EXTERNALLY-ATTAINED FUNCTIONALITY IN NETWORK CHALCOGENIDE GLASSES exemplified by RADIATION-INDUCED EFFECTS

INTRODUCTION – Part A

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C O N T E N T
Part I: Introduction

1. Chalcogenide Vitreous Semiconductors (ChVS) as typical example of network glasses:
- **Short characterization of network glasses – I**
- **Short characterization of network glasses – II**
- **ChVSs – general definition;**
- **ChVS as polymers;**
- **ChVS semiconductors;**
- **ChVS as glasses;**
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--- Break – 17 pages ---

C O N T E N T
Part I: Introduction

2. Structural specificity of ChVSs (continuation):
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Short characterization of network glasses – I

GENERAL DEFINITIONS

NETWORK GLASSes:

✍ **glass-type matrix**
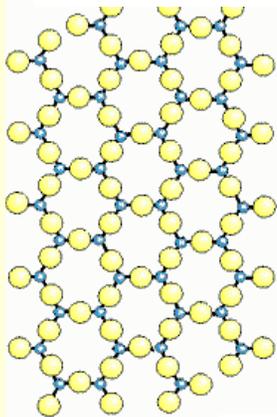(no long-range ordering because of deviations in bond lengths and angels)

✍ **infinite matrix**
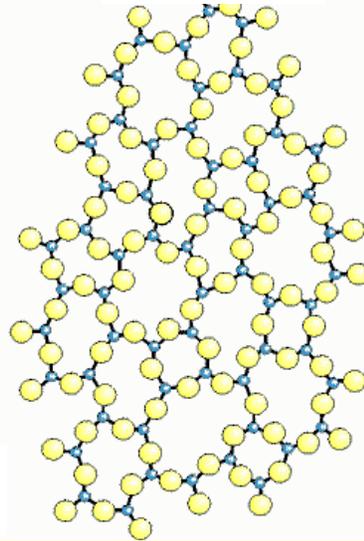(no any space constraints; surface imperfections and defects are ignored)

✍ **full saturation of interatomic bonding**
(no separate atoms like modificators beyond a network; all atoms are fully incorporated into a glass skeleton)

Crystalline   **Glassy**

A comparison of covalent-bonded crystalline and glassy-like A_2B_3 structures after Zachariasen:

each **blue cation** is three-fold coordinated and **yellow anion** is two-fold coordinated despite *structural disordering*
(in both crystalline and glassy-like objects) –
*effect of keeping
in local atomic coordination*

Short characterization of network glasses – II

GENERAL DEFINITIONS

Keeping in local atomic coordination does not mean keeping in structural ordering: the locally-ordered structural elements involving a few atoms can be arbitrary interconnected in a space, resulting in a full destroying of any ordering at the more extended length scale.

Each skydiver has
a simple set of symmetry rules
for himself
(two dissolved hands in the parties)

as well as

a simple set of symmetry rules
for bonding with neighbors
(hand-to-hand keeping),

while *there is a sufficient flexibility for different patterns of ordering* to be formed
on the scale of a few body lengths.

[Adapted from: *Salmon P.S. Nature Materials 2002 1 87-88*]

ChVSs – general definition

Chalcogenide vitreous semiconductors (ChVSs)
or, for simplicity, **chalcogenide glasses –**
the typical example of network glasses

represent themselves as
chemical compounds of
chalcogen atoms (S, Se or Te, but not O)
with some elements from
IV-th and V-th groups of the Periodic Table (typically As, Sb, Bi, Ge, etc.)
obtained by conventional melt quenching.

ChVSs – the unique disordered solids, being simultaneously

ℜ **Inorganic polymers**, in terms of their chemical nature,

ℜ **semiconductors**, in terms their electronic nature,

ℜ **glasses**, in terms of their thermodynamic nature.

ChVSs as polymers

In terms of their chemical nature,

ChVSs are <u>inorganic polymers</u>
(no long-range ordering while infinite-bonded polymer matrix)

with ♣ <u>fully-saturated covalent-bonded network</u>

(the feature No 1 – there are no separate atoms and atomic groups beyond polymer backbone)

and ♣♣ <u>spatially uniform distribution of elementary atomic groups</u>

(the feature No 2 – local ordering within more or less small atomic fragments uniformly distributed throughout a network is still possible).

Chemical elements in ChVS composition:

- two-fold coordinated **chalcogens S, Se and Te** (analogues of anions);
- three-fold coordinated **pnictogens P, As, Sb and Bi** (analogues of cations I);
- four-fold coordinated **tetragens (or tathogens) Si and Ge** (analogues of cations II).

Alternative chemical terminology:

Chalcogenide glasses $\Rightarrow$

Pnictochalcogenide glasses $\Rightarrow$ (P, As, Sb, Bi) – (S, Se, Te)

Tetrachalcogenide glasses $\Rightarrow$ (Si, Ge) – (S, Se, Te)

Pnictotetrachalcogenide glasses $\Rightarrow$ (P, As, Sb, B) – (Si, Ge) – (S, Se, Te)

ChVSs as semiconductors

In terms of their electronic nature,

ChVSs are semiconductors

only because of short-range ordering in the structure

(in terms of Gubanov, it means that we deal with **localization of electronic states in the valence- and conductive-band "tails"**),

which gives an additional number of unexpected and controversial features:

- **band-gap-related electronic properties** (p-type electrical conductivity, large Stocks shift of photolumonescence, etc.), revealed simultaneously with **high optical transmittance and absence of paramagnetic centers**;

- effect of **Fermi-level pinning** or **non-doping ability** (full saturation of covalent bonding in respect to the known $8 - N$ rule without typical donor and/or acceptor states within band gap).

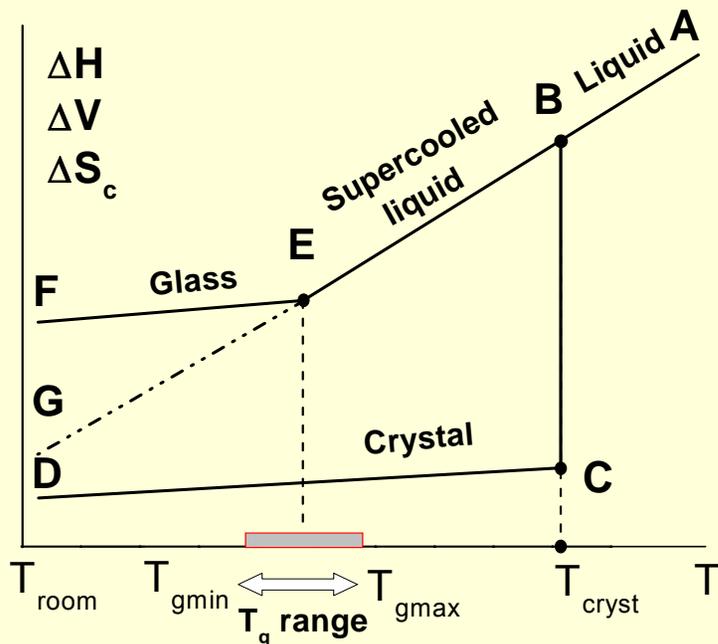**[Goryunova N.A. and Kolomiets B.T. Glasses semiconductors. –**
USSR Invention Diploma No 98: Appl. No. OT-7460 from 26.11.1969. Prior. Jan. 1955]

ChVSs as glasses

In terms of their thermodynamic nature,

ChVSs are <u>glasses,</u>

being obtained via conventional melt quenching technological route in a metastable state of supercooled liquid with its character feature – structural disordering.

ΔH
ΔV
ΔS_c

F — Glass
E
Supercooled liquid
B — Liquid A
G
D
Crystal
C

T_{room} T_{gmin} ⟷ T_{gmax} T_{cryst} T
T_g range

Enthalpic diagram
illustrating "thermodynamic" origin
of structural disordering in ChVS
frozen during quenching from melt liquid

Measure of structural disordering:
- ΔH – an excess of enthalpy;
- ΔV – an excess of free volume;
- ΔS_c – an excess of configurational entropy.

Specific temperatures:
T_{room} – near-room temperature;
T_g – glass transition temperature;
T_{cryst} – crystallization temperature.

Thermodynamic equilibrium states:
- AB – melt liquid;
- BE – supercooled liquid;
- EG – extrapolated supercooled liquid;
- CD – melt-grown crystal;
- EF – "as-prepared" glass.

