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SHORT-RANGE ORDER AND SPATIAL ATOMIC DISTRIBUTION MODEL FOR SEMICONDUCTING GLASSY ALLOY $As_{.35}Se_{.30}Te_{.35}$ BY X-RAY DIFFRACTION

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ABSTRACT

A study was carried out on the radial atomic distribution of amorphous alloy $As_{.35}Se_{.30}Te_{.35}$, using the data supplied by X-ray diffraction of its samples, which were obtained using the melt-quench method. Short-range order was determined by interpreting the Radial Distribution Function (RDF), using a theoretical expression which takes into account the variation in the atomic scattering factors with **s** (scattering vector module), and approximating them to polynomial functions. The tetra- and tri-coordinated arsenic hypotheses, quoted in the literature for glassy alloys containing this element, were taken into consideration. The result of the study is that, for the alloy in question, only the tri-coordinated arsenic hypothesis is compatible with the structural information obtained experimentally. According to this coordination for the arsenic, a spatial atomic distribution model was generated, using the conveniently modified Metropolis-Monte Carlo random method. This model consists of triangular pyramids with arsenic atoms at some of their vertices, joined together forming a network. A comparative analysis of the main structural parameters of this model revealed their good agreement with the values given in the literature for similar alloys.

INTRODUCTION

The knowledge of amorphous solids, materials whose atomic distribution lacks long-range order [1], is one of the most active fields of research in the physics of condensed materials today. The great interest in these materials is largely due to their ever increasing applications in modern technology. Their possibilities in the immediate future are huge, based on characteristic properties such as electronic excitation phenomena, chemical reactivity and inertia, superconductivity, etc. Within twenty years, an industry with a great future, the transformation of different types of energy (light, heat, and chemical energy, among others) into electricity, will use large quantities of non-crystalline substances [2]. The data processing and storing industry will also use these materials, during the present decade. Their application in the manufacture of heat, corrosion and abrasion-resistant products will also increase considerably, as well as in catalysis for the manufacture of water desalinization membranes, among other basic chemical activities.

For all these reasons, we may agree with Ovshinsky [3] in that, if the ages of Mankind take their names from the materials which predominate in them, the next century will be called the Glass Age. The current years are marking the transition from the age of ordered materials (crystalline state) to the age of those lacking long-range order (amorphous state).

Among glassy materials, chalcogenides are remarkable for their semiconducting properties. Kolomiets [4] proved that chalcogenide glasses behave as intrinsic semiconductors and that their electric conductivity is not altered by the addition of impurities. Later on, Spear performed carrier mobility measurements in selenium glasses, and Tauc et al. [5] studied semiconducting properties in amorphous germanium. But these materials began to grow in importance in 1968, the year in which Ovshinsky [6,7] discovered and published the switching phenomenon in chalcogenide glasses.

Glassy solids, though lacking long-range order, do have short-range order in their bonds with first neighbours, up to a few atomic diameters, showing a characteristic spectrum in the diffractogram. Given the close relationship between macroscopic properties and structure, it is interesting to know the atomic distribution of a glassy solid and to establish short-range structural models, as every amorphous material possesses such a structure, which conditions its macroscopic behaviour.

This work shows the structural information for the glassy alloy $As_{.35}Se_{.30}Te_{.35}$, supplied by its Radial Distribution Function (RDF), obtained from the X-ray diffraction intensities; after analyzing this information, the coordination hypotheses were formulated, making it possible to establish the short-range order of the material.

Based on these hypotheses and on the geometric restrictions imposed by the experimental RDF, a spatial atomic distribution model was generated, using the Metropolis-Monte Carlo random method. An analysis of the main parameters (coordinations and bond lengths and angles) of this model shows their good agreement with the values quoted in the literature for similar alloys.

THEORETICAL ASPECTS

Structural research in all kinds of materials is based fundamentally on the interpretation of the phenomenon of radiation diffraction by the solid. Although several kinds of radiation are used as instruments for detecting atomic positions, X radiation is the most widely used, due to its simple technology. It was used for obtaining structural information on the semiconducting glassy alloy $As_{.35}Se_{.30}Te_{.35}$.

The well-known electromagnetic wave diffraction theory, for a spatial atomic configuration, makes it possible to deduce a relation between diffracted intensity in a given direction and the relative positions of the atoms in the material. When this relation is applied to an amorphous material, in which it is possible to postulate that these positions are completely randomly oriented, the diffracted intensity in each direction, expressed in electronic units (e.u.), is given by Debye's relation [8]

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

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

In order to obtain structural information on a glassy solid, it is necessary to determine the relative positions between the atoms of the material from a set of diffracted intensities; in this sense, Zernicke and Prins [9] applied the Fourier transformation to a function of the diffracted intensities, obtaining an expression of the variation in atomic density with the distance to an arbitrary atom in the material.

