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Structure of the $Cu_{15}As_{34}Se_{51}$ amorphous alloy by extended X-ray absorption fine structure spectroscopy

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Abstract

The structure of the $Cu_{15}As_{34}Se_{51}$ amorphous alloy has been studied by X-ray absorption spectroscopy to determine the chemical environment of the three elements. Data are in accordance with the fourfold Cu coordination and an increase in the As and Se coordination numbers, compared with the coordination obtained for the amorphous As_2Se_3 compound.

1. Introduction

It has been shown [1] that the addition of a transition series element in amorphous material can lead to changes in their resistivity. The family obtained by adding Cu to the As–Se glasses is interesting because the electrical conductivity increases and the activation energy decreases by Cu addition. These electronic properties are related to a structure in which atoms are assumed to be tetrahedrally coordinated [2]. The aim of the present work is to determine the distance and the coordination of the components.

The electrical properties of Cu–As–Se amorphous alloy system has been attributed to the formation of Cu–Se bonds [3]. Electrical conduction at room temperature may be due to the electronic structure associated with these bonds rather than those of a As–Se or Se–Se bond [2].

The short range order of some alloys of this family has been investigated [3,4]. X-ray diffraction methods have been applied to determine the bonding and topology features of $Cu_{15}As_{34}Se_{51}$ glassy semiconductor [5,6]. Combined X-ray diffraction and X-ray absorption methods have been used in a study of $Cu_8As_{26}Se_{66}$ and $Cu_{26}As_{37}Se_{37}$ glasses [7,8] in which the As/Se ratio differs and the Cu concentration spans the range of glass formation.

Experimentally, the metal atoms are tetrahedrally coordinated [2,9,10] and the general structural model proposed by Liu and Taylor [11] gives a tetrahedral structure when Cu is added to the

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glasses. Extended X-ray absorption fine structure (EXAFS) spectroscopy is a useful technique to determine pair distances and coordination numbers separately for the three components. It has been recently used for other alloys of the same Cu–As–Se amorphous family [12]. The average coordination number will be calculated from the EXAFS data and compared with that obtained from wide angle X-ray diffraction spectroscopy. Monte Carlo methods will be used to construct a model of the structure [13–15]. The EXAFS experiments have been performed at the three absorption K-edges of the Cu, As and Se elements at room temperature. Initially three samples were selected with compositions $Cu_8As_{26}Se_{66}$, $Cu_{26}As_{37}Se_{37}$ and $Cu_{15}As_{34}Se_{51}$. The large difference in Cu concentration will provide data from which differences in the structure of these three composition can be determined. Results for $Cu_8As_{26}Se_{66}$ and $Cu_{26}As_{37}Se_{37}$ samples have been reported [7,8]. In the present work, EXAFS experiments are reported on the $Cu_{15}As_{34}Se_{51}$ composition and are compared with the previous X-ray diffraction studies. EXAFS investigations have been performed on some $Cu_x(As_{0.4}Se_{0.6})_{100-x}$ samples at the Cu K-edge by Hunter et al. [4] and by Laderman et al. [16] in a wide range of Cu concentration. In this work, the selected value for x ($x = 15$) differs from those previously reported. EXAFS data are analyzed taking into account the theoretical backscattering phase and amplitude functions which avoid the problem of references compounds.

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 quartz ampoule, which was then heated at 950°C for 4 h. During melting, the tube was rotated in order to mix the constituents to ensure a homogeneous liquid [17].

EXAFS experiments were carried out on the EXAFS-III beamline at D.C.I. storage ring (Orsay) with an electron beam energy of 1.85 GeV and an average current of 250 mA. Data were collected with a fixed exit monochromator using two Si(311) crystals in transmission mode; detection was made using two ion chambers filled with air. The fast EXAFS data acquisition operation mode [18] was used to collect at least ten spectra to improve the signal to noise ratio. Energy resolution was estimated to be better than 2 eV based on the Cu foil 3d near edge feature [19]. The energy calibration was monitored using the Cu foil sample, and was set as 8991 eV at the first maximum above the edge.

