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# Neutron diffraction study on the medium and short-range order of ternary chalcogenide glasses

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Glasses from $Ge_xAs_{40-x}S_{60}$, $Ge_xAs_{40-x}Se_{60}$, $Ge_xSb_{40-x}S_{60}$ and $Ge_xSb_{40-x}Se_{60}$ families have been investigated by neutron diffraction. The well expressed "first sharp diffraction peak" of the neutron spectra at $\mathbf{Q} = 10$–$14\ \text{nm}^{-1}$ has been explained by a pseudo-binary model of the structure of studied chalcogenide glasses. The amplitude of this interference maximum increases with Ge-content in all investigated samples. Experimental radial distribution functions show that the basic structural units, $GeS(Se)_4$ tetrahedra and $As(Sb)S_3$ or $As(Sb)Se_3$ pyramids persist in glassy state for the whole range of studied compositions. Crystal-like model distribution functions have been used to describe the short-range order observed. A shortening of heteropolar bonds in S-containing glasses as well as an increase of heteropolar bonds length in Se-containing glasses has been found. *© 1999 Kluwer Academic Publishers*

## 1. Introduction

Amorphous chalcogenide materials (glasses and thin films) are semiconductors with promising optical and electronic properties. Some of them are used in optical devices such as lenses and windows for infrared spectral region, wave-guides and image recording media [1]. Since the early 1955, when the first experimental work on amorphous chalcogenide semiconductors [2] has been published, this class of glasses has been intensively investigated, because of the potentialities for a purposeful improvement and modification of their physical parameters by composition variation. The observed structural dependence of the physical and physico-chemical properties have stimulated numerous investigations of their short range order (SRO) as well as of their medium range order (MRO) [3–8]. The SRO can be studied by direct structural methods: infrared and Raman spectroscopy, electron, X-ray and neutron diffraction, Mössbauer spectroscopy etc. However, the interpretation of the obtained results is always difficult because of a non-periodic arrangement of the atoms (structural disorder). That is why the structure of binary glasses with stoichiometric compositions has been usually determined. Some investigations on the structure of ternary chalcogenide glasses composed of nonstoichiometric compounds are also available [9–12]. A general result of all structural studies is that depending on the composition and synthesis conditions, the bulk glasses consist of different kind of motives (coordination polyhedra, chains) forming band structure, continuous two- or three-dimensional network. It follows from the spectroscopic and diffraction data that these structural units are predominantly of the same character as in the crystalline materials. Investigations on chalcogenide compounds including nonstoichiometric ingredients show that even in such type of glasses the main structural units may be preserved [3, 13].

The purpose of the present paper is to describe the short and medium range order in the ternary $Ge_xAs(Sb)_{40-x}S(Se)_{60}$ glasses on the basis of comparison of neutron scattering data with a model distribution of interatomic distances. Putting Me instead of As and/or Sb, and X instead of S and/or Se, the system $Ge_xMe_{40-x}X_{60}$ can be denoted as $(Me_2X_3)_y(GeX_{1.5})_{1-y}$. The investigated family of glasses is composed, as can be seen from the last formula, of one stoichiometric and one nonstoichiometric component. These compositions can be considered as chalcogen deficient. Thus, the study of SRO and MRO of ternary chalcogenide glasses which consist of stoichiometric and nonstoichiometric components can provide us new information on the structure of this type of glasses.

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## 2. Experimental

### 2.1. Samples preparation

Ge-As(Sb)-S(Se) samples were prepared by the melt quenching method generally adopted for chalcogenide glasses. Appropriate quantities (8 g total per batch) of 5N purity elements As, S, Se, Sb and Ge were sealed into fused quartz ampoules (14–16 mm in diameter), after evacuating them to 10 Pa. The mixtures were heated in a rotating furnace up to 1230 K for 24 hours and then air quenched. The chemical composition of the prepared glasses was checked by means of a TRACOR NORTHERN TN-2000 scanning microprobe X-ray analyser. The determined composition was in correspondence with the original mixture of chemical elements and a maximal deviation of $\Delta x/x < 1\%$ was found. The compositions of the investigated glasses are listed in Table I. The synthesized glasses were mechanically ground and the ~100 $\mu$m powder was poured in vanadium containers. The probes were controlled for crystallinity by X-ray diffraction. All samples were found to be amorphous except for sample No. 7 where a small amount of two crystalline phases of pure selenium and antimony selenide ($Sb_2Se_3$) was detected.

The macroscopic density $\rho$ of Ge-As(Sb)-S(Se) glasses was measured by the Archimed method with xylol as reference medium. The average $\rho$- values were obtained with an accuracy of ±1% and are given in Table I. The calculated $\rho_{oi}$-value of atomic density of $i$-type atoms is shown in the last column of Table I.

### 2.2. Neutron scattering measurements

Neutron interference functions $i(\mathbf{Q})$, $\mathbf{Q} = 4\pi \sin\theta/\lambda$, were obtained at $T = 297$ K by means of two different instruments:

(a) E3 diffractometer equipped with a linear position sensitive detector (PSD) installed at BER-II reactor, Hahn-Meitner-Institut, Berlin and,

(b) SPN-100 diffractometer installed at LVR-15 reactor, NPI, Rez near Prague.

