Journal of Non-Crystalline Solids 86 (1986) 251–260
North-Holland, Amsterdam

STRUCTURAL MODELS FOR SEMICONDUCTOR $As_{0.20}Se_{0.50}Te_{0.30}$ GLASS ALLOY BY X-RAY DIFFRACTION

J. VÁZQUEZ, P. VILLARES and R. JIMÉNEZ-GARAY

Departamento de Fisica, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real (Cádiz), Spain

Received 4 February 1986

Two structural models of the bulk $As_{0.20}Se_{0.50}Te_{0.30}$ amorphous alloy have been built by a random Monte Carlo technique. These models are in good agreement with the atomic radial distribution function obtained by X-ray diffraction. The first model was made to fit the hypothesis of coordinated tetrahedral As, and the second to fit the hypothesis of threefold As coordination. The structural parameters of both models are in agreement with those mentioned in the literature for similar alloys.

1. Introduction

Amorphous semiconductors, a group of non-crystalline materials, are at present of great technological interest. In the 1950s, Kolomiets [1] highlighted an intrinsic semiconductor behaviour in chalcogenide glasses. Later, Ovshinsky [2] discovered the switching phenomenon presented by these materials.

Because of these as well as other electronic, magnetic and optical properties, the interest in amorphous materials has increased considerably in recent years. However, although the atomic structure of crystalline solids is well established, that of amorphous solids remains unknown.

Here we report the results of an X-ray radial distribution analysis of $As_{0.20}Se_{0.50}Te_{0.30}$ alloy. In this work we have tried to construct two short-range models of this compound by an aleatory method.

2. Experimental

The $As_{0.20}Se_{0.50}Te_{0.30}$ sample used was obtained from commercial As, Se and Te of 99.999% purity. Appropriate proportions of the elements were sealed in a quartz ampoule under a neutral He atmosphere and then melted [3]. The molten mixture was rotated for three days inside a furnace at temperatures above 600°C and then quenched in ice–water bath.

The solid obtained from the quenching was ground to a fine powder (< 325 mesh), which was compacted by pressure into a brick of approximately 30 × 12 × 1 mm^3. No evidence of crystallinity was found in a conventional X-ray diffraction experiment.

The diffraction intensities were measured on a Siemens diffractometer equipped with a bent graphite monochromator, scintillation counter and standard electronics. The radiation used was Mo $K\alpha(\lambda = 0.71069$ Å).

Four series of data were collected in the interval $6° \leqslant 2\theta \leqslant 120°$, two with increasing angles of 2θ and the other two in reverse. A step size of $\Delta(2\theta) = 0.2°$ was used from 6° to 70°, and of $\Delta(2\theta) = 0.5°$, from 70° to 120°. Times were measured by keeping 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 average, with a maximum deviation of 4%.

The density of the material measured with a pycnometer was 4.93 g/cm^3 with an estimated error of ±2%.

3. Radial distribution function

The observed intensities were corrected for background, polarization and multiple scattering, and normalized into electron units.

The radial distribution function (RDF) 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 $f_i f_j/(\sum_i x_i f_i)^2$ products and $G(r)$ is

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

begin

$$F(S) = si(s)$$

and

$$i(s) = \frac{I_{\mathrm{e.u.}} - \sum_i x_i f_i^2}{\left(\sum_i x_i f_i\right)^2}$$

where x_i is the atomic fraction of the ith element, with i = As, Se, Te; and $I_{\mathrm{e.u.}}$ represents the resulting intensity values after corrections.

The $F(s)$ function was theoretically extended to $s_{\max} = 30$ 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 et al. [4].

