MIT 3.071
Amorphous Materials

10: Electrical and Transport Properties

Juejun (JJ) Hu

After-class reading list

- Fundamentals of Inorganic Glasses
  - Ch. 14, Ch. 16
- Introduction to Glass Science and Technology
  - Ch. 8
- 3.024 band gap, band diagram, engineering conductivity

Basics of electrical conduction

- Electrical conductivity

$$\sigma = \sum_i n_i Z_i e \mu_i$$

$$\boldsymbol{v}_{\boldsymbol{i}} = \mu_i \boldsymbol{E}$$

- Einstein relation

$$D_i = \frac{\mu_i k_B T}{Z_i e}$$

$$\Rightarrow \quad \sigma = \frac{1}{k_B T} \cdot \sum_i \left(Z_i e\right)^2 n_i D_i$$

σ : electrical conductivity

n : charge carrier density

Z : charge number

e : elementary charge

μ : carrier mobility

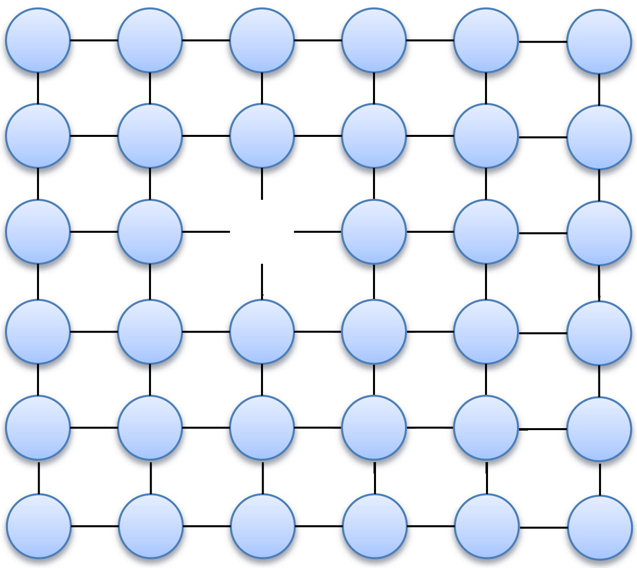
D : diffusion coefficient

$\boldsymbol{v}$: carrier drift velocity

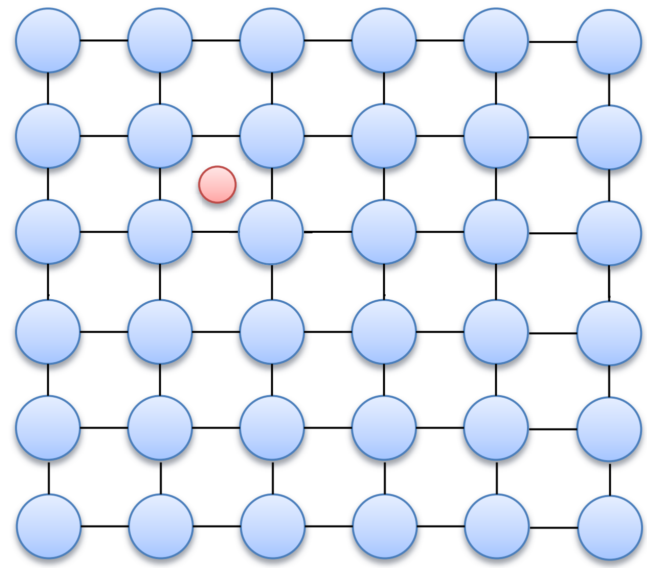
$\boldsymbol{E}$: applied electric field

Both ions and electrons contribute to electrical conductivity in glasses

Ionic conduction in crystalline materials



Vacancy mechanism



Interstitial mechanism

Ionic conduction pathway in amorphous solids

Comparison of Li transport pathways figure removed due to copyright restrictions. See: Figure 8: Adams, S. and R. Prasada Rao. "Transport Pathways for Mobile Ions in Disordered Solids from the Analysis of Energy-scaled Bond-valence Mismatch Landscapes." Phys. Chem. Chem Phys. 11 (2009): 3210-3216.

- There are low energy "sites" where ions preferentially locate
- Ionic conduction results from ion transfer between these sites
- Ionic conduction is thermally activated

2-D slices of regions with Li site energies below a threshold value in Li_2O-SiO_2 glasses

Phys. Chem. Chem. Phys. **11**, 3210 (2009)

A tale of two valleys

- Assuming completely random hops, the average total distance an ion moves after M hops in 1-D is:

$$r = d \cdot \sqrt{M}$$

- Average diffusion distance:

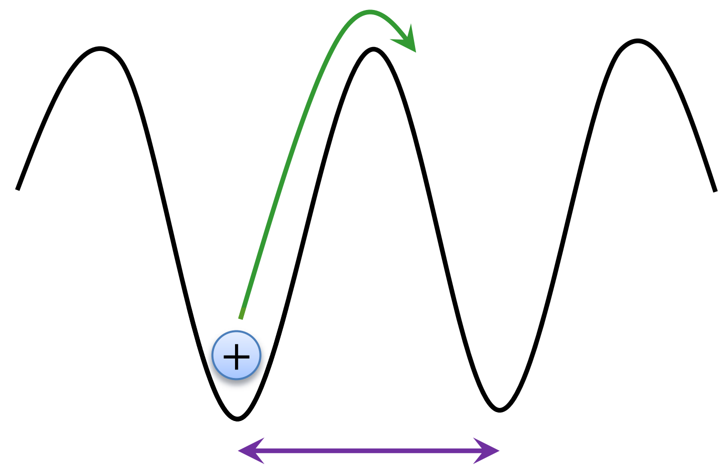
$$r = \sqrt{2\tau D} \qquad \text{(1-D)}$$