Naturally-attained functionality of ChVSs – I

NATURALLY-ATTAINED FUNCTIONALITY of ChVSs
is determined by their main features:

- **high transmittance in IR spectral region from visible up to 20-25 μm** including
two commercial telecommunication windows at 3-5 and 8-12 μm
(since absorption bands of main ChVS-forming structural units are in far IR spectral region);

- **optical memory effects**
(because of high sensitivity to absorbed light photoexposure);

- **electrical memory effects**
(because of phase-changing ability in some ChVS compositions at the edge of glass-forming region).

Naturally-attained functionality of ChVS – II

Examples of possible application

Photograph of a chalcogenide glass rod
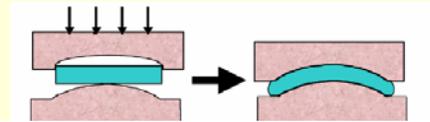
Sketch of molding route to make chalcogenide glass lense

Molded lenses with diffractive or spheric surfaces

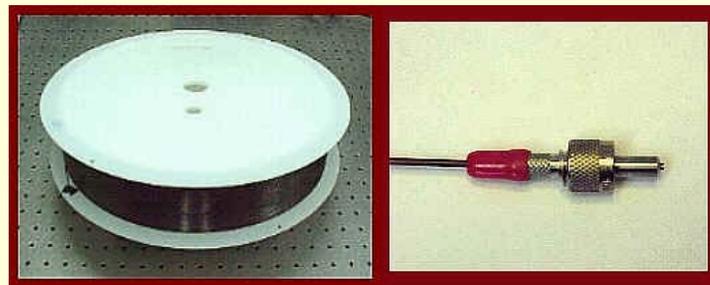Finished optical elements, prepared for IR device application

Naturally-attained functionality of ChVSs – III

Examples of possible application

Night vision camera equipped with ChVS lens and taken photograph
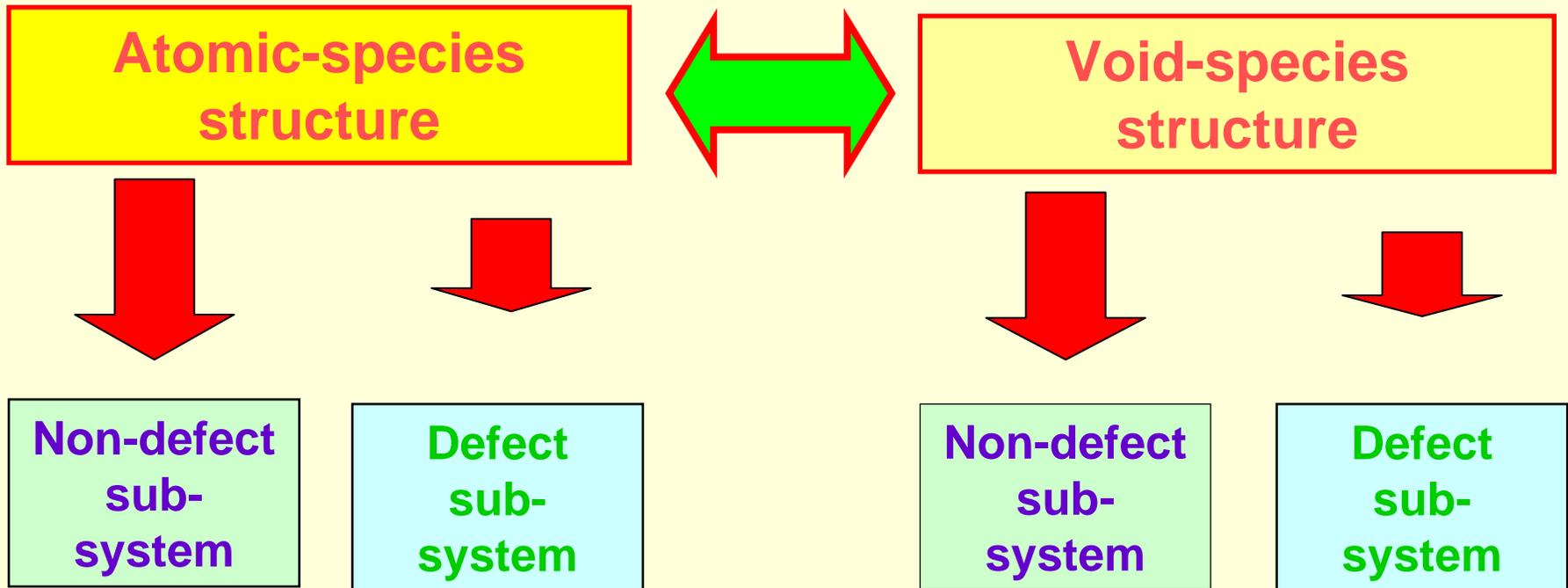

ChVS-based IR fibres

ChVS-based re-writable CD

Naturally-attained functionality of ChVS – IV

MAIN MANUFACTURERS in the field of ChVS-based optoelectronics

Product	Manufacturer	Glass composition	Typical application
AMTIR-1 AMTIR-3 C1 C2	Amorphous Materials Inc. *(Garland, Texas, USA)*	$Ge_{33}As_{12}Se_{55}$ $Ge_{28}Sb_{12}Se_{60}$ As-Se-Te As_2Se_3	IR lenses IR lenses Telecommu-nication fibers
GASIR 1/0108 GASIR 2/0308	UMICORE IR Glass *(Acigne, France)*	$Ge_{22}As_{20}Se_{58}$ $Ge_{20}Sb_{15}Se_{65}$	IR lenses IR lenses
OVONICS	Energy Conversion Devices Inc. *(Rochester Hills, Michigan, USA)*	$Ge_2Sb_2Te_5$, $GeSb_2Te_4$, Ge_4SbTe_5, InSbTe, $SnSb_2Te$	Flash memory; CD/RW; DVD/RW

Levels of structural organization of ChVS

Atomic-species structure	⟷	Void-species structure

Non-defect sub-system	Defect sub-system	Non-defect sub-system	Defect sub-system

Non-defect atomic-species structure of ChVS – I

Atomic species – glass-forming structural units (s.u.) randomly distributed within a network (pyramidal $AsS_{3/2}$ atomic groups; in the case of non-stoichiometric ChVSs, another types of s.u. appear in atomic-species structure, such as $AsS_{4/2}$, $S_{2/2}$, etc.)

Length scales of order in ChVSs
(in terms of S.R. Elliott [Nature, 1991, v. 354, 445-452]):

♣ **short-range order ShRO** **(0.2-0.5 nm)** within individual coordination polyhedra;

ShRO in ChVSs is described by
      number and types of nearest neighbors around an origin atom,
      nearest-neighbor bond-length,
      bond angle,
      fraction of wrong homopolar chemical bonds per coordination polyhedron, etc.

Non-defect atomic-species structure of ChVS – II

**Length scales of order in ChVSs
(in terms of S.R. Elliott [Nature, 1991, v. 354, 445-452]):**

♣ **medium-range order MRO** – the next highest level of structural organization beyond ShRO, stretched **from 0.5 to 2.0 nm**;

Three types of MRO in ChVSs:
♣♣ **near-MRO (~0.5 nm),**
which describes the type of connection between individual coordination polyhedra (corner-, edge- or face-sharing s.u.);
♣♣ **intermediate-MRO (~0.5-0.8 nm),**
which describes the well-defined relative orientations in mutually-interconnected coordination polyhedra, which, thereby, can be accepted as the "super-structural" units *s.s.u.* or, in other words, the aggregates of basic polyhedra connected together
to form regular rings or three-dimensional clusters;
♣♣ **far-MRO (~0.8-2.0 nm),**
which describes the local dimensionality of covalent-bonded glass network;
the local dimensionality of 3 corresponds to structural isotropy,
the local dimensionality of 2 – to layer-like connection between s.u.,
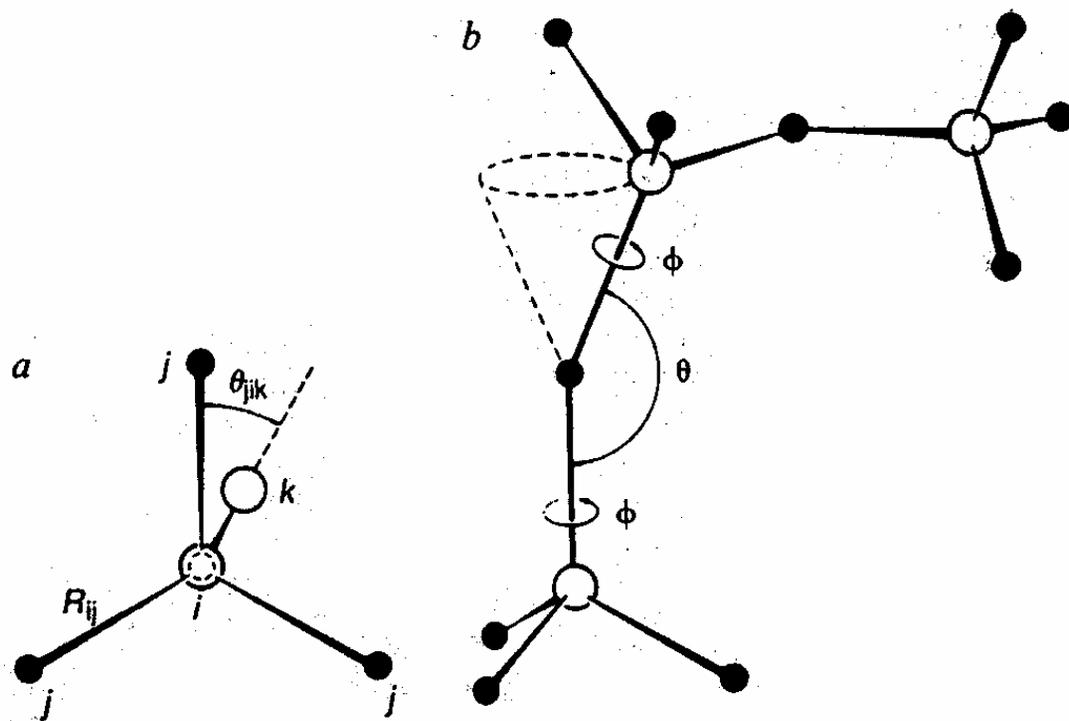the local dimensionality of 1 – to chain-like connection between s.u. and
the local dimensionality of 0 – to isolated clusters in a glass network.

