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Topological features of $Cu_{15}As_{34}Se_{51}$ glassy semiconductor

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The addition of one d-element in binary chalcogenide glasses produces important changes in its physical behaviour [1]. Copper added to the As–Se amorphous alloy systems has been studied by many authors [2, 3], and significant modifications of its properties, such glass transition, net work connectivity and electrical conductivity, are seen. The material stability is improved because of an increase in the average coordination number. The electrical resistivity is lower when copper is present, as can be expected.

It is well-known that the electrical conduction of amorphous semiconductors strongly depends on the short-range structure [4]. In a previous work [5] the short-range order of $Cu_{15}As_{34}Se_{51}$ has been studied by X-ray diffraction from analysis of its radial distribution function (RDF). A conclusion of this work was that the structure is made up of a tetrahedral framework centred on copper atoms, there also being some centred on arsenic atoms. Furthermore, the existence of three-fold coordinated selenium atoms justifies the high connectivity of the structure (3.05 ± 0.1 atoms).

On the basis of this short-range order, a 1.07 nm radius spherical model has been build up by a random method described elsewhere [6–8], appropriate for materials obtained by the melt-quenching method. According to the experimental density ($4.87 \pm 0.15\,\mathrm{g\,cm^{-3}}$) of the compound, the model is made up of 200 atoms, of which 30 are copper, 70 arsenic, and 100 selenium, if we take into account the material composition.

The geometrical fitting of the structure has been carried out by comparison between the RDF of the model and the experimental one, multiplied by a theoretical function [9], simulating the shape and finite size of the model. In Fig. 1 both functions are shown after the model refinement being its quadratic standard deviation $\varepsilon^2 = 0.0242$, calculated as

$$\varepsilon^2 = \frac{1}{N}\,|\mathrm{RDF}_{\mathrm{exp}}(r_i) - \mathrm{RDF}_{\mathrm{mod}}(r_i)|^2$$

where r_i is the radial distance and N the number of points where the comparison is accomplished. ε^2 serves as criterion to decide the validity of the model.

TABLE I Coordination distributions in the final (initial) performed models

Type of atom	Coordination				
	4	3	2	1	0
Cu	15 (24)	9 (3)	5 (2)	1 (1)	–
As	12 (21)	28 (12)	20 (26)	9 (11)	1 (0)
Se	–	48 (28)	35 (48)	16 (21)	1 (3)

The atom coordination distributions of the initial state of the model (in brackets) and after the refinement process are given in Table I. It should be pointed out that the increase of the average coordination of selenium atoms in the final model (from 2.0 atoms to 2.3 atoms) is in agreement with the statement formulated from the RDF analysis. This situation, together with the presence of four-fold coordinated arsenic atoms, indicates a drastic breakdown of the 8-N rule which is verified when a no d-element is added to the As–Se amorphous alloy system [2].

If the coordination of atoms is related to the topological disorder, the bonding distance and angle distributions convey to us the geometrical disorder. Table II shows the averaged bonding distances (ABD) and angle (ABA) with standard deviations. As can be observed, the Se–X ABDs are further from the sum of covalent radii than the As–X ABDs, especially Cu–Se, indicating a smaller covalent character of this bond. On the other hand, As–As, As–Se and Se–Se ABDs approach the values obtained by us for other alloys containing As–Se [6, 7]. Finally, the calculated average radius of the first coordination sphere in the model is equal to that obtained for the first peak position of experimental RDF [5] (2.43 ± 0.01 and 2.44 ± 0.01 atoms, respectively).

