

## METALLIC GLASSES: STRUCTURAL MODELS

E. Nassif, Depto. de Física, Facultad de Ingeniería, U.B.A.  
Paseo Colón 850 (1063) BUENOS AIRES, ARGENTINA

**INTRODUCTION:** Many models have been proposed in the last few years to describe the structure of metallic glasses. These models can be regarded as microscopical descriptions of the atomic arrangement in the system considered, in which the fundamental unit is formed by a single atom or a group of atoms. In order to check the validity of any of these models, the ability of the proposed structure to reproduce the main macroscopical features of the analyzed system must be tested. From a structural point of view our most important macroscopical parameters in the case of a disordered system are basically two: the structure factor  $S(Q)$  and any of the atomic distribution functions [RDF( $r$ ),  $g(r)$  or  $G(r)$ ]. To define therefore the efficiency of a definite kind of structural model, it is necessary to know accurately the experimental values of those functions, as well as their partial components from which they can be obtained as a linear combination.

As we shall see this has been possible only in a few experimental investigations up to now, making difficult to draw conclusions about the fit of the different known models to the atomic structure of the studied system. The aim of this talk is to give a summary of the attempts made up to the present in order to describe by structural models the atomic arrangement in metallic glasses, showing also why the structure factors and atomic distribution functions cannot be always experimentally determined with a reasonable accuracy.

**STRUCTURE FACTORS AND DISTRIBUTION FUNCTIONS:** The structure factor for a one-component system can be defined as:

$$S(Q) = I_{\text{coh}}(Q) / N f^2(Q) \quad (1)$$

where  $Q = |\vec{Q}' - \vec{Q}_0| = 4\pi \sin\theta/\lambda$  is the absolute value of the scattering vector,  $\lambda$  is the radiation wavelength,  $2\theta$  the scattering angle and  $I_{\text{coh}}(Q)/N$  the coherently scattered intensity per atom.

$$I_{\text{coh}}(Q) = \langle |A(Q)|^2 \rangle = f^2(Q) \langle \sum_j \sum_k \exp[-i\vec{Q}(\vec{r}_j - \vec{r}_k)] \rangle \quad (2)$$

where  $f(Q)$  is the atomic scattering factor,  $A(Q)$  is the amplitude of the scattered radiation and  $\vec{r}_j$  the position of the atom  $j$ . (The brackets  $\langle \rangle$  denote the statistical average).

In the case of a two-component system, there are three different definitions for the structure factor, following three different formalisms. Considering the definition of Ashcroft and Langreth (1) we have, for the total structure factor of a binary alloy:

$$S^{\text{AL}}(Q) = \frac{I_{\text{coh}}(Q)}{N \langle f^2(Q) \rangle} = \sum_i \sum_j (c_i c_j)^{1/2} \frac{f_i(Q) f_j(Q)}{\langle f^2(Q) \rangle} S_{ij}^{\text{AL}}(Q) \quad (3)$$

where  $\langle f^2(Q) \rangle = c_1 f_1^2(Q) + c_2 f_2^2(Q)$  being  $c_{i,j}$  the atomic concentrations of the atoms of the species  $i, j$  respectively and  $S_{ij}(Q)$  the partial structure factors, which verify:

$$\lim_{Q \rightarrow \infty} S_{ij}^{\text{AL}}(Q) = 0 \quad ; \quad \lim_{Q \rightarrow \infty} S_{ii}^{\text{AL}}(Q) = \lim_{Q \rightarrow \infty} S_{jj}^{\text{AL}}(Q) = 1$$

In the Faber-Ziman formalism (2) the structure factor can be written as follows:

$$S^{\text{FZ}}(Q) = \left[ \frac{I_{\text{coh}}(Q)}{N} - \{ \langle f^2(Q) \rangle - \langle f(Q) \rangle^2 \} \right] / \langle f(Q) \rangle^2$$

$$= \sum_i \sum_j \frac{c_i c_j f_i(Q) f_j(Q)}{\langle f(Q) \rangle^2} S_{ij}^{\text{FZ}}(Q) \quad (4)$$

with  $\langle f(Q) \rangle = c_1 f_1(Q) + c_2 f_2(Q)$  and where  $\{ \langle f^2(Q) \rangle - \langle f(Q) \rangle^2 \} = c_1 c_2 (f_1 - f_2)^2$  is a term usually known as the "Laue monotone diffraction", and the partial structure factors verify:

$$\lim_{Q \rightarrow \infty} S_{ij}^{FZ}(Q) = 1 \quad \forall i, j \quad i, j = 1, 2$$

