Midgap electronic states in amorphous pnictide and chalcogenide semiconductors

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Motivation: why pnictides and chalcogenides

Amorphous pnictides/chalcogenides* exhibit **significant photo-and current-induced changes** whose nature is not well understood.

* pnictogens – P,As,Sb, chalcogens – S,Se,Te

Applications:

- **$Ge_2Sb_2Te_5$** and **AgInSbTe** – the most common phase-change materials used in writable (DVD-RAM) and rewritable (DVD-RW, PCM) storage media.
- **Se** – the most common photoconductor used in photocopying.
- **Bi_2Te_3** – one of the best performing thermoelectrics.

Motivation: why midgap states
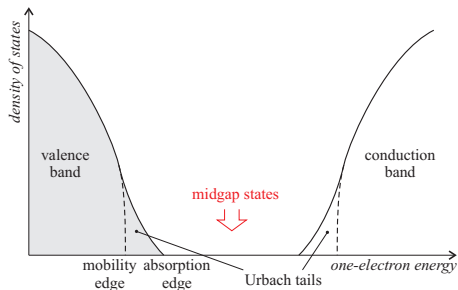
Identified by ▶ see Experiments

- ▶ light-induced ESR
- ▶ light-induced midgap absorption
- ▶ threshold for doping by metals

The induced concentration of midgap states is 10^{20} cm^{-3} (1 per 200 atoms) so that they

- ▶ influence population and trapping of electron and holes;
- ▶ are absorption and recombination centers;
- ▶ are supposed to be intimately related to light-induced structural changes.

Outline

- Structural and electronic properties of pnictides and chalcogenides: short overview
- Midgap states: current state of the problem, open questions, the underlying idea of our approach
- Our model of midgap states and how does it answer the posed questions
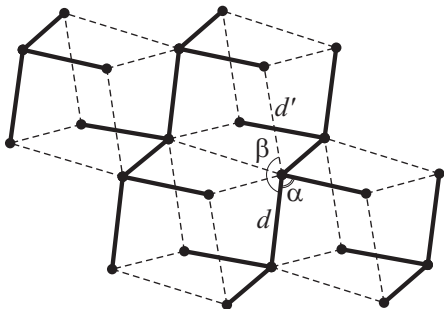
Outline

What materials will we consider?

Pnictides and chalcogenides

- ▸ with average 5-6 valence electrons per atom
- ▸ excluding light elements and heavy elements
- ▸ with small variance in electronegativity, $\Delta\varepsilon_p \ll t_{pp\sigma}$
- ▸ *for example*: As, Se, $As_x Se_{1-x}$, $Ge_x Se_{1-x}$
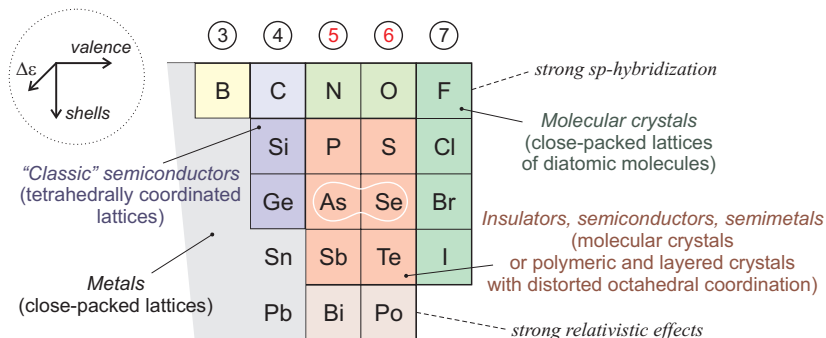
Structural motifs: distorted octahedral coordination

GeTe, rhombohedral As
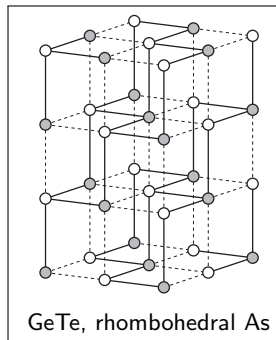
- Right-angled geometry: $90° \lesssim \alpha < 109°$
- Secondary bonding: $d' < r_{vdW}^{A} + r_{vdW}^{B}$ and additionally $\beta > 160°$ (back-bonding) ▸ see Secondary bonding
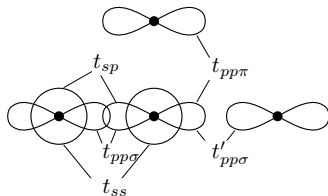- Trans-influence: $d > r_{cov}^{A} + r_{cov}^{B}$

But

- some covalent or secondary bonds may be missing, especially for elements of group VI and VII;
- competing tetrahedral coordination for elements of group IV.

Electronic structure: degeneracy of the covalent network
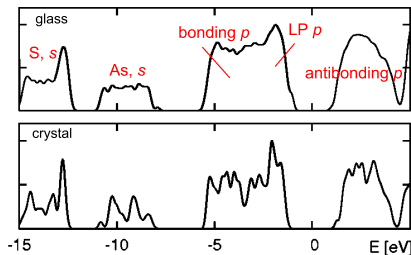
EDOS for As_2S_3 (Simdyankin, Elliott, 2004)

Transfer integrals

- ▶ *s*-orbitals do not contribute to bonding
  — it is the network of $pp\sigma$-bonds ($pp\sigma$-network)

- ▶ $pp\sigma$-bonds themself do not form 3D solid
  — the structure is determined by the balance of

  - secondary bonding $\qquad\qquad$ $t'^2_{pp\sigma}/2t_{pp\sigma}$
  - hybridization or *sp*-interaction $\quad$ $t^2_{sp}/(\varepsilon_p - \varepsilon_s - t_{pp\sigma})$
  - $pp\pi$-interaction (usually small) $\quad$ $t^2_{pp\pi}/2t_{pp\sigma}$

