Structure 1

- ✓ Glass formation in chalcogenide system
- ✓ Structural models

Explaining glass formation?

- ✓ As for glass formation in the chalcogenide system, there are theories, concepts, criteria, semi-empirical rules, and models.

- ✓ All of these would be divided into three groups as follows*;
  - ➢ Structural–chemical
  - ➢ Kinetic
  - ➢ Thermodynamic (energetic)

- ✓ The differences between these groups are rather indistinct, and quite often those concepts overlap from one group to another. Even now, the harmonic combination of the most important elements of each of the three groups of theories into a three-in-one concept that can be applied to the prognosis of new chemically different glass-forming systems remains unresolved.

* Semiconducting Chalcogenide Glass I, p. 1.

Glass formation

- ✓ There seem to be two ways to solve the glass formation prognosis problem in the absence of a unified concept of glass-formation that connects its structural–chemical, kinetic, and thermodynamic aspects.

- ✓ The first method is based on experiences and related to using 'the periodical regularities' in glass formation, which allows the qualitative evaluation of GFA in simple chalcogenide systems.

  - ➢ Elements of a same Group play similar structural/chemical role.
  - ➢ The 8-N rule would estimate CN of each constituent atom, though not applicable all the time
  - ➢ In two- and three-component chalcogenide alloys, replacing one of the components of 4th (Ge, Sn), 5th (As, Sb, Bi), or 6th (S, Se, Te) main subgroups by an element with a greater atomic number decreases the glass forming region, possibly due to the increase in the metallization degree of covalent bonds.
  - ➢ In ternary systems, there is a decreasing tendency of glass formation: S>Se>Te, As>P>Sb, Si>Ge>Sn.

Glass formation

- ✓ The role of stable electronic configurations in glass-forming ability of ChG (Funtikov, 1994).
  - ➢ One of the principal conditions for glass formation is the structural-configurational equilibrium between the low- and high-molecular-weight forms of atomic groups in melts (solutions) at the synthesis temperature.
  - ➢ This equilibrium is related to the electron configuration equilibriums in the atoms that make up all of these groups.
  - ➢ For example, elemental sulfur or selenium can form glass, which can produce in the molten state both types of molecular groups, i.e., cyclic X_8 and chain X_n molecules in this case, possessing the same free energy and existing in equilibrium with one another.

- ✓ Glasses can be treated as a modification of metastable highly disperse multi-component eutectics or frozen lyophilic colloidal solutions (Funtikov, 1996).
  - ➢ An ideal glass is a multicomponent eutectic in which the number of components is comparable, in the order of magnitude, to a feasible total number of structural elements of the short-range order.

* Semiconducting Chalcogenide Glass I, p. 10.

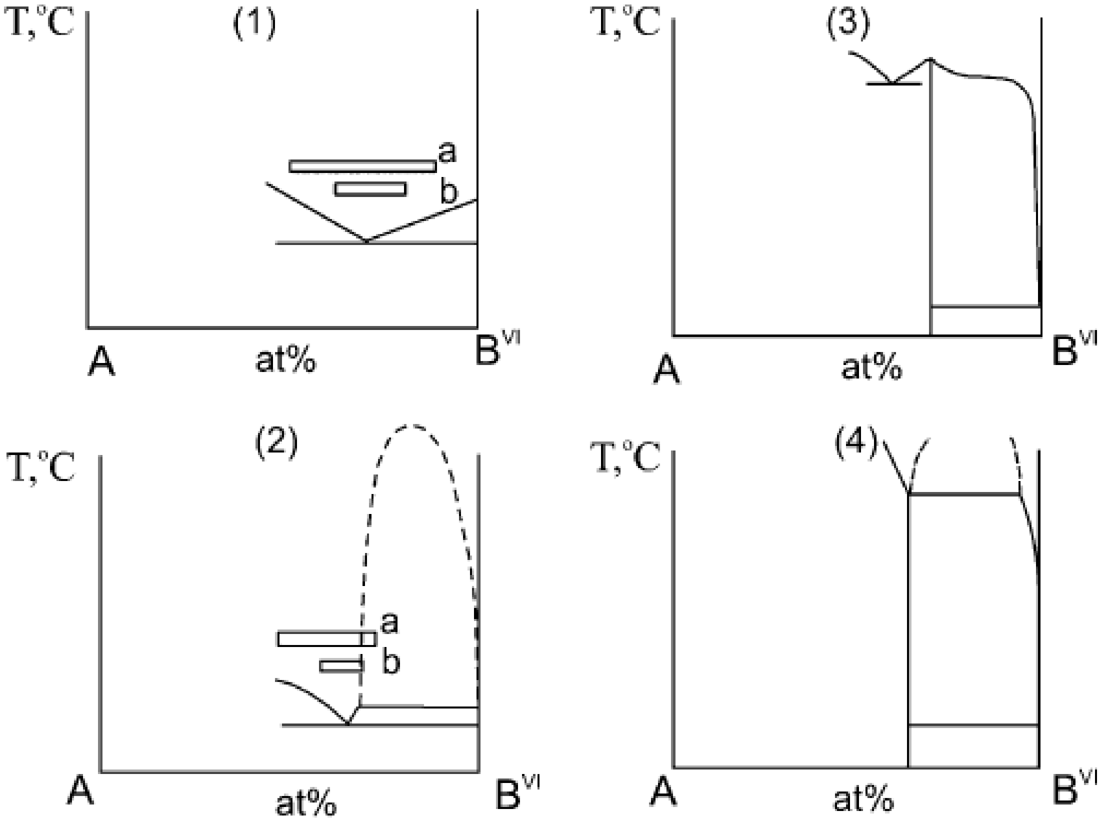


FIG. 2. Types of phase diagrams of binary chalcogenide systems (Minaev, 1982): (1) the glassforming type with the chalcogens-enriched eutectic; (2) the glassforming eutectic type with the phase liquation in the chalcogens-enriched region; (3) the non-glass-forming type with the sharp liquidus rise in the chalcogens-enriched region; (4) the same as 3 but with the phase liquation; (a) the Glass-formation region at the quick quenching of melt; (b) the glass-formation region at the slow cooling of melt.

Semiconducting Chalcogenide Glass I, p. 11.

Criterion for glass formation: one example

- ✓ Sun-Rawson's criterion for glass formation of individual oxide, the energy of chemical or covalence-ion binding (CIB) of substance per one averaged atom is given by the sum of products of energies of certain chemical bonds E_i, the portion of atoms bounded by such bond M_i, and the half-value of their valence CN K_i
  - ➢ SR criterion $$E_{\mathrm{CIB}} = \frac{\sum_i E_i M_i (K_i/2)}{\sum_i M_i}$$

- ✓ Minaev modifies the SR criterion to account for the effect of liquidus temperature.
  - ➢ SRM criterion $$\mathrm{GFA} = \frac{E_{\mathrm{CIB}}}{T_{\mathrm{liq}}}$$

Semiconducting Chalcogenide Glass I, p. 15.