Non-defect atomic-species structure of ChVS – III

Length scales of order in ChVSs
(in terms of S.R. Elliott [Nature, 1991, v. 354, 445-452]):

Schematic illustrations showing some elements of ShRO (a) and MRO (b) in v-GeX$_2$ (X – chalcogen atom):

i, j and k – types of atoms;
θ_{ijk} – bond angle;
R_{ij} – nearest-neighbor bond-length;
ϕ – dihedral angle.
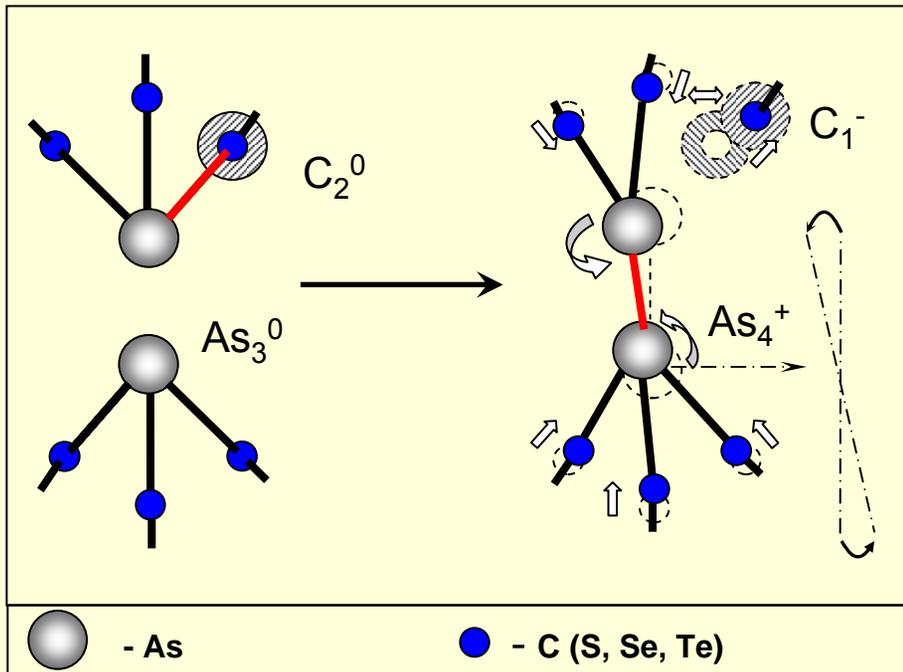
Non-defect atomic-species structure of ChVS – IV

Length scales of order in ChVSs
(in terms of S.R. Elliott [Nature, 1991, v. 354, 445-452]):

♣ **long-range order LRO** within whole glass bulk **(>2.0 nm)** is absent;
sometimes, LRO is associated with <u>macroscopic inhomogeneities and large-scale imperfections</u>
(voids, column-grown morphology, bubbles remaining, etc.).

Defect atomic-species structure of ChVS – I

Specific kind of structural defects in ChVSs – **coordination topological defects (CTDs)** – can be considered as **local deviations from full saturation of covalent-like chemical bonding within a glass network**, typically caused by external influences.
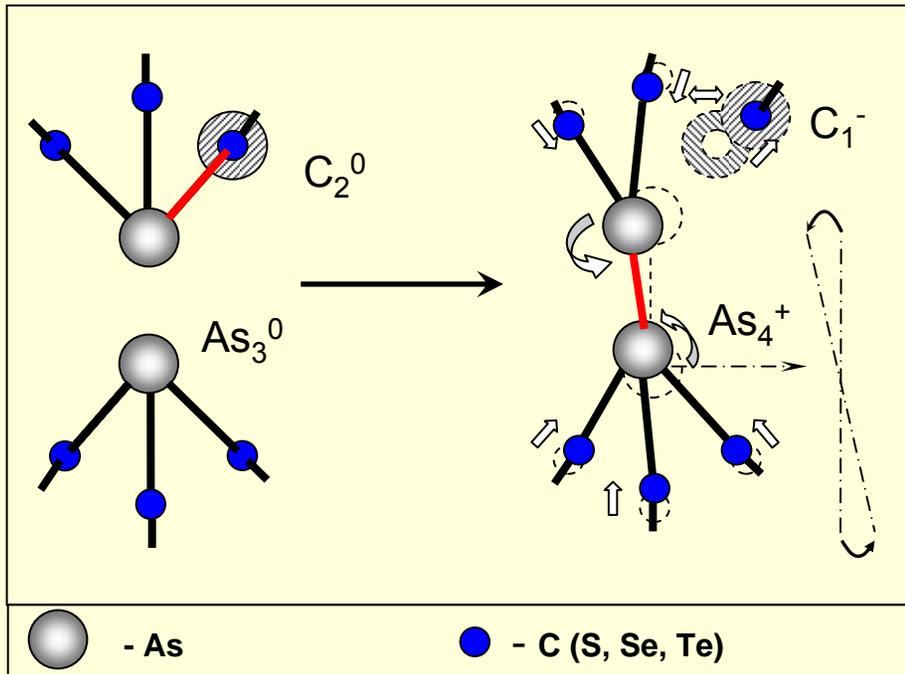

C_2^0

As_3^0

C_1^-

As_4^+

- As   - C (S, Se, Te)

CTDs appear in a glassy-like network

♣ by **pairs** (**under- and over-coordinated, negative and positive ones, but always – diamagnetic**), providing full conserving of average bonding and electroneutrality of the sample;

♣ in the result of **destruction-polymerization transformations** or **bond-switching reactions** – one covalent bond is destroyed, but another one is formed instead of the former in its nearest vicinity (finally, two atoms of a glassy-like network obtain local atomic coordination, which does not comply the well-known $8 - N$ rule.

Schematic presentation showing CTD-pair formation in v-As_2C_3 (the upper index in defect signature (superscript) means electrical charge of atom, and the lower one (subscript) – coordination number). Instead of heteropolar As-C bond, the homopolar As-As bond is formed. This process is accompanied by sufficient atomic displacements at ShRO and MRO nanostructural levels (indicated by arrows).

Defect atomic-species structure of ChVS – II

C_2^0

As_3^0

C_1^-

As_4^+

⬤ - As   🔵 - C (S, Se, Te)

CTDs in ChVVs: short historical overview

Electronic configurations of CTDs were proposed, taking into account **Anderson's postulate on negative U-centres** in ChVSs. It was assumed that all states within band gap corresponded to double-paired carriers with opposite spins, their energies forming a quasi-continuous spectrum.

According to this postulate, N. Mott, E. Davis and R. Street put forward the model of **CTDs in the form of D-centres or unsaturated "dangling" bonds**.

Later, the model of **C-centres** or **valence alternation pairs (VAPs)** was developed by M. Kastner, D. Adler and H. Fritzsche and,
finally,
Kastner's model of **intimate valence alternation pairs (IVAPs),** considering Coulomb interaction between opposite charged CTDs, was proposed.

