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# Structure of glassy AsTe: the effect of adding a small quantity of Cu or Ag

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## Abstract

The structure of the glasses  $\text{Cu}_{0.1}\text{AsTe}$  and  $\text{Ag}_{0.1}\text{AsTe}$  is studied by using the method of isotopic substitution in neutron diffraction. It is found that the addition of metal atoms  $M$  ( $=\text{Cu}$  or  $\text{Ag}$ ) does not significantly affect the structure of glassy AsTe on either the short- or intermediate-range length scales. Cu and Ag both take coordination numbers in excess of four in an As–Te network that is compact by comparison with its As–S and As–Se counterparts. In high- $M$ -content  $M$ –As–Te glasses, Cu and Ag again take coordination numbers greater than four and the absence of significant ionic conductivity for the Ag-based materials is attributed to a compact As–Te network that restricts pathways along which silver ions can move.

## 1. Introduction

Arsenic telluride glasses, which are at the heart of several amorphous compounds that have found practical application as switching and memory devices [1–3], have different physico-chemical properties to their sulphide and selenide counterparts. For example, their formation requires faster quench rates and the materials have a relatively high electrical conductivity. Furthermore, whereas the addition of Ag to As–S and As–Se can produce glasses with an appreciable ionic conductivity [4], Ag–As–Te glasses remain semiconductors even when a large amount of silver is incorporated [5, 6]. By comparison, although Cu(I) is isoelectronic with Ag(I), its solubility in As–S glasses is small [7] and its addition to As–Se or As–Te does not promote the formation of ionically conducting materials [4, 8].

A prerequisite for understanding this behaviour is detailed information on the microscopic structure of As–Te and  $M$ –As–Te ( $M = \text{Cu}$  or  $\text{Ag}$ ) glasses. The former have been investigated in detail by Ma *et al* [9] using extended x-ray absorption fine-structure (EXAFS) and differential anomalous x-ray scattering (DAS) methods. Structural information on  $M$ –As–Te systems is, however, limited. With the exception of glassy  $\text{AgAsTe}_2$  [10] and  $\text{Cu}_2\text{As}_3\text{Te}_4$  [11], which

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have been studied in detail by using the method of isotopic substitution in neutron diffraction, and glasses on the  $(\text{Ag}_2\text{Te})_x(\text{AsTe})_{1-x}$  ( $0 \leq x \leq 0.3$ ) pseudo-binary tie line, which have been investigated by using the EXAFS method [12], other studies of M–As–Te glasses have been restricted to the  $x$ -ray or neutron diffraction total-structure-factor level [13–18].

The object of this paper is to present neutron diffraction (ND) results on the changes in structure that occur when a small quantity of Cu or Ag is added to glassy AsTe to form  $\text{M}_{0.1}\text{AsTe}$ . On this addition, the glasses remain semiconductors and the electrical conductivity at 20 °C increases by a factor of approximately three from  $\approx 5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$  [4]. By isotopically substituting the M atom it is feasible to simplify the complexity of correlations associated with a single neutron diffraction experiment on glassy  $\text{M}_{0.1}\text{AsTe}$  by the application of difference function methods [19, 20]. It is thereby possible to obtain information on the coordination environments of the metal and matrix ( $\mu = \text{As}$  or  $\text{Te}$ ) atoms separately. The matrix-atom correlations in a three-component glass can then be compared with those in the pure network former AsTe to ascertain the effect on the structure of the network-modifying metal atoms.

## 2. Theory

In a neutron diffraction experiment on a three-component M–As–Te glass the coherently scattered intensity can be represented by the total structure factor

$$F(k) = A[S_{\text{AsAs}}(k) - 1] + B[S_{\text{TeTe}}(k) - 1] + C[S_{\text{AsTe}}(k) - 1] + D[S_{\text{MM}}(k) - 1] + E[S_{\text{MAs}}(k) - 1] + F[S_{\text{MTe}}(k) - 1] \quad (1)$$

where  $A = c_{\text{As}}^2 b_{\text{As}}^2$ ,  $B = c_{\text{Te}}^2 b_{\text{Te}}^2$ ,  $C = 2c_{\text{As}}c_{\text{Te}}b_{\text{As}}b_{\text{Te}}$ ,  $D = c_{\text{M}}^2 b_{\text{M}}^2$ ,  $E = 2c_{\text{M}}c_{\text{As}}b_{\text{M}}b_{\text{As}}$  and  $F = 2c_{\text{M}}c_{\text{Te}}b_{\text{M}}b_{\text{Te}}$ . In these equations  $c_{\alpha}$  and  $b_{\alpha}$  are, respectively, the atomic fraction and coherent scattering length of chemical species  $\alpha$ , the magnitude of the scattering vector is denoted by  $k$ , and the so-called Faber–Ziman partial structure factors  $S_{\alpha\beta}(k)$  are related to the partial pair distribution functions  $g_{\alpha\beta}(r)$  through

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2 r n_0} \int_0^{\infty} k [S_{\alpha\beta}(k) - 1] \sin(kr) dk \quad (2)$$

where  $n_0$  is the atomic number density. If diffraction experiments are made on two M–As–Te glasses that are identical in every respect, except that the isotopic composition of the metal is changed from M to  ${}^{\text{M}}$ M such that  $b_{\text{M}} > b_{\text{M}}$ , the difference between the resultant total structure factors gives the first-order difference function

$$\Delta_{\text{M}}(k) = {}^{\text{M}}F(k) - {}^{\text{M}}F(k) = D' [S_{\text{MM}}(k) - 1] + E' [S_{\text{MAs}}(k) - 1] + F' [S_{\text{MTe}}(k) - 1] \quad (3)$$

