Materials Chemistry and Physics, 32 (1992) 63–71

A theoretical method for determining basic parameters for the short-range order of amorphous ternary alloys, using X-ray diffraction

J. Vázquez, M. Casas-Ruiz, R. A. Ligero and R. Jiménez-Garay
Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real, Cádiz (Spain)

(Accepted February 18, 1992)

Abstract

A procedure was developed for determining theoretical expressions for the area under the first radial distribution function (RDF) peak, and for the relative coordination numbers (n_{ij}) which depend on the coordination hypotheses and on the number of bonds between atoms of a single element or a pair. In this method, two important facts were taken into account. On one hand, the products of atomic factors are functions of s (the scattering vector module) and so cannot always be considered constant; they were therefore approximated by the polynomial functions which best fit the results obtained for the atomic factors given in the International Tables. On the other hand, we considered the influence of the structural hypotheses (coordinations, existence of certain types of bond) on the area and coordination numbers mentioned, and obtained expressions for these parameters which enable us to postulate the most probable local order. In order to test the reliability of the method, it was applied to a set of alloys, quoted in the literature, and the theoretical results agreed very satisfactorily with the experimental values.

Introduction

Amorphous materials themselves are nothing new. The iron-rich siliceous glasses found in the moon rocks, brought back by the Apollo missions, are billions of years old. Man has been making glasses (mainly silica) for centuries, as is proven by the coloured glass used artistically in cathedrals and other buildings during the Middle Ages. What is relatively recent is the scientific study of amorphous solids, and interest in them grows daily as new glasses are obtained, some of which have a promising technological future. Proof of the growing interest in these solids is the number of scientific works published yearly on the subject, which has increased threefold since the seventies and is still growing.

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 first neighbours. 'Amorphous' and 'non-crystalline' are therefore synonymous terms, whereas 'glass' is the non-crystalline material exhibiting a characteristic transition temperature [1] 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 coordination of the material [2], so an understanding of its local order is very important, as it can be related to other physical properties of the material.

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

When interpreting the radial atomic distribution function (RDF), obtained from the X-ray diffraction intensities of a glassy solid, the area under the first peak of the curve is related to the relative coordination 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, $R_{ij}(s) = f_i(s)f_j(s)/(\Sigma_i x_i f_i(s))^2$, remain practically constant and equal to $Z_iZ_j/(\Sigma_i x_i Z_i)^2$ throughout the whole interval of s (scattering vector

0254-0584/92/$5.00

module) in which the measurements are carried out. This is not always true, as in some cases $R_{ij}(s)$ varies considerably with s [3].

This work takes into account, on one hand, that the atomic scattering factors are functions of the Bragg angle [3] and, on the other, that the coordination hypotheses for a certain element in the alloy. Both considerations made it possible to calculate, according to the literature [4–6], theoretical expressions of the parameters which depend on the alloy, and of the coordination hypotheses which appear in the theoretical expression of the area under the first peak, and in those of the average coordination numbers. The theoretical results were applied to the analysis of the short-range order of different glassy alloys; the results agree with the experimental values.

Theoretical background and motivation

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 is possible to postulate that the mentioned positions are randomly orientated, the intensity diffracted in each direction, expressed in electronic units (e.u.), is given by Debye's equation [7]

$$I_{\mathrm{e.u.}} = \sum_{n,m} f_n f_m \frac{\sin s r_{nm}}{s r_{nm}} \tag{1}$$

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 [8] applied the Fourier transformation to a function of the diffracted intensities, thus obtaining an expression of the variation of the atomic density with distance to an arbitrary atom in the material.

A strict evaluation of Debye's equation involves considering the atomic scattering factors as functions of the Bragg angle through magnitude s, a consideration which was taken into account by Finbak [9], afterwards by Waser and Schomaker [10] and later by Warren [3]. According to the latter author, the following relationship is found for the radial atomic distribution function:

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

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 function $P_{ij}(r)$ is defined by

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

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

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + rG(r) \tag{4}$$

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 to say, its average coordination), it is necessary to obtain the area under the first RDF peak given by the expression

$$\mathrm{Area} = \frac{2}{\pi} \sum_{i,j} x_i \frac{n_{ij}}{r_{ij}} \int_a^b r P_{ij}(r)\, dr \tag{5}$$

