Materials Chemistry and Physics, *25* (1990) 399–416

ON THE GENERATION, BY A RANDOM METHOD, OF SPATIAL ATOMIC CONFIGURATIONS OF SOME Cu-As-Se SYSTEM GLASSY ALLOYS

J.VAZQUEZ, P. VILLARES, E. MARQUEZ and R. JIMENEZ-GARAY
Facultad de Ciencias. Universidad de Cádiz. Puerto Real, Cádiz.
(Spain)

Received: December 27, 1989; accepted: February 12, 1990

ABSTRACT

Atomic structure models of the semiconducting glassy alloys $Cu_xAs_{0.5-x}Se_{0.5}$ (x=0.05, 0.10, 0.20) were generated from short-range order information, supplied by the corresponding radial distribution functions deduced from the intensities given by X-ray diffraction experiments carried out on samples of these alloys obtained by quenching the molten mixtures of their elements. The Metropolis-Monte Carlo random method was used in the making of the models, conveniently modified and bearing the tetracoordinated copper hypothesis in mind. A comparative analysis of the main structural parameters of these models revealed the good agreement of the same with the values given in the literature for similar alloys.

INTRODUCTION

Amorphous solids have been used by man for centuries, although the nature, structure and properties of these materials have been obscure,in most cases, until lately. Due to the development of the atomic theory, interest in the structure of all kinds of materials has grown considerably. Although, initially, this interest only referred to crystalline substances, it has later been extended powerfully to amorphous solids [1-3]. Nowadays, one of the most active fields in solid state research is the study of non-crystalline materials, that is, those whose atomic distribution lacks long-range order, although they do have short-range order in their bonds with first neighbours, up to a few atomic diameters, giving a characteristic spectrum in the

0254-0584/90/$3.50

diffractograms. A point of great interest in the study of glassy materials is their atomic distribution and the making of short-range order structural models, a structure that every amorphous material has and which will greatly condition its macroscopic behaviour. A knowledge of the structure of solids in general, and amorphous materials in particular, is basic when trying to establish a formal theory in order to explain the above mentioned properties.

Se-based chalcogenide glasses usually exhibit high resistivity values, which imply certain limitations in their application, as well as difficulties in their electric measurements. Some authors [4] note that the addition of elements with d orbitals to chalcogenide materials can produce significant changes in their electrical properties. Specifically, the addition of copper produces a strong increase in the conductivity of glassy alloys composed of arsenic and selenium, as well as an even stronger decrease in their conduction activation energy. Cu-As-Se system glassy alloys also exhibit interesting switching properties, which depend on the copper content, and the memory effect, which makes them adequate for the production of electronic devices [5]. In this work, tridimensional models of the short-range order of the alloys $Cu_xAs_{0.5-x}Se_{0.5}$ with x=0.05 (MI), x=0.10 (MII) and x=0.20 (MIII) have been made, using the conveniently modified Metropolis-Monte Carlo random method [6]. In the making of these models, we have taken into account the geometric and coordination conditions deduced by ourselves [7] from the radial distribution function (RDF) of each composition obtained by X-ray diffraction.

THEORETICAL BACKGROUND

The basic object of the determination of the structure of an amorphous solid is to build tridimensional atomic models which verify, as a necessary condition, the structural information obtained experimentally from the analysis of the radial atomic distribution function and which, at the same time, agree as much as possible with the known physical-chemical properties of the material under study and of its elements.

There is a wide range of methods for generating structural models of glassy solids, from those based on initial crystalline configurations, whose positions are modified following different techniques, to those starting from a totally random initial state, in order to guarantee that the generated model will not be influenced by the restrictions originated by the starting conditions, besides atomic configuration generation techniques based on the minimization of the system's energy. Although all of these methods can give satisfactory results, as in the case of amorphous Se [8], in which the theoretical structure was generated from the crystalline positions of one hundred atoms of the material, submitted to a random alteration process until the experimental spectrum of the amorphous material was described [9], however, it seems that, among the random base methods, the Metropolis-Monte Carlo method is the most adequate for describing the short-range order of a glassy solid obtained through quenching of its molten mixture, as it seems to simulate the structural characteristics of this kind of alloy very well.

In this work, a variation of the Monte Carlo method, similar to the procedure used by Rechtin et al. [10], was used. The variations refer mainly to the geometric and coordination conditions, which imply a certain semi-randomness in the construction of the atomic configuration.

There are two stages in the model building process: Generation of the initial configuration and refinement of the initial model.

Generation of the initial configuration

In order to establish the position of the atoms that will generate the models, it is necessary to choose the volume in which they will be located. Bearing in mind that the RDF, $4\pi r^2$ (r), where (r) is the atomic density of the material, is a function which only depends on the distance r to a random atom taken as reference, the sphere is usually considered to be the most adequate geometric space in which to locate a model.

