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GERMANIUM COORDINATION HYPOTHESES AND SPATIAL ATOMIC DISTRIBUTION IN THE GLASSY ALLOY $Ge_{0.20}Bi_{0.06}Se_{0.74}$

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ABSTRACT

A radial atomic distribution study of the amorphous alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$ was performed from the X-ray diffraction data of the samples obtained by quenching the molten material. Short-range order information was obtained by interpreting the Radial Distribution Function data, using a theoretical expression which takes into account the variation of the atomic scattering factors with s (the scattering vector module) and approximates them to polynomic functions. The tri- and tetra-coordinated germanium hypotheses, suggested in the literature for glassy alloys containing this element, were found to be compatible with the experimentally obtained structural information. Spatial atomic distribution models were generated, considering the coordination hypotheses suggested for the germanium, using the adequately modified Metropolis-Monte Carlo method. A comparative analysis of the structural parameters of these models showed good agreement with the values given in the literature for similar alloys.

INTRODUCTION

The study of the structure, properties and behaviour of non-crystalline solids is relatively new, although man has been using them since ancient times and, in some cases, in large quantities. Solid state and crystallinity were traditionally treated as synonyms in texts on condensed matter, but since the sixties, one of the most active research fields in solid state physics has been the study of non-crystalline materials, in which the atomic distribution has no trace of long-range order. These solids do,

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however, have short-range order in their bonds with first neighbours, up to a few atomic diameters, showing a characteristic spectrum in the diffraction diagram. An understanding of the spatial atomic distribution and the establishment of the short-range order structure of a material are of great interest when trying to explain its macroscopic properties.

An important aspect to consider in amorphous solids is their metastable energetic state, unlike crystalline solids, which are in a stable thermodynamic balance. Amorphous solids can be said to exhibit relative energy minima, whereas crystalline solids show absolute minima. The change from the amorphous to the crystalline phase means a release of energy, but in order for this to happen an energy barrier (activation energy) must be overcome; when this is high enough, compared to the thermal agitation energy, the non-crystalline solid is stable and can maintain its properties at room temperature for thousands of years [1]. In the case of chalcogenides with polivalent elements, stability is due precisely to the presence of this type of element, which modifies the properties because of the formation of tri-dimensional structural units. The polivalent atoms which stabilize the structures of the chalcogenides are mainly arsenic and germanium, as they form spatial units with chalcogens, breaking their complex structural formation and contributing to the establishment of more homogeneous structures for the alloys belonging to this kind of system, a fact which can explain some of their properties.

This work analyzes the short-range order of the glassy alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$, from Radial Distribution Function (RDF) data determined from X-ray diffraction intensities. The experimental value of the area under the first RDF peak was compared to the one obtained theoretically [2,3] as a coordination function of the germanium, and bearing in mind that the products of the atomic scattering factors, $R_{ij}(s)=f_i(s)f_j(s)/(\sum_i x_i f_i(s))^2$, depend on the Bragg angle, θ, through s (scattering vector module) and cannot always be approximated by the constant value $Z_i Z_j/(\sum_i x_i Z_i)^2$. The aforementioned comparison shows that, for this alloy, the tetra- and tri-coordinated germanium hypotheses quoted in the literature [4-6] can be considered as valid. Based on these germanium coordination hypotheses, spatial atomic distribution models were generated, using a semi-random method which takes into account the geometrical restrictions imposed by the experimental RDF. An analysis of the parameters (bond lengths and angles) of these models shows good agreement with the values quoted in the literature for similar alloys.

EXPERIMENTAL PROCEDURE AND TREATMENT OF THE X-RAY INTENSITIES

Eight 1g bulk samples of the glassy alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$ were prepared from its 99.999%-pure components. The adequately sifted elements were introduced into quartz ampoules, which were successively filled with inert gas (He) 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 oxy-acetylene burner, maintaining an interior residual pressure of 10^{-3} torr, and kept in a rotary furnace at 975°C for 24 hours, after which they were quenched in water at room temperature. The pulverized samples of the alloy were radiated in an automatic SIEMENS D500 diffractometer, using MoKα (λ=0.71069 Å), confirming their glassy nature. The intensity of the radiation diffracted by the samples was measured at fixed counts (4,000) 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 value of the Bragg angle. Three types of slits 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.

Table I. Characteristics of the diffractometric system of measurement.

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

The intensities obtained in arbitrary units (a.u.)were corrected to background, polarization and multiple scattering, normalized to electronic units (e.u.) [2,7] and corrected for the incoherent component. The process of fitting the experimental intensities to the independent scattering function of the compound, using the expression [2]

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

resulted in the following adjustment constants: $K_1=13.17$, $K_2=5.5\cdot10^{-4}$. 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 were obtained:

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

giving way to the interference function, $F(s) = s\cdot i(s)$, in the interval (0-14,48)Å^{-1}, through whose Fourier transformation the radial atomic distribution function was obtained:

$$4\pi r^2\rho(r) = 4\pi r^2\rho_o + rG(r) \qquad (3)$$

where $\rho(r)$ represents the local atomic density affected by the Fourier transformation of the products of atomic factors, and ρ_o 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 4.77 gcm^{-3}, with a relative error under 3%.