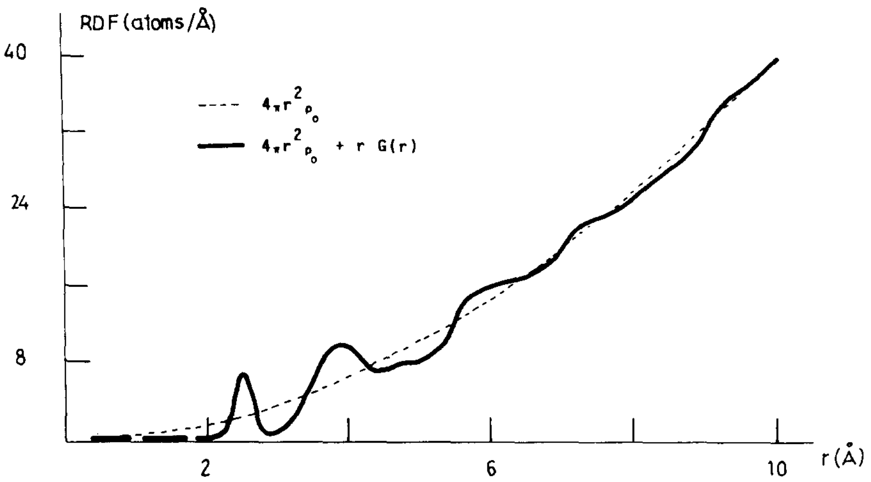

Fig. 1. Radial distribution function.

The RDF after theoretical extension of the experimental data has been plotted in fig. 1.

The analysis of experimental RDF may be summarized by the values given in table 1. The general features shown by the RDF of the $As_{0.20}Se_{0.50}Te_{0.30}$ amorphous alloy, are very similar to those found in the radial distribution analysis of the amorphous alloys systems As–Se and As–Te [5,6].

The first peak, corresponding to the first-neighbour distance, is found in the interval defined as (2.05 Å, 2.90 Å), which does not allow any bond between the different elements to be discarded.

The area under the first peak was calculated by means of Simpson's formula and that under the second with the method proposed by Stesiv [7]. Errors were estimated.

The value of the area under the first peak of the RDF is a parameter which permits the estimation of short-range order in the material; for this reason, an analytical method has been developed to relate this area to the number of bonds between all the pairs of elements in the material [8].

Assuming coordination N for one of the elements of the alloy, an analytical expression has been obtained for the aforementioned area as a function of N

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

Peak	r(Å)	Area (atoms)	Δ
1st	2.53	2.10	0.10
2nd	3.85	6.90	0.20

and of the number of bonds of one type between pairs of elements in the compounds, which is defined as:

$$\text{Area} = \frac{1}{100\left(\sum_j x_j Z_j\right)^2} \times \left[Z_2(\alpha Z_2 + 2\gamma Z_3) + \left[h + Z_2(\beta Z_2 - 2\delta Z_3)\right] N + 2(Z_2 - Z_3)^2 a_{33}\right], \tag{3}$$

where α, β, γ, δ, y, h are specific characteristics of each alloy, as they only depend on the concentration of each element, the corresponding atomic number and the coordination.

As previous authors [9,10] propose tetrahedral coordination for As or similar elements in binary and ternary alloys with chalcogens, and others [11,12] attribute coordination three to As in this kind of compound, both tendencies have been considered in this study. Thus, two short-range models are proposed for the $As_{0.20}Se_{0.50}Te_{0.30}$ alloy, one based on the tetrahedral As hypothesis and the other considering As as threefold coordinated.

Given that the theoretical expression of the area under the first peak in the RDF is valid for all values of coordination N of a determined element in the alloy, it has been used in the description of short-range orders in the compound for each one of the hypotheses mentioned.

The characteristic parameters of the material corresponding to the analytical development analysis carried out previously have the following values:

$h = 21548 \quad \alpha = 55 \quad \beta = -5 \quad \gamma = 82.5 \quad \delta = 7.5$

and the area under the first peak of the RDF for each of the cited hypotheses is given by:

$$\text{Area} = 2.0323 + 0.0042 a_{33} \tag{4}$$

for the tetrahedral As hypothesis, and

$$\text{Area} = 2.1023 + 0.0042 a_{33} \tag{5}$$

for the threefold As coordination.

