Q_1'' = 1.38 \text{ \AA}^{-1}$, using a value for $d(\text{As-As})$ taken from a modelling study [40]. The agreement between these values is within $\approx 10\%$,

as for the other values of Q_1'' for AX_2 -type materials obtained earlier [3]. However, for this, and for related materials, the void distribution is not known (but is likely to be qualitatively different from that characteristic of AX_2 -type glasses because of the local two-dimensionality associated with the pnictogen atoms in V–VI compounds). Hence, more accurate estimates, based on (6) or (10) (which may themselves be inappropriate), cannot yet be made. It is necessary to analyse the distribution of interstitial voids in realistic models of these materials and thence to calculate $S_{cc}(Q)$ in terms of partial correlation functions involving the voids.

The origin of the FSDP in the case of the three-coordinated amorphous elemental pnictogens (P, As) is less easy to understand on the basis of (5), (6) or (10) if, as for elemental Si or Ge, the atom itself is taken as the cluster motif. However, if instead, for the case of a-As the trigonal pyramidal $AsAs_{3/3}$ unit is chosen (by analogy with the case of As chalcogenides), then the inter-cluster separation appearing in (5) and (6) is the second-neighbour As–As distance, or $d = 3.76 \text{ \AA}$ [2]. Use of the simple formula (5) with this value (since the size-difference parameter ϵ is not known) yields the estimate $Q_1'' \approx 1.25 \text{ \AA}^{-1}$ in reasonable agreement with the experimental value [8], $Q_1 \approx 1 \text{ \AA}^{-1}$. Of course, for such pyramidal units, with asymmetric bonding configurations, a local layer-like topology will result. As a consequence, interstitial voids will not be distributed with spherical symmetry with respect to the $AsAs_{3/3}$ units, and so (5) will no longer strictly be valid.

In some cases, e.g. for the case of glassy As_2O_3 or P_2O_5 [17] or potassium silicates [51], more than one pre-peak is observed in the low- Q region of the structure factor. These features are not fully understood, but may be due to not one but several shells of chemically ordered interstitial voids around cation-centred clusters (or the influence of the network-modifying cations in the latter case). A proper insight into the structural origin of these multiple pre-peaks awaits a detailed analysis of the void distribution of realistic structural models of these materials.

The observed scaling [16] of the FSDP position with primary bond length, $r_1(A-X)$, for different AX_2 (and other) glasses is naturally understandable from examination of (10). This predicts that the dimensionless product $Q_1''r_1$ should be given by

$$Q_1''r_1 \approx 3\pi(1 - \epsilon/2)(1 + 1.3\Delta)/4 \quad (11)$$

and calculated values for this product are shown in table 1 for a number of AX_2 -type glasses. The average value is $Q_1''r_1 \approx 2.65$, which compares very well with the experimental value [16] of 2.5. Variations of the estimates given in the table from this value could be due to uncertainties in the value of the parameter ϵ .

In addition, the present model for the origin of the FSDP can be used to rationalize the behaviour of this peak in chalcogenide glasses with optical illumination. It has been observed that the FSDP intensity decreases on illumination, a manifestation of the photostructural effect (see [52] for a recent review of this topic). The photostructural effect has been ascribed to a photo-induced change involving an increase in the fluctuations of the bond angles subtended at the chalcogen atoms (see [52] and references cited therein) caused, at least in the case of the arsenic chalcogenides glasses, by a process of photo-induced bond twisting. If this type of chalcogen motion is indeed responsible for the photostructural effect in chalcogenide glasses, then it is very likely that the photo-induced disordering of the chalcogen positions will cause a concomitant decrease in the degree of chemical ordering of interstitial voids around cation-centred clusters, since the size and position of the voids are mostly determined by the 'boundaries' of the chalcogen atoms. As a consequence, it is expected that

the magnitude of $S_{cc}(Q)$, and hence of the FSDP, will also diminish. This proposal for the structural origin of the photo-induced change in FSDP intensity awaits a void analysis of structural models which have been systematically altered to simulate the photostructural effect.

Finally, it should be noted that recent modelling studies [53] of the glassy AgI-AgPO₃ system, using the reverse Monte Carlo approach [54], have also identified the origin of the FSDP as arising from voids in the network structure, in this case caused by the introduction of the doping salt, AgI.