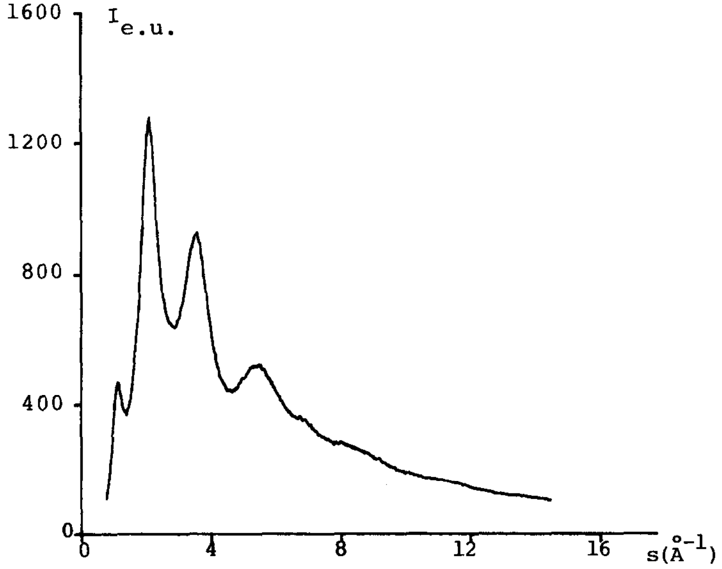


Fig. 1. Intensities in electron units.

Due to the limitations imposed by the experimental data on the interval of s *versus* the one 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 in [8] was carried out, based on the one proposed by Shevchick [9], consisting of adjusting the experimental data of the interference function to the theoretical function

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

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 $(7.94\text{-}10.83)\text{Å}^{-1}$ interval. The initial values of the parameters were: C=2.57 atoms and r=2.45 Å. A Fourier transformation was applied to this function, giving way to the extended RDF of the alloy, shown in Fig. 2, which supplied the structural information shown in Table II.

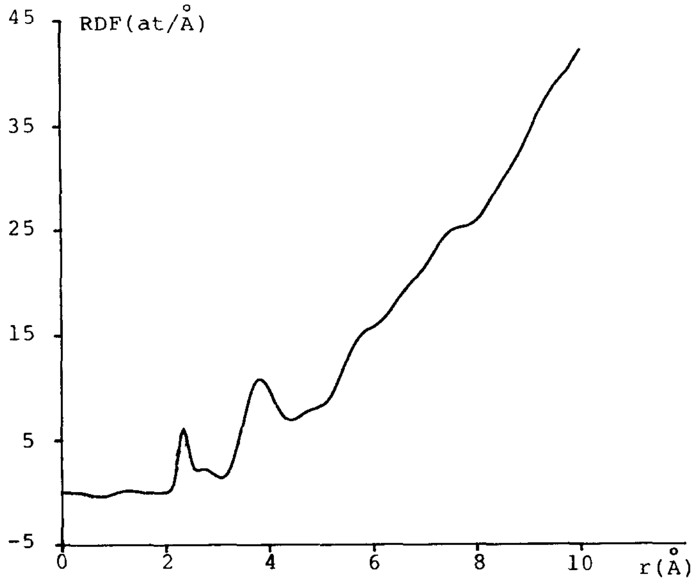


Fig. 2. Radial Distribution Function.

Table II. RDF characteristics.

Maximun	1	2
Position (Å)	2.35	3.85
Limits (Å)	2.00-3.05	3.15-4.40
Averaged angle (deg)	109.9	
Area (atoms)	2.62	6.94
Error	±0.1	±0.2

RDF ANALISIS AND GERMANIUM COORDINATION HYPOTHESES

An analysis of the structural data supplied by the radial atomic distribution function of the alloy under study shows, among other things, that the definition interval of the first peak, corresponding to the first coordination sphere of the alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$ (Ge=1, Bi=2, Se=3), is such that all types of bond are possible among the different elements of the alloy, as can be deduced by comparing the mentioned interval to the bond lengths, r_{ij}, of all possible pairs quoted in the literature, as shown in Table III.

Table III. Bond lengths.

Pair	r_{ij}(Å)	Ref.
Ge-Ge	2.52	[10]
Ge-Bi	2.68	[11]
Ge-Se	2.37	[12]
Bi-Bi	2.92	[11]
Bi-Se	2.62	[11]
Se-Se	2.34	[11]

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; that is, the average coordination number of the material. This area is related to certain structural parameters, the relative average coordination numbers, n_{ij}, which represent the average number of j-type atoms surrounding an arbitrary i-type atom. This area is usually expressed according to the relation

$$\text{Area} = \frac{1}{(\sum_{i} x_i Z_i)^2} \sum_{ij}\sum x_i n_{ij} Z_i Z_j \qquad (5)$$

where Z_i and Z_j are the atomic numbers of elements i and j respectively; however, when products $R_{ij}(s)$ vary with the scattering angle, Vázquez and Sanz [13]; following the method described by Warren [7], have deduced, more strictly, that the area under the first RDF peak is related to the relative coordination numbers through the expression

$$\text{Area} = \frac{2}{\pi} \sum_{ij}\sum x_i \frac{n_{ij}}{r_{ij}} \int_a^b r P_{ij}(r)\,dr \qquad (6)$$

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

$$P_{ij}(r) = \frac{1}{2}\int_0^{s_m} R_{ij}(s)\cos s(r - r_{ij})ds \qquad (7)$$

s_m being the upper measurement limit.

