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A STUDY ON SHORT-RANGE ORDER IN SOME ALLOYS OF THE Cu–As–Se GLASSY SYSTEM BY X-RAY RADIAL DISTRIBUTION ANALYSIS

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Abstract—The radial atomic distribution was studied in the amorphous alloys $Cu_xAs_{0.5-x}Se_{0.5}$, with $x = 0.05$ (MI), $x = 0.10$ (MII) and $x = 0.20$ (MIII), using X-ray diffraction data of samples of these alloys obtained by quenching the molten material. The short-range order proposed was determined through the interpretation of the radial distribution function (RDF), using a theoretical expression which takes into account the variation in the atomic dispersion factors with s (scattering vector module) and approximating them to polynomic functions. Different coordination hypotheses for Cu, quoted in the literature on glassy alloys containing this element, were taken into account. The result of the study is that tetracoordinated Cu is the hypothesis which best agrees with the experimentally-obtained structural information, so the most probable short-range order for the Cu–As–Se system alloys studied is made up of tetrahedral units centred on interlaced copper and arsenic atoms, forming a network.

Keywords: Glasses, structure, short-range order, chalcogenide.

1. INTRODUCTION

It is a well-known fact that amorphous materials have a metastable energetic state, so external agents such as light, heat, electron radiation or the electric field, among others, can produce substantial changes in their structure. If we bear in mind that many properties of materials, such as glass transition temperature, crystallization temperature and rate, thermal and electric conductivity, optical constants, chemical activity, etc. are considerably affected by structural changes, it is obvious that the field of application of amorphous materials is getting wider every day.

Se-based chalcogenide glasses, unlike those containing Te, usually exhibit high resistivity values implying certain limitations for their application, as well as difficulties in electrical measurements. Some authors [1] point out that the addition of elements with d orbitals to chalcogenide glasses can produce considerable changes in their electrical properties. Specifically, the addition of Cu produces a strong increase in conductivity in the As and Se glassy systems, as well as an even stronger decrease in conduction activation energy. These Cu, As and Se alloys also exhibit interesting switching properties which depend on the Cu content, as well as the memory effect, which makes them appropriate for the manufacture of electronic devices [2].

It must also be pointed out that the glass transition temperature of the amorphous materials in the Cu–As–Se system increases with the Cu content, oscillating around 450 K [3], which means they are relatively stable. It must be noted that the stability of these chalcogenide glasses with polivalent elements is in fact due to the presence of this type of element, which modifies the properties by forming tridimensional structural units. The polivalent atoms that stabilize the structures of the chalcogenide glasses are mainly arsenic and germanium, as they form spatial units with the chalcogenes, breaking up their characteristic complex structure and contributing to the establishment of more homogeneous structures for the glassy alloys belonging to this kind of system, a fact which explains some of the properties mentioned.

The analysis of the short-range structure of the $Cu_xAs_{0.5-x}Se_{0.5}$ alloys, with $x = 0.05$ (MI), $x = 0.10$ (MII) and $x = 0.20$ (MIII), was done bearing in mind the aforementioned reasons, from the information supplied by the radial distribution function (RDF) of each of the alloys, obtained by X-ray diffraction. The experimental values of the area under the first RDF peak were compared with those obtained theoretically for this magnitude [4, 5] as a coordination function of copper, and bearing in mind that the functions $R_{ij}(s) = f_i(s)f_j(s)/[\Sigma_i x_i f_i(s)]^2$ depend on the scattering angle [6] and cannot always be approximated by the constant value $Z_iZ_j/(\Sigma_i x_iZ_i)^2$.