where  $D' = c_{\text{M}}^2 (b_{\text{M}}^2 - b_{\text{M}}^2)$ ,  $E' = 2c_{\text{M}}c_{\text{As}}b_{\text{As}}(b_{\text{M}} - b_{\text{M}})$  and  $F' = 2c_{\text{M}}c_{\text{Te}}b_{\text{Te}}(b_{\text{M}} - b_{\text{M}})$ . Formation of the first-order difference function eliminates from  $F(k)$  those correlations not involving the metal atoms and there is a cancellation of many of the systematic errors associated with the data analysis procedure [20]. The complexity of correlations associated with the total structure factor can also be reduced by forming the difference function

$$\begin{aligned} \Delta F'(k) &= {}^{\text{M}}F(k) - b_{\text{M}}\Delta_{\text{M}}(k)/(b_{\text{M}} - b_{\text{M}}) = {}^{\text{M}}F(k) - b_{\text{M}}\Delta_{\text{M}}(k)/(b_{\text{M}} - b_{\text{M}}) \\ &= A [S_{\text{AsAs}}(k) - 1] + B [S_{\text{TeTe}}(k) - 1] + C [S_{\text{AsTe}}(k) - 1] + D'' [S_{\text{MM}}(k) - 1] \end{aligned} \quad (4)$$

where  $D'' = -c_{\text{M}}^2 b_{\text{M}} b_{\text{M}}$ . With this combination the M– $\mu$  correlations are eliminated from the total structure factor and the effect of any systematic errors will be small since  $\Delta F'(k)$  dominates  $F(k)$  [20]. The real-space functions corresponding to  $F(k)$ ,  $\Delta_{\text{M}}(k)$  and  $\Delta F'(k)$

are denoted by  $G(r)$ ,  $\Delta G_M(r)$  and  $\Delta G'(r)$  respectively and are obtained from equations (1), (3) and (4) by substituting for the  $S_{\alpha\beta}(k)$  with the  $g_{\alpha\beta}(r)$ . The mean number of particles of type  $\beta$  contained in a volume defined by two concentric spheres of radii  $r_i$  and  $r_j$ , centred on a particle of type  $\alpha$ , is given by

$$\bar{n}_\alpha^\beta = 4\pi n_0 c_\beta \int_{r_i}^{r_j} r^2 g_{\alpha\beta}(r) dr. \quad (5)$$

### 3. Experimental method

The glasses were prepared by using a procedure designed to avoid contamination [21]. The elemental components were sealed within silica ampoules (5 mm inner diameter, 1 mm wall thickness) and thoroughly mixed in a rocking furnace prior to quenching in an ice/salt-water mixture at  $-5^\circ\text{C}$ . The glasses AsTe,  $^{\text{N}}\text{Cu}_{0.1}\text{AsTe}$ ,  $^{65}\text{Cu}_{0.1}\text{AsTe}$ ,  $^{107}\text{Ag}_{0.1}\text{AsTe}$  and  $^{109}\text{Ag}_{0.1}\text{AsTe}$  were made using elemental As (99.9999%), Te (99.999%),  $^{\text{N}}\text{Cu}$  (99.999%),  $^{65}\text{Cu}$  (99.7% enrichment),  $^{107}\text{Ag}$  (97.8% enrichment) or  $^{109}\text{Ag}$  (98.5% enrichment), where 'N' denotes the natural isotopic abundance of copper. The AsTe was made in batches of about 7 g by quenching from  $500^\circ\text{C}$ , the  $\text{Cu}_{0.1}\text{AsTe}$  was made in batches of about 5 g by quenching from  $600^\circ\text{C}$  and the  $\text{Ag}_{0.1}\text{AsTe}$  was made in batches of about 4.6 g by quenching from  $500^\circ\text{C}$ . The scattering length values are  $b(\text{As}) = 6.58(1)$  fm,  $b(\text{Te}) = 5.80(3)$  fm,  $b(^{\text{N}}\text{Cu}) = 7.718(4)$  fm,  $b(^{65}\text{Cu}) = 10.60(19)$  fm,  $b(^{107}\text{Ag}) = 7.480(11)$  fm and  $b(^{109}\text{Ag}) = 4.216(11)$  fm [22]. The weighting factors for the  $S_{\alpha\beta}(k)$  appearing in the various formulae are given in table 1.

**Table 1.** Weighting factors on the  $S_{\alpha\beta}(k)$  (in mb (b standing for barns)) in equations (1), (3) and (4) for glassy AsTe and  $\text{M}_{0.1}\text{AsTe}$ .

Function	$S_{\text{AsAs}}(k)$	$S_{\text{TeTe}}(k)$	$S_{\text{AsTe}}(k)$	$S_{\text{MM}}(k)$	$S_{\text{MAs}}(k)$	$S_{\text{MTe}}(k)$
$^{\text{AsTe}} F(k)$	108.2(3)	84.1(9)	191(1)	—	—	—
$^{\text{N}} F(k)$	98.2(3)	76.3(8)	173.1(9)	1.351(1)	23.03(4)	20.3(1)
$^{65} F(k)$	98.2(3)	76.3(8)	173.1(9)	2.55(9)	31.6(6)	27.9(5)
$\Delta_{\text{Cu}}(k)$	—	—	—	1.20(9)	8.6(6)	7.6(5)
$\Delta F'_{\text{Cu}}(k)$	98.2(3)	76.3(8)	173.1(9)	-1.86(3)	—	—
$^{107} F(k)$	98.2(3)	76.3(8)	173.1(9)	1.269(4)	22.32(5)	19.7(1)
$^{109} F(k)$	98.2(3)	76.3(8)	173.1(9)	0.403(2)	12.58(4)	11.09(6)
$\Delta_{\text{Ag}}(k)$	—	—	—	0.866(4)	9.74(6)	8.6(1)
$\Delta F'_{\text{Ag}}(k)$	98.2(3)	76.3(8)	173.1(9)	-0.715(2)	—	—

