Origin of the First Sharp Diffraction Peak in the Structure Factor of Covalent Glasses

S. R. Elliott
Department of Chemistry, University of Cambridge, Cambridge, United Kingdom

(Received 7 March 1991)

A model is proposed for the "first sharp diffraction peak" (FSDP) in glasses. The FSDP is a chemical-order prepeak due to interstitial volume around cation-centered structural units. Calculated FSDP positions of some covalent glasses agree well with experiment, and the anomalous temperature and pressure dependences of the FSDP can be understood in terms of density effects.

PACS numbers: 61.42.+h

There is much current interest in the medium-range order (MRO) of covalent glasses [1]. MRO can be regarded as comprising structural correlations, say, in the range ~5–10 Å, in *excess* of those expected for an ideal Zachariasen-type continuous-random network (CRN) characterized by a random dihedral-angle distribution [1]. Examples of MRO include preferred values of dihedral angle and also "superstructural" units, such as rings or clusters of atoms, present in a proportion greater than expected for an ideal CRN [2].

One manifestation of MRO in covalently bonded glasses is the so-called "first sharp diffraction peak" (FSDP) (or "prepeak") in the structure factor $S(Q)$. The FSDP is anomalous in a number of ways [3]: There is a negligible change in the real-space correlation function whether or not the FSDP is included in the Fourier transformation of $S(Q)$, indicating that the FSDP is a manifestation of rather subtle intermediate-range correlations; the intensity of the FSDP reversibly *increases* with increasing temperature [4], unlike the other features in $S(Q)$ which behave in the normal manner expected from the Debye-Waller function; and finally the FSDP is more sensitive than the other peaks in $S(Q)$ to the application of pressure, its intensity decreasing with increasing pressure [5,6]. Although the FSDP occurs at widely varying values of scattering vector Q_1 for different glasses (see Refs. [3,7]), the FSDPs lie at approximately the *same* positions [8] when the structure factor for each glass is plotted against the reduced coordinate Q_1r_1, where r_1 is the nearest-neighbor bond length. Table I shows experimental values of Q_1 of AX_2-type glasses and calculated values Q_1', scaled to the values pertaining to v-SiO$_2$; it can be seen that the two sets of values are in remarkably close agreement.

Very recently, a well-defined, but as-yet unexplained, correlation has been demonstrated between values of Q_1r_1 for the FSDP and the reduced wave vector $\Omega = \omega_m c/v$ corresponding to the low-frequency "boson" peak in Raman spectra [9] (where ω_m is the frequency of the boson peak, v is the sound velocity in the glass, and c

TABLE I. Positions of the first sharp diffraction peak (FSDP) for AX_2 glasses. Q_1 are experimental values, Q_1' are values obtained by scaling the value corresponding to a-SiO$_2$ using the primary bond length $r_1(A\text{-}X)$, and Q_1'' are values obtained from Eq. (3) or (4) using the cation-cation distances $d(A\text{-}A)$.

Glass (AX_2)	Q_1 (Å^{-1})	$r_1(A\text{-}X)$ (Å)	$d(A\text{-}A)$ (Å)	Q_1' (Å^{-1})	Q_1'' (Å^{-1})
SiO$_2$	1.52 [a]	1.61 [b]	3.12 [c]	(1.52)	1.51 [Eq. (3)]
SiO$_2$ (pressurized)	1.69 [a]	1.63 [a]	2.9 [d]	· · ·	1.63 [Eq. (3)]
GeO$_2$	1.55 [e]	1.74 [e]	3.18 [e]	1.41	1.48 [Eq. (3)]
BeF$_2$	1.63 [f]	1.54 [f]	3.09 [f]	1.59	1.53 [Eq. (3)]
ZnCl$_2$	1.09 [g]	2.29 [g]	3.7 [g]	1.07	1.16 [Eq. (4)]
GeS$_2$	1.04 [h]	2.23 [i]	3.78 [j]	1.10	1.17 [Eq. (4)]
GeSe$_2$	1.01 [k]	2.38 [k]	3.57 [k]	1.02	1.11 [Eq. (4)]

