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Local order hypotheses and spatial atomic distribution in the glassy alloy $Cu_{0.05}Ge_{0.15}Te_{0.80}$ by X-ray diffraction

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The radial atomic distribution was studied in the amorphous alloy $Cu_{0.05}Ge_{0.15}Te_{0.80}$, using X-ray diffraction data of samples obtained by quenching. The short-range order was determined through the interpretation of the radial distribution function (RDF), using a theoretical expression which takes into account the variation in the atomic scattering factors with s, the modulus of the scattering vector. The tetra- and di-coordinated copper hypotheses, quoted in the literature, were considered. The result of the study is that only the tetracoordinated copper hypothesis is compatible with the structural information obtained experimentally. A spatial atomic distribution model was generated according to this copper coordination, using the conveniently modified Monte Carlo method. A comparative analysis of the parameters of this model revealed good agreement with the values given in the literature for similar alloys.

1. Introduction

Amorphous solids have been used by man for centuries, although the nature, structure and properties of these materials have been obscure, in most cases, until lately. Due to the development of the atomic theory, interest in the structure of all kinds of materials has grown considerably. Although, initially, this interest only referred to crystalline substances, it has later been extended powerfully to amorphous solids [1–3]. Nowadays, one of the most active fields in solid-state research is the study of non-crystalline materials, that is, those whose atomic distribution lacks long-range order, although they do have short-range order in their bonds with first neighbours, up to a few atomic diameters, giving a characteristic spectrum in the diffractograms. A point of great interest in the study of glassy materials is their atomic distribution and the making of short-range order structural models, a structure that every amorphous material has and which will greatly condition its macroscopic behaviour.

This work analyzes the local order of the semiconducting glassy alloy $Cu_{0.05}Ge_{0.15}Te_{0.80}$, 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 [4,5] as a coordination function of the copper and taking into account that the functions

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

depend on the scattering angle [6] and cannot always be approximated by a constant value

$$Z_i Z_j/\Big(\sum_i x_i Z_i\Big)^2 .$$

Based on the abovementioned analysis and on the geometrical restrictions imposed by the experimental RDF, a spatial atomic distribution model was generated, using the Monte Carlo random method. An analysis of the main parameters of the model (coordinations, bond lengths and angles) shows good agreement with the values quoted in the literature for similar alloys.

2. Experimental methods

The samples of the glassy alloy $Cu_{0.05}Ge_{0.15}Te_{0.80}$

were prepared in bulk form, from 99.999% pure Cu, Ge and Te. These elements were introduced into quartz ampoules, sealed at a pressure of 10^{-3} Torr and heated in a rotating furnace at 1100°C for 72 h. The melt was quenched in liquid nitrogen to obtain the glass. The density of the material was experimentally measured using a pycnometric method at a constant temperature, the average value of the series of measurements being 5.48 g cm^{-3}, with a relative error under 3.5%. The pulverized samples of the alloy were radiated in an automatic Siemens D500 diffractometer, using Mo Kα ($\lambda = 0.71069$ Å) confirming their glassy nature. Four series of measurements were done in the $5° \leqslant 2\theta \leqslant 110°$ 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. Radial distribution function and short-range order hypotheses

The observed intensities were corrected for background, polarization and multiple scattering, and normalized into electron units [4,7]. The radial distribution function is calculated as

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + rG(r)\,, \tag{1}$$

where ρ_0 is the mean atomic distribution over the sample, directly deduced from the experimental density, $\rho(r)$ the local atomic density which is affected by the Fourier transform of the

$$f_i(s) f_j(s) \Big/ \Big(\sum_i x_i f_i(s)\Big)^2$$

products and $G(r)$ is given by

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

Here $F(s) = si(s)$ and

$$i(s) = \Big(I_{\mathrm{e.u.}} - \sum_i x_i f_i^2(s)\Big) \Big/ \Big(\sum_i x_i f_i(s)\Big)^2\,,$$

