F.-J. Haug

Optical properties:

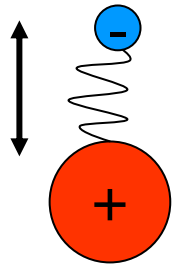
Dispersion and absorption

PV-lab
IMT NEUCHATEL

Dispersion (frequency dependence)

Very simple model: oscillator with damping

e.g. movement of electrons against cores



$$m\ddot{x} + 2\beta\dot{x} + \omega_0^2 x = eE_0 e^{-i\omega t}$$

inertia — damping — restoring force — harmonic driving force

Amplitude of driven oscillator

$$x_0 = \frac{eE_0}{m}(-\omega^2 - 2i\beta\omega + \omega_0^2)$$

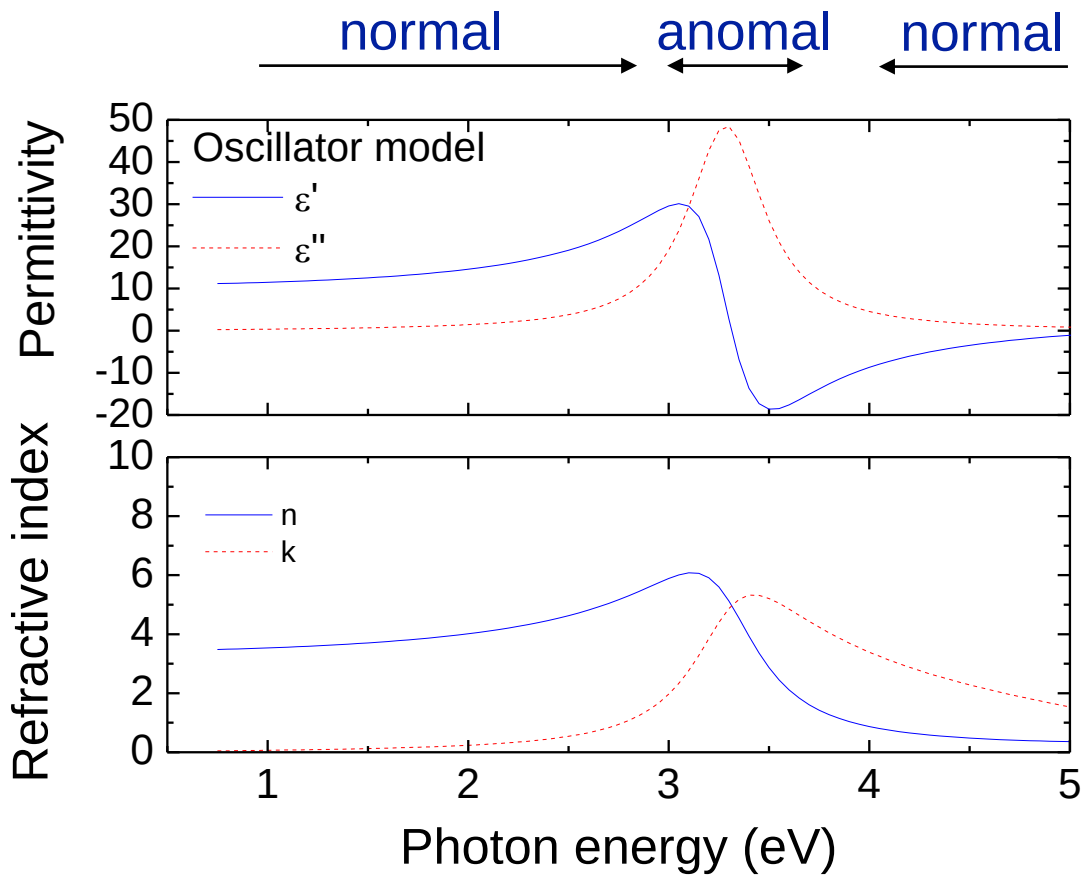
Dipole moment and macroscopic polarization:

$$P = \frac{N}{V}p = \frac{N}{V}ex_0 \overset{!}{=} \varepsilon_0(\varepsilon - \varepsilon_\infty)\cdot E$$

Find dielectric function:

$$\varepsilon(\omega) = (n + i\kappa)^2 = \varepsilon_\infty + \frac{e^2 N}{\varepsilon_0 m V}\frac{1}{(\omega_0^2 - 2i\beta\omega - \omega^2)}$$

Dispersion



Relation: $\epsilon' + i\epsilon'' = (n + i\kappa)^2$

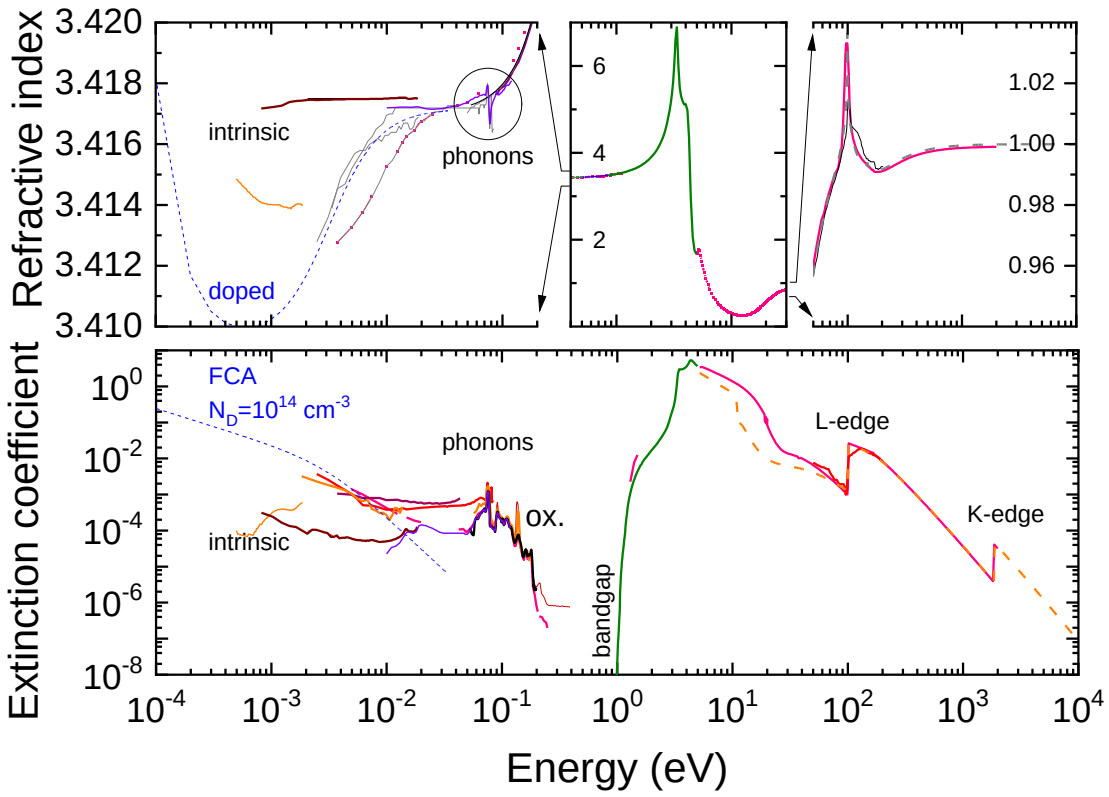
refractive index — extinction coefficient

Shape of permittivity dispersion: Lorentzian

normal dispersion:
higher permittivity for higher energy;
necessary for spectral splitting of prisms, also shine or “lustre” of diamonds

anomal dispersion:
opposite trend, normally not observed because in absorbing region

Frequency ranges of dispersion (e.g. c-Si)



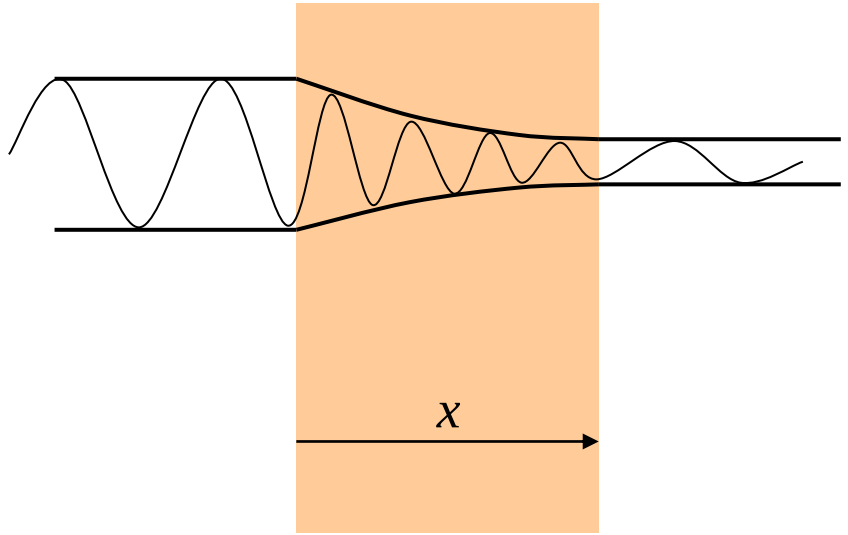
Frequency dependence of contributions to polarizability arising from
a) free electron plasma (depending on doping, can be up to vis)
b) lattice vibrations (IR)
c) displacement of electrons (vis and UV)
d) interactions with core electrons (X-ray regime)

Afsar, J. IR waves, (1994)
Green, Sol. En. Mat. (2008)
Palik, Handbook of Opt. Const.