[a] Reference [34].
[b] Reference [3].
[c] Reference [33].
[d] Reference [35].
[e] A. J. Leadbetter and A. C. Wright, J. Non-Cryst. Solids **7**, 37 (1972).
[f] A. J. Leadbetter and A. C. Wright, J. Non-Cryst. Solids **7**, 156 (1972).
[g] J. A. E. Desa, A. C. Wright, J. Wong, and R. N. Sinclair, J. Non-Cryst. Solids **51**, 57 (1982).
[h] C. Lin, L. E. Busse, S. R. Nagel, and J. Faber, Phys. Rev. B **29**, 5060 (1984).
[i] L. Cervinka, D. Smotlacha, and L. Tichy, J. Non-Cryst. Solids **97-98**, 183 (1987).
[j] A. Feltz, M. Pohle, H. Steil, and G. Herms, J. Non-Cryst. Solids **69**, 271 (1985).
[k] S. Susman, K. J. Volin, D. G. Montague, and D. L. Price, J. Non-Cryst. Solids **125**, 168 (1990).

is the speed of light).

Many attempts have been made to explain the origin of the FSDP in glasses (see, e.g., Refs. [2,3]). These can be divided into two classes: One assumes 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; the other treats the FSDP as simply being the first (i.e., lowest Q), and most intense, peak of a rapidly decaying structure factor $D_m(Q)$ accounting for "intermolecular"-type correlations in real space between "clusters," if the overall measured structure factor $S(Q)$ can be partitioned into two terms, viz. $D_m(Q)$ and $f_m(Q)$ [where $f_m(Q)$ is an *intra*molecular form factor], as for molecular liquids [10,11]. The first viewpoint has found favor in the past because many of the crystalline analogs of chalcogenide glasses have *layered* structures, and this layer motif has been taken to be the repeating structural unit in the glass, with the position of the FSDP, Q_1, determined by the interlayer separation D via the relation $Q_1 \sim 2\pi/D$ [4,12-14]. More recently the role of interlayer correlations between locally 2D structural arrangements in the glass (not necessarily the same as in a crystalline arrangement) has also been stressed [15,16]. However, it is most unlikely that this quasicrystalline picture involving interlayer correlations is generally valid. Some glasses (e.g., SiO_2) clearly exhibit FSDPs, yet there is no evidence in these cases for the structure in either crystalline or amorphous form being layerlike or locally two dimensional. Furthermore, the FSDP of, e.g., $GeSe_2$ persists into the *liquid* phase [17-19], seeming to rule out a microcrystalline explanation for its origin. Finally, x-ray-scattering experiments on very thin films of a-$GeSe_2$ have revealed that $S(Q)$ is independent of film thickness [20], indicating that preferential layerlike correlations probably do not exist.

Other authors [3,21] have emphasized that packing considerations, perhaps involving (ill-defined) clusters, are responsible for the FSDP. One example where this is indubitably true concerns as-deposited amorphous arsenic [22] and arsenic sulphide [8] films, where the scattering from quasispherical As_4 and As_4S_4 molecules, respectively, has been shown to give rise to an intense FSDP. For well-annealed films or bulk glasses the structural identification of the "clusters" is more problematic [3]. However, it is significant that many experimental and theoretical studies have shown that the FSDP for, say, an AX_2 glass (e.g., $GeSe_2$) is determined by *cation*-centered (primarily cation-cation, e.g., Ge-Ge) correlations. For instance, differential anomalous x-ray-scattering measurements on a-$GeSe_2$ [20,23], x-ray-scattering measurements on a series of $GeSe_2$-$GeTe_2$ glasses [24], Ge isotopic-substitution neutron-diffraction studies of liquid $GeSe_2$ [19], and molecular dynamics and other computer simulations of the structure of glassy and liquid $GeSe_2$ [25-27] all lead to this conclusion, implying that Ge-centered clusters are the structural units associated with the formation of the FSDP in a-$GeSe_2$. It has also been proposed [2,21,28] that the FSDP arises, not from intercluster correlations themselves, but from the presence of zones of low atomic occupancy [28]. These low-density regions can then serve to define the spatial extent of the clusters [21].

