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Invited Lecture

STRUCTURAL AND PHASE TRANSFORMATIONS IN CONDENSED SELENIUM

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At normal pressure selenium exists in several forms of condensed state: crystalline (hexagonal Se_n, α -, β -, γ -monoclinic Se₈, monoclinic Se₈), rhombohedral Se₆, α - and β -cubic Se, amorphous Se (red, brown and black Se), 4 liquid modifications, vitreous selenium. Structural and phase transformations taking place at heating as well as at cooling (or at constant temperature) of all above indicated selenium forms have been considered. The analysis of transformations inside of different Se forms and between them has been made on the base of the concept of the polymeric-polymorphoid structure of glass and glass-forming liquid using data of diffractometry, IR-, Raman- and UV-photoelectron spectroscopy as well as results of heat capacity alterations in the range of Se glass transition and enthalpy of transformation of non-crystalline Se forms into others.

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1. Introduction

Multiformity of crystalline and non-crystalline selenium (solid and liquid) requires a special attention to the initial point, to the position from which the analysis of structural phase transformations can be carried out for this "simple" (with or without quotes marks) glass-forming substance. Transformations in substances taking place under external factors, turning out the system from its equilibrium state, are directly related to the substance properties. The latter, according to the main principle of the physical-chemical analysis of Kurnakov and Tananaev [1, 2] depends on the most important aspects of the physical-chemical essence of substances: the chemical composition, the structure, the dispersity.

Ultra-dispersive media are macroscopic assemblies of microscopic particles with dimensions of 1-10 nm. Distinctive features of surface states are clearly demonstrated in such systems [3]. During producing substances by chemical deposition, by condensation from a vapor phase or by other methods, ultra-dispersive particles (to the greater or lesser extent) join together, demonstrating the internal dispersion that is directly related to the rupture of chemical bonds, change of hybridization, and nanometer-scale pores, characteristic for many film samples. The main feature of ultra-dispersive powder media is the external dispersion.

Plurality of non-crystalline solid selenium requires a more accurate terminology. Up to now, there is no a clear division between amorphous and vitreous states. The following are the most popular viewpoints: "the vitreous state is a particular case of the amorphous state" [4, p.223]; "there is no reason to divide qualitatively the state of amorphous solids, obtained by evaporation or electro-deposition methods, and glasses, obtained by the super-cooling liquid method" [5]; "there are no grounds to identify amorphous and vitreous states" [6, p.231]. To avoid the existing terminological confusion, we have proposed [7, 8] to divide non-crystalline substances into two classes: vitreous

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and ultra-dispersive (non-vitreous powders and films) substances. We will follow such terminology in this work using the definition "amorphous state" only in citations.

It is obvious that structural transformations in non-crystalline substances take place with the alteration of their structure. What are the structures of different modifications of non-crystalline selenium? Are they related to structures of numerous crystalline forms, and, if yes, in what way? There are no complete answers for these questions till now. And the reason is, from our viewpoint, the absence of a generally acknowledged objective concept of structures of non-crystalline substances, vitreous in particular.

The concept of Frankenheim (1835) [9], Lebedev (1921) [10], Zahariasen (1932) [11], the para-crystalline concept of Hoseman (1950) [12], the polymeric-crystallite concept of Poray-Koshitz (1959) [13], and the concept of "clusters of structurally-independent poly-forms" of Goodman (1975) [14] reflect, to some extent, the objective glass structure, but they are either too general or contain notions which contradict the experimental facts. The latter concept is based on crystallites – the smallest crystals consisting of a small number of unit cells [13]. In the last years, the very interesting concept of Popescu and Bradaczek [15, 16] is in progress. This concept based on Hoseman's ideas develops the microparacrystalline model of the intermediate-range order in non-crystalline substances.

In this work, the analysis of structural and phase transformation in condensed selenium is carried out on the base of the concept of the polymeric nanoheteromorphous structure of non-crystalline substances [17] and its particular case – individual glass-forming chemical substances (ICS) – the concept of the polymeric-polymorphoid glass and glass-forming liquid structures (before the work [18]) – it was called "the concept of polymeric polymorphous-crystalloid structures [8, 17-19]. We will also apply this concept to ultra-dispersive – non-crystalline non-vitreous, "amorphous" – forms of selenium. The experience of such applications, related to the consideration of silicon and carbon structures [8, 20], has shown that the advancing of the more general concept of polymeric-polymorphoid (nanoheteromorphous) structure of non-crystalline substances will have not many differences from its "vitreous" forerunner. One of them / the change of the process (and the notion) of "glass-formation" into the process (the notion) of the transformation of substances from crystalline, liquid, vapor phase, dissolved states into the ultra-dispersive state / consists in some kind of "amorphization" without the glass formation and the corresponding glass transition temperature T_g .

The following ideas are laid at the base of the concept of the polymeric-polymorphoid structure of glass and glassforming liquid:

- glass and glass-forming liquid (GL) are built (more or less) of co-polymerized structural fragments of different polymorphous modifications (PM) without a long-range order – polymorphoids (before there was called– crystalloids [18]);

- the polymorhoid (the crystalloid) is a crystal structure fragment consisting of a group of atoms connected with chemical bonds in accordance with rules of the stereometric ordering inherent to one of crystalline PMs without a translation symmetry of the crystal. There is no long-range order (LRO) due to a minimum size in polymorphoid – two neighboring unit cells of the crystal structure which could be mutually translated;

- the intermediate-range order is a stereometrically defined combination (topology) of shortrange orders within polymorphoid's borders that is characterized by parameters of all short-range orders (SRO): coordination numbers, inter-atom distances, inter-bond angles as well as dihedral angles inherent to a given PM; the intermediate-range order has dimensions, at least along one of three crystallographic axes, which are less than two periods of the crystal lattice, otherwise it would be a crystallite;

- under external impacts, mutual transformations take place between polymorphoids of different PMs and copolymerization or depolymerization of polymorphoids occurs:

$$T, P, Ph, E, H \dots$$

$$A_x + B_1 + C_m + \dots + Z_x \iff A_p + B_q + C_r + \dots + Z_y$$
(1)

where A, B, C....Z are polymorphous modifications of substances which fragment's (polymorphoid's) concentrations k, l, m, ... p, q, r ... x, y change depending on external conditions (the temperature T, the pressure P, the irradiation Ph, the electric field E, the magnetic field H and others) from 0 to 100% (a crystalline substance); the concentration ratio of different polymorphoids in glass and glass-forming liquids is a fundamental physical-chemical characteristic of these states of substances that allows to develop standards of their structure;

The concept of the polymeric-polymorphoid structure of glass and glass-forming liquid (CPPSGGL), based on above mentioned ideas, unites objective notions of earlier concept as well as many notions on structures of non-crystalline substances, expressed by many authors and analyzed in [8, 17-19].

2. Different forms of condensed states and some properties of selenium under the normal pressure

At the normal pressure selenium exists in several forms of condensed state: crystalline (hexagonal^{*} Se_n with the melting temperature of $T_m = 217$ °C, α -monoclinic Se₈ with $T_m = 144$ °C, β -monoclinic Se₈ with $T_m = 100$ °C, γ -monoclinic Se₈, rhombohedric Se₆ with $T_m = 120$ °C, orthorhombic Se, α - and β -cubic Se, obtained as films), ultra-dispersive "amorphous" (red, brown and black Se), 4 liquid forms obtained as a result of the melting of crystalline PMs at above mentioned T_m and vitreous Se [21-26].

