A STRUCTURAL MODEL OF THE AMORPHOUS ALLOY $As_{0.40}Se_{0.30}Te_{0.30}$ BY RANDOM TECHNIQUE

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An analysis is performed of the atomic radial distribution function of the amorphous alloy $As_{0.40}Se_{0.30}Te_{0.30}$, obtained from the quenching of the molten mixture of the elements. A spherical-shaped model of this alloy has been studied by means of the random Monte Carlo method. The model describes the experimental radial distribution function quite well.

1. Introduction

Progress in glass science has been considerable in the last years. Interest in vitreous chalcogenides was stimulated first by their infrared transmission and later by their semiconduction and switching properties [1,2]. The features of these properties depend strongly on the structure.

Here we report the results of an X-ray radial distribution analysis and a short-range structure model of the amorphous alloy $As_{0.40}Se_{0.30}Te_{0.30}$.

2. Experimental

The $As_{0.40}Se_{0.30}Te_{0.30}$ sample used was prepared from elements of 5 N purity. Appropriate amounts of the finely powdered components were put into silica tubes, evacuated and sealed under a He atmosphere. They were kept in a rotatory furnace at 600°C for 3 days, ensuring a perfect melt and reaction of the components. Finally, the tubes were quenched in an ice-water bath.

The solid obtained from the quenching was ground to a fine powder (<325 mesh), which was compacted into a brick shape. No evidence of crystallinity was found in a conventional X-ray diffraction experiment.

The diffraction intensities were measured with a Siemens diffractometer equipped with a bent graphite monochromator, scintillation counter and standard electronics. The radiation used was Mo Kα (λ = 0.71069 Å).

Four series of data were collected in the interval $6^\circ \leqslant 2\theta \leqslant 120^\circ$, two in increasing angles of 2θ, and the other two in reverse. From 6° to 70°, step sizes of $\Delta(2\theta) = 0.2^\circ$ were used, and from 70° to 120° of $\Delta(2\theta) = 0.5^\circ$. Times were measured by taking a fixed number of counts (N = 4000).

The intensity assigned to each observation point was the mean value of those measured at that point. Most of the averaged values lie within 3% of the mean, with a maximum deviation of 5%. The density of the material measured with a pycnometer was 5.49 g/cm^3 with an estimated error of ±3%.

3. Radial distribution function (RDF)

The observed intensities were corrected for background, polarization and multiple scattering. Warren's method [3] was used in the last correction. Compton scattering was evaluated, taking into consideration the efficiency of the monochromator, and following the procedure described by Shevchik [4].

The intensities were put into electron units by means of the high-angle method, and the incoherent scattering subtracted.

The interference function $F(s)$ was calculated, and theoretically extended to s_{max} = 30 Å^{-1}, to avoid spurious oscillations in the RDF below the first signif-