Once the spatial characteristics of the initial configuration are decided, the next step is to determine N, the number of atoms that can be located in this space using the relationship

$$N = (\rho_o A/M_a)V \qquad (1)$$

where ρ_o is the experimentally measured density, A is Avogadro's number, M_a is the atomic mass of the composition unit and V is the volume chosen for the generation of the model.

As the models generated from a number of positions equal to the above mentioned number of atoms are low in coordination, although they fit correctly from a geometric point of view, it is necessary to modify the initial configuration by saturating the chosen volume with positions, increasing coordination. In order to generate the coordinates (x_1, x_2, x_3) of the positions corresponding to the initial configuration, series of three random numbers (a_1, a_2, a_3) are used, belonging to the interval $(0 \le a_i \le 1)$, resulting in the coordinates through the expression

$$x_i = (2a_i - 1)R \quad (i = 1, 2, 3) \tag{2}$$

if condition $\Sigma_i x_i^2 \leq R^2$ is verified, R being the radius of the sphere constituting the model.

Each position generated must also meet the following restrictions, which have already been mentioned:

(i) The distance between two first neighbours must be within the definition interval of the first experimental RDF peak.

(ii) The bond angle with two immediate positions must be inside the interval (ϕ_{min}, ϕ_{max}), which are the extreme limits of this angle, according to the literature [11].

(iii) The number of atoms of each kind, in the first coordination sphere, given as the maximum acceptable coordination for each one of them.

When any of these conditions is not met, the position created is rejected, and another is generated, until the whole volume is saturated. Then the positions with lowest coordination are eliminated, until the number of remaining positions is equal to the number of atoms compatible with the experimental density, and the different kinds of atoms in the alloy are assigned semirandomly to the positions. These atoms must verify the equation system

$$\sum_{i=1}^{3} n_i = N, \qquad n_i/a'_i = K \text{ (K=proportionality constant)} \tag{3}$$

where n_i is the number of i-type atoms in the whole of N, which can be located in the chosen volume, and a'_i is the concentration of element **i** in 100 atoms of material.

Once the initial atomic configuration is established, the next step is to find the corresponding reduced RDF, $rG_{mod}(r)$, by simulating a diffraction process in the model. In order to compare this function to the experimental one, the sample and the model must be of similar shape and dimensions. The spherical shape is simulated by multiplying function $rG_{exp}(r)$ by the one proposed by Mason [12], given by

$$D(r) = 1.0 - 1.5(r/2R) + 0.5(r/2R)^3 \tag{4}$$

and which represents the probability of finding a distance r inside a sphere with a radius R.

The comparison of the two reduced RDFs is done through the average quadratic deviation, ε^2, which is used as a criterium for deciding on the validity of the configuration generated and which is given by the expression

$$\varepsilon^2 = (1/M') \sum_{i=1}^{M'} (r_i G_{exp}(r_i) D(r_i) - r_i G_{mod}(r_i))^2 \quad (5)$$

for the r_i's corresponding to the M' points taken in the comparison.

Refining the initial model

The process of modifying the initial configuration until a final structure is obtained, whose RDF adequately fits the experimental value of said function, is known as refining the model, and has two stages: Refining positions and thermal factors.

The process of refining atomic positions was carried out using the Metropolis-Monte Carlo method [6], consisting essentially of randomly modifying the initial position of an atom, accepting the new position if the average quadratic deviation between the experimental RDF and the generated model diminishes, and if the restrictive conditions imposed in the generation of the initial configuration are met with. The development of this technique begins by randomly determining the atom which will change positions, for which all the atoms in the model are numbered from 1 to N and then a number a is generated, within the interval (0,1), and through the relationship

$$M = \text{Integer}\ (a\ N + 1) \quad (6)$$

the number M of the atom that will change its position is obtained.

This atom is then moved from its previous position to a new one, following a randomly chosen direction, for which another two random numbers, b and c, inside the same interval, are taken, and through the expressions

$$\phi = 2\pi b \qquad \theta = \pi c \quad (7)$$

we obtain the spherical coordinates (ϕ,θ) defining the random direction of the move whose origin is in the chosen atom M, resulting in its new position M_t, Fig. 1, being given by the relationships

$$\begin{aligned} x' &= x + P \operatorname{sen} \theta \cos \phi \\ y' &= y + P \operatorname{sen} \theta \operatorname{sen} \phi \quad (8) \\ z' &= z + P \cos \theta \end{aligned}$$

where (x,y,z) are the coordinates of M, and P is the amplitude of the displacement. P is arbitrarily established, and can be modified as the refinement process advances, varying according to the literature [13] between 0.5 Å at the beginning of the process to 0.1 Å at the end, in order to achieve a faster convergence. Lower values for P have no physical sense, as they are masked by thermal agitation.

