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Atomic configurations generation by a random method for glassy alloy $Ge_{0.14}As_{0.43}Te_{0.43}$

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Three different models of the amorphous alloy $Ge_{0.14}As_{0.43}Te_{0.43}$, obtained by quenching the molten mixture of the elements, were built by computer simulation of an X-ray diffraction experiment, taking the tetra- and tricoordinated germanium hypotheses into account. The main structural parameters of these models were analysed and the results did not vary greatly from those given in the literature for similar alloys.

1. Introduction

As a result of the development of the atomic theory, interest in the structure of matter has increased. Although this interest initially only referred to crystalline substances, it is also possible to extend it to amorphous compounds [1–3]. The study of the structure of solid materials, both glassy and crystalline, is an important consideration when attempting to explain the macroscopic properties observed in them, and it is absolutely necessary when trying to establish a formal theory to explain these properties.

The glassy alloys in the Ge–As–Te system are highly conductive [4], and also exhibit the switching phenomenon and the memory effect [5–11]. In this paper, three-dimensional models of the short-range order for alloy $Ge_{0.14}As_{0.43}Te_{0.43}$, which belongs to the above glassy system, have been generated, using the Metrópolis–Monte Carlo random method [12], accordingly modified. In building these models, the geometric and coordination conditions obtained by ourselves [13] through the experimental radial distribution function (RDF) were taken into account.

2. Theory

The basic object of determining the structure of an amorphous solid is to construct atomic models which verify experimentally obtained structural information and are in agreement with the physical and chemical properties of the material.

Although there are many methods for building atomic models of the structure of amorphous materials, it appears that, among the random base methods, the Metrópolis–Monte Carlo method is the most adequate for describing short-range order in a glassy solid obtained by quenching its molten mixture, as it is the one that best simulates the structural characteristics of this type of alloy.

For this work, a variation of the Monte Carlo method has been used, similar to the procedure used by Rechtin *et al.* [14]. The variations refer mainly to the geometric and coordination conditions, which imply semirandomness in the construction of the atomic configuration.

There are two stages in the process of building the model: generation of the initial configuration, and refining of the initial model.

2.1. Generation of the initial configuration

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

Once the space characteristics of the initial configuration are decided, the next step is to determine N, the number of atoms that can be located in it, depending on the experimental density of the material. As the models generated from a number of positions equal to the above number of atoms are low in coordination even if they are adjusted correctly from a geometric point of view, it is necessary to modify the initial configuration by saturating the chosen volume with positions, which increases coordination. The positions thus generated must meet with the restrictions already mentioned.

(i) The first restrictive condition refers to the fact that the distance between two first-neighbour positions must be inside the definition interval of the first RDF peak.

(ii) The second restriction is related to the possible variation interval of the bond angle. This interval is obtained by establishing the extreme positions that two atoms can occupy, which, together with the reference position, determine the angle. Considering $(r_{1\min}, r_{1\max})$ and $(r_{2\min}, r_{2\max})$ to be the limit radii which correspond to the first and second coordination spheres, the extreme positions mentioned above, which are shown in Fig. 1, are defined by $(r_{1\min}, r_{2\max})$ and $(r_{1\max}, r_{2\min})$, and we obtain from these

$$\begin{aligned} \phi_{\min} &= 2\sin^{-1}\frac{r_{2\min}}{2r_{1\max}} \\ \phi_{\max} &= 2\sin^{-1}\frac{r_{2\max}}{2r_{1\min}} \end{aligned} \qquad (1)$$

which are the limits of the bond angle interval.