$$r = \sqrt{6\tau D} \qquad \text{(3-D)}$$

$$\Rightarrow \quad D = \frac{1}{2}\nu d^2 \qquad \text{(1-D)}$$

$$\Rightarrow \quad D = \frac{1}{6}\nu d^2 \qquad \text{(3-D)}$$

Electric field E = 0



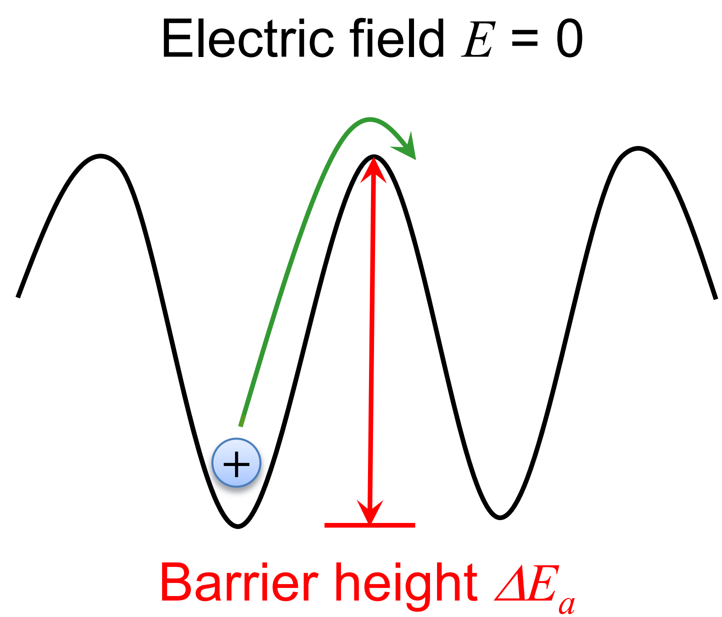
Average spacing between adjacent sites: d

- For correlated hops:

$$D = \frac{1}{6} f \nu d^2 \qquad 0 < f < 1$$

Ion hopping frequency: ν

A tale of two valleys



- Attempt (vibration) frequency: ν_0
- Frequency of successful hops (ion hopping frequency):

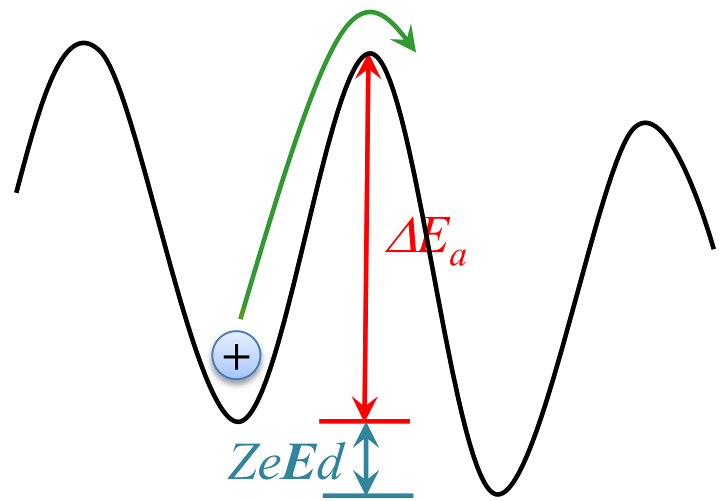
$$\nu = \nu_0 \exp\left(-\frac{\Delta E_a}{k_B T}\right)$$

$$\Rightarrow \quad D = \frac{1}{6} f \nu_0 d^2 \exp\left(-\frac{\Delta E_a}{k_B T}\right)$$

- Equal probability of hopping along all directions: zero net current

A tale of two valleys

Electric field $\boldsymbol{E} > 0$



- Energy difference between adjacent sites: $Ze\boldsymbol{E}d$
- Hopping frequency $\rightarrow$:

$$v_{\rightarrow} = \frac{1}{2} v_0 \exp\left(-\frac{\Delta E_a}{k_B T} \right)$$

- Hopping frequency $\leftarrow$:

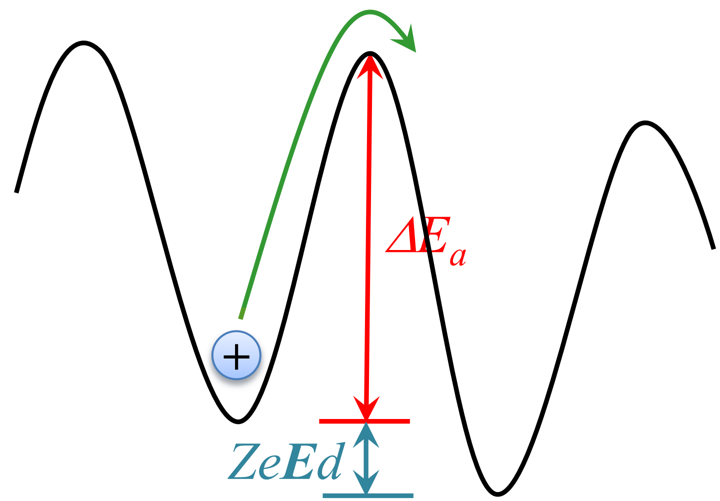
$$v_{\leftarrow} = \frac{1}{2} v_0 \exp\left(-\frac{\Delta E_a + Ze\boldsymbol{E}d}{k_B T} \right)$$

- Net ion drift velocity:

$$\boldsymbol{v} = \left(v_{\rightarrow} - v_{\leftarrow} \right) \cdot d = \frac{v_0 Ze\boldsymbol{E}d^2}{2k_B T} \cdot \exp\left(-\frac{\Delta E_a}{k_B T} \right)$$

A tale of two valleys

Electric field $\boldsymbol{E} > 0$



- Ion mobility

$$\mu = \frac{v_0 Zed^2}{2k_B T} \cdot \exp\left(-\frac{\Delta E_a}{k_B T}\right)$$

