Materials Chemistry and Physics, 33 (1993) 245–253

A study of short-range order and atomic arrangement in the glassy alloy $Cu_{0.03}Ge_{0.20}Te_{0.77}$ by X-ray diffraction

M. Casas-Ruiz, J. Vázquez, R. A. Ligero and R. Jiménez-Garay
Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real, Cádiz (Spain)

(Received April 8, 1992; accepted July 24, 1992)

Abstract

The radial atomic distribution of the amorphous alloy $Cu_{0.03}Ge_{0.20}Te_{0.77}$ was studied using the X-ray diffraction data supplied by samples obtained through quenching. The short-range order was determined by interpreting the radial distribution function (RDF), using a theoretical expression that takes into account the variation in the atomic scattering factors with s (the scattering vector module) and approximates them to polynomic functions. The tetra- and dicoordinated-copper hypotheses, quoted in the literature for glassy alloys containing this element, were considered. The result of the study is that, for the alloy in question, only the tetracoordinated-copper hypothesis is compatible with the structural information that was obtained experimentally. A spatial atomic distribution model was generated in accord with this copper coordination, using a conveniently modified Monte Carlo (random) method. A comparative analysis of the main structural parameters of this model revealed good agreement with the values given in the literature for similar alloys.

1. Introduction

Amorphous materials have been used by man since remote times. Over 3000 years ago, the Phoenicians developed an important industry based on the manufacture of glass objects from the quartz-rich sands of the Lebanese coast. Despite their long history, the nature, structure and properties of amorphous solids have remained almost unknown until recently [1]. Although some studies were done on this type of material during the first half of this century, glassy solids have been the object of detailed studies since the 1960s, owing to their great fundamental and technological importance [2].

An amorphous solid is one that does not possess the long-range order (periodicity) characteristic of crystalline materials, but does have a certain local order in its bonds with first neighbours. 'Amorphous' and 'non-crystalline' are therefore synonymous terms, whereas 'glass' is a non-crystalline material that exhibits a characteristic transition temperature [3] from the more energetic glass phase to the minimal-energy crystalline phase. The temperature at which the glass–crystal transition takes place is related to the average coordination of the material [4], making it very important to understand its local order, which can be related to other physical properties exhibited by the material.

This work presents an analysis of the short-range order of the semiconducting glassy alloy $Cu_{0.03}Ge_{0.20}Te_{0.77}$, from the X-ray diffraction intensities of samples of this alloy, using the fact that the scattering atomic factors are functions of the Bragg angle [5]. After finding the coordination of copper that best explained the experimentally obtained structural information, a spatial atomic distribution model was generated, using a semi-random method that takes into account the geometric restrictions imposed by the radial distribution function (RDF). Analysis of the parameters (bond lengths and angles) of the generated model shows good agreement with the data presented in the literature for similar alloys.

2. Experimental

2.1. Preparing the samples and obtaining the diffracted intensities

The samples of glassy alloy $Cu_{0.03}Ge_{0.20}Te_{0.77}$ were prepared in bulk from 99.999% pure copper, germanium and tellurium, which were pulverized to a grain size of less than 40 μm and added in the proper amounts to obtain 12 g of the compound. The material was homogeneously mixed (in order to obtain the greatest possible contact surface

0254-0584/93/$6.00

between the particles and so encourage the reaction) and put into quartz tubes, which were submitted to an iterative process of filling and emptying with inert gas (He) in order to avoid possible oxidation of the samples. The capsules were sealed with an oxy-acetylene burner, while the residual pressure was less than 10^{-3} torr. The resulting ampoules were kept at 1100 °C for 72 h in a rotary furnace, rotating at 1/3 rpm, and then quenched in liquid nitrogen, which supplied the necessary cooling rate for obtaining the glass. In order to make ingots for studying other physical (electric) properties, the material was extracted by dissolving the quartz in a mixture of hydrofluoric acid and hydrogen peroxide. The samples were homogeneous from a macroscopic point of view, and presented the conchoidal fracture characteristic of solids with random atomic distribution. The density was pycnometrically determined using pieces of the material of adequate size, at constant temperature; the series of measurements gave an average value of 5.43 g cm^{-3}, with a relative error of less than 3%.

Part of the material was pulverized to a particle size of less than 40 μm and pressed into bricks of approximately $20 \times 20 \times 1$ mm, X-ray diffraction showed that the compound did not exhibit the peaks characteristic of the crystalline phase, thus confirming the glassy nature of the alloy.

