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## LETTER TO THE EDITOR

# Intermediate-range order in glasses and liquids†

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**Abstract.** Many glasses and liquids exhibit a first sharp diffraction peak that is evidence for intermediate-range order caused by regularities in the packing of structural units. These tend to cluster around particular values of the wavevector when scaled by the nearest-neighbour distance or the mean inter-atomic spacing. The first sharp diffraction peak is distinguished from the pre-peak in binary metallic glasses, which occurs at higher wavevectors when scaled in this way.

Many glasses exhibit a pronounced first sharp diffraction peak (FSDP) in the structure factor  $S(Q)$  (Moss and Price 1985). This peak is remarkably sensitive both to methods of sample preparation and treatment as well as to variables such as composition, temperature, and pressure. According to data tabulated in Moss and Price (1985), the wavevector  $Q_1$  at which the FSDP occurs has typical values corresponding to  $Q_1 r_1 \approx 2.5$  or  $Q_1 d_s \approx 4.5$ , where  $r_1$  is the nearest-neighbour distance and  $d_s$  is the mean inter-atomic spacing ( $\rho^{-1} = (\pi/6)d_s^3$ ). In fact, the structure factors  $S(Qr_1)$  scaled in this way have a similar appearance in a wide variety of glasses, even when the analogous crystal structures have different dimensionality (Wright *et al* 1985, Price *et al* 1987).

The small wavevector and relative sharpness of the FSDP, compared with the larger- $Q$  part of the structure factor, has been ascribed to the persistence into the glassy state of layers found in some of the analogous crystalline compounds (Phillips 1981, Busse and Nagel 1981). However, the ubiquitous nature of the peak, as described above, can be more readily understood in terms of the concept of random packing of structural units (Moss and Price 1985). According to this picture, the sharp peak results from the competition between the form factor for the structural unit, which falls rapidly with increasing  $Q$ , and a structure factor for the positions of the units, which rises with increasing  $Q$  over the region in question.

Further support for this view comes from the fact that many liquids also exhibit an FSDP. The peaks observed in chalcogenide glasses (for example, in  $\text{As}_2\text{Se}_3$  (Uemura *et al* 1978) and  $\text{GeSe}_2$  (Susman *et al* 1988)) frequently persist into the liquid state. More surprisingly, a number of equi-atomic liquid alloys of the form AM, where A is an alkali metal and M a group-IV metal, have recently been found to exhibit sharp peaks in the neighbourhood of  $Q = 1 \text{ \AA}^{-1}$  (Saboungi *et al* 1987, 1988a, b). The experimental structure

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**Table 1.** Positions  $Q_1$  of the first peak in the diffraction pattern of some inter-metallic liquids, scaled by the nearest-neighbour distance  $r_1$  and the mean inter-atomic spacing  $d_s$  ( $\rho^{-1} = (\pi/6) d_s^3$ ).

System	$Q_1$ ( $\text{\AA}^{-1}$ )	$r_1$ ( $\text{\AA}$ )	$Q_1 r_1$	$d_s$ ( $\text{\AA}$ )	$Q_1 d_s$
Oxide and halide glasses					
$B_2O_3^\dagger$	1.57	1.36	2.14	2.90	4.55
$SiO_2^\dagger$	1.55	1.61	2.50	3.07	4.75
$GeO_2^\dagger$	1.55	1.74	2.70	3.12	4.83
$BeF_2^\dagger$	1.63	1.54	2.51	2.92	4.76
$ZnCl_2^\dagger$	1.09	2.29	2.49	3.76	4.10
Chalcogenide glasses					
$P_{40}Se_{60}^\dagger$	1.16	2.29	2.66	3.78	4.38
$Si_{32}Se_{68}^\dagger$	1.02	2.30	2.35	3.92	3.99
$Si_{24}Te_{76}^\dagger$	1.04	2.60	2.69	4.09	4.25
$GeS_2^\dagger$	1.04	2.22	2.31	3.76	3.91
$GeSe_2^\dagger$	1.01	2.37	2.39	3.86	3.90
$As_2Se_3^\dagger$	1.27	2.44	3.10	3.77	4.79
$As_2S_3^\dagger$	1.26	2.28	2.87	3.66	4.61
Elemental semiconducting glasses					
$Se^\dagger$	1.88	2.37	4.56	3.89	7.32
$P(\text{red})^\dagger$	1.04	2.29	2.38	3.54	3.69
$As^\dagger$	1.03	2.49	2.56	3.69	3.80
$Ge^\dagger$	1.89	2.46	4.43	3.64	6.88
Metallic glasses ('pre-peak')					
$Co_{80}P_{20}^\dagger$	2.30	2.34	5.38	2.77	6.37
$Ni_{38}Zr_{62}^\dagger$	1.62	2.66	4.30	3.31	5.36
$Ni_{40}Ti_{60}^\dagger$	1.90	2.60	4.94	3.03	5.76
Metallic glasses (main peak)					
$Co_{80}P_{20}^\dagger$	3.16	2.34	7.39	2.77	8.75
$Ni_{38}Zr_{62}^\dagger$	2.62	2.66	6.97	3.31	8.67
$Ni_{40}Ti_{60}^\dagger$	2.91	2.60	7.57	3.03	8.82
$Fe^\dagger$	3.09	2.55	7.88	—	—
Equi-atomic liquid alloys					
$NaPb^\ddagger$	1.25	3.19	3.99	3.96	4.95
$KPb^\S$	0.96	3.12	3.00	4.45	4.27
$RbPb^\ddagger$	0.93	3.10	2.88	4.58	4.26
$CsPb^\ddagger$	0.92	3.09	2.84	4.87	4.48
$NaSn^\parallel$	1.06	3.00	3.18	3.86	4.09
$KSn^\ddagger$	0.96	2.97	2.85	4.37	4.19
$RbSn^\ddagger$	0.92	2.95	2.71	4.30	3.96
$CsSn^\ddagger$	0.90	2.94	2.65	4.69	4.22
$CsSb^\nabla$	0.95	2.84	2.70	4.29	4.52

$^\dagger$  Moss and Price (1985), p 81, table 1.