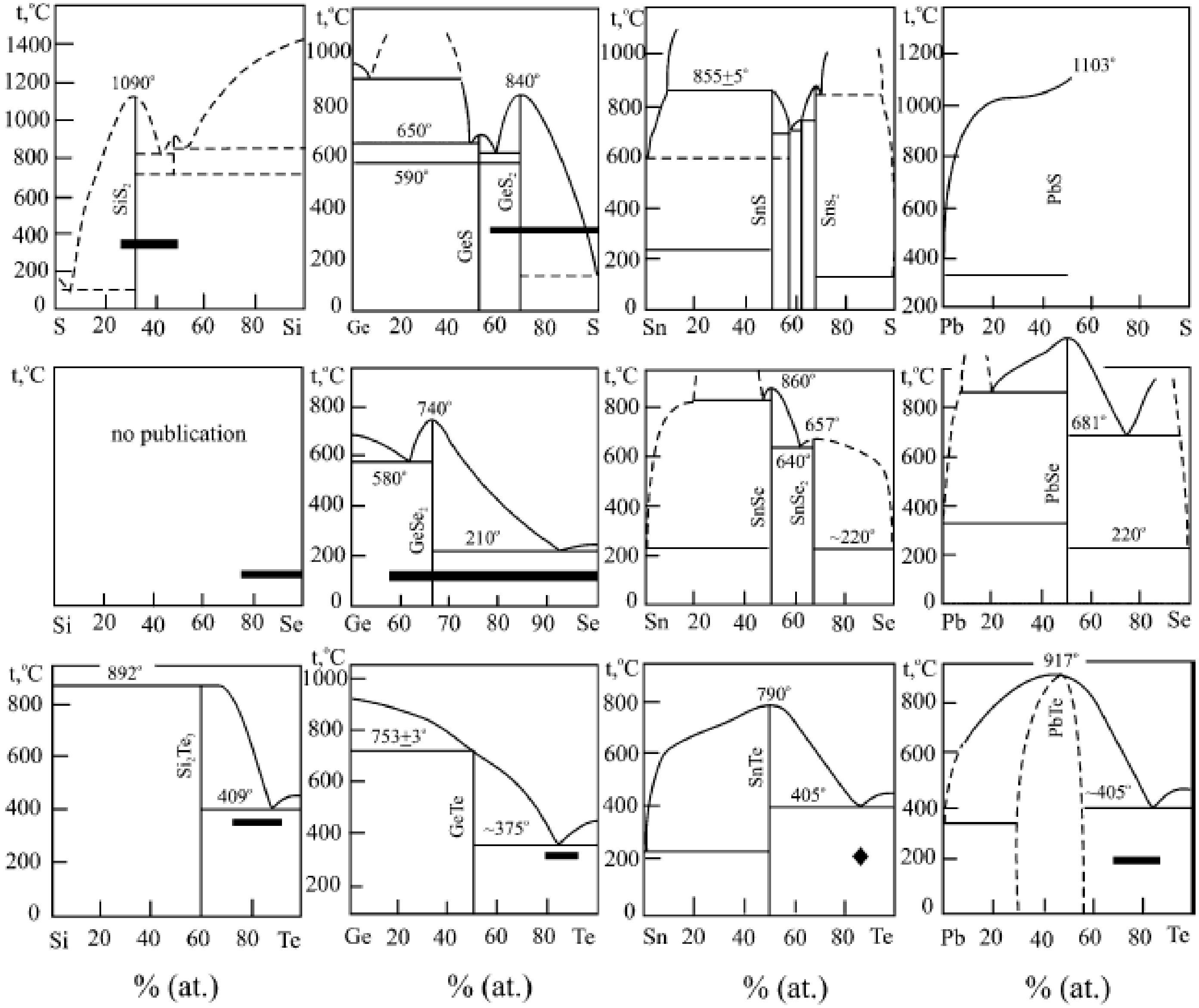


FIG. 6. Phase diagrams and glass-formation regions (bold lines, rhombs) in systems $A^{IVA}-B^{VI}$ (Minaev, 1991).

Semiconducting Chalcogenide Glass I, p. 24.

- ✓ The SRM criterion is successful to explain glass formation of many simple chalcogenide systems.

- ✓ GFA of chalcogens carried out in accordance with the SRM criterion
  - ➢ For energies of homopolar bonds of sulfur, selenium, and tellurium of 266, 184, and 168 kJ/mol/K and melting temperatures of 119.3, 217, and 449.8 C, respectively,
  - ➢ Their glass-formation abilities are 0.678, 0.375, and 0.231 kJ/mol/K.

- ✓ GFA given by the SRM criterion is based on the physical–chemical essence and the energetic in part, but not based on the kinetic aspect.

- ✓ Since glass formation depends on cooling rate, integration of statistical data concerning critical cooling rates and the comparison with calculated values of the glass-formation ability may be needed in order to fully describe the glass formation.

Semiconducting Chalcogenide Glass I, p. 15.

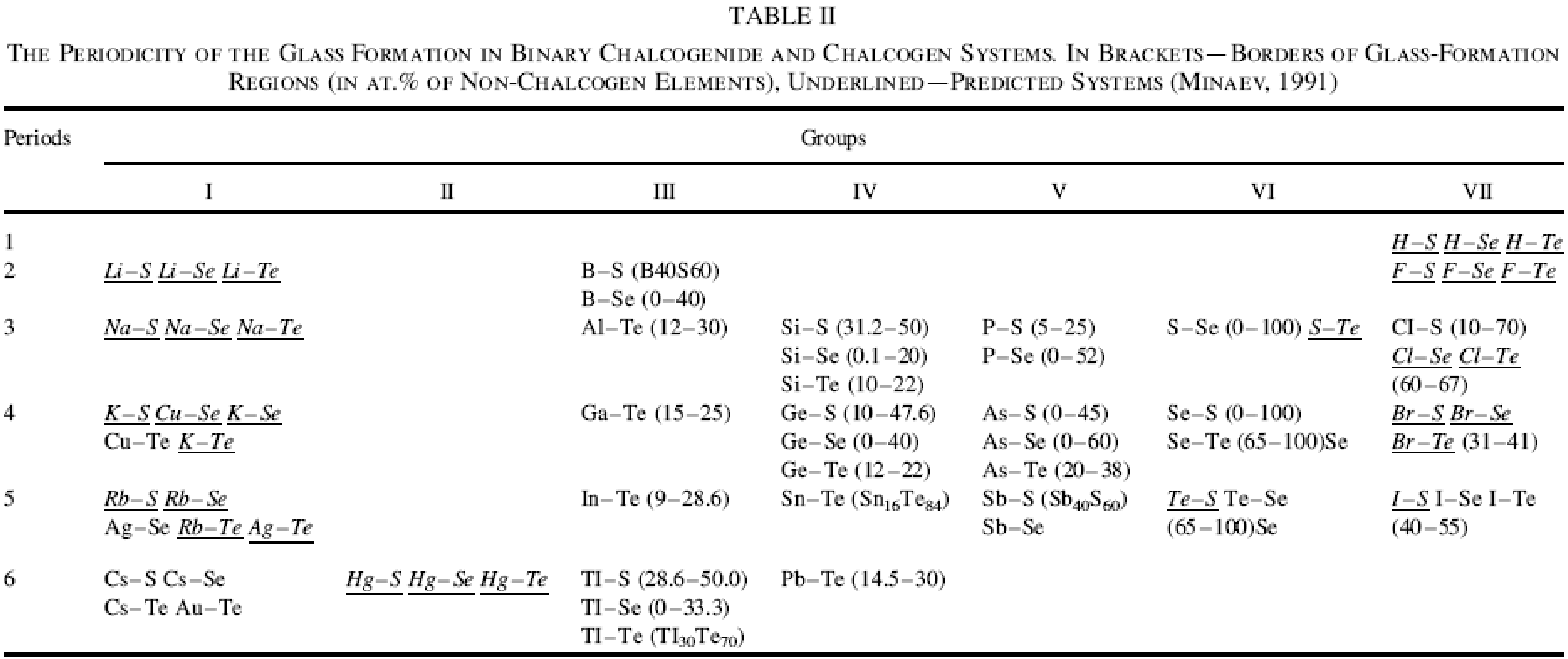


TABLE II

THE PERIODICITY OF THE GLASS FORMATION IN BINARY CHALCOGENIDE AND CHALCOGEN SYSTEMS. IN BRACKETS—BORDERS OF GLASS-FORMATION REGIONS (IN AT.% OF NON-CHALCOGEN ELEMENTS), UNDERLINED—PREDICTED SYSTEMS (MINAEV, 1991)

