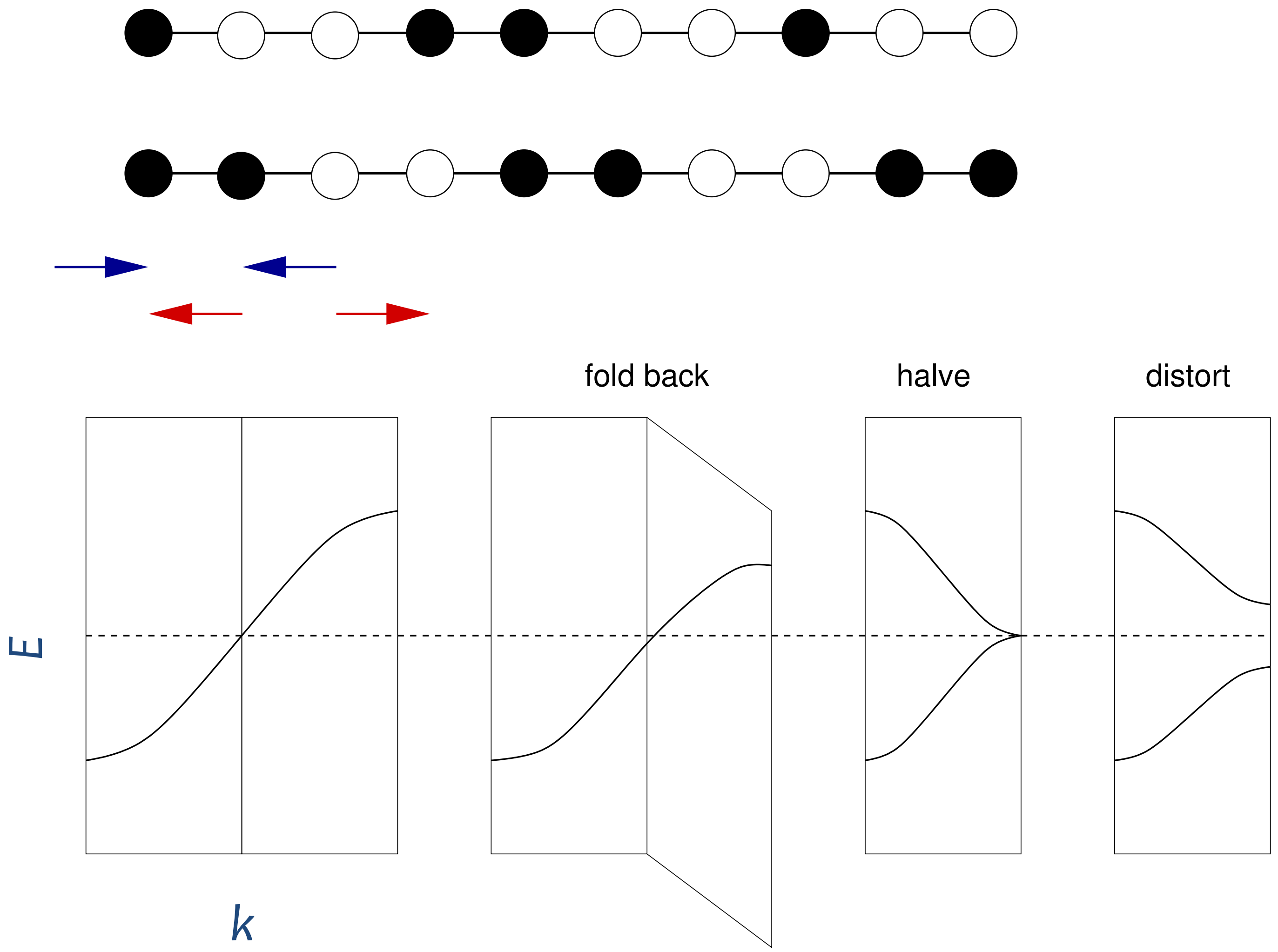
The Peierls distortion seen in 1D chains: The simplest model for a gap.

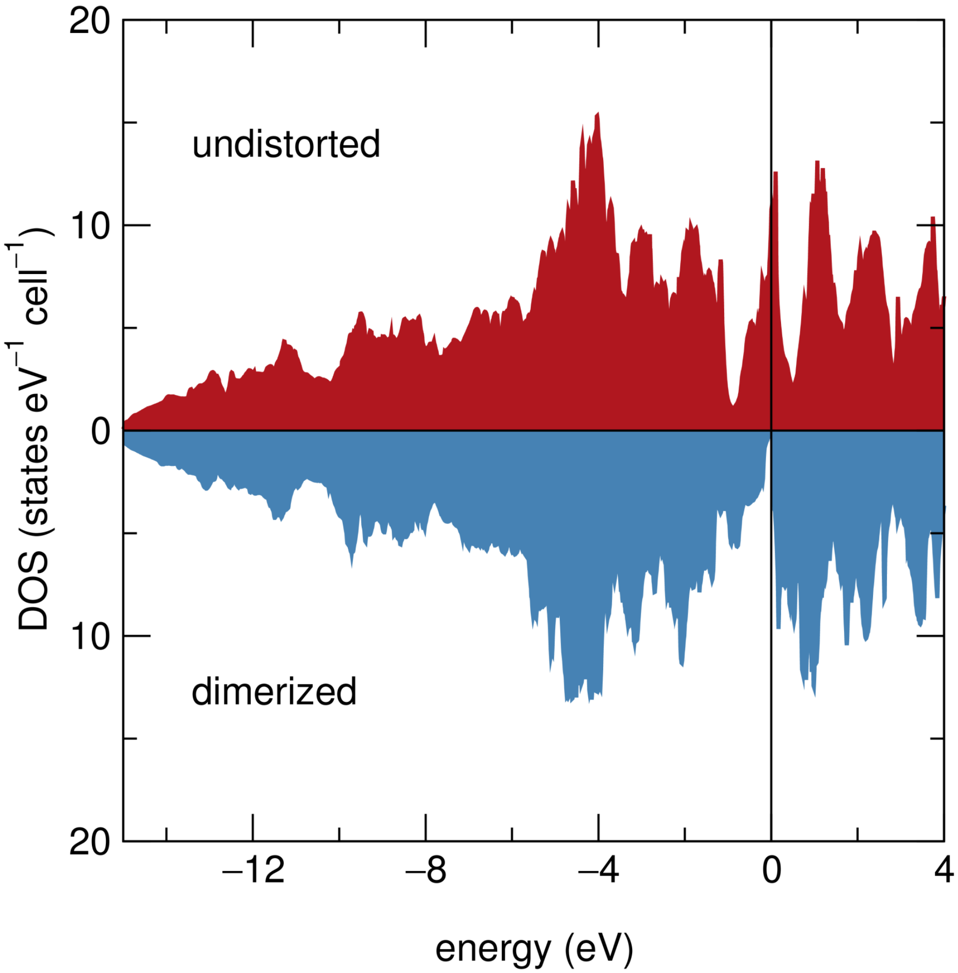


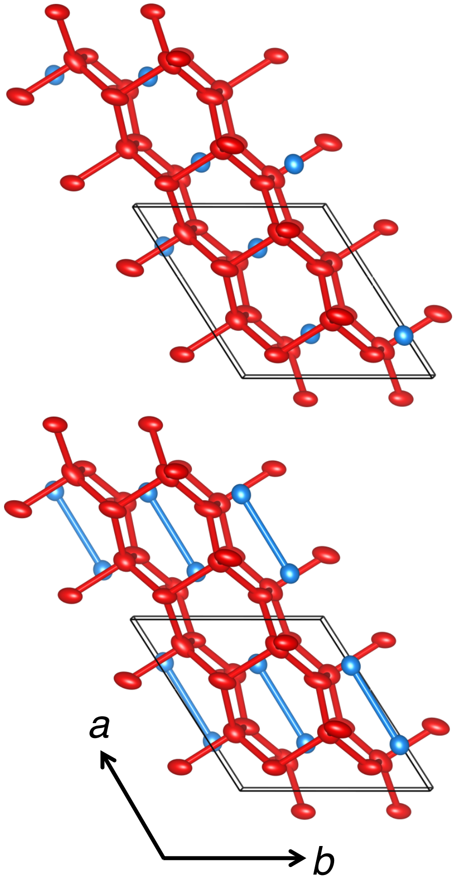
Note that we go from being valence-imprecise to being valence precise: Now two electrons *per* unit cell.