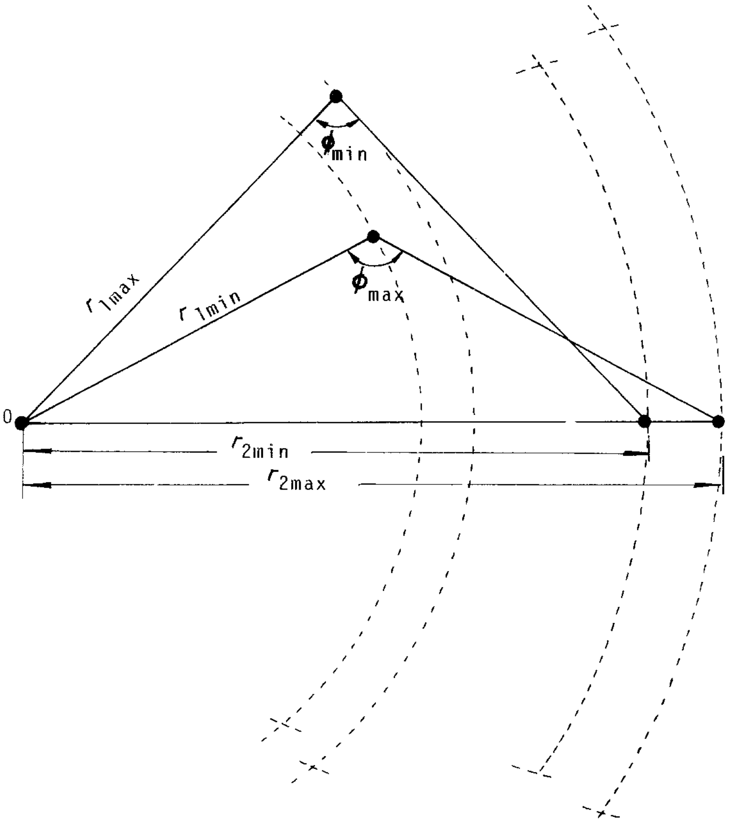

Figure 1 Limits of the bond angle interval.

Another condition to consider is the number of the atoms of each type, in the first coordination sphere, which is given as the maximum coordination for each of them.

When any of these conditions is not met, the position created is rejected and another is generated, and so on until the whole volume is saturated. Then, the positions with the lowest coordination are eliminated until what is left is a number equal to that of the atoms compatible with the experimental density, and the different types of atom are assigned to the positions in a semi-random way.

Once the initial atomic configuration is established, the next step is to find the corresponding reduced RDF, $rG_{\mathrm{mod}}(r)$, by simulating a diffraction process in the model. In order to compare this function with the experimental one, it is essential that the sample and the model be of similar size and shape. Simulation of the spherical sample is obtained by multiplying the function $rG_{\mathrm{exp}}(r)$ by that proposed by Mason [15], which is given by:

$$D(r) = 1.0 - 1.5\left(\frac{r}{2R}\right) + 0.5\left(\frac{r}{2R}\right)^3 \quad (2)$$

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

Comparison of the two reduced RDFs is done by mean square deviation, ε^2, which is used as a criterion for deciding on the validity of the generated configuration and is given by the expression

$$\varepsilon^2 = \frac{1}{M}\sum_{i=1}^{M}\left[r_i G_{\mathrm{exp}}(r_i) D(r_i) - r_i G_{\mathrm{mod}}(r_i)\right]^2 \quad (3)$$

for the r_i which correspond to the M points taken in the comparison.

2.2. Refining the initial model

The object of this process is to find the atomic configuration whose reduced RDF best fits the experimental one; there are two stages: position refining and thermal factor adjustment.

The atomic position refining process is done using the Metròpolis–Monte Carlo technique [12], which consists basically of randomly modifying the initial position of a randomly chosen atom, and accepting the new position if the restrictions imposed by the experimental RDF are complied with and, at the same time, mean square deviation decreases.

When using this technique the amplitude, P, of the atomic movements is arbitrarily fixed and can be modified throughout the refinement process, varying, according to Alberdi [16], from 0.05 nm at the beginning of the process to 0.01 nm at the end, in order to achieve a quicker convergence. Values lower than 0.01 nm have no physical meaning, as they are masked by thermal vibration.

Position refining is considered finished when the computation time necessary to obtain a valid movement is too large and mean square deviation does not sensibly improve.