Propagation and absorption in media

Wave vector: defined with **effective** wavelength

$$k = \frac{2\pi}{\lambda_{eff}} = \frac{2\pi \cdot n}{\lambda_0}$$



Field amplitude and intensity (n complex):

$$E(x,t) = E_0 \exp\{i((n + i\kappa)kx - \omega t)\}$$

$$|E(x,t)|^2 = \left|E_0 \exp\{i((n + i\kappa)kx - \omega t)\}\right|^2$$

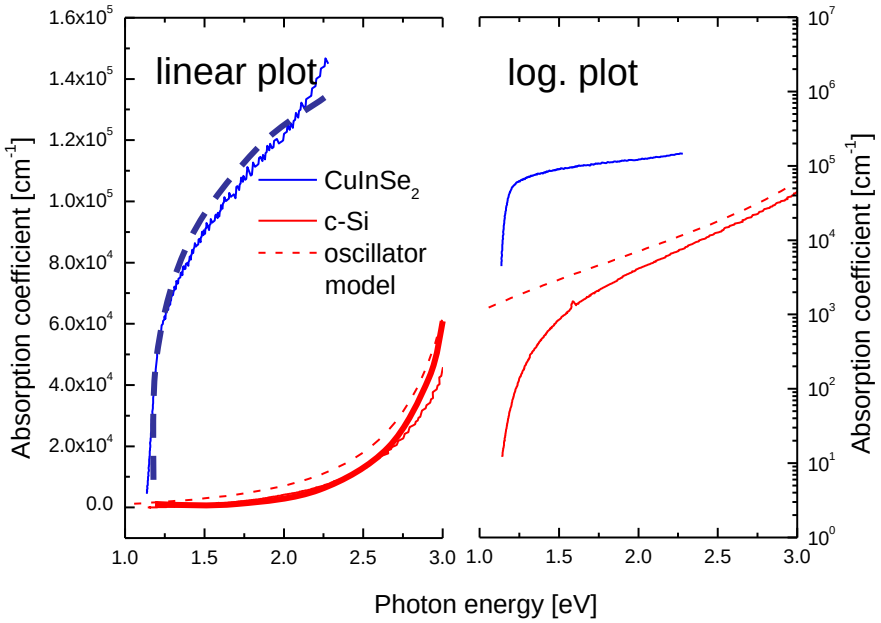
$$= |E(x,t)|^2 \exp\{-\underbrace{(2\kappa \cdot 2\pi/\lambda)}_{\alpha}x\}$$

Absorption coefficient: responsible for exponential decay of intensity

$$\alpha = 4\pi\kappa/\lambda$$

Absorption coefficient

Absorption and band gap



Oscillator model: no gap behaviour

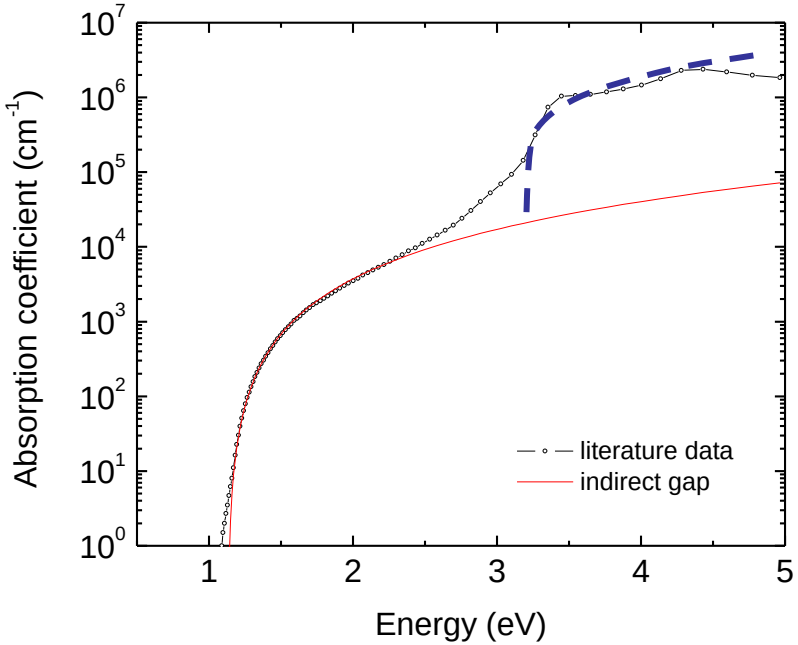
Strong absorbers (GaAs, $CuInSe_2$):

$\alpha \sim (E - E_g)^{1/2}$ (direct gap)

Weak absorbers (c-Si):

$\alpha \sim (E - E_g)^{2}$ (indirect gap)

In c-Si: both mechanisms



in vis and near IR (400 nm to 1000):

indirect gap dominates,

$\alpha \sim (E - 1.13\text{eV})^{1/2}$ is OK in Vis

direct gap in UV (< 400 nm)

Green, Sol. En. Mat. 2008

Electronic and optic properties of materials with lattice

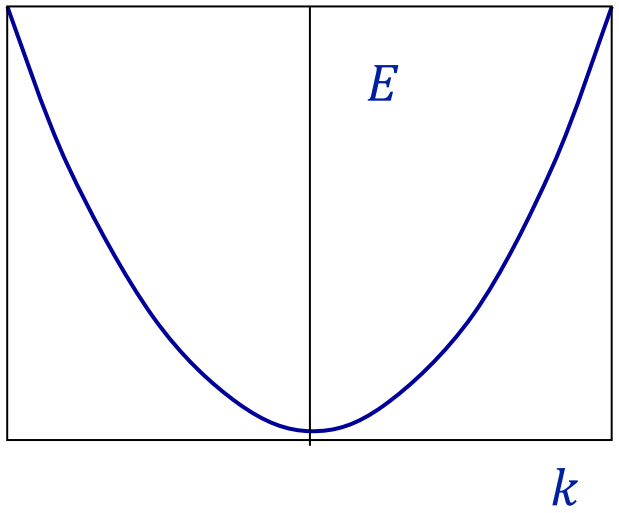
Energy bands and the reduced scheme (1D)

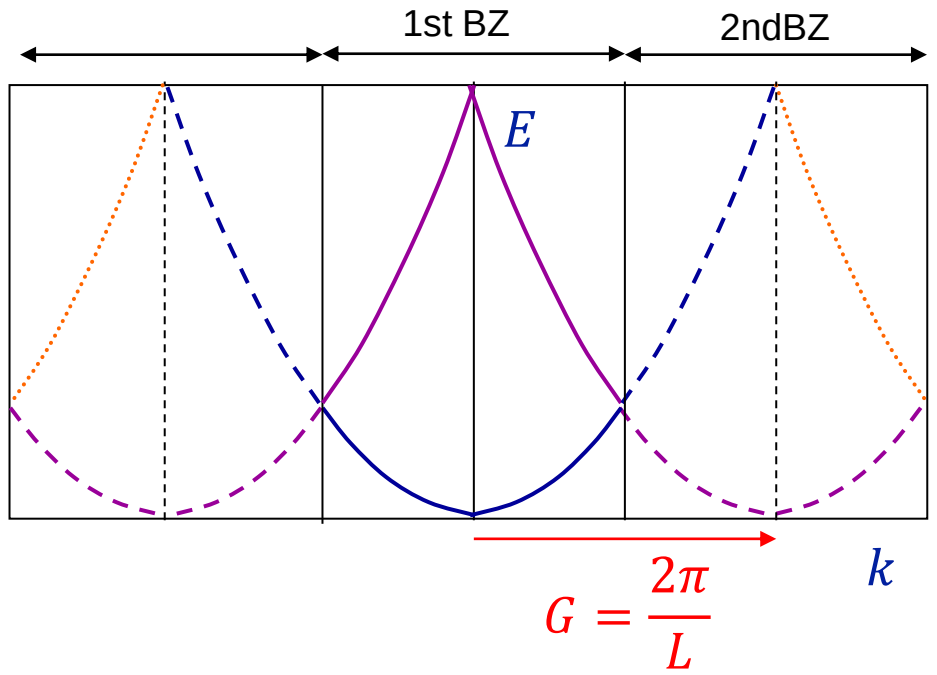
free electron energy in 1D: express electron momentum p by wave vector k (DeBroglie)

$$E = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$$

Periodic potential: Application of Bloch theorem gives rise to periodicity in $E(k)$ with reciprocal lattice vector G

$$E = \frac{(\hbar k)^2}{2m} = \frac{\hbar^2 (k + nG)^2}{2m} \qquad G = \frac{2\pi}{L},\ n = 0, \pm 1, \pm 2, \ldots$$