seshadri@mrl.ucsb.edu

Charge carrier concentration and the filling-driven Mott transition

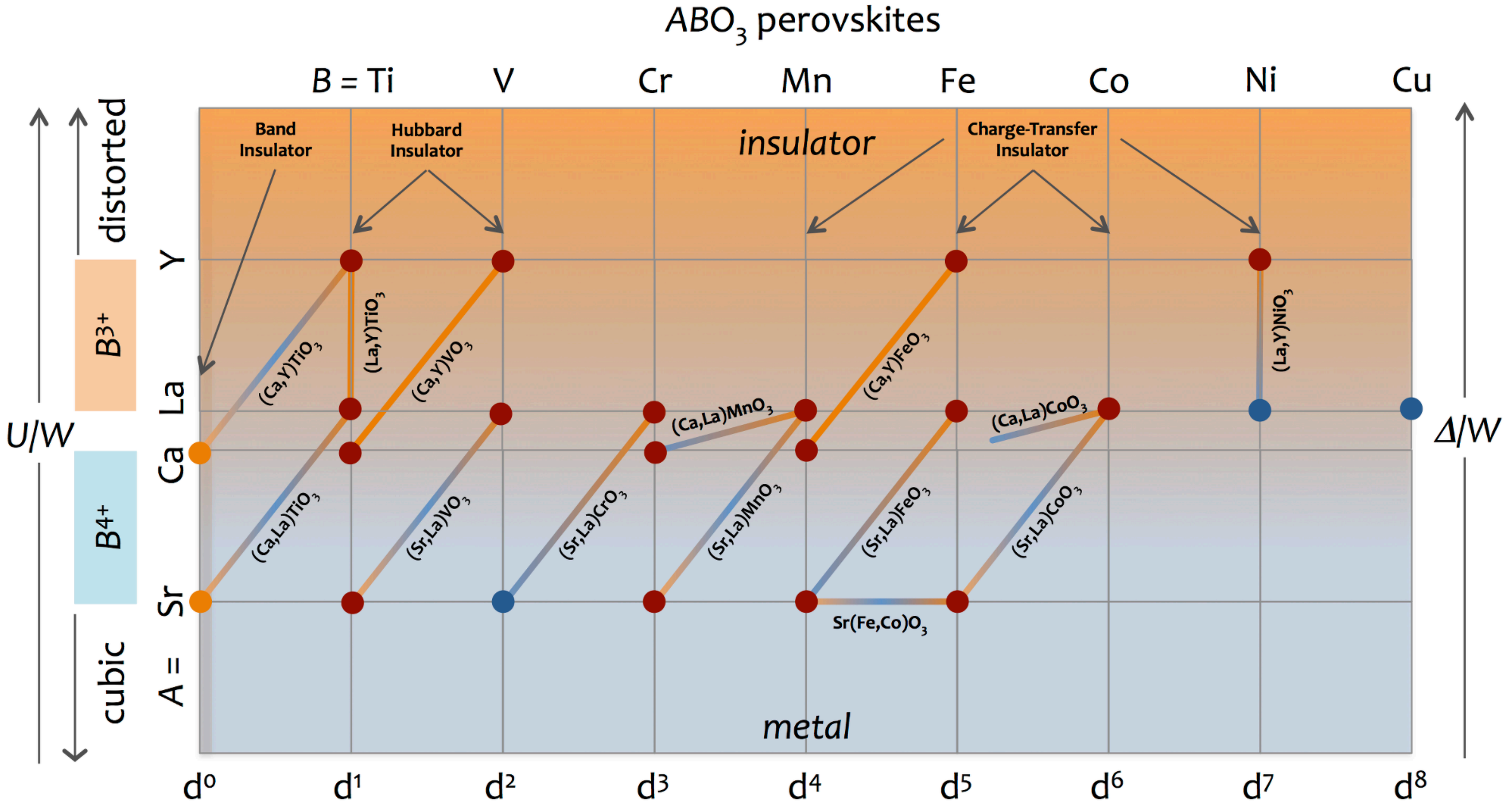
A real-world example of Peierls: MnB_4





Knappschneider *et al.*, Peierls-distorted monoclinic MnB4 with a Mn-Mn bond, *Angew. Chem. Int. Ed.* **53** (2014) 1684–1688.

Charge carrier concentration and the filling-driven Mott transition



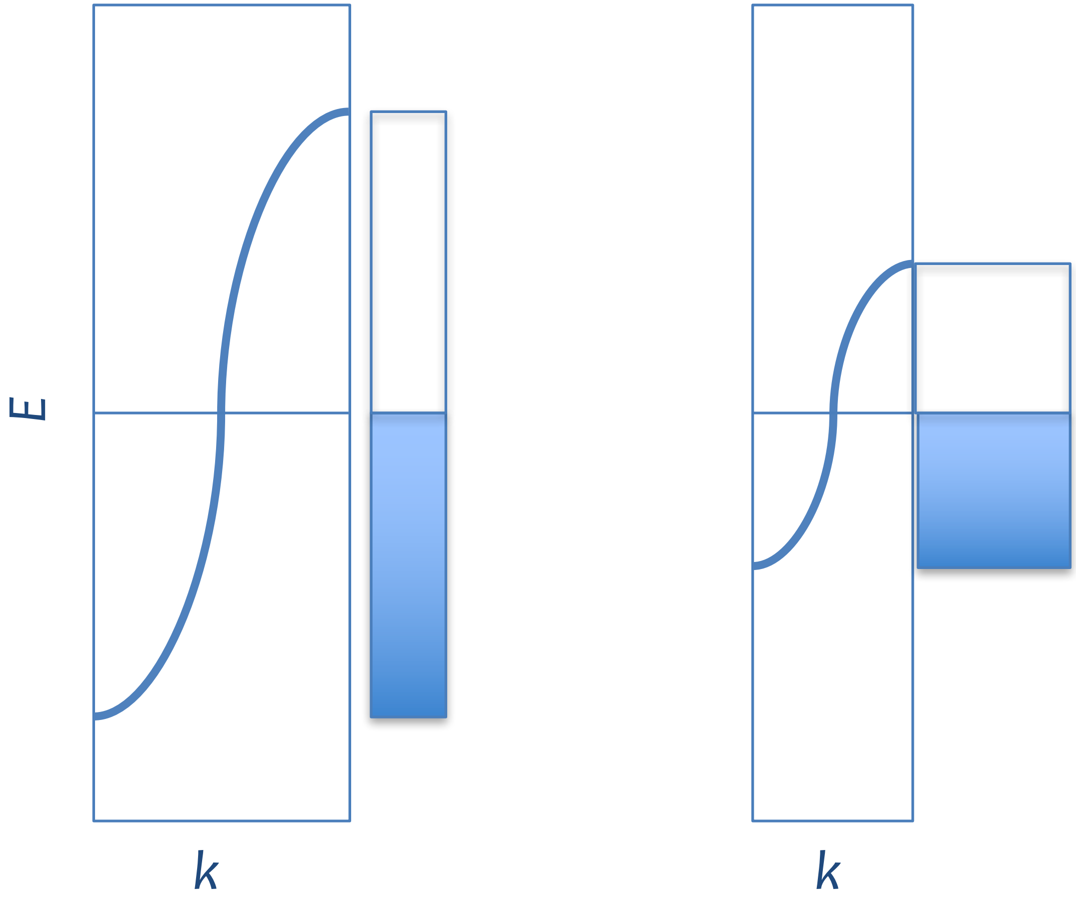
Band theory (Wilson theory) and DFT would suggest that any departure from a band insulator should give rise to metallic behavior. This is wrong. Look close to $SrTiO_3$ and $CaTiO_3$.

seshadri@mrl.ucsb.edu

Charge carrier concentration and the filling-driven Mott transition

Consider the 1D chain again, at half-filling. Assume Peierls does not take place.

The system remains metallic no matter how far apart the atoms, which cannot be right. Mott: "… this is against common experience, and, one might say, common sense"