where x_i and $f_i(s)$ are the atomic fraction and the scattering atomic factor of element i in the alloy. The $F(s)$ function was theoretically extended to $s_{\max} = 30$ $\mathrm{Å}^{-1}$ to avoid spurious oscillations in $G(r)$ below the first significant maximum due to the lack of data for high s, with the method described by d'Anjou and Sanz [8]. The RDF after theoretical extension of the experimental data has been plotted in fig. 1. The analysis of experimental RDF supplied the following structural information: position of the first two maximum values 2.70 Å and 4.25 Å; limits of the first peak: 2.20–3.15 Å; area under the latter: 2.54 ± 0.1 atoms; average bond angle: 103.8°. This analysis shows, among other things, that the definition interval of the first peak, corresponding to the first coordination sphere of alloy $\mathrm{Cu_{0.05}Ge_{0.15}Te_{0.80}}$ (Cu = 1, Ge = 2, Te = 3), 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.

A parameter of great interest when postulating short-range order 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

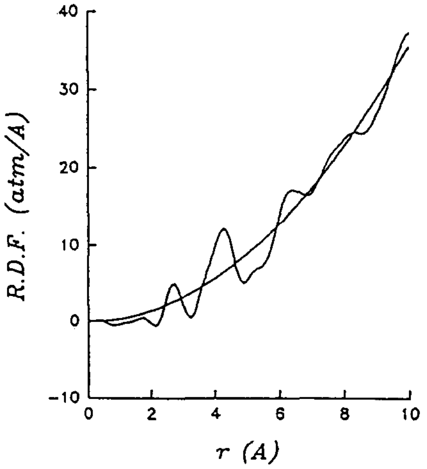

Fig. 1. Radial distribution function.

the scattering angle, Vázquez and Sanz [6], following the method described by Warren [7], deduced that the area under the first RDF peak is related to certain structural parameters, the relative coordination numbers n_{ij}, through the expression

$$\text{area}=\frac{2}{\pi}\sum_{i,j}x_i\frac{n_{ij}}{r_{ij}}\int_a^b rP_{ij}(r)\,\mathrm{d}r\,, \tag{3}$$

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

$$P_{ij}(r)=\frac{1}{2}\int_0^{s_\mathrm{m}}\frac{f_i(s)f_j(s)}{[\sum_i x_i f_i(s)]^2}\cos[s(r-r_{ij})]\,\mathrm{d}s\,, \tag{4}$$

s_m being the upper limit of the measurement.

The structural information obtained from the analysis of the experimental radial atomic distribution, together with some physical–chemical properties of the alloys and their elements, give way to hypotheses on the local order of amorphous materials. 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. [5] to deduce the following relation from eq. (3):

$$\text{area}=\frac{1}{50\pi}\left[\left(h+\beta A_{22}-\delta\sum_{i,j\neq 1}A_{ij}\right)N+\alpha A_{22}\right.$$
$$\left.+\gamma\sum_{i,j\neq 1}A_{ij}+P\left(\sum_{i=j\neq 1}A_{ij}-\sum_{\substack{i,j\neq 1\\ i\neq j}}A_{ij}\right)a_{ij}\right], \tag{5}$$

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

$$A_{ij}=\frac{1}{r_{ij}}\int_a^b rP_{ij}(r)\,\mathrm{d}r\,. \tag{6}$$

This work evaluates parameters A_{ij} by adjusting functions $R_{ij}(s)$ by the corresponding straight regression lines, fig. 2, thus obtaining the values shown in table 1, which were calculated according to the literature [6] from the bond lengths, r_{ij}, given in table 1, and the coefficients of the mentioned straight regression lines.