6. Temperature dependence of the FSDP

The anomalous temperature dependence of the FSDP in chalcogenide materials [9] can also be understood in the framework of the present model. Vashishta *et al* [36–38] have shown, using molecular dynamics and other computer simulations of the structure of glassy and liquid GeSe₂, that *only the FSDP in the structure factor exhibits an anomalous increase in peak intensity with decreasing density at constant temperature*; at fixed density, *all peaks in $S(Q)$ decrease in intensity with increasing temperature in the normal manner expected of the Debye–Waller factor*. Thus, the isobaric temperature dependence of the scattering intensity, I , can be expressed as

$$(\partial I / \partial T)_p = (\partial I / \partial T)_\rho + (\partial I / \partial \rho)_T (\partial \rho / \partial T)_p. \quad (12)$$

For all peaks in $S(Q)$ other than the FSDP, $(\partial I / \partial T)_p$ is a *negative* function since $(\partial I / \partial T)_\rho$ is negative due to the Debye–Waller factor and, although $(\partial I / \partial \rho)_T$ is nearly zero or positive [38], the thermal expansivity, $(\partial \rho / \partial T)_p$ is *almost always negative*. For the FSDP, $(\partial I / \partial T)_\rho$ is still of course negative, but now $(\partial I / \partial \rho)_T$ is also *negative* [38], the same sign as $(\partial \rho / \partial T)_p$, and hence the sign of the overall isobaric temperature dependence of the FSDP intensity depends on the balance between the two terms on the right-hand side of (12), but $(\partial I / \partial T)_p$ is generally positive.

The temperature dependence of the FSDP intensity for *vitreous SiO₂* is, by contrast, apparently rather anomalous in its behaviour. Recent neutron scattering measurements [53, 55] have shown that the *FSDP intensity anomalously decreases with increasing temperature*, while x-ray scattering measurements show *no temperature dependence whatsoever of the FSDP intensity* [55]. This surprising behaviour can be understood in terms of three factors: the very low thermal expansivity of vitreous silica [56] (which is typically an order of magnitude, or more, lower than that of other glasses); the difference in relative scattering factors of Si and O atoms for x-rays and neutrons; and the large average bond angle subtended at the O atoms compared with the corresponding angle in other AX₂-type glasses.

Consider first the case of the scattering of neutrons by vitreous SiO₂. Examination of (9) shows that one contribution to the concentration–concentration correlation function $S_{cc}(Q)$ is the *inter-cluster* term, $S_{11}(Q)$. While this quantity will obviously contain the cation–cation (A–A) correlation term (see section 8), if the angle subtended at the anion X is large and near 180° (as it is for v-SiO₂ where the average angle is $\bar{\theta}_X \approx 145^\circ$) then inter-tetrahedral O–O (fourth-neighbour) correlations will be relatively well defined (i.e. the static disorder for this separation will be relatively small irrespective of dihedral angle variations). In this case, therefore, O–O correlations will also be expected to contribute, in principle, to the inter-cluster term $S_{11}(Q)$, and hence to $S_{cc}(Q)$. However, since the neutron scattering length for

oxygen is greater than that for silicon, $b_O > b_{Si}$, these O–O correlations will produce the dominant contribution to the pre-peak in $S_{cc}(Q)$, i.e. to the FSDP. Although the *static* disorder associated with such fourth-neighbour O–O correlations is expected to be relatively small, the *dynamic* disorder (associated with thermal vibrations) will be considerably larger and strongly temperature dependent since such thermal fluctuations arise essentially from the combined fluctuations in the *three* intervening bond angles (two angles subtended at Si atoms and one at the bridging O atom). Hence, the Debye–Waller factor $(\partial I/\partial T)_\rho$, the first term in (12), will be large and negative, and much larger than the second factor in (12) which is anomalously small anyway for $v\text{-SiO}_2$ because the thermal expansivity term, $(\partial \rho/\partial T)_p$, is so small. Thus, the experimentally observed [53, 55] negative sign for $(\partial I/\partial T)_\rho$ for the FSDP of $v\text{-SiO}_2$ for the case of neutron scattering can be understood.

