Physicochemical properties

- ✓ Properties in general
- ✓ Properties of some representative ChGs

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Structure-property relation

- In a liquid state, the flowing property (viscosity) depends not only on the amplitude of the particle oscillations (atoms or molecules) but also on the character and strength of the chemical bonds between particles.

- The chemical bond is the fundamental cause that determines the transition from the liquid state either to crystalline or to non-crystalline state.

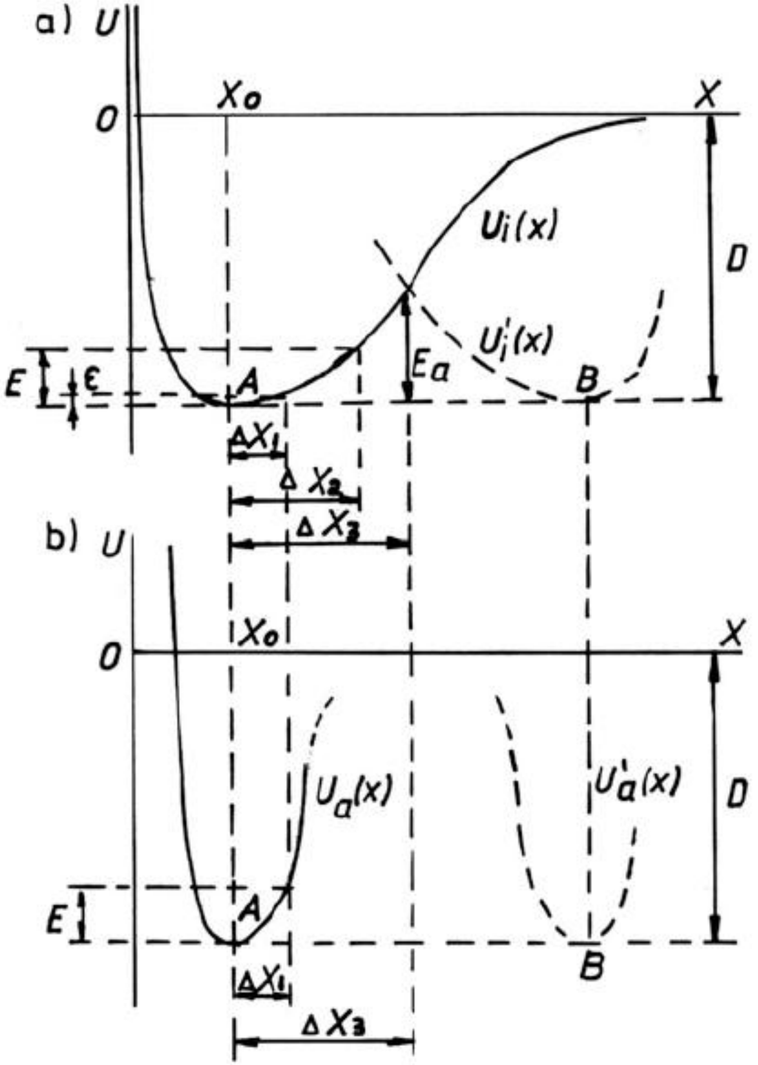


Figure 2.1. The potential energy U as a function of the inter-atomic distance x.
a - for polar materials: $|U_i(x)|$ b - for covalent materials: $|U_a(x)|$

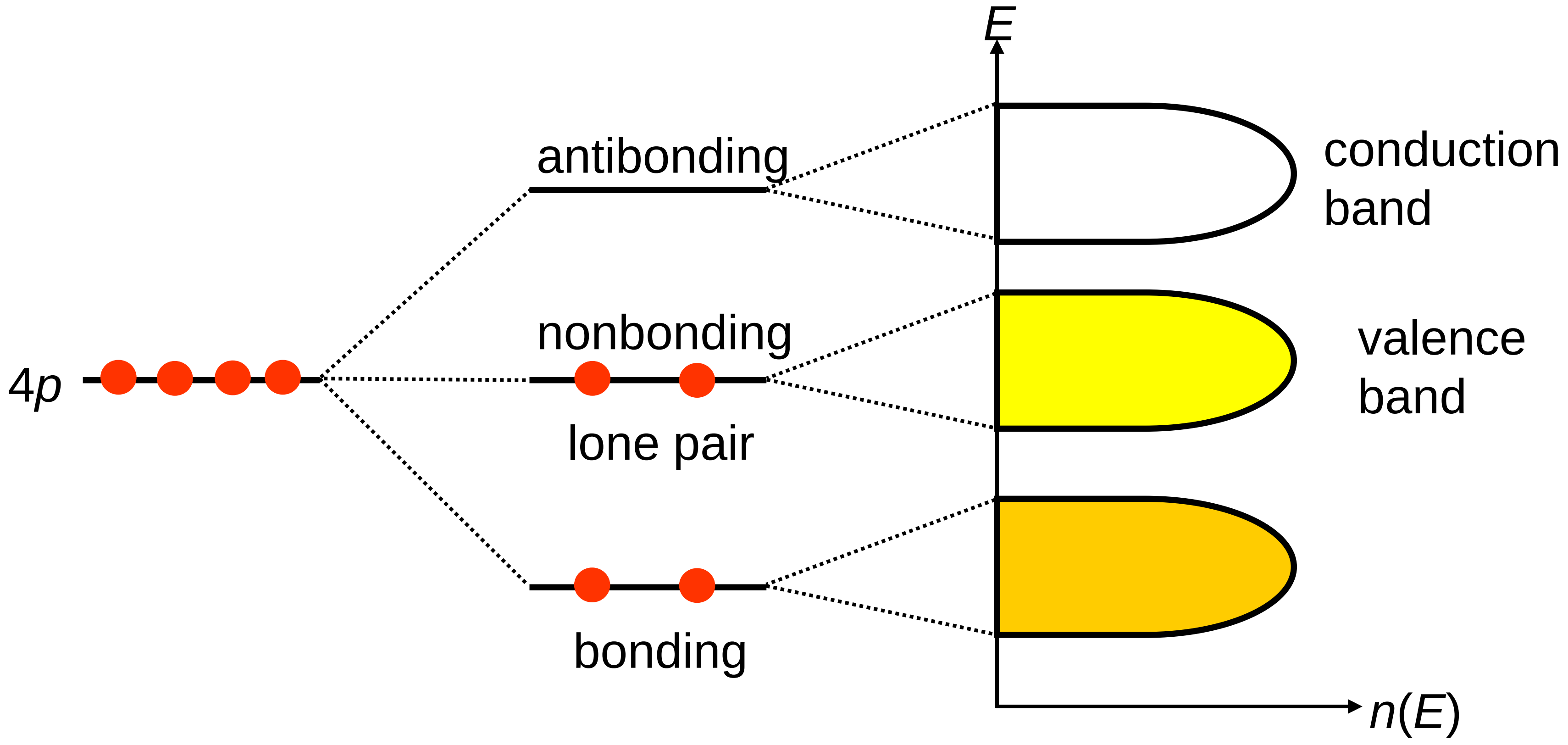
Popescu book, p. 105

Structure-property relation

- Glass-forming ability is related to the number of lone-pair electrons.
- In amorphous chalcogenides which are sometimes called “lone-pair semiconductors”, the valence bond is formed by the lone-pair electrons which occupy the middle part between bonding and anti-bonding orbitals.
- The existence of lone-pair electrons is connected with presence of the specific network defects, which are absent in the substances that do not contain lone-pair electrons.
- In thin amorphous films, the thickness or the surface to volume ratio is important in addition to temperature, nature of the substrate, pressure of the gaseous traces.
- Under the action of various physical factors (light, temperature, pressure, mechanical shocks, etc.) the amorphous films can be modified.

Electronic structure of chalcogen elements

- ✓ The lone pair electrons form valence band



E

antibonding

conduction band

nonbonding

valence band

4*p*

lone pair

bonding

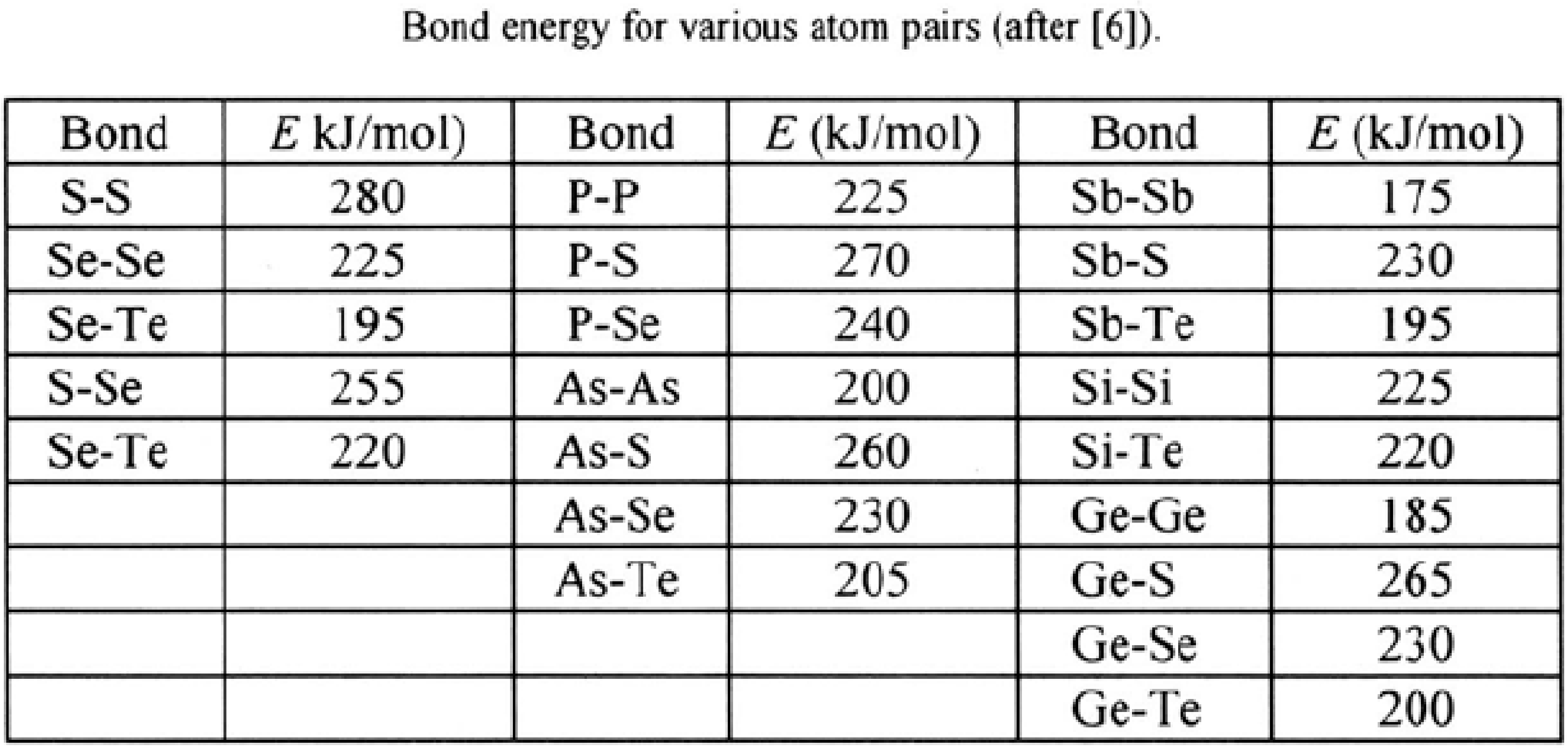
n(*E*)

Se atom: $4s^2p^4$ Se molecule ($z = 2$) Solid Se

❖ R. Zallen, The physics of amorphous solids, John Wiley & Sons, 1983.

Structure-property relation

- The thermo-physical and mechanical properties of ChG depend on the structural and energetic factors. The formation of structural units at the atomic scale is correlated with the bond energy and to the preparation conditions.



Bond energy for various atom pairs (after [6]).

Bond	*E* kJ/mol)	Bond	*E* (kJ/mol)	Bond	*E* (kJ/mol)
S-S	280	P-P	225	Sb-Sb	175
Se-Se	225	P-S	270	Sb-S	230
Se-Te	195	P-Se	240	Sb-Te	195
S-Se	255	As-As	200	Si-Si	225
Se-Te	220	As-S	260	Si-Te	220
		As-Se	230	Ge-Ge	185
		As-Te	205	Ge-S	265
				Ge-Se	230
				Ge-Te	200

[6] D. Linke, Proc. Intern. Conf. “Amorph. Semic. ’78”, Pardubice, Czechoslovakia, Vol. 1, p. 78, 1978.

Structure-property relation

- The typical glass formers, except for BeF_2, are oxides and chalcogenides.
- The chalcogen atoms have two covalences, and bridge two adjacent units.
- They can also bridge themselves, as in the case of vitreous S and Se, forming macromolecular chain polymers.