For the refining of thermal factors, the corresponding coordination spheres are defined according to the experimental RDF, and $\sigma_0 = 0.01$ nm is taken as the initial value of the isotropic factor. The set of values for σ_i which best adjust the model-reduced RDF to the experimental one is calculated by an iterative least square method, in successive cycles until variation for σ_i is less than 10^{-4} nm.

Once the refining process is finished, the resulting atomic configuration is suitable for carrying out a statistical evaluation of the main structural parameters of the alloy (coordinations, bond lengths, bond angles, etc.).

3. Description and analysis of the generated models

The mathematical space which may be considered adequate for generating the possible structural models of the alloy $Ge_{0.14}As_{0.43}Te_{0.43}$ is the volume limited by a spherical surface with a radius of 1 nm, the space which best verifies the condition of being large 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 of the alloy which can be placed in the volume according to the experimental density ($\varrho_0 = 5.51\,\text{g}\,\text{cm}^{-3}$) [13] is 142, distributed in the following manner: 20 Ge atoms, 61 As atoms and 61 Te atoms.

The generation of atomic positions was carried out by finding the cartesian coordinates from three random numbers, and bearing in mind all the geometric and coordination conditions which must be met with, deduced from analysis of experimental RDF [13], and which in this case are:

(i) the distance between first neighbours must be inside the interval (0.225 nm, 0.305 nm), which defines the first experimental RDF peak;

(ii) the bond angle between an atom and two of its first neighbours can vary between 70° and 150°, as is inferred from the extreme positions (0.225 nm, 0.435 nm) and (0.305 nm, 0.345 nm) which the two atoms that determine the angle together with the reference atom can occupy.

(iii) The coordination attributed to each element must be such that the weight mean coordination for the model agrees with that obtained experimentally.

Keeping in mind the tetra- and tricoordinated germanium hypotheses, expounded and theoretically confirmed in [13], and which agree with the conclusions reached by Betts *et al.* [17], a theoretical model has been generated, imposing the condition of tetracoordinated Ge (Ge(4)) and another model with the condition of tricoordinated Ge (Ge(3)).

3.1. Structural models based on the Ge(4) and Ge(3) hypotheses

Considering the coordination and geometric restrictions already mentioned, 200 positions were generated for each of the models, and were reduced to 142, the number predicted from experimental density, by eliminating those with lowest coordination. The following step was the assignment of atoms to their proper positions in each model, placing the germanium atoms in the maximum coordination positions, being 4 in the first model and 3 in the second, whereas the other elements were randomly placed in the remaining positions. The reduced RDF for each configuration was found, and was compared to the experimental RDF, modified by the finite size simulation function [15], with the result that the mean square deviation between the theoretical and experimental functions was 0.201 47 nm in the case of Ge(4) and 0.246 50 nm in the case of Ge(3).

TABLE I Position refining process for Ge(4) and Ge(3) models

Model	P (nm)	Movement intervals	Squared deviation (nm)
Ge(4)	0.05	1–394	0.006 83
	0.03	395–467	0.004 41
	0.01	468–585	0.003 06
Ge(3)	0.05	1–443	0.005 78
	0.03	444–505	0.003 64
	0.01	506–657	0.001 87

Considering that the initial models were suitable for obtaining a relatively quick reduced-RDF adjustment to the experimental RDF, the next step was position refining by successive atom movements of amplitude P, adding the restriction of not allowing movements which mean a break in germanium atom bonds, and so maintain the coordination predicted for this element in each case.

Throughout the position refining process, both models behaved as shown in Table I, in which mean square deviation refers to the last movement in each interval. The position refining process was considered finished for each model when the number of rejected movements was too high and the mean square deviation did not vary significantly.

The last step in the building of structural models of the alloy $Ge_{0.14}As_{0.43}Te_{0.43}$ was thermal factor refining. This was carried out by defining the five coordination spheres whose extreme radii are shown in Table II; by using the iterative least square method already mentioned, the isotropic factor values, σ_i, shown in Table II for both atomic configurations, were found for each sphere.

After finishing the thermal factor refining process, the square deviations between the theoretical and experimental values of $rG(r)$ were reduced to 0.002 97 nm for the tetrahedric germanium model and to 0.001 81 nm for the tricoordinated germanium model. The reduced RDF for each model is shown in Fig. 2a and b, together with the experimental RDF, after the refining process.

The space representations of both configurations are shown in Figs 3 and 4, which reflect tetrahedrons centred on germanium atoms, in the case of the tetracoordinated germanium, and triangular pyramids with one vertex occupied by this element, in the case of tricoordinated germanium. Both the tetrehedrons and the triangular pyramids are joined together forming networks of structural elements which form each of the models.

These theoretical models, built by random methods and taking into account the structural information

TABLE II Thermal factor refining for Ge(4) and Ge(3) models

Coordination sphere order	r_{min} (nm)	r_{max} (nm)	σ_i (nm)	
			Ge(4)	Ge(3)
1st	0.000	0.300	0.009 77	0.009 75
2nd	0.300	0.480	0.008 55	0.009 12
3rd	0.480	0.670	0.011 30	0.009 80
4th	0.670	0.830	0.013 08	0.012 65
5th	0.830	1.000	0.011 20	0.012 52

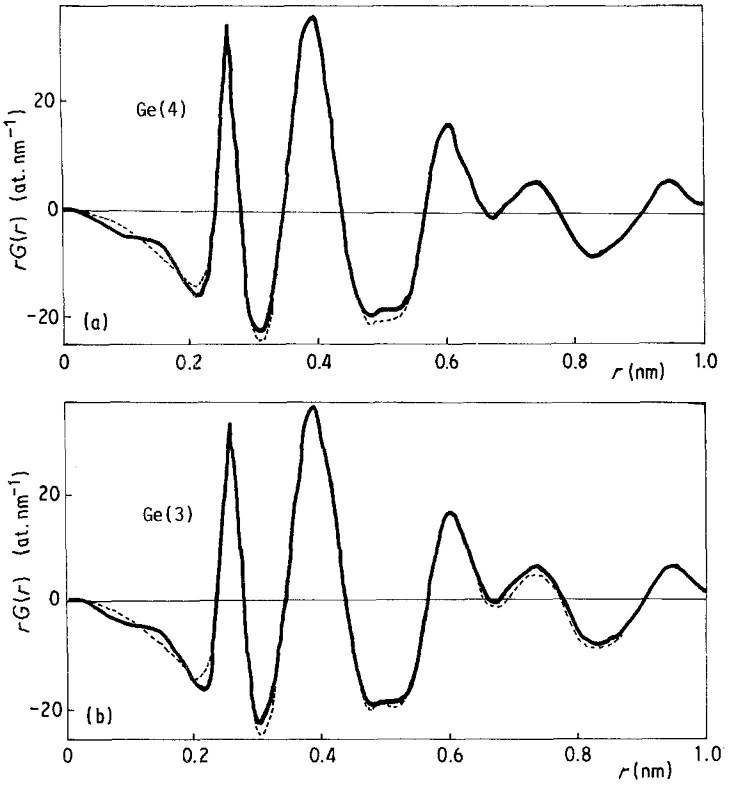

Figure 2 Representations of (– – –) calculated and (——) experimental RDFs.

obtained from experimental RDF, should be as representative as possible of the actual structure of the alloy in question. One way of estimating concordance between these models and the atomic arrangement of the alloy is to analyse the main structural parameters, coordinations and mean bond distances which can be obtained from them.

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

Table III shows the coordinations for each element in the alloy $Ge_{0.14}As_{0.43}Te_{0.43}$ in each of the generated models, and, in parentheses, the coordinations predicted theoretically from the corresponding hypotheses [13]. For each model we may observe the existence of coordination defects, a fact which shows the presence of atoms with non-saturated bonds, which may be partly justified by the finite nature of the models. In the Ge(4) model, 50% of the dicoordinated arsenic atoms (As(2)) and 75% of the monocoordinated tellurium atoms (Te(1)) are less than 0.2 nm away from the surface of the sphere that encloses the model, and can saturate their bonds with other elements outside it. In much the same way, in the Ge(3)-based

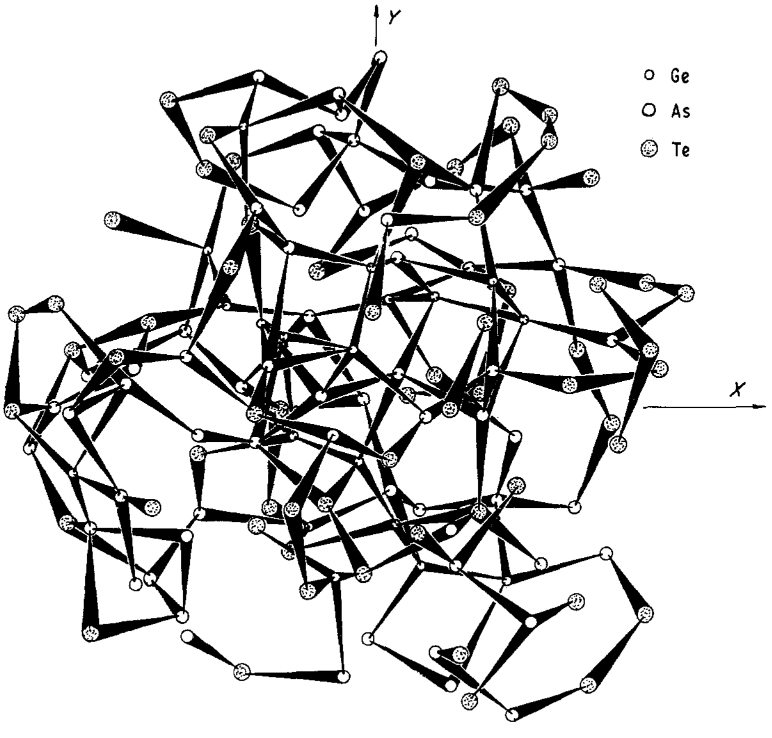

Figure 3 Spatial representation of the model of alloy $Ge_{0.14}As_{0.43}Te_{0.43}$ by hypothesis of four-fold coordinated germanium.