For the case of x-ray scattering, the situation is different. The scattering factor for silicon is greater than that for oxygen, $f_{Si} > f_O$, and so Si–Si inter-tetrahedral correlations will now make the dominant contribution to $S_{cc}(Q)$ and hence to the FSDP. We expect the Debye–Waller term, $(\partial I/\partial T)_\rho$ to be appreciably less negative than for the case of neutron scattering because the dynamic disorder term will be smaller, being determined essentially only by the fluctuations of a *single* bond angle (that subtended at the intervening O atom). Regarding the second factor in (12), although the thermal expansivity is very small in $v\text{-SiO}_2$, nevertheless, it is still non-zero at temperatures above room temperature [56] (i.e. $(\partial \rho/\partial T)_p$ is small and negative); thus, since the other term $(\partial I/\partial \rho)_T$ is negative for the FSDP, the second factor in (12) will therefore be positive (but small). We suppose, therefore, that for temperatures above ambient, the two additive factors in (12) have approximately the same magnitude (but opposite signs) for $v\text{-SiO}_2$, thereby accounting for the fact that the FSDP has been observed to be temperature independent when measured by x-ray scattering [55].

If this interpretation is correct, we therefore predict that this accidental cancellation of terms, leading to a null temperature dependence of the x-ray FSDP for $v\text{-SiO}_2$ will no longer occur at *low* temperatures. At temperatures below ≈ 200 K, the thermal expansivity coefficient for $v\text{-SiO}_2$ changes sign [56] (i.e. $(\partial \rho/\partial T)_p$ becomes positive), and we expect, therefore, that correspondingly the FSDP intensity measured by x-rays in this régime should *decrease* with increasing temperature, as observed in neutron scattering at higher temperatures [53, 55].

Our present picture for the origin of the FSDP in terms of a chemical ordering of voids around cation-centred clusters allows a natural interpretation of the anomalous (negative) sign of the term $(\partial I/\partial \rho)_T$ in (12). As the density of the material is increased, obviously the void volume is progressively reduced. Thus, the factor $(b_1 - b_2)^2$ ($1 = \text{atom or cluster}$; $2 = \text{void}$) multiplying $S_{cc}(Q)$ in the expression for the scattering cross section (equation (2)) systematically decreases as the void fraction decreases, i.e. with increasing density. However, a general expression for the term $(\partial I/\partial \rho)_T$, based on our void-related model, cannot yet be given; a computer-based study of the effect of pressure, and hence of the overall density, on the void distribution in a model, and thence on the calculated FSDP, is required and awaits future work. Nevertheless, we believe that our void-related picture can provide a general rationalization for the temperature-dependent behaviour of the FSDP, independent of composition, such as that observed [9] in $\text{As}_x\text{S}_{1-x}$ glasses, where the temperature dependence of $I(Q_1)$ is the same for all values of x when scaled to T_g .

Finally, in this section, we consider the behaviour of the *position* of the FSDP, Q_1 ,

with temperature. For the case of B_2O_3 studied using neutron diffraction [57], it has been found that Q_1 decreases with increasing temperature, apparently linearly, in the glassy state. The value of the thermal shift coefficient, defined as [38]

$$\alpha = -(1/Q_1)(\partial Q_1/\partial T)_p \quad (13)$$

in this case is $\alpha \approx 2 \times 10^{-5} \text{ K}^{-1}$. In the liquid state, beyond T_g , the linear rate of decrease of Q_1 with T is much greater; $(\partial Q_1/\partial T)_p$ is about eight times that for the glass. Similar temperature-dependent behaviour has been found [9] for glassy As_2Se_3 ; in this case $\alpha \approx 1.2 \times 10^{-4} \text{ K}^{-1}$. By contrast, Q_1 for $v\text{-SiO}_2$, as measured also by neutron diffraction [55], shows only a very small thermal shift, with a coefficient $\alpha \approx 10^{-5} \text{ K}^{-1}$.

As for the temperature dependence of the FSDP intensity discussed above, that for the FSDP position can also be written as the sum of two terms [38]:

$$\alpha = -(1/Q_1)(\partial Q_1/\partial T)_p - (1/Q_1)(\partial Q_1/\partial \rho)_T(\partial \rho/\partial T)_p. \quad (14)$$

The computer simulations of Iyetomi *et al* [38] have provided separate estimates for the two terms in (14), $(\partial Q_1/\partial T)_p$ and $(\partial Q_1/\partial \rho)_T$, for the cases of glassy and liquid $GeSe_2$. (Such quantities cannot be obtained experimentally; all that is measured is the net change, cf (13).) These theoretical estimates (for $GeSe_2$) give a value for the temperature shift factor, α , which is comparable to that observed experimentally in glassy chalcogenides (e.g. As_2Se_3 [9]), with the first term in (14) being dominant, even though the absolute magnitudes of Q_1 resulting from the simulations are larger than those observed experimentally.

