Structural studies on Te-rich Ge-Te melts

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Abstract

The structure of liquid $Ge_{15}Te_{85}$, $Ge_{25}Te_{75}$ and $Ge_{33}Te_{67}$ alloys has been studied by neutron- and X-ray diffraction. Datasets obtained by the two techniques have been modelled simultaneously with the reverse Monte Carlo simulation method. As a result, the first coordination numbers and nearest neighbour distances for the studied alloys were estimated. On the base of the experimental data, Ge-Ge bonding appears to be present in liquid $Ge_{25}Te_{75}$ and $Ge_{33}Te_{67}$. It has been found that temperature dependences of the physico-chemical properties correlate with the structural changes in liquid $Ge_{15}Te_{85}$.

1. Introduction

It has been established long ago that liquid chalcogenes and many binary chalcogenides exhibit anomalous temperature and composition dependencies of various physical properties in the liquid state [1-3]. Among them is the Ge-Te system, which is characterized by one congruently melting compound GeTe (ϑ_{melt} = 725 °C) and two eutectics at 49.85 at.% Te (ϑ_{eut} = 720 °C) and 85 at.% Te (ϑ_{eut} = 375 °C), respectively [4, 5]. In addition, a phase with the stoichiometry $GeTe_4$ was found by crystallization of amorphous alloys around the $Ge_{20}Te_{80}$ composition [6].

Proceeding from the assumption that the physical properties of the liquid alloys are closely related to the topological and chemical short-range order (SRO), the anomalous behaviour of the physical properties of the Ge-Te melts has been explained by the existence of some structural units (clusters) and by the structural changes occurring with variation of temperature or composition (e.g. [7-12]). However, due to the fact that various physical properties showed the anomalies (maxima and minima) at different compositions, quite different structural models and existence of various structural units in the liquid Ge-Te alloys have been suggested.

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For example, a maximum on the composition dependences of the electrical resistivity and thermoelectric power observed at around 67 at.% Te by Valiant and Faber [7] was interpreted as an indication of the existence of $GeTe_2$ compound in the liquid phase. Tsuchiya has assumed the existence of molecular associations with the stoichiometry Ge_1Te_6 after analysis of the temperature and composition dependences of the specific heat, isothermal compressibility, density and thermal expansion of the Te-rich Ge-Te alloys [8, 9].

The liquid eutectic alloy $Ge_{15}Te_{85}$ shows interesting temperature-dependent features. Tschirer et al. [10, 11] found that the electrical resistivity decreases by nearly two orders of magnitude within 100 °C above the eutectic temperature. Herwig and Wobst [12] observed that the temperature dependences of the dynamic viscosity for Te-rich Ge-Te melts show positive deviations from the Arrhenius plot below ~525 °C and the activation energy of viscous flow for liquid $Ge_{15}Te_{85}$ increases appreciably with decreasing temperature close to ϑ_{eut}. Terzieff et al. [13] observed a minimum of the magnetic susceptibility at the $Ge_{15}Te_{85}$ composition, which disappears at temperatures about 100 °C above ϑ_{eut}. These results have been interpreted in terms of some "clusters of atoms", which exist after melting and disappear when the temperature is 100 – 150 °C above the eutectic point.

The atomic structure of liquid Ge-Te alloys has been studied in a number of diffraction measurements so far. Neumann et al. [14, 15] combined neutron and X-ray scattering data for molten $Ge_{15}Te_{85}$ and determined the partial correlation functions for Te-Te and Ge-Te pairs up to 600 °C. They assumed that the low temperature melt is built-up from pure Te regions and α-GeTe like clusters, and the locally ordered regions are destroyed with increasing temperature.

Based on the analysis of the neutron weighted total pair correlation function Nicotera et al. [16] concluded that the structure of the liquid $Ge_{17.5}Te_{82.5}$ alloy can be represented by a model with fourfold coordinated Ge atoms and threefold coordinated Te atoms.

Kameda et al. [17] assumed that there exists a chemical order in Te-rich Ge-Te liquid alloys based on the bonding between Ge and Te atoms, but the bonding and local atomic order in liquid, amorphous and crystalline state are significantly different according to their opinion. Yoshioka et al. [18] carried out neutron diffraction and EXAFS measurements on liquid $Ge_{15}Te_{85}$ and assumed that the bonding state between Ge and Te decreases and becomes weak with increasing temperature. It has been suggested that a strong temperature dependence of the properties of the $Ge_{15}Te_{85}$ melt may be explained as a transition from covalent to ionic character of the Ge-Te bonding.

Bichara, Bergman et al. [19, 20] related the anomalous temperature dependence of the density of liquid $Ge_{15}Te_{85}$ to a reorganization of the first coordination shell and interpreted this as a gradual change from a Peierls distorted to a less Peierls distorted structure. It has been suggested that the structural changes undergone by $Ge_{15}Te_{85}$ melt mainly consist in an increase of Te neighbours around Ge.

In this work we performed X-ray and neutron diffraction measurements on the liquid alloys $Ge_{15}Te_{85}$, $Ge_{25}Te_{75}$ and $Ge_{33}Te_{67}$. The experimental data are simulated with the reverse Monte-Carlo

(RMC) technique [21, 22] and the partial structure factors and pair distribution functions obtained are analyzed.

2. Experimental procedure

The Ge-Te alloys were prepared from germanium and tellurium pieces of high purity (99.999 %) by melting at 800 °C in evacuated and sealed quartz ampoules.

Neutron diffraction experiments were carried out with the liquid and amorphous materials diffractometer SLAD at NFL, Studsvik [23]. The samples were filled into quartz glass capillaries (6 mm diameter and 0.2 mm wall thickness) and sealed under vacuum. The incident wavelength of neutrons was 1.116 Å. The measurements have been performed in the Q-range between 0.4 and 10.4 $Å^{-1}$. Structure factors were obtained from the scattering intensities after corrections and normalization to a vanadium standard, which were done with the CORRECT program described in [24].