Periods	Groups						
	I	II	III	IV	V	VI	VII
1							*H–S* *H–Se* *H–Te*
2	*Li–S* *Li–Se* *Li–Te*		B–S (B40S60) B–Se (0–40)				*F–S* *F–Se* *F–Te*
3	*Na–S* *Na–Se* *Na–Te*		Al–Te (12–30)	Si–S (31.2–50) Si–Se (0.1–20) Si–Te (10–22)	P–S (5–25) P–Se (0–52)	S–Se (0–100) *S–Te*	Cl–S (10–70) *Cl–Se* *Cl–Te* (60–67)
4	*K–S* *Cu–Se* *K–Se* Cu–Te *K–Te*		Ga–Te (15–25)	Ge–S (10–47.6) Ge–Se (0–40) Ge–Te (12–22)	As–S (0–45) As–Se (0–60) As–Te (20–38)	Se–S (0–100) Se–Te (65–100)Se	*Br–S* *Br–Se* *Br–Te* (31–41)
5	*Rb–S* *Rb–Se* Ag–Se *Rb–Te* *Ag–Te*		In–Te (9–28.6)	Sn–Te ($Sn_{16}Te_{84}$)	Sb–S ($Sb_{40}S_{60}$) Sb–Se	*Te–S* Te–Se (65–100)Se	*I–S* I–Se I–Te (40–55)
6	Cs–S Cs–Se Cs–Te Au–Te	*Hg–S* *Hg–Se* *Hg–Te*	Tl–S (28.6–50.0) Tl–Se (0–33.3) Tl–Te ($Tl_{30}Te_{70}$)	Pb–Te (14.5–30)			

Semiconducting Chalcogenide Glass I, p. 40.

Just some of the structural models

- ✓ A good structural model should explain 1) property-composition relationship, 2) atomic arrangements in IRO as well as SRO, and possess 3) general applicability for as many systems as possible.

- ✓ The most famous concepts of glass structure are the crystalline concept of Frankenheim (1835, 1851) and Lebedev (1921, 1924), in which for the first time an hypothesis was offered regarding glass formation and polymorphism; the concept of polymeric structure (Mendeleev, 1864; Sosman, 1927; Tarasov, 1959, 1979, and others); the concept of a continuous random network of Zachariasen (1932); the polymeric crystallite concept of Porai-Koshits (1959), which with some success combines three previous concepts; the concept of clusters of structural-independent poly-forms of Goodman (1975), which develops the ideas of Frankelgeim–Lebedev, and the concept of polymeric polymorphous-crystalloid structure of Minaev (1991).*

  - ➢ **Chemically ordered continuous random network model**
  - ➢ **Polymeric polymorphous-crystalloid structure model**
  - ➢ **Topological model based on the bond-constraint theory**

* Semiconducting Chalcogenide Glass I, ch. 1.

Chemically ordered continuous random network

- ✓ Continuous random network (Zachariasen, 1932)
- ✓ Chemically ordered continuous random network (Lucovsky and Hayes, 1979)
- ✓ Stereo chemically defined structure (Gaskell, 1981)

  - ➢ Structural role of constituents; in view of Coulombic interaction
    - ◆ Network former
    - ◆ Network modifier
    - ◆ Intermediate

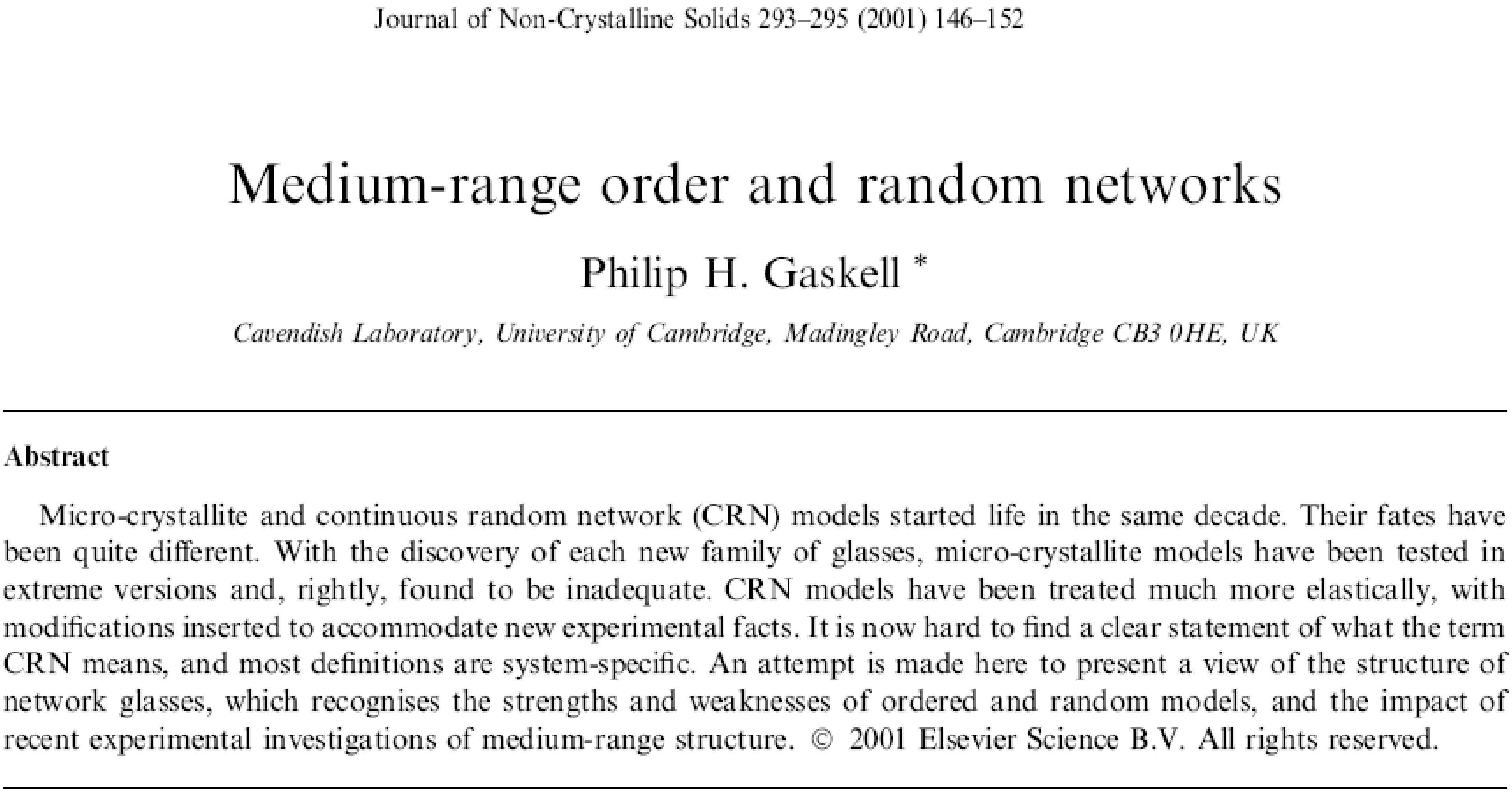
- ✓ Can this classification be applied to the amorphous covalent solids too?
    - ◆ Strong covalent ChG
    - ◆ Weak covalent ChG

- ✓ Difficult to explain evidence of simultaneous influence of different polymorphs on properties and structure of glass, and its crystallization as different polymorphs.
- ✓ Difficult to support plural experimental clues indicating presence of IRO.

Polymeric polymorphous-crystalloid structure

- ✓ Micro-crystallite concept (Lebedev, 1924)
- ✓ Polymeric crystallite concept (Porai-Koshits, 1959)
- ✓ Polymeric polymorphous-crystalloid structure (Minaev, 1991)
- ✓ Nano-paracrystallite (Popescu, 2005)

- ✓ Some explanations
- ➢ Glass formation is the process of generation, mutual transformation and copolymerization of structural fragments of various polymorphs of crystal substance without an LRO (crystalloids).
- ➢ The crystalloid is a fragment of crystal structure consisting of a group of atoms connected by chemical bonds.
- ➢ In every non-crystalline substance there are two or more SROs, two or more IROs, and there is no LRO.
- ➢ Glass structure is not absolutely continuous, and there are separate broken chemical bonds and other structural defects.
- ✓ Validity not tested for multi-component glasses, even for ternary glasses.



