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Analysis of short-range order and structural model in the glassy semiconductor $Ge_{0.20}Sb_{0.20}Se_{0.60}$ by X-ray diffraction

I. Quiroga, J. Vázquez, P. Villares and R. Jiménez-Garay
Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real, Cádiz, Spain

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An X-ray radial atomic distribution (RDF) study of the amorphous alloy $Ge_{0.20}Sb_{0.20}Se_{0.60}$ was performed. Short-range order information was obtained by interpreting the RDF data using a theoretical expression which takes into account the variation of the atomic scattering factors with s, the scattering vector modulus. The existence of tetra- and tri-coordinated germanium atoms, suggested in the literature for glassy alloys containing this element, was found to be compatible with the experimentally obtained structural information. A spatial distribution model was generated according to these two possible coordinations for germanium, using the conveniently modified Metropolis Monte Carlo method. The model exhibits tetrahedral units on germanium atoms, forming a network with triangular pyramids with a germanium atom at some vertices. A comparative analysis of the parameters of this model showed good agreement with the values given in the literature for similar alloys.

1. Introduction

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 electric 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.

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 polyvalent elements, stability is due precisely to the presence of this type of element, which modifies the properties because of the formation of tri-coordinated structural units. The polyvalent 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 $Ge_{0.20}Sb_{0.20}Se_{0.60}$ 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 [2–4] as a coordination function of the germanium, and bearing in mind that the products of the atomic scattering factors,

$$R_{ij}(s)=f_i(s)f_j(s)\left[\sum_i x_i f_i(s)\right]^{-2},$$

depend on the Bragg angle, θ, through s (scattering vector modulus) and cannot always be approximated by the constant value $Z_iZ_j/(\sum_i X_iZ_i)^2$. The aforementioned comparison shows that, for this alloy, the tetra- and tri-coordinated germanium hypotheses quoted in the literature [5–7] can be considered as valid. Based on these germanium coordination hypotheses, a spatial atomic distribution model was 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 this model shows good agreement with the values quoted in the literature for similar alloys.

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

The samples of the glassy alloy $Ge_{0.20}Sb_{0.20}Se_{0.60}$ were prepared in bulk from 99.99% pure germanium, antimonium and selenium which were pulverized to a grain size of less than 40 µm, and weighed to obtain 8 g of the compound. The material was homogeneously mixed (in order to attain the greatest possible contact surface 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) 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 120 h in a rotary furnace, rotating at 1/3 rpm, and then quenched in ice water, which supplied the necessary cooling rate for obtaining the glass.

The pulverized samples of the alloy were X-rayed by use of an automatic Siemens D500 diffractometer, using Mo Kα ($\lambda=0.71096$ Å), confirming their glassy nature. The intensity of the diffracted radiation 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.

The diffraction intensities I_{au} obtained in arbitrary units were corrected for background, polarization, absorption and multiple scattering [8], normalized to electronic units (eu) [2,8] and corrected for the incoherent component. Once the intensities in electronic units and the corresponding atomic fractions, x_i, of the different elements in the alloy, were known, and with the atomic scattering factors f_i, the reduced intensities, $i(s)$, were obtained from

$$i(s)=\frac{I_{eu}(s)-\sum_i x_i f_i^2(s)}{[\sum_i x_i f_i(s)]^2}\,, \tag{1}$$

which give the interference function $F(s)=si(s)$, from which the $G(r)$ function is obtained by applying a Fourier transformation and from this, the radial atomic distribution function

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

representing the number of neighbours of an arbitrary atom, at a certain distance. $\rho(r)$ is the local atomic density affected by the Fourier transformation of the products of the atomic factors, and ρ_0 is the average experimental density of the material. This density was experimentally measured using a pycnometric method at constant temperature, the average value of the series of measurements being 4.69 g cm^{-3}, with a relative error less than 3%.