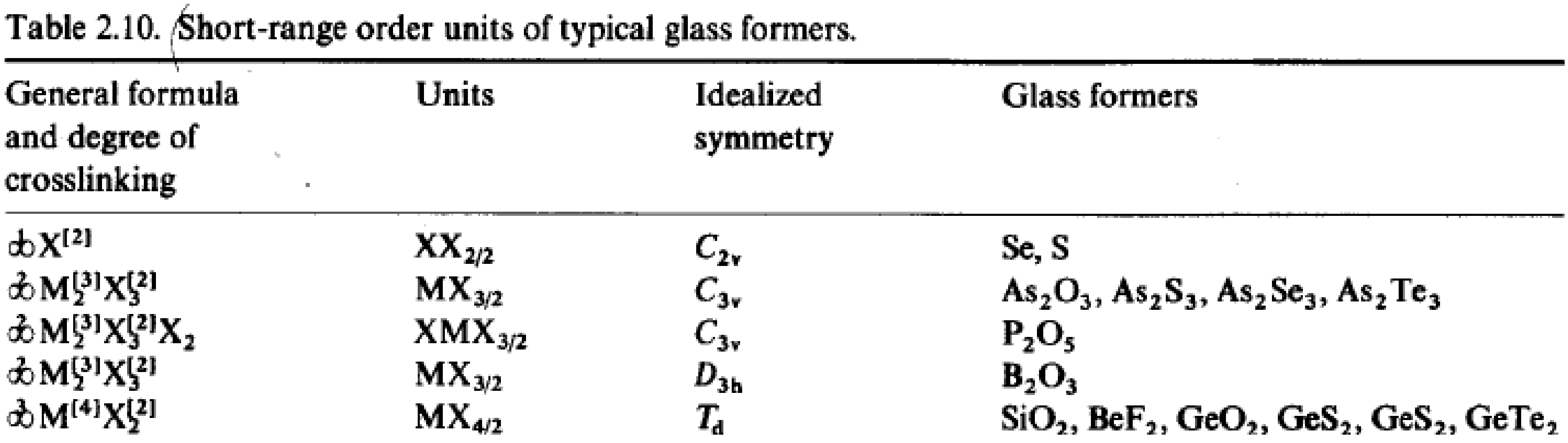


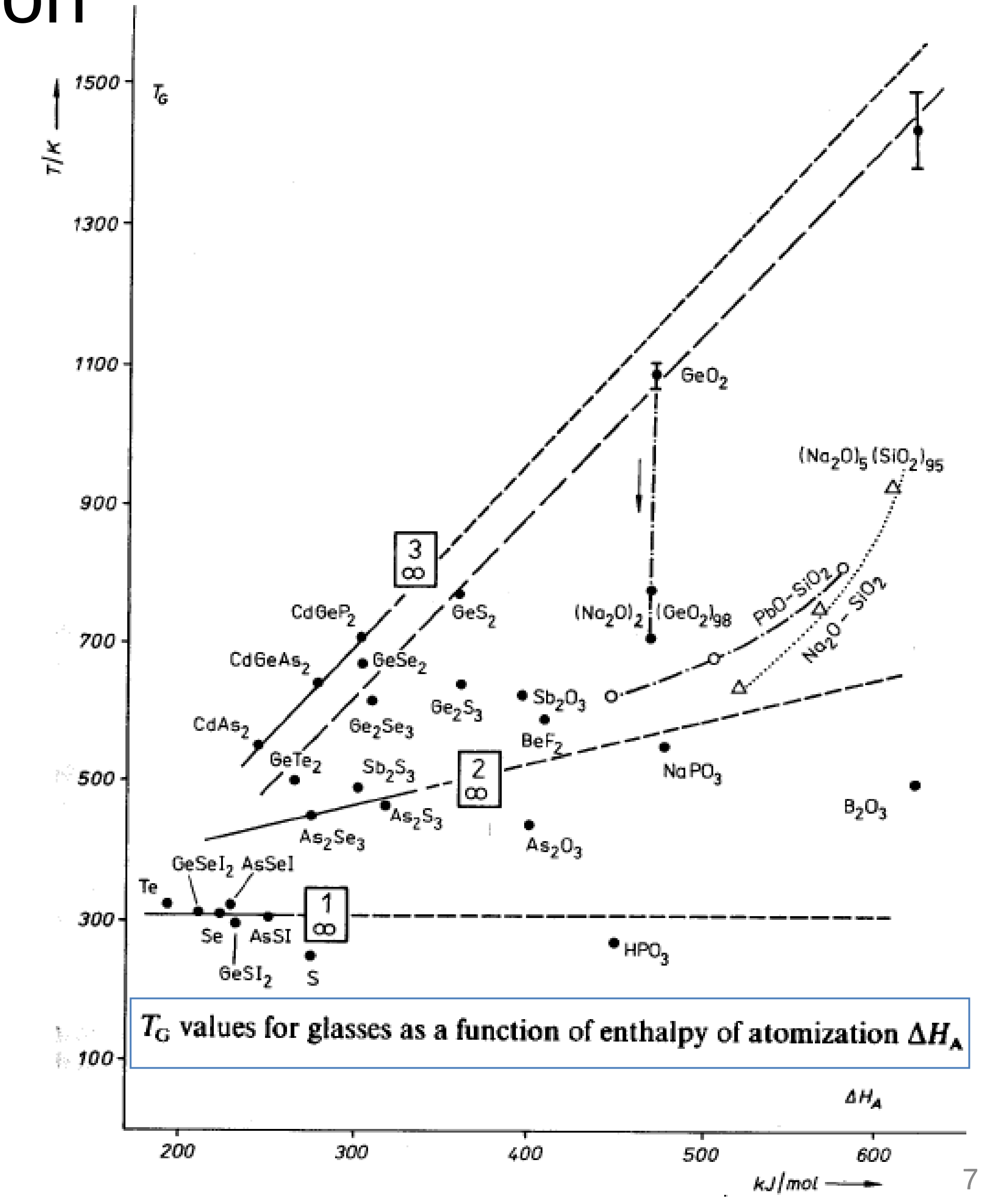
Table 2.10. Short-range order units of typical glass formers.

General formula and degree of crosslinking	Units	Idealized symmetry	Glass formers
${}^{1}_{\infty}X^{[2]}$	$XX_{2/2}$	C_{2v}	Se, S
${}^{2}_{\infty}M^{[3]}_{2}X^{[2]}_{3}$	$MX_{3/2}$	C_{3v}	As_2O_3, As_2S_3, As_2Se_3, As_2Te_3
${}^{2}_{\infty}M^{[3]}_{2}X^{[2]}_{3}X_2$	$XMX_{3/2}$	C_{3v}	P_2O_5
${}^{2}_{\infty}M^{[3]}_{2}X^{[2]}_{3}$	$MX_{3/2}$	D_{3h}	B_2O_3
${}^{3}_{\infty}M^{[4]}X^{[2]}_{2}$	$MX_{4/2}$	T_d	SiO_2, BeF_2, GeO_2, GeS_2, GeS_2, $GeTe_2$

Feltz book, p. 91.

Structure-property relation

- The glass transition temperature appears to depend on the bond energy between constituent atoms.
- T_g also depends on the structure of glasses; it tends to increase with increasing dimensionality of glass structure in general.
- The highest T_g values are those of glasses with 3-dimensional cross-linking of short-range order units.



T_G values for glasses as a function of enthalpy of atomization ΔH_A

Feltz book, p. 109.

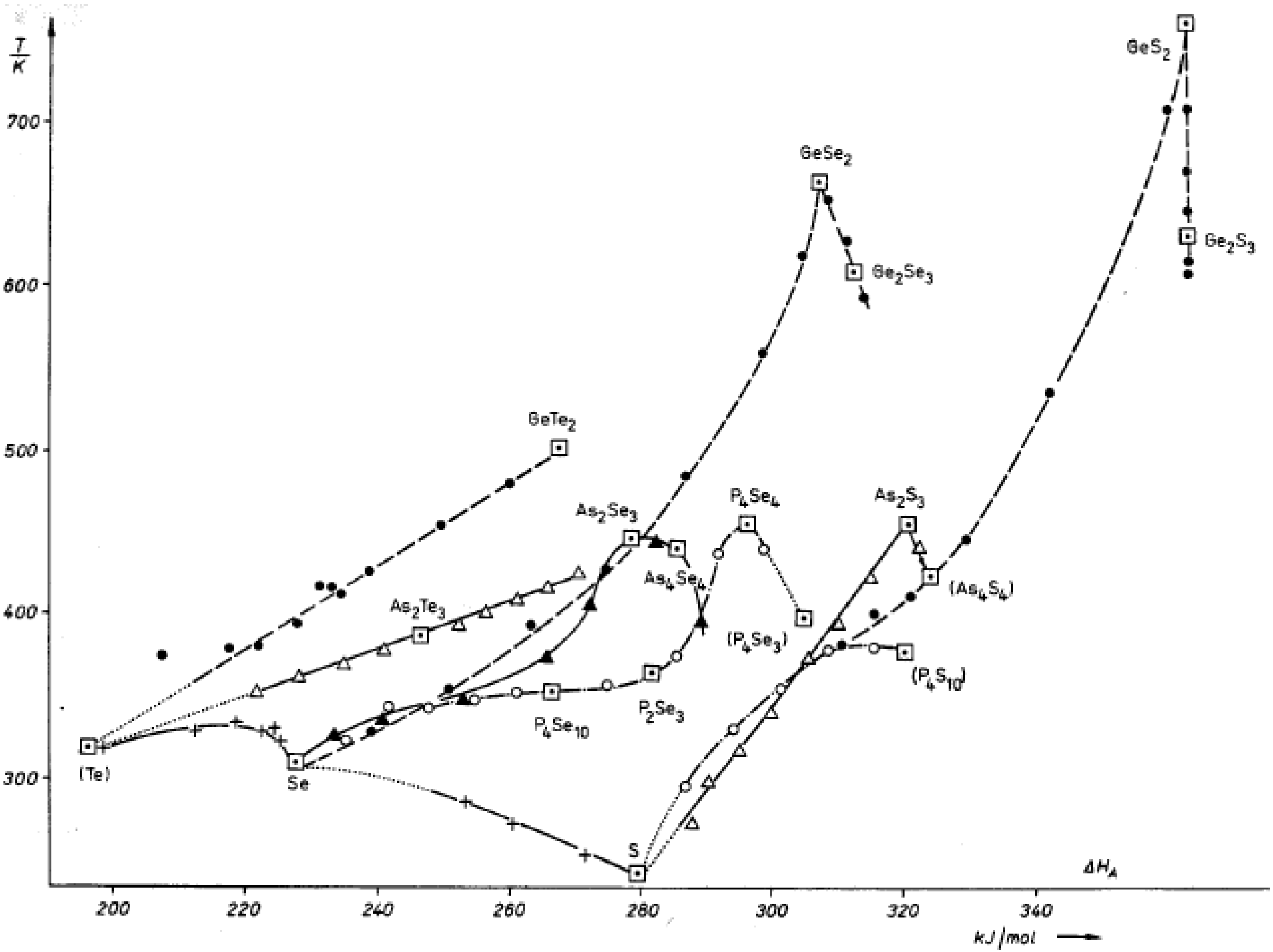


Fig. 2.46. T_G values of typical chalcogenide glass-forming systems as a function of the enthalpy of atomization (according to Linke).

Feltz book, p. 111.

Metal-insulator transitions

Transition	Electron wave functions		Characteristic energies	Change at the MIT	Criterion for localization
	Metal side of transition	Insulator side of transition			
Bloch	Extended	Extended	Bandwidth B	Partly filled bands → all bands filled or empty	—
Mott	Extended	Localized	Electron-electron correlation energy e^2/r_{ij}, U	Correlation-induced localization	$U > B$
Anderson	Extended	Localized	Width of the distribution of random site energies W	Disorder-induced localization	$W > B$

- R. Zallen, The physics of amorphous solids, John Wiley & Sons, 1983.

Electronic conduction of semiconductors

- ✓ Bandgap decreases on amorphization in conventional semiconducting materials.
  - ➢ Broadening of electronic density of states
  - ➢ Formation of tail states in the bandgap

- ✓ Conductivity decreases due to decrease in drift mobility.
  - ➢ More frequent electron scattering by the phonons
  - ➢ Decrease of the mean free path

- ✓ Only elemental Se or Te exhibits an increased bandgap in the amorphous phase among covalent systems.
  - ➢ Weaker inter-chain bonds and stronger intra-chain bonds

- W. Welnic et al, Nature Mater. 5 (2006) 56.

The mobility edge

✓ Localized electronic charge carriers

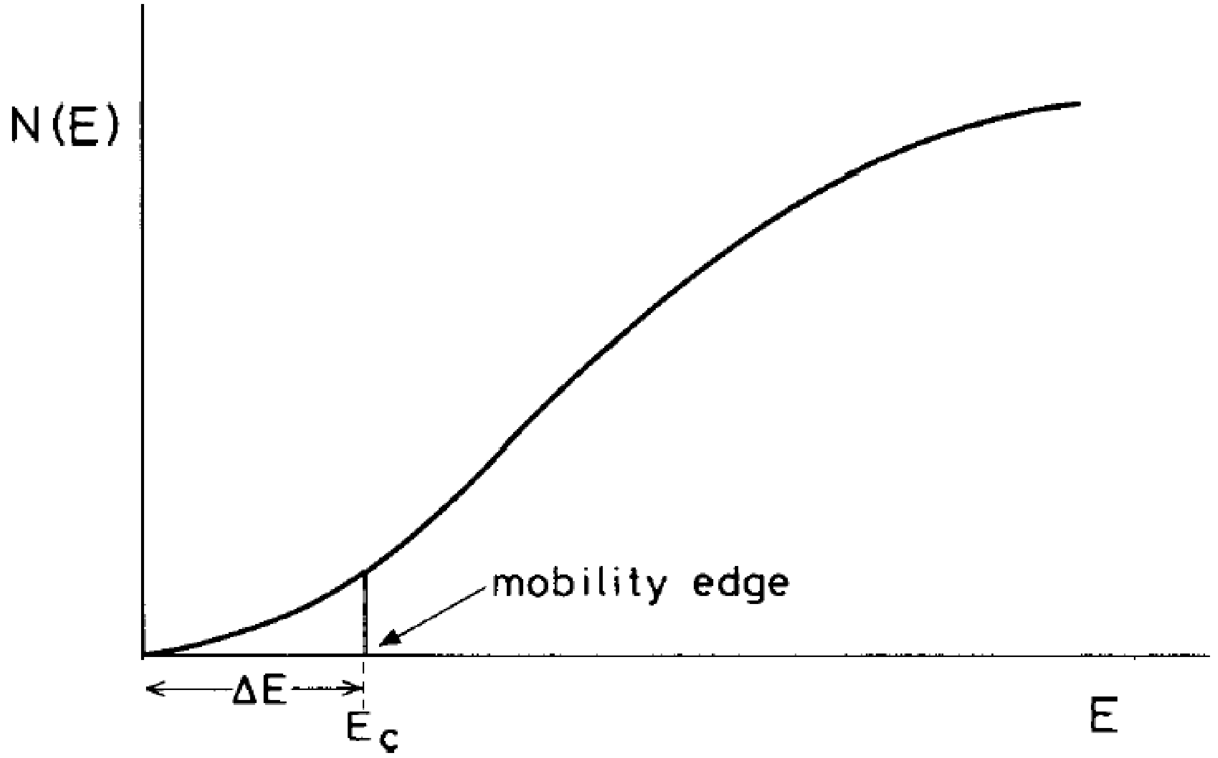


Fig. 1. The density of states in the conduction band of a non-crystalline material, showing the mobility edge E_c separated by an energy $\Delta \mathbf{E}$ from the band edge.