In order to obtain structural information on the material, the samples were submitted to X-ray diffraction analysis. The intensity of the diffracted radiation was measured in an automatic Siemens D500 powder diffractometer with Bragg–Brentano geometry by reflection. The proper narrow frequency interval, centred around the frequency of the radiation used, was selected with a bent graphite monochromator. The device was equipped with a scintillation detector with a Tl-enriched NaI photosensitive window.

As the detection system used consists of counting the number of randomly detected photons, with the statistical error depending on the number of photons that reach the detector, the intensities were measured while fixing the number of counts and digitally registering the time taken to do them, thus keeping the error constant throughout the series. The number of pulses was fixed at 4000, keeping the relative error under 1.5%. The intensities diffracted by the samples were measured in the range of s ($=(4\pi/\lambda)\sin\theta$) from 0.77 to 14.48 Å^{-1}, using Mo Kα ($\lambda = 0.71069$ Å), and supplying the generator with a power of 50 kW at 30 mA. Four series of measurements were carried out: two ascending and two descending, at the Bragg 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 value of the four measurements done for each angle was taken as the intensity of the radiation diffracted by the samples.

2.2. *Obtaining structural data*

The mentioned intensities were corrected for background, polarization and multiple scattering [5], in order to eliminate the radiation that does not carry structural information. Figure 1 shows these corrected intensities expressed in arbitrary units.

The intensities were normalized to electronic units (e.u.) using the high angle technique [5], according to which, for high values of s, the experimental intensity curve should oscillate around the independent scattering curve in decreasing amplitude. The normalization method [6] consisted of fitting, by least squares, the experimental curve $I(s)$ (in arbitrary units) to the independent scattering curve $f(s)$, minimizing the function

$$S = \sum_{i=1}^{M} [f(s_i) - k_1 I(s_i) \exp(-k_2 s_i^2)]^2 \qquad (1)$$

where k_1 and k_2 are two adjustment parameters, and the factor $\exp(-k_2 s_i^2)$ is used for simulating a damping of the oscillations as the angle increases. The normalized intensities were corrected for the Compton effect, resulting in the coherent spectrum $I_{\mathrm{e.u}}(s)$ from which the reduced intensities are obtained:

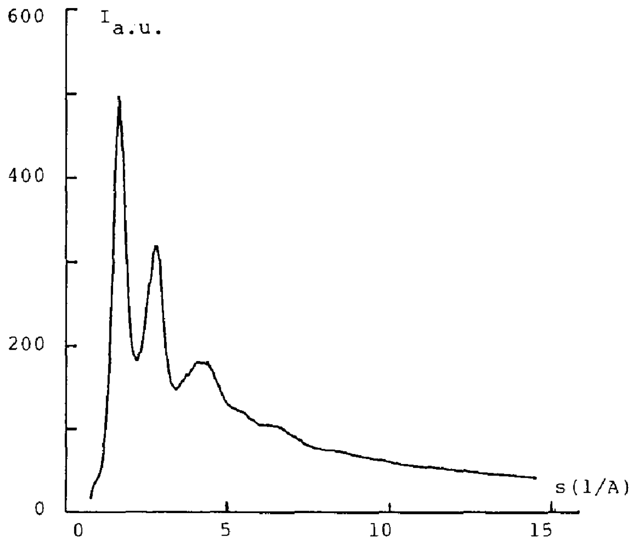

Fig. 1. Intensity (arbitrary units) of the radiation diffracted by the samples, corrected by background, polarization and multiple scattering.

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

which give the interference function $F(s)=s\times i(s)$, from which the function $G(r)$ is obtained by applying a Fourier transform and, from this, the radial atomic distribution function (RDF):

$$4\pi r^2\rho(r)=4\pi r^2\rho_0+rG(r) \tag{3}$$

representing the number of neighbours of an arbitrary atom, at a certain distance. $\rho(r)$ is the local atomic density affected by the Fourier transform of the products of atomic factors, and ρ_0 is the average experimental density.

The spurious oscillations that appear in the RDF for low values of r, owing to the lack of experimental data for high values of s, make it necessary to extend the interference function to those values of s for which the said function tends toward zero. The extension was carried out using the method described in the literature [7], based on the one proposed by Shevchik [8], according to which, for high values of s, the experimental interference function may be approximated by

$$F_{\mathrm{theoretical}}(s)=\frac{C}{r}\exp\frac{(-\sigma^2 s^2)}{2}\sin(sr) \tag{4}$$

where C, r and σ are parameters obtained by least-squares adjustment from the initial values C_1, r_1 and σ_1, which represent the area, the position and the half-width of the first RDF peak evaluated up to $s=14.48$ Å^{-1}, the maximum value for which data were obtained with the experimental device in use. A Fourier transform was applied to the interference function, extended up to 30 Å^{-1}, giving the RDF shown in Fig. 2, which supplied the following structural information: positions of the first two maximum values, 2.75 and 4.25 Å; limits of the first peak, 2.20–3.20 Å; area under the latter, 2.44 ± 0.1 atoms; average bond angle, 101.2°.

