Structure Investigations on $Se_{1-x}Te_x$ Melts by Neutron Scattering and X-ray Diffraction

W. Hoyer*, B. Kunsch, M. Suda**, and E. Wieser***

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Neutron scattering results on $Se_{1-x}Te_x$ melts ($x = 0.3, 0.6, 0.8$) obtained at 460 °C are combined with earlier X-ray diffraction data. The behaviour of the number and distance of nearest neighbours is discussed with respect to chemical short-range order and transition from twofold to threefold coordination. For $Se_{70}Te_{30}$ the radial concentration correlation function $4\pi r^2 \varrho_{CC}(r)$ has been evaluated. It shows clearly the preferred formation of unlike pairs (Se-Te) within the chains.

1. Introduction

Liquid Selenium-Tellurium mixtures are very interesting with regard to their structure. The question arises in which way the transition proceeds from the Selenium-like structure with twofold coordination in zig-zag chains or Se_8-rings to the threefold coordination in the quasicrystalline structure of liquid Tellurium. Moreover chemical short-range order has to be expected taking into account the predominantly covalent nature of the chemical bonds in this system.

The structure of Selenium-Tellurium melts has been studied extensively using X-ray diffraction [1]. According to these results zig-zag chains are dominating up to about 50 at.% Te. The proportion of Se_8-rings decreases rapidly with increasing Te content and rising temperature. Above 50 at.% Te beside the chains increasing amounts of atomic arrangements with threefold coordination are formed. Concerning the distribution of Se and Te within the chains a slight preference of Se-Te pairs has been observed in [1].

Neutron scattering investigations on liquid Se-Te melts in the whole concentration region are reported in [2]. The transition to threefold coordination at about 50 at.% Te found in [1] has been confirmed in this investigation. The scattering curves up to 60 at.% Te are in good agreement with a model of nearly free rotating random chains with Se-Te substitution. For Te-rich melts a quasi-crystalline As-type network with Se-Te chains (Te concentration 60 at.%) has been assumed.

In a neutron scattering experiment with high maximum momentum transfer ($Q_{\max} = 250\ \text{nm}^{-1}$, $Q = (4\pi/\lambda)\sin\Theta$) on $Se_{0,25}Te_{0,75}$ at 414 °C the fine structure of the first peak in the radial distribution function has been resolved [3]. The evaluation of partial coordination numbers leads to the conclusion that 15% of Te are arranged in threefold coordination. This proportion increases up to 75% at 541 °C.

In the present work neutron scattering investigations on liquid $Se_{1-x}Te_x$ with $x = 0.3$, 0.6, and 0.8 are combined with X-ray diffraction results from [1] in order to obtain more detailed information about the atomic scale structure of this system especially in connection with chemical short-range order. The neutron scattering results from [2] are also considered for the discussion. The consideration of the results of several independent experiments enhances the reliability in the interpretation of parameters like number of nearest neighbours or distances of higher coordination spheres which are strongly influenced by experimental uncertainties (e.g. termination effect). The comparison of X-ray diffraction and neutron scattering results is of interest because of the reversal in the relation of the scattering power of the two components (neutrons:

$$b_{Se} = 0.80 \cdot 10^{-12}\ \text{cm}\,, \quad b_{Te} = 0.58 \cdot 10^{-12}\ \text{cm}\,,$$

X rays:

$$f_{Se}(Q=0) = 34\ \text{e.u.}\,, \quad f_{Te}(Q=0) = 52\ \text{e.u.})\,.$$

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* Technische Hochschule Karl-Marx-Stadt, Sektion Physik/EB, X-9001 Karl-Marx-Stadt, PSF 964, DDR.

** Forschungszentrum Seibersdorf, Physikinstitut, A-2444 Seibersdorf, Austria.

*** Zentralinstitut für Kernforschung Rossendorf, Akademie der Wissenschaften der DDR, X-8051 Dresden, PSF 19, DDR.

Reprint requests to Dr. W. Hoyer, TH Karl-Marx-Stadt, Sektion Physik/EB, PSF 964, X-9001 Karl-Marx-Stadt.

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2. Experimental

Neutron scattering experiments were carried out on $Se_{1-x}Te_x$ melts ($x = 0.3, 0.6, 0.8$) at 460 °C using the experimental equipment described in [4]. The samples were sealed under vacuum in cylindrical silica containers of 10 mm inner diameter and 1 mm wall thickness. The scattering patterns were recorded in the region from $Q = 2.5$ to $Q = 89\,\mathrm{nm}^{-1}$ using a wave length of 0.108 nm.