2. EXPERIMENTAL PROCEDURE

2.1. *Preparation of the samples*

The samples of the three alloys were prepared in bulk form, from 99.999%-pure Cu, As and Se, pulverized to grains smaller than 40 μm. The three elements were homogeneously mixed in the adequate proportions, in each case, in order to obtain 7 g of the

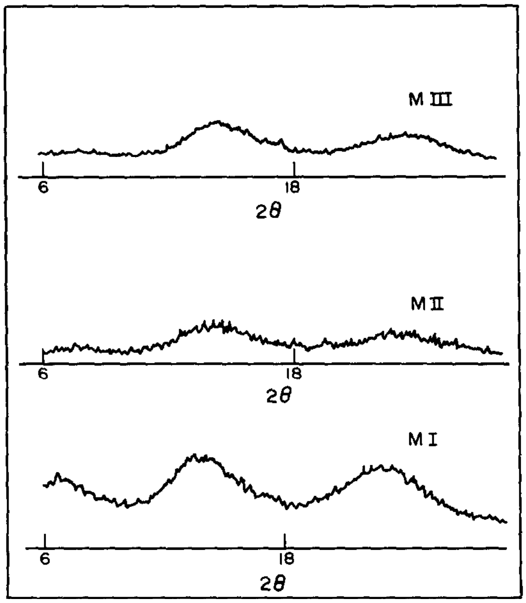


Fig. 1. Diffractograms of the three alloys.

composition desired. The samples were put into quartz ampoules and subjected to an alternating process of filling and vacuuming of inert gas (He) until a residual pressure of 10^{-3} torr was reached. The ampoules were sealed with an oxyacetylene burner, in order to avoid a possible oxidation of the alloy during the thermal process, and put into a rotary furnace at 1000°C, guaranteeing the melting of the three elements. Thanks to the rotation device of the furnace, the ampoules turned at 1/3 rpm, in order to ensure the homogeneity of the molten material. After 6 h under these stirring and heating conditions, the ampoules were quenched in air, producing the glassy material in this system.

The quartz ampoules were corroded in a mixture of hydrofluoridic acid and hydrogen peroxide, in order to take the alloys out. Part of the samples were pulverized and pressed into $20 \times 20 \times 1\ \mathrm{mm}^3$ tablets, and it was checked by X-ray diffraction that the compounds did not exhibit the characteristic peaks of a crystalline phase. Figure 1 shows the diffractograms corresponding to each of the alloys. The density of each alloy was determined by a pycnometric method at a constant temperature. The average values obtained from the series of measurements carried out, with relative errors always below 3%, were: $4.75\ \mathrm{g\,cm^{-3}}$, $4.90\ \mathrm{g\,cm^{-3}}$ and $5.06\ \mathrm{g\,cm^{-3}}$ for alloys MI, MII and MIII, respectively.

2.2. *X-Ray diffraction intensity measurements*

The intensities of the radiations diffracted by the samples were measured in an automatic SIEMENS D500 powder diffractometer with Bragg–Brentano geometry by reflection. The proper selection of an X-ray wavelength was obtained with a curved graphite monochromator. The device was equipped with a scintillation detector, with a Tl-enriched photosensitive NaI window.

Table 1. Characteristics of the diffractometric system of measurement

Angular interval (deg)	$\Delta(2\theta)$ (deg)	Divergence slit (deg)
5–23	0.2	0.3
20–70	0.2	1
67–70	0.2	3
70–110	0.5	3

Since the detection system used consists of counting the number of photons randomly received, whose statistical error depends on the number of photons that reach the detector, the intensities were measured by determining the number of counts and digitally registering the time it took to carry them out, so the error is kept constant throughout the whole series of measurements. The number of pulses was determined as 4000, so the relative error was kept below 1.5%. The intensities diffracted by the samples were measured in the range of s $(=4\pi/\lambda \sin\theta)$ from 0.77 to $14.48\ \text{Å}^{-1}$ using a radiation of MoK_α ($\lambda = 0.71069$ Å), supplying the generator with a power of 50 kV–30 mA. Four series of measurements were carried out, two ascending and two descending in Bragg's angle. In order that the sample surface radiated at low and high angles would be approximately the same, three types of slits were used, whose divergence slits, intervals of use and angular increases are shown in Table 1.

The average of the four measurements carried out for each angle was taken as the intensity of the radiation diffracted by the samples.

2.3. *Treatment of the X-ray intensities*

The above-mentioned intensities were corrected, as usual, as to background, polarization and multiple scattering [7], in order to eliminate the part of the radiation which does not carry structural information. Figure 2 shows these corrected intensities in arbitrary units for each alloy.