3. RDF analysis and copper coordination hypotheses

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 $Cu_{0.03}Ge_{0.20}Te_{0.77}$ (Cu = 1, Ge = 2, Te = 3), is such that all types of bond are possible between the different elements in the compound, as may be observed by comparing the mentioned interval to the bond lengths r_{ij} of all possible pairs, quoted in the literature and shown in Table 1.

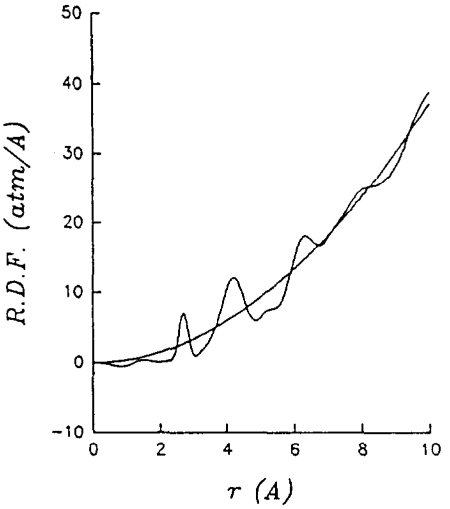

Fig. 2. Experimental radial distribution function of the $Cu_{0.03}Ge_{0.20}Te_{0.77}$ alloy. The parabola corresponds to $4\pi r^2\rho_0$.

TABLE 1. Bond lengths

Pair	r_{ij} (Å)	Ref.
Cu–Cu	2.58	9
Cu–Ge	2.39	10
Cu–Te	2.53	10
Ge–Ge	2.51	11
Ge–Te	2.58	10
Te–Te	2.71	7

Bearing in mind that the Te–X bonds (X = Cu, Ge, Te) ought perhaps to contribute most to the diffraction spectrum, it seems reasonable to assume that the first maximum RDF value is within the values defining the bond lengths of the corresponding pairs, which agrees with the average weighted value, 2.67 Å, of these three types of bond. Owing to the RDF's character as a probability function, the positions of its maximum values can be interpreted as the average distances between the different coordination spheres and an arbitrary reference atom. Specifically, the abscissa of the first maximum value 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 number of atoms which, on average, surround an arbitrary reference atom — in other words, the average coordination number of the material. Bearing in mind the physical meaning of this area, and the fact that the products of atomic factors, $R_{ij}(s)=f_i(s)f_j(s)/[\Sigma_i x_i f_i(s)]^2$, are functions of the scattering angle, Vázquez and Sanz [12], following the method described by Warren [5], have come to the conclusion that the area under the first RDF peak is related to certain structural parameters, the relative coordination numbers n_{ij}, through the expression

$$\text{area} = \frac{2}{\pi}\sum_{ij} x_i \frac{n_{ij}}{r_{ij}} \int_a^b rP_{ij}(r)\,\mathrm{d}r \tag{5}$$

r_{ij} being the average distance between an i-type atom and a j-type atom, a and b the limits of the first RDF peak and $P_{ij}(r)$ a function defined as follows:

$$P_{ij}(r) = \frac{1}{2}\int_0^{s_m} R_{ij}(s)\cos[s(r-r_{ij})]\,\mathrm{d}s \tag{6}$$

where s_m is the upper measurement limit.

The structural information obtained from the analysis of the experimental RDF, together with the physicochemical properties of the alloys and their constituent elements, allow us to hypothesize on the local order of glassy materials. These hypotheses, reflected in the relative coordination numbers and therefore in the number of chemical bonds, a_{ij}, between the different pairs of elements in the material, led Vázquez *et al.* [13] to deduce, from eqn. (5), the following relationship:

$$\text{area} = \frac{1}{50\pi}\left[\left(h + \beta A_{22} - \delta\sum_{i,j\neq 1} A_{ij}\right)N + \alpha A_{22} + \gamma\sum_{i,j\neq 1} A_{ij} + P\left(\sum_{i=j\neq 1} A_{ij} - \sum_{i,j\neq 1,\, i\neq j} A_{ij}\right)a_{ij}\right] \tag{7}$$