The number of bonds of each type present in the proposed model are indicated in Table III. Beside each are the corresponding quantities of a hypothetical model with an ideal aleatory distribution of first neighbours, used as a reference. In this calculation we have taken into consideration that our model presents 111 dangling bonds over 620 in total (of which 37 could

TABLE II Averaged bonding distances (ABD) and angles (ABA) of different bonds present in the model

Bond	ABD (nm)	SCR* (nm)	Standard distances (nm)
Cu–Cu	0.229 ± 0.015	0.234	0.256 metal
Cu–As	0.242 ± 0.011	0.237	0.253 [10]
Cu–Se	0.245 ± 0.010	0.233	0.242 [10]
As–As	0.243 ± 0.009	0.240	0.249 a-As 0.241 [7]
As–Se	0.244 ± 0.011	0.236	0.241 [7]
Se–Se	0.240 ± 0.009	0.232	0.240 a-Se 0.240 [7]
Angle	**ABA (deg)**		
X–Cu–X	108 ± 25		
X–As–X	110 ± 18		
X–Se–X	106 ± 21		

*Sum of covalent radii.

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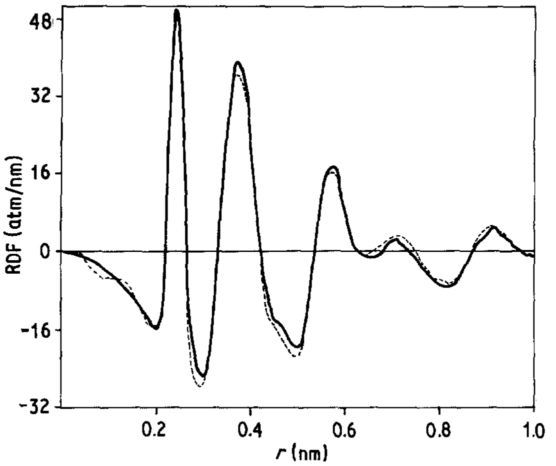

Figure 1 Geometrical fitting of the performed model. $\varepsilon^2 = 0.0242$, (——) model, (– – –) experimental values.

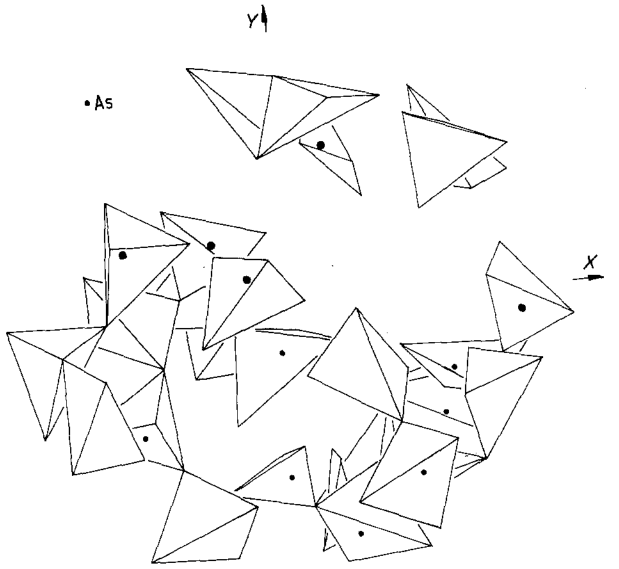

Figure 2 Schematic spatial representation of the tetrahedral clusters, (●) centred on As atoms.

be satisfied with hypothetical external neighbours). After Borisova [1], the chemical interaction of copper with arsenic and selenium is the result of the participation of the $4s^1$ electron of copper in the Cu–Se chemical bond and the formation of the donor–acceptor Cu : As bond. In this way, one of the Cu–X bonds will always be a Cu–Se bond and the other three would be satisfied according to kinetic criteria, i.e. a distribution directly proportional to the concentration of the elements in the alloy.