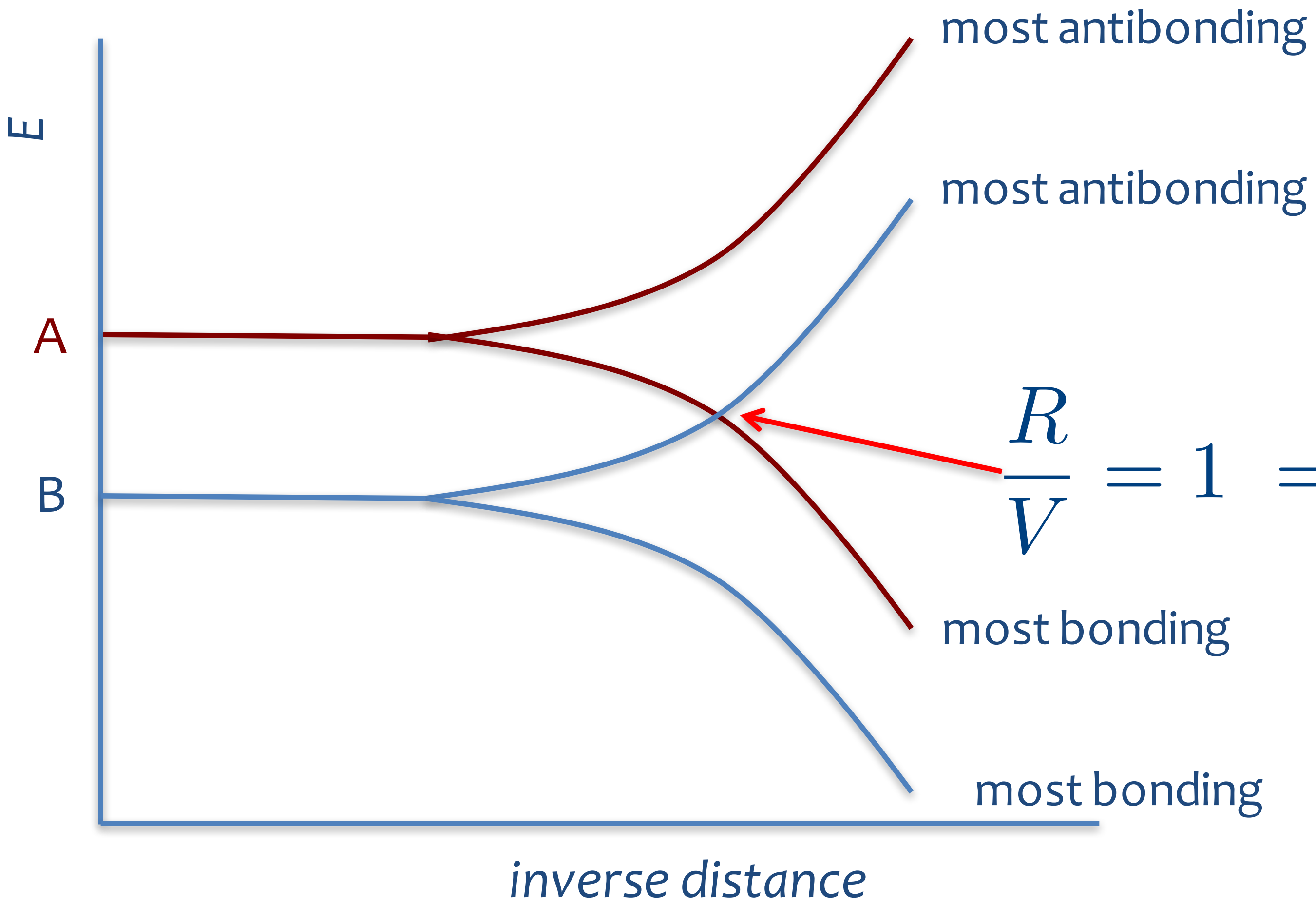


seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Charge carrier concentration and the filling-driven Mott transition

This familiar picture of atomic orbital levels interacting and spreading out as they approach, is **not** a band-structure picture. This picture captures the Herzfeld criterion discussed previously.

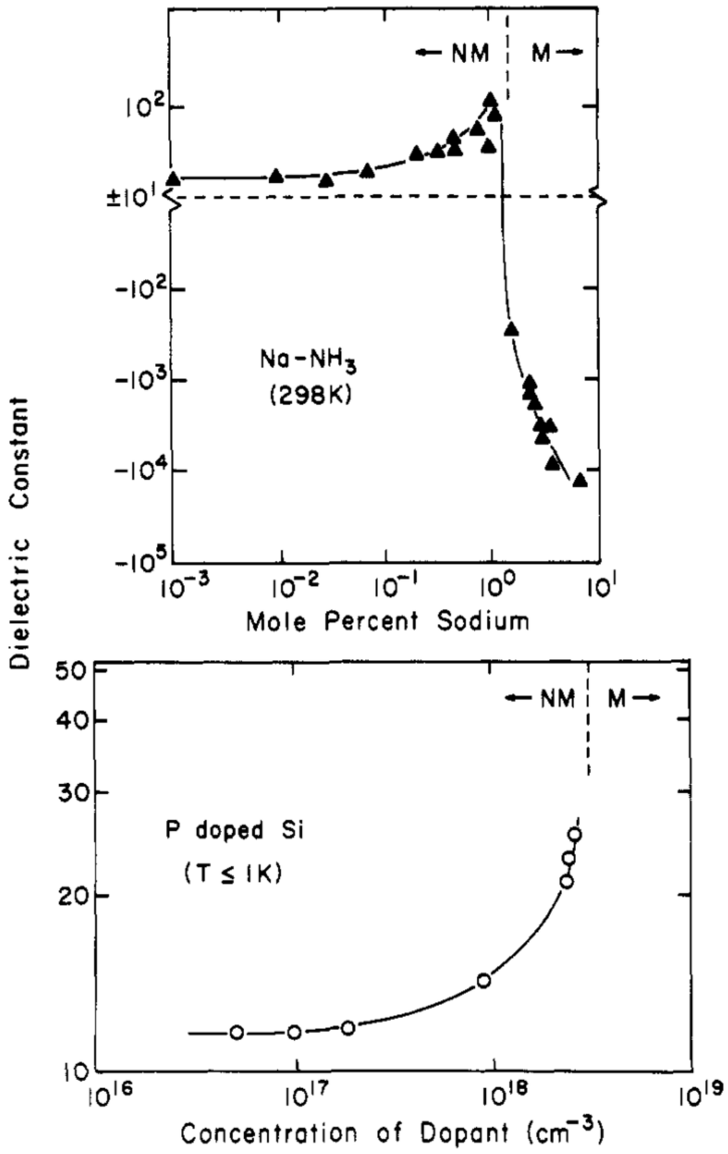


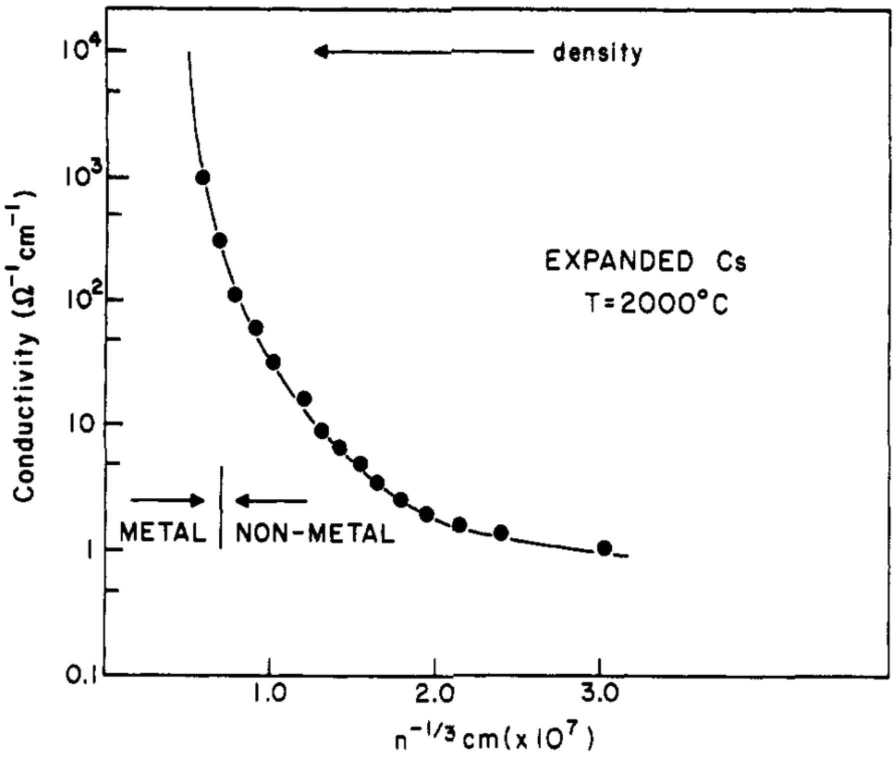
$$\frac{R}{V} = 1 \implies \epsilon_r = \infty$$

related picture with atoms and potentials

Charge carrier concentration and the filling-driven Mott transition

Examples of composition (band-filling) dependent non-metal to metal transitions:





Edwards and Sienko, *Acc. Chem. Res.*

seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Charge carrier concentration and the filling-driven Mott transition

Consider the case of expanded Cs, which for convenience, can be treated as a chain. When the atoms are infinitely separated, the energy required to remove an electron is the ionization energy IE = 3.89.

The energy required to place an electron on neutron Cs is the electron affinity EA = 0.47 eV.

The energy cost to transfer an electron is the difference, referred to as the Hubbard *U*.