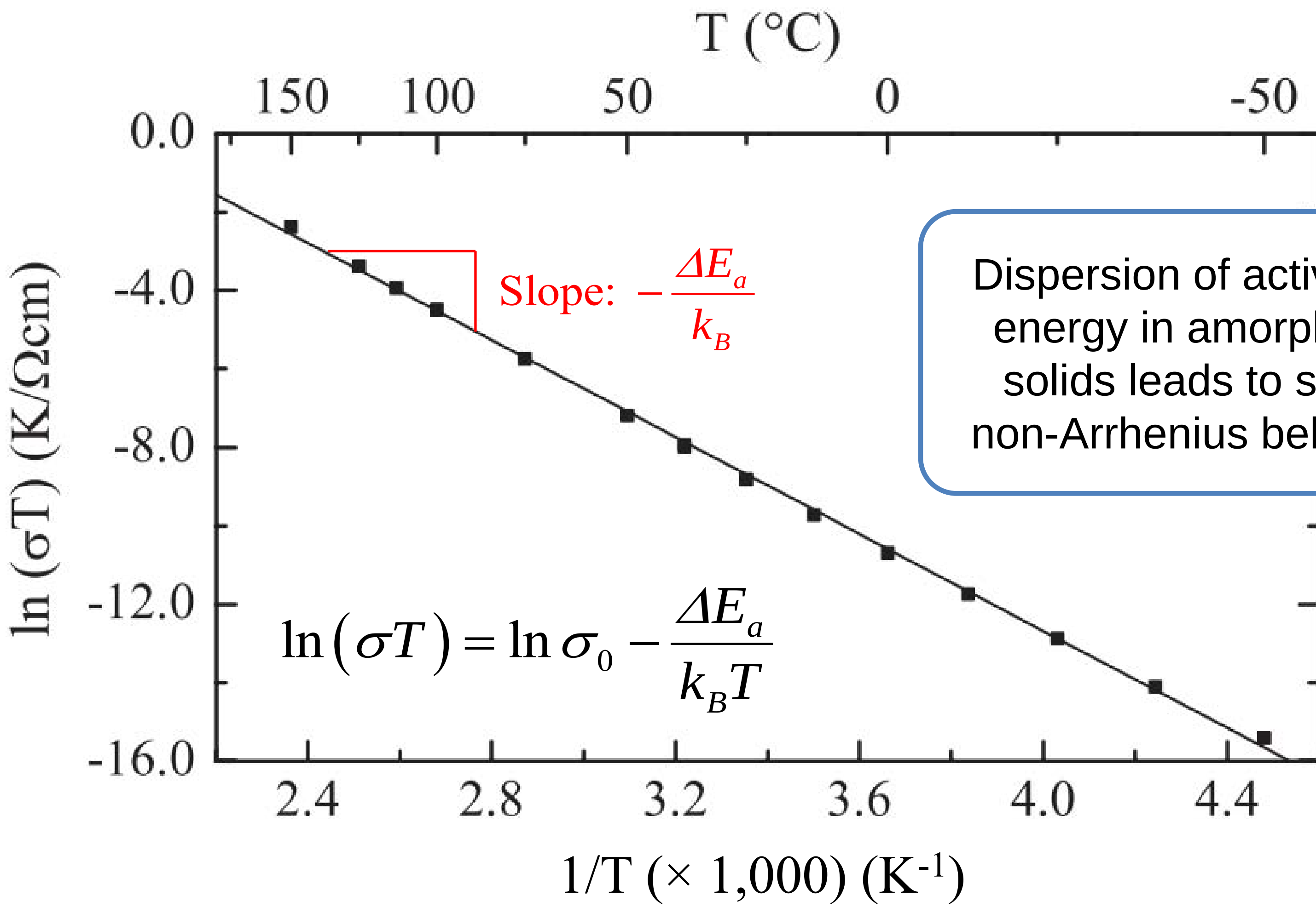
- Electrical conductivity (1-D, random hop)

$$\sigma = \frac{n v_0 \left(Zed\right)^2}{2k_B T} \cdot \exp\left(-\frac{\Delta E_a}{k_B T}\right)$$

- Einstein relation (3-D, correlated hops)

$$\sigma = \frac{1}{k_B T}\left(Ze\right)^2 nD = \frac{f n v_0 \left(Zed\right)^2}{6k_B T} \cdot \exp\left(-\frac{\Delta E_a}{k_B T}\right) = \frac{\sigma_0}{T} \exp\left(-\frac{\Delta E_a}{k_B T}\right)$$

Temperature dependence of ionic conductivity



Dispersion of activation energy in amorphous solids leads to slight non-Arrhenius behavior

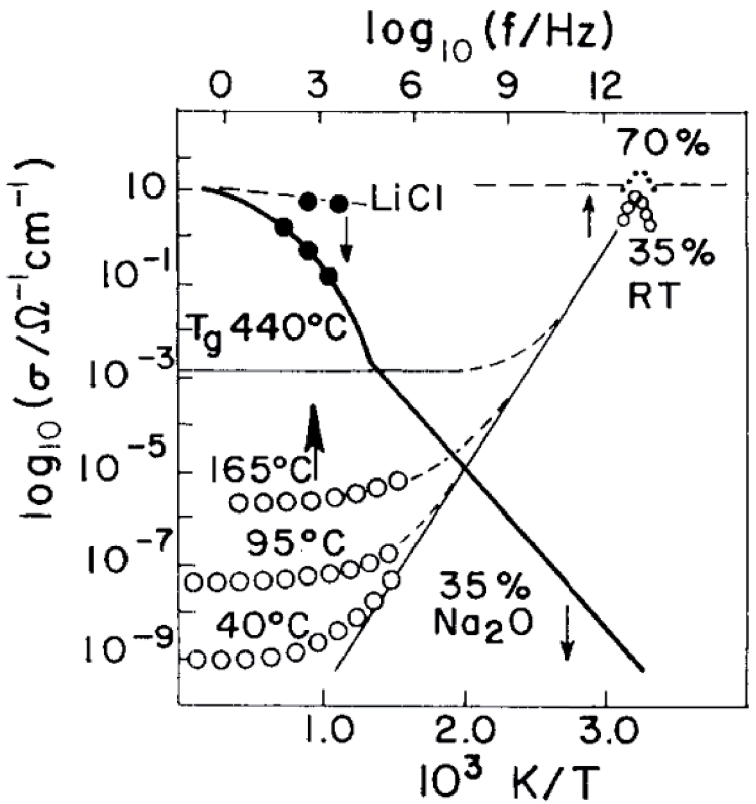
Phys. Rev. Lett. **109**, 075901 (2012)

Theoretical ionic conductivity limit in glass

$$\sigma = \frac{\sigma_0}{T} \cdot \exp\left(-\frac{\Delta E_a}{k_B T} \right) \qquad \sigma_0 = \frac{f n v_0 \left(Zed \right)^2}{6 k_B}$$