Table 2
Coordination numbers for both models

Tetrahedral coordination for As, As(4)	$n_{11} = 0.8$	$n_{12} = 2$	$n_{13} = 1.2$
	$n_{21} = 0.8$	$n_{22} = \frac{19 + 2a_{33}}{50}$	$n_{23} = \frac{28.5 - 2a_{33}}{50}$
	$n_{31} = 0.8$	$n_{32} = \frac{28.5 - 2a_{33}}{30}$	$n_{33} = \frac{2a_{33}}{30}$
Threefold coordination for As, As(3)	$n_{11} = 0.6$	$n_{12} = 1.5$	$n_{13} = 0.9$
	$n_{21} = 0.6$	$n_{22} = \frac{28 + 2a_{33}}{50}$	$n_{23} = \frac{42 - 2a_{33}}{50}$
	$n_{31} = 0.6$	$n_{32} = \frac{42 - 2a_{33}}{30}$	$n_{33} = \frac{2a_{33}}{30}$

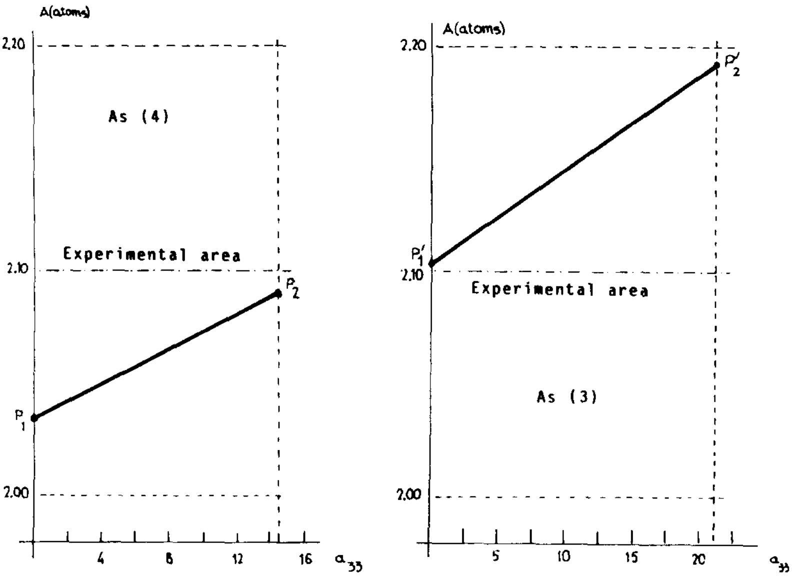

Fig. 2. Area of first peak versus number of Te–Te bonds for both hypotheses.

These are linear functions which depend only on a_{33}, the number of Te–Te bonds in the alloy.

The corresponding coordination numbers are listed in table 2. From both the area expressions (4) and (5) and the listed values, the number of Te–Te bonds is deduced to vary in the interval $0 \leqslant a_{33} \leqslant 14.25$ in the case of tetrahedral As and in $0 \leqslant a_{33} \leqslant 21$ when As is considered to be threefold coordinated.

The area as a function of a_{33}, represented in fig. 2 for both hypotheses, is limited in the first case between points P_1 and P_2, where it takes the values:

$$\text{Area}(P_1) = 2.032 \text{ atoms} \quad \text{Area}(P_2) = 2.092 \text{ atoms}$$

and in the second case between P'_1 and P'_2, where the values are

$$\text{Area}(P'_1) = 2.102 \text{ atoms} \quad \text{Area}(P'_2) = 2.191 \text{ atoms},$$

these values being within the experimental error.

Therefore, for the construction of the short-order structure model, structural units of the type $AsX_{4/2}$ (X: As, Se, Te) and $AsX_{3/2}$ (X: As, Se, Te) are proposed for the first and second hypotheses respectively.