X-ray diffraction experiments were carried out at the BW5 experimental station [25] at HASYLAB, DESY. The samples were filled and sealed into quartz capillaries of 2 mm in diameter and with wall thickness of about 0.02 mm. The energy of the radiation was 125 keV. The scattered intensity was measured between 0.4 and 20 $Å^{-1}$. Statistical error at the tail of the curve was less than 0.2%. Raw data were corrected for detector dead-time, background, polarization, absorption, and variations in detector solid angle.

3. Experimental results

The neutron diffraction measurements on the $Ge_{15}Te_{85}$ alloy were performed in the liquid state up to 740 °C and in the supercooled state at 345 °C. The X-ray scattering curves of liquid $Ge_{15}Te_{85}$ were recorded at 380, 450, 550 and 650 °C. Attempts to supercool the liquid sample melted with a light-spot heater at the BW5 synchrotron station were unsuccessful. The experimental structure factors of liquid and amorphous (redrawn from [26]) $Ge_{15}Te_{85}$ are shown in figure 1. $Ge_{25}Te_{75}$ and $Ge_{33}Te_{67}$ alloys were measured at 550 °C and 750 °C respectively; the structure factors are shown in figure 2.

The shape of the experimental structure factors depends on the temperature as well as on the composition of the alloys. It is seen from figure 3 that the height of the first, $S(Q^{I})$, and the second, $S(Q^{II})$, maximum for the $Ge_{15}Te_{85}$ alloy exhibit strong but different temperature dependences: $S(Q^{I})$ at first increases when the temperature rises up to 450 – 550 °C, and then decreases at 650 °C; $S(Q^{II})$ decreases continuously with increasing temperature. It is to be mentioned that density of $Ge_{15}Te_{85}$ changes non-monotonously above the melting point with a maximum close to 500 ^{o}C [8, 9]. Such an anomalous temperature behaviour of the density and the intensity of the first maximum in the $S(Q)$ of liquid $Ge_{15}Te_{85}$ should be reflected by some structural changes in the short-range order. Bergman et al. [20] assign the changes of $S(Q)$ to an increase of the number of Te neighbours around Ge atoms. In their analysis they do not consider the possible changes of Te-Te correlations. Taking into account that pure liquid Te exhibits similar anomalous behaviour (see e.g. figures 1-3 of reference [20]) this simplification may limit the validity of their argumentation. In our opinion it is not possible to determine what exactly has changed in the SRO of binary Ge-Te alloys only from the total structure factors or pair distribution functions. Therefore further analysis will be carried out on the partial functions derived with the help of RMC.

4. RMC simulations

Since the first publication on the reverse Monte Carlo technique [21], it has been illustrated in a number of studies that RMC is a useful tool for modelling of the atomic structure of non-crystalline substances and determination of the partial pair correlation functions and other structural parameters (for details of the technique the reader is referred to a comprehensive review of R. McGreevy [22]). Recently we have proven that reliable partial structure factors and partial pair correlation functions of a binary liquid alloy can be obtained with two independent diffraction curves if additional physical information (e.g. atomic size differences or coordination constraints) can be built in the simulation [27]. Due to different values of the X-ray atomic scattering factors ($f_{Ge}(0)$ = 32 e.u., $f_{Te}(0)$ = 52 e.u.) and the neutron scattering lengths (b_{Ge} = 8.185 fm, b_{Te} = 5.8 fm [28]) for Ge and Te and application of plausible physical constraints one may expect to obtain a reliable picture of the atomic distribution in Ge-Te alloys.

In the present work, coupled simulations of the X-ray and neutron diffraction measurements were carried out with boxes of 15000 - 20000 atoms. The densities of liquid alloys were taken from [20, 29]. Initial configurations were obtained by hard sphere simulation runs, i.e. fitting no experimental data but applying hard sphere cut-offs and coordination constraints. For all compositions the cut off distances between Ge-Te and Te-Te pairs were 2.3 Å and 2.5 Å respectively. For $Ge_{15}Te_{85}$ Ge-Ge bonding was eliminated by setting the minimum distance r_{GeGe} to 3.5 Å. In case of $Ge_{33}Te_{67}$ and $Ge_{25}Te_{75}$ alloys runs with r_{GeGe} = 2.3 Å were also carried out. In these runs Ge-Ge coordination constraints were also applied by restricting the average Ge-Ge coordination number between 2.3 Å and 3.2 Å.

As an example, the RMC simulated and experimental total structure factors for liquid $Ge_{15}Te_{85}$ (380 °C), $Ge_{25}Te_{75}$ (550 °C) and $Ge_{33}Te_{67}$ (750 °C) are plotted in figure 2. The agreement between the experimental $S_{X,N}^{\exp}$ and the simulated $S_{X,N}^{RMC}$ structure factors was judged by the value of

$$\chi_{X,N}^2 = \frac{\sum_i (S_{X,N}^{RMC}(Q_i) - S_{X,N}^{\exp}(Q_i))^2}{\sigma_{X,N}^2} \qquad (1)$$

where σ is a parameter of RMC chosen appropriately to determine the ratio of accepted moves. Subscripts X and N refer to X-ray or neutron diffraction data. The value of σ was usually between 0.0015 and 0.003, depending on the temperature and composition. However, it was always kept constant when χ^2 was investigated as the function of the coordination constraints. The maximum random atomic displacement was 0.2 Å and the ratio of accepted moves was usually between 0.2 and 0.4.

5. Discussion

5.1. $Ge_{15}Te_{85}$ eutectic alloy

The partial structure factors and pair distribution functions for liquid $Ge_{15}Te_{85}$ simulated with RMC are shown in figure 4. On the base of Raman scattering data we assumed in our previous paper [26] that there are no Ge-Ge bonds in amorphous $Ge_{15}Te_{85}$. It is reasonable to assume that this also holds for liquid $Ge_{15}Te_{85}$ in the vicinity of the melting point. The existence of the Ge-Ge bonds cannot be ruled out at elevated temperatures. The weight of the Ge-Ge partial structure factor is so small that for this composition the diffraction measurements are not conclusive concerning the existence of the Ge-Ge bonds. This is well seen from Table 1 where the weights of the partial structure factors for the alloys studied are given.

The partial structure factors and pair distribution functions are strongly temperature dependent (figure 4). At 380 ^{o}C (just above melting) both $g_{TeTe}(r)$ and $g_{GeTe}(r)$ have a distinct first minimum; Te-Te and Ge-Te coordination numbers are 1.7 and 3.7 respectively. At elevated temperatures the first minimum of $g_{TeTe}(r)$ becomes more and more shallow and the overlap between the first and second coordination spheres is stronger. The differences between the partial pair distribution functions at 550 °C and 650 °C are small and the data for 550 °C are therefore not shown in figure 4. The nearest neighbour distances r_{ij} and coordination numbers N_{ij} for all temperatures calculated up to the first minimum of $r^2g_{TeTe}(r)$ are given in Table 2.

From the temperature evolution of the Te-Te and Ge-Te partial pair correlation functions and coordination parameters (figure 4 and Table 2) it is seen that in accordance with the physico-chemical properties, the temperature induced structural changes in liquid $Ge_{15}Te_{85}$ are very pronounced in the temperature interval from ϑ_{eut} = 375 °C up to 450 °C, and they are not so strong at higher temperatures. It can be also observed that there is a slight increase in the Ge-Te coordination number and Ge-Te nearest distance. The changes of the respective values for the Te-Te pairs are comparable. As pure elemental Te shows a similar behaviour in the supercooled region [30], our results suggest that the addition of Ge stabilizes the low-temperature structure of liquid Te and the structural transformations of the eutectic $Ge_{15}Te_{85}$ alloy cannot be assigned only to changes in $g_{GeTe}(r)$ as it was suggested in [20].

Figure 5 gives the Te-Ge-Te bond angle distribution for the liquid $Ge_{15}Te_{85}$ derived with the help of RMC. A striking feature is the usual artificial peak at 60°. Apart from that, it can be concluded that the bond angle distribution has a maximum around 100°, which is broadened with increasing temperature. This suggests that with increasing temperatures tetrahedral local order transforms to a more dense atomic arrangement. This is in line with conclusions made by Bergman et al. [20] on the base of neutron diffraction and density measurements in liquid $Ge_{15}Te_{85}$.

5.2. $Ge_{25}Te_{75}$ alloy

The structure of liquid $Ge_{25}Te_{75}$ was modelled in a series of the simulation runs where the number of Ge-Ge neighbours was varied. Figure 6 shows the partial structure factors and partial pair distribution functions of liquid $Ge_{25}Te_{75}$ at 550 °C obtained with different values of the Ge-Ge coordination number ($N_{GeGe} = 0$, $N_{GeGe} = 0.6$ and $N_{GeGe} = 1.0$). It has been found that for $N_{GeGe} < 1.6$ the quality of the fit was not so sensitive to the number of Ge-Ge pairs as in the case of $Ge_{33}Te_{67}$ (this will be seen later). It can also be observed that changes in $g_{GeGe}(r)$ and $g_{GeTe}(r)$ compensate each other. From the shape of the first peak in $g_{GeGe}(r)$ it appears that N_{GeGe} should not be higher than 0.8 – 1 for the $Ge_{25}Te_{75}$ composition. The values of the nearest neighbours and the coordination numbers for liquid $Ge_{25}Te_{75}$ at 550 °C estimated with the constraint $N_{GeGe} = 0.6$ are given in Table 3. It should however be mentioned that the first coordination shell in $g_{TeTe}(r)$ is not well defined on the right hand side.

The Te-Ge-Te bond angle distribution for the liquid $Ge_{25}Te_{75}$ was also determined from the simulation. This result will be discussed together with the respective data for the $Ge_{33}Te_{67}$ composition.

5.3. $Ge_{33}Te_{67}$ alloy

GeX_2 (X = S, Se, Te) glasses and melts belong to the most intensely investigated disordered systems. Maruyama et al. studied liquid Ge-chalcogen mixtures by time of flight neutron diffraction [31]. In works [32-34] the structure of amorphous and liquid $GeSe_2$ was investigated by neutron diffraction with isotopic substitution. It was found that both states comprise edge- and corner sharing tetrahedral units. It was also shown that 25(5) % of Ge and 20(5) % of Se atoms are involved in homopolar bonds. While Ge-Se melts can be vitrified up to at least 40 at.% Ge content [35] Ge-Te glasses can be obtained only in the vicinity of the eutectic point (15 at.% Ge), where the melt can be deeply supercooled. Though a detailed and in depth explanation of this phenomenon is certainly far beyond the scope of our paper two remarks can be made here: i) there are two stable crystalline compounds (GeSe and $GeSe_2$) in the Ge_xSe_{1-x} system. The existence of competing crystal structures may enhance the glass forming ability (especially for $x \geq 1/3$); ii) it has been shown [36] that there are no Ge-Ge bonds in vitreous Ge_xTe_{1-x}. ($0.16 \leq x \leq 0.20$). Therefore it can be concluded that in contrast with the Ge-Se system the formation of Ge-Ge bonds is not favourable in Ge-Te glasses. This is also supported by the fact that upon solidification liquid Ge_xTe_{1-x} ($x < 0.5$) alloys segregate into two phases (GeTe and Te) without Ge-Ge bonds.

Several different simulation runs were carried out to study the structure of liquid $Ge_{33}Te_{67}$. It has been found that the diffraction data cannot be well fitted if a large minimum Ge-Ge distance ($r_{GeGe} = 3.5$ Å) is assumed, i.e. when Ge-Ge bonds are excluded. The fit was significantly improved when the minimum Ge-Ge distance was set to be 2.3 Å and the average Ge-Ge coordination number was raised to 1.5 – 2: the χ^2 value (Eq. 1) for X-ray data decreased by about 70 - 80% (see figure 7). Parts of the experimental neutron structure factor for liquid $Ge_{33}Te_{67}$ and the structure factors simulated with N_{GeGe}

= 0 and N_{GeGe} = 1.5 are compared in figure 8. It is noteworthy that the sum of Ge-Ge and Ge-Te coordination numbers remained about 4.8 ± 0.2 in all cases. Regardless the constraints used in RMC (coordination numbers or nearest neighbour distances) the Ge-Te bond length was about 2.85 Å for the liquid $Ge_{33}Te_{67}$.