❖ N. Mott, Electrons in glass, Nobel Lecture, December 8, 1977.

The mobility gap

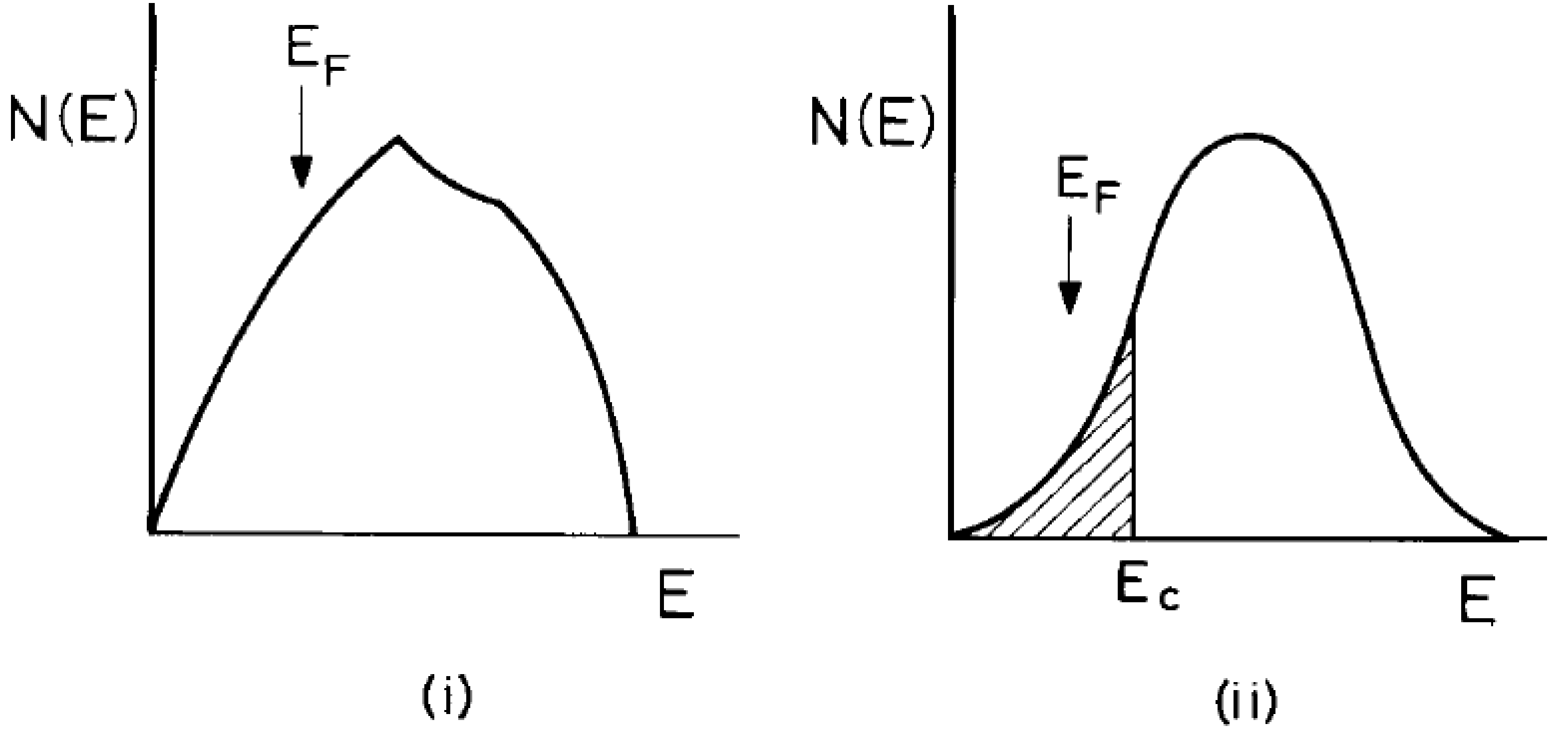
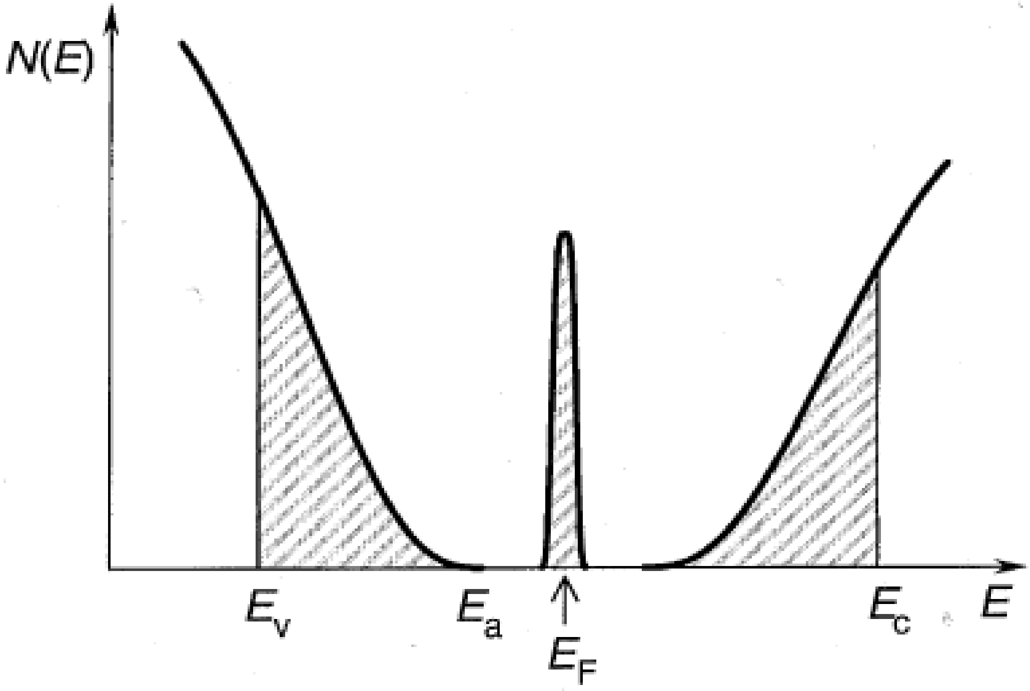


Fig. 3. Density of states in a metallic conduction band, with states occupied up to a limiting Fermi energy E_F. (i) is for a crystal, (ii) for an amorphous or liquid material, with localized states shaded and a mobility edge at E_c.

- N. Mott, Electrons in glass, Nobel Lecture, December 8, 1977.

Deep localized states of amorphous chalcogenide

- ✓ Intrinsically introduced;
  - ➢ Dangling bonds, valence alternating pairs, vacancies, etc
  - ➢ Charged defects
- ✓ Fermi level pinning

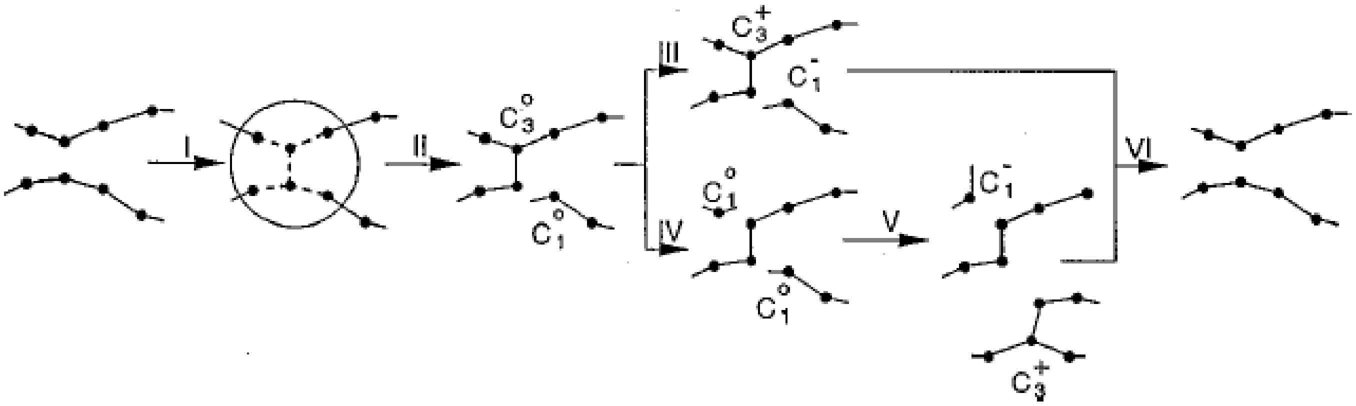


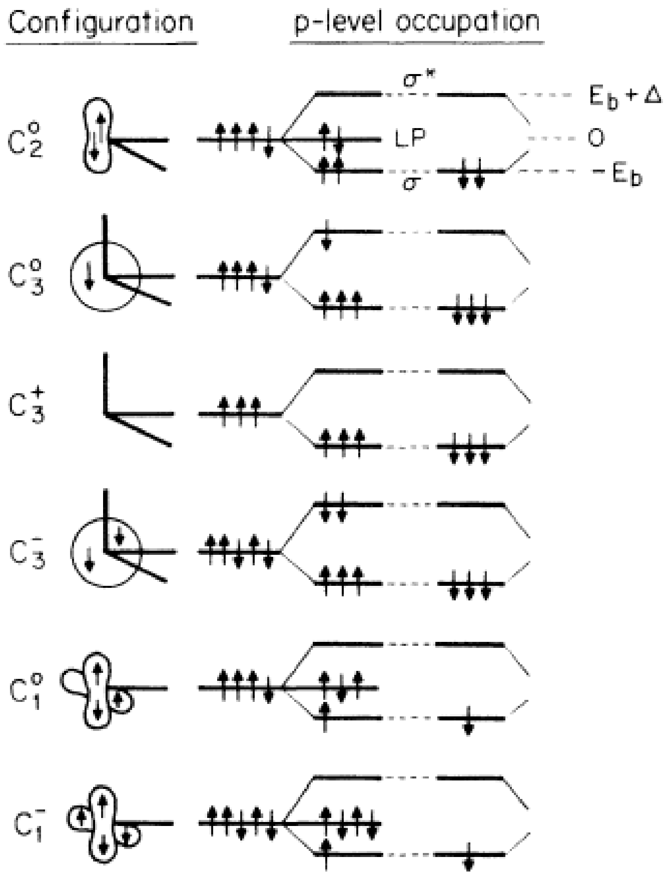
❖ N. Mott, Electrons in glass, Nobel Lecture, December 8, 1977.

Valence alternation pair (VAP)

- ✓ Presence of ‘deep’ gap states
  - ➢ Supported by luminescence, photoinduced optical absorption and activation energy for electrical conduction…
  - ➢ No ESR signals; charged defects

$$2C_2^0 \rightarrow C_3^+ + C_1^-$$





- ❖ Kastner, Adler, Fritzsche, Phys. Rev. Lett. 37 (1976) 1504.
- ❖ Kolobov et al, Phys.Rev. B 58 (1998) 12004.

Electrical conduction

- In the case of non-metallic solids, the temperature dependence of electrical conductivity follows an Arrhenius relationship.

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT} \right)$$

- For transport of electrons or holes in the band states, it is a consequence of the exponential dependence of the charge carrier density.

- For transport, by hopping process between localized centers, of ions or electrons in polarons, the mobility or the diffusivity is subject to thermal activation.

- The type of charge carriers and the causes of the electron localization depend on the composition and structure.

Diffusion

- ✓ Thermal energy keeps the atoms vibrating vigorously about their lattice positions, continually bumping into each other and exchanging energy with their neighbors and surroundings.

- ✓ Every now and then, an atom will gain sufficient energy to leave its mooring and migrate.

$$D = D_0 \, exp\left(-\frac{Q}{kT}\right)$$

Mass transport

- ✓ Diffusion in potential gradient, i.e., driving force, f

$$J_i = c_i v_{drift} = \frac{c_i D_i}{kT} f$$

- ✓ Differences in chemical potential and electric potential; electrochemical potential

$$J_k = -\frac{c_k D_k}{kT}\frac{d\tilde{\eta}_k}{dx} = -\frac{c_k D_k}{kT}\left(\frac{d\tilde{\mu}_k}{dx} + z_k e\frac{d\phi}{dx}\right)$$

Ionic conduction

- ✓ Transport of charged particles can make electrical conduction.

$$I_i = z_i e J_{ion} = \frac{z_i e c_{ion} D_{ion}}{kT} f = -\frac{z_i e c_{ion} D_{ion}}{kT}\left[z_i e \frac{d\phi}{dx} \right]$$