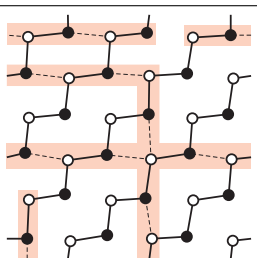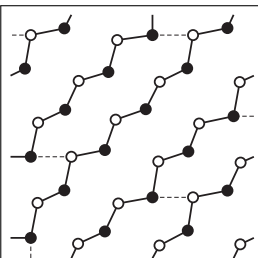## $pp\sigma$-networks: three classes

Project the Fock matrix onto valence p-orbitals (see ⟨▸ method⟩ and its ⟨▸ illustration⟩) and mark all the resulting elements $\gtrsim 0.5 t_{pp\sigma}$
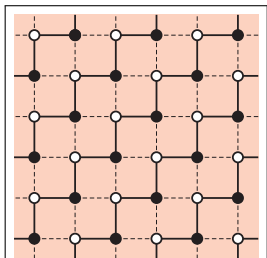
strong back-bonding
($t'_{pp\sigma}/t_{pp\sigma} > 0.5$)
As, As$_2$Te$_3$, GeTe
poor glassformers

weak back-bonding
(on average)
As$_2$Se$_3$, Se
glassformers

negligible back-bonding
($t'_{pp\sigma}/t_{pp\sigma} < 0.2$)
As$_2$O$_3$, GeSe$_2$
glassformers

Outline

Midgap states: Conceptual developments
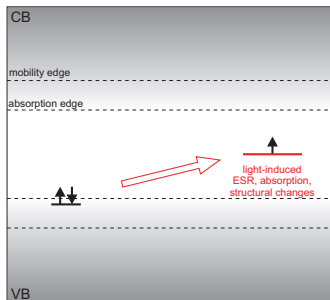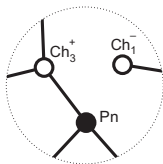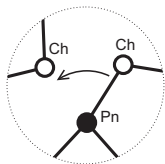
1. Midgap states originate from coordination defects whose ground state is charged (Street, Mott, 1975)
2. They pair up into positively charged overcoordinated atom and negatively charged undercoordinated – VAP (Kastner, Adler, Fritzsche, 1976; Pollard, Joannopoulos, 1979)
3. Defects can move and be created by bond switching, which is the underlying mechanism for light-induced phenomena

Midgap states: Open questions

1. Microscopic realization of the defects.
2. What is the effective-U, that is the difference between the energies of charged and neutral defects?
3. What are barriers for the bond switching?
4. Two kinds of paired defects: one can be easily created upon light illumination and then annihilates and another are stable.

Brute-force approach does not provide the solution

Ab-initio molecular dynamics:
(Drabold *et al.* since 90s, Elliott *et al.* 2000s)

- ▶ 4 orbitals per atom
- ▶ 200 atoms in a supercell
- ▶ cooled from melted crystal and equilibrated for 100 ps

Summary of results:

⇒ Reproduce bulk properties well (DOS, structure factor)

⇒ Conceptually consistent with theories of midgap state

but for study of structural defects

⇒ Are they reproducible? ▶ see example

⇒ Do they provide representative sampling of the glass?

⇒ Bond switching was not studied

⇒ Prone to systematic errors:
  - Inaccurate parametrization
  - Too fast cooling or improper initial configuration
  - Too small linear size (6 atoms in periodic boundary conditions)

More efficient approach: cluster in a proper environment

1. Guess the geometry of the structural defect
2. Put it in a proper environment
3. Optimize the geometry

A. Systematic studies (simplified models):
   - Joannopoulos, Pollard, Vanderbilt, 1979-81
   - **We add secondary bonding**
B. Case studies (realistic calculations):
   - O'Reilly, Kelly, 1981 – As
   - . . .
   - Simdyankin, Elliott *et al.* 2005 – As_2S_3
   - **We propose novel configurations**

Methods for electronic structure calculations ▸ details

A. Extended Hubbard model:
- ▸ *use* RHF/SUHF ▸ see SUHF
- ▸ *check by* exact diagonalization for small systems
- ▸ *check by* DMRG for large systems

B. Realistic calculations:
- ▸ *use* semiempirical PM6 (`MOPAC`): 4 valence + polarization *d*-orbitals, NDDO (only Coulomb integrals in multipole approx. for interatomic elements), RHF/ROHF+post-HF
- ▸ *check by* ab-initio MP2 or DFT in GTO (`Firefly`) for small
- ▸ *check by* ab-initio DFT in PW (`Abinit`) for periodic systems

Technical limitations: PM6 parametrization was not designed for pnictide/chalcogenide semiconductors
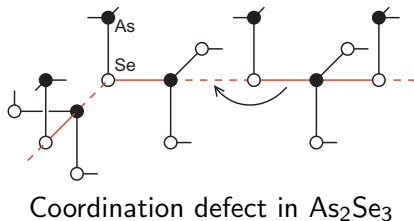
Our approach: idea

(i) Secondary bonding is essential

(ii) Lowest energy motions are collective

$\implies$
- linearly extended defects
- barrierless bond switching

less moving oxygens

Si

moving oxygens

most moving oxygen
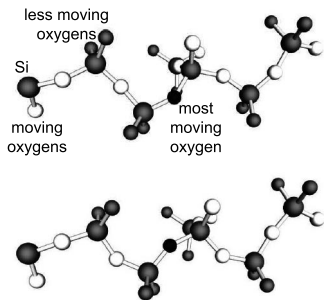
Two-level system in SiO_2
(Reinisch, Heuer, 2005)

As

Se

Coordination defect in As_2Se_3

Outline

Single coordination defect (without lone pairs involved)

