

## GLASSY MATERIALS CLARIFIED THROUGH THE EYES OF HYPERVALENT BONDING CONFIGURATIONS

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A characteristic ability of chemical bond in glass-forming substances to form both “normal” and hypervalent configurations (HVC) is considered as the origin of glass specificity and glass formation itself. The development of this idea is observed from early 1980’s to the present-day investigations, namely, from the notions about three-centre bonds coexisting with “normal” two-centre covalent bonds in continuous random network, through specification of the nature and parameters of HVC in particular glasses by means of quantum-chemical modeling and, finally, to the understanding of the collective behavior of HVC in terms of self-organization. Experimental features of glasses, whose explanation are still unclear up to now (e.g., high melt viscosity, low-temperature anomalies, optically-induced anisotropy, etc.), were used for both initiating and development of this approach. As a result, a new way of understanding and managing of the properties of glassy materials is formulated.

(Received November 15, 2000; accepted January 29, 2001)

*Keywords:* Glass, Hypervalent bonding configuration, Quasimolecular defect

### 1. Introduction

Glasses are non-crystalline solids which are obtained by cooling a melt at a rather slow rates of about 10 K/s and lower, a condition that permits to obtain a bulk material of a considerable thickness, from few millimeters to tens of centimeters. Although this definition looks too “technological”, it permits to separate glasses as a specific group of materials and to formulate two fundamental questions concerning the specificity. Really, there seems to be no a sharp gap among a wide range of non-crystalline materials, from amorphous silicon to glassy SiO<sub>2</sub> or As<sub>2</sub>S<sub>3</sub>. Note, however, that one can prepare the latter two substances in the form of both film and glass (e.g., a-SiO<sub>2</sub> and g-SiO<sub>2</sub>), but one can obtain only a-Si or a-Si:H, and not bulk g-Si or g-Si:H. A common explanation of this fact is that glass-forming melts are very *viscous* and thus show a tendency to supercooling, when the melt structure is “frozen” as solid. But a natural question is *why* these melts are so viscous?

The second question is *why* bulk glass *exists* at all? If one consider amorphous solid as a continuous random network (CRN, the well known term after Zachariasen-Warren [1,2]) consisting of ordinary covalent bonds (e.g. Si-Si for a-Si and Si-O for g-SiO<sub>2</sub>) there is no an essential difference between, say, Si and SiO<sub>2</sub>, although only the latter can form bulk glass. A vulgar explanation is that the ≡Si-Si≡ bonding configuration is more “rigid”, and, therefore, less stable in the form of three-dimensional (3D) CRN, as compared with the ≡Si-O-Si≡ configuration that has the -O- bridge as a flexible element. Nevertheless, even in the latter case covalent bond remains a rigid formation, whose parameters cannot be altered significantly, so that an ideal 3D CRN realizes hardly in SiO<sub>2</sub> [3]. In order eliminate the down internal stress arising due to distorted covalent bonds, CRN is supposed to be interrupted periodically by means of bond breaking, either in the form of single *dangling bonds* (DB) or, what is more effective, by forming the “cuts” that contain certain “soft” bonds in order to connect adjacent CRN pieces (one of the earliest models of this sort was proposed by Robertson [4]). Thus, for

construction of a mechanically stable non-crystalline network one needs some alternative bonding states. This general demand was formulated by Ovshinsky [5] in terms of “bond option” as a necessary condition for amorphization. The question is what is the nature of “bond option” that ensure stability of bulk non-crystalline structure, i.e. formation of glass?

The two problems can be resolved simultaneously on the basis of hypervalent configurations (HVC) representing specific bonding states that (i) provide quasi-polymerization of a melt, so ensuring its high viscosity, and (ii) throw out internal stress due to intrinsic softness and flexibility, so providing the existence of a mechanically stable solid. The concept of HVC, as the origin of glass formation and the microscopic basis for explanation of various properties of glass, was introduced by Dembovsky 20 years ago [6] and continues to develop successfully up to now (e.g., [7]). This concept in its development is presented here.

The paper is organized as follows. Section 2 considers the period of 1980-1990’s, when the three-centre bond (TCB) model was used as a reckon model for HVC. This model allowed us to explain not only the phenomenon of glass formation but also all general features of glasses such as a mysterious tendency for increase of the first coordination number in glass and/or in glass-forming melt as compared with crystalline counterpart, low-temperature anomalies and low-frequency (“boson”) peak in Raman scattering, magnetic effects, etc. Since the study was carried out on qualitative or semi-quantitative level, this period was denoted as “qualitative” one. The existence of TCB in glasses, however, needs special arguments, and the following “quantitative” period was devoted to quantum-chemical calculations of alternative bonding configurations in glasses (Section 3). During this study a wide variety of bonding configurations including low-energy HVC were found, TCB being only a particular case of them. In Section 4 we discuss the collective behavior of HVC that cannot be ignored when considering most of glass properties, the glass transition phenomena and medium-range order first of all. In this section the notions about symmetry, of information, self-organization are applied to the glass problems.

## 2. Qualitative period

### 2.1. Defects in glasses

Considering CRN as an ideal glass structure one should conclude that each HVC represents a *defect* in such a network consisting of ordinary covalent bonds, which are the same as for the crystalline lattice of the substance under consideration. It is tempting, therefore, to draw parallels between defects in glasses and crystals, but the similarity occurs to be less than the difference, as it was shown fairly by Popescu and Bradaczek [8]. This is the reason that, contrarily to defects in crystal, there is no a generally accepted definition of “defect” in glass, and our specification given in Table 1 is only once more attempt to notify the term.

Our classification is based on the fact that the main crystal feature, translational long-range order (LRO) is absent in glass, in which only short-range order (SRO) persists unambiguously. Because SRO, at least in the covalent-bonded glasses under consideration, is determined by the bond geometry, then one can distinguish *chemical bond defects* in glasses as an alternative for *structural defects* in crystal, as it is shown in Table 1. (Of course, this classification is rather conditional since change in bonding leads to a local change in geometry, i.e. in local structure on the scale of SRO).

Deviation from ordinary bond can be made in three ways, two of which are well known in glass science as *wrong bonds* (e.g. As-As or S-S instead of ordinary As-S bond in  $As_2S_3$ ) or *VAP* (valence alternation pairs) after Kastner, Adler and Fritsche [9]. The both deviations, however, deals with one and the same type of bond, common two-centre two-electron covalent bond. The third possibility, formation of chemical bond of a quite different character, was not studied seriously, although the notions about certain “soft” and/or “weak” bonds, as well as about “intercluster” or “intermolecular” bonding of unknown nature, arise permanently in the literature. Below we shall treat the third possibility in the form of hypervalent configurations (HVC) of a definite nature.