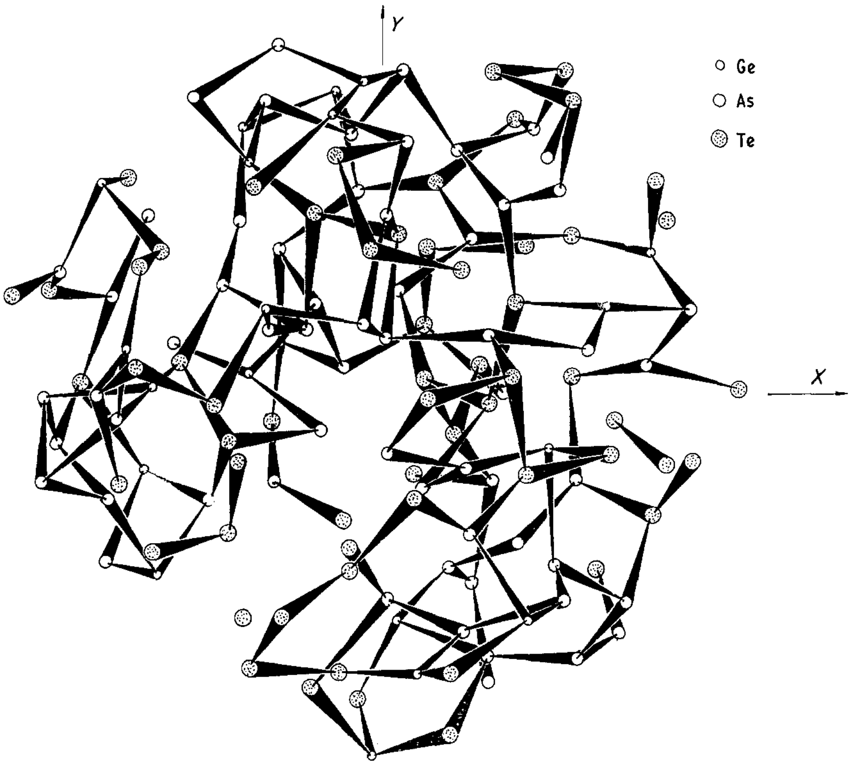

Figure 4 Spatial representation of the model of alloy $Ge_{0.14}As_{0.43}Te_{0.43}$ by hypothesis of three-fold coordination for germanium.

structural configuration, 33% of the As(2) atoms and 65% of the Te(1) atoms are also less than 0.2 nm away from the surface of the model. The monocoordinated As atoms, which appear in both configurations, may exhibit bond defects that cannot be explained by the finite size of the models. It is also important to note the presence of overcoordinated atoms, Te(3) and As(4), which is in accordance with the literature [18, 19] on alloys containing these elements.

Another interesting aspect of the generated models is the mean bond length in the different pairs of elements in the alloy, to be compared to those of the other similar compositions; this will result in more accurate information on the validity of the models.

Table IV shows the mean bond distances of all possible pairs in each model. It may be observed that these distances are very similar in both configurations: in the least favourable case, the difference is less than 1.5%.

The great similarity in bond distances for both of the generated models, together with the fact that the theoretical $rG(r)$ fits the experimental $rG(r)$, in both the Ge(4) and the Ge(3) configurations, gives substance to the idea that the actual structure of the material is formed by a network of structural units centred on Ge(4) and Ge(3) atoms, which coexist simultaneously in the same model, a fact which has led us to build a theoretical atomic configuration based on this hypothesis.

3.2. Structural model based on the simultaneous Ge(4) and Ge(3) hypotheses

This model was generated in much the same way as that described above, with the only difference that breakdown in germanium atom bonds was allowed so that some of them would take tetracoordination and others would take tricoordination, as presupposed.

The initial configuration and its reduced RDF were obtained; the latter was compared to experimental RDF, and, as in the case of Ge(4), mean square deviation was found to be 0.201 47 nm. During the position refining process, 377 moves with an amplitude of 0.05 nm were made; on reaching a deviation of 0.008 70 nm, the amplitude was reduced to $P = 0.03$ nm until move number 481, in which $\varepsilon = 0.003\,44$ nm, continuing with moves of 0.01 nm up to move number 618, in which the refining process was considered finished with a mean square deviation of 0.001 89 nm. Fig. 5 shows the experimental and model $rG(r)$s.

Fig. 6 shows a space representation of the created atomic configuration, in which appear tetrahedra

TABLE III Model coordinations

Model	Atom type	Coordination				
		4	3	2	1	0
Ge(4)	Ge	20(20)	0(0)	0(0)	0(0)	0(0)
	As	17(0)	22(61)	19(0)	3(0)	0(0)
	Te	0(0)	10(0)	36(61)	15(0)	0(0)
Ge(3)	Ge	0(0)	20(20)	0(0)	0(0)	0(0)
	As	0(10)	42(51)	15(0)	4(0)	0(0)
	Te	0(0)	15(10)	27(51)	17(0)	2(0)

TABLE IV Averaged bonding distances

Bond	$\langle d \rangle$ (nm)	
	Ge(4)	Ge(3)
Ge–Ge	0.252	0.251
Ge–As	0.265	0.262
Ge–Te	0.260	0.257
As–As	0.257	0.254
As–Te	0.259	0.259
Te–Te	0.260	0.260