The normalization of electronic units (e.u.) was done bearing in mind the high-angle technique [7], according to which, for high values of s, the experimental intensity curve should oscillate around the independent scattering curve of the structure. The normalization method [4] consisted of fitting, by least-square, the experimental curve $I(s)$ in arbitrary units to the independent scattering curve $f(s)$, by minimizing the function

$$S = \sum_{i=1}^{N} [f(s_i) - K_1 I(s_i)\exp(-K_2 s_i^2)]^2, \qquad (1)$$

where K_1 and K_2 are two adjustment parameters, and the factor $\exp(-K_2 s_i^2)^2$ is used as an adequate mathematical function for simulating a reduction in the amplitude of the oscillations for increasing angles. The normalized intensities were corrected for the

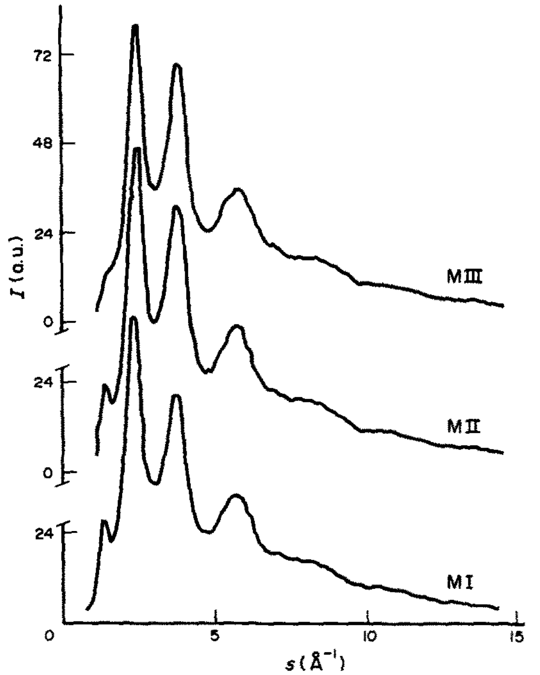


Fig. 2. Corrected intensities in arbitrary units.

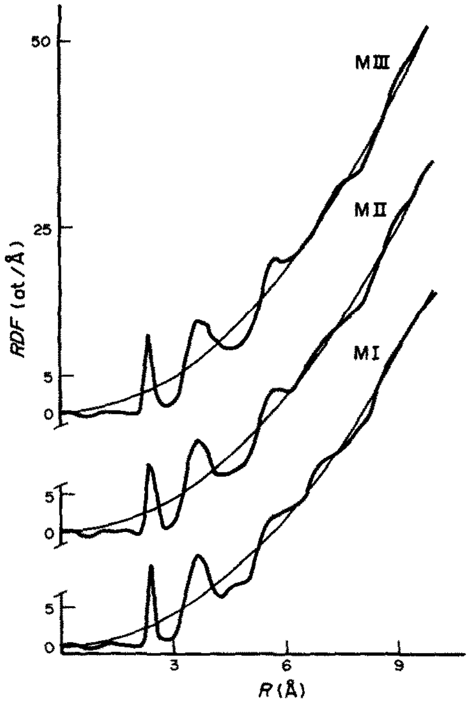


Fig. 3. Radial distribution functions.

Compton effect, the coherent spectrum $I_{e.u.}(s)$ being obtained from which the reduced intensities are, in turn, obtained

$$i(s)=\frac{I_{e.u.}(s)-\sum_i x_i f_i^2(s)}{\left[\sum_i x_i f_i(s)\right]^2}, \qquad (2)$$

where x_i and $f_i(s)$ are the atomic fraction and the atomic dispersion factor of an i-type atom, respectively.

The application of a Fourier transformation to the interference function, $F(s)=s\cdot i(s)$, resulted in the relationship

$$G(r)=\frac{2}{\pi}\int_0^{s_{max}} F(s)\sin sr\, ds, \qquad (3)$$

s_{max} being the maximum limit for which there are experimental data.