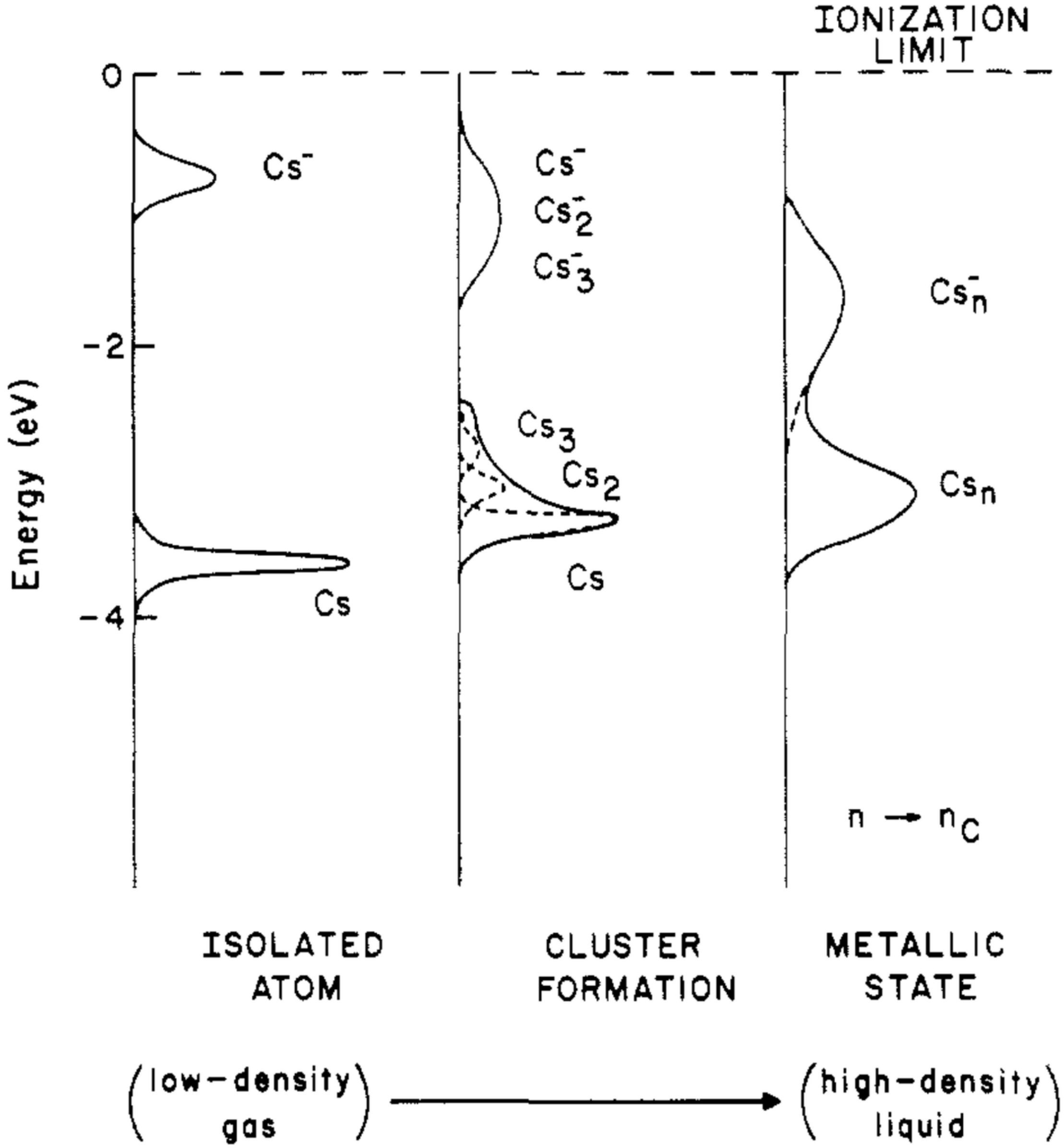
$$U = IE - EA = 3.42\ \text{eV}$$

This is the potential energy barrier required to be overcome, in order for electrons to hop.

Hopping is favored by the kinetic energy or bandwidth.

seshadri@mrl.ucsb.edu

Charge carrier concentration and the filling-driven Mott transition



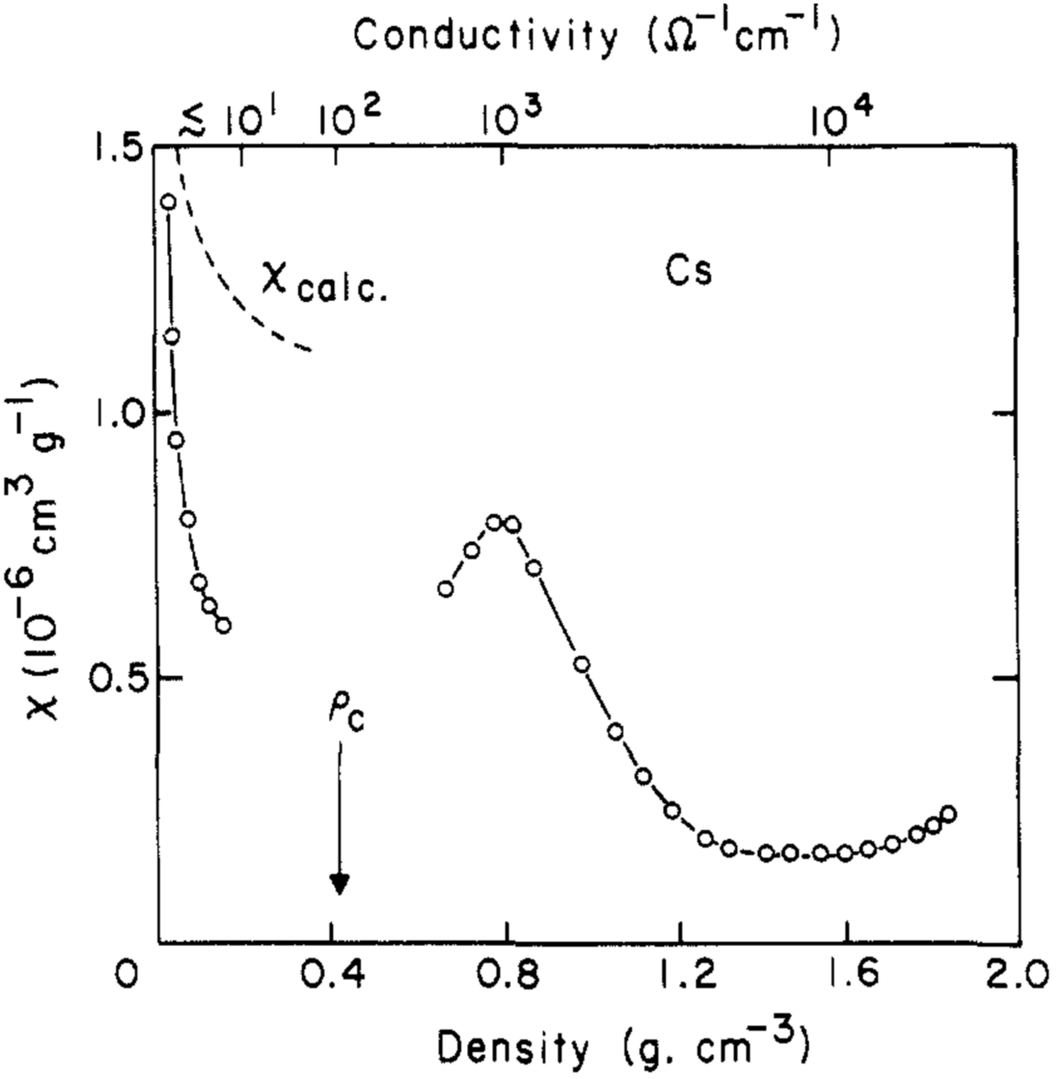
Approximate energetics for the metallization of Cs.

Edwards and Sienko, *Acc. Chem. Res.*

seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Charge carrier concentration and the filling-driven Mott transition



Consequences for magnetism: When the charge carriers are *localized*, they can carry spin.

Magnetism is therefore frequently associated with non-metal to metal transitions.

Edwards and Sienko, *Acc. Chem. Res.*

seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Charge carrier concentration and the filling-driven Mott transition

The Mott treatment of when the threshold concentration is crossed, is based on Thomas-Fermi screening:

$$\varphi = \frac{q}{r}\exp(-k_s r) \quad \text{with} \quad k_s \propto \frac{n_0^{1/3}}{a_0}$$

When the strength of the screening overcomes the Coulombic repulsion U, at a critical number density of carriers n_c and the **Mott criterion** is fulfilled:

$$n_c^{1/3} a_0 \approx 0.25$$

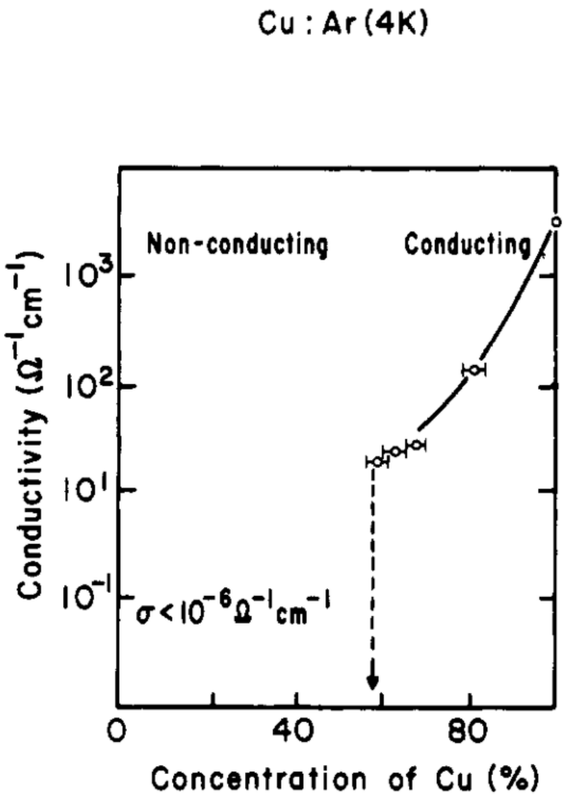
where a_0 is the hydrogenic Bohr radius.