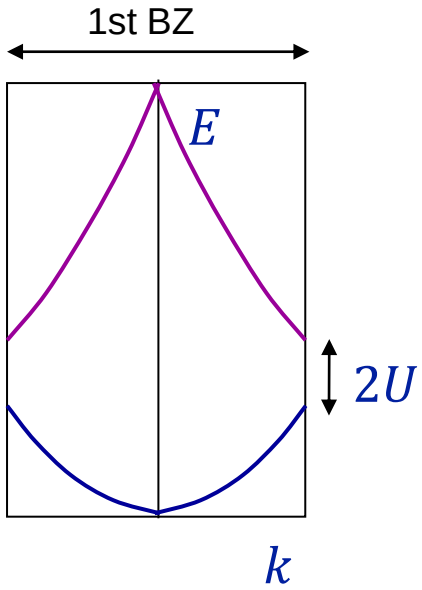
Energy gaps due to weak potential

One example of a periodic potential: $U = const.$

Splitting at boundaries of 1st BZ by $2U$

Alternatively, definition by Fourier components

$U = U_1(\exp ikx + \exp -ikx)$ for cos-shape potential

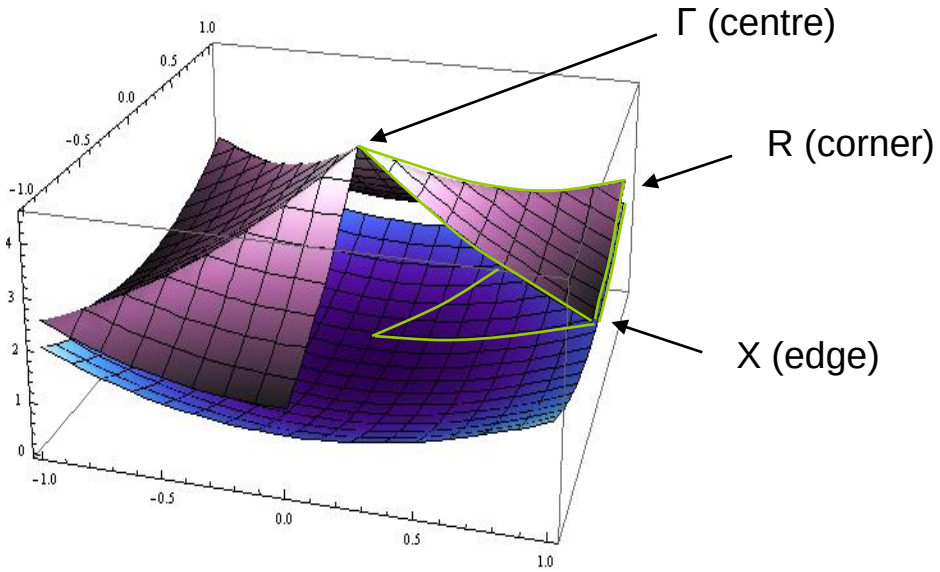


Projections of energy bands (2D)

free electron energy in 2D:

energy surface:

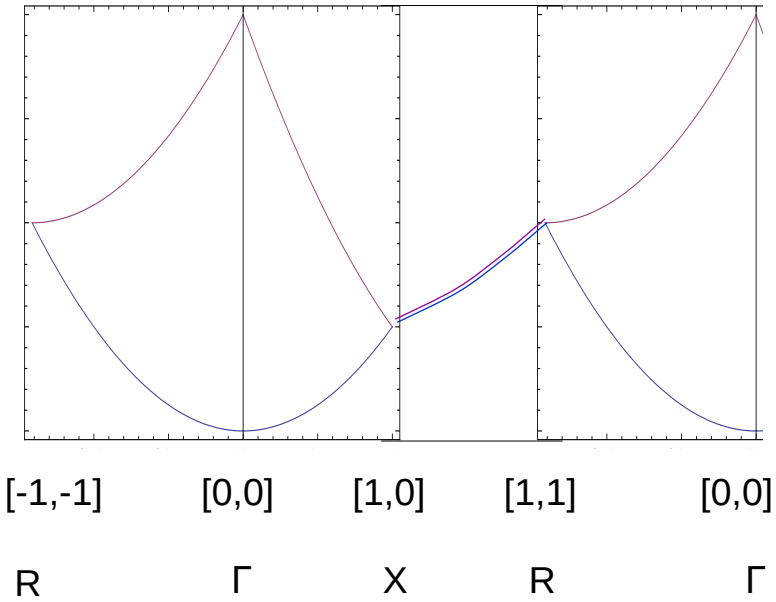
$$E = \frac{p^2}{2m} = \frac{\hbar^2\left(k_x^2 + k_y^2\right)}{2m}$$



(corner sliced open for illustration)

1D representation of 2D:

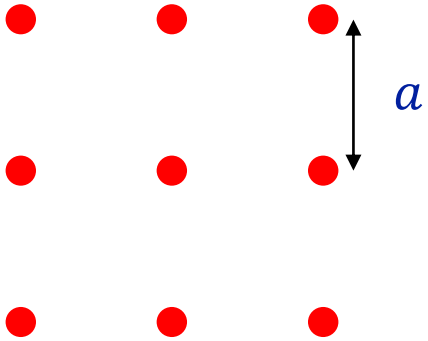
follow lines of high symmetry



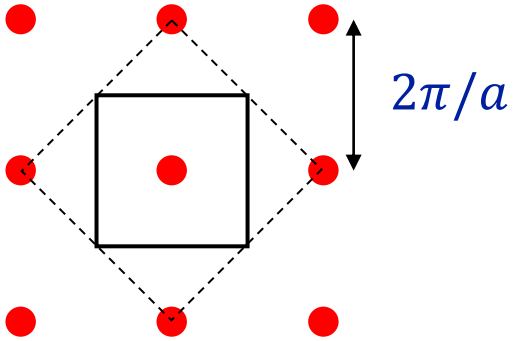
Relation between real and reciprocal space

Example:

square lattice in 2D real space



=> square lattice also in reciprocal space



Elementary cell: smallest cell that represents the lattice

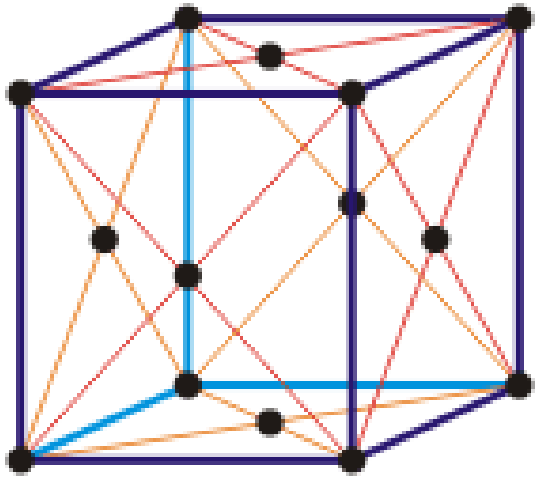
Wigner-Seitz cell: construction rule for a common elementary cell

- draw lines to all neighbours
- construct a perpendicular plane (2D: line) at half-distance

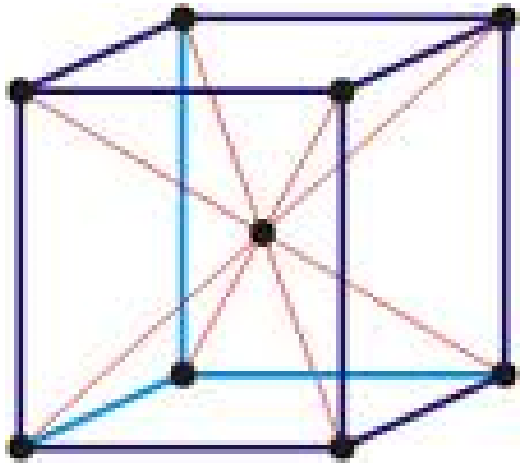
The Wigner Seitz cell of reciprocal space is called the **first Brillouin zone** (1st BZ)

Reciprocal lattice in 3D (e.g. fcc for Si)

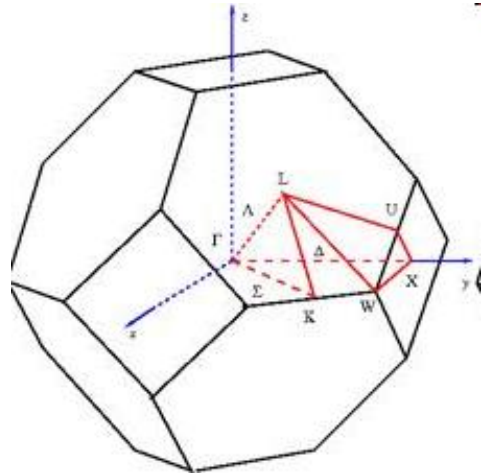
Real lattice:
face centred cubic (fcc)



Reciprocal lattice:
body centred cubic (bcc)