When approximating functions $R_{ij}(s)$ by the straight regression lines, $F'_{ij}(s)=A_{0ij}s + A_{1ij}$, of the corresponding pairs of elements which make up the alloy, relation (6) can be written as

$$\text{Area} = \frac{2}{\pi}\sum_{ij}\sum x_i n_{ij} A_{ij} \qquad (8)$$

an expression in which

$$A_{ij}=\frac{1}{2r_{ij}}\int_a^b r\left[\int_0^{s_m} F'_{ij}(s)\cos s(r-r_{ij})ds\right]dr=$$

$$=\frac{1}{2r_{ij}}[B_{1ij}+B_{2ij}+r_{ij}(B_{3ij}+B_{4ij})] \qquad (9)$$

and where B_{kij} (k=1,2,3,4) are given by the relations

$$B_{1ij}=(A_{0ij}s_m+A_{1ij})\frac{\cos s_m a'_{ij}-\cos s_m b'_{ij}}{s_m}; \qquad B_{2ij}=A_{0ij}\ln\frac{|a'_{ij}|}{b_{ij}}$$

$$B_{3ij}=\int_{a'_{ij}}^{b'_{ij}}\frac{\sin s_m x}{x}dx; \quad B_{4ij}=A_{0ij}\left[\frac{1-\cos s_m b'_{ij}}{b'_{ij}} - \frac{1-\cos s_m a'_{ij}}{a'_{ij}}\right]$$

with $a'_{ij} = a - r_{ij}$, $b'_{ij}= b - r_{ij}$ and $x = r - r_{ij}$.

The structural information obtained from the analysis of the experimental radial distribution function, together with the known physical-chemical properties of the alloys and their constituent elements, give way to hypotheses on the local order of amorphous materials. These hypotheses, reflected in the n_{ij}s and, therefore, in the number of chemical bonds between the different pairs of elements in an alloy, have made it possible for Vázquez et al. [3] to deduce the following relation from equation (8), according to the literature [2]:

$$\text{Area}=\frac{1}{50\pi}[(h+\beta A_{22}-\delta\sum_{i,j\neq 1} A_{ij})N+\alpha A_{22}+\gamma\sum_{i,j\neq 1} A_{ij}+P(\sum_{i=j\neq 1} A_{ij}-\sum_{\substack{i,j\neq 1\\ i\neq j}} A_{ij})a_{ij}] \qquad (10)$$

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 material, a_{ij} is the number of bonds between types i and j, and P is a parameter worth 2 when, in variable a_{ij}, i=j, and -1 if i≠j.

In this work, functions $R_{ij}(s)$ were approximated by the straight regression lines of the corresponding pairs of elements, whose coefficients, A_{0ij}, A_{1ij}, appear in Table IV. From these coefficients, and using expression (9), parameters A_{ij} were evaluated, and are also shown in Table IV.

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

Pair	A_{0ij}	A_{1ij}	A_{ij}
Ge-Ge	-5.04×10^{-3}	0.7558	1.1255
Ge-Bi	23.12×10^{-3}	2.0373	3.3849
Ge-Se	-4.54×10^{-3}	0.8055	1.3022
Bi-Bi	192.57×10^{-3}	5.4394	8.8966
Bi-Se	27.58×10^{-3}	2.1704	3.3136
Se-Se	-3.93×10^{-3}	0.8585	1.4356

Bearing in mind the models based on the germanium coordination scheme proposed by Hilton et al, [4], and following the hypotheses postulated by Betts et al, [5], the possibility of proposing structural units for the configuration of the short-range order of the sample under study with tetra-, tri-, and di-coordinated germanium is analyzed. In order to do this, it is necessary to determine the theoretical area as a function of the coordination, N, attributed to the germanium atoms in this alloy. The characteristic parameter h=74.0826 was calculated, as well as those depending on the coordination hypotheses [3]:

$\alpha = -130$ $\beta = 0$ $\gamma = 148$ $\delta = 0$ for N=4
$\alpha = -198$ $\beta = 17$ $\gamma = 222$ $\delta = 18{,}5$ for N=3 and N=2

From these data and the tabulated A_{ij}'s, and using relation (10), the following expressions were obtained:

$$\begin{aligned} \text{Area} &= 0.7678 + 0.0472a_{33} && \text{for } N=4 \\ \text{Area} &= 0.1138 + 0.0472a_{33} && \text{for } N=3 \qquad (11) \\ \text{Area} &= -0.5401 + 0.0472a_{33} && \text{for } N=2 \end{aligned}$$

which are used to postulate the short-range order of the alloy. These relations may be observed to be functions of the number of Se-Se bonds, a_{33}, making it possible to limit the variability field of the theoretical area. The comparison of these theoretical areas to the experimental area allows us to define variation intervals of a_{33} for each germanium coordination hypothesis in the alloy in question.

On the other hand, as the theoretical areas are functions of the relative coordination numbers, which depend on the coordination number, N, of a certain element in the alloy [2], <u>i.e.</u>, the germanium, it is necessary to determine the variability field of a_{33} due to the restriction imposed by the intrinsically positive nature of the n_{ij}s.

When proposing local order models of glassy alloys, the intersection of both intervals supplies the possible variability field of parameter a_{33}, which can be used to discern which coordination hypothesis is the most probable.

In the amorphous alloy $Ge_{0.20}\ Bi_{0.06}\ Se_{0.74}$, in which the area is expressed as a function of a_{33}, the average coordination numbers, n_{ij}, which include a_{33}, can be written, according to the literature [2]:

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

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

where a'_i is the percentage of element i in the compound.

Expressions (11) of the theoretical area, together with the corresponding experimental area with the margin of error of ±0.1 atoms, shown in Table II, determine the variation intervals of a_{33} (a magnitude which is always positive) for each germanium coordination hypothesis, shown in Table V. On the other hand eqns. (12) give the expressions of n_{22} and n_{23}, which establish the new limits for magnitude a_{33}, shown in Table V together with their intersections with the intervals defined by the experimental area. To illustrate the theoretical calculations carried out, Fig. 3 shows the theoretical area under the first RDF peak, <u>versus</u> the number of Se-Se bonds, a_{33}, according to the tetra-, tri- and di-coordinated germanium hypotheses.