From eqn (3), the radial distribution function (RDF) is immediately deduced

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

where $\rho(r)$ is the local atomic density which is affected by the Fourier transformation of the products $R_{ij}(s)=(f_i(s)f_j(s))/([\Sigma_i x_i f_i(s)]^2)$ and ρ_0 is the average experimental atomic density of the material expressed in atoms per cubic angstrom. The spurious oscillations which appear in the radial atomic distribution function for small values of r, due to the lack of experimental data for high values of s, make it necessary to extend the interference function up to 30 Å^{-1}, a value for which function $F(s)$ tends towards zero. The extension was carried out using the method described in the literature [8], based on the one proposed by Shevchik [9] according to whom, for high values of s, the experimental interference function can be approximated by

$$F_{\text{theoretical}}(s)=C/r\,\exp\left(\frac{-\sigma^2 s^2}{2}\right)\sin sr, \qquad (5)$$

where C, r and σ are parameters obtained by least-square adjustment from the initial values C_1, r_1 and σ_1, which represent the area, the position and the half-width of the first RDF peak, deduced from eqn (3) for $s_{max}=14.48$ Å^{-1}, the maximum value for which data have been obtained with the device used. The Fourier transformation was applied to the extended interference functions, resulting in the RDFs shown in Fig. 3 for each of the alloys, and from which the structural information in Table 2 was obtained.

3. RESULTS AND DISCUSSION

3.1. *Analysis of the RDFs*

The analysis of the structural data supplied by the radial atomic distribution functions of the alloys studied shows, among other things, that the definition interval of the first peak, corresponding to the first coordination sphere, in each of the compositions in the Cu–As–Se system (Cu = 1, As = 2, Se = 3), is

Table 2. Structural information supplied by the experimental RDFs

Alloy	MI		MII		MIII	
Maximum	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

such that all types of bonds between the different elements of the three alloys considered are possible, as may be deduced by comparing these intervals with the bond lengths, r_{ij}, of all possible pairs quoted in the literature and shown in Table 3.

Bearing in mind that Se–X bonds (X = Cu, As, Se) are perhaps those which should contribute most to the diffraction spectrum, it seems logical to think that the first RDF maximum is between the values which define the bond lengths of the corresponding pairs, which agrees with the average weighed values of these three kinds of bond, which vary between 2.36 and 2.37 Å for the three alloys studied. Given the character of the RDF as a probability function, the positions of its maximum values can be interpreted as the average distances of the different coordination spheres to an arbitrary atom taken as a reference origin; specifically, the abscissa of the first maximum represents the average distance between first neighbours.

A parameter of great interest, when trying to postulate short-range models of a glassy solid, is the area enclosed under the first RDF peak, as it represents the number of atoms which, on average, surround any given atom, that is, the average coordination number of the material. This area is related to certain structural parameters, the relative mean coordination numbers n_{ij}, which represent the average number of j-type atoms surrounding any given i-type atom.

The above-mentioned area is frequently expressed as

$$\text{area} = \frac{1}{\left(\sum_i x_i Z_i\right)^2} \sum_i \sum_j n_{ij} x_i Z_i Z_j, \qquad (6)$$

where Z_i, Z_j are the atomic numbers of elements i and j, respectively; however, in a more accurate consideration, when the functions $R_{ij}(s)$ vary considerably with the scattering angle, Vázquez and Sanz [6] have deduced a more exact expression for the area of the first RDF peak, following the method described by Warren [7] and considering that the products $R_{ij}(s)$ can be approximated by polynomes in n-order s. This expression is

$$\text{area} = \frac{2}{\pi} \sum_i \sum_j x_i \frac{n_{ij}}{r_{ij}} \int_a^b r P_{ij}(r)\,\mathrm{d}r, \qquad (7)$$

where a and b are the limits of the first RDF peak and $P_{ij}(r)$ is a function defined by

$$P_{ij}(r) = 1/2 \int_0^{s_m} \frac{f_i(s) f_j(s)}{\left[\sum_i x_i f_i(s)\right]^2} \cos s(r - r_{ij})\,\mathrm{d}s. \qquad (8)$$

The structural information obtained from the analysis of the experimental radial atomic distribution, together with some physical–chemical properties of the alloys and their elements, give way to hypotheses on the local order of amorphous materials. Considering the ternary glassy alloy $A_{a'_1} B_{a'_2} D_{a'_3}$ for every 100 atoms of material, the mentioned hypotheses are:

(i) Element A, copper in the present case, has coordination N, no matter what the composition of the alloy, and the average coordination numbers of this element with all those bonded to it are proportional to their respective percentual concentrations.