TABLE III Bonds number in an aleatory distribution and in the proposed model

Bond	Random	Model
Cu–Cu	9	4
Cu–As	40	30
Cu–Se	41	60
As–As	41	28
As–Se	83	94
Se–Se	43	39

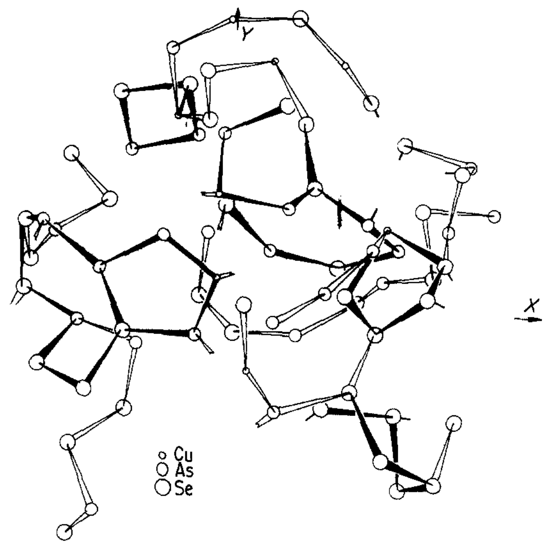

Figure 3 Rings (full bonds) and branched chains (empty bonds) present in the model.

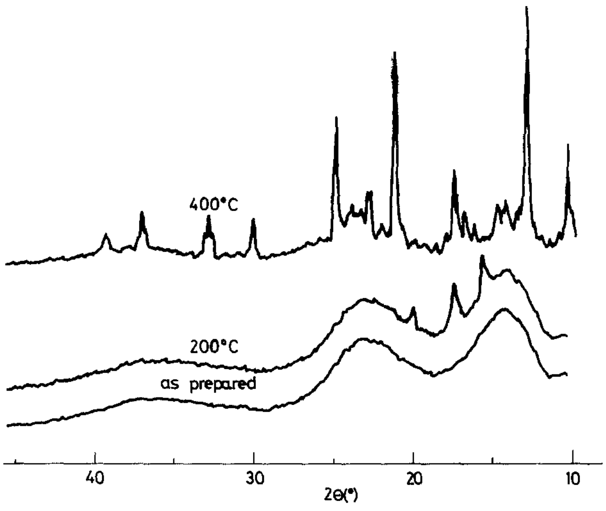

Figure 4 X-ray diffraction patterns after thermal treatment for the outline temperatures (Mo$K\alpha$ = 0.0711 nm).

If we admit the preceding statement and the average coordination of the elements proposed by us previously [5], (i.e. 4, 3.53 and 2.53 for copper, arsenic and selenium, respectively), an aleatory distribution of the remaining bonds would give rise to 6, 33 and 54 Cu–Cu, Cu–As and Cu–Se, respectively. This result is very near to the situation presented by the

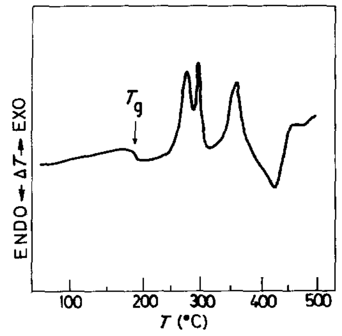

Figure 5 DTA thermogram of the alloy ($10°C\,min^{-1}$ and 20 mg weight).

model; thus we can state that the Cu–Se bond is really more probable than Cu–Cu or Cu–As. The less covalent character of the former would influence drastically the decrease of electrical resistivity, as proposed by Haifz *et al.* [3].

Two topologies can be distinguished in the resulting structure: on the one hand a network consisting of tetrahedra centred on copper and arsenic atoms, on the other hand a distribution of rings and chains made up of arsenic and selenium atoms, the proportions of which are near the crystalline phases appearing when thermal treatment is accomplished [3].

This structural result seems to indicate a mixture of phases in the alloy. It is consistent with the X-ray diffraction pattern (Fig. 4) after two different thermal treatments (200 and 400° C for 1 h). The crystalline phase appearing at 200° C (near $T_g = 174°$ C) is not present in the sample heat treated at 400° C. This behaviour is corroborated by the DTA thermogram (Fig. 5) where three exothermic peaks can be observed before the melting point.

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