Wigner Seitz cell:
truncated octahedron



Band diagrams of the fcc lattice

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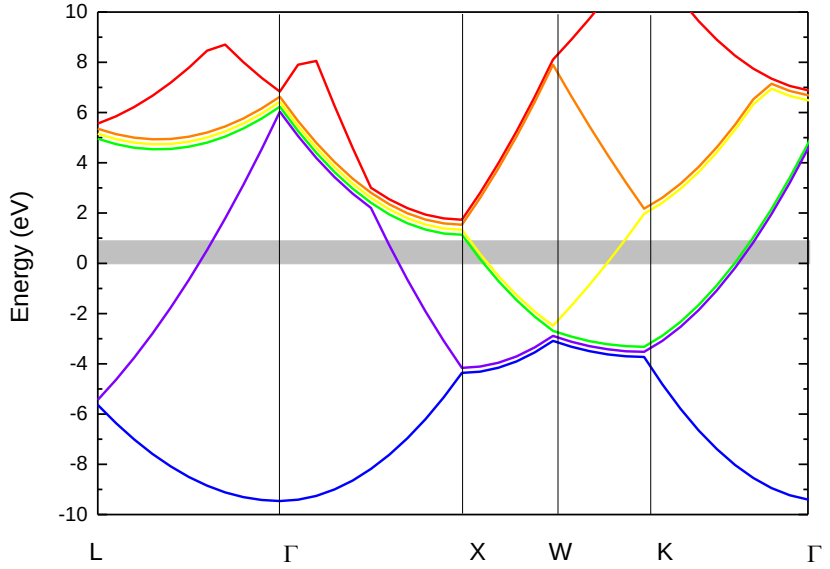
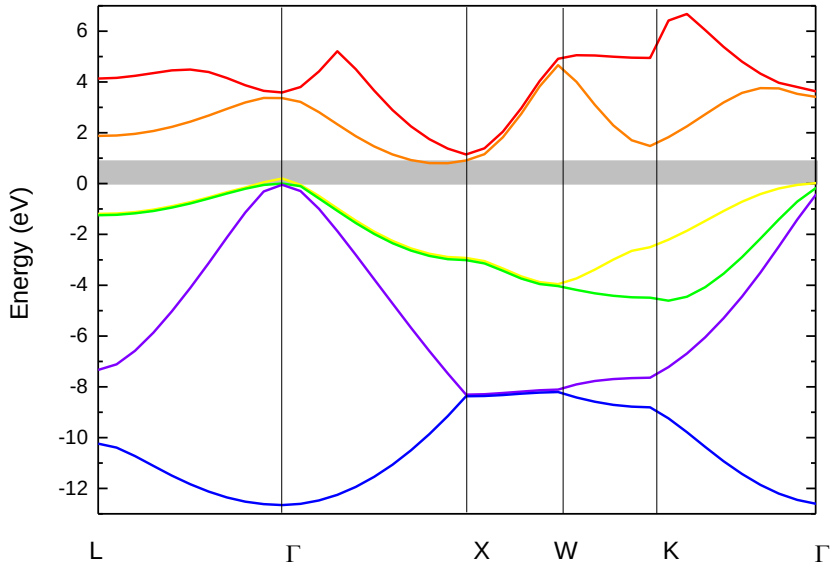
Free electron bands



Band diagram of c-Si



Formation of band gap:

VBM: rounding of intersection at Γ (heavy and light holes + split off band)

CBM: 85% towards X (6 equivalent minima in the [100] directions, “pockets”)

indirect gap: 1.13 eV

direct gap $\Gamma_{VB} \rightarrow \Gamma_{CB}$: ca. 3 eV

Indirect absorption in c-Si

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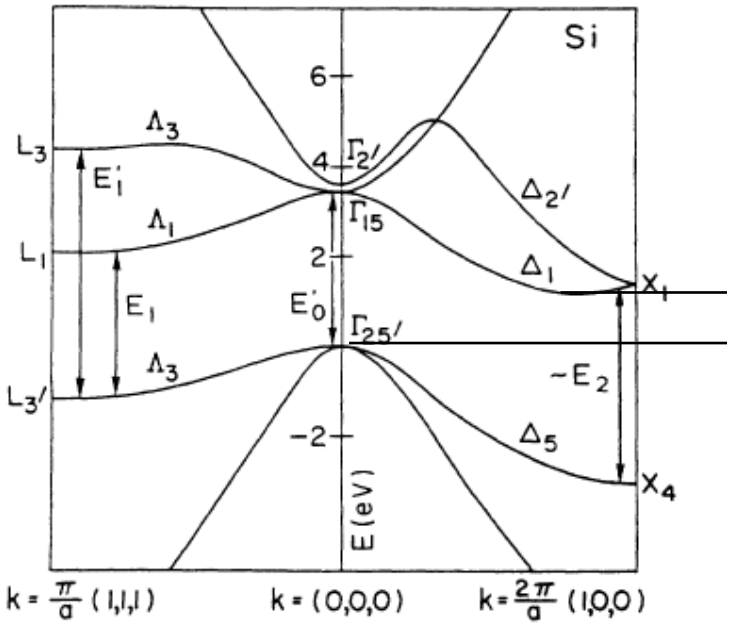
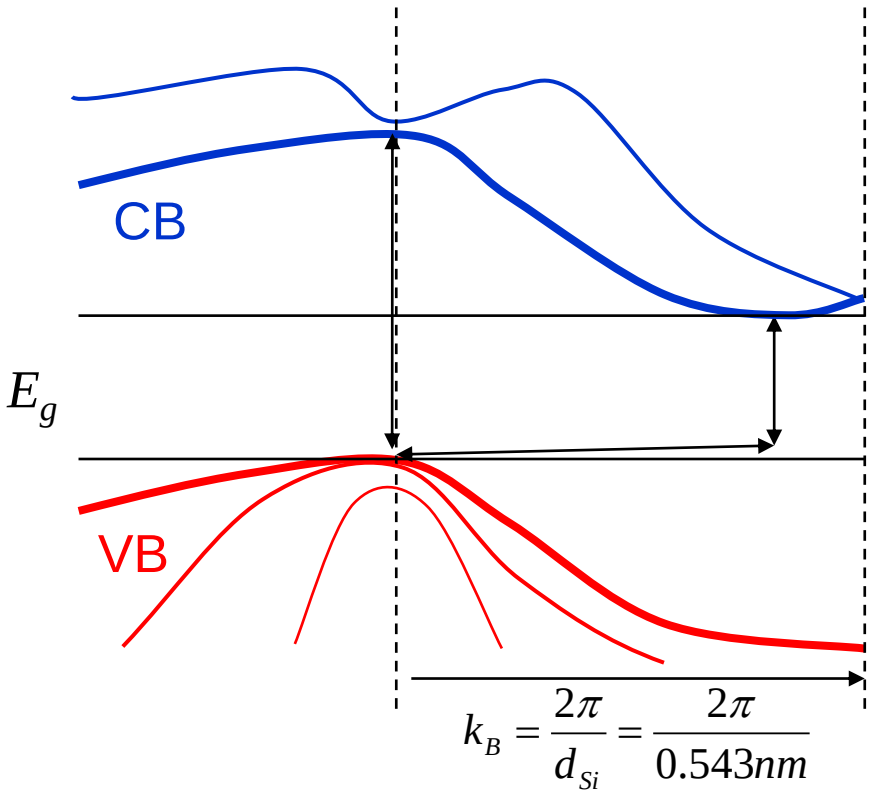
Band diagram of c-Si around gap





direct transitions > 3eV : E'_0/E_1 or E_2 (vertical VBM to CB)

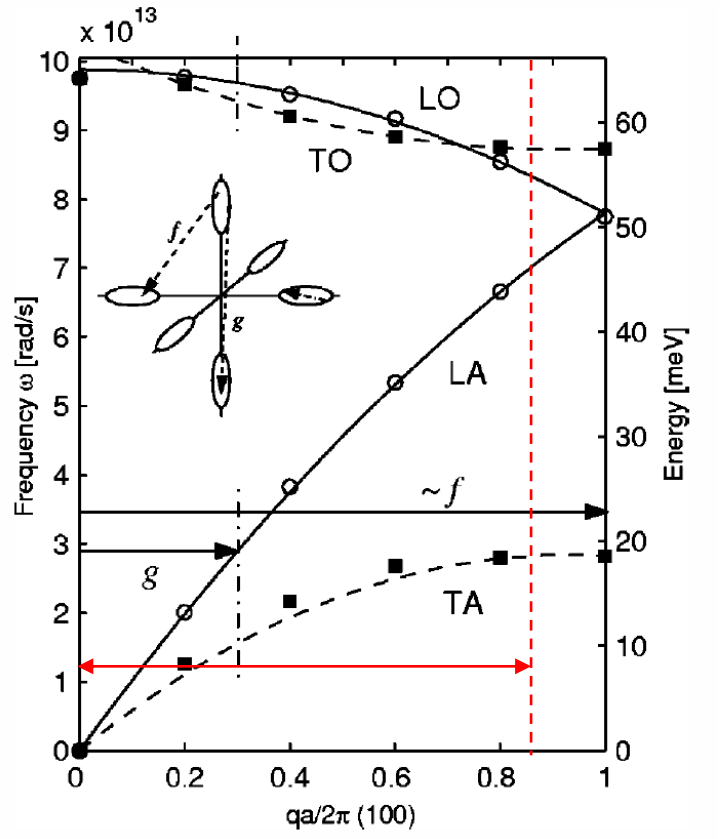
indirect transitions >1.13 eV (from VBM to CBM)