Consideration of (14) gives an immediate explanation for why the temperature shift of Q_1 should be much larger in the liquid state than in the glassy state, e.g. as observed in B_2O_3 [57]. The thermal expansivity term, $(\partial \rho/\partial T)_p$, is obviously considerably larger in the liquid state [57], resulting in the two additive factors in (14) having comparable magnitudes, and since the computer simulation results of Iyetomi *et al* show that the first term, $(\partial Q_1/\partial T)_p$, is also larger in the liquid state, the increase in α by almost an order of magnitude for B_2O_3 can be accounted for quantitatively.

The origin of the much smaller value of the temperature shift factor, α , for $v\text{-SiO}_2$ observed experimentally [55] can be traced to the very low thermal expansivity of this material at temperatures above ambient. In this case, only the first term in (14) will contribute significantly to α ; moreover, this factor may also be anomalously small in $v\text{-SiO}_2$ owing to the peculiarities of the structural changes with temperature of this material.

Our model for the origin of the FSDP in terms of the chemical ordering of interstitial voids allows a structural interpretation for the various terms in (14). In particular, the factor, $(\partial Q_1/\partial \rho)_T$ can be understood if the increase in density is assumed to be associated with a decrease in the inter-tetrahedral distance $d = r(A-A)$ for the case of AX_2 -type materials (or the equivalent separation for other materials). In this case, it can be seen from (5) and (6) that Q_1 should increase, i.e. the factor $(\partial Q_1/\partial \rho)_T$ should be positive, as found in computer simulations [38]. The first term $(\partial Q_1/\partial T)_p$ in (14) is less easy to understand in such simple terms since, in the absence of a detailed analysis of the structural changes occurring in simulated models (e.g. [38]), it is not possible to predict how, in general, the thermal expansion of the network structure with increasing temperature (as a result of anharmonicity in the interatomic potentials) is compensated by structural changes (presumably involving

relative rotations of connected polyhedral units) in order to maintain constant overall density.

7. Pressure dependence of the FSDP

As a function of increasing pressure, the FSDP of chalcogenide glasses [13, 14] and of silica [15] rapidly decreases in intensity and shifts in position to higher values of Q , unlike the other peaks in $S(Q)$.

The rapid decrease of the FSDP intensity with increasing pressure is immediately understandable from a consideration of the factor $(\partial I/\partial \rho)_T$, which is negative for the FSDP as discussed above, since the pressure dependence of the FSDP intensity, $(\partial I/\partial p)_T$ is related to it via the equation

$$(\partial I/\partial p)_T = (\rho/B)(\partial I/\partial \rho)_T \quad (15)$$

where B is the bulk modulus. A computer modelling study [38] (of a-GeSe₂) has shown that $(\partial I/\partial \rho)_T \approx -3 \text{ (g cm}^{-3}\text{)}^{-1}$ for the case of the FSDP; equation (15) then predicts that $(\partial I/\partial p)_T \approx -0.1 \text{ kbar}^{-1}$, assuming a representative value [58] of 150 kbar for the bulk modulus of chalcogenide glasses. For the case of a-GeSe₂, the high-pressure x-ray data of Tanaka [14] indicate that $(\partial I/\partial p)_T \approx -0.17 \text{ kbar}^{-1}$, in reasonable agreement with the predicted value. As mentioned in section 6, an *a priori* calculation of the factor $(\partial I/\partial \rho)_T$, and hence of the pressure dependence of the FSDP intensity, awaits a future investigation of the effect of density on the void distribution in realistic structural models of chalcogenide and oxide glasses.

The simultaneous shift in position of the FSDP to higher values of Q with increasing pressure has been observed in computer simulations [38], and is readily understandable [3] in terms of the quantity $(\partial Q_1/\partial \rho)_T$ on the basis of the present model for the origin of the FSDP in terms of (5) (or (6)). In the case of (permanently) pressure-densified vitreous silica, magic-angle spinning ²⁹Si NMR studies [59] have revealed that the effect of pressure is to cause a decrease in the average value of the bond angle, θ_O , subtended at the oxygen atoms, by approximately 5°, implying a reduction in the Si-Si separation to $d \approx 2.9 \text{ Å}$. Structural modelling using molecular dynamics supports this conclusion [15], although this change is not readily discernible in neutron scattering data [15, 60]. Use of this value of d , with (5), yields an estimate for $Q_1'' \approx 1.63 \text{ Å}^{-1}$, in good agreement with the experimental value [15, 60] of $Q_1 \approx 1.69 \text{ Å}^{-1}$ for v-SiO₂ in a pressure-densified state.