R. Street was the first who used CTD-concept to explain reversible photostructural transformations in thin layers of ChVSs, connecting their origin with a so-called **exciton self-trapping.**

**EXTERNALLY-ATTAINED FUNCTIONALITY
IN NETWORK CHALCOGENIDE GLASSES
exemplified by
RADIATION-INDUCED EFFECTS**

To Be Followed by

Part B of Introduction

EXTERNALLY-ATTAINED FUNCTIONALITY IN NETWORK CHALCOGENIDE GLASSES exemplified by RADIATION-INDUCED EFFECTS

Introduction Continued – Part B

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'Feb. 22, 2006

Non-defect void-species structure of ChVS – I

Void species – free-volume nanovoids within glassy-like network stabilized technologically during melt quenching:
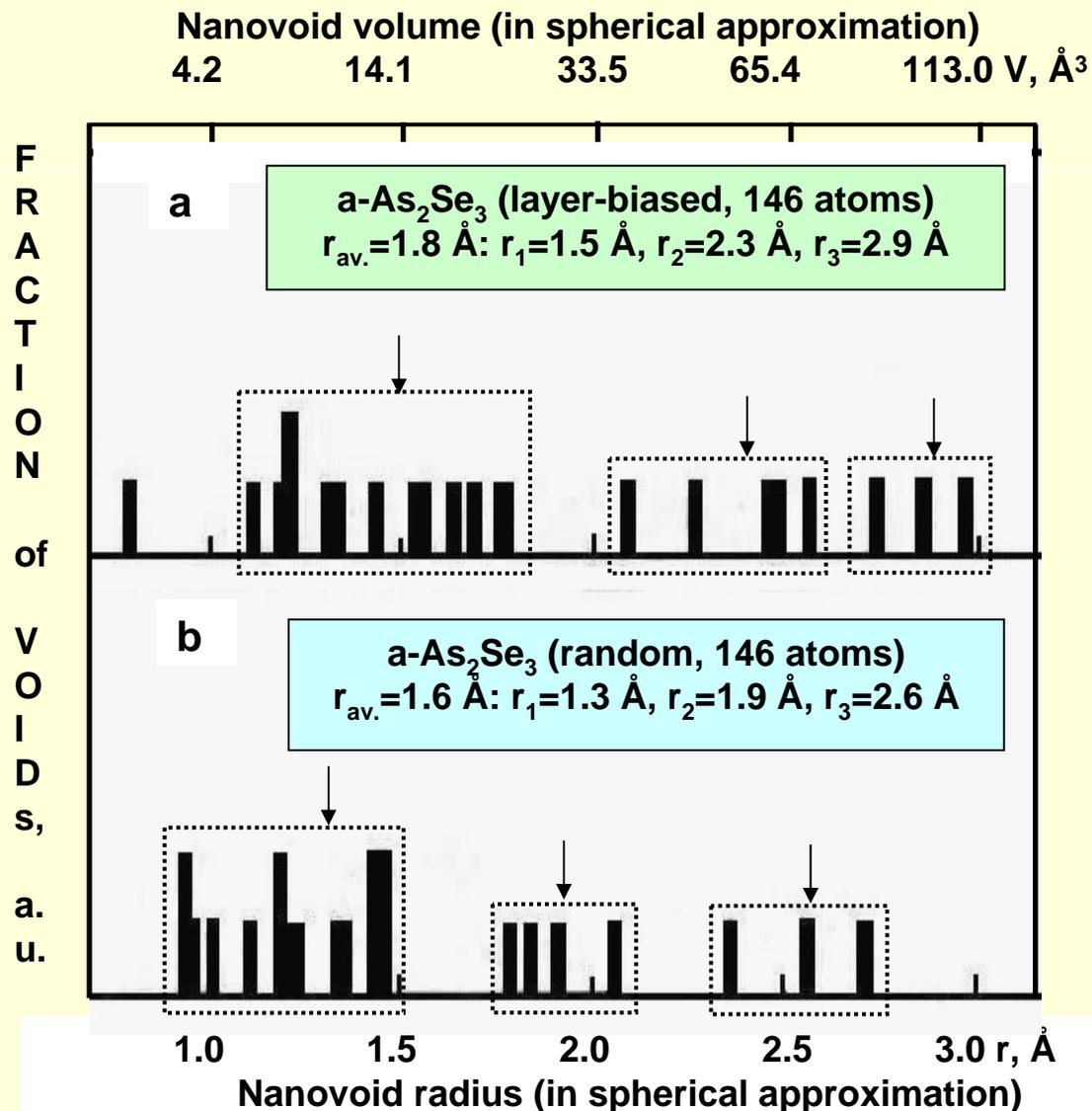
• *BFSA-based free-volume nanovoids* (BFSA – bond-free solid angle) –
stereometric specificity in local bond-charge density distribution around network-forming atoms (*from ~10-15 Å³ up to ~30-50 Å³*);

• *quasi-network fluctuational free-volume nanovoids* –
technologically-frozen atomic fluctuations such as network deformations including boundary shifts of bridge chalcogen atoms (*from 5-10 Å³ up to 40 Å³*);

• *geometrical free-volume nanovoids* –
topological inconsistencies between different glass-forming s.u. such as $AsS_{3/2}$ pyramids and $GeS_{4/2}$ tetrahedra (*up to ~100 Å³, the lower size limit is difficult to estimate*)

Size-distribution of free-volume nanovoids (topology) within a glass-forming network is determined mainly by
> glass composition (1) and
> glass-preparation technology (2).

Non-defect void-species structure of ChVS – II

Theoretical models

Nanovoid volume (in spherical approximation)

4.2   14.1   33.5   65.4   113.0 V, Å³

F R A C T I O N   of   V O I D s,   a. u.

a — a-As₂Se₃ (layer-biased, 146 atoms)
$r_{av.}=1.8$ Å: $r_1=1.5$ Å, $r_2=2.3$ Å, $r_3=2.9$ Å

b — a-As₂Se₃ (random, 146 atoms)
$r_{av.}=1.6$ Å: $r_1=1.3$ Å, $r_2=1.9$ Å, $r_3=2.6$ Å

1.0   1.5   2.0   2.5   3.0 r, Å
Nanovoid radius (in spherical approximation)

Interpretation in terms of Popescu M.
[Popescu M.A. *J. Non-Cryst. Solids*, 1980, <u>35-36</u>, 549]

<u>*Calculation procedure:*</u>
Starting from a given position inside the model, the distance to the nearest atom was calculated.
Afterwards, giving small aleatory moves to the position of the initial hole centre, it were retained only those moves which led to a higher radius of the hole.
Finally, the maximum radius of hole was calculated. Repeating this procedure at different starting positions inside chosen model, the complete void-radius distribution was obtained.

Non-defect void-species structure of ChVS – III

BFSA-based free-volume nanovoids

Interpretation in terms of
BOND-FREE SOLID ANGLE (BFSA) concept
of M.Kastner [Kastner M. *Phys. Rev. B*, v. 7, No 12, 5327-5252]

Local bond-charge density distribution around some network-forming atoms in ChVS:

| Chalcogen | Pnictogen | Tetragen |

C_2^0

BFSA$_0 \approx 0.72$ sphere

P_3^0

BFSA$_0 \approx 0.5$ sphere

T_4^0

BFSA$_0 \approx 0$ sphere

Non-defect void-species structure of ChVS – IV

## Quasi-network fluctuational free-volume nanovoids
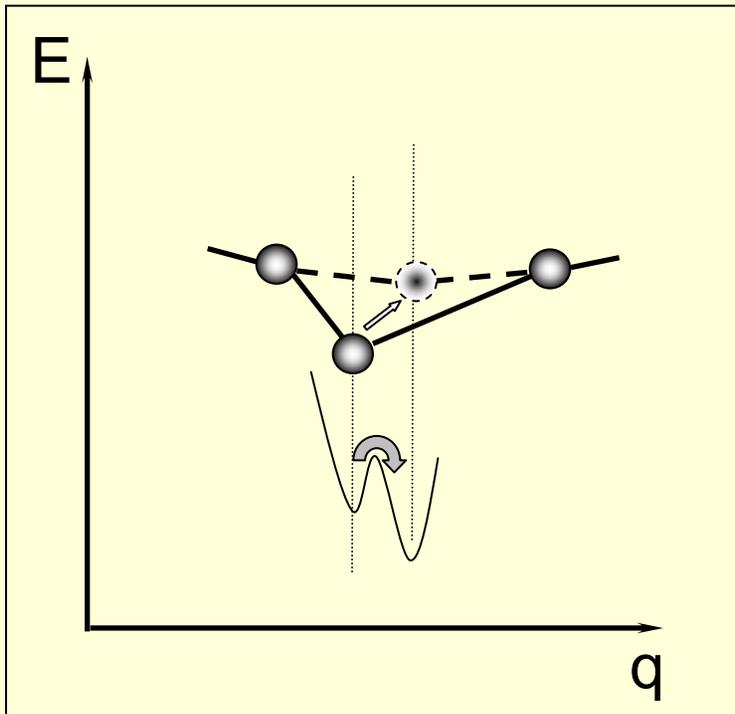
Boundary shifts/displacements
(atomic fluctuations)
of bridge chalcogen atoms
within a so-called <u>soft atomic configuration</u>
(–Cl–**Cl**–Cl– chain)
described by double-well potential
(q – configurational coordinate).

