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Basic parameters for the short-range order of amorphous ternary alloys with applications to practical cases

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A procedure was considered for determining theoretical expressions of the area under the first radial distribution function (RDF) peak, and of the relative co-ordination numbers, n_{ij} which depend on the co-ordination hypotheses and on the numbers of bonds between elements of a single type of pair. In this method, two important facts were taken into account. First, the products of atomic factors are functions of s (the scattering vector module) and so they cannot always be considered constant; they were therefore approximated by polynomic functions which best fitted the results obtained from the atomic factors given in international tables. Secondly, consideration of the influence of the structural hypotheses (co-ordinations, existence of certain types of bond) on the area and co-ordination numbers mentioned enabled the most probable local order to be postulated. In order to test the reliability of this method, the method was applied to a set of alloys, quoted in the literature, and the theoretical results obtained agreed very satisfactorily with the experimental values.

1. Introduction

Knowledge of amorphous solids is one of the most active fields of research in the physics of condensed materials today [1]. The great interest in these materials is largely due to their ever increasing applications in modern technology. Their possibilities in the immediate future are huge, based on characteristic properties such as electronic-excitation phenomena, chemical reactivity and inertia, and superconductivity.

An amorphous solid is a material which does not have the long-range order (periodicity) characteristic of crystalline materials, although it does have a certain local order in its bonds with its first neighbours. *Amorphous* and *non-crystalline* are therefore synonymous terms, whereas a *glass* is a non-crystalline material exhibiting a characteristic transition temperature [2] from the more energetic glass phase to the minimal-energy crystalline phase. The temperature at which the glass–crystal transition takes place is proportional to the average co-ordination of the material [3], so an understanding of its local order is very important, as this can be related to other physical properties of the material.

The method which, to date, has proven to be most efficient for structural research in all types of solids is the interpretation of the diffraction phenomenon of radiation diffracted by the solid. Although several types of radiation are used for detecting atomic positions, the most frequently used is X-ray radiation, because of its simple technology. X-rays were used to obtain structural information on the glassy materials considered in this work.

When interpreting the radial atomic distribution function (RDF), obtained from the X-ray diffraction (XRD) intensities of a glassy solid, the area under the first peak of the curve is related to the relative co-ordination numbers, n_{ij}, in order to postulate the short-range order of the material. It is a well-known fact that this area also depends on the atomic numbers of the constituent elements of the alloys, when the products of the atomic scattering factors, $R_{ij}(s) = f_i(s)f_j(s)/[\sum_i x_i f_i(s)]^2$, remain practically constant and equal to $Z_iZ_j/(\sum_i x_iZ_i)^2$ throughout the whole interval of s (the scattering vector module) in which the measurements are carried out. This is not always true, as in some cases $R_{ij}(s)$ varies considerably with s [4].

This work takes into account that the atomic scattering factors are functions of Bragg's angle [4] and the co-ordination hypotheses for a certain element in the alloy. These two considerations made it possible to calculate, using the literature [5–8], theoretical expressions of the parameters which depend on the alloy, and of the co-ordination hypotheses which appear in the theoretical expression of the area under the first peak, and in those of the average co-ordination numbers. The theoretical results were applied to an analysis of the short-range order of different glassy alloys; the results agree with the experimental values.

2. Theoretical background

The classical theory of electromagnetic-wave diffraction, for a spatial configuration of atoms, makes it possible to deduce a relationship between the diffracted intensity in a given direction and the relative positions of the atoms in the material. When this relationship is applied to a glassy material in which it

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is possible to postulate that the positions are randomly oriented, the intensity diffracted in each direction, expressed in electronic units (*e.u.*), is given by Debye's equation [9]

$$I_{e.u.} = \sum_{n,m} f_n f_m \frac{\sin sr_{nm}}{sr_{nm}} \qquad (1)$$

where $s = (4\pi/\lambda)\sin\theta$, f_n and f_m are the scattering factors of atoms n and m, respectively, and r_{nm} is the distance between those atoms.

The problem of obtaining structural information on a glassy solid involves determining the relative positions between the atoms of the material from a set of diffracted intensities, and in this sense Zernicke and Prins [10] applied a Fourier transformation to a function of the diffracted intensities, thus obtaining an expression for the variation of the atomic density with the distance to an arbitrary atom in the material.

