A study of short-range order and atomic arrangement in the glassy semiconductor $As_{0.20}Se_{0.40}Te_{0.40}$ by X-ray diffraction

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An X-ray radial atomic distribution (RDF) study of the amorphous alloy $As_{0.20}Se_{0.40}Te_{0.40}$ 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 arsenic atoms, suggested in the literature for glassy alloys containing this element, was found to be compatible with the experimentally obtained structural information. A spatial atomic distribution model was generated according to these two possible coordinations for arsenic, using the conveniently modified Metropolis Monte Carlo method. The model obtained exhibits tetrahedral units on arsenic atoms, forming a network with triangular pyramids with an arsenic 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

The nature, structure and properties of amorphous solids have remained virtually unknown. Although some studies were done on this class of material in the first half of this century, glassy semiconductors have been the object of intense studies in recent years, thanks to revised fundamental and technological interest since the sixties [1]. Among the glassy semiconductors, chalcogenides are of importance from a technological point of view, due to their electrical behaviour. They exhibit switching and memory effects [2], as well as photostructural changes and optical memory [3], among other differential properties. These materials lack long-range order in their structure, although they do exhibit short-range order in their bonds with first neighbours, up to a few atomic diameters. The lack of structural periodicity in glassy solids implies a metastable state of greater energy than that of the corresponding crystalline material, a fact which justifies glass–crystal phase transitions that can be related to the observed electrical and optical properties. It is well known that the temperature at which this transition takes place is proportional to the average coordination of the material [4] and this is of importance to the understanding of local order, as well as other macroscopic properties, which are largely determined by the short-range structure present in all glassy materials.

This work analyzes the local order of the semiconducting glassy alloy $As_{0.20}Se_{0.40}Te_{0.40}$, from data obtained from the radial distribution function (RDF) determined from X-ray diffraction intensities. The experimental value of the area under the first RDF peak was compared to the one obtained theoretically [5,6] as a coordination function of the arsenic and taking into account that the functions

$$R_{ij}(s) = f_i(s) f_j(s) \Big/ \Big(\sum_i x_i f_i(s) \Big)^2$$

depend on the scattering angle [7] and cannot always be approximated by a constant value $Z_i Z_j / (\sum_i x_i Z_i)^2$. Based on the abovementioned analysis and on the geometrical restrictions imposed by the experimental RDF, a spatial atomic distribution model was generated, using the Metropolis Monte Carlo random method. An analysis of the main parameters of the model (coordinations, bond lengths and an-

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gles) shows good agreement with the values quoted in the literature for similar alloys.

2. Experimental procedure

The bulk samples of the glassy alloy $As_{0.20}Se_{0.40}Te_{0.40}$ were prepared from commercial 99.999% pure As, Se and Te, as described in ref. [8]. The density of the material was determined from pieces of adequate size, using a pycnometric method at a constant temperature. The average value obtained from the series of measurements carried out was 5.21 g cm^{-3}, with a relative error of less than 3%.

Part of the alloy was pulverized to a particle size of less than 40 μm, and pressed into $20\times20\times1$ mm^3 bricks. The absence of crystalline peaks was checked by X-ray diffraction, confirming the glassy nature of the solid. The intensities of the radiation diffracted by the sample were measured in an automatic Siemens D500 powder diffractometer, equipped with a bent graphite monochromator and a scintillation detector. Mo Kα radiation was used ($\lambda=0.71069$ Å). Four series of measurements were done in the $5°\leq\theta\leq110°$ range, two for increasing and two for decreasing scattering angles, using an angular interval of 0.2° in the 5–70° scan and of 0.5° in the 70–110° scan. These measurements were done fixing the number of counts at 4000, and digitally registering the time it took to detect them. The average value of the four measurements was taken as the radiation intensity at each observation point.