Comparing both formalisms one can easily state that  $(S^{AL}(Q) - 1)/(S^{FZ}(Q) - 1) < 1$  and  $\lim_{Q \rightarrow \infty} S^{FZ}(Q) = \lim_{Q \rightarrow \infty} S^{AL}(Q) = 1$  which means, that the Faber-Ziman formalism is more sensitive to the oscillations of the structure factor. The Ashcroft-Langreth formalism, is, on the other hand, simpler, more sensible to concentration fluctuations and with the advantage that it does not diverge when  $\langle f \rangle = 0$ , which occurs in the case of negative scattering lengths usual in some neutron diffraction experiments.

A third description of the structure factor is that given by the Bhatia-Thornton formalism (3) in terms of which the structure factor can be written as follows:

$$\begin{aligned} S^{BT}(Q) &= \frac{I_{coh}(Q)}{\langle f^2(Q) \rangle} \\ &= \frac{\langle f(Q) \rangle^2}{\langle f^2(Q) \rangle} S_{NN}(Q) + \frac{c_1 c_2 \{f_1(Q) - f_2(Q)\}^2}{\langle f^2(Q) \rangle} S_{CC}(Q) + \\ &\quad + 2 \langle f(Q) \rangle \frac{\{f_1(Q) - f_2(Q)\}}{\langle f^2(Q) \rangle} S_{NC}(Q) \end{aligned} \quad (5)$$

where  $S_{NN}(Q)$ ,  $S_{CC}(Q)$  are, respectively, the partial structure factors of the correlations between number density fluctuations and of the correlations between concentration fluctuations;  $S_{NC}(Q)$  is the partial structure factor of the cross correlations between concentration fluctuations and density fluctuations. They can be expressed in the form:

$$S_{NN}(Q) = \frac{1}{N} \langle N^*(Q) N(Q) \rangle ; \quad S_{CC}(Q) = \frac{M}{V} \langle C^*(Q) C(Q) \rangle$$

$$S_{NC}(Q) = \text{Re} \langle N^*(Q) C(Q) \rangle$$

being  $N(Q)$  and  $C(Q)$  the Fourier transform of the local deviation in the total number density and in the concentration, respectively. It can be shown that:

$$\lim_{Q \rightarrow \infty} S^{BT}(Q) = 1 = \lim_{Q \rightarrow \infty} S_{NN}(Q) = \lim_{Q \rightarrow \infty} S_{CC}(Q) ; \quad \lim_{Q \rightarrow \infty} S_{NC}(Q) = 0$$

Comparing the Bhatia-Thornton formalism with those previously seen, it can be stated that the total structure factors are numerically identical in the BT and the AL formalisms, being however the interpretation of the structure in terms of the partial structure factors completely different. The Bhatia-Thornton formalism is particularly useful to describe the structure of substitutional alloys, in which the atomic size of the components is almost equal ( $R_1 \cong R_2$ ) and can be verified  $S_{NC} = 0$ . Since the partial structure factor of the correlations between concentration fluctuations,  $S_{CC}$ , is extremely sensitive to those fluctuations, this formalism is also particularly effective in those systems with a strong chemical short range order (CSRO). (In the Faber-Ziman formalism, on the other hand, one has for substitutional alloys  $S_{11}^2 = S_{22}^2 = S_{12}^2$ ).

