The first sharp diffraction peak in glasses and in other amorphous substances

LETTER TO THE EDITOR

The first sharp diffraction peak in glasses and in other amorphous substances

E A Chechetkina

Institute of General and Inorganic Chemistry, Leninsky Prospekt 31, Moscow 117907, Russia

Abstract. It is shown that there exists a numerical relationship between the position of the first sharp diffraction peak, Q_1, and the first interatomic distance, r_1, which obeys a simple equation $d = ar_1 + b$ where $d = 2\pi/Q_1$ is the equivalent distance and the coefficients (a, b) specify the group of amorphous substances—glasses, amorphous metals and semiconductors, liquids of a definite nature. The scale of medium-range order $\xi = d/r_1$ is introduced and it is proposed that the ξ–r_1 plot could be used for classification of amorphous structures.

The first sharp diffraction peak (FSDP) is an intriguing feature in the diffraction patterns of glasses and other amorphous substances, and is intensively discussed in contemporary literature (see, for example, [1,2]). It is described as 'sharp' because of a relatively small halfwidth corresponding to the 20–40 Å region of structural correlations associated with medium-range order (MRO). The MRO dimension may be evaluated also from the FSDP position ($Q_1 \simeq 1.0$ Å^{-1} for chalcogenide glasses, and $\simeq 1.5$ Å^{-1} for oxide glasses etc) using the equivalent distance

$$d = 2\pi/q_1 \tag{1}$$

(which takes the values $\simeq 6$ Å and $\simeq 4$ Å, respectively). However, one should keep in mind that d is a 'conditional' value which has the sense of a real distance only in the framework of the layer model of the FSDP ([3] etc), which can hardly be taken as correct without additional physical arguments for glasses of the non-layered type (e.g. SiO_2) or liquids.

In the past decade a few attempts have been made to connect Q_1 with the position of the first peak in the radial distribution function, r_1. First, Wright et al [4] demonstrated a remarkable similarity of four glasses when using the coordinates $S(Q)$ versus Qr_1, the FSDP being located at

$$Q_1 r_1 \simeq 2.5. \tag{2}$$

Moss and Price [5], expanding the range of glasses (G) and introducing amorphous metals (A) into their consideration, have obtained

$$Q_1 r_1 = 2.14\text{–}3.10 \qquad \text{for G} \tag{3}$$

$$Q_1 r_1 = 4.3\text{–}5.3 \qquad \text{for A.} \tag{4}$$

Strictly speaking, they used the term 'pre-peak' for amorphous metals instead of FSDP for glasses; however, this difference, reflecting only the intensity and halfwidth of the peak, is relative. For example, in samples from one glass-forming system Se_xP_{1-x}, the strong and sharp first peak existing at $x = 0.5$ becomes a weak and wide one for $x > 0.85$ and almost disappears in pure Se ($x = 1$) [6]; however, the 'FSDP' observed in its evolution with changing chemical composition remains the same. On the other hand, the very weak 'pre-peak' in the amorphous metals Ni_xTi_{1-x} becomes the strongest peak in the diffraction pattern when using neutron diffraction instead of x-ray diffraction [7].

Later Price *et al* [8] investigated a correlation between Q_1d_s (d_s is the mean interatomic spacing obtained from the density data) and Q_1r_1; however, this is actually the d_s versus r_1 correlation. Finally, Elliott [1], in an analysis based on the model of cation-centred soft clusters, has applied Bletry's expression for tetravalent monatomic materials (a-Si etc)

$$Q_1 = 3\pi/2D \tag{5}$$

(where D is the atom/void diameter) to tetrahedral AX_2 glasses (SiO_2 etc), with $D = r(A-A)$ considered as the nearest-neighbour cation–cation separation. Since $r(A-A) \simeq 2r_1$ (e.g. in the Si–O–Si fragment), one obtains $Q_1 \simeq 3\pi/4r_1 \simeq 2.36/r_1$ or

$$Q_1r_1 \simeq 2.4. \tag{6}$$

This result is very similar to the initial empirical evaluation by Wright *et al* [4]—see equation (2). However, note that the glasses analysed in [4] were SiO_2, GeS_2, B_2O_3 and $AsS_{1.66}$, the latter two not being tetrahedral, and therefore this agreement is ambiguous.