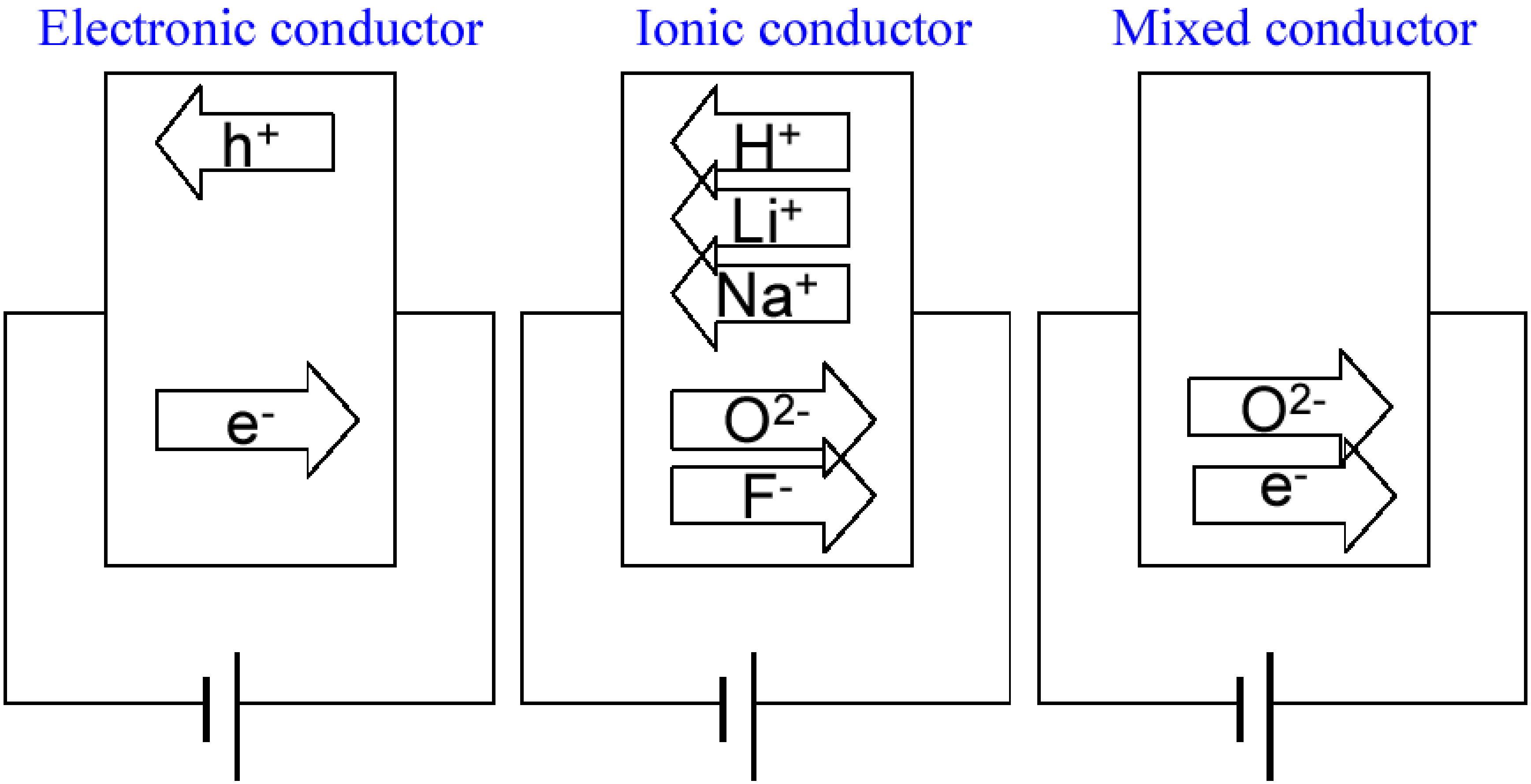
$$\sigma_{ion} = \frac{z_i^2 e^2 c_{ion} D_{ion}}{kT} = \frac{z_i^2 e^2 c_{def} D_{def}}{kT}$$

- ✓ Generalized electrical conductivity;

$$I_i = -\sigma_i \frac{d\phi}{dx} = |z_i| e v_{d,i} c_i \text{ and } \mu_{d,i} = -\frac{v_{d,i}}{d\phi / dx}$$

$$\sigma_i = \sum_i c_{d,i} e |z_i| \mu_{d,i}$$

Charge carriers in solids



Ionic conduction of solids

- ✓ Transport number, $t_{ion} > 0.98$: solid electrolyte or ionic conductor

$$1 = \frac{\sigma_e}{\sigma_{total}} + \frac{\sigma_h}{\sigma_{total}} + \frac{\sigma_{ion}}{\sigma_{total}} = t_e + t_h + t_{ion}$$

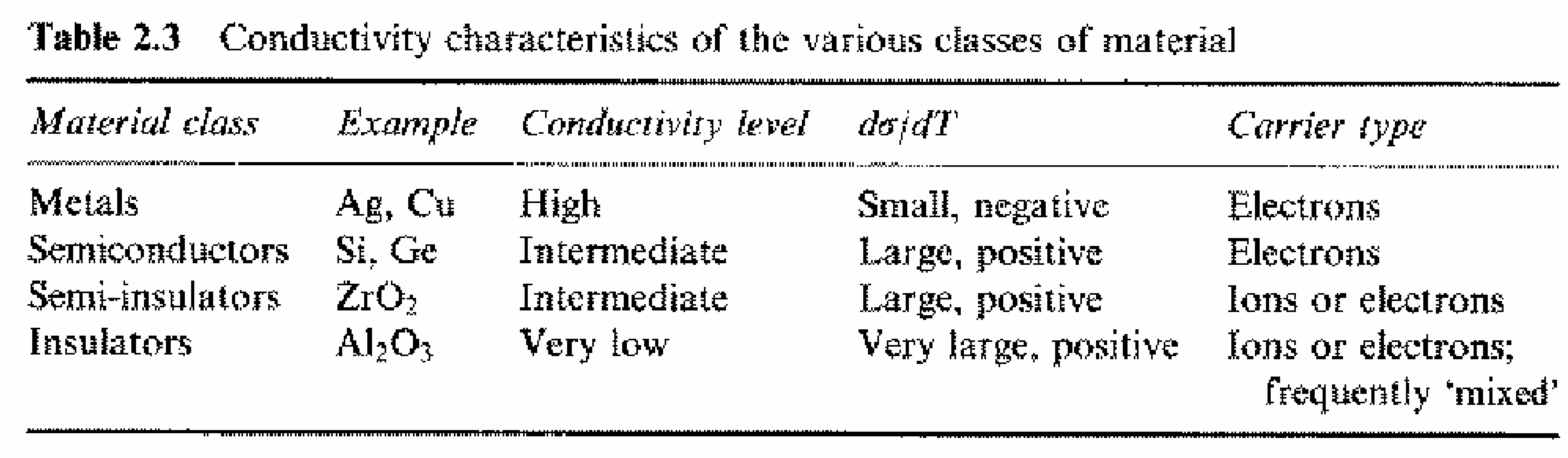
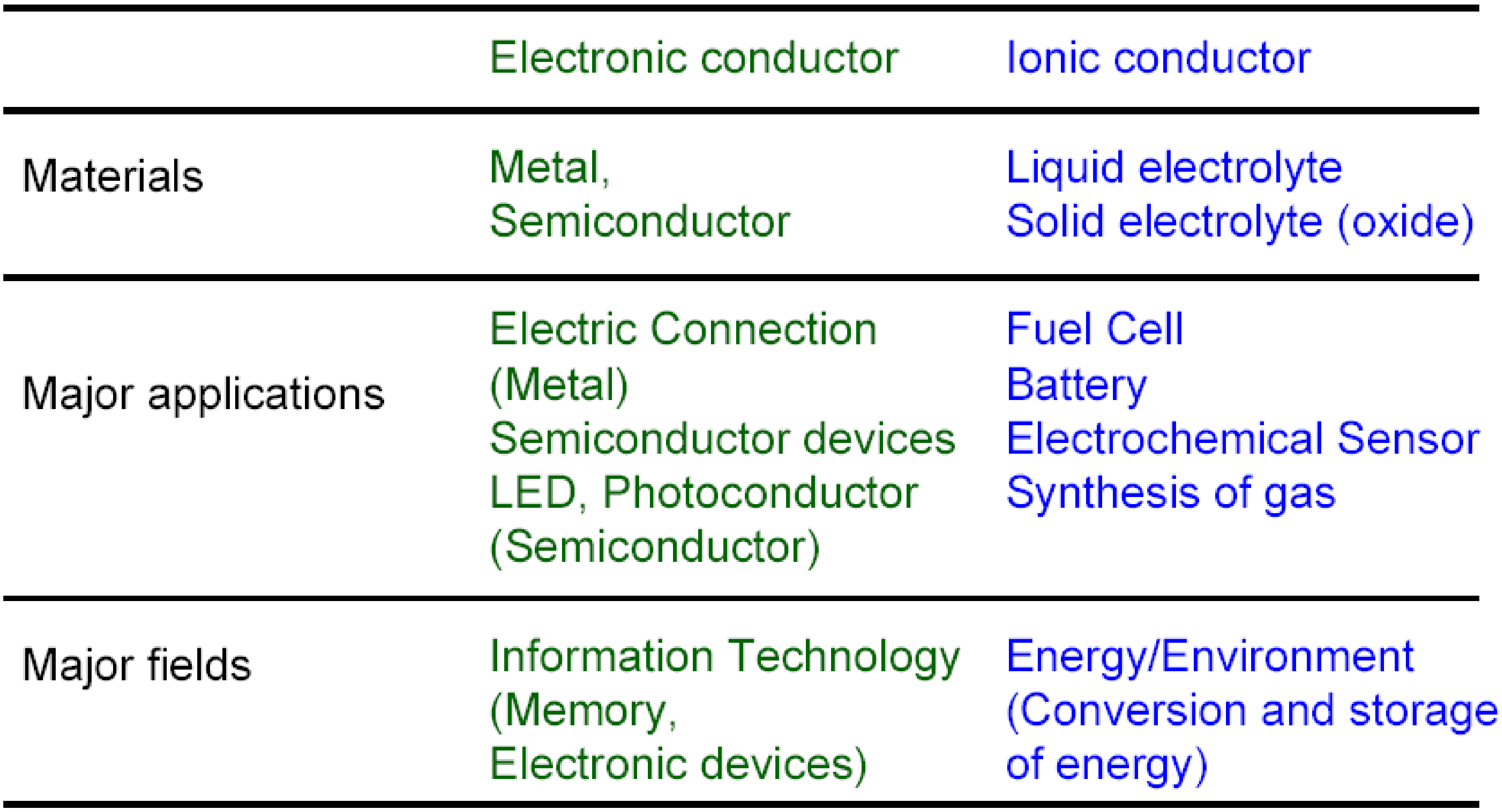


Table 2.3 Conductivity characteristics of the various classes of material

Material class	*Example*	*Conductivity level*	*dσ/dT*	*Carrier type*
Metals	Ag, Cu	High	Small, negative	Electrons
Semiconductors	Si, Ge	Intermediate	Large, positive	Electrons
Semi-insulators	ZrO_2	Intermediate	Large, positive	Ions or electrons
Insulators	Al_2O_3	Very low	Very large, positive	Ions or electrons; frequently 'mixed'

Moulson and Herbert, Electroceramics, 2nd ed, Wiley, 2003.

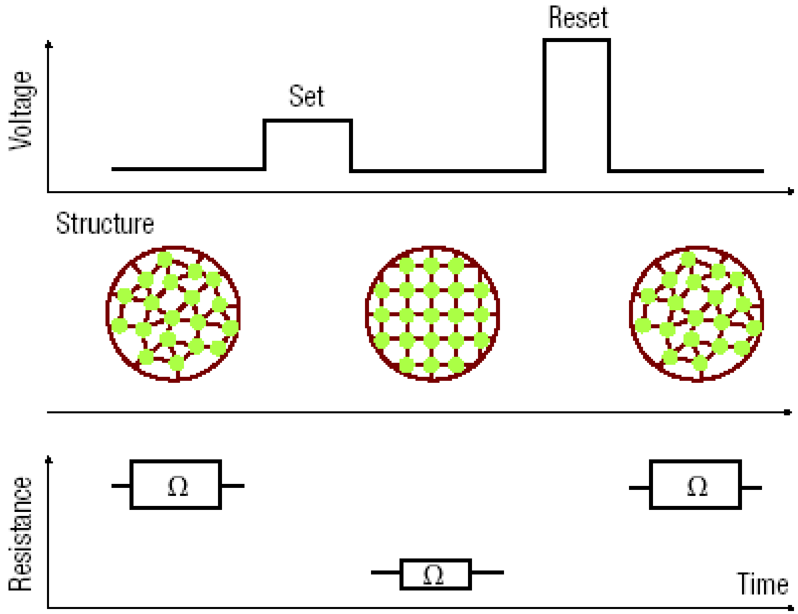
Applications



	Electronic conductor	Ionic conductor
Materials	Metal, Semiconductor	Liquid electrolyte Solid electrolyte (oxide)
Major applications	Electric Connection (Metal) Semiconductor devices LED, Photoconductor (Semiconductor)	Fuel Cell Battery Electrochemical Sensor Synthesis of gas
Major fields	Information Technology (Memory, Electronic devices)	Energy/Environment (Conversion and storage of energy)

Applications; electronic conduction

- ✓ Phase change memory and much more
  - ➢ “Chalcogenides are already important in optical storage discs and fibers. They are now being proposed as the basis for solid-state memory technologies.”

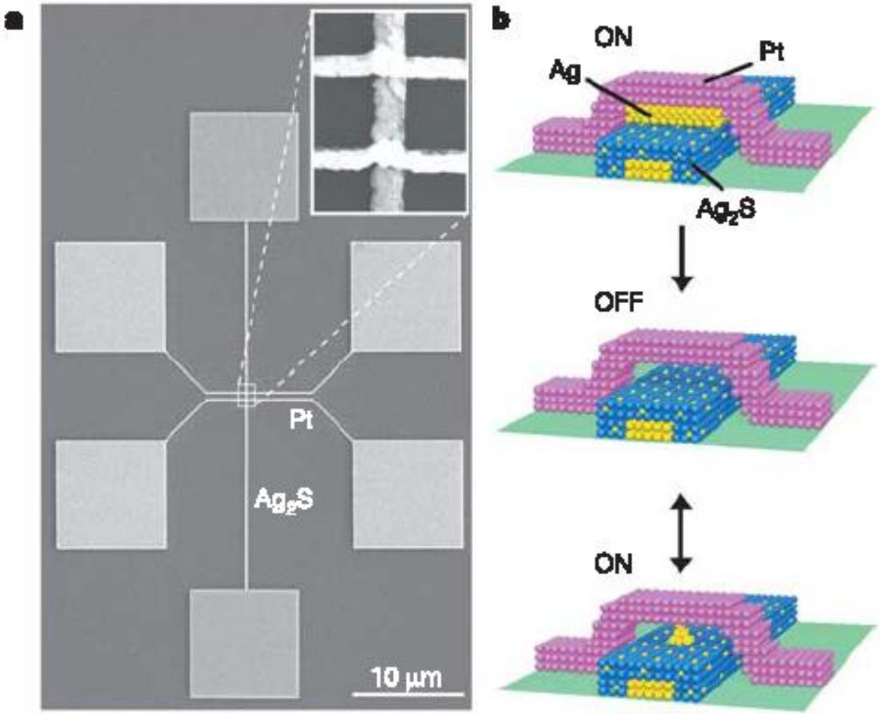


- ❖ Greer and Mathur, Nature 437 (2005) 1246.
- ❖ Wuttig, Nature Mater. 4 (2005) 265.