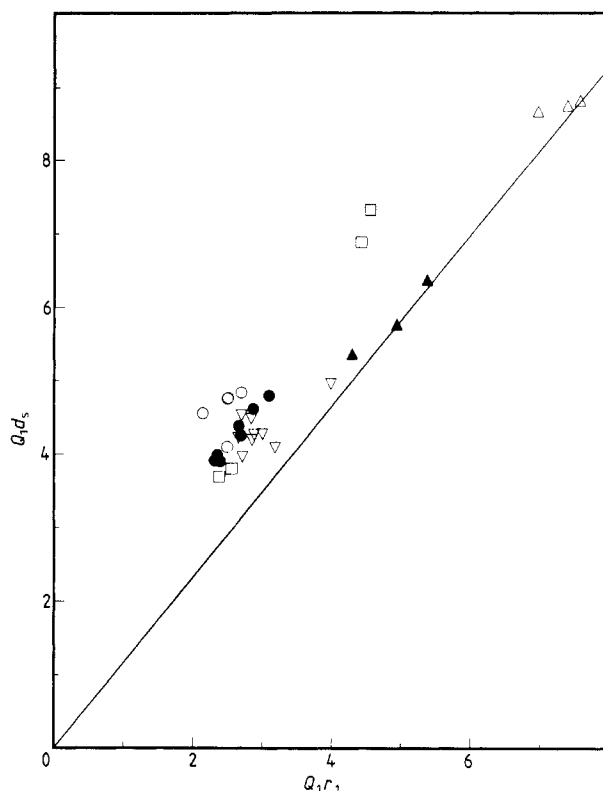
$^\ddagger$  Saboungi *et al* (1988a, b).

$^\S$  Saboungi *et al* (1987).

$^\parallel$  Alblas *et al* (1983).

$^\nabla$  Lamparter *et al* (1984).

factors can be reproduced by a model involving  $A_4M_4$  molecules as the basic structural units (Saboungi *et al* 1987); such units can also be identified in the crystal structures of these alloys. A similar peak has been observed in liquid CsSb and ascribed to Sb chain units (Lamparter *et al* 1984).



**Figure 1.** Wavevectors  $Q_1$  of peaks in the structure factors of some liquids and glasses, scaled by the nearest-neighbour distance  $r_1$ , and the mean atomic spacing  $d_s$ .  $\circ$ , oxide and halide glasses, FSDP;  $\bullet$ , chalcogenide glasses, FSDP;  $\nabla$ , inter-metallic liquids, FSDP;  $\square$ , elemental semiconducting glasses, first peak;  $\blacktriangle$ , metallic glasses, pre-peak;  $\triangle$ , metallic glasses, main peak. The full line represents the limit for dense random packing,  $d_s = 1.162 r_1$ .

Values for the positions  $Q_1$  of the FSDP, scaled by  $r_1$  and  $d_s$ , are listed in table 1 and plotted in figure 1. The data for amorphous solids compiled by Moss and Price are included in addition to those for the liquids discussed above. The first peaks in the structure factors of both oxide, halide and chalcogenide glasses, and also the inter-metallic liquids, are clustered in the region around  $Q_1 r_1 \approx 2.5$  and  $Q_1 d_s \approx 4.5$ . The only exception is liquid NaPb for which the thermodynamic and transport data indicate that  $\text{Na}_4\text{Pb}_4$  molecules are not energetically stable (Saboungi *et al* 1988a, b). Also included in this  $Q$ -region are the elemental semiconducting glasses phosphorus and arsenic, the basic structural units in these cases being  $\text{P}_4$  and  $\text{As}_4$  tetrahedra.

The FSDP should be distinguished from the well known pre-peak in metallic glasses with two metallic species, such as  $\text{Ni}_x\text{Zr}_{1-x}$  or  $\text{Ni}_x\text{Ti}_{1-x}$ , which is associated with minority species ordering (Ni in these examples) (Steeb and Lamparter 1984). In this case  $Q_p r_1$  takes values in the range 4.3–5.0, where  $Q_p$  is the wavevector of the pre-peak. The openness of the minority species structure therefore resembles the tetrahedral packing in a-Ge, for instance, where  $Q_1 r_1 = 4.43$ . More recently, pre-peaks have also been observed in Al–Mn and Al–Mn–Si glasses (Matsubara *et al* 1988, Robertson *et al* 1988), where they have been associated with discrete, well separated Mn–Mn distances found

in the icosahedral and  $\alpha$ -phases of these materials, in both of which distinct ordered tetrahedra exist.

The main peak in metallic glasses, on the other hand, generally agrees with the well known Ehrenfest relation for a dense packing of hard spheres,  $Qr_1 \approx 5\pi/2 = 7.5$ . For example, elemental amorphous iron has  $Q_1r_1 = 7.88$ .

The data in figure 1 follow an approximate straight line, indicating some regularity in the relation between  $d_s$  and  $r_1$ . For a one-component dense random packing of hard spheres,  $d_s/r_1 = 1.162$ . As seen from figure 1, this relation represents a lower bound for the experimental data. The nearest approach to the dense-random-packing limit is found for the metallic glasses. The systems exhibiting FSDPs are by their nature more open structures, as are the tetrahedrally coordinated elemental semiconductors silicon and germanium.

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