TETRAHEDRAL BONDING IN THE GLASSY SEMICONDUCTOR $Cu_{15}As_{34}Se_{51}$

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An X-ray diffraction radial-distribution study of the $Cu_{15}As_{34}Se_{51}$ alloy obtained by the melt-quench method, has been performed. We reject a model with As three-fold and Se two-fold coordinated. The short-range order may be a tetrahedral framework centered on Cu and some on As atoms. The Cu–Se bond may be responsible for its electrical resistivity.

1. Introduction

Chalcogenide glasses are in general characterised by high values of resistivity, involving certain limitations in their applications, as well as difficulty in electrical measurements. Borisova [1] has shown that the addition of some d-elements in amorphous material can lead to significant changes in their resistivities. In this way Haifz et al. [2] attribute these changes in electrical behaviour of compounds of the Cu–As–Se amorphous alloy system to the formation of Cu–Se bonds. In this way the electrical conduction at room temperature would be due to the electronic structure associated with these bonds rather than those of As–Se or Se–Se bonds. The aim of this study is to investigate the short-range order of this alloy by X-ray diffraction methods. Electrical resistivity measurements carried out by Márquez et al. [3] on the sample used in the diffraction experiment yielded similar values (1.2×10^6 Ω cm of Haifz et al. against 7.9×10^5 Ω cm of Márquez et al.) indicating similar electrical behaviours. If the electrical conduction of amorphous semiconductors depends strongly on the short-range structure [4], a comparison of the structure proposed in the early work with our results will be possible.

X-ray diffraction is a basic method in structural research. Amorphous materials, which lack long-range order, are resolved by means of an analysis of the radial distribution function (RDF). This is obtained as the Fourier transform of an experimental intensity function.

2. Experimental

Amorphous bulk materials were prepared by the usual melt-quench technique, the constituents Cu, As and Se (4N purity) were weighed and sealed in an evacuated and inerted quartz ampoule, which was then heated at 950°C for 4 h. During the melt process the tube was rotated in order to intermix the constituents to ensure homogeneization of the melt.

A standard X-ray diffraction pattern did not show any crystallinity remains. The intensities were collected using a scintillation counter. Averaged values lay within 5% of the mean. The mean density of the solid was 5.1 ± 0.2 g cm^{-3}.

3. Radial distribution function

The RDF(r) is calculated as:

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

where ρ_0 and $\rho(r)$ represent, respectively, the mean atomic distribution and the local atomic density. $G(r)$ stands for the Fourier transform of a function of experimental intensities:

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

with

$$F(s)=si(s)\quad\text{and}\quad i(s)=\frac{I_{\mathrm{eu}}-\sum x_i f_i^2}{(\sum x_i f_i)^2},$$

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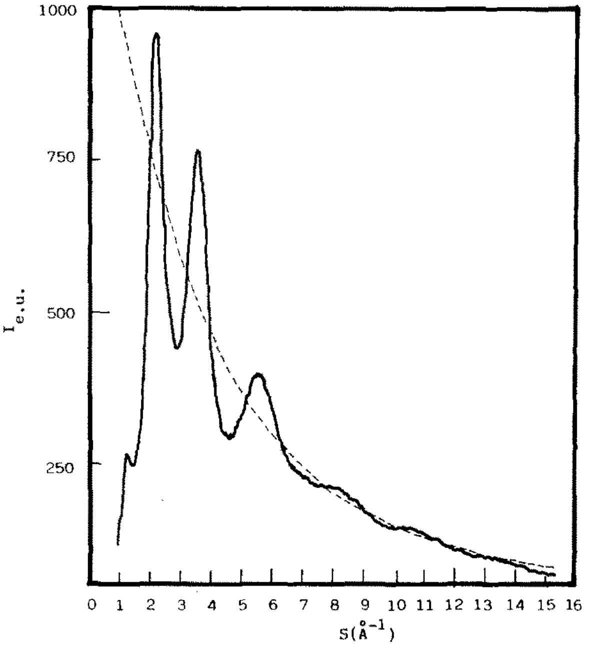


Fig. 1. Normalized experimental intensities (full line) and structure-independent dispersion curve (dotted line) in electronic units.

where x_i is the atomic fraction of element i with i = Cu, As, Se and I_{eu} represents the resulting intensity values in electronic units after correction. Fig. 1 represents I_{eu} where the oscillation on the structure-independent dispersion curve is observed.