Applications; ionic conduction

- ✓ Memory (R-RAM) and others (battery, fuel cell and more)

- ✓ Quantized conductance atomic switch;
  - ➢ Controlling the formation and annihilation of an atomic bridge at the crossing point between two electrodes.



❖ Terabe et al, Nature 433 (2005) 48.

Electronic conduction

- The activation energies of ChGs are different; they usually decrease with increasing content of heavy atoms, corresponding to the reduction of the optical band gap, and thus the mobility gap.
- The activation energy of the majority of the glasses corresponds to about half the optical band gap.
- The σ_0 values of ChGs are usually between 10^2 and 10^4 $\Omega^{-1}\text{cm}^{-1}$, which are in the order of magnitude of typical crystalline semiconductors.

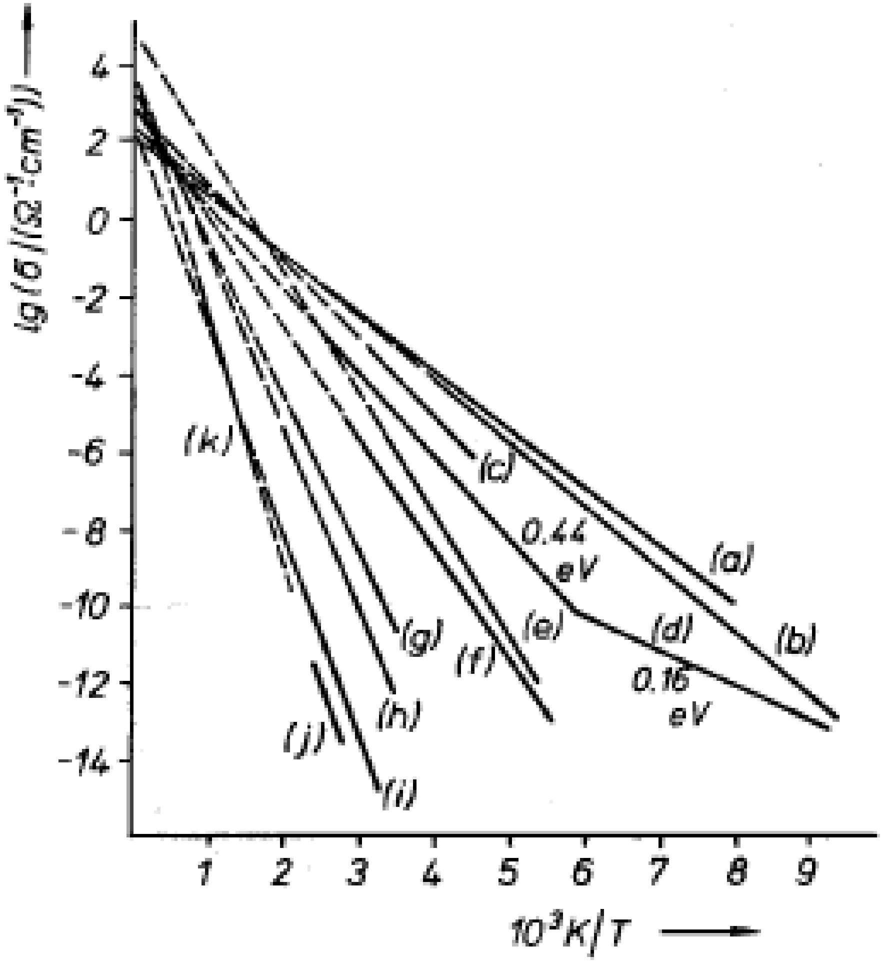


Fig. 4.13. Temperature dependence of the electrical conductivity of semiconducting glasses and amorphous layers. (a) GeTe, (b) $Tl_2As_2SeTe_3$, (c) As_2Te_3, (d) $As_{10}Se_3Te_{12}$, (e) $CdGeAs_2$, (f) $Tl_2As_2Se_3$, (g) $As_6Sb_4Se_{15}$, (h) As_2Se_3, (i) Ge_2Se_3, (j) As_2S_3, (k) Se.

Feltz book, p. 331

Electronic conduction

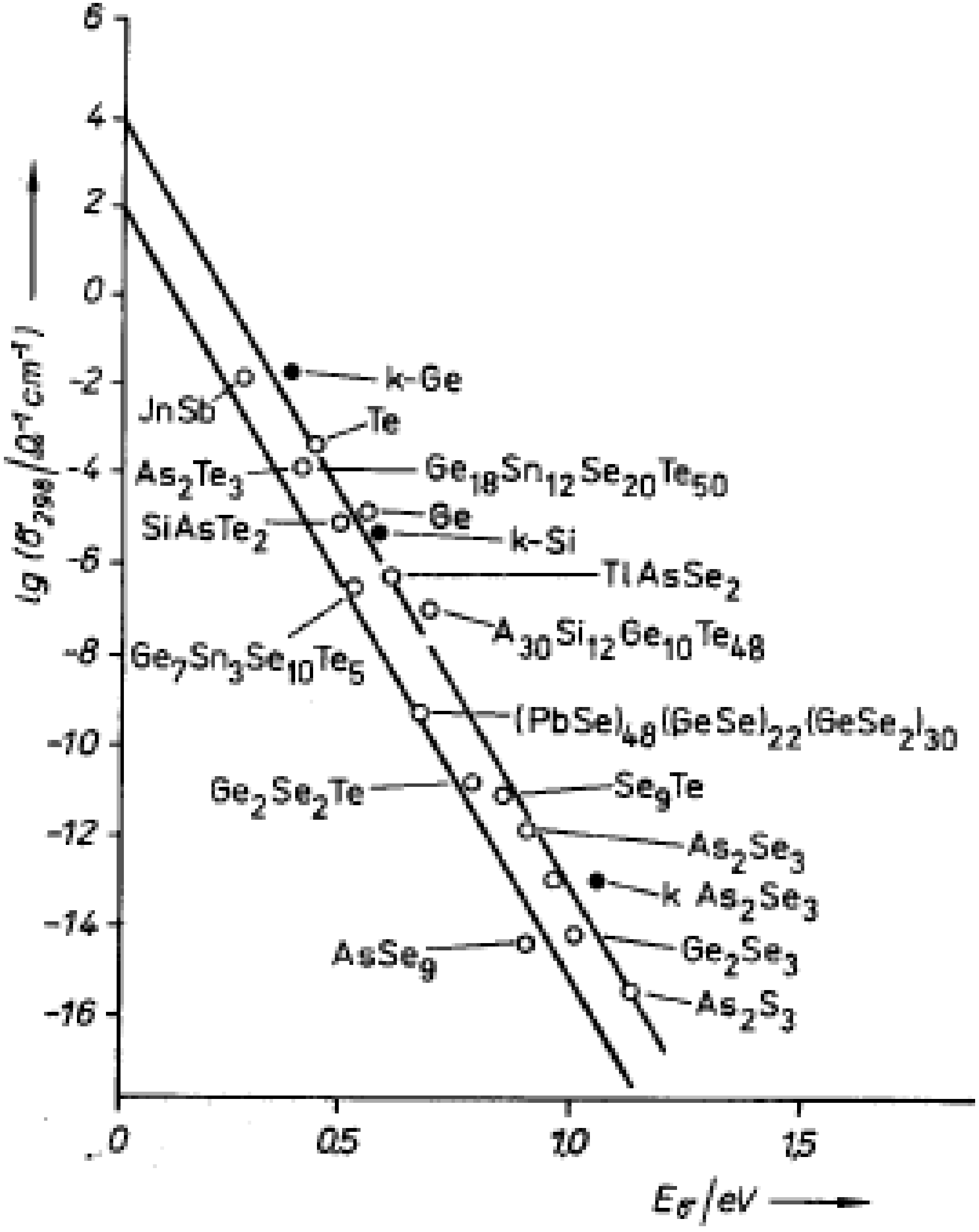


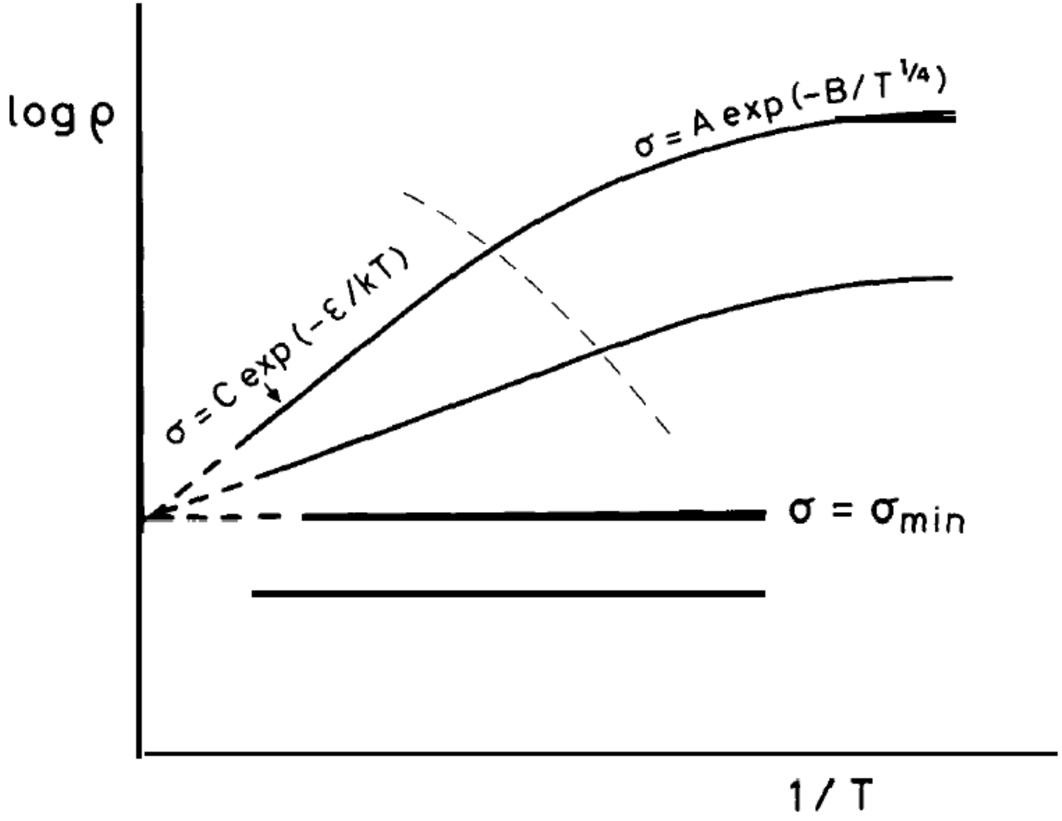
Fig. 4.14. Relationship between conductivity at 298 K and activation energy for amorphous, semiconductors. (●): crystalline substances.

Feltz book, p. 332.

Conduction by hopping

- ✓ Variable range hopping in glasses
  - ➢ Phonon-assisted quantum-mechanical tunneling of an electron from one localized state to another.
  - ➢ The determination of the most probable jump distance leads to the Mott's $T^{-1/4}$ law.

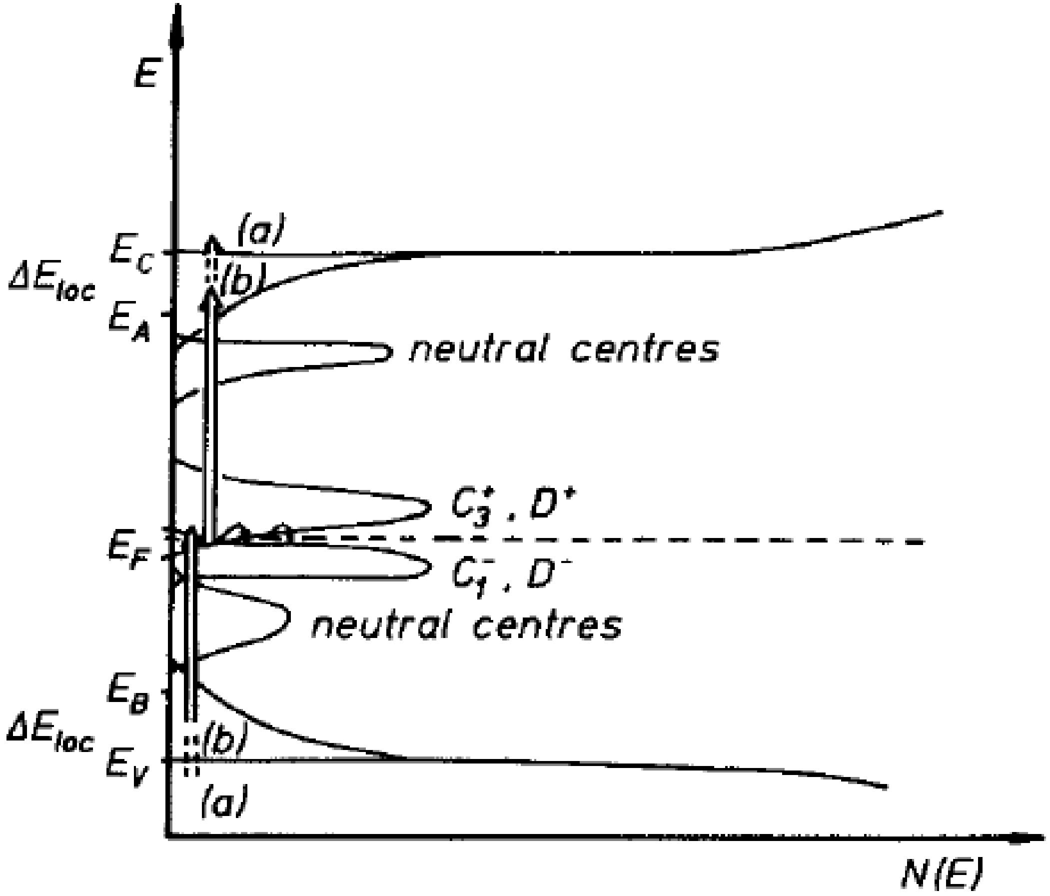
$$\sigma = \sigma_0 e^{-\left(\frac{T_0}{T}\right)^{\frac{1}{d+1}}}$$



- ❖ N. Mott, Phil. Mag. 19 (1969) 835.
- ❖ N. Mott, Electrons in glass, Nobel Lecture, December 8, 1977.