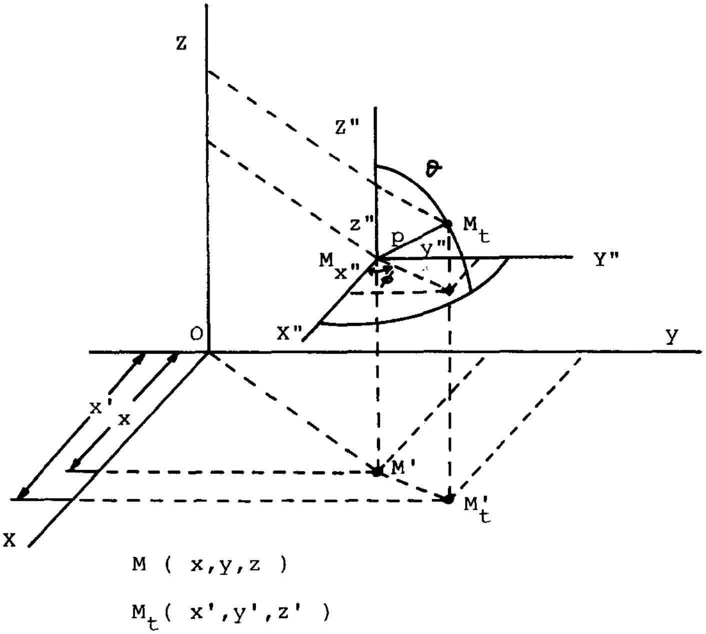

Fig. 1. Random movement of atoms in the refining process.

The position refining process is considered finished when the computation time necessary to obtain a valid movement is excessively long, and the average quadratic deviation does not considerably improve.

For refining the thermal factors, the corresponding coordination spheres are defined according to the experimental RDF, and σ_0=0.1 Å is taken as the initial value of the isotropic factor. The set of values for σ_i which best fits the reduced RDF of the model to the experimental RDF is calculated by an iterative method of least squares, in successive cycles, until the variation of σ_i is less than 10^{-3} Å.

Once the refinement process is finished, the resulting atomic configuration is the adequate one for carrying out a statistical evaluation of the main structural parameters of the alloy under study (coordinations, bond lengths and angles, etc.).

GENERATION AND DESCRIPTION OF THE MODELS

The spatial atomic configurations of the above mentioned Cu-As-Se system alloys were made bearing in mind the considerations deduced from the interpretation of the radial atomic distribution functions of the corresponding samples, which means that any of the generated models will be such that its theoretical RDF will be as similar as possible to the one determined [7] from the intensity measurements obtained in the X-ray diffraction experiment carried out on the material.

Bearing in mind the analysis done by Domínguez et al. [7] on the coordination of copper in this ternary glassy system, the models that have been made are based on the tetracoordinated copper hypothesis, this element taking the electrons necessary for sp^3 hybridation from some arsenic and selenium atoms, which increase their coordination to 4 and 3 respectively.

The mathematical space considered as adequate for the generation of possible structural models of the alloys under study is the volume limited by a spherical surface with a radius of 10Å, as it best verifies the condition of being large enough to conveniently represent the samples, from a statistical point of view, and small enough for the computation time not to be too long. The total number of atoms which, according to the experimental densities in Table I [7], can be located in this volume, are shown in Table II together with the number of atoms of each kind corresponding to each of the alloys studied.

Table I. Structural information supplied by the experimental RDFs.

Alloy	MI		MII		MIII	
Maximun	1	2	1	2	1	2
Position (Å)	2.40	3.70	2.40	3.70	2.40	3.80
Limits (Å)	2.20-2.90		2.20-2.80		2.10-2.90	
Averaged angle (deg)	100.9		100.9		104.7	
Area (at.)	2.66	6.98	2.93	7.03	3.23	7.09
Error	±0.1	±0.2	±0.1	±0.2	±0.1	±0.2

Table II. Number of atoms in each model.

Alloy	Total	Cu	As	Se
MI	157	8	71	78
MII	163	16	64	83
MIII	171	34	51	86

The atomic positions were generated by determinig the Cartesian coordinates from three random numbers, as explained above, bearing in mind the geometric and coordination conditions that must be met with, deduced from the analysis of the experimental RDF [7], shown in Table I and which, in this case, are:

(i) The distance between first neighbours must be enclosed within the limits of the first experimental RDF peak, shown in Table I for each alloy.

(ii) The bond angle between an atom and two of its first neighbours can vary between the values ϕ_{min} and ϕ_{max}, deduced from the extreme positions that can be occupied by the two atoms which, together with the reference atom, determine the bond angle.

(iii) The coordination attributed to each element must be such that the weighed average coordination of the model agrees with the experimentally obtained one.