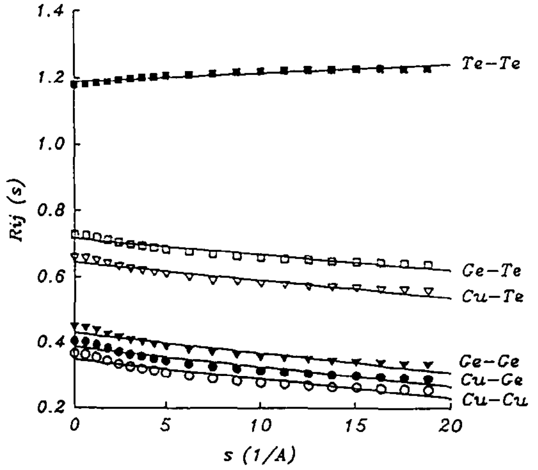

Fig. 2. Straight regression lines fitted to values of $R_{ij}(s)$.

Table 1
Bond lengths and A_{ij} parameters

Pair	r_{ij} (Å)	Ref.	A_{ij}
Cu-Cu	2.58	[9]	0.5335
Cu-Ge	2.39	[10]	0.5684
Cu-Te	2.53	[10]	1.0231
Ge-Ge	2.51	[11]	0.6797
Ge-Te	2.58	[10]	1.0858
Te-Te	2.71	[8]	1.9951

In order to express the area under the first RDF peak as a function of the coordination, N, assigned to the copper atoms in this alloy, the characteristic parameter $h=2.6934$, and those depending on the coordination hypotheses, were calculated [5,12]

$$\alpha=-95,\quad \beta=-5,\quad \gamma=155\,,$$
$$\delta=-5\quad \text{for } N=2 \text{ and } N=4\,.$$

The following expressions of the area were obtained from these data and from parameters A_{ij}, using eq. (5):

$$\text{area}=1.8610+6.4\times10^{-3}a_{33}\quad \text{for } N=2\,,$$
$$\text{area}=1.9902+6.4\times10^{-3}a_{33}\quad \text{for } N=4\,, \tag{7}$$

which are of basic interest when trying to formulate hypotheses on the short-range order of the alloy in question. These expressions may also be observed as being functions of the number of Te–Te bonds, a_{33}, a fact which makes it possible to limit the variability field of the theoretical area.

In order to generate a local order model of alloy $Cu_{0.05}Ge_{0.15}Te_{0.80}$ it is necessary to establish the average coordinations 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 [9,13] propose two-fold coordination for copper in similar compounds, others [14,15] attribute tetrahedral coordination to copper in ternary alloys with chalcogens; both hypotheses must be taken into consideration.

Bearing in mind that, for each value of N, relationships (7) 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 [16], the suitable coordination for 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 which contain parameter a_{33}, are given [4,12] by the expressions

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

$$n_{23}=\frac{\gamma-(100\delta+a'_1a'_3)N/100-2a_{33}}{a'_2}, \qquad (8)$$

which allow us to obtain for $N=2$ an average value $\langle a_{33}\rangle=63.88$. Considering the relationships (7) with $N=2$ for the area under the first peak 2.27 atoms was obtained; as may be observed, this is considerably less than that obtained experimentally, a fact which led to the rejection of coordination 2 for the copper 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 [14]. Under this hypothesis, the coordination numbers n_{22} and n_{23} are positive for the values of a_{33} within the interval [51.0–79.5] and relationships (7) give for the area under the first RDF peak an expression which is in good agreement with the experimentally determined value, within the ±0.1 atoms 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. Model description and results

The procedure used for the elaboration of the short-range order structure model is similar to that used by Esquivias and Sanz [17]. This structure is refined with the help of the well-known random technique of Metropolis Monte Carlo.

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 a 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 leads to the best fit of the theoretical $rG(r)$ to the experimental value was calculated with the least-squares method. The refining process was considered finished after 433 valid movements and the mean-square deviation was 0.026 Å. Fig. 3 shows the reduced RDF of the model and the experimental RDF after the refining process. Fig. 4 shows a spatial representation of the generated atomic configuration, in which one may observe tetrahedrons centred on copper and germanium atoms. Both structural units are interlinked, forming a network which constitutes the possible 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. Fifty 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.