Whereas the total structure factors are almost directly available from the experimental data through  $I_{\text{coh}}(Q)$  (which is indeed the measured diffracted intensity of the radiation, subsequently corrected for sample absorption, polarization, incoherent or Compton scattering and finally normalized (4)), the distribution functions have a more complicated mathematical treatment from experimental data but their physical meaning remain much more evident than that of the structure factors. The so called radial distribution function  $RDF(r)$  defined as:

$$RDF(r) = 4\pi r^2 \rho(r) \quad (6)$$

(where  $\rho(r)$  is the local atomic density at a distance  $r$  from a given atom), measures the number of atoms in a spherical shell of radius  $r$  and thickness unity, and verifies:

$$\lim_{r \rightarrow \infty} RDF(r) = 4\pi r^2 \rho_0$$

(with  $\rho_0$  being the mean atomic density of the glass). By integration of the  $RDF(r)$  between two consecutive minima, one can compute the coordination number, that means, the number of atoms located between distances  $R_l$  and  $R_u$  from

a given atom:

$$Z^p = \int_{R_1}^{R_u} \text{RDF}(r) \, dr \quad (7)$$

where  $R_1, R_u$  define usually the minima just by a maximum of the  $\text{RDF}(r)$  determining the  $p$ -th shell and therefore the  $p$ -th coordination number  $Z^p$ . Although the  $\text{RDF}$  is quite useful, the pair probability function  $g(r)$  is more closely related to the scattering pattern (as we shall see later) and is defined as follows:

$$g(r) = \frac{\rho(r)}{\rho_0} \quad (8)$$

where  $\lim_{r \rightarrow \infty} g(r) = 1$ .

The most frequently used distribution function is, however, the so called pair correlation function (also called the reduced atomic distribution function)  $G(r)$ , which can be expressed, following the Faber-Ziman formalism, as:

$$G(r) = 4\pi r \rho_0 [g(r) - 1] = 4\pi r [\rho(r) - \rho_0] \quad (9)$$

verifying  $\lim_{r \rightarrow \infty} G(r) = 0$ .

This atomic distribution function has the advantages, in comparison with those previously seen, that the density fluctuations can be more clearly appreciated and that his expression as function of the structure factor is simpler, which can be shown in the following:

$$G(r) = 4\pi r \rho_0 [g(r) - 1] = \frac{2}{\pi} \int_0^{\infty} Q[S(Q) - 1] \text{sen}(Q \cdot r) \, dQ \quad (10)$$

$$\begin{aligned} S(Q) &= 1 + 4\pi \rho_0 \int_0^{\infty} r [g(r) - 1] \frac{\text{sen}(Q \cdot r)}{Q} \, dr \\ &= 1 + \int_0^{\infty} G(r) \frac{\text{sen}(Q \cdot r)}{Q} \, dr \end{aligned} \quad (11)$$

The total pair correlation function can be written also as a function of the partial terms like:

$$G^{FZ}(r) = \sum_{i,j} \frac{c_i c_j f_i f_j}{\langle f \rangle^2} G_{ij}(r) \quad (12a)$$

$$G^{AL}(r) = \sum_{i,j} \frac{c_i c_j f_i f_j}{\langle f \rangle^2} G_{ij}(r) \quad (12b)$$

$$G^{BT}(r) = \frac{\langle f \rangle^2}{\langle f^2 \rangle} G_{NN}(r) + \frac{c_1 c_2 (f_1 - f_2)^2}{\langle f^2 \rangle} G_{CC}(r) + \frac{2 \langle f \rangle (f_1 - f_2)}{\langle f^2 \rangle} G_{NC}(r) \quad (12c)$$

in the Faber-Ziman, Ashcroft-Langreth and Bhatia-Thornton formalisms, respectively.

Two important features must be remarked:

- i) the expressions of the total structure factor and the total pair correlation function as function of the partial contributions in the Ashcroft-Langreth formalism are asymmetric, and
- ii) the partial distribution functions ( $g_{ij}(r)$ ,  $\rho_{ij}(r)$  and  $G_{ij}(r)$ ) are the same in the Faber-Ziman and the Ashcroft-Langreth formalisms. This is not true, however, for the partial structure factors.