where h, α, β, γ and δ are parameters that depend on the alloy and on the coordination hypothesis, N is the coordination attributed to a certain element in the material, P is a parameter equal to 2 when, in the variable a_{ij}, $i=j$ and equal to -1 if $i\neq j$, and A_{ij} is determined by the following relation:

$$A_{ij} = \frac{1}{r_{ij}}\int_a^b rP_{ij}(r)\,\mathrm{d}r \tag{8}$$

A theoretical evaluation of the area under the first RDF peak according to eqn. (7), as a function of the coordination N attributed to the copper, requires calculation of the parameters A_{ij}. According to the literature [12], the calculation of these parameters involves establishing the order of the polynomes in s, which approximate the functions $R_{ij}(s)$; in this work, the mentioned functions were adjusted to the straight regression lines of the corresponding pairs of elements in the alloy, whose equations, $F'_{ij}(s) = A_{0ij}s + A_{1ij}$, are shown in Fig. 3. Parameters A_{ij}, given in Table 2, were calculated according to the literature method [14] from the bond lengths r_{ij} given in Table 1 and the coefficients A_{0ij} and A_{1ij} of the aforementioned straight regression lines, given in Table 2.

In order to express the area in question as a function of the coordination N assigned to the copper atoms in this alloy, the characteristic parameter ($h = 1.8304$) and those depending on the coordination hypotheses were calculated [15]:

$\alpha = -71 \quad \beta = -3 \quad \gamma = 151 \quad \delta = -3$
for $N = 2$ and $N = 4$

From these data and the tabulated A_{ij}, and using eqn. (7), the following expressions were obtained:

$$\begin{aligned} \text{area} &= 1.9323 + 5.1\times10^{-3}a_{33} \quad \text{for} \quad N=2 \\ \text{area} &= 2.0141 + 5.1\times10^{-3}a_{33} \quad \text{for} \quad N=4 \end{aligned} \tag{9}$$

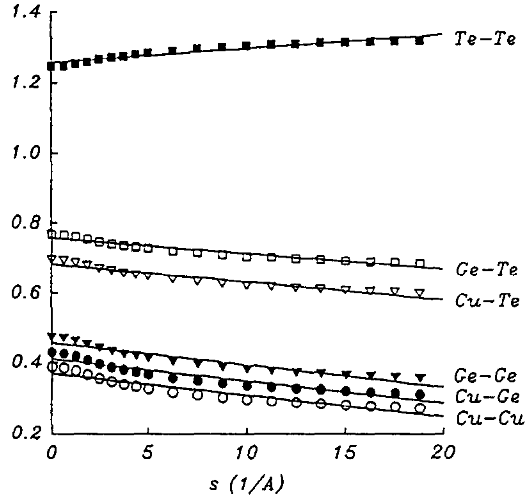

Fig. 3. Straight regression lines fitted to values of $R_{ij}(s)$ of the corresponding pairs of elements in the alloy studied.

TABLE 2. Coefficients of straight regression lines fitted to values of $R_{ij}(s)$ and A_{ij} parameters

Pair	A_{0ij}	A_{1ij}	A_{ij}
Cu–Cu	-5.96×10^{-3}	0.3574	0.5251
Cu–Ge	-6.05×10^{-3}	0.3965	0.6412
Cu–Te	-5.14×10^{-3}	0.6601	1.0819
Ge–Ge	-6.06×10^{-3}	0.4399	0.7410
Ge–Te	-4.48×10^{-3}	0.7322	1.1367
Te–Te	3.27×10^{-3}	1.2166	1.9301

which may be used for postulating the short-range order of the alloy. These relationships are functions of the number of Te−Te bonds, a_{33}, limiting the variability field of the theoretical area.

In order to generate a local-order model of alloy $Cu_{0.03}Ge_{0.20}Te_{0.77}$, it is necessary to establish the average coordination of its constituent elements, which involves attributing a certain coordination to the copper. This is a relatively difficult question, as there is no single coordination hypothesis in the literature for this element in other compounds. Whereas some authors [9, 16] propose twofold coordination for the copper in similar compounds, others [17, 18] propose tetrahedral coordination for copper in ternary alloys with chalcogens; both hypotheses must be taken into consideration.

Bearing in mind that, for each value of N, eqns. (9) vary linearly with the number of Te−Te bonds, and that the relative coordination numbers n_{22} and n_{23} also depend on N, it is possible to obtain, according to the literature [19], the suitable coordination of the copper by determining the variation interval of a_{33} for which the relative coordination numbers are positive and, at the same time, the theoretically obtained area is within the margin of error of the experimental area. In order to do this, the relative coordination numbers that contain parameter a_{33} are given [6, 15] by the expressions

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

$$n_{23}=\frac{\gamma-[100\delta+a'_1a'_3]N/100-2a_{33}}{a'_2} \qquad (10)$$

which allow us to obtain for $N=2$ an average value $\langle a_{33}\rangle=56.5$. Considering eqn. (9) with $N=2$, a value of 2.22 is obtained for the area under the first RDF peak; 2.22 atoms, as may be observed, is considerably less than the value obtained experimentally, a fact that led to the rejection of coordination 2 for the Cu in the alloy studied.

