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Frontiers of self-organization in covalent-bonded glassy networks: a complexity originates from mixed *molecular-clustering* and *chain-crossing* in glassy germanoselenides Ge-Se

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Compositional trends in topological organization of fully-saturated covalent networks are considered at the example of binary Ge-Se glasses. It is shown that previously announced reversibility window, detected in this system with temperature-modulated differential scanning calorimetry as compositional range of under-marginal non-reversing heat flow, does not correspond to real intermediate phase in terms of global optimally-constrained connectivity. The observed structural complexity is attributed to *topological pseudo-self-organization*, e.g. effect originated from mixed over-constrained molecular-clustering and optimally-constrained inter-cluster chain crossing.

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Today, the nature of self-organization is in a sphere of tight interest for a great number of scientists working on solid state systems with mathematical-statistical modelling approaches [1,2]. These systems usually consist of a very large number of inherent components, which makes nearly impossible to build them artificially within developed computational techniques. Therefore, understanding the processes leading towards self-organization in real condensed matter objects is still an actual task. In this view, the topological self-organization of disordered networks offers unique possibility to test existing theoretical models.

Among materials possessing a stretched network structure, the chalcogenide glasses (the glassy-like alloys of IV-V group elements with S, Se or Te quenched from melt [3]) are one of the most convenient objects in view of their excellent glass-forming ability, which allows covalent disordered networks of wide connectivity by chalcogen variation only. Assuming covalent bonds as Lagrangian constraints of constituting atoms, different elastic-topological phases can be introduced in such glassy backbones. According to the Phillips-Thorpe rigidity percolation theory [4,5], these covalent-bonded networks are characterized by three distinct elastic phases in dependence on their composition (defined by mean coordination number Z, e.g. average number of covalent chemical bonds per atom) – the floppy, intermediate and rigid. The networks having number of constraints per atom n_c less than space dimensionality are considered to be under-constrained (floppy, F); those with greater n_c are attributed to over-constrained (rigid and stressed, RS); and networks with n_c just equal to space dimensionality are optimally-constrained (rigid but unstressed, or isostatically rigid). Topological self-organization occurs, if network keeps its optimal atomic arrangement as long as possible (through change in a glass composition) to avoid stresses, caused by over-constrained structural fragmentation [6,7]. As a result, the solitary percolation transition from floppy F to rigid-stressed RS network splits into two points revealing a self-organized phase, formed by optimally-constrained glassy structures.

That is why the covalent-bonded networks of binary germanoselenides Ge-Se, which form glasses within a wide concentration domain from pure glassy g-Se (Z = 2.00) to near-stoichiometric g-GeSe$_2$ (Z = 2.67), can be considered as one of canonical systems to study the phenomenon of topological self-organization. The compositional boundaries of intermediate phase in g-Ge-Se were determined previously within $2.40 < Z < 2.52$ range (a so-called reversibility window) using marginality of non-reversing heat flow in temperature-modulated differential scanning calorimetry (DSC) study as a criterion [8-10]. However, these boundaries were not confirmed experimentally by means of synchrotron x-ray diffraction and x-ray absorption fine structure measurements [11], the reversibility window being considered only as an artefact of both the restraints during temperature-modulated DSC (single modulation frequency used), as well as time pre-history of a glass [12-15]. Recent attempts for more precise justification of compositional boundaries of reversibility window in g-Ge-Se through better glass homogenization [10], in fact, did not change anything in regard to a major question on the possible origin of non-reversing heat flow anomaly in temperature-modulated DSC. So we come back to this system once more to clarify its realistic topological specificity.

In our consideration we will rely on the previous structural inspection of this system with high-resolution XPS [16], supported by quantum-chemical modelling for molecular- and network-forming clusters [13,17,18]. XPS peaks of Ge 3*d* and Se 3*d* core-level electrons were fitted with a number of doublets corresponding to each specific chemical environment of the network sites. Fitting parameters, such as peak position or binding energy (BE), area (*A*) and FWHM (full width at half maximum) are summarized in Table 1 and 2 for Se and Ge 3*d* core level electrons, respectively. The doublets in Se 3*d* XPS spectra with primary components at ~54.6 eV, ~54.2 eV and ~53.8 eV were attributed to Se-**Se**-Se, Ge-**Se**-Se and Ge-**Se**-Ge structural fragments, respectively. The doublet in Ge 3*d* XPS spectra with main component at ~30.3 eV was assigned to $(Se)_2$>**Ge**<$(Se)_2$ regular environment (regular $GeSe_4$ tetrahedrons).