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

Some authors ignore this expression, as 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, which is true only when the atomic scattering factors, f_i, can be considered independent of s and therefore constant and equal to the atomic numbers Z_i. Only under this hypothesis can the identity of the two expressions of the area under the first RDF peak be proven, since, by substituting the equation for $P_{ij}(r)$ in relationship (5), the result is

$$\mathrm{Area} = \frac{1}{\pi} \sum_{i,j} x_i \frac{n_{ij}}{r_{ij}} \frac{Z_i Z_j}{\left(\sum_i x_i Z_i\right)^2} S \tag{6}$$

where

$$S=\int_a^b r\,\frac{\sin s_m(r-r_{ij})}{r-r_{ij}}\,dr$$

is an integral which, by carrying out the successive variable changes $x=r-r_{ij}$ and $y=s_m x$, gives way to

$$S=[\cos s_m(a-r_{ij})-\cos s_m(b-r_{ij})]s_m^{-1} + r_{ij}\int_{y_1}^{y_2}\frac{\sin y}{y}\,dy \qquad (7)$$

a relationship where $y_1=s_m(a-r_{ij})<0$, $y_2=s_m(b-r_{ij})>0$, and s_m, which proceeds from the lack of experimental data for very high values of s, can be identified as infinite, being the upper limit of a Fourier transformation, whereby $S=r_{ij}\pi$ and expression (6) turns into

$$\text{Area}=\frac{\sum_{i,j} x_i n_{ij} Z_i Z_j}{\left(\sum_i x_i Z_i\right)^2} \qquad (8)$$

thus proving that it is a particular case of the more general relationship (5).

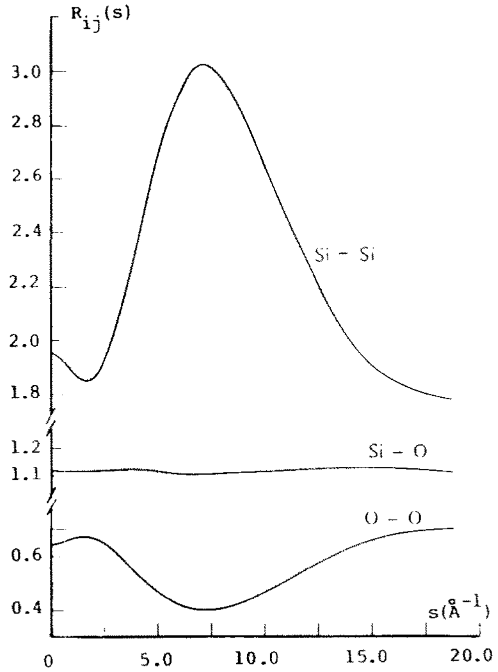

Fig. 1. Representation of functions $R_{ij}(s)$ *versus* s in amorphous SiO_2.

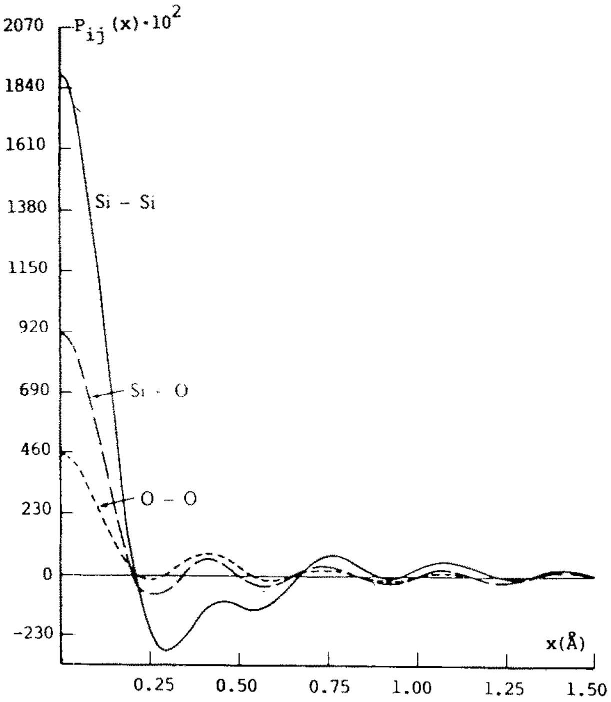

Fig. 2. Representation of functions $P_{ij}(x)$ *versus* x for the different pairs of elements in amorphous SiO_2.