A strict evaluation of Debye's equation for ternary alloys $A_{x1}B_{x2}C_{x3}$ (x_i, i=1,2,3 atomic fraction of element i) makes it necessary to consider the atomic scattering factors as functions of Bragg's angle through magnitude s, as in the process carried out by Finbak [10], later by Waser and Schomaker [11], and later still by Warren [12]. According to the latter, the following relation is found for the radial atomic distribution function:

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

where G(r) is the Fourier transformation of the interference function, ρ_o is the average atomic density of the material, n_{ij} is the number of j-type atoms surrounding an i-type atom, r_{ij} is the distance between them, and function $P_{ij}(r)$ is given by

$$P_{ij}(r) = \frac{1}{2}\int_0^{s_m} \frac{f_i(s) f_j(s)}{(\sum_i x_i f_i(s))^2} \cos s(r - r_{ij}) ds \qquad (3)$$

where s_m is the maximum value of s for which there are experimental data. By defining a function

$$\rho(r) = \frac{1}{2\pi^2 r_{ij}} \sum \frac{n_{ij}}{r_{ij}} x_i P_{ij}(r)$$

representing the local atomic density affected by the Fourier transformation of the product of atomic factors, relation (2) changes thus:

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

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

In order to evaluate the average number of first neighbours of an arbitrary atom, that is to say, its average coordination, it is necessary to find the area under the first RDF peak, given by the expression

$$\text{Area} = \frac{2}{\pi}\sum_{ij} x_i \frac{n_{ij}}{r_{ij}} \int_a^b rP_{ij}(r) dr \qquad (5)$$

where a and b are the abscissae of the limits of said peak. The quoted area is, as can be seen, related to the relative coordination numbers, n_{ij}, reflecting the hypotheses on the local order of glassy materials; these hypotheses obviously have an influence on the number of chemical bonds between the different pairs of elements in an alloy, and have made it possible for Vázquez et al. [13] to deduce the following relationship from eqn. (5), according to the literature [14]:

$$\text{Area} = \frac{1}{50\pi}\left[(h+\beta A_{22}-\delta \sum_{i,j\neq 1} A_{ij})N+\alpha A_{22}+\gamma\sum_{i,j\neq 1} A_{ij}+P(\sum_{i=j\neq 1} A_{ij}-\sum_{\substack{i,j\neq 1\\ i\neq j}} A_{ij})a_{ij}\right] \quad (6)$$

where h, α, β, γ and δ are parameters which depend on the alloy and on the coordination hypotheses, N is the coordination attributed to a certain element in the alloy, P is a parameter which is equal to 2 when, in the variable a_{ij}, i=j, and to -1 if i≠j, and A_{ij} is determined by

$$A_{ij} = \frac{1}{r_{ij}} \int_a^b rP_{ij}(r)dr \quad (7)$$

The aforementioned relation makes it possible to theoretically evaluate the area under the first RDF peak as a function of the coordination attributed to a certain element in the alloy. The agreement between the value thus calculated and the experimentally obtained value makes it possible to establish the short range order hypotheses for the material, and to generate the most probable spatial atomic distribution model.

Although there are many methods for generating structural models of amorphous materials, the Metropolis-Monte Carlo method seems to be the most appropriate, among the random methods, for describing the local order of a glassy solid obtained by quenching, as is the case of the alloy in question, and for simulating the structural characteristics of this type of materials.

In this work, a variation on the Monte Carlo method is used, similar to the procedure used by Rechtin et al. [15] and described in detail in [16]. The variations refer to the geometrical and coordination restrictions imposed by the experimental RDF, which imply a certain semi-randomness in the generation of the atomic configuration. In order to build the model, one must first determine the number of atoms which, according to the experimental density, can be located within an adequate volume, and a number of positions is semi-randomly generated, greater than the number of atoms quoted in order to avoid a low coordination in the model. The positions with lowest coordination are then eliminated, and the different kinds of atom are randomly assigned to the rest, thus obtaining the initial configuration. Its reduced RDF, $rG_{mod}(r)$, is determined by simulating a diffraction process in this configuration, and it is compared to the experimental RDF by mean square deviation, used as a criterion for deciding on the validity of the generated configuration.

Once the initial atomic configuration is accepted, we proceed to its refining, which basically consists of randomly modifying the initial position of a randomly chosen atom, and accepting the new position if, while all the restrictions imposed by the experimental RDF are met with, the mean square deviation diminishes. The refining process is considered finished when the calculating time necessary in order to obtain a valid movement is too long and the mean square deviation does not considerably improve.

Once the refining process is finished, it is possible to compare the values of the model's main parameters (coordination, bond lengths and angles) to those quoted in the literature for similar alloys, in order to obtain the optimum approximation to the true structure of the material.

EXPERIMENTAL

Preparation and irradiation of the samples

The samples of semiconducting glassy alloy $As_{.35}Se_{.30}Te_{.35}$ were prepared in bulk form, by melting its elements and quenching the molten mixture, in order to avoid nucleation and crystalline growth, highly probable processes near the melting point. Commercial As, Se and Te, of 99.999 % purity, were pulverized to a grain size under 40 μm, and mixed homogeneously in adequate proportions, in order to obtain 7g samples of the compound. The samples were put into quartz ampoules, which were submitted to an iterative process of filling with inert gas He, and emptying, until a residual pressure of 10^{-3} torr was reached, in order to avoid oxidation. Under these internal pressure conditions, the ampoules were sealed with an oxy-acetylene burner, and put into a heating furnace at 600°C for 72 hours, turning at 1/3 r.p.m. in order to ensure homogeneity. The ampoules were then quenched in ice-water.

