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# Local atomic environment in amorphous Ge<sub>15</sub>Te<sub>85</sub>

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## Abstract

The structure of amorphous Ge<sub>15</sub>Te<sub>85</sub> has been studied by neutron and x-ray diffraction. Experimental data have been modelled simultaneously with the reverse Monte Carlo simulation method. The contrast between structure factors together with the application of some plausible physical constraints allowed the separation of the three partial pair correlation functions and determination of Ge and Te local environment.

## 1. Introduction

Amorphous chalcogenides show several interesting phenomena such as electric switching [1] and optical phase change recording [2]. Ge<sub>15</sub>Te<sub>85</sub> is one of the most extensively studied alloys that can serve as a relatively simple model for systems of direct industrial interest (Ge–Sb–Te, Ge–As–Te, etc [3]). Despite considerable experimental efforts [4–8] the structure of amorphous Ge<sub>15</sub>Te<sub>85</sub> is still not completely known. Open questions are the short range order (environment of Ge and Te atoms) and the origin of the prepeak in the neutron diffraction pattern.

To understand the structure of a binary amorphous system even at a very basic level it is necessary to know the three partial pair correlation functions. In some favourable cases this can be achieved by neutron diffraction with isotopic substitution. This option is prohibitively expensive in the case of Ge<sub>15</sub>Te<sub>85</sub> as the natural abundance of Te<sup>122</sup>—the only isotope that could give sensible contrast—is very low. Though the contrast between x-ray and neutron diffraction data is satisfactorily high it is *not* possible to analyse them in the traditional frame of data evaluation where *three* experimental datasets should be combined to obtain partial correlation functions.

On the other hand if *a priori* knowledge can be included in the course of evaluation then the separation of the three partial structure factors may become possible with only two independent

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measurements. Reverse Monte Carlo (RMC) simulation [9, 10] is a straightforward tool for coupling experimental data with additional constraints. Its capability of giving reliable partial structure factors (or partial pair correlation functions) by modelling only one measurement has already been demonstrated several times [10].

The aim of the present paper is the structural study of amorphous Ge<sub>15</sub>Te<sub>85</sub> by modelling simultaneously x-ray and neutron diffraction data. In the case of amorphous Ge<sub>15</sub>Te<sub>85</sub>, Ge–Ge bonding can be ruled out on the basis of Raman scattering measurements [6]. Applying it as a constraint in reverse Monte Carlo simulation will help to separate the three partial pair correlation functions and estimate the number of nearest neighbours for Ge and Te atoms.

## 2. Experimental details

The amorphous Ge<sub>15</sub>Te<sub>85</sub> alloy was prepared by the melt spinning technique. The precursor alloy was produced from Ge and Te of 99.999% purity by melting in a sealed quartz ampoule under vacuum.

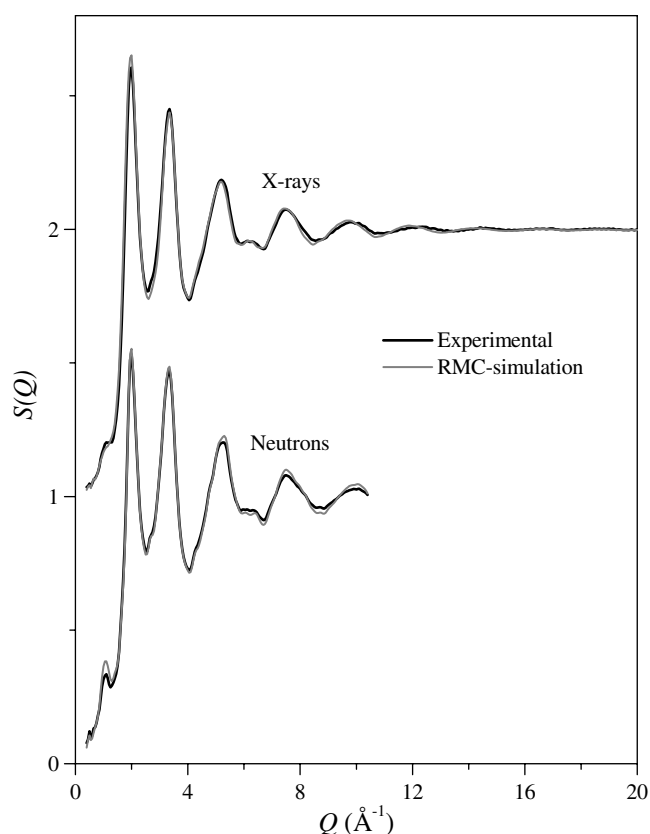
Neutron diffraction experiments were carried out with the liquid and amorphous materials diffractometer SLAD at NFL, Studsvik [11]. The powdered sample was contained in a thin-walled vanadium container. The incident wavelength of neutrons was 1.11 Å. The scattered intensity was measured between 0.4 and 10.4 Å<sup>-1</sup>. The static structure factor was obtained from the scattering intensities after applying corrections for absorption, multiple scattering and inelasticity followed by normalization to a vanadium standard, which were done with the CORRECT program described in [12].