Journal of Non-Crystalline Solids 293–295 (2001) 146–152

Medium-range order and random networks

Philip H. Gaskell *

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

Abstract

Micro-crystallite and continuous random network (CRN) models started life in the same decade. Their fates have been quite different. With the discovery of each new family of glasses, micro-crystallite models have been tested in extreme versions and, rightly, found to be inadequate. CRN models have been treated much more elastically, with modifications inserted to accommodate new experimental facts. It is now hard to find a clear statement of what the term CRN means, and most definitions are system-specific. An attempt is made here to present a view of the structure of network glasses, which recognises the strengths and weaknesses of ordered and random models, and the impact of recent experimental investigations of medium-range structure. © 2001 Elsevier Science B.V. All rights reserved.

- ✓ Models evolve but usually become more complicated to incorporate;
    - New experimental data on existing glass forming systems
    - New results obtained from (*ab initio*) simulations
    - Newly found glass forming systems
- ✓ Assumptions must not be needlessly multiplied.*
- ✓ There's more than one way to skin a cat.**

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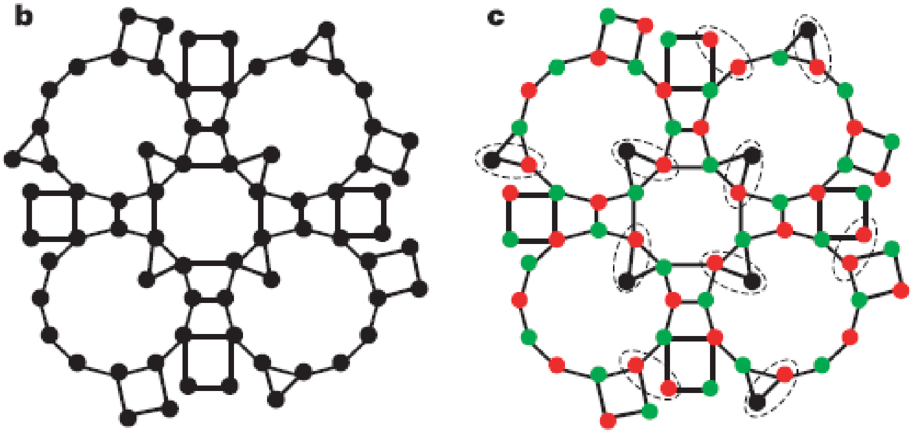
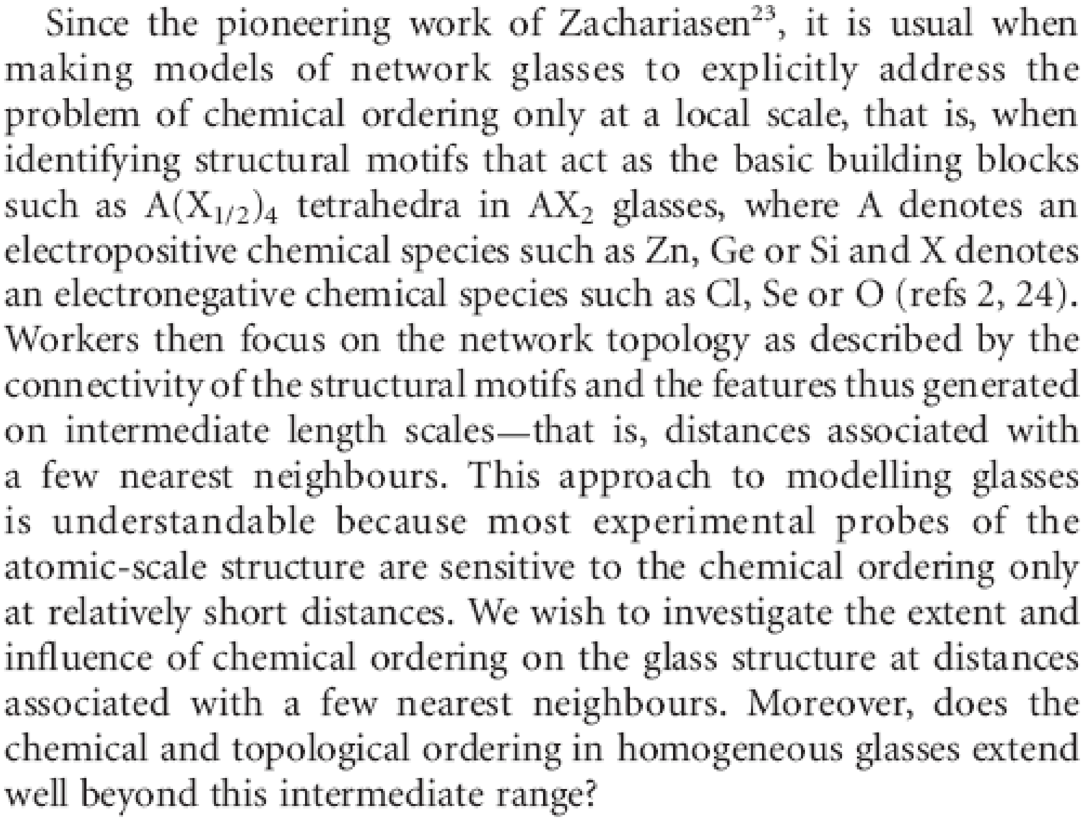
* http://en.wikipedia.org/wiki/Occam's_razor

** Deng Xiaoping



- ✓ Topological ordering and chemical ordering in ChGs
  - ➢ Ordering in the short range
  - ➢ Ordering in a medium range


Since the pioneering work of Zachariasen[23], it is usual when making models of network glasses to explicitly address the problem of chemical ordering only at a local scale, that is, when identifying structural motifs that act as the basic building blocks such as $A(X_{1/2})_4$ tetrahedra in AX_2 glasses, where A denotes an electropositive chemical species such as Zn, Ge or Si and X denotes an electronegative chemical species such as Cl, Se or O (refs 2, 24). Workers then focus on the network topology as described by the connectivity of the structural motifs and the features thus generated on intermediate length scales—that is, distances associated with a few nearest neighbours. This approach to modelling glasses is understandable because most experimental probes of the atomic-scale structure are sensitive to the chemical ordering only at relatively short distances. We wish to investigate the extent and influence of chemical ordering on the glass structure at distances associated with a few nearest neighbours. Moreover, does the chemical and topological ordering in homogeneous glasses extend well beyond this intermediate range?

Salmon et al, Nature 435 (2005) 75.

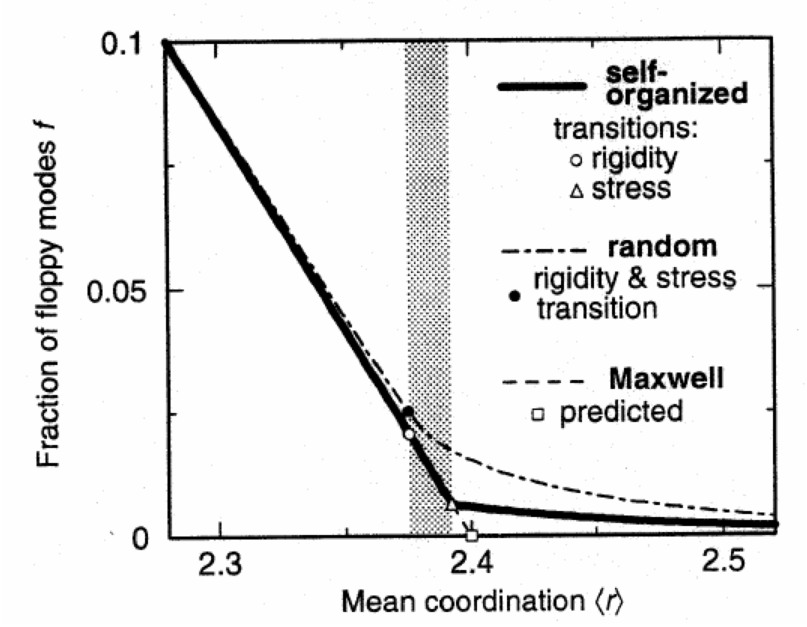
Topological model and bond constraint theory

- ✓ Idea of mechanical constraint counting (Philips, 1979)
- ✓ Floppy mode and mean-field rigidity threshold at Z=2.40 (Thorpe, 1983)
- ✓ Structural transition from 2D to 3D at [Z]=2.67 (Tanaka, 1989)
- ✓ Intermediate phase in addition to floppy and rigid phases (Boolchand, 2001)

- ✓ Assumption
  - ➢ For a network possessing well-defined local structures, inter-atomic forces must form a hierarchical order. The strongest covalent forces between nearest neighbors serve as Lagrangian (mechanical) constraints defining the elements of local structure (building blocks). Constraints associated with the weaker forces of more distant neighbors must be intrinsically broken leading to the absence of long-range order.
  - ➢ Glass forming tendency is optimized when the number of Lagrangian local-bonding constraints per atom, n_c, just equals the number of degrees of freedom.
  - ➢ Implicitly assume that [Z] is indiscriminate in species of valence bonds. The chemical property is obscured, and instead the topological nature emerges.

