Electrical and optical properties II

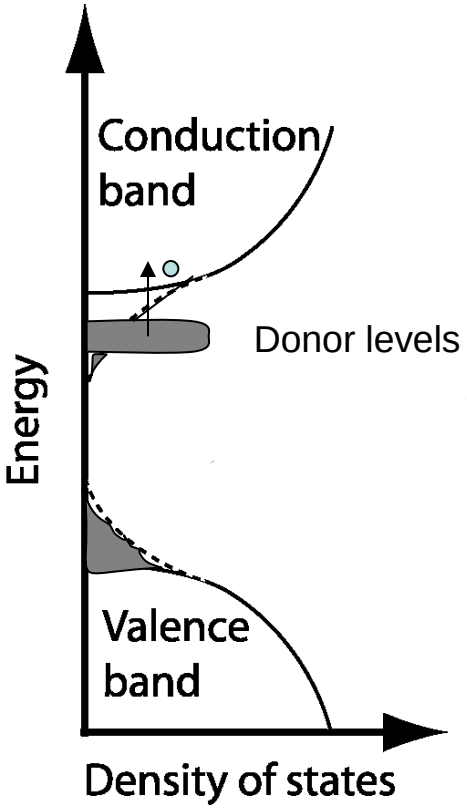
Amorphous semiconductors and insulators

Outline

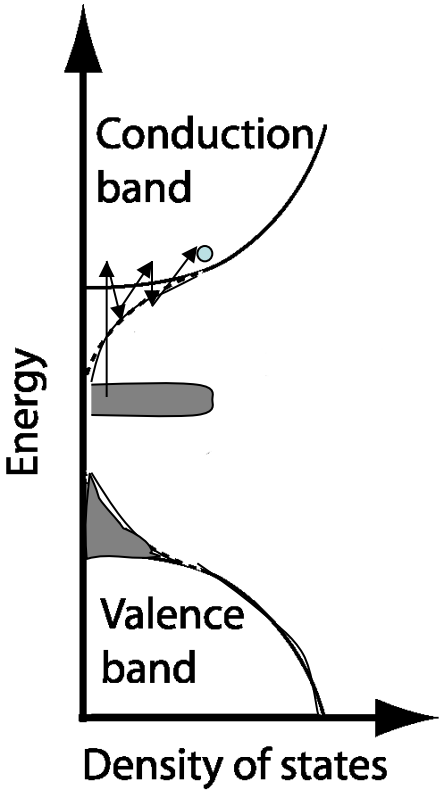
- Semiconductors $E_g < 4$ eV
- Insulators $E_g > 4$ eV
- Conduction mechanisms
- Excitations of electrons from localized states at the Fermi level to the conduction band (or holes to the valence band)
- Trapping in empty gap states
- Hopping between localized states at the Fermi level
- Optical properties: Polaron absorption, Urbach tails

Band conduction

- Donors to conduction band

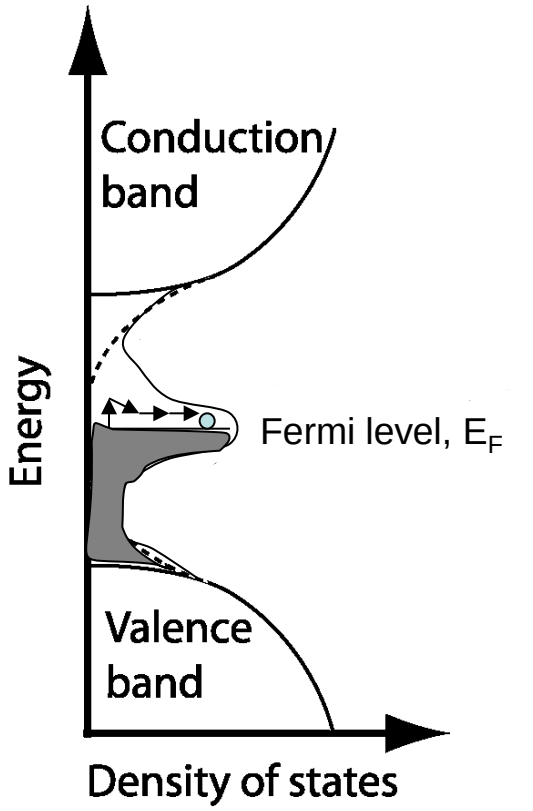


- Multiple trapping

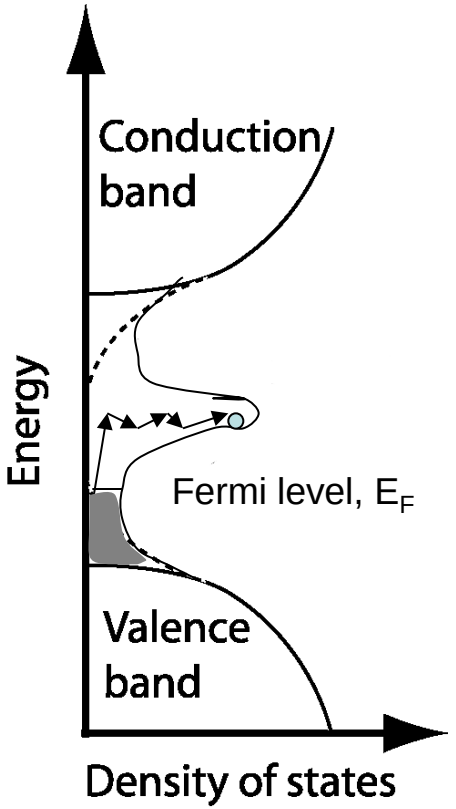


Hopping conductivity

- Hopping at the Fermi level – ”R-hopping”



- R-E hopping



Conductivity: Semiconductors

- Semiconductors: $\sigma = ne\mu_e + pe\mu_h$
- Generally: $$\sigma = e\int D(E)\mu(E)f(E)(1-f(E))dE$$
- f(E) – Fermi-Dirac distribution function
- D(E) – density of states
- μ(E) – mobility
- Amorphous material with mobility edge at E_c
- μ(E) ~0 for localized states in the band gap.
- f(E)(1-f(E)) ~ exp[-(E-E_F)/k_BT], if E-E_F>>k_BT

Amorphous semiconductors/insulators

- Case of electron conduction
- Excitation of electrons from E_F to the conduction band. The main contribution comes from E~E_c.

$$\sigma \approx eD(E_c)\mu_e k_B T \exp[-(E_c - E_F)/k_B T]$$

- Similar equation is obtained for hole conduction
- Prefactor: Mott suggested $\sigma_0 \sim e^2/\hbar L_i$
- Of the order of the ”minimum metallic conductivity”, and L_i is an inelastic scattering length