In the first experiment the spectra were measured at two positions of PSD and at two different wavelengths, respectively. At small $2\theta$ angle position, neutrons with $\lambda = 0.245$ nm from PG monochromator were used, and thus covering the range of $\mathbf{Q} = 3{-}36\,\text{nm}^{-1}$. In the range of $2\theta = 30{-}110\,^{\circ}$, neutrons with $\lambda = 0.0937$ nm from Cu monochromator permitted us to reach $\mathbf{Q}_{\text{max}} = 109.4\ \text{nm}^{-1}$. Both measured parts of the diffraction spectra were connected and recalculated in equidistant $\mathbf{Q}$-distribution.

In the second experiment (constant step, $\Delta\mathbf{Q} = 0.5\,\text{nm}^{-1}$) neutrons with $\lambda = 0.09$ nm from a bent Si monochromator were used. The shorter wavelength has permitted to measure the interference functions to higher value of $\mathbf{Q}$, $\mathbf{Q} = 3.6{-}126\ \text{nm}^{-1}$.

### 2.3. Calculation procedure

Before the Fourier transformation, standard corrections of neutron spectra were applied: (a) for inelastic scattering (Placzek correction), (b) for multiple scattering; (c) for the presence of absorbed $H_2$ or $H_2O$ on the surface and in the sample volume; (d) for neutron absorption; (e) for scattering on the vanadium sample container and (f) for PSD efficiency.

The Fourier transformation was realized by multi-atomic-type Debye equation where the modification function used was in the form proposed by Lorch.

The measured first sharp diffraction peak (FSDP) was analysed by the Scherrer formula. The linear size

TABLE I Chemical composition and densities of the studied $Ge_{40-x}As(Sb)_xS(Se)_{60}$ samples

| Sample no. | Ge (at %) | As (at %) | Sb (at %) | Se (at %) | S (at %) | $\rho$ (g/cm$^3$) | $\rho_{oi}$ (at/Å$^3$) |
|---|---|---|---|---|---|---|---|
| 1 | — | 40 | — | — | 60 | 3.18 | 0.0389 |
| 2 | — | — | 40 | — | 60 | 3.53 | 0.0441 |
| 3 | 4 | 36 | — | — | 60 | 3.12 | 0.0382 |
| 4 | 5 | — | 35 | — | 60 | 4.04 | 0.0385 |
| 5 | 10 | 30 | — | 60 | — | 4.49 | 0.0351 |
| 6 | 10 | 30 | — | — | 60 | 3.03 | 0.0372 |
| 7 | 10 | — | 30 | 60 | — | 5.38 | 0.0356 |
| 8 | 15 | — | 25 | — | 60 | 3.75 | 0.0462 |
| 9 | 15 | — | 25 | 60 | — | 5.08 | 0.0336 |
| 10 | 20 | — | 20 | — | 60 | 3.58 | 0.0442 |
| 11 | 22 | 18 | — | — | 60 | 2.96 | 0.0366 |
| 12 | 25 | 15 | — | — | 60 | 2.96 | 0.0366 |
| 13 | 25 | — | 15 | — | 60 | 3.43 | 0.0371 |
| 14 | 27 | 13 | — | — | 60 | 2.95 | 0.0366 |
| 15 | 27 | — | 13 | — | 60 | 3.37 | 0.0384 |
| 16 | 32 | 8 | — | — | 60 | 2.96 | 0.0368 |
| 17 | 32 | 8 | — | 60 | — | 4.34 | 0.0341 |
| 18 | 35 | — | 5 | — | 60 | 3.16 | 0.0375 |
| 19 | 35 | — | 5 | 60 | — | 4.55 | 0.0340 |
| 20 | 36 | 4 | — | 60 | — | 4.34 | 0.0342 |
| 21 | 36 | 4 | — | — | 60 | 2.96 | 0.0368 |
| 22 | 38 | — | 2 | — | 60 | 3.16 | 0.0387 |
| 23 | 40 | — | — | — | 60 | 3.02 | 0.0377 |

TABLE II Positions (nm) of the coordination maxima PI of model RDFs

| Composition | P1a | P1b | P2a | P2b | P3 | P4 | P5 |
|---|---|---|---|---|---|---|---|
| Ge | 0.248 | — | — | — | — | 0.482 | 0.590 |
| GeS | 0.2485 | 0.267 | 0.332 | — | 0.391 | 0.473 | — |
| $GeS_2$ | 0.224 | — | 0.352 | — | 0.446 | — | 0.593 |
| GeSe | 0.262 | — | 0.340 | 0.391 | — | 0.480 | 0.544 |
| $GeSe_2$ | 0.223 | — | 0.356 | — | 0.435 | — | 0.519 |
| Sb | — | — | 0.323 | — | — | 0.458 | 0.573 |
| $Sb_2S_3$ | 0.263 | — | 0.343 | — | 0.397 | 0.454 | 0.515 |
| $Sb_2Se_3$ | 0.263 | — | 0.363 | — | — | 0.453 | 0.60 |
| As | 0.271 | — | — | — | 0.412 | — | 0.585 |
| $As_2S_3$ | 0.229 | — | 0.353 | — | 0.435 | — | 0.585 |
| $As_2Se_3$ | 0.228 | — | 0.359 | — | 0.433 | — | 0.60 |
| AsS | 0.230 | 0.271 | 0.363 | — | — | 0.453 | 0.60 |
| AsSe | 0.230 | — | 0.368 | — | — | 0.460 | 0.60 |

of clusters $L$ is given by $L = \frac{k\lambda}{\beta \cos 2\vartheta}$, where $\beta$ is the full width at half maximum (FWHM) of the peak profile, $2\theta$ is the diffraction angle, and $k = \frac{4}{3}\sqrt[3]{\frac{\pi}{6}} = 1.0747$ in the case of spherical clusters.