Mapping onto the extended Hubbard–Peierls model
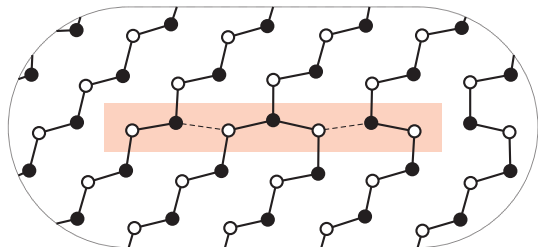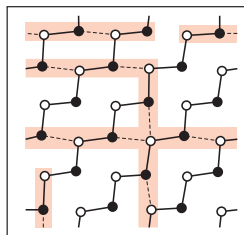
- ▶ Lowest energy motions in glasses do not change the topology of interconnections
- ▶ One orbital per atom of the chain (inline *p*-orbital) ▸ see details
- ▶ Electron-electron interaction in ▸ extended Hubbard model
- ▶ Electron-phonon interaction in adiabatic approximation:
  – transfer integrals depends on the bond length,
  – on-site energies depends on the environment ▸ see details

Extended Hubbard–Peierls model: Hamiltonian
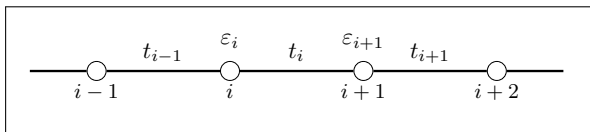
$$H^{tot} = \sum_i \Big\{ \; \varepsilon_i n_i - t_i T_i \qquad \text{one-electron Hamiltonian}$$
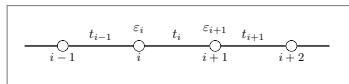
$$+ U n_i^\uparrow n_i^\downarrow + V n_i n_{i+1} \qquad \text{on-site and inter-site e-e repulsion}$$

$$+ \frac{(\varepsilon_i - \varepsilon_i^0)^2}{2\alpha} + \frac{(t_i - t_i^0)^2}{2\beta} \Big\} \qquad \text{lattice energy}$$

- ε_i and t_i are electron on-site energies and transfer integrals
- $n_i = n_i^\uparrow + n_i^\downarrow$, $n_i^s = c_{i,s}^+ c_{i,s}$ are occupation-number operators
- $T_i = \sum_s \left(c_{i,s}^+ c_{i+1,s} + c_{i+1,s}^+ c_{i,s} \right)$
- $c_{i,s}^+ / c_{i,s}$ are spin-s ($\uparrow$ or $\downarrow$) creation/annihilation operators

Extended Hubbard–Peierls model: parameters

$$H^{\text{tot}} = \sum_i \left\{ \varepsilon_i n_i - t_i T_i + U n_i^\uparrow n_i^\downarrow + V n_i n_{i+1} + \frac{(\varepsilon_i - \varepsilon_i^0)^2}{2\alpha} + \frac{(t_i - t_i^0)^2}{2\beta} \right\}$$

Typically
$$\varepsilon_i^0 = (-1)^i \epsilon, \qquad t_i^0 = t + (-1)^i \delta/2,$$

ϵ is variance in electronegativity (polymethineimine, poly-CHN),
δ is built-in dimerization (cis-polyacetylene).

	on-site	inter-site
one-electron	ϵ	δ
electron-phonon interaction	α	β
electron-electron interaction	U	V

Relation to other models

Full model:

$$\sum_i \left\{ \varepsilon_i \mathsf{n}_i - t_i \mathsf{T}_i + U \mathsf{n}_i^\uparrow \mathsf{n}_i^\downarrow + V \mathsf{n}_i \mathsf{n}_{i+1} + \frac{(\varepsilon_i - \varepsilon_i^0)^2}{2\alpha} + \frac{(t_i - t_i^0)^2}{2\beta} \right\}$$

Extended Hubbard model – electron-electron interaction only:

$$\sum_i \left\{ \varepsilon_i \mathsf{n}_i - t_i \mathsf{T}_i + U \mathsf{n}_i^\uparrow \mathsf{n}_i^\downarrow + V \mathsf{n}_i \mathsf{n}_{i+1} \phantom{+ \frac{(t_i - t_i^0)^2}{2\beta}} \right\}$$

Su–Schrieffer–Heeger (SSH) model – electron-phonon interaction only:

$$\sum_i \left\{ \varepsilon_i \mathsf{n}_i - t_i \mathsf{T}_i \phantom{+ U \mathsf{n}_i^\uparrow \mathsf{n}_i^\downarrow + V \mathsf{n}_i \mathsf{n}_{i+1}} + \frac{(t_i - t_i^0)^2}{2\beta} \right\}$$

Simplified model of polaron:

$$\sum_i \left\{ \varepsilon_i \mathsf{n}_i \phantom{- t_i \mathsf{T}_i} + U \mathsf{n}_i^\uparrow \mathsf{n}_i^\downarrow \phantom{+ V \mathsf{n}_i \mathsf{n}_{i+1}} + \frac{(\varepsilon_i - \varepsilon_i^0)^2}{2\alpha} \phantom{+ \frac{(t_i - t_i^0)^2}{2\beta}} \right\}$$

Hydrogen passivated arsenic chain
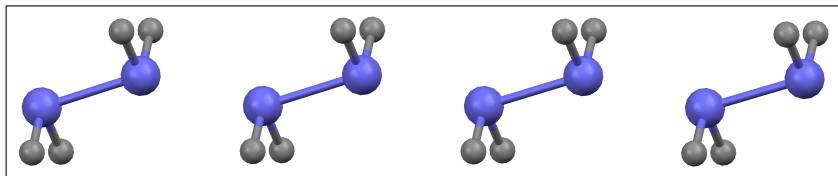
Geometry of As_2H_4–As_2H_4

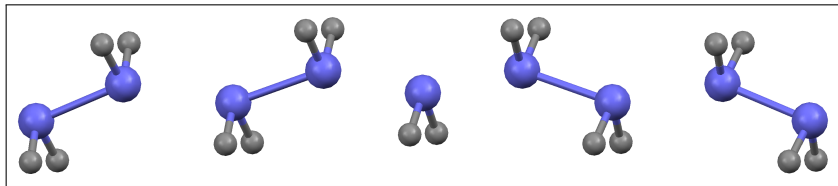|	d_{AsAs},Å	d'_{AsAs},Å	β_{AsAsAs}	E_{bind},eV
PM6	2.463	3.06	148°	0.17
MP2	2.483	3.57	177°	0.13
Ref.*	(2.441)	3.53	(180°)	0.10