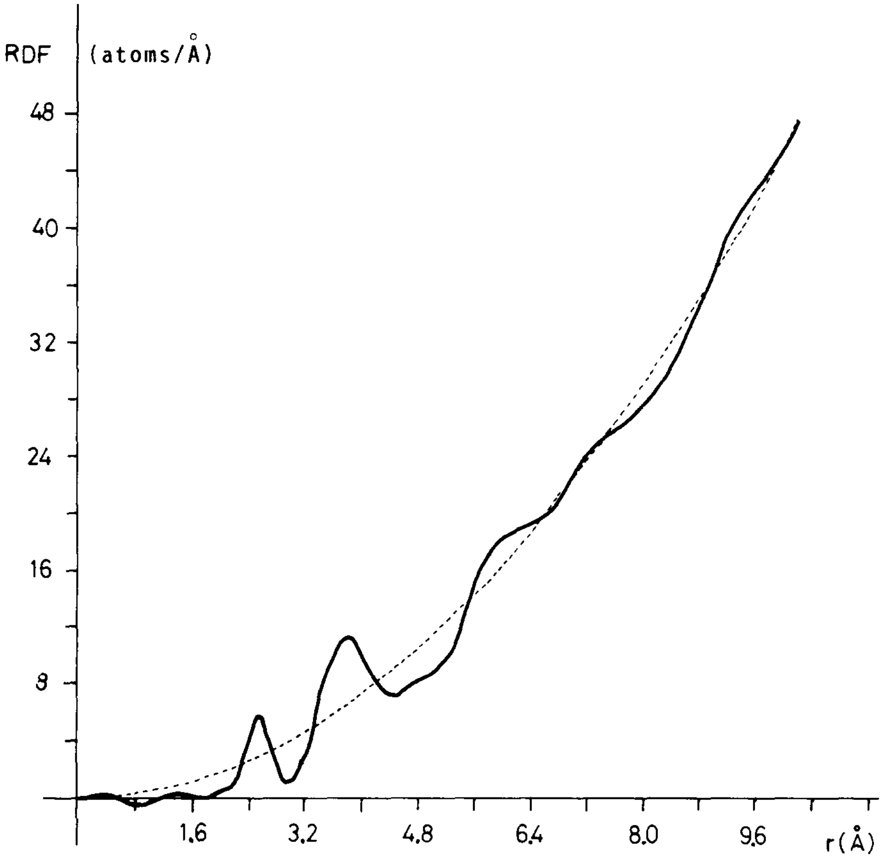

Fig. 1. Radial distribution function.

icant maximum due to the lack of high-s data, by the method described by D'Anjou and Sanz [5].

The RDF, after the theoretical extension of the experimental data, is plotted in fig. 1.

The analysis of the RDF may be summarized by the values given in table 1.

The area under the first peak was calculated with Simpson's formula, and the area under the second peak with the method proposed by Stesiv [6], errors were estimated.

The first peak is located in the interval (2.00 Å, 2.90 Å), this corresponds to first-neighbour distance, which means that no bonds between the different elements of the alloy can be discarded.

Table 1
Peak positions and area under the peaks of the RDF. Errors are estimated

Peak	r (Å)	Area (atoms)	Δ
first	2.50	2.40	0.10
second	3.85	6.96	0.20

The area under the first maximum is related to the main structural parameters by the expression

$$A = \frac{1}{\pi} \sum_{i,j} x_j \frac{n_{ij}}{r_{ij}} \Bigg\{ (A_{0ij} s_\mathrm{m} + A_{1ij}) \times \frac{\cos s_\mathrm{m} a'_{ij} - \cos s_\mathrm{m} b'_{ij}}{s_\mathrm{m}} + A_{0ij} L \frac{|a'_{ij}|}{b'_{ij}} + r_{ij} A_{1ij} \int_{b'_{ij}}^{a'_{ij}} \frac{\sin s_\mathrm{m} x}{x} \, \mathrm{d}x + r_{ij} \left[A_{0ij} \left(\frac{1 - \cos s_\mathrm{m} b'_{ij}}{b'_{ij}} - \frac{1 - \cos s_\mathrm{m} a'_{ij}}{a'_{ij}} \right) \right] \Bigg\} , \tag{1}$$

after results obtained by Vázquez and Sanz [7], deduced from a linear regression fit of the products $f_i f_j/(\Sigma_i x_i f_i)^2$ versus s, over the angle interval tabulated. A_{0ij} and A_{1ij} are the coefficients in the fit.

The value of the area under the first peak of the experimental RDF, allows structural units to be proposed in the form $AsX_{3/2}$ and $AsX_{4/2}$ (X: As, Se, Te), and allows As–As bonds, given the high proportion of this element in the sample.

4. The description of the model and results

The procedure used in developing the model with short-range order structure is similar to that employed by Esquivias and Sanz [8]. The initial model was based on a hypothesis drawn from the value of the area under the first peak of the experimental RDF. A sphere of 10 Å radius was considered adequate to represent the material from a statistical point of view.