Using the crystal-like structural model of glasses, the radial distribution functions (RDFs) were calculated under the assumption of Gaussian distribution of interatomic distances in glasses with maxima at the corresponding crystal structure values, $R_i$:

$$\mathrm{RDF} = C \sum \frac{n_i}{2a_i\sqrt{\pi}} \left(\frac{R}{R_i}\right)^2 \exp\left(-\left(\frac{R - R_i}{2a_i}\right)^2\right),$$

where $n_i$ is the number of atoms on the $i$th coordination sphere of the crystalline structure, $a_i$ is the width of $i$th Gaussian which increases proportionally to $4D\sqrt{R_i}$. The calculated peak positions of starting materials necessary for the building of model RDFs are given in Table II.

## 3. Results and discussion

The registered neutron interference functions are very sensitive to the chemical composition of the studied glassy systems. Although the structure factors, $S(\mathbf{Q})$, are comparable for all samples, in case of several curves drastic changes of the FSDP amplitude were observed (see Fig. 1). The presence of FSDP is detected in all $S(\mathbf{Q})$-curves at $\mathbf{Q} = 10-14\,\mathrm{nm}^{-1}$. The measured $S(\mathbf{Q})$ and interference functions are shown in Figs 1, 2. The experimental spectra, taken up to 120 $\mathrm{nm}^{-1}$ have no more than 7 interference maxima (e.g., for sample No. 9 they are located at 13.5, 24.6, 39.6, 59.7, 74.0, 85.8 and 103.7 $\mathrm{nm}^{-1}$). The RDFs calculated according to the above described procedure are shown in Figs 3–5.

### 3.1. The main structural units in chalcogenide glasses

The structural investigations of binary chalcogenide glasses have proved that their main structural units are

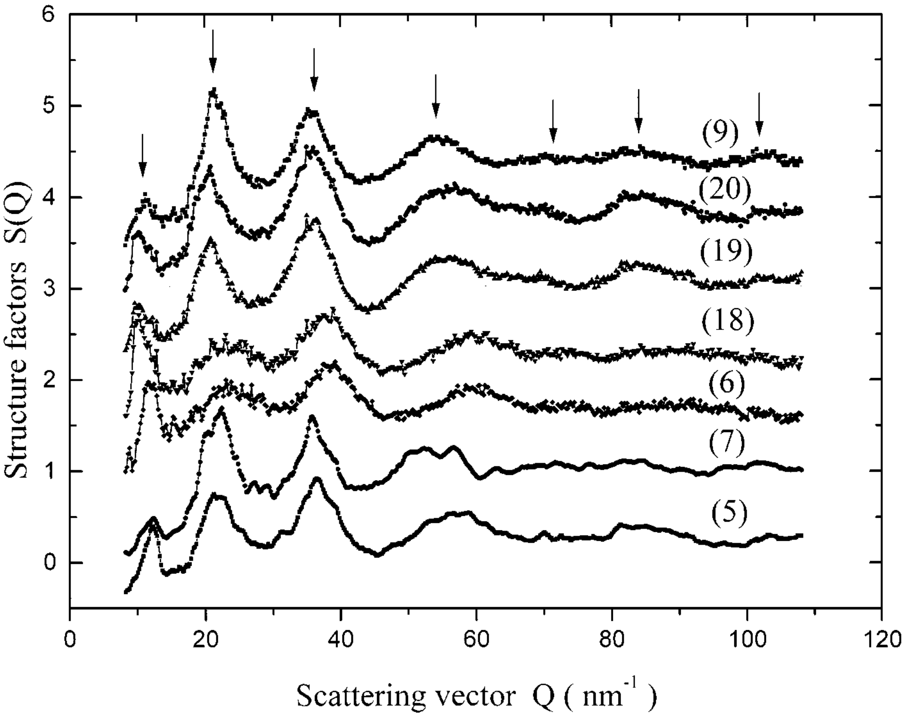

*Figure 1* Neutron structure factors of samples No. 5–7, 9 and 18–20.

predominantly the same as in the respective crystals, [4, 6, 9, 10, 13–15]. The Ge, As (Sb) and chalcogen atoms are 4-, 3- and 2-fold coordinated, respectively, and the homopolar bonds are highly suppressed.

The main structural units in stoichiometric $GeX_2$ are $GeX_4$ tetrahedra [6, 10, 13]. High resolution neutron diffraction study of crystalline, glassy and liquid $GeSe_2$ demonstrates that corner- and edge-shared $GeSe_4$ tetrahedra are the base structural units in glassy and crystalline state and they persist even in the liquid at 1084 K [16]. In $Ge_xSe_{1-x}$ with $0.33 < x < 0.40$, the glass is composed of $GeSe_4$ and $Se_3Ge$-$GeSe_3$ units [17]. Street and Biegelsen [18] have proposed the formation of Ge-Ge bonds in Ge-rich chalcogenides to explain their photoluminescence and optical data. EXAFS data of Ge-rich Ge-Se alloys [14, 15] have shown that Ge and Se maintain 4- and 2-fold coordination, but the structure becomes increasingly disordered with increasing of the Ge concentration. This great structural disorder led Phillips [17] to suggest that $Ge_2(Se_{1/2})_6$ ethane-like units might comprise the amorphous network.