However, it appears that Ge-Ge coordination number of 1.5 - 2 is too high for this composition. This is quite close to the value which would be obtained for the random distribution of Ge and Te atoms (i.e. when 1/3 of the neighbours of Ge atoms are other Ge atoms). Moreover, when we applied the constraint $N_{GeGe} \geq 1$ then artificial sharp features appeared on the Ge-Ge partial pair distribution functions. Therefore we assume that the real number of Ge-Ge atoms is smaller, and N_{GeGe} = 0.6 is chosen for a further analysis. The RMC simulated (with N_{GeGe} = 0.6) and experimental total structure factors for the liquid $Ge_{33}Te_{67}$ are compared in figure 2. The respective partial structure factors and pair distribution functions are plotted in figure 9.

It is noteworthy that in comparison with liquid $Ge_{25}Te_{75}$ the first and the second maxima in the Te-Te pair distribution function shift to lower *r*-values and become slightly sharper (see figure 10 and Table 3). This suggests that the structure becomes more compact in the latter case. The first maximum in the Ge-Te pair distribution function for liquid $Ge_{33}Te_{67}$ is virtually not changing as compared to that of liquid $Ge_{25}Te_{75}$. But the second maximum in the $g_{GeTe}(r)$ for liquid $Ge_{33}Te_{67}$ is smeared out in comparison with liquid $Ge_{25}Te_{75}$. These changes are obviously related to an increased Ge concentration. There seems to be a tendency of reducing the number of Te-Te bonds.

A formation of Ge-Ge bonds in liquid $Ge_{33}Te_{67}$ was also found in the EXAFS study of Hosokawa et al [37]. They reported 3.2 – 3.25 Å both for the Ge-Ge and Ge-Te bond length in liquid $GeTe_2$ at 700 °C. These distances are remarkably longer than those determined by us (2.9 Å and 2.81 Å respectively). It is not clear where the differences originate. However as we already mentioned it was not possible to fit the experimental data using RMC with the constraint r_{GeGe} > 3 Å. Taking into account rather high weights of Ge-Te partials both in X-ray and neutron diffraction patterns (Table 1) the reliability of the nearest neighbour distances derived with RMC is also very high. It should also be mentioned that the useful EXAFS data range in [37] extends only up to 7 – 8 $Å^{-1}$. As the XANES region extends up to 3 – 4 $Å^{-1}$ it remains to be seen how accurately these values could be determined on the base of such a limited data range.

The Te-Ge-Te bond angle distribution in liquid $Ge_{25}Te_{75}$ and $Ge_{33}Te_{67}$ derived with RMC are shown in figure 11. Except for the artificial peak at about 60°, which often appears in configurations obtained with RMC, the following features should be noted: i) there is a maximum in the Te-Ge-Te bond angle distribution for liquid $Ge_{25}Te_{75}$ at about 100°; ii) the maximum position in the Te-Ge-Te bond angle distribution for liquid $Ge_{33}Te_{67}$ is situated at about 90°. These findings suggest that the atomic packing is more compact in liquid $Ge_{33}Te_{67}$ as compared to $Ge_{25}Te_{75}$ alloy as it was already concluded from the analysis of the Te-Te and Ge-Te nearest neighbour distances. The shift of the peak in the bond angle distribution curve to 90° and the appearance of the maximum at ~ 160° for liquid

$Ge_{33}Te_{67}$ give evidence of a structural transformation from tetrahedral towards octahedral local ordering with increasing Ge content.

Summary

1) There are significant differences in the local atomic order of liquid $Ge_{15}Te_{85}$ at low temperatures up to about 450 °C including the supecooled liquid state and at the temperatures above 450 °C. The structural transformations of the $Ge_{15}Te_{85}$ alloy are connected with the changes both in $g_{GeTe}(r)$ and $g_{TeTe}(r)$.
2) It is assumed that there are no Ge-Ge bonds in liquid $Ge_{15}Te_{85}$ close to the melting point but they may exist at higher temperatures. It follows from the analysis of the experimental data that Ge-Ge bonding appears when Ge content is increased. Thus Ge-Ge bonding seems to be present in liquid $Ge_{25}Te_{75}$ and $Ge_{33}Te_{67}$.
3) It can be assumed that the temperature at which the structural changes in the Te-rich Ge-Te alloys occur is related to their Ge content. Indeed, taking into account the composition and temperature dependences of the density, sound velocity and other physical properties of liquid Te and Ge-Te alloys [29, 30] and the results of our structural investigations it can be concluded that addition of Ge (up to about 15 - 20 at.% Ge) to Te stabilizes the low-temperature liquid structure.
5) We assume that there is a connection between the glass forming ability of Ge-Te alloys and Ge-Ge/Ge-Te bonding. It is probable that a higher number of Ge-Te bonds stabilizes the low temperature liquid structure and for the alloys with a high glass-forming ability (around $Ge_{15}Te_{85}$ composition) the liquid-liquid phase transformations take place above the liquidus line. On the other hand a high number of Ge-Ge bonds is not favourable in the Te-rich Ge-Te alloys. This is also supported by the fact that upon solidification liquid Ge-Te alloys segregate into two phases – GeTe and Te – without Ge-Ge bonds.

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Table 1. The X-ray W_{ij}^{X} (at Q = 0) and neutron W_{ij}^{N} weights of the partial structure factors for the investigated Ge-Te alloys.

Composition	W_{TeTe}^{X}	W_{TeTe}^{N}	W_{GeTe}^{X}	W_{GeTe}^{N}	W_{GeGe}^{X}	W_{GeGe}^{N}
$Ge_{15}Te_{85}$	0.814	0.641	0.176	0.319	0.010	0.040
$Ge_{25}Te_{75}$	0.689	0.464	0.282	0.434	0.029	0.102
$Ge_{33}Te_{67}$	0.589	0.344	0.357	0.485	0.054	0.171

Table 2. The nearest neighbour distances r_{ij} and coordination numbers N_{ij} for amorphous and liquid $Ge_{15}Te_{85}$.