4. Models' description and results

The procedure used for the elaboration of the short-range order structure model is similar to that used by L. Esquivias et al. [13]. This structure is

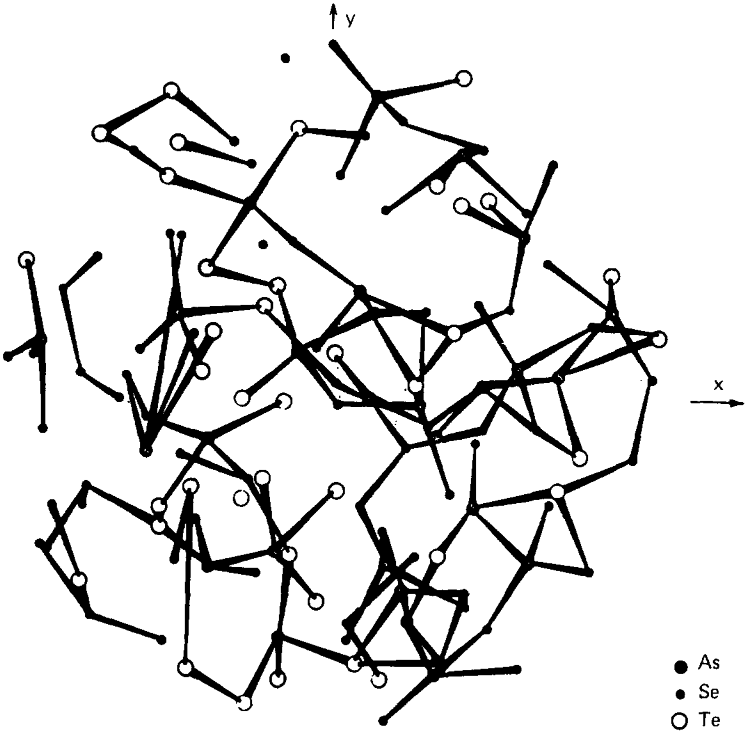

Fig. 3. Spatial representation of the model of $As_{0.20}Se_{0.50}Te_{0.30}$ alloy by hypothesis of fourfold-coordinated As.

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 ($\sigma = 0.10$ 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 fitting of the theoretical RDF(red.) to the experimental value was calculated with the least-squares method.

In the first model, where hypothetically the As is fourfold coordinated, after 620 valid movements, the standard deviation was 0.0367. Fig. 3 shows a spatial model representation. Fig. 4 corresponds to both the experimental and calculated RDF.

A second model for the $As_{0.20}Se_{0.50}Te_{0.30}$ alloy was built on the hypothesis of As being threefold coordinated. After 371 valid movements, the standard deviation was 0.0249. Fig. 5 corresponds to a spatial model representation. Fig. 6 shows both the experimental and calculated RDF.

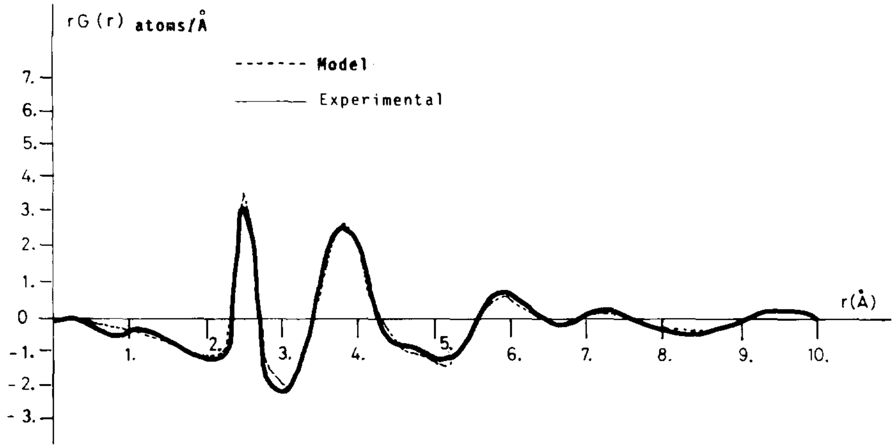

Fig. 4. Representation of calculated (dotted line) and experimental (solid line) RDFs by hypothesis of fourfold-coordinated As.