3. Obtaining the radial distribution function. Local order hypotheses

The observed intensities were corrected, as usual, for background, polarization, absorption and multiple scattering [9], in order to eliminate the portion of radiation which does not carry structural information. The correction of incoherent intensities and the determination of the interference function make it necessary to express the experimental intensities in electronic units (eu), as the atomic factors and Compton intensities are tabulated in these units. The normalization to electronic units was done using the high angle technique [9], and the normalized intensities were corrected for the Compton component, obtaining the spectrum of coherent intensities $I_{eu}(s)$ used to determine the interference function

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

where x_i and $f_i(s)$ are the atomic fraction and the scattering atomic factor of element i in the alloy. The function $F(s)$ was extended up to $s_{max}=30$ $Å^{-1}$, in order to avoid the spurious oscillations which appear in the RDF when small values of r are considered, due to the lack of experimental data for high values of s. The extension was done using the method described by D'Anjou and Sanz [10], based on the one proposed by Shevchik [11]. A Fourier transformation was applied to the extended interference function, obtaining the radial distribution function

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

where ρ_0 is the average experimentally measured density of the material, $\rho(r)$ represents the local atomic density affected by the Fourier transformation of products $R_{ij}(s)$, and the function $G(r)$ is given by

$$G(r)=\frac{2}{\pi}\int_0^{s_{max}} F(s)\sin sr\,ds. \tag{3}$$

The experimental RDF, shown in fig. 1, supplied the structural information shown in table 1. The general characteristics exhibited by the RDF of glassy alloy $As_{020}Se_{0.40}Te_{0.40}$ (As=1, Se=2, Te=3) are very similar to those found in the analysis of the radial distribution of amorphous alloys belonging to the As–Se and As–Te systems [12,13]. The interval defined by the first RDF peak, corresponding to the distances between first neighbours, is such that bonds are possible between all pairs of elements in the material.

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 average coordination number of the material. Bearing in mind the physical meaning of this area, and the fact that the products $R_{ij}(s)$ are functions of the scattering angle, Vázquez and Sanz [7], following the method described by Warren [9], deduced that the area under the first RDF peak is related to cer-

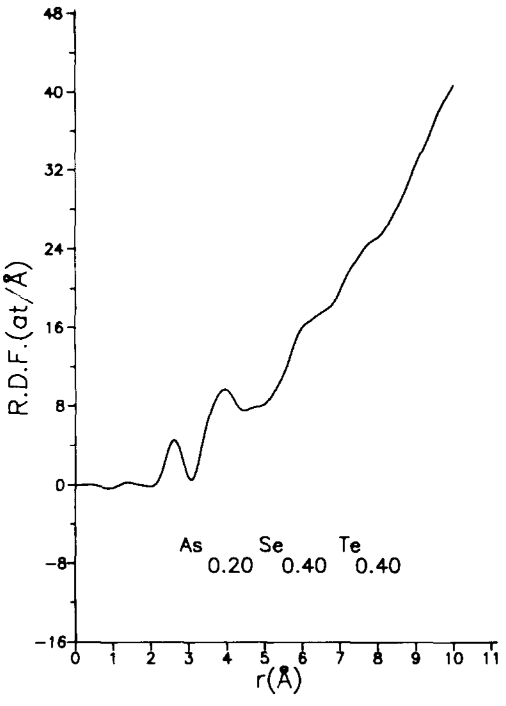

Fig. 1. Radial distribution function.

Table 1
RDF characteristics

maximum	1	2
position (Å)	2.60	3.95
limits (Å)	2.20–2.95	3.20–4.45
averaged angle (deg)	98.86	
area (atoms)	2.21	6.92
error	±0.1	±0.2

tain structural parameters, the relative coordination numbers n_{ij}, through the expression

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

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

$$P_{ij}(r) = \frac{1}{2} \int_0^{s_m} R_{ij}(s) \cos[s(r - r_{ij})]\, \mathrm{d}s \,, \tag{5}$$

where s_m is the upper limit of the measurement.

The structural information obtained by analyzing the experimental RDF, together with the physical-chemical properties of the alloys and of their constituent elements, make it possible to postulate the nature of the local order of the glassy materials. These hypotheses, which are reflected in the relative coordination numbers and, therefore, in the number of chemical bonds between the different pairs of elements in the material, have made it possible for Vázquez et al. [6] to deduce the following relation from eq. (4):

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

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

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

This work evaluates parameters A_{ij} by adjusting functions $R_{ij}(s)$ by the corresponding straight regression lines, thus obtaining the values shown in table 2, which were calculated through the method described by Vázquez and Sanz [7]. The distances between the different pairs used are also shown in table 2, together with the corresponding references.