Due to the characteristic fragility of these materials, and in order to obtain ingots of the alloy which could be used to carry out electrical measurements, the samples were taken out of the capsules by dissolving the latter in a mixture of hydrofluoridic acid and oxygen peroxide. The material looked homogeneous, from a macroscopic point of view, and exhibited the concoidal fracture characteristic of solids with random atomic distribution.

Part of the material was pulverized and pressed into bricks of approximately 20x20x1 mm^3, and tested by X-ray diffraction for the characteristic peaks of a crystalline phase, which it did not show, as can be seen in the diffractogram shown in Fig. 1, thus confirming the glassy nature of the alloy.

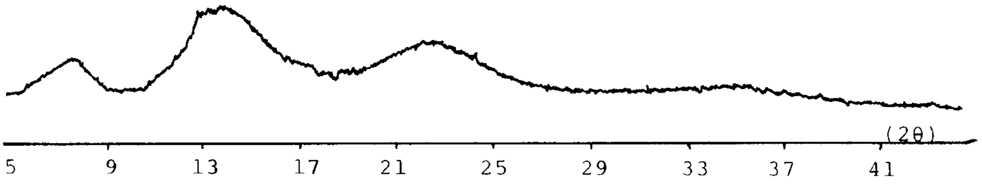

Fig. 1. Diffractogram of alloy $As_{.35}Se_{.30}Te_{.35}$.

The density of the material was determined by a pycnometric method at a constant temperature. The average value obtained, after performing a series of measurements, was 5.12 gcm^{-3}, with a relative error under 3%.

In order to obtain structural information on the alloy in question, the samples were submitted to X-ray diffraction processes. The intensities of the diffracted radiations were measured in an automatic SIEMENS D500 powder diffractometer with Bragg-Brentano geometry by reflection. The proper selection of a narrow frequency interval centred on the frequency of the radiation used was obtained with a bent graphite monochromator. The device is equipped with a scintillation detector, with a Tl-enriched NaI photosensitive window.

Since the detection system used consists of counting the number of photons perceived randomly, whose statistical error depends on the number of photons that reach the detector, the intensities were measured by fixing the number of counts and digitally registering the time used in making them; the error throughout the series of measurements is thus kept constant. The number of impulses was fixed at 4,000, the relative error being kept under 1.5%. The intensities diffracted by the samples were measured in the 0.77 $Å^{-1}$ to 14.48 $Å^{-1}$ range, using MoK_{α} radiation (λ=0.71069 Å), and supplying the generator with a power of 50 KV-30 mA. Four series of measurements were performed, two ascending and two descending, at Bragg's angle, using an angular interval of 0.2° in the 5° to 70° scan, and 0.5° in the 70° to 110° scan. The average values of the four measurements carried out for each angle were taken as the intensities of the radiations diffracted by the samples.

Treatment of the X-ray intensities.

These intensities were corrected as to background, polarization and multiple scattering [12], in order to eliminate the part of radiation which does not carry structural

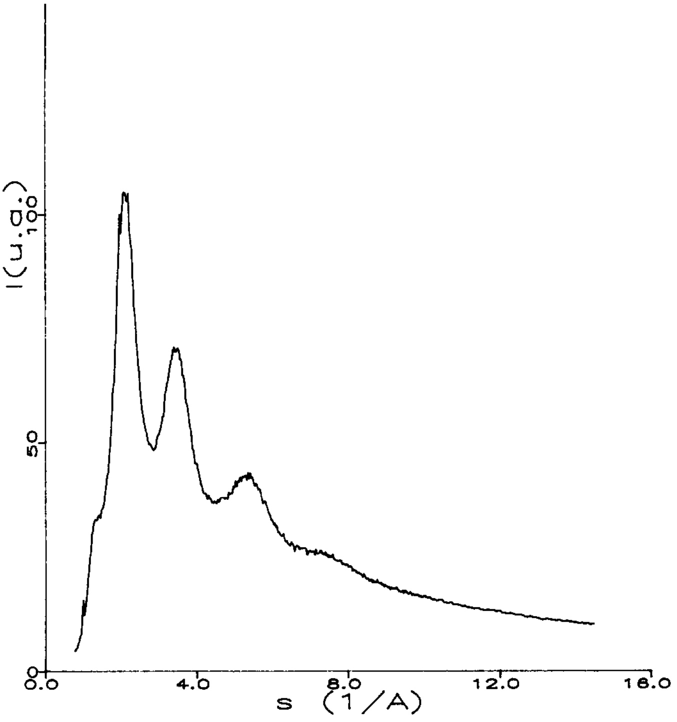

Fig. 2. Corrected intensities in arbitrary units.

information. Figure 2 shows these corrected intensities, expressed in arbitrary units.