*Klinkhammer, Pyykko, 1995

Neutral coordination defect in arsenic chain

Su–Schrieffer–Heeger (SSH) model do work

Compare predictions of SSH model

$$H^{tot} = \sum_i \left\{ -t_i T_i + \frac{t_i^2}{2\beta} \right\}$$

with semiempirical ROHF calculations of $(AsH_2)_{21}$ chain

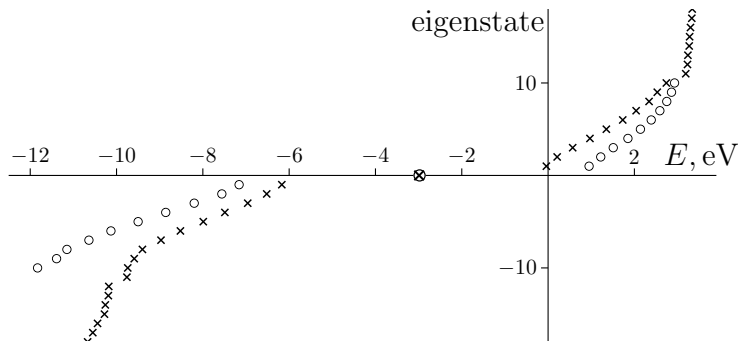**Note:** Coordination defect does not change the "environment"

- deviations in H–H bond lengths are less than $0.001\,\text{Å}$
- deviations in H–As–H angles are less than $0.2°$
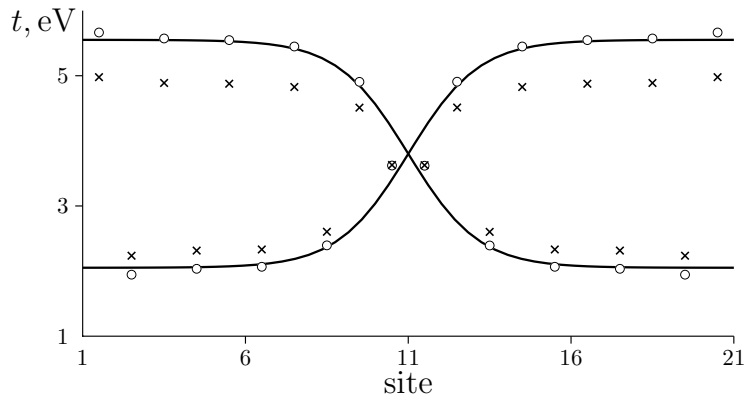
Neutral coordination defect in arsenic chain

Eigenvalues

- crosses – full semiempirical calculations,
- circles – one-orbital approximation.
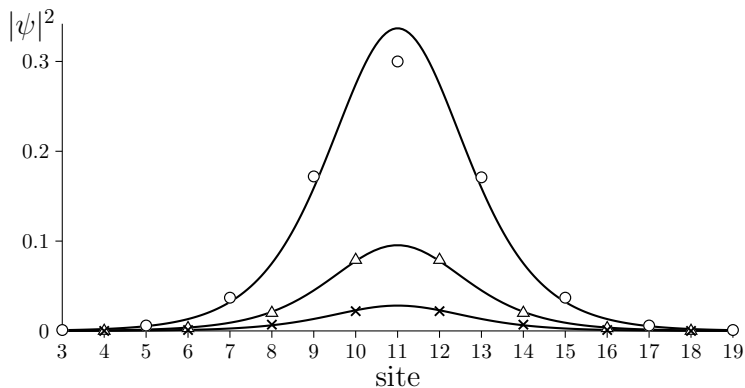
Neutral coordination defect in arsenic chain

Transfer integrals

- crosses – bare,
- circles – renormalized,
- solid line – as predicted by SSH model.

Neutral coordination defect in arsenic chain

Midgap eigenfunction

- ▶ circles – As p_z-AOs (73%-contribution),
- ▶ triangles – As s-AOs (21%),
- ▶ crosses – all other AOs (6%),
- ▶ solid lines – as predicted by SSH model.

Outline

Linearly extended defects

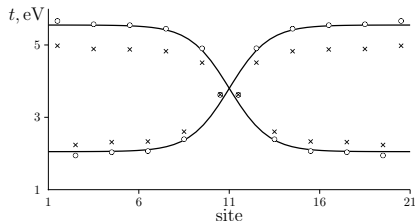Two estimates for the linear size ξ of a coordination defect:

- decay length of the midgap eigenfunction
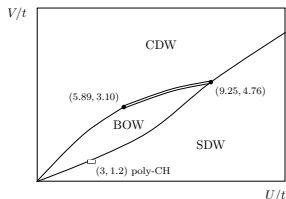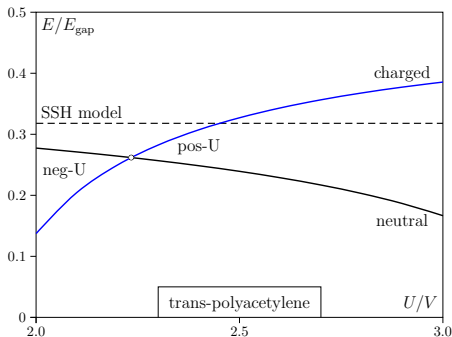
$$\xi = 2 \ln \left(t/t' \right)^{-1}$$

- soliton semiwidth in the Su–Schrieffer–Heeger model

$$\xi = \frac{t + t'}{t - t'}$$

Both give $\xi > 3$ for $t'/t > 0.5$ (strong secondary bonding)