In $As_2S_3$ and $As_2Se_3$ glasses the main pyramidal structure of the crystals is also preserved [4, 6]. The local order is described by specific atomic clusters

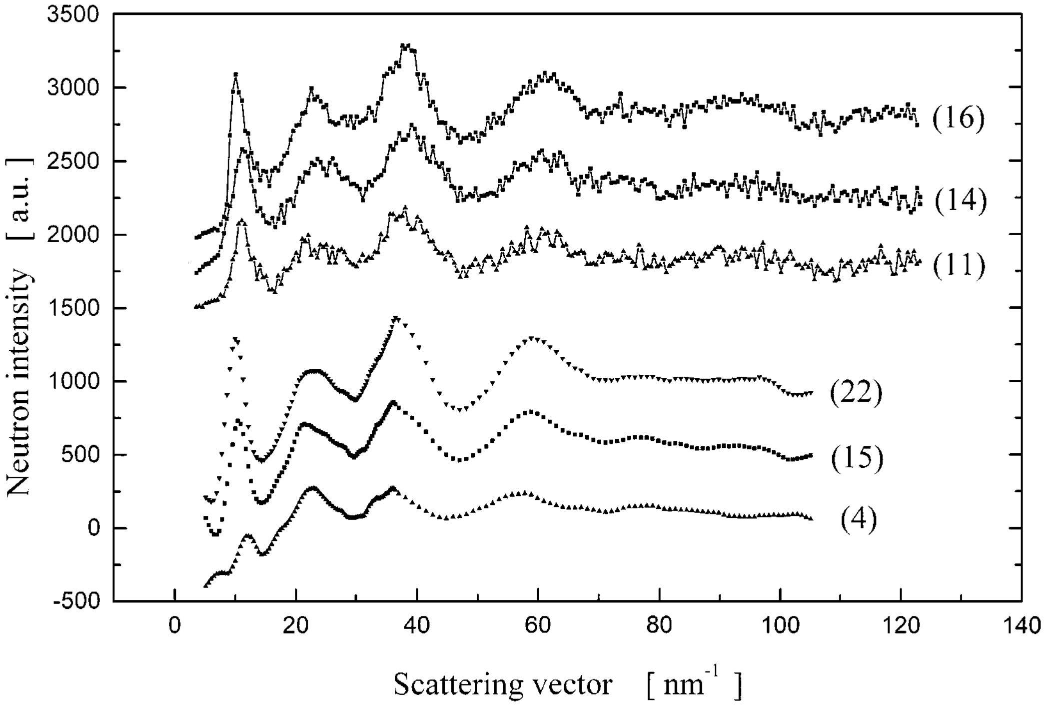

*Figure 2* Neutron scattering spectra of glasses No. 4, 11, 14–16 and 22.

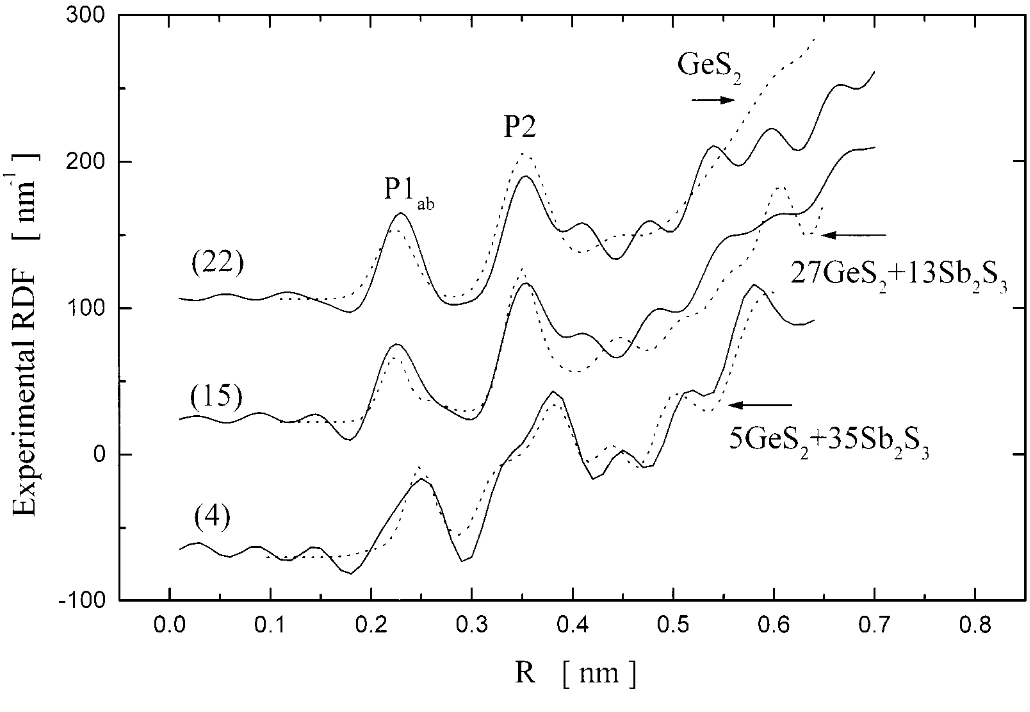

*Figure 3* Experimental and model RDFs of samples 4, 15 and 22.