Samples were prepared by grinding, sieving and then selecting particles < 10 μm in size by floating the powder. The particles were then spread on a tape. About two layers of tape were used to fabricate samples with an adequate absorption jump ($0.1 \le \Delta\mu x \le 1.0$) and a maximum for the total absorption less than 1.5 ($\mu x \le 1.5$).

3. Results

Fig. 1 shows the extended X-ray absorption spectra at the K-edge of the three components of the sample $Cu_{15}As_{34}Se_{51}$. The same sample thickness was used for all measurements.

A classical procedure has been used to analyze the EXAFS spectrum [20]: above the edge, the signal background was removed by a multi-iteration curve smoothing procedure. The analysis of the EXAFS signal to obtain the position of the neighbours around the absorber atom has been carried out using the well known EXAFS expression [21]

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} \exp\left(-2k^2\sigma_j^2\right) \exp\left(-\Gamma_j R_j/k\right) \times f_j(k) \sin\left[2kR_j + \phi_j(k)\right]. \quad (1)$$

This expression describes the EXAFS oscillations for a Gaussian distribution of neighbours around the absorbing atom, in the single scattering theory and in the plane-wave approximation. k is the wave vector of the photoelectron, which is related to the electron mass, m_e, and with the threshold energy, E_0, by

$$k = \left[(2m_e/h^2)(E - E_0)\right]^{1/2}. \quad (2)$$

N_j is the average coordination number for the Gaussian distribution of distances centered at the R_j value, σ_j is the Debye–Waller contribution, $\phi_j(k) = 2\delta(k) + \gamma_j(k)$ is the phase shift, $\delta(k)$ and $\gamma_j(k)$ being the central and backscattering atom phase shifts, respectively, $f_j(k)$ is the amplitude function of the backscattering atoms and Γ_j is related to the mean free path of the photoelectron.

Fig. 2 shows the Fourier transform of the $k^3\chi(k)$ weighted signals for the alloy; a Hanning window was used within an interval from 3 to 14 Å^{-1}. These transforms are related to the radial distribution functions (RDF) of atoms surrounding the three component atoms. The first coordination spheres are given by the mean peaks centered about 2 Å. EXAFS information from amorphous material is related only to the first coordination sphere because the EXAFS signal is only sensitive to the short range order.

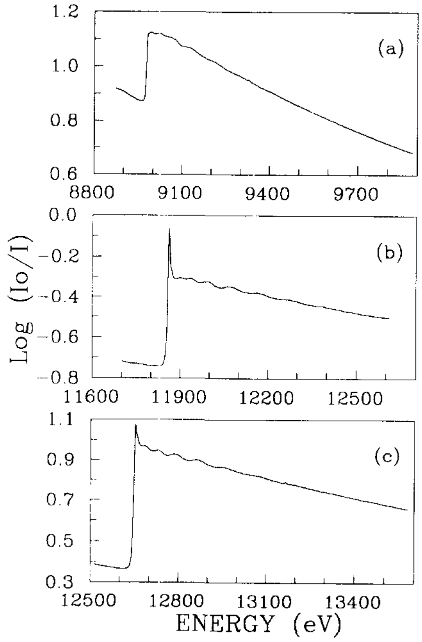

Fig. 1. Room temperature EXAFS spectra of the $Cu_{15}As_{34}Se_{51}$ amorphous alloy taken at: (a) Cu K-edge, (b) As K-edge and (c) Se K-edge.

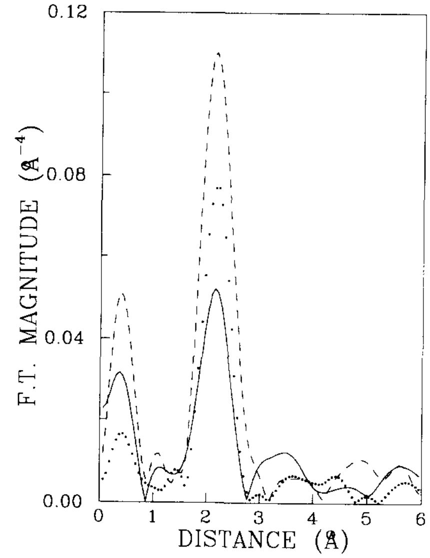

Fig. 2. Fourier transform of the $k^3\chi(k)$ weighted EXAFS signal of the $Cu_{15}As_{34}Se_{51}$ amorphous alloy at the Cu-edge (———), As-edge (– – – – –) and Se-edge (· · · · · ·).