8. Compositional dependence of the FSDP

Two aspects of the behaviour of the FSDP with composition can be considered: the first concerns the case when the *network-forming* cations (A) or anions (X) are changed (at constant overall chemical composition) in say, AX₂-type glasses; the second involves the incorporation of *network-modifying* ions.

Susman *et al* [11] have discussed the behaviour of the FSDP intensity for four AX₂-type glasses (A = Si, Ge; X = S, Se). They assumed that the FSDP comprises contributions from both $S_{AA}(Q)$ and $S_{AX}(Q)$ partial structure factors and that these are combined together by atomic concentration and neutron scattering length factors according to the Ashcroft-Langreth formalism [61], namely

$$I \propto (c_A b_A^2 S_{AA} + 2c_A^{1/2} c_B^{1/2} b_A b_X S_{AX}) / (c_A b_A + c_X b_X)^2. \quad (16)$$

By making the assumption that the values of the partial structure factors $S_{\text{Ge-Ge}}(Q_1)$ and $S_{\text{Ge-Se}}(Q_1)$ contributing to the FSDP at Q_1 , taken from molecular dynamics simulations [36], are transferable to all other AX_2 -type glasses, these authors [11] obtained estimates for the FSDP intensity $I(Q_1)$ which correctly accounted for the trends observed experimentally (namely that $I(Q_1)$ appears to be systematically larger for the sulphide of a particular cation, A, than for the selenide of the same cation [11]). However, *absolute* quantitative agreement was poor, discrepancies of a factor of two being found in some cases.

This method suffers from the crucial assumption of transferability of $S_{ij}(Q_1)$ values for glasses of a particular type. Moreover, the values for $S_{\text{Ge-Ge}}(Q_1)$ and $S_{\text{Ge-Se}}(Q_1)$ taken by Susman *et al* [11] from simulation results [36] are appreciably different from those found recently using isotopic substitution neutron diffraction [35]. Furthermore, this treatment assumes that the FSDP peak *height* is the important factor, implying that the width of the FSDP is invariant in all cases. However, the FWHM of the FSDP for these four AX_2 -type glasses appears to vary by almost a factor of two, and so considerations of the height alone of the FSDP are insufficient.

In our model for the origin of the FSDP, based on a picture of a packing of clusters and voids, the total structure factor in the Bhatia-Thornton formalism [41] is given by [49] (cf (2))

$$S^{\text{BT}}(Q) = (1/\bar{b}^2) \left[\bar{b}^2 S_{\text{NN}}(Q) + 2\bar{b} \Delta b S_{\text{NC}}(Q) + (\Delta b)^2 S_{\text{CC}}(Q) \right] \quad (17)$$

and for the effectively single-component (cluster) packing under consideration (where $b_2 \equiv b_v = 0$), the weighting factor, W , for $S_{\text{cc}}(Q)$, and hence of its pre-peak (namely the FSDP) is given by $W = b_{\text{A}}^2/\bar{b}^2$ (cf (16)) if it is assumed that cation-cation (A-A) separations mainly serve to define the inter-tetrahedral correlations contributing to $S_{\text{cc}}(Q)$ (see (8) and (9)). (Note, however, that an anion-anion contribution may be significant in the case of $\nu\text{-SiO}_2$, where the bond angle subtended at the anion is larger than in the chalcogenides—see section 6.)

If it is assumed that the void distribution is the *same* for Si and Ge chalcogenides, differences in the integrated intensity of the FSDP are then due to the weighting factor, W . Estimates for the relative intensities may be made using appropriate values of neutron scattering length giving the ratios $I(\text{SiS}_2)/I(\text{SiSe}_2) = 4.3$ and $I(\text{GeS}_2)/I(\text{GeSe}_2) = 2.3$, compared with the experimental values quoted by Susman *et al* [11] (in terms of peak heights) namely 2.6 and 1.9, respectively. If, however, experimental integrated intensities (areas) of the FSDP are considered, the ratio, e.g. for the Ge chalcogenides, becomes $I(\text{GeS}_2)/I(\text{GeSe}_2) = 3.4$. The theoretical estimates, based on weighting factors alone, are in reasonable agreement with the experimental values for the peak intensities, and certainly account for the trends observed between sulphides and selenides.