The measured intensities were put on an absolute scale by comparison with a Vanadium standard of identical dimensions. At the end of the correction and normalization procedure the normalization factor was adjusted using the Krogh Moe normalization condition [5] for the structure factor $S(Q)$. The change of the normalization factor was smaller than 10% for $Se_{70}Te_{30}$ and $Se_{20}Te_{80}$ but reached 23% in the case of $Se_{40}Te_{60}$. As reason for the latter large deviation we assume a somewhat incorrect position of the sample in the furnace.

Multiple scattering was treated as described in [4] using the tables of [6] which are in good agreement with the results of [7] for our sample dimensions. The calculated contribution of multiple scattering was in the range of 15% and 19% for $x = 0.3$ and $x = 0.8$, respectively. These theoretical values were adapted in such a way, that the experimental $S(0)$ values coincided with $S(0)$ values evaluated from compressibility data. The change of the multiple scattering amounted to less than 10% of its absolute value. The presented results correspond to $S(0)$ values estimated as in [1] from the compressibility of the solid alloys ($S(0)$ between 0.028 and 0.019 for x between 0.3 and 0.8). Compressibility data calculated from the sound velocity of Se-Te melts according to [8] yield $S(0)$ values between 0.086 and 0.115 in the same x-range. An evaluation of our neutron scattering results with these larger $S(0)$ decreases the change of the normalization factor necessary to fulfil the Krogh Moe condition. However, the resulting difference of the $S(Q)$ curves is smaller than 2% and therefore within the error limits. The absorption correction was carried out according to [9]. For the Placzek correction [10] we used a concentration averaged atomic mass.

3. Results

Figure 1 shows the structure factors evaluated from our neutron scattering data. Figure 2 presents

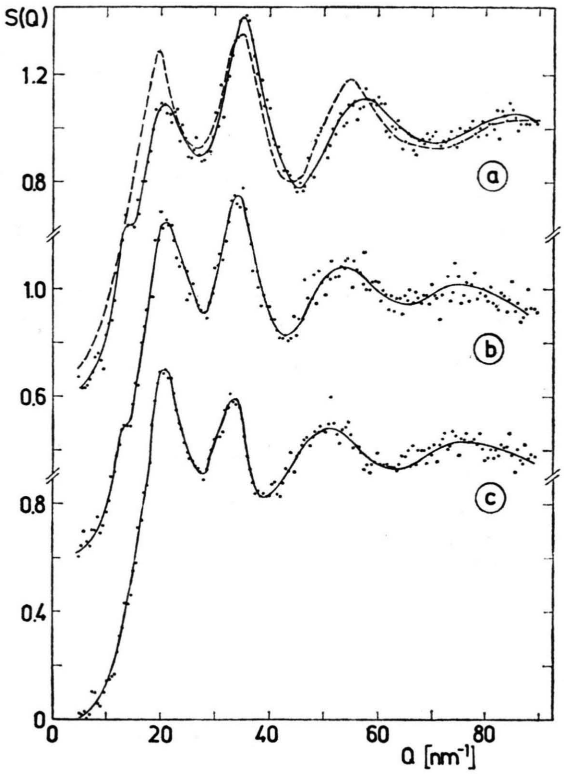

Fig. 1. Experimental structure factors of $Se_{1-x}Te_x$ at 460 °C, a) $x = 0.3$; b) $x = 0.6$; c) $x = 0.8$; --- X-ray diffraction $x = 0.3$.

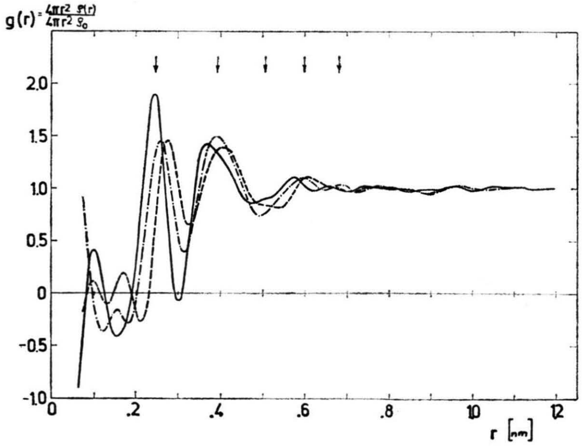

Fig. 2. Total pair correlation functions of $Se_{1-x}Te_x$ at 460 °C —— $x = 0.3$; ·–·–· $x = 0.6$; ---- $x = 0.8$ (arrows indicate the atomic distances in a free rotating mixed $Se_{70}Te_{30}$ chain).

the corresponding total pair correlation functions $g(r) = \varrho(r)/\varrho_0$ ($\varrho(r)$ local average particle density, ϱ_0 average particle density). For comparison the X-ray result for $Se_{70}Te_{30}$ is also shown in Figure 1. Our results are in good agreement with [2]. Values for the distance of nearest neighbours r_1 and their number N_1 are given in Table 1. The N_1-values were determined by integration up to the first minimum in $4\pi r^2 \varrho(r)$.

Figure 3 shows the N_1-values and Fig. 4 the concentration dependence of the nearest neighbour distance of the present work together with the results from [1] and [2].

x	r_1(nm)	N_1
0.3	0.242	2.16
0.6	0.257	2.26
0.8	0.275	2.42

Table 1. Values for the distance of nearest neighbours r_1 and their number N_1.

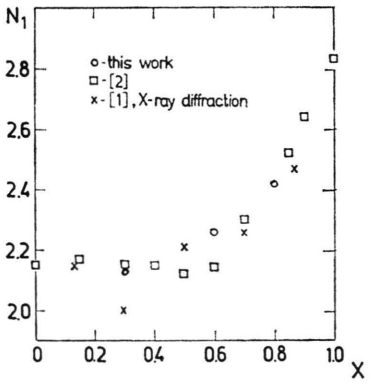

Fig. 3. Concentration dependence of the number of nearest neighbours in $Se_{1-x}Te_x$.

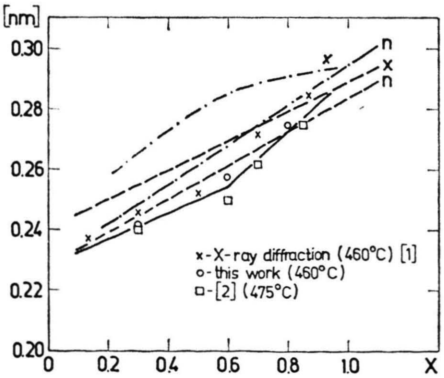

Fig. 4. Concentration dependence of the nearest neighbour distance in $Se_{1-x}Te_x$. —— experimental results; ---- mixed random chains; –·–·– pure Se-chains and Te in threefold coordination.

Using the method developed in [11] the partial structure factors $S_{NN}(Q)$ and $S_{CC}(Q)$ were evaluated for the composition $Se_{70}Te_{30}$. According to [11] the following relation is valid for binary systems

$$S(Q)_{BT} = \frac{\langle b\rangle^2}{\langle b^2\rangle} S_{NN}(Q) + \frac{(b_A - b_B)^2}{\langle b^2\rangle} S_{CC}(Q) + \frac{2\langle b\rangle (b_A - b_B)}{\langle b^2\rangle} S_{NC}(Q)$$

(b_A, b_B scattering amplitudes of the elements A and B). The Bhatia-Thornton structure factor $S(Q)_{BT}$ is related to the structure factor $S(Q)$ by

$$S(Q)_{BT} = (\langle b\rangle^2 S(Q) + c_A c_B (b_A - b_B)^2)/\langle b^2\rangle$$

(c_A, c_B concentrations of the elements A and B, respectively). $S_{NN}(Q)$ and $S_{CC}(Q)$ describe the Fourier transform of the spatial correlations of particle density fluctuations and concentration fluctuations, respectively. Neglecting contributions by the function $S_{NC}(Q)$, which depends on cross-correlations between particle density and concentration fluctuations, $S_{NN}(Q)$ and $S_{CC}(Q)$ were obtained from the $S(Q)_{BT}$ curves measured by neutron scattering (this work) and X-ray diffraction [1]. The justification to neglect $S_{NC}(Q)$ in our case is discussed in Section 6. By Fourier transformation we calculated the radial concentration correlation function

$$4\pi r^2 \varrho_{CC}(r) = (2r/\pi) \cdot \int Q(S_{CC}(Q)/c_A c_B - 1) \sin(Qr)\, dQ$$

shown in Figure 5. In order to reduce the termina-

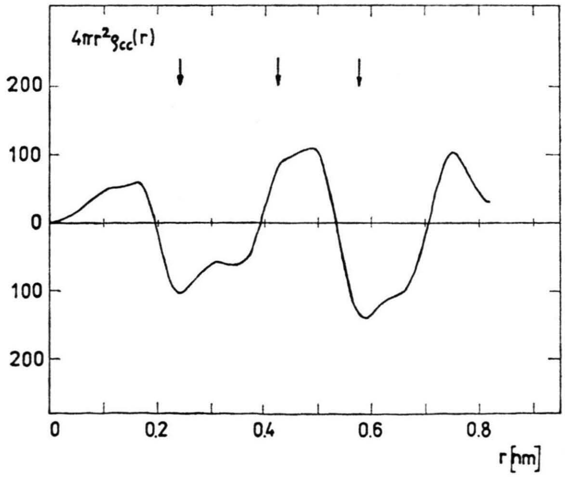

Fig. 5. Concentration correlation function $4\pi r^2 \varrho_{CC}(r)$ for $Se_{70}Te_{30}$ (arrows indicate positions of maxima in $g(r)$).

tion effect an exponential damping factor e^{-aQ^2} ($a = 0.0008\ \mathrm{nm}^2$) was used.

4. Conclusions from the Behaviour of Number and Distance of Nearest Neighbours

According to Fig. 3 the average number of nearest neighbours N_1 is practically independent of concentration up to 60 at.% Te. This leads to the conclusion that the structure does not change in this region and is essentially determined by zig-zag chains with twofold coordination in agreement with the result of [2] that the structure factors for these compositions are well reproduced by the model of nearly free rotating chains.

The absolute value of N_1 is somewhat too high for a chain model. Taking into account the chain ends we expect $N_1 \approx 2$. The shift of the experimental N_1 to approximately 10% higher values may be explained by the limited integration length when Fouriertransforming the data ($81-95\ \mathrm{nm}^{-1}$) [12]. By integration up to $Q_{\max} = 135\ \mathrm{nm}^{-1}$, values of $N_1 \approx 1.85$ have been obtained in [1].

The coordination numbers N_1 evaluated from neutron scattering curves coincide within the error limits with the X-ray diffraction results. This confirms that the Se-rich melts consist only of chains and do not contain threefold coordinated atoms (typical for the As-like structure). The experimental coordination number corresponds to a weighted average of the number of Se-Se, Te-Te, and Se-Te pairs. The weight factors are determined by the product of the corresponding scattering amplitudes.

Theoretical N_1-values for different models were calculated using the relation

$$N_1 = (c_A b_A^2 N_{AA} + c_B b_B^2 N_{BB} + 2\, c_A b_A b_B N_{AB}) / \langle b \rangle^2 .$$

For infinite chains with maximum short-range order, i.e. with the maximum possible number of unlike pairs (Se-Te), we find for $x = 0.3$ $N_1^x = 1.96$, and $N_1^n = 1.98$ and for $x = 0.6$ $N_1^x = 1.95$, and $N_1^n = 1.97$ for X-ray diffraction and neutron scattering, respectively. For chains with a lower amount of unlike pairs, $N_1^x \approx N_1^n$. In contrast any contribution of threefold coordination leads to $N_1^x > N_1^n$. Assuming a structure with all Te arranged in threefold coordination we obtain for $x = 0.3$ $N_1^x = 2.60$, and $N_1^n = 2.22$ and for $x = 0.6$ $N_1^x = 2.88$, and $N_1^n = 2.50$, respectively.

Concerning the distribution of Se and Te within the chains the coordination number N_1 provides no information. E.g. a concentration of $x = 0.3$ and the assumption that chains are built up solely by Se or Te lead to $N_1^x = 2.08$ and $N_1^n = 2.04$. The small difference in comparison to the chain with maximum short-range order is non-significant due to the experimental uncertainties.