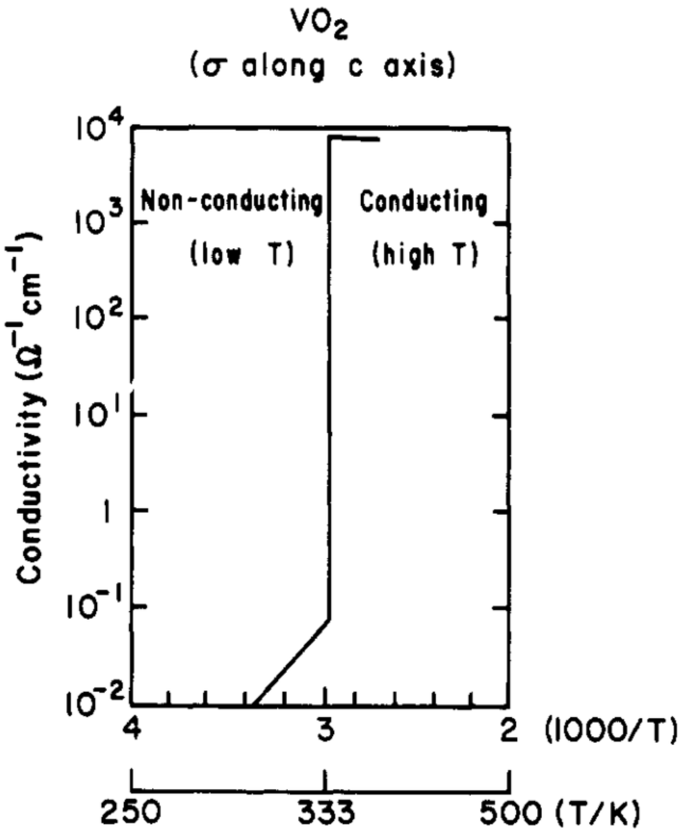
This should be a first-order phase transition, although that has not been easy to verify.

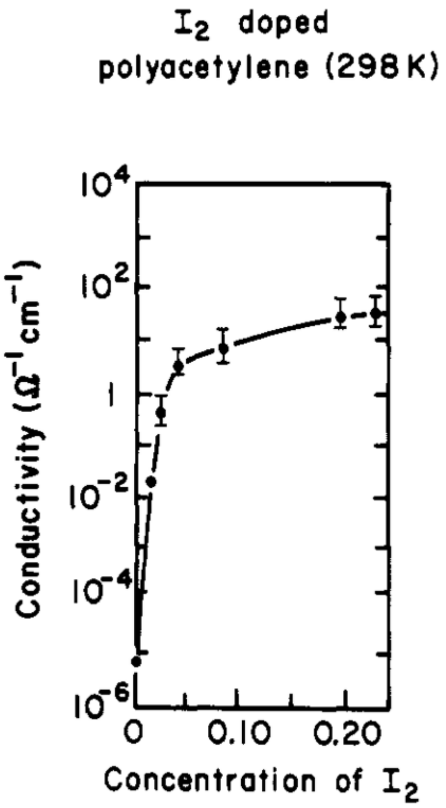
seshadri@mrl.ucsb.edu

Charge carrier concentration and the filling-driven Mott transition

Some more examples:


Cu : Ar (4K)

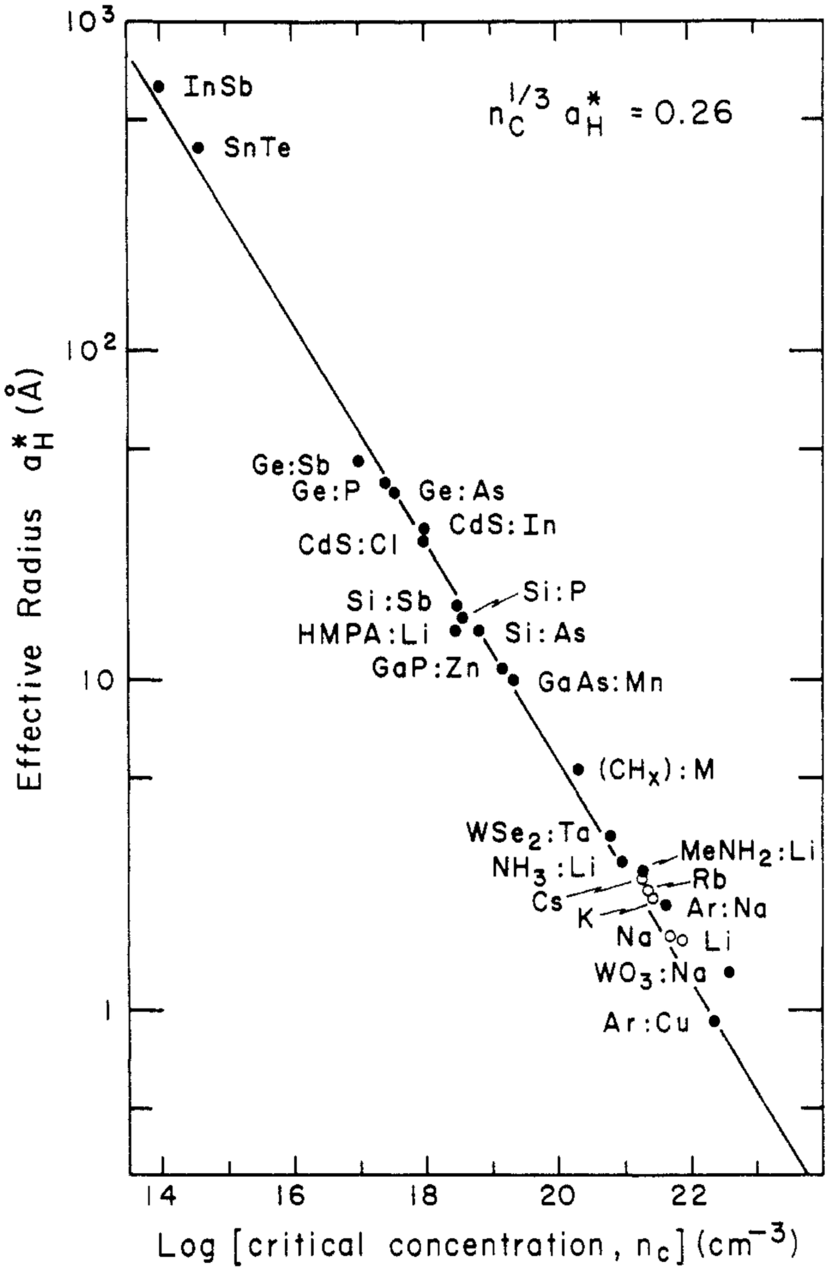

VO_2
(σ along c axis)


I_2 doped
polyacetylene (298 K)

Edwards and Sienko, *Acc. Chem. Res.*

seshadri@mrl.ucsb.edu

Charge carrier concentration and the filling-driven Mott transition



Manifestations of the Mott criterion.

Note that a large Bohr radius should correspond to a high mobility.

Remember:

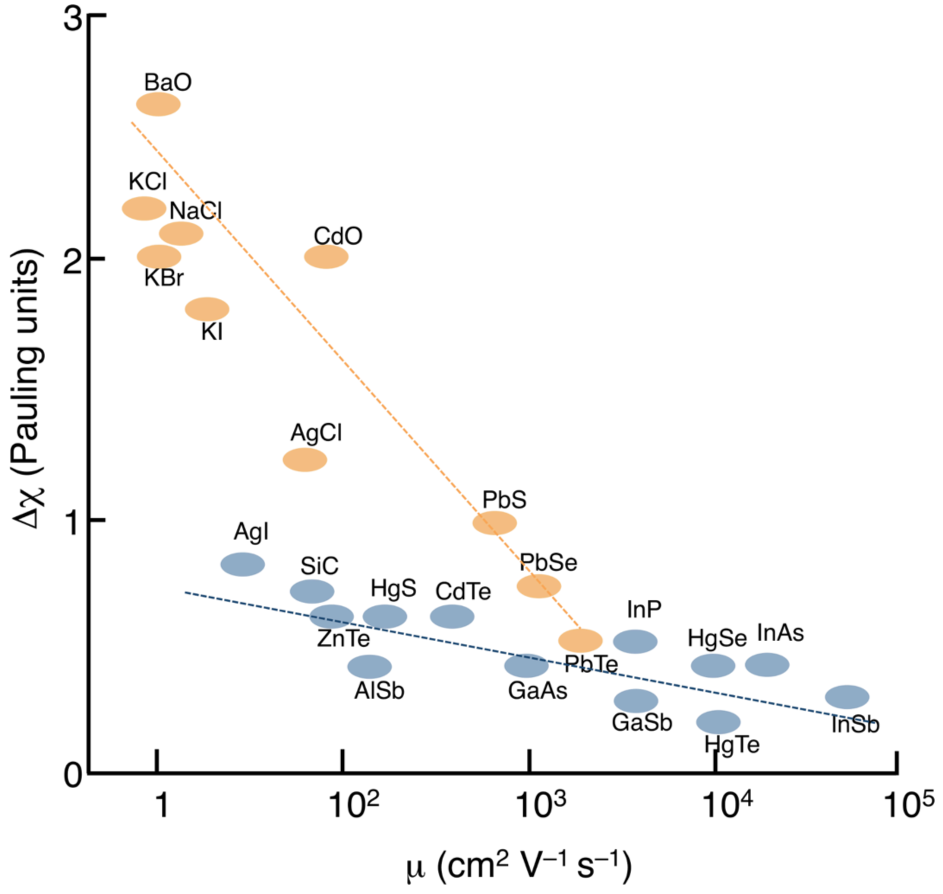
$$\sigma = ne\mu$$

Edwards and Sienko, *Acc. Chem. Res.*

seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Charge carrier concentration and the filling-driven Mott transition



But large intrinsic μ is associated with small electronegativity differences.

Adapted from R. E. Newnham, *Properties of Materials*

Edwards and Sienko, *Acc. Chem. Res.*

seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Charge carrier concentration and the filling-driven Mott transition

The Mott minimum metallic conductivity (originally argued for disordered systems):

$$n_c^{1/3} a_0 \approx 0.25$$

implies that at the transition:

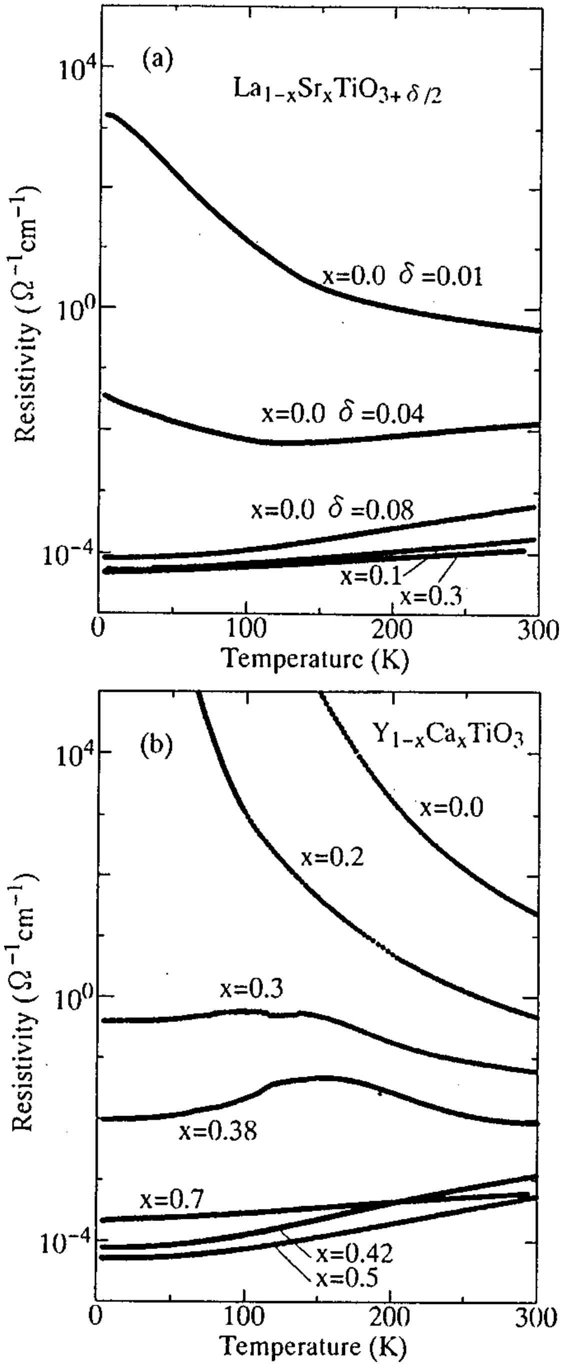
$$\sigma_{\mathrm{M}} = Ce^2/(\hbar a_0)$$

This is a fixed value of the conductivity, usually close to 100 S cm^{-1}, or correspondingly, there is a maximum metallic resistivity, close to 0.01 Ω cm.

Möbius, The metal-semiconductor transition in three-dimensional disordered systems-reanalysis of recent experiments for and against minimum metallic conductivity, *J. Phys. C: Solid State Phys.* **18** (1985) 4639–4670.

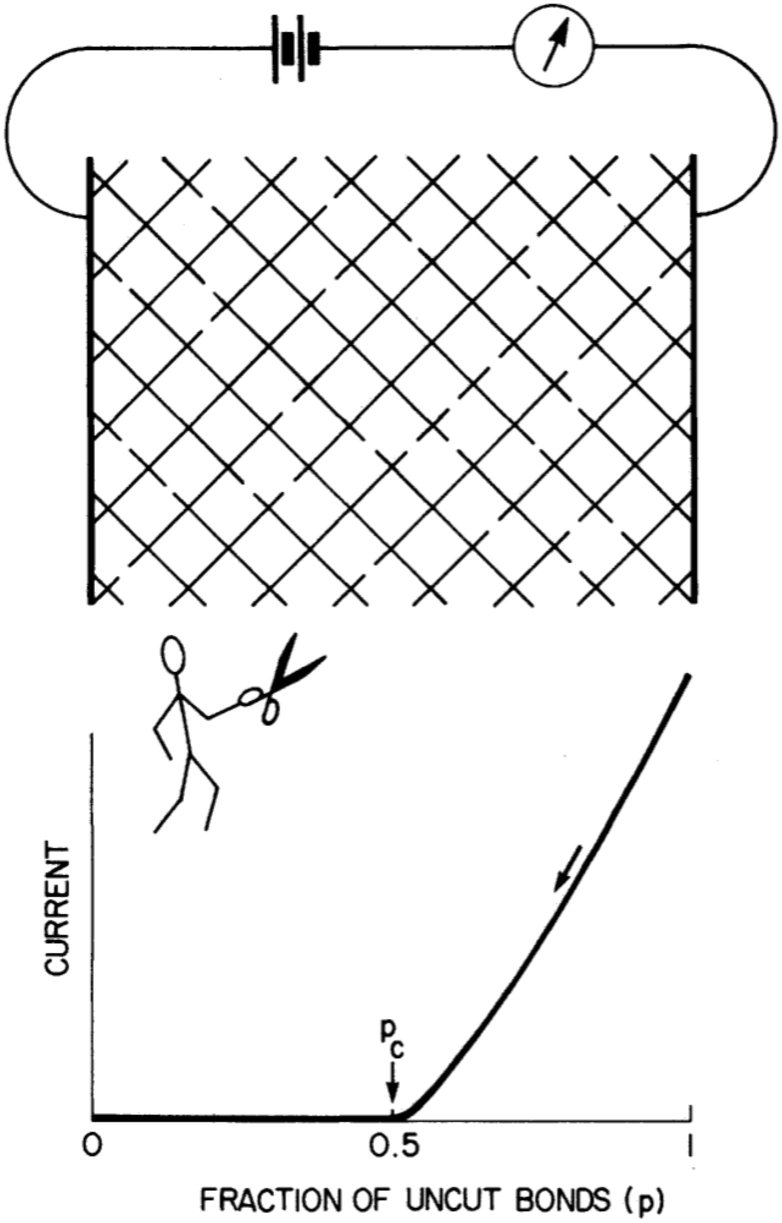
Charge carrier concentration and the filling-driven Mott transition

Examples:



seshadri@mrl.ucsb.edu

Percolation *etc.* [Closely following the text by R. Zallen]



This figure, from page 137 of Zallen, describes the problem in a 2D square mesh.