If 'chains crossing' model [19,20] was valid for binary Ge_xSe_{100-x} glasses, three types of possible nearest Se neighbour configurations are expected: Se-**Se**-Se, Ge-**Se**-Se and Ge-**Se**-Ge (the analyzed core level is written in bold font). At the same time, only one Ge environment $(Se)_2$>**Ge**<$(Se)_2$ (i.e. Ge atoms incorporated within $GeSe_{4/2}$ tetrahedron) should exist. Then, it is possible to determine theoretically the content of each atomic environment for all the investigated glass compositions (see A^0 values in Table 1 and 2). Each of the indicated fragments should contribute a separate doublet in the corresponding core level spectrum. It is evident from a comparison of the peak area, *A* (experimental) and A^0 (predicted by 'chain-crossing' model) that this model is obeyed only for Se-rich compositions (Ge_5Se_{95}, Ge_8Se_{92} and $Ge_{10}Se_{90}$). Starting from g-$Ge_{12}Se_{88}$, significant deviation from 'chains crossing' occurs.

So, we were forced to introduce another model possible for the structure of g-Ge-Se, the 'outrigger raft' (ORR) model based on the existence of clusters of appropriate glass-forming units (such as ones character for high-temperature modification of crystalline $GeSe_2$) [21].

Table 1. Numerical parameters of Se 3d$_{5/2}$ fit components in Se 3d core level XPS spectra, attributed to different atomic environments around Se atoms.

Se-**Se**-Se species

Glass	BE	FWHM	*A*	A_0
Se	54.60	0.71	100	100
Ge$_5$Se$_{95}$	54.56	0.70	81	79
Ge$_8$Se$_{92}$	54.52	0.70	70	65
Ge$_{10}$Se$_{90}$	54.50	0.69	61	56
Ge$_{12}$Se$_{88}$	54.48	0.69	56	45
Ge$_{14}$Se$_{86}$	54.49	0.69	51	34
Ge$_{20}$Se$_{80}$	54.49	0.69	32	0
Ge$_{23}$Se$_{77}$	54.49	0.70	22	0
Ge$_{25}$Se$_{75}$	54.48	0.70	11	0
Ge$_{30}$Se$_{70}$				

Se-**Se**-Ge species

Glass	BE	FWHM	*A*	A_0
Se				
Ge$_5$Se$_{95}$	54.14	0.75	19	21
Ge$_8$Se$_{92}$	54.17	0.58	25	35
Ge$_{10}$Se$_{90}$	54.15	0.60	33	44
Ge$_{12}$Se$_{88}$	54.17	0.60	33	55
Ge$_{14}$Se$_{86}$	54.15	0.60	35	66
Ge$_{20}$Se$_{80}$	54.15	0.60	36	100
Ge$_{23}$Se$_{77}$	54.13	0.65	35	81
Ge$_{25}$Se$_{75}$	54.13	0.78	44	67
Ge$_{30}$Se$_{70}$	54.19	0.86	29	29

Ge-**Se**-Ge species

Glass	BE	FWHM	*A*	A_0
Se				
Ge$_5$Se$_{95}$				
Ge$_8$Se$_{92}$	53.75	0.50	5	0
Ge$_{10}$Se$_{90}$	53.74	0.49	6	0
Ge$_{12}$Se$_{88}$	53.80	0.54	11	0
Ge$_{14}$Se$_{86}$	53.81	0.52	14	0
Ge$_{20}$Se$_{80}$	53.82	0.66	32	0
Ge$_{23}$Se$_{77}$	53.81	0.73	43	19
Ge$_{25}$Se$_{75}$	53.80	0.73	45	33
Ge$_{30}$Se$_{70}$	53.77	0.75	71	71

These ORR clusters consist of two edge-shared (ES) tetrahedrons connected with four corner-shared (CS) ones as it is arbitrary shown in Fig. 2. If one recalculated the ratio between Ge atoms in ES tetrahedrons and those belonging to CS surrounding in this structure, it is 1:2, which is quite close to the ratio between observed doublets in Ge core level XPS spectra in Table 2 for samples with *x* ≥ 20. So, the second doublet with primary component at ~30.5 eV was assigned to ES tetrahedrons.