Table 1. Comparison of defects in crystal and glass.

Crystal	Glass
1. IDEAL STRUCTURE	
Ideal lattice with perfect long-range order (LRO)	Continuous random network (CRN) with perfect short-range order (SRO)
2. PRINCIPAL DEFECTS	
Structural ones: 0D (vacancies, interstitials) 1D (dislocations) 2D (grain boundaries) 3D (voids)	Chemical bonding ones: Another neighbour («wrong bond») Another coordination (VAP) Another type of bonding (HVC, etc.)
3. PRINCIPAL FEATURES	
Thermo-mechanical stability up to $T_m$ , the melting point Low-viscosity melts Inability for supercooling (not more than few degrees below $T_m$ ) A wide range of properties that are well understood by means of structural defects	Softening at $T_g \approx (2/3)T_m$ , $T_g$ is the glass transition temperature High-viscosity melts Wide glass-transition region $T_g - T_m$ (tens/hundreds degrees) A number of «anomalies», such as low-temperature anomalies, low-frequency «boson» peak, medium-range order, etc., that are poorly understood up to now

## 2.2. Hypervalency and quasimolecular defects

As far as 20 years ago Dembovsky [6] emphasized a strange structural peculiarity observed in chalcogenide glasses and glass-forming melts, namely, the fact that the first coordination number,  $Z_1$ , for them can be *higher* than that in crystalline counterparts (see examples in Table 2). In fact, the existing model of glass structure implies  $Z_1(\text{glass}) \leq Z_1(\text{cryst})$ , the equality corresponding to ideal CRN, and the decrease to CRN containing defects of the most probable dangling bond type. Even if one consider the VAP-type defects after [9], i.e.  $C_3^+C_1^-$  (C denotes chalcogen atom, upper index is the charge, bottom index is coordination or the number of covalent bonds per atom), one obtains the equality since such combination of over-coordinated and under-coordinated atoms gives  $\langle Z_1(\text{VAP}) \rangle = 2$  as for chalcogen atom in crystal.

Table 2. Documented cases for an increased first coordination number ( $Z_1$ ) in glassy semiconductors in the glassy (*g*), liquid (*l*), and amorphous film (*a*) state as compared with crystal (*c*). The method is X-ray excepting ref. [13] using EXAFS

Substance ( $T_m$ )	State	Temperature, K	$Z_1$	Ref.	
S (391K)	<i>c</i>		2.0	[10]	
	<i>l</i>	373	2.4		
		403	2.4		
		443	2.45		
		473	2.4		
		523	2.6		
Se (494K)	<i>c</i>		2.0	[11]	
	<i>g</i>		2.1		
		<i>l</i>	503		2.7
			573		2.9
		703	2.5		
	<i>a</i>	room	2.2		[12]
30		2.15	[13]		
As <sub>2</sub> S <sub>3</sub> (600K)	<i>c</i>		<2.4>	[14]	
	<i>g</i>		<2.9>		
	<i>l</i>	693	<2.6>		
As <sub>2</sub> Se <sub>3</sub> (670K)	<i>c</i>		<2.4>	[14]	
	<i>g</i>		<2.8>		
	<i>l</i>	723	<2.8>		

Using this peculiarity, Dembovsky succeeded in 1981 [6] in connecting together two unrelated, at the first glance, ideas of that time, namely, the electronic  $\Psi$ -criterion for glass formation [15] and the model of quasimolecular defects (QMD) [16]. The Dembovsky's criterion [15] establishes an optimum-high concentration of lone-pair electrons (LP) relatively to all the valence shell electrons,  $\Psi=0.5-0.66$ , as an intrinsic property of glass formers. The Popov's QMD model [16] postulates a special defects, which are based on three-centre bonds (TCB) that was suggested previously for understanding of chemical bonding in polyhalide and halide-rare gas molecules. Because TCB in glass is not a free molecule, being built up into covalent network, Popov [16] called this defect "quasimolecular"; QMD were used there as an alternative to VAP for understanding the electro-optical properties of glassy semiconductors. A point connecting both ideas is the fact that QMD is formed from ordinary covalent bond by means of LP-electrons, as it is illustrated in Fig. 1. Thus, the electronic  $\Psi$ -criterion is connected probably with TCB concentration, which is too small (if TCB exist at all) when a relatively low LP concentration  $\Psi < 0.5$  takes place, and too large when  $\Psi > 0.66$ ; in the latter case TCB represent the main bonding state (this is just the case of molecules  $I_3^-$ ,  $XeF_2$ , etc.) and not a defect.

One can see that TCB shown in Fig. 1 contains 2 super-coordinated atoms ( $C_3$  instead of normal  $C_2$ ), a fact that can be compared with the increased  $Z_l$  values in Table 2. Strictly speaking, super-coordination and hypervalency are not equivalent terms. Hypervalency is considered usually as the presence of more than 8 electrons in the valence shell; it is a well-known phenomena for the molecules containing the IV-VI group elements [18]. Note that free atom of oxygen or chalcogen (S, Se, Te) contains 6 electrons: four p-electrons (which form the valence band in the condensed state of chalcogenide glassy semiconductors [19]) and two low-laying s-electrons, which are usually not shown, as it is done in Fig. 1. Then, only the middle atom in TCB shown in Fig. 1 is a hypervalent one (4 electrons of TCB, 2 electrons from  $\sigma$ -bond, 2 p-electrons as LP, and 2 s-electrons as LP give 10 electrons in sum) while the left  $C_3$  atom is not hypervalent, being only super-coordinated. On the other hand, QMD/TCB in Fig. 1 can be considered as a definite hypervalent configuration (HVC) that contains two three-fold coordinated atoms. Note, that VAP is not HVC, since  $C_3^+$  corresponds to 8 electrons in the valence shall, and not a super-coordinated defect since the averaged coordination number for VAP is 2.

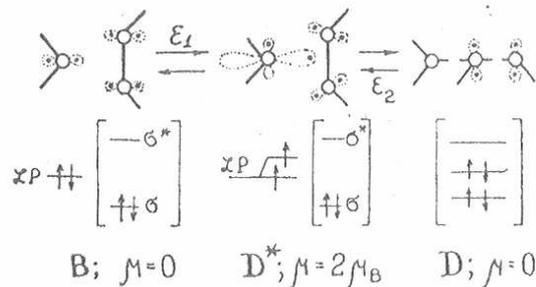


Fig. 1. Scheme for formation of the simplest TCB in g-Se. Left state is the basic state ( $B$ ) representing two adjacent covalent chains; right state is the defect state ( $D$ ) in the form of QMD after [16]; the both states are diamagnetic due to electron pairing on corresponding molecular orbitals, which are shown at the second line (LP is the lone-pair orbital). Intermediate paramagnetic state  $D^*$ , that corresponds to formation of TCB by means of the "harpoon" mechanism, is given after [17].