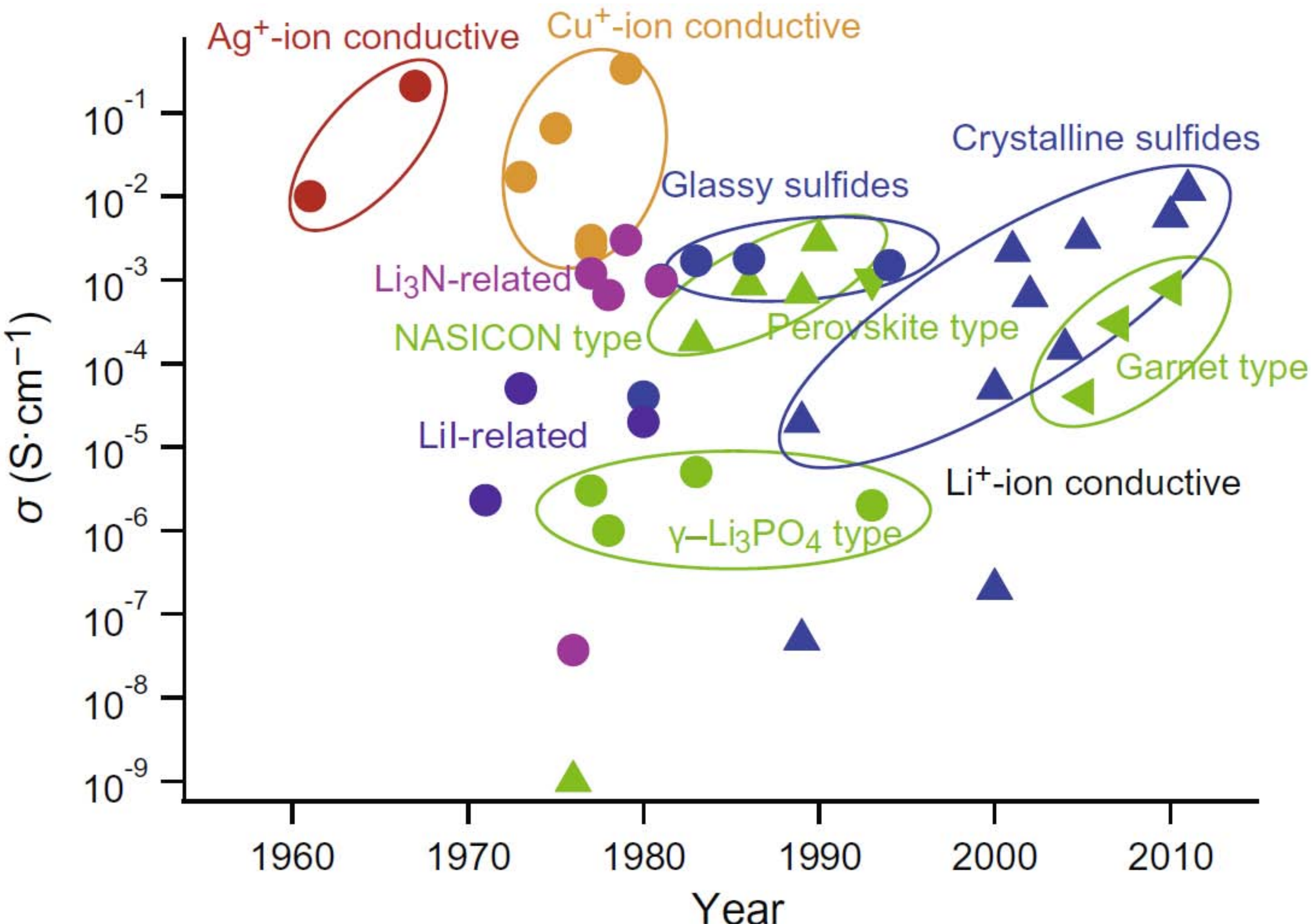
Note that σ_0 has a unit of Ω·cm/K

- When $T \to \infty$, $\sigma \to \sigma_0 / T$
- Extrapolation of the Arrhenius plot agrees with infrared spectroscopic measurements in ionic liquids (molten salts)



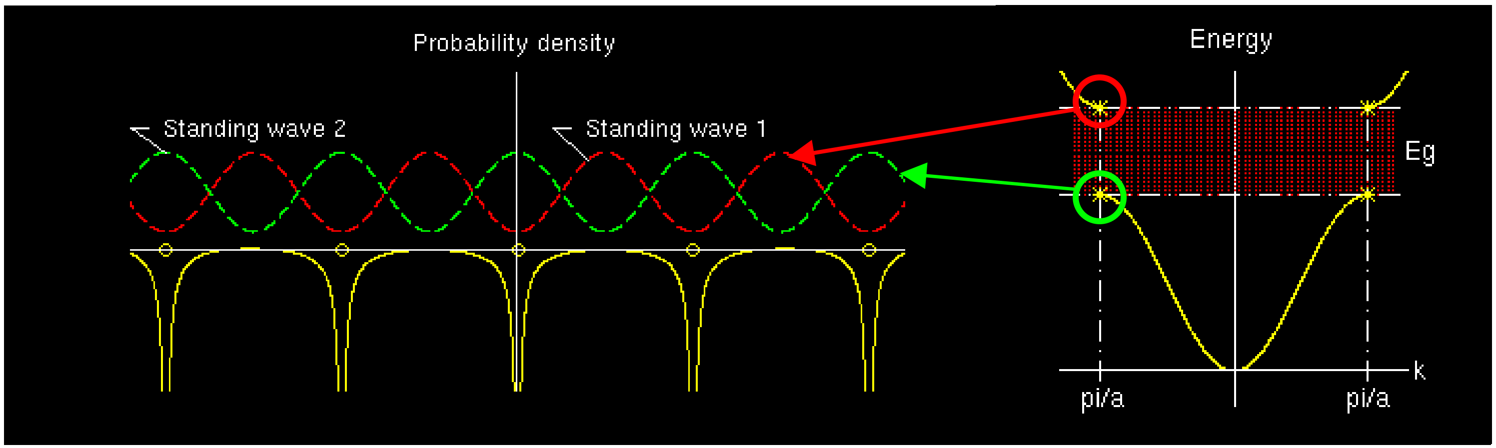
Solid State Ionics **18&19**, 72 (1986)
Annu. Rev. Phys. Chem. **43**, 693 (1992)

Fast ion conductors / superionic conductors



Acta Mater. **61**, 759 (2013)

Band structures in defect-free crystalline solids



- ✓ All electronic states are labeled with real Bloch wave vectors k signaling translational symmetry
- ✓ All electronic states are extended states
- ✓ No extended states exist in the band gap