Considering the geometric and coordination restrictions already mentioned, 200, 230 and 250 positions were generated for the models of alloys MI, MII and MIII respectively, and they were reduced to 157, 163 and 171, the values predicted from the experimental densities, by eliminating the positions with the lowest coordination. The next step was to assign the atoms to their respective positions in each model, placing the copper atoms in tetracoordinated positions and the other elements randomly in the rest. The reduced RDF was determined for each configuration, and compared to the experimental RDF, modified by the finite size simulation function [12], which revealed that the above mentioned initial configurations were adequate for making them evolve and obtaining from them the most probable spatial models of the alloys under study. These initial atomic distributions were then adjusted by successive movements of their atoms, of amplitude P, with the added restriction of not allowing moves implying a break in copper atom bonds, therefore keeping the coordination predicted for this element in each case.

During the position refining process, the models evolved as shown in Table III, in which the average quadratic deviation refers to the last movement in each interval. The position refining process was considered finished when the number of rejected movements was too high and the average quadratic deviation did not vary significantly.

Table III. Position refining process for each alloy.

Alloy	P(Å)	Movement intervals	Squared deviation (Å)
	0.5	1-394	0.1162
MI	0.3	395-502	0.0560
	0.1	503-552	0.0296
	0.5	1-354	0.0895
MII	0.3	355-452	0.0382
	0.1	453-573	0.0260
	0.5	1-342	0.1202
MIII	0.3	343-466	0.0425
	0.1	467-617	0.0221

The last step in the building of the structural models of the three Cu-As-Se system alloys studied was refining the thermal factors. This was done by defining five coordination spheres, whose extreme radii are shown in Table IV, and by using the above mentioned iterative method of least squares, the isotropic factors, σ_i, shown in Table IV, were found for each coordination sphere of each one of the alloys under consideration.

Table IV. Thermal factor refining for each alloy.

Coordination sphere	r_{min}(Å)			r_{max}(Å)			σ_i(Å)		
order	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII
1st	0.00	0.00	0.00	3.00	3.00	2.60	0.0826	0.0968	0.0940
2nd	3.00	3.00	2.60	5.00	4.90	4.80	0.0961	0.0989	0.0968
3rd	5.00	4.90	4.80	6.60	6.30	6.70	0.1048	0.0994	0.1096
4th	6.60	6.30	6.70	8.20	8.10	8.20	0.1082	0.1130	0.1022
5th	8.20	8.10	8.20	10.00	10.00	10.00	0.1115	0.1049	0.1314

Once the thermal factor refining process was finished, the quadratic deviations between the theoretical and experimental values of function rG(r) were reduced to 0.0261 Å, 0.0255 Å and 0.0196 Å for compositions MI, MII and MIII respectively. The reduced RDF of each model after the refining process is shown in Fig. 2, (a, b, c) together with the corresponding experimental RDF.