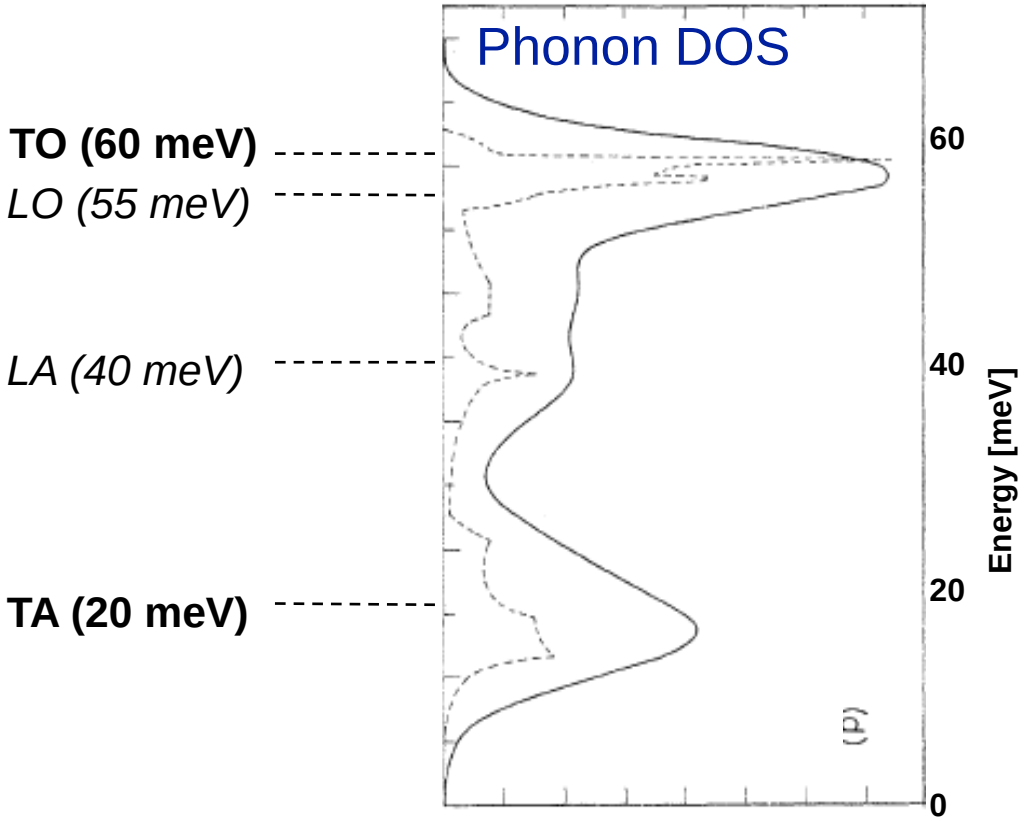
require “horizontal” component, e.g. **phonon** assistance

Lautenschlager, PRB 36(9) 4821 (1987)

Phonons: small energy, large momentum

Phonon band diagram, starting like $\omega = ck$ (sound wave)





at 85% of [100]: 20 meV (TA) and ca. 60 meV TO (no longitudinal excitation by light)

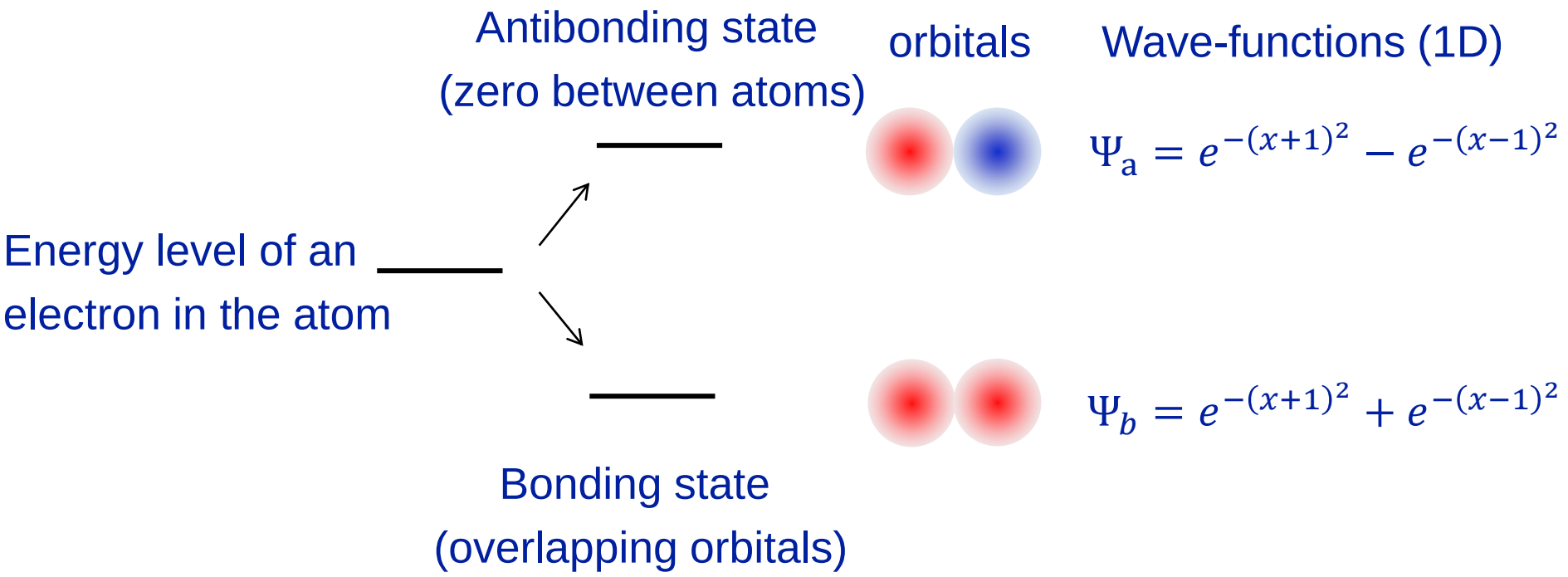
Brockhouse, PRL 1959
Pop, JAP 96(9) 4998 (2004)

Smith, PRL 26(11) 642 (1971)

Origin of band-gaps in materials with short-range order

Orbitals and energy states

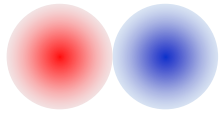
Example: molecule, e.g. H_2

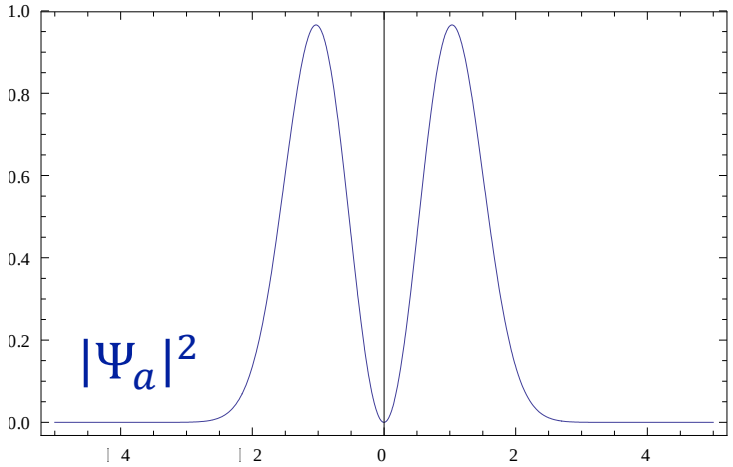


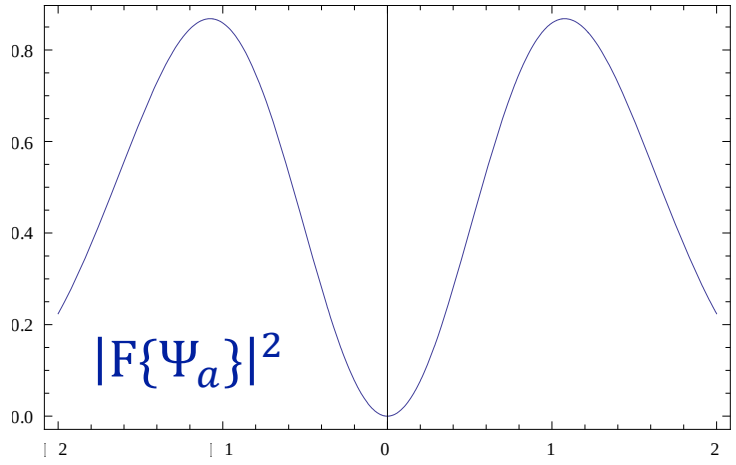
Binding energy separates bonding state (occupied) and antibonding state (free)

Shape of wave-functions (1D)

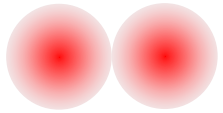
$$\Psi_a = e^{-(x+1)^2} - e^{-(x-1)^2}$$

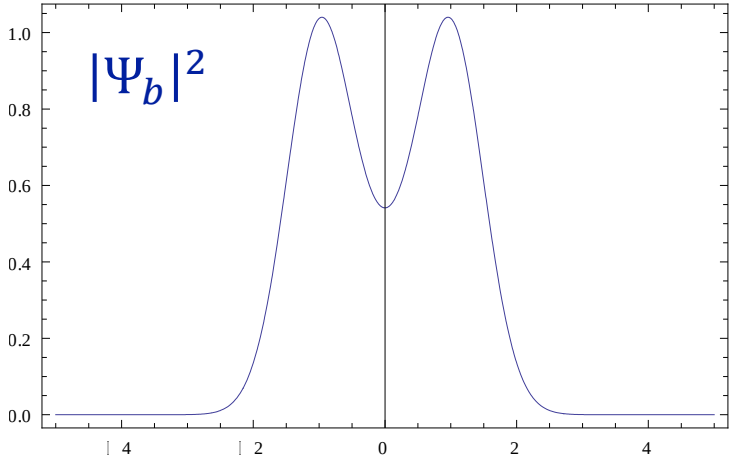


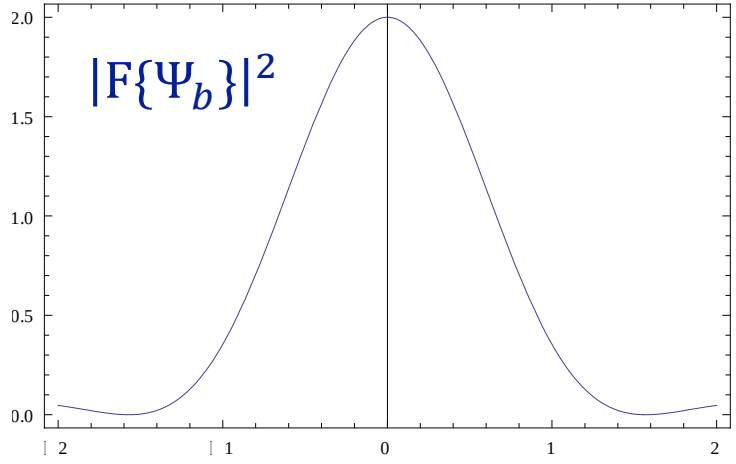




$$\Psi_b = e^{-(x+1)^2} + e^{-(x-1)^2}$$

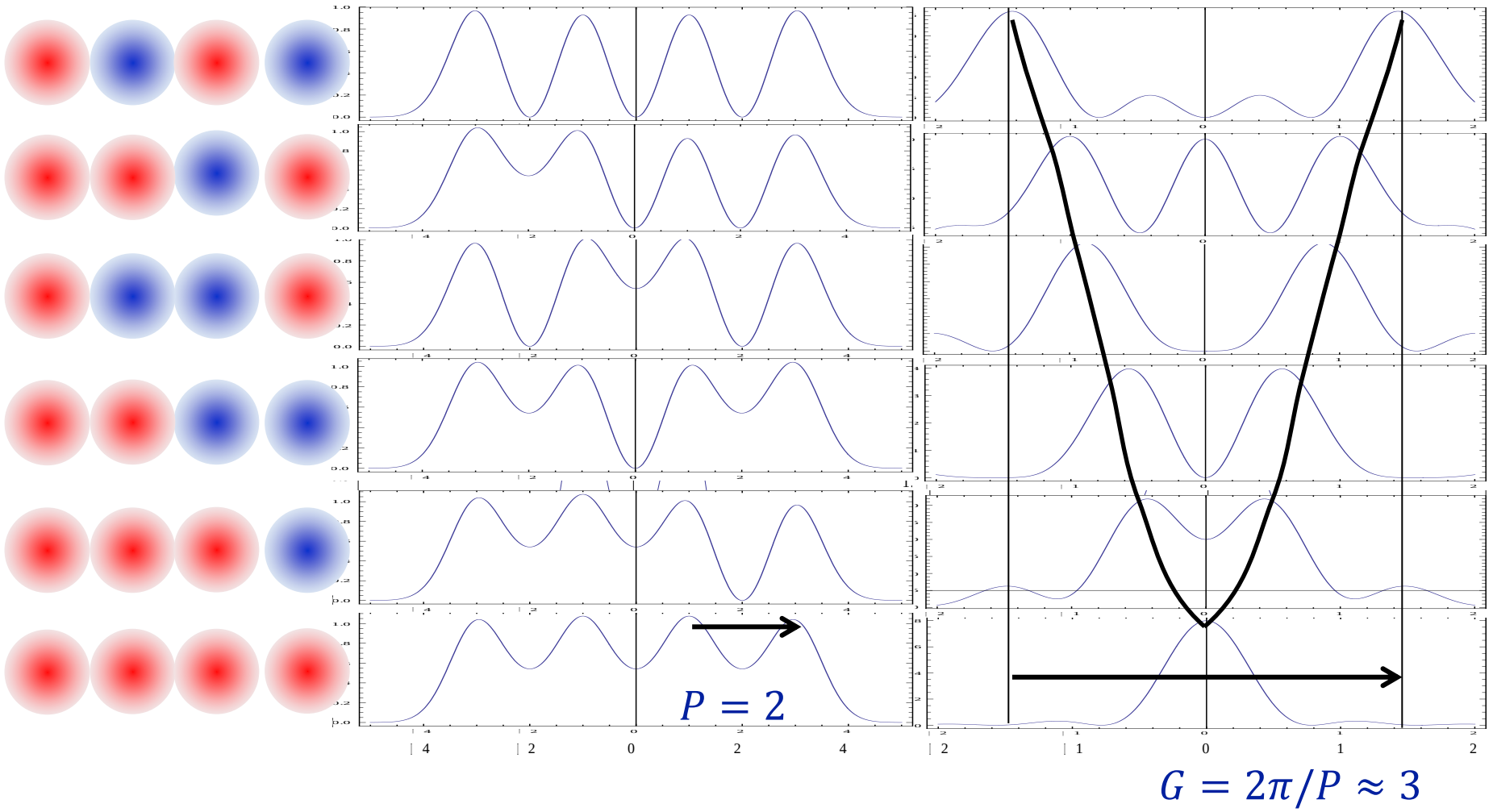






A chain of four atoms

$|\Psi|^2$ $|F\{\Psi\}|^2$ (reciprocal coordinate)



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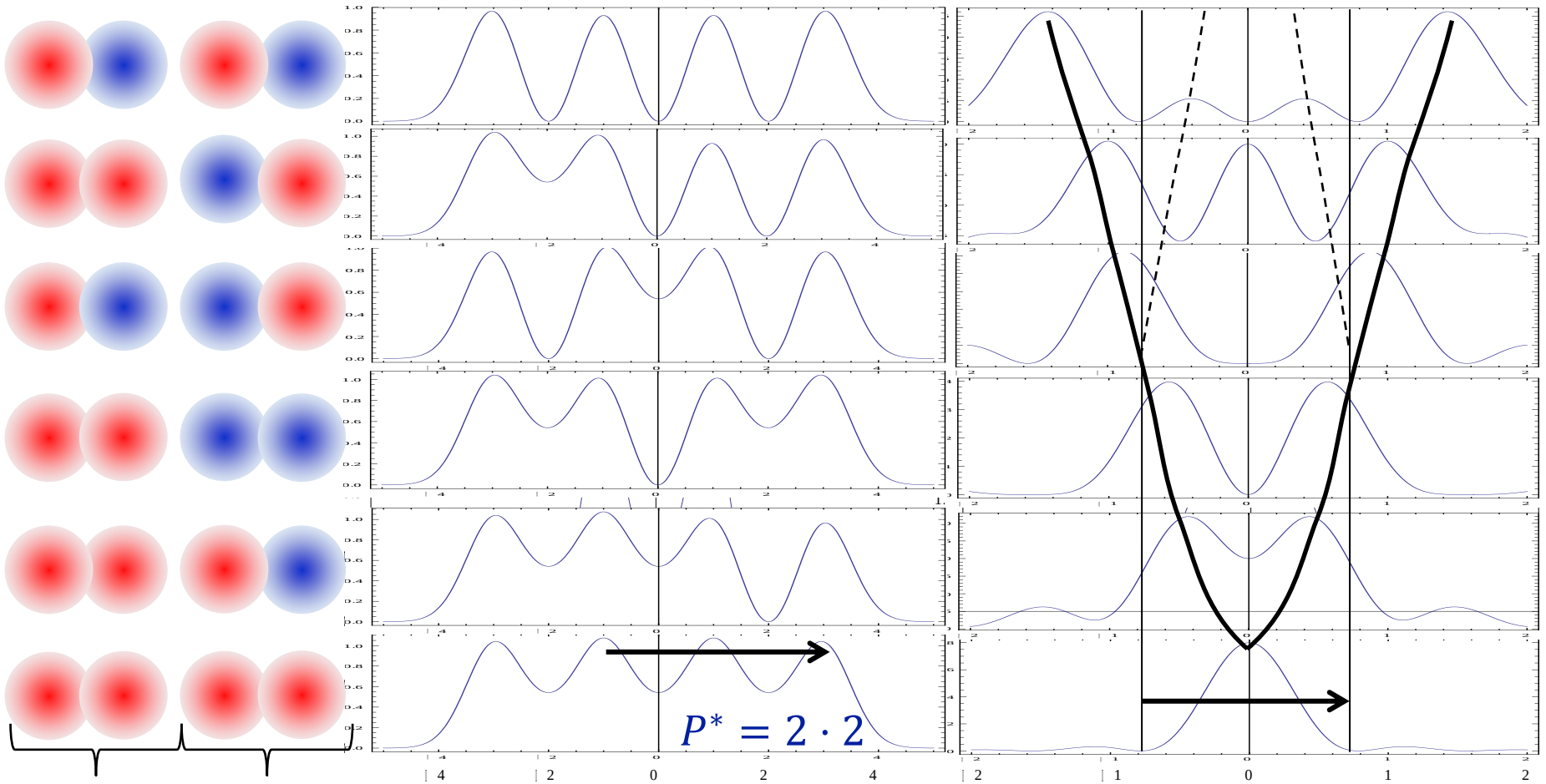
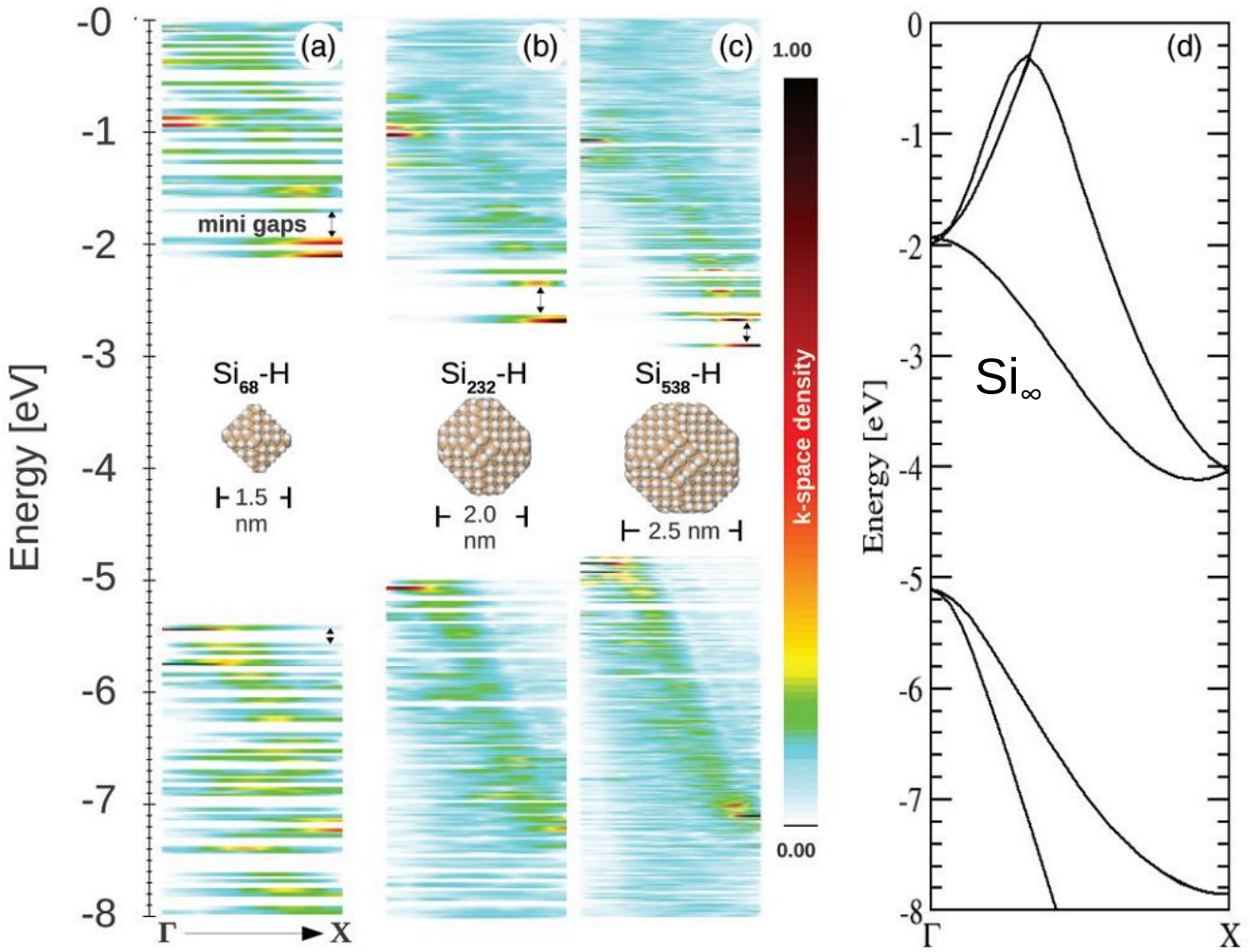
A “chain” of two molecules