In 1991 there appeared an evidence in favor of the QMD/TCB model. As a result of MD simulation for 64-atomic cell in the temperature range 350-720 K, it was found by Hohl and Jones [20] that both a-Se and l-Se have  $Z_l = 2.1-2.2$ , and that the three-fold coordinated atoms concentration is as high as 16-17%. The main defect type was found to be linear  $C_3-C_3$  configuration, which was compared by the authors of [20] with QMD shown in Fig. 1.



paramagnetic state of TCB, e.g. in the form shown in Fig.1 as  $D^*$ , allowed us to propose a possible influence of magnetic field on viscosity. Note that such experiments are senseless from traditional point of view, if one considers glass as a typical diamagnetic. We, however, not only detected the effect both in the constant [29] and the pulsed [30] magnetic fields, but obtained a surprisingly large value of the effect in the latter case shown in Fig. 3.

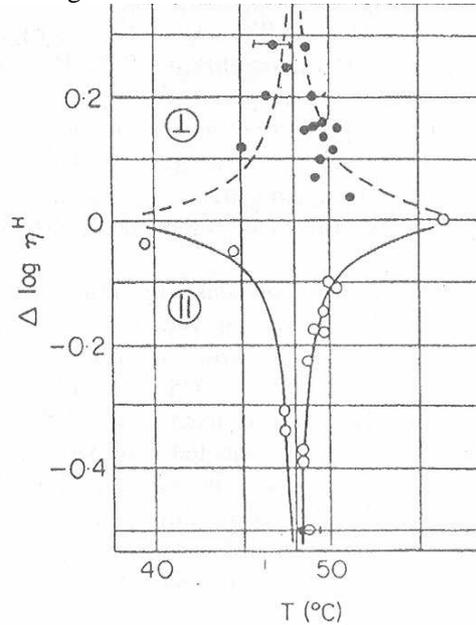


Fig. 3. Influence of the pulsed magnetic field ( $f=50\text{Hz}$ ,  $H=240\text{ Oe}$ ) on viscosity of softened selenium glass ( $T_g \approx 300\text{K}$ ) / after [30] /. The magnitude of the effect is estimated as  $\Delta \log \eta = \log \eta^H - \log \eta^0$ , where  $\eta^H$  is viscosity under the action of magnetic field, and  $\eta^0$  is viscosity without the field at the same temperature. Note that terminal points correspond to the change of viscosity by a factor of 2÷3. Viscosity was measured by the penetration method, so “⊥” corresponds to the transversal field as compared with the direction of moving of the probing rod, “∥” corresponds to the longitudinal field.

There are three unpredicted peculiarities of the effect: (i) a definite relation between the field frequency and the sample temperature; (ii) anisotropy, i.e. increase or decrease of viscosity in dependence on the field direction; and (iii) weakness of the field, whose energy is incommensurably small as compared with thermal energy,  $\mu_B H \ll kT$ . The two peculiarities were interpreted in [27] in the following way. First, the field acts most effectively when it fits into a resonance with the thermally-activated acts of TCB formation, i.e. with the frequency of periodic generation of paramagnetic  $D^*$  states shown in Fig. 1. Second, this state can throw its electronic “harpoon” (see Fig. 1) to one or another of adjacent selenium chains; the option is random when other conditions being equal, but it becomes directed when magnetic field acts on an unpaired spin of the “harpoon”; as a result, linear TCB are “born” principally in the field direction, and the subsequent bond switching by means of TCB acquires an anisotropic component. The third peculiarity, an extreme weakness of the field, is the most surprising since any orientational effect due to the field should be destroyed by thermal motion. Note, however, that viscous flow is a collective process, and a specific collective behavior of HVC considered in Section 4 can explain this peculiarity, too.

Recently we have renewed these experiments using both *temperature* of a sample and *frequency* of the field as variables. Isothermal runs from 219.2 K to 324.3 K indicate the shift of resonance frequency from 37.7 Hz to 58.7 Hz, that corresponds to activation energy  $\varepsilon = 0.71\text{ eV}$  (with  $\nu_0 = 8 \cdot 10^{12}\text{ Hz}$ , the main valent frequency of Se, as pre-exponent. This value coincides practically with  $\varepsilon^*_{D^*} = 0.68\text{ eV}$  in Fig. 2, being somewhat higher (note, however, that  $\varepsilon$  is the barrier and  $\varepsilon^*_{D^*}$  is the level). Thus, the elementary act of formation of paramagnetic transition state of HVC underlies this effect.

### 2.3.2. Low-temperature anomalies and low-frequency Raman scattering

Low-temperature anomalies (LTA) in glasses as compared with corresponding crystals are usually connected with a specific behavior of heat capacity and heat transfer, although acoustic, dielectric, etc., peculiarities are also observed [31]. As a rule, LTA are considered in two temperature regions. In the first, at  $T < 2$  K, the excess heat capacity,  $C_p(\text{gl}) > C_p(\text{cr})$ , and the suppressed heat transfer  $\kappa(\text{gl}) < \kappa(\text{cr})$  are observed. In the second, at  $2 < T < 50$  K, there is a peak on the  $C_p/T^3$  temperature dependence, and a plateau on  $\kappa(T)$ . The heat transfer behavior is illustrated in Fig. 4b with Se as an example. The two LTA temperature regions can be compared, at least phenomenologically, with the two frequency regions of anomalous behavior of low-frequency Raman scattering (LFRS), namely, with the excess scattering at  $\omega < 10$   $\text{cm}^{-1}$ , and with the so-called “boson” peak having a maximum at  $\omega = 20\text{--}60$   $\text{cm}^{-1}$ , the peak position being dependent primary on the glass composition.