In order to express the area under the first RDF peak as a function of the coordination N, assigned to the As atoms in this alloy, the characteristic parameter of the alloy $h = 24.2715$, and those depending on

Table 2
Bond lengths and A_{ij} parameters

Pair	r_{ij} (Å)	Ref.	A_{ij}
1–1	2.49	[14]	0.9120
1–2	2.38	[15]	1.0675
1–3	2.62	[16]	1.7294
2–2	2.34	[15]	1.1425
2–3	2.54	[15]	1.5079
3–3	2.71	[10]	2.9329

Table 3
Theoretical results obtained for the coordination hypotheses of the arsenic atom

N	Coordination numbers n_{ij}, $i,j\neq 1$	Variation intervals for parameter a_{33}		Intersection of intervals
		defined by the n_{ij} parameters	defined by limits of error of the experimental area	
3	$n_{22}=0.05a_{33}$ $n_{23}=1.4-0.05a_{33}$	$0\leq a_{33}\leq 28$	$8.19\leq a_{33}\leq 23$	$8.19\leq a_{33}\leq 23$
4	$n_{22}=0.05a_{33}$ $n_{23}=0.95-0.05a_{33}$	$0\leq a_{33}\leq 19$	$10.96\leq a_{33}\leq 25.78$	$10.96\leq a_{33}\leq 19$

the coordination hypothesis, were calculated with the following results [6]:

$$\alpha=0,\quad \beta=0,\quad \gamma=80,\quad \delta=0,\quad \text{for } N=3\,;$$
$$\alpha=0,\quad \beta=0,\quad \gamma=110,\quad \delta=10,\quad \text{for } N=4\,.$$

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

$$\text{area}=1.9995+0.0135a_{33},\quad \text{for } N=3\,;$$
$$\text{area}=1.9620+0.0135a_{33},\quad \text{for } N=4 \qquad (8)$$

and used for postulating the short-range order of the alloy. These relations may be observed to be functions of the number of Te–Te bonds, a_{33}, a fact which makes it possible to limit the variability field of the theoretical area.

In order to generate a local order model of the alloy $As_{0.20}Se_{0.40}Te_{0.40}$, it is necessary to establish the average coordinations of its constituent elements, which implies attributing a certain coordination to the arsenic. This is a relatively complicated question, as there is not just one coordination hypothesis in the literature for this element in other compounds. Whereas some authors [17,18] propose tetrahedral coordination for arsenic or similar elements in binary and ternary alloys with chalcogens, others [19,20] attribute three-coordination to the arsenic in these types of compounds, so both hypotheses must be considered.

Bearing in mind that relationship (8) for each value of N varies 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 [21], an adequate coordination for arsenic, by determining the variation interval for a_{33} in which the relative coordination numbers are positive and, at the same time, the theoretically obtained area within the margin of error of the experimental area. Table 3 shows the expressions for n_{ij}, $i,j\neq 1$, as functions of a_{33} for the tetra- and tri-coordinated arsenic hypotheses, as well as the variation intervals for the number of Te–Te bonds defined by the positive nature of the n_{ij} and by the margin of error of ±0.1 atoms in the experimental area, together with the intersection of these intervals.

In order to illustrate our calculations, fig. 2 shows the theoretically calculated areas versus the number of Te–Te bonds for the two valid As coordination hypotheses in $As_{0.20}Se_{0.40}Te_{0.40}$. This figure shows the variation intervals of a_{33} in which the theoretical areas are simultaneously compatible with the experimental area and with the corresponding coordination numbers.

An analysis of the interval intersections leads to the conclusion that in this alloy, the tetra- and tri-coordinated arsenic hypotheses are compatible with the structural information obtained from the experimental data. Therefore, the most probable short-range order may be a network of tetrahedral units centered on arsenic atoms, coexisting with others in which this element occupies one of the vertices of triangular pyramids, while the rest are taken by any of the other kinds of atoms which make up the material.