Effective-U is close to zero

Phase diagram of the extended Hubbard model

- ▶ Effective-U is negative if CDW dominates and positive if SDW dominates.
- ▶ For Coulomb interaction $2 \lesssim U/V \lesssim 3$ (dominating BOW), and the effective-U is order of magnitude smaller than U.
- ▶ In substances with strong electron-phonon interaction (large α) we can observe the transition from positive- to negative-U.
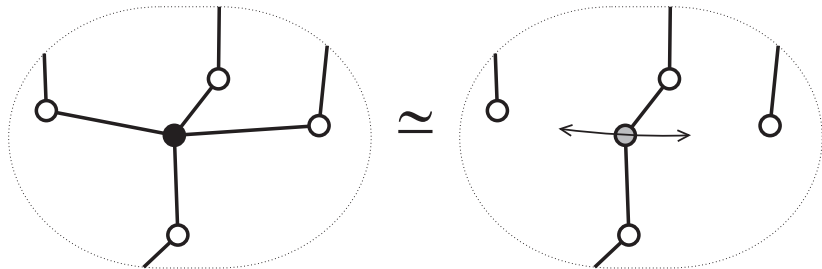
Barrierless bond switching

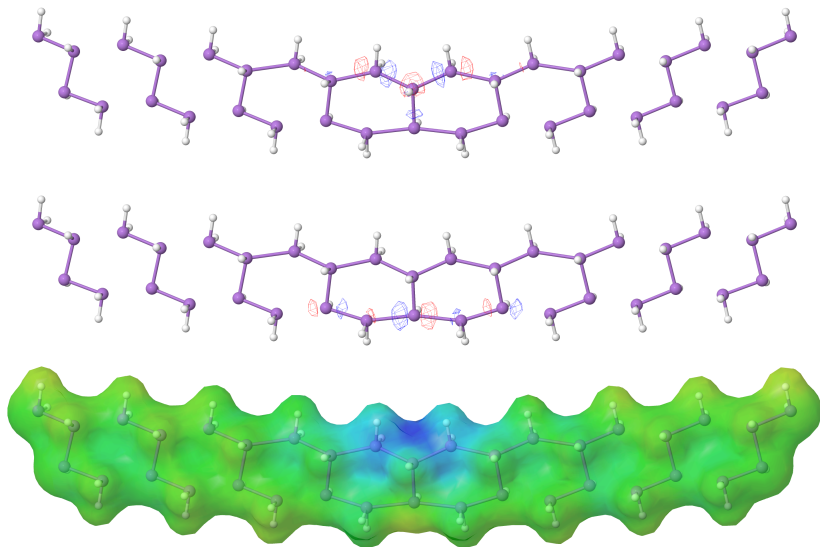Su–Schrieffer–Heeger model with zero variance in electronegativity

$$H^{\text{tot}} = \sum_i \left\{ \underbrace{-t(d_i)\mathsf{T}_i + \Phi^{\text{in}}(d_i)}_{1} + \underbrace{\Phi^{\text{ext}}_i(d_i)}_{2} \right\}$$

1. Motion of the coordination defect (soliton) in isolated chain is free.
2. Φ^{ext}_i pins the soliton, but we know in SiO_2 glass this motion can be almost barrierless (in two level systems).

Double arsenic chain

Topologically stable pair of coordination defects

Summary

In amorphous pnictide and chalcogenide semiconductors

1. Electronic and structural properties are strongly influenced by the secondary bonding.
2. There exist coordination defects linearly extended up to 10 atoms.
3. Major part of them are involved in two level systems.
4. The latter are responsible for light- and current-induced structural changes.

What is next?

▶ Simulations: we propose configurations for systematic search of two level system.

▶ Simulations: we are interested to apply our analysis of the Fock matrix to realistic simulations.

▶ Excited states: in our research only ground state was investigated.

▶ Experiments: modern spectroscopy can answer many questions.

Outline

Light-induced phenomena

Prolonged subgap illumination of glassy-As_2Se_3 causes changes[1] orders of magnitude larger than those in crystalline form, oxide glasses, or amorphous tetrahedral semiconductors:

- ESR (electron spin resonance) saturating at 10^{20} cm^{-3} upon illumination.
- Photodarkening (red-shift of the optical absorption edge) and rise of midgap absorption.
- Decrease of the main PL (photoluminescence) band and increase of a subgap excited PL.
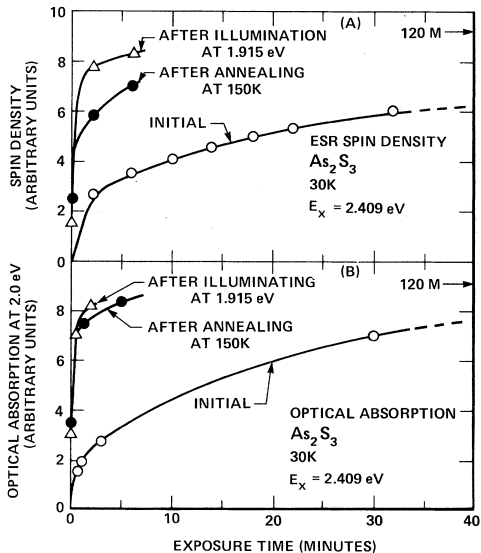- Volume expansion by a few percent[2].

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[1]Shimakawa K, Kolobov A, Elliott S R, Adv Phys 44, 475 (1995)

[2]Tanaka K, Saitoh A, Terakado N, J Optoelectronics Adv Mater 8, 2058 (2006)