The normalization to electronic units (e.u.) was done bearing in mind the high angle technique [12], according to which, for high values of s, the experimental intensity curve must oscillate around the independent scattering curve, with a decreasing amplitude. The normalization method [14] consisted of adjusting, by least squares, the experimental curve I(s) in arbitrary units to the independent scattering curve f(s), by minimizing the function.

$$S = \sum_{i=1}^{M} (f(s_i) - K_1 I(s_i)\exp(-K_2(s_i)^2))^2 \qquad (8)$$

where K_1 is a normalization constant and the term $\exp(-K_2(s_i)^2)$ is related to the Debye Waller temperature factor, which diminishes as the angle and temperature increase. The normalized intensities were corrected for the Compton effect, resulting in the coherent spectrum, $I_{e.u.}(s)$, from which the reduced intensities are obtained:

$$i(s) = \frac{I_{e.u.}(s) - \sum_i x_i f_i^2(s)}{(\sum_i x_i f_i(s))^2} \qquad (9)$$

which give way to the interference function, F(s) = s·i(s) and from which the radial atomic distribution function given by eqn. (4) is obtained, by applying a Fourier transformation.

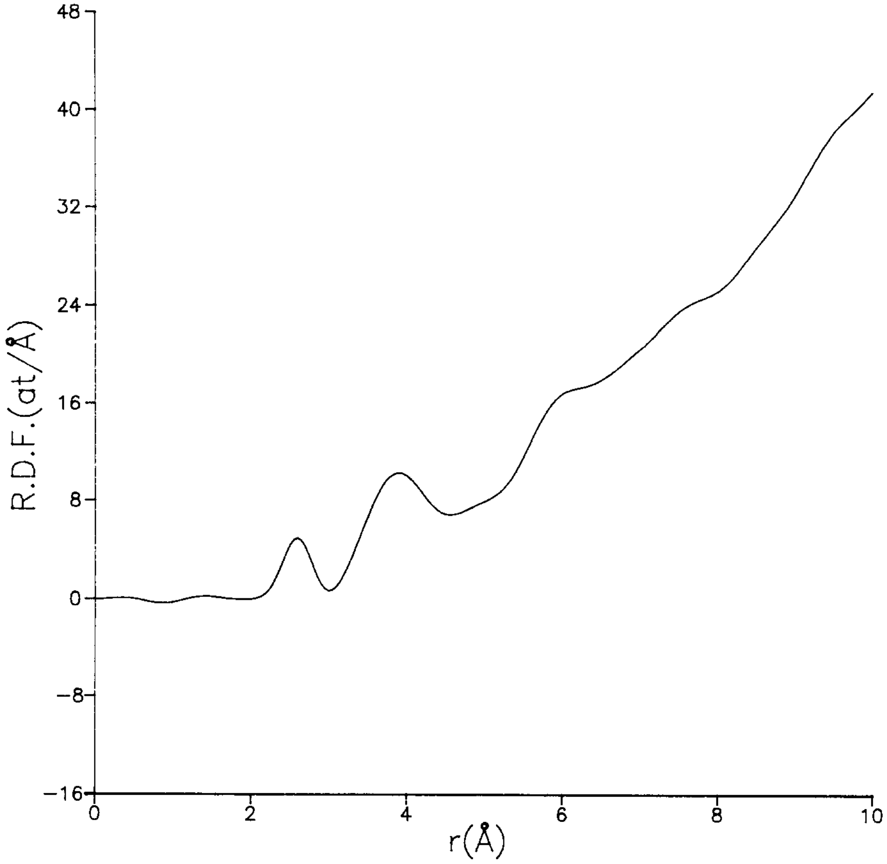

Fig.3. Radial distribution function.

The spurious oscillations which appear in the RDF for low 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 those values of s for which this function tends towards zero. The extension was done using the method described in the literature [17], based on the one proposed by Shevchik [18], according to whom, for high values of s, the experimental interference function can be approximated by

$$F_{theoretical}(s) = \frac{C}{r} \exp\frac{(-\sigma^2 s^2)}{2} \sin s\, r \qquad (10)$$

where C, r and σ are parameters obtained by an iterative method of square leasts from the initial values C_1, r_1 and σ_1, representing the area, the position and the half-width of the first RDF peak evaluated up to s = 14.48 $Å^{-1}$, which is the maximum value for which data have been obtained with the experimental device used. A Fourier transformation was applied to the interference function, extended up to 30 $Å^{-1}$, thus obtaining the RDF shown in Fig. 3, which supplied the following structural information: Position of the two first maximum values: 2.60 Å and 3.90 Å; limits of the first peak: 2.00-2.95 Å; area under the first peak: 2.23 ±0.1 atoms; average bond angle: 97.18°.

ANALYSIS OF RDF AND SHORT-RANGE ORDER

The analysis of the structural data supplied by the radial atomic distribution function shows, among other things, that the definition interval of the first peak, corresponding to the first coordination sphere of alloy $As_{.35}Se_{.30}Te_{.35}$ (As=1, Se=2, Te=3), is such that all types of bonds are possible among the different elements of the compound, as can be deduced by comparing the mentioned interval to the bond lengths, r_{ij}, of all possible pairs, quoted in the literature and shown in Table I.