4. Generation and analysis of the spatial atomic distribution model

One's main object, when determining the struc-

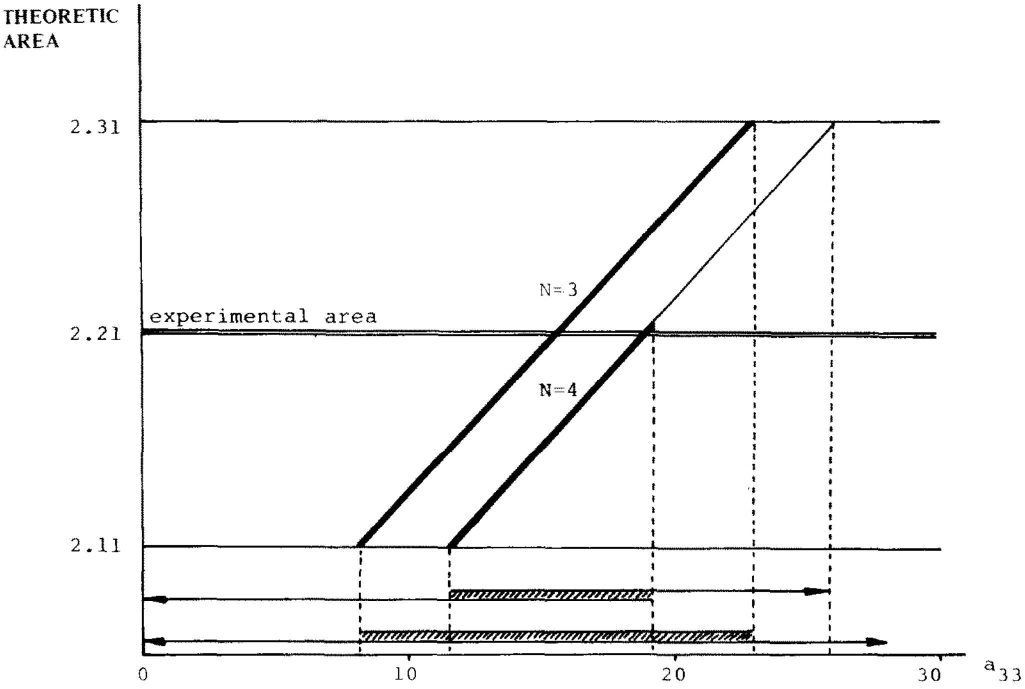

Fig. 2. Areas of first peak plotted against number of Te–Te bonds.

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

The process used for building the model, described at length by Vázquez et al. [22], comprises two stages: generating the initial configuration and refining it. During the first stage, 200 positions were semi-randomly created in the volume limited by a 10 Å radius spherical surface, in which, according to the experimental density, 135 atoms were to be located, as follows: 27 As atoms, 54 Se atoms and 54 Te atoms. This number of atoms is large enough to statistically represent the material, and small enough not to require too much calculating time. The generated positions meet the following requirements imposed by the information supplied by the experimental RDF:

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

(ii) The bond angle must be within the 66–180° range obtained, according to the literature [23], from the extreme radii of the first two coordination spheres.

(iii) The number of atoms of each kind in the first coordination sphere, which is given as a maximum acceptable coordination for each one of them. In the case of the alloy $As_{0.20}Se_{0.40}Te_{0.40}$, bearing in mind the postulated local order, a maximum coordination of four was considered for the arsenic, allowing it to evolve to three-coordination.

The positions obtained were reduced to a number equal to the number of atoms compatible with the experimental density by eliminating those with lowest coordination; the different kinds of atom were semi-randomly assigned to the corresponding positions. The reduced RDF of the initial configuration, $rG_{\mathrm{mod}}(r)$, was determined, simulating a diffraction process in the configuration. This function was compared to the $rG_{\mathrm{exp}}(r)$ multiplied by the expression proposed by Mason [24] and the two RDFs were compared by mean-square deviation, ϵ^2, used as a criterion for deciding on the validity of the generated configuration.

The second stage in the building of the model is the refining stage, which was done using the Metropolis Monte Carlo method [25] and consisted of modifying the initial position of a randomly chosen atom, by movements of arbitrary amplitude, *P*, and in random directions. These movements must meet all the conditions imposed by the experimental RDF, plus the additional restriction of only breaking one bond, at the most, in each arsenic atom, in order to keep the coordinations which were predicted for this element when the local order of the alloy was postulated. During the position refining process, the model evolved as shown in table 4, in which the mean-square deviation refers to the last movement in each interval. The position refining process was considered finished when the number of rejected movements was too large, and the mean-square deviation did not considerably improve. Fig. 3 shows the reduced RDF of the model and the experimental RDF after refining the positions and the thermal factors of the alloy under study.