X-ray diffraction experiments were carried out at the BW5 experimental station [13] at HASYLAB, Hamburg. The powdered amorphous sample was filled into a quartz capillary of 2 mm in diameter with wall thickness of about 0.02 mm. The energy of the radiation was 125 keV (0.101 Å). Scattered intensities were measured between 0.5 and 20 Å<sup>-1</sup>. Raw data were corrected for detector dead-time, background, polarization, absorption, and variations in detector solid angle [13]. Experimental neutron and x-ray structure factors can be seen in figure 1.

## 3. RMC simulations

For details of the reverse Monte Carlo technique we refer to a recent review [10]. To check for possible dependence on starting configuration or simulation box size, runs were carried out with 4000, 20 000 and 32 000 atoms. Apart from the high-*r* behaviour of the pair correlation functions ( $r > 22$  Å), which is not accessible with the smallest box, the results show systematic no box size dependence. The density in the amorphous state was taken to be 0.0282 Å<sup>-3</sup> [14]. Minimum distances between Te–Te, Te–Ge and Ge–Ge pairs were 2.5, 2.3 and 3.5 Å, respectively. Three different sets of additional coordination constraints were applied in the amorphous state: in the ‘tetrahedral’ model each Ge atom should have four Te neighbours between 2.5 and 3.1 Å. In the ‘3–4’ model Ge atoms were allowed to be either threefold or fourfold coordinated by Te, and in the ‘3–4–5’ model one Ge atom had three, four or five Te neighbours. Te atoms were forced to have either one or two Te neighbours in each case. These constraints were usually satisfied by at least 96–98% of the atoms. Initial configurations were obtained by hard sphere simulation runs, i.e. fitting no experimental data but applying hard sphere cut-offs and coordination constraints.

In principle, separation of  $g_{\text{TeTe}}(r)$  and  $g_{\text{GeTe}}(r)$  on the basis of two measurements can be carried out in the region of the first peak if  $g_{\text{GeGe}}(r)$  is zero in this range, i.e. when only  $g_{\text{TeTe}}(r)$



**Figure 1.** Experimental structure factors (*black curves*) and their reverse Monte Carlo fits for the 'tetrahedral' model (*light curves*). The x-ray structure factor is shifted by 1 for clarity.

and  $g_{\text{GeTe}}(r)$  contribute to the total pair correlation functions. For the Ge<sub>15</sub>Te<sub>85</sub> composition,