An analysis of the intersection of intervals shows that, although the three coordinations proposed for germanium are theoretically possible, the lower the coordination, the less probable it is. The variation interval of the number of Se-Se bonds, in which the model can evolve, decreases; coordinations 3 and 2 for the germanium are therefore improbable, especially the latter, a fact which agrees with the conclusions reached by Ligero <u>et al</u>. [6].

Table V. Theoretical results obtained for the coordination hypotheses of the germanium atom.

		Variation intervals for parameter a_{33}		
N	Coordination numbers n_{ij}, $i,j \neq 1$	Defined by the n_{ij} parameters	Defined by limits of error of the experimental area	Intersection of intervals
4	$n_{22}=-12.6 + 1/3a_{33}$ $n_{23}= 14.8 - 1/3a_{33}$	37.8 - 44.4	37.12 - 41.36	37.8 - 41.36
3	$n_{22}=-17.7 + 1/3a_{33}$ $n_{23}= 20.35 - 1/3a_{33}$	53.1 - 61.05	50.98 - 55.22	53.1 - 55.22
2	$n_{22}=-22.8 + 1/3a_{33}$ $n_{23}= 25.9 - 1/3a_{33}$	68.4 - 77.7	64.83 - 69.07	68.4 - 69.07

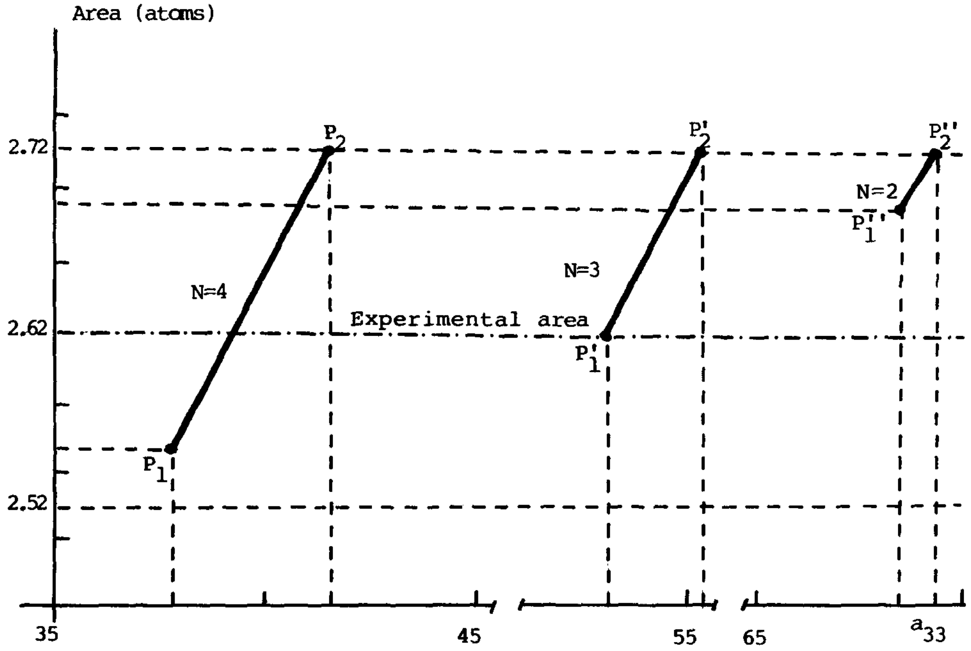


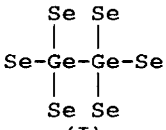
Fig. 3. Areas of first peak plotted against number of Se-Se bonds.

Bearing in mind the values of the n_{ij}s corresponding to the extremes of the a_{33} intervals, it may be postulated that the short-range order of the alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$ evolves between the extreme situations indicated; therefore, the models which verify the average coordination numbers of the extreme values may be considered as the most probable structural models.

On the other hand, considering that the structural units proposed must be compatible with the average coordination numbers calculated according to the established hypotheses, and taking n types of different units, the number of bonds of element 1, a_{1i}, with all the elements in the alloy, can be written, according to the literature [2], thus:

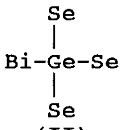
$$\sum_{\substack{R=1 \\ i\neq 1}}^{n} x_R a_{1iR} = a_{1i} \qquad (13)$$

where x_R is the number of R-type units in 100 atoms of material, and a_{1iR} is the number of bonds between types 1, i in structural element R, making it possible to propose different structural units, as long as their different bonds verify the above relation. If structural elements of types (I), (II), (III)



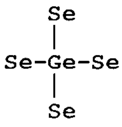
$$\begin{array}{ccccccc} & & \mathrm{Se} & & \mathrm{Se} & & \\ & & | & & | & & \\ \mathrm{Se} & - & \mathrm{Ge} & - & \mathrm{Ge} & - & \mathrm{Se} \\ & & | & & | & & \\ & & \mathrm{Se} & & \mathrm{Se} & & \end{array}$$

(I)



$$\begin{array}{ccccc} & & \mathrm{Se} & & \\ & & | & & \\ \mathrm{Bi} & - & \mathrm{Ge} & - & \mathrm{Se} \\ & & | & & \\ & & \mathrm{Se} & & \end{array}$$

(II)



$$\begin{array}{ccccc} & & \mathrm{Se} & & \\ & & | & & \\ \mathrm{Se} & - & \mathrm{Ge} & - & \mathrm{Se} \\ & & | & & \\ & & \mathrm{Se} & & \end{array}$$

(III)

are proposed, which of course agree with the tetrahedral coordination for Ge and with the hypothesis stating that the Ge bonds with every element in the sample, we must deduce that only eight type-(I) units and four type-(II) units are compatible with the stated considerations.