Table I. Bond lengths.

Pair	r_{ij}(Å)	Ref.
As-As	2.49	[19]
As-Se	2.38	[20]
As-Te	2.62	[21]
Se-Se	2.34	[20]
Se-Te	2.54	[20]
Te-Te	2.71	[17]

Bearing in mind that the Te-X bonds (X=As, Se, Te) are perhaps the ones which should most contribute to the diffraction spectrum, it would seem logical to suppose that the first RDF maximum is between the values defining the bond lengths of the corresponding pairs, which is in good agreement with the weighed average value, 2.62 Å, for these three types of bond. Given the

RDF's character 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; the abscissa of the first maximum value, in particular, represents the average distance between first neighbours.

A parameter of great interest, when postulating short-range models of a glassy solid, is the area enclosed under the first RDF peak, as it represents the average coordination of the material. In order to theoretically evaluate this area according to eqn. (6), depending on the N-coordination attributed to the As, it is necessary to calculate parameters A_{ij}. Bearing in mind that, according to the literature [22], the finding of these parameters implies the establishment of the order of the polynomials in s, which approximate the functions $R_{ij}(s) = f_i(s)f_j(s)/(\Sigma x_i f_i(s))^2$, in this work the functions mentioned were adjusted to the straight regression lines of the corresponding pairs of elements of the alloy, whose eqns., $F'_{ij}(s) = A_{0ij}s + A_{1ij}$, are shown in Fig. 4. Parameters A_{ij}, shown in Table II, were calculated according to the literature [23], from the bond lengths, r_{ij}, given in Table I, and the coefficients A_{0ij} and A_{1ij} of the mentioned straight regression lines, shown in Table II.

Table II. Coefficients of straight regression lines fitted to values of $R_{ij}(s)$ and A_{ij} parameters.

Pair	A_{0ij}	A_{1ij}	A_{ij}
As-As	$-5.24\text{x}10^{-3}$	0.6690	0.9551
As-Se	$-5.06\text{x}10^{-3}$	0.6903	1.0574
As-Te	$1.36\text{x}10^{-4}$	1.0767	1.8666
Se-Se	$-4.87\text{x}10^{-3}$	0.7123	1.1449
Se-Te	$7.63\text{x}10^{-4}$	1.1109	1.6364
Te-Te	$1.59\text{x}10^{-2}$	1.7300	3.1249

In order to express the area under the first RDF peak as a function of the coordination, N, assigned to the arsenic atoms in this alloy, the characteristic parameter h=41.5489, and those depending on the coordination hypotheses, were calculated [13]:

α=-10, β=0, γ=70, δ=0, for N=3
α=-18.08 β=2.69, γ=126,54, δ=18.85, for N=4

The following expressions of the area were obtained from these data and from parameters A_{ij}, using equation (6):

$$\text{Area}=2.1791 + 0.0127a_{33}, \qquad \text{for } N=3$$
$$\text{Area}=2.0706 + 0.0127a_{33}, \qquad \text{for } N=4 \qquad (11)$$

which are of basic interest when trying to formulate hypotheses on the short-range order of the alloy in question. These expressions may also be observed as being functions of the number of Te-Te bonds, a_{33}, a fact which makes it possible to limit the variability field of the theoretical area.

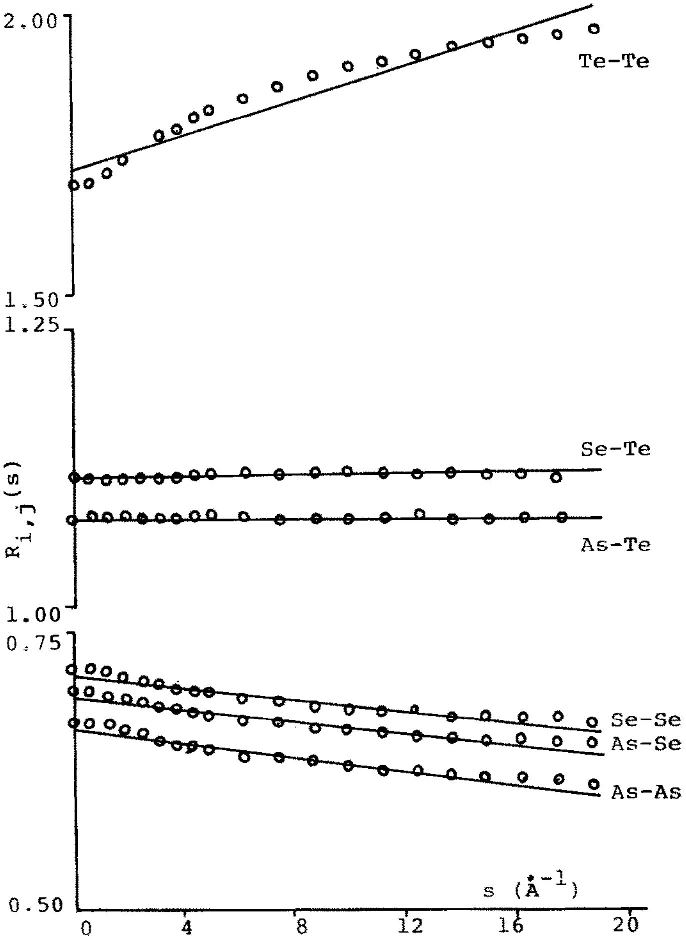

Fig. 4. Straight regression lines fitted to values of $R_{ij}(s)$.