Photoinduced ESR and subgap absorption

spin density reaches 10^{20} cm^{-3}

Photoinduced midgap absorption
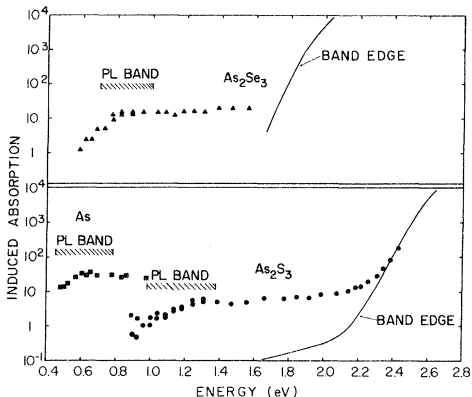
Photoluminescence after bandgap irradiation ◂ return ▸ more
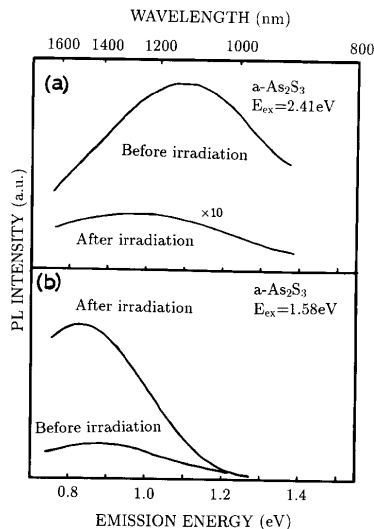
$T = 4.2\,\mathrm{K}$
$E_{\mathrm{irr}} = 2.41\,\mathrm{eV}$

Threshold switching in chalcogenides
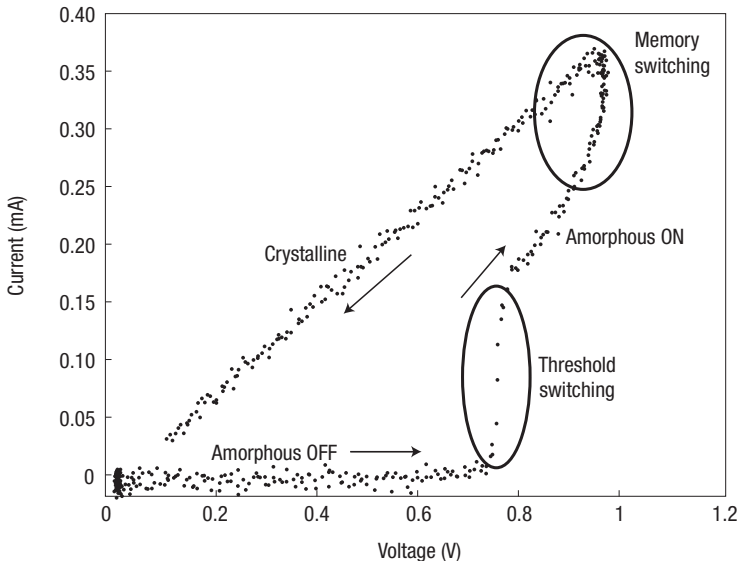
Secondary bonding: pnictogen chains

Can we consider secondary bonds as some kind of bonds?

d=2.49 Å   d'=3.04 Å
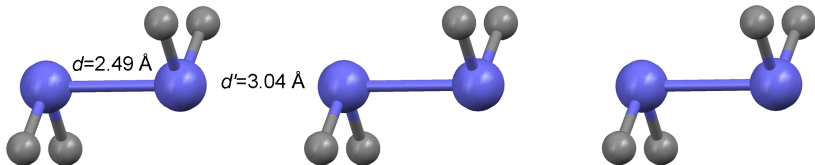
Infinite hydrogen-passivated arsenic chain (plane waves, LDA, HGH psp)

- ▶ Right-angled coordination
- ▶ Strong secondary bonding: $d' \ll 2r_{vdW}$ and perfect alignment
- ▶ Trans-influence: $d > 2r_{cov}$ (2.43 Å for isolated As_2H_4)
- ▶ Dimer and infinite chain have principally the same geometry

Secondary bonding: halogen molecules

Can we consider secondary bonds as some kind of bonds?

Br$_2$–Br$_2$ (aug-ccpVTZ, MP2; lowest p-MO)
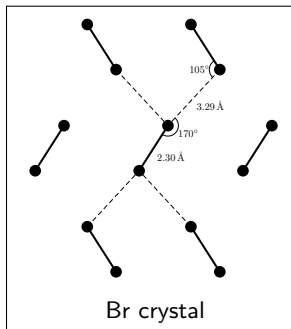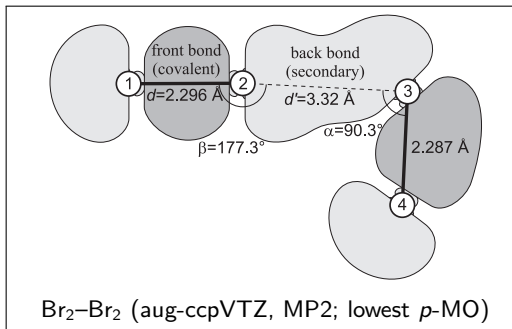
Br crystal

- ▶ Right-angled coordination: $\alpha \approx 90°$
- ▶ Secondary bonding: $d' < 2r_{vdW}$ and $\beta \approx 180°$
- ▶ Trans-influence: $d > 2r_{cov}$ (left molecule is elongated)
- ▶ Dimer and crystal have principally the same geometry

Secondary bonding in trans-polyacetylene

$pp\pi$ bonding

		C_2H_4	C_4H_6	C_6H_8	...	infinite	cis	trans
d, Å	C=C	1.34	1.34	1.35			1.37	1.36
d', Å	C–C*	—	1.47	1.45			1.44	1.44

* Not a single covalent bond, but covalent+secondary bond, single C–C bond length is 1.52 Å.

Molecular orbital picture of the secondary bonding

Yes, we can consider secondary bonds as bonds

3c4e model

4c4e model
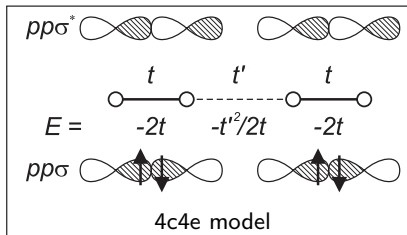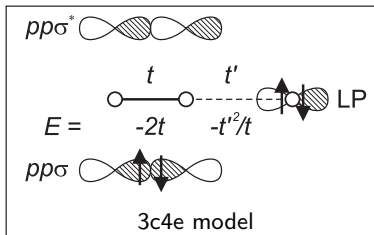
- ▶ One-orbital approximation: t_{ss} are negligible, $t_{sp} \ll \varepsilon_p - \varepsilon_s$, of all pp-integrals $pp\sigma$-integrals t and t' dominate, other p-orbitals are not in resonance.
- ▶ Effects of e-e interaction only renormalize one-electron parameters, i.e. Hartree–Fock approximation is valid.