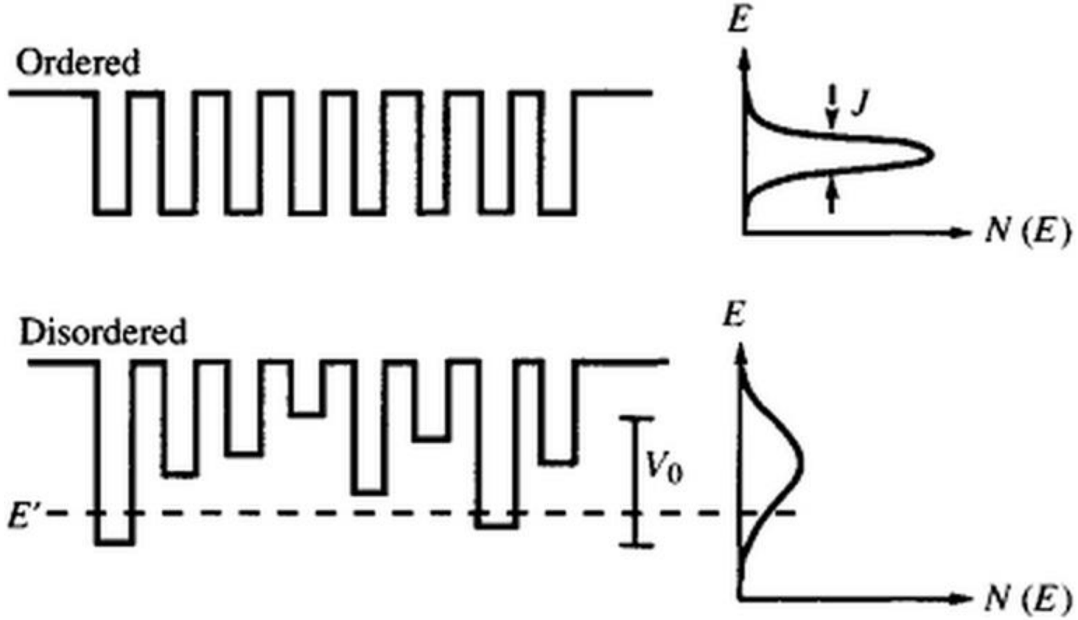
Band structures in defect-free crystalline solids

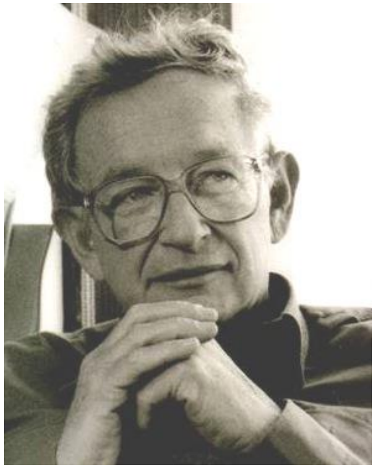
In the band gap, wave equation solutions have complex wave vectors k