The  $G_{NN}(r)$  partial pair correlation function in the BT formalism represents the topological short range ordering (TSRO), whereas  $G_{CC}(r)$  are related to the chemical short range ordering (CSRO) and  $G_{NC}(r)$  represents the size effect, which is caused by different atomic volumes of the components (see, for example, Wagner and Ruppensberg (5a) or Chieux and Ruppensberg (5b)), and equals zero in the case of substitutional alloys.

Unfortunately, the distribution functions, being one dimensional, are not capable of discriminating between closely related models of the structure of metallic glasses, such as the dense random packing of hard spheres or the polyhedral model (that we shall see in the second part of this talk), and more details about the structure must be determined. For this reason, it is of the greatest impor-

tance to calculate the partial structure factors (which means also the partial distribution functions), in order to determine the local atomic arrangement in metallic glasses. In the case of binary alloys, three partial functions,  $S_{11}(Q)$ ,  $S_{12}(Q)$  and  $S_{22}(Q)$  (or their corresponding  $S_{NN}(Q)$ ,  $S_{NC}(Q)$  and  $S_{CC}(Q)$ ) must be calculated. This can be done quite readily, in principle, by measuring three independent total scattering functions  $S(Q)$  and solving for the three unknowns  $S_{ij}(Q)$  or  $S_{NC}(Q)$ , since  $S(Q)$  is the weighted sum of the three partial functions. The weighting factors depend upon the atomic concentration  $c_i$  and the scattering factor  $f_i$  of the element  $i$  in the alloy, as we can see following, for example, eq. (4):

$$S_{\text{Tot}}(Q) = w_{11}S_{11}(Q) + w_{22}S_{22}(Q) + 2w_{12}S_{12}(Q) \quad (13)$$

with:

$$w_{ij} = c_i c_j f_i f_j / \langle f \rangle^2$$

(Faber-Ziman formalism). Equation (13) can be re-written in matrix notation like:

$$[T(Q)] = [w(Q)] [R(Q)] \quad (14)$$

with:

$$[T(Q)] = \begin{bmatrix} S_{\text{Tot}}^1(Q) \\ S_{\text{Tot}}^2(Q) \\ S_{\text{Tot}}^3(Q) \end{bmatrix} ; [R(Q)] = \begin{bmatrix} S_{11}(Q) \\ S_{22}(Q) \\ S_{12}(Q) \end{bmatrix}$$

$$[w(Q)] = \begin{bmatrix} w_{11}^1 & w_{22}^1 & w_{12}^1 \\ w_{11}^2 & w_{22}^2 & w_{12}^2 \\ w_{11}^3 & w_{22}^3 & w_{12}^3 \end{bmatrix}$$

where  $[R(Q)]$  corresponds to the three partial structure factors,  $[w(Q)]$  represents the weighting factors for different scattering abilities, and  $[T(Q)]$  are the total structure factors observed experimentally for each independent event. The solution for the partial structure factors can be written as:

$$[R(Q)] = [w(Q)]^{-1} [T(Q)] = [V(Q)] [T(Q)] \quad (15)$$

A unique solution is found for  $[R(Q)]$  only if the determinant of  $[w]$  is different from zero. A measure of how good the equations system is conditioned is given by  $|w|_h$ , the normalized determinant of the system of three equations whose value can be, at most 1. Unfortunately, in most experimental cases, the normalized determinant for metallic glasses is very small, giving thus an indication of the difficulties to be expected in order to solve equation (15). That means, even very small experimental uncertainties lead to drastic uncertainties in the resulting partial functions, making therefore very difficult to decide whether a definite structural model describes the atomic arrangement of a glassy metal in a better way than others.

In order to separate the partial structures measuring the total structure factors by three different experiments, several methods are used. In principle they can be divided into four kinds:

- a) the three different radiation techniques using X-rays, neutrons and electrons (see, for example, Paasche (6));
- b) the isotope-enrichment technique for neutron diffraction in which the scattering power of the constituents are varied by using different isotopes (see Sperl (7));
- c) the polarized neutron technique which is applicable to magnetic materials; d) the anomalous scattering technique for both X-rays and neutrons (see Waseda (8)) and of course;
- e) any assortment of the above techniques as, for example a combination of X-rays with the isotope-enrichment technique (Nold (9)) or a combination of X-rays with the polarized-neutron technique (see, for example, Sadoc and Dixmier (10)). From all these attempts to separate the partial structures the most succesful was that performed by Sperl (7) for the  $Ni_{81}B_{19}$  metallic glass, using the isotope enrichment technique for neutron diffraction, who had a value of 0.51 for the determinant of  $|w|_n$ .