$|\Psi|^2$ $|\mathrm{F}\{\Psi\}|^2$ (reciprocal coordinate)



$G = 2\pi/P^* = 2\pi/4 \approx 1.5$

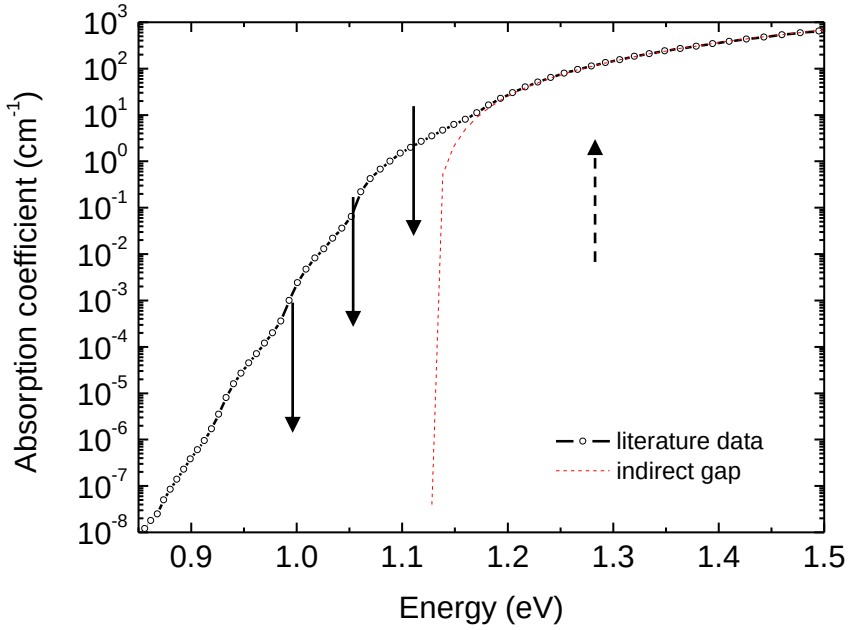
Correct MO theory for Si nanoparticles

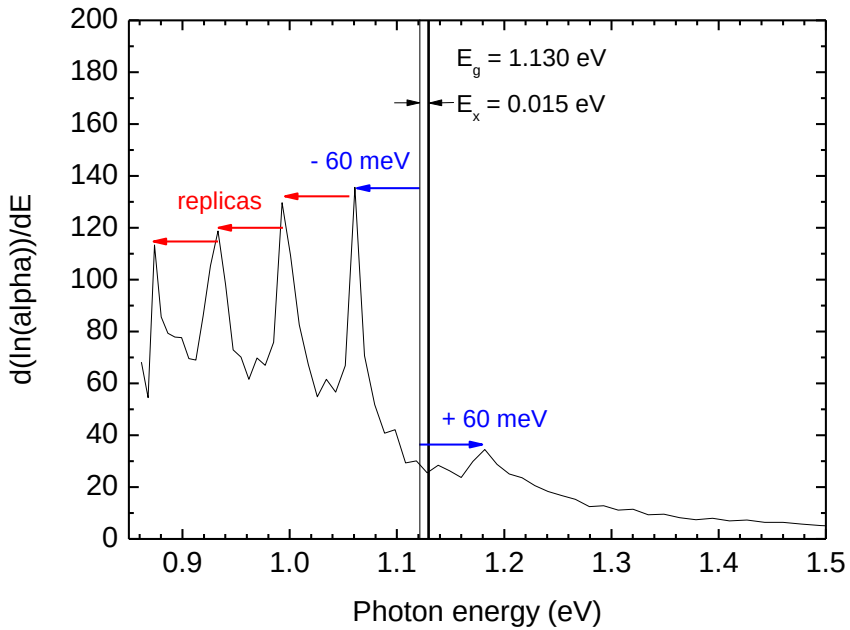


Hapala, PRB (2013)

Absorption below the gap signature of disorder

Close-up of low absorption region in c-Si





Weakly absorbing tail below gap

Fine structure:

- large signatures at ± 60 meV
- weak signatures at ± 20 meV

Explanation: lattice vibrations (phonons) mediate absorption

below gap: lattice must provide phonons (cooling)

above gap: phonons are emitted (heating)

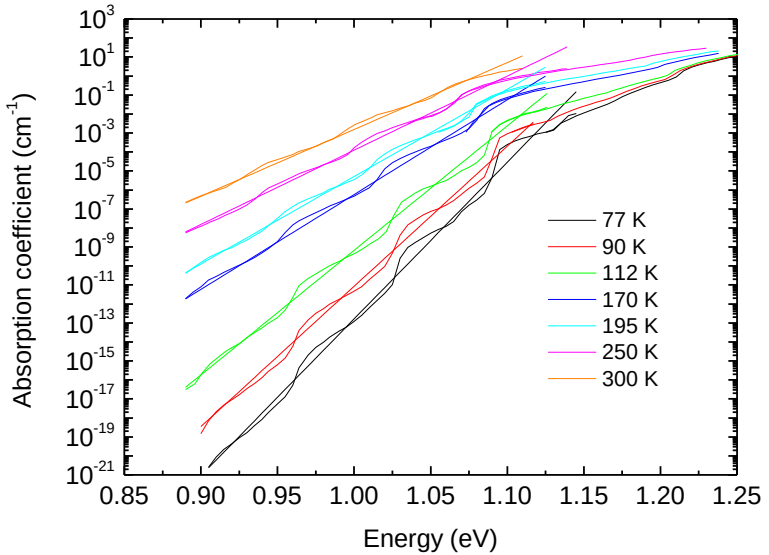
Haynes, JPCS 1959

Vouk, JPC 1977

Cody, JNCS 1992

Close up: sub-gap absorption

Temperature dependence of ultra-low absorption:
(use generalized Planck radiation law to inverse photoluminescence yield)