There are, however, practical cases in which it may be observed that the approximation considering functions R_{ij} as constant and equal to $Z_iZ_j/(\Sigma_i x_i Z_i)^2$ is inaccurate enough to influence the short-range order postulated for the material. In relation to this, Fig. 1 [3] shows R_{ij} *versus* s for all possible pairs of elements in amorphous SiO_2. Relationship (8), based on the constancy of the atomic scattering factors, is obviously a good approximation for the pair Si—O, but very inaccurate for the pairs Si—Si and O—O. Analogously, Fig. 2 [3] shows functions $P_{ij}(x)$ *versus* x for the same pairs as in the previous figure. In addition to the ripples due to the errors in finishing the series, the curve for Si—Si is observed to have a sharp negative wing just outside the main peak, and the curve for O—O has a positive region at the end of the main peak. These positive or negative regions are a consequence of the shapes of the $R_{ij}(s)$ curves. A relatively broad, though not complete, analysis of cases such as amorphous SiO_2 seems to make it advisable to express products $R_{ij}(s)$ through the mathematical functions which best fit the results obtained from the atomic scattering factors given in the International Tables. In this sense, Vázquez and Sanz [4] have developed an analytical method for evaluating the area under the first RDF peak, in which 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, the authors [4] propose the following expression:

$$\text{Area}=\frac{2}{\pi}\sum_{i,j} x_i n_{ij} A_{ij} \qquad (9)$$

with

$$A_{\mathrm{ij}}=\frac{1}{r_{\mathrm{ij}}}\int_{a} rP_{\mathrm{ij}}(r)\,\mathrm{d}r=\frac{1}{2r_{\mathrm{ij}}}\left[B_{1\mathrm{ij}}+B_{2\mathrm{ij}}+r_{\mathrm{ij}}(B_{3\mathrm{ij}}+B_{4\mathrm{ij}})\right],$$

the functions $B_{k\mathrm{ij}}$ ($k=1, 2, 3, 4$) being given by the relationships

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

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

$$B_{3\mathrm{ij}}=\int_{a'_{\mathrm{ij}}}^{b'_{\mathrm{i,j}}}\frac{\sin s_{\mathrm{m}}x}{x}\,\mathrm{d}x,$$

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

where $A_{0\mathrm{ij}}$ and $A_{1\mathrm{ij}}$ 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 $a'_{\mathrm{ij}}=a-r_{\mathrm{ij}}$ and $b'_{\mathrm{ij}}=b-r_{\mathrm{ij}}$.

Equation (9) is, as may be observed, a function of the relative coordination numbers, n_{ij}, and therefore of the number of chemical bonds, a_{ij}, between the i-type and j-type elements of the alloy. This fact made it possible to develop analytical methods [5, 6] for expressing the area under the first RDF peak as a function of the coordination of one type of element in the material and to the number of bonds between pairs of atoms.

Short-range order: basic parameters

Analytically determining the parameters which depend on the alloy and on the coordination hypotheses

A theoretical evaluation of the average coordination of a glassy alloy, from its radial atomic distribution function, 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 coordination for some element in the alloy. This will enable us to attribute a coordination to a certain element, according to its properties and to the coordination proposed in the literature for the same element in similar alloys. The postulated coordination 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 the experimental error, the coordination hypothesis may be considered adequate; otherwise, the hypothesis is rejected and another one is tested. On the other hand, it is a well-known fact that, in glassy alloys, we may postulate the absence of bonds between certain types of elements, either because of the low concentration of one of them, or because the energy of this type of bond makes it very improbable in comparison to others. It is therefore very important that the theoretical expression of 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.*[6] have proposed theoretical expressions of the area which reflect both the coordination hypotheses for a certain element, and the possible absence of different types of bond in the material.