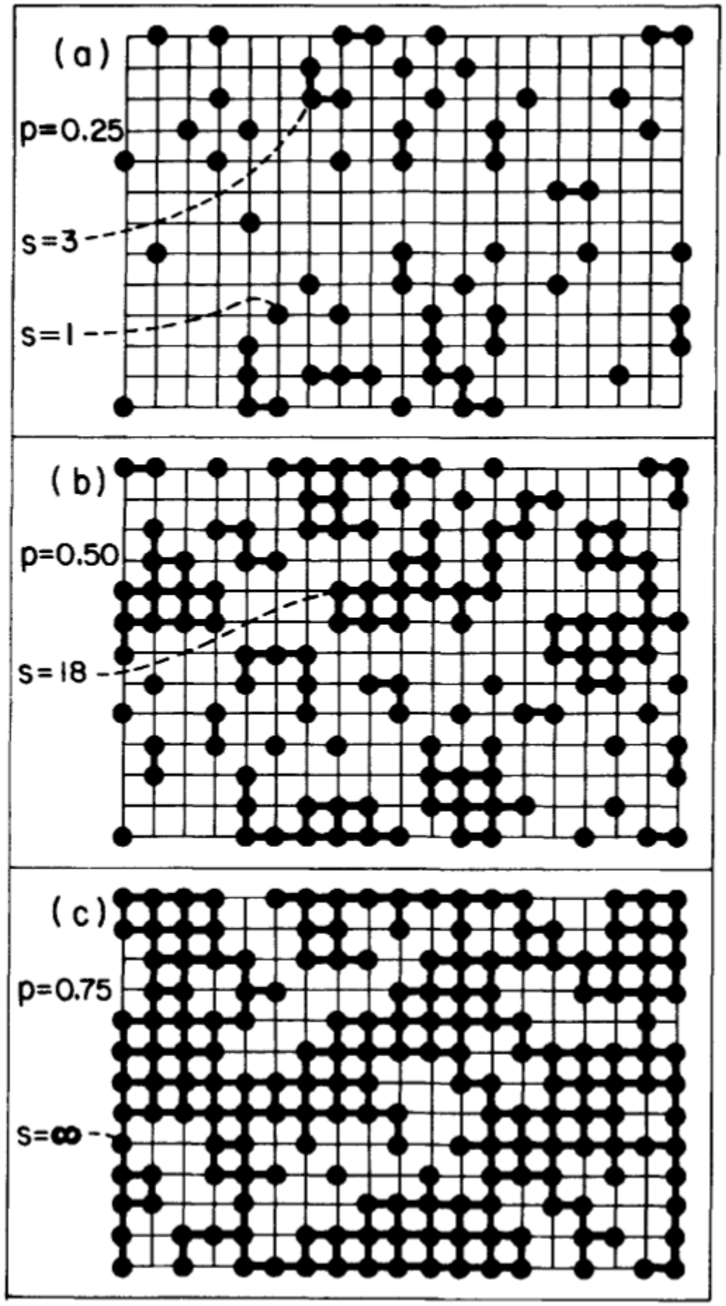
At some *precise* critical number of random snips, current flow stops.

This is an example of *bond percolation* as opposed to *site percolation*.

R. Zallen, *The Physics of Amorphous Solids*, Wiley-VCH, 2004.

seshadri@mrl.ucsb.edu

Percolation *etc.* [Closely following the text by R. Zallen]



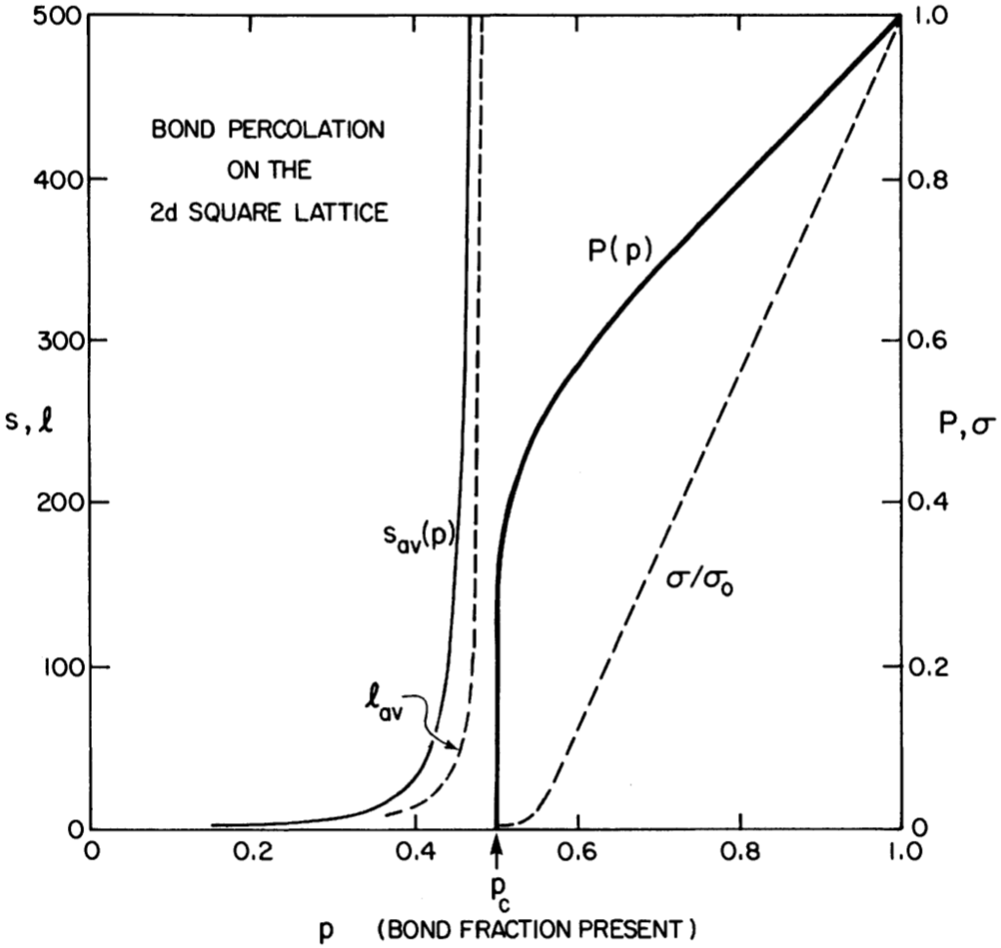
This figure is from page 143 of Zallen.

This shows site percolation on a square lattice, with different site filling fractions *p*. For *p* = 0.75 in (c), the cluster formed by connecting neighboring atoms spans the whole lattice, and a *percolation path* is created.

R. Zallen, *The Physics of Amorphous Solids*, Wiley-VCH, 2004.

seshadri@mrl.ucsb.edu

Percolation *etc.* [Closely following the text by R. Zallen]



This figure is from page 146 of Zallen.

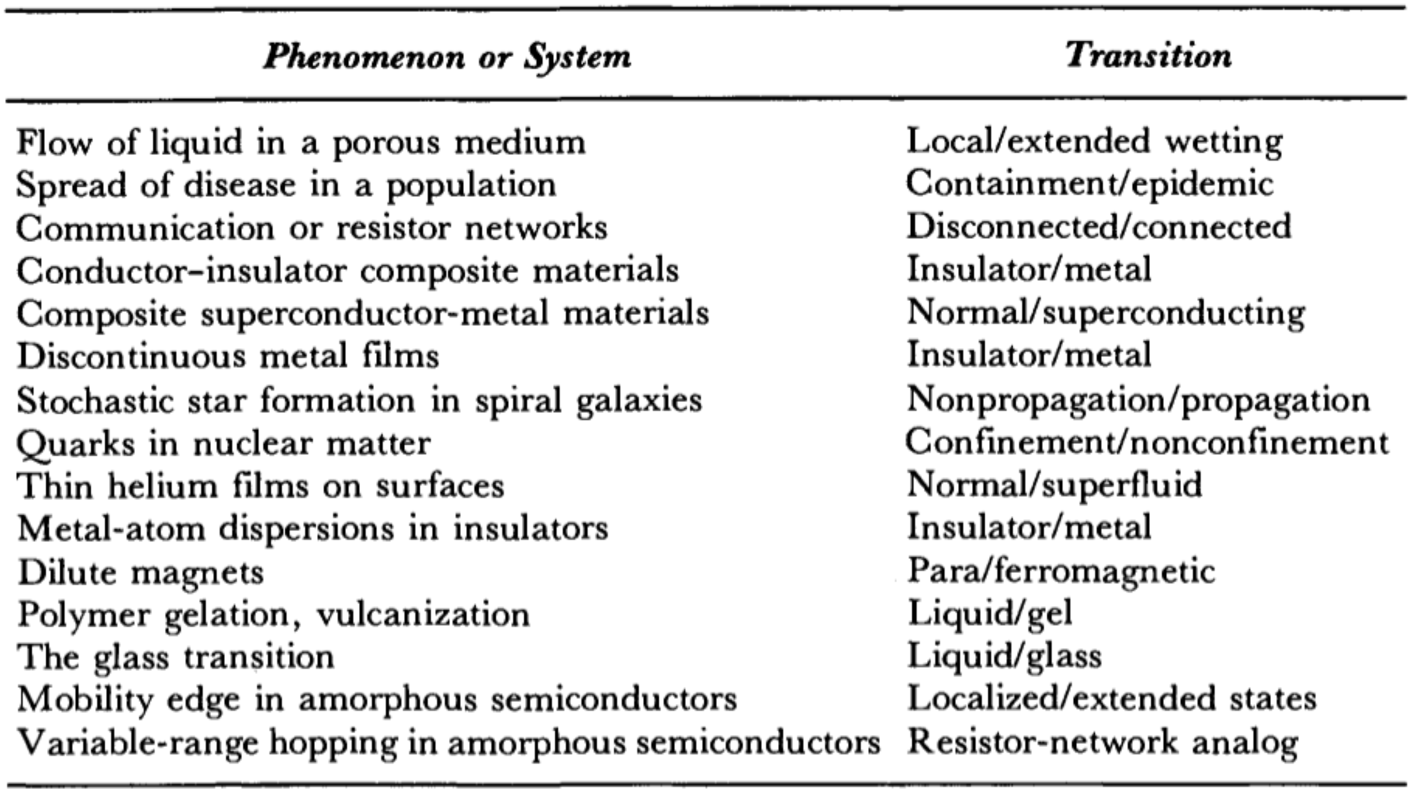
Computer simulations on a large square lattice; $s_{av}(p)$ is the average cluster size, and $P(p)$ is the percolation probability.