In the present work, tetracoordinated copper ($N=4$) has been assumed, accepting the necessary electrons for the sp^3 hybridization of some tellurium atoms, which increase their coordination by one unit [17]. Under this hypothesis, the coordination numbers n_{22} and n_{23} are positive for values of a_{33} within the interval [38.08–76.88], and eqns. (9) give for the area under the first RDF peak an expression that is in good agreement with the experimentally determined value, within the ±0.1 atom margin of error. This analysis leads us to the conclusion that, in the alloy in question, the most probable short-range order can be described as a network of tetrahedral units centred on copper atoms together with other tetrahedrons centred on germanium atoms. All of these structural units would be joined by ramified chains, made up of an excess of tellurium atoms.

4. Generation of the spatial model and discussion of the results

When determining the structure of a glassy solid, our main object is to build a spatial atomic distribution model that verifies the structural information obtained experimentally and, at the same time, agrees with the physicochemical properties of the material. Of all the different methods for generating structural models of amorphous solids, the Monte Carlo method seems to be the most suitable for describing the short-range order of a glassy material obtained by quenching, and the one that best simulates the structural characteristics of this type of alloy.

A variation of the Monte Carlo method, similar to the procedure used by Rechtin *et al.* [20], was therefore used for building the atomic model of the alloy $Cu_{0.03}Ge_{0.20}Te_{0.77}$. The variations refer to the geometric and coordination conditions imposed by the experimental RDF, which imply a certain semi-randomness in the building of the atomic configuration.

The process used to generate the model, described in depth by Vázquez *et al.* [21], has two stages: generation of the initial configuration and refining of the same. In the first stage, 200 positions were semi-randomly created in the volume enclosed by a spherical surface of radius 10 Å in which, according to the experimental density, 124 atoms must be situated, distributed as follows: 4 Cu atoms, 25 Ge atoms and 95 Te atoms. This number of atoms is large enough to represent the material statistically, and small enough not to take too much calculating time. The generated positions comply with the following conditions, imposed by the structural 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 between an atom and two of its first neighbours can vary between the values $\Phi_{min}=60°$ and $\Phi_{max}=180°$, deduced [22] 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 average weighted coordination agrees with the experimentally obtained one.

The positions were reduced to a number equal to the number of atoms compatible with the experimental density, by eliminating those with the lowest coordination. The atoms were assigned to their respective positions, placing the copper atoms in tetracoordinated positions and the others randomly among the rest of the positions. The reduced RDF, $rG_{\mathrm{mod}}(r)$, of the initial configuration was determined by simulating a diffraction process. This function was compared to the $rG_{\mathrm{exp}}(r)$ multiplied by the expression proposed by Mason [23]:

$$D(r) = 1.0 - 1.5\left(\frac{r}{2R}\right) + 0.5\left(\frac{r}{2R}\right)^3 \qquad (11)$$

which represents the probability of finding a distance r inside a sphere whose radius is R. The comparison of the two RDFs was done by mean square deviation, used as a criterion for deciding the validity of the generated configuration.

The second stage in building the model is refining it, using the Metropolis–Monte Carlo technique [24], which consists of modifying the initial position of a randomly chosen atom, through movements of arbitrary amplitude P and in random directions. These movements must obey all the conditions imposed by the experimental RDF, and the additional restriction of not breaking any copper bonds, in order to keep the coordination predicted for this element when postulating the local order of the alloy. During the refining process, the model evolved as shown in Table 3, where 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 high and the mean square deviation did not improve considerably. Figure 4 shows the experimental reduced RDF and the model RDF, after the process of refining the positions and the thermal factors was completed.