With the improvement of the experimental techniques, better data can be obtained because of the new developments of more intense sources and efficient detectors.

Some of these techniques (energy dispersive X-ray diffraction (EDXD) or time of flight measurements with pulsed neutrons) enable us to carry out measurements of the scattered intensities up to  $Q=40\text{\AA}^{-1}$ , which permits the evaluation of high resolution Fourier transforms which can provide a more detailed description of nearest neighbour interactions in binary metallic glasses. Measurements of extended X-ray absorption fine structure (EXAFS) and Mossbauer spectroscopy provide us a rather accurate information about the local atomic structure. For a more detailed description of the separation methods and of these new techniques see, for example, Waseda (8), Hafner (11) or Egami (12).

**STRUCTURAL MODELS:** A comparison between the structure of the amorphous state and that of the liquid state shows (see, for example, Waseda (8)) that the general features of the structure of the former are similar to those of the latter, except for a shoulder on the second peak observed in both  $S(Q)$  and  $g(r)$  in the amorphous diagrams. From the similarity of the gross features of the  $S(Q)$  and  $g(r)$  for metallic glasses, the fundamental configuration of atoms should be considered as liquid like. On the other hand, the ratio  $(r_2/r_1)$  between the positions of the second peak ( $r_2$ ) and of the first peak ( $r_1$ ) in the amorphous state (about 1.67), is rather similar to the values obtained for the  $c/a$  ratio in close packed hexagonal structures (1.63) and for the  $(r_3/r_1)$  ratio in a fcc structure (1.73), falling rather far away from the values of  $(r_2/r_1)$  and  $(r_3/r_1)$  for the liquid state (about 1.86 and 2.70 respectively). This implies that the short range order of near neighbours in metallic glasses is affected more or less by the atomic arrangement of the crystalline state.

From these considerations the two basic tendencies that exist in the formulation of structural models for metallic glasses can be well understood: on one side (i) the microcrystalline disorder models (also called stereochemi-

cally defined models), on the other side (ii) the topological disordered models.

#### i) Microcrystalline models

These models are based on the similitudes that have been observed between the short range order in metallic glasses and the corresponding crystalline phase at the same concentration or in the same concentration range. Hamada et al (13) proposed a structural model for the Fe-B metallic glass, consisting on "crystalline-embryos" with a bcc structure (similarly to crystalline Fe<sub>3</sub>B) surrounded by a statistical atomic distribution in the boundary regions between the embryos.

The total structure factor  $S(Q)$  calculated with this model reproduces acceptably some structural features seen with the experimental  $S(Q)$  like the reduction of the shoulder on the right hand side of the second maximum of the structure factor with increasing boron content.

A good agreement between the model and the measured data was also observed in Ag<sub>48</sub>Cu<sub>52</sub> (14) and Fe<sub>75</sub>P<sub>25</sub> (15) metallic glasses, proposing in both cases a fcc structure for the crystalline embryos.

Kuhnast et al (16) presented a microcrystalline model to explain the structure of amorphous Ni<sub>66</sub>B<sub>34</sub>, starting from the crystalline phase Ni<sub>3</sub>B with which he could successfully described the local ordering for  $r < 6\text{\AA}$ . Although a good agreement could be found in all these cases, efforts to obtain agreement for other materials have been unsuccessful. Cargill (17) has showed that in order to fit the experimental structure factors with these models, too many parameters (such as sizes and strain distributions of the microcrystals) must be varied.