Table 2. Numerical parameters of Ge 3d$_{5/2}$ fit components in Ge 3d core level XPS spectra, attributed to different atomic environments around Ge atoms

$(Se)_2$>**Ge**<$(Se)_2$ CS species

Glass	BE	FWHM	*A*	A_0
Ge$_5$Se$_{95}$	30.39	0.73	100	100
Ge$_8$Se$_{92}$	30.39	0.73	100	100
Ge$_{10}$Se$_{90}$	30.35	0.72	100	100
Ge$_{12}$Se$_{88}$	30.31	0.65	97	100
Ge$_{14}$Se$_{86}$	30.31	0.67	83	100
Ge$_{20}$Se$_{80}$	30.31	0.67	67	100
Ge$_{23}$Se$_{77}$	30.35	0.72	66	100
Ge$_{25}$Se$_{75}$	30.23	0.73	70	100
Ge$_{30}$Se$_{70}$	30.21	0.70	70	100

$(Se)_2$>**Ge**<$(Se)_2$ ES species

Glass	BE	FWHM	*A*	*A_0*
$\mathbf{Ge_5Se_{95}}$				
$\mathbf{Ge_8Se_{92}}$				
$\mathbf{Ge_{10}Se_{90}}$				
$\mathbf{Ge_{12}Se_{88}}$	30.79	0.44	3	0
$\mathbf{Ge_{14}Se_{86}}$	30.76	0.62	17	0
$\mathbf{Ge_{20}Se_{80}}$	30.45	0.90	33	0
$\mathbf{Ge_{23}Se_{77}}$	30.45	0.90	34	0
$\mathbf{Ge_{25}Se_{75}}$	30.45	0.90	30	0
$\mathbf{Ge_{30}Se_{70}}$	30.45	0.82	30	0

The ratio between doublets in Se core level XPS spectra (Table 1) also supports this assumption for g-Ge_xSe_{100-x} with $x \geq 20$. The ES $GeSe_{4/2}$ tetrahedrons can be also the reason for almost step-like increase beyond $x = 20$ composition in the FWHM parameter of the fitted component responsible for Ge-**Se**-Ge species (Table 1). At the same time, the FWHM of all other core level peaks assigned to Se-**Se**-Ge and Se-**Se**-Se structural species remains almost unchanged with glass composition, supporting the assumption made.

On the other hand, the almost constant ratio of peaks in Ge core level spectra attributed to ES and CS $GeSe_{4/2}$ tetrahedrons as obtained by fitting procedure (Table 2), suggests that most of Ge atoms participate in the formation of structural units proper to high-temperature modification of crystalline $GeSe_2$ in all glass compositions starting from $x \cong 20$ onward.

Thus, Se and Ge core level XPS spectra do not yield any evidence for structural signature of intermediate phase in a sense of self-organization, in good agreement with recent results obtained by XRD and XAFS [11]. In other words, we cannot distinguish any special optimally-constrained ($n_c = 3$) structural units, which could be continuously formed within $20 \leq x < 26$ range to constitute the reversibility window in this system, as claimed by means of temperature modulated DSC [8-10].

Starting from the percolation point ($x = 20$), all Ge atoms should participate in the formation of a so-called ORR-like structures consisting of ES $GeSe_{4/2}$ tetrahedrons surrounded by four CS ones (two from each side). Such over-constrained ORR cluster for $x = 30$ glass is shown in Fig. 1 as typical example.

The network of other glasses within $20 \leq x < 30$ range should contain extra Se atoms according to a glass composition. They can be attached to the bridges between different ORR clusters or to the places of Se-Se dimers, filling a significant amount of inner free volume proper to high-temperature modification of crystalline $GeSe_2$.