In order to elaborate a local order model of a glassy material, it is necessary to establish the mean coordinations of its elements. In the case of alloy $As_{.35}Se_{.30}Te_{.35}$, it is a relatively complex matter to attribute a certain coordination to the arsenic, given the wide range of hypotheses quoted in the literature for its different compounds. Some authors [24,25] propose tetrahedral coordination for arsenic or similar elements in binary and ternary alloys with chalcogens while others [26,27] attribute tri-coordination to arsenic in this kind of compounds, which means that both hypotheses must be considered.

In order to establish the most adequate coordination hypothesis in the present case, it is necessary to compare the theoretical areas, for each value of N, to the experimental area. The relations (11) are observed to vary linearly with the number of Te-Te bonds. Since the area is a function of the relative coordination numbers, which in turn depend on the coordination number, N, of a certain element, arsenic, in the alloy [14], 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} parameters. When local order models of amorphous materials are proposed, the mentioned interval supplies the possible range in which the structure develops.

According to the literature [14], if the area is expressed as a function of the number of Te-Te bonds, the n_{ij}'s, which contain

Table III. Theoretical results obtained for the coordination hypotheses of the arsenic atom.

N	Coordination numbers $n_{ij}, i, j \neq 1$	Variation intervals for parameter a_{33}		
		Defined by the n_{ij} parameters	Defined by limits of error of the experimental area	Intersection of intervals
3	$n_{22}=-0.1583 + 0.0667a_{33}$ $n_{23}= 1.1083 - 0.0667a_{33}$	$2.37 \leq a_{33} \leq 16.62$	$-3.87 \leq a_{33} \leq 11.88$	$2.37 \leq a_{33} \leq 11.88$
4	$n_{22}=-0.0103 + 0.0667a_{33}$ $n_{23}= 0.0718 - 0.0667a_{33}$	$0.15 \leq a_{33} \leq 1.08$	$4.68 \leq a_{33} \leq 20.43$	———

parameter a_{33}, are given for each value of N by the expressions shown in Table III, together with the variation intervals of a_{33} defined by the relative coordination numbers. On the other hand, the comparison of the experimental area, with its margin of error of ±0.1 atoms, to the theoretical area, defines a new variation interval of the number of Te-Te bonds for each coordination considered for the arsenic, intervals which are shown in Table III together with their intersections with those corresponding to the positive character of the n_{ij}'s.

The analysis of the intersection of intervals leads to the conclusion that, in this alloy, the tetracoordinated arsenic hypothesis is incompatible with the structural information obtained from the experimental data and, therefore, the most probable short-range order can be described as a network of $AsX_{3/2}$ structural units (X=As, Se, Te) forming triangular pyramids in which at least one vertex is occupied by an arsenic atom.

GENERATION AND ANALYSIS OF THE SPATIAL MODEL

The basic aim of determining the structure of an amorphous solid is to make tridimensional atomic models, which necessarily verify the structural information obtained experimentally from the analysis of the radial atomic distribution function, and at the same time are as close as possible to the known physical-chemical properties of the material in question and of its elements.

The spatial atomic distribution model of alloy $As_{.35}Se_{.30}Te_{.35}$ was randomly generated, but bearing in mind the tricoordinated arsenic hypothesis, which is compatible with the experimentally obtained structural information.

The mathematical space considered adequate, for the generation of the spatial atomic configuration, is the volume enclosed by a 10 Å-radius spherical surface, as it best verifies the condition of being big enough to conveniently represent the sample, from a statistical point of view, and small enough for the computation time not to be too long. The number of atoms that can be placed in this volume according to the experimental density is 137, distributed as follows: 48 As atoms, 41 Se atoms and 48 Te atoms.

The atomic positions were generated by determining the cartesian coordinates from three random numbers [16], and bearing in mind the geometrical and coordination conditions which must be met with, deduced from the analysis of the experimental RDF and which are the following:

(i) The distance between first neighbours must be within the limits of the first peak of the radial distribution function.

(ii) The bond angle between an atom and two of its first neighbours can vary between the values ϕ_{min}=63.3° and ϕ_{max}=180°, [16] 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 mean coordination of the model is in agreement with the experimentally obtained one.