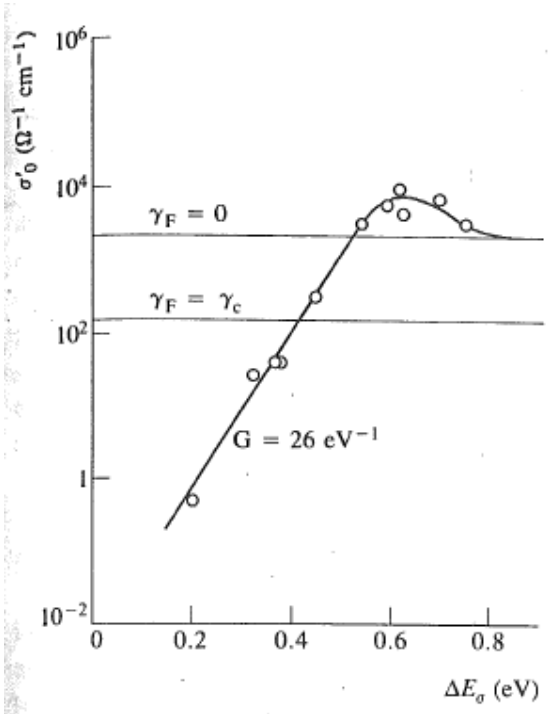
Meyer-Neldel rule

- $\Delta E=E_c-E_F$ depends on temperature
- Fermi level sinks towards mid-gap as T increases.
- Mobility edge changes due to thermal expansion and electron-phonon coupling
- Approx: $\Delta E(T)=\Delta E(0)-\gamma T$

$$\sigma = \sigma_0 \exp(\gamma / k_B) \exp[-\Delta E(0) / k_B T]$$

- Exp. a-Si:H (vary doping)

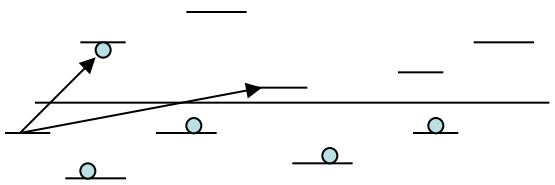
$$\sigma_0^{'} = \sigma_0 \exp(\gamma / k_B) = \sigma_0 \exp(G \Delta E(0))$$



Source: Elliott, Physics of amorphous materials

Hopping conductivity - 1

- Phonon-assisted tunneling between localized states at the Fermi level



- Competition between energy needed for the hop and the influence of spatial separation on the probability for a hop

- Wave function:

$$\psi(r) \sim \exp(-\alpha r)$$

- Tunneling probability from state i to j

  ~exp(-2ar$_{ij}$)

- Possibility to gain energy from a phonon

  ~exp (-ΔE/k_BT)

- Balance between these terms depends on temperature and spatial separation

Hopping conductivity - 2

- Mobility $\mu = eD/k_BT = e\gamma r^2/6k_BT$, where D is the diffusion coefficient and γ is the hopping rate
- Conductivity prefactor:

$$\sigma_0 \approx \gamma_0 e^2 r_{ij}^{\ 2} D(E_F)/6$$

- Conductivity:

$$\sigma_{ij} = \sigma_0 \exp(-\Delta E / k_{\mathbf{B}} T) \exp(-2\alpha r_{ij})$$

- Consider that an electron can hop to sites within radius r and energy ΔE
- The optimal hop occurs when only one site can be reached.

Variable range hopping - 1

- An electron can reach N sites where

$$N = 4\pi r^3 D(E_F)\,\Delta E/3$$

- N=1 → $\Delta E = 3/4\pi r^3 D(E_F)$
- Maximise the conductivity by minimising the exponent, x, in the e^{-x} function:

$$\frac{d}{dR}\left(2\alpha r + 3/4\pi r^3 D(E_F)k_B T\right) = 0$$

$$\Rightarrow r_m = \left(\frac{9}{8\pi\alpha D(E_F)k_B T}\right)^{1/4}$$

Variable range hopping - 2

- Finally we obtain (Mott's law)

$$\sigma = \sigma_0 \exp(-(T_o / T)^{1/4})$$

$$T_0 = \frac{512\alpha^3}{9\pi D(E_F)k_B}$$

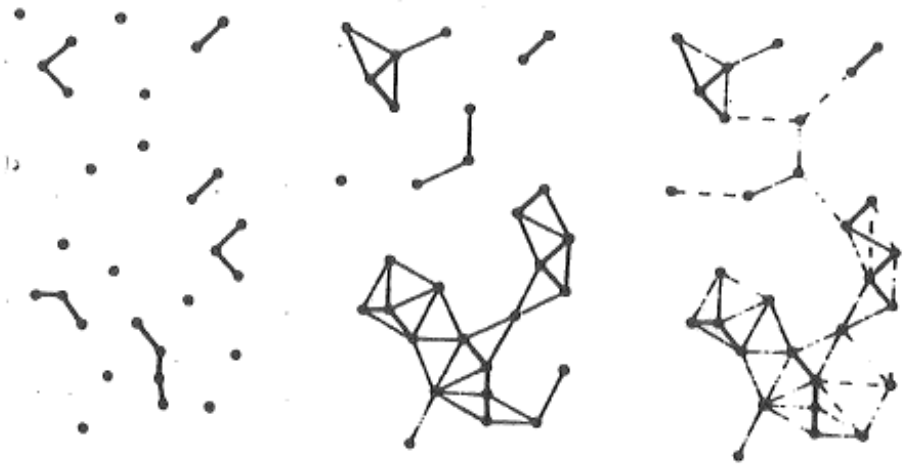
- Typically $1/\alpha$~10 Å, r_m depends on localized DOS, but may be of the order of 1-10 nm
- For localized states in the band gap

  $D(E_F) \sim 10^{18} – 10^{19}$ cm^{-3} eV^{-1}

Percolation treatment

- We only considered a single hop
- In reality we have a complicated resistor network with a wide (exponential) spread of conductances
- A percolation treatment gives Mott's law, except for a numerical constant in T_0.

$$\sum_{j \neq i} \sigma_{ij} (V_i - V_j) = 0$$



Largest σ's

Smaller ones →

The percolation path appears:

$\sigma \sim \sigma(\text{critical})$

Source: Overhof, Festkörperprobleme

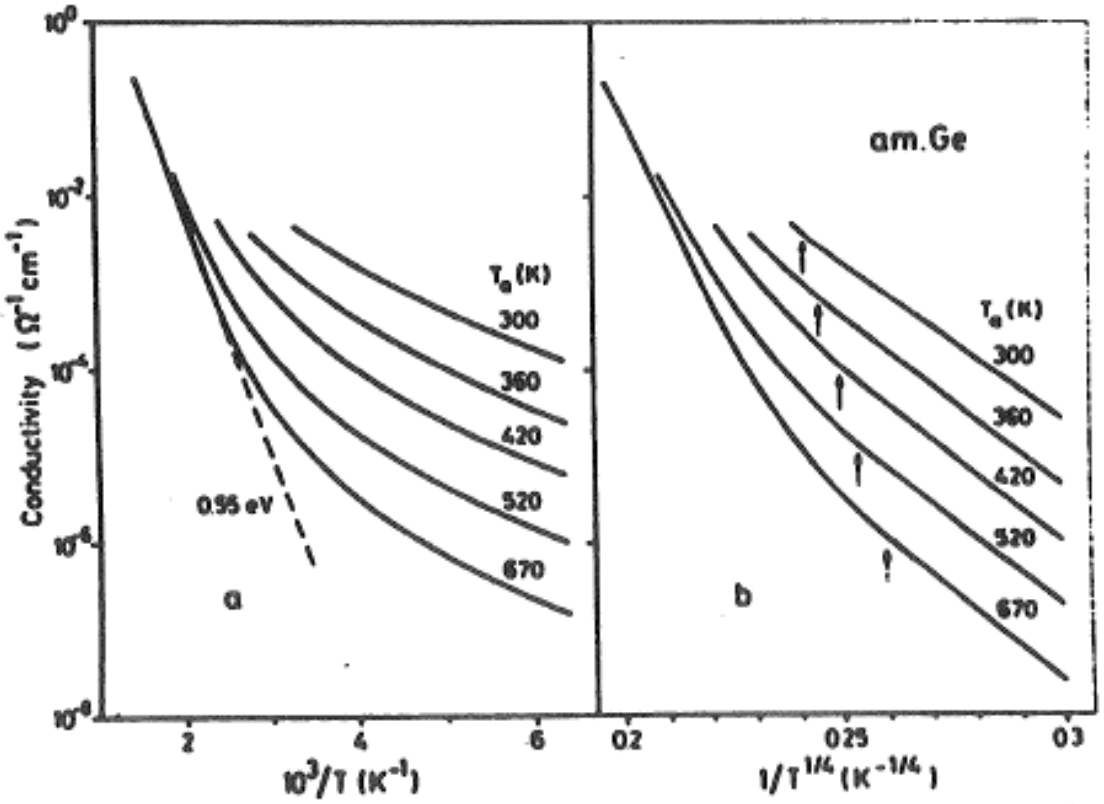
Hopping vs. band conduction

- The exponent in Mott's law becomes different in case of two dimensions and if $D(E_F)$ varies rapidly around E_F
- Variable range hopping is favored by low temperature and a large localized DOS
- Band conduction is favored by high temperature and a low localized DOS
- Crossover: Compare terms $\sim\exp(-2\alpha r_{ij})$ and $\sim\exp(-(E_c-E_F)/k_BT)$

Ex: amorphous Ge

- Conductivity plotted in two different ways

Band



VRH

Source: Overhof, Festkörperprobleme 16 (1976)

Multiple trapping - 1

- Trapping of electrons from the conduction band, or generally from ”transport states”
- p(r,t) –probability that a transport state is occupied
- $p_i(r,t)$ – probability that trap state ”i” is occupied
- w_i – capture rate
- r_i – release rate

- Trapping equations

$$P(r,t) = p(r,t) + \sum_i p_i(r,t)$$

$$\frac{\partial p_i(r,t)}{\partial t} = w_i\, p(r,t) - r_i\, p_i(r,t)$$

$$\frac{\partial P(r,t)}{\partial t} = g(r,t) - \mu E \nabla p(r,t)$$

- Here g is the rate of excitation of carriers to the transport states

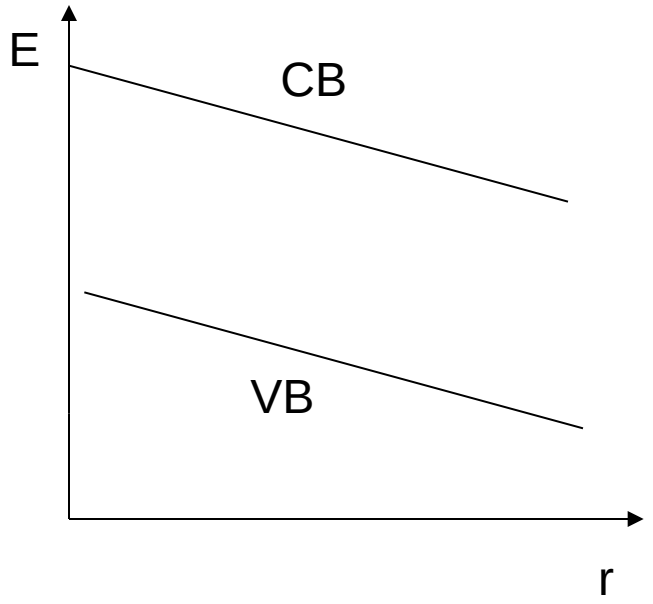
Multiple trapping - 2

- These equations form the basis for the transient photoconductivity method for measuring localized band gap states
- In an insulator material, charge carriers will be generated in the transport states by thermal excitation from the Fermi level
- Maybe excitation to the conduction band
- Trap-controlled hopping: Excitation to a maximum of the localized DOS; the lower lying empty states act as traps
- Conductivity proportional to the average release rate
- Power-law distribution of release rates (for example exponential band tails) – very long time-dependent transients – DC conductivity may be difficult to observe
- Conductivity related to the cutoff of the power-law distribution

High field concuction

- Apply a high voltage, V, i.e. a high electric field, F, to the sample
- Energy depends on position: E=E(0)-eFr
- Band conduction: Excitation from donors, space charge limited conduction with traps
- Hopping conduction

- Electron energies vary with position – ”tilted energy bands”



Donors: Band conduction

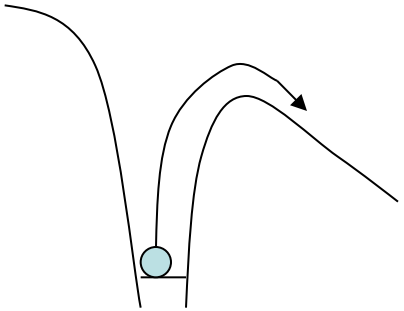
- Poole-Frenkel effect
- Coulomb potential
- The electron has to climb an energy barrier to the conduction band
- Current density

$$J = J(0)\exp(\beta F^{1/2} / kT)$$

$$\beta = e^3 / \pi\varepsilon\varepsilon_0$$

- Exp: β differs from this value

- Donor state



- $E=E_0 - e^2/4\pi\varepsilon_0\varepsilon r - eFr$

$$\frac{dE}{dr} = 0 \Rightarrow r_m = (e / 4\pi\varepsilon_0\varepsilon F)^{1/2}$$