According to such consideration and in good agreement with [13,16-18], we can argue that ORR clustering motif (two ES and four CS $GeSe_{4/2}$ tetrahedrons, terminated from both sides by homopolar Se-Se bonds as first suggested by Bridenbaugh et al. yet in 1979 [21]), is a basic network-forming structural unit for Ge-Se glasses within $20 \leq x < 30$ concentration range.

This structural unit consists of three parts, the central $GeSe_2$ core ($n_c = 3.67$) and two adjusting left- and right-sided $Ge_{2.5}Se_6$ cores ($n_c = 3.35$) as it is shown in Fig. 1. Within such geometrical consideration, the central core consists of two ES $GeSe_{4/2}$ tetrahedrons, while left- and right-sided cores are built of two CS tetrahedrons each. These cores form a so-called cluster “body” (see Fig. 2). Other components involve two homopolar Se-Se bonds (Se-Se dimers or “ears”) terminating both sides of CS $GeSe_{4/2}$ tetrahedrons (shadowed ellipses in Fig. 1) and inter-cluster Se-based bridges (“legs”) between CS tetrahedrons of different ORR clusters (shadowed half-ellipses in Fig. 1). Therefore, the left- and right-sided parts of each ORR cluster involve the five-member rings of $(Ge)_{1/2}$-Se-Se-$(Ge)_{1/2}$-Se-$(Ge)_{1/2}$ composition. In view of steric constraints within this rigid ORR structural configuration ($n_c > 3.00$), two free-volume spaces (atomic-deficient holes or voids) of lower electron density appear next to the central ES tetrahedrons.

Thus, this ORR clustering motif in g-Ge-Se can be easily imagined as a separate “puzzle” block (as it shown in Fig. 2), which involves the following constituent elements:

- the central over-constrained RS (rigid and stress) cluster “body” ($n_c > 3.00$),
- the under-constrained F homoatomic Se-Se cluster “ears” ($n_c < 3.00$),
- the four inter-cluster “legs” of variable topological rigidity depending on the number of bridging Se atoms between neighbouring ORR clusters and
- the two low electron density voids attached to the central part of ORR cluster.

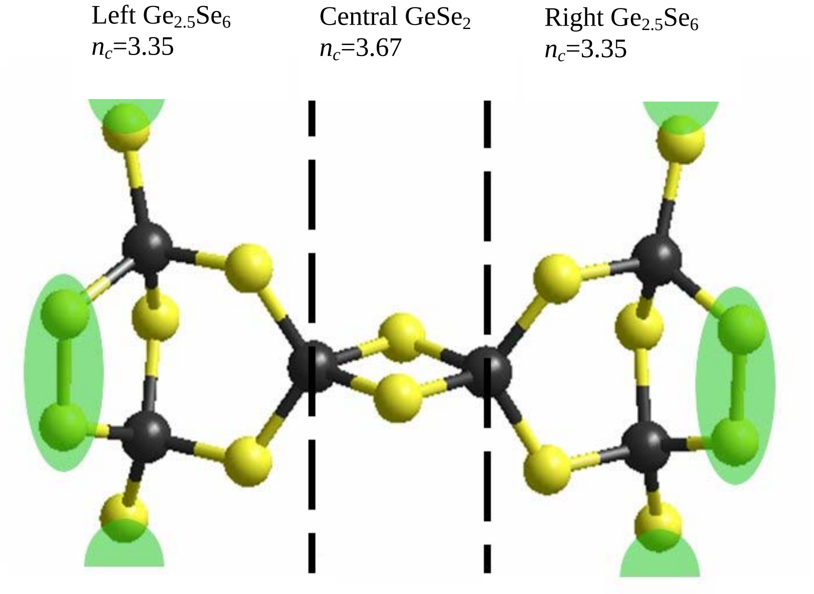


Fig. 1. ORR "body-ears-legs" clustering motif in g-Ge-Se built of interconnected cluster "bodies"(two central ES $GeSe_{4/2}$ tetrahedrons neighboured by two left- and two right-sided CS $GeSe_{4/2}$ tetrahedrons), left- and right-adjusted Se-Se "ears" (shadowed ellipses), and four inter-cluster "legs" (shadowed half-ellipses).