Coordination defects are observed in both models, indicating the presence of atoms with unsatisfied bonds. This may be justified by the finite character of the model.

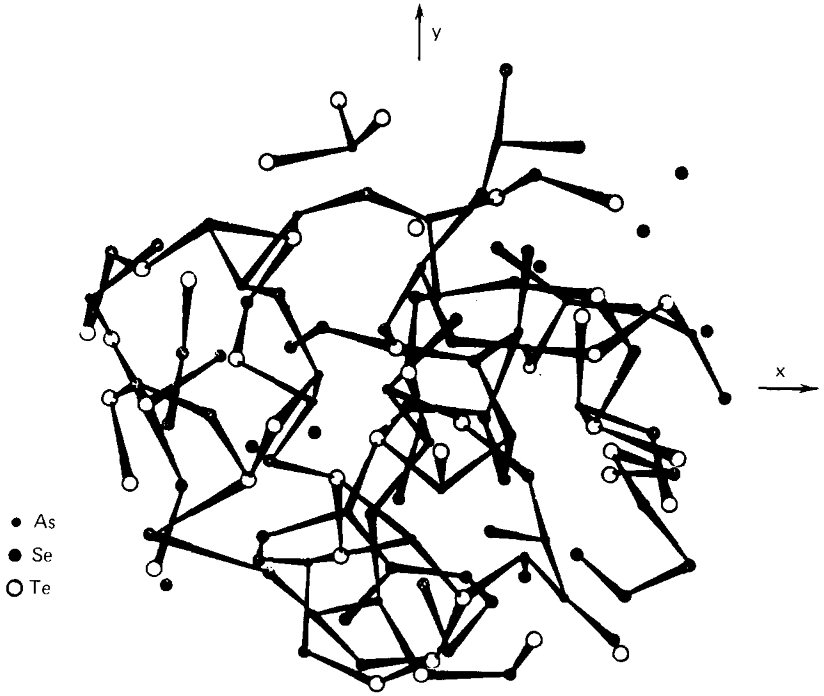

Fig. 5. Spatial representation of the model of $As_{0.20}Se_{0.50}Te_{0.30}$ alloy by hypothesis of threefold coordination for As.

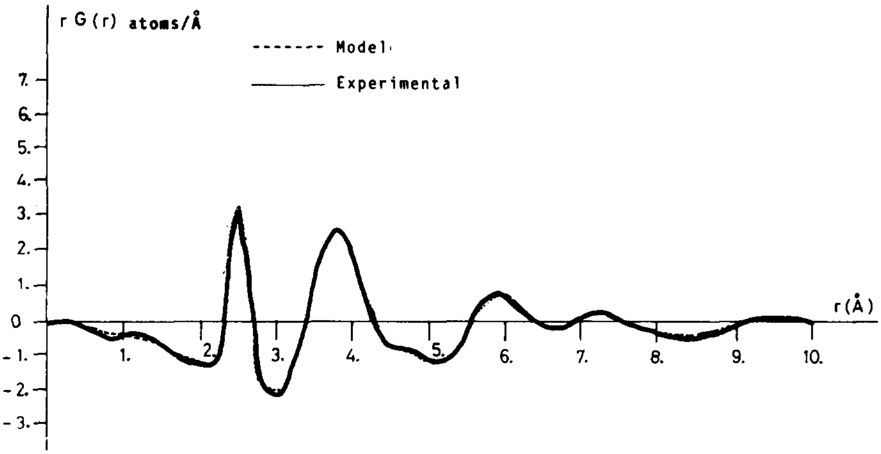

Fig. 6. Representation of calculated (dotted line) and experimental (solid line) RDFs by hypothesis of threefold coordination for As.