TABLE 3. Position-refining process for model

P (Å)	Movement intervals	Squared deviation (Å)
0.5	1–263	0.037
0.3	264–302	0.028
0.1	303–360	0.021

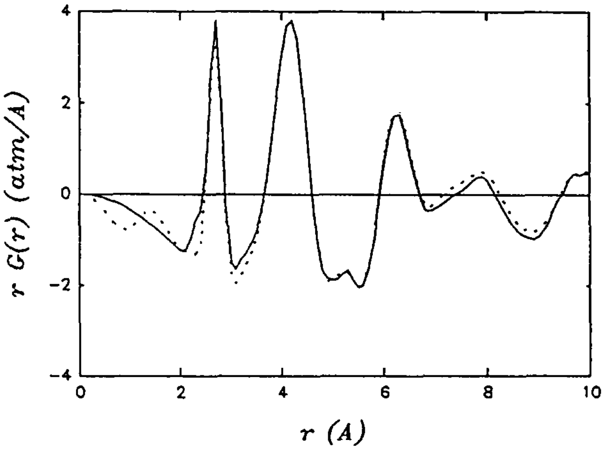

Fig. 4. The functions $rG_{\mathrm{exp}}(r)D(r)$ and $rG_{\mathrm{mod}}(r)$ of the final model (dashed and solid lines, respectively) once the thermal isotropic refinement was accomplished.

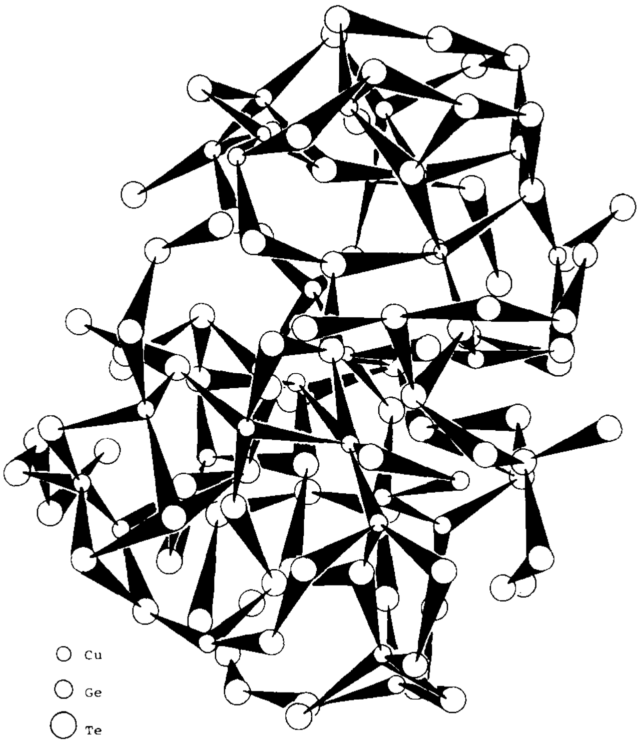

Fig. 5. Spatial representation of the generated model of the alloy $Cu_{0.03}Ge_{0.20}Te_{0.77}$.

The poor fit observed in the $0<r<2$ Å region between the reduced RDFs (Fig. 4) is explained by the assumption in the generated model that, on the basis of the first-neighbour distance obtained from the experimental RDF, distances of less than 2 Å are not possible.

The spatial representation of the generated atomic distribution is shown in Fig. 5, in which one may observe tetrahedrons centred on copper and germanium atoms. Both structural units are interlinked, forming a network that constitutes the possible structure of the alloy.

This theoretical model, which is randomly generated and which takes into consideration the structural information obtained from the experimental RDF, must be as representative as possible of the true structure of the alloy in question. One way of estimating the agreement between this model and the atomic distribution of the compound is by analyzing its main structural parameters (coordinations, average bond lengths, etc.).

An important point to bear in mind when statistically analyzing the generated model is the comparison of the resulting coordinations of its elements and those of the structural units, which, according to the established hypotheses, can be postulated from the information supplied by the experimental data. Table 4 shows the coordinations of each element in the atomic model of the alloy and, in parentheses, the coordinations which were theoretically predicted based on the tetracoordinated-copper hypothesis. Dangling bonds are observed in this spatial distribution, indicating the presence of atoms with unsaturated bonds; this can be partly justified by the finite size of the model. Many of these dangling bonds belong to atoms that are less than a first-neighbour distance away from the surface of the sphere, and can be saturated with possible atoms outside it. In the case of elements with two or more dangling bonds, they are admittedly due to the limitation of the distribution, when the atom in question is less than 1.1 Å away from the surface of the model. This possibility takes into account both the distance between first neighbours and the average bond angle. In the generated model 50% of unsaturated atoms are less than 2 Å away from the spherical surface enclosing it, and cannot therefore be considered infra-coordinated as they can bond with external atoms. However, the existence of dangling bonds is inherent to the method of preparation of chalcogenide glasses.

Another interesting aspect of the generated model is the average bond lengths in the different pairs of elements in the material, and relating their values of those quoted in the literature for similar compounds. Table 5 shows the average bond lengths between pairs of elements. It is seen that the values obtained agree with data from the literature, since, with the exception of the Cu–Ge bond lengths, which are not considered statistically significant, all values differ by less than 2% from those previously reported.