Since intra-molecular coupling is dominant in the above ORR cluster within $2.40 < Z < 2.60$ compositional range [13], the overall glass-forming process in g-Ge-Se looks like a superposition of

(1) *inter-cluster linking* between four outer Ge atoms belonging to neighbouring ORR clusters (the first compositional trend, which can be conditionally characterized as *chain-crossing network-forming motif*) and

(2) *increase in the number of inner Se atoms* attached to the place of Se-Se dimer in left- and right-sided $Ge_{2.5}Se_6$ cores (the second compositional trend, which can conditionally accepted as *molecular-clustering motif*).

Both compositional trends keep an optimal 2:4 ratio between ES and CS $GeSe_{4/2}$ tetrahedrons, required to form over-constrained "body" of ORR cluster (RS-distinguished in Fig. 2) [16].

Strict examination of possible compositional trends in binary g-Ge-Se within cation-interlinking network-cluster approach [17,18] testifies that optimally-constrained (n_c = 3.00) inter-cluster $-(Ge)_{1/4}-Se-Se-(Ge)_{1/4}-$ bridges between ORR clusters are preserved when changing glass composition from $Z = 2.545$ to 2.43.

The rest Se atoms (from 2 to 6) form left/right-sided "ears" at the places of Se-Se dimers (the principle of space filling with these building blocks are reflected by Fig. 3 and 4). This balance between molecular-clustering and chain-crossing is satisfied at low energy cost within $2.43 < Z < 2.545$ range of compositions [13,17,18]. Beyond this domain, the optimal interconnection between ORR clusters through $-(Ge)_{1/4}-Se-Se-(Ge)_{1/4}-$ bridges is destroyed, being the reason for compositional peculiarities of non-reversing heat flow values in temperature-modulated DSC [8-10].

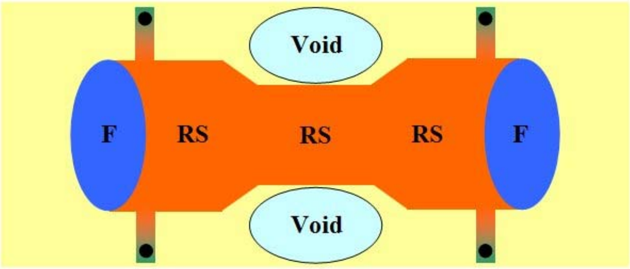
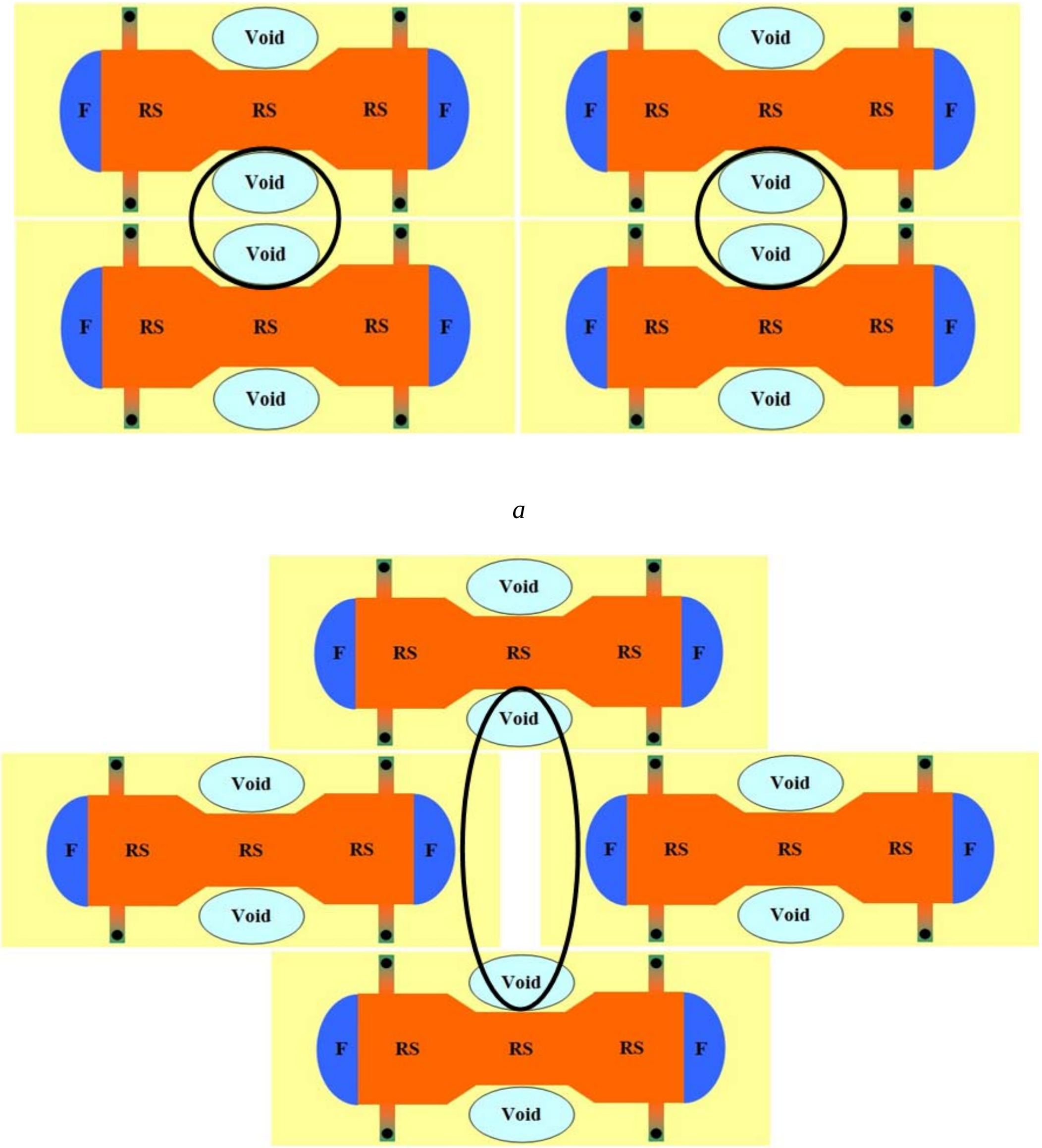