Temperature	r_{TeTe} (Å)	r_{GeTe} (Å)	N_{TeTe}	N_{GeTe}	N_{TeX}
Amorphous*	2.73	2.62	1.62	3.95	2.32
380 °C	2.75	2.70	1.7	3.7	2.4
450 °C	2.85	2.77	1.9	4.0	2.6
550 °C	2.88	2.82	1.9	4.0	2.6
650 °C	2.83	2.77	1.9	4.6	2.7

* [28] (XRD + ND + RMC, "tetrahedral" model)

Table 3. The nearest neighbour distances r_{ij} and coordination numbers N_{ij} for liquid $Ge_{25}Te_{75}$ at 550 °C and $Ge_{33}Te_{67}$ at 750 °C.

Alloy	r_{TeTe} (Å)	r_{GeTe} (Å)	r_{GeGe} (Å)	N_{TeTe}	N_{GeTe}	N_{GeGe}
$Ge_{25}Te_{75}$	3.10	2.81	2.5	2.1	4.2	0.5*
$Ge_{33}Te_{67}$	2.81	2.81	2.9	0.8	4.1	0.6*

* these values were applied as the constraints in RMC simulations.

Figure captions

Figure 1. Experimental structure factors of $Ge_{15}Te_{85}$ alloys.

Figure 2. Experimental (*circles*) and RMC simulated (*lines*) structure factors of liquid $Ge_{15}Te_{85}$, $Ge_{25}Te_{75}$ and $Ge_{33}Te_{67}$. Just every 5th experimental point is shown for $Q > 4.5$ Å^{-1} for clarity.
Simulation constraints:
$Ge_{15}Te_{85}$ – $N_{GeGe} = 0$; $r_{TeTe} = 2.5$ Å; $r_{GeTe} = 2.3$ Å; $r_{GeGe} = 3.5$ Å;
$Ge_{25}Te_{75}$ – $N_{GeGe} = 0.6$; $r_{TeTe} = 2.5$ Å; $r_{GeTe} = 2.3$ Å; $r_{GeGe} = 3.5$ Å;
$Ge_{33}Te_{67}$ – $N_{GeGe} = 0.6$; $r_{TeTe} = 2.5$ Å; $r_{GeTe} = 2.3$ Å; $r_{GeGe} = 2.3$ Å.

Figure 3. Temperature dependences of $S(Q^{I})$ and $S(Q^{II})$ for the $Ge_{15}Te_{85}$ alloy.

Figure 4. Temperature evolution of the RMC-simulated partial structure factors and partial pair correlation functions of liquid $Ge_{15}Te_{85}$.

Figure 5. Te-Ge-Te bond angle distribution in liquid $Ge_{15}Te_{85}$ in dependence on temperature.

Figure 6. Partial pair distribution functions of liquid $Ge_{25}Te_{75}$ at 550 °C simulated with different values of N_{GeGe}.

Figure 7. Dependence of the fit quality χ^2 for liquid $Ge_{33}Te_{67}$ at 750 °C on the constraint N_{GeGe}.

Figure 8. The experimental neutron structure factor of liquid $Ge_{33}Te_{67}$ at 750 °C and the structure factors simulated with $N_{GeGe} = 0$ and $N_{GeGe} = 1.5$.

Figure 9. Partial structure factors and partial pair correlation functions of liquid $Ge_{33}Te_{67}$ at 750 °C (simulated with $N_{GeGe} = 0.6$).

Figure 10. Comparison of the RMC-simulated partial pair distribution functions for liquid $Ge_{25}Te_{75}$ and $Ge_{33}Te_{67}$ alloys.

Figure 11. Te-Ge-Te bond angle distribution in liquid $Ge_{25}Te_{75}$ at 550 °C and $Ge_{33}Te_{67}$ at 750 °C.

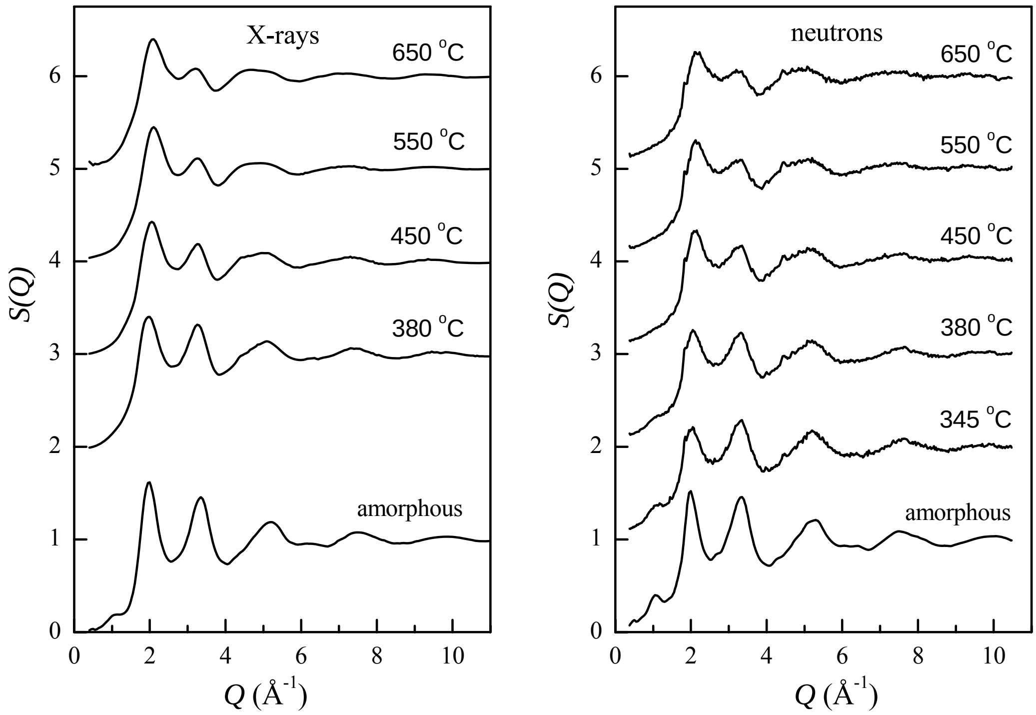

Figure 1. Experimental structure factors of $Ge_{15}Te_{85}$ alloys.