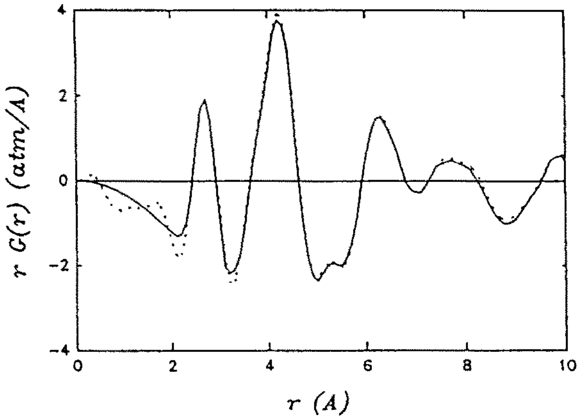

Fig. 3. Representations of (---) experimental and (—) calculated RDFs.

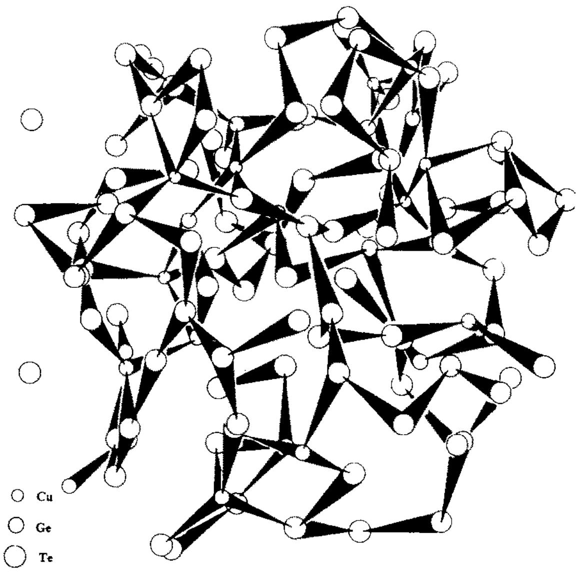

Fig. 4. Spatial representation of the model of alloy $Cu_{0.05}Ge_{0.15}Te_{0.80}$.

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 2 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 Cu–Ge bond lengths which are not considered statistically significant, all the other values differ less than 3% from those previously reported.

Table 2
Averaged bonding distances (Å)

Bond	$\langle d_{ij} \rangle$	Ref.
Cu–Ge	2.69	this work
	2.39	[10]
Cu–Te	2.71	this work
	2.64	a)
Ge–Ge	2.77	this work
	2.70	[19]
Ge–Te	2.64	this work
	2.65	[20]
Te–Te	2.70	this work
	2.70	[20]
	2.71	[8]

a) Estimation by means of Schomacker and Stevenson's formula [18].

Table 3
Averaged bonding angles (deg)

Type	$\langle \alpha \rangle$	Material	Ref.
Cu	107.9	$Cu_{0.05}Ge_{0.15}Te_{0.80}$	this work
	107.8	$Cu_{0.20}As_{0.30}Se_{0.50}$	[21]
	106.6	$Cu_{0.05}As_{0.50}Te_{0.45}$	[14]
Ge	107.9	$Cu_{0.05}Ge_{0.15}Te_{0.80}$	this work
	107.5	$Ge_{0.05}As_{0.20}Te_{0.75}$	[20]
	108.0	$Ge_{0.20}As_{0.40}Se_{0.40}$	[11]
Te	110.5	$Cu_{0.05}Ge_{0.15}Te_{0.80}$	this work
	110.6	$As_{0.40}Se_{0.30}Te_{0.30}$	[22]

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 3 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%.

5. Conclusions

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

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

Considering the tetracoordinated copper hypothesis, a model of the spatial atomic distribution of the alloy was built, using the Metropolis Monte Carlo random method and bearing in mind the geometric conditions, deduced from the radial atomic distribution function obtained by X-ray diffraction of the samples.

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

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