DESCRIPTION AND ANALYSIS OF THE GENERATED MODELS

The basic aim of 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. These models were generated using a variation of the Monte Carlo method, similar to the procedure followed by Rechtin *et al*. [14], which seems to be the most adequate for describing the short-range order of a glassy material obtained through quenching. The variations of this procedure refer to the geometrical and coordination conditions imposed by the experimental RDF, which imply a certain semi-randomness in the building of the atomic configuration.

The mathematical space considered suitable for generating the possible structural models of the alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$ is the volume limited by a 10 Å radius spherical surface, which is large enough to statistically represent the sample, and small enough not to require too much calculation time. The number of atoms which, according to the experimental density, can be located in this volume is 141, distributed as follows: 28 Ge atoms, 9 Bi atoms and 104 Se atoms.

The atomic positions were generated by finding their cartesian coordinates from three random numbers [15] and bearing in mind all the geometrical and coordination conditions deduced from the analysis of the experimental RDF, and which in this case are the following:

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

(ii) The bond angle between an atom and two of its first neighbours may vary between 62° and 180°, as may be deduced [10] from the extreme radii of the first two coordination spheres represented by the limits of the first two RDF peaks.

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

Bearing in mind the tetra- and tri-coordinated germanium hypotheses, theoretically confirmed as being the most probable, two theoretical models were generated, imposing the condition of tetra-coordinated germanium, Ge(4), and tri-coordinated germanium, Ge(3), respectively.

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

Considering the aforementioned geometrical and coordination conditions, 200 positions were generated in each model, and reduced to 141, the number predicted from the experimental density, by eliminating those with the lowest coordination. The next step was to assign the atoms to their positions in each model, placing the Ge atoms in the positions with maximum coordination (4 in the first model and 3 in the second), the other elements being randomly placed in the rest. The reduced RDF, rG(r), was determined for each configuration, and compared to the experimental RDF, modified by the finite size simulation function [16]. The mean square deviation between the theoretical and experimental functions was 1.3951 Å in the case of Ge(4) and 0.9322 Å in the case of Ge(3).

The initial models were considered to be suitable for obtaining a relatively speedy adjustment of the theoretical and experimental reduced RDFs; so the positions were refined by successive atom movements, of arbitrary amplitude P and in random directions, adding the restriction of not allowing movements which break Ge atom bonds, thus keeping the coordination postulated for this element in each case.

During the position refining process, both models evolved as shown in Table VI, where the 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 became too high and the mean square deviation did not significantly improve. The last step in the generation of structural models of the alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$ was the thermal factor refining process, for which five coordination spheres were defined according to the experimental rG(r), and the initial value of the isotropic factor was taken as $\sigma_0=0.1$ Å. The set of values, σ_i, which best fitted the model RDF to the experimental RDF was calculated by an iterative least square method, in successive cycles, until σ_i varied less than 10^{-3} Å.

Table VI. Position refining process for Ge(4) and Ge(3) models.

Model	P(Å)	Movement intervals	Squared deviation (Å)
Ge(4)	0.5	1-650	0.0432
	0.3	651-720	0.0283
	0.1	721-792	0.0195
Ge(3)	0.5	1-231	0.0469
	0.3	232-342	0.0295
	0.1	343-357	0.0219

Once the thermal factor refining process was finished, the mean square deviation between the theoretical and experimental values of rG(r) was reduced to 0.0184 Å for the tetrahedral germanium model, and 0.0211 Å for the tri-coordinated germanium model. The reduced RDF of each model after the refining process is shown in Figs. 4a and b, together with the experimental RDF.

The spatial representations of both configurations appear in Figs. 5 and 6, showing tetrahedrons centered on germanium atoms, in the case of the tetra-coordinated germanium, and triangular pyramids with a vertex occupied by this element, in the case of the tri-coordinated germanium. Both the tetrahedrons and the triangular pyramids are joined together forming networks of the constituent structural elements of each model.

These theoretical models, generated by random methods and considering 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 these models and the atomic distribution of the alloy consists of analyzing the main structural parameters (coordinations and average bond lengths).