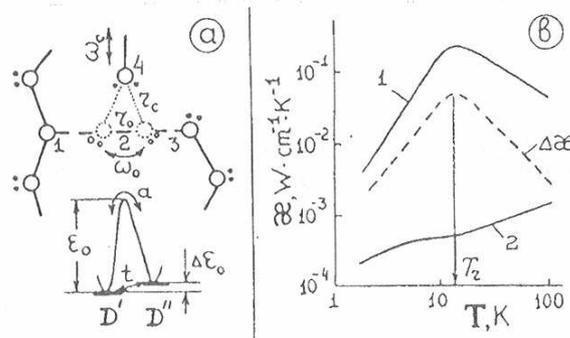


Fig. 4. (a) Model for understanding LTA and LFRS from one and the same TCB point of view, and (b) experimental data for heat transfer in glassy (2) and polycrystalline (1) Se. The figure is from ref. [17].

A detailed description of experiments and models concerning LTA and LFRS up to 1990 is given in our book [32]. They are not changed appreciably up to now, although new, more refined, models, were suggested. For the purpose of this brief review it is enough to use the pioneer concepts of two-level states realized in two-well potentials (TWP) after Anderson-Halperin-Varma [33] and W. Phillips [34], and of soft atomic configurations (SAC) after Klinger-Karpov [35]. SAC is attributed to a special microscopic region of 3 atoms, 1-2-3, in which the middle atom 2 possesses an extremely small quasi-elastic constant,  $\beta_0 \ll \beta$ , a property that corresponds to a wide shallow atomic potential, both one-well and two-well. After Klinger [36] SAC are responsible for a number of glass features, and SAC concentration was estimated to be as high as 1-10%.

The first realistic chemical-bonding image for such SAC/TWP was given by means of the TCB model, as it is shown in Fig. 4a. Due to electron delocalization, TCB are much more flexible and “soft” than ordinary two-centre covalent bond, and the middle hypervalent atom of TCB, being probably in TWP with  $\beta_0 \ll \beta$ , can vibrate also with correspondingly lowered frequency  $\omega_0 \ll \omega$ , where  $\omega$  is the frequency of main valent vibration of covalent bond (e.g., 20  $\text{cm}^{-1}$  and 250  $\text{cm}^{-1}$ , respectively, for g-Se). This hypothetical model was confirmed later by quantum-chemical study of  $\text{SiO}_2$  [37], in which it was found that the stretched  $\equiv\text{Si-O-Si}\equiv$  linkage is a TCB with a soft atomic potential with  $\beta_0/\beta \approx 10^{-2}$  and vibrational band at 60  $\text{cm}^{-1}$  known as the “boson” peak for  $\text{SiO}_2$ . The fact that HVC really possess “soft” potentials which often become two-well ones, was confirmed also by our quantum-chemical investigations (see, e.g., Fig. 5 in Section 3 below).

### 2.3.3. Quasi-polymerization of glass-forming melt and mechanical stability of solid glass

It is generally accepted that glass-forming melts have a polymeric nature, i.e. CRN persists without important damage at the melt temperatures. This is a quite unusual behavior as compared with

other, non-glass-forming covalent substances, whose crystals are known to acquire metallic or ionic character after melting. On the other hand, it was shown by one of the authors [38] that crystals of glass formers have a relatively low melting points as compared with non-glass-forming substances, and this fact was interpreted as an ability of glass formers to generate a sub-system of alternative bonds (e.g., TCB-subsystem) which accumulate excess thermal energy, so providing the preservation of the main subsystem of covalent bonds (CB). Since CB and TCB transform one into another (see  $CB \leftrightarrow TCB$  in Fig. 1) the both sub-systems are in a dynamical interaction, and there appears a dynamical *quasi-polymeric melt* consisting of temporary covalent fragments linked together by means of HVC. The question is how large should be the concentration of TCB in order to provide an effective quasi-polymerization? Our estimations for Se made with the use of various experimental data considered in the limits of a definite model [27] gives equilibrium TCB concentrations from 10% at  $T_m = 494$  K to 30% at the boiling point  $T_b \approx 950$  K. These values can be compared with the concentration of soft atomic configurations after Klinger [36] who estimated  $N(\text{SAC}) \approx 1-10\%$  in solid glass, as well as with the value of 16-17% of  $C_3-C_3$  states in both *g*-Se and *l*-Se after Hohl and Jones [20]. Thus, an idea of quasi-polymerization in glass-forming melt seems to have a numerical justification.

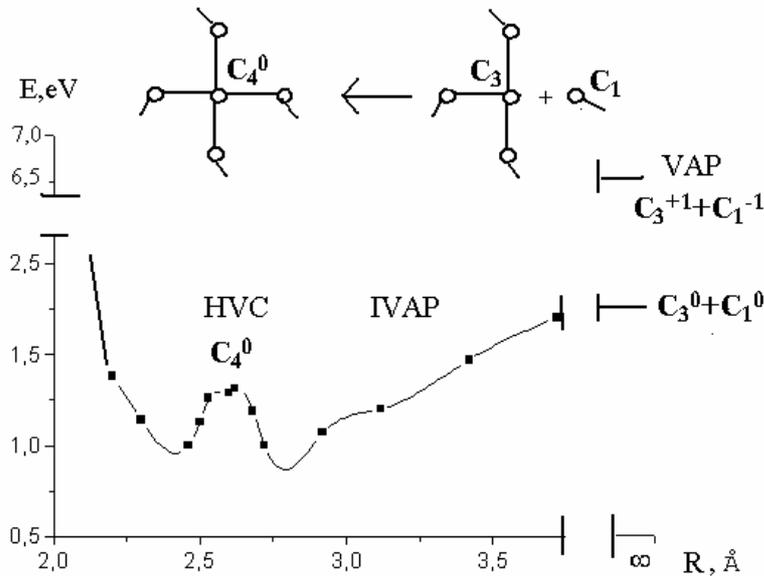


Fig. 5. Formation of four-coordinated diamagnetic neutral HVC in Se in the process of decreasing of the distance between the neutral VAP constituents (after [47]).

When temperature decreases, concentration of equilibrium HVC/TCB falls, e.g. up to 1% for *g*-Se at  $T_g$  after [27]. The question of how much of “soft” HVC is enough for throwing up the mechanical stress in a rigid covalent network below  $T_g$  remains open. It seems likely that the critical TCB concentration is minimal in 1D CRN (Se-type), medium in 2D CRN ( $B_2O_3$ -type), and maximum in 3D CRN ( $SiO_2$ -type). In any case concentration of TCB should be much more than equilibrium one due to the “freezing” of structure below  $T_g$ , which probably leads to freezing of defects in it. In addition, during its freezing CRN can generate super-equilibrium TCB in the stressed regions. Really, at quantum-chemical study of  $SiO_2$  it was shown that when a “normal” two-centre covalent bond  $\equiv Si-O-Si \equiv$  is stretched, it elongates and transforms into soft TCB  $\equiv Si \cdots O \cdots Si \equiv$  [37], thus generating special bonds that needs to glue the “cuts” in a rigid CRN [3,4]. Thus, both quasi-polymerization of glass-forming melt and mechanical stability of solid glass, although being realized in quite different temperature range, at  $T > T_m$  ( $T_m$  is the melting point of crystalline counterpart) and at  $T < T_g$  ( $T_g$  is the glass transition temperature, which is normally  $2/3$  of  $T_m$ ), are connected with an ability of HVC to heal the damages in covalent network that arise there due to thermal and mechanical stress, respectively.