Kittel, *Introduction to Solid State Physics*, Ch. 7

Anderson localization in disordered systems

- Localization criterion: $V_0 / J > 3$

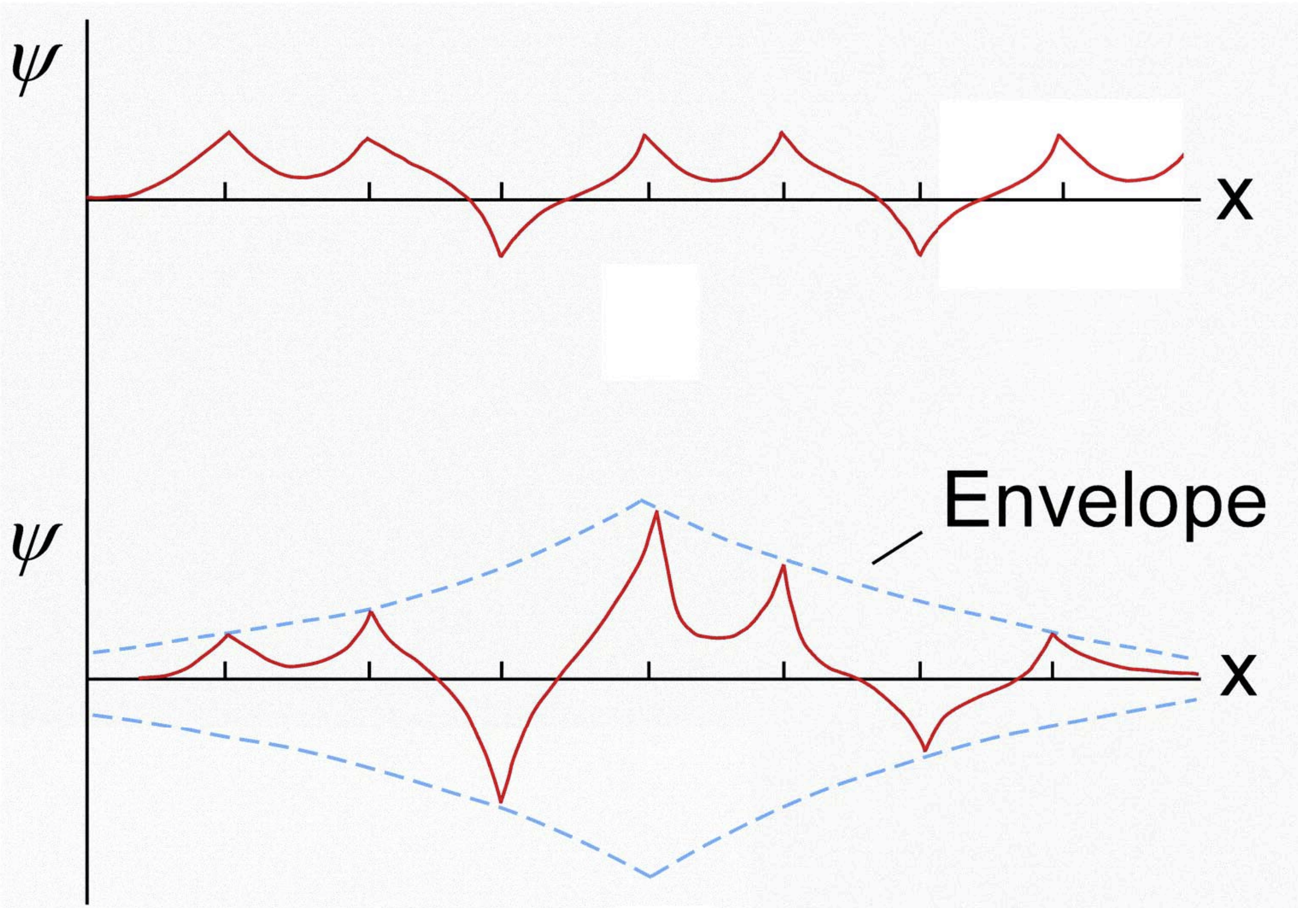




P. W. Anderson

Disorder leads to (electron, photon, etc.) wave function localization

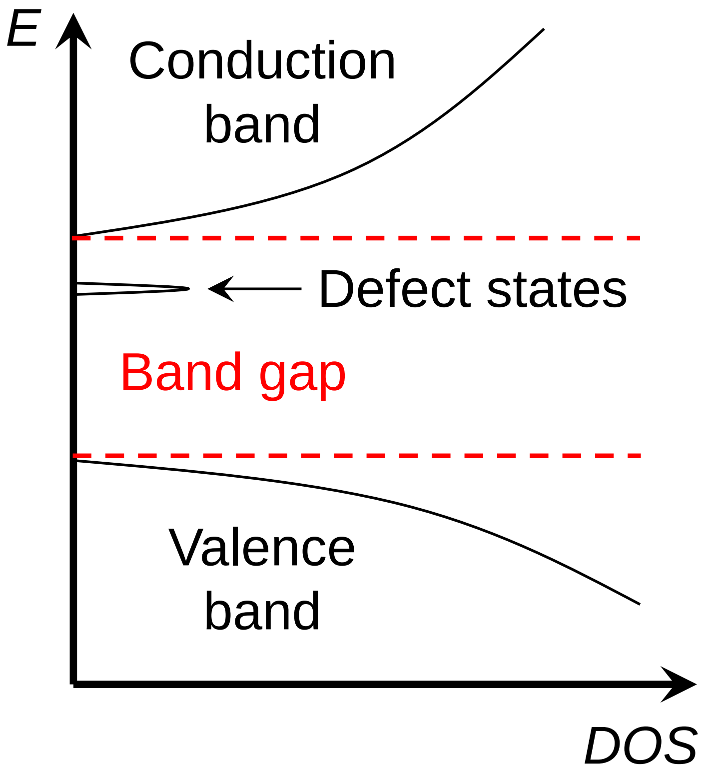
Anderson localization in disordered systems



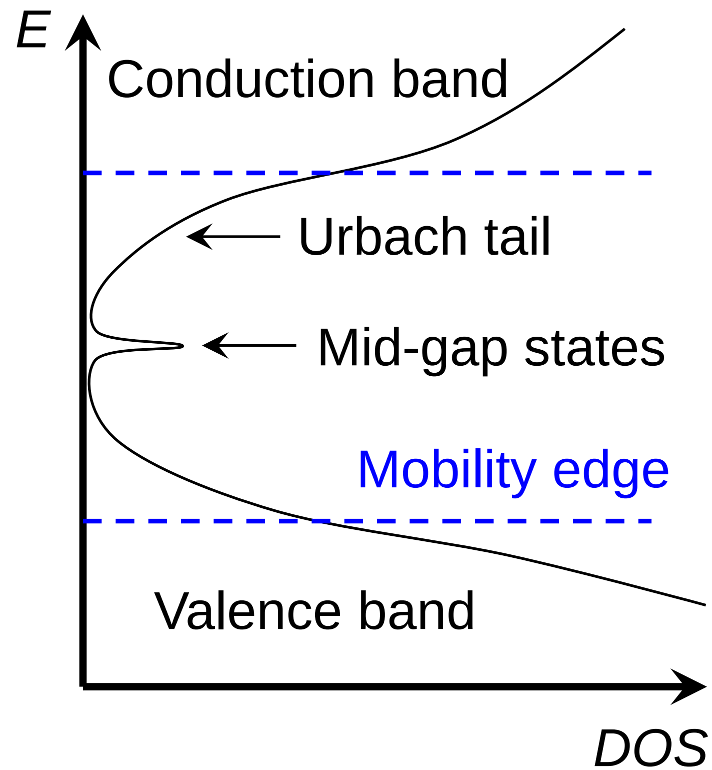
Extended states (Bloch states)

Localized states

Density of states (DOS) in crystalline and amorphous solids



Crystalline solids



Amorphous solids

Extended state conduction

- Extended state conductivity:

$$\sigma_{ex} = ne\mu_{ex}$$

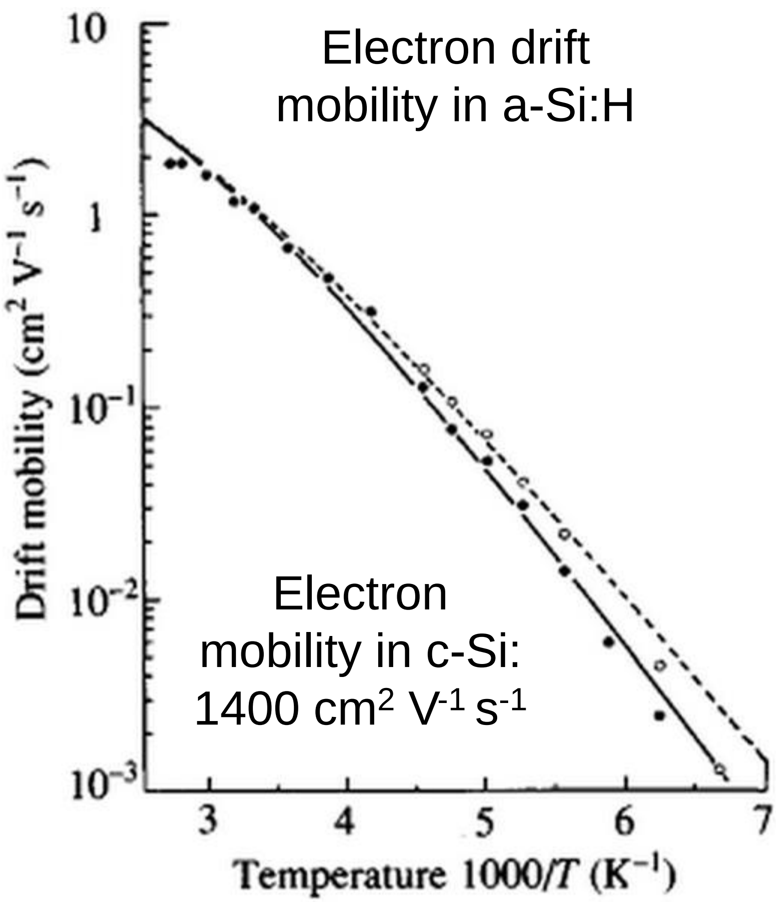
$$\mu_{ex} = \left(1 - f_{trap}\right)\mu_0$$