R. Zallen, *The Physics of Amorphous Solids*, Wiley-VCH, 2004.

seshadri@mrl.ucsb.edu

Percolation *etc.* [Closely following the text by R. Zallen]

Where is percolation applicable?



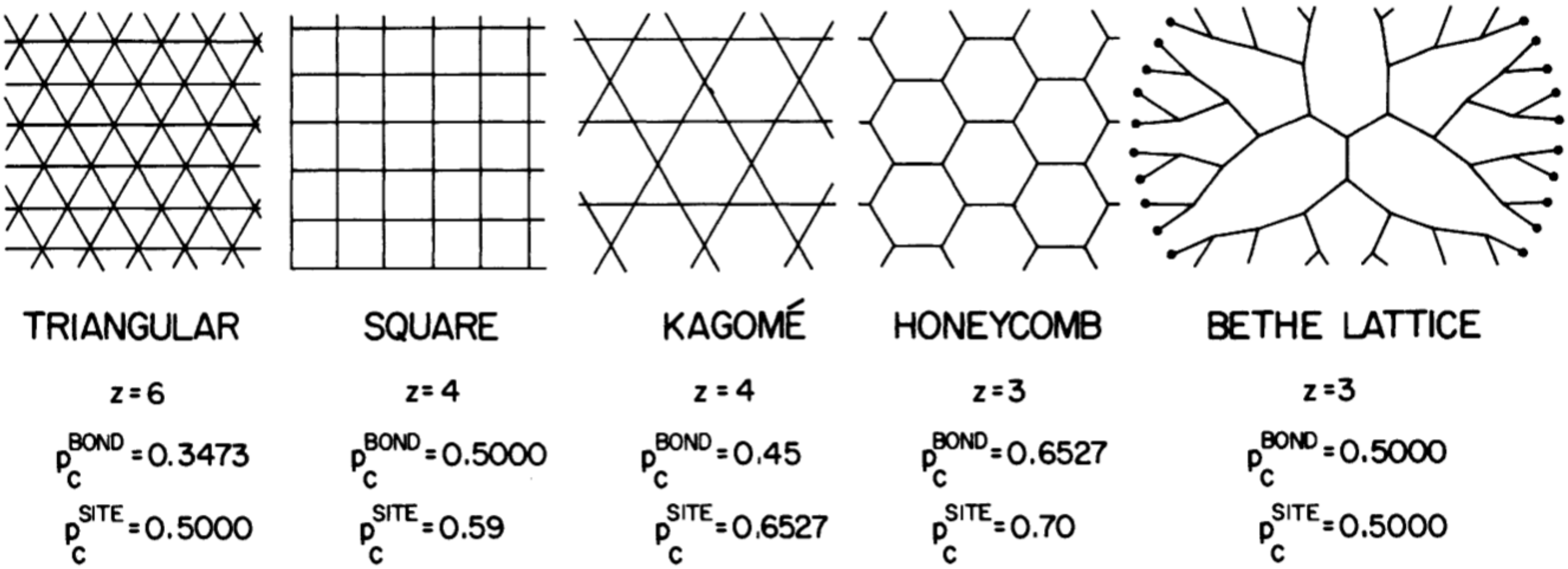
Phenomenon or System	*Transition*
Flow of liquid in a porous medium	Local/extended wetting
Spread of disease in a population	Containment/epidemic
Communication or resistor networks	Disconnected/connected
Conductor–insulator composite materials	Insulator/metal
Composite superconductor-metal materials	Normal/superconducting
Discontinuous metal films	Insulator/metal
Stochastic star formation in spiral galaxies	Nonpropagation/propagation
Quarks in nuclear matter	Confinement/nonconfinement
Thin helium films on surfaces	Normal/superfluid
Metal-atom dispersions in insulators	Insulator/metal
Dilute magnets	Para/ferromagnetic
Polymer gelation, vulcanization	Liquid/gel
The glass transition	Liquid/glass
Mobility edge in amorphous semiconductors	Localized/extended states
Variable-range hopping in amorphous semiconductors	Resistor-network analog

This table is from page 148 of Zallen.

R. Zallen, *The Physics of Amorphous Solids*, Wiley-VCH, 2004.

Percolation *etc.* [Closely following the text by R. Zallen]

Different lattices:



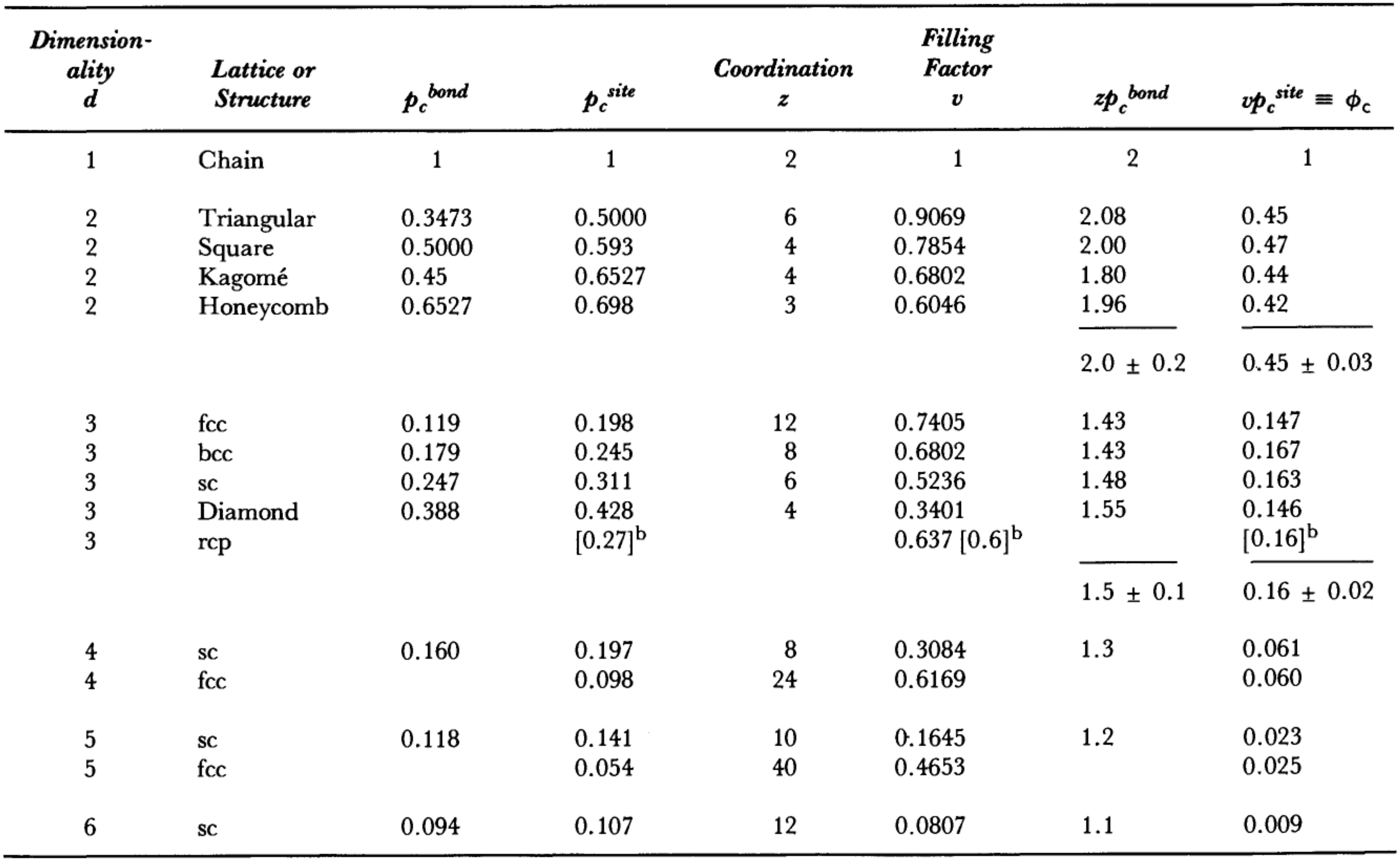
TRIANGULAR	SