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Copper coordination hypotheses and structural model in the glassy semiconductor $Cu_{0.08}Ge_{0.18}Te_{0.74}$ by X-ray diffraction

M. CASAS-RUIZ, J. VÁZQUEZ, R. A. LIGERO, R. JIMÉNEZ-GARAY
Faculty of Science, University of Cádiz, Apdo. 40, Puerto Real, Cádiz, Spain

The radial atomic distribution was studied in the amorphous alloy $Cu_{0.08}Ge_{0.18}Te_{0.74}$, using X-ray diffraction data of samples obtained by quenching the molten material. The short-range order proposed was determined through the interpretation of the radial distribution function, using a theoretical expression which takes into account the variation in the atomic scattering factors with s (scattering vector module) and approximating them to polynomic functions. Different coordination hypotheses for copper, quoted in the literature on glassy alloys containing this element, were taken into account. The result of the study is that tetracoordinated copper is the hypothesis which most agrees with the experimentally obtained structural information. According to this coordination for copper, a spatial atomic distribution model was generated, using the Monte-Carlo random method. A comparative analysis of the main structural parameters of this model revealed its good agreement with the values given in the literature for similar alloys.

1. Introduction

In the last decades, amorphous materials have been the subject of intense study prompted by fundamental and technological interest [1]. 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 electrical 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. Chalcogenide glasses with polyvalent elements exhibit properties which are the result of the formation of three-dimensional structural units. These polyvalent atoms, which stabilize the chalcogenide structures, are preferably arsenic and germanium, which form space units with the chalcogen elements, break their characteristic complex structural formations and contribute to the establishments of more homogeneous structures for the glassy alloys belonging to this type of system, a fact which explains some of their properties. Despite substantial progress in the structural study of the glassy solids, basic problems remain, such as quantitative characterization of the atomistic disorder [2]. Experimentally, the presence of disorder means that one can measure only averaged properties and an accurate determination of the individual atomic coordinates is impossible. Theoretically, non-crystalline semiconductors are particularly difficult to model, because the interatomic interactions that are responsible for short-range order, depend strongly on atomic and chemical environments.

This work analyses the local order of the semiconducting glassy alloy $Cu_{0.08}Ge_{0.18}Te_{0.74}$, from data obtained from the radial distribution function (RDF) determined from X-ray diffraction intensities. The experimental value of the area under the first RDF peak was compared to that obtained theoretically [3–5] as a coordination function of copper and taking into account 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 a constant value $Z_iZ_j/(\Sigma_i x_i Z_i)^2$. Based on the above analysis and on the geometrical restrictions imposed by the experimental RDF, a spatial atomic distribution model was generated, using the Monte-Carlo random method. An analysis of the main parameters of the model (coordinations, bond lengths and angles) shows good agreement with the values quoted in the literature for similar alloys.

2. Experimental procedure and treatment of the X-ray intensities

Bulk samples, weighing 12 g, of the glassy alloy $Cu_{0.8}Ge_{0.18}Te_{0.74}$ were prepared from its 99.999% pure components. The adequately sifted elements were introduced into quartz ampoules, which were successively filled with inert gas (helium) and emptied in order to achieve a very low oxygen concentration, thereby avoiding any possible oxidation in the material. The ampoules were sealed using an oxyacetylene burner, maintaining an interior residual pressure of 10^{-3} torr (1 torr = 133.322Pa) and kept in a rotary

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furnace at 1100 °C for 72 h, after which they were quenched in liquid nitrogen. The pulverized samples of the alloy were radiated in an automatic Siemens D500 diffractometer, using MoK_α(λ = 0.071 069 nm), confirming their glassy nature. The intensity of the radiation diffracted by the samples was measured at fixed counts (4000) in the 5°–110° angular interval, four scans being carried out, two ascending and two descending, in order to obtain the average values of the intensities corresponding to each Bragg angle value. Three types of slit were used, whose angular opening, usage interval and angular increase are shown in Table I, so that the sample surface radiated at low and high angles should be approximately the same.

The intensities, I, obtained in arbitrary units were corrected to background, polarization and multiple scattering, normalized to electronic units (e.u.) [3, 7] and corrected for the incoherent component. The process of fitting the experimental intensities to the independent scattering function of the compound, using the expression [3]

$$I_{e.u.}(s) = K_1 I_{a.u.}(s) e^{-K_2 s^2} \quad (1)$$

resulted in the following adjustment constants: $K_1 = 12.79$, $K_2 = 1.91 \times 10^{-3}$. Once the intensities (in e.u.) shown in Fig. 1, and the corresponding atomic fractions, x_i, of the different elements in the alloy, were known, the reduced intensities, i, were obtained

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

TABLE I Characteristics of the diffractometric system of measurement

Angular interval (deg)	Δ(2θ)(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

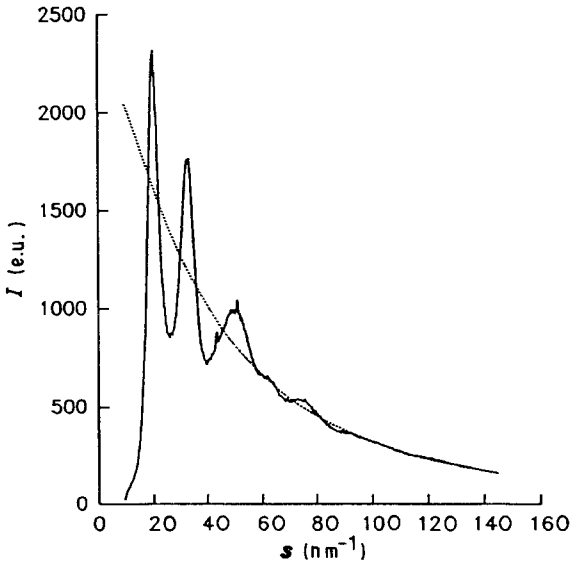


Figure 1 Intensities in electron units. (···) f (s), (—) $I_{e,u}$ (s).

giving the interference function, $F(s) = s.i(s)$, in the interval (0–144.8) nm^{-1} through whose Fourier transformation the radial atomic distribution function was obtained

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + rG(r) \quad (3)$$

where $\rho(r)$ represents the local atomic density affected by the Fourier transformation of the products of atomic factors, and ρ_0 is the average atomic density of the material. This density was experimentally measured using a pycnometric method at a constant temperature, the average value of the series of measurements being 5.54 g cm^{-3}, with a relative error under 3%.

Owing to the limitations imposed by the experimental data on the interval of s versus that demanded by the Fourier integral, there are oscillations in the RDF which do not correspond to the atomic diffraction behaviour of the alloy. In order to eliminate them, the extension method described by d'Anjou and Sanz [8] was carried out, based on that proposed by Shevchick [9], consisting of adjusting the experimental data of the interference function to the theoretical function

$$F(s) = \frac{C}{r} \exp\frac{(-\sigma^2 s^2)}{2} \sin sr \quad (4)$$

from initial values of C and r which represent the area under the first peak and its position in the RDF, σ being the half-width of the peak in question. The adjustment was carried out in the (71.6– 92.1) nm^{-1} interval. The initial values of the parameters were $C = 2.86$ atoms and $r = 0.270$ nm. A Fourier transformation was applied to this function, giving the extended RDF of the alloy, shown in Fig. 2, which supplied the structural information shown in Table II.

3. Observations and results

3.1. Analysis of the RDF

The analysis of the structural data supplied by the radial atomic distribution function of the alloy

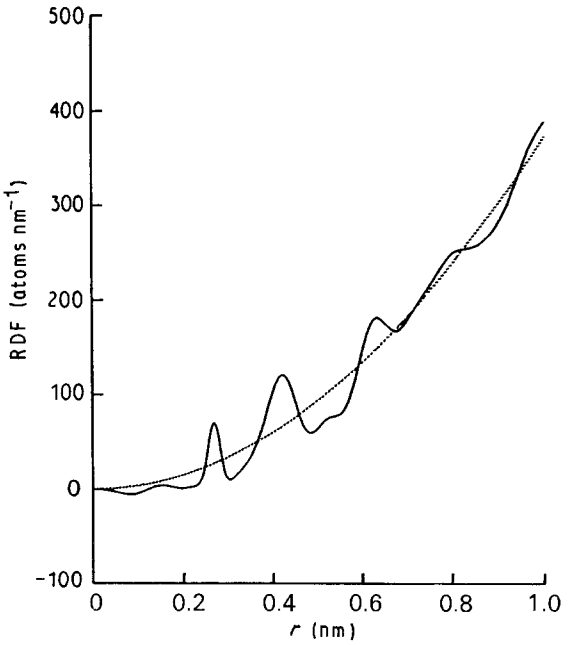


Figure 2 Radial distribution function. (—) $4\pi r^2 \rho(r)$, (···) $4\pi r^2 \rho_0$.

TABLE II RDF characteristics

	Maximum	
	1	2
Position (nm)	0.270	0.420
Limits (nm)	0.220–0.310	0.310–0.485
Averaged angle (deg)	102.1	
Area (atoms)	2.58	6.83
Error	±0.1	± 0.2

studied, shows among other things that the definition interval of the first peak, corresponding to the first coordination sphere, of alloy $Cu_{0.08}Ge_{0.18}Te_{0.74}$ (Cu = 1, Ge = 2, Te = 3), is such that all types of bond between the different elements are possible, as may be deduced by comparing this interval with the bond lengths, r_{ij}, of all possible pairs quoted in the literature and shown in Table III.

Bearing in mind that Te–X bonds (X = Cu, Ge, Te) 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 value, 0.265 nm, of these three kinds of bond, in the alloy 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

$$\text{Area} = \frac{1}{\left(\sum_i x_i Z_i\right)^2} \sum_i \sum_j n_{ij} x_i Z_i Z_j \qquad (5)$$

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

$$\text{Area} = \frac{2}{\pi} \sum_i \sum_j x_i \frac{n_{ij}}{r_{ij}} \int_a^b r P_{ij}(r)\,\mathrm{d}r \qquad (6)$$

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

$$P_{ij}(r) = \frac{1}{2} \int_0^{s_m} \frac{f_i(s) f_j(s)}{\left[\sum_i x_i f_i(s)\right]^2} \cos s(r - r_{ij})\,\mathrm{d}s \qquad (7)$$

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 hundred 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 $N(N \neq C_1)$, the number of bonds of this type of atom is [5]

$$a_1 = Na'_1 = C_1 a'_1 \pm |x|$$

$|x|$ being the variation in the number of bonds of said element, when its coordination changes from C_1 to N;

(iv) when the coordination of element A changes, the coordinations of elements B and D may increase or decrease, so the number of bonds of these elements is given by

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

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

Taking this hypothesis into account, Vázquez *et al.* [4] deduced the following relation from Equation 6 and according to the literature [3]

$$\text{Area} = \frac{1}{50\pi}\left[\left(h + \beta A_{22} - \delta \sum_{ij \neq 1} A_{ij}\right)N + \alpha A_{22} + \gamma \sum_{ij \neq 1} A_{ij} + P\left(\sum_{i=j \neq 1} A_{ij} - \sum_{\substack{i,j \neq 1 \\ i \neq j}} A_{ij}\right)a_{ij}\right] \qquad (8)$$

where h, α, β, γ and δ are parameters which depend on the alloy and on the coordination hypotheses, N is the

TABLE III Bond lengths

Pair	r_{ij} (nm)	Reference
Cu–Cu	0.258	[10]
Cu–Ge	0.239	[11]
Cu–Te	0.253	[11]
Ge–Ge	0.251	[12]
Ge–Te	0.258	[11]
Te–Te	0.271	[8]

coordination attributed to a certain element, in the alloy, P is a parameter equal to 2 when, in the variable a_{ij}, $i = j$, and -1 if $i \neq j$, and A_{ij} is determined by

$$A_{ij} = \frac{1}{r_{ij}} \int_a^b r P_{ij}(r) \mathrm{d}r \qquad (9)$$

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 of the alloy, whose equations $F'_{ij}(s) = A_{0ij}s + A_{1ij}$, are shown in Fig. 3. Parameters A_{ij}, shown in Table IV, were calculated according to the literature [6], from the bond lengths, r_{ij}, given in Table III, and the coefficients A_{0ij} and A_{1ij} of the mentioned straight regression lines, shown in Table IV.

In order to express the area under the first RDF peak as a function of the coordination, N, assigned to the copper atoms in this alloy, the characteristic parameter $h = 4.6769$, and those depending on the coordination hypotheses, were calculated [4, 5]: $\alpha = -68$, $\beta = -8$, $\gamma = 140$, $\delta = -8$ for $N = 2$ and $N = 4$.

The following expressions for the area were obtained from these data and from parameters A_{ij}, using Equation 8:

$$\text{Area} = 1.9258 + 0.0053a_{33} \qquad N = 2 \qquad (10a)$$
$$\text{Area} = 2.1420 + 0.0053a_{33} \qquad N = 4 \qquad (10b)$$

TABLE IV Coefficients of straight regression lines fitted to values of R_{ij} (s) and A_{ij} parameters

Pair	$A_{0ij}(\times 10^{-3})$	A_{1ij}	A_{ij}
Cu–Cu	− 6.04	0.3695	0.5492
Cu–Ge	− 6.11	0.4100	0.6539
Cu–Te	− 5.05	0.6824	1.0651
Ge–Ge	− 6.11	0.4548	0.7399
Ge–Te	− 4.33	0.7569	1.1388
Te–Te	3.95	1.2576	1.9535

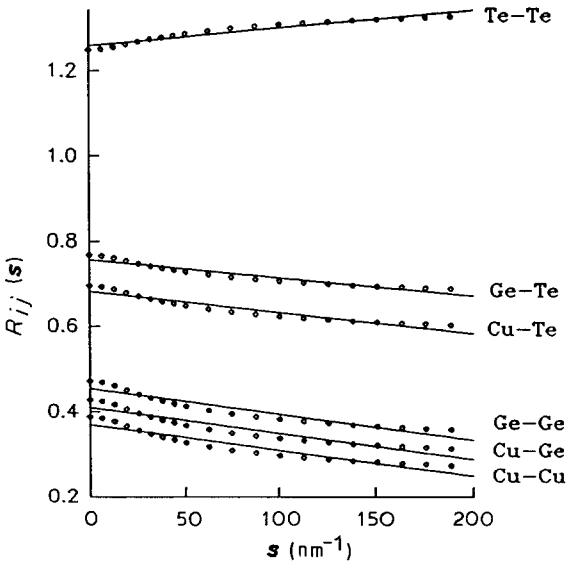


Figure 3 Straight regression lines fitted to values of R_{ij} (s).

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.

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 alloy $Cu_{0.08}$ $Ge_{0.18}$ $Te_{0.74}$, it is a relatively complex question to attribute a certain coordination to copper, 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 copper atoms [10]. The structure of Cu_2O may be explained considering an sp hybridation of the Cu [11–13], 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 alloy under study, because tellurium is in the same group of the Periodical Table as oxygen. If we admit a coordination of 2 for copper, the electrons which need to take this element would be supplied by some tellurium atoms, whose coordination would become 3.

In order to determine whether the above coordination hypothesis is valid, Equations 10a and b were applied with $N = 2$ and an average value of a_{33}, 54.8, being obtained for the area under the first RDF peak; 2.22 atoms, which, as may be observed, is considerably less than that obtained experimentally, a fact which led to the rejection of coordination 2 for the copper in the alloy studied.

Another frequent hypothesis in the literature is coordination 4 for copper. With RDF studies as a basis, some authors postulate the existence of tetracoordinated copper atoms in chalcogenide glasses. Hunter *et al.* [14], from studies of the EXAFS spectrum, attribute four first neighbours to the copper, a value which is also found in other compounds of this element such as CuFeS [11], Cu_3AsS_4 [11], and CuAsI [10]. In the present work, tetracoordinated copper ($N = 4$) has been assumed, accepting the necessary electrons for the sp^3 hybridation of some tellurium atoms, which increase their coordination by one unit [15]. Under this hypothesis, Equations 10a and b give, for the area under the first RDF peak, an expression which is in good agreement with the experimentally determined value, within the ± 0.1 atom margin of error. These relationships are observed to vary linearly with the number of Te–Te bonds, and because 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 [3, 5], 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 Te–Te bonds, the n_{ij} s, which contain parameter a_{33}, are given [3, 5] by the expressions

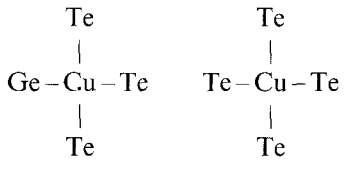
$$n_{22} = \frac{\alpha + [100\beta + a'_1(a'_3 - a'_2)]N/100 + 2a_{33}}{a'_2}$$

$$n_{23} = \frac{\gamma - [100\delta + a'_1 a'_3]N/100 - 2a_{33}}{a'_2} \qquad (11)$$

which allow us to write the relative coordination numbers shown in Table V, together with the variation intervals of parameter a_{33} defined by the $n_{ij}s$. On the other hand, the comparison of the experimental area, with its margin of error $\pm$ 0.1 atoms, to the theoretical area, defines a new variation interval of the number of Te–Te bonds, which is shown in Table V together with its intersection with that corresponding to the positive character of the $n_{ij}s$. To illustrate the theoretical calculations carried out, Fig. 4 shows the theoretical area under the first RDF peak versus a_{33}, according to the tetracoordinated copper hypothesis.

Bearing in mind the values of the $n_{ij}s$ corresponding to the extremes of the a_{33} interval, it may be postulated that the material of the alloy 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 alloy considered in which, together with tetrahedral units centred on copper atoms, such as



there are other tetrahedra centred on germanium atoms. All of these structural units would be joined by ramified chains, made up of an excess of tellurium atoms [16, 17].

4. Model description and analysis

The main object, when determining the structure of glassy solids, is to build spatial atomic distribution models which verify the experimentally obtained structural information and, at the same time, agree with the physical–chemical properties of the materials. The Monte Carlo method seems to be the most adequate for describing the short-range order of a glassy material obtained by quenching.

The process used for building the model, described at length by Vázquez *et al.* [18], comprises two stages: generating the initial configuration and refining it. During the first stage, 200 positions were semi-randomly created in the volume limited by a 1.0 nm radius spherical surface, in which, according to the experimental density, 124 atoms were to be located, as follows: 10 copper atoms, 22 germanium atoms and 92 tellurium atoms. This number of atoms is large enough to represent statistically the material, and small enough not to require too much calculating time. The generated positions meet the following requirements imposed by the information supplied by the experimental RDF.

(i) The distance between two first neighbours must be within the interval defined by the first RDF peak.

(ii) The bond angle must be within the 60° – 180° range obtained, according to the literature [19], from the extreme radii of the first two coordination spheres.

(iii) The number of atoms of each kind in the first coordination sphere, which is given as a maximum acceptable coordination for each one of them. In the case of the alloy $Cu_{0.08}$ $Ge_{0.18}$ $Te_{0.74}$, bearing in mind the postulated local order, a maximum coordination of four was considered for the copper.

The positions obtained were reduced to a number equal to the number of atoms compatible with the experimental density by eliminating those with lowest coordination; the different kinds of atom were semi-randomly assigned to the corresponding positions. The reduced RDF of the initial configuration, $rG_{\mathrm{mod}}(r)$, was determined, simulating a diffraction process in the configuration. This function was compared to the $rG_{\mathrm{exp}}(r)$ multiplied by the expression proposed by Mason [20] and the two RDFs were compared by mean-square deviation, ε^2, used as a criterion for deciding on the validity of the generated configuration.

The second stage in the building of the model is the refining stage, which was done using the Metropolis

TABLE V Theoretical results obtained for the alloy $Cu_{0.08}Ge_{0.18}Te_{0.74}$

Coordination numbers n_{ij}, $i,j \neq 1$	Variation intervals for parameters a_{33}		Intersection of intervals
	Defined by the n_{ij} parameters	Defined by limits of error of the experimental area	
$n_{22} = (-82.08 + 2a_{33})/18$	$41.04 \leq a_{33} \leq 74.16$	$63.77 \leq a_{33} \leq 101.51$	$63.77 \leq a_{33} \leq 74.16$
$n_{23} = (148.32 - 2a_{33})/18$			

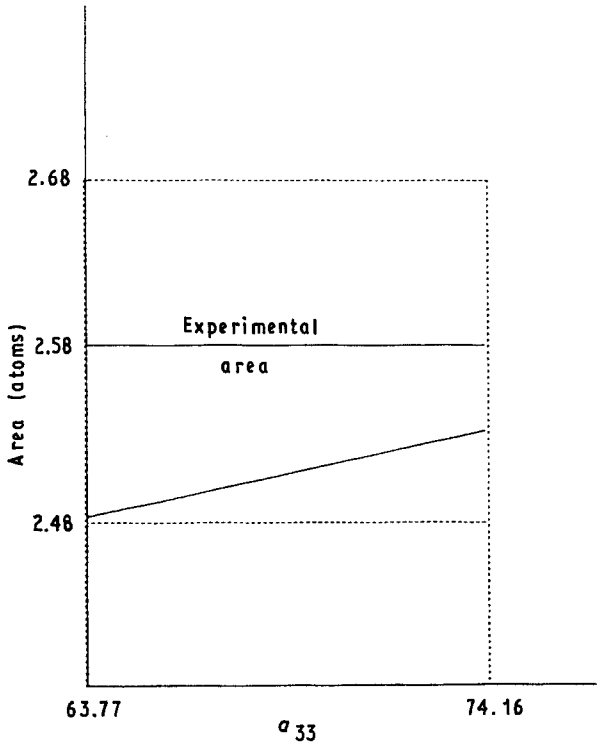


Figure 4 Area of first peak plotted against number of Te–Te bonds.

Monte Carlo method [21] and consisted of modifying the initial position of a randomly chosen atom, by movements of arbitrary amplitude, P, and in random directions. These movements must meet all the conditions imposed by the experimental RDF, plus the additional restriction of not allowing moves implying breaks in the bonds of copper atoms, therefore keeping the predicted coordination for this element when the local order of the alloy was postulated. During the position-refining process, the model evolved as shown in Table VI, in which the mean-square deviation refers to the last movement in each interval. The position-refining process was considered finished when the number of rejected movements was too large, and the mean-square deviation did not considerably improve. Fig. 5 shows the reduced RDF of the model and the experimental RDF after refining the positions and the thermal factors of the alloy under study. Fig. 6 shows a spatial representation of the generated atomic configuration, in which one may observe tetrahedra centred on copper and germanium atoms. Both structural units are interlinked, forming a network which constitutes the possible structure of the alloy.

TABLE VI Position refining process

P (nm)	Movement intervals	Squared deviation (nm)
0.05	1 – 314	0.0090
0.03	315 – 362	0.0072
0.01	363 – 523	0.0044

Dangling bonds are observed in this spatial distribution, as is frequent in amorphous materials. Many of these dangling bonds belong to atoms which are less than a first neighbour's distance away from the surface of the sphere, and may be saturated with atoms situated outside it. In the case of elements with two or more dangling bonds, they may be due to the finite size of the model, when the atom in question is less than 0.11 nm away from the surface limiting the configuration. This possibility takes into account both the distance between first neighbours and the average bond angle. Of the dangling bonds observed in the

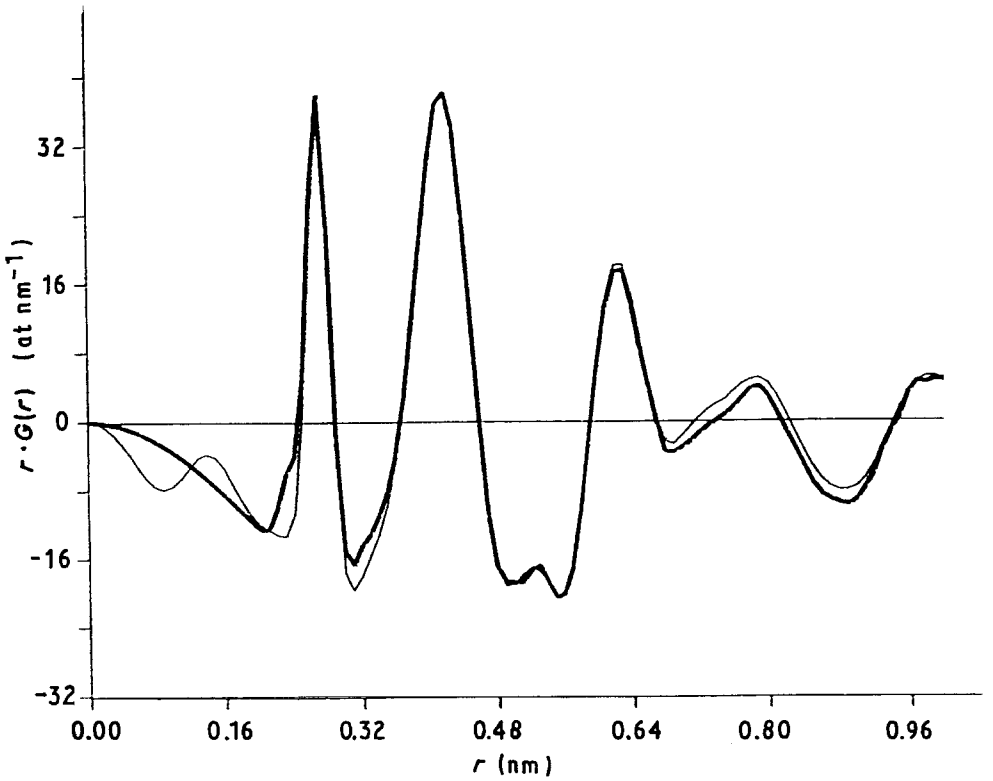


Figure 5 Representation of (—) calculated and (——) experimental RDFs.

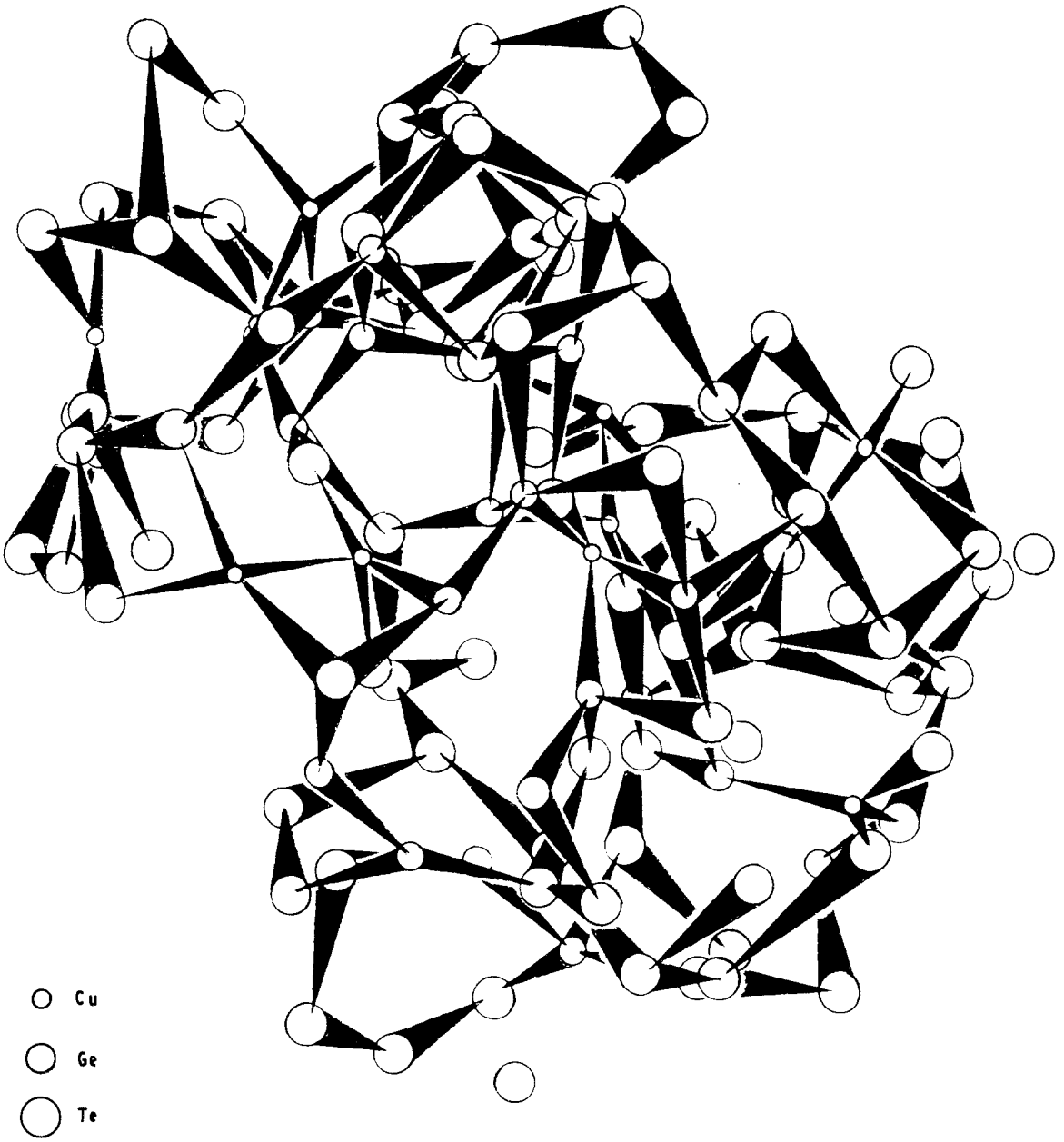


Figure 6 Spatial representation of the model of alloy $Cu_{0.08}Ge_{0.18}Te_{0.74}$.

model, 36% belong to atoms which are not in a position allowing them to be saturated with possible external neighbours. However, the existence of dangling bonds is a consequence inherent to the preparation of chalcogenide glasses.