However, Blétry [62] has shown, through a systematic study of a number of structural models, that the intensity of the pre-peak in $S_{\text{cc}}(Q)$ itself also depends on the concentration of voids and on the degree of chemical short-range ordering that is present, characterized by the Cargill-Spaepen [63] chemical order parameter ζ (< 0) which is defined as

$$\zeta = (n_{12}^{\text{d}} - n_{12})/n_{12}^{\text{d}} \quad (18)$$

where n_{12}^{d} is the reference heteroatomic coordination number of the chemically disordered alloy (with the same packing fraction). Of course, it is entirely reasonable

that both the void concentration and ζ should vary from material to material, and consequently $I(Q_1)$ would be expected to vary concomitantly.

For the case of say AX_2 -type materials, systematic changes in these quantities would be expected for different materials. For instance, as the anion X changes from $O \rightarrow S \rightarrow Se$, the average bond angle subtended at the anion, θ_X , decreases; this systematic change has an effect on the packing arrangement of the $AX_{4/2}$ tetrahedra and hence on the void distribution in that the anion packing density increases [50] and hence the spheres associated with the $AX_{4/2}$ tetrahedra overlap. Furthermore, as the cation A changes from $Si \rightarrow Ge$ (for the chalcogenides), the MRO in the glass changes dramatically from being locally one-dimensional (caused by almost complete edge-sharing of tetrahedra) to being locally two-dimensional (with part corner and part edge-sharing connections), respectively [1, 2], becoming three-dimensional for the corresponding oxides. Thus, on this basis alone, the void distribution is expected to be significantly different in different materials with concomitant effects on $S_{cc}(Q)$. Unfortunately, in the absence of knowledge about the void distribution in (models of) materials such as SiS_2 or GeS_2 , it is not possible to speculate further on the compositional behaviour of the FSDP in this regard. Consideration of this point awaits future work.

The other kind of compositional variation of the FSDP to be considered here concerns the incorporation into the glass structure of network-modifying ions, such as alkalis or silver. In general, the intensity of the FSDP decreases markedly upon the addition of modifier atoms [18–21, 51] (see figure 3) and, in certain cases (e.g. the silver germanium chalcogenides [19, 20]), the FSDP is suppressed almost completely. It is difficult to account for this dramatic behaviour in terms of the explanations of the FSDP proposed previously in the literature and summarized in section 3. However, our interpretation of the origin of the FSDP in terms of the chemical ordering of interstices around clusters lends itself to a natural explanation.

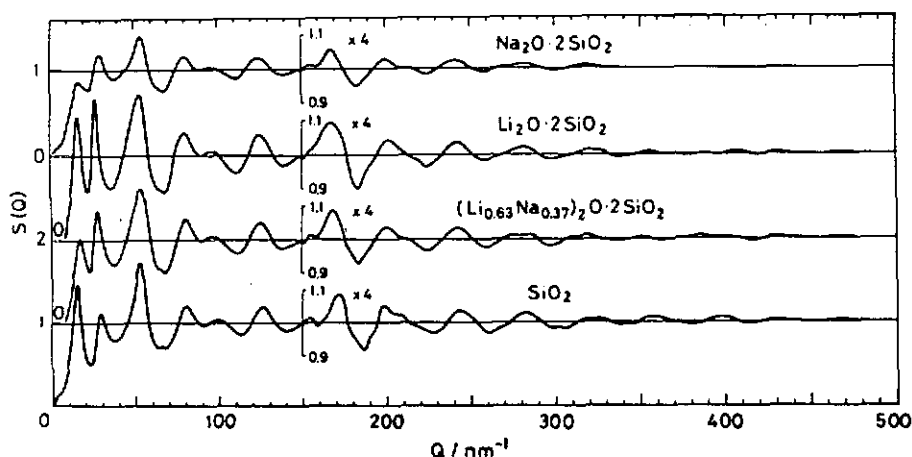


Figure 3. Measured total structure factors for glassy silica and binary alkali silicates [18], including a mixed alkali composition for which the net neutron scattering length for the alkali cations is zero.

Within the framework of the rather crude model we envisage for the global (packing) structure of covalent glasses, it is reasonable to assume that the network-modifier ions occupy what were previously the (largest) interstices in the structure.