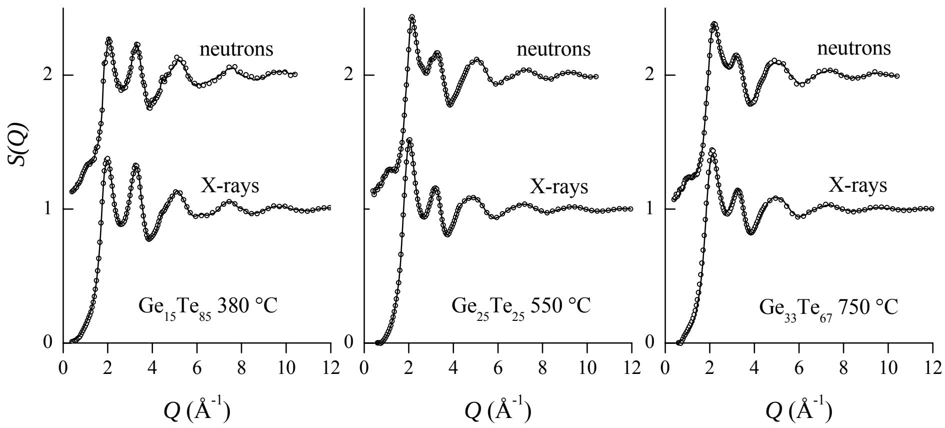

Figure 2. Experimental (*circles*) and RMC simulated (*lines*) structure factors of liquid $Ge_{15}Te_{85}$, $Ge_{25}Te_{75}$ and $Ge_{33}Te_{67}$. Just every 5th experimental point is shown for $Q > 4.5$ Å^{-1} for clarity. Simulation constraints:

$Ge_{15}Te_{85}$ – $N_{GeGe} = 0$; $r_{TeTe} = 2.5$ Å; $r_{GeTe} = 2.3$ Å; $r_{GeGe} = 3.5$ Å;

$Ge_{25}Te_{75}$ – $N_{GeGe} = 0.6$; $r_{TeTe} = 2.5$ Å; $r_{GeTe} = 2.3$ Å; $r_{GeGe} = 3.5$ Å;

$Ge_{33}Te_{67}$ – $N_{GeGe} = 0.6$; $r_{TeTe} = 2.5$ Å; $r_{GeTe} = 2.3$ Å; $r_{GeGe} = 2.3$ Å.

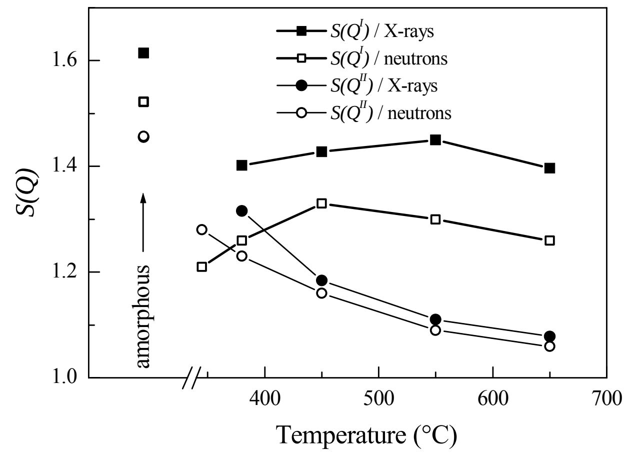

Figure 3. Temperature dependences of $S(Q^{\mathrm{I}})$ and $S(Q^{\mathrm{II}})$ for the $Ge_{15}Te_{85}$ alloy.

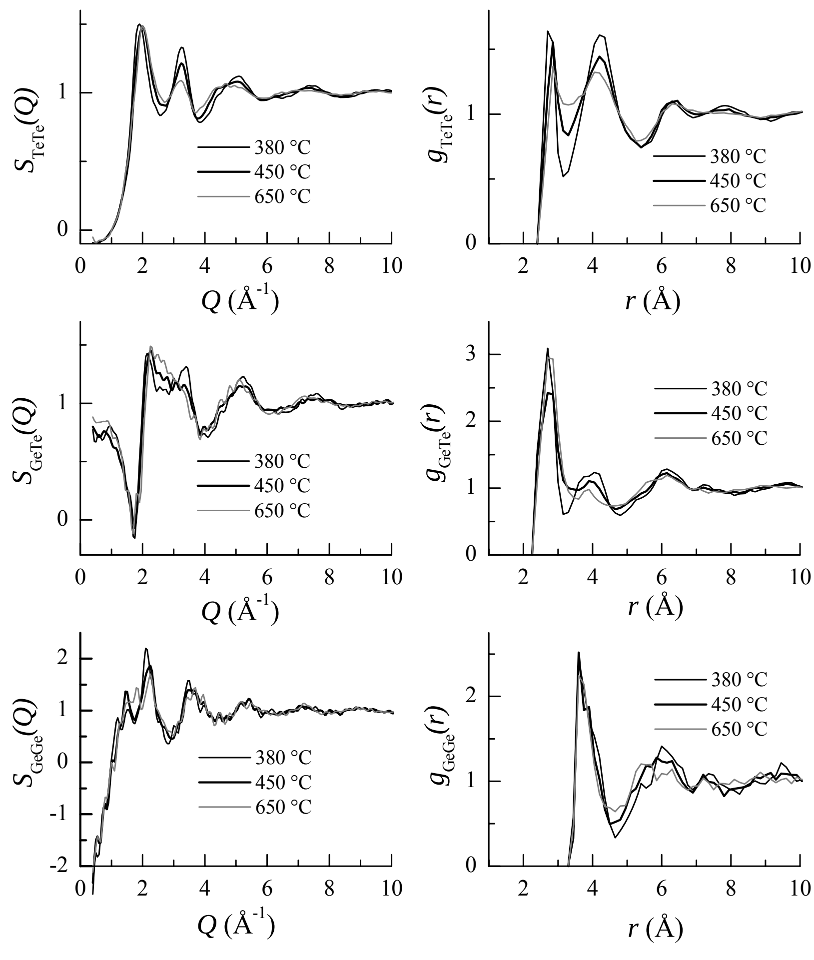

Figure 4. Temperature evolution of the RMC-simulated partial structure factors and partial pair correlation functions of liquid $Ge_{15}Te_{85}$.