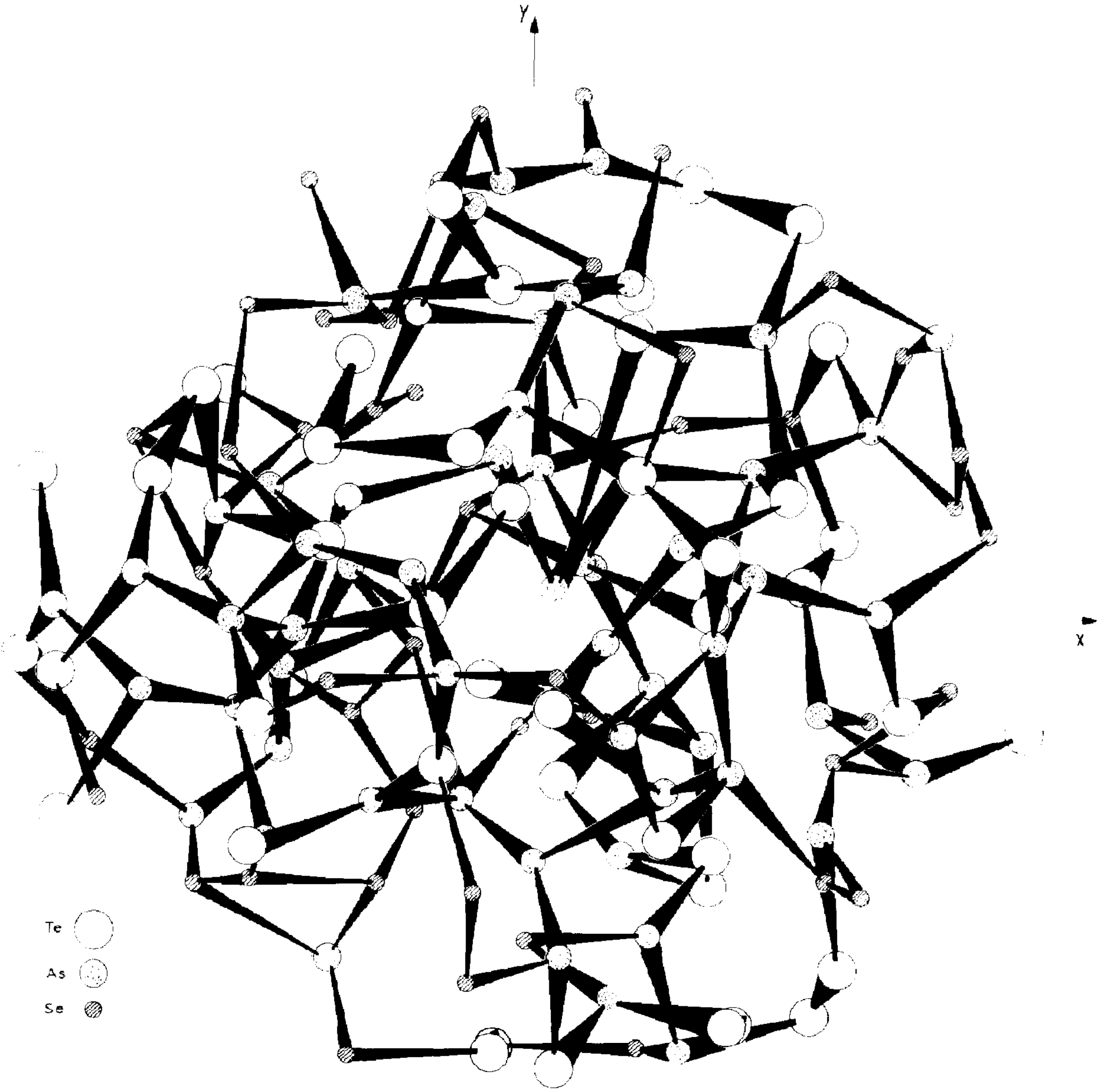

Fig. 2. Spatial representation of the model of the $As_{0.40}Se_{0.30}Te_{0.30}$ alloy.