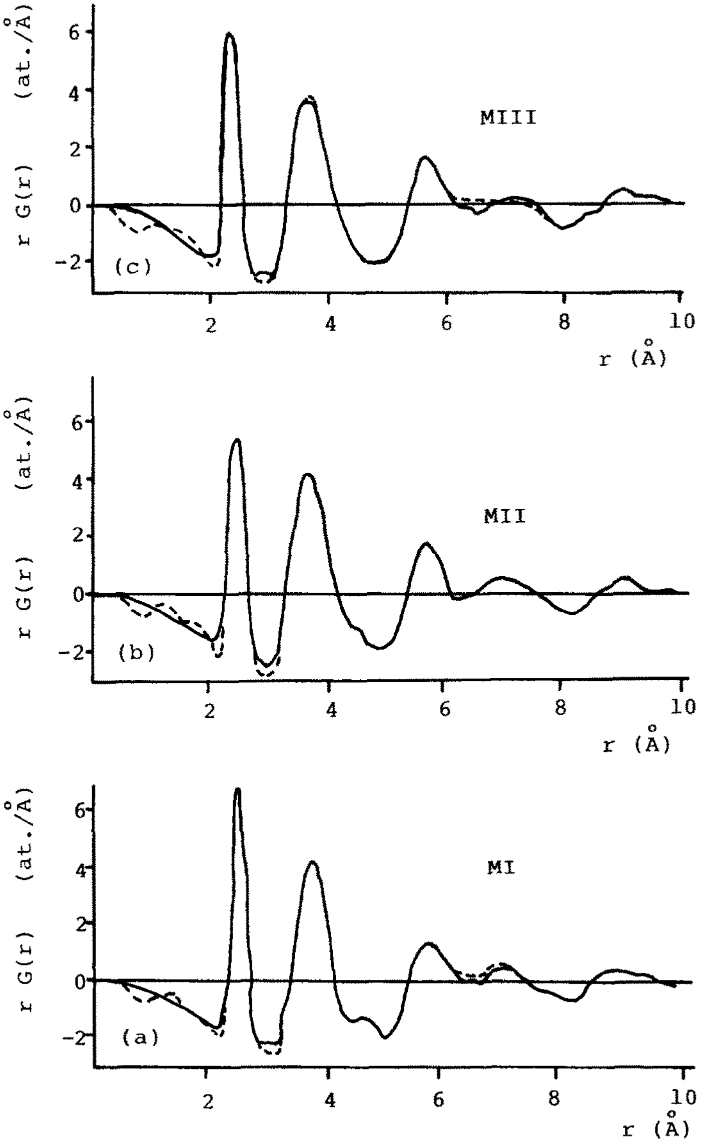

Fig. 2. (a,b,c). Representations of (----) calculated and (——) experimental RDFs.

The spatial representation of the atomic distribution of alloy MI is shown in Fig. 3, where tetrahedric units centred on copper atoms may be observed to coexist with other tetrahedric units centred on those arsenic atoms whose coordination has increased to four. Figure 4 is a spatial representation of the network of tetrahedrons centred on Cu or As atoms for alloy MII. Both kinds of tetrahedrons are joined together, either directly or by chains of selenium atoms forming networks of structural elements which constitute each one of the models.These theoretical models, generated by random methods and taking into account the structural information obtained from the experimental RDF, must be as representative as possible of the real structure of the composition under consideration. One way of estimating the agreement between these models and the atomic distribution of the corresponding alloys is to analyze the main structural parameters, coordinations and average bond lengths obtained from them.

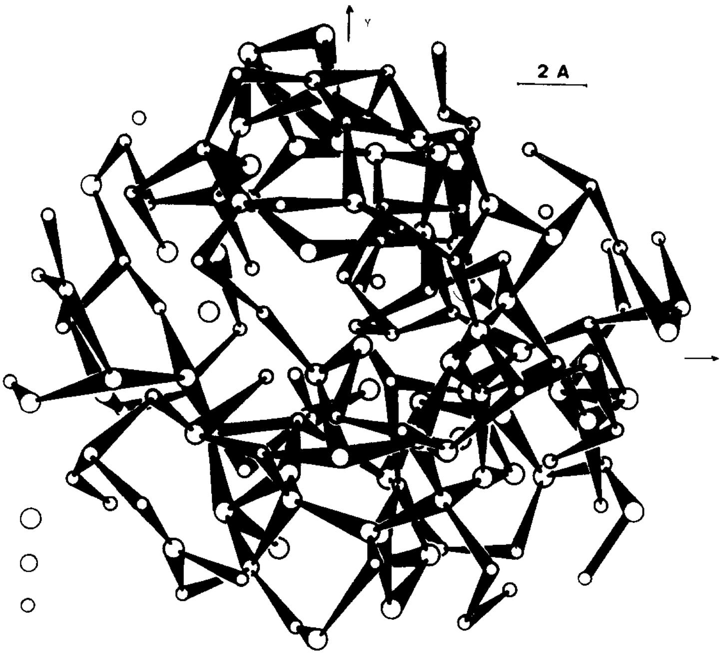

Fig. 3. Spatial representation of the model of alloy MI.