Considering the geometrical and coordination restrictions mentioned, 200 positions were generated and reduced to 137, the value predicted from the experimental density, by eliminating the positions with the lowest coordination. The next step was to assign the atoms to their respective positions, placing the arsenic atoms in tricoordinated positions and the other elements randomly in the rest. The reduced RDF of the initial configuration was determined and compared to the experimental RDF, modified by the finite size simulation function proposed by Mason [28], showing that the configuration was adequate for developing and obtaining from it the most probable spatial model of the alloy in question. This initial atomic distribution was then adjusted by successive moves of its atoms in random directions, adding the restriction of not allowing moves implying breaks in the bonds between arsenic atoms, therefore keeping the predicted coordination for this element. The amplitude, P, of the atomic moves is arbitrarily fixed and can be modified throughout the refining process, varying according to the literture [29] between 0.5 Å at the beginning of the process and 0.1 Å at the end, in order to achieve a faster convergence.

During the position refining process, the model evolved as follows: after 402 0.5 Å amplitude movements, the mean square deviation was 0.0390 Å; during the next 73 movements, 0.3 Å in amplitude, the deviation was reduced to 0.0292 Å, and after 110 movements at P=0.1 Å, the refining process was considered finished with a mean square deviation of 0.0205 Å, as the number of rejected moves was too large and the deviation did not improve noticeably. Figure 5 shows the reduced RDF of the model after the refining process, together with the corresponding experimental RDF. The spatial representation of the atomic distribution of alloy $As_{.35}Se_{.30}Te_{.35}$ is shown in Fig. 6, where triangular pyramids with arsenic atoms in some of their vertices may be observed. These pyramids are joined together either directly or by chains of chalcogen atoms, forming networks of structural elements which make up the model.

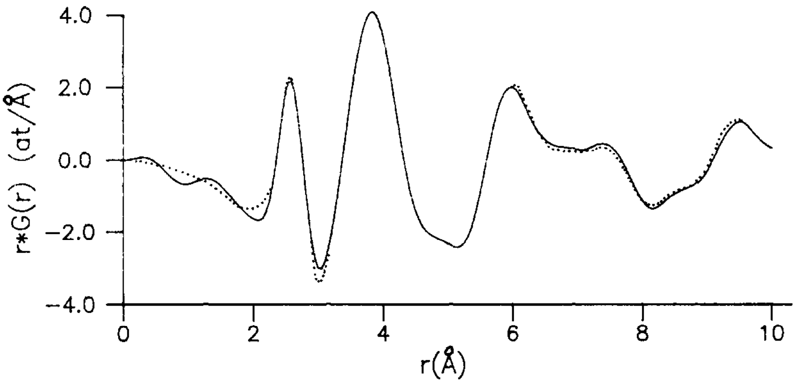

Fig. 5. Representations of (– – – – –) calculated and (————) experimental RDFs.

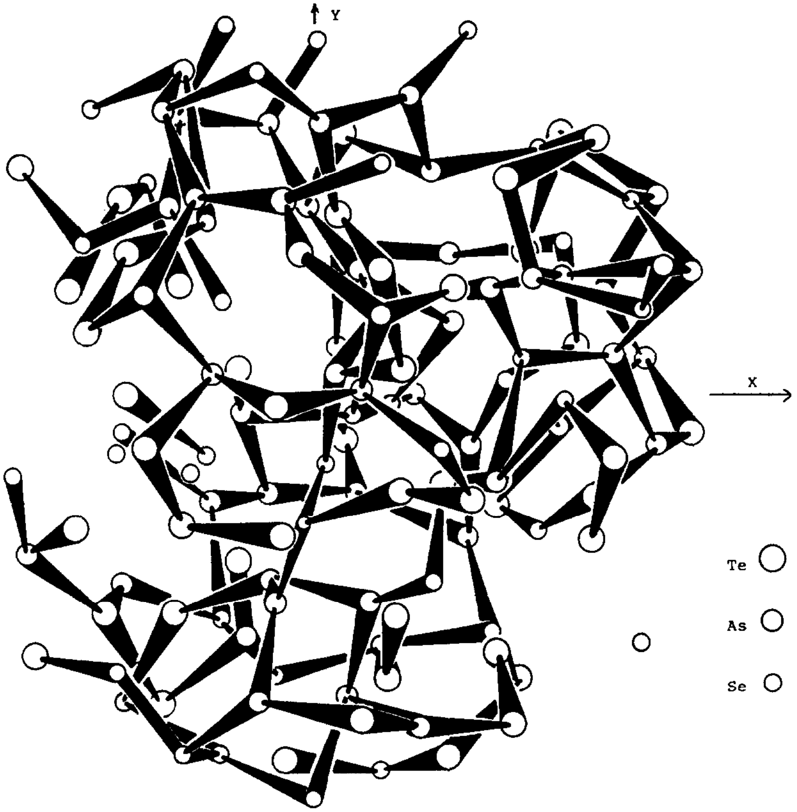

Fig. 6. Spatial representation of the model of alloy $As_{.35}Se_{.30}Te_{.35}$.

This theoretical model, generated randomly and bearing in mind the structural information obtained from the experimental RDF, must be as representative as possible of the true structure of the alloy under consideration. One way of estimating the concordance between this model and the atomic distribution of the compound is by analyzing the main structural parameters, coordinations and average bond lengths obtained from it.