Table 4
Position refining process

P (Å)	Movement intervals	Squared deviation (Å)
0.5	1–240	0.0257
0.3	241–279	0.0170
0.1	280–335	0.0122

Fig. 4 shows a spatial representation of the generated atomic configuration, in which one may observe tetrahedrons centred on arsenic atoms, and triangular pyramids with this element in one of their vertices. Both structural units are interlinked, forming a network which constitutes the possible structure of the alloy.

Dangling bonds are observed in this spatial distribution, as is frequent in amorphous materials. Many of these dangling bonds belong to atoms which are less than a first neighbour's distance away from the surface of the sphere, and may be saturated with atoms situated outside it. In the case of elements with two or more dangling bonds, they may be due to the finite size of the model, when the atom in question is less than 1.1 Å away from the surface limiting the configuration. This possibility takes into account both the distance between first neighbours and the average bond angle. Thirty 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

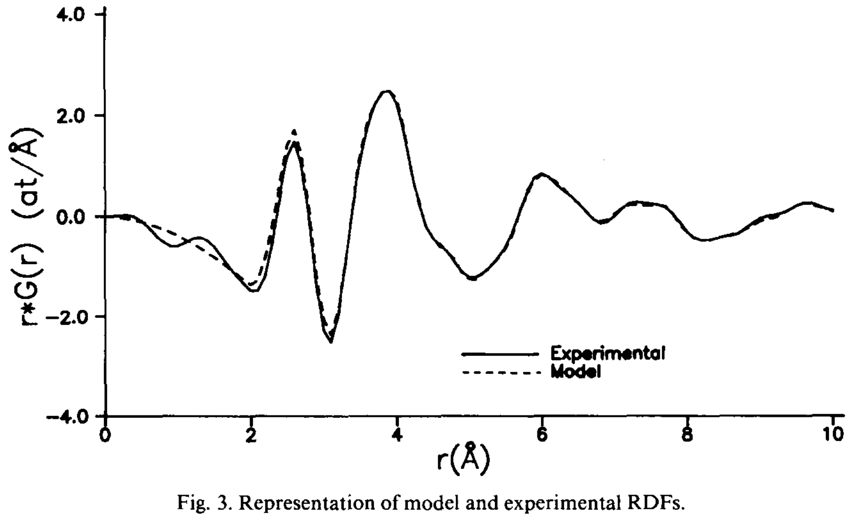

Fig. 3. Representation of model and experimental RDFs.

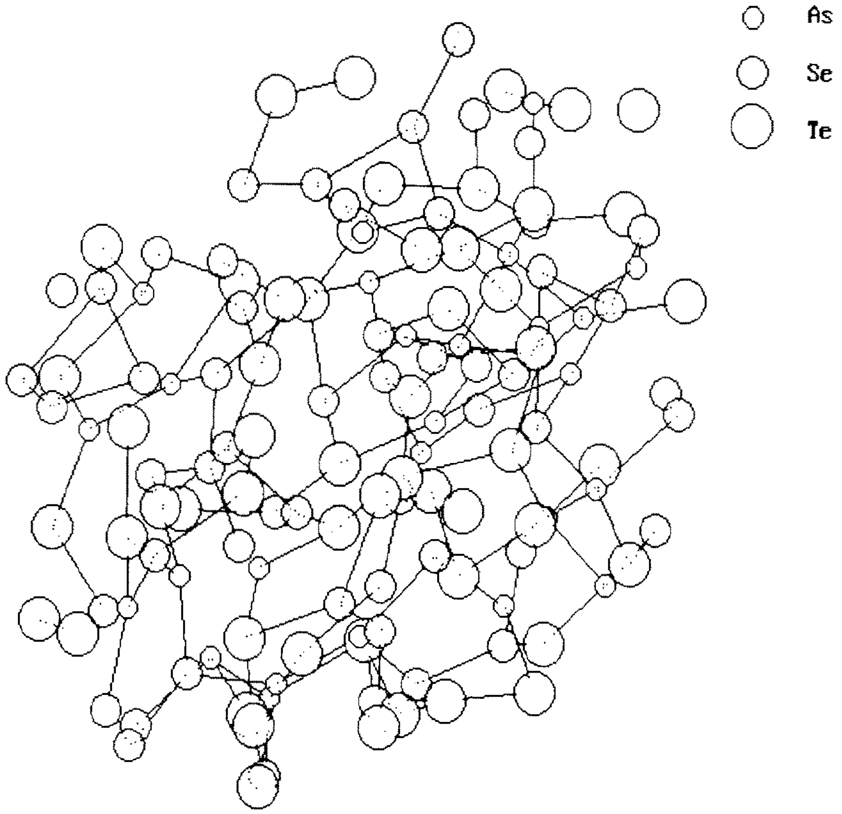

Fig. 4. Spatial representation of the model of alloy $As_{0.20}Se_{0.40}Te_{0.40}$.

structural parameters (bond lengths and angles) obtained from the model, and relating their values to those quoted in the literature for similar compounds. Table 5 shows the average bond lengths between the different pairs of elements. The values calculated for the bond lengths may be observed to agree very acceptably with the bibliographical data.