Non-defect void-species structure of ChVS – V

Geometric origin of void-species structure in crystalline counterparts of ChVS:

an example of GeS$_2$

The total fraction of geometrical free volume ($\sim$50-100 Å^3) – 25-30 % in dependence on ChVS composition.
Steric inconsistencies between structural units within glass-forming backbone – the main source of geometrical nanovoids: **1D-dimensional** (S$_{2/2}$ chains and rings), **2D-dimensional** (AsS$_{3/2}$ pyramids) and **3D-dimensional** (GeS$_{4/2}$ tetrahedra)


| a | b | c |
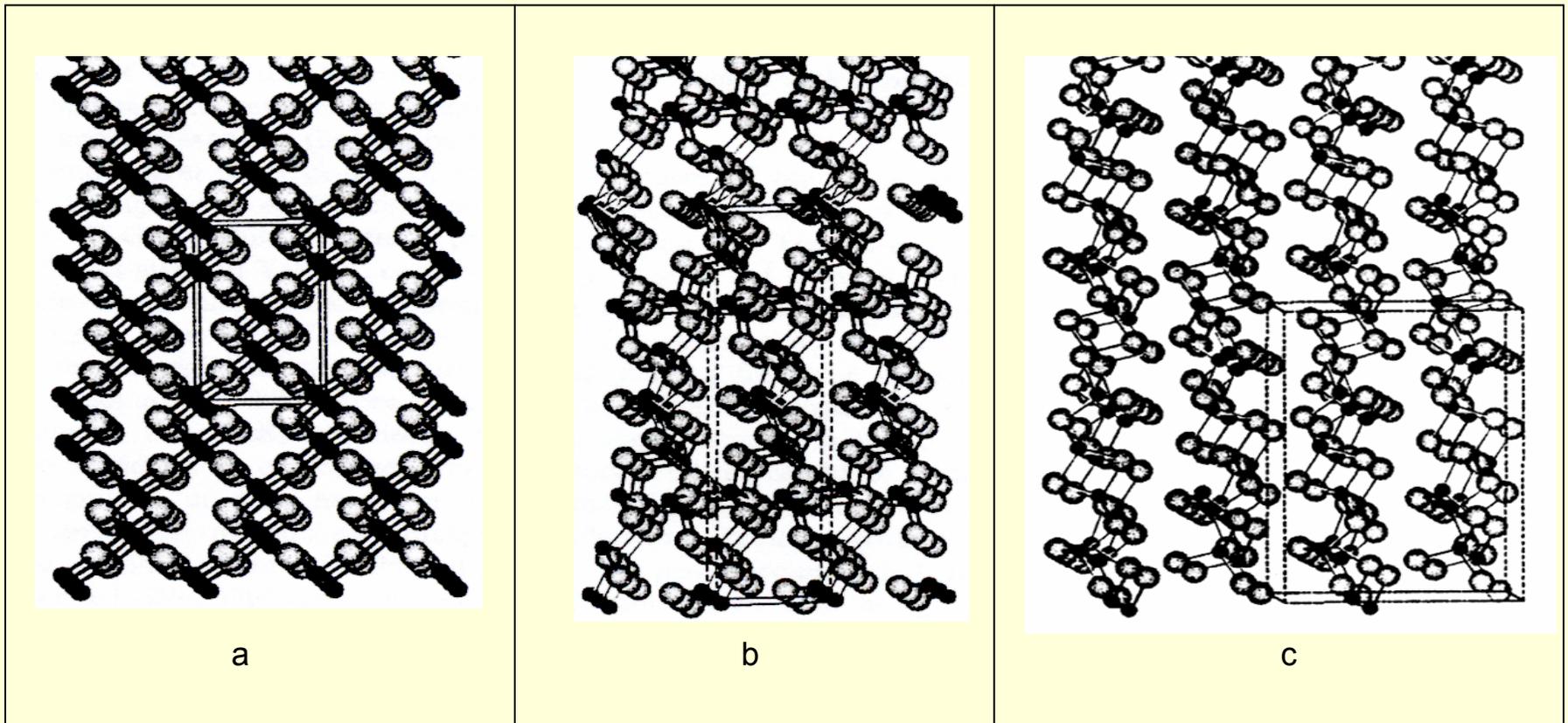
Typical fragments of crystalline structure of high-temperature α- (a), low-temperature β- (b) and high pressure II- (c) modifications of GeS$_2$
(Ge atoms are denoted by small solid circles and S atoms – by large open circles)
[Adapted from: Miyauchi K., Qiu J., Shojiya M., Kawamoto Y. and Kitamura N., *J. Non-Cryst. Solids* 279 (2001) 186-195].

Defect void-species structure of ChVS – I

On the topological origin
of defect-related void-species structure in ChVS

- As

- C (S, Se, Te)
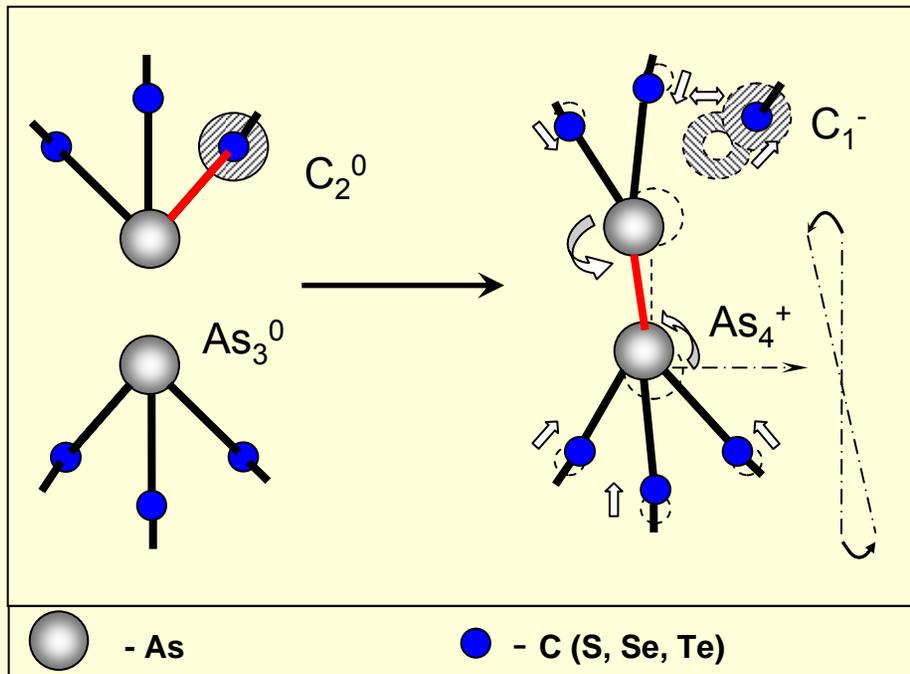
**Schematic presentation
showing MRO structural transformations
accompanied by free volume appearance
in a vicinity of as-formed CTD-pair in v-As$_2$S$_3$**

Formation of **As-As** covalent chemical bond instead of destroyed **As-S** one (nearby positively charged CTD) leads to **the local densification of atomic network**, while in the vicinity of the negatively charged CTD **atomic packaging is released** due to free volume appearance (crosshatched).

The lack of one covalent chemical bond at the negatively charged CTD and its shift along existing bond towards neighboring directly-bonded atom leads to the appearance of free-volume (nano)void (identified by PALS measurements).