Thus, in this simple interstice-stuffing picture, a decrease in the intensity of the FSDP is predicted if the modifier ion has a positive neutron scattering length b_m , since now the contrast factor $(b_1 - b_2)^2$ multiplying $S_{cc}(Q)$ in the relation for the total structure factor (equation (17)) is dramatically reduced (when $b_2 \equiv b_m$) compared to the unstuffed state, where $b_2 \equiv b_v = 0$. The progressive decrease in $I(Q_1)$ with increasing modifier content (e.g. in Ag-Ge-S glasses [20]) is therefore understandable in terms of the progressive filling of the voids around the 'clusters' and the consequent decrease in the magnitude of density fluctuations. Of course, if the incorporation of ions results in a concomitant decrease in the degree of chemical ordering of ions and/or voids around clusters, due perhaps to a modifier-induced change in the structure of the framework material, then the intensity of the pre-peak in $S_{cc}(Q)$ will also decrease for this reason.

A similar alloying-induced reduction in the intensity of the first peak in the structure factor of a-Ge has been observed in the case of amorphous Ge-Mo films [64]. This behaviour can be understood in exactly the same way if this first peak is identified as an FSDP due to the chemical ordering of interstitial voids around the Ge atoms [42]; it can be assumed to a first approximation that the Mo atoms simply fill these voids, thereby reducing the magnitude of the density fluctuations.

Conversely, if the network-modifying atom has a negative neutron scattering length ($b_m < 0$), the above considerations predict that the FSDP should increase with incorporation of the modifier because the contrast of density fluctuations is thereby enhanced. This surprising behaviour has, in fact, been observed for the case of lithium disilicate glass [18, 51] (see figure 3); the scattering length of Li is $b_{Li} = -2.1$ fm. Examination of the scattering data shown in figure 3 shows that the intensity of the FSDP of $Li_2O \cdot 2SiO_2$ is, in fact, comparable with that of pure SiO_2 , but a more valid comparison is with the structure factor of the mixed alkali glass, $(Li_{0.63}Na_{0.37})_2O \cdot 2SiO_2$ for which the compositionally weighted average scattering length of the modifier is zero, $\bar{b}_m = 0$. The FSDP intensity of the pure Na glass is appreciably less, and that of the pure Li glass is appreciably higher, than that of this 'zero-scattering' material, in accord with the predictions of our model.

Of course, the addition of network-modifier atoms to silica causes the production of non-bridging oxygen (NBO) defects which, for the disilicate composition, are almost entirely contained in Q_3 units [2] ($SiO_{4/2}$ tetrahedra with one NBO each). This depolymerization of the silicate network, caused by the incorporation of modifier ions, results in the formation of a topologically two-dimensional structure of the covalently bonded silicate sub-lattice in the case of the disilicate composition containing only Q_3 structural units. This local two-dimensionality of the structure will almost certainly result in a change in the distribution of interstitial void volume; this redistribution may be the cause of the appearance of multiple pre-peaks in the structure factor, instead of a single FSDP, in the case of potassium disilicate glasses [51], particularly since the molar volume of the glass increases with addition of K, i.e. more interstitial volume must be introduced. In this sense, the effect of incorporating network modifiers in SiO_2 at the disilicate composition is topologically equivalent to replacing oxygen by the chalcogens S or Se in GeO_2 (where now the two-dimensionality arises from edge-sharing of Ge-centred chalcogen-containing tetrahedra). In both cases, the void distribution is expected to be appreciably different between the 2D-like structure and the parent 3D-like structure, implying that $S_{cc}(Q)$ should also be different. This is, we believe, why the FSDP intensity of the 'zero-scattering' modified glass is not precisely the same as that of pure SiO_2 in figure 3.

9. Conclusions

In this paper we have presented a new interpretation for the origin of the first sharp diffraction peak (FSDP), which is ubiquitously observed in covalent network glasses and liquids. This model is based upon the premise that the FSDP is a pre-peak in the concentration-concentration structure factor, arising from the chemical ordering of interstitial voids around cation-centred 'clusters' in the structure. This approach is capable of predicting, in a quantitative fashion, the positions of the FSDP for a wide range of covalent oxide and chalcogenide glasses. The anomalous temperature and pressure dependences of the FSDP intensity are rationalized in terms of density effects. The suppression of the FSDP by the incorporation of network-modifying ions (e.g. alkalis) into the framework structure, and the anomalous enhancement of the FSDP associated with the incorporation of Li, are naturally explained by assuming that the modifiers occupy the interstitial voids.

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