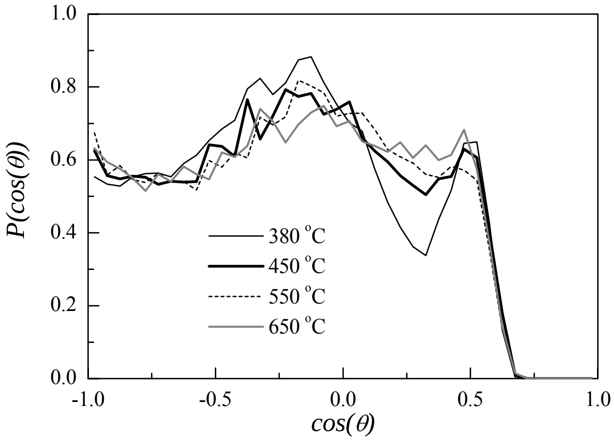

Figure 5. Te-Ge-Te bond angle distribution in liquid $Ge_{15}Te_{85}$ in dependence on temperature.

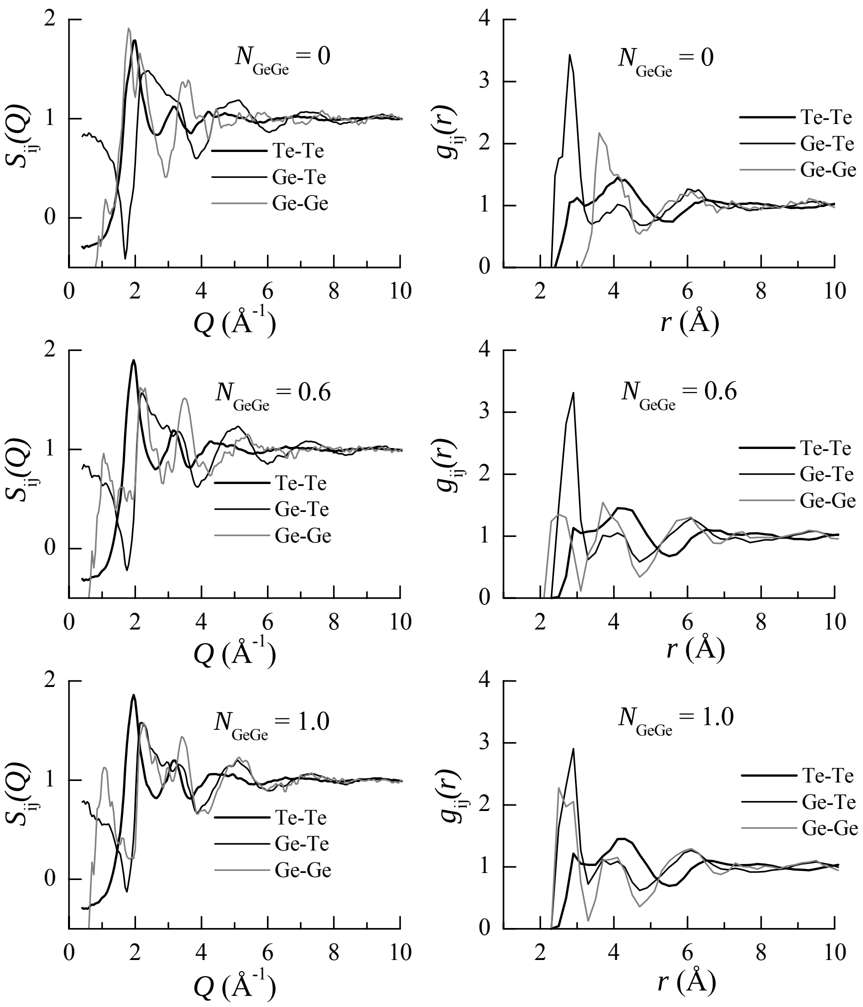

Figure 6. Partial pair distribution functions of liquid $Ge_{25}Te_{75}$ at 550 °C simulated with different values of N_{GeGe}.

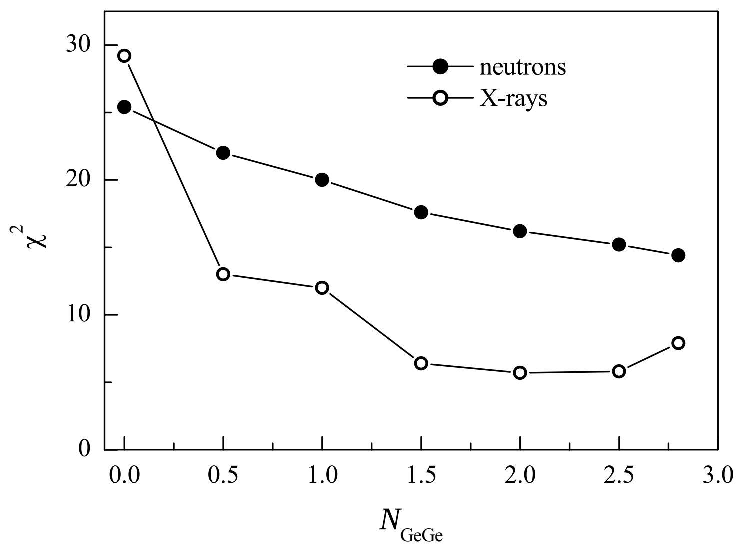

Figure 7. Dependence of the fit quality χ^2 for liquid $Ge_{33}Te_{67}$ at 750 °C on the constraint N_{GeGe}.