According to the mentioned authors, in the case of the ternary glassy alloy $\mathrm{A}_{a'_1}\mathrm{B}_{a'_2}\mathrm{D}_{a'_3}$ for every hundred atoms of material, where elements, A, B and D are assigned subscripts 1, 2 and 3 respectively, supposing that element A has N-coordination in the compound and that the average coordination numbers, n_{1k}, of this element, with all those it is bonded to, are proportional to their respective percentual concentrations, equation (9) gives us

$$\mathrm{Area}=\frac{1}{50\pi}\left[\frac{\mathrm{N}_{a'_1}}{\sum_k a'_k}\left(\sum_k a'_k\mathrm{A}_{1k}+\sum_{k\neq 1}a'_k\mathrm{A}_{1k}\right)+2\sum_{\substack{\mathrm{i,j}\neq 1\\ \mathrm{i}\leqslant \mathrm{j}}}a_{\mathrm{ij}}\mathrm{A}_{\mathrm{ij}}\right] \tag{10}$$

where k obviously cannot take the values of the subscripts representing elements which are not bonded to element A. In this equation it is observed that, once element A is subscripted 1, the number of bonds between pairs of elements is represented by a_{ij}, $\mathrm{i,j}\neq 1$. Bearing in mind that the total number of bonds, a_{i}, of element i is given by the expression $a_{\mathrm{i}}=2a_{\mathrm{ii}}+\Sigma_{\mathrm{i}\neq \mathrm{j}}a_{\mathrm{ij}}$, it is possible to change relationship (10) in such a way that it is a function only of the coordination attributed to element A in the compound and of the number of bonds between specific pairs of elements. In order to do this, two parallel mathematical developments are carried out from the last equation for the area, using the expression for a_{ij} deduced from the one for a_i, depending on whether $i=j$ or $i\neq j$. The following expression is thus obtained for the area under the first RDF peak:

$$A=\frac{1}{50\pi}\left[hN+a_2A_{22}-a_3((A_{22}-2A_{23})\delta_{ij}-(1-\delta_{ij})A_{33})+P\left(\sum_{i=j\neq 1}A_{ij}-\sum_{\substack{i,\,j\neq 1\\ i\neq j}}A_{ij}\right)a_{ij}\right] \tag{11}$$

where P is a parameter worth 2 if $i=j$, and -1 if $1\neq j$, h being a specific characteristic of each alloy given by the relationship

$$h=\frac{a'_1}{\sum_k a'_k}\left[\sum_k a'_kA_{1k}+\sum_{k\neq 1}a'_kA_{1k}+pa'_3((A_{22}-2A_{23})\delta_{ij}-(1-\delta_{ij})A_{33})-qa'_2A_{22}\right] \tag{12}$$

where parameters p and q are worth 1 when multiplying concentrations, a'_k, of elements bonded to element A, and zero otherwise. By use of the symbol δ_{ij} (Kronecker's delta), relationships (11) and (12) condense two expressions for the area and another two for parameter h, when $i=j$ and when $i\neq j$.

Variations in the coordinations of the elements in a compound obviously influence the theoretical area under the first RDF peak. If an unusual coordination N is attributed to element A in the alloy, it may involve the electronic transference between all or some of the elements present in the material, which is reflected in the number of chemical bonds between atoms of the different types of element in the solid and, consequently, in the area under the first RDF peak. When expressing this magnitude, therefore, certain parameters should be included which depend on the coordination hypotheses. If the normal coordinations of the different elements in the sample are denoted by C_i, the number of bonds for element A will be

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

$|x|$ being the variation in the number of bonds for the element in question when it goes from coordination C_1 to N. Elements B and D can simultaneously change their coordinations and, therefore, the number of bonds in them is given by

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

where $|y_i|$ represents the variation in the number of bonds for element i. Considering that the variation in the number of bonds of a given element is equal to the number of electrons it transfers, and that this variation is proportional to the percentual concentration of the said element, the following system of equations results:

$$|x|=\sum_{i\neq 1}|y_i|; \qquad \frac{|y_i|}{a'_i}=K'$$

(K' = proportionality constant)

whence the following relationship is obtained for the number of bonds of element i:

$$a_i=C_ia'_i\pm\frac{a'_1a'_i(|N-C_1|)}{\sum_{i\neq 1}a'_i}$$

which enables us to find the expressions that depend linearly on the N-coordination attributed to type A

$$a_2-a_3=\alpha+\beta N,\quad a_3=\gamma-\delta N \tag{13}$$

where parameters α, β, γ and δ, which depend on the specific characteristics of the alloy and on the coordination variations of the different constituent elements, are related among themselves through the equations

