Neutron and X-ray Scattering on Liquid Eutectic Ge–Te, Sn–Te and Pb–Te Alloys

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From neutron and X-ray diffraction investigations on liquid $Ge_{15}Te_{85}$, $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ alloys the coordination numbers and nearest neighbour distances of these systems are obtained. The partial structure factors and partial pair correlations reveal that the short-range order of the eutectic Ge–Te melt differs from that of the eutectic Sn–Te and Pb–Te melts.

Key words: Neutron scattering; X-ray scattering; short-range order; liquid alloys; eutectic Ge–Te; Sn–Te and Pb–Te melts.

1. Introduction

All binary alloy phase diagrams of tellurium with fourth group elements have an eutectic on the tellurium-rich side near 85 at-% tellurium (Massalski [1]). Besides with the exception of the Si–Te system, these eutectics are built-up from $X_{0.5}Te_{0.5}$ (X = Ge, Sn, Pb) and pure Te. Whereas the crystalline phases SnTe and PbTe in the temperature range above the eutectic line form a cubic structure (NaCl-lattice), the compound GeTe shows a phase transition from the trigonal As-structure (α-phase) to the cubic NaCl-structure (β-phase) at 25 K above the eutectic temperature (Feltz [2]).

From measurements of the heat capacity of the eutectic Ge–Te melt Castanet and Bergman [3] concluded the existence of a second order phase transition in the liquid state.

For the liquid Sn–Te and Pb–Te alloys, the negative enthalpy of mixing measured by Predel et al. [4] indicates the tendency of compound formation in the sense of Sauerwald's classification [5].

According to Tschirner et al. [6] the electrical resistivity of liquid $Ge_{15}Te_{85}$ decreases by nearly two orders of magnitude within about 100 K above the eutectic temperature. In contrast, the resistivity of liquid $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ shows only a very weak dependence on temperature.

Herwig and Wobst [7] determined the dynamical viscosity of these liquid eutectic alloys. Whereas the Arrhenius plot of the viscosity of liquid Sn–Te and Pb–Te eutectic alloys is nearly linear, liquid $Ge_{15}Te_{85}$ shows a distinct deviation from linearity. Within approximately 100 K above the eutectic line the activation energy of viscous flow increases strongly with decreasing temperature.

Neutron scattering investigations on molten $Ge_{17.5}Te_{82.5}$ alloys have been performed by Nicotera et al. [8]. The distance and nearest neighbour coordination number increase with increasing temperature. The total coordination number has been considered consistent with a structure model where Ge is fourfold and Te is threefold coordinated.

From neutron and X-ray diffraction experiments on liquid $Ge_{15}Te_{85}$ alloys Neumann et al. [9, 10] determined partial structure factors and pair correlation functions in dependence on temperature. On the basis of partial distances and coordination numbers of TeTe and GeTe pairs a structure model assuming an inhomogeneous liquid at low temperatures has been discussed. According to this model the low temperature melt is built-up from pure Te-regions consisting of two- and threefold bonded Te-atoms and GeTe-regions having the short-range order of α-GeTe.

2. Neutron Scattering on Liquid $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$

Neutron diffraction experiments on liquid eutectic $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ alloys in dependence on temperature were performed at channel 2 of the Rossendorf research reactor. Experimental arrangement, measuring conditions and data reduction procedure were described by Neumann, Matz and Hoyer

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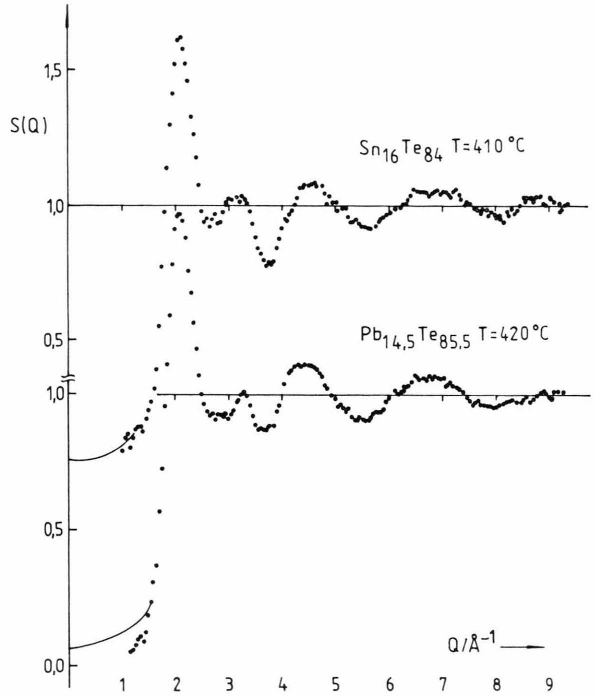