### 2.3.4 TCB as non-rigid molecule and related properties

TCB with characteristic soft atomic potentials belong formally to the well known class of non-rigid molecules ( $\text{NH}_3$ ,  $\text{LiAlF}_4$ , etc.) that possess a number of additional movements such as inversion, rotation, etc., and corresponding additional degrees of freedom. A fundamental distinction, however, is that TCB is not a free molecule, therefore, its ability to such movements is suppressed by a rigid covalent environment. The latter, in turn, behaves differently above and below  $T_g$ , thus, TCB is either frozen up into an immobile CRN at  $T < T_g$  or exists in a changeable medium above  $T_g$ , so acquiring new degrees of freedom.

Besides, there may realize more than one type of TCB in one and the same substance, a property that means an ability for *isomerism* in the TCB-subsystem. Various types of TCB-isomers (structural or tautomers, optical or enantiomers, topological isomers as well as dynamical isomers arising due to inversion, rotation, etc.) was considered by Dembovsky [39,40] and used by him for interpretation of excess entropy below  $T_g$  (zero or residual entropy,  $S_0$ ) and above  $T_g$  (configurational entropy,  $S_c$ ). It was shown that the both CB-subsystem and TCB-subsystem give contributions into  $S_0$  and  $S_c$ ; the CB-subsystem due to common disordering and subsequent distortion of bond lengths and bond angles, and TCB-subsystem due to isomerism.

The results of model calculations, which was made using Se and  $\text{SiO}_2$  as typical examples of “fragile” and “strong” glass-formers, are presented in Table 3. It is seen that the TCB contribution for both  $S_0$  and  $S_c$  is higher in “strong”  $\text{SiO}_2$  than in “fragile” Se, a fact that will be confirmed by our later calculations showing that HVC are formed more easily in  $\text{SiO}_2$  than in Se (see Section 3). On the other hand, the number of *conformational* degrees of freedom,  $f_{cfm}$ , is higher in Se. This is not surprising, because 1D CRN of Se gives more possibilities for TCB to realize different invertomers and rotamers than 3D CRN of  $\text{SiO}_2$ . This result correlates also with an enhanced density of “configurons” characteristic for “fragile” liquids after Angell [41].

Table 3. Interpretation of experimental data for the residual ( $S_0$ ) and configurational ( $S_c$ ) entropies after [39,40].  $S_0$  and  $S_c$  in [cal/mol K]. CB and TCB mean the covalent bond and the

TCB contributions, respectively;  $f_{cfm}$  is the number of conformational degrees of freedom.

Substance	$S_0$ (0K- $T_g$ )	$S_0(\text{TCB})/$ $/S_0(\text{CB})$	$S_c$ ( $T_m$ )	$S_c(\text{TCB})/$ $/S_c(\text{CB})$	$f_{cfm}$
Se	0.90	0.09	1.42	0.34	11.4
$\text{SiO}_2$	0.91	0.70	0.40	0.88	1.6

In conclusion of this “qualitative” section it should be emphasized one more property of HVC considered on the basis of the TCB model, namely, the TCB ability to form chiral and dipolar anisotropic centres [42], which manifests themselves in experiments of optically-induced anisotropy and gyrotropy (see, e.g., [43]). As it will be shown below by quantum-chemical modeling, HVC can really form such centres including those having an extremely large dipole momentum.

## 3. Quantitative period

### 3.1. Introductory remarks

As we saw, the TCB model of HVC proved to be very useful for the understanding of glass formation and glass properties, however, it should be confirmed and specified by direct calculations of possible alternative bonding states in glasses. The two calculation works for Se [20] and  $\text{SiO}_2$  [37] cited above were shown to be quite comparable with the TCB model. Nevertheless, in order to consider this problem fundamentally, we carried out a series of quantum-chemical calculations for chalcogenide [44-48, 49-51], oxide [52-62], and halide [63,64] glasses. The structures were studied in the cluster

approximation, the cluster size (up to tenths of atoms) was chosen large enough to exclude terminal effects on the active region under consideration.

When using quantum-chemical methods, the classical notions about localized two-centre (or three-centre) bonds, valency, the “octet” rule, etc., become vague. Instead, notions of distribution of electron density, of polarization and electron correlation effects, of fractional charge and bond order etc., arise. The term “valency” becomes less convenient than the term “coordination”. We, however, keep the term HVC, but will understand *hypervalency* as over-coordination in comparison with a normal coordination of an atom in crystalline counterpart under ambient pressure (e.g. each chalcogen atom having coordination more than 2 is considered as hypervalent; however, VAP which contains a pair of sub- and over-coordinated atoms does not form HVC, as before).

Although quantum-chemical methods give a valuable information about bonding states, the characteristics states depend strongly on the method used. The most reliable non-empirical methods (*ab initio* schemes) need too much time as compared with semi-empirical methods like MNDO. The latter, however, are not very reliable, and their results should be proved in ambiguous cases by *ab initio* calculations. Thus, a usual methodology was to use initially MNDO and then test the most interesting configurations by means of non-empirical methods using more and more refined approximations. Thus, the method of calculation is a very significant part of quantum-chemical calculations, and it is discussed specially in each original paper, to which the reader is referred. Here we will consider only the main results and their interpretations.

### 3.2. Chalcogenide glasses

**Sulfur**, as the lightest chalcogen, was investigated firstly on the MNDO level (for Se this method becomes less reliable, and will be used only as a first rough approximation) [44,45] and then with the use of non-empirical methods with different approaches [46]. There was found two groups of HVC: (i) in charged systems, when a positively or negatively charged fragment interacts with an infinite chain, and (ii) in neutral systems, where a series of HVC was found, 3 of them being metastable, i.e. has a local minima, including four-coordinated  $S_4^0$ . Possible ways of non-breaking switching of covalent bonds by means of such HVC were investigated [44,45]. The most interesting result obtained is that VAP is *not* a negative- $U^{eff}$  defect, as it is generally accepted; this role is played by either VAP-dipole  $>S-S$  ( $C_3^+-C_1^-$  center, two atoms of which are directly linked together, and not isolated as in classical VAP model [9]) or the hypervalent  $C_4^0$  configuration.