A strict evaluation of Debye's equation involves considering the atomic scattering factors as functions of Bragg's angle via the magnitude s, a consideration which was taken into account by Finbak [11], and later by Waser and Schomaker [12] and even later by Warren [4] According to Warren, the following relationship is found for the RDF

$$\frac{2r}{\pi}\sum_{ij} x_i \frac{n_{ij}}{r_{ij}} P_{ij}(r) = 4\pi r^2 \rho_0 + rG(r) \qquad (2)$$

where x_i is the atomic fraction of element i, $G(r)$ is the Fourier transformation of the interference function, ρ_0 is the average atomic density of the material, r_{ij} is the distance between an i-type atom and a j-type atom, and the function $P_{ij}(r)$ is defined by

$$P_{ij}(r) = \frac{1}{2}\int_0^{s_m} \frac{f_i(s)f_j(s)}{\left[\sum_i x_i f_i(s)\right]^2}\cos s(r - r_{ij})\,\mathrm{d}s \qquad (3)$$

where s_m is the maximum value of s for which experimental data are available. By defining a function, $\rho(r) = (2\pi^2 r)^{-1}\sum_{ij} x_i n_{ij} r_{ij}^{-1} P_{ij}(r)$, representing the local atomic density affected by the Fourier transformation of the atomic factor products, Equation 2 changes into

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + r\,G(r) \qquad (4)$$

which represents the average number of atoms surrounding a reference atom at a distance r.

When evaluating the average number of first neighbours of an arbitrary atom (that is, its average coordination), it is necessary to obtain the area under the first RDF peak given by the expression

$$\text{Area} = \frac{2}{\pi}\sum_{ij} x_i \frac{n_{ij}}{r_{ij}} \int_a^b r\,P_{ij}(r)\,\mathrm{d}r \qquad (5)$$

where a and b are the abscissae of the limits of the peak.

Some authors ignore this expression, since they consider that the traditional relationship of the area as a function of the atomic numbers of the elements is equally accurate in all possible cases; but this is true only when the atomic scattering factors, f_i, can be considered to be independent of s and therefore to be constant and equal to the atomic numbers Z_i. There are, however, practical cases in which it may be observed that the approximation of considering the functions R_{ij} to be constant and equal to $Z_i Z_j/(\sum_i x_i Z_i)^2$ is sufficiently inaccurate to influence the short-range order postulated for the material. In relation to this, Fig. 1 [4] shows R_{ij} versus s for all possible pairs of elements in amorphous SiO_2. The traditional relationship of the area, based on the constancy of the atomic scattering factors, is obviously a good approximation for the pair Si–O, but is very inaccurate for the pairs Si–Si and O–O. A relatively broad, though not complete, analysis of cases such as amorphous SiO_2 seems to make it advisable to express the products $R_{ij}(s)$ by mathematical functions which best fit the results obtained from the atomic scattering factors given in international tables. In this sense, Vázquez and Sanz [5] have developed an analytical method for evaluating the area under the first RDF peak in which the products $R_{ij}(s)$ are expressed by n-order polynomials in s. When these polynomials are of the first order, as is frequently the case, Vázquez and Sanz [5] proposed the following expression:

$$\text{Area} = \frac{2}{\pi}\sum_{ij} x_i n_{ij} A_{ij} \qquad (6)$$

with

$$A_{ij} = \frac{1}{r_{ij}}\int_a^b rP_{ij}(r)\,\mathrm{d}r$$

$$= \frac{1}{2r_{ij}}[B_{1ij} + B_{2ij} + r_{ij}(B_{3ij} + B_{4ij})]$$

and the addends, $B_{kij} (k = 1, 2, 3, 4)$, being given by the relationships

$$B_{1ij} = (A_{0ij}s_m + A_{1ij})\frac{\cos s_m a'_{ij} - \cos s_m b'_{ij}}{s_m}$$