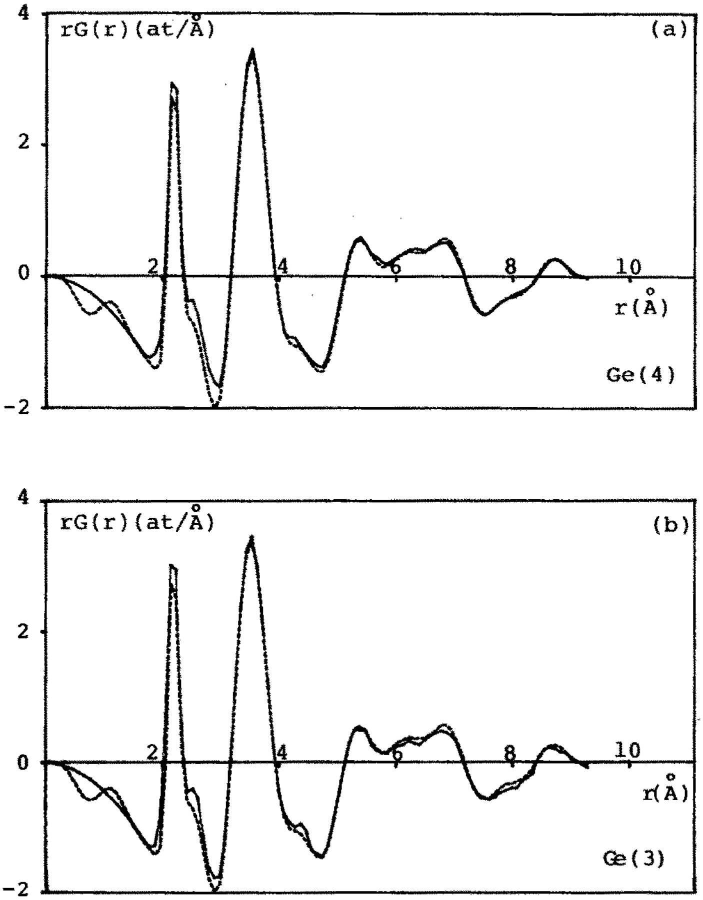


Fig. 4. Representations of(———) calculated and (·······) experimental RDFs.

An important point to consider, when statistically analyzing the generated models, is the comparison between the resulting coordinations of their elements and those of the structural units, which, according to the established hypotheses, may be postulated from the information supplied by the experimental RDF. Table VII shows the coordinations of each element in the alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$ in each of the generated models, and, in brackets, the coordinations which were theoretically predicted from the corresponding hypotheses. Coordination defects are observed in each model, indicating the presence of atoms with dangling bonds which may be justified, in part, by the finite nature of the models. In model Ge(4), 60% of the mono-coordinated Se (Se(1)) atoms are less than 2 Å away from the surface of the sphere, and may be saturated with atoms situated outside it. Similarly, in the Ge(3)-based structural configuration, 76% of the Se(1) atoms are also less than 2 Å away from the surface of the model.

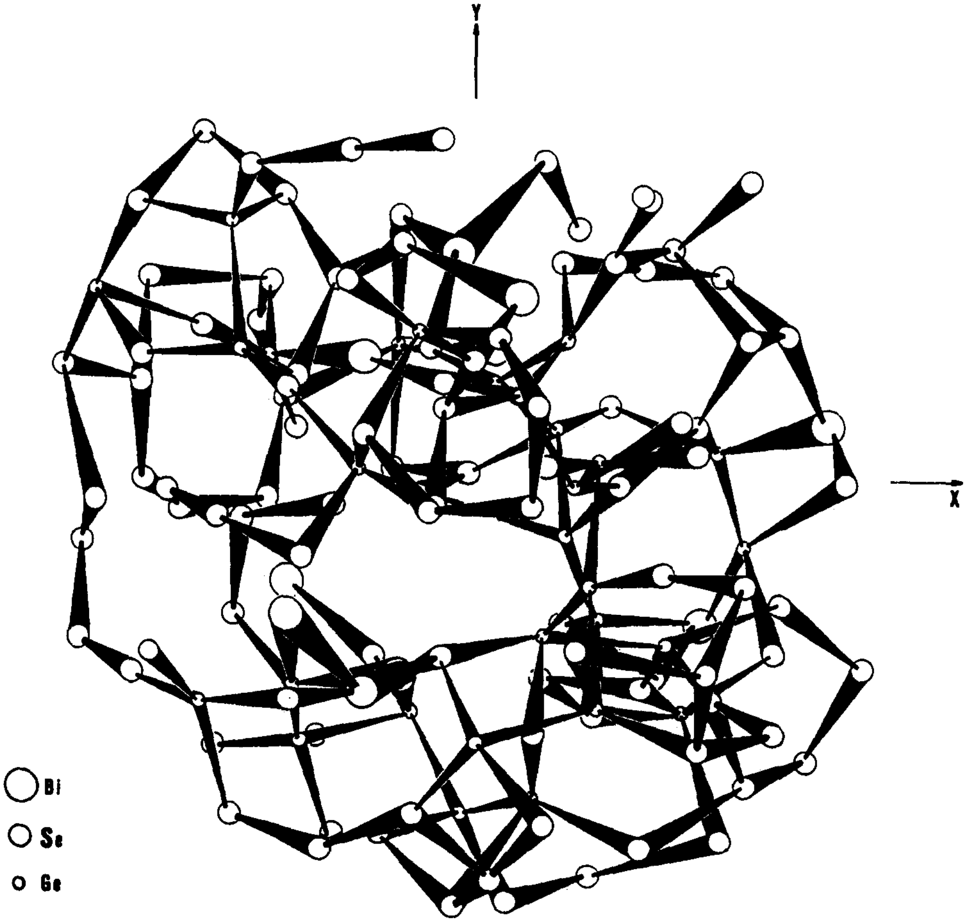


Fig. 5. Spatial representation of the model of alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$ by hypothesis of four-fold coordinated germanium.