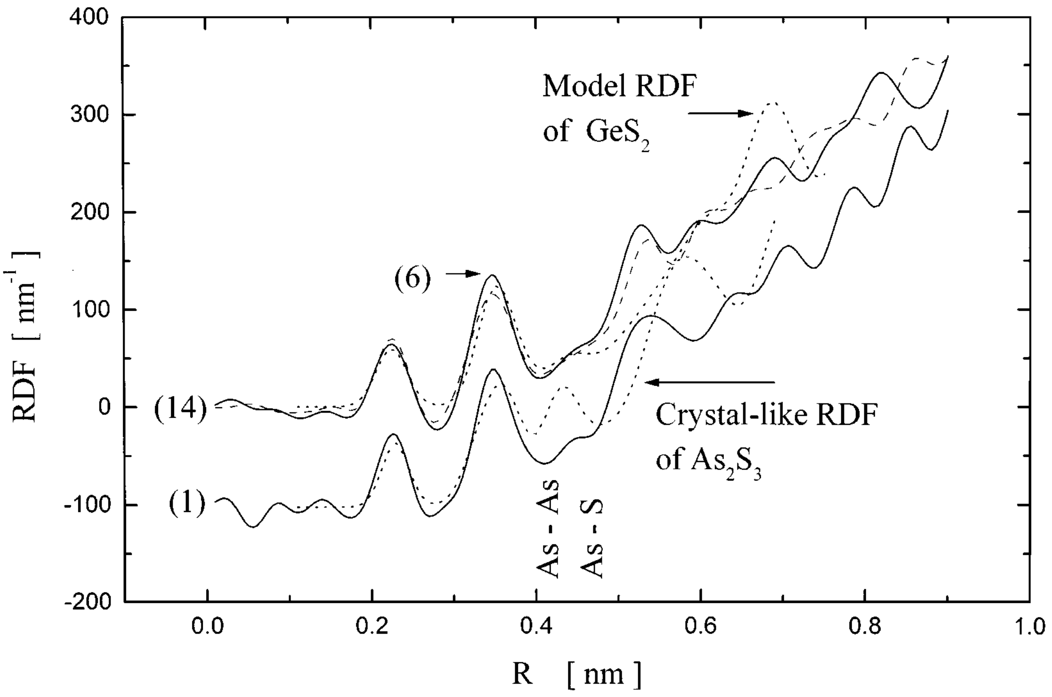

*Figure 4* Comparison of experimental and crystal-like model RDF of samples 1, 6 and 14.

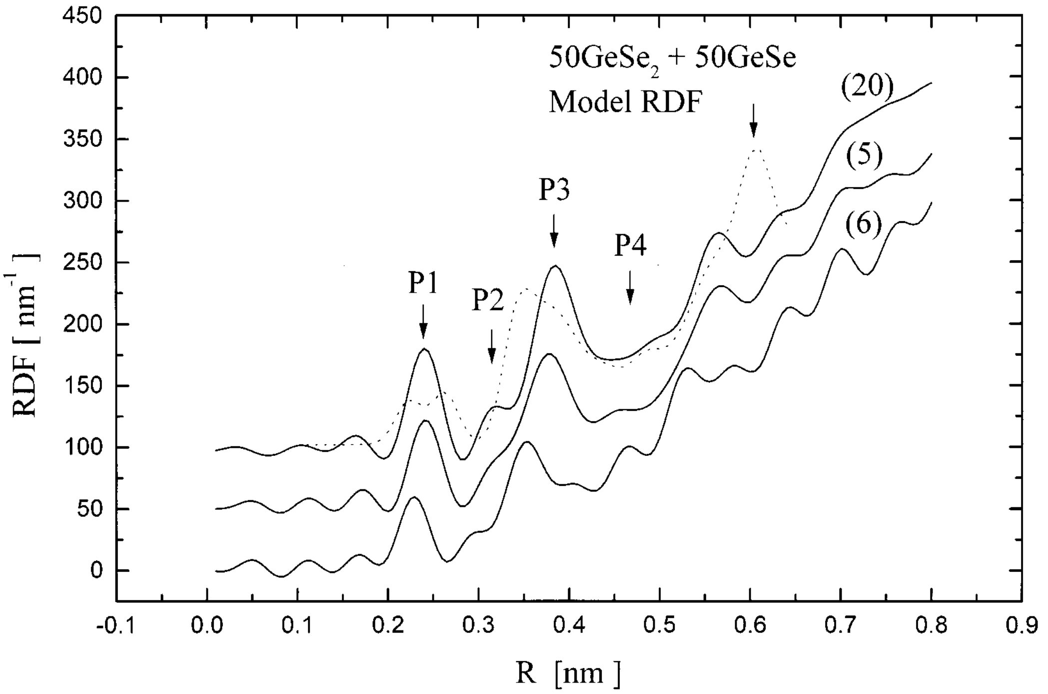

*Figure 5* RDFs of samples 5, 6 and 20. A model distribution function of a glass with composition 50GeSe$_2$ + 50GeSe is drawn by dashed line.

which are composed of AsX$_3$ pyramids. Mössbauer experiments on As$_2$S$_3$ and As$_2$Se$_3$ glasses undoubtedly show the predominant 2-fold coordination of chalcogen atoms analogous to the bonding in orpiment structure [19]. In As$_x$S$_{1-x}$ at x > 0.4 the glass is apparently composed of AsS$_3$ and S$_2$As-AsS$_2$ units [4].