4. Discussion

Data have been fitted in the k- and R-spaces (Fig. 3) by comparison of experimental filtered data and the spectra calculated by Eq. (1); finally, a mean square fitting has been carried out in k-space to obtain better parameters. $f_j(k)$ and $\phi_j(k)$ have been taken as those reported by Mckale et al. [22]. In order to reduce the number of EXAFS parameters we have taken into account the different hypotheses previously described in the literature [1,5,6]; as can be seen below, the hypotheses fix some parameters in the EXAFS data analysis.

The first model we consider is one in which As and Se fit the ‘octet’ rule [23] and gives for them a coordination of 3 and 2, respectively. This model has been tested by trying to fit the three EXAFS spectra taken at Cu, As, Se K-edges. It is possible to fit the As and Se data with the 3 and 2 coordinations but the coordination of Cu atoms would then be in the range from 2 to 3 which is inconsistent with the data on the area under the first peak in the RDF.

According to Borisova [1], the chemical interaction of Cu with As and Se is due to the partici-

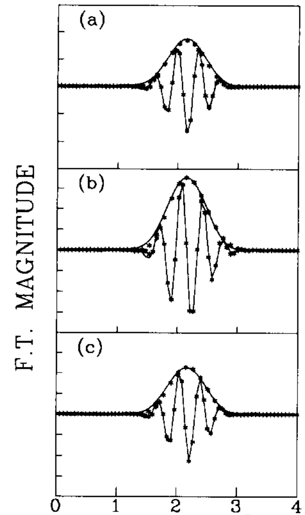

Fig. 3. Comparison between experimental (points) and calculated (———) of the modulus and imaginary part of the filtered EXAFS data in R-space at: (a) Cu K-edge, (b) As K-edge and (c) Se K-edge.

pation of the $4s^1$ electron of copper in the Cu–Se chemical bond and the formation of a donor–acceptor Cu : As bond, and the unshared pair of electrons of the As atom are donated to the vacant 4p orbit of the Cu atom. This process could produce a Cu sp^3 hybridization and an increase in the coordination of some As atoms so that the structural units appearing in the glasses would be four-coordinated As atoms (1Cu and 3Se atoms) and four-coordinated Cu atoms (1As and 3Se). This Cu coordination could likewise be satisfied by d^3s 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 [5]. This model will be called, in the following, the neutral model.

In the short-range order model, it is assumed that Cu is covalently bonded to As and Se atoms in a ratio of two to three, implying that 2/5 of the As atoms will have coordination 4 and 3/5 of the Se atoms coordination 3. In this model, the formation of Cu–Cu bonds is ignored because of their low concentration. These models do not fit, properly, the EXAFS spectra, because the Cu–Cu contribution is necessary to have a good fitting of the Cu environment with that deduced from the spectra.

From our EXAFS data fitting, we propose a model intermediate between the neutral Cu model and the short-range order model. We assume the Cu atoms have a Cu–Se chemical bond through the formation of sp^3 hybrids with the $4s^1$ electron of copper and thus a coordination 4 for the Cu atoms, and the coordination of As and Se atoms being relatively the same as in the As_2Se_3

Table 1
Set of values obtained as the best fit of EXAFS signal

Sample	Edge pair	E_0	ΔE_0	N	d (Å)	σ (Å^2)	Γ (Å^{-2})	ϵ ($\times 10^{-5}$)
As_2Se_3 (c)	[As] As–Se	11 857.6	5.0	2	2.41	0.08	0.9	1.45
	As–Se			1	2.42	0.08		
	[Se] Se–As	12 643.7	3.0	2	2.42	0.08	0.9	2.39
$AsSe_3Ag$ (c)	[As] As–Se	11 857.6	13.0	3	2.41	0.105	2.5	1.88
$Cu_{15}As_{34}Se_{51}$	[Cu] Cu–Cu	8976.8	−7.7	0.50	2.23	0.097	1.66	3.54
	Cu–As			1.00	2.35	0.098		
	Cu–Se			2.50	2.37	0.097		
	[As] As–Cu	11 857.5	−3.4	0.44	2.35	0.068	1.66	8.90
	As–Se			3.00	2.42	0.068		
	[Se] Se–Cu	12 646.4	−6.0	0.61	2.37	0.075	1.66	4.84
	Se–As			2.00	2.42	0.075		