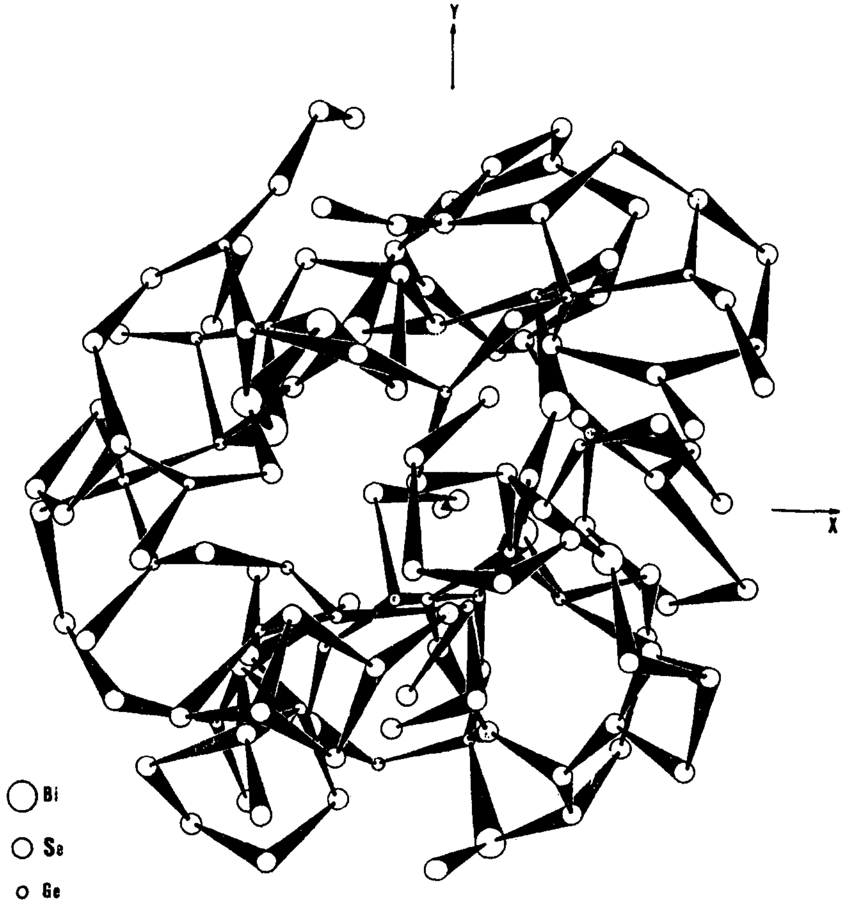


Fig. 6. Spatial representation of the model of alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$ by hypothesis or three-fold coordinated germanium.

Table VII. Model coordinations.

Model	Atom type	Coordination				
		4	3	2	1	0
Ge(4)	Ge	28(28)	0(0)	0(0)	0(0)	0(0)
	Bi	2(0)	3(9)	3(0)	1(0)	0(0)
	Se	0(0)	29(0)	59(104)	15(0)	1(0)
Ge(3)	Ge	0(0)	28(28)	0(0)	0(0)	0(0)
	Bi	0(0)	7(9)	2(0)	0(0)	0(0)
	Se	0(0)	38(0)	49(104)	15(0)	2(0)

Another important aspect of the generated models is the comparison of the average bond lengths of the different pairs of elements in the alloy to those found in similar alloys. This gives more accurate information on the validity of the models. Table VIII shows the average bond lengths of all possible pairs in each model. These lengths are similar in both configurations, the difference being less than 1.5% in the most unfavourable case.

Table VIII. Averaged bonding distances.

Bond	<d>(Å)	
	Ge(4)	Ge(3)
Ge-Ge	2.52	2.50
Ge-Bi	2.63	2.62
Ge-Se	2.48	2.45
Bi-Bi	2.65	2.64
Bi-Se	2.59	2.58
Se-Se	2.46	2.43

The great resemblance between the bond lengths in both generated models, together with the good adjustment of the theoretical and experimental rG(r)'s in the Ge(4)- and Ge(3)-based spatial atomic configurations, allow us to assume that the true structure of the material is made up of a network of structural units centered on Ge(4) and Ge(3) atoms, coexisting simultaneously in the same model; a theoretical atomic configuration based on this hypothesis was therefore built.

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

This model was generated using the same process described above, the only difference being that the breaking of germanium atom bonds was allowed, so that some of them would have tetrahedral coordination and others would be tri-coordinated.

The initial configuration and its reduced RDF were obtained; this was then compared to the experimental RDF, and, as in the case of Ge(4), the mean square deviation was found to be 1.3951 Å. During the position refining process, 629 movements, 0.5 Å in amplitude, were carried out, until a deviation, ε , of 0.0354 Å was achieved; the amplitude was then reduced to P=0.3 Å up to movement 676, in which ε =0.0229 Å; the amplitude was further reduced to 0.1 Å up to movement 740, where the refining process was considered finished with a mean square deviation of 0.0136 Å.

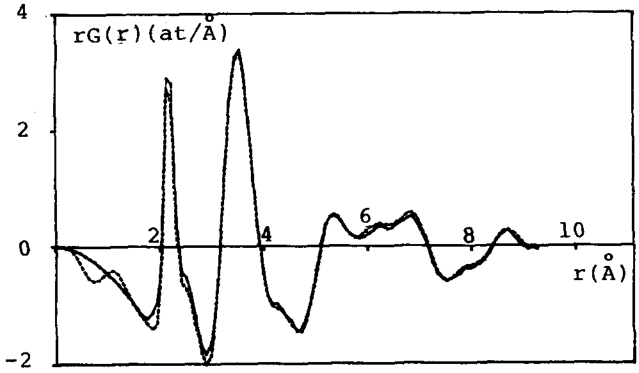


Fig. 7. Representation of (———) calculated and (-------) experimental RDFs for model based on the simultaneous Ge(4) and Ge(3) hypotheses.