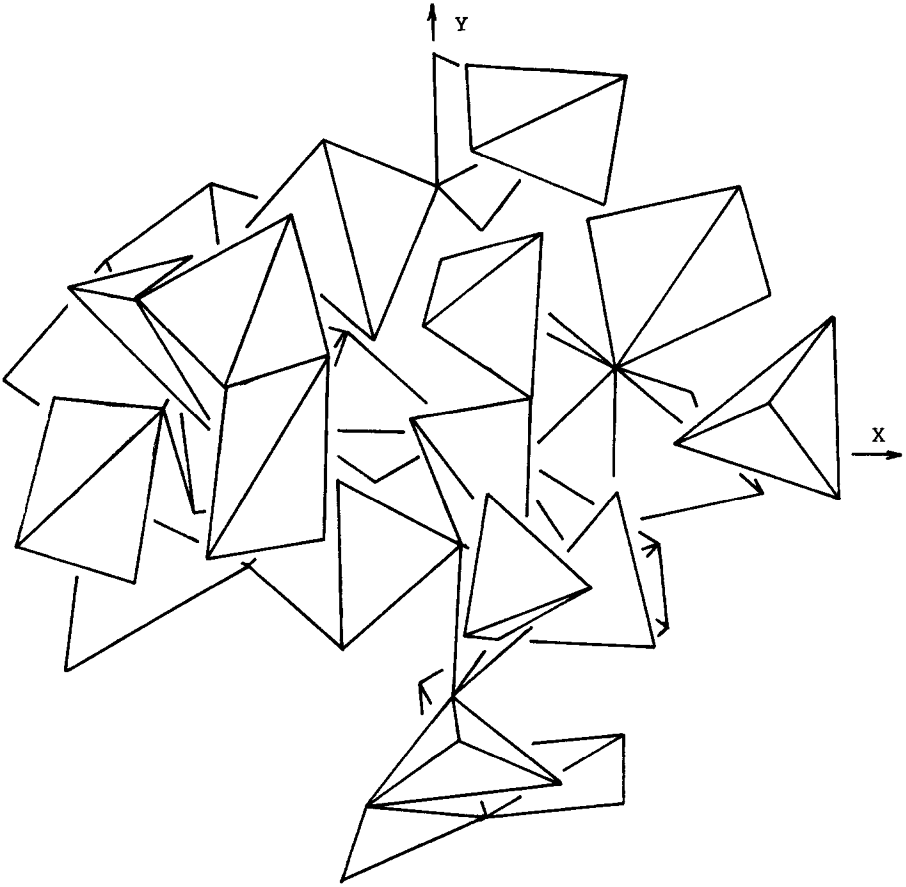

Fig. 4. Spatial representation of tetrahedral framework of alloy MII.

An important point to bear in mind when statistically analyzing the generated models is the comparison of the coordinations which result from their elements, and those of the structural units which, according to the established hypotheses, can be postulated from the information given by the experimental RDF.

Table V shows the coordinations of each element in the models corresponding to the three alloys and, in brackets, the coordinations which were theoretically predicted from the corresponding hypotheses [7]. In all the models, the existence of coordination defects may be observed, a fact which reveals the presence of atoms with unsaturated bonds, and which can be partly explained by the finite nature of the models. Thus, in the case of alloy MII, 65% of the bicoordinated arsenic atoms (As(2)) and 80% of the monocoordinated selenium atoms (Se(1)) are located less than 2 Å from the surface of the sphere limiting the model, and can therefore saturate their bonds with other elements located outside it. The monocoordinated arsenic atoms which appear in the three configurations can exhibit some bond defects, not explainable by the finite size of the models but which, as is a well-known fact, are an inherent consequence of the preparation method of chalcogenide glasses. It is also important to note the presence of overcoordinated atoms, As(4) and Se(3), in agreement with the tetracoordinated copper hypothesis and which is quoted in the literature [7] for alloys containing these elements.

Table V. Number of atoms with their coordination in each model.

Alloy	Atom type	Coordination				
		4	3	2	1	0
	Cu	8(0)	0(0)	0(0)	0(0)	0(0)
MI	As	9(11)	40(60)	17(0)	4(0)	1(0)
	Se	0(0)	21(13)	35(65)	19(0)	3(0)
	Cu	16(16)	0(0)	0(0)	0(0)	0(0)
MII	As	17(21)	29(44)	14(0)	4(0)	0(0)
	Se	0(0)	21(27)	39(56)	20(0)	3(0)
	Cu	34(34)	0(0)	0(0)	0(0)	0(0)
MIII	As	11(39)	30(13)	9(0)	2(0)	0(0)
	Se	0(0)	25(63)	46(22)	13(0)	1(0)

Another interesting aspect of the generated models is the average bond length between the different pairs of elements which constitute the material, as it reveals the agreement existing between the mentioned lengths, calculated theoretically from experimental data of the analyzed alloy, and those already known for other like compounds, giving a criterium for establishing the validity of the models.

Table VI shows the average bond lengths of all possible pairs in each one of the alloys. It may be observed that these distances are very similar in the three compounds, as in the most unfavourable case the difference is below 3.2%.

Table VI. Averaged bonding distances.

Bond	<d>(Å)		
	MI	MII	MIII
Cu-Cu	2.47	2.55	2.49
Cu-As	2.48	2.47	2.46
Cu-Se	2.41	2.42	2.47
As-As	2.45	2.41	2.42
As-Se	2.45	2.43	2.42
Se-Se	2.43	2.41	2.44

Figure 5 represents, as an example, the bond length histograms for the different kinds of pairs of elements in alloy MIII, since, being the one with the highest copper concentration, the number of bonds of each kind must be more representative from a statistical point of view.