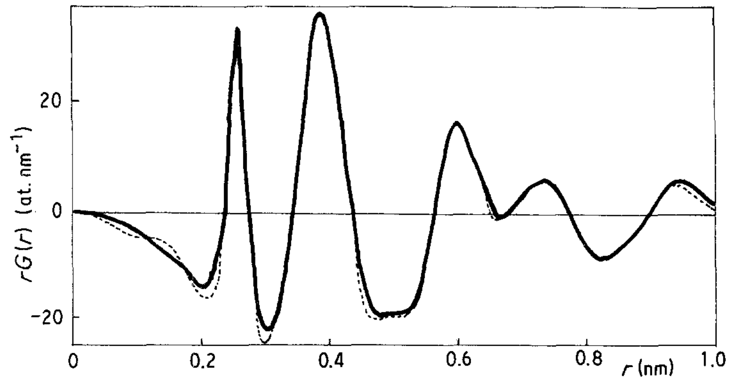

Figure 5 Representation of (– – –) calculated and (——) experimental RDFs for model based on the simultaneous Ge(4) and Ge(3) hypotheses.

centred on germanium atoms and triangular pyramids with this element in one of their vertices. Both structural units are interlaced, forming a network which is the structure of the alloy.

In this model, as in those generated previously, there are bond defects. Many of these defects belong to atoms which are less than a first neighbour's distance away from the periphery of the sphere, and could be saturated by hypothetical external neighbours. In the case of elements with two or more bond defects, it may be admitted that these could be due to the finite size of the model, when the atom in question is less than 0.11 nm away from the surface; this possibility takes into account both the mean distance between first neighbours and the mean bond angle. The model contains 13.20% of bond defects pertaining to atoms which are not in a situation that would allow them to be saturated by possible external neighbours. However, the existence of bond defects is a consequence inherent to the method of preparation of chalcogenide glasses.

The mean bond distances calculated for this model were compared to those of the other alloys of similar elements cited in the literature, with the following results.

(i) The mean value of the Ge–Ge bond lengths, theoretically calculated, is 0.253 nm, which is relatively higher than 0.247 nm, the value found for this bond in films of amorphous Ge [20]; however, it is close to the distance of 0.251 nm belonging to the Ge–As–Se system [21], and practically the same as the value of the Ge–Ge distance in amorphous germanium, which is 0.254 nm [22].

(ii) The Ge–As and Ge–Te bond lengths are 0.247 and 0.259 nm, respectively, very similar to the distances cited in the literature [21, 23–27] for these bonds.

(iii) In the case of As–As, the generated model gave a mean bond length of 0.256 nm, a value which is close, by defect and by excess, to 0.259 and 0.253 nm, which are the lengths of this bond in alloys $As_{0.20}Se_{0.50}Te_{0.30}$ [19] and $Al_{0.10}As_{0.40}Te_{0.50}$ [28], respectively; and it is practically equal to the 0.257 nm found for this bond in the glassy composition $As_{0.45}Se_{0.10}Te_{0.45}$ [29].

(iv) The As–Te bond length found for the theoretical model is 0.261 nm, which is in accordance with the 0.258 nm length in alloy $As_{0.45}Se_{0.10}Te_{0.45}$ [29], and the sum of covalent radii in the elements [27].

(v) The model gave a value of 0.262 nm for the Te–Te bond; this is very close to 0.260 nm, which is the pertinent length in alloy $As_{0.40}Se_{0.30}Te_{0.30}$ [30], and it is exactly the same as the length cited in the literature [28, 31] for the compositions $Al_{0.20}As_{0.40}Te_{0.40}$ and $Al_{0.23}Te_{0.77}$.