Conduction pathways

- ✓ Transport in band states
- ✓ Migration in the band tails
- ✓ Hopping between localized states



The neutral centres at the band edges correspond to the partial generation of homonuclear bonds. Three contributions to the conductivity should be distinguished: excitation to band states (a), excitation to localized states in the region $\Delta E_{1\mathrm{oc}}$ (b), and electron jump conduction in the region of the Fermi energy (c).

❖ Feltz book, p. 329.

Doping or chemical modification?

- ✓ In general, ‘doping’ doesn’t work in the case of ChG.
  - ➢ Fermi level pinning
  - ➢ The empirical 8-*N* rule

- ✓ Certain additives can cause large increases in the electrical conductivity.
  - ➢ In a-As or in ChGs with high concentrations of transition metals, the E_F is shifted inside a band, making VRH the dominant conduction mechanism.
  - ➢ In Ge-Se(S)-Bi, where the conduction type changes from p- to n-type at 9-10% of Bi, the E_F remains in the energy gap.
  - ➢ In pure a-Se, only few hundreds ppm of chlorine increase the conductivity by orders of magnitude and probably change the conduction type.

❖ E. Mytilineou, J. Optoelectronic and Advanced Materials, 4 (2002) 705.

General properties

- ChGs are chemically stable materials in normal conditions. They are not greatly affected by the aggressive media, are not soluble in water and do not dissolve in organic solvents.

- Nevertheless, various external factors (electromagnetic radiation, particle beams, electric and magnetic fields, etc.) cause particular modifications of interest in various applications.

- ChGs are less stable in alkali solutions. The chemical stability of ChGs increases in the order of S < Se < Te, which is proved by the increase of the value of the activation energy of dissolution and of the alkali concentration wherein the glass dissolution takes place.

- The introduction of the halogens in As-Ch glasses leads to the destruction of the compact character of the glass network, thus decreasing their chemical stability. The elements of the group IV elements increase their stability by the formation of the tetrahedral structural units.

Popescu book, ch. 2.

General properties

- The density of ChGs is higher than that of the oxide glasses and the micro-hardness is essentially lower. The highest hardness values were found in the sulphur systems (Ge-S, Ge-As-S, Ge-As-S-I) and the lowest values were found in glasses with atomic chains (i.e. S-Se).

- The micro-hardness and the density of the semiconducting glasses decrease linearly with the increase of the temperature. As a function of composition, T_g of ChGs changes in a wide range of 230 ~ 770 K. The introduction of halogens in As-Ch glass leads to the abrupt decrease of T_g, while the introduction of tetrahedral elements increases T_g.

- The As-Ch glasses exhibit high expansion coefficients of (8~20) X 10^{-6} K^{-1}. The introduction of halogens in As-Ch leads to the increase of up to 50 X 10^{-6} K^{-1}. The halogenated glasses exhibit high thermo-plasticity in a large range of temperatures.

Popescu book, ch. 2.

Properties of amorphous sulfur

✓ *Mechanical and thermal properties*

- The plastic sulphur is prepared by stretching the liquid sulphur from the boiling point, or by drawing filaments from hot liquid sulphur. After several hours of storage at room temperature the material becomes hard and brittle, which was explained by the transition from plastic sulphur to micro-crystalline α-sulphur.

- The density of the plastic sulphur is 2.01. Glass transition temperature depends on the cooling rate of the melt, in the range of 230~520 K.

- Sulphur can be quenched as a thin film. Slowly quenched polymeric sulphur is yellow. The polymer quickly quenched to 76 K is red, because it contains small molecules.

- The thermal conductivity of sulphur is about 0.29 W/m.K at 0 °C. Sulphur ranks with mica and wood among the best thermal insulators.

Popescu book, ch. 2.

Properties of amorphous sulfur

✓ *Electrical and optical properties*

- The plastic sulphur is a good insulator. Under high pressure it transforms into the metallic form, which at temperatures below 10 K becomes superconducting.

- The thin films of sulphur deposited in vacuum at room temperature show resistivit values of the order of 10^{17} Ω.cm. Its dielectric constant is 4.

- By transformation in plastic sulphur the colour is changed in orange-red till brownish and the transparency is lost. The refractive index for melted sulphur is n = 2.068 at 400 nm and n = 1.927 at 568 nm.

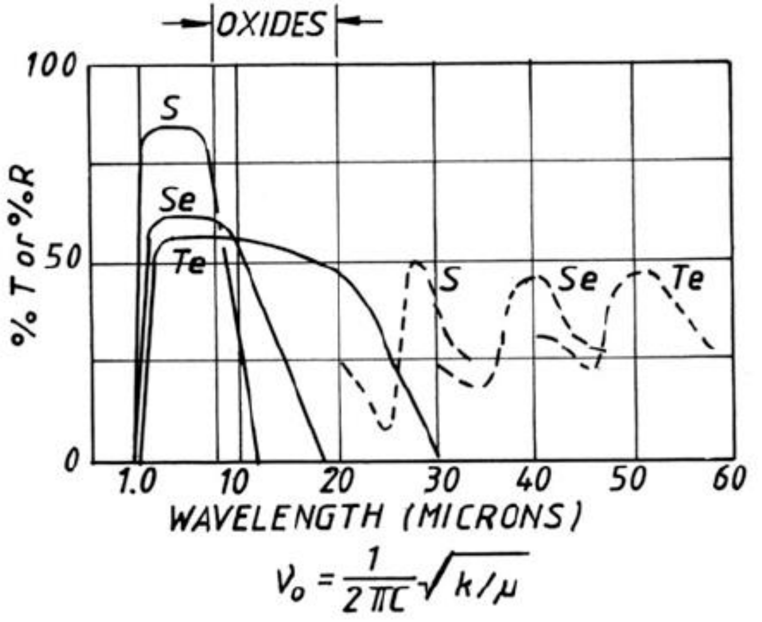


Figure 2.3. The transmission spectra of sulphur, selenium and tellurium (after [36]).

Popescu book, ch. 2.

Properties of amorphous selenium

- ✓ *Mechanical and thermal properties*

- ➢ The vitreous selenium obtained by cooling the melt is composed from Se_8 rings and long selenium chains. By storage selenium crystallizes at the room temperature.

- ➢ Nucleation of crystallization has been found to be heterogeneous because of the fact that the distribution of the crystallization nuclei hardly changes with the heating time at a given temperature situated above ~60 °C.

- ➢ The amorphous selenium films are different from the melt-quenched selenium in its weight fraction of Se_8 rings. The structure of amorphous selenium films depends on the deposition conditions, i.e. substrate temperature, deposition rate, etc.

Popescu book, ch. 2.

Properties of amorphous selenium

- Vitreous selenium is soluble in sulfuric acid and slightly soluble in carbon disulphide. It is insoluble in water and alcohol. The organic solvents as alcohol, benzene, toluene, chloroforms, etc. produce the transformation of a-Se into “red” crystalline form. The solvents as quinoline, aniline, pyridine, etc. leads to the transformation of a-Se into metallic Se.

- The density of vitreous Se is 4.27 g/cm^3 and increases to 4.79 g/cm^3 when amorphous selenium is converted into the metallic form. In liquid the density is 3.99 g/cm^3 at 220 °C.

- Amorphous selenium is rather a soft material. Its hardness is 2.0 on the Moss scale (as compared to Pb: 1.5 and Cu: 2.5-3.0).

- The thermal expansion coefficient is 5.6 X 10^{-5} 1/K while that of hexagonal (metallic) selenium is 3.2 X 10^{-5} 1/K. The thermal conductivity at 20 °C is 2 X 10^{-3} W/cm.K for both a-Se and metallic Se.

Popescu book, ch. 2.

Properties of amorphous selenium

- ✓ *Electrical and dielectric properties*

- ➢ The resistivity of glassy selenium at room temperature is ~10^{12} Ω.cm. The thermal activation energy obtained from resistance-temperature measurements is ~1.7 eV.

- ➢ In thin evaporated films of a-Se the effective mobility of electrons is ~5 X 10^{-3} cm^2/V.s and ~0.14 X 10^{-3} cm^2/V.s for holes. The dielectric constant ranges from 5.97 to 6.60.

Popescu book, ch. 2.

Properties of amorphous selenium

✓ *Optical properties*

- The optical bandgap of selenium is 2.1 eV. The absorption edge is situated at 540 nm for a-Se and 620 nm for hexagonal Se and for liquid selenium at 220 °C.
- The activation energy found from photoconductivity measurements is 2.5 eV. This value agrees approximately with the wavelength at which the absorption constant begins to fall down rapidly. This value agrees, also, with the energy associated with the Se-Se bond, which is 225kJ/mol.
- The refractive index has a maximum value of n = 3.13 at about 500 nm. In the infrared range n = 2.46.

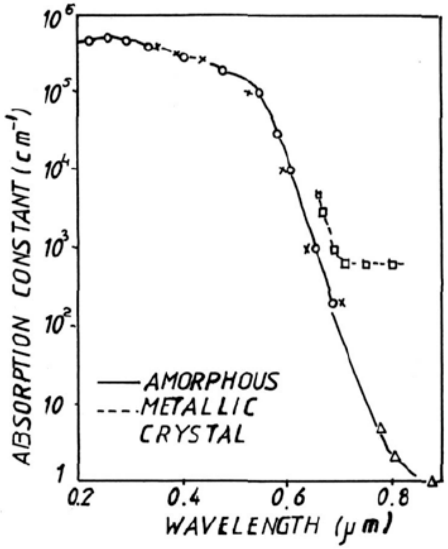


Figure 2.7. Absorption in selenium: —— amorphous ------- crystalline, metallic Se.

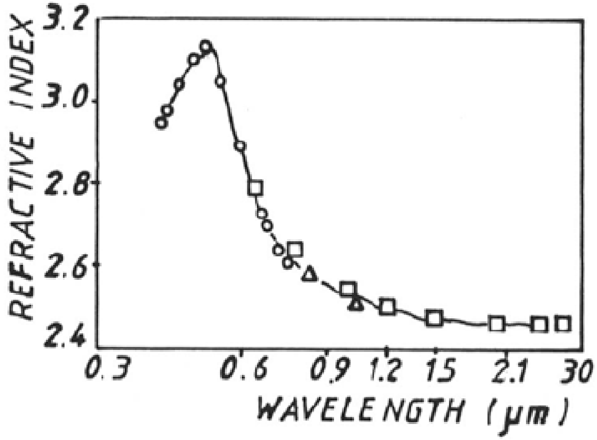


Figure 2.8. The refractive index for selenium.

Popescu book, ch. 2.

Properties of amorphous tellurium

✓ *Mechanical and thermal properties*

➢ Glassy state of tellurium can be reached only through very high cooling rates. Rates corresponding to ~10^{10} K/s are necessary to get thin amorphous film. Amorphous films can be also obtained by condensation from vapors on substrates cooled at 77 K.

➢ Changes in the density show that melting destroys the ordered chain structure of the crystalline tellurium only partially. Thus, one gets a mixture of chain molecules, whose average length decreases when temperature is raised.

➢ The electrical conductivity increases when the viscosity decreases and this behavior indicates that the metallic character is related to the increase of the density of broken bonds.

Popescu book, ch. 2.

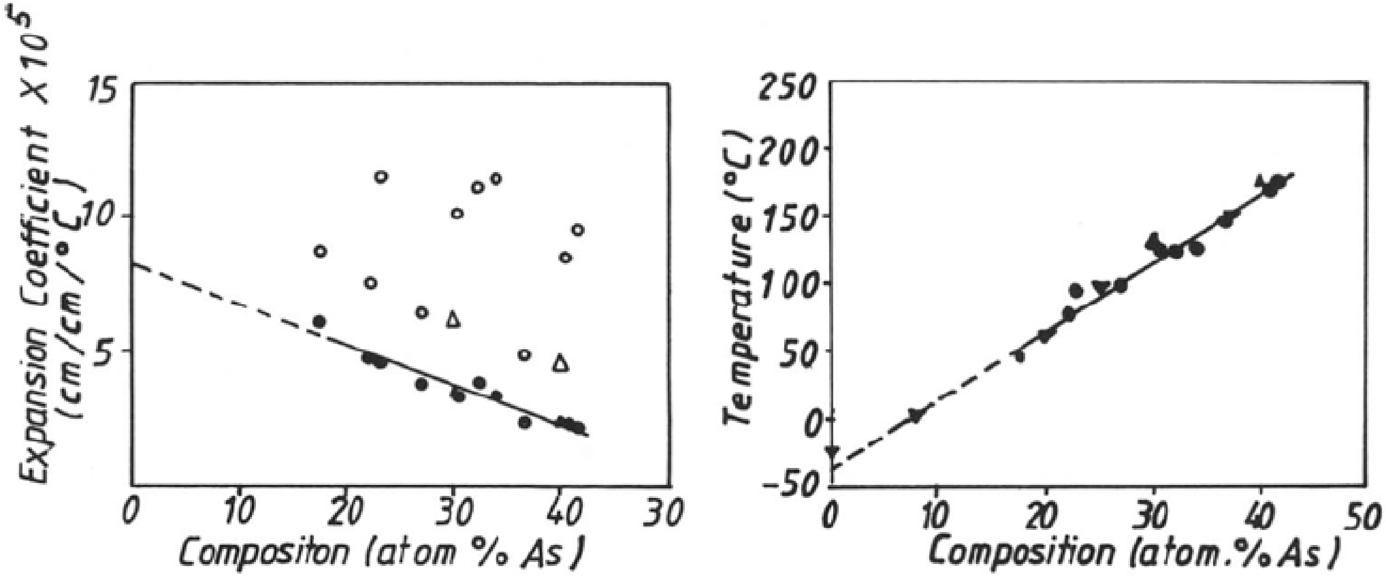
Properties of amorphous tellurium

✓ *Electrical and optical properties*

- The electrical conductivity at room temperature is 10^{-4} $S^{-1}cm^{-1}$. The thermal activation energy is 0.44 eV. Between 77 and 170 K the Mott law $T^{-1/4}$ is valid and the activation energy is 0.046 eV.
- The electrical conductivity increases during melting and for further heating. This effect is related to the increase of the co-ordination number of tellurium.
- By amorphization the absorption edge shifts toward short wavelengths. The shift of the absorption edge is accompanied by the decrease of the refractive index from 5.3 (for polycrystalline tellurium) to 3.4 for amorphous tellurium.
- The essential decrease of the refractive index of the amorphous tellurium as compared to polycrystalline tellurium was explained by the change of the effective number of nearest neighbors in the disordered material on the account of the disorder between atom chains. The optical gap of amorphous tellurium is 0.9 eV.