It follows from X-ray diffraction investigation of As$_2$S$_3$Ge$_x$ glasses that the basic structural units are predominantly the same as in the relevant (As$_2$S$_3$ and Ge) crystalline materials. The number of Ge-S and Ge-Ge bonds increases with an increasing Ge content. There is no evidence of Ge-As bonds formation in these glasses. In samples with over stoichiometry of Ge, direct As-As bonds have been observed. Clusters of amorphous Ge were detected at high Ge content [5]. In the case of GeS$_2$-As$_2$S$_3$ glassy system a small variation of As$_2$S$_3$ content in GeS$_2$ is accompanied by a large change in T$_g$ [20]. The authors explain this experimental fact by the presence of very different local surrounding of Ge and As atoms in the glasses-GeS$_4$ tetrahedron with Ge-atom at the centre and AsS$_3$ pyramid, respectively. X-ray diffraction investigations on Ge-Sb-S glasses also have proved the presence of two main types of structural units [3].

The structural arrangement in chalcogenides beyond the first coordination shell (MRO) has also been a matter of consideration [21–23]. Our previous X-ray investigations on $Ge_xAs(Sb)_{40-x}S(Se)_{60}$ glasses and thin films [24–26] have shown the presence of MRO in the amorphous structure. The FSDP and a new peak (called pre-FSDP) were observed in the structure factor curves and they were attributed to a high level of structural organisation in the MRO. In the present investigation new evidence of the MRO of the investigated glasses have been obtained.

### 3.2. $As(Sb)_2S(Se)_3$-$GeS(Se)_{1.5}$ glasses

In view of the results and statements cited in 3.1. the interpretation of the obtained structural parameters is based on the "two mode", pseudo-binary model of the glass structure. $As(Sb)S_3$ pyramids and $GeS(Se)_4$ tetrahedra are accepted to be the main glassy network constituents which form SRO and the neutron interference functions, respectively. The presence of two or three kinds of ordering (SRO) in the glasses makes difficult the unambiguous interpretation of RDF peaks, $Pn, n > 1$. Similarly, the excess of Ge ($GeX_{1.5}$) makes further complications in the interpretation.

### *3.2.1. $Ge_xSb_{40-x}S_{60}$ glasses*

The compositional dependence of the main structural units is treated on the basis of the Ge-Sb-S system. Neutron interference functions corresponding to the samples Nos. 4, 15 and 22 are presented in Fig. 2. From the Scherrer formula applied to FSDP it is found that the mean cluster size decreases from 1.46 to 1.28 nm. As follows from the neutron scattering experiments, in spite of the fact that these values are quite close for the two end compositions ($GeS_{1.5}$ and $Sb_2S_3$), it is evident that they are built by different structural units: 2 to 4 $GeS_4$ tetrahedra, edge- and corner-shared, and bands of -Sb-S-Sb- chains, respectively. At a high Ge content, where the composition is close to that of $GeS_{1.5}$ the glass structure could also be considered as similar to the $GeX_2$ layered network. In this region, however, the Ge-Ge bonding and the depolimerization of both corner-shared and edge-shared tetrahedra increase. The effect is in accordance with a decrease of the glass transition temperature $T_g$ [27] and with the molecular cluster network model [28]. As it follows from molecular dynamics calculation [16, 28], FSDP of Ge-Sb-S glasses is mainly due to Ge-Ge correlation in the 0.4–0.8 nm range. In Fig. 2 the FSDP amplitude of the sample No. 22 is nearly 500% higher than the same value for the sample No. 4. This increase of FSDP correlates with the increase of Ge-content in the samples, i.e. with the augment of the $GeX_4$ tetrahedra quantity, and is similar to that, observed in Ge-Sb-S glasses by X-ray diffraction [22, 24]. In these studies a significant difference in MRO of $GeS_2$ (intensive FSDP) and $Sb_2S_3$ (very small FSDP) was found. Accepting the interpretation of the authors of Ref. 22 and 24, it can be supposed that two kinds of basic MRO elements are available in the investigated glasses: a part of a chain of corner-shared tetrahedra extracted from the high temperature form of crystalline $GeS_2$ (as in the glassy $GeS_2$) and a part of a crystal-like $(Sb_2S_3)n$ bands (as in the glassy $Sb_2S_3$). This fact can explain the reason of the low FSDP amplitude of the sample No. 4 in Fig. 2. The kink located at $\sim$18 $nm^{-1}$ in $S(\mathbf{Q})$ for sample 4 may be attributed to the MRO features of amorphous $Sb_2S_3$. According to Ref. 22 the ordering of the $(Sb_2S_3)_n$ bands in amorphous $Sb_2S_3$ is characterized by a greater interband separation than in the crystal. From the position of FSDP of the sample No. 4 an interband separation of $\sim$0.53 nm is estimated, while the interband separation of the crystalline $Sb_2S_3$ is 0.21 nm.