$$\alpha=C_2a'_2-C_3a'_3-C_1\beta,$$

$$\beta=\delta-\epsilon,\quad \gamma=C_3a'_3+C_1\delta$$

where $|\epsilon|=a'_1a'_2/\Sigma_{1\neq 1}a'_i$, $|\delta|=a'_1a'_3/\Sigma_{i-1}a'_i$. Parameters δ and ϵ reflect the evolution of the coordinations of elements 1 and $i\neq 1$ as the compound takes form. When one of these type of elements increases its coordination and the other decreases it, the corresponding parameter is positive; if both types increase or decrease their coordinations, it is negative; and the parameter is annulled when element 1 or $i\neq 1$ keeps its coordination, in which case i cannot take the value of the subscript of the indicated element. These parameters, which depend on the coordination hypotheses of the elements in the material, are introduced into relationship (11) using equation (13), and the following expression is thus obtained for the area under the first RDF peak:

$$\mathrm{Area} = \frac{1}{50\pi}\left[(h+\beta \mathrm{A}_{22}-\delta \mathrm{Q})\mathrm{N}+\alpha \mathrm{A}_{22}+\gamma \mathrm{Q} + \mathrm{P}\left(\sum_{i=j\neq 1} \mathrm{A}_{ij} - \sum_{\substack{i,j\neq 1\\ i\neq j}} \mathrm{A}_{ij}\right)a_{ij}\right] \tag{14}$$

which is a function of the coordination postulated for element A and of the number of bonds among a single type of pairs of elements, and where parameter Q is defined by the relationship

$$\mathrm{Q} = \delta_{ij}\sum_{\substack{i,j\neq 1\\ i\neq j}} \mathrm{A}_{ij} + (1-\delta_{ij})\sum_{i=j\neq 1} \mathrm{A}_{ij} \tag{15}$$

The expression of the theoretical area, deduced above, enables us to find, according to the experimental area, the variation interval of the number of bonds between the elements of a certain pair, for each coordination hypothesis. This fact is very useful when choosing the most adequate coordination for the elements which usually make up compounds with different coordinations.

Deducing the relative coordination numbers

The relative coordination 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 coordination, N, attributed to a certain element; and bearing in mind the restrictions imposed by its intrinsically positive nature, it is possible to choose the most adequate value for N.

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

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

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

From the equation $a_i = 2a_{ii} + \Sigma_{i\neq j} a_{ij}$, and considering relationship (13), expressions are obtained for the coordination numbers n_{ij} (i, j ≠ 1) as functions of the number of a_{ij} bonds. In order to find these expressions, two parallel deductions were carried out, according to whether i = j or i ≠ j, with the following result:

$$n_{22} = \frac{\alpha + \gamma(1-\delta_{ij}) + [(\beta - \delta(1-\delta_{ij}))\sum_k a'_k + a'_1(\delta_{ij} p a'_3 - q a'_2)]\mathrm{N}/\sum_k a'_k + p a_{ij}}{a'_2}$$

$$n_{23} = \frac{[\gamma - (\delta \sum_k a'_k + a'_1 p a'_3)\mathrm{N}/\sum_k a'_k]\delta_{ij} + (1-3\delta_{ij})a_{ij}}{a'_2}$$

$$n_{33} = \frac{[\gamma - (\delta \sum_k a'_k + a'_1 p a'_3)\mathrm{N}/\sum_k a'_k](1-\delta_{ij}) - (1-3\delta_{ij})a_{ij}}{a'_3} \tag{16}$$

condensing, through the symbol δ_{ij}, the two possible expressions for each one of the coordination numbers deduced. The fact that these numbers must be positive or null 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 one 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.

Application to some practical cases

The method described, for determining the parameters enabling us to postulate 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 literature. Different structural hypotheses were used, and the theoretical results obtained agree with the mentioned experimental data, confirming the reliability of the theoretical method developed. This work shows the theoretical analysis of the five alloys considered most representative of the set studied, whose experimental values are shown in Table 1. The constituent elements of each alloy were subscripted 1, 2 and 3 in the order in which they appear in the alloy. The coordination hypotheses used for obtaining the parameters which define the possible local order are shown in Table 2, where C'_i ($i = 2, 3$) represents the coordination of element i in the compound. The existence of bonds between all