(ii) The total number of i-type bonds, a_i, is given by

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

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

(iii) If the normal coordinations of the different elements in the sample are called C_i, and it is assumed that element A has a coordination of N ($N \geqslant C_1$), the number of bonds of this type of atom is

$$a_1 = Na'_1 = C_1 a'_1 + x,$$

x being the increase in the number of bonds of the said element, when its coordination changes from C_1 to N.

(iv) When the coordination of element A increases, the coordinations of elements B and D may increase

Table 3. Bond lengths

Pair	r_{ij} (Å)	Ref.
Cu–Cu	2.58	10
Cu–As	2.53	11
Cu–Se	2.42	11
As–As	2.57	12
As–Se	2.38	13
Se–Se	2.34	13

Table 4. Straight regression lines fitted to the values of $R_{ij}(s)$

Pair	$F'_{ij}(s)$		
	MI	MII	MIII
Cu–Cu	$-3.78 \times 10^{-3}s + 0.7479$	$-3.69 \times 10^{-3}s + 0.7574$	$-3.48 \times 10^{-3}s + 0.7769$
Cu–As	$-2.36 \times 10^{-3}s + 0.8567$	$-2.22 \times 10^{-3}s + 0.8676$	$-1.91 \times 10^{-3}s + 0.8899$
Cu–Se	$-1.96 \times 10^{-3}s + 0.8839$	$-1.81 \times 10^{-3}s + 0.8951$	$-1.48 \times 10^{-3}s + 0.9182$
As–As	$-3.56 \times 10^{-4}s + 0.9812$	$-1.56 \times 10^{-4}s + 0.9936$	$2.71 \times 10^{-4}s + 1.0193$
As–Se	$1.97 \times 10^{-4}s + 1.0124$	$4.12 \times 10^{-4}s + 1.0252$	$8.71 \times 10^{-4}s + 1.0516$
Se–Se	$7.89 \times 10^{-4}s + 1.0445$	$1.02 \times 10^{-3}s + 1.0578$	$1.51 \times 10^{-3}s + 1.0850$

or decrease, so the number of bonds of these elements is given by

$$a_i = C_i a'_i \pm y_i \quad (i \neq 1),$$

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

Taking this hypothesis into account, Vázquez *et al.* [5] have deduced the following relation from eqn (7) and according to the literature [4]:

$$\text{area} = 1/50\pi\left[\left(h + \beta A_{22} - \delta \sum_{i,j \neq 1} A_{ij}\right)N + \alpha A_{22} + \gamma \sum_{i,j \neq 1} A_{ij} + P\left(\sum_{i,j \neq 1} A_{ij} - \sum_{\substack{i,j \neq 1 \\ i \neq j}} A_{ij}\right)a_{ij}\right], \quad (9)$$

where h, α, β, γ and δ are characteristic parameters of each alloy, N is the coordination attributed to a certain element of the same, P is a parameter worth 2 when, in the variable a_{ij}, $i = j$, and -1 if $i \neq j$, and A_{ij} is determined by

$$A_{ij} = \frac{1}{r_{ij}} \int_a^b r P_{ij}(r)\, dr. \quad (10)$$

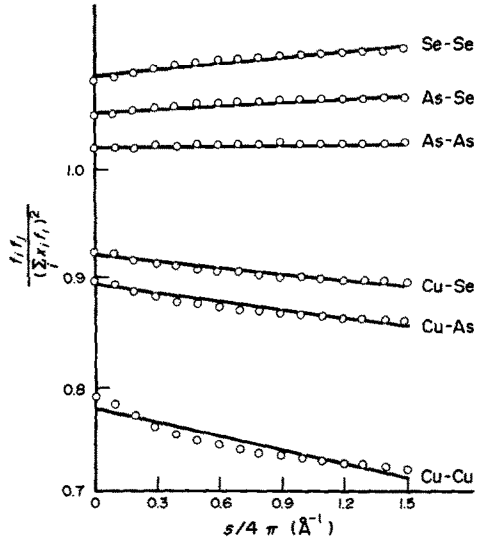


Fig. 4. Straight regression lines fitted to the values of $R_{ij}(s)$ in alloy MIII.