Fig. 1. Total structure factors of molten $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ measured by neutron scattering.

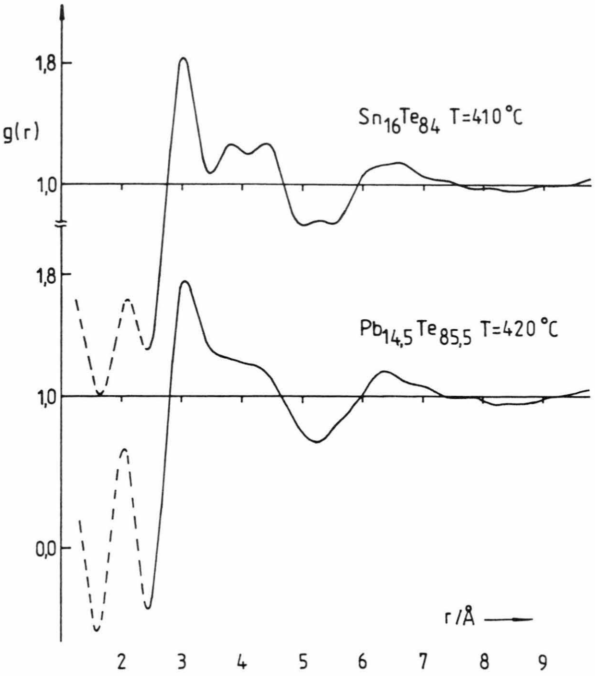

Fig. 2. Total pair correlation function of molten $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ computed from the structure factors of Figure 1.

Table 1. Pair distances and coordination numbers of nearest neighbours vs. temperature (neutron scattering).

$T/°C$	$Sn_{16}Te_{84}$		$Pb_{14.5}Te_{85.5}$	
	$r^1/Å$	N^1_{sym}	$r^1/Å$	N^1_{sym}
410	3.00	3.2	–	–
420	3.00	3.3	3.05	3.6
450	3.00	3.2	3.05	3.4
500	3.00	3.4	3.05	3.3
550	–	–	3.05	3.6
650	3.00	3.1	3.05	3.4
750	–	–	3.05	3.6

[11]. The structure factors, $S(Q)$, of liquid $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$, calculated according to the Faber and Ziman definition [12], are shown as functions of the momentum transfer $Q = 4\pi/\lambda \sin\theta$ (λ-wave length, θ-half scattering angle) in Figure 1. Because temperature induced changes are absent, only the structure factors near the eutectic temperature for both liquid melts are given. The general shape of $S(Q)$ is similar for both alloys.

For the calculation of the pair correlation functions, $g(r)$, are shown in Fig. 2; the structure factors were extrapolated to $Q=0$ [11]. The pair correlation functions of liquid $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ differ essentially at about 3.5 Å. Whereas $g(r)$ of liquid $Sn_{16}Te_{84}$ has a minimum there, the first and second coordination shells of liquid $Pb_{14.5}Te_{85.5}$ overlap strongly. Consequently, the determination of the number of nearest neighbours for the latter eutectic melt seems to be possible only by using the method of the symmetrized first peak of the radial distribution function. The distances and coordination numbers of nearest neighbours, compiled in Table 1, show that in contrast to liquid $Ge_{15}Te_{85}$, the eutectic SnTe and PbTe melts are not undergoing a change of the short-range order in the investigated temperature range.