This result was confirmed recently on **selenium** investigated *ab initio* [47]. It is seen in Fig. 5 that, like in S, VAP/IVAP in Se is a positive- $U^{eff}$  defect since its diamagnetic state,  $C_3^+C_1^-$ , lies higher than its paramagnetic state  $C_3^0C_1^0$ . When VAP constituents become nearer, the energy decreases due to electrostatic interaction, however, IVAP has no a local minimum, which is realized only when the structure converts into four-coordinated  $Se_4^0$  diamagnetic defect which is a negative- $U^{eff}$  defect that possesses also soft two-well low-energy potential shown in Fig. 5. The two-well potential (TWP) originates from the fact that the bonds surrounding  $Se_4^0$  atom are not equivalent since one pair is more “soft” and longer than another (2.7 Å and 2.4 Å, respectively). A possible bond exchange between the pairs can be considered as a specific “inversion” in accordance with the notions about HVC as a non-rigid quasimolecule (see Section 2.3.4).

Sulfur and selenium are two elementary representatives of **chalcogenide glasses** known also as glassy semiconductors. As such, their main problems are: (i) the nature of band tails and of localized states in the gap, and (ii) an absence of the doping effect, that is a fundamental feature of crystalline semiconductors. A hypothesis that just HVC (in a model form of TCB) provide the both peculiarities was formulated by Dembovsky as far as 1989 [48]. The present-day quantum-chemical modeling made on S and  $As_2S_3$  [49] shows a possibility that localized states within the gap, that pin the Fermi level, originates from VAP-dipoles and HVC. For **GeS<sub>2</sub>**, however, there was obtained another structure of the gap, when HVC contribute into the band tails, while the un-doping effect arises probably due to a specific destruction behavior of impurity atoms, which are transformed into a singlet form having such number of bonds that corresponds to the “8-N” rule [50].

GeS<sub>2</sub> is also a glass in which HVC with a large dipole momentum, up to 5D and higher, were found [51]. It is interesting that one of such HVC ( $Ge_5S_3$ , bottom index is coordination) has both low-

polar (HVC-1) and high-polar (HVC-2) forms divided by a small (10 kcal/mole) barrier. Thus, a dynamical HVC( $1 \leftrightarrow 2$ ) structure represents a non-rigid molecule with TWP. In addition, in the process of such an inversion a dipole emission can appear, a property that should be searched in a special experiment. A possible existence of large dipoles change the picture of the gap: it was shown recently that such defects can give both localized states and a quasi-continuous distribution of density of states in the vicinity of  $E_{c(v)}$  [7].

### 3.3 Oxide glasses

The general representatives of this group, namely,  $\text{SiO}_2$  [52-55],  $\text{GeO}_2$  [54-56],  $\text{B}_2\text{O}_3$  [52, 57-59],  $\text{P}_2\text{O}_5$  [60], as well as the  $\text{B}_2\text{O}_3+\text{Li}_2\text{O}$  [61] and  $\text{SiO}_2+\text{Li}_2\text{O}$  [61-62] systems with modifiers were investigated. The HVC formation was shown to be more typical here than in chalcogenide glasses, however, the HVC stability decreases within the row  $\text{SiO}_2 > \text{GeO}_2 > \text{B}_2\text{O}_3 > \text{P}_2\text{O}_5$ . Namely, there is a number of metastable, i.e. having a local minimum, HVC in  $\text{SiO}_2$  and  $\text{GeO}_2$ , their number decreases in  $\text{B}_2\text{O}_3$ , and vanishes in  $\text{P}_2\text{O}_5$ , where only unstable HVC that arises as transition states in the process of bond switching were found. Much attention was paid to investigation of various fragments of CRN in the form of cycles  $\text{C}_n$  ( $n=2-8$ ) and the ways of their destruction which takes place under real conditions due to thermal or mechanical stress. HVC, which are formed when the fragments interact, take an active part in the processes of bond rearrangement including non-breaking switching of bonds that provides low-energetic mechanisms of atomic transport.

Modeling of IR-spectra for  $\text{SiO}_2$  and  $\text{GeO}_2$  was made on the MNDO-PM3 level, so the results should be considered as semi-quantitative. However, it was shown [55] that the main features of spectra for crystalline counterparts are reproduced quite well, as well as the glassy spectra modelled by "normal" fragments of CRN. Introduction of HVC makes the spectra more complex, with filling the gaps between the lines and a low-frequency shift, which was expected from initial notions about HVC as non-rigid configurations with elongated and weakened bonds having relatively low quasi-elastic constants.

The influence of the modifier ( $\text{Li}_2\text{O}$ ) on  $\text{B}_2\text{O}_3$  [61] consists in the primary formation of the O-Li-O bridges that initiates the interaction of boron atoms belonging to adjacent layers, so forming hypervalent  $\equiv\text{B}-\text{O}-\text{B}\equiv$  links and changing the 2D CRN characteristic for  $\text{B}_2\text{O}_3$  into 3D CRN. The links are rather strong, a fact that corresponds to the well known facts of increase of density, of glass transition temperature, and of viscosity when the  $\text{Li}_2\text{O}$  concentration is increased. When  $\text{B}_2\text{O}_3$  is substituted for  $\text{SiO}_2$ , the links, however, become more soft and weak, and the process of network destruction competes with the process of quasi-polymerization [62]. As a result, the increase of density is much less pronounced, and a strong decrease in viscosity is observed when incorporating of  $\text{Li}_2\text{O}$  into  $\text{SiO}_2$ . The Li migration through the network was also modelled in [62] as a definite way along the potential surface; such a pioneering investigation has a direct relation to the problem of super-ionic conductivity in glasses.