We can now summarize the basic properties of the microcrystalline models, following Gaskell (18):

- i) In a A<sub>1-x</sub>B<sub>x</sub> alloy, one of the possible local configuration of A and B atoms is preferred basically on energetic grounds.
- ii) This arrangement thus represents the dominant coordination polyhedron over a wide range of concentrations  $C_A$

and radius ratios  $R_A/R_B$ , being the coordination number of the B species (the smaller atoms) relatively independent of these quantities.

iii) Differences in structure with concentration and character of A and B atoms, and the distinction between amorphous and crystalline phases, are described by variations in the way local structural units are interconnected.

iv) There is a potential local structure equivalence of the crystalline and amorphous phases.

v) In this kind of models, the long range order disappears because of the random orientation of the microcrystals.

Historically, the validity of such "embryo-models" was supported by some X-ray small angle scattering and transmission electron microscopy measurements that showed the existence of a number of inhomogeneities in the amorphous state.

#### ii) Topological disorder models

These structural models (often called homogeneous disordered models) can be separated in two main groups: a) dense random packing of hard spheres (DRPHS); b) dense random packing of coordination polyhedra (DRPCP).

a) DRPHS Models: They are the natural extension of the structural models originally employed in the description of monoatomic liquids and are based on the general similarities of  $S(Q)$  and  $g(r)$  between the liquid and amorphous states. The starting point of all these models is the hard sphere model first proposed by Bernal (19). The spheres are dense in the sense that no "internal holes" great enough to accommodate another sphere can be found, and they are at random because only weak interactions are present between spheres separated by four or five atomic diameters. That means, there are no regions of long range order as in the crystalline structures.

In Bernal's model, the topology is described in terms of polyhedra (also called "Bernal holes") in which the vertices are defined by the sphere centers. Bernal found 5 different types of polyhedra: 1) tetrahedra, 2) octahedra,

3) archimedean trigonal prisms, 4) archimedean antiprisms, 5) tetragonal dodecahedra. The introduction of archimedean polyhedra prevents from any long range order and from the realization of the ideal structure precisely. This model was later improved by J.L. Finney (20), who obtained the radial distribution function for a dense random packing of about 8000 hard spheres with much better resolution than previously available.

Finney's model was used to fit the experimental values of the reduced radial distribution function  $G(r)$  obtained by Cargill (17) for the  $Ni_{76}P_{24}$  metallic glass. The results were rather satisfactory since we take into account that only one parameter namely the atomic size ( $R_{Ni}=R_P$ ) was varied.

Polk (21) proposed a model consisting of a Bernal structure (DRPHS) which is primarily metallic, with the metalloid (the smaller atoms) filling some of the larger holes inherent in the random packing. Polk suggested that it is this special relationship between the metal and the metalloid which could lead to the stabilization of the amorphous structure. Unfortunately, none of the holes are as large as originally believed by Polk, not allowing, therefore, their filling up by the metalloid atoms. Polk (22) later generalized his view of the DRPHS void-filling model to allow the metal atoms to occupy random packing structures somewhat less dense than those of Bernal and Finney, which should provide more larger holes to accommodate the metalloid atoms.

Ichikawa (23) constructed a DRPHS model suggesting some modifications of Bennett's criterion (24). Bennett's algorithm consisted on adding spheres to an initial equilateral triangle formed by three spheres, enumerating all possible sites for which an added sphere would be in hard contact with three spheres already in the cluster, but would not overlap with any of them and selecting among them the nearest to the center of the cluster. In his model, Ichikawa introduced a measure of the tetrahedral perfection of the pocket formed by three spheres, defined as:

$$T = r_{ij}^{\max} / (R_i + R_j) \quad (16)$$

where  $r_{ij}^{\max}$  is the maximum distance between the centers of spheres  $i$  and  $j$  in the distribution of three spheres, and  $R_i$  and  $R_j$  are their radius respectively. In this model the assembly of hard spheres with diameter  $T$  is considered, in which the tetrahedron of four spheres is first constructed. Then the other spheres are arranged in a growing process of tetrahedral clusters, under the condition that the desired sphere occupies only the position of having been in contact with three spheres of surface within the distance  $T$ . Thus, deviation from the condition  $T=1.0$  allows the formation of a slightly deformed tetrahedron. Ichikawa suggested that the model calculation with the parameter  $T=1.2$  (which corresponds to a relatively rigid packing of tetrahedrons) is more compatible with the experimental data for the amorphous state. He showed also that the packing became obscure for  $T=2.0$ , that is the fundamental tetrahedra are distorted, and in this case the splitting of the second peak in both  $S(Q)$  and  $g(r)$  is no longer observed, a fact that is in good agreement with the experimental results for the liquid state. This means that the amorphous structure requires something to be added to the simple model structure of hard sphere liquids. In fact more rigid configurations of atoms must be considered, this corresponding to the introduction of the parameter for tetrahedral perfection.

The main problem of this kind of model is that if atomic arrangements in the amorphous metal-metalloid alloys were truly like those of spheres in such dense random packings, then the metalloid atoms would have the same average surroundings as the noble or transition metal atoms, a fact that, as showed by several experimental observations, is unlikely. Binary DRPHS models with smaller spheres representing metalloid atoms and with no metalloid-metalloid nearest neighbours is probably a more realistic structural model for the metal-metalloid amorphous alloys, than simple dense random packing of equal size hard spheres

with metal and metalloid atoms occupying random sites. Such a model was proposed by Sadoc et al (25) who used Bennett's algorithm to construct hard sphere packings with two sizes of spheres in which the smaller spheres, representing metalloid atoms, were not allowed to occupy adjacent sites. The introduction of small spheres requires the large spheres to form a looser random packing to provide enough large holes to accommodate the small spheres. This tendency could be even observed in the liquid state, as suggested by this author (26) for the Ni-B melt.

Cargill and Kirkpatrick (27) obtained a rather good fitting of the experimental RDF( $r$ ) with a binary DRPHS model using Bennett's global criterion for rare earth-transition metal alloys, namely  $Tb_{33}Fe_{67}$ ,  $Gd_{36}Fe_{64}$  and  $Gd_{18}Co_{32}$ . Waseda et al (25,28) used a binary model based on the previous works from Ichikawa (23) and Cargill and Kirkpatrick (27), to describe the experimental behaviour of the partial structure factors  $S_{ij}(Q)$  and pair distribution functions  $g_{ij}(r)$  for amorphous Fe-P and Cu-Zr. An important improvement of binary DRPHS models was that made by Connell (29) and von Heimendahl (30) who relaxed the model through energy minimization of the assumed pair potential. It is important to note that the relaxation does not conserve the original topology, which means that one has to make a topological analysis after the structure was relaxed. Boudreaux (31) relaxed a DRPHS model using a Lennard-Jones potential for the Fe-B system at different concentrations finding a coordination number of 6.6 around the boron atoms. This leads Finney (32) to propose a model based on local structural units (trigonal prisms) with six iron atoms around a boron one, like in crystalline  $Fe_3B$  (cementite structure) with the rest of the boron atoms distributed as a "statistical adhesive" between the molecular units. Some investigators (see, for example, Gaskell (18)) questioned this criterion, pointing out that the model gives a poor information about that "statistical cement". Another improvement of the DRPHS models has been carried out through softening of the hard spheres,

allowing them to oscillate around their equilibrium sites with a defined frequency which corresponds to a given temperature. This leads to a broadening of the first coordination shell in the pair correlation functions. With such dense random packing of about 5000 soft spheres, Blétry (33) obtained rather satisfactory results to fit the very accurately experimental results of the partial structures determined by Spexl (7) with the  $\text{Ni}_{81}\text{B}_{19}$  amorphous alloy. Other calculations based on the same experimental data were made by Beyer and Hoheisel (34) using molecular dynamics and taking a Lennard-Jones potential for a system under conditions similar to those of the liquid state. Though this model made reasonable predictions for the values of the  $G_{\text{Ni-Ni}}(r)$  and  $G_{\text{Ni-B}}(r)$  partial pair correlation functions, the values of the experimental  $G_{\text{B-B}}(r)$  show considerable differences with those predicted by the model. Furthermore, the assumption that the glassy alloy could be handled as a binary liquid alloy on thermal equilibrium at high temperatures seems to be unlikely.