3. X-ray Diffraction on Liquid $Ge_{15}Te_{85}$, $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$

The experimental intensities of the liquid eutectic alloys were measured with a θ-θ-diffractometer using Mo-K_α radiation and a focussing monochromator of pyrolytic graphite placed in front of the detector. The data reduction procedure was carried out as described by Hoyer et al. [13]. Because of the high vapour pressure of tellurium the intensities were determined in

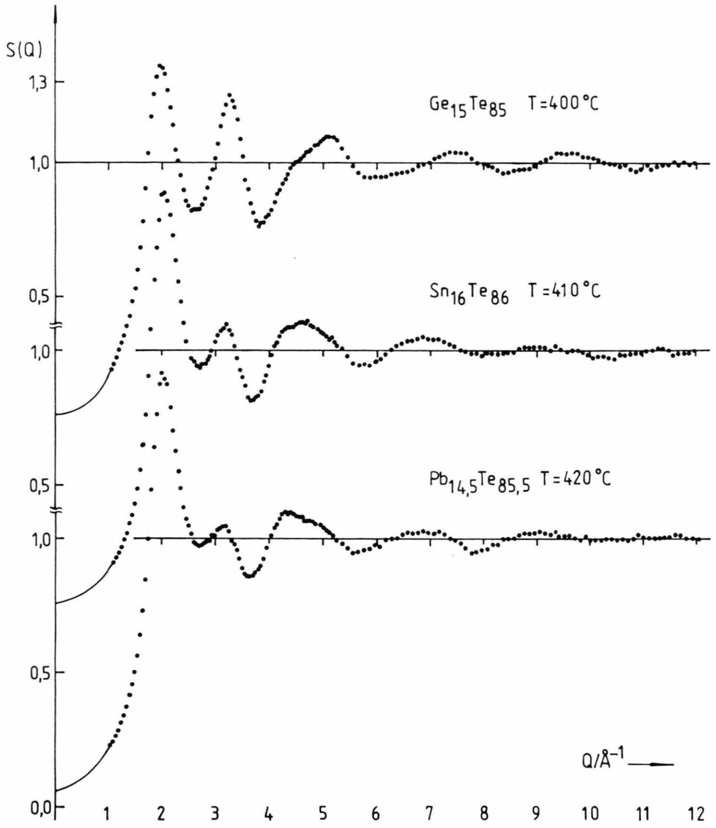

Fig. 3. Total structure factors of molten $Ge_{15}Te_{85}$, $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ measured by X-ray scattering.

several runs over the Q-range from 1 $Å^{-1}$ to 8 $Å^{-1}$ and from 5 $Å^{-1}$ to 12 $Å^{-1}$. After correction and normalization the averaged parts of the structure factors were assembled to the final structure factors given in Figure 3. As in the case of the neutron scattering experiments, the structure factors of liquid $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ are similar while that of $Ge_{15}Te_{85}$ differs distinctly, especially the relative heights of the first and second maxima.

The pair correlation functions of the liquid eutectics change systematically with increasing atomic number of the fourth group element (Figure 4, Table 2). The height of the first maximum decreases with increasing atomic number. In contrast to the liquid Sn–Te and Pb–Te eutectic, the Ge–Te eutectic has a deep first minimum in $g(r)$. The second maximum of $g(r)$ for the Ge–Te eutectic is higher than those of the other alloys. The distance of the first coordination shell increases with increasing atomic number. The greatest alteration in the first distance takes place at the transition from Ge to Sn. The liquid $Ge_{15}Te_{85}$ alloy has the lowest number of nearest neighbours. The first coordination numbers of $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ are nearly equal. Of course the determination of the number of nearest neighbours is rather uncertain for the Pb–Te eutectic because of the strong overlap of the first and second coordination shells.

Table 2. First distances and first coordination numbers determined with the method of symmetrization N^1_{sym} and integration up to the first minimum N^1_{min} as well as the height of the first maximum of the pair correlation function (X-ray scattering).