Properties of As-S glass

- For increasing concentration of arsenic in the system As-S, the stability against crystallization increases. The glass with the content of 6 at.% As crystallizes at room temperature in a day with the formation of rhombic sulfur, while the glass of composition As_2S_5 cannot be crystallized by thermal annealing.



a.

b.

Figure 2.19. The expansion coefficient (a) and the softening temperature (b) in As-S glasses.

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Electrical and dielectric properties. The temperature dependence of the electrical conductivity (d.c.) was investigated. For the most part of the amorphous semiconductors, and for a very large temperature range, the following relation is valid:

$$\sigma = \sigma_o \exp(-E_\sigma/kT) \tag{2.55}$$

where σ_o is a proportionality coefficient and E_σ is the activation energy.

For relatively high temperatures the preexponential factor, σ_o, is considerably lower than in other amorphous semiconductors **($10^3 \div 10^4\ \Omega^{-1}\mathrm{cm}^{-1}$)** and takes the values in the interval **$6 \div 8\ \Omega^{-1}\mathrm{cm}^{-1}$** and even **$9\ \Omega^{-1}\mathrm{cm}^{-1}$** [96]. The results obtained on samples of

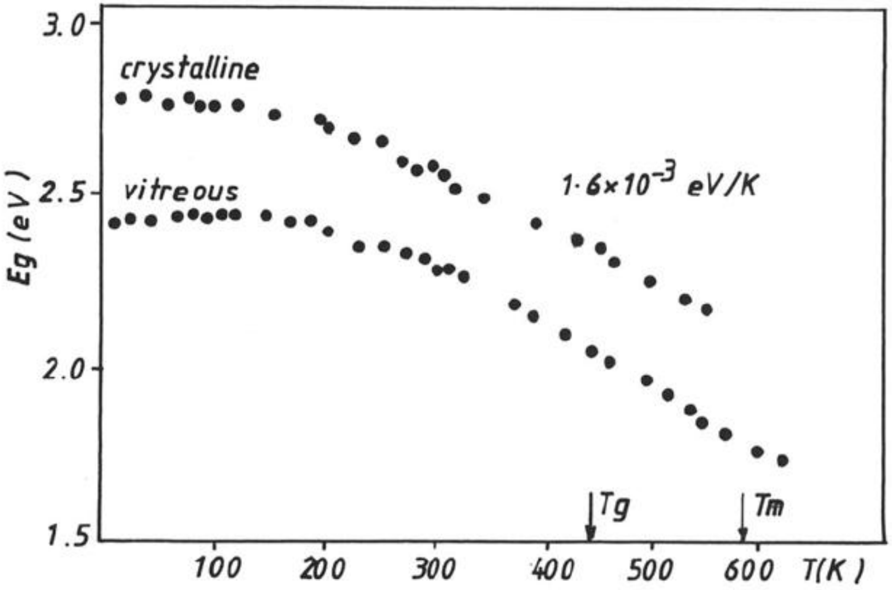

Figure2.22. Dependence on temperature of the absorption edge of crystalline and glassy As_2S_3.

Permittivity, refractive index and density in the glassy system As_xS_{1-x}.

x	ε	n_∞	d(g/cm^3)
0.10	4.6	1.98	2.29
0.14	4.9	2.04	2.42
0.20	5.3	2.10	2.38
0.25	5.9	2.17	2.73
0.33	6.9	2.30	2.99
0.40	8.0	2.39 2.38-2.41*	3.18
0.44	7.0	2.38	3.24

* experimental

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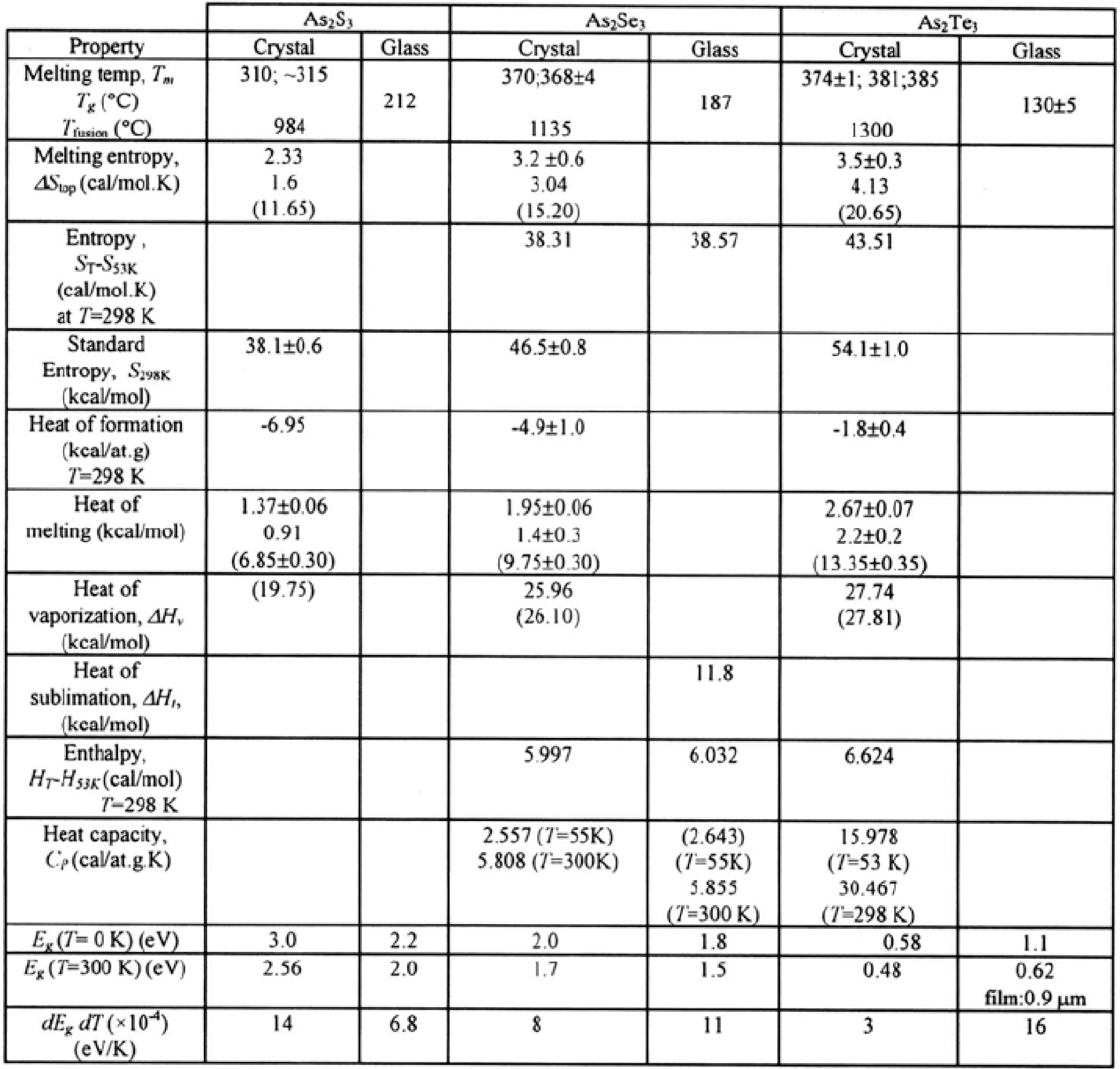
Thermodynamical and some electronic properties of As_2Ch_3 glasses [28, 65,146-150].



	As_2S_3		As_2Se_3		As_2Te_3	
Property	Crystal	Glass	Crystal	Glass	Crystal	Glass
Melting temp, T_m T_g (°C) T_{fusion} (°C)	310; ~315 984	212	370;368±4 1135	187	374±1; 381;385 1300	130±5
Melting entropy, ΔS_{top} (cal/mol.K)	2.33 1.6 (11.65)		3.2 ±0.6 3.04 (15.20)		3.5±0.3 4.13 (20.65)	
Entropy , S_T-S_{53K} (cal/mol.K) at T=298 K			38.31	38.57	43.51	
Standard Entropy, S_{298K} (kcal/mol)	38.1±0.6		46.5±0.8		54.1±1.0	
Heat of formation (kcal/at.g) T=298 K	-6.95		-4.9±1.0		-1.8±0.4	
Heat of melting (kcal/mol)	1.37±0.06 0.91 (6.85±0.30)		1.95±0.06 1.4±0.3 (9.75±0.30)		2.67±0.07 2.2±0.2 (13.35±0.35)	
Heat of vaporization, ΔH_v (kcal/mol)	(19.75)		25.96 (26.10)		27.74 (27.81)	
Heat of sublimation, ΔH_t, (kcal/mol)				11.8		
Enthalpy, H_T-H_{53K} (cal/mol) T=298 K			5.997	6.032	6.624	
Heat capacity, C_P (cal/at.g.K)			2.557 (T=55K) 5.808 (T=300K)	(2.643) (T=55K) 5.855 (T=300 K)	15.978 (T=53 K) 30.467 (T=298 K)	
E_g (T= 0 K) (eV)	3.0	2.2	2.0	1.8	0.58	1.1
E_g (T=300 K) (eV)	2.56	2.0	1.7	1.5	0.48	0.62 film:0.9 μm
$dE_g\ dT$ (×10^{-4}) (eV/K)	14	6.8	8	11	3	16

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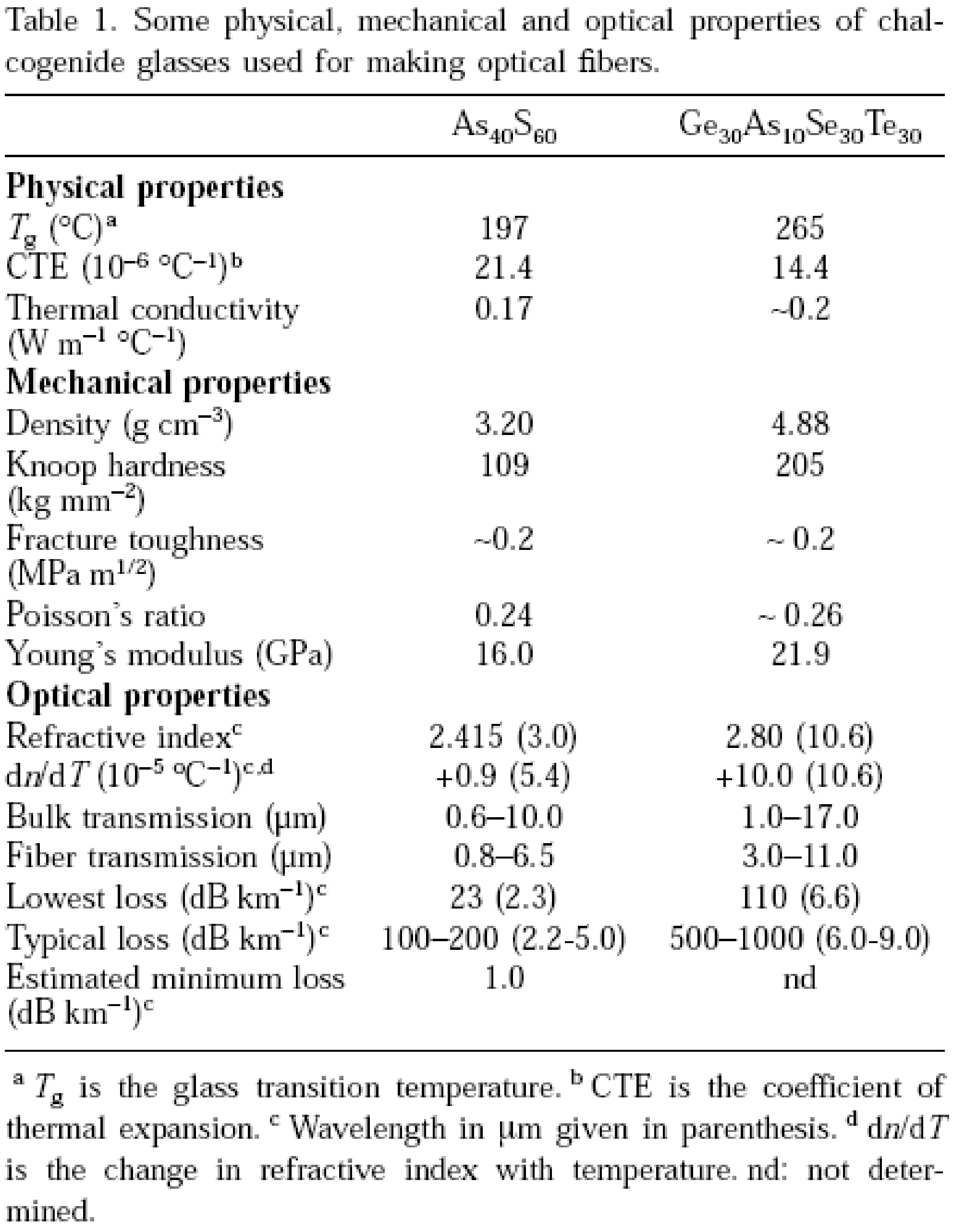

Table 1. Some physical, mechanical and optical properties of chalcogenide glasses used for making optical fibers.