Space charge limited currents

- At high applied voltages, charge may be injected from the contact into a close so called space charge region in the conduction band of an insulator
- Space charge limited currents: $J \sim V^2$
- Single trap level decreases the current but does not modify the voltage dependence
- Broad distribution of trap levels
- Exponential DOS: $D(E) = N_0 \exp(-E / kT_0)$
- Current becomes: $J \sim V^{1+T_0/T}$

High field hopping

- Low fields, ohmic region: Variable range hopping, Mott's law
- Moderate fields $eFr<k_BT$ treated by percolation theory

$$\sigma(F) = \sigma(0)\exp(-CeFr_p / kT)$$

- Other exponential dependences also possible

- Very high fields: $eFr>>k_BT$
- Electrons "hop down" in high E-field
- Accessible states: $N=4\pi r^3 eFrD(E_F)/3$
- Mott argument, N=1

$$\sigma = \sigma_0^{hf} \exp(-(F_o / F)^{1/4})$$

$$F_0 = \frac{64\alpha^4}{e\pi D(E_F)}$$

How to distinguish these phenomena?

- See which eqn. gives the best fit to exp?
- But there may be crossovers between different mechanisms
- Examine the derivative of the current is very useful

$$\Delta = \frac{d(\ln \sigma)}{d(1/F)} \cong nAF^{1-n}$$

- We can determine the exponent n!

- We can write in the form:
- $J \sim F^m \exp(-A/F^n)$

TABLE I. Values of the parameters m and n for different high-field conduction mechanisms.

Conduction mechanisms		n	m
Isotropic percolation, moderate fields		−2	...
Directed percolation, moderate fields		−1	...
Poole's law		−1	0
Poole–Frenkel conduction		−0.5	0.5 or 1
Space-charge-limited conduction		0	>2
High-field percolation theory		0.25	...
(hopping or tunneling)	or	0.33	
Particle-particle tunneling		1	1
Field ionization		1	0

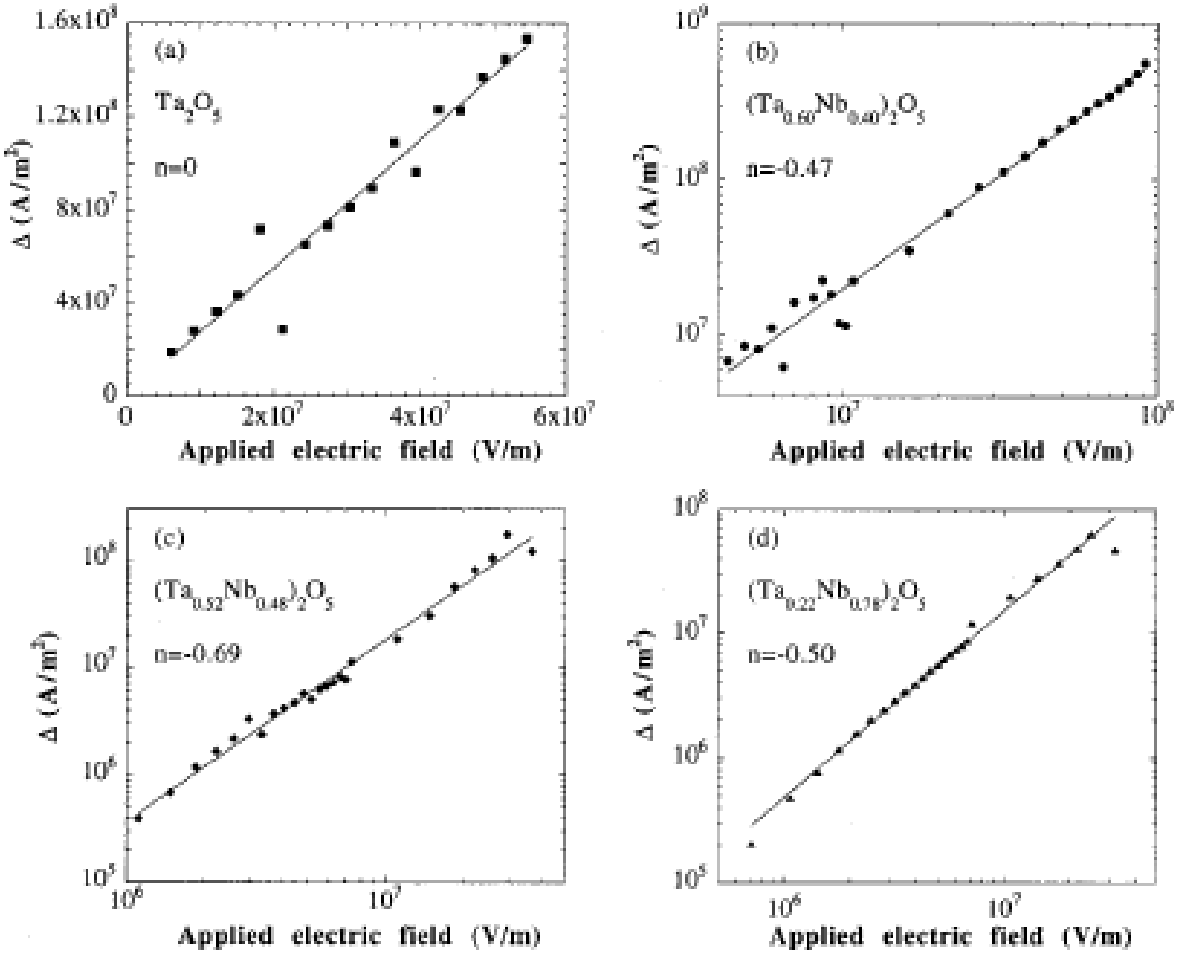
- Analogous method for the temperature dependence

Ex: Amorphous $Ta_xNb_yO_5$ films

- Ta2O5:
- Space charge limited conduction

- Other films:
- Poole-Frenkel conduction

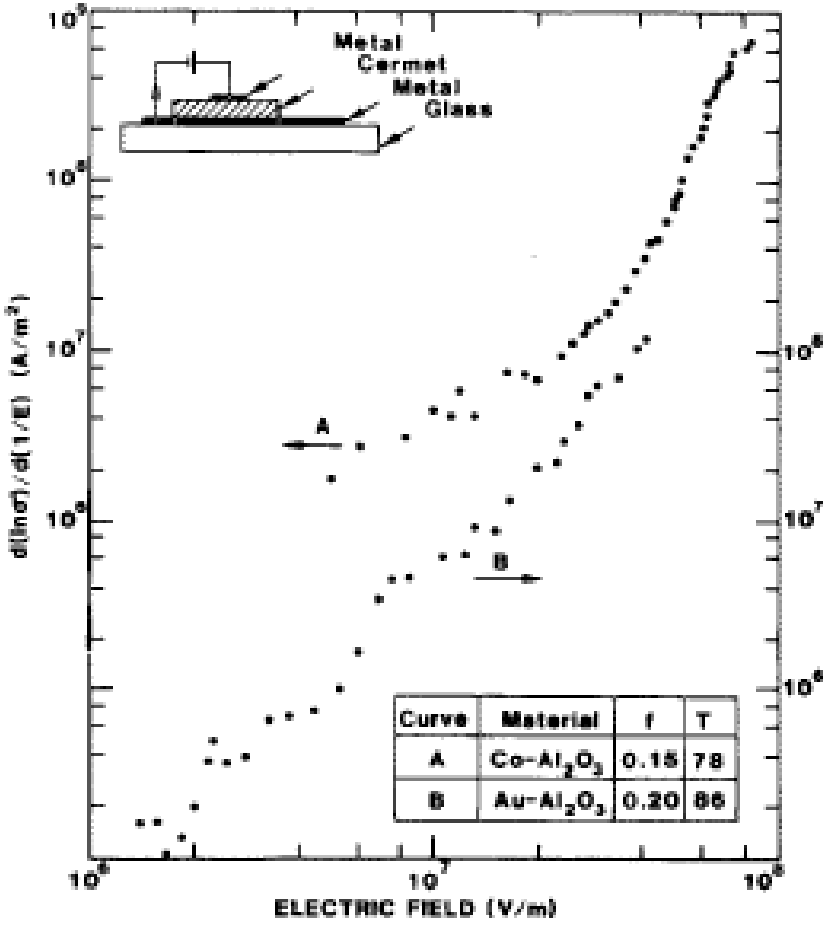
- a-SiO_2 (not shown) n=-1, i.e. high field hopping



Source: Strömme et al.

Ex: Metal-insulator composites

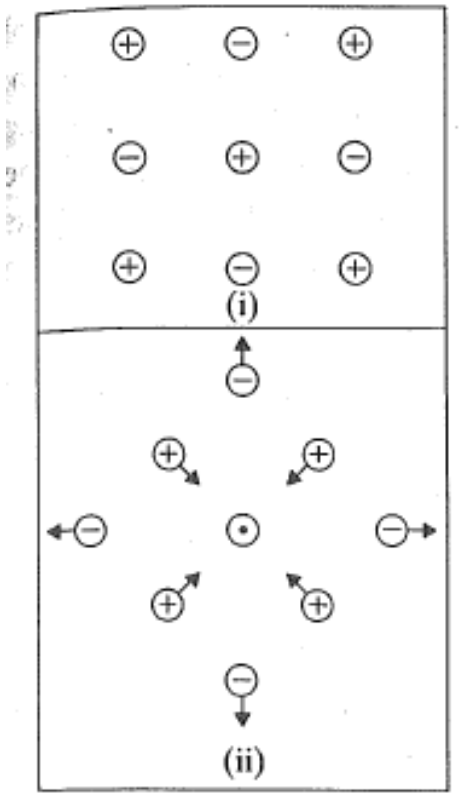
- Au-Al_2O_3: n=-1
- Points to high field hopping at moderate fields
- Co-Al_2O_3: n=0, then much higher –n
- Detailed mechanism unknown
- n=0 may point to the importance of trap states in this material



Polarons - 1

- A charge carrier in a material always distorts the surroundings - even in crystal
- Lower energy state
- Strong electron-phonon interaction – the carrier may become self-trapped
- Large polaron: Extends over several atomic distances
- Small polaron: atomic distance

- Ionic material



Source: Elliott, Physics of amorphous materials

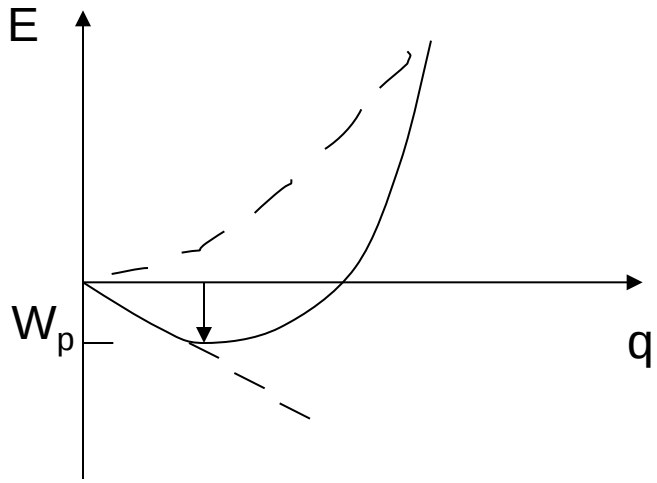
Electron-phonon interaction

- Fröhlich model: Interactions with longitudinal optical phonons
- Coupling constant

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar}\sqrt{\frac{m}{2\hbar\omega_{LO}}}\left(\varepsilon_\infty^{-1} - \varepsilon(0)^{-1}\right)$$

- Weak coupling: $\alpha << 1$
- Strong coupling: $\alpha >> 1$
- Measurable parameters

- Energy as a function of ”configuration”, q



Polarons - 2

- Polaron binding energy $W_H = \alpha^2 \hbar \omega_{LO} / 3\pi$
- Polaron radius, β^{-1} $\beta = \frac{e^2 m}{12\pi\varepsilon_0 \hbar^2 \sqrt{\pi}} \left(\varepsilon_\infty^{-1} - \varepsilon(0)^{-1} \right)$
- The polaron sits in a potential well and can be transported by hopping between these wells.
- Polarons in conduction band: The charge carrier concentration, n can be high and constant, if E_F is in the band, while the mobility is small and thermally activated
- Excitation of carriers into the band: Both n and μ are thermally activated

Polaron hopping - 1

- An occupied site has a lower energy than an unoccupied site
- Energy from phonons make the transition possible
- An atomic distortion momentarily brings the energy level of an occupied site into coincidence with a neighboring unoccupied site, in order for the charge transfer to take place
- Adiabatic regime: Electron transfer faster than vibrational motion → several forward-backward hops
- Nonadiabatic regime: Small probability of electron transfer during a lattice vibration. Gives similar results to VRH, but there we considered only an electron gaining energy from a single phonon.
- At all but the lowest temperatures, multiphonon processes are important.