	$r^1/Å$	N^1_{sym}	N^1_{min}	$g(r^1)$
$Ge_{15}Te_{85}$	2.75	2.1	2.2	1.70
$Sn_{16}Te_{84}$	2.95	2.5	2.8	1.63
$Pb_{14.5}Te_{85.5}$	3.05	2.6	–	1.40

The differences between the coordination numbers shown in Table 1 and 2 are mainly caused by the different Q-ranges of the X-ray and neutron diffraction experiments. The area under the first maximum of $g(r)$ decreases with increasing upper integration limit.

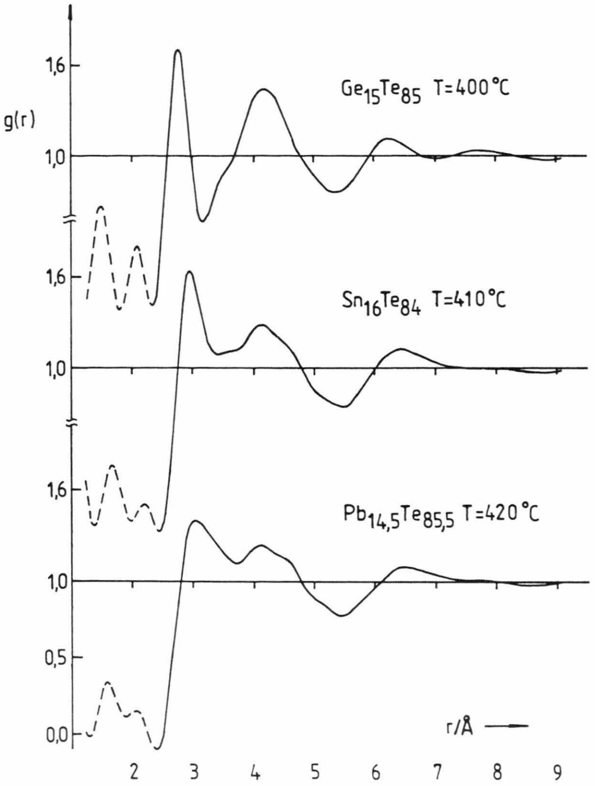

Fig. 4. Total pair correlation function of molten $Ge_{15}Te_{85}$, $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ computed from the structure factors of Figure 3.

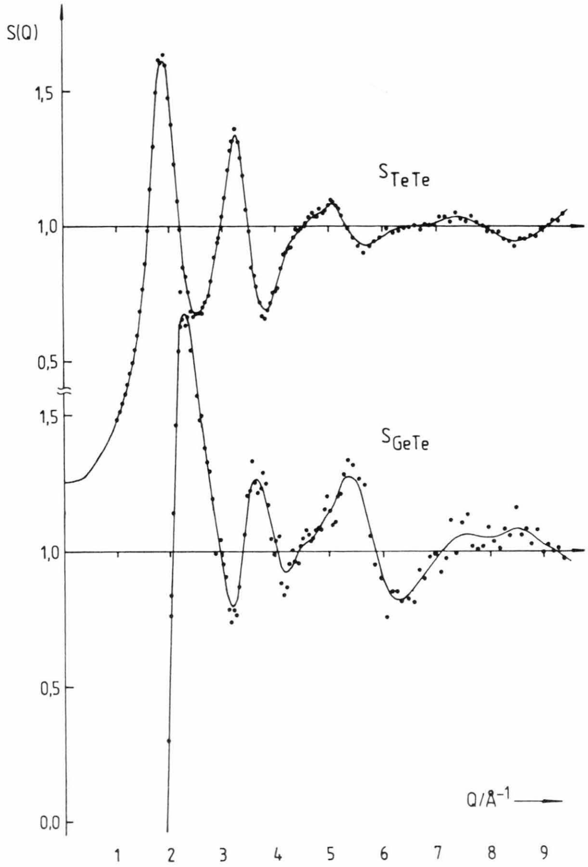

Fig. 5. Partial structure factors S_{GeTe} and S_{TeTe}.

4. Partial Structure Factors and Pair Correlation Functions

In the Faber-Ziman form the total structure factor $S(Q)$ is expressed by partial structure factors $S_{ij}(Q)$ in the following way:

$$S(Q)=\sum_{i,j}\frac{c_i c_j b_i b_j}{\langle b\rangle^2}S_{ij}(Q)=\sum_{i,j}w_{ij}S_{ij}(Q) \tag{1}$$

with $\langle b\rangle=\sum_i c_i b_i$.

Here c_i denote the relative atomic concentrations and b_i the scattering lengths of the elements constituting the sample. In the case X-ray diffraction the scattering length b_i is replaced by the Q-dependent atomic form factor $f_i(Q)$.

For the $Ge_{15}Te_{85}$ alloy the following equations for neutron and X-ray diffraction were derived:

$$\begin{aligned} S_n(Q)&=0.628\,S_{\mathrm{TeTe}}(Q)+0.332\,S_{\mathrm{GeTe}}(Q)\\ &\quad+0.04\,S_{\mathrm{GeGe}}(Q),\\ S_X(Q)&=0.814\,S_{\mathrm{TeTe}}(Q)+0.176\,S_{\mathrm{GeTe}}(Q)\\ &\quad+0.01\,S_{\mathrm{GeGe}}(Q). \end{aligned} \tag{2}$$

In this equation in the case of X-ray diffraction the weighting factors w_{ij} were calculated with the atomic numbers of the elements $Z_i=f_i(Q=0)$.

Because of the small weighting factor of the Ge–Ge contribution it seems to be possible to neglect the partial structure factor $S_{\mathrm{GeGe}}(Q)$. For the calculation of the partial structure factors $S_{\mathrm{TeTe}}(Q)$ and $S_{\mathrm{GeTe}}(Q)$, shown in Figure 5, the normalization $\sum w_{ij}=1$ and the Q-dependent X-ray atomic form factor have been

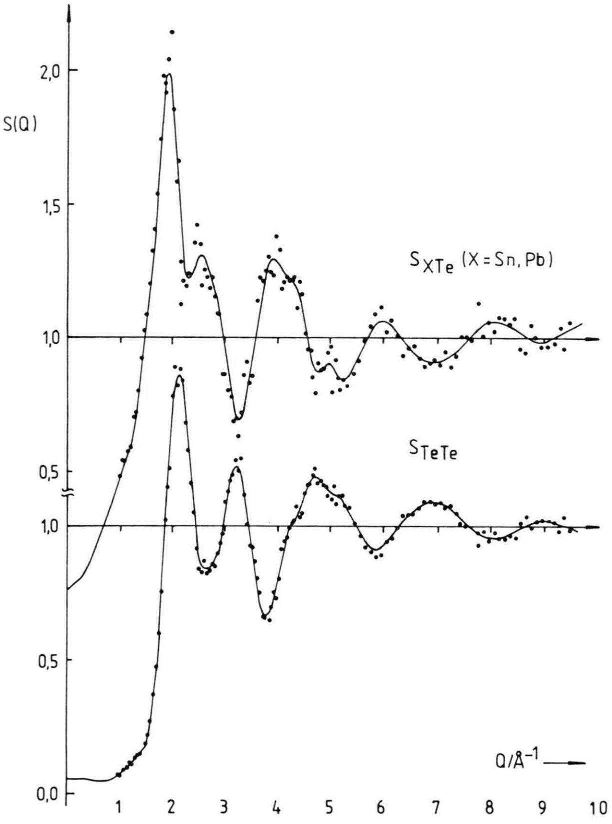

Fig. 6. Partial structure factors S_{TeTe} and S_{XTe} (X = Sn, Pb).