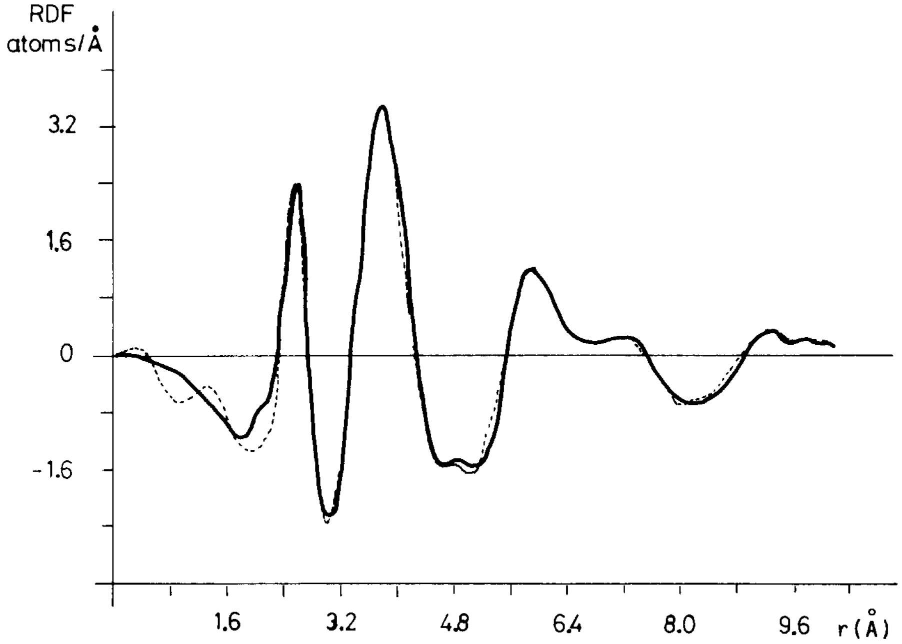

Fig. 3. Representation of calculated (continuous line) and experimental (dotted line) RDFs.

The structure is refined with the help of the well-known Metropolis Monte Carlo technique. On starting the refinement process, we assumed a shift value of $\Delta r = 0.3$ Å. Afterwards, it was reduced to $\Delta r = 0.1$ Å as the refinement advanced in order to obtain fast convergence.

Initially, a constant temperature factor ($\sigma = 0.1$ Å) was considered. After the refinement process, it was taken as a constant value for every coordination sphere, but differing one from another. The set of σ_i values which gave the best fit of the theoretical RDF (red.) to the experimental value, was calculated with the least-squares method.

After 419 valid movements, the standard deviation was 0.0198. Fig. 2 shows a spatial model representation. Fig. 3 corresponds to both experimental and calculated RDF (red.). Coordination deficient Se and Te atoms are observed in the model. Of them, 86% of Te atoms and 100% of Se atoms are less than 2 Å and 1 Å, respectively, from the spherical surface limiting the model, thus being able to satisfy their bonds with other atoms on the other side of the surface.

Mean bonding distances for the different atom pairs as well as their mean-squared deviations, are dis-

Table 2
Averaged bonding distances (Å)

Bond	$\langle d \rangle$ (Å)	Squared deviation
As–As	2.46	0.25
As–Se	2.55	0.18
As–Te	2.50	0.22
Se–Se	2.38	0.23
Se–Te	2.55	0.20
Te–Te	2.60	0.17

Table 3
Averaged bonding angles (degrees). The numbers in parentheses represent the coordination of the atom

Type	$\langle \alpha \rangle$ (deg.)	Squared deviation
As(4)	106.33	25.73
As(3)	109.87	21.09
Se(3)	106.72	20.02
Se(2)	105.49	21.68
Te(3)	110.90	26.38
Te(2)	104.66	22.68

played in table 2. These distances agree with those found in the literature for similar alloys [9–12], as in the most unfavorable case – the As–Se bonds – the difference is not larger than 5%.

The average bonding angles are displayed in table 3. All of them seem to have acceptable values, since the first distortion that one may expect for an amorphous material is in the bonding angles.

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