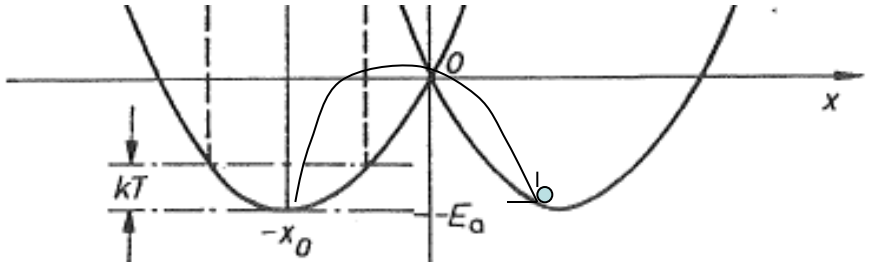
Polaron hopping - 2

- Polaron hopping energy W_H
- Disorder energy, W_D
- Activation energy:
  $W = W_H + W_D/2$
  (if W_D small)

$$\sigma = \sigma_0 \exp[-(\Delta E + W)/k_B T]$$

- Thermopower does not depend on W!
- Hall effect also activated.

- Hopping process:



- In addition disorder may cause the bottom of the two wells to be at different energies

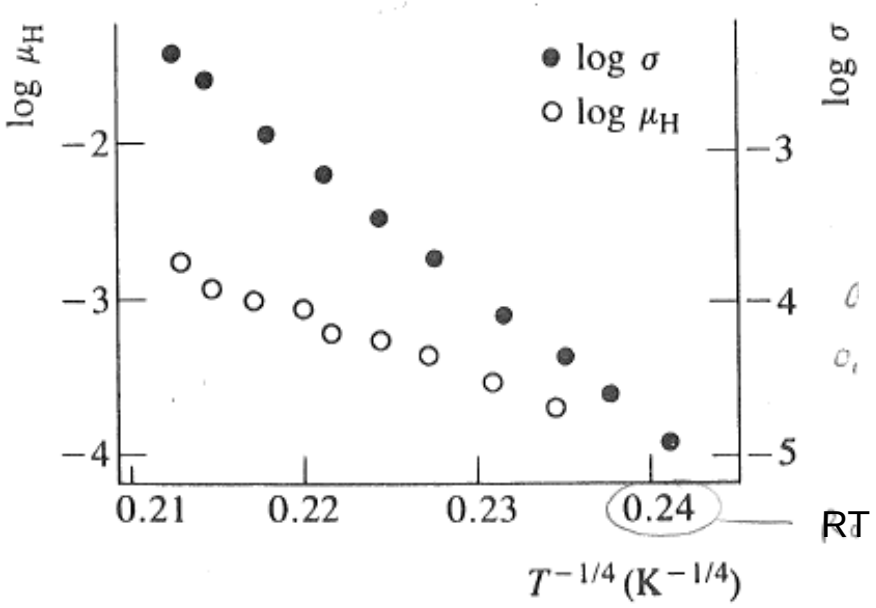
VRH of polarons

- Polaron sites on a lattice: Thermally activated conduction
- Disorder in positions of sites: Variable range hopping

$$\sigma = \sigma_0 \exp(-(T_o / T)^{1/4})$$

- Important in transition metal oxides and glasses with transition metal ions

- Ex: V_2O_5-P_2O_5 glass
- Conductivity and Hall mobility



Source: Elliott, Physics of amorphous materials

Polarons or electrons?

- Jonker plot: S vs. ln σ for samples with varying stoichiometry or doping

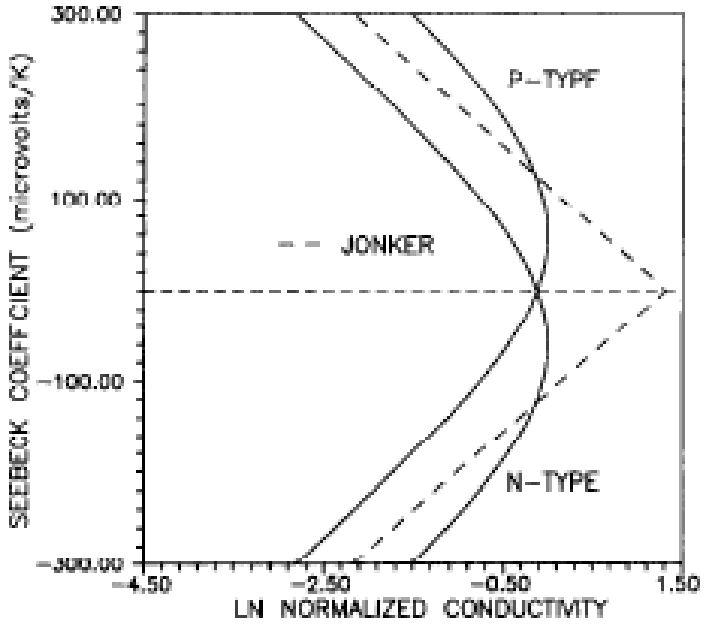


FIG. 1. Seebeck coefficient vs logarithm of conductivity for *p*-type and *n*-type small polaron systems as compared to typical semiconductor (Jonker) behavior.

- Example:

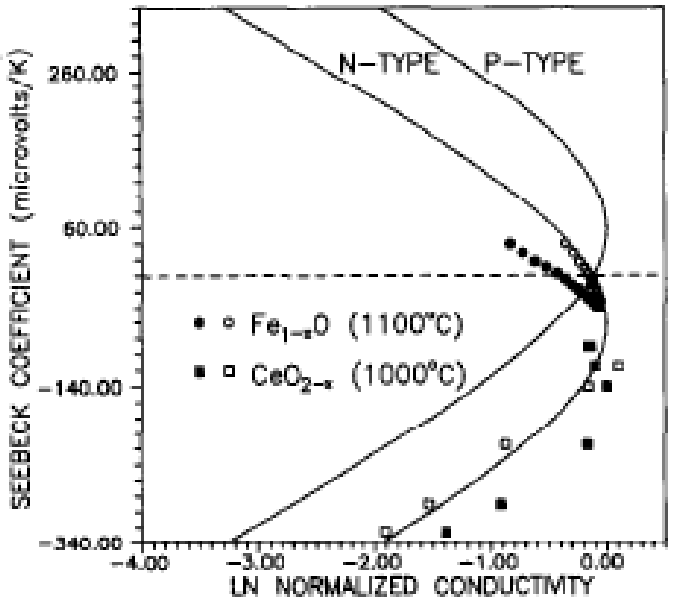


FIG. 2. *N*-type small polaron Jonker plots for CeO_2 (*6*) and FeO (*17*). The raw CeO_2 data (closed squares) have been corrected for changes in the Nv product (*10*) (open circles).