The samples were characterized using a TA Instruments Thermal Analyst 2000 differential scanning calorimeter operating at a heating rate of  $10^\circ\text{C min}^{-1}$ . A glass transition temperature of  $135(2)^\circ\text{C}$  (onset) or  $137(2)^\circ\text{C}$  (mid-point) was measured for glassy AsTe in agreement with the values reported elsewhere [4, 23–26]. Glass transition temperatures of  $137(2)^\circ\text{C}$  (onset) or  $146(2)^\circ\text{C}$  (mid-point) and  $129(2)^\circ\text{C}$  (onset) or  $136(3)^\circ\text{C}$  (mid-point) were measured for the  $\text{Cu}_{0.1}\text{AsTe}$  and  $\text{Ag}_{0.1}\text{AsTe}$  samples respectively. The former values for  $\text{Cu}_{0.1}\text{AsTe}$  are larger than the glass transition temperature of  $129^\circ\text{C}$  given by Borisova [4] whereas the latter values for  $\text{Ag}_{0.1}\text{AsTe}$  are in agreement. Number densities of  $0.0325 \text{ \AA}^{-3}$  (AsTe),  $0.0342 \text{ \AA}^{-3}$  ( $\text{Cu}_{0.1}\text{AsTe}$ ) and  $0.0336 \text{ \AA}^{-3}$  ( $\text{Ag}_{0.1}\text{AsTe}$ ) were calculated from the mass densities quoted in reference [4].

The diffraction experiments on the AsTe and  $\text{Ag}_{0.1}\text{AsTe}$  glasses were made using the instrument D4B at the Institut Laue–Langevin, Grenoble with an incident neutron wavelength

of 0.6991 Å. The diffraction experiments on the  $\text{Cu}_{0.1}\text{AsTe}$  glasses were made using the SANDALS instrument at the ISIS pulsed neutron source, Rutherford Appleton Laboratory. The glasses were in the form of coarsely ground lumps and were held at room temperature ( $\approx 23^\circ\text{C}$ ) in cylindrical thin-walled (0.1 mm) vanadium containers of internal diameter of 8.8 mm ( $\text{AsTe}$  and  $\text{Cu}_{0.1}\text{AsTe}$ ) or 6.8 mm ( $\text{Ag}_{0.1}\text{AsTe}$ ). Each complete experiment comprised the measurement of the diffraction patterns for the sample in its container, the empty container, the background with the sample absent and a vanadium rod of dimensions comparable to the sample for normalization purposes. The measured intensity for a cadmium neutron-absorbing rod of similar diameter to the sample was also collected in the D4B experiment to account for the effect of the sample self-shielding on the background count rate at small scattering angles [27]. The D4B data analysis followed the scheme given in reference [20] and the SANDALS data analysis was made using the ATLAS suite of programs [28]. In the latter, the  $^{123}\text{Te}$  resonance at 2.334 eV [29], which could be observed in the diffraction patterns taken for the 18 different detector groups arranged at scattering angles between  $3.8^\circ$  and  $36.5^\circ$ , was eliminated by truncating the data for each group at a suitable incident neutron wavelength. The  $F(k)$  were constructed by merging all those diffraction patterns from the different groups that showed good agreement.

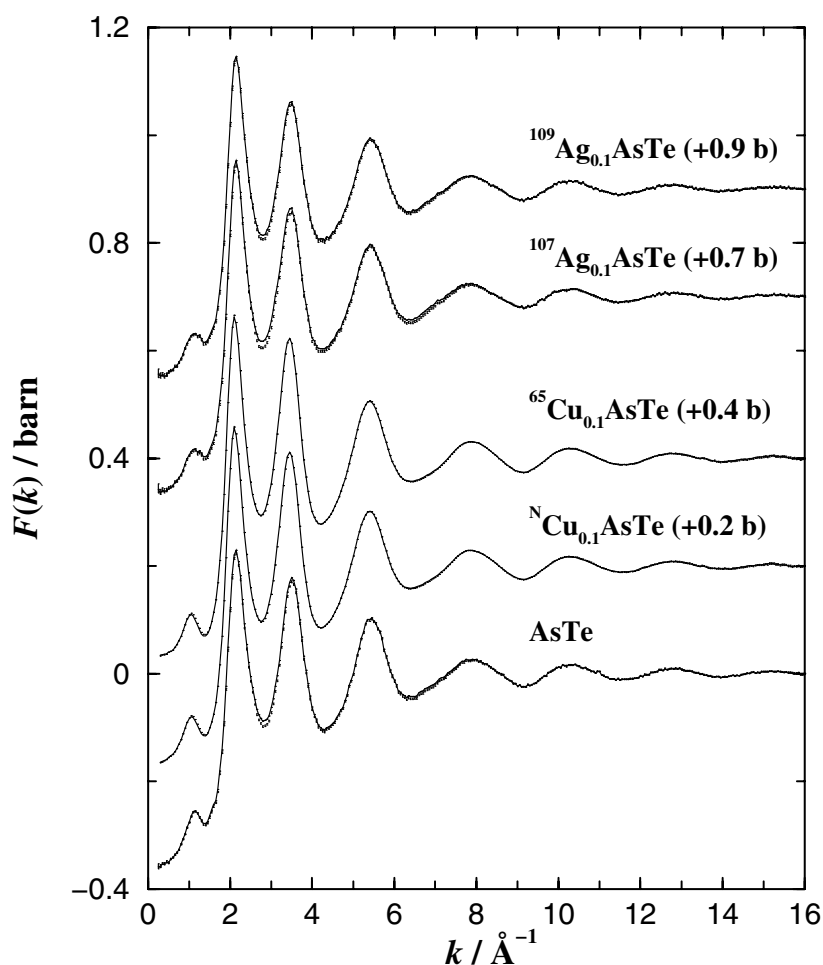
The efficacy of the data correction procedure, and hence the reliability of the measured data, was tested by checking that each final  $F(k)$  function tends to the correct high- $k$  limit, obeys the usual sum-rule relation, and that there is good overall agreement between  $F(k)$  and the Fourier back-transform of the corresponding  $G(r)$  after the unphysical low- $r$  oscillations are set to their calculated  $G(0)$  limit [20]. It was also ensured that the derived difference functions are properly behaved. The measured  $k$ -space data sets extend to  $16\text{ \AA}^{-1}$  and all of the data were used when Fourier transforming into  $r$ -space.