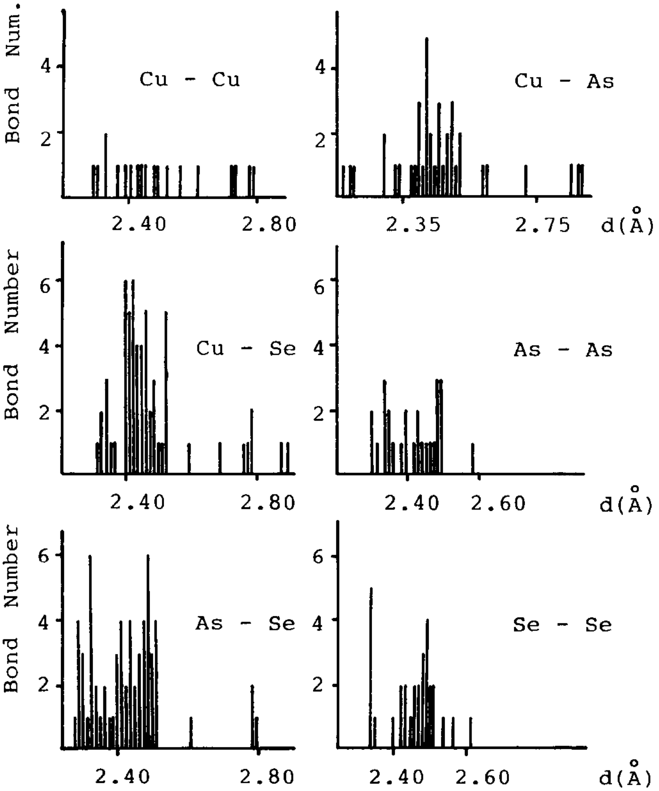

Fig. 5. Histograms of the distances in the pairs of elements of alloy MIII.

When it is wished to note that a theoretically generated model adequately represents the true structure of an amorphous alloy, a parameter which contributes to this aim is the average bond angle of each element with two of its first neighbours. In the case of the three Cu-As-Se system alloys, six different kinds of angles have been established, attending to the type and coordination of the atom in the vertex. These angles can have atoms of any kind at the ends of their sides, as long as their coordinations allow the formation of the corresponding angle. Bearing this in mind, the average values, $<\alpha>$, of the bond angles for the six different kinds of atoms in the vertex in each of the models, have been found and are shown in Table VII. In the three compounds studied, the average values of the bond angles, whose vertices are occupied by Cu, As or Se atoms, vary in the intervals (107.8 - 109.2)°, (108.4 - 109.6)° and (107.9 - 109.8)° respectively, which are, as can be seen, values very close to 109.5°, the angle in the centre of the regular tetrahedron.

Table VII. Averaged bonding angles for each alloy.

Type and coordination of the atom in the vertex	$<\alpha>$(deg)		
	MI	MII	MIII
Cu(4)	109.24	109.13	107.8
As(4)	107.45	107.27	108.42
As(3)	109.81	106.46	111.35
As(2)	107.91	114.41	109.12
Se(3)	107.99	105.88	108.28
Se(2)	110.23	113.66	107.54

ANALYSIS OF THE GENERATED MODELS

One way of estimating the degree of concordance between the theoretically elaborated spatial atomic distribution and the true structure of an alloy, consists of analyzing the main structural parameters which can be extracted from the former, relating their values to those quoted in the literature for other compounds like the one under study.

In this work, the average bond lengths shown in Table VI are compared to those of other alloys of similar elements quoted in the literature, in the following way:

(i) The average value of the Cu-Cu lengths, theoretically calculated for each one of the alloys studied, varies between

2.47 Å in composition MI and 2.55 Å in MII. It may be observed that the latter value is very close to 2.58 Å, the Cu-Cu bond length quoted in the literature [14], while the former differs somewhat more from the mentioned value, but the low copper concentration in alloy MI makes the number of bonds of this kind very small, so its comparative analysis may not be significant from a statistical point of view.

(ii) The Cu-As lengths are very similar in the three generated models, slightly below 2.53 Å, the length quoted for this bond by some authors [15], up to the point that in the most unfavourable case the difference with the quoted value is lower than 2.7%.

(iii) In the case of Cu-Se, the generated models give an average bond length of 2.43 Å, practically the same as the value of 2.42 Å quoted in the literature [15] for this bond.

(iv) The As-As bond length obtained theoretically varies between 2.41 Å and 2.45 Å. The former value is very close to 2.40 Å, the sum of the covalent radii [16] of the atoms involved in the bond, and exactly the same as the As-As length in alloy $Ge_{0.20}As_{0.40}Se_{0.40}$ [17]. In the case of alloy MI, the theoretically calculated length of 2.45 Å is in good agreement with the 2.49 Å quoted in the bibliography [18,19] for the As-As bond length in amorphous arsenic.

(v) The theoretical models give an average value of 2.43 Å for the As-Se bond, a value which is very close, in defect and in excess, to 2.46 Å and 2.41 Å, the lengths of this bond in alloys $As_{0.45}Se_{0.10}Te_{0.45}$ [20] and $Ge_{0.20}As_{0.40}Se_{0.40}$ [17] respectively, and exactly the same as the value found for this bond [21,22] in the binary glassy composition As_2Se_3.