The spurious oscillations which appear in the RDF for low values of r, due to the lack of experimental data for high values of s, make it necessary to extend the interference function to those values of s for which said function tends towards zero. The extension was carried out using the method described in the literature [9] based on the one proposed by Shevchik [10], according to which, for high values of s, the experimental interference function may be approximated by

$$F_{\text{theoretical}}(s)=(C/r)\exp(-\sigma^2 s^2/2)\sin sr\,, \tag{3}$$

were 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 transformation was applied to the interference function, extended up to 30 Å^{-1}, thus obtaining the RDF shown in fig. 1, which supplied the following structural information. Position of the first two maximum values: 2.50 Å and 3.85 Å; limits of the first peak: 2.05–3.00 Å, area under the latter: 2.64±0.1 atoms, average bond angle 100.70°.

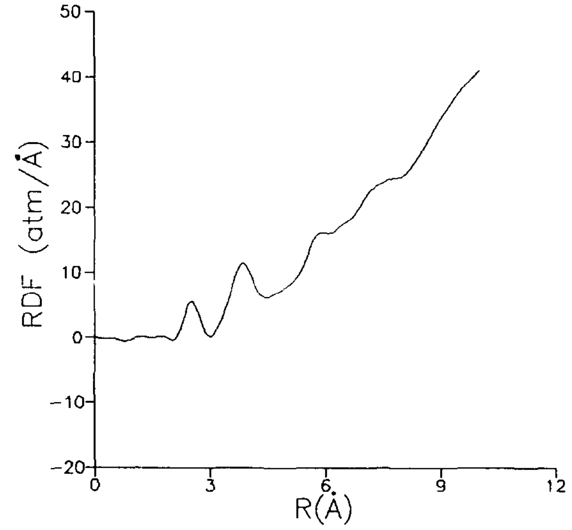

Fig. 1. Radial distribution function.

3. RDF analysis and germanium coordination hypotheses

The definition interval of the first peak of the RDF of the alloy $Ge_{0.20}Sb_{0.20}Se_{0.60}$, (Ge = 1, Sb = 2, Se = 3) which corresponds to the first coordination sphere, is such that all types of bond are possible between the different elements in the material, 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.

Analysis of the experimental RDF shows a fact which is very interesting when carrying out a model of the short-range order of a glassy solid: the area under the first peak represents the number of atoms which, on average, surround any given one taken as a reference, i.e. the average coordination number for the material.

Table 1
Bond lengths and A_{ij} parameters

Pair	r_{ij} (Å)	Ref.	A_{ij}
Ge-Ge	2.52	[11]	1.0632
Ge-Sb	2.62	[12]	1.8735
Ge-Se	2.37	[13]	1.2714
Sb-Sb	2.80	[12]	3.4641
Sb-Se	2.56	[12]	1.8794
Se-Se	2.32	[12]	1.4169

Bearing in mind the physical significance of this area, and that the products $R_{ij}(s)$ are functions of the scattering angle, Vázquez and Sanz [14], following the method described by Warren [8], have concluded that the area under the first RDF peak is related to certain structural parameters, the relative coordination numbers, n_{ij}, by the expression

$$\text{area} = \frac{2}{\pi} \sum_i \sum_j x_i \frac{n_{ij}}{r_{ij}} \int_a^b r P_{ij}(r)\, \mathrm{d}r\,, \tag{4}$$

where r_{ij} is the average distance between a type i and type j atom, a and b the limits of the first RDF peak and $P_{ij}(r)$ a function defined by

$$P_{ij}(r) = \frac{1}{2} \int_0^{s_\mathrm{m}} \frac{f_i(s) f_j(s)}{[\sum_i x_i f_i(s)]^2} \cos[s(r - r_{ij})]\, \mathrm{d}s\,, \tag{5}$$

s_m being the upper measurement limit.

The structural information obtained by analysis of the experimental RDF, together with certain physical-chemical properties of the alloys and their elements, give way to hypotheses on the local order of glassy alloys. The hypotheses, reflected in the relative coordination numbers, n_{ij}, and consequently in the number of chemical bonds between the different pairs of elements in a material, have allowed Vázquez et al. [4] to deduce, from eq. (4), the relationship

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

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

$$A_{ij} = \frac{1}{r_{ij}} \int_a^b r P_{ij}(r)\, \mathrm{d}r \tag{7}$$

and Q is given by

$$Q = \delta_{ij} \sum_{\substack{i,j \neq 1 \\ i \neq j}} A_{ij} + (1 - \delta_{ij}) \sum_{i=j\neq 1} A_{ij}\,,$$

where δ_{ij} is Kronecker's delta.