Fig. 2. Glass-building "puzzle" block of g-Ge-Se involving over-constrained rigid-stress "body" RS with four optimally-constrained inter-cluster "legs" (black bold pointed), under-constrained floppy "ears" F and two attached voids.



a

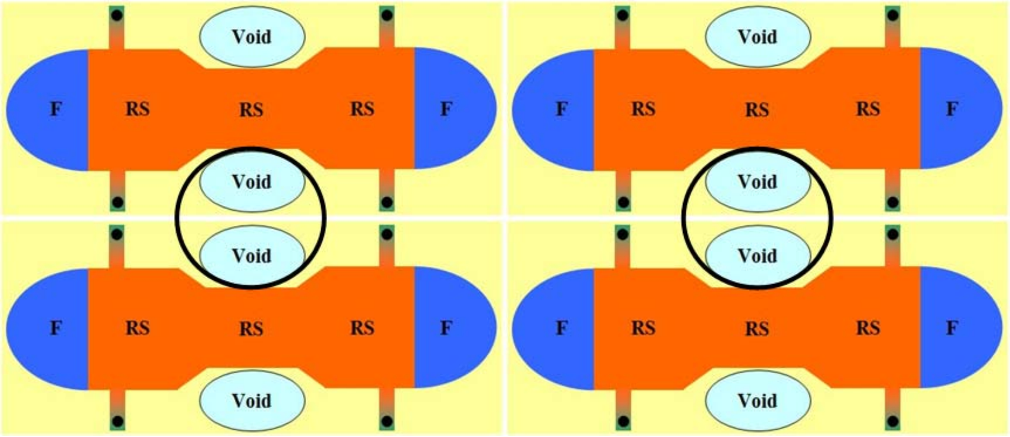
b

Fig. 3. A "puzzle" principle of space filling in g-Ge-Se by ORR clusters with short Se chains in the "ears" (Z is close to 2.545), through regular (a) and irregular (b) packing.