#### 4. Results

The measured  $F(k)$  for glassy  $\text{AsTe}$ , shown in figure 1, has a first sharp diffraction peak (FSDP) at  $1.14(2)\text{ \AA}^{-1}$  which is a signature of intermediate-range atomic ordering [30] and can be attributed to As–As correlations [9]. This feature is not destroyed when the metal atoms are added and appears at  $1.07(2)\text{ \AA}^{-1}$  for  $\text{Cu}_{0.1}\text{AsTe}$  and  $1.13(2)\text{ \AA}^{-1}$  for  $\text{Ag}_{0.1}\text{AsTe}$ . The intermediate-range ordering giving rise to the FSDP in the  $\text{M}_{0.1}\text{AsTe}$  glasses is not associated with M-atom correlations as shown by the absence of a FSDP in the measured first-order difference functions  $\Delta_{\text{M}}(k)$  illustrated in figure 2.

The real-space functions  $\Delta G_{\text{M}}(r)$  were obtained by Fourier transforming the corresponding  $\Delta_{\text{M}}(k)$  both before and after the application of a cosine window function (figure 3). The effect of the latter was to smooth the data but altered neither the peak positions nor coordination numbers. It is found that the  $\Delta G_{\text{M}}(r)$  have well defined first peaks at  $2.56(2)\text{ \AA}$  for  $\text{Cu}_{0.1}\text{AsTe}$  and  $2.80(2)\text{ \AA}$  for  $\text{Ag}_{0.1}\text{AsTe}$  which extend over the ranges  $2.15 \leq r (\text{\AA}) \leq 3.07$  and  $2.21 \leq r (\text{\AA}) \leq 3.31$  respectively.

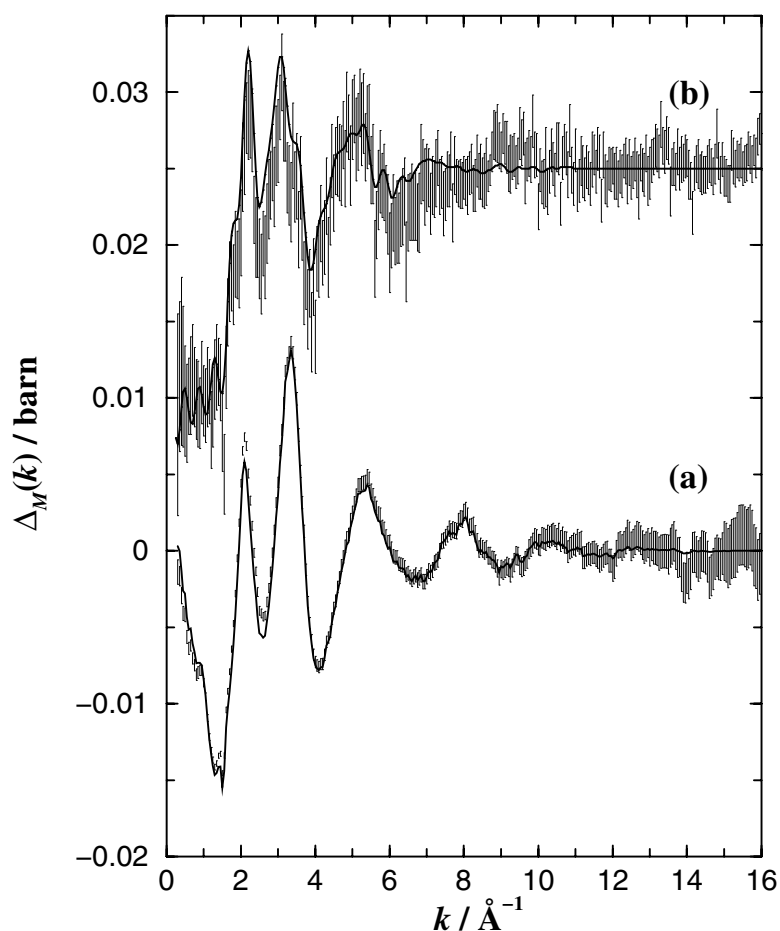
It is not possible to unambiguously identify those correlations contributing to the first peak in  $\Delta G_{\text{Cu}}(r)$  since its range encompasses typical Cu–Te, Cu–As and Cu–Cu bond lengths [17, 31]. Recent  $^{125}\text{Te}$  Mössbauer experiments on  $\text{Cu}_{0.3529}\text{AsTe}$  glasses suggest that Te atoms are bonded to Cu [32] and the copper content of the present  $\text{Cu}_{0.1}\text{AsTe}$  glasses is small which gives a large Cu–Cu nearest-neighbour distance of  $8.5\text{ \AA}$  if the Cu atoms are uniformly distributed. Also, fourfold coordination of Cu in chalcogenide glasses is often assumed [33, 34]. The first peak in  $\Delta G_{\text{Cu}}(r)$  was therefore analysed using several different scenarios to find  $\bar{n}_{\text{Cu}}^{\text{Te}}$  wherein  $\bar{n}_{\text{Cu}}^{\text{As}}$  was fixed at 0, 1, 2, 3 or 4 with  $\bar{n}_{\text{Cu}}^{\text{Cu}} = 0$ . However, in