TABLE 4. Model coordinations

Atom	Coordination				
	4	3	2	1	0
Cu	4 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Ge	17 (25)	6 (0)	2 (0)	0 (0)	0 (0)
Te	1 (0)	31 (12)	48 (83)	13 (0)	2 (0)

Another parameter that is often used for obtaining information on the structure of a glassy solid is the average bond angle, $\langle\alpha\rangle$, of each element with two of its first neighbours. This is why the average values of these angles are usually compared with those given in the literature. Table 6 shows these values for the model, together with those quoted in the literature for similar alloys; and Fig. 6 shows the angular distribution histograms for the different elements in the vertex. In this table, it may be observed that all the calculated values can be considered acceptable, if we bear in mind that a distortion of the bond angle is typical of glassy solids and that, in the most

TABLE 5. Averaged bond distances

Bond	Material	$\langle d_{ij}\rangle$ (Å)	Ref.
Cu–Ge	$Cu_{0.03}Ge_{0.20}Te_{0.77}$	2.63	this work
	sum of covalent radii	2.39	10
Cu–Te	$Cu_{0.03}Ge_{0.20}Te_{0.77}$	2.59	this work
	$Cu_{0.05}As_{0.50}Te_{0.45}$	2.62	17
		2.64	a
Ge–Ge	$Cu_{0.03}Ge_{0.20}Te_{0.77}$	2.68	this work
	Ge crystallized	2.70	26
Ge–Te	$Cu_{0.03}Ge_{0.20}Te_{0.77}$	2.73	this work
	Ge Te film	2.75	27
Te–Te	$Cu_{0.03}Ge_{0.20}Te_{0.77}$	2.73	this work
	$Ge_{0.10}As_{0.20}Te_{0.70}$	2.70	28
	$Al_{0.23}Te_{0.77}$	2.71	8

[a] Estimation by means of Schomacker and Stevenson's formula [25].

TABLE 6. Averaged bond angles

Type	$\langle\alpha\rangle$ (degrees)	Material	Ref.
Cu	109.4	$Cu_{0.03}Ge_{0.20}Te_{0.77}$	this work
	107.8	$Cu_{0.20}As_{0.30}Se_{0.50}$	21
	106.6	$Cu_{0.05}As_{0.50}Te_{0.45}$	17
Ge	107.8	$Cu_{0.03}Ge_{0.20}Te_{0.77}$	this work
	107.5	$Ge_{0.05}As_{0.20}Te_{0.75}$	28
	108.0	$Ge_{0.20}As_{0.40}Se_{0.40}$	11
Te	108.0	$Cu_{0.03}Ge_{0.20}Te_{0.77}$	this work
	107.0	$As_{0.45}Se_{0.10}Te_{0.45}$	29
	106.8	$As_{0.20}Se_{0.50}Te_{0.30}$	30

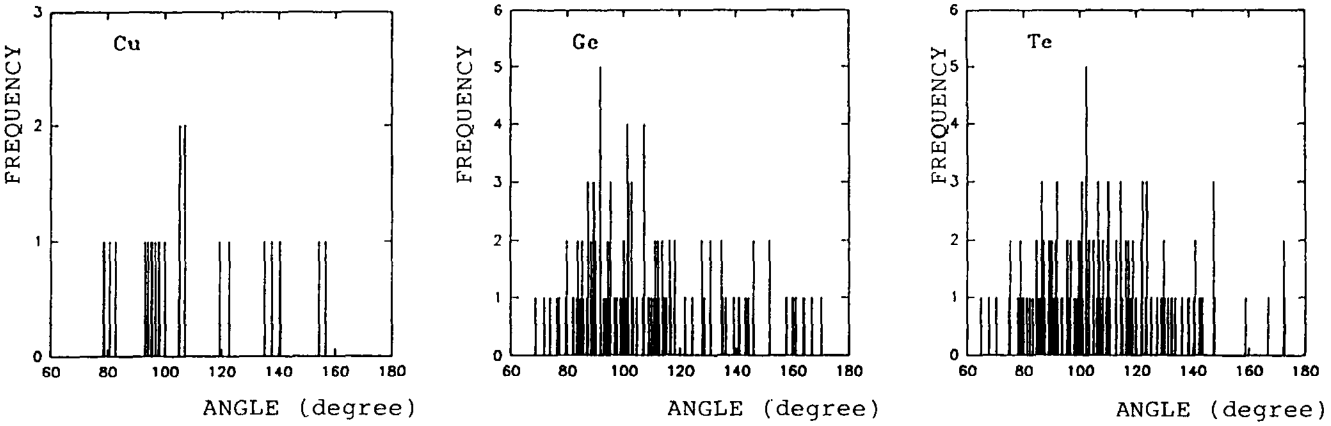

Fig. 6. Bond-angle histograms for the different elements of the alloy.

unfavourable case, the difference between the bond angles in the model and the values quoted in the literature is less than 2.5%.