μ_0 : free mobility

f_{trap} : fraction of time in trap states

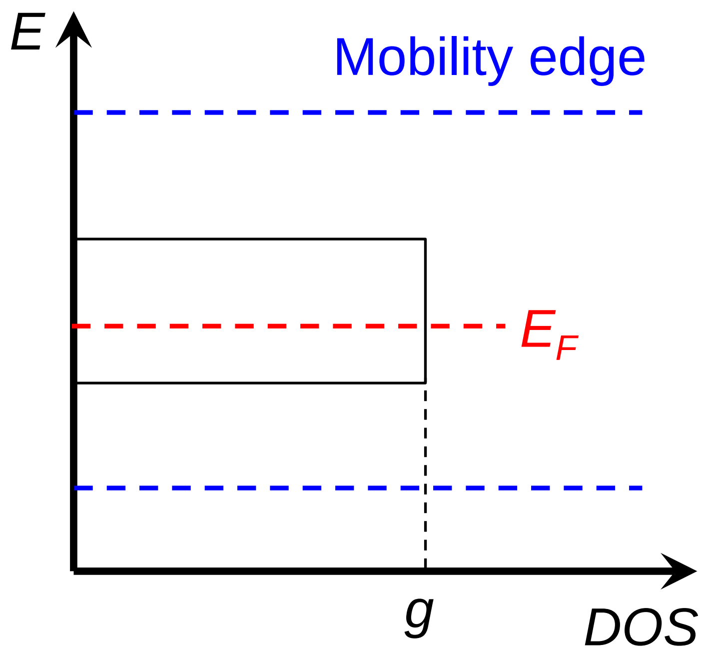
- Drift mobility μ_{ex} increases with temperature ($T \to \infty, f_{trap} \to 0$)
- Extended state conductivity follows Arrhenius dependence

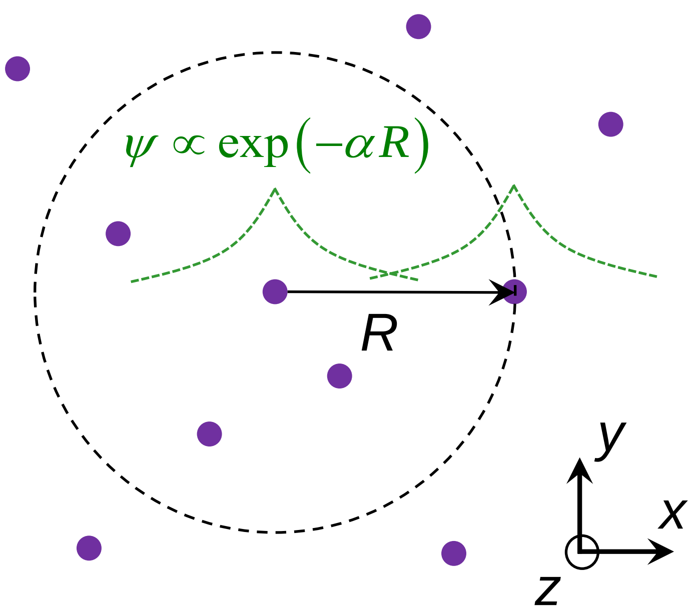
R. Street, *Hydrogenated Amorphous Silicon*, Ch. 7



Hopping conduction via localized states

- Fixed range hopping: hopping between nearest neighbors
  - Hopping between dopant atoms at low temperature
- Variable range hopping (VRH)
  - Hopping between localized states near E_F





Variable range hopping

- Hopping probability $P \propto \exp\left(-2\alpha R - \frac{\Delta E}{k_B T}\right) \propto \sigma_{VRH}$
- Within distance R, the average minimal energy difference ΔE is:

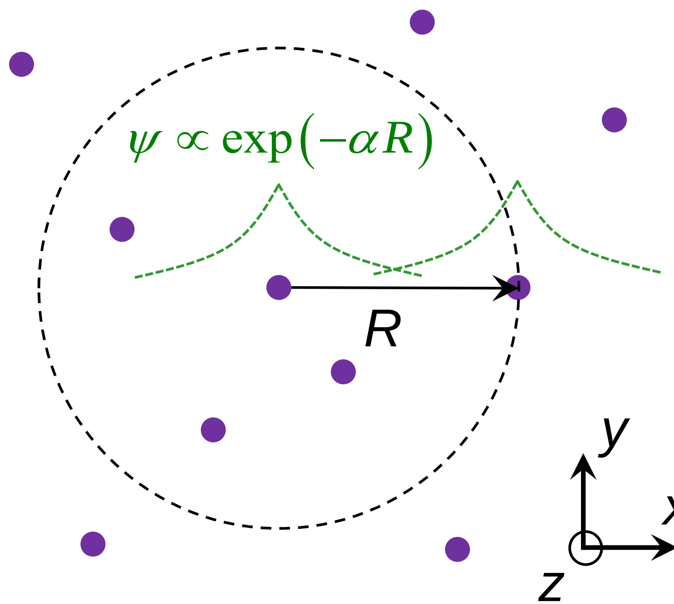
$$\Delta E = \frac{3}{4\pi R^3 g}$$

- Optimal hopping distance:

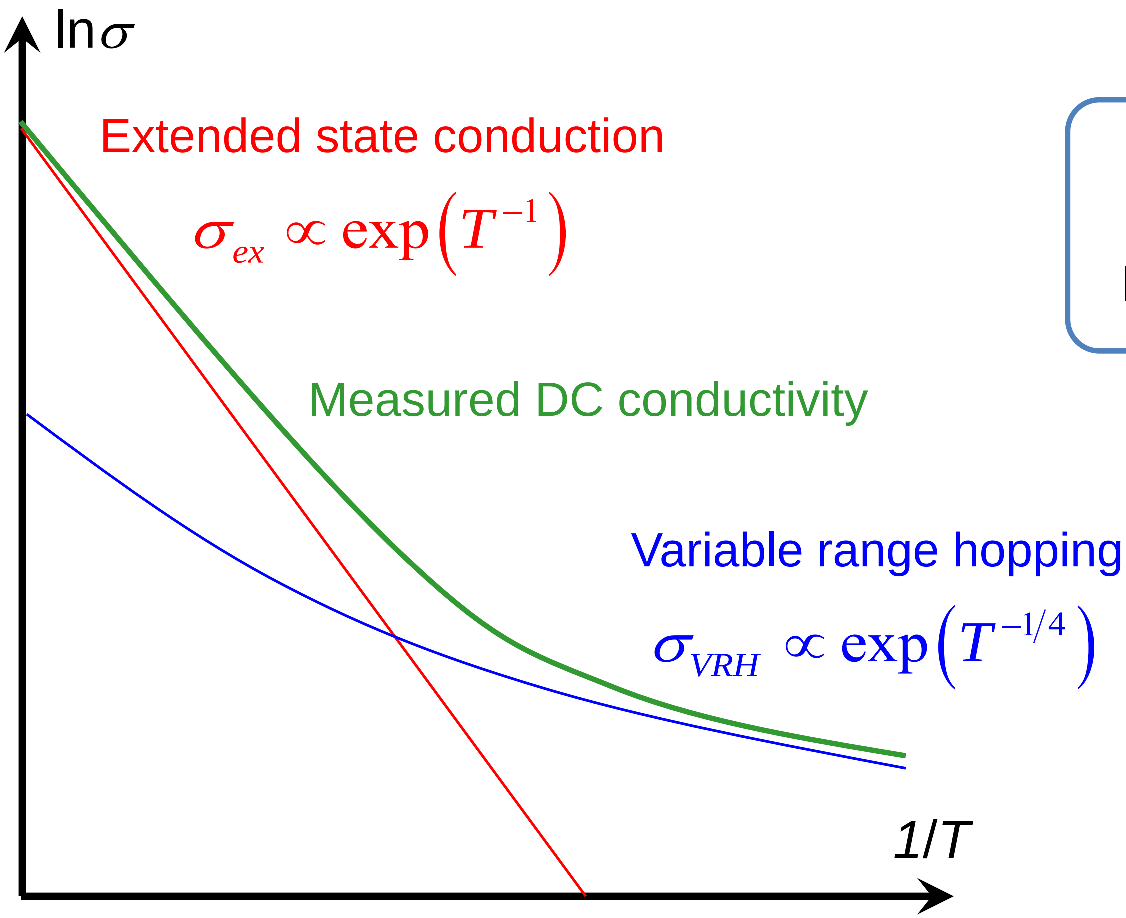
$$R = \left(8\pi g \alpha k_B T/9\right)^{-1/4}$$