Source: Nell et al, Solid State Chem. 1989

Some optical effects

- Strong absorption for energies higher than the band gap, E_g.
- The shape of the interband absorption is modified (broadened) because of the breakdown of the k-selection rule
- At lower energies various absorption phenomena may be present:
- Polaron absorption in the near infrared or thermal infrared
- Absorption involving exponential band tails (Urbach tails)
- Weak absorption from defect and impurity states

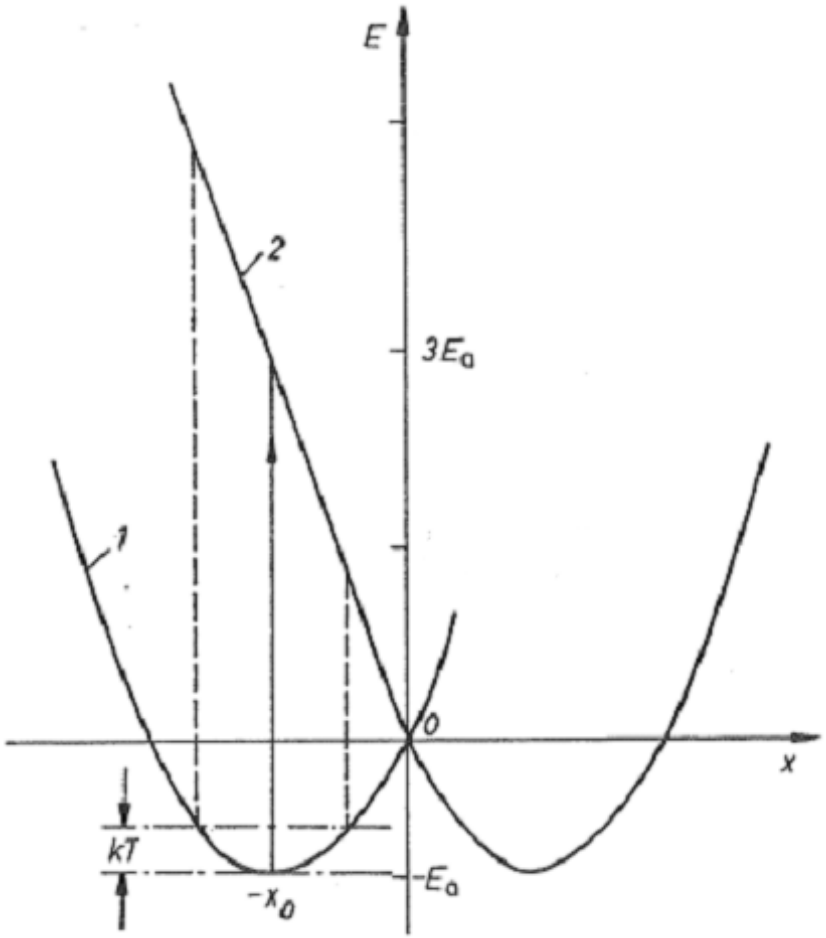
Polaron absorption

- Optical transition: Two-site model
- Absorption centered around energy $4W_H$
- Optical conductivity:

$$\sigma_1(\omega) \sim \exp\left[\frac{-(\hbar\omega - 4W_H)^2}{16 W_H k_B T}\right]$$

if $k_B T > E_{LO}$

- Low T: Phonon broadening

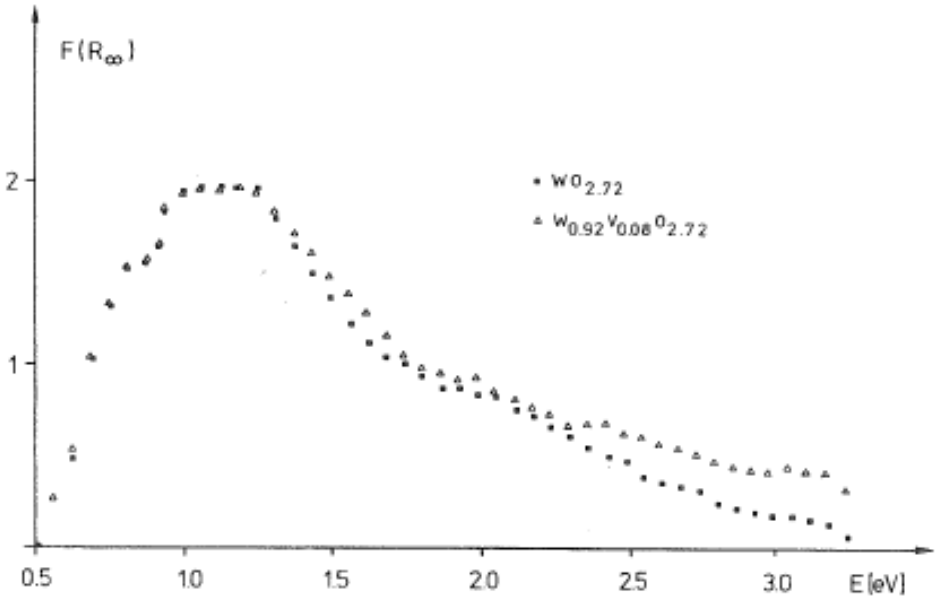


Source: Elliott, Physics of amorphous materials

Polaron absorption: Exp

- Most studied in TiO_2 and WO_3
- Ex: $WO_{2.72}$ and V-doped material
- Absorption peak centered at ~1 eV
- Present in crystals
- Amorphous WO_3 doped with protons or Li^+: Electrochromism due to polaron absorption

Defects: O vacancies

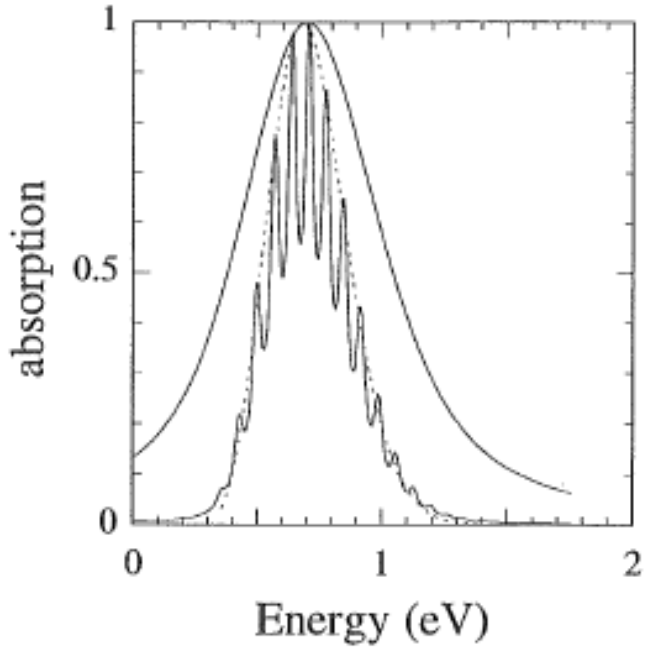


Source: Salje et al.