The qualitative correspondence of the experimental RDFs with crystal-like model RDFs of the end member compounds $Sb_2S_3$ and $GeS_{1.5}$ is demonstrated in Fig. 3. Sample No. 22 containing only 2 at % Ge with a structure, very close to that of $GeS_{1.5}$, is given as an example. As is estimated in Ref. 29, $GeS_{1.5}$ contains an amount of 14% Ge-Ge bonds. In any case the contribution of the Ge-Ge bonds at 0.248 nm should be situated between P1 and P2. The expected broadening of P1 is not visible, as it can be seen from Fig. 3. That is why the influence of the Ge-Ge bonds is considered as week and the used model is pseudo-binary. The coincidence of the model with the experimental RDF for the sample No. 4, where the $Sb_2S_3$ content is $\sim$74%, appears particularly good. The possibility of =Ge=S/S=Ge= chain formation (consisting of 2 to 4 tetrahedra) is a question of terminology; a more adequate picture is the 2 to 4-member $GeS_4$ clusters, connected via S-atoms with $SbS_3$ chains. For all glasses of the Ge-Sb-S system the first coordination maximum in the RDFs is complex and can be approximated by two Gaussians P1a and P1b, The peak parameters (position ($R_i$), FWHM ($2w_i$), and area), are summarized in Table III. According to the performed crystal-like calculations, Table II, P1 is due to Sb-S and Ge-S correlations in the basic structural units of the glass: $SbS_3$ pyramid with three-fold coordinated Sb-atom at the apex, and $GeS_4$ tetrahedra with Ge-atom at the centre. The pseudo-binary character of this glassy system can be also clearly traced out in the compositional dependence of SRO. The transition from $Sb_2S_3$-rich to $GeS_{1.5}$-rich glasses gives an increase to well expressed transformations of RDF: (a) The first coordination maximum shifts towards the shorter distances by 0.01 nm; (b) The second peak of $Sb_2S_3$-rich composition is double ($R2a = 0.332$ nm and $R2b = 0.381$ nm). For the samples Nos. 15 and 22 this peak is located at $R2 = 0.35$ nm; (c) The small P3 maximum is displaced from 0.453 to 0.400 nm. All these structural effects could be explained using the contribution of the SRO of the constituents.

### *3.2.2. Substitution of Sb by As*

Our previous investigations have shown that the sensitivity towards structural changes of physical and physico-chemical properties of $Ge_xAs_{40-x}X_{60}$ and $Ge_xSb_{40-x}X_{60}$ families is better expressed in the As-containing glasses [25]. This fact has been explained by the presence of higher degree of ionicity of the Sb-X bonds with a respect to the As-X bonds (e.g., 40%

TABLE III RDF peak parameters[a] of Ge-Sb(As)-S(Se) glassy system

|  | $Ge_5Sb_{35}S_{60}$ |  |  | $Ge_{27}Sb_{13}S_{60}$ |  |  | $Ge_{38}Sb_2S_{60}$ |  |  |
|---|---|---|---|---|---|---|---|---|---|
| RDF peaks | $R_i$ | $W_i$ | Area | $R_i$ | $W_i$ | Area | $R_i$ | $W_i$ | Area |
| $P1_a$ | 0.224 | 0.015 | 0.38 | 0.226 | 0.021 | 2.56 | 0.228 | 0.018 | 2.36 |
| $P1_b$ | 0.251 | 0.023 | 2.60 | 0.265 | 0.023 | 0.74 | 0.252 | 0.018 | 0.49 |
| $P2_a$ | 0.332 | 0.017 | 1.89 | 0.350 | 0.024 | 4.96 | 0.352 | 0.025 | 4.80 |
| $P2_b$ | 0.382 | 0.031 | 7.97 |  | — |  |  | — |  |
| P3 | 0.446 | 0.018 | 2.19 | 0.415 | 0.042 | 6.90 | 0.413 | 0.03 | 4.14 |
| P4 | 0.523 | 0.048 | 7.63 | 0.481 | 0.021 | 3.54 | 0.476 | 0.022 | 3.3 |
|  | $Ge_{10}As_{30}Se_{60}$ |  |  | $Ge_{10}As_{30}S_{60}$ |  |  | $Ge_{36}As_4Se_{60}$ |  |  |
| $p^1$ | 0.242 | 0.018 | 3.55 | 0.221 | 0.019 | 2.45 | 0.240 | 0.018 | 3.32 |
| $p^2$ | 0.318 | 0.018 | 1.20 | 0.294 | 0.017 | 0.97 | 0.318 | 0.015 | 1.081 |
| $p^3$ | 0.374 | 0.028 | 7.034 | 0.350 | 0.025 | 5.26 | 0.382 | 0.028 | 8.13 |
| $p^4$ | 0.457 | 0.050 | 8.16 | 0.410 | 0.032 | 4.49 | 0.452 | 0.035 | 6.4 |
| $p^5$ | 0.567 | 0.046 | 17.6 | 0.460 | 0.017 | 2.03 | 0.494 | 0.019 | 0.75 |

[a] All peak positions $R_i$ are in (nm).

for the Sb-Se and 20% for the As-Se bonds). As far as the elements As and Sb belong to the same group of the Periodic Table, they form isomorphous units with the chalcogens. The main differences between the Ge-As-X and Ge-Sb-X neutron diffraction curves are due to the difference in the respective interatomic distances Me-X. Thus, the observed lack of splitting in the first RDF maximum P1 for the As-containing glasses, (see Fig. 4 and Table III), is due to the nearly equal As-X and Ge-X distances (see Table II). Even the increase in Ge amount from 10 to 36 at % causes a shift of $R$ only by 0.0016 nm, which value is near to the experimental error limits. Similarly to the Sb-containing glasses, two structural units—pyramids and tetrahedra—are supposed to form two parts of the shape of the maxima, however situated closely enough and can not be distinguished. From same reasons it is hardly to find any difference between the first peaks of the $S(\mathbf{Q})$ curves for Se-containing glasses in Fig. 1 (Nos. 19 and 20). The RDF distances in the first coordination sphere $R_1$ are almost equal $-0.242$ and 0.240 nm, respectively. Small amount of Sb or As (of about 5 at %) in the presence of more than 80% of $GeS_2$ [29] in these compositions can not influence significantly the curves shape. When the amount of As-Se or Sb-Se bonds prevails, i.e., at small $x$, the Ge-As-X and Ge-Sb-X curves differ significantly; e.g., the obtained $R_1$ value is 0.242 nm for $Ge_{10}As_{30}Se_{60}$, and 0.259 nm for $Ge_{10}Sb_{30}Se_{60}$. This difference follows from the different bond length in the respective structural units once more. (The difference $\Delta R_i = 0.04$ nm for $Sb_2Se_3$ and $GeSe_2$, while for $As_2Se_3$ and $GeSe_2$ $\Delta R_i = 0.005$ nm.)