In this Letter, we ascribe the FSDP to a prepeak in the concentration-concentration partial structural factor $S_{CC}(Q)$ (in the Bhatia-Thornton formalism [29]) due to chemical short-range ordering of interstices around cation-centered clusters. Our picture of the structure, of say an AX_2 glass, for this purpose is thus an aggregate of soft (i.e., overlapping) cation-centered quasispherical clusters separated by the cation-cation distance $d = r_{AA}$, each cluster being surrounded by an equal number of spherical voids at a distance D. This simplified model obviously makes no reference to the positions of the anions X 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 [30] 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. In this situation, the general expression for the neutron-scattering cross section in the Bhatia-Thornton formalism [29] reduces to [30]

$$\frac{d\sigma}{d\Omega} = \frac{N_a b_a^2 (S_{NN} + S_{CC})}{2} \tag{1}$$

[where N_a and b_a are the number and scattering length, respectively, of the (cationic) atoms and $S_{NN}(Q)$ is the number-number partial structure factor], since the scattering length b_v of a void is zero and also since the number-concentration partial structure factor $S_{NC}(Q)$ is zero for a substitutional mixture of equally sized spheres. Equation (1) may be compared with the equivalent Faber-Ziman relation expressed in terms of atom-atom partial correlation functions, which reduces in this situation to

$$\frac{d\sigma}{d\Omega} = N_a b_a^2 S_{aa}(Q) . \tag{2}$$

Thus, it can be seen [30] that the first peak in the measured structure factor $S_{aa}(Q)$, i.e., the FSDP at Q_1, corresponds to the prepeak in $S_{CC}(Q)$, indicative of short-range chemical ordering, and the second peak at Q_2 corresponds to the first peak in $S_{NN}(Q)$. Blétry has shown that

$$Q_1 = 3\pi/2d \tag{3}$$

in the case where atoms and voids have the same diameter, $d=D$. When there is a size difference, given by the ratio $\delta=D/d=1+\varepsilon$, the FSDP peak is shifted to the value [30]

$$Q_1=\frac{3\pi(1-\varepsilon/2)}{2d}. \tag{4}$$

The above relations can be used to obtain estimates for the position of the FSDP of, for example, AX_2 glasses, if values for $d=r(A\text{-}A)$, the nearest-neighbor cation-cation separation, and $D=r(A\text{-}V)$, the average cation-void separation, are known. In the case of a-SiO$_2$, these quantities have been found during our recent void analysis [31] of a molecular-dynamics structural model [32]. A well-defined nearest-neighbor peak in the Si-void partial radial distribution function (RDF) was observed at $D=3.2$ Å which, taken together with the value [32,33] for the Si-Si separation $d=3.12$ Å, yields an estimate for the position of the FSDP of $Q_1=1.51$ Å^{-1}, using Eq. (3) (the size-difference parameter ε is nearly zero in this case). This theoretical estimate is very close to the value observed experimentally (see Table I).

This approach can be extended to other AX_2 glasses. However, this analysis is hampered because of our paucity of knowledge concerning the distribution of voids in the structure of these materials. Nevertheless, the most important parameter in determining Q_1 is $d=r(A\text{-}A)$ and this can often be inferred approximately from experimental scattering data or from the partial RDFs resulting from modeling studies. Furthermore, a very rough estimate for the average cation-void distance D, and hence an indication of the magnitude of the size-difference parameter ε, can be obtained for other AX_2 glasses by scaling the values corresponding to v-SiO$_2$. For example, if it is assumed that the average distance between void center and the "boundary" of the anion atom (corresponding to the van der Waals radius R) is constant, an estimate for D can be obtained by scaling with respect to $r_1(A\text{-}X)$, d, and R. In this way, theoretical values for the FSDP position Q_1'' can be obtained using Eqs. (3) and (4), and are given in Table I. It can be seen that in general there is good agreement between theoretical estimates and experimental values of Q_1.

Blétry [30] has already considered the case of the elemental amorphous materials, a-Ge and Si. In the absence of twofold-coordinated chalcogen atoms, the structural packing is somewhat tighter and the "clusters" in this case are the atoms themselves. Thus, d is now simply the nearest-neighbor interatomic separation and, since this is appreciably smaller than the separation $r(A\text{-}A)$ in say AX_2 glasses, the FSDP position is at a correspondingly *larger* value of Q [30].