**Figure 1.** The measured total structure factor  $F(k)$  (equation (1)) for the AsTe and  $M_{0.1}\text{AsTe}$  ( $M = \text{Cu}$  or  $\text{Ag}$ ) glasses. The bars represent the statistical errors on the data points and the solid curves are the Fourier back-transforms of the corresponding  $G(r)$  after the unphysical low- $r$  features are set to their calculated  $G(0)$  limit. The  $G(r)$  for glassy AsTe is shown in figure 5—see later.

high-Cu-content Cu–As–Se glasses a short Cu–Cu distance of 2.7 Å has been observed [31] so an estimate of  $\bar{n}_{\text{Cu}}^{\text{Cu}}$  was also obtained assuming no Cu–As correlations and four Te around Cu. The results, which are summarized in table 2, show that *irrespective* of the interpretation scheme the average coordination number of copper  $\bar{n}_{\text{Cu}} > 4$  provided there is some degree of Cu–Te bonding. The range of the first peak in  $\Delta G_{\text{Ag}}(r)$  covers typical Ag–Te and Ag–Ag bond distances [10] and while Ag–As bonds are not anticipated [31] their presence cannot be entirely ruled out. The same analysis scheme used for the  $\text{Cu}_{0.1}\text{AsTe}$  glass was therefore employed and it was found that, *irrespective* of the scenario, the average coordination number of silver  $\bar{n}_{\text{Ag}} > 4$  provided there is some degree of Ag–Te bonding (see table 2).

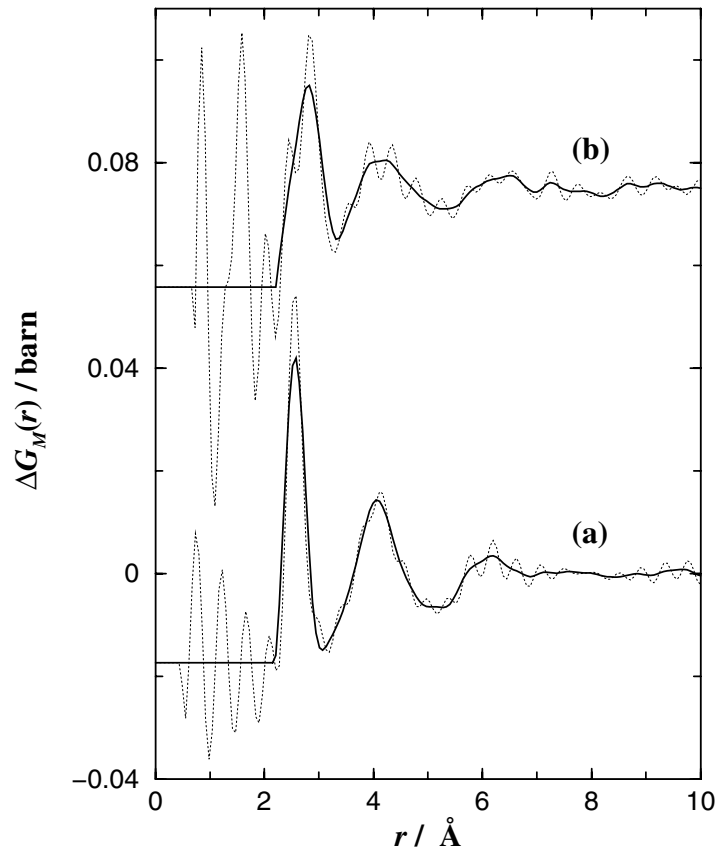
The  $\Delta F'(k)$  difference functions for the  $\text{Cu}_{0.1}\text{AsTe}$  and  $\text{Ag}_{0.1}\text{AsTe}$  glasses are compared with  $F(k)$  for glassy AsTe in figure 4. Each  $\Delta F'(k)$  function has an FSDP, at  $1.10(2) \text{ \AA}^{-1}$  for  $M = \text{Cu}$  and  $1.14(2) \text{ \AA}^{-1}$  for  $M = \text{Ag}$ , which is at a comparable position to the FSDP in



**Figure 2.** The measured first-order difference function  $\Delta_M(k)$  (equation (3)) for the glasses (a)  $\text{Cu}_{0.1}\text{AsTe}$  and (b)  $\text{Ag}_{0.1}\text{AsTe}$  (+0.25 b). The bars represent the statistical errors on the data points and the solid curves are the Fourier back-transforms of the corresponding  $\Delta G_M(r)$  given by the solid curves in figure 3.

$F(k)$  for glassy AsTe. This indicates that the intermediate-range ordering in glassy AsTe is not significantly altered by incorporation of the metal atoms.

The total pair distribution function  $G(r)$  for glassy AsTe (figure 5) has a first peak at  $2.57(2)$  Å and extends over the range  $2.26(2) \leq r$  (Å)  $\leq 2.95(2)$ . Its assignment to As–Te correlations alone gives  $\bar{n}_{\text{As}}^{\text{Te}} = 2.5(2)$  in disagreement with the ‘8 –  $N$ ’ rule [35]. However, in the EXAFS and DAS experiments of Ma *et al* [9], As–As, Te–Te and As–Te bonds of length  $2.48(1)$  Å,  $2.85(2)$  Å and  $2.70(2)$  Å were found with corresponding coordination numbers of  $\bar{n}_{\text{As}}^{\text{As}} = 1.6(2)$ ,  $\bar{n}_{\text{Te}}^{\text{Te}} = 0.4(2)$  and  $\bar{n}_{\text{As}}^{\text{Te}} = 1.4(2)$ . The range of the first peak in  $G(r)$  therefore encompasses typical As–As and Te–Te homopolar bonding distances and its integration assuming  $\bar{n}_{\text{As}}^{\text{As}} = 1.6$  and  $\bar{n}_{\text{Te}}^{\text{Te}} = 0.4$  also gives  $\bar{n}_{\text{As}}^{\text{Te}} = 1.5(2)$  such that the As and Te atoms each have a complete shell of eight outer electrons. The first peak in both of the  $\Delta G'(r)$  functions also occurs at  $2.57(2)$  Å (figure 5). As for the case of glassy AsTe it was interpreted assuming  $\bar{n}_{\text{As}}^{\text{As}} = 1.6$  and  $\bar{n}_{\text{Te}}^{\text{Te}} = 0.4$  whence its integration gave  $\bar{n}_{\text{As}}^{\text{Te}} = 1.4(2)$  for both the copper- and silver-modified glasses. The short-