In this work, in order to evaluate the A_{ij} parameters, the $R_{ij}(s)$ functions have been adjusted to the corresponding regression straight lines, and the values shown in table 1 have been calculated by the method described by Vázquez and Sanz [14].

Bearing in mind the models based on the germanium coordination scheme proposed by Hilton et al. [5], and following the hypotheses postulated by Betts et al. [6], 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 parameters $h=32.3632$ and $Q=3.7587$ were calculated, as well as those depending on the coordination hypotheses [4]:

$$\alpha=-60,\quad \beta=0,$$
$$\gamma=120,\quad \delta=0,\quad \text{for } N=4\,;$$
$$\alpha=-100,\quad \beta=10,$$
$$\gamma=180,\quad \delta=15,\quad \text{for } N=3 \text{ and } N=2\,.$$

From these data and the tabulated A_{ij}, and using relation (6), the following expressions were obtained:

$$\text{area}=2.3724+0.0143a_{33},\quad \text{for } N=4\,;$$
$$\text{area}=2.3048+0.0143a_{33},\quad \text{for } N=3\,;$$
$$\text{area}=2.2371+0.0143a_{33},\quad \text{for } N=2\,, \qquad (8)$$

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 [4], i.e. 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}.

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

In amorphous $Ge_{0.20}Sb_{0.20}Se_{0.60}$, 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 [4], as

$$n_{22}=\frac{\alpha+[100\beta+a'_1(a'_3-a'_2)]N/100+2a_{33}}{a'_2}\,,$$
$$n_{23}=\frac{\gamma-(100\delta+a'_1a'_3)N/100-2a_{33}}{a'_2}\,, \qquad (9)$$

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

Expressions (8) of the theoretical area, together with the corresponding experimental area with margins of error of ±0.1 atoms, determine the variation intervals of a_{33} (a magnitude which is always positive) for each germanium coordination hypothesis, shown in table 2. On the other hand, eqs. (9) give the expressions for n_{22} and n_{23}, which establish new limits for the magnitude of a_{33}, shown in table 2 together with their intersections with the intervals defined by the experimental area.

To illustrate the theoretical calculations carried out, fig. 2 shows the theoretical area under the first RDF peak, versus 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 germanium are therefore improbable, especially the latter, a fact which agrees with the conclusions reached by Ligero et al. [7]. This fact allow us to assume that the true structure of the material is made up of a network of structural units centered on tetra- and tri-coordinated germanium atoms, coexisting simultaneously in the same model; a theoretical atomic configuration based on this hypothesis was therefore built.

Table 2
Theoretical results obtained for the coordination hypotheses of the germanium atom

N	Coordination numbers n_{ij}, $i,j\neq 1$	Variation intervals for parameters a_{33}		
		defined by the n_{ij} parameters	defined by limits of error of the experimental area	intersection of intervals
4	$n_{22}=-1.4+0.1a_{33}$ $n_{23}=3.6-0.1a_{33}$	14–36	11.72–25.71	14–25.71
3	$n_{22}=-2.3+0.1a_{33}$ $n_{23}=4.95-0.1a_{33}$	23–49.5	16.45–30.43	23–30.43
2	$n_{22}=-3.2+0.1a_{33}$ $n_{23}=6.3-0.1a_{33}$	32–63	21.18–35.17	32–35.17