$$\left(2\alpha R + \frac{\Delta E}{k_B T}\right)_{\min} = 4\alpha^{\frac{3}{4}}\left(\frac{2}{9\pi g k_B T}\right)^{\frac{1}{4}}$$

$$\Rightarrow \sigma_{VRH} \propto \exp\left(T^{-1/4}\right)$$

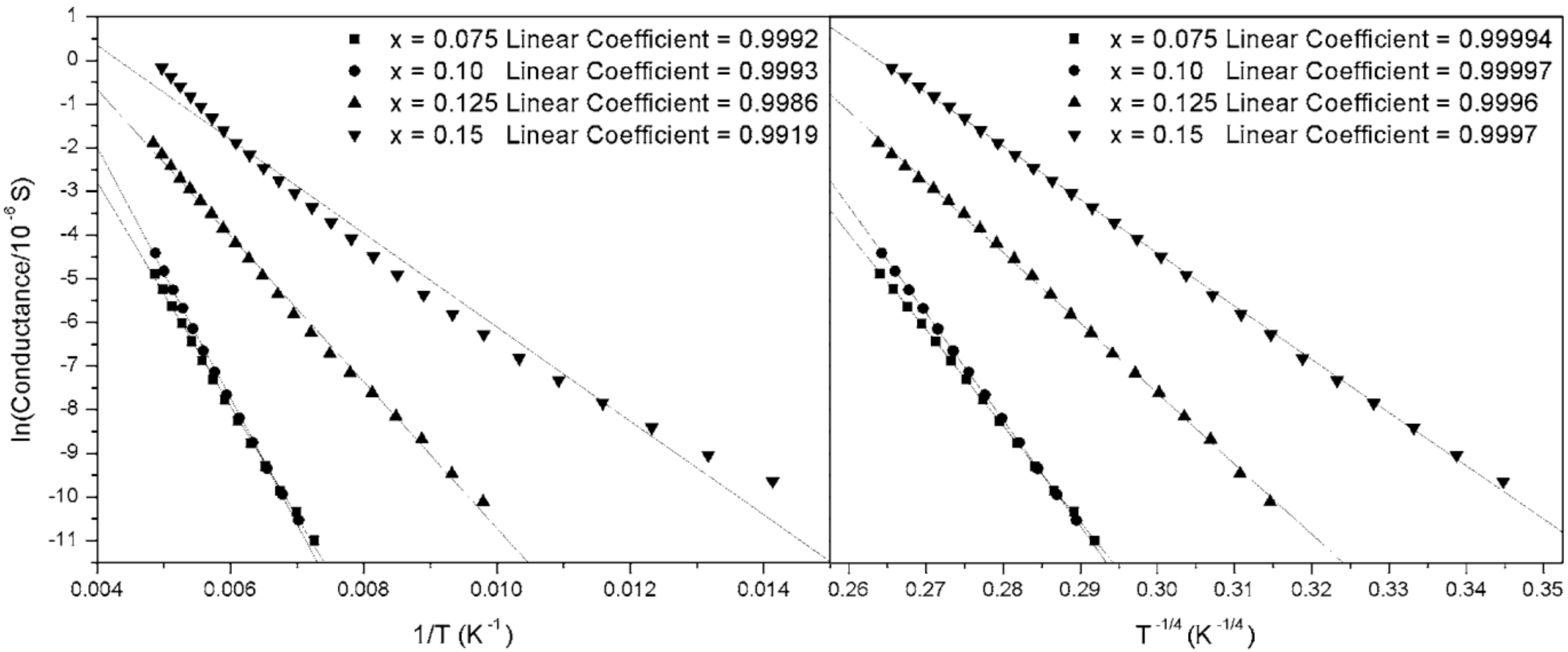


DC conductivity in amorphous semiconductors



VRH is most pronounced at low temperature

VRH in As-Se-Te-Cu glass



- ✓ Near room temperature, mixed ionic and extended state conduction
- ✓ At low temperature, variable range hopping dominates

J. Appl. Phys. **101**, 063520 (2007)

Summary

- Basics of electrical transport
  - Conductivity: scalar sum of ionic and electronic contributions

$$\sigma = \sum_i n_i Z_i e \mu_i \qquad \boldsymbol{v_i} = \mu_i \boldsymbol{E}$$

  - Einstein relation

$$D_i = \frac{\mu_i k_B T}{Z_i e} \Rightarrow \sigma = \frac{1}{k_B T} \cdot \sum_i \left(Z_i e\right)^2 n_i D_i$$

- Ionic conductivity
  - Occurs through ion hopping between different preferred “sites”
  - Thermally activated process and non-Arrhenius behavior

$$\sigma = \frac{\sigma_0}{T} \cdot \exp\left(-\frac{\Delta E_a}{k_B T}\right) \qquad \sigma_0 = \frac{fnv_0\left(Zed\right)^2}{6k_B}$$

Summary

- Electronic structure of amorphous semiconductors
  - Anderson localization: extended vs. localized states
  - Density of states
  - Mobility edge
  - Band tail and mid-gap states
- Extended state conduction
  - Free vs. drift mobility
  - Thermally activated process
- Localized state conduction
  - Fixed vs. variable range hopping
  - Mott's $T^{-1/4}$ law of VRH