Therefore, we believe that just the conservation of inter-ORR- cluster linkages in the form of optimally-constrained bridges is a reason for marginal values of non-reversing temperature-modulated DSC signal in g-Ge-Se observed within the reversibility window (between $Z = 2.40$-2.43 and $Z = 2.53$-2.55) and mistakenly accepted as a signature of self-organized phase [8-10]. In reality, the network of g-Ge-Se in $2.43 < Z < 2.545$ compositional range are not optimally-constrained in a sense of global connectivity, since they consist of over-constrained ($n_c > 3.00$) structural blocks (RS ORR "bodies") interconnected by optimally-constrained -$(Ge)_{1/4}$-Se-Se-$(Ge)_{1/4}$- inter-cluster "legs" ($n_c = 3.00$), in full agreement with conclusions made in [16]. This feature can be accepted only as an evidence for *pseudo-self-organized* phase rather, than strong topological self-organized phase in g-Ge-Se [13,18]. According to the present consideration, the latter is expected in much narrower compositional domain centred near $Z \approx 2.40$-2.43, in good agreement with theoretical predictions [4,5].

So, the glass-forming trends within binary g-Ge-Se can be conditionally imagined like as overall space filling with ORR-like "puzzles", each of them being built of interconnected $GeSe_{4/2}$ tetrahedrons (two interconnected central ES $GeSe_{4/2}$ tetrahedrons with two left- and two right-attached CS $GeSe_{4/2}$ tetrahedrons). Hence, the "puzzle body" is topologically over-constrained (e.g. RS) having $n_c > 3.00$, while the adjusted "puzzle ears" (left- and right-sided Se chains) are topologically floppy F with $n_c < 3.00$ constraints (Fig. 2).

Thereby, under above consideration we can note that within $2.43 < Z < 2.545$ compositional range in the structure of g-Ge-Se, the optimally-constrained (n_c = 3.00) *inter-cluster linkage* prevails over *molecular clustering*, denoting the compositional boundaries for *topological pseudo-self-organization* in this binary glass-forming system.



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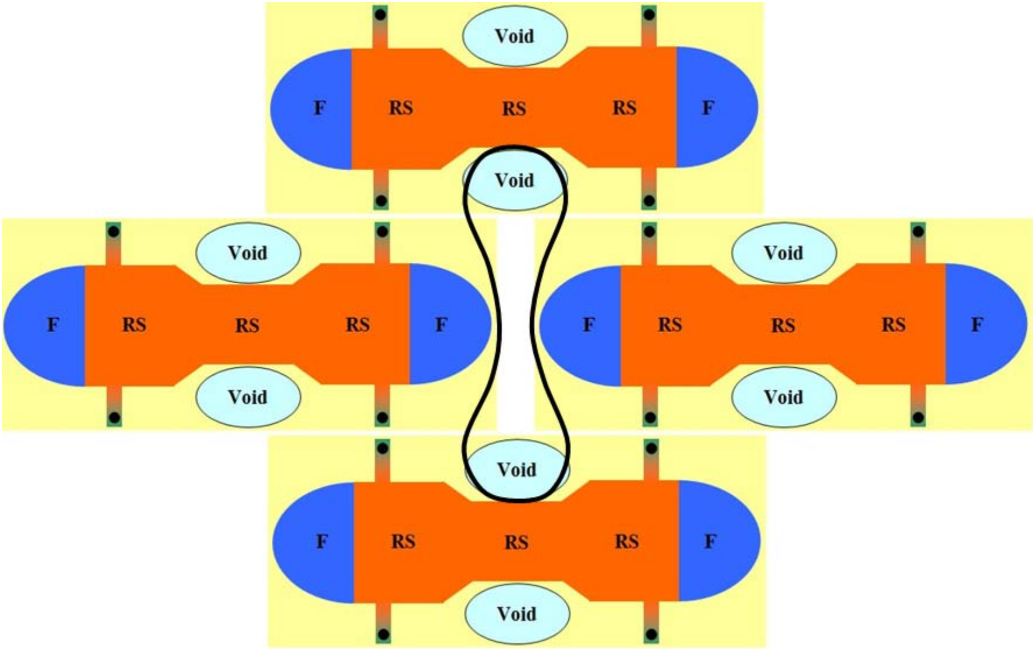

b

Fig. 4. A "puzzle" principle of space filling in g-Ge-Se by ORR clusters with longer Se chains in the "ears" (Z is close to 2.43) through regular (a) and irregular (b) packing.