Bearing in mind that, according to the literature [6], the evaluation of the parameters A_{ij} implies the establishment of the order of the polynomes in s which approximate the functions $R_{ij}(s)$, in this work these functions have been fitted to the straight regression lines of the corresponding pairs of elements which constitute each alloy and whose equations, $F'_{ij}(s) = A_{0ij}s + A_{1ij}$, are shown in Table 4. Figure 4 shows, as an example, the above-mentioned straight lines for composition MIII.

In order to evaluate the parameters A_{ij}, eqn (10), which may be written as

$$A_{ij} = \frac{1}{2r_{ij}}[B_{1ij} + B_{2ij} + r_{ij}(B_{3ij} + B_{4ij})], \quad (11)$$

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

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

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

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

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

where $a'_{ij} = a - r_{ij}$, $b'_{ij} = b - r_{ij}$ and $x = r - r_{ij}$, has made it possible to calculate the values in Table 5.

In order to express the area under the first RDF peak according to the coordination, N, which can be attributed to the Cu in the Cu–As–Se system alloys studied, the following characteristic parameters have

Table 5. A_{ij} parameters

Pair	A_{ij}		
	MI	MII	MIII
Cu–Cu	1.1771	1.2631	1.2049
Cu–As	1.3354	1.4828	1.3133
Cu–Se	1.4186	1.4683	1.4012
As–As	1.5497	1.6928	1.5715
As–Se	1.6343	1.6232	1.6953
Se–Se	1.6386	1.5726	1.8347

been calculated for each of them, in agreement with the literature [5]:

$$h = 5.6122 \quad \alpha = 35.26 \quad \beta = -0.26$$

$$\gamma = 97.37 \quad \delta = -2.63 \quad \text{for MI;}$$

$$h = 13.2690 \quad \alpha = 21.11 \quad \beta = -1.11$$

$$\gamma = 94.44 \quad \delta = -5.56 \quad \text{for MII;}$$

$$h = 20.9850 \quad \alpha = -5 \quad \beta = -5$$

$$\gamma = 87.5 \quad \delta = -12.5 \quad \text{for MIII.}$$

From these data, the corresponding parameters A_{ij} and using eqn (9), the following expressions have been determined for the area:

$$\text{area} = 2.3740 + 0.0879N - 0.0010a_{33} \quad \text{for MI}$$

$$\text{area} = 2.1794 + 0.1873N + 2.42 \times 10^{-4}a_{33} \quad \text{for MII}$$

$$\text{area} = 1.8386 + 0.3534N + 1.99 \times 10^{-4}a_{33} \quad \text{for MIII} \qquad (12)$$

which, as may be observed, are functions of the coordination postulated for Cu, so they are an interesting basis to discern when it comes to elaborating hypotheses on the short-range order of the compounds in this system. It is also obvious that these expressions are functions of the number of Se–Se bonds, a_{33}, a fact which makes it possible to limit the variability field of the theoretical area.

3.2. *Short-range order hypotheses*

In order to build a local order model of a glassy material, it is necessary to establish the average coordinations of its elements. In the case of the Cu–As–Se system, it is a relatively complex question to attribute a certain coordination to Cu, due to the variety of hypotheses that appear in the literature for the coordination of this element in the different compounds it forms. For example, in Cu_2O the atoms of the metal have a coordination of 2, linked to two oxygen atoms, and these, with a coordination of 4, are linked to four Cu atoms [10]. The structure of Cu_2O may be explained considering an *sp* hybridation of the Cu [13, 14], which results in one of the orbitals remaining empty, while the other is occupied by an electron. The first could be used to accept electrons donated by oxygen atoms, while the second, which possesses an electron, would bond with another oxygen atom. We can assume an analogous structure for the alloys under study, as Se is in the same group of the Periodical Table as oxygen. If we admit a coordination of 2 for Cu, the electrons which need to take this element would be supplied by some As and Se atoms, whose coordination would turn into 4 and 3, respectively.