TABLE 1. RDF characteristics of the analyzed alloys

Alloy	First peak		Area (at.)	Ref.
	a (Å)	b (Å)		
$As_{0.20}Se_{0.50}Te_{0.30}$ (M1)	2.05	2.90	2.10	[11]
$Al_{0.20}As_{0.20}Te_{0.60}$ (M2)	2.20	3.05	2.18	[12]
$Ge_{0.14}As_{0.43}Te_{0.43}$ (M3)	2.25	3.05	2.42	[13]
$Cu_{0.20}As_{0.30}Se_{0.50}$ (M4)	2.10	2.90	3.23	[14]
$Cu_{0.08}Ge_{0.18}Te_{0.74}$ (M5)	2.20	3.10	2.58	[15]

TABLE 2. Coordination hypotheses

Alloy	N	C_1	C_2	C_3	C'_2	C'_3
M1	4	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 3. Parameters related to the coordination hypotheses

Alloy	α	β	γ	δ
M1	55	−5	82.5	7.5
M2	−30	−10	75	−15
M3	43	0	114	7
M4	−5	−5	87.5	−12.5
M5	−68	−8	140	−8

TABLE 4. Average bond lengths for each alloy

Pair	r_{ij} (Å)					ref.				
	M1	M2	M3	M4	M5	M1	M2	M3	M4	M5
1–1	2.49	2.86	2.51	2.58	2.58	[16]	[20]	[23]	[26]	[26]
1–2	2.38	2.43	2.44	2.53	2.39	[17]	[21]	[23]	[27]	[17]
1–3	2.68	2.53	2.58	2.42	2.53	[18]	[17]	[17]	[27]	[17]
2–2	2.34	2.49	2.57	2.57	2.51	[17]	[16]	[24]	[24]	[23]
2–3	2.54	2.68	2.58	2.38	2.58	[17]	[18]	[24]	[17]	[17]
3–3	2.71	2.83	2.60	2.34	2.71	[19]	[22]	[25]	[17]	[19]

pairs of elements in all alloys was postulated, except in M2, where the absence of Al−Al bonds was presumed [12]. Bearing in mind the mentioned structural hypotheses, and using the previously deduced theoretical expressions, the values shown in Table 3 were calculated, corresponding to the parameters that depend on the specific characteristics of each alloy and on the coordination variations of its elements. Table 4 shows the average bond lengths, which were used for calculating parameters A_{ij} and h, shown in Table 5.

Through eqn. (14), and using the set of parameters obtained, the theoretical expressions of the area shown in Table 6 were deduced. These expressions, together with the experimental areas (Table 1) with an error of ± 0.1 atoms, made it possible to determine the variation intervals for a_{ij} (i, j$\neq$1), shown in Table 6. Equations (16) supply the relative coordination numbers, which, due to their intrinsically positive nature, define the new limits for magnitude a_{ij}, shown in Table 6 together with their intersections with the intervals corresponding to the margin of error of the experimental area. These coordination numbers are such that the sum of those corresponding to one type of element with all those bonded to it is equal to the coordination postulated for that element. Thus in the case of alloy M5, where tetra-coordinated copper is postulated, and the electrons necessary for the sp^3 hybridation of the copper are supplied by the tellurium, the coordinations are: four for the copper and the germanium, and 86/37 for the tellurium. The same results are obtained by adding the n_{ij}s 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. This figure shows the intervals in which the theoretical areas are simultaneously compatible with the experimental area and the corresponding coordination numbers.

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

Conclusions

The described theoretical method enables us to test different structural hypotheses in relation to the coordinations or the absence of some types of bond, as the expressions deduced for the relative coordination numbers and for the area under the first RDF peak depend on these hypotheses. On the other hand, when deducing this area the polynomial functions were used which best fit the products of the atomic factors in those cases in which said magnitudes differ greatly from the approximate values $Z_iZ_j/(\Sigma_i x_i Z_i)^2$, a fact which is of great interest when accurately evaluating the average number of first neighbours in a glassy alloy.