To avoid spurious oscillations in $G(r)$ due to the lack of high-s (scattering vector modulus) data, theoretical extension of the data was carried out by means of a method based on that described by Shevchick and Paul [5] and D'Anjou and Sanz [6]. In the present case, the fitting was carried out between 7.75 and 10.32 Å^{-1} reaching a variance of 0.9% between theoretical and experimental functions, as shown in fig. 2.

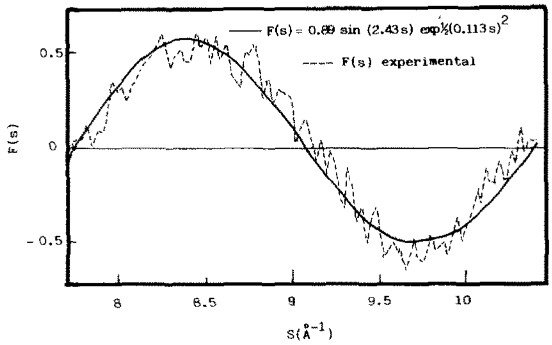


Fig. 2. Fitting interval for theoretical extension of experimental interference function.

The RDF(r) after theoretical extension of the experimental data in $F(s)$ up to s = 30 Å^{-1} have been plotted in fig. 3.

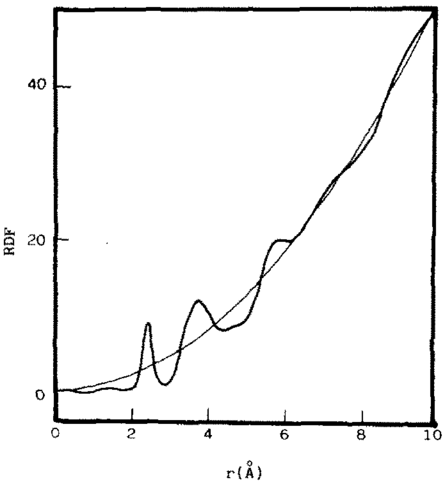


Fig. 3. Radial distribution function (RDF).

4. Results and discussion

The analysis of experimental RDF(r) of the present alloy is summarized by the values given in table 1.

The limits of the first peak, which corresponds to the first near-neighbour distances, do not allow us to reject any kind of bond between the different elements in the alloy, because the whole of the standard bond distances are included between these limits. The first peak position (2.44 Å) is very close to the 2.42 Å of the Cu–Se bond distance, in such a way that it seems to indicate an important amount of these bonds in the alloy. The area under the first peak represents the average value of first neighbours (i.e. the atomic network connectivity). As the ideal average coordination value for amorphous chalcogenides is 2.45 at. [7], the obtained value of 3.05 at. indicates a great network connectivity and therefore a probable loss of the covalent behaviour of As and Se atoms.

On the other hand, the theoretical expression of the

Table 1
Main RDF characteristics

Peak	Position(Å)	Limits(Å)	Area(at.)	Error
1	2.44±0.01	2.00–2.90	3.05	±0.1
2	3.77±0.01	-	11.6	±0.2

area under the first peak is,

$$A=\frac{1}{(\sum x_i Z_i)^2}\sum_i\sum_j x_i Z_i Z_j n_{ij},$$

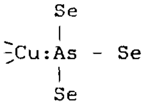
where x_i and Z_i are the fraction and atomic number of element i, respectively, and n_{ij} the average number of i-type atoms in the first coordination sphere of a j-type atom. Using the experimental area A, values of n_{ij} may be proposed from the following hypotheses:

(A) Copper coordination. If n is the mean coordination of Cu and As, Se fit the $8-N$ rule, that is mean coordination of 3 and 2, respectively, an expression for the area is obtained in the form:

$$A=2.11+0.11\ n.$$

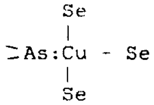
As the terms n_{ii} are approximately 10^{-3}, given the similarity in atomic numbers (Z_i), they have been ignored. With this expression and the experimental area, the value obtained for n is between 7 and 10, which is not probable for this kind of alloys obtained by the melt-quench method. Besides, this would not agrée with the experimental density. Therefore, we have rejected this model where As and Se fit the "octet" rule. This result agrees with those obtained for other alloys in this system studied by Liang et al. [8].