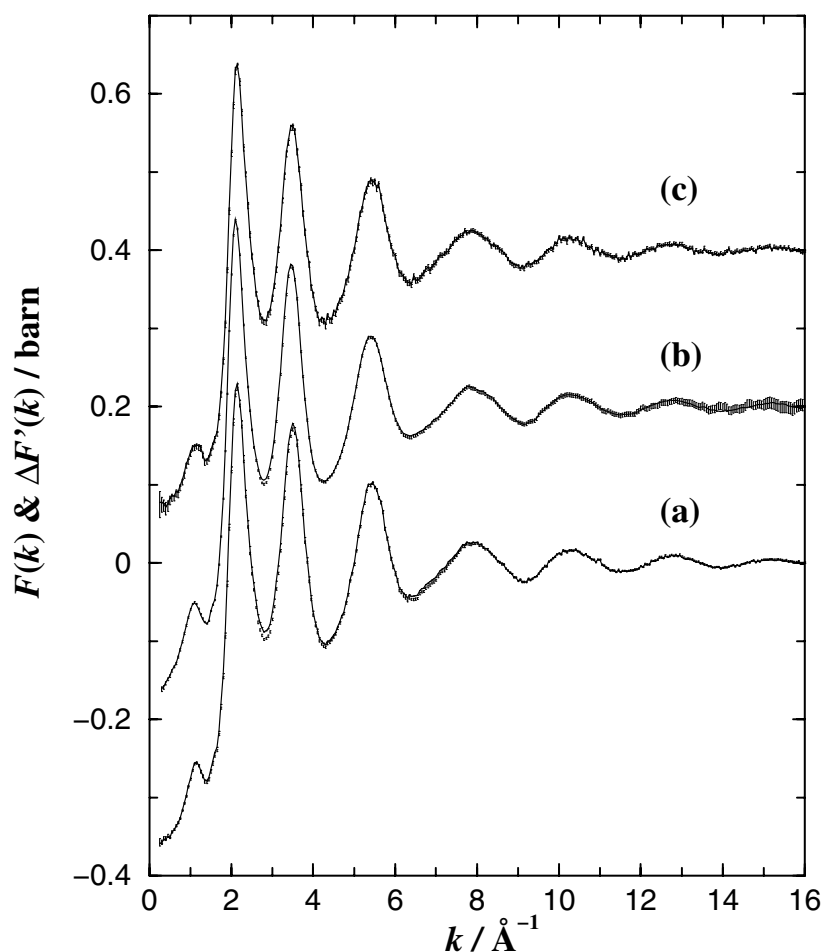


**Figure 3.** The real-space function  $\Delta G_M(r)$  for the glasses (a)  $\text{Cu}_{0.1}\text{AsTe}$  and (b)  $\text{Ag}_{0.1}\text{AsTe}$  (+0.075 b) obtained by Fourier transforming the  $\Delta_M(k)$  given in figure 2 either before (dotted curves) or after (solid curves) the application of a cosine window function. The unphysical low- $r$  oscillations of the latter have been set to the  $\Delta G_M(0)$  limit.

**Table 2.** Coordination numbers obtained from the first peak in  $\Delta G_M(r)$  for the  $\text{M}_{0.1}\text{AsTe}$  glasses.

Function	$\bar{n}_M^{\text{Te}}$	$\bar{n}_M^{\text{As}}$	$\bar{n}_M^{\text{M}}$	$\bar{n}_M$
$\Delta G_{\text{Cu}}(r)$	4.7(1)	—	—	4.7(1)
	3.5(1)	1	—	4.5(1)
	2.4(1)	2	—	4.4(1)
	1.3(1)	3	—	4.3(1)
	0.1(1)	4	—	4.1(1)
	4	—	0.4(1)	4.4(1)
$\Delta G_{\text{Ag}}(r)$	4.7(2)	—	—	4.7(2)
	3.6(2)	1	—	4.6(2)
	2.5(2)	2	—	4.5(2)
	1.4(2)	3	—	4.4(2)
	0.2(2)	4	—	4.2(2)
	4	—	0.8(2)	4.8(2)