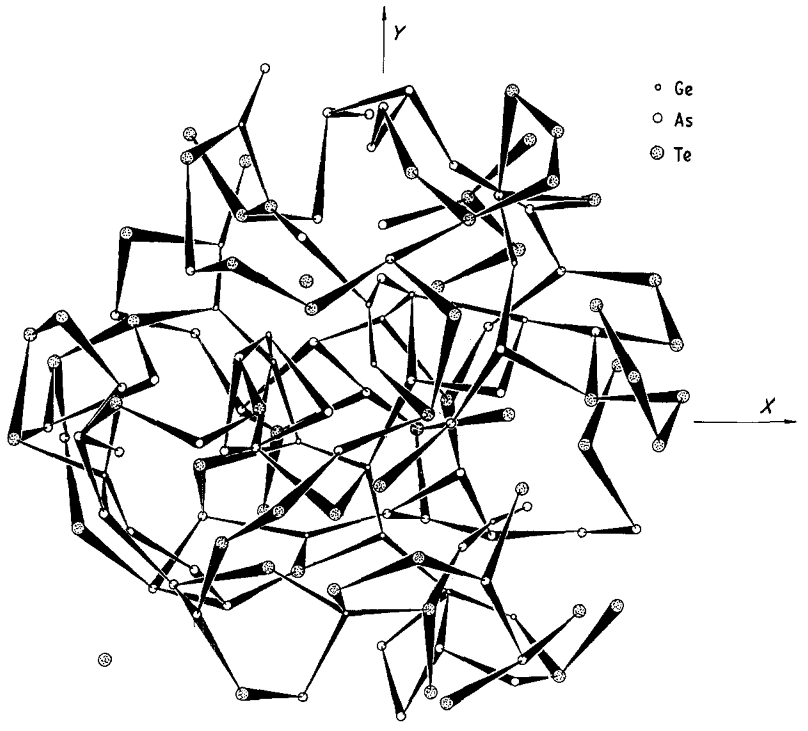

Figure 6 Spatial representation of model based on the simultaneous Ge(4) and Ge(3) hypotheses.

TABLE V Averaged bonding angles

Type	⟨α⟩ (deg)	Material	Reference
Ge	112.0	$Ge_{0.14}As_{0.43}Te_{0.43}$	Present work
	108.0	$Ge_{0.20}As_{0.40}Se_{0.40}$	[21]
	109.5	Tetrahedric angle	–
As	107.3	$Ge_{0.14}As_{0.43}Te_{0.43}$	Present work
	108.2	$As_{0.45}Se_{0.10}Te_{0.45}$	[29]
	107.1	AsSe glass	[32]
	106.7	$As_{0.20}Se_{0.50}Te_{0.30}$	[19]
Te	106.5	$Ge_{0.14}As_{0.43}Te_{0.43}$	Present work
	106.8	$As_{0.20}Se_{0.50}Te_{0.30}$	[19]
	107.0	$As_{0.45}Se_{0.10}Te_{0.45}$	[29]
	102.0–109.5	TeGe glass	[33]

Detailed analysis of the theoretical values shows, as we have seen, close accordance between these values and bibliographic data, so they may be considered to represent the bond lengths in the actual structure of the alloy.

Another interesting parameter which supplies information on the actual atomic structure of a glassy solid is the mean bond angle of each element with two of its first neighbours. It is therefore usual to carry out a comparative analysis of the mean values of these angles and those obtained through bibliographical data. Table V shows these values for the model, together with those quoted in the literature for similar compounds. It may be observed that all the values calculated can be considered acceptable, if we take into account that bond-angle distortion is typical of glassy materials and that, in the least favourable case, the difference between the bond angles in the model and the values quoted in the literature was less than 3.5%.

4. Conclusions

Three space models of the glassy alloy $Ge_{0.14}As_{0.43}Te_{0.43}$ were built, using the Metrópolis–Monte Carlo random technique; the geometric conditions, deduced from the radial distribution function obtained by X-ray diffraction, were taken into account.

The tri- and tetracoordinated germanium hypotheses propounded in the literature were also considered for the building of the models.

The first two models, Ge(4) and Ge(3), gave very similar structural data, a fact which leads us to believe that the theoretical model that best fits the actual structure of the compound is one in which tetracoordinated germanium atoms and tricoordinated germanium atoms coexist.

The model based on this hypothesis may be described as a tridimensional network of covalent bonds, some of which are centred on germanium atoms, forming tetrahedra, and the rest of which are arranged following the edges of a triangular pyramid, one of whose vertices is occupied by a germanium atom. These structural units are joined together by arsenic and tellurium atoms or chains of atoms that form a compact network.

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