Similar peak by intercalation of H^+, Li^+

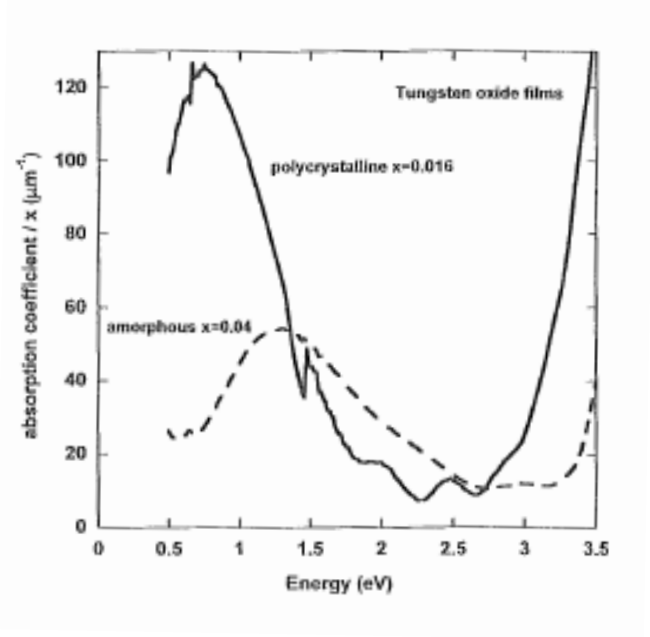
Ex: WO_3

- Fröhlich model, but intermediate polaron
- Phonon broadening



Source: Bo Sernelius, LiU

- Experiment on Li-doped WO_3 films
- Polaron radius 6-7 Å



The optical band gap

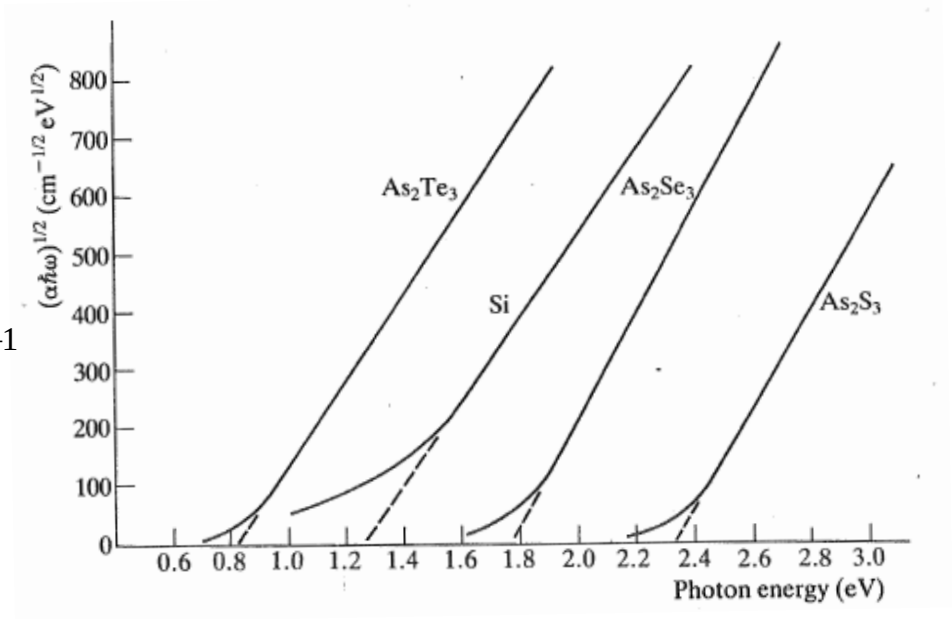
- Assume that the DOS in the valence and conduction bands vary as power laws of energy with indices p and q, respectively
- Good approximation close to band edges (mobility edges)

$$\omega\alpha(\omega) \sim \omega^2 \varepsilon_2(\omega) \sim (\hbar\omega - E_g)^{p+q+1}$$

- Parabolic bands

$$\omega\alpha(\omega) \sim (\hbar\omega - E_g)^2$$

- Extrapolation gives ”Tauc gap”
- Is it the ”true” band gap?



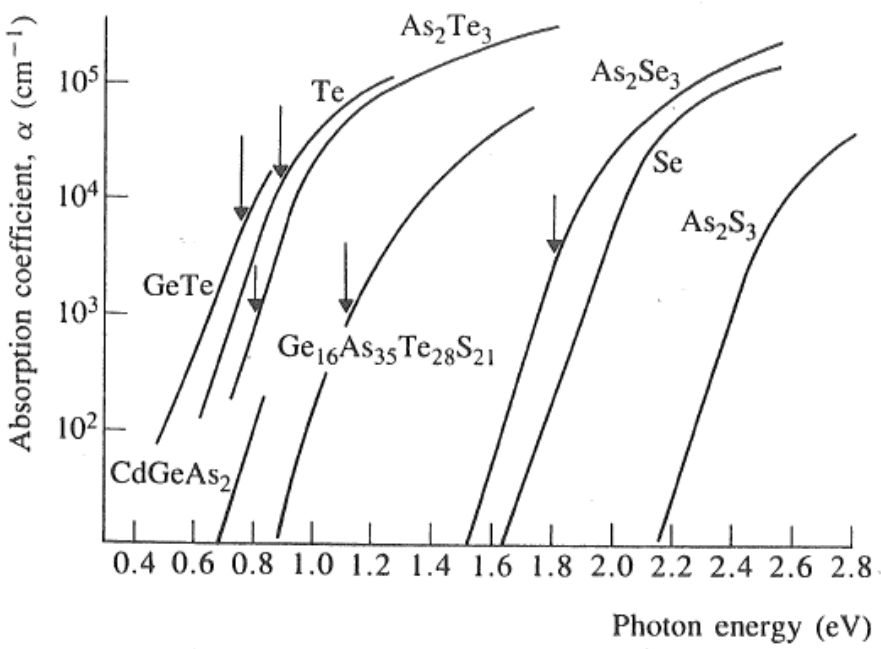
Source: Elliott, Physics of amorphous materials

Urbach (band) tail

- At lower energies we see an Urbach tail
- Extended to localized state transitions
- Exponential DOS

$$\alpha(\omega) \sim \exp[-A(T)(E_U - \hbar\omega)]$$

- Structural disorder
- Defect bands have lower optical absorption strength and are difficult to observe



Source: Elliott, Physics of amorphous materials

Ex: TiO_2 thin films

- Polycrystalline films by sputtering
- More sub-stoichiometric as Ar/O_2 ratio in the sputter gas decreases
- Oxygen vacancies
- Urbach tail seen for all samples (oscillations are not real!)
- Polaron absorption at low oxygen content