Topological model and bond constraint theory

- ✓ Basic ideas
  - ➢ For a 3d network, the number of degrees of freedom, $n_d = 3$.
  - ➢ In covalent solids, there are two types of near-neighbor bonding forces; bond-stretching (α-forces) and bond-bending (β-forces). The number of Lagrangian bond-stretching constraints per atom is $n_\alpha = Z/2$, and of bond-bending constraints is $n_\beta = 2Z-3$.
  - ➢ For the case when all α- and β-constraints are intact and no dangling ends, $n_c = n_\alpha + n_\beta = n_d$ which results in Z=2.4.



Source of figure: M. F. Thorpe, M. V. Chubynsky in Properties and Applications of Amorphous Materials, Ed. M. F. Thorpe, L. Tichy, Kluwer Academic Press, Dordrecht, p. 61, 2001.

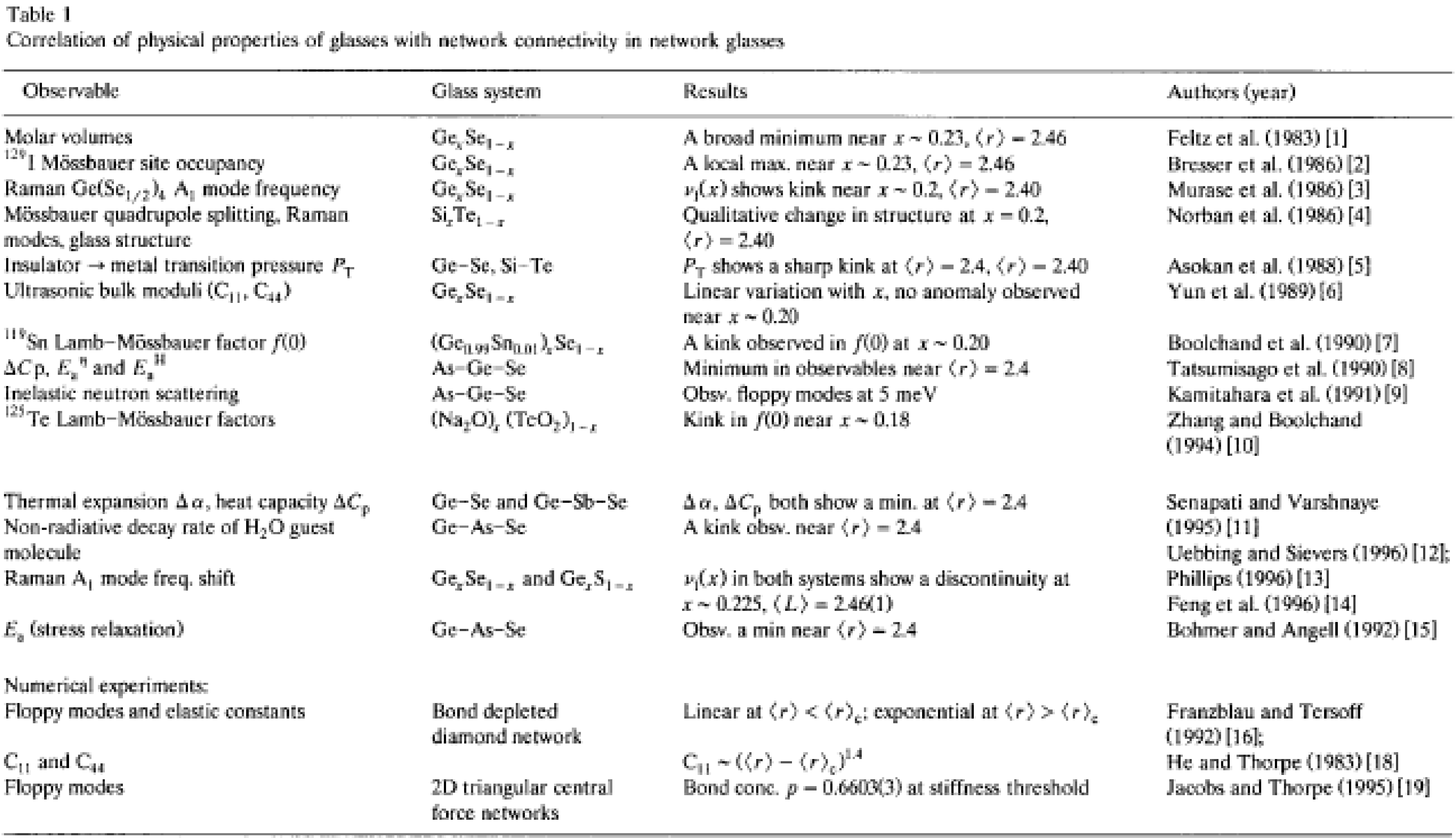


Table 1

Correlation of physical properties of glasses with network connectivity in network glasses

Observable	Glass system	Results	Authors (year)
Molar volumes	Ge_xSe_{1-x}	A broad minimum near $x \sim 0.23$, $\langle r \rangle = 2.46$	Feltz et al. (1983) [1]
^{129}I Mössbauer site occupancy	Ge_xSe_{1-x}	A local max. near $x \sim 0.23$, $\langle r \rangle = 2.46$	Bresser et al. (1986) [2]
Raman $Ge(Se_{1/2})_4$ A_1 mode frequency	Ge_xSe_{1-x}	$\nu_1(x)$ shows kink near $x \sim 0.2$, $\langle r \rangle = 2.40$	Murase et al. (1986) [3]
Mössbauer quadrupole splitting, Raman modes, glass structure	Si_xTe_{1-x}	Qualitative change in structure at $x = 0.2$, $\langle r \rangle = 2.40$	Norban et al. (1986) [4]
Insulator → metal transition pressure P_T	Ge–Se, Si–Te	P_T shows a sharp kink at $\langle r \rangle = 2.4$, $\langle r \rangle = 2.40$	Asokan et al. (1988) [5]
Ultrasonic bulk moduli (C_{11}, C_{44})	Ge_xSe_{1-x}	Linear variation with x, no anomaly observed near $x \sim 0.20$	Yun et al. (1989) [6]
^{119}Sn Lamb–Mössbauer factor $f(0)$	$(Ge_{0.99}Sn_{0.01})_xSe_{1-x}$	A kink observed in $f(0)$ at $x \sim 0.20$	Boolchand et al. (1990) [7]
ΔCp, E_a^{η} and E_a^{H}	As–Ge–Se	Minimum in observables near $\langle r \rangle = 2.4$	Tatsumisago et al. (1990) [8]
Inelastic neutron scattering	As–Ge–Se	Obsv. floppy modes at 5 meV	Kamitahara et al. (1991) [9]
^{125}Te Lamb–Mössbauer factors	$(Na_2O)_x(TeO_2)_{1-x}$	Kink in $f(0)$ near $x \sim 0.18$	Zhang and Boolchand (1994) [10]
Thermal expansion $\Delta\alpha$, heat capacity ΔC_p	Ge–Se and Ge–Sb–Se	$\Delta\alpha$, ΔC_p both show a min. at $\langle r \rangle = 2.4$	Senapati and Varshnaye (1995) [11]
Non-radiative decay rate of H_2O guest molecule	Ge–As–Se	A kink obsv. near $\langle r \rangle = 2.4$	Uebbing and Sievers (1996) [12];
Raman A_1 mode freq. shift	Ge_xSe_{1-x} and Ge_xS_{1-x}	$\nu_1(x)$ in both systems show a discontinuity at $x \sim 0.225$, $\langle L \rangle = 2.46(1)$	Phillips (1996) [13] Feng et al. (1996) [14]
E_a (stress relaxation)	Ge–As–Se	Obsv. a min near $\langle r \rangle = 2.4$	Bohmer and Angell (1992) [15]
Numerical experiments:			
Floppy modes and elastic constants	Bond depleted diamond network	Linear at $\langle r \rangle < \langle r \rangle_c$; exponential at $\langle r \rangle > \langle r \rangle_c$	Franzblau and Tersoff (1992) [16];
C_{11} and C_{44}		$C_{11} \sim (\langle r \rangle - \langle r \rangle_c)^{1.4}$	He and Thorpe (1983) [18]
Floppy modes	2D triangular central force networks	Bond conc. $p = 0.6603(3)$ at stiffness threshold	Jacobs and Thorpe (1995) [19]

Feng et al, J. Non-Cryst. Solids 222 (1997) 137.

Journal of Non-Crystalline Solids 240 (1998) 1–21

Microscopic origin of the glass forming tendency in chalcohalides and constraint theory

M. Mitkova [1], P. Boolchand *

compositions. We think that glass compositions residing near or close to the predicted compositions result from optimally constrained *random networks* with halogen atoms progressively terminating the network backbone. On the other hand, glass compositions residing away from the predicted compositions are also optimally constrained but consist of *molecular fragments* that are formed at specific stoichiometries controlled by the coordination chemistry of respective cations. A perusal of the available literature reveals a general pattern; although constraint theory cannot predict the morphology of the glass structure, it does impose bounds on possible structures. In none of the glass

PHYSICAL REVIEW B VOLUME 54, NUMBER 7 15 AUGUST 1996-I

Evidence concerning the effect of topology on electrical switching in chalcogenide network glasses

R. Aravinda Narayanan
Department of Physics, Indian Institute of Science, Bangalore 560 012, India

S. Asokan*
Department of Instrumentation, Indian Institute of Science, Bangalore 560 012, India

A. Kumar
Department of Physics, Indian Institute of Science, Bangalore 560 012, India

(Received 29 March 1996)

Electrical switching properties of Ge-As-Te glasses have been investigated over a wide range of mean coordination numbers ($\langle r\rangle$) in a single composition tie line. The results obtained clearly indicate the modulation of the composition dependence of switching fields by network topology. Distinct change is observed in the slope of the composition dependence of switching field, at $x=25$ ($\langle r\rangle=2.4$) and $x=52.5$ ($\langle r\rangle=2.67$), which correspond to mechanical and chemical thresholds, respectively. Present results also rule out the earlier suggestions such as shifting of percolation threshold to higher $\langle r\rangle$ values and the likelihood of two isolated rigidity percolation thresholds in such glass systems. [S0163-1829(96)02531-3]

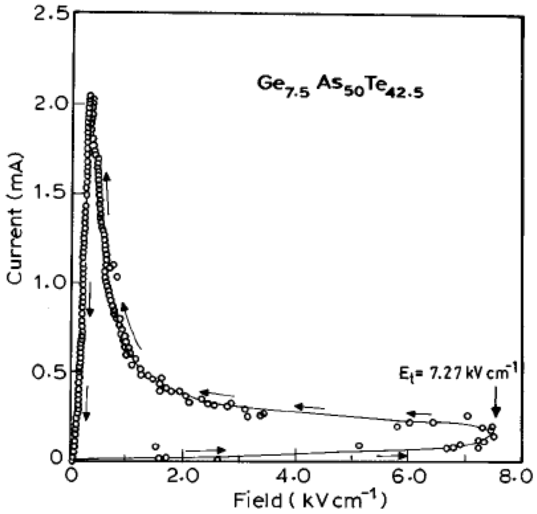


FIG. 1. *I-V* characteristics of a representative $Ge_{7.5}As_{50}Te_{42.5}$ glass.

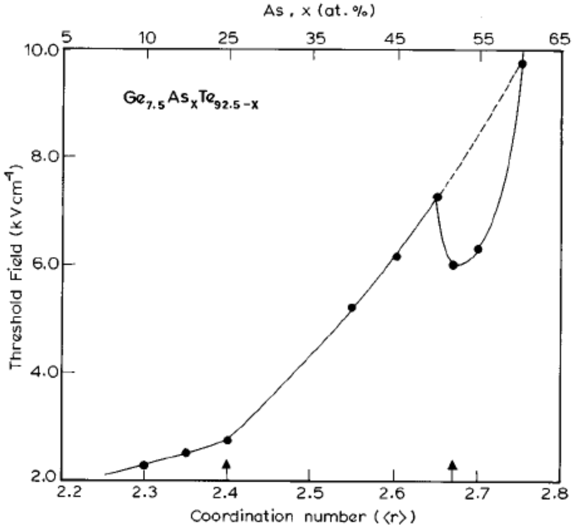


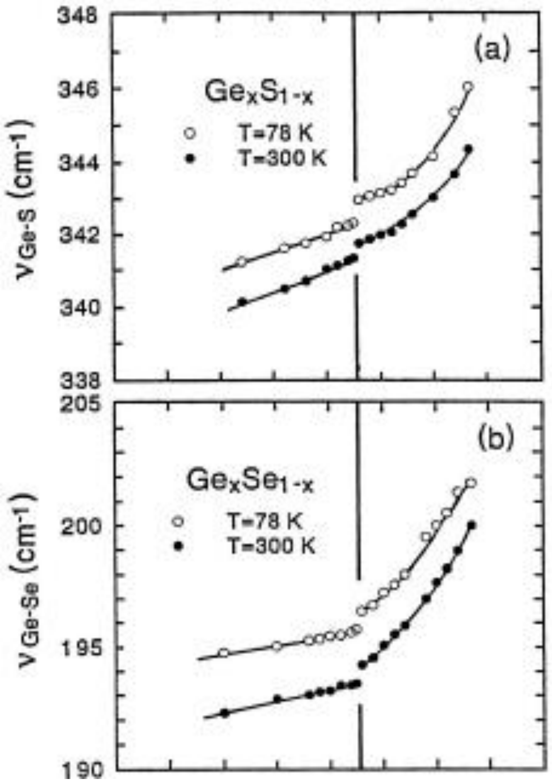
FIG. 2. Composition dependence of the electrical switching fields (E_t) of $Ge_{7.5}As_xTe_{92.5-x}$ glasses. The vertical arrows at $\langle r\rangle=2.4$ and 2.67 indicate the mechanical and chemical thresholds, respectively.

Direct Evidence for Stiffness Threshold in Chalcogenide Glasses

Xingwei Feng, W. J. Bresser, and P. Boolchand
Department of Electrical and Computer Engineering and Computer Science, University of Cincinnati, Cincinnati, Ohio 45221-0030

(Received 10 February 1997)

Raman scattering in $\mathrm{Ge}_x X_{1-x}$ glasses, X = S or Se, reveals that the frequency of A_1 modes of corner-sharing $\mathrm{Ge}(X_{1/2})_4$ tetrahedra displays a discontinuous jump between $x = 0.225$ and $x = 0.230$, which coincides with a minimum in the nonreversing heat flow at the glass transition T_g established from modulated differential scanning calorimetry. These results constitute direct evidence for a stiffness threshold at a mean coordination $\langle r \rangle_c = 2.46(1)$, which is well described by mean-field constraint counting procedures. [S0031-9007(97)03283-3]



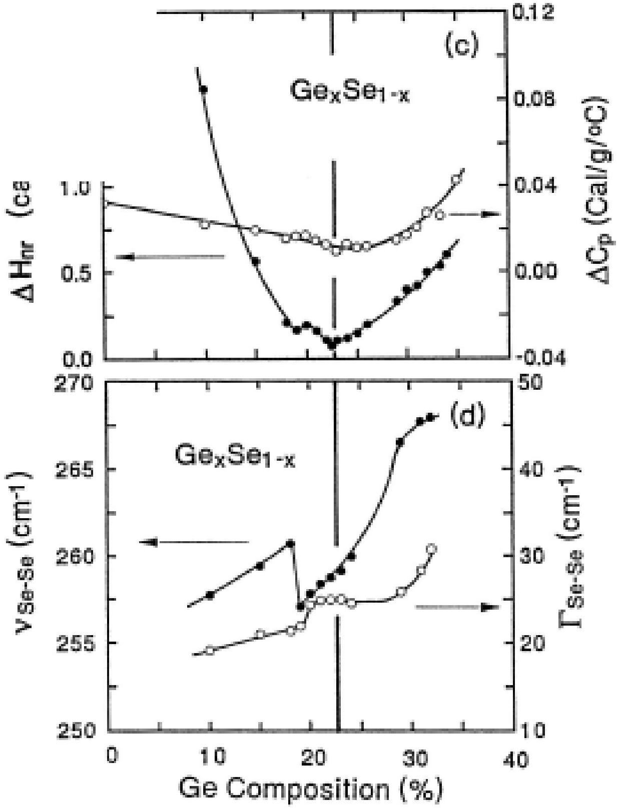


FIG. 3. (a) A_1 mode frequency of CS $\mathrm{Ge(S_{1/2})_4}$ units and (b) $\mathrm{Ge(Se_{1/2})_4}$ units, (c) relative changes in nonreversing heat flow $\Delta H_{\mathrm{nr}}(T_g)$ (filled circles) and specific heat change $\Delta C_p^{\mathrm{rev}}$ (open circles) from MDSC measurements, and (d) A_1 mode frequency of Se_n chains or rings (filled circles) and mode linewidth (open circles), each studied as a function of Ge concentration x in indicated binary glasses. The lines drawn through data points are to guide the eye.

PHYSICAL REVIEW B VOLUME 39, NUMBER 2 15 JANUARY 1989-I

Structural phase transitions in chalcogenide glasses

Keiji Tanaka
Department of Applied Physics, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

(Received 7 March 1988)

The composition dependence of the structural and electronic properties in chalcogenide glasses suggests that there exists a structural phase transition at the average coordination number of 2.67. Materials having smaller coordination numbers are characterized by molecular structures, and otherwise three-dimensional networks govern the properties. The result is discussed in light of topological and percolative arguments.

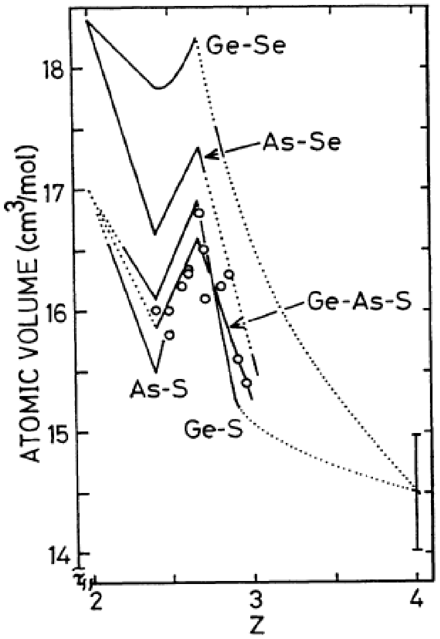


FIG. 2. The atomic volumes for various chacogenide glasses as a function of the average coordination number Z. The present results for Ge-As-S glasses are plotted by circles. Solid lines for binary alloys show representative tendencies with an accuracy of ±0.1 cm^3/mol. Dotted lines depict estimated behaviors.

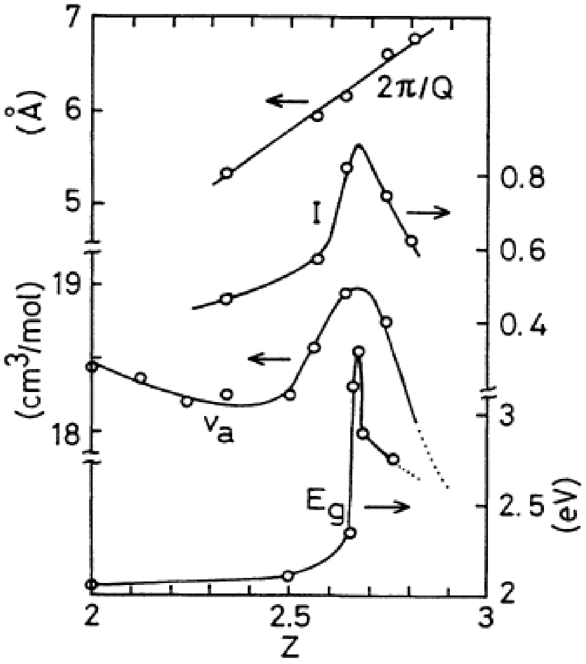


FIG. 10. The atomic volume v_a, the optical band-gap energy E_g, the FSDP position $2\pi/Q$, and the normalized FSDP intensity I for Si-Se glasses as a function of the average coordination number Z.

Journal of Optoelectronics and Advanced Materials Vol. 3, Nr. 3, September 2001, p. 703 - 720er

DISCOVERY OF THE INTERMEDIATE PHASE IN CHALCOGENIDE GLASSES

P. Boolchand, D. G. Georgiev, B. Goodman[a]

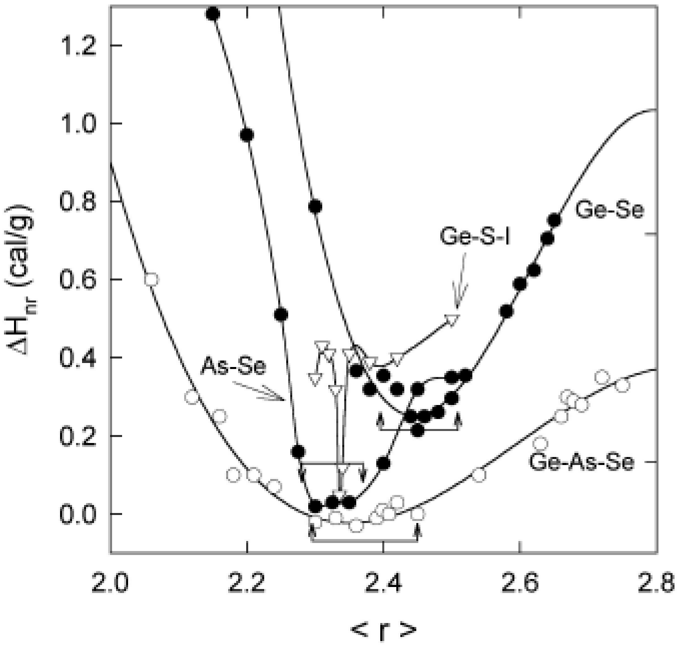


Fig. 4. Non-reversing heat, DH_{nr}, as a function of mean coordination number <r> for four different glass systems. The Ge-As-Se ternary shows the widest window (Ref. 5) while the Ge-S-I the narrowest (Ref. 7).