Why the dimerization pattern does not depend on the chain length?
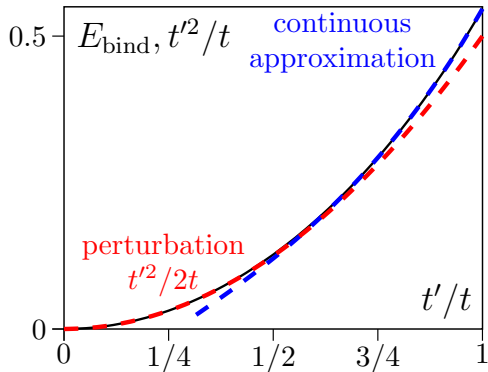
Electronic binding energy per dimer for an infinite chain ▸ see Peierls transition
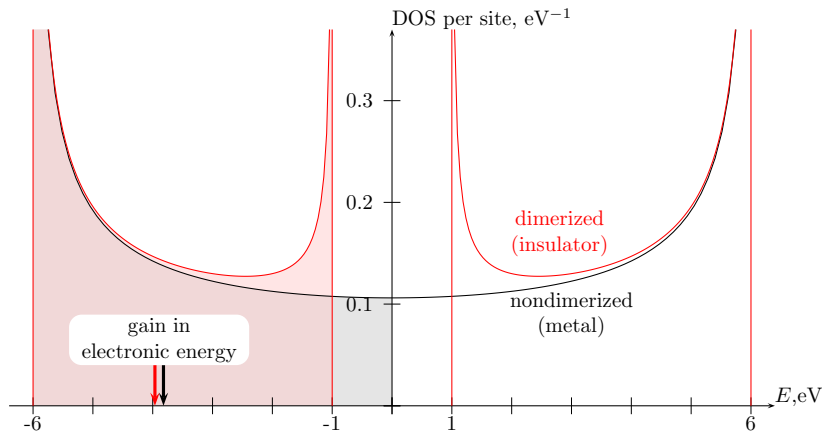
By optimizing the energy of SSH model over bond lengths we obtain dimerized (i.e. with alternating bond lengths) ground state due to Peierls transition: dimerization lowers the top of the valence band.

Peierls transition in 3D ◂ back

1. Take simple cubic lattice.
2. Apply 1D SSH models to p_x, p_y, p_z orbitals separately (use $pp\sigma$ bonding), but count the total number of electrons.
3. By optimizing the geometry one will obtain
   - α-As crystal for 3 p-electrons per atom,
   - gray-Se crystal for 4 p-electrons per atom,
   - crystal of diatomic molecules for 5 p-electrons per atom.

Isolating bonding electrons

A. Implicit electron-electron interaction (H is the Fock matrix):

$$H = \begin{pmatrix} H_{\mathsf{sys}} & H_{\mathsf{int}}^+ \\ H_{\mathsf{int}} & H_{\mathsf{env}} \end{pmatrix}$$

$$\tilde{H}_{\mathsf{sys}} = H_{\mathsf{sys}} + H_{\mathsf{int}}^+ \left(E - H_{\mathsf{env}}\right)^{-1} H_{\mathsf{int}}$$

- ▶ Joannopoulos, Yndurain, 1974: self-consistently, the environment is approximated by Bethe lattice.
- ▶ Our approach (for midgap states only):
  - fix E at the middle of the bandgap (no resonance),
  - valence s- and polarization d-orbitals can be treated by perturbation theory,
  - orthogonal p-orbitals are weakly coupled.

B. Explicit electron-electron interaction:

- ▶ Nontrivial, we assume that the renormalization is insensitive to small changes in the environment.

Electron-phonon interaction
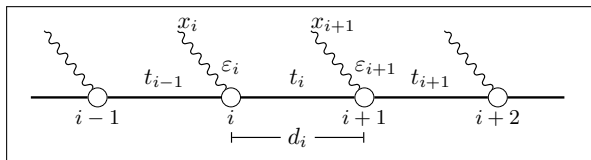
Two sets of configurational coordinates:

- d_i are bond lengths determining $t_i = t(d_i)$,
- x_i describe the interaction between the chain and its surrounding as in polaron models $\varepsilon_i = \varepsilon(x_i, d_i, d_{i-1})$.

Total energy:

$$E^{\text{tot}} = \langle \text{electronic energy} \rangle \left(\{ \varepsilon_i, t_i \} \right) + \langle \text{lattice energy} \rangle \left(\{ x_i, d_i \} \right)$$

Approximation:

$$\langle \text{lattice energy} \rangle \left(\{ x_i, d_i \} \right) = \sum_i \frac{\left(\varepsilon_i - \varepsilon^{(0)} \right)^2}{2\alpha} + \sum_i \frac{\left(t_i - t^{(0)} \right)^2}{2\beta}$$

Arsenic chain: mapping onto 1D model

$\phi \setminus \psi$	Elements $\langle\phi\|H\|\psi\rangle$ in eV				Their renormalization		
	$p_\parallel$	s	$p_\perp$	s_H	Δ, eV	sp-only	no sp
on-site $p_\parallel$	-4.9	-0.6	0.2	0.1	$+1.2$	60%	-25%
s		$-13.$	0.9	-4.0			
$p_\perp$			-4.4	-7.6			
s_H				-5.0			
front bonds $p_\parallel$	4.9	2.8	-0.8	0.6	$+0.7$	50%	1%
s		-0.7	0.4	-0.1			
$p_\perp$			1.3	0.4			
back bonds $p_\parallel$	2.3	-1.0	0.7	-0.2	-0.3	35%	10%
s		0.0	0.2	-0.1			
$p_\perp$			0.5	0.2			