One important point to bear in mind, when statistically analyzing the generated model, is the comparison of the resulting coordinations of its elements to those of the structural units which, according to the established hypotheses, can be postulated from the information supplied by the experimental data. Table IV shows the coordinations of each element in the atomic model of the alloy and, in brackets, the coordinations predicted theoretically from the tricoordinated arsenic hypothesis. Coordination defects are observed in the model, showing the presence of atoms with unsaturated bonds, partly justifiable by the finite size of the model. Sixty-four per cent of the Se atoms and 52% of the mono-coordinated Te atoms are less than 2 Å from the surface of the sphere limiting the model, and can therefore saturate their bonds with other elements outside it. It is also important to point out the presence of overcoordinated atoms, Se(3) and Te(3), a fact which is in agreement with the literature [30] on alloys containing these elements.

Table IV. Model coordinations.

Atom type	Coordination			
	3	2	1	0
As	45(48)	3(0)	0(0)	0(0)
Se	11(0)	16(41)	11(0)	3(0)
Te	2(0)	33(48)	13(0)	0(0)

Another interesting aspect of the generated model is the knowledge of the average bond lengths of the different pairs of elements in the material: As-As 2.51 Å, As-Se 2.49 Å, As-Te 2.51 Å, Se-Se 2.43 Å, Se-Te 2.53 Å, and Te-Te 2.59 Å. The concordance between these lengths, theoretically calculated from the experimental data of the analyzed alloy, and those known for other similar compounds, is a criterion for establishing the validity of the model. In this work, the comparative analysis of the mentioned lengths with the bibliographical data was done as follows:

(i) The average As-As bond length, theoretically calculated, is approximated by defect and by excess to 2.53 Å and to 2.47 Å, which are the lengths of this bond in alloys $Al_{.10}As_{.40}Te_{.50}$ [21] and $As_{.20}Se_{.50}Te_{.30}$ [30] respectively; it also coincides with the As-As bond length quoted in the literature [31] for rhombohedric arsenic.

(ii) The average value of the As-Se bond length in this model is slightly higher than the sum of covalent radii of the elements, but very near 2.43 Å [32], which is the length of this bond in glassy solid As_2Se_3, and equal to the value quoted in the literature [30] for the mentioned bond in amorphous alloy $As_{.20}Se_{.50}Te_{.30}$.

(iii) In the case of the As-Te length, the theoretical model supplied a value which, although slightly lower than the 2.58 Å of this bond length in alloy $As_{.45}Se_{.10}Te_{.45}$ [33], is practically the same as the 2.52 Å and 2.50 Å found in glassy compunds $As_{.20}Se_{.50}Te_{.30}$ [30] and $As_{.40}Se_{.30}Te_{.30}$ [34], respectively.

(iv) The comparison of the Se-Se bond length in the generated spatial atomic distribution, to the data found in the literature [35-37], shows that the former is slightly higher, although the difference is never over 4%. If we also take into account that the value obtained in this study is similar to the 2.40 Å [36,37] of trigonal and amorphous selenium, it may be admitted that the theoretically deduced average Se-Se length is adequate for glassy alloy $As_{.35}Se_{.30}Te_{.35}$.

(v) The Se-Te length in this model is acceptably enclosed between 2.58 Å and 2.49 Å, the length of this bond in alloys $As_{.45}Se_{.10}Te_{.45}$ [33] and $As_{.20}Se_{.50}Te_{.30}$ [30] respectively, and almost exactly equal to 2.54 Å, sum of the covalent radii of the elements.

(vi) The generated spatial structure gives an average Te-Te bond length slightly lower than the 2.67 Å corresponding to this length in compound $As_{.45}Se_{.10}Te_{.45}$ [33], but very close to the 2.62 Å of this bond in alloys $Ge_{.14}As_{.43}Te_{.43}$ [38] and $Al_{.20}As_{.40}Te_{.40}$ [21], which allows us to consider it as adequate in this study.

The analysis of the theoretical values therefore shows good agreement between these values and the bibliographical data, so they may be considered as representative of the bond lengths in the true structure of the alloy.

CONCLUSIONS

According to the radial atomic distribution function of the alloy studied, obtained from X-ray diffraction data, and with the coordination hypotheses for arsenic quoted in the literature, the consideration of tri-coordinated arsenic was found to correctly explain the average number of first neighbours experimentally determined for the compound in question.

The use of the most approximate expression of the area under the first RDF peak made it possible to discard tetrahedral coordination for the arsenic, as it did not allow us to find a number of Te-Te bonds that, while keeping coordination numbers n_{22} and n_{23} positive, would at the same time give a theoretical area within the margin of error of the experimental area.

Considering the tricoordinated arsenic hypothesis, a model of the spatial atomic distribution of the alloy was built, using the Metropolis-Monte Carlo random method and bearing in mind the geometric conditions, deduced from the radial atomic distribution function obtained by X-ray diffraction of the samples.

According to the analysis of the model, the structure of the material can be described as a tridimensional network of covalent bonds with tricoordinated arsenic atoms at one of the vertices of the triangular pyramids, joined together directly or by chalcogen atoms, making the structure compact.

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