The scaling of the FSDP position with primary bond length $r_1(A\text{-}X)$ for different AX_2 glasses (see Table I) is naturally understandable from Eq. (3) since, if the bond angle subtended at the anion, θ_x, remains constant, $d=r(A\text{-}A)$ scales directly with r_1. However, if θ_x also *decreases* as $r_1(A\text{-}X)$ increases (e.g., for SiO$_2$→ GeSe$_2$), the increase in Q_1 (caused by the diminution in d due to the decrease in θ_x) is offset by an increasingly sublinear contribution of the size-effect term $(1-\varepsilon/2)$ in Eq. (4), with the overall result that effectively Q_1 remains scaled by the bond-length factor $r_1(A\text{-}X)$.

This model also enables the effects of pressure to be understood. Measurements of the FSDP of chalcogenide glasses at high pressure [5,6], and of permanently densified v-SiO$_2$ after the application of pressure [34], have revealed that Q_1 increases and the FSDP intensity decreases with increasing pressure. Magic-angle-spinning ^{29}Si NMR studies [35] of pressure-densified v-SiO$_2$ have revealed that the average bond angle θ_0 decreases by approximately 5°, implying a reduction in the Si-Si separation to $d\sim2.9$ Å. Structural modeling using molecular dynamics supports this picture, although the changes are not readily discernible in neutron-scattering data [34]. Use of this value of d_1 with Eq. (3) yields an estimate for $Q_1\sim1.63$ Å^{-1}, in good agreement with the experimental value [34] of $Q_1\sim1.69$ Å^{-1} (see Table I). The marked decrease in intensity of the FSDP with increasing pressure [5,6,34] is also understandable. Application of pressure causes a densification of the glass structure [34], i.e., a diminution of the interstitial volume. Thus, it is expected that the FSDP intensity should correspondingly decrease.

The anomalous temperature dependence of the FSDP [4] in chalcogenide glasses can also be understood in the framework of the present model. Vashishta and coworkers [25-27] have shown, using molecular dynamics and other computer simulations of the structure of a-GeSe$_2$, 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. The anomalous temperature dependence of the intensity of the FSDP is thus due to the decrease in density of the glass with increasing temperature as the liquid state is approached. This behavior is predicted by the present model since the FSDP intensity is expected to scale with the amount of void volume clustered around cation-centered units in the structure.

Note added.—Penfold and Salmon [36] have very recently reported isotopic-substitution neutron-diffraction data on liquid GeSe$_2$ which are in accord with the interpretation proposed in this paper. They find unambiguous evidence from the partial correlation functions that cation-cation (Ge-Ge) correlations are the dominant contribution to the FSDP. Further, they find a prepeak in in the *atom-based* $S_{CC}(Q)$, in contrast to the predictions from molecular-dynamics simulations (Vashishia *et al.* [37]).

[1] S. R. Elliott, J. Non-Cryst. Solids **97-98**, 159 (1987).