Despite of some data concerning $As_2S_3$ glasses [4, 19] which include the presence of As-As bond, the amount of As-As bonds and thus of $As_4S_4$ clusters (if available) in the investigated Ge-As-S(Se) family should be very small because no maxima were available at $R = 0.271$ nm (see for comparison Fig. 4 and Table II).

From the $S(\mathbf{Q})$ and RDF analysis a conclusion can be drawn that despite of the nonstoichiometric composition of the $Ge_xAs(Sb)_{40-x}S(Se)_{60}$ glasses their SRO can be approximated by a pseudo-binary model. In this model the main structural units are $GeX_4$ tetrahedra and $MeX_3$ pyramids although some amount of Me-Me bounds is expected to exist.

### 3.2.3. The role of the Chalcogen atom

The substitution of S by Se at fixed amount of As and Ge leads to a decrease of the FSDP intensity for all investigated glasses, e.g., FSDP of the sample No. 5 is about 20% lower than the corresponding maximum of the sample No. 6 The similar trend can be seen in the Sb-containing glasses (see curves Nos. 18 and 19, Fig. 1). This result is in accordance with our previous work [25], proving the stronger structural dependence of the properties of Ge-As-S glasses and thin films than the Ge-As-Se ones. For all S-containing glasses a certain decrease of the second $S(\mathbf{Q})$ maximum, P2, and its broadening effect is observed. As it is known, the S-containing binary glasses are less ordered than the Se-containing ones. It can be supposed that the same effect occurs in the investigated ternary glasses which fact leads to the observed differences in P2. The sensitivity of the first coordination sphere to the type of the chalcogen atom, S or Se, at fixed Ge and As content is demonstrated in Fig. 5. The first coordination peak position at $R = 0.221$ nm of the sample No. 6 related to that of As-S ($R = 0.229{-}0.230$ nm) and Ge-S ($R = 0.224{-}0.248$ nm) in the binary crystals indicates a slight shortening of heteropolar bonds in the glassy state. The higher stability of $GeS_4$ tetrahedra with respect to $AsS_3$ pyramids leads to the conclusion that some of $AsS_3$ polyhedra could be deformed. This effect can be explained by a break-down of the endless -S-As-S-As- chains at the transition into the glassy state. Than, in this process the chain fragments are connected through S-atoms with $GeS_4$ polyhedra in more compact groups.

An opposite effect is observed in the Se-containing systems. The first coordination maximum of the sample No. 5 (with distances $R = 0.228{-}0.23$ nm for As-Se and $R = 0.223 - 0.262$ nm for Ge-Se) is fixed at 0.242 nm. As can be seen from Fig. 5 the first coordination maximum in the RDF model related to $50\%GeSe_2 + 50\%GeSe$ strongly differs from the experimental curves. At the same time the $GeSe_2$ RDF fit of the sample No. 22, Fig. 3, is more convenient. That is why the amount of GeSe structural units can be considered as negligible. As a result a conclusion is drawn that the first coordination sphere distances in Ge-As-Se glasses increase. The comparison of the crystal-like model RDF with that obtained from the experiment shows that the pseudo-binary model of SRO is a good approach for the first two coordination spheres, up to 0.4 nm. A more important difference is the appearance of the small RDF peak in the region of 0.294–0.318 nm. It is absent on the RDF of low Ge-content glasses and is shifted to higher distances with S→Se substitution. The only structural effect connected with S↔Se substitution in Ge-Sb-X glasses detected on neutron scattering data could be attributed to the atomic (ionic) size of $Se^{2-}$ and $S^{2-}$.

## 4. Conclusions

The results from neutron scattering experiments carried out on $Ge_xAs(Sb)_{40-x}S(Se)_{60}$ glasses show that the basic structural units, $GeS(Se)_4$ tetrahedra and $As(Sb)S_3$ or $As(Sb)Se_3$ pyramids persist in the glassy state for the whole range of studied compositions. The crystal-like model distribution functions describe very well the experimentally observed RDFs for the first two coordination spheres, although the investigated families contain one nonstoichiometric component. The appearance of a new coordination maximum between the first two RDF peaks in glasses with high ($>10$ at %) Ge content is probably due to the formation of two-member clusters of edge-shared $GeS(Se)_4$ tetrahedra. The proposed pseudo-binary model explains the existence of well expressed FSDP the amplitude of which increases with the Ge-content in all ivestigated glasses.

A shortening of the heteropolar bonds in the S-containing glasses as well as an increase of the heteropolar bonds in the Se-containing glasses has been found.

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