Let us consider two examples of possible packing ways for these building blocks ("puzzles") in a space:

- *the regular packing* when each ORR cluster shares two optimally-constrained -$(Ge)_{1/4}$-Se-Se-$(Ge)_{1/4}$- bridges with its neighbor (Fig. 3a and 4a) and

- *the irregular packing* when each ORR cluster shares one optimally-constrained -$(Ge)_{1/4}$-Se-Se-$(Ge)_{1/4}$- bridge with each neighbor (Fig. 3b and 4b).

For the first case (the regular packing), the appeared low electron density voids are surrounded exclusively by *negatively-charged environment* of Se^{2-}(CS-$GeSe_{4/2}$) – $2Se^{2-}$(ES-$GeSe_{4/2}$) – Se^{2-}(CS-$GeSe_{4/2}$) – Se^{2-}(CS-$GeSe_{4/2}$) – $2Se^{2-}$(ES-$GeSe_{4/2}$) – Se^{2-}(CS-$GeSe_{4/2}$) type, while *mixed negative-neutral environment* of Se^{2-}(CS-$GeSe_{4/2}$) – $2Se^{2-}$(ES-$GeSe_{4/2}$) – Se^{2-}(CS-$GeSe_{4/2}$) – nSe^{0}(Se_n-chain) – Se^{2-}(CS-$GeSe_{4/2}$) – $2Se^{2-}$(ES-$GeSe_{4/2}$) – Se^{2-}(CS-$GeSe_{4/2}$) – nSe^{0} (Se_n-chain) is character for surrounding of voids in the case of irregular packing.

It is interesting to note that these network-forming tendencies principally differ in view of their compositional dependence. Surrounding of the voids character for regular packing (Fig. 3a and 4a) does not change upon the composition, since it is fixed near ORR clusters (dense-arranged "puzzles"), the volume of corresponding voids remains nearly the same (e.g. does not depend on short or long Se chains in the "puzzle ears"). On the other hand, the voids of irregular packing (Fig. 3b and 4b) are more stretched-shaped (hole-arranged "puzzles"), reducing their volume with Se content because of increase in the number of Se atoms involved into edges of ORR clusters ("puzzle ears").

The further experiments exploring unique possibilities of void-sensitive nanostructural probes in disordered substances, such as positron annihilation lifetime spectroscopy [22-24], would shed more light on real preferences for topological-structural organization in this canonical system.

Conclusion

Unusual effect of *topological pseudo-self-organization* character for covalent-bonded networks of glassy germanoselenides g-Ge_xSe_{100-x} was treated in terms of structural complexity originated from *mixed molecular-clustering* and *chain-crossing* motifs.

This case of topological-structural evolution occurs, when rigid glass-forming units (either optimally- or over-constrained) are interlinked via optimally-constrained inter-cluster bridges within the same covalent-bonded backbone. The structural evolution in $2.43 < Z < 2.545$ domain of g-Ge-Se involves the formation of over-constrained rigid-stressed RS molecular units (ORR clusters or "puzzle bodies") having different number of Se atoms in "ears", which are interlinked preferentially via optimally-constrained -$(Ge)_{1/4}$-Se-Se-$(Ge)_{1/4}$- "legs". The "puzzle bodies" are composed of two central ES $GeSe_{4/2}$ tetrahedrons connected with two left-attached and two right-attached CS ones.

Two different kinds of inter-ORR-cluster arrangement are interesting in this structure, which correspond to *regular* and *irregular packing* of ORR clusters in a space with two and one $(Ge)_{1/4}$-Se-Se-$(Ge)_{1/4}$- shared bridges, respectively. These network-forming tendencies are principally different in view of their compositional trends. The regular packing is accompanied by formation of inner voids which volumes are compositionally independent (the dense-arranged "puzzles" forming *negatively-charged atomic environment*), while intercluster voids of irregular packing demonstrate more extended volumes enriched with Se content (the hole-arranged "puzzles' forming *mixed negative-neutral atomic environment*). The latter is supposed to be more plausible for binary g-Ge-Se in view of character compositional dependence of molar volume.

So this model of *topological pseudo-self-organization* in covalent-bonded networks of glassy germanoselenides g-Ge_xSe_{100-x} can be conditionally outlined as "*hole puzzles*" model.

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