These MRO transformations associated with free-volume nanovoids offer necessary conditions for CTDs **stabilization** in a glassy-like network, preventing their **backward disappearing**. **Additional CTD-conserved bond-switching act without change in bond type** – space separation between over- and under-coordinated atoms within CTD-pair at the final stage.
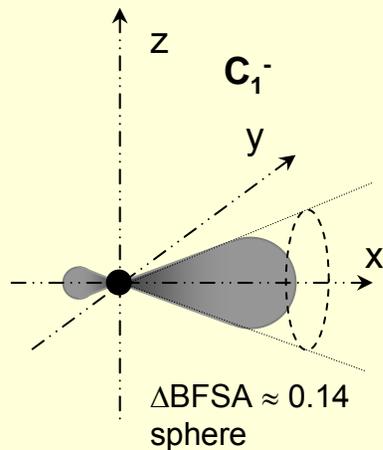
Defect void-species structure of ChVS – II

Additional BFSA-based input
## in defect void-species structure of ChVS
in terms of M.Kastner [Kastner M. *Phys. Rev. B*, v. 7, No 12, 5327-5252]

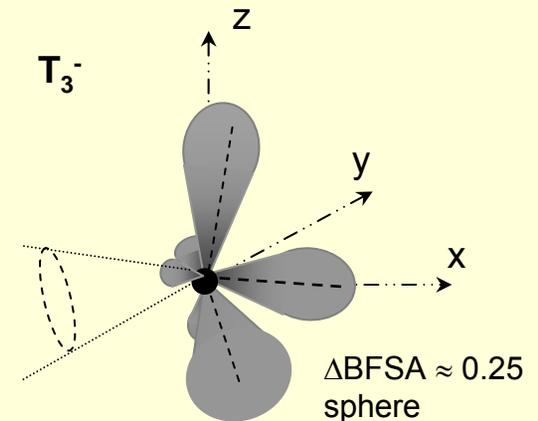### Local bond-charge density distribution around some defect configurations in ChVS

Negativelly-charged under-coordinated chalcogen atoms: C_1^- defects

C_1^-

z

y

x

$\Delta BFSA \approx 0.14$ sphere

Negativelly-charged under-coordinated pnictogen atoms: P_2^- defects

P_2^-

z

y

x

$\Delta BFSA \approx 0.17$ sphere
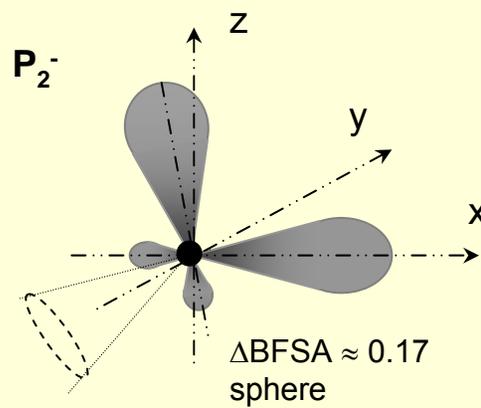
Negativelly-charged under-coordinated tetragen atoms: T_3^- defects

T_3^-

z

y

x

$\Delta BFSA \approx 0.25$ sphere

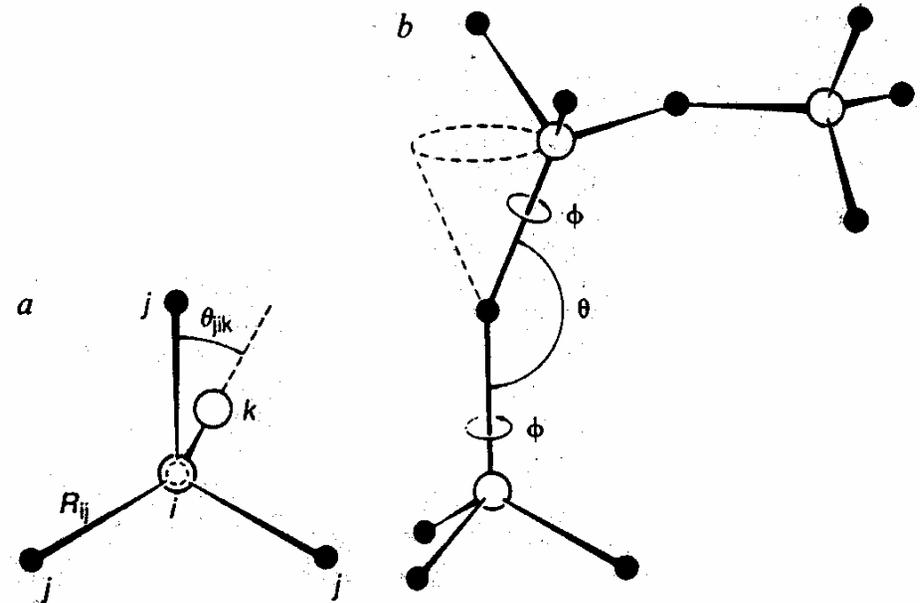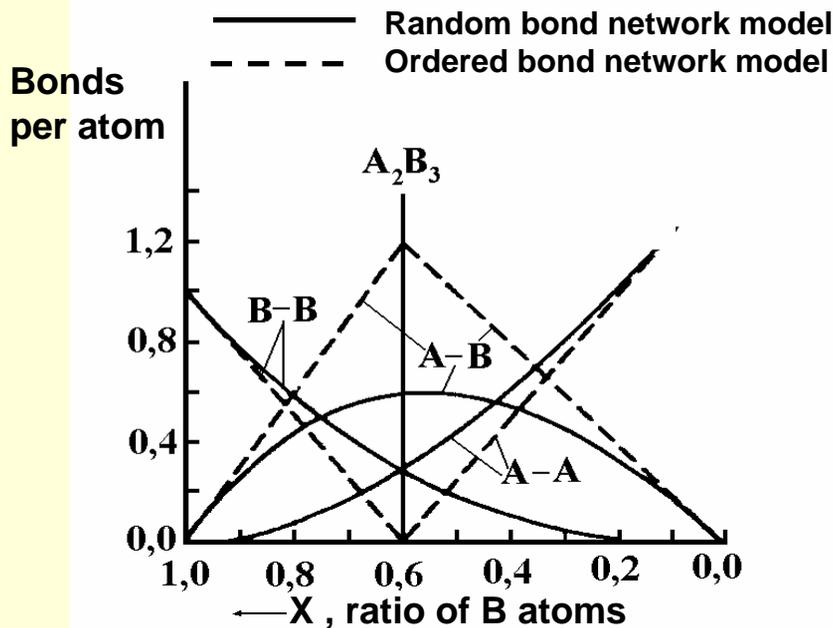# Disorder in non-defect covalent-bonded glass networks – I

Can we change DISORDER in covalent-bonded glass networks ?

CTD-free NETWORKs
(a) full saturation of covalent bonding (no local deviations from *8-N* rule)
(b) uniform distribution of electrical charge (no local electrical charges)

| Chemical disorder (bond statistics or covalent bond distribution)	Topological disorder (atomic- and void-species arrangement)

Covalent bond statistics in v-A_2B_3 within random and ordered bond network models.

Schematic illustration showing deviations in bond angle θ_{ijk}, nearest-neighbour bond-length R_{ij} and dihedral angle ϕ in v-GeX_2 (after S.R. Elliott, 1991).

Disorder in non-defect covalent-bonded glass networks – II

Can we change DISORDER in covalent-bonded glass networks ?

CTD-free NETWORKs	
Chemical disorder (bond statistics or covalent bond distribution)	**Topological disorder** (atomic- and void-species arrangement)
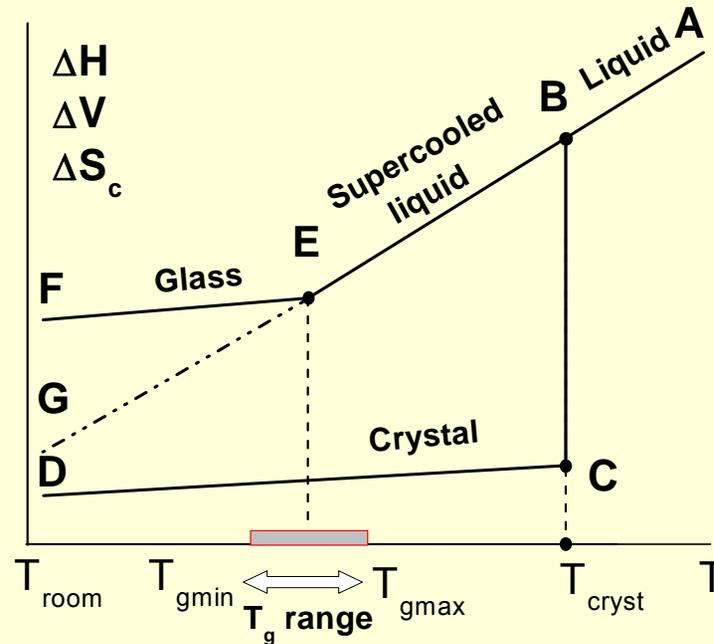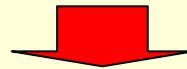
Enthalpic diagram illustrating "technological" origin of structural disordering in ChVS frozen during quenching from melt liquid
(ΔH, ΔV and ΔSc – excesses of enthalpy, free volume and configurational entropy)

Disorder in defect covalent-bonded glass networks

Can we change DISORDER in covalent-bonded glass networks ?