5. Conclusions

According to the radial atomic distribution function of the alloy in question, obtained from the X-ray diffraction data, and from the copper coordination hypotheses quoted in the literature, the tetracoordinated-copper hypothesis was found to most correctly explain the average number of first neighbours determined experimentally for this composition.

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 tetracoordinated copper which, while keeping the coordination numbers n_{22} and n_{23} positive, give a theoretical area within the margin of error of the experimental area.

Considering the tetracoordinated-copper hypothesis, a spatial atomic distribution model of the alloy was built, using the Monte Carlo (random) method and taking into account 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 tetrahedrons centred on copper atoms, coexisting with other tetrahedrons 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.

Acknowledgement

The authors are grateful to the Junta de Andalucía for their financial support.

References

1 W. H. Zachariasen, *J. Am. Chem. Soc., 54* (1932) 3841.
2 N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials,* Clarendon, Oxford, 1979.
3 S. R. Elliott, *Physics of Amorphous Materials,* Longman, Harlow, UK, 1984.
4 J. Cornet and J. Schneider, in G. H. Frischat (ed.), *The Physics of Non-Crystalline Solids,* Trans Tech Publications, Aedermannsdorf, Switzerland, 1977.
5 B. E. Warren, *X-ray Diffraction,* Addison-Wesley, Reading, MA, 1969.
6 J. Vázquez, L. Esquivias, P. Villares and R. Jiménez-Garay, *Ann. Fis. B, 81* (1985) 223.
7 A. D'Anjou and F. Sanz, *J. Non-Cryst. Solids, 28* (1978) 319.
8 N. J. Shevchick, *Ph.D. Thesis,* Harvard University, 1972.
9 R. B. Heslop and K. Jones, *Inorganic Chemistry,* Elsevier, Amsterdam, 1976.
10 L. Pauling, *Uniones Químicas,* Kapelusz, Buenos Aires, 1969.
11 N. de la Rosa-Fox, L. Esquivias, P. Villares and R. Jiménez-Garay, *Phys. Rev. B, 33* (1986) 4094.
12 J. Vázquez and F. Sanz, *Ann. Fis. B, 80* (1984) 31.
13 J. Vázquez, P. Villares and R. Jiménez-Garay, *Mater. Lett., 4* (1986) 485.
14 M. Domínguez, J. Vázquez, P. Villares and R. Jiménez-Garay, *J. Phys. Chem. Solids, 52* (1991) 567.
15 J. Vázquez, M. Casas-Ruiz, R. A. Ligero and R. Jiménez-Garay, *Mater. Chem. Phys., 32* (1992) 63.
16 E. Gutiérrez Rios, *Química Inorgánica,* Reverte, Barcelona, 1978.
17 J. Vázquez, E. Márquez, N. de la Rosa-Fox, P. Villares and R. Jiménez-Garay, *J. Mater. Sci., 23* (1988) 1709.
18 M. Casas-Ruiz, J. Vázquez, R. A. Ligero and R. Jiménez-Garay, *J. Mater. Sci.,* in press.
19 R. A. Ligero, J. Vázquez, P. Villares and R. Jiménez-Garay, *J. Mater. Sci., 22* (1987) 4357.
20 M. D. Rechtin, A. L. Renninger and B. L. Averbach, *J. Non-Cryst. Solids, 15* (1974) 74.

21 J. Vázquez, P. Villares, E. Márquez and R. Jiménez-Garay, *Mater. Chem. Phys.*, *25* (1990) 399.

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

23 G. Mason, *Nature (London)*, *217* (1968) 733.

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

25 F. D. Bloss, *Crystallography and Crystal Chemistry*, Holt, Rinehart and Winston, New York, 1977.

26 R. W. Haisty and H. Krebs, *J. Non-Cryst. Solids*, *1* (1969) 399.

27 A. G. Kolaichuk and A. G. Kogut, *Sov. Phys.-Crystallogr.*, *15* (1970) 294.

28 R. A. Ligero, J. Vázquez, P. Villares and R. Jiménez-Garay, *Mater. Lett.*, *5* (1987) 301.

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

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