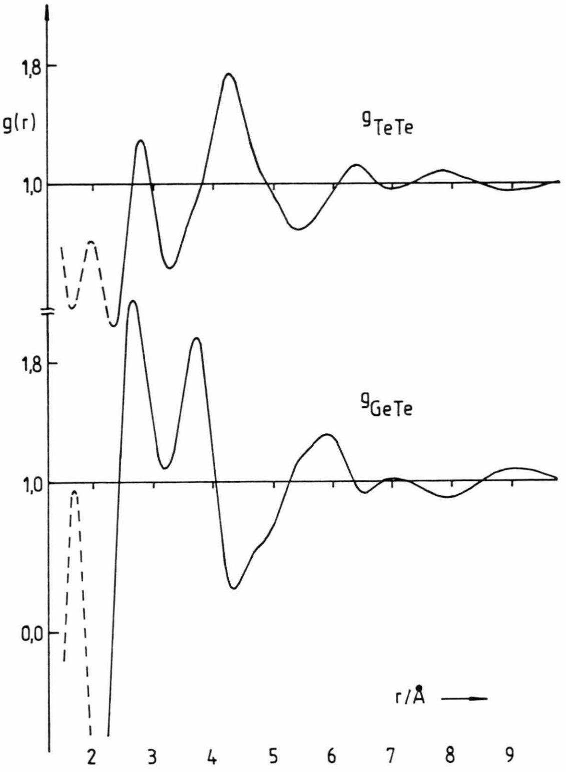

Fig. 7. Partial pair correlation functions g_{TeTe} and g_{GeTe} computed from the partial structure factors of Figure 5.

considered. The greater fluctuations of S_{GeTe} are caused by the lower weighting factors. The application of the same approximation for the determination of partial structure factors is not possible for the eutectic Sn–Te and Pb–Te melts. Owing to the small differences between the weighting factors for the case of X-ray and neutron scattering for both, Sn–Te and Pb–Te alloys, a small determinant of the equation system (c.f. (2)) results. Consequently, the method used for the Ge–Te eutectic can not be employed.

But from the discussion given in the foregoing paragraphs one can conclude that the short-range order of the $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ alloys is quite similar. Therefore it should be possible to use the method of the isomorphic substitution for the calculation of $S_{TeTe}(Q)$ and $S_{XTe}(Q)$ (X = Sn, Pb). This method presupposes that the elements Sn and Pb are equal in view of the physico-chemical behaviour in the corresponding eutectic melts.

Following this way, $S_{TeTe}(Q)$ and $S_{XTe}(Q)$ (X = Sn, Pb) have been calculated using the total structure factors determined by X-ray diffraction with the help of the equations

$$\begin{aligned} S^{t}_{SnTe}(Q) &= 0.714\, S_{TeTe}(Q) + 0.262\, S_{SnTe}(Q) \\ &\quad + 0.024\, S_{SnSn}(Q), \\ S^{t}_{PbTe}(Q) &= 0.622\, S_{TeTe}(Q) + 0.333\, S_{PbTe}(Q) \\ &\quad + 0.045\, S_{PbPb}(Q). \end{aligned} \tag{3}$$

Disregarding the contribution of the last term in each of the equations, $S_{TeTe}(Q)$ and $S_{XTe}(Q)$ (X = Sn, Pb) have been calculated (see Figure 6). The partial structure factors were smoothed with an eleven points convolution according to Savitzky and Golay [14] before Fourier transformation. The smoothing effect can be seen from Figs. 5 and 6.

From the comparison of the partial pair correlation functions in Figs. 7 and 8 it is clear that the short-range order of the low temperature $Ge_{15}Te_{85}$ melt differs distinctly from those of the liquid $Sn_{16}Te_{84}$ alloy and $Pb_{14.5}Te_{85.5}$ alloy. The Te–Te correlation function of the liquid Ge–Te eutectic has a low first