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 6 shows these values for the model, together with those quoted in the literature for similar alloys. All the calculated values can be considered acceptable, bearing in mind that a distortion of the bond angle is typical of glassy materials and that, in the most unfavourable case, the difference between the bond angles in the model and the values quoted in the literature was less than 2.2%.

Table 5
Averaged bonding distances (Å)

Bond	Material	$\langle d_{ij} \rangle$	Ref.
As–As	$As_{0.20}Se_{0.40}Te_{0.40}$	2.59	a)
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.59	[26]
	As_4S_4	2.59	[27]
As–Se	$As_{0.20}Se_{0.40}Te_{0.40}$	2.53	a)
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.52	[26]
	$As_{0.40}Se_{0.30}Te_{0.30}$	2.55	[8]
As–Te	$As_{0.20}Se_{0.40}Te_{0.40}$	2.55	a)
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.55	[26]
	sum of covalent radii	2.58	[15]
Se–Se	$As_{0.20}Se_{0.40}Te_{0.40}$	2.47	a)
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.47	[26]
	$As_{0.45}Se_{0.10}Te_{0.45}$	2.44	[28]
Se–Te	$As_{0.20}Se_{0.40}Te_{0.40}$	2.56	a)
	$As_{0.40}Se_{0.30}Te_{0.30}$	2.55	[8]
	$As_{0.45}Se_{0.10}Te_{0.45}$	2.58	[28]
Te–Te	$As_{0.20}Se_{0.40}Te_{0.40}$	2.61	a)
	$Ge_{0.14}As_{0.43}Te_{0.43}$	2.62	[23]
	$Al_{0.23}Te_{0.77}$	2.62	[29]

[a] This work.

Table 6
Averaged bonding angles (deg)

Type	⟨α⟩	Material	Ref.
As	110.2	$As_{0.20}Se_{0.40}Te_{0.40}$	a)
	109.9	$As_{0.40}Se_{0.30}Te_{0.30}$	[8]
	109.5	$As_{0.20}Se_{0.50}Te_{0.30}$	[26]
Se	108.7	$As_{0.20}Se_{0.40}Te_{0.40}$	a)
	107.7	$As_{0.45}Se_{0.10}Te_{0.45}$	[28]
	106.7	$As_{0.40}Se_{0.30}Te_{0.30}$	[8]
	107.5	Se glass	[30]
Te	109.3	$As_{0.20}Se_{0.40}Te_{0.40}$	a)
	107.0	$As_{0.45}Se_{0.10}Te_{0.45}$	[28]
	102.0–109.5	Te Ge glass	[31]

a) This work.

5. Conclusions

According to the radial atomic distribution function of the alloy studied, obtained from X-ray diffraction data and by analyzing the arsenic coordination hypotheses quoted in the literature, both tetrahedral and tri-coordinated arsenic were found to be possible in this alloy, as they correctly explain the experimentally determined average number of first neighbours.

By using the most approximate expression of the area under the first RDF peak, a number of Te–Te bonds was found for each of the arsenic's coordinations such that, while keeping coordination numbers n_{22} and n_{23} positive, the theoretical area is within the margin of error of the experimental area.

Considering the tetrahedral arsenic hypothesis, a spatial atomic distribution model of the alloy was built, using the Metropolis Monte Carlo random method, allowing the arsenic atoms to evolve to three-coordination, and bearing in mind the geometrical conditions deduced from the experimental radial distribution function.

According to the analysis of the model, the structure of the material may be described as a three-dimensional network of covalent bonds, arranged tetrahedrally around arsenic atoms, or else as triangular pyramids with atoms of this element in one of their vertices. Both basic structural units may be joined together either directly (by one atom linked to more than one arsenic atom), or by chains of Se and Te atoms.

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