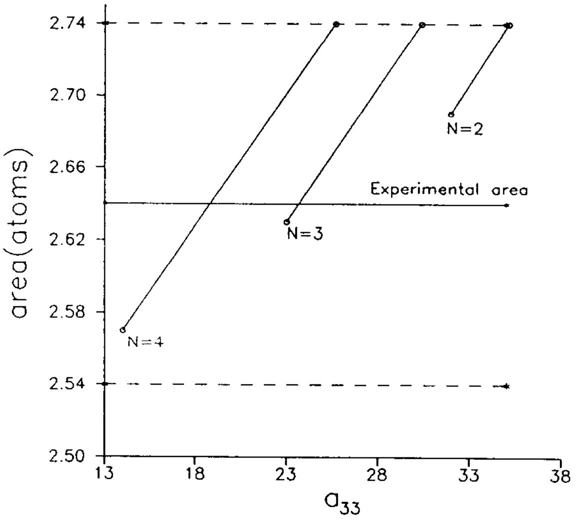

Fig. 2. Area of first peak versus number of Se–Se bonds.

4. Model description and results

The procedure used for the elaboration of the short-range order structure model is similar to that used by Esquivias et al. [15]. This structure is refined with the help of the well-known random technique of Metropolis Monte Carlo. The breaking of germanium atom bonds was allowed, so that some of them would have tetrahedral coordination and others would be tri-coordinated.

At the start of the refining process, we assumed a shift value of $\Delta r=0.3$ Å. Later it was reduced to $\Delta r=0.1$ Å at the same time as the refining was advanced in order to obtain fast convergence.

Initially, a constant temperature factor ($\sigma=0.1$ Å) was considered. After the refining process, it was taken as a constant value for every coordination sphere but differing from one to another. The set of σ_i values which lead to the best fit of the theoretical $rG(r)$ to the experimental value was calculated by the least-squares method. The refining process was considered finished after 539 valid movements and the mean-square deviation was 0.018 Å. Fig. 3 shows the reduced RDF of the model and the experimental RDF after the refining process and fig. 4 shows a spatial representation of the resulting atomic configuration, in which there appear tetrahedrons centered on germanium atoms, and triangular pyramids with this element in one of their vertices. Both structural

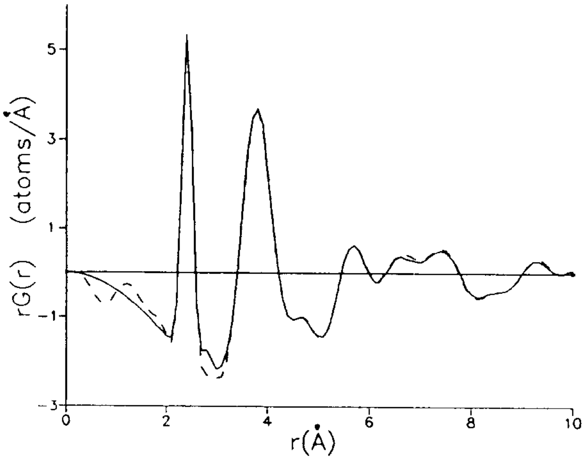

Fig. 3. Representations of calculated (——) and experimental (---) RDFs.