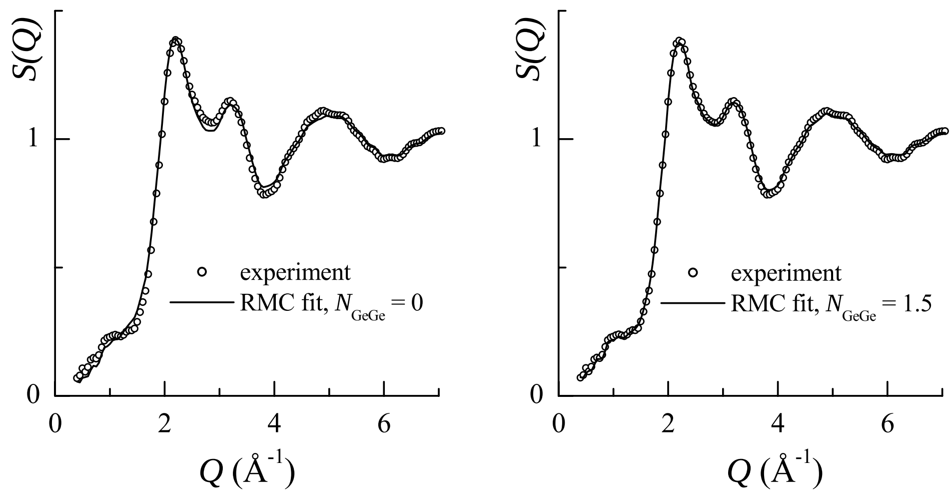

Figure 8. The experimental neutron structure factor of liquid $Ge_{33}Te_{67}$ at 750 °C and the structure factors simulated with $N_{GeGe} = 0$ and $N_{GeGe} = 1.5$.

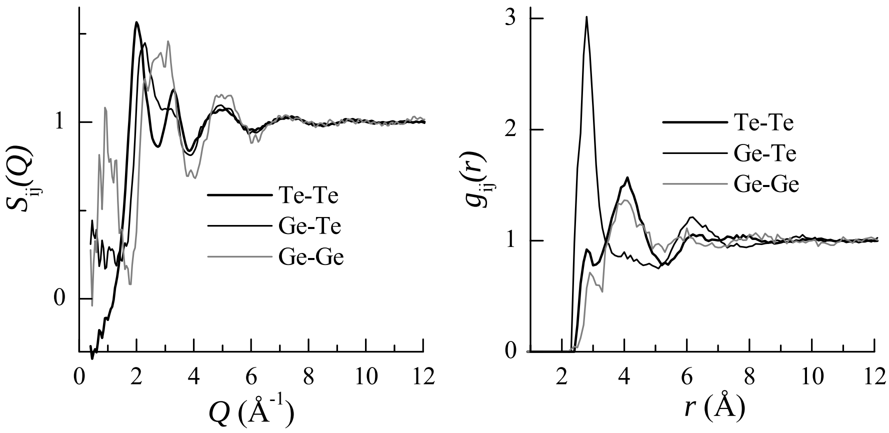

Figure 9. Partial structure factors and partial pair correlation functions of liquid $Ge_{33}Te_{67}$ at 750 °C (simulated with $N_{GeGe} = 0.6$).

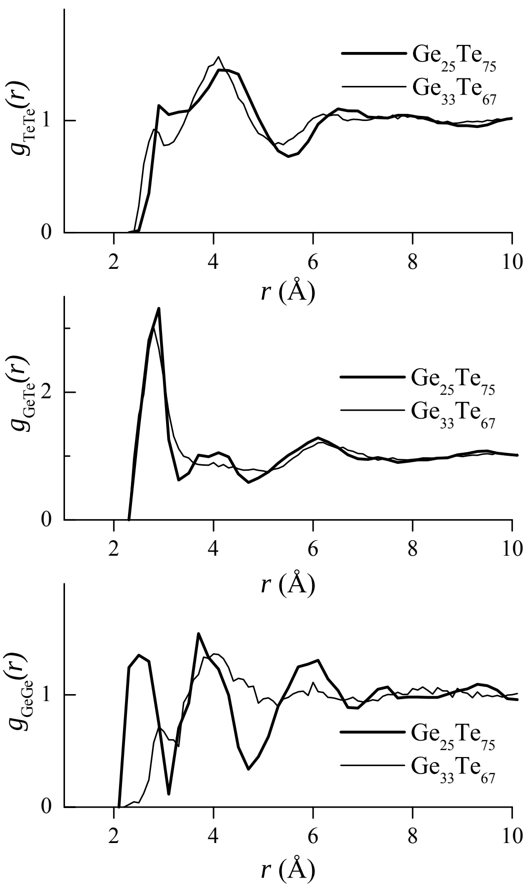

Figure 10. Comparison of the RMC-simulated partial pair distribution functions for liquid $Ge_{25}Te_{75}$ and $Ge_{33}Te_{67}$ alloys.

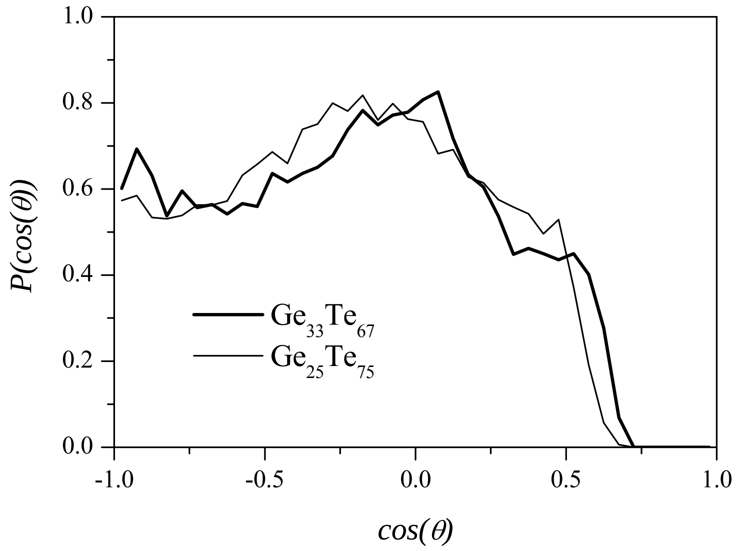

Figure 11. Te-Ge-Te bond angle distribution in liquid $Ge_{25}Te_{75}$ at 550 °C and $Ge_{33}Te_{67}$ at 750 °C.