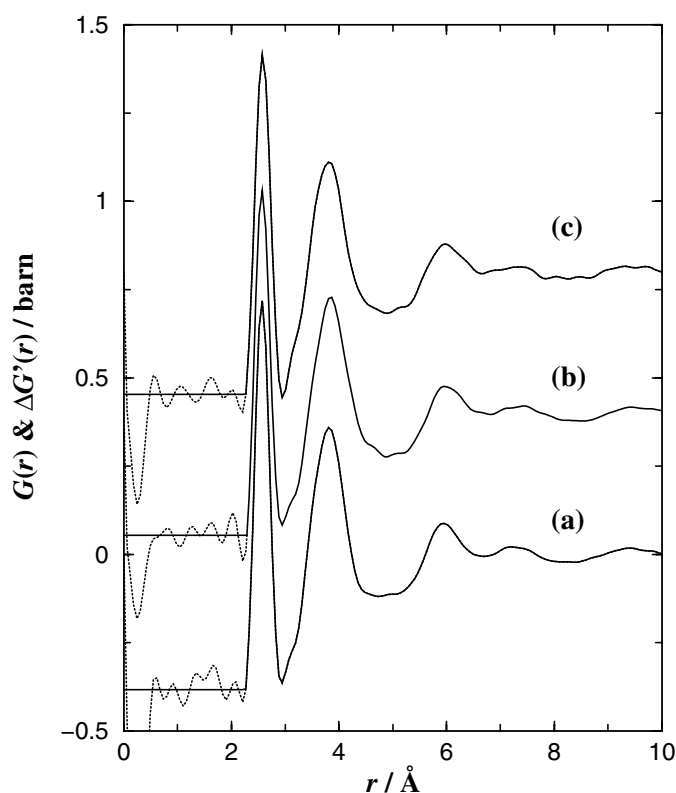


**Figure 4.** Comparison of (a) the total structure factor  $F(k)$  for glassy AsTe with the difference function  $\Delta F'(k)$  (equation (4)) for the glasses (b)  $\text{Cu}_{0.1}\text{AsTe}$  (+0.2 b) and (c)  $\text{Ag}_{0.1}\text{AsTe}$  (+0.4 b). The bars represent the statistical errors on the data points and the solid curves are the Fourier back-transforms of the corresponding  $r$ -space functions given by the solid curves in figure 5.

range ordering of the network former is not therefore destroyed on incorporating the copper or silver atoms.

## 5. Discussion

The average coordination number of Cu,  $\bar{n}_{\text{Cu}}$ , in glassy  $\text{Cu}_{0.1}\text{AsTe}$  is greater than four (see table 2) provided it is not exclusively bound to arsenic atoms, a scenario that is supported by the  $^{125}\text{Te}$  Mössbauer experiments of Fourmentin *et al* [32]. A similar observation has been made by Liu [11] who applied the method of isotopic substitution in neutron diffraction to study the structure of the ternary telluride glass  $(\text{Cu}_2\text{Te})_{0.25}(\text{AsTe})_{0.75}$ . In this work the first peak in  $\Delta G_{\text{Cu}}(r)$  gave a coordination number  $\bar{n}_{\text{Cu}} \approx 5$  irrespective of the analysis scenario wherein copper was assumed to have either different combinations of matrix atoms (As or Te) as nearest neighbours or, following reference [31], one copper atom in addition to matrix



**Figure 5.** Comparison of (a) the total pair distribution function  $G(r)$  for glassy AsTe with the difference function  $\Delta G'(r)$  for the glasses (b)  $\text{Cu}_{0.1}\text{AsTe}$  (+0.4 b) and (c)  $\text{Ag}_{0.1}\text{AsTe}$  (+0.8 b) obtained by Fourier transforming the functions given by the error bars in figure 4. The unphysical low- $r$  oscillations about the  $G(0)$  or  $\Delta G'(0)$  limits are shown by the broken curves.

atoms. It is therefore apparent that copper can take coordination numbers greater than four in telluride glasses, in contrast with the assumption of fourfold coordination made in constructing previous models of these materials from total x-ray and neutron diffraction patterns [13–17].

The addition of Ag to glassy AsTe also results in a metal-atom coordination number greater than four since silver is not exclusively bound to arsenic atoms (see table 2). The latter follows from the near immiscibility of Ag and As at room temperature and  $^{125}\text{Te}$  Mössbauer experiments on  $\text{Ag}_{0.3529}\text{AsSe}_x\text{Te}_{1-x}$  ( $0 \leq x \leq 1$ ) glasses which show preferential bonding of Te to Ag [6]. Furthermore, a coordination number  $\bar{n}_{\text{Ag}} > 4$  has been observed for glassy  $(\text{Ag}_2\text{Te})_{0.5}(\text{As}_2\text{Te}_3)_{0.5}$  wherein Ag has 2.9(2) Te nearest neighbours at 2.80(3) Å and 2.8(4) Å nearest neighbours at 3.03(2) Å [10]. Crystalline complexes in which Cu(I) or Ag(I) have close metal neighbours in addition to three or four non-metal atoms at normal distances are also reported [36].

The observation of a coordination number for coordination of copper or silver with *matrix* atoms,  $\bar{n}_{\text{M}}^{\mu}$ , greater than four is not the usual expectation for chalcogenide glasses, at least those based on sulphur and selenium. When the covalent component to the bonding is important and the d-electron states are not involved, fourfold coordination of these metal atoms is often assumed [33, 34]. The present neutron diffraction work shows that this picture will break down in  $\text{M}_{0.1}\text{AsTe}$  glasses provided  $\bar{n}_{\text{M}}^{\text{M}} = 0$  (see table 2), i.e. since exclusive M–As bonding

is ruled out by Mössbauer studies [6, 32]  $\bar{n}_M^\mu$  will be *greater* than four. Indeed, this picture also breaks down in several M–As–S [19] and M–As–Se [31, 37] glasses although in these systems  $\bar{n}_M^\mu$ -values of *less* than four have been observed. Alternatively, if  $\bar{n}_M^\mu \leq 4$  in  $M_{0.1}$  AsTe glasses, in keeping with comparable sulphide- and selenide-based systems, then there must be short M–M nearest-neighbour distances even at low metal-atom concentrations in order to account for the area under the first peak in  $\Delta G_M(r)$ .

When a small amount of the network modifier M is added to the network former AsTe no significant change is observed in its short-range ordering. Provided there is a degree of homopolar bonding, the ‘8 – N’ rule holds for the matrix atoms and there is no need to invoke fourfold coordination of arsenic [13–16, 18]. Furthermore, little change is observed in the FSDP which occurs at  $\approx 1 \text{ \AA}^{-1}$  in  $F(k)$  for the network former, i.e. the modifier has little effect on the intermediate-range ordering of the matrix atoms. This observation has previously been made for other low-modifier-content glasses such as  $(\text{Ag}_2\text{S})_{0.096}(\text{As}_2\text{S}_3)_{0.904}$  [19] and  $(\text{Ag}_2\text{Se})_{0.096}(\text{As}_2\text{Se}_3)_{0.904}$  [11, 38] where  $\text{Ag}_2\text{X}$  is the modifier and X denotes a chalcogen. Other experiments on the structure of M–As–X chalcogenide glasses show, however, that when a large amount of network modifier is added, the intermediate-range ordering of the network former is changed: the FSDP in  $F(k)$  for the network former is eliminated in the reciprocal-space function describing the  $\mu$ – $\mu$  correlations in the modified glass [10, 31]. Nevertheless, even in these cases no evidence could be found to support destruction of the short-range ordering of the matrix atoms as shown by the comparison of tables 3 and 4 where  $r_{\mu\mu}$  denotes the nearest-neighbour matrix–matrix-atom separation.