One way of estimating the concordance between the generated atomic configuration and the actual structure of the alloy under study, is by analysing the structural parameters (bond lengths and angles) obtained from the model, and relating their values to those quoted in the literature for similar compounds. Table VII shows the average bond lengths between the different pairs of elements. It is observed that the values obtained agree with data from the literature because, with the exception of the Cu–Cu bond lengths which are not considered statistically significant, all the other values differ less than 3% from those previously reported.

Another interesting parameter which supplies information on the true structure of a glassy solid is the average bond angle between each element and two of

TABLE VII Averaged bonding distances

Bond	Material	$\langle d_{ij} \rangle$ (nm)	Reference
Cu–Cu	$Cu_{0.08}Ge_{0.18}Te_{0.74}$	0.271	Present work
		0.258	[a]
Cu–Ge	$Cu_{0.08}Ge_{0.18}Te_{0.74}$	0.246	Present work
	sum of covalent radii	0.239	[11]
Cu–Te	$Cu_{0.08}Ge_{0.18}Te_{0.74}$	0.267	Present work
		0.264	[b]
	$Cu_{0.05}As_{0.50}Te_{0.45}$	0.262	[15]
Ge–Ge	$Cu_{0.08}Ge_{0.18}Te_{0.74}$	0.256	Present work
	amorphous Ge	0.254	[23]
	$Ge_{0.10}As_{0.20}Te_{0.70}$	0.253	[24]
	$Ge_{0.14}As_{0.43}Te_{0.43}$	0.253	[19]
Ge–Te	$Cu_{0.08}Ge_{0.18}Te_{0.74}$	0.259	Present work
	$Ge_{0.14}As_{0.43}Te_{0.43}$	0.259	[19]
Te–Te	$Cu_{0.08}Ge_{0.18}Te_{0.74}$	0.269	Present work
	$Ge_{0.10}As_{0.20}Te_{0.70}$	0.270	[24]
	$Al_{0.23}Te_{0.77}$	0.271	[8]

[a] Estimation of the average value between the pure metal and Cu_2S [10].

[b] Estimation by means of Schomacker and Stevenson's formula [22].

TABLE VIII Averaged bonding angles

Type	$\langle\alpha\rangle$ (deg)	Material	Reference
Cu	107.0	$Cu_{0.08}Ge_{0.18}Te_{0.74}$	Present work
	107.8	$Cu_{0.20}As_{0.30}Se_{0.50}$	[18]
	106.6	$Cu_{0.05}As_{0.50}Te_{0.45}$	[15]
	106.2	$Cu_{0.15}As_{0.40}Te_{0.45}$	[15]
Ge	106.8	$Cu_{0.08}Ge_{0.18}Te_{0.74}$	Present work
	107.5	$Ge_{0.05}As_{0.20}Te_{0.75}$	[24]
	108.0	$Ge_{0.20}As_{0.40}Se_{0.40}$	[12]
Te	106.9	$Cu_{0.08}Ge_{0.18}Te_{0.74}$	Present work
	107.0	$As_{0.45}Se_{0.10}Te_{0.45}$	[25]
	106.8	$As_{0.20}Se_{0.50}Te_{0.30}$	[26]
	102.0–109.5	TeGe glass	[27]

its first neighbours. The average values of these angles are therefore usually compared to those given in the literature. Table VIII shows these values for the model, together with those quoted in the literature for similar alloys. All the calculated values can be considered acceptable, bearing in mind that a distortion of the bond angle is typical of glassy materials and that, in the most unfavourable case, the difference between the bond angles in the model and the values quoted in the literature was less than 1.5%.

5. Conclusions

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

By using the most approximate expression of the area under the first RDF peak, it was possible to find a number of Te–Te bonds for tetra-coordinated copper which, while keeping the coordination numbers, n_{22} and n_{23}, positive, gives a theoretical area within the margin of error of the experimental area.

Considering the tetracoordinated copper 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 generated model, the three-dimensional structure of the studied alloy can be described as a network of tetrahedra centred on copper atoms, coexisting with other tetrahedra whose centres are occupied by tetracoordinated germanium atoms, making the network more compact. These tetrahedral units can be joined together either directly or by chains of tellurium atoms.

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