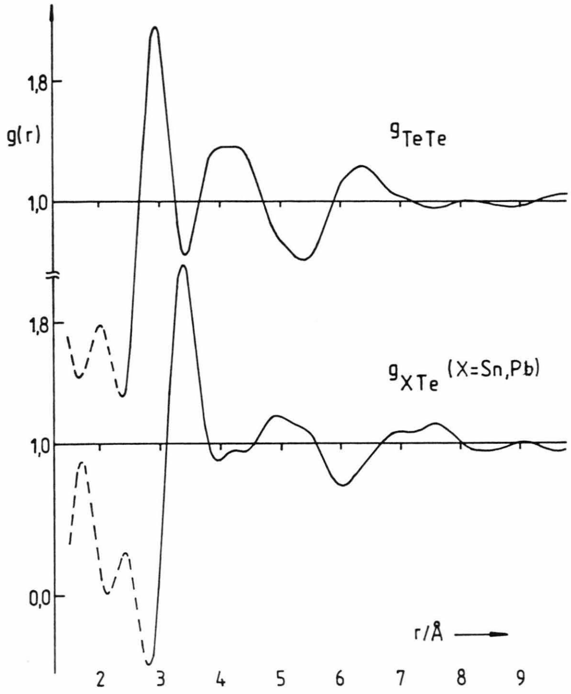

Fig. 8. Partial pair correlation functions g_{TeTe} and g_{XTe} (X = Sn, Pb) computed from the partial structure factors of Figure 6.

Table 3. Partial coordination numbers (integration up to the first minimum) and partial distances (X = Ge, Sn, Pb).

	N^{I}_{TeTe}	N^{I}_{XTe}	N^{II}_{XTe}	r^{I}_{TeTe}/Å	r^{I}_{XTe}/Å
$Ge_{15}Te_{85}$	1.8	3.1	6.3	2.80	2.65
$Sn_{16}Te_{84}$	3.1	4.6	–	2.95	3.40
$Pb_{14.5}Te_{85.5}$	3.2	4.8	–	2.95	3.40

maximum and a high second maximum, whereas this correlation function of the other two eutectics is characterized by a high first maximum and a low, broad second maximum.

Great differences also exist between the mixed correlation functions. The Ge–Te correlation function shows two well-resolved peaks. This means that the first and second coordination spheres are well developed. In contrast, the X–Te distribution function has only one sharp maximum.

The partial distances and coordination numbers, given in Table 3, are significantly lower for the liquid Ge–Te eutectic than for the liquid Sn–Te and Pb–Te eutectic.

5. Discussion

The experimental results on liquid $Ge_{15}Te_{85}$ alloy confirm the structure model reported by Neumann et al. [10]. According to this model, the eutectic Ge–Te melt at temperatures near the eutectic point is built-up from two kinds of associates: chain-like coordinated tellurium atoms and GeTe associates, corresponding to the structure of the α-GeTe phase. The partial coordination numbers $N^{I}_{TeTe} = 1.8$ for the Te–Te correlation and $N^{I}_{GeTe} = 3.1$ and $N^{I}_{GeTe} = 6.3$ for the first and second coordination shell of the Ge–Te correlation imply a short-range order quite similar to that of the crystalline phases of the eutectic. From the comparison of the partial distances $r^{I}_{TeTe} = 2.80$ Å and $r^{I}_{GeTe} = 2.65$ Å with the distances $r^{I}_{TeTe} = 3.20$ Å and $r^{I}_{GeTe} = 2.97$ Å, calculated from the atomic radii of the elements, one can conclude that the bonds of the associates in the eutectic Ge–Te melt should be rather tight.

In contrast, in the liquid Sn–Te eutectic and Pb–Te eutectic another type of short-range order seems to exist. The coordination numbers of nearest neighbours of both eutectics are significantly greater than in the eutectic Ge–Te melt. The first distances of the Sn–Te and Pb–Te correlation $r^{I}_{XTe} = 3.40$ Å (X = Sn, Pb) nearly agree with the distances $r^{I}_{SnTe} = 3.22$ Å and $r^{I}_{PbTe} = 3.55$ Å determined from the atomic radii of the elements.

The short-range order of liquid $Sn_{16}Te_{84}$ and $Pb_{14.5}Te_{85.5}$ alloy is possibly that of a network-like structure, where a Te atom has two or three Te neighbours, whereas a Sn or Pb atom is surrounded by at least four Te atoms.

As reported by Neumann et al. [10], a dissociation process of the associates in the liquid $Ge_{15}Te_{85}$ alloy takes place with increasing temperature. The partial as well as the total numbers and distances of first neighbours increase. The short-range order of the eutectic high temperature Ge–Te melt obviously resembles that of the eutectic Sn–Te and Pb–Te melt.

Further neutron diffraction experiments (wide angle scattering up to high Q-values and small angle scattering) are planned in order to get a deeper understanding of the detailed nature of the short-range order of the discussed liquid eutectics.

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