In order to determine whether the above coordination hypothesis is valid, relationships (12) were applied with $N = 2$ and considering the term dependent on a_{33} as negligible, the following values being obtained for the area under the first RDF peak: 2.54, 2.55 and 2.55 for alloys MI, MII and MIII, respectively, which, as may be observed, are considerably less than those obtained experimentally, a fact which led to the rejection of coordination 2 for the Cu in the compositions studied in the Cu–As–Se system.

Another frequent hypothesis in the literature is coordination 4 for Cu. With RDF studies as a basis, some authors postulate the existence of tetracoordinated Cu atoms in glassy alloys of the system under study. Hunter *et al.* [15], from studies of the EXAFS spectrum, attribute four first neighbours to the Cu, a value which is also to be found in other compounds of this element such as CuFeS [13], Cu_3AsS_4 [13] and CuAsI [10]. In the present work, tetracoordinated Cu ($N = 4$) has been assumed, accepting the necessary electrons for the sp^3 hybridation of some arsenic and selenium atoms, which increase their coordination by one unit [16, 17]. Under this hypothesis, relationships (12) give the following values for the area under the first RDF peak:

$$2.7256 - 10^{-3}a_{33} \quad \text{for MI}$$

$$2.9296 + 2.42 \times 10^{-4}a_{33} \quad \text{for MII}$$

$$3.2522 + 1.99 \times 10^{-4}a_{33} \quad \text{for MIII,}$$

expressions which are in good agreement with the experimentally-determined values, within the ±0.1 atoms margin of error. These relationships are observed to vary linearly with the number of Se–Se bonds, and since the area is a function of the relative coordination numbers, which in turn depend on the coordination number, N, of a particular element, copper, in the alloy [4], it is necessary to determine the variation interval of a_{33} due to the restrictions imposed by the intrinsically positive nature of the n_{ij}s.

When local order models of amorphous materials are proposed, the above-mentioned interval supplies the possible margin within which the structure evolves.

If the area is expressed as a function of the number of Se–Se bonds, the n_{ij}s, which contain parameter a_{33}, are given [4] by the expressions

$$n_{22} = \frac{\alpha + [(100 - (a'_2 + a'_3))/100]\beta N + 2a_{33}}{a'_2}$$

$$n_{23} = \frac{\gamma - [(100 - (a'_2 + a'_3))/100]\delta N - 2a_{33}}{a'_2} \qquad (13)$$

which allow us to write, for each composition, the relative coordination numbers shown in Table 6,

Table 6. Coordination numbers n_{ij}, $i, j \neq 1$, and variation intervals of parameter a_{33} and of the area for each alloy

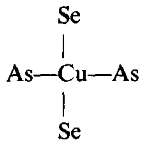
Alloy	Coordination numbers n_{ij}, $i, j \neq 1$	Variation intervals	
		Parameter a_{33}	Area
MI	$n_{22} = 0.7824 + 0.0444a_{33}$ $n_{23} = 2.1755 - 0.0444a_{33}$	0–49.0	2.726–2.677
MII	$n_{22} = 0.5167 + 0.05a_{33}$ $n_{23} = 2.4166 - 0.05a_{33}$	0–48.33	2.930–2.941
MIII	$n_{22} = -0.3 + 0.0666a_{33}$ $n_{23} = 3.25 - 0.0666a_{33}$	4.5–48.75	3.253–3.262

together with the variation intervals of parameter a_{33} and of the area under the first RDF peak.

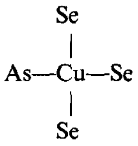
In Table 6 it may be observed that the intervals of a_{33} are very similar in the three alloys, which may be attributed to the fact that they all have the same Se percentage. The good agreement between the values of the theoretical areas throughout the interval and those obtained experimentally, shown in Table 2, also must be noted, as well as the little change in this parameter throughout the a_{33} interval, which may be explained by the similarity in the atomic factors of the three elements in the system, especially arsenic and selenium.