Indeed, in the first model 25% of the Se atoms and 17% of the Te present onefold coordination, but they are all found at less than 2 Å from the surface limiting the model, and thus it is possible for them to form bonds with other atoms located beyond the surface, to complete adequate coordination. It should be pointed out that in this model 10% of the Se atoms and 12% of the Te atoms present threefold coordination, these atoms always establishing bonds between tetrahedral units, or between these and chains.

As for the second model, it must be pointed out that 65% of the Se atoms and 77% of the Te atoms with coordination one are found at distances less than 2 Å from the surface limiting the model, thus being able to satisfy their bonds with atoms outside this surface.

The mean bonding distances calculated for each model are shown in table 3

The mean value of the As–As bonding length in model As(4) is 2.59 Å, which is relatively greater than that of this bond in amorphous As obtained by other authors [14,15] although it is close to the 2.51 Å of the aforementioned bond in the rhombohedral As [16].

It is important to stress that the theoretical value coincides exactly with the As–As distance in the molecular unit As_4S_4 [17] and is slightly higher than the covalent distance of this element [18].

It is possible that As–As bonds are present in the alloy studied, these being relatively longer than the typical covalent bonds due to circumstances similar to those found in the As_4S_4 molecule [17].

For the second model, As(3) a distance of 2.47 Å has been found. This value is very close to the length of the bond in amorphous As [14,15].

The bonding length found for As–Se is 2.52 Å in the first model and 2.49 Å in the second. These values are slightly higher than the 2.38 Å obtained as the sum of the covalent radii of these elements. However, it is very close to the 2.43 Å [19] in the amorphous alloy As_2Se_3.

Table 3
Averaged bonding distances $\langle d_{ij} \rangle$ for both models

Models	Bond	$\langle d_{ij} \rangle$ (Å)
Tetrahedrical coordination for As, As(4)	As–As	2.59
	As–Se	2.52
	As–Te	2.55
	Se–Se	2.45
	Se–Te	2.48
	Te–Te	2.48
Threefold coordination for As, As(3)	As–As	2.47
	As–Se	2.49
	As–Te	2.52
	Se–Se	2.47
	Se–Te	2.49
	Te–Te	2.57

The As–Te distances obtained for each model are 2.55 Å and 2.52 Å respectively. Both values, the first more than the second, are close to the deduced bond length for this pair as a sum of the covalent radii [18], which is found to be 2.58 Å.

The mean values of the theoretical Se–Se bond lengths are 2.45 Å and 2.47 Å respectively. On comparison with those found in the literature [20–22] it is seen that these are relatively higher, although in neither case is the difference higher than 6%. If, in addition, it is kept in mind that the values found in this study are similar to the 2.40 Å [21,22] of the trigonal and amorphous forms of Se, it is admissable that the values obtained are adequate for the $As_{0.20}Se_{0.50}Te_{0.30}$ alloy.

The Se–Te bond lengths that have been obtained are 2.48 Å in the first model and 2.49 Å in the second. These values are slightly lower than 2.54 Å, the sum of the covalent radii of the elements forming the bond, but much closer to 2.45 Å [23] found for binary $Se_{0.70}Te_{0.30}$ alloy.

Table 4
Averaged bonding angles $\langle \alpha \rangle$ for both models. The numbers in brackets represent the atom coordination

Models	Type	$\langle \alpha \rangle$ (deg)
Tetrahedral coordination for As, As(4)	As(4)	106.70
	Se(3)	105.52
	Te(3)	106.81
	Se(2)	111.42
	Te(2)	111.21
Threefold coordination for As, As(3)	As(3)	109.48
	Se(3)	105.54
	Te(3)	108.43
	Se(2)	111.71
	Te(2)	104.57

In the case of the Te–Te bond, the mean lengths obtained are 2.48 Å and 2.57 Å for each of the models. These values are clearly lower than 2.71 Å, the length found for this bond in the amorphous alloy $Al_{0.23}Te_{0.77}$ [4], but are closer to the 2.62 Å of the Te–Te distance in the $Al_{0.23}Te_{0.77}$ alloy [24] for a phase-separated model.