CTD-related NETWORKs	
Coordination disorder (local Z-deviations: over-under-coordinated atomic pairs or CTDs)	**Electrostatic disorder** (local Q-deviations: negative-positive electrical charge excesses)

C_2^0

As_3^0

C_1^-

As_4^+
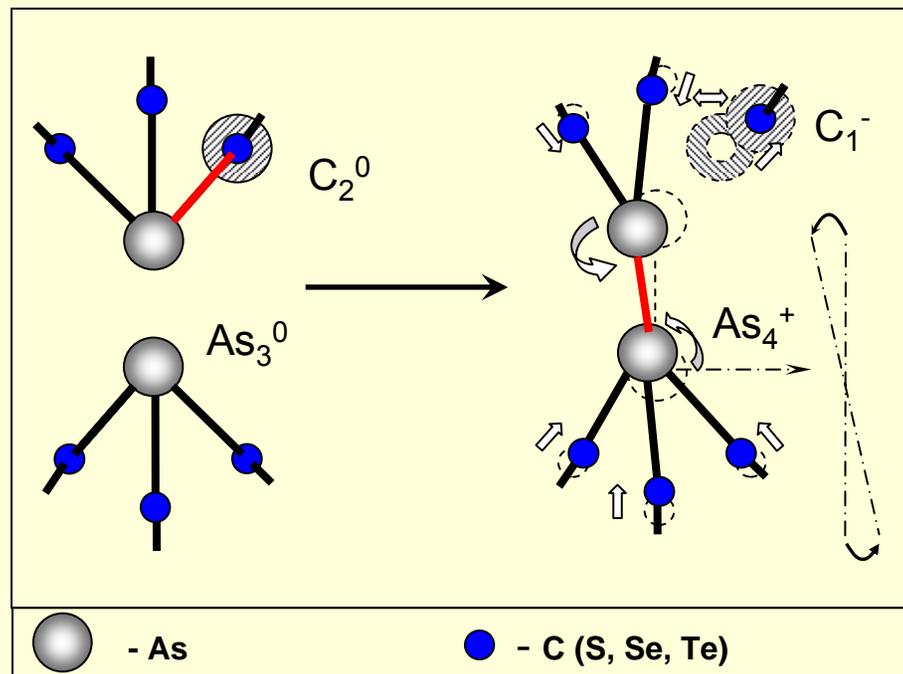
Schematic presentation showing local Z- and Q-deviations in ChVS owing to CTD formation (an example of v-As_2C_3)

- As

- C (S, Se, Te)

Limitation factors for radiation stability of ChVS

Can we change DISORDER in covalent-bonded glass networks ?

CTD-free NETWORKs	
Chemical disorder (bond statistics or covalent bond distribution)	**Topological disorder** (atomic- and void-species arrangement)

CTD-related NETWORKs	
Coordination disorder (local Z-deviations: over-under-coordinated atomic pairs or CTDs)	**Electrostatic disorder** (local Q-deviations: negative-positive electrical charge excesses)

From one hand,
ChVS will be positively distinguished by high radiation stability

??? "Confirmations" ???

The first report on radiation tests in ChVS-based ovonic threshold switches:
[Ovshinsky S.R., Eans E.J., Nelson D.L., Fritzsche H. Radiation hardness of ovonic devices. –
IEEE Trans. Nucl. Sci., 1968, 15, No.6, 311-321]

🕸🕸🕸 **Specific experimental constraints and disadvantages of these tests:** 🕸🕸🕸

✆ *the compositional constraint*
by selection of **Te-based ChVSs with high saturation of covalent bonding** and, consequently, small defect formation ability;

✆ *the technological constraint*
by **cathode-sputtered films with very small thickness** of about 1 μm;
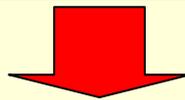
✆ *the limitation factors of radiation treatment*
by too small absorbed doses chosen **without any respect to the sensitivity threshold of ChVSs** (in spite of huge energies E>>1 MeV of neutron flux, X-rays or γ-quanta).

Pre-conditions for high radiation sensitivity in ChVS

Can we change DISORDER in covalent-bonded glass networks ?

CTD-free NETWORKs	
Chemical disorder (bond statistics or covalent bond distribution)	Topological disorder (atomic- and void-species arrangement)

| CTD-related NETWORKs	
Coordination disorder (local Z-deviations: over-under-coordinated atomic pairs or CTDs)	Electrostatic disorder (local Q-deviations: negative-positive electrical charge excesses)

BUT ⬇ BUT

From the other hand,

ChVSs will be sensitive to external influences,

because of
- **high steric flexibility** proper to glassy-like network with low average coordination
- relatively large content of **structurally intrinsic free volume** frozen near glass transition
- specific **lp-character of electronic states localized at a valence-band top**

An enthalpic paradigm of externally-attained functionality

ΔS_c

, measured in configuration entropy ΔS_c

ΔS_c
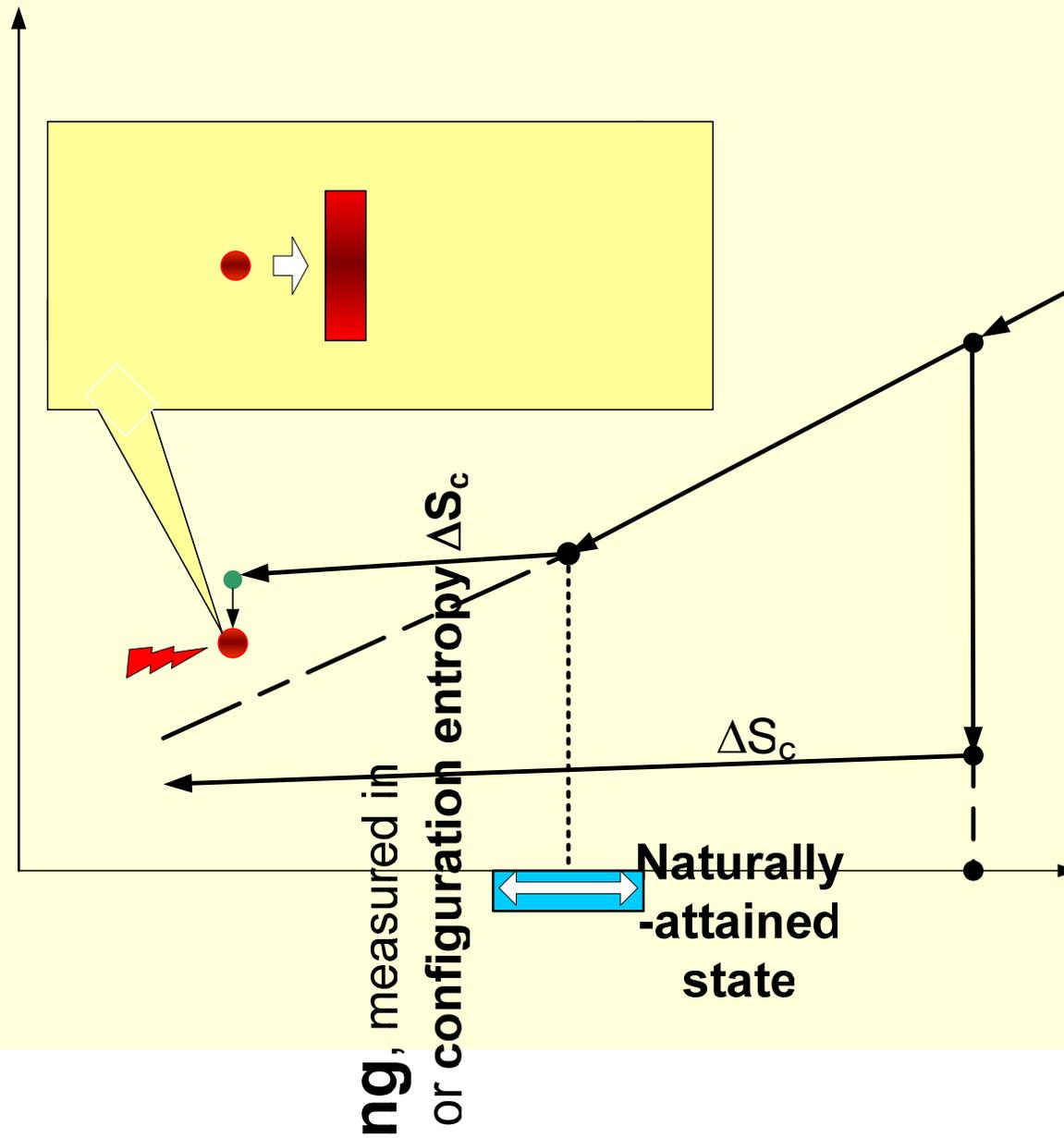
Naturally -attained state

**Externally-a
with differen
of *structura
in respect to
naturally-a

Thermodynamic origin of externally-attained functionality in ChVSs – II

A sequence of correlations for radiation-induced external functionality

First level of correlations:

Naturally-Attained State
(in G point)
is a direct function of:
Glass Composition + Melt-Quenching Technology + Natural Physical Ageing

Second level of correlations:

Physical Ageing
is a direct function of
Disordering
**(chemical/topological – CTD-free;
chemical/topological/coordination/electrostatic – CTD-related networks)**

Third level of correlations:

Disordering
is dependent on
External Influence ≡
≡ Externally-Attained Functionality
(deviation from G point)

A comparison between naturally- and externally-attained functionality in ChVS

On the controversy and structurally-intrinsic interconnections between naturally-attained and radiation-induced externally-attained functionality in ChVS

Natural physical ageing (NPhA)	Expected result of external influence
General rule of NPhA: NPhA as infinitely-stretched time-dependent process always tends the system ***towards a more thermodynamically-equilibrium state*** close to the extrapolated states of supercooled liquid, this process being followed by free-volume (alternatively – configurational entropy or enthalpy) release.	***Any tendencies are possible*** (ordering and/or disordering ones) in dependence on glass composition, technical parameters and conditions of external treatment.
Dynamics of NPhA is strictly developed ***towards replacing of more quick relaxation processes by slower ones***, showing the known stretched-exponential behaviour (the KWW relaxation).	External influence (irradiation) accelerates the NPhA so that ***the quicker time-dependent components become dominant***, while stretched-exponential behaviour left unchangeable.
Main consequences **of <u>new radiation-induced external functionality</u> in ChVSs:**	
• **additional input in NPhA** **(<u>to stabilize or change (to modify)</u> their exploitation properties);** • **acceleration effects in post-irradiation NPhA** **(<u>to accelerate or attain more quickly</u> the final more equilibrium state).**	

Methodology of radiation-induced effects in ChVS – I

**Radiation-induced effects –
the best example of externally-attained functionality in ChVSs**

Pre-condition No 1: correct choice of ChVS (bulk samples):
- **direct synthesis in evacuated quartz ampoules**
- **standard rocking-furnace technique followed by air quenching**
- **additional air-annealing of ingots near T_g during 3 to 5 h**
- **plates about 1 to 2 mm in thickness polished with 1 μm alumina**

Pre-condition No 2: correct choice of irradiation facility
(main advantages of ^{60}Co γ-irradiation – the typical example of high-energy photon flux treatment):

✺ **Average energy of ^{60}Co γ-quanta is as high as 1.25 MeV,**
which is greater than the dual rest energies of electrons (1.02 MeV), determining the high-energetic character of the observed RIEs.
✺✺ **γ-irradiation is characterized by a high penetration ability**
and, consequently, a high uniformity of the produced structural changes throughout the sample thickness.
✺✺✺ **γ-irradiation does not cause any direct atomic displacements**
resulting in surface macro-damages, craters or cracks, proper to high-energetic corpuscular radiation (accelerated electrons, protons, neutrons).
✺✺✺✺ **Nuclear transmutations**
(such as induced by reactor neutrons) essentially restricted experimental possibilities for RIEs observation do not take place during γ-irradiation.
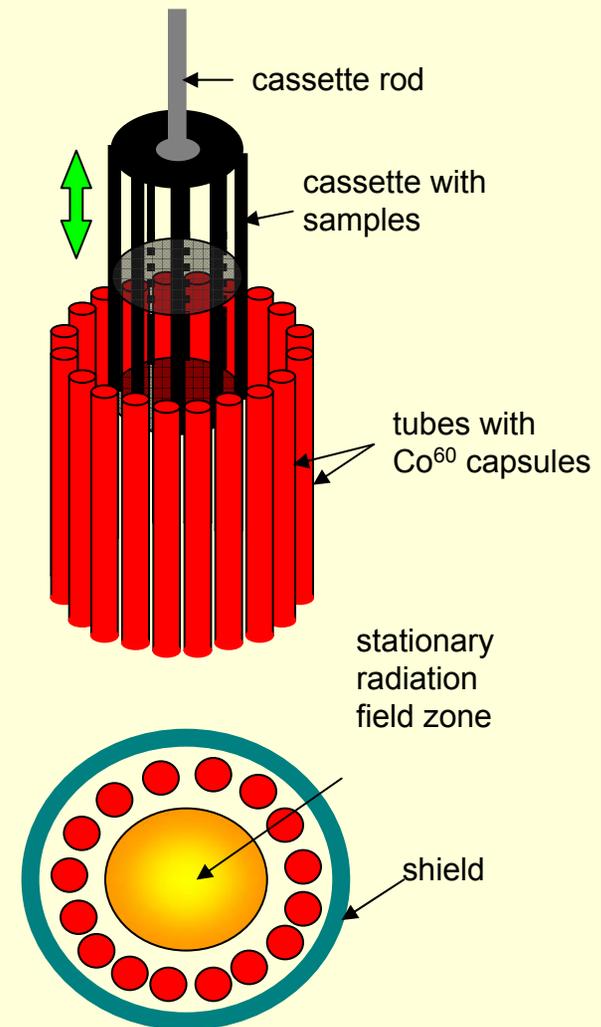
Methodology of radiation-induced effects in ChVS – II

Numerical parameters and geometry of γ-irradiation set-up:

Radiation treatment is usually performed in the normal conditions of **stationary radiation field**, created in <u>a closed cylindrical cavity</u> by <u>a number of concentrically established</u> <u>^{60}Co (E=1.25 MeV) radioisotope capsules</u>.

The accumulated doses of Φ=0.1-10.0 MGy were chosen with account of the previous results of I.A. Domoryad (1960-s).

<u>The absorbed dose power</u> P was chosen from a few up to 25 Gy/s.

The P value determined the maximum temperature of <u>accompanying thermal heating</u> in irradiating chamber. This temperature did not exceed 310-320 K during prolonged γ-irradiation (more than 10 days), provided dose power P<5 Gy/s, but it reached even 380-390 K at the dose power of ~25 Gy/s.

cassette rod

cassette with samples

tubes with Co^{60} capsules

stationary radiation field zone

shield

Research chronology for radiation-induced effects in ChVS

Main stages of RIEs study

<u>**I.A. Domoryad**</u> **(Inst. of Nuclear Physics, Tashkent, Uzbekistan): 1960-s ÷ 1980-s.**

<u>**Sh.Sh. Sarsembinov**</u> **(Kazakh State Univer., Alma-Ata, Kazakhstan): 1980-s.**

<u>**L.F. Konorova**</u> **et al. (A.F. Ioffe Physical-Technical Inst., St.-Petersburg, Russia): 1980-s.**

<u>**National Centre for Radiation Research and Technology**</u> **(Cairo, Egypt): 1990-s ÷ now.**

> **In the early 80-s, the complex and comprehensive experimental investigations of RIEs (^{60}Co γ-irradiation) in As_2S_3-based ChVSs, has been started in**
> **Lviv Sci&Res. Inst. of Materials of Sci.&Res. Co "Carat" (Lviv, Ukraine)**

Other important research in the field of RIEs in ChVSs:

✦ effect of γ-induced electrical conductivity in v-As-S(Se)-Te **(T. Minami et al., 1972);**

✦ X-ray diffraction study of γ-induced structural transformations in v-As_2S_3 and v-As_2Se_3 **(Yu.G. Poltavtsev et al., 1973);**

✦ electron-induced long-wave shift of fundamental optical absorption edge in v-$As_2S(Se)_3$ **(A.V. Moskalionov, 1976);**

✦ thermally-stimulated conductivity in γ-irradiated v-$AsS_{3.5}Te_{2.0}$ i**(T. Minami et al., 1977);**

✦ neutron-induced effects in v-GeS_x and v-As_2S_3 **(P. Macko et al., 1977);**

✦ ESR study of paramagnetic counterparts of radiation-induced defects in ChVS **(P.C. Taylor et al., 1978;**
   N. Kumagai et al., 1984; I.V. Chepeleva, 1987 and E.A. Zhilinskaya et al., 1990);

✦ γ-induced structural relaxation in v-Se **(R. Calemczuk et al., 1981);**

✦ radiation-induced effects in ChVS-based optical fibers **(A.M. Andriesh et al., 1984 and A.Ya. Vinokurov at al., 1988);**

✦ electron-induced crystallization in the ternary Ge-Sb-Se glasses **(S.I. Kalinich et al., 1986).**