Bearing in mind the values of the n_{ij}s corresponding to the extremes of the a_{33} intervals, it may be postulated that the material of each one of the alloys has a short-range order which evolves between the extreme situations indicated, so those models that verify the average coordination numbers of the extreme values mentioned may be considered as the most probable structural models.

According to these hypotheses, short-range order models may be proposed for the alloys considered in the Cu–As–Se glassy system in which, together with tetrahedral units centred on copper atoms, such as



$$\begin{array}{c} \mathrm{Se} \\ | \\ \mathrm{As{-}Cu{-}As} \\ | \\ \mathrm{Se} \end{array}$$



$$\begin{array}{c} \mathrm{Se} \\ | \\ \mathrm{As{-}Cu{-}Se} \\ | \\ \mathrm{Se} \end{array}$$

there are other tetrahedra centred on arsenic atoms. All of these structural units would be joined by ramified chains, made up of an excess of arsenic and selenium atoms [18, 19].

4. CONCLUSIONS

According to the radial atomic distribution functions of the different alloys studied in the Cu–As–Se glassy system, obtained from the X-ray diffraction data and with the different copper coordination hypotheses quoted in the literature, it has been found that the consideration of tetracoordinated copper best explains the average number of first neighbours determined experimentally for each of the compositions analysed.

The use of the most approximate expression of the area under the first RDF peak has made it possible to discard two-coordination for the copper, as it has in copper oxide, as this coordination implies a considerably smaller theoretical area than that obtained experimentally for each of the alloys.

The structural configuration which most agrees with the experimental data in all cases is a network of tetrahedral units centred on Cu atoms, which coexist with other tetrahedra whose centres are taken up by As atoms. These units can be joined together directly or through Se atoms, due to the high concentration of this element in the samples and its strong tendency to form chains.

REFERENCES

1. Borisova Z. U., *Glassy Semiconductors*. Plenum Press, New York (1981).
2. Adler D., Schwartz B. B. and Steele M. C. (Editors) *Physical Properties of Amorphous Materials*. Plenum Press, New York (1985).
3. Vázquez J., Ligero R. A., Villares P. and Jimenez-Garay R., *Thermochim. Acta* **157**, 181 (1990).
4. Vázquez J., Esquivias L., Villares P. and Jimenez-Garay R., *Ann. Fis.* **B81**, 223 (1985).
5. Vázquez J., Villares P. and Jimenez-Garay R., *Mater. Lett.* **4**, 485 (1986).
6. Vázquez J. and Sanz F., *Ann. Fis.* **B80**, 31 (1984).
7. Warren B. E., *X-ray Diffraction*. Addison–Wesley, Reading (1969).
8. D'Anjou A. and Sanz F., *J. non-crystalline Solids* **28**, 319 (1978).
9. Shevchick N. J., PhD thesis, Harvard University (1972).
10. Heslop R. B. and Jones K., *Inorganic Chemistry*. Elsevier, Amsterdam (1976).
11. Bloss F. D., *Crystallography and Crystal Chemistry*. Holt, Rinehart and Winston, New York (1977).
12. Vázquez J., Marquez E., Villares P. and Jimenez-Garay R., *Mater. Lett.* **4**, 360 (1986).
13. Pauling L., *Uniones Quimicas*. Kapelusz, Buenos Aires (1969).
14. Gutierrez Rios E., *Quimica Inorgánica*. Reverte, Barcelona (1978).
15. Hunter S. H., Biennenstack A. and Hayes T. M., *The Structure of Non-Crystalline Materials* (Edited by P. H. Gaskell). Taylor and Francis, London (1977).
16. Vázquez J., Marquez E., de La Rosa-Fox N., Villares P. and Jimenez-Garay R., *J. Mater. Sci.* **23**, 1709 (1988).
17. Esquivias L. and Sanz F., *J. non-crystalline Solids* **72**, 165 (1985).
18. Corb B. W., Wei W. D. and Averbach B. L., *J. non-crystalline Solids* **53**, 29 (1982).
19. Ligero R. A., Vázquez J., Villares P. and Jimenez-Garay R., *J. Mater. Sci.* **22**, 4357 (1987).