2.1. Crystalline polymorphous modifications and liquids obtained at melting

The summary (Table 1) of allotropic selenium forms and some of their characteristics is given in [25].

Red monoclinic selenium is characterized by the *cis*-configuration in the arrangement of four sequentially bonded atoms in the circular molecule of Se₈. The monoclinic unit cell of α - and β -selenium contains 4 Se₈ molecules, γ -selenium – 8. α -monoclinic selenium has the following parameters of the unit cell: a=905.4 pm, b=908.3 pm, c=1160 pm. The valency angle is equal to 105.9°, the dihedral angle φ = 101.0° [24]. The hexagonal PM consists of spiral chains with the *trans*-configuration arrangement of atoms in the 4-member fragment of the chain (Fig. 1 [24, p.259]). The spiral chains with the identity period of 3 are connected in the crystal lattice of the trigonal syngony with the following parameters of the unit cell: a=436.8 pm, c=495.8 pm. The valency angle is equal to 103.1°. The dihedral angle φ , characterizing the degree of the chain twisting, reaches 100.6°, approaching to the value of the angle in the Se₈ molecule [24].

Data on rhombohedric Se₆ are given in Table 1. The dihedral angle is $76.2\pm0.4^{\circ}$. The hexagonal unit cell contains 3 molecules of Se₆ [27].

Judging from the values of lattice constants of allotropic forms of selenium, the polymorphoids dimensions (which must not exceed at least the doubled value of the lattice constant [28]) of trigonal selenium are less than 9.916 Å. For α -monoclinic it is 23.220 Å, for rhombohedric selenium – less than 22.724 Å. These values correspond to the values that are typical for the nanoscale heterogeneity regions ("pseudo phases") which are inherent, according to Poray-Koshits [29], to glasses without crystalline inclusions. Such heterogeneities are due to the density fluctuations in glass, as usually admitted [30]. However, the cause of such fluctuations is not shown. The concept of the polymeric-polymorphoid structure of glass reveals this cause. The density fluctuation in glass originates from interchange of polymorphoids of different polymorphous modifications in its polymeric structure which naturally have different densities.

The thermodynamically stable allotropic modification of selenium is trigonal selenium.

^{*} as it can be seen from the following text, many authors call this polymorphous modification, trigonal

Relaxation processes in metastable polymorphous modifications (MSPM) of selenium under temperature become apparent at the phenomenological level as polymorphous transformations "monoclinic PM \rightarrow hexagonal PM" (in a monocrystalline sample the beginning of the transformation is registered after heating at 70 °C during 630 min) [31] and the transformation "rhombohedric PM \rightarrow hexagonal PM" at the temperatures higher than 105 °C [27]. α -monoclinic Se melts at 144 °C and spontaneously transforms into trigonal selenium; β -modification melts at temperatures higher than 100 °C [24]. The curves of the differential scanning calorimetry (the heating rate: 10 °C/min) of rhombohedric selenium show the endothermic melting peak at 120 °C [27]. All these transformations are irreversible that demonstrates the monotropic character of the transformations. The heating of the hexagonal PM leads to its melting at 217 °C [24].



Fig. 1. The structure of selenium crystalline modifications.

a – trigonal selenium r₁ (the shortest distance Se-Se in the chain of selenium atoms) – 237.3 pm; r₂ (the distance from a selected atom to four second atoms neighbors belonging to three selenium spirals) – 342.6 pm; b – the *trans*-configuration of selenium chains; v - the valency angle (103.1°); φ - the dihedral angle (100.6°); c – the "crown" structure of Se₈ molecules in monoclinic Se α - and β -modifications; v = 105.9° (α - modification); φ = 101.0° (α -modification) [24].

		~		1001	-		T			
		Spiral chains	2.37	103.1	2	4.366	-	4.954	Melting	4.819
1.	Trigonal	Se _n							217-221	[24]
2.	α-monoclinic	Rings	2.32	105.9	2	9.054	9.083	11.601	Transformation into	4.390
		Se ₈							trigonal 140-160	[24]
3.	β-monoclinic	Rings	2.34	105.5	2	12.85	8.07	9.31	Transformation into	
	•	Se ₈							trigonal 140-180	
4.	α-cubic	-	2.97	-	6	2.970	-	-	-	
5.	β-cubic	-	2.48	-	4	5.755	-	-	-	
6.	Rhombohedric	Rings	2.35	101.1	-	11.362	-	4.429	Transformation into	4.710
		Se ₆							trigonal 120-135	[27]
7.	Ortho-rhombic	-	-	-	-	26.32	6.88	4.34	Transformation into	
									trigonal	
									105	
Non-crystalline										
8.	Red	Rings	2.33		~2.4	-	-	-	≈ T _{room}	4.270
	amorphous	_								[24]
9.	Black	-	-		-	-	-	-		
	amorphous									
10.	Vitreous	Chains and	2.33	105	2-2.2	-	-	-	Softening	4.280
		rings	2.46						30	[24]
11.	Melt	~								4.010
										[24]
			•			•		•	<u> </u>	

Table 1. Allotropic selenium forms.

а

Å

The

 K_1

number

coordination

The

bond

length

Å

Molecular

composition

No.

Name

Crystalline

The bond

angle,

deg.

Unit cell constants

b

Å

с

Å

The transformation

temperature T, °C

Density, g.cm⁻³

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The properties of different-temperature liquids are very different. The main difference between the highest-temperature liquid and other liquid forms is its thermodynamical stability in a rather wide range of temperatures. It can be called the stable glass-forming liquid (SGFL). Lowtemperature liquids crystallize rather fast. They can be called unstable glass-forming liquids (USGFL).

2.2. Vitreous selenium. Structure of liquid and vitreous selenium

In sixties of the last century it was considered that vitreous selenium was a mixture of two structures of polymeric spiral chains and 8-member ring molecules that are connected by Van der Waals forces. Conclusions on the structural model were made up mainly on the base of indirect evidences, as Lucovsky writes [32]. "The presence of chains is inferred from the high viscosity of amorphous selenium at its melting point"^{*}, the presence of Se₈ rings – from its partial solvability in CS_2 .

To calculate the structural equilibrium of the "ring \Leftrightarrow chain" in the selenium melt, the experiment of cooling the melt from 490 K (217 °C) and 700 K (427 °C), carried out by Brieglieb as long ago as 1929 [35], was used. The samples obtained were dissolved in CS₂. It was presumed that selenium, dissolved in CS₂, exists in glass as molecules of Se₈. In the first case (the cooling from 217 °C), 40% of glass were dissolved, in the second case (the cooling from 427 °C) only 18% were dissolved.

According to data [36], the content of the Se₈ monomer at temperatures, some what higher than T_m (217 °C) is ~ 40%, and at temperatures near 427 °C - ~ 25%.

It could be assumed that the viscosity of the melt at decreasing of the Se₈ ring concentration should increase with the temperature increase. However, this assumption was not confirmed experimentally. The viscosity of the selenium SGFL at temperatures somewhat higher than the melting point (~ 217 °C) is rather high (30 poises), but it decreases continuously with the temperature increase [37]. Poltavtsev analyzed in his work [38] the curves of radial atoms distribution of melted selenium [39,40], compared them with his own data [41] and came to the conclusion that there existed a coexistence of spiral atom chains (structural elements of hexagonal PM) and a small fraction of 8-member rings (structural elements of monoclinic modifications). With the temperature increase up to 300 °C, the fraction of chain structural elements (*trans*configurations) decreases and the fraction of 8-member rings (*cis*-configurations) increases that conforms to data of the viscosity decrease reported by Nemilov [37]. Besides, according to the Poltavtsev's opinion, structural elements appear in the melt as lower-temperatures formations including 6-member rings of Se₆. At the further temperature increase, the contraction of atoms chains takes place, and this contributes to the viscosity decrease as well.

For the first time, Popescu (1978) [42] proposed the possibility to register variations of the equilibrium ratio "chains – rings" using measurements of the characteristic peaks at 4.75 Å of the radial distribution function calculated from the x-ray diffraction pattern. At the substrate temperature changes (from 30 °C to 70 °C), the glass was deposited to, and the maximum of this ratio was found at 50 °C. In this work "a special kind of ordering at not too large scale" was observed, that exceeded the limit of the short-range order. Popescu wrote that "for the explanation of the structure of a-Se ("amorphous Se") it is necessary to assume more order than the simple retaining of the bond distance and bond angle of the parent crystal". We think that Popescu actually for the first time proposed to fix the intermediate-range order in glass "extracting" it from crystalline substance. We followed this way as well (after Popescu), before we formulated our definition of the intermediate-range order (1995-1996) [19, 43-46] that was discussed above.

^{*} This is a typical example of the terminological confusion, described in the Introduction. Some researchers understand the notion "amorphous" as the state of red non-crystalline selenium precipitated from selenitic solutions as dispersive colloidal particles [21-24] or black selenium obtained from red selenium by heating at 310 K [24, 33]. Others, like in this case [32], give to vitreous selenium, obtained by cooling the melt, the name "amorphous". And, at last, in the work [34] concerning the investigation of the Raman-spectrum of "amorphous" selenium, nothing was said about either its color or the method of production. Readers were given possibilities to take decisions themselves about which form of condensed selenium the author dealt with.

Let us, however, come back to the experiment described above [35, 36]. The rings concentration of Se₈, changed approximately two times (from ~ 40 to 18-25%) at the temperature decrease in the first case from 490 K and in the second case from 700 K. This modification practically does not change the corresponding IR-spectra [47]. Moreover, the IR-spectrum almost did not changed after the extraction in CS₂ [48]. What can we say about the decrease of the Se₈ ring concentration according to these results?

The most important contribution to solve this problem was given in the papers of Keezer and Lucovsky [47, 49].

These papers have shown that:

1) α -monoclinic selenium dissolves in CS₂ very easily and the dissolution rate does not depend on illumination in the range of the band-gap and it is significantly higher than the absorption edge:

2) trigonal Se does not dissolve at all experimental conditions; and

3) a-selenium ("amorphous Se") can be dissolved but only under illumination with the photon energy > 2.3 eV (λ > 0.54 µm – the green and shorter radiation). Doesn't it follow that Se₈ rings, dissolving in CS₂, are formed in non-crystalline selenium only under illumination?

In the Lucovsky's work [49] molecular spectra of compact vitreous selenium were interpreted on the base of the chain structure that is characterized by the irregular sequence of statistically distributed *cis*- and *trans*-configurations formed by the third and forth Se atoms. The part of the chain is shown on Fig. 2.



Fig. 2. Regions with cis- and trans-configurations in the chain structure of vitreous selenium [49].

Taking into account above given data on solutions of different selenium forms as well as IR-[48] and Raman-spectra (the latter – Fig. 3 – practically coincide in works [34] and [50]) that were generalized by Popov [25] in Table 2, the suggestion on the chain structure, constructed of *cis*- and *trans*-configurations of atoms, seems to be quite convincing. Besides, the experimental radial distribution function of vitreous selenium coincides rather well with the curve calculated in accordance with this model [51].

A similar model, "the model of the disordered chain in Se", was proposed by Misawa and Suzuki [52, 53] based on data of the neutron scattering method. In this model, it is proposed to consider "amorphous selenium not as a mixture of "cycloocta-selenium" molecules and polymeric chains but as a model that "includes a molecule having both ring and chain conformations of Se in a single molecule". Bőhmer and Angell [54] consider this model as a reconciliation between old Brieglieb's experiments on selenium solutions with Lucovsky's objections against the Se₈ rings presence in a significant amount [49]. It must be noted that the model of Misawa and Suzuki includes structural units of three-coordinated Se as well, which are responsible for many interesting properties of "amorphous" selenium.



Fig. 3. Recorder curves of the Raman spectra of trigonal (top), α -monoclinic (bottom) and amorphous selenium (middle) at liquid temperature [34, 50].

In the Kolobov's work [55] on the structural investigation of "amorphous selenium" by the Extended X-Ray Absorption Fine Structure (EXAFS) method, data on the presence of three-coordinated states in the amount of ~ 20% are given that follows from measurements of the average coordination number of selenium that equals approximately to 2.2.

Let us consider one more peculiarity of the vitreous selenium structure. As long ago as fifties of the last century, Richter et al. [56, 57], based on papers on the X-ray distribution function, came to the conclusion that vitreous selenium is a mixture of 6-member ring molecules Se_6 and long chains of selenium atoms. This model was criticized by Lucovsky as unconvincing [58].

In seventies, several authors [59-61] carried out experiments and energy calculations of X-ray and UV-photoelectron spectra of trigonal and amorphous selenium that showed the possibility of the existence of Se_6 molecules in "amorphous selenium".

In 1989, Miyamoto [27] grew selenium crystal from the saturated solution of carbon sulfide that was identified with the help of the X-Ray analysis as a new allotropic rhombohedric modification of selenium. The crystallographic parameters of this phase are given in Table 1. The allotropic form consists of 6-member ring Se₆. The differential scanning calorimetry determined that the rhombohedric modification melted at 120 °C.

Miyamoto thinks that the probability of the formation of Se_6 rings at the rhombohedric crystals growth from CS_2 is very small. He thinks that these molecules came from dissolved vitreous selenium. Further, Miyamoto reminded that the model of Richter and Herre, proposed in 1958 [57], corresponded to the radial distribution function of vitreous selenium. Besides, the peak at 5.7 Å for all vitreous selenium types, registered by them, could be explained only with the help of their model – the model including 6-member rings in the vitreous-Se structure. Miyamoto proposed a new model of vitreous selenium consisting of three types of the atom arrangement: Se_8 ring, Se_6 rings and polymeric chains – the model in which the content of each component depends on the method of glass production.

Based partially on above information, in works [62, 63, 28] the conclusion was drawn that vitreous selenium is constructed of tangles of chains consisting of fragments of 8- and 6-member rings of monoclinic and rhombohedric PMs and fragments of chains of hexagonal selenium.

IR-absorption in the range of 50-300 cm ⁻¹								Raman-scattering				
Vitreous selenium	Position, cm ⁻¹	95	120	135	230	254	Drift, cm ⁻¹	110- 115	140	235	250- 256	
	Character	Peak	Shoulder	Peak	Shoulder	Peak	Character	Peak	Shoulder	Shoulder	Peak	
α- monoclinic	Position, cm ⁻¹	92- 97	120	-	-	254	Drift, cm ⁻¹	113	-	-	250	
selenium	Character	Doublet	Peak	-	-	Peak	Character	Peak	-	-	Peak	
Trigonal selenium	Position, cm ⁻¹	-	-	144	230	-	Drift, cm ⁻¹	-	143	237	-	
	Character	-	-	Peak	Peak	-	Character	-	Peak	Peak	-	

Table 2. The main vibration modes evidenced in IR-absorption and Raman-scattering of selenium [25].

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2.3 Non-crystalline ultra-dispersive forms of selenium

Popescu in his work of 1978 [42], following Andrievsky et al. [64] and Richter [65], divides non-crystalline selenium into two forms: a-Se-I and a-Se-II. He includes in the first group selenium, deposited on a substrate at low temperatures, in the second group selenium produced at high temperatures and bulk vitreous selenium. Analyzing previous information of selenium structures, obtained with the help of IR-spectroscopy, Raman-spectroscopy, DTA and others [64, 66, 67] as well as his own information obtained from the radial distribution (got from x-ray scattering) distribution, Popescu has come to the conclusion that the non-crystalline selenium structure consists of 8-member ring monomers and chain polymers. The main components of vitreous selenium are chains and in a-Se-I – rings. Judging from the context, Popescu takes a-Se-I as non-crystalline non-vitreous ("amorphous", ultra-dispersive from our viewpoint) selenium. We have already mentioned changes of the ratio "rings/chains", obtained by Popescu, depending on substrate temperatures in the range of 30...70 °C. Further, Popescu has mentioned that the transformation of a-Se-I into a-Se-II is possible at the annealing.

In works [21, 22], non-crystalline non-vitreous "amorphous selenium" is divided into red, brown and black selenium. Feltz wrote only about red (the density of 4.27 g/cm^3) and black selenium.

3. Structural and phase transformations at cooling of different forms of liquid selenium

Judging from the information of the paragraph 2.1, the high-temperature stable liquid selenium is constructed from polymorphoids of different PMs – trigonal, monoclinic and rhombohedric (to the lesser extent). Two modifications exist in liquid mainly as fragments of Se_8 and Se_6 rings and partially as ring structures themselves. Besides, there are three-coordinated selenium atoms in liquid.

Practically, all information on liquid has been obtained by the extrapolation of the glass structure. The IR- and Raman-spectra as well as diffractometer data in the vitreous state with corresponding data of different (but not all) crystalline PMs were compared. For example, we could not find data on IR- and Raman-spectra of rhombohedric selenium. After all, based on these data and corresponding responses in vitreous selenium, one can judge at least approximately about a fraction of the rhombohedric PM in non-crystalline forms of selenium.

Moreover, of course, there are no direct structural (spectroscopic and diffractometric) investigations of the liquid state itself. Information on the structure of liquid, obtained from data on glass, does not take into account the relaxation changes in glass transition processes.

Let us try to analyze these changes on the base of the concept of the polymericpolymorphoid structure of glass and glass-forming liquid.

The temperature range under the melting point of hexagonal PM is characterized by the stability of the high-temperature PM down to, apparently, very low temperatures. Moreover, in the same time this region can be divided into sub-regions with rather fuzzy borders where two other PMs – monoclinic and rhombohedric – demonstrate the metastability properties (at relatively low temperatures), and regions where they are unstable (at higher temperatures up to T_m of the hexagonal PM) and monotropically (irreversibly) transform into the single stable hexagonal modification.

These sub-regions are shown on Fig. 4, partially adopted from [46, 28] and enriched with the new information material. On the diagram of different forms of the condensed state, shown on Fig. 4, one can easily observe structural – without the phase border formation – transformations in liquid, super-cooled liquid, glass and ultra-dispersive forms (red, brown and black) as well as phase transformations "crystal \rightarrow liquid", "liquid \rightarrow crystal", "crystal \rightarrow crystal", "glass \rightarrow crystal", "ultra-dispersive state \rightarrow crystal". This diagram reflects the relation between relaxation processes taking place at temperature changes in crystalline, vitreous, ultra-dispersive and liquid states, super-cooled liquid included.



Fig. 4. Varieties of condensed states of Se (see description in the text).

According to the CPPSGGL of ICS and the more general concept of the polymeric nanoheteromorphous structure of glass and glass-forming liquid, containing any number of components [17, 28], at the cooling of any glass-forming liquid there is co-polymerization of fragments of substance with different structures, formed in the process of melting, which have no long-range order. Such <u>co-polymerization of different-structured on the nanolevel</u>, <u>nanoheteromorphous</u> <u>fragments is the fundamental source of glass-formation excluding a possibility of long-range</u> <u>organization</u>.

For glass-forming liquids of individual chemical substances, different-structured copolymerized fragments without LRO are polymorphoids of different PMs [68], formed as the result of the melting of the very high-temperature PM.

The gradual viscosity increase at the melt's cooling is just the consequence of the copolymerization process of different-structured polymorphoids. In the case liquids contain fragments with the same structures, the viscosity increases stepwise and crystalline solids are formed.

At the cooling temperature lower than the melting point $T_{m(h)}$ of the very high-temperature selenium PM – the hexagonal stable PM (SPM) – liquid, containing polymorphoids of different PMs, gets into the temperature region of stability of this PM (Fig. 4). This region is also the region of instability of metastable PMs (MPM) – monoclinic (from 217 °C to 70 °C [31]) and rhombohedric (from 217 °C to 105 °C [27]). Therefore, in addition to the process of co-polymerization of polymorphoids of different PMs, natural at the cooling of glass-forming liquid, the process of the decomposition of polymorphoids of monoclinic and rhombohedric PMs and their transformation into polymorphoids of the stable hexagonal PM takes place.

Thus, at the temperature decrease of super-cooled glass-forming liquid, the concentration of polymorphoids of the hexagonal PM increases continuously and concentrations of polymorphoids of monoclinic and rhombohedric PMs decrease continuously.

The decomposition of polymorphoids of these MPM, related to the chemical bonds rupture, is nothing else but the depolymerization process in substances. This process "feeds" super-cooled liquid with new portions decomposed, liquid, fragments of low-temperature PMs. It can be said that just this process is the main cause of the delayed transformation of glass-forming liquids in solids. Without this process, the polymerization of glass could be realized significantly faster.

Thus, the glass transition process in selenium is the indivisible processes of "copolymerization – depolymerization" – copolymerization of polymorphoids of hexagonal, monoclinic and rhombohedric PMs and depolymerization of the forming copolymer due to the decomposition of instable polymorphoids of two latter PMs [28, 46, 69].

Temperature intervals of stability and instability of structural fragments of metastable PMs of selenium approximately correspond to temperature intervals of stability and instability of low-temperature polymorphous modifications in the crystalline state (Fig. 4), the polymorphous transformation temperature of which is a "prototype" of the glass transition temperature [62]. Polymorphous transformations in crystalline states take place with the heat absorption at transformations from low-temperature PMs to the high-temperature PM and with the "calorification" at the reverse transformation [70]. The same processes take place at structural fragments transformations of different PMs in glass and liquids.

In the temperature interval $T_m...T_g$ polymorphoids of selenium metastable PMs are instable and, therefore, get decomposed and transformed into stable in this interval polymorphoids of the hexagonal PM. It is obvious that this process takes place, like in the crystalline substance, with the endothermic effect (heat absorption). But, during the annealing of glass-forming liquid the heat is actively taken from the substance, in the result of which, in accordance with the Le Chatelier principle (the temperature decrease causes the equilibrium drift in the direction that is accompanied by the heat absorption [71]), the decomposition processes of MPM polymorphoids and the formation process of SPM polymorphoids become slower and, at a certain temperature, are interrupted. The processes are interrupted because the heat removal rate, due to the temperature decrease, becomes equal to the heat absorption rate due to the endothermic effect at the polymorphoids transformation "MPM \rightarrow SPM", i.e the transformation of polymorphoids of monoclinic and rhombohedric PMs into the hexagonal PM. With the termination of the decomposition of MPM polymorphoids, the depolymerization process of the forming copolymer, the process of "feeding" of super-cooled liquid with decomposed – "liquid" – fragments of MPM polymorphoids is terminated as well. Super-cooled liquid transforms into glass. And the temperature, at which the process "copolymerization-depolymerization" is terminated in super-cooled liquid, is the glass transition temperature (at the melt cooling) T_g . The T_g is completely dependent on the heat removal rate from the cooled melt. The higher the cooling rate and the faster the heat removal, the sooner the transformation process of MPM polymorphoids into SPM polymorphoids is terminated, the higher the glass transition temperature T_g and the smaller the interval " $T_m...T_g$ ", the lesser the quenched substance loses formed at the melting of polymorphoids of monoclinic and rhombohedric selenium modifications and more glass properties will approach to properties of metastable PMs.

At the cooling rate of melt (V_{cool}) higher than the critical cooling rate (V_{cr}), which is equal to ~ 20 K.min⁻¹ for selenium, the copolymerization process of polymorphoids of different PMs prevails over the depolymerization process and liquid, increasing its viscosity, transforms into glass – the copolymer of structural fragments of different PMs – with lower glass transition temperature T_g .

By developing the glass transition temperature definition, proposed in [62], it can be said: the glass transition temperature at the cooling of melt (T_g) is the temperature of the termination of the copolymerization process of polymorphoids of SPM and MPM in monotropic substances (polymorphoids of HTPM and LTPM in enantiotropic substances).

Thus, in the process of cooling of glass-forming liquid, its structure is not got frozen [24, 30] but significantly changes before its fragments without long-range order (polymorphoids) are copolymerized into glass ($V_{cool} > V_{cr}$) or (after the transformation of all MPM polymorphoids into SPM polymorphoids is completed) into the high-temperature PM ($V_{cool} < V_{cr}$). In the case of selenium it will be the hexagonal PM.

It is obvious that the critical cooling rate of glassforming melt depends both on the copolymerization rate of stable and unstable polymorphoids in the $T_{m(h)}...T_g$ interval and the depolymerization rate of the substance, i.e. the decomposition rate of polymorphoids which is instable in this interval and their transformation into stable polymorphoids (SPM).

Because the glass-formation process is the "product of synthesis" of these two processes, the following conclusion can be made: the critical cooling rate necessary for the glass-formation process is inversely proportional to the difference of copolymerization and depolymerization rates:

$$V_{cr} = K \frac{1}{V_{copol} - V_{depol}},$$
(2)

where *K* is a coefficient of proportionality.

The greater $V_{copol} - V_{depol}$, the lesser V_{cr} . The lesser $V_{copol} - V_{depol}$, the greater V_{cr} . When the difference goes to zero, V_{cr} goes to the infinity and super-cooled liquid goes to the instantaneous crystallization. Copolymerization and depolymerization rates are apparently dependent only on the substance nature.

As to relaxation processes at the cooling of low-temperature selenium liquids – liquids, formed as the result of the melting of monoclinic PMs (α - at 144 °C [24] and β - (at 100 °C [24]) and the rhombohedric PM (at 105 °C [27], we could not find any information. It may be assumed that the high cooling rate can vitrify these liquids with the obtaining of glass samples whose properties are different from those of the glass samples, obtained by cooling of the melt of the hexagonal PM, because of the significant difference of the concentration ratios of different PMs' polymorphoids in such samples. Could it be a way to obtain new perspective forms of vitreous selenium?

At insufficient cooling rates, low-temperature liquids will pass, evidently, through the phase transformation "liquid \rightarrow crystal". The latter will be the stable crystal modification – hexagonal selenium.

4. Formation of super-cooled liquid at heating of vitreous selenium and its relaxation at temperature increase

Formation of super-cooled liquid from the vitreous state in glass-forming ICS is directly related to the glass transition temperature T_g . In its turn, T_g is genetically related to the polymorphous transformation temperature in the crystalline T_{tr} and located in the same temperature range, coinciding with T_{tr} or somewhat differing from it, depending on the melt cooling rate [62]. For example, for GeS₂ T_g and T_{tr} are equal to 495 °C and 497 °C, respectively [24], for As₂S₃ 175(180) °C and 175 °C [72], for P₄Se₄ – 180 °C and 192 °C [72], for P₂O₅ – 380 °C and 378 °C (the active stage of the transformation [73]).

And finally, for selenium $T_g \approx 37 \pm 10$ °C [54], for monoclinic MPM $T_{tr} \sim 70$ °C [31], and for rhombohedric MPM $T_{tr} = 105$ °C [27].

Investigations of viscosity-elasticity properties and stress relaxations in vitreous selenium, made by Bömer and Angell [54], have shown that, at the glass in the temperature range of 27-42 °C, the fraction of ring configuration quickly decreases, and the fraction of chain conformation quickly increases in the softening glass structure. Such change of the ratio "rings/chains" was identified by the authors as the phase transformation between ring and chain structures.

From the position of the concept of the polymeric-polymorphoid glass structure these facts are considered as a structural transformation of monoclinic MPM polymorphoids into stable hexagonal PM (SPM) polymorphoids in the vitreous selenium phase, as a latent pre-crystallization period, preceding the crystallization of the hexagonal SPM. The beginning of such crystallization in glass is registered at 50 $^{\circ}$ C [50] (Fig. 4).

It is seen from above data that the relaxation processes in vitreous selenium at its heating are similar to those in crystalline (the transformation of MPM polymorphoids into SPM polymorphoids – "MPM \rightarrow SPM") but they begin at lower temperatures. In our opinion, this is related to the fact that the internal energy of the disordered glass network is higher than that of the corresponding crystal as well as to the heterogeneity of the glass structure and the activation role of hexagonal SPM fragments located there.

Actually, atoms in monoclinic and rhombohedric crystalline PMs are located in regularly arranged rings, and glass consists of fragments of such rings, alternating in chains with hexagonal PM fragments [49]. For the structural transformation of metastable PM fragments into stable hexagonal PM fragments in glass, there is no need to disrupt chemical bonds in rings and reconstruct the ring structure into the chain structure. It is sufficient to "straighten" ring fragment into spiral chains that requires significantly lesser energy. Moreover, glass already contains a part of structural fragments as sections of hexagonal chains. And as the result, the transformations of monoclinic and rhombohedric PMs fragments into hexagonal PM fragments in glass begin on 30-70 °C earlier than in crystalline MPMs.

Thus, the glass formation temperature at heating (T_g^+) is nothing else but the temperature of the beginning of the active stage of the transformation of low-temperature PM polymorphoids into high-temperature PM polymorphoids, accompanied by the decomposition of the formers, i.e. by the rupture of chemical bonds in glass, its depolymerization, its viscosity decrease and the high-temperature PM polymorphoids formation.

In the case of selenium, it is the decomposition of monoclinic and rhombohedric PMs polymorphoids and their transformation into the hexagonal PM polymorphoids.

The given definition of T_g^+ is a development of the notion of the softening temperature proposed in [62].

At the heating of super-cooled liquid in the interval of $T_g...T_m$, it can crystallize (it can be seen on the Se example (Fig. 4) as the hexagonal PM at ≥ 50 °C as a result of the termination of the transformation process of monoclinic and rhombohedric PMs polymorphoids into this PM. Apparently, there is such a critical heating rate of super-cooled liquid at which this process has no time to terminate and super-cooled liquid, by-passing the stage of crystallization, becomes an usual equilibrium liquid with higher T_m .

5. Structural transformations in selenium at annealing below T_g

How does glass-forming substance behave, selenium in particular, characterized by the monotropic polymorphous transformation in the crystalline state, at the exposition at a constant temperature (the annealing) below T_g ? So far, we considered that below T_g in a monotropic glass-forming substance the transformation process of the low-temperature metastable PM polymorphoids into polymorphoids of the PM, stable in the whole interval of the solid existence, continues, i.e. monoclinic and rhombohedric PMs polymorphoids transform into hexagonal PM polymorphoids in this case as well. But this process, due to low temperatures, goes on very slowly, and at the normal temperature it can continue for years (the glass ageing process [74]).

This thesis results from the definition of a monotropic substance (experiencing the irreversible transformation [21, 23]).

But now, the work of Stephens [75] has come to the field of our vision. In this work, the change of the heat capacity, C_p , in the glass transition temperature range at the heating of the vitreous selenium sample (T_g^+) depending on the annealing time at 300.4 K (the heating rate was the same: 20 K/min) was measured by the differential scanning calorimetry method (DSC). In all cases, the heat capacity increased as a result of passing over T_g^+ (Fig. 5 [75]), the heating was accompanied by the endothermic effect. This fact is well known for all glasses actually. However, what is the cause of the endothermic effect? Moreover, why did the heat capacity increase is more than two times higher for the sample, tempered during 2450 min, comparing with the sample, annealed during 5 min? The author [75] did not answer these questions. The Feltz's monograph [24], where this experiment was described, did not answer this questions as well.



Fig. 5. Heat capacity versus temperature for Se in the region of its glass transition after annealing for various times at 300.4 K (27.2 °C) [75].

The concept of the polymeric-polymorphoid glass structure answers both questions. As it was said above, the transformation of the crystalline low-temperature PM into the high-temperature PM is always accompanied by the endothermic effect [70]. Glass is a copolymer of polymorphoids of both PMs. At the heating of glass, the structural transformation of low-temperature PM polymorphoids into high-temperature PM polymorphoids at T_g^+ begins, that is naturally accompanied by the endothermic effect.

The answer to the second question about the thermal capacity increase at the time increase lower T_g happens to be rather sudden on the face of it. In the annealing process, vitreous selenium behaves as a enantiotropic substance and not as a monotropic substance. The longer the annealing time, the greater number of polymorphoids of the hexagonal PM, stable in the crystalline state, transforms in polymorphoids of a low-temperature metastable PM, apparently monoclinic. And all the higher the endothermic effect at the heating of vitreous selenium, enriched with fragments of this MPM which transforms higher T_g into the stable hexagonal PM with the heat absorption.

The enantiotropic behavior of vitreous selenium below Tg is also confirmed by the Gobrecht's experiment [76], carried out as long ago as sixties of the last century. Only the exothermal effect of crystallization at ≈ 100 °C and the endothermic effect of the melting (Fig. 6) are revealed on the thermogram of freshly-prepared fast-quenched melted selenium, i.e. the endothermic effect, characterizing the glass transition temperature, is absent. And only after the annealing during several days at the temperature of 24 °C, a peak appeared that increased with the annealing time increase (like in the Stephens's experiment [75]!) and was described by the author as an endothermic transition. This peak appeared due to the slow formation of the state that (according to the author) decomposed at the glass transition temperature Tg between 35 and 45 °C. The author did not explain which state is formed during the annealing and why it decomposed at 35...45 °C with the heat absorption, registered as the endothermic peak Tg. The concept of the polymeric-polymorphoid structure of glass gives a clear answer to these questions. Below Tg (like in the Stephens's experiment [75]) the structural transformation takes place: polymorphoids of the hexagonal PM transforms into polymorphoids of the monoclinic (and, possibly, the rhombohedral) PM, and they, accumulating with the annealing time increase in the greater amounts, give the increasing endothermic effect of the transformation of metastable PMs into the high-temperature stable PM registered as T_g.

This effect becomes even greater apparently due to the fact that vitreous selenium at the illumination with the light of the > 2.3 eV energy [49], corresponding to $\lambda < 0.54 \,\mu$ m, i.e. the visible spectrum, forms the 8-member rings that is evidenced by its appearing ability to be solved in CS₂. It is natural to assume that more heat is absorbed at the transformation of Se₈ rings into hexagonal chains in the T_g region [54] than at the transformation of chain *cis*-fragments into also chain-like *trans*-fragments. In the latter case, there is no necessity to break chemical bonds connecting atoms in the ring.

As the result of the analysis of these facts, we must make corrections in our Figure, published earlier in [28] and given here as Fig. 4. The work [28] has shown that the transformation "polymorphoids MSPM \rightarrow polymorphoids SPM" takes place both in the super-cooled liquid and glass. The given facts shows that this correspond to reality only in the temperature region of the super-cooled liquid. Below T_g – in glass – the reverse transition takes place that is shown in the new version of the figure.

It is interesting that the absence of T_g on DSC curves immediately after the tempering of glass-forming liquid is observed not only in selenium but in vitreous H₂O as well [76]. However, the endothermic effect appears at 136 ± 1 K after the annealing of the sample at 130 K during 1 hour and the second scanning. And in this work also, the author did not explain neither the causes of the T_g appearance after the annealing. It is understandable. In the time of publication of experiments with glass-forming selenium and water, there was no a concept of structures of glass and glass-forming liquid that was able to explain the physical-chemical essence of such "strange" behavior of vitreous water and selenium. And only the conception of polymeric-polymorphoid structure of glass and glass-forming liquid can give the clear explanation for the effect revealed.

So, monotropic selenium in the vitreous state behaves as a substance with the enantiotropic transformation in the process of the cooling and the annealing below T_g .

In principle, this fact is predicted by the thermodynamics of polymorphous transformations. For example, in the work [78, p. 64] it is said: "As the most important practical consequence from the thermodynamics of polymorphous transformations, it should be pointed out to the possibility of transformations of enantiotropic polymorphous systems into monotropic polymorphous systems, and vice versa, under different impacts". In this case, such factor is the substance being in the vitreous state (in contrast to the crystalline state).

The analysis of the experiment on the vitreous selenium annealing (Fig. 5 [75]) allows to make the conclusion that the similar thermal capacity increase at T_g^+ will also take place as the result of the quenching rate increase of melted selenium. As we showed before, the higher the quenching rate, the lesser MPM polymorphoids have time to transform into SPM polymorphoids in the interval $T_m...T_g^-$ and the more MPM fragments are formed at the cooling below T_g . As the result, the MPM polymorphoids concentration in quickly quenched glass will be higher than that in glass, quenched with the lesser rate, which, in its turn, will be enriched with stable hexagonal PM polymorphoids.



Fig. 6. Differential enthalpy analysis of vitreous selenium [76].

It follows that, at the heating of glass, the thermal capacity of fast-quenched glass in the range of the glassformation temperature T_g will be higher than that of glass, cooled with the lesser rate, i.e. the thermal capacity higher T_g increases not only with the annealing time lower T_g but also with the melt cooling rate increase. This regards not only to selenium but to enantiotropic substances as well.

In connection with the above, the equality of thermal capacities of fast- and slow-quenched glasses, showed in Feltz's monograph (Fig. 7 [24, p. 62]), is rather surprising. In our opinion, the thermal capacity peak of fast-quenched glass in the T_g region must be significantly higher than that of slow-quenched glass – see the peak depicted by us as a dash-line.

Further, judging from the upper part of the Feltz' Figure, the thermal capacity of fastquenched glass is greater than that of slow-quenched glass. This fact puts some thought into mind. In fast-quenched glass the polymorphoid ratio HTPM:LTPM is lesser than that of slow-quenched glass. And, as it was indicated before, the HTPM thermal content is higher than that of LTPM [70]. According to this logic, fast-quenched glass must have lesser thermal capacity because it contains lesser HTPM polymorphoids with higher thermal capacity. Feltz showed the reverse picture. What is it related to? May be, it is related to that the glass heat capacity (which, of course, is greater than that of the crystal) increases with the increase of degree of nanoheteromorphism– the differentstructuring on the nanometric level in glass? Related to dimensions of separate fragments of the copolymerized structure (they are obviously smaller at the fast-quenching)? Related to the vicinity of the concentration ratio "HTPM:LTPM" to 1?



Fig. 7. The temperature dependence of the entalphy H and the thermal capacity C_p at direct and reverse transitions "melt – vitreous state" $q_B > q_A$ (q – cooling and heating rates); T_g – the glasstransition temperature; T_2 – the freezing temperature [24].

Which viewpoint is true here? To answer this question, additional experiments are necessary on determinations of quantitative ratios of polymorphoids in glass, quenched with different rates and/or annealed below and higher T_g) and on measurements of the thermal capacity of corresponding samples.

Seemingly, in future the concentration ratio of polymorphoids in glass can be evaluated not only from data of X-ray and neutron diffractometry and Raman-spectroscopy (by band intensity ratios of different PMs) but also from data on thermal capacities in glass formation regions (at the heating of glass) comparing with the data of heat capacities of the polymorphous transformation HTPM \rightarrow LTPM in crystals.

6. Structural and phase transformations of ultra-dispersive ("amorphous") selenium

Unfortunately, there are no systematic investigations of structural and phase transformations yet both in the range of the ultra-dispersive phase and outside its boundaries, at the crystallization of ultra-dispersive selenium.

As it was mentioned before, there are data on red, brown and black ultra-dispersive Se obtained from selenite solutions as colloid particles of the different grades of dispersion [21, 23]. It is

interesting that red monoclinic modifications of crystalline Se, consisting of 8-member rings, are obtained from CS_2 solutions. Red amorphous selenium dissolves in CS_2 also well, from what in some works, summarized in [79], the conclusion has been made that it also consists mainly of 8-member rings. The same color of these selenium different forms is not apparently casual.

According to data [32, 80, 81], IR-spectra of red "amorphous" selenium and red α monoclinic selenium are very similar. Spectra of monoclinic selenium and black "amorphous" selenium are somewhat more different, and more different is the vitreous selenium spectrum (Fig. 8 [32, 80, 81]) where the band at 135 cm⁻¹ and the shoulder at 230 cm⁻¹ are close to bands of trigonal Se [32]. At the same time, the Raman-spectrum of vitreous Se (bands at 110-115, 140, 235, 250-256 cm⁻¹) is actually a superposition of spectra of monoclinic (bands at 113 cm⁻¹ and 250 cm⁻¹) and trigonal (bands at 143 cm⁻¹ and 237 cm⁻¹) selenium (Fig. 3 [34], Table 2 [25]).

Data on enthalpies of transformations are given in [82-84]:

12.56 ±1.67 kJ/mole						
red amorphous seleni	um \rightarrow	trigonal selenium				
5	5.024±1.67 k.	J/mole				
vitreous selenium	\rightarrow	trigonal selenium				

Both transformations can be considered as phase transformations "non-crystalline substance \rightarrow crystal" with corresponding "calorification" of the crystallization heat.



Fig. 8. a) IR spectra of red and black amorphous Se [80, 81]; b) IR spectra of Se-glass and α -monoclinic Se [32].

The same authors [82-84] reported data according to that, at slow heating of red amorphous selenium, its transformation into powder-like black selenium takes place with the endothermic effect of 0.42 kJ/mole. This transformation begins at 37 $^{\circ}$ C.

As we have already mentioned, according to Popescu [42], a-Se-I, deposited on a cold substrate and different from vitreous a-Se-II in lesser amount of chain formations and in more amount of ring formations, can be transformed into a-Se-II at annealing, i.e. ultra-dispersive ("amorphous") selenium transforms into vitreous selenium at heating.

One should not forget that red monocrystalline monoclinic selenium, containing 8-member rings, transform irreversible into grey trigonal chain selenium at 70 $^{\circ}$ C [31].

Thus, all non-crystalline forms of solid selenium can be lined up in one hypothetic line in which they are connected by sequential transformations under the temperature:

-	- 0.42 kJ/mole			5.024 kJ/mole				
red a-Se	\rightarrow	black a-Se	\rightarrow	vitreous g-Se	\rightarrow	trigonal crystalline Se		

The obtaining of missing data on the transformation of black a-Se into vitreous selenium and also on the heat absorption by vitreous selenium before the moment of its crystallization (with the calorification) can allow to qualitatively evaluate limits of concentration rates of polymorphoids of low-temperature and hexagonal PMs in each form of solid non-crystalline selenium. The additional condition of such evaluation is the obtaining of data on ratios of ring's fragments and closed rings in non-crystalline forms of selenium.

Let us consider two more experimental facts related to red ultra-dispersive selenium and its transformations.

The work [23, p. 8] has shown that the red "amorphous" form transforms into the red monoclinic PM form at the temperature somewhat lower 70 °C, and into the grey hexagonal PM form at higher temperatures. We can see that selenium loses the monotropic properties and becomes enantiotropic not only in the vitreous state but in the ultra-dispersive "amorphous" state as well. It is interesting that in this case the transformation temperature into the crystalline hexagonal PM coincides with the temperature of the beginning of recrystallization of the monocrystalline monoclinic PM into the hexagonal PM (70 °C [31]). Isn't it the evidence that red ultra-dispersive selenium has very high concentration of Se₈ rings, which rupture requires higher temperature than for the *cis* \rightarrow *trans* transformation in glass (27-42 °C [54])?

Works [85,86] describe the experiment on the endothermic crystallization of "red amorphous selenium" into the monoclinic metastable phase in the Calve calorimeter at 312 K (\approx 39 °C) during 42 min. The crystallization of approximately 30% of selenium was accompanied by the thermal absorption of 0.35 kJ/mole, from which the author made the conclusion that the complete crystallization would require 1 kJ/mole (??). The author emphasized that the endothermic effect of crystallization was registered in the direct experiment where there was no necessity to carry out any thermo-chemical calculations. The results of the experiment are shown on Fig. 9.



Fig. 9. Crystallization of red amorphous selenium; 1 – x-ray diffraction pattern of the original amorphous selenium; 2 – x-ray diffraction pattern of selenium after heat treatment at 312 K for 42 min; 3 – endothermic peak of crystallization of amorphous selenium (calorimetric date) [85, 86].

We have already described a similar experiment, carried out in works [83, 84] and then repeated in works [87, 88]. "Red amorphous selenium" transformed into the black powder at the slow heating. The endothermic effect was observed at that. The transformation temperature from different authors did not exceed limits of 30-53 °C. Selenium T_g is in this limit, that is the beginning of the "rings-chains" transformation in the Bemer's and Angel's experiment [54], described above.

According to the polymeric-polymorphoid concept of glass-formation, T_g is the beginning of the active stage of the transformation of low-temperature PM polymorphoids into high-temperature PM polymorphoids. This thesis is confirmed by examples of such glass-forming substances as SiO₂, GeO₂, AsSe, BeF₂ and some others [62]. This transformation takes place with the endothermic effect for all of them.

From the other side, no cases are known at which the crystallization process of a noncrystalline substance was accompanied by the endothermic effect.

What is happening with the sample of "red amorphous selenium" in this case?

The temperature of 39 °C, at which "red amorphous selenium" is heated, is in the equilibrium range of ring-like and chain-like, *cis*- and *trans*-fragments of the selenium structure. The exposure at this temperature promotes the association and the consequent crystallization of red monoclinic selenium modifications, and simultaneously, the transformation of ring fragments into chain ones that leads to the transformation of "red amorphous selenium" into black one with the endothermic effect as shown in works [83, 84]. Examples of the simultaneous formation of two different modifications of substances are well known. For example, quartz and cristobalite crystallize simultaneously from tridymite (SiO₂) at its electrolysis in the work of Flörke [89]. In the described experiment, red amorphous selenium transforms into the red monoclinic crystalline phase which amounts 30% of initial "red amorphous selenium". In the rest 70% of the powder, the process of the transformation of monoclinic selenium polymorphoids into trigonal selenium polymorphoids takes apparently place, i.e. "red amorphous selenium", at least partially, transforms into black selenium and, possibly, into vitreous selenium. This process is followed by the endothermic effect that compensates with excess the exothermal effect of the crystallization of 30% red monoclinic selenium. In our opinion, this experiment must be repeated with the description that is more thorough in conditions and characteristics of phases obtained.

The given information on ultra-dispersive selenium forms develops into an unified picture shown in the right part of Fig. 4.

At the fast heating, red selenium "gets through" stages of the transformation into black selenium and consequent glass-formation, and crystallizes higher 70 °C. At the slow heating, red selenium transforms into black one, passing through the stage of the formation of brown selenium with consequent or simultaneous glass-formation, and then glass crystallizes at \geq 50 °C as the hexagonal PM.

At the annealing below 37 $^{\circ}$ C, red ultra-dispersive selenium can crystallize as red monoclinic selenium. At the annealing higher 77 $^{\circ}$ C, it can crystallize as hexagonal selenium passing the stages of the transformation into black and, possibly, into vitreous selenium.

At the fast heating, black selenium crystallizes in the region of 70 °C. At slow heating, it transforms into glass and crystallizes at \geq 50 °C.

7. Conclusion

To avoid a terminological confusion "amorphous – vitreous", in this work, like in works [7, 8], the division of solid non-crystalline substances into two classes is accepted: vitreous and ultradispersive (powder-like and film-like non-vitreous). All non-crystalline non-vitreous forms of solid selenium – red, brown, black "amorphous" selenium relates to the second class.

The consideration of structural (in limits of one phase) and phase transformations in condensed selenium is carried out on the base of the concept of the polymeric-polymorphoid structure of glass and glass-forming liquid [8, 18, 19, 28].

According to this concept, all forms of non-crystalline selenium are constructed of copolymerized in the greater (glass) or lesser extent (liquid, ultra-dispersive forms) structural

fragments of crystal lattices of trigonal, monoclinic and – in some cases – rhombohedric modifications without a long range order (polymorphoids). Polymorphoids of different PMs form chain structures consisting of *trans*-configurations of chain fragments of the hexagonal PM and *cis*-configurations of fragments of eight- and six-member rings. Some chains form "stars", in which centers three-coordinated selenium atoms are located. Besides, non-crystalline selenium contains, in the greater (ultra-dispersive forms) or lesser (glass) extent, separate eight-member and (in some cases) six-member ring selenium molecules.

Under external factors, temperature in particular, the inter-transformation takes place of different PM polymorphoids and changes of their concentration ratios that is the fundamental characteristic of the condensed state of substances, in this case – selenium.

Non-equilibrium non crystalline individual chemical substances, selenium included, "memorize" all inherited crystalline modifications and, getting into conditions of the stable existence of one of these PMs, relax (fast or slowly) in the direction of formation of this modification which is the equilibrium phase in these conditions.

The glass-formation process is an indivisible (two in one) process "copolymerization – depolymerization": copolymerization of high-temperature and low-temperature PMs polymorphoids (for selenium – hexagonal, monoclinic and rhombohedric PMs) and depolymerization of the forming polymer due to the decomposition of low-temperature PMs polymorphoids which are unstable in the glass transition range (for selenium – monoclinic and rhombohedric PMs).

The glass transition temperature at the cooling of melt (T_g) is the temperature of the termination of the copolymerization process of high-temperature PM polymorphoids (for selenium – hexagonal PM) and low-temperature PMs polymorphoids (for selenium – monoclinic and rhombohedric PMs).

The glass-formation temperature at the heating of glass (T_g^+) is the temperature of the beginning of the active stage of the decomposition and the transformation of low-temperature PMs polymorphoids (for selenium – monoclinic and rhombohedric PMs) into high-temperature PM polymorphoids (for selenium – hexagonal PM), accompanied by the rupture of many chemical bonds in glass, its depolymerization, the viscosity decrease and the formation of high-temperature PM polymorphoids (for selenium – hexagonal PM).

The nature of thermal effects in non-crystalline substances is directly related to the nature of thermal effects at polymorphous transformations of crystalline polymorphous modifications. Thus, at the transformation of low-temperature PMs into the high-temperature PM (for example, monoclinic or rhombohedric selenium PM into hexagonal PM), the heat is always absorbed. From this, the endothermic effect is generated at the heating of glass in the T_g^+ region or at the transformation of ultra-dispersive red selenium into black one.

Monotropic selenium in the crystalline state, which is characterized by the irreversible transformation of low-temperature PMs (monoclinic and rhombohedric) into the high-temperature PM, demonstrates enantiotropic properties in the non-crystalline state. Below the glass transition temperature, hexagonal PM polymorphoids transform into polymorphoids of, for example, monoclinic PM. This property allows, at the annealing below T_g (37±10 °C), to "accumulate" low-temperature PMs polymorphoids. The consequent heating take place with significantly greater endothermic effect increasing, for example, the thermal capacity in the glass-formation region or allowing to detect T_g in samples where it was absent before the annealing.

The "accumulation" of additional monoclinic PM polymorphoids in non-crystalline red selenium leads to its crystallization.

A non-crystalline individual chemical substance is the continuum - the continuous connected set – of atomic structures characterized by the concentration ratio (changing under external factors and time) of co-polymerized (to the larger extent – glass, to the lesser extent – ultra-dispersive films and powders) polymorphoids – fragments of crystal lattices of different polymorphous modifications of the given substance without the translation symmetry (the long-range order).

The authors expect that among readers of this paper a researcher may be found who will repeat and update all experiments, described here, in conditions of the strict repeatability of results and using samples obtained from the same sort of the investigated substance. He (or she) will also define more exactly the general picture of structural and phase transformations in condensed selenium shown in this paper.

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