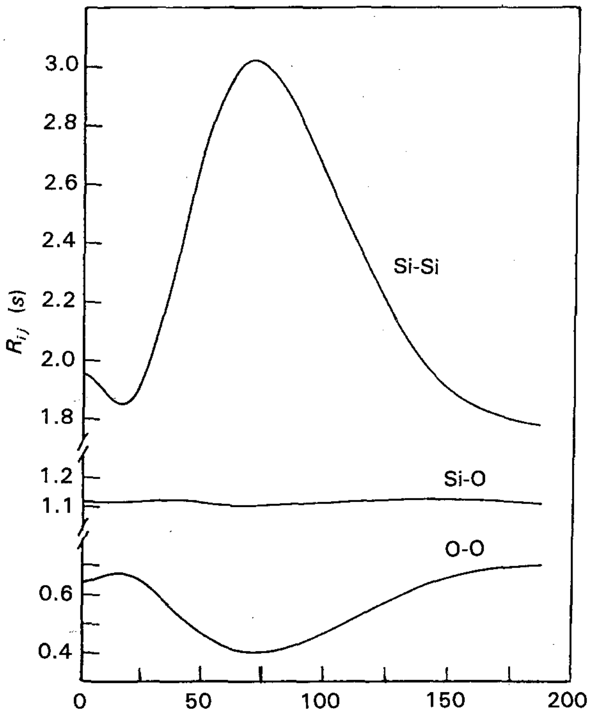

Figure 1 Representation of the functions $R_{ij}(s)$ in amorphous SiO_2.

$$B_{2ij} = A_{0ij}\ln\frac{|a'_{ij}|}{b'_{ij}}$$

$$B_{3ij} = \int_{a'_{ij}}^{b'_{ij}}\frac{\sin s_m x}{x}\mathrm{d}x$$

$$B_{4ij} = A_{0ij}\left[\frac{1-\cos s_m b'_{ij}}{b'_{ij}} - \frac{1-\cos s_m a'_{ij}}{a'_{ij}}\right]$$

where A_{0ij} and A_{1ij} are the slope and the zero-ordinate, respectively, of the straight regression line corresponding to the product of the scattering factors of atoms, i, j; and $a'_{ij} = a - r_{ij}$; and $b'_{ij} = b - r_{ij}$. In relation to this, Fig. 2 [13] shows the function $R_{ij}(s)$ for possible pairs of elements in amorphous $Al_{0.20}As_{0.20}Te_{0.60}$.

Equation 6 is, as may be observed, a function of the relative co-ordination numbers, n_{ij}, and therefore it is a function of the number of the chemical bonds, a_{ij}, between the i-type and j-type elements of the alloy. This fact made it possible to develop analytical methods [6, 7] for expressing the area under the first RDF peak as a function of the co-ordination of one type of element in the material and of the number of bonds between pairs of atoms.

2.1. Basic parameters which depend on the alloy and on the co-ordination hypotheses

A theoretical evaluation of the average co-ordination of a glassy alloy, from its RDF involves determining the area under the first peak of this function as accurately as possible. This parameter will influence the formulation of short-range-order hypotheses, so it is useful to relate this area to a parameter representing the postulated co-ordination for some element in the alloy. This will enable a co-ordination to be attributed to a certain element, according to its properties and to the co-ordination proposed in the literature for the same element in similar alloys. The postulated co-ordination is substituted in the theoretical expression of the area, and the value obtained for this magnitude is compared to the area enclosed by the first experimental RDF peak. If the difference between the two values is within experimental error, the co-ordination hypothesis may be considered adequate; otherwise, the hypothesis should be rejected and another one is tested. On the other hand, it is a well-known fact that, in glassy alloys, the absence of bonds between certain types of elements may be postulated, either because of the low concentration of one of the elements, or because the energy of that type of bond makes its occurrence very improbable in comparison with other bonds. It is therefore very important that the theoretical expression for the area should reflect the existence or non-existence of the possible bonds between the different pairs of elements in the compound, in order to compare the experimental area to the theoretical areas obtained through different hypotheses on bonded elements. In this sense, Vázquez *et al.* [7] proposed theoretical expressions for the area which reflect both the co-ordination hypotheses for a certain element, and the possible absence of different types of bond in the material.