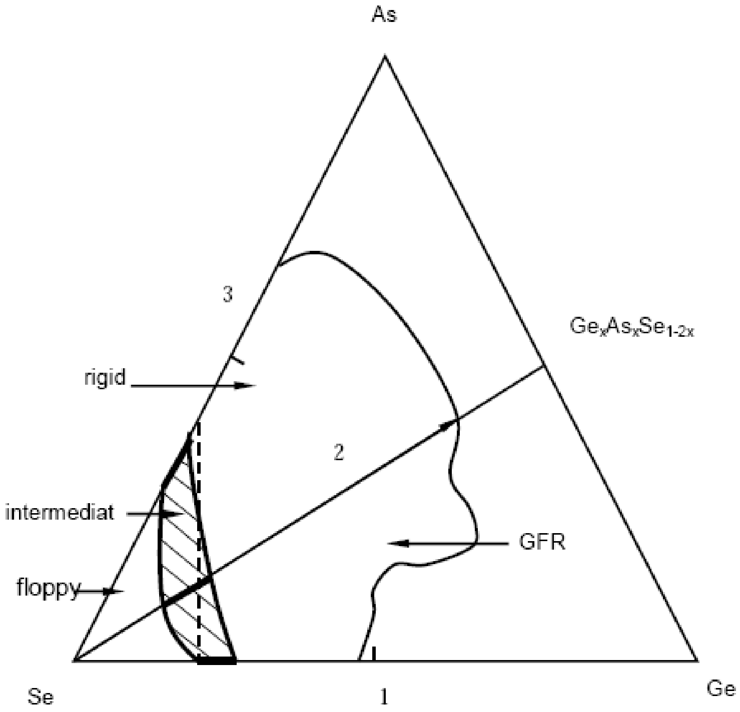
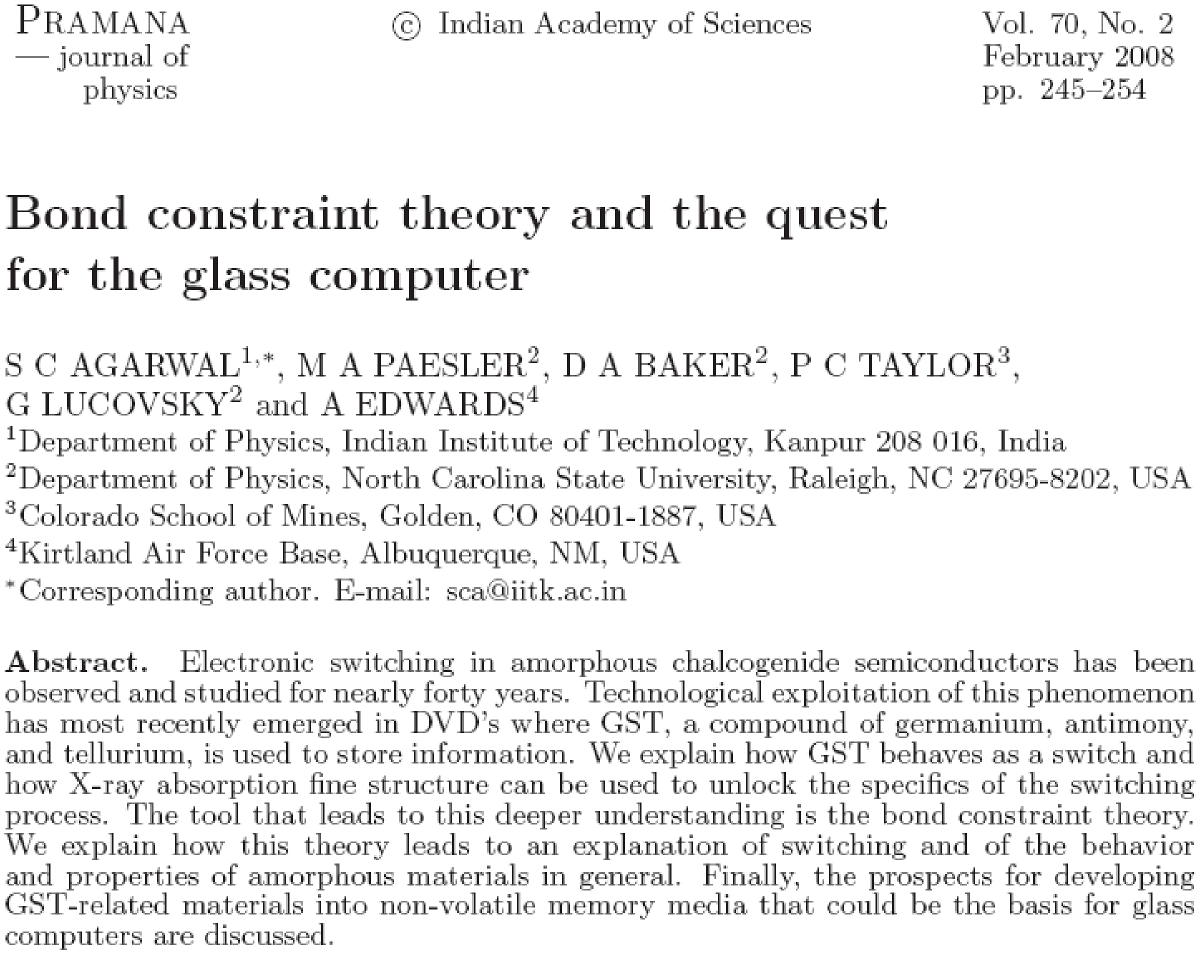


Fig. 5. The glass-forming region in the Ge-As-Se ternary glass system. The broken line corresponds to <r> = 2.40. The shaded region gives the opening of the intermediate phase between the floppy and the rigid phases, and it straddles the <r> = 2.40 line.

Topological model and bond constraint theory

- ✓ Applicability and limitations(?)
  - ➢ Explain many simple (binary) bulk glasses consisting of strong covalent bonds



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Bond constraint theory and the quest for the glass computer

S C AGARWAL[1,*], M A PAESLER[2], D A BAKER[2], P C TAYLOR[3],
G LUCOVSKY[2] and A EDWARDS[4]
[1]Department of Physics, Indian Institute of Technology, Kanpur 208 016, India
[2]Department of Physics, North Carolina State University, Raleigh, NC 27695-8202, USA
[3]Colorado School of Mines, Golden, CO 80401-1887, USA
[4]Kirtland Air Force Base, Albuquerque, NM, USA
*Corresponding author. E-mail: sca@iitk.ac.in

Abstract. Electronic switching in amorphous chalcogenide semiconductors has been observed and studied for nearly forty years. Technological exploitation of this phenomenon has most recently emerged in DVD's where GST, a compound of germanium, antimony, and tellurium, is used to store information. We explain how GST behaves as a switch and how X-ray absorption fine structure can be used to unlock the specifics of the switching process. The tool that leads to this deeper understanding is the bond constraint theory. We explain how this theory leads to an explanation of switching and of the behavior and properties of amorphous materials in general. Finally, the prospects for developing GST-related materials into non-volatile memory media that could be the basis for glass computers are discussed.

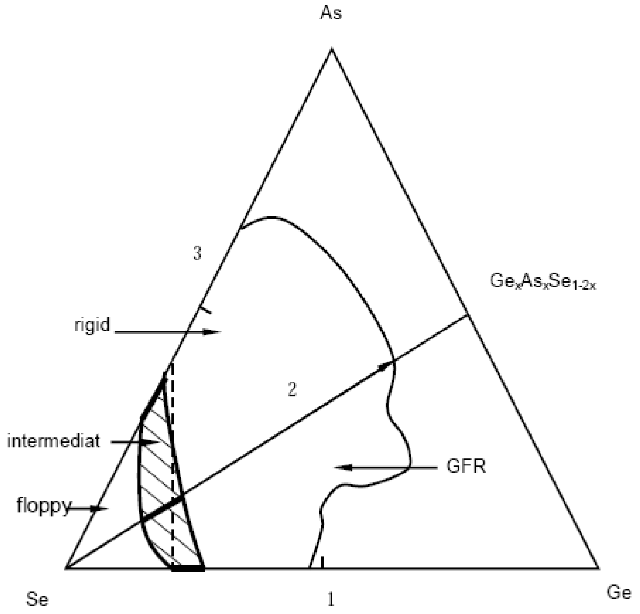

Fig. 5. The glass-forming region in the Ge-As-Se ternary glass system. The broken line corresponds to <r> = 2.40. The shaded region gives the opening of the intermediate phase between the floppy and the rigid phases, and it straddles the <r> = 2.40 line.