**Table 3.** Matrix-atom nearest-neighbour correlations in M–As–X glasses. X–X correlations do not appear under the first peak in the  $r$ -space function describing the matrix atoms except in the case of the telluride glasses.

Glass	$r_{\mu\mu}(\text{\AA})$	$\bar{n}_{\text{As}}^X$	$\bar{n}_{\text{As}}^{\text{As}}$	$\bar{n}_X^X$	Reference
$\text{Cu}_{0.1}\text{AsTe}$	2.57(2)	1.4(2)	1.6	0.4	Present work
$(\text{Cu}_2\text{Se})_{0.25}(\text{AsSe})_{0.75}$	2.42(2)	2.8(2)	0	—	[31]
		2.3(2)	1	—	
$(\text{Ag}_2\text{S})_{0.096}(\text{As}_2\text{S}_3)_{0.904}$	2.28(1)	3.1(2)	—	—	[19]
$(\text{Ag}_2\text{S})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$	2.27(1)	3.0(2)	—	—	[19]
$(\text{Ag}_2\text{Se})_{0.096}(\text{As}_2\text{Se}_3)_{0.904}$	2.42(2)	3.1(2)	—	—	[11]
$(\text{Ag}_2\text{Se})_{0.25}(\text{AsSe})_{0.75}$	2.42(2)	2.5(2)	0	—	[31]
		2.0(2)	1	—	
$\text{Ag}_{0.1}\text{AsTe}$	2.57(2)	1.4(2)	1.6	0.4	Present work
$(\text{Ag}_2\text{Te})_{0.5}(\text{As}_2\text{Te}_3)_{0.5}$	2.63(2)	3.2(2)	0	—	[10]
		2.1(2)	0.8	0.9	

The general observation that the addition of a small amount of M to AsTe does not significantly affect the short-range order of the matrix atoms also holds for low-M-content M–As–S and M–As–Se glasses. The question therefore arises as to why the electrical conductivity of these telluride glasses is higher than those of their sulphide and selenide counterparts. An explanation lies in the enhanced metallic character of tellurium that leads to a more compact network in keeping with  $^{57}\text{Fe}$  Mössbauer results on the Ag–As–Se–Te system [39] together with a packing fraction calculation based on the number density of As–X (X = S, Se, Te) glasses [4] and the covalent radii of the chemical species [40]. The latter shows an increase in the packing fraction by 29% when S is replaced by Te in glassy  $\text{As}_2\text{X}_3$  and by 15% when Se is replaced by Te in glassy AsX. Incorporated metal atoms can

**Table 4.** Matrix-atom nearest-neighbour correlations in some network-forming glasses.

Glass	Method	$r_{\mu\mu}$ (Å)	$\bar{n}_{As}^X$	$\bar{n}_{As}^{As}$	$\bar{n}_X^X$	Reference
As <sub>2</sub> S <sub>3</sub>	EXAFS	2.26	3.1	—	—	[42]
	EXAFS	2.28(1)	3.0(1)	—	—	[43]
	ND	2.28(2)	3.1(2)	—	—	[44]
AsSe	ND	2.42(2)	2.4(2)	0	—	[31]
			2.0(2)	1	—	
As <sub>2</sub> Se <sub>3</sub>	ND	2.42(2)	3.0(2)	—	—	[11]
AsTe	EXAFS/DAS	2.48(1) As–As	1.4(2)	1.6(2)	0.4(2)	[9]
		2.85(2) Te–Te				
	ND	2.70(2) As–Te				
	ND	2.57(2)	1.5(2)	1.6	0.4	Present work
As <sub>2</sub> Te <sub>3</sub>	EXAFS/DAS	2.47(1) As–As	2.2(2)	0.8(2)	0.9(2)	[9]
		2.83(2) Te–Te				
		2.69(2) As–Te				

thereby adopt environments in which they take coordination numbers in excess of four either by bonding exclusively to matrix atoms or to a combination of matrix and other metal atoms. Packing fraction calculations based on the number density of M–As–X glasses with *high* Ag and Cu contents [4] and the covalent radii of the chemical species [40] also show the arsenic telluride structure to be relatively compact. For example, the packing fraction of the matrix atoms increases by 37% when S is replaced by Te in glassy AgAsX<sub>2</sub> and by 15% when Se is replaced by Te in glassy Ag<sub>0.7</sub>AsX<sub>1.5</sub>. This feature may therefore account for the absence of ionic conductivity when large quantities of silver are incorporated, i.e. the As–Te network has insufficient ‘pathway volume’ to allow for the free movement of silver ions [41].

## 6. Conclusions

The addition of a small amount of Cu or Ag to glassy AsTe does not significantly affect its short- or intermediate-range atomic ordering, at least on the difference function level at which the present experiments were conducted. The Cu and Ag atoms are incorporated to form a nearest-neighbour environment in which their coordination number is greater than four in an As–Te network that is compact by comparison with its As–S and As–Se counterparts. In high-M-content M–As–Te glasses, Cu and Ag again take coordination numbers greater than four and the absence of significant ionic conductivity for the Ag-based materials is attributed to a compact As–Te network that restricts the pathways along which silver ions can move.

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