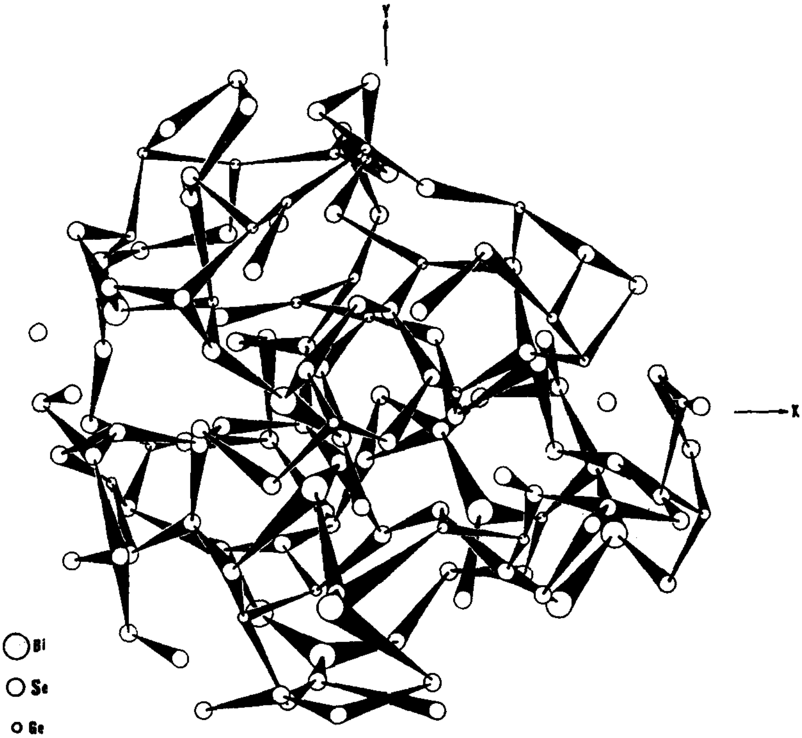


Fig. 8. Spatial representation of model based on the simultaneous Ge(4) and Ge(3) hypotheses.

Figure 7 shows the experimental and model rG(r)s. Figure 8 shows a spatial representation of the resulting atomic configuration, in which appear tetrahedrons centered on germanium atoms, and triangular pyramids with this element in one of their vertices. Both structural units are interlinked, forming a network which may represent the true structure of the alloy.

In this model, as in those generated before, there are dangling bonds. Many of these belong to atoms which are less than a first neighbour's distance away from the surface and can therefore be saturated with hypothetical outside neighbours. In the case of elements with two or more dangling bonds, they are probably due to the finite size of the model, when the atom in question is less than 1.1 Å away from the surface; this possibility simultaneously takes into account both the bond length between first neighbours and the average bond angle. Twenty-five percent of the dangling bonds in the model belong to atoms which are not in a situation which allows them to be saturated with possible external neighbours. However, the existence of dangling bonds is inherent to the method of preparation of chalcogenide glasses.

Table IX. Averaged bonding distances of model based on the simultaneous Ge(4) and Ge(3) hypotheses.

Bond	Material	<d>(Å)	Ref.
Ge-Ge	$Ge_{0.20}Bi_{0.06}Se_{0.74}$	2.53	a
	$Ge_{0.14}As_{0.43}Te_{0.43}$	2.53	[10]
	amorphous Ge	2.54	[17]
Ge-Bi	$Ge_{0.20}Bi_{0.06}Se_{0.74}$	2.63	a
	sum of covalent radii	2.68	[11]
Ge-Se	$Ge_{0.20}Bi_{0.06}Se_{0.74}$	2.48	a
	$Ge_{0.20}As_{0.40}Se_{0.40}$	2.48	[18]
Bi-Bi	$Ge_{0.20}Bi_{0.06}Se_{0.74}$	2.67	a
	sum of covalent radii	2.90	[11]
Bi-Se	$Ge_{0.20}Bi_{0.06}Se_{0.74}$	2.60	a
	sum of covalent radii	2.62	[11]
Se-Se	$Ge_{0.20}Bi_{0.06}Se_{0.74}$	2.45	a
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.45	[19]
	$As_{0.45}Se_{0.10}Te_{0.45}$	2.44	[20]

[a] This paper

One way of estimating the agreement between the generated atomic configuration and the true structure of the alloy under study is by analyzing the structural parameters (bond lengths) obtained from the model, relating their values to those quoted in the literature for similar compounds. Table IX shows the average bond lengths between the different pairs of elements in the model based on the simultaneous Ge(4) and Ge(3) hypotheses. The values calculated for the bond lengths show a very acceptable agreement with the bibliographical data, so this generated model may be considered as representative of the true structure of glassy alloy $Ge_{0.20}Bi_{0.06}Se_{0.74}$.

CONCLUSIONS

According to the radial atomic distribution function of the alloy in question, obtained from X-ray diffraction data, and from the analysis of the different germanium coordination hypotheses quoted in the literature, tetrahedral coordination was found to be the most probable for the germanium, not discarding the possibility of tri-coordinated germanium, as both coordinations correctly explain the average number of experimentally determined first neighbours.

By using the most approximate expression of the area under the first RDF peak, it was possible to find a number of Se-Se bonds for each germanium coordination 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.

The tetra- and tri-coordinated germanium hypotheses were used to build the models. The first two Ge(4) and Ge(3) models gave very similar structural data, leading us to believe that the theoretical model which would best fit the true structure of the compound is that in which tetra- and tri-coordinated germanium atoms co-exist.

The model based on this hypothesis can be described as a tri-dimensional network of covalent bonds, some of which are centered on germanium atoms, forming tetrahedrons, the rest being distributed following the edges of triangular pyramids, at least one of whose vertices is occupied by a germanium atom. These structural units can be joined together either directly or by selenium atoms, given the high concentration of this element in the samples and its great tendency to form chains, thus making the network compact.

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