The distances for nearest neighbours r_1 were determined from X-ray diffraction as well as neutron diffraction with high precision. In the region up to 60 at.% Te the X-ray diffraction results are about 0.004 nm larger than the corresponding neutron values r_1^n as shown in Figure 4. Theoretical values for r_1 were calculated assuming different structure models using the relation

$$r_1 = (c_A b_A^2 N_{AA} r_{AA} + c_B b_B^2 N_{BB} r_{BB} + 2\, c_A b_A b_B N_{AB} r_{AB}) / N_1 \langle b \rangle^2$$

(r_{mn} = distance of an atomic pair m-n).

Thereby for r_{SeSe} the value for pure Se chains $r_{\mathrm{SeSe}} = 0.234$ nm [1] and for r_{TeTe} in chains the value for twofold coordination in solid Te $r_{\mathrm{TeTe}} = 0.286$ nm [13] were used. For r_{SeTe} the average of these two values has been used. For Te in threefold coordination $r_{\mathrm{TeTe}} = 0.295$ nm [1]. Figure 4 contains theoretical curves for the concentration dependence of r_1^x and r_1^n for mixed chains with random distribution of Se and Te and for the case of pure Se chains and Te in threefold coordination. Both model curves lie too high and the difference $r_1^x - r_1^n$ is significantly larger than 0.004 nm. On the other hand a difference $r_1^x - r_1^n$ 0.004 nm is obtained for chains with a maximum number of Se-Te pairs

$$(x = 0.3 - r_1^x = 0.253\ \mathrm{nm}, \quad r_1^n = 0.248\ \mathrm{nm}; \quad x = 0.6 - r_1^x = 0.267\ \mathrm{nm}, \quad r_1^n = 0.263\ \mathrm{nm}).$$

Although these theoretical values are also somewhat too high they show the best agreement with the experiment. According to Fig. 4 the nearest neighbour distances for the case of completely threefold coordinated Te show the largest discrepancy to the experimental result. This confirms the assumption of a pure chain structure up to 60 at.% Te.

In summary the behavior of the nearest neighbour distances leads to the conclusion that the chains with a maximum possible number of Se-Te pairs determine the structure of the melts with Te concentration up to 60 at.%.

The steep rise of the coordination number N_1 above 60 at.% Te can only understood by assuming the occurrence of threefold coordination. Provided that the experimental value $N_1 = 2.45$ for $Se_{20}Te_{80}$ is also by about 0.2 too large as in the case of the Se-rich melts, an amount of about 30% atoms with threefold coordination has been estimated. For this proportion of threefold coordination $N_1^x \approx N_1^n$ ($N_1^x = 2.25$, $N_1^n = 2.20$). With increasing probability of threefold coordination this difference increases. An amount of 30% threefold coordinated Te-atoms for $Se_{20}Te_{80}$ at 460 °C is in good agreement with the observed increase of threefold coordination from 15% at 414 °C to 75% at 541 °C for $Se_{25}Te_{75}$ [3]. Moreover the r_1 values calculated for $Se_{20}Te_{80}$ with 30% threefold coordination ($r_1^x = 0.281$ nm, $r_1^n = 0.275$ nm) agree also very well with the experiment.

5. Conclusions from the Distance of Higher Coordination Shells

The peak in $g(r)$ around 0.4 nm seems to be due to the superposition of two non-resolved peaks at about 0.375 and 0.425 nm, respectively. This is suggested by the obvious asymmetry of this peak for the compositions $x = 0.3$ and $x = 0.8$. According to [2] these subpeaks become resolved at $x = 0.85$ and $x = 0.92$, respectively. Obviously the position of these two subpeaks depends only very weakly on composition.

Free rotating pure Se-Se chains show with a nearest neighbour distance of 0.234 nm and a bond angle of 105.5° (this corresponds to trigonal Selenium) a second neighbour distance of 0.37 nm. Free rotating ordered Se-Te chains exhibit a second neighbour distance of 0.42 nm taking the average values for nearest neighbour distances and bond angles in the trigonal crystalline phases of Se and Te, respectively. These two second neighbour distances may cause the two subpeaks in the second $g(r)$-maximum. The shift of the resulting peak to larger r with increasing Te concentration from $x = 0.3$ to $x = 0.6$ can be explained by an increase of the relative amount of the subpeak at about 0.425 nm.

The peak in $g(r)$ between 0.575 and 0.600 nm is shifted towards larger r with increasing Te concentration in the range of 30 to 60 at.% but remains nearly unchanged in position at higher Te contents. This leads to the conclusion that also this peak corresponds to an intra-chain distance. Above 60 at.% Te the composition of the chains does not change remarkably because the excess Te forms the As-like network.