On the other hand, bearing in mind that the number of Te–Te bonds is small in both models, these may be considered analytically insignificant.

As regards the averaged bonding angles shown in table 4, it is observed that all the values are acceptable, since the first distortion that may be expected for an amorphous material is in the bonding angles.

5. Conclusions

Using X-ray diffraction data, we have built two structural models for amorphous $As_{0.20}Se_{0.50}Te_{0.30}$ alloy. These models may be described as a three-dimensional framework of covalent bonds either tetrahedrally oriented around the As atoms or with the As atoms threefold coordinated forming trigonal pyramids. Both basic structural units can be connected either directly through an atom which is bonded with more than one As atom, or by means of Se and Te atoms by way of chains.

References

[1] B.T. Kolomiets, Phys. Stat. Sol. 7 (1964) 359.
[2] S.R. Ovshinsky, Phys. Rev. Lett. 21 (1968) 1450.
[3] E. Márquez, P. Villares and R. Jiménez-Garay, J. Non-Cryst. Solids 74 (1985) 195.
[4] A. D'Anjou and F. Sanz, J. Non-Cryst. Solids 28 (1978) 319.
[5] J. Chang and D.B. Dowe, J. Non-Cryst. Solids 16 (1974) 72.
[6] O. Uemura, Y. Sagara, M. Tsushima, T. Kamikawa and T. Satow, J. Non-Cryst. Solids 33 (1979) 71.
[7] Y.T. Stesiv, Sov. Phys. Cryst. 18 (1973) 306.
[8] J. Vázquez, L. Esquivias, P. Villares and R. Jiménez-Garay Anales de Fisica, to be published.
[9] D.L. Price, M. Misawa, S. Susman, T.I. Morrison, G.K. Shenoy and M. Grimsditch, J. Non-Cryst. Solids 66 (1984) 443.
[10] Z.U. Borisova, Glassy Semiconductors (Plenum, New York, 1981).
[11] J.R. Fitzpatrick and C. Maghrabi, Phys. Chem. Glasses 12 (1971) 105.
[12] L. Cervinka and A. Hruby, J. Non-Crystal. Solids 48 (1982) 231.
[13] L. Esquivias and F. Sanz, J. Non-Cryst. Solids 70 (1985) 221.
[14] H. Krebs and R.Z. Steffen, Anorg. Allg. Chem. 327 (1964) 224.
[15] G.N. Greaves and E.A. Davis, Phil. Mag. 29 (1974) 1201.
[16] S. Itoh, T. Fujiwara and M. Okazaki, J. Non-Cryst. Solids 50 (1982) 49.
[17] A.J. Apling, A.J. Leadbetter and A.C. Wright, J. Non-Cryst. Solids 23 (1977) 369.
[18] L. Pauling, Uniones Quimicas (Kapelusz, Buenos Aires, 1969).
[19] Y. Sagara, O. Uemura, S. Okuyama and T. Satow, Phys. Stat. Sol. (a) 31 (1975) K33.
[20] H.A. Grimminger, Dissertation, Technische Hochschule, Stuttgart (1955).
[21] B.W. Corb, W.D. Wei and B.L. Averbach, J. Non-Cryst. Solids 53 (1982) 29.
[22] R.W. Fawcett, C.N.J. Wagner and G.S. Cargill, J. Non-Cryst. Solids 8–10 (1972) 369.
[23] R. Bellissent and G. Tourand, J. Non-Cryst. Solids 35–36 (1980) 1221.
[24] L. Esquivias and F. Sanz, J. Non-Cryst. Solids 72 (1985) 165.