Through the developed procedure, it is possible to postulate certain structural characteristics and

TABLE 5. Values of parameters A_{ij} and h obtained for $s_m = 12$ Å^{-1}

Alloy	A_{ij}						h
	1–1	1–2	1–3	2–2	2–3	3–3	
M1	1.0707	1.1186	1.8885	1.1778	1.8334	3.0638	22.6048
M2	0.1417	0.3463	0.6354	1.1012	1.7829	2.8337	−25.4865
M3	0.9376	0.9488	1.5577	0.9975	1.6123	2.6009	12.6039
M4	1.2049	1.3133	1.4012	1.5715	1.6953	1.8347	20.9832
M5	0.5492	0.6539	1.0651	0.7399	1.1388	1.9535	4.6769

TABLE 6. Theoretical results obtained for the different alloys

Alloy	Theoretical area	Coordination numbers n_{ij}, i,j≠1	Variation intervals for parameter a_{ij}, i,j≠1		
			Defined by the n_{ij} parameters	Defined by limits of error of the experimental area	Intersection of intervals
M1	$2.0636+0.0073a_{33}$	$n_{22}=(19+2a_{33})/50$ $n_{23}=(28.5-2a_{33})/50$ $n_{33}=2a_{33}/30$	$0 \leqslant a_{33} \leqslant 14.25$	$0 \leqslant a_{33} \leqslant 18.68$	$0 \leqslant a_{33} \leqslant 14.25$
M2	$2.2421-0.0023a_{23}$	$n_{22}=(45-a_{23})/20$ $n_{23}=a_{23}/20$ $n_{33}=(75-a_{23})/60$	$0 \leqslant a_{23} \leqslant 45$	$0 \leqslant a_{23} \leqslant 70.48$	$0 \leqslant a_{23} \leqslant 45$
M3	$2.4228+0.0048a_{33}$	$n_{22}=(43+2a_{33})/43$ $n_{23}=(74.94-2a_{33})/43$ $n_{33}=2a_{33}/43$	$0 \leqslant a_{33} \leqslant 37.47$	$0 \leqslant a_{33} \leqslant 20.25$	$0 \leqslant a_{33} \leqslant 20.25$
M4	$3.2522+0.0002a_{33}$	$n_{22}=(-9+2a_{33})/30$ $n_{23}=(97.5-2a_{33})/30$ $n_{33}=2a_{33}/50$	$4.5 \leqslant a_{33} \leqslant 48.75$	$0 \leqslant a_{33} \leqslant 389$	$4.5 \leqslant a_{33} \leqslant 48.75$
M5	$2.1420+0.0053a_{33}$	$n_{22}=(-82.08+2a_{33})/18$ $n_{23}=(148.32-2a_{33})/18$ $n_{33}=2a_{33}/74$	$41.04 \leqslant a_{33} \leqslant 74.16$	$63.77 \leqslant a_{33} \leqslant 101.51$	$63.77 \leqslant a_{33} \leqslant 74.16$

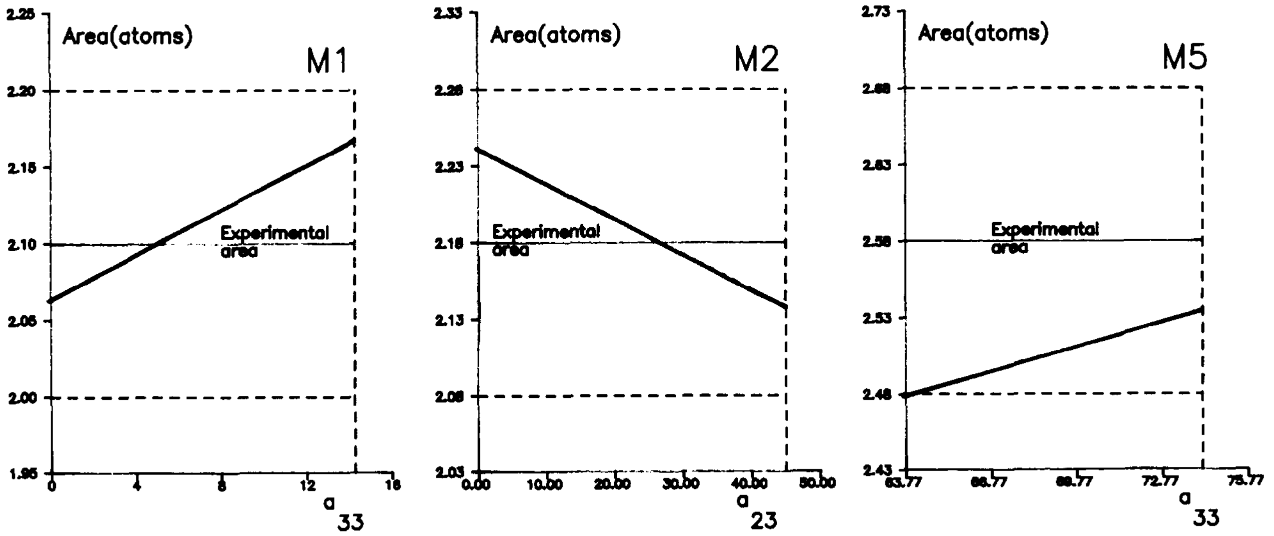

Fig. 3. Area of the first RDF peak *versus* the number of a_{ij} bonds (i,j≠1) for alloys M1, M2 and M5.