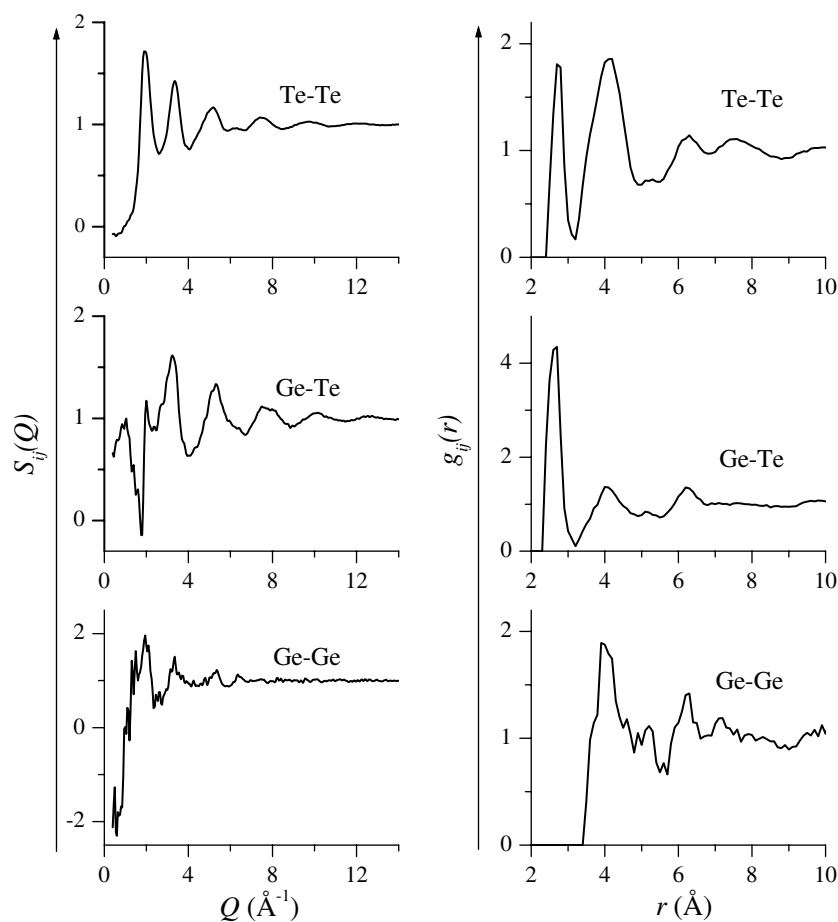
$$g^X(r < 3.5 \text{ \AA}) \approx 0.836g_{\text{TeTe}}(r) + 0.157g_{\text{GeTe}}(r) \quad (1)$$

$$g^N(r < 3.5 \text{ \AA}) = 0.641g_{\text{TeTe}}(r) + 0.319g_{\text{GeTe}}(r). \quad (2)$$

Due to the  $Q$ -dependence of the weights of the corresponding partial structure factors the relation is not exact for x-rays. However, it is not a problem for RMC as during the simulation pair correlation functions are transformed to reciprocal space and then recombined by the exact  $Q$ -dependent weights to obtain the model x-ray structure factor.

#### 4. Discussion

Simulated partial structure factors and partial pair correlation functions are shown in figure 2. From the partial correlation functions the number of nearest neighbours for Ge and Te atoms were calculated. The nearest neighbour distances and Te–Te and Ge–Te coordination numbers together with some derived quantities (average Te coordination number, average number of neighbours/atom, x-ray and neutron weighted total coordination numbers) are given in table 1. It is seen that the weighted coordination numbers obtained by RMC depend only weakly on the coordination constraints applied. Ge–Te and Te–Te coordination numbers are determined mainly by the coordination constraints applied (especially for the 'tetrahedral'



**Figure 2.** Partial structure factors and pair correlation functions generated by RMC for the ‘tetrahedral’ model.

**Table 1.** Partial, average ( $\langle N \rangle = 0.85N_{\text{Te}} + 0.15N_{\text{GeTe}}$ ), neutron and x-ray weighted total coordination numbers ( $N_n = 0.641N_{\text{TeTe}} + 0.319N_{\text{GeTe}}$ ,  $N_x = 0.836N_{\text{TeTe}} + 0.157N_{\text{GeTe}}$ ) and the nearest neighbour distances  $r$  of amorphous  $\text{Ge}_{15}\text{Te}_{85}$ .

Model	$N_{\text{TeTe}}$	$N_{\text{GeTe}}$	$\langle N_{\text{Te}} \rangle$	$\langle N \rangle$	$N_x$	$N_n$	$r_{\text{GeTe}}$ (Å)	$r_{\text{TeTe}}$ (Å)
‘Tetrahedral’	1.62	3.95	2.32	2.56	1.98	2.30	2.62	2.73
‘3–4’	1.79	3.40	2.39	2.54	2.03	2.23	2.63	2.74
‘3–4–5’	1.71	3.63	2.35	2.54	2.0	2.26	2.62	2.72

model). However, there is a weak and non-systematic dependence on the box size. The estimated uncertainty is about 0.2 and 0.05 for the Ge–Te and Te–Te coordination numbers, respectively. The quality of the fit was the same in the three models tested.