All the above Q_1 versus r_1 dependences may be represented as

$$d = ar_1 \tag{7}$$

or in the form of the dotted lines in figure 1. To be more specific I have expanded the range of substances considered and most importantly, distinguished the points/substances in the $d-r_1$ plot in accordance with their belonging to the following groups: glasses—G; amorphous metals and semiconductors—A; liquid halogens—H; liquid and APb and ASn—P and S, respectively. It is seen from figure 1 that similar points tend to group around specific lines

$$d = ar_1 + b \tag{8}$$

differing in the coefficients a, b. Interestingly, in such a representation the chemical formula and the dimensionality of, say, glass are of no importance. On the other hand, while only one correlation line is revealed for each of the groups A, H, S, P, there are two correlation lines for glasses, G and G', along with a transition between them at $r_1 \simeq 2.3$ Å.

Since d may be related to the dimension of medium-range order (MRO), and r_1 with that of short-range order (SRO), the correlation lines in figure 1 can be converted into the scaled form shown in figure 2, where the scale of MRO is

$$\xi = d/r_1 = 2\pi/Q_1r_1 \tag{9}$$

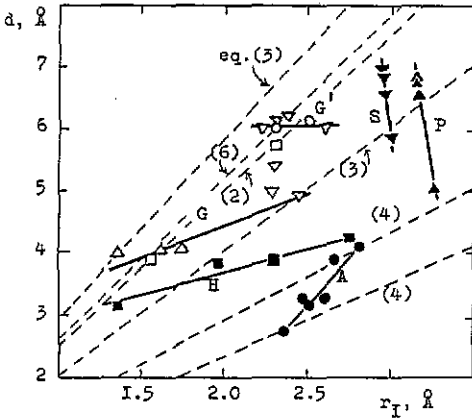which may be calculated with the use of (8):

$$\xi = a + b/r_1. \tag{10}$$

Figure 1. The equivalent distance for the FSDP, $d = 2\pi/Q_1$, versus the first interatomic distance, for ($\triangle$) oxide glasses (B_2O_3, SiO_2, GeO_2), ($\square$) halide glasses (BeF_2, $ZnCl_2$), (∇) chalcogenide glasses (GeS_2, As_2S_3, $P_{40}Se_{60}$, $Si_{32}S_{68}$, $GeSe_2$, As_2Se_3, $Si_{24}Te_{76}$), ($\bigcirc$) elementary glasses (P, As), ($\bullet$) amorphous metals and semiconductors ($Co_{80}P_{20}$, Ge, Si, $Ni_{40}Ti_{60}$, $Ni_{35}Zr_{65}$, $Al_{90}Fe_5Ce_5$), ($\blacksquare$) liquid halogens (F_2, Cl_2, Br_2, I_2), ($\blacktriangledown$ and $\blacktriangle$) liquid ASn and APb, respectively, where A = Cs, Rb, K, Na. Substances in the groups are arranged in order of increasing r_1. The Q_1- and r_1-data are from [9] (Si), [10] ($Al_{90}Fe_5Ce_5$), [11] (H group), [8] (S group) and [5] (all others).
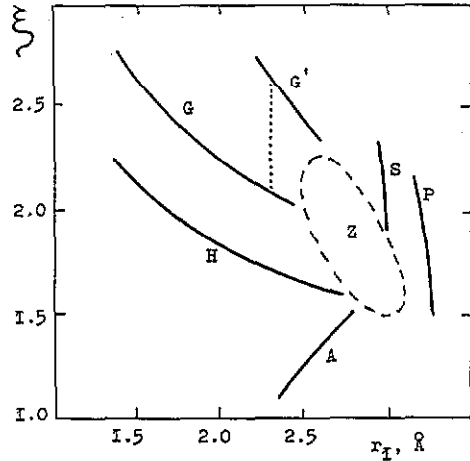
Figure 2. The scale of the MRO (10) in different families of amorphous structures (annotation as for figure 1). Coefficients a and b in (10) correspond to the lines in figure 1, taking values for G, G', H, A, S, P of, respectively, $a = 1.10$, 0, 0.94, 3.62, -18.1, -15.2 and b (Å) = 2.27, 6.1, 1.78, -5.89, 60.1, 54.7.