(vi) In the case of the Se-Se bond whose average lengths vary between 2.41 Å and 2.44 Å, the former of these values is observed as being practically equal to the 2.40 Å of the Se-Se length in composition $Ge_{0.20}As_{0.40}Se_{0.40}$ [17], and in amorphous selenium [23] , while the latter is very slightly lower than the 2.45 Å quoted in the literature [24] for this bond in alloy $As_{0.20}Se_{0.50}Te_{0.30}$ and exactly the same as the Se-Se length in composition $As_{0.45}Se_{0.10}Te_{0.45}$ [20].

A detailed analysis of the theoretical values obtained shows, as has been pointed out, a very good agreement between these values and the bibliographical data; they can therefore be considered as representative of the bond lengths in the true structure of the alloys under study.

The average values of the bond angles shown in Table VII were analyzed, a great similarity being observed between these values and the characteristic angle of the typical tetrahedric disposition; the most probable atomic configurations of the alloys studied could therefore be formed basically by tetrahedric structural units.

CONCLUSIONS

Spatial atomic distribution models were made for the glassy alloys belonging to the Cu-As-Se system, MI, MII and MIII, using the Metropolis-Monte Carlo random method, and bearing in mind the geometrical conditions deduced from the radial atomic distribution function obtained by X-ray diffraction.

The frequently quoted tetracoordinated copper hypothesis was also taken into consideration, thus implying an increase in coordination in some As and Se atoms.

According to the analysis of the generated models, the tridimensional structure of the studied alloys can be described as a network of tetrahedrons centred on copper atoms, coexisting with other tetrahedrons whose centres are occupied by tetracoordinated arsenic atoms, making the network more compact. These tetrahedric units can be joined together by arsenic and selenium atoms or by chains of the latter element.

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. MAT 88-0561).

REFERENCES

1 W. Zacharaisen, J. Am. Chem. Soc., 54 (1932) 3841.

2 B. E. Warren, H. Krutter and O. Morning Star, J. Am. Ceram. Soc., 19 (1936) 202.

3 J. Biscoe and B.E. Warren, J. Am. Ceram. Soc., 21 (1938) 287.

4 Z. U. Borisova, Glassy Semiconductors, Plenum Press, New York, 1981.

5 D. Adler, B. B. Schwart and M. C. Steele (Éds.), Physical properties of amorphous materials, Plenum Press, New York, 1985.

6 M. Metropolis, A. W. Rosebluth, M. N. Rosebluth and A. M. Teller, J. Chem Phys., 21 (1953) 1087.

7 M. Domínguez, J. Vázquez, P. Villares and R. Jiménez-Garay, J. Non-Cryst. Solids., Study on the short-range order in some alloys of the Cu-As-Se glassy system by X-ray radial distribution analysis (submitted).

8 P. H. Gaskell, J. Phys. C 12 (1979) 7321.

9 M. Misawa and K. Suzuki, J. Phys. Soc. (Japan), 44 (1978) 1612.

10 M. D. Rechtin, A. L. Renninger and B. L. Averbach, J. Non-Cryst. Solids, 15 (1974) 74.

11 R. A. Ligero, J. Vázquez, P. Villares and R. Jiménez-Garay, J. Mater. Sci., 23 (1988) 1598.

12 G. Mason, Nature, 217 (1968) 733.

13 C. Alberdi, PhD thesis, Navarra University, Navarra, 1979.

14 R. B. Heslop and K. Jones, Inorganic Chemistry, Elsevier, Amsterdam, 1976.

15 F. D. Bloss, Crystallography and Crystal Chemistry, Holtz, Rinehart and Wiston, New York, 1977.

16 L. Pauling, Uniones químicas, Kapelusz, Buenos Aires, 1969.

17 N. de la Rosa-Fox, L. Esquivias, P. Villares and R. Jiménez-Garay, Phys. Rev., B33 (1986) 4094.

18 H. Krebs and R. Z. Steffen, Anorg. Allg. Chem., 327 (1964) 224.

19 G. N. Greaves and E. A. Davis, Phil. Mag., 29 (1974) 1201.

20 J. Vázquez, E. Márquez, P. Villares and R. Jiménez-Garay, Mater. Lett., 4 (1986) 360.

21 Y. Sagara, O. Uemura, S. Okuyama and T. Satow, Phys. Stat. Sol., 31a (1975)K33.

22 K. S. Liang, J. Non-Cryst. Solids, 18 (1975) 197.

23 R. W. Fawcett, C. N. J. Wagner and G. S. Cargill, J. Non-Cryst. Solids, 8-10 (1972) 369.

24 J. Vázquez, P. Villares and R. Jiménez-Garay, J. Non-Cryst. Solids, 86 (1986) 251.