[2] S. R. Elliott, *Physics of Amorphous Materials* (Longman, London, 1990), 2nd ed.
[3] S. C. Moss and D. L. Price, in *Physics of Disordered Materials,* edited by D. Adler, H. Fritzsche, and S. R. Ovshinsky (Plenum, New York, 1985), p. 77.
[4] L. E. Busse and S. R. Nagel, Phys. Rev. Lett. **47**, 1848 (1981); L. E. Busse, Phys. Rev. B **29**, 3639 (1984).
[5] H. Tsutsu, K. Tamura, and H. Endo, Solid State Commun. **52**, 877 (1984).
[6] Ke. Tanaka, J. Non-Cryst. Solids **90**, 363 (1987); Philos. Mag. Lett. **57**, 183 (1988).
[7] D. L. Price, S. C. Moss, R. Reijers, M. L. Saboungi, and S. Susman, J. Phys. C **21**, L1069 (1988); J. Phys. Condens. Matter **1**, 1005 (1989).
[8] A. C. Wright, R. N. Sinclair, and A. J. Leadbetter, J. Non-Cryst. Solids **71**, 295 (1985).
[9] V. N. Novikov and A. P. Sokolov, Solid State Commun. **77**, 243 (1991).
[10] D. G. Montague, M. R. Chowdhury, J. C. Dore, and J. Reed, Mol. Phys. **50**, 1 (1983).
[11] M. Misawa, J. Chem. Phys. **93**, 6774 (1990).
[12] A. A. Vaipolin and E. A. Porai-koshits, Fiz. Tverd. Tela (Leningrad) **5**, 683 (1963) [Sov. Phys. Solid State **5**, 497 (1963)].
[13] J. C. Phillips, J. Non-Cryst. Solids **43**, 37 (1981).
[14] P. M. Bridenbaugh, G. P. Espinosa, J. E. Griffiths, J. C. Phillips, and J. P. Remeika, Phys. Rev. B **20**, 4140 (1979).
[15] Ke. Tanaka, J. Non-Cryst. Solids **97-98**, 391 (1987).
[16] L. Cervinka, J. Non-Cryst. Solids **90**, 371 (1987); **106**, 291 (1988).
[17] O. Uemura, Y. Sagara, and T. Satow, Phys. Status Solidi a **32**, K91 (1975); O. Uemura, Y. Sagara, D. Muno, and T. Satow, J. Non-Cryst. Solids **30**, 155 (1978).
[18] S. Susman, D. L. Price, K. J. Volin, R. J. Dejus, and D. G. Montague, J. Non-Cryst. Solids **106**, 26 (1988).
[19] I. T. Penfold and P. S. Salmon, J. Phys. Condens. Matter **2**, SA233 (1990).
[20] P. H. Fuoss and A. Fischer-Colbrie, Phys. Rev. B **38**, 1875 (1988).
[21] T. G. Fowler and S. R. Elliott, J. Non-Cryst. Solids **92**, 31 (1987).
[22] M. F. Daniel and A. J. Leadbetter, Philos. Mag. B **44**, 509 (1981).
[23] P. H. Fuoss, P. Eisenberger, W. K. Warburton, and A. Bienenstock, Phys. Rev. Lett. **46**, 1537 (1981).
[24] S. C. Moss, in *Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors* (Taylor and Francis, London, 1974), p. 17.
[25] P. Vashishta, R. K. Kalia, and I. Ebbsjö, Phys. Rev. B **39**, 6034 (1989).
[26] P. Vashishta, R. K. Kalia, G. A. Antonio, and I. Ebbsjö, Phys. Rev. Lett. **62**, 1651 (1989).
[27] H. Iyetomi, P. Vashishta, and R. K. Kalia, Phys. Rev. B **43**, 1726 (1991).
[28] S. Veprek and H. U. Beyeler, Philos. Mag. B **44**, 557 (1981).
[29] A. B. Bhatia and D. E. Thornton, Phys. Rev. B **2**, 3004 (1970).
[30] J. Blétry, Philos. Mag. B **62**, 469 (1990).
[31] S. L. Chan and S. R. Elliott, Phys. Rev. B **43**, 4423 (1991).
[32] B. P. Feuston and S. H. Garofalini, J. Chem. Phys. **89**, 5818 (1988).
[33] L. F. Gladden, J. Non-Cryst. Solids **119**, 318 (1990); (private communication).
[34] S. Susman, K. J. Volin, R. C. Liebermann, G. D. Gwanmesia, and Y. Wang, Phys. Chem. Glasses **31**, 144 (1990); S. Susman, K. J. Volin, D. L. Price, M. Grimsditch, J. P. Rino, R. K. Kalia, P. Vashishta, G. Gwanmesia, Y. Wang, and R. C. Liebermann, Phys. Rev. B **43**, 1194 (1991).
[35] R. A. B. Devine, R. Dupree, I. Farnan, and J. J. Capponi, Phys. Rev. B **35**, 2560 (1987).
[36] I. T. Penfold and P. S. Salmon, Phys. Rev. Lett. **67**, 97 (1991).
[37] P. Vashishta *et al.*, Phys. Rev. B **41**, 12197 (1990).