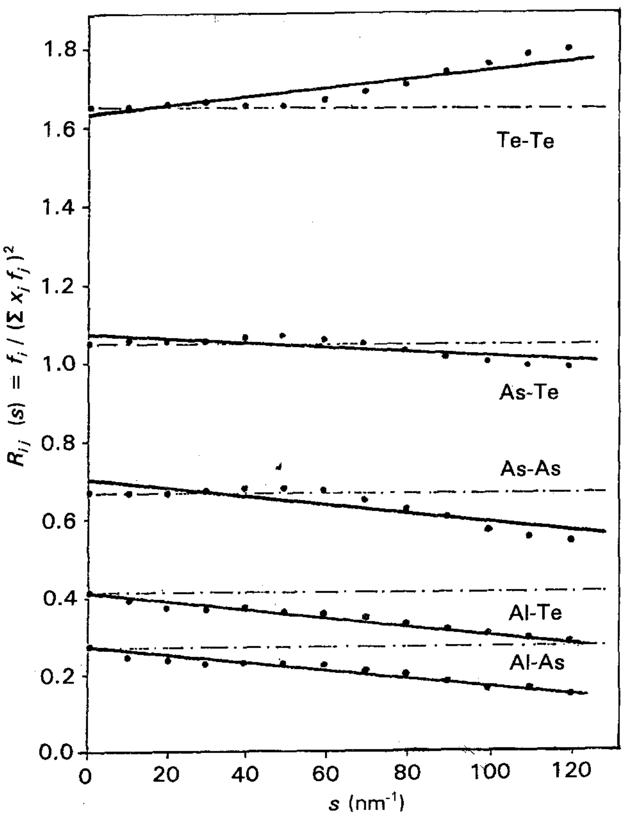

Figure 2 Straight regression lines fitted to the values of $R_{ij}(s)$ in the alloy $Al_{0.20}As_{0.20}Te_{0.60}$.

The structural information obtained from the analysis of the experimental RDF, together with some physical–chemical properties of the alloys and their elements, permits hypotheses on the local order of amorphous materials. Consider a ternary glassy alloy, $A_{a'_1}$ $B_{a'_2}$ $D_{a'_3}$, for every 100 atoms of material the hypotheses are as follows.

1. Element A has co-ordination N, no matter what the composition of the alloy, and the average co-ordination numbers of this element with all those bonded to it are proportional to their respective percentage concentrations.
2. The total number of i-type bonds, a_i, is given by

$$a_i = 2a_{ii} + \sum_{i \neq j} a_{ij} \tag{7}$$

where a_{ij} is the number of chemical bonds between i-type and j-type elements.

3. If the normal co-ordinations of the different elements in the sample are called C_i, and it is assumed that element A has a coordination $N(N \gtrless C_1)$, the number of bonds of this type of atom is

$$a_1 = Na'_1 = C_1a'_1 \pm |x|$$

$|x|$ being the variation in the number of bonds of the element, when its co-ordination changes from C_1 to N.

4. When the co-ordination of element A changes, the co-ordinations of elements B and D may increase or decrease, so the number of bonds of these elements is given by

$$a_i = C_ia'_i \pm 1|y_i|, \quad (i \neq 1)$$

where $|y_i|$ represents the variation in the number of i-type bonds.

Taking these hypotheses into account, Vázquez *et al.* [8] have deduced the following relation using Equation 5 and results in [6, 7]:

$$\text{Area} = \frac{1}{50\pi}\left[(h + \beta A_{22} - \delta Q)N + \alpha A_{22} + \gamma Q + P\left(\sum_{i=j\neq 1} A_{ij} - \sum_{i,j\neq 1, i\neq j} A_{ij}\right)a_{ij}\right] \quad (8)$$

where h, α, β, γ and δ are characteristic parameters of each alloy; P is a parameter equal to 2 when $i = j$ in the variable a_{ij}, and equal to -1 if $i \neq j$; and Q is defined by the relationship

$$Q = \delta_{ij} \sum_{i,j\neq 1, i\neq j} A_{ij} + (1 - \delta_{ij}) \sum_{i=j\neq 1} A_{ij}$$

δ_{ij} is the Kronecker delta.

The previous expression of the theoretical area enables, according to the experimental area, the variation interval of the number of bonds between the elements of a certain pair to be found, for each co-ordination hypothesis. This fact is very useful when choosing the most adequate co-ordination for the elements which usually make up compounds with different co-ordinations.

2.2. Relative co-ordination numbers

The relative co-ordination numbers, n_{ij}, of the different pairs of elements of a compound, are a very interesting set of parameters when postulating the short-range order of a glassy solid. These parameters, which represent the average number of j-type atoms surrounding an i-type atom, can be related to the co-ordination, N, attributed to a certain element; bearing in mind the restrictions imposed by the intrinsically positive nature of n_{ij}, it is possible to choose the most adequate value for N.

When postulating the absence of bonds between certain types of element, the corresponding n_{ij}s are zero. As it is always possible to assign the subscript 1 to one of these types, considering the hypothesis mentioned above to the effect that the average co-ordination numbers of this element with all the elements, k, bonded to it, are proportional to their respective percentage concentrations, the following expressions are obtained:

$$n_{1k} = \frac{a'_k N}{\sum_k a'_k}, \quad n_{k1} = \frac{a'_1 N}{\sum_k a'_k}$$

which depend on the co-ordination attributed to element A. Bearing in mind that the relative co-ordination numbers are given by $n_{ij} = a_{ij}/a'_i$, expressions can be deduced for the $n_{ij}(i, j \neq 1)$ enabling the short-range order of the solid to be hypothesized.

From Equation 7, Vázquez *et al.* [8] deduced the following expressions for the co-ordination numbers $n_{ij}(i, j \neq 1)$ as functions of the number of a_{ij} bonds:

$$\begin{aligned} n_{22} = \Bigg\{\alpha + \gamma(1 - \delta_{ij}) + \Bigg[(\beta - \delta(1 - \delta_{ij}))\sum_k a'_k \\ + a'_1(\delta_{ij} p a'_3 - q a'_2)\Bigg] N\left(\sum_k a'_k\right)^{-1} + P a_{ij}\Bigg\}(a'_2)^{-1} \\ n_{23} = \Bigg\{\left[\gamma - \left(\delta \sum_k a'_k + a'_1 p a'_3\right) N \left(\sum_k a'_k\right)^{-1}\right]\delta_{ij} \\ + (1 - 3\delta_{ij}) a_{ij}\Bigg\}(a'_2)^{-1} \qquad (9) \\ n_{33} = \Bigg\{\left[\gamma - \left(\delta \sum_k a'_k + a'_1 p a'_3\right) N \left(\sum_k a'_k\right)^{-1}\right](1 - \delta_{ij}) \\ - (1 - 3\delta_{ij}) a_{ij}\Bigg\}(a'_3)^{-1} \end{aligned}$$

condensing, by the symbol δ_{ij}, the two possible expressions for each of the co-ordination numbers deduced. The fact that these numbers must be positive or zero makes it possible to find the variation of the number of bonds, a_{ij}, for each value attributed to N. The intersection of this interval with the interval deduced from the experimental area, is extremely useful for choosing the value of N which best agrees with the structural information supplied by the RDF, when postulating the local order of the material.

3. Application to practical cases

The method described in the literature [8], for determining the parameters enabling postulation of the short-range order of an amorphous solid, was applied to a relatively wide set of glassy alloys whose experimental data are quoted in the bibliography, shown in Table I. Different structural hypotheses were used, and the theoretical results obtained agree with the experimental data mentioned above, confirming the reliability of the theoretical method quoted. This work shows the theoretical analysis of the five alloys considered to be most representative of the set studied; their experimental values are shown in Table I. The constituent elements of each alloy were given the subscripts 1, 2 and 3 in the order in which they appear in the alloy. The co-ordination hypotheses used for obtaining the parameters which define the possible local order are shown in Table II, $C'_i (i = 2, 3)$ represents the co-ordination of element i in the compound. The existence of bonds between all pairs of elements in all alloys was postulated, except in M2, where the absence of Al–Al bonds was presumed [13].

TABLE I RDF characteristics of the alloys analysed

Alloy	First peak		Area (atoms)	Reference
	a (nm)	b (nm)		
M1, $As_{0.35}Se_{0.30}Te_{0.35}$	0.200	0.295	2.23	[14]
M2, $Al_{0.20}As_{0.50}Te_{0.30}$	0.210	0.300	2.36	[15]
M3, $Ge_{0.05}As_{0.20}Te_{0.75}$	0.235	0.305	2.05	[16]
M4, $Cu_{0.10}As_{0.40}Se_{0.50}$	0.220	0.280	2.93	[17]
M5, $Cu_{0.05}Ge_{0.15}Te_{0.80}$	0.220	0.315	2.54	[18]

TABLE II Co-ordination hypotheses

Alloy	N	C_1	C_2	C_3	C'_2	C'_3
M1	3	3	2	2	2	2
M2	4	3	3	2	> 3	> 2
M3	3	4	3	2	> 3	> 2
M4	4	1	3	2	> 3	> 2
M5	4	1	4	2	4	> 2

TABLE III Parameters related to the co-ordination hypotheses

Alloy	α	β	γ	δ
M1	− 10	0	70	0
M2	75	5	37.5	− 7.5
M3	− 101.56	2.89	165.80	3.95
M4	21.11	− 1.11	94.44	− 5.56
M5	− 95	− 5	155	− 5

Bearing in mind the structural hypotheses mentioned, and using the previously quoted theoretical expressions, the values shown in Table III were calculated, corresponding to parameters that depend on the specific characteristics of each alloy and on the co-ordination variations of its elements. Table IV shows the average bond lengths used for calculating the parameters A_{ij} and h (shown in Table V).

Using Equation 8, and the set of parameters obtained, the theoretical expressions of the area shown in Table VI were deduced. These expressions, together with the experimental areas (Table I) with an error of $\pm$ 0.1 atoms, made it possible to determine the variation intervals for $a_{ij}(i, j \neq 1)$, shown in Table VI. Equations 9 supply the relative co-ordination numbers, which, due to their intrinsically positive nature, define the new limits for the magnitude a_{ij}, shown in Table VI, together with their intersections with the intervals corresponding to the margin of error of the experimental area. These co-ordination numbers are such that the sum of those corresponding to one type of element with all those bonded to it is equal to the co-ordination postulated for that element. Thus, in the case of the alloy M5, where tetra-co-ordinated copper is postulated and the electrons necessary for the sp^3 hybridization of the copper are supplied by tellurium, the co-ordinations are: four for the copper and the germanium, and 35/16 for the tellurium. The same results are obtained by adding the n_{ij} with a fixed i and $j = 1, 2, 3$ for each element.

To illustrate the theoretical calculations, Fig. 3 shows the theoretical areas obtained versus the number of a_{ij} bonds $(i, j \neq 1)$ for three of the alloys studied. Fig. 3 shows the intervals in which the theoretical areas are simultaneously compatible with the experimental area and the corresponding co-ordination numbers.

The agreement between the theoretically deduced parameters and those obtained from the experimental data makes it possible to select the most adequate co-ordination hypotheses in order to establish the most probable short-range order of a glassy solid.

4. Conclusion

The theoretical method quoted enables different structural hypotheses to be tested in relation to the co-ordinations or the absence of some types of bond, since the expressions for the relative co-ordination numbers and for the area under the first RDF peak depend on these hypotheses. On the other hand, when deducing this area polynomial functions were used which best fitted the products of the atomic factors in those cases in which the magnitudes differ greatly from the approximate values, $Z_iZ_j/(\sum_i x_iZ_i)^2$; this fact

TABLE IV Average bond lengths for each alloy

Pair	r_{ij} (nm)					Reference				
	M1	M2	M3	M4	M5	M1	M2	M3	M4	M5
1–1	0.249	0.286	0.251	0.258	0.258	[19]	[23]	[27]	[30]	[30]
1–2	0.238	0.243	0.244	0.253	0.239	[20]	[24]	[27]	[31]	[20]
1–3	0.262	0.253	0.258	0.242	0.253	[21]	[20]	[20]	[31]	[20]
2–2	0.234	0.249	0.257	0.257	0.251	[20]	[19]	[28]	[28]	[27]
2–3	0.254	0.268	0.258	0.238	0.258	[20]	[25]	[28]	[20]	[20]
3–3	0.271	0.283	0.260	0.234	0.271	[22]	[26]	[29]	[20]	[22]

TABLE V Values of the parameters A_{ij} and h obtained $s_m = 120\ \mathrm{nm}^{-1}$

Alloy	A_{ij}						h
	1–1	1–2	1–3	2–2	2–3	3–3	
M1	0.9551	1.0574	1.8666	1.1449	1.6364	3.1249	41.5489
M2	0.1744	0.5242	0.8184	1.3318	2.3689	3.9239	− 20.6958
M3	0.6959	0.7017	1.1604	0.7423	1.2002	1.9377	3.3202
M4	1.2631	1.4828	1.4683	1.6928	1.6232	1.5726	13.2693
M5	0.5335	0.5684	1.0231	0.6797	1.0858	1.9951	2.6934

TABLE VI Theoretical results obtained for the different alloys

Alloy	Theoretical area	Co-ordination numbers $n_{ij}(i, j \neq 1)$	Variation intervals for the parameter $a_{ij}(i, j \neq 1)$		
			Defined by the n_{ij} parameters	Defined by the limits of error of the experimental area	Intersection of intervals
M1	$2.1791 + 0.0127a_{33}$	$n_{22} = (-4.75 + 2a_{33})/30$ $n_{23} = (33.25 - 2a_{33})/30$ $n_{33} = 2a_{33}/35$	$2.37 \leq a_{33} \leq 16.62$	$0 \leq a_{33} \leq 11.88$	$2.37 \leq a_{33} \leq 11.88$
M2	$2.5369 - 0.0033a_{23}$	$n_{22} = (112.5 - a_{23})/50$ $n_{23} = a_{23}/50$ $n_{33} = (37.5 - a_{23})/30$	$0 \leq a_{23} \leq 37.5$	$23.30 \leq a_{23} \leq 83.91$	$23.30 \leq a_{23} \leq 37.5$
M3	$1.9770 + 0.0036a_{33}$	$n_{22} = (-84.64 + 2a_{33})/20$ $n_{23} = (142.7 - 2a_{33})/20$ $n_{33} = 2a_{33}/75$	$42.32 \leq a_{33} \leq 71.35$	$0 \leq a_{33} \leq 48.06$	$42.32 \leq a_{33} \leq 48.06$
M4	$2.9290 + 2.42 \times 10^{-4}\ a_{33}$	$n_{22} = (20.67 + 2a_{33})/40$ $n_{23} = (96.68 - 2a_{33})/40$ $n_{33} = 2a_{33}/50$	$0 \leq a_{33} \leq 48.34$	$0 \leq a_{33} \leq 417.36$	$0 \leq a_{33} \leq 48.34$
M5	$1.9904 + 0.0064a_{33}$	$n_{22} = (-102 + 2a_{33})/15$ $n_{23} = (159 - 2a_{33})/15$ $n_{33} = a_{33}/40$	$51.0 \leq a_{33} \leq 79.5$	$70.25 \leq a_{33} \leq 101.5$	$70.25 \leq a_{33} \leq 79.5$

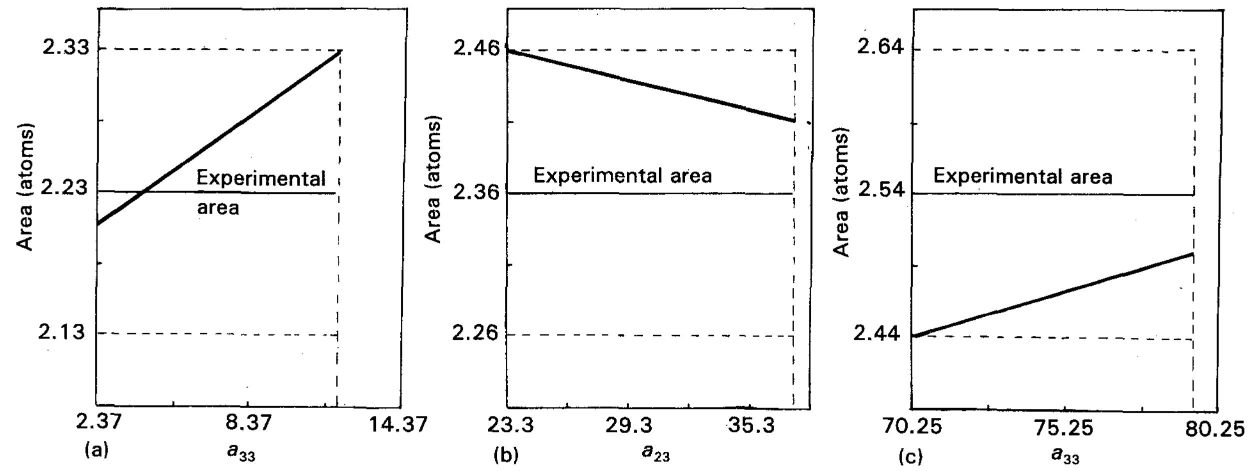

Figure 3 Area of the first RDF peak versus the number of a_{ij} bonds $(i, j \neq 1)$ for the alloys (a) M1, (b) M2, and (c) M5.

is of great interest when accurately evaluating the average number of first neighbours in a glassy alloy.

Because of the procedure used, it is possible to postulate certain structural characteristics and to obtain the average theoretical co-ordination of a solid from them; this was compared to the experimentally determined co-ordination. If the difference is within the experimental error, it may be considered that the hypotheses describe the most probable local order of the material.

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