to obtain, from these, the average theoretical coordination of a solid, which is compared to the experimentally determined coordination. If the difference is within the experimental error, it may be considered that the hypotheses describe the most probable local order of the material.

Acknowledgements

The authors are grateful to Aurora Rice for translating this paper into English, and to the Comisión Interministerial de Ciencia y Tecnología for their financial support (project no. PB88-0463).

References

1 S. R. Elliott, *Physics of Amorphous Materials,* Longman, Harlow, 1984.
2 J. Cornet and J. Schneider, in G. H. Frischat (ed.), *The Physics of Non-Crystalline Solids*, Trans. Tech. Publications, Claustahl-Zellerfeld, Germany, 1977.
3 B. E. Warren, *X-Ray Diffraction*, Addison-Wesley, Reading, MA, 1969.
4 J. Vázquez and F. Sanz, *Ann. Fis., B80* (1984) 31.
5 J. Vázquez, L. Esquivias, P. Villares and R. Jiménez-Garay, *Ann. Fis., B81* (1985) 223.
6 J. Vázquez, P. Villares and R. Jiménez-Garay, *Mater. Lett., 4* (1986) 485.
7 P. Debye, *Ann. Physik, 46* (1915) 809.
8 F. Zernicke and J. A. Prins, *Z. Physik, 41* (1927) 184.
9 C. Finbak, *Acta Chem. Scand, 3* (1949) 1279.
10 J. Waser and V. Schomaker, *Rev. Modern Phys., 25* (1953) 671.
11 J. Vázquez, P. Villares and R. Jiménez-Garay, *J. Non-Cryst. Solids, 86* (1986) 251.
12 P. Olano, C. Alberdi and F. Sanz, *An. Fis., 76* (1980) 237.
13 R. A. Ligero, J. Vázquez, P. Villares and R. Jiménez-Garay, *J. Mater. Sci., 22* (1987) 4357.
14 M. Domínguez, J. Vázquez, P. Villares and R. Jiménez-Garay, *J. Phys. Chem. Solids, 52* (1991) 567.
15 M. Casas-Ruiz, R. A. Ligero, J. Vázquez and P. Villares, *10th General Conference of the Condensed Matter Division,* Lisbon, 1990, p. 41.
16 G. N. Greaves and E. A. Davis, *Phil. Mag., 29* (1974) 1201.
17 L. Pauling, *Uniones Químicas,* Kapelusz, Buenos Aires, 1969.
18 J. Cornet and D. Rossier, *J. Non-Cryst. Solids, 12* (1973) 85.
19 A. d'Anjou and F. Sanz, *J. Non-Cryst. Solids, 28* (1978) 319.
20 W. B. Pearson, *Lattice Spacings and Structures of Metals and Alloys*, Pergamon, London, 1957.
21 R. W. G. Wyckoff, *Crystal Structures,* Wiley, New York, 1963.
22 P. Chering and P. Unger, in W. Cooper (ed.), *The Physics of Selenium and Tellurium, Pergamon, London, 1969.*
23 N. de la Rosa-Fox, L. Esquivias, P. Villares and R. Jiménez-Garay, *Phys. Rev., B33* (1986) 4094.
24 J. Vázquez, E. Márquez, P. Villares and R. Jiménez-Garay, *Mater. Lett., 4* (1986) 360.
25 J. Vázquez, P. Villares and R. Jiménez-Garay, *Mater. Lett., 4* (1986) 171.
26 R. B. Heslop and K. Jones, *Inorganic Chemistry,* Elsevier, Amsterdam, 1976.
27 F. D. Bloss, *Crystallographic and Crystal Chemistry,* Holt, Rinehart and Winston, New York, 1977.