E_0, the energy threshold; ΔE_0, the energy shift; N, the number of neighbours; R, the distance; σ, the Debye–Waller factor; Γ, the mean free path contribution factor; ϵ, the residual parameter. The fitting of the crystalline As_2Se_3 and $AsSe_3Ag$ are given for comparison.

compounds but with the addition of Cu atoms increases their coordination numbers.

In order to fit the EXAFS spectra, we have assumed the copper coordination to be one Se bonded atom and the three others to be bonded atoms as three numbers proportional to the stoichiometry in the sample; with this hypothesis, coordination numbers consistent with the EXAFS data are given in Table 1. In order to calculate the Se–Cu partial coordination we have corrected it by the stoichiometric factor 15/61 (a similar correction has been made for As–Cu partial coordinations) and the Se–As and As–Se coordination has been taken as the same as in crystalline As_2Se_3 and glass compound (i.e., two As atoms around the Se and three Se around an As atom) and the same Debye–Waller factor was assumed for all the pairs which contributed to the peak. In order to begin the fitting procedure, the distances have been taken as the averaged bonding distances given by the model of this structure [6], and it can be pointed out that they are a very good approximation.

In Table 1 the coordination number of each atom and the obtained distances and other EXAFS parameters are given. The ϵ parameter gives the deviation of the calculated EXAFS spectrum from the experimental data. To evaluate ϵ, we have defined the residual parameter as $\epsilon^2 = (1/N)\Sigma(\text{data}_i - \text{model}_i)^2$. It must be noted that the obtained coordinations are $n(\text{Cu}) = 4$; $n(\text{As}) = 3.44$, $n(\text{Se}) = 2.61$, which gives a mean coordination of 3.1, which is, within errors of measurement, the same as that obtained from the RDF measurements (3.05 ± 0.1) [5] on the same type of sample.

The pre-edge structure may give information about site geometry and valence state and the X-ray absorption near edge structure (XANES) region contains stereo-chemical information (e.g., bond angles). Fig. 4 shows the XANES spectra of the $Cu_{15}As_{34}Se_{51}$ amorphous sample at the Cu, As and Se K-edges by comparison with two other alloys of the Cu–As–Se family. We observe that valence state does not depend, within errors of measurement, on the relative concentration of the elements because the threshold position is unshifted. The Cu absorption edge is not affected by the Cu concentration nor by the As/Se ratio. On the other hand, the As and Se K-edge XANES spectra differ in the features at 11 870 and 12 660 eV. A comparison with the As_2Se_3 crystalline reference compound shows that these difference are in accordance with the monotonic increase of their As and Se coordination numbers which make different environments for the atoms [24].

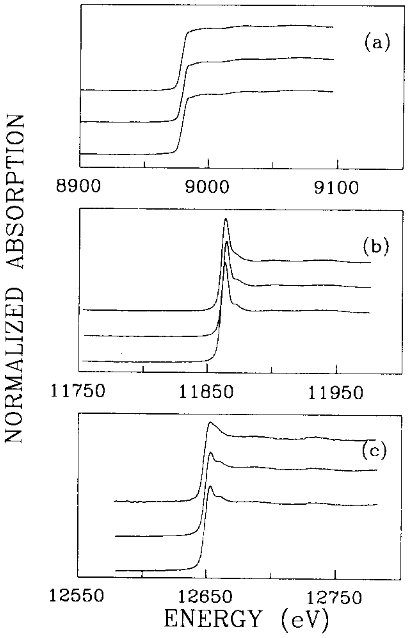

Fig. 4. Comparison of XANES spectra at the three absorption edges for different samples: $Cu_8As_{26}Se_{66}$, $Cu_{15}As_{34}Se_{51}$ and $Cu_{26}As_{37}Se_{37}$ (respectively from above to below) (a) Cu K-edge, (b) As K-edge and (c) Se K-edge.