(B) Neutral Cu model. After Borisova [1], the chemical interaction of Cu with As and Se 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, given the unshared pair of electrons of the As atom in the vacant 4p orbits of the Cu atom. This would produce a Cu sp^3 hybridization, and an increase in the coordination of some As atoms, so that the structural units described below would appear in the glass:



$$\gtrdot\mathrm{Cu{:}}\underset{\displaystyle\mathrm{Se}}{\overset{\displaystyle\mathrm{Se}}{\mathrm{As}}}-\mathrm{Se}$$

and



$$>\mathrm{As{:}}\underset{\displaystyle\mathrm{Se}}{\overset{\displaystyle\mathrm{Se}}{\mathrm{Cu}}}-\mathrm{Se}$$

The aforementioned Cu coordination could likewise be satisfied by d^3s hybridization also tetrahedral, or by dsp^2 hybridization which is square planar and could form a ring framework within the tetrahedral network. Nevertheless, the participation of d-orbitals in the bond confers greater instability and is considered less probable. On the other hand, the fabrication method used implies a greater preponderance of kinetic rather than thermodynamic criteria. Therefore, the probability that the electronic pair is provided by As or Se, is only proportional to their concentrations in the alloy.

(C) Short-range order. If we suppose that Cu is covalently bonded to As and Se atoms in a ratio of two to three, then of every five sp^3 orbitals, two are shared with As and three with Se, implying that 2/5 of the As atoms will have coordination 4 and 3/5 of the Se atoms coordination 3. This would result in a mean coordination of

$$n(\mathrm{As})=3.53,\quad n(\mathrm{Se})=2.53.$$

These results lead to a value of the area under the first peak which fits the obtained experimental value. The formation of Cu–Cu bonds has not been taken into account, given their low concentration.

From EXAFS studies in alloys of this system, Hunter et al. [9] also rejected a model with As three-fold and Se two-fold coordinated and proposed an increase in the coordination of both elements, as well as four-fold coordination for Cu. In this study [9] the possible existence of four-fold coordinated Se is admitted, thus an expression for the area as a function of the Se coordination (n) and the number of As–Se bonds (x) has been calculated,

$$A=1.663+0.544\ n-4.71\times10^{-4}x.$$

This expression is represented in fig. 4, only as a function of n, as the third term is of the order of 10^{-3} and is not significant. The shaded area in fig. 4 corresponds to a negative amount of four-fold coordinated Se atoms, which is illogical. On the other hand,

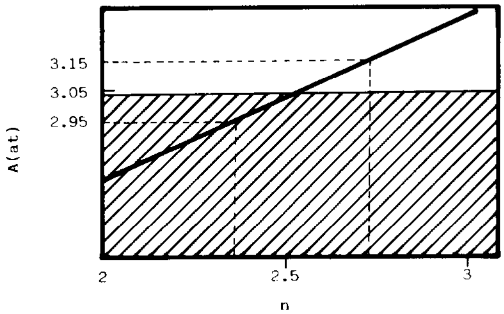


Fig.4. First peak area versus Se coordination number.

the experimental area (3.05 at.) is close to the upper limit of the shaded zone indicating the low probability of tetrahedric Se in this alloy.

The short-range structure of this amorphous alloy is found between the possible values of the straight line of fig. 4. This would result in a tetrahedral framework centered on Cu atoms, there also being some centered on As atoms which would contribute to a greater continuity of the network, verified by the experimental average coordination number. It is probable that there exits a framework of deformed rings intermingled with the tetrahedra if the Cu hybridization is square planar.

References

[1] Z.U. Borisova, Glassy semiconductors (Plenum Press, New York, 1981).
[2] M.M. Haifz, M.M. Ibrahim, M.M. Dongol and F.H. Hammad, J. Appl. Phys. 54 (1983) 1950.
[3] E. Márquez, J. Vázquez, P. Villares and R. Jiménez-Garay, II Simposio Iberico de Fisica de la Materia Condensada (P3-20) Sevilla, 1986.
[4] N. Mott and E.A. Davis, Electronic processes in non-crystalline materials, 2nd Ed. (Clarendon Press, Oxford, 1979).
[5] N.J. Shevchick and W. Paul, J. Non-Cryst. Solids 8-10 (1972) 369.
[6] A. D'Anjou and F. Sanz, J. Non-Cryst. Solids 28 (1978) 319.
[7] J.C. Phillips, Phys. Stat. Sol. 101b (1980) 473.
[8] K.S. Liang, A. Biennenstock and C.W. Bates, Phys. Rev. B10 (1974) 1528.
[9] S.H. Hunter, A. Biennenstock and T.M. Hayes (Taylor and Francis, London, 1977) p.73.