### 3.4. Halide glasses

Two typical representatives,  $\text{BeF}_2$  [63] and  $\text{ZnCl}_2$  [64] were investigated. The general conclusion is that HVC here is less pronounced than in chalcogenide and, especially, in oxide glasses. On the other hand, one should take into account that CRN of both  $\text{BeF}_2$  and  $\text{ZnCl}_2$  is based on the three-centre bonds  $\text{Be}-\text{F}-\text{Be}$  or  $\text{Zn}-\text{Cl}-\text{Zn}$  that have a two-centre component [63,64]. However, in accordance with the definition of hypervalency taken in this Section 3, these TCB are not HVC. The existence of super-coordinated HVC (e.g. containing  $\text{Zn}_5$  or  $\text{Zn}_6$  atoms instead of "normal"  $\text{Zn}_4$  one) is possible, but such HVC are unstable and can exist only at the process of bond switching (e.g., at viscous flow taking place in a high-temperatures region) or under a strong stress from adjacent rigid CRN (a situation that cannot be excluded in a solid glass). As a result of an increased ionic component of bonding, the most large dipolar states were obtained just in halides, namely, up to 15-20D in  $\text{ZnCl}_2$  [64] and 7-15D in  $\text{BeF}_2$  [63]. A comparative analysis of  $\text{AX}_2$  ( $\text{SiO}_2\text{-GeO}_2\text{-GeS}_2\text{-BeF}_2\text{-ZnCl}_2$ ) glasses from the point of view of realization, destruction and transformation of various fragments including HVC is given in ref. [65].

## 4. Collective behavior of HVC

### 4.1. Cluster approach

This approach is the most wide-spreading one beginning from the classical work of Adam and Gibbs [66] who postulated a cooperatively rearranging regions, that exist in glass-forming liquids and whose size is temperature dependent. Since then many cluster (domain, etc.) models were suggested, and the main problem seems to be the nature of *boundary* that separates a cluster from others and that is an active region for cluster rearrangement. The above-mentioned “cuts” in CRN, which are filled with “weak/soft” bonds [3,4], can imply such a boundary. In turn, HVC, being naturally such bonds, seems to be a good candidate for an active element of inter-cluster boundary which is shown in Fig. 6d.

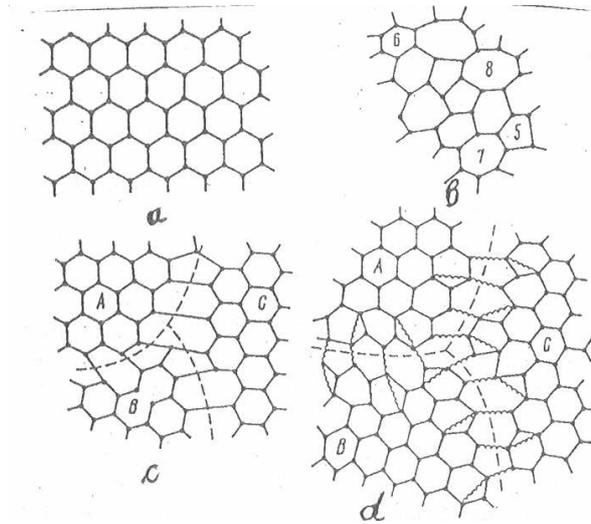


Fig. 6. Models of glass structure: (a) ideal CRN, (b) CRN containing rings of different size, (c) a rigid-boundary super – stressed clustered network, and (d) a soft - boundary clustered network after [32, p.191].

In such cluster model the structure of glass is considered as consisting of clusters divided by the HVC-boundary, the cluster size and the HVC population of the boundary being depending on temperature. It seems likely that equilibrium concentration of HVC decreases when cooling, a process that leads to the increase of the cluster size and/or the decrease of HVC population of boundary. At some critical temperature this population becomes so low that collective behavior of HVC becomes impossible, the boundary becomes rather rigid, and clusters become “frozen” in the sense that they cannot change its size and transform one into another. This picture was considered on the semi-quantitative level using the data of jump of heat capacity at glass transition, with Se (1D), B<sub>2</sub>O<sub>3</sub> (2D) and SiO<sub>2</sub> (3D) as examples, in the frames of a specific model that accounts both vibrational and configurational contributions into this jump [67]. The main conclusion was that the excess vibrational density of states existing above  $T_g$  can be associated with the collective behavior of HVC, which are interconnected at  $T > T_g$  and do not correlate at lower temperatures.

Experiment shows, however, that not all type of motions are frozen below  $T_g$  (remember, e.g., the well known  $\beta$ -relaxation processes). Moreover, the large-scale structure transformations can realize in solid glass under definite conditions, e.g., when a low-energy light ( $h\nu < E_{opt}$ ) after its passing through a bulk glass (As<sub>2</sub>S<sub>3</sub>) gives an obvious diffraction picture [43]. This experiment was interpreted in [68] as a result of action of such a light directly on the TCB-subsystem. The latter was supposed to exist in the form of inter-cluster boundary which, being consisting of relatively weak bonds, can be excited by the sub-gap light with subsequent formation of *gigantic non-crystalline clusters* and *gigantic lattices* having inter-plane distance as large as 3-5  $\mu$ . Due to the collective behavior of soft HVB, no cracking of solid glass is observed, in spite of a dramatic change of glass structure which transforms from ordinary isotropic one to highly anisotropic one.

#### 4.2. The symmetry approach

When glass acquires anisotropy, its order apparently increases. This process would be described quantitatively, however, there was no a definite evaluation of order for this case up to 1996, when Dembovsky and Koz'min [69] suggested a method of numerical evaluation of order from the most general symmetry point of view. The method is based on a simple equation  $Q=I-P/3n$  (where  $Q$  is the index of order,  $P$  is the number of independent coordinates needed to fix an  $n$ -atomic molecule in the Cartesian coordinate system) which was applied to various molecules of different symmetry including non-rigid molecules. It was shown that "order"  $Q$  represents a new geometrical informational index, and "disorder"  $I-Q$  can be compared with the Shannon's entropy of information. The  $Q$  value was shown to depend on the point group of symmetry, the dimensionality, and the number of structural degrees of freedom of the molecule under consideration. Some later [70] this method was expanded to a large molecular systems including a model glass considered as a system consisting of two bonding subsystem: the covalent bond (CB) one and the HVC one. The reader can see numerical examples of calculation of order,  $Q$ , for different covalent polyhedra and different dimensionality of CRN which they form in original [70]. The order in HVC-subsystem is of a special interest because this is a labile sub-structure which should be responsible for anisotropic effects in glasses. In accordance with the Curie's principle of superposition of symmetry (it connects the symmetry of external influence, the symmetry of structure, and the symmetry of properties), both the symmetry of field (which is, e.g., polar-tensorial for uniaxial pressure, or polar-vectorial for the electric component of the linearly polarized light) and the symmetry of HVC (e.g., TCB in Fig. 1 has the  $C_1$  point group of symmetry, that is chiral and dipolar) should determine both the existence and the character of anisotropic effects in glasses.