For comparison in Fig. 2 intra-chain bond distances in mixed free rotating chains are shown for the case of $Se_{70}Te_{30}$.

6. Concentration Fluctuations and Short-Range Order

In Fig. 5 the function $4\pi r^2 \varrho_{CC}(r)$ obtained by Fourier transformation from $S_{CC}(Q)$ is shown for the $Se_{70}Te_{30}$ melt. The radial concentration correlation function $4\pi r^2 \varrho_{CC}(r)$ enables to determine the Cowley-Warren short-range order parameters α_i for the i-th neighbour shell according to [14]. Supposed that $S_{NC}(Q) = 0$

$$\alpha_i = N_i^{-1} \int_{r_i-\varepsilon}^{r_i+\varepsilon} 4\pi r^2 \varrho_{CC}(r)\,\mathrm{d}r$$

(N_i coordination number for the i-th neighbour shell, $r_i - \varepsilon$ to $r_i + \varepsilon$ distance region characterizing the i-th coordination shell). α_i becomes negative if the probability to find unlike atomic pairs in the corresponding coordination shell is higher than in the case of random distribution. According to Fig. 5 $4\pi r^2 \varrho_{CC}(r)$ shows negative values in the r range of the first coordination shell and consequently positive values for next-nearest neighbours and so on. This gives a direct confirmation of the assumption that the distribution of Se and Te within the chains shows a strong short-range order with preferred formation of Se-Te pairs. From the curve in Fig. 5 a value $\alpha_1 = -2.5$ has been evaluated. The absolute value of α_1 is, however, unexpectedly large.

In the evaluation of $S_{CC}(Q)$ we neglected contributions by $S_{NC}(Q)$. It is possible to show the justification of this procedure for a chain structure. According to [11] the function $\varrho_{NC}(r)$, the Fourier transform of $S_{NC}(Q)$, is connected with the partial local particle densities $\varrho_{ij}(r)$ in the following way

$$\varrho_{NC}(r) = c_A c_B \{c_A[\varrho_{AA}(r)/c_A - \varrho_{AB}(r)/c_B] - c_B[\varrho_{BB}(r)/c_B - \varrho_{BA}(r)/c_B]\}.$$

Integration over the i-th coordination shell leads to the expression

$$\begin{aligned}&\int 4\pi r^2 \varrho_{\mathrm{NC}}(r)\,\mathrm{d}r\\ &= c_{\mathrm{A}} c_{\mathrm{B}} \{c_{\mathrm{A}}[\alpha^i_{\mathrm{AA}}/c_{\mathrm{A}} - \alpha^i_{\mathrm{AB}}/c_{\mathrm{B}}]\\ &\qquad - c_{\mathrm{B}}[\alpha^i_{\mathrm{BB}}/c_{\mathrm{B}} - \alpha^i_{\mathrm{BA}}/c_{\mathrm{B}}]\}\\ &= c_{\mathrm{A}} c_{\mathrm{B}}[\alpha^i_{\mathrm{AA}} + \alpha^i_{\mathrm{AB}} - \alpha^i_{\mathrm{BB}} + \alpha^i_{\mathrm{BA}}]\end{aligned}$$

using $c_{\mathrm{A}}\alpha^i_{\mathrm{AB}} = c_{\mathrm{B}}\alpha^i_{\mathrm{BA}}$. In the above equation we introduced the values α^i_{mn} as the number of n-atoms as neighbours of the i-th shell around a m-atom. In a chain the number of i-th neighbours is two, independent of the kind of the considered central atom. Therefore $\alpha^i_{\mathrm{SeSe}} + \alpha^i_{\mathrm{SeTe}} = \alpha^i_{\mathrm{TeTe}} + \alpha^i_{\mathrm{TeSe}}$, and consequently the integral over $4\pi r^2 \varrho_{\mathrm{NC}}(r)$ taken in the region of one coordination shell vanishes. In such a range of distances compensating oscillations of $4\pi r^2 \varrho_{\mathrm{NC}}(r)$ may occur in connection with differences in the distances r_{ij} of different atomic pairs. In our case we assume a well ordered distribution of unlike atoms and therefore these possible oscillations are small.

The Fourier transform of $(S_{\mathrm{NN}}(Q) - 1)$ is in good agreement with $g(r)$ shown in Figure 2.

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