	$As_{40}S_{60}$	$Ge_{30}As_{10}Se_{30}Te_{30}$
Physical properties		
T_g (°C)[a]	197	265
CTE (10^{-6} °C^{-1})[b]	21.4	14.4
Thermal conductivity (W m^{-1} °C^{-1})	0.17	~0.2
Mechanical properties		
Density (g cm^{-3})	3.20	4.88
Knoop hardness (kg mm^{-2})	109	205
Fracture toughness (MPa $m^{1/2}$)	~0.2	~ 0.2
Poisson's ratio	0.24	~ 0.26
Young's modulus (GPa)	16.0	21.9
Optical properties		
Refractive index[c]	2.415 (3.0)	2.80 (10.6)
dn/dT (10^{-5} °C^{-1})[c,d]	+0.9 (5.4)	+10.0 (10.6)
Bulk transmission (μm)	0.6–10.0	1.0–17.0
Fiber transmission (μm)	0.8–6.5	3.0–11.0
Lowest loss (dB km^{-1})[c]	23 (2.3)	110 (6.6)
Typical loss (dB km^{-1})[c]	100–200 (2.2-5.0)	500–1000 (6.0-9.0)
Estimated minimum loss (dB km^{-1})[c]	1.0	nd

[a] T_g is the glass transition temperature. [b] CTE is the coefficient of thermal expansion. [c] Wavelength in μm given in parenthesis. [d] dn/dT is the change in refractive index with temperature. nd: not determined.

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Properties of Ge-S and Ge-Se glasses

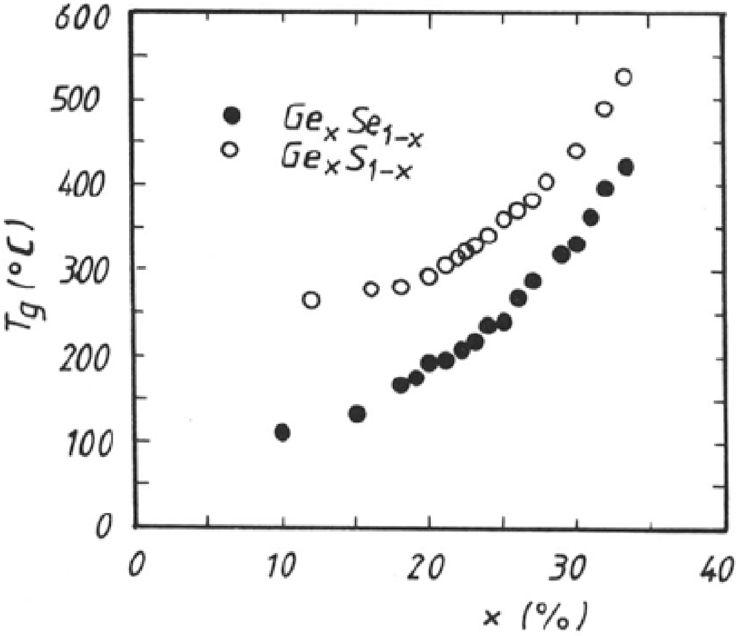

Figure 2.49. (a) The glass transition temperature T_g of Ge-S glasses (•) and of Ge-Se glasses (o) [176,177].

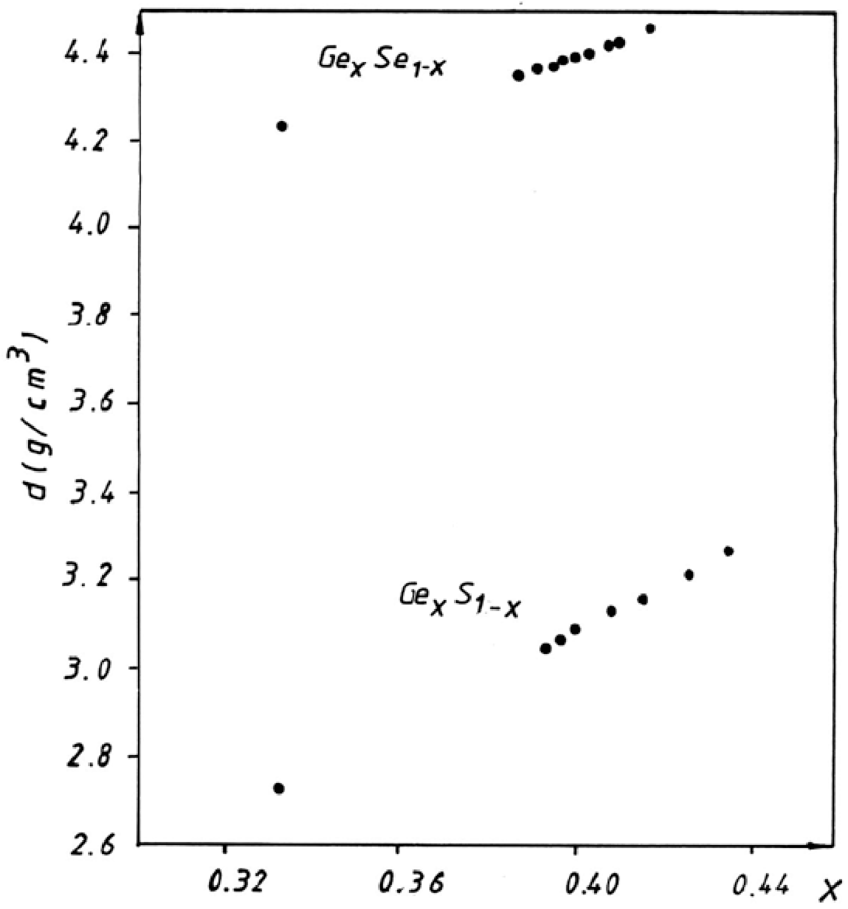

Figure 2.50. The densities in the glassy systems Ge-S and Ge-Se.

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Properties of Ge-S and Ge-Se glasses

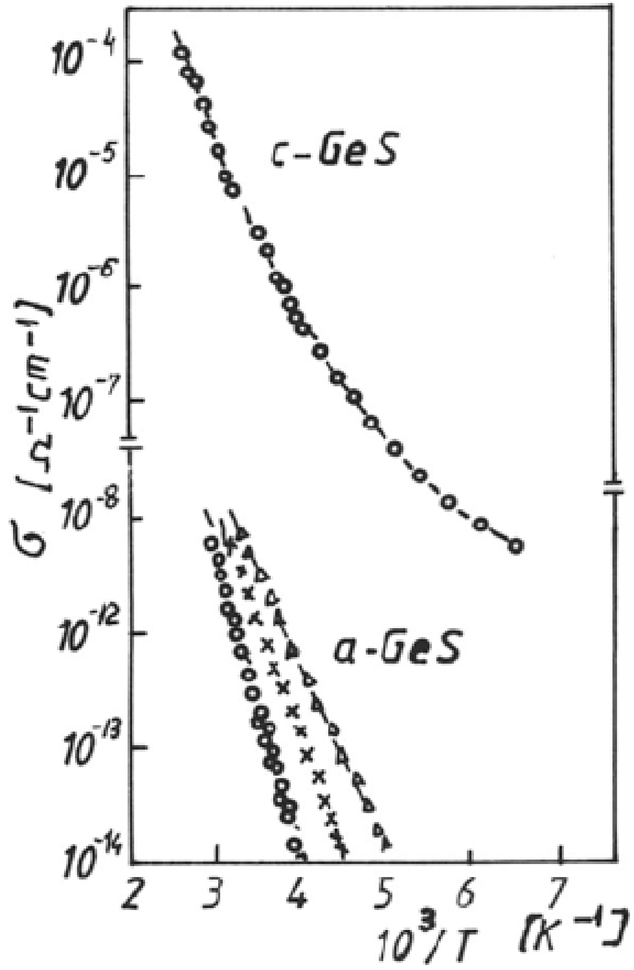

Figure 2.51. The temperature dependence of conductivity for crystalline and amorphous GeS layers.
(deposition temperatures: • 220 °C × 230 °C Δ 250 °C).

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Properties of Ge-S and Ge-Se glasses

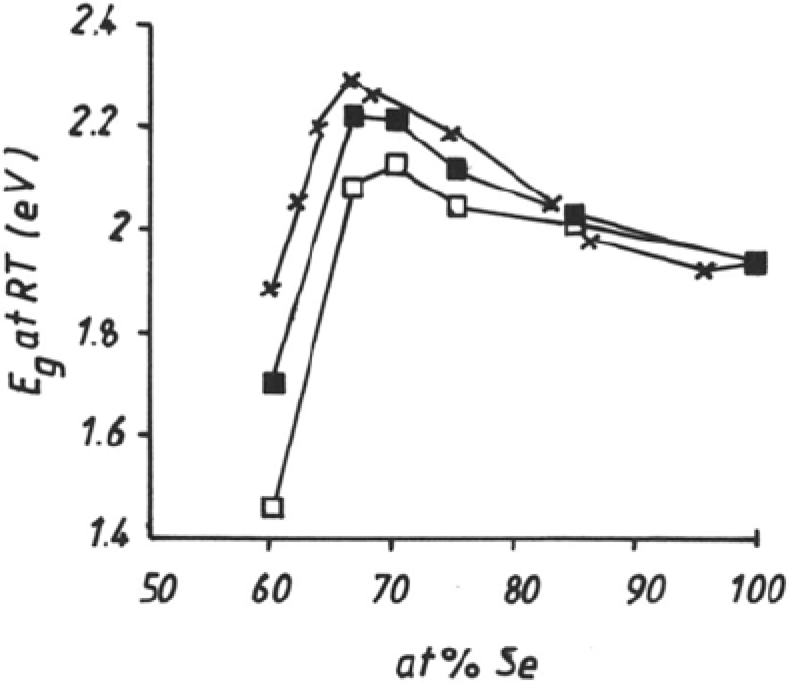

Figure 2.53. The optical gap in Ge_xSe_{1-x} films.
× PECVD films, virgin ■ annealed films □ evaporated films,

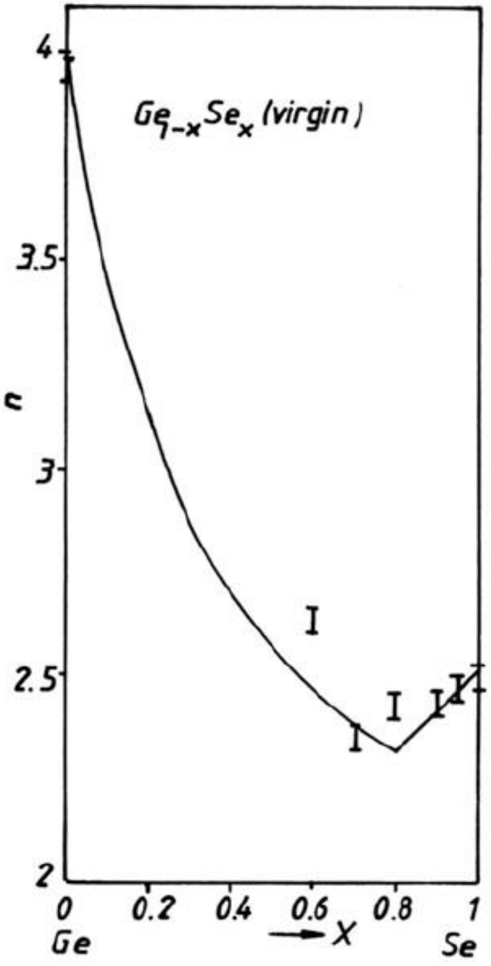

Figure 2.54. The refractive index as a function of atomic concentration, x, for the $Ge_{1-x}Se_x$ system. The solid curve indicates the calculated value.

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Properties of Ge-Te glass

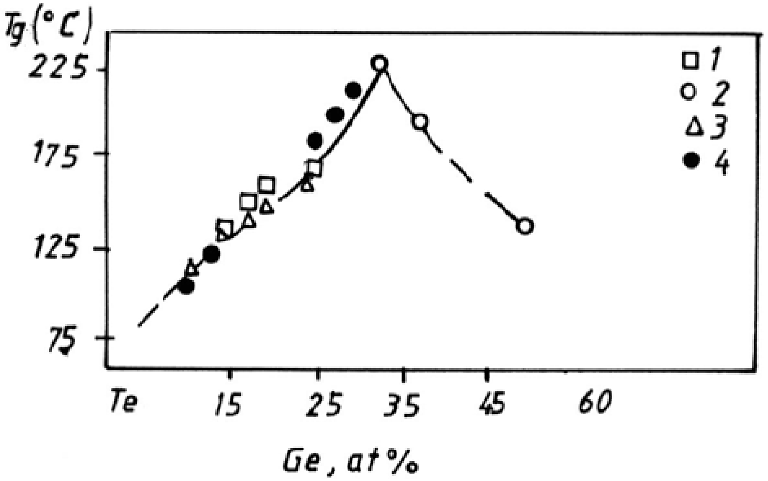

Figure 2.56. The evolution of the T_g in Ge-Te glassy alloys. The samples were prepared [194] by: 1 - spray cooling 3- splat cooling 2- cathode sputtering 4-cooling in NaCl solution [195].

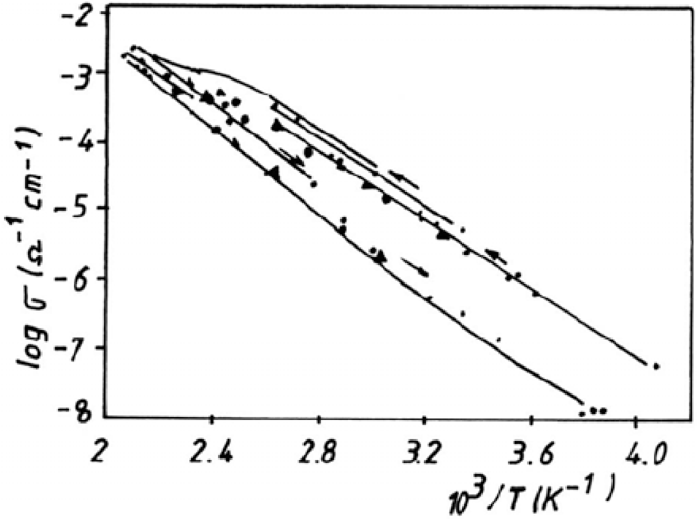

Figure 2.57. Electrical conductivity of sputtered **$GeTe_2$** films versus reciprocal temperature. Film thickness: **(•) 45.5 µm** **(Δ) 1.10 µm**. Activation energy at 25 °C is 0.51 eV on heating and 0.59 eV on cooling.

Popescu book, ch. 2.