Both experimental datasets can be fitted reasonably well with the ‘tetrahedral’ model. It can also be seen that if no 100% fourfold coordination of Ge is required than  $N_{\text{GeTe}}$  decreases while  $N_{\text{TeTe}}$  increases. As a result of the two counteracting effects, x-ray and neutron-weighted total coordination numbers—the observable quantities—remain insensitive to the model applied. A common feature of these models is that the average Te coordination number

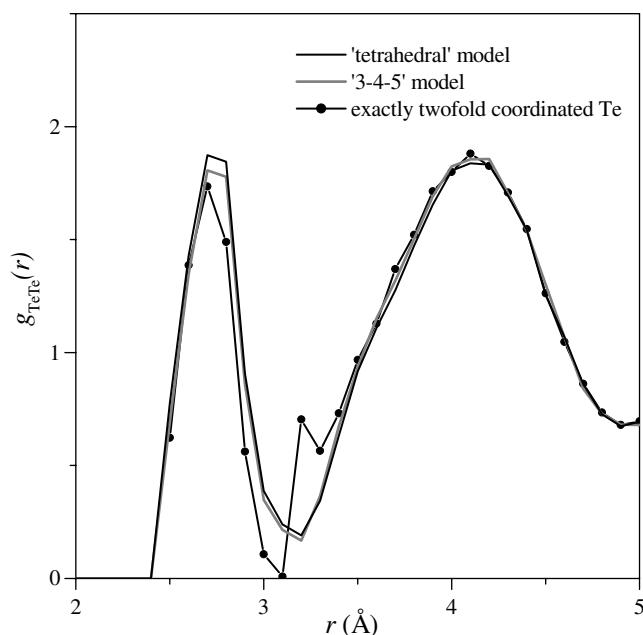


Figure 3. Te–Te partial pair correlation functions simulated with different coordination constraints.

$\langle N_{\text{Te}} \rangle$  is significantly larger than 2 and the average coordination number  $\langle N \rangle$  is about 2.55. This value ( $\langle N \rangle = 2.55$ ) lies between a characteristic parameter of the rigidity percolation threshold ( $\langle N \rangle = 2.4$ ) suggested by Philips and Thorpe [15] and that of a topological threshold in chalcogenide glasses ( $\langle N \rangle = 2.67$ ) found by Tanaka [16]. A set of simulation runs was carried out to check whether this is necessary to fit diffraction data or it is just an artefact of the simulation. In these runs Ge atoms were forced to have exactly four Te neighbours ( $N_{\text{GeTe}} = 4$ , therefore  $N_{\text{TeGe}} = 0.706$ ) while Te atoms had to have on the average 1.294 Te neighbours. Figure 3 shows Te–Te partial correlation functions simulated with different coordination constraints. It is clearly seen that a spike appears at  $\sim 3.2$  Å, which is a consequence of the constraint applied to Te–Te coordination. The area below the first peak in  $g_{\text{TeTe}}(r)$  cannot be reduced to the value required by a twofold coordinated Te model without introducing artefacts, indicating that a proportion of Te atoms is threefold coordinated in amorphous Ge<sub>15</sub>Te<sub>85</sub>. It is remarkable that with 100% fourfold coordination for Ge and 100% twofold coordination for Te the average coordination number would be 2.3, a value below 2.4, the rigidity percolation threshold.

Kameda *et al* [5] suggested 2.59 Å for the first Ge–Te distance and 2.76 Å for the Te–Te covalent distance. On the other hand Ichikawa *et al* [8] proposed a model in which the Ge–Te coordination number is close to 6, the Ge–Te bond length is 2.68 Å and there are no Te–Te bonds. The large freedom in the interpretation of diffraction data is the consequence of the small separation of Ge–Te and Te–Te peaks in  $r$ -space. (It is to be mentioned that the measurement in [8] was carried out up to  $32 \text{ \AA}^{-1}$ .)