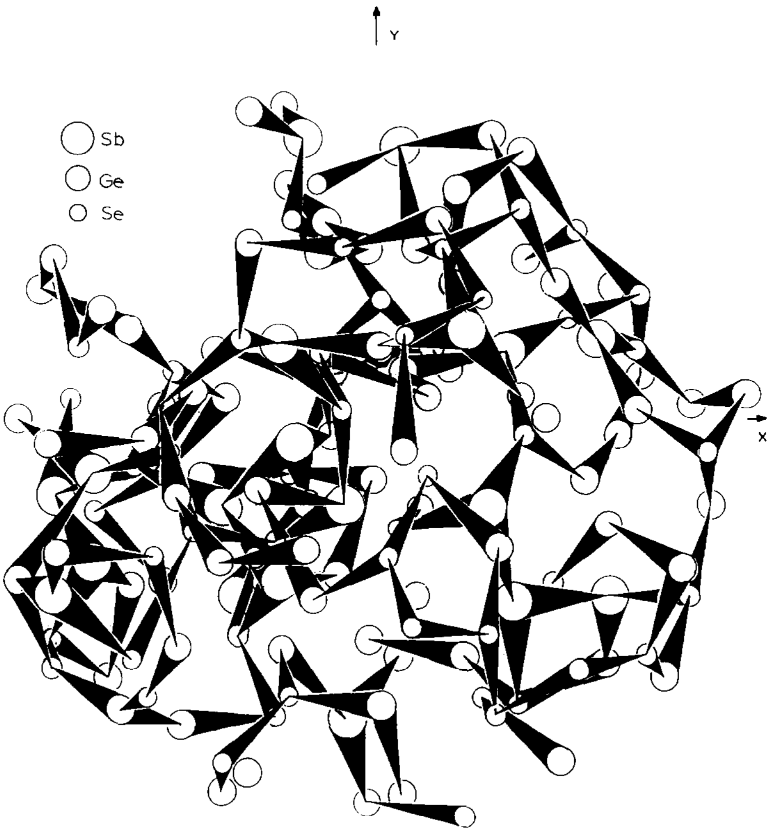

Fig. 4. Spatial representation of the model of the $Ge_{0.20}St_{0.20}Se_{0.60}$ alloy.

units are interlinked, forming a network which may represent the true structure of the alloy.

Coordination defects are observed in the model, indicating the presence of atoms with unsaturated bonds. Many of these dangling bonds belong to atoms which are less than a first-neighbour distance away from the surface of the model, and may be saturated with atoms situated outside it. Forty percent of the dangling bonds observed in the model 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 analyzing 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 3 shows the average bond lengths between the different pairs of elements. It is observed that the values obtained agree with data from the literature since, with the exception of the Sb–Sb bond lengths which are not considered statistically significant, all the other values differ by 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 its first neighbours. The average values of these angles are therefore usually compared to those given in the literature. Table 4 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 dis-

Table 3
Average bond distances (Å)

Bond	Material	⟨d⟩	Ref.
Ge–Ge	$Ge_{0.20}Sb_{0.20}Se_{0.60}$	2.51	a)
	$Ge_{0.14}As_{0.43}Te_{0.43}$	2.53	[11]
	amorphus Ge	2.54	[16]
Ge–Sb	$Ge_{0.20}Sb_{0.20}Se_{0.60}$	2.56	a)
	sum of covalent radii	2.62	[12]
Ge–Se	$Ge_{0.20}Sb_{0.20}Se_{0.60}$	2.49	a)
	$Ge_{0.20}As_{0.40}Se_{0.40}$	2.48	[17]
Sb–Sb	$Ge_{0.20}Sb_{0.20}Se_{0.60}$	2.58	a)
	sum of covalent radii	2.80	[12]
Sb–Se	$Ge_{0.20}Sb_{0.20}Se_{0.60}$	2.53	a)
	$Sb_{0.40}Se_{0.60}$	2.58	[18,19]
Se–Se	$Ge_{0.20}Sb_{0.20}Se_{0.60}$	2.45	a)
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.45	[20]
	$As_{0.45}Se_{0.10}Te_{0.45}$	2.44	[21]

a) Present work.

Table 4
Average bond angles (deg)

Type	⟨α⟩	Material	Ref.
Ge	107.7	$Ge_{0.20}Sb_{0.20}Se_{0.60}$	a)
	107.5	$Ge_{0.05}As_{0.20}Te_{0.75}$	[22]
	108.0	$Ge_{0.20}As_{0.40}Se_{0.40}$	[17]
Sb	108.3	$Ge_{0.20}Sb_{0.20}Se_{0.60}$	a)
	111.0	$Ge_{0.20}Sb_{0.15}Se_{0.65}$	[23]
Se	108.0	$Ge_{0.20}Sb_{0.20}Se_{0.60}$	a)
	106.7	$As_{0.40}Se_{0.30}Te_{0.30}$	[24]

a) Present work.

tortion 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 3%.

5. Conclusions

According to the radial atomic distribution function of the $Ge_{0.20}Sb_{0.20}Se_{0.60}$ alloy, obtained from the 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 for 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 model, which can be described as a three-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, and give 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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