Owing to application of the notions about symmetry to the non-crystalline case, it became possible to treat the glass transition and the isotropy→anisotropy transition from the most general point of view, e.g. as the *breaking of symmetry* [71,72]. On the other hand, the two non-equilibrium phase transitions differ in the underlying process, which is *orientation* of HVC in the case of the isotropy→anisotropy transition [71], and which is the appearance of additional *dynamical degrees of freedom* connected with the above-mentioned dynamical isomers (rotamers and invertomers) of HVC arising above  $T_g$  [72]. In the latter case the notions about a special Shubnikov's antisymmetry (black-white or sign symmetry) are necessary, and for the first time glass transition is considered as the breaking of *antisymmetry* in isotropic non-crystalline medium.

#### 4.3. The bond wave approach

Another type of collective behavior in the HVC-subsystem can be realized in the form of *bond wave* that means a spatio-temporal correlation between the acts of bond exchange  $CB \leftrightarrow HVC$ . The bond wave model was introduced firstly when discussing thermodynamic features of glass-forming substances [38], and then was tested and developed when considered first sharp diffraction peak (FSDP), a well-known fingerprint of medium range order [73,74], glass transition [75], fracture [76], and viscosity [77,78]. One can see a "photo" of bond wave (BW) at a given moment in Fig. 7. Corresponding model of FSDP belongs obviously to the group of quasi-layer models, whose main problem is to explain the existence of FSDP in the substances that have no a 2D crystalline counterpart (an elegant solution of this problem is given in [79]). Note that within the frames of the BW model the dimensionality of CRN is of no matter since CRN is only a medium in which the bond wave, as a totality of equidistant planes populated with HVC, moves. Such a particular structure should give not only FSDP located at  $Q_l = 2\pi/d$  at about  $1\text{\AA}^{-1}$  but also the  $Q_A = 2\pi/\Lambda$  reflex at about  $0.1\text{-}0.01\text{ \AA}^{-1}$ , which can be detected using suitable methods (e.g. synchrotron diffraction); this is not an exotic experiment because such situation is well known and investigated in the case of smectic liquid crystals or lamellar phases of liquid membranes.

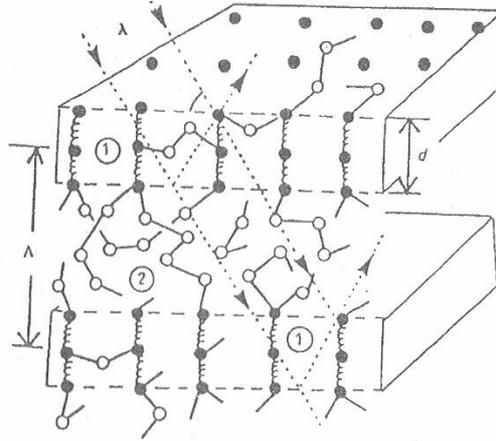


Fig. 7. An element of the bond-wave structure which gives the reflex  $Q_1=2\pi/d$  corresponding to FSDP after [75]. Short lines are covalent bonds, springs are HVC (in the form of TCB),  $\lambda$  is the wavelength.

Since bond waves are organized by means of HVC, the HVC concentration, which depends on temperature, is the critical parameter for the BW existence and behavior. The higher temperature the more population of the HVC-layer (see “1” in Fig. 7) and/or smaller the interlayer distance, which is the BW wavelength at the same time (see  $\lambda$  in Fig. 7). Conversely, when temperature falls, may be realized a situation when  $\lambda$  becomes so large that interlayer correlation vanishes, and BW stops its propagation through CRN. This case was compared with the glass transition that corresponds, therefore, to the 3D-BW→2D-BW transition [75]. 3D bond waves means the moving system of the HVC-populated layers which, therefore, excite all the structure, ensuring its total mobility. 2D bond waves spread only within the stopped layers populated with correlated HVC, and corresponding processes (possibly those known as  $\beta$ -relaxation) can proceed only in these restricted regions/layers.

Bond wave as a self-organized structure can be realized only in *open system*. Glass-forming liquid under manipulation (cooling or heating, under mechanical stress when measuring viscosity, etc.) is an open system, as well as a solid glass under one or another testing influence. Such systems are known to be sensitive to *information* from an external source [80]. Thus, our experiments on the influence of weak magnetic field on viscosity of softening Se glass (see Fig. 3) can be interpreted in the following way. Viscous flow proceeds by means of the thermally-activated bond waves [77,78], whose direction of spreading is determined by external mechanical field, which can be considered as *information field*  $\underline{M}$  (vector) for flowing liquid. Since there is an intermediate paramagnetic state ( $D^*$  in Fig. 1) arising at the acts of bond exchange, which are precursors of switching of bonds, BW is sensitive to magnetic field, therefore, it represents the second information field  $\underline{H}$  (vector). Thus, viscous flow acquires an additional component which depends on the relative  $\underline{M}$  versus  $\underline{H}$  direction, as it is really observed (Fig. 3). Note that information field should not be strong (although a definite threshold should exist) because it does not compete with “thermal motion”. Temperature, as the state parameter, and informational field, as the parameter of self-organization, executes different functions. Thermal energy provides the acts of bond exchange and hence the existence of BW as a definite dissipation pattern; information field gives the direction of BW, i.e. determines a concrete structure that realizes in glass-forming liquids and then freezes in solid glass. We need a “strong” influence of high temperature for supporting an intense bond wave process, however, without a “weak” information field BW not only non-regulated but hardly exists at all.

## 5. Conclusions

Glass is considered as a complex system consisting of two bonding subsystems, a passive subsystem of ordinary rigid covalent bonds, and an active subsystem of alternative bonds which are, possibly, of the hypervalent character. Just the latter subsystem, which determines specificity of the glassy state, needs a careful investigation on different levels: microscopic one (e.g., investigation of

different bonding states by means of quantum-mechanics), mesoscopic one (modeling of their behavior on the scale of medium-range order), and macroscopic one (considering glass as a complex system under real conditions, when self-organization within the HVC-subsystem becomes a significant factor). This approach needs introduction of a new, unusual (for glassy science) notions about symmetry, information, etc., but it can give us not only a new understanding of glass nature but also new, informational technologies for glassy materials – a worthy goal for the new millenium.

### Acknowledgements

The authors wish to thank Prof. M. Popescu for the support and discussion of this paper, Prof. L. Ferrari for his interest and support of recent magneto-viscous experiments, and Dr. A. S. Zyubin for discussion of Section 3. This work was supported by Russian Foundation for Fundamental Research (Grant No. 00-03-32646 and 98-03-32531).

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