b) DRPCP models: The DRPHS models seen before start from the similarity of the pair correlation functions in the liquid and in the amorphous states. While this remains obviously true for the long and medium range structure, the more recent diffraction experiments support the point of view that the short range order in the amorphous phase may be similar to the crystalline structure. Thus one may begin with larger local units having the desired coordination and a topology borrowed from the crystalline structure. The model is built by a random stacking of these local units. In this sense some investigators (see, for example, Gaskell (19)) supported this kind of models because they allow a better description of the CSRO (chemical short range order) than the DRPHS models. The opposite argument is that the dense random packing of coordination polyhedra models doesn't take into account satisfactorily the random elements, namely the disorder. Two of the most important DRPCP models are those proposed by Takeuchi (35) and Wright (36) for monoatomic systems

based on geometrical considerations. As showed by Hoare and Pal (37), the icosahedron is the 13-atoms cluster configuration with the lowest energy. The icosahedron can be separated in 20 almost regular tetrahedra. Considering all atoms of the icosahedron as equivalent, the whole amorphous structure can be idealized as an array of tetrahedral units. The model is constructed in such a way that each new tetrahedron is put above one of three faces of the previous tetrahedron so that the vertex of the new tetrahedron comes to the farthest distance from the origin. The average coordination number obtained in this way for the first shell is about 13.4 which agrees rather well with the values obtained experimentally for most of the metallic glasses. Sperl (7) presented a very good agreement between the normalized atomic distances  $(r_i/r_1)_{i=1,2,\dots}$ , obtained from his experimental partial pair correlation function  $G_{Ni-Ni}(r)$  and the values taken from Wright's (36) and Takeuchi's (35) models. Other DRPCP models considering larger fundamental units have been presented, such as that of Kuhnast et al (16), who proposed a dense random packing of icosahedral units to describe the structure of amorphous  $Ni_{71}B_{29}$ . Finally, another important DRPCP model, successfully employed for the Pd-Si amorphous alloy, is that presented by Gaskell (38) who takes as fundamental units a trigonal prism (with 6 Pd atoms around a Si atom) as well as a trigonal prism capped with three half-octahedra (9 Pd atoms around a Si atom) with a similar topology as the cementite structure (crystalline  $Fe_3C$ ). The model was relaxed using Lennard-Jones potentials and supplementary conditions to maintain the coordination after the relaxation procedure. This structural model was also employed to reproduce the above mentioned experimental data of Sperl (7). The results were not very satisfactory: a better agreement between the model and the measured data for the pair correlation function would require a greater diameter of the metalloid atoms. Furthermore, the first boron-boron atomic distance calculated with this model is somewhat smaller than the one obtained from the experimental curves.

The essential features of the homogeneous disordered models (DRPHS and DRPCP) can be thus summarized as follows:

- i) In a  $A_{1-x}B_x$  amorphous alloy, the smaller atoms B, are mainly surrounded by A atoms. This has been experimentally demonstrated for some glassy metals and it seems to be a general phenomenon in these materials.
- ii) The atomic arrangement in local coordination polyhedra is essentially at random and dictated by geometrical (radius ratio) and compositional factors alone. There is no preference, energetic or otherwise, for a particular local symmetry or coordination number so that the average local geometry becomes a function of the radius ratio and the concentration of each species (as pointed out by Jansen (39)).

**CONCLUSIONS:** We can summarize the former discussions saying that three main descriptions can be found for the structure of metallic glasses: a) Stereochemically defined models; b) Dense random packing of hard or soft spheres; and c) Dense random packing of polyhedral units.

There are obvious similarities between these three types of models. In each case the structure consists of a dense, space filling arrangement of local structural units. The unit, however, can range from a single atom through a group containing, say, five or seven atoms to a cluster of several hundreds. The topological disordered models, however, seem to describe the structure of glassy metals in a better way than the microcrystalline models and to provide a more realistic framework in which one can analyze the mechanical, magnetic and electronic properties of these materials. In view of the increased information contact it is of the greatest importance that not only total but also partial distribution functions might be accurately determined for these amorphous alloys and in this way there would be a lot of experimental work to do.

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