5. Conclusions

Our fit gives a fourfold coordination for the Cu atoms and a coordination of 3.44 and 2.61 for the As and Se atoms, respectively, in accordance with the RDF measurements. We propose a structural model in which the copper is always bonded to one selenium atom and the other three bonds are occupied by Cu, As and Se proportionately to their concentrations in a sample. The increase of the As and Se coordination is caused by the addition of the Cu which forms As–Cu and Se–Cu bonds in addition to the As–Se bonds in the As_2Se_3 compound.

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References

[1] Z.U. Borisova, Glassy Semiconductors (Plenum, New York, 1981).

[2] K.S. Liang, A. Bienenstock and C.W. Bates, Phys. Rev. B10 (1974) 1528.

[3] M.H. Haifz, M.M. Ibrahim, M.M. Dongol and F.H. Hammad, J. Appl. Phys. 54 (1983) 1950.

[4] S.H. Hunter, A. Bienenstock and T.M. Hayes, in: The Structure of Non-Crystalline Materials, ed. P.H. Gaskell (Taylor and Francis, London, 1977) p. 73.

[5] J.M. Conejo, N. de la Rosa-Fox, L. Esquivias and R. Jiménez-Garay, Mater. Lett. 4 (1986) 481.

[6] N. de la Rosa-Fox and L. Esquivias, J. Mater. Sci. Lett. 7 (1988) 105.

[7] D. Gómez-Vela, L. Esquivias and C. Prieto, in: The Physics of Non-Crystalline Solids, ed. L. David Pye, W.C. LaCourse and H.J. Stevens (Taylor and Francis, London, 1992) p. 86.

[8] D. Gómez-Vela, L. Esquivias and C. Prieto, Phys. Rev. B48 (1993) in press.

[9] S. Neov, M. Baeva, I. Gerassmore and M. Nikiforova, Phys. Status Solidi A57 (1980) 795.

[10] Z.M. Saleh, G.A. Williams and P.C. Taylor Phys. Rev. B40 (1989) 10557.

[11] J.Z. Liu and P.C. Taylor, Solid State Commun. 70 (1989) 81.

[12] C.Y. Yang, M.A. Paesler and D.E. Sayers, Phys. Rev. B36 (1987) 980; 36 (1987) 9160; 39 (1989) 10342.

[13] L. Esquivias and F. Sanz, J. Non-Cryst. Solids 70 (1985) 221.

[14] N. de la Rosa-Fox, L. Esquivias, P. Villares and R. Jimenez-Garay, Phys. Rev. B33 (1986) 4094.

[15] D. Gomez-Vela, L. Esquivias and C. Prieto, Phys. Status Solidi B169 (1992) 303.

[16] Z.S. Laderman, A. Bienenstock and K.S. Liang, Solar Energy Mater. 8 (1982) 15.

[17] A.E. Owen, in: Electronic and Structural Properties of Amorphous Semiconductors, ed. P.G. Le Comber and J. Mort (Academic Press, London, 1973) p. 161.

[18] C. Prieto, P. Lagarde, H. Dexpert, V. Briois, F. Villain and M. Verdaguer, Measur. Sci. Tech. 3 (1992) 325.

[19] See, for instance, the 'Report on the International Workshops on Standard and Criteria', ch. 195, in: X-Ray Absorption Fine Structure, ed. S.S. Hasnain (Ellis Horwood, London, 1991).

[20] B.K. Teo, EXAFS: Basic Principles and Data Analysis, Inorganic Chemistry Concepts, Vol. 9 (Springer, Berlin, 1986).

[21] B.K. Teo and Lee, J. Am. Chem. Soc. (1979) 2815.

[22] A.G. Mckale, B.W. Veal, A.P. Paulikas, S.K. Chan and G.S. Knapp, J. Am. Chem. Soc. 110 (1988) 3763.

[23] N.F. Mott, Adv. Phys. 3 (1967) 49.

[24] V. Mastelaro, S. Benazeth, R. Ollitrault-Fichet, A. Ibañez, H. Dexpert and J. Duque, in: Proc. 2nd Europ. Conf. on Progress in X-Ray Synchrotron Radiation Research p. 659, ed. E. Balerna, E. Bernieri and S. Mobilio (SIF, Bologna, 1990) p. 659.