The EXAFS technique gives the possibility to probe the environment of Ge and Te atoms separately by carrying out the measurements at the corresponding absorption edges. Several EXAFS studies have been carried out on Ge–Te glasses in the past decade [6, 7, 17, 18]. Bond lengths and Debye–Waller factors reported in these works are given in table 2. It can

**Table 2.** Bond lengths  $r$ , coordination numbers  $N$  and Debye–Waller factors  $\sigma$  in Ge–Te glasses determined by diffraction and EXAFS. In [9, 10] sample compositions are far from  $\text{Ge}_{15}\text{Te}_{85}$ ; therefore, coordination numbers are not shown.

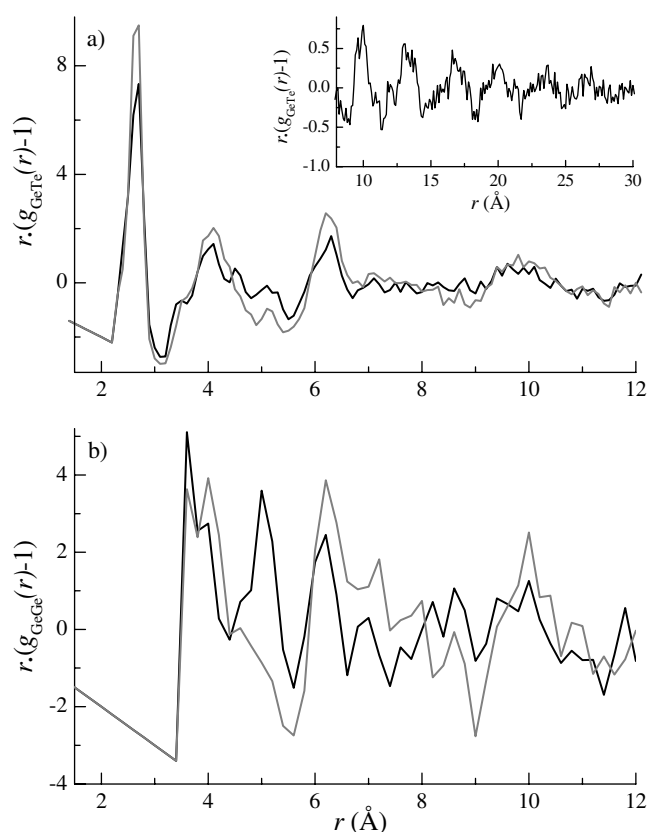
Method	Reference	$r_{\text{GeTe}}$ (Å)	$r_{\text{TeTe}}$ (Å)	$N_{\text{GeTe}}$	$N_{\text{TeTe}}$	$\sigma_{\text{GeTe}}$ (Å)	$\sigma_{\text{TeTe}}$ (Å)
ND + XRD	This study	2.62–2.63	2.72–2.74	3.40–3.95	1.62–1.79	0.3	0.3
ND	[5]	2.59	2.76	—	—	—	—
XRD	[6]	2.62(1)	2.78(1)	4.14(2)	1.27(3)	0.11(1)	0.12(1)
EXAFS	[6]	2.605	—	—	—	—	—
EXAFS	[7]	2.60	2.78	3.6	1.2	0.05	0.053
ND	[8]	2.68	—	6.3(4)	—	0.30	—
EXAFS	[16]	2.59/2.61	—	—	—	0.076/0.081	0.063
EXAFS	[17]	2.60	—	—	—	—	—

be seen that the Ge–Te bond lengths (about 2.60 Å) determined by Ge K-edge measurements are shorter than the values obtained in the present study (2.62–2.63 Å). On the other hand, the Te–Te first distance of [7] (2.78 Å) is longer than our value (2.73 Å). This discrepancy is most likely due to the insufficient spatial resolution provided by diffraction experiments: if it is not restricted by the experimental data or other constraints then RMC tends to mix neighbouring peaks in  $r$ -space. Two remarks should be made here:

- (1) EXAFS results are not always internally consistent. For example, the separation of Te–Ge and Te–Te shells in [7] led to  $N_{\text{TeGe}} = 1.3$ , which would imply that  $N_{\text{GeTe}} = 7.4$ , an obviously unreliable value.
- (2) While the limited resolution of diffraction experiments makes the separation of Te–Te and Ge–Te peaks extremely difficult (if not impossible), it does not affect the validity of *negative* statements: if a model is not compatible with *any* experimental evidence then it should be excluded.