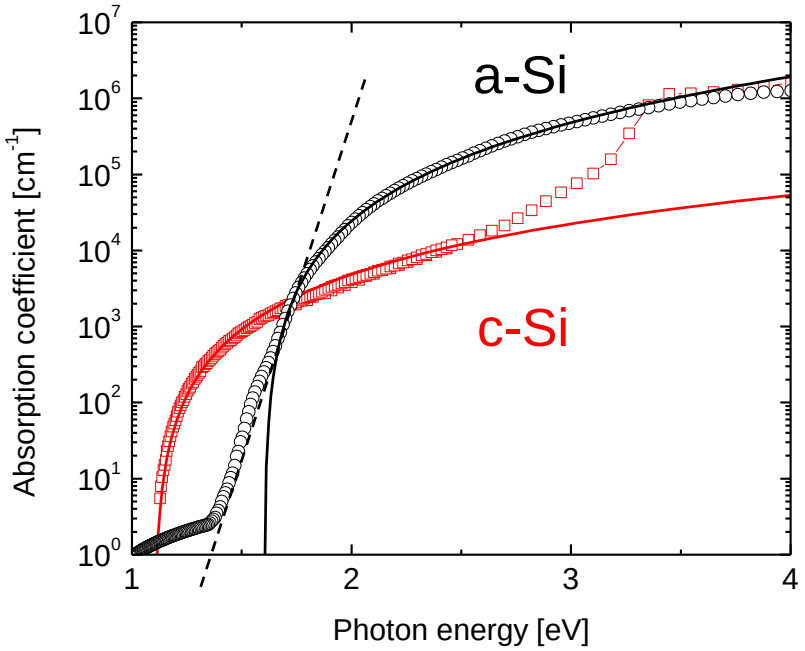
Crude approximation:
$\alpha(E) = \alpha_0 \exp(E/E_U)$
where E_U is the Urbach energy
(or Urbach slope)

at low temperature:

- Absorption drops massively (cold lattice can provide fewer phonons)
- Steps become more prominent (less thermal broadening)
- Average slope changes (up to about 10 meV)

McFarlane, PR 1958
Daub, PRL 1995
Trupke, JAP 2003

Absorption in a-Si



Identical absorption for E > 3.2 eV:

corresponding electron wavelength (DeBroglie)

$$\lambda = \sqrt{\frac{h^2}{2mE}} = 0.7\text{nm}$$

Same as near range order!

Electron waves with E > 3 eV don't feel the disorder

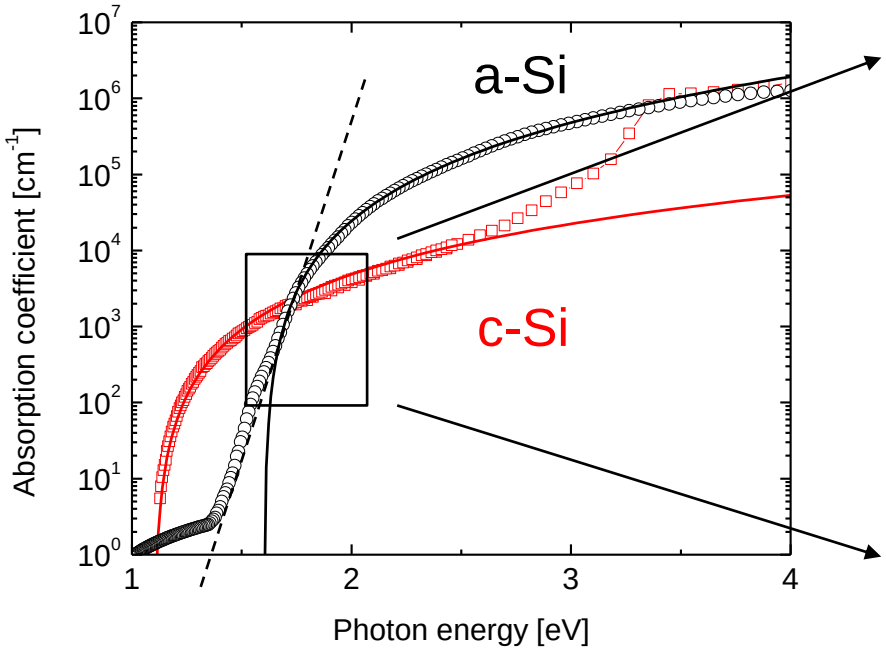
Indirect band gap ~1.75 eV

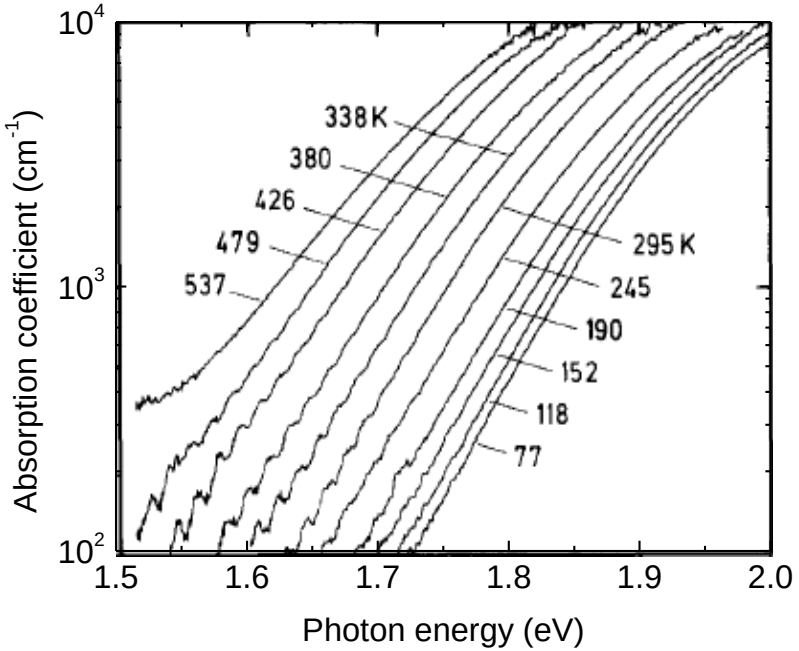
Exponential absorption tail below the gap

Higher absorption in visible

Band edge absorption in a-Si

Absorption tail is associated with disorder (combination of structural and thermal)





Urbach absorption $\alpha(E) = \alpha_0 \exp(E/E_U)$

In device quality material: E_U ~ 50 meV at RT

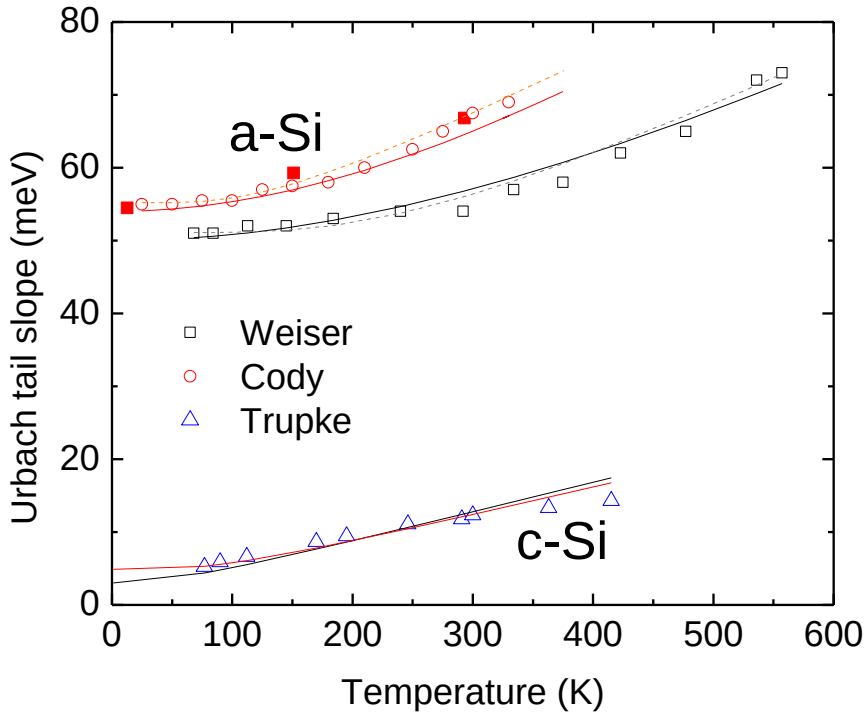
flattening at high T similar to c-Si (but with different numerical values)

Cody, PRL 1981
Weiser, JNCS 1989

Disorder and Urbach absorption

Hypothesis: disorder of the displacement contributes to absorption signature,

regardless whether thermal or static; $E_U(T) = \sqrt{E_U^2(0) + (\gamma kT)^2}$



Low T: static disorder dominates (c-Si: almost zero)

High T: similar temperature dependence (curvature)

Cody, J. de Physique 1981

Stutzmann, Phil Mag Lett. 1992

Summary

Bandgaps

- in crystals: bands and gaps as consequence of periodicity and binding potential
- in disordered materials: overlap of discrete states with increasing delocalization

Absorption below gap (Urbach region):

- in crystals:
  explained by thermal “disorder”
  (a very ordered phenomenon explained by phonons)
- in disordered materials:
  a combination of structural and thermal disorder