Note that the case $Q_1 r_1 \simeq$ constant (equations (2), (6)) corresponds to ξ = constant (equation (9)), which is incorrect even within a given group of amorphous substances—see figure 2. Other equations, (3) and (4), are somewhat better, since they actually establish limits for ξ in two groups (glasses and amorphous metals)—see figure 1, where each dotted line corresponds to a definite ξ. However, only in the present work are the specific $\xi(r_1)$ dependences obtained.

The region $\xi < 1$ is not shown in figure 2, because it corresponds to the absence of MRO. Theoretically when only SRO is present one obtains $\xi = 0.8$–0.9 (p 849 in [12]) and just such values are realized in liquid elementary metals (one may use tabulated data on Q_1 and r_1 from [13] to test this statement). Thus, in amorphous structures having SRO only, the first peak in the diffraction pattern is *not* the FSDP either in sense (MRO is absent) or in value ($\xi < 1$). For example, in liquid Si the first peak corresponds to $\xi = 0.92$ ($Q_1 = 2.72$ Å^{-1} and $r_1 = 2.50$ Å after [13]), while in amorphous Si the appearance of a new peak is at $Q_1 = 1.95$ Å^{-1} [9], and so $\xi = 1.3$ points to the appearance of MRO in the solid state, and only this peak is an FSDP. On the other hand, in substances demonstrating an FSDP the scale of the MRO is not higher than 3, the largest ξ-values being achieved in glasses (figure 2).

Particular curves in figure 2 appear to rotate around a centre Z, leaving free a forbidden zone around the axis or rotation. The question is of whether this zone is really forbidden or whether there is a special group(s) of amorphous substances occupying it. Correspondingly, are the spaces between the lines/curves in figures 1, 2 free from substances of other groups and/or of the same group that have not been analysed here?

Since r_1 is simply the strongest bond length, a second question arises: what are the bonding/structure features in different groups of amorphous substances that are hidden behind the particular $d(r_1)$ and $\xi(r_1)$ relations? The existence of a general equation (8), satisfying all the groups, points to a general origin of the FSDP irrespective of the mode of chemical bonding, structure motif, formula and amorphization (glass formation) ability. Discovery of this origin seems to be an important prerequisite for achieving an understanding of the nature of the amorphous state.

References

[1]   Elliott S R 1991 *Phys. Rev. Lett.* **67** 711

[2]   Reijers H T, Saboungi M-L, Price D L, Richardson J W, Volin K W and van der Lugt W 1989 *Phys. Rev.* B **40** 6018

[3]   Busse L 1984 *Phys. Rev.* B **29** 3639

[4]   Wright A C, Sinclair R N and Leadbetter A J 1985 *J. Non-Cryst. Solids* **71** 295

[5]   Moss S C and Price D L 1985 *Physics of Disordered Materials* ed D Adler, H Fritzsche and S R Ovshinsky (New York: Plenum) p 77

[6]   Price D L, Misawa M, Susman S, Morrison T I, Shenoy G K and Grimsditch M 1984 *J. Non-Cryst. Solids* **66** 43

[7]   Boldrick M S, Lee D and Wagner C N J 1988 *J. Non-Cryst. Solids* **106** 60

[8]   Price D L, Moss S C, Saboungi M-L and Susman S 1989 *J. Phys.: Condens. Matter* **1** 1005

[9]   Roorda S, Sinke W C, Poate J M, Jacobson D C, Dierker S, Dennis B S, Eaglesham D J, Spaepen F and Fuoss P 1991 *Phys. Rev.* B **44** 3702

[10]   Hsiesh H Y, Egami T, He Y, Poon S J and Shiflet G J 1991 *J. Non-Cryst. Solids* **135** 248

[11]   Misawa M 1989 *J. Chem. Phys.* **91** 2575

[12]   Klug H P and Alexander L E 1974 *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials* (New York: Wiley)

[13]   Waseda Y 1981 *Prog. Mater. Sci.* **26** 1