Debye–Waller factors for Ge–Te bonds determined by EXAFS curve fitting procedures are usually much smaller than peak widths obtained by simulation of diffraction data. The spatial resolution of EXAFS experiments is usually better as they are carried out up to  $k = 16\text{--}18 \text{ \AA}^{-1}$  (due to a factor of 2 in the definition of  $k$ , the electron wavenumber, this corresponds to (roughly)  $32\text{--}36 \text{ \AA}^{-1}$  in the diffraction terminology). However, the principal reason is different: as is pointed out by Lee *et al* [19], the Debye–Waller factor in EXAFS theory is *not* a true mean square displacement as it contains a term depending on the correlated motion of the absorber and backscatterer atoms (see equations 3.21–3.23 of [19]).

A characteristic feature of the neutron structure factor is the prepeak at  $\sim 1.03 \text{ \AA}^{-1}$ . As it has much smaller amplitude for the x-ray case, it is reasonable to assume that the prepeak is related to Ge–Te or Ge–Ge correlations, which have larger contribution to the neutron scattering pattern. Comparison of the partial structure factors (figure 2) shows that the prepeak can be undoubtedly assigned to Ge–Te correlations. The presence of a prepeak is usually considered as evidence of a medium range order. As prepeaks can be found in systems of rather different nature (e.g.  $\text{CCl}_4$  and other simple molecular liquids, some molten alloys, covalent glasses) it is not obvious how to relate their position to  $r$ -space characteristics. Reverse Monte Carlo simulation on the other hand offers a simple way for investigating this question: omitting the prepeak from the fitted range of neutron data can reveal the underlying  $r$ -space feature. For this reason two independent RMC runs have been carried out starting from the same ‘raw’ configuration. In figure 4 the two corresponding functions— $r(g_{\text{GeTe}}(r) - 1)$  and  $r(g_{\text{GeGe}}(r) - 1)$ —are compared. It is remarkable that correlations extend up to 30 Å or further even if the prepeak region ( $0.4\text{--}1.7 \text{ \AA}^{-1}$ ) is not included in the fit (see the inset of figure 4(a)).



**Figure 4.** Effect of the prepeak on the structural models generated by RMC: (a)  $r(g_{\text{GeTe}}(r) - 1)$ , (b)  $r(g_{\text{GeGe}}(r) - 1)$ ; *black curves*: without fitting the prepeak; *light curves*: fitting the whole neutron data range.

Therefore in our case there is no obvious connection between the prepeak and the existence of the medium range correlations. On the other hand, peaks in the first–third neighbours range are much more pronounced if the whole neutron data range ( $0.4\text{--}10.4 \text{ \AA}^{-1}$ ) is modelled. In line with the above changes, some features of  $g_{\text{GeGe}}(r)$  also become stronger (see the plot in figure 4(b)). Though the statistics is much weaker here the tendency of a separation of the first and the second Ge–Ge coordination shells is clearly observable if the prepeak is included in the fit.

As the Te–Te partial pair correlation function remained practically insensitive to the fitting range of neutron data it can be reasonably assumed that the prepeak is a consequence of enhanced Ge–Te correlations in the first–third coordination shells.

## 5. Conclusions

The present study shows that

- (i) the average coordination number of amorphous Ge<sub>15</sub>Te<sub>85</sub> alloy is larger than 2.4, the rigidity percolation threshold, but less than 2.67, the topological threshold;
- (ii) the average Te-coordination number is larger than 2;



- (iii) the prepeak in the experimental structure factors originates mainly from correlations between central Ge atoms and Te atoms belonging to their first–third coordination spheres;
- (iv) Ge–Te correlations extend up to  $\sim 30$  Å.

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