Strong back-bonding, hydrogens mimic stronger front bonds, s-orbitals do not contribute to bonding, but renormalize $t_{pp\sigma}$ via sp-integrals, orthogonal p-orbitals interact weakly, $pp\pi$-interaction is weak, renormalization of ε is essential.
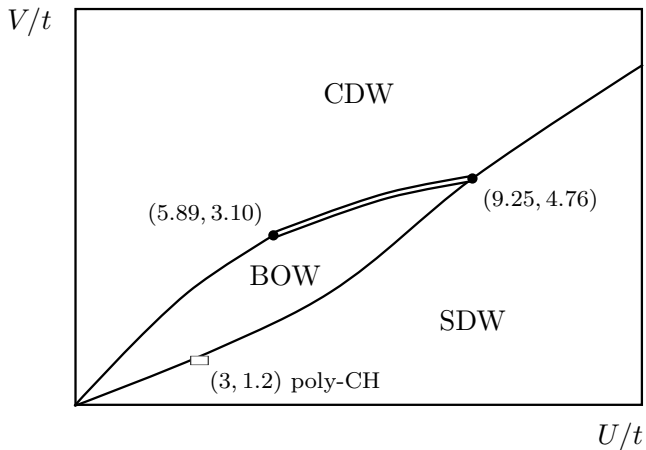
Extended Hubbard model
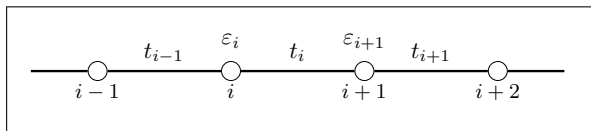
$$
\begin{aligned}
H^{el} = \sum_i \Big\{ \; & \varepsilon_i n_i && \text{on-site energy} \\
& - t_i \left(c_{i,s}^+ c_{i+1,s} + c_{i+1,s}^+ c_{i,s} \right) && \text{hopping between sites} \\
& + U n_i^\uparrow n_i^\downarrow + V n_i n_{i+1} \Big\} && \text{on-site and inter-site repulsion}
\end{aligned}
$$

- $c_{i,s}^+/c_{i,s}$ are spin-s ($\uparrow$ or $\downarrow$) creation/annihilation operators,
- $n_i = n_i^\uparrow + n_i^\downarrow$, $n_i^s = c_{i,s}^+ c_{i,s}$ are occupation-number operators,
- t_i is hopping matrix element (electron transfer integral) between sites i and $i+1$.

Computational chemistry of back-bonding ◂ back

in polyacetylene, elemental As, Te, Br etc.

- ▶ Fixed charge and topology of interconnections: TB
- ▶ Otherwise: semiempirical methods at RHF/ROHF level, use spin-restricted UHF to describe accurately SDW ▸ see SUHF
- ▶ Accurate calculations: post-HF methods, in particular MP2, are robust
- ▶ DFT optimized for closed shell systems is unpredictable for interactions between closed shell systems
  - neutral soliton in trans-polyacetylene is too wide for BLYP and B3LYP (Ref.2)
  - Cubic- to rhombohedral-As transition pressure is 20 GPa for LDA and 30 GPa for GGA (Silas *et al.* 2008)

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1. P. Pyykko, Strong closed-shell interactions in inorganic chemistry, Chem. Rev. 97, 597 (1997)
2. T. Bally, D. A. Hrovat, W. T. Borden, Attempts to model neutral solitons in polyacetylene by ab initio and density functional methods, Phys. Chem. Chem. Phys. 2, 3363 (2000)

Spin-constrained UHF method

ROHF underestimates SDW, UHF overestimates it. To fix this we use SUHF method (Andrews *et al.* 1991) by adding the term
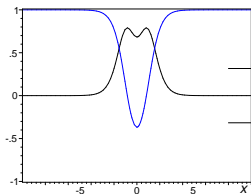
$$\mu \, \mathsf{tr} \left[\left(\rho^\uparrow - \rho^\downarrow \right) O \right]^2$$

to UHF energy functional, minimize it, and calculate UHF energy, here ρ is the density matrix, O is the basis functions overlap matrix, and μ is a parameter.

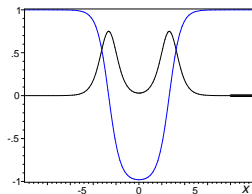# Mechanism of current-induced structural changes
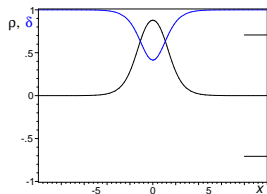
polaron is stable   bipolaron is unstable   and transforms into pair of solitons

Here:

- Black curve is electronic density of midgap states, ρ.
- Blue curve is dimerization amplitude, δ.
- Energy levels of the midgap states are shown as bars.
- Energy unit is scaled so that 1 corresponds to $E_{\mathrm{gap}}/2$.

Positively charged overcoordinated chalcogen

Bond angle for Ch_3^+ coordination defect represented by small molecules. In the second row the deviation from the experimental value $94.4°$ is shown to illustrate the accuracy of the methods. The symmetry C_3 corresponds to a rotator geometry, C_{3v} — to buckled graphene. For $S(AsH_2)_3^+$ the energies of both conformations differ by less than 0.1 eV.

		PM3	PM6	RHF	B3LYP	MP2
SH_3^+ $(\Delta\alpha_{exp})$	C_{3v}	+2.5	+3.7	+2.2	+0.1	+0.4
$S(PH_2)_3^+$	C_3	120	112	108	107	106
$S(AsH_2)_3^+$	C_3	116	114	109	107	105
$S(AsH_2)_3^+$	C_{3v}	109	107	102	100	98
$Se(AsH_2)_3^+$	C_{3v}	107	92	98	97	95

- ▸ Simdyankin, Elliott *et al.* 2005, As_2S_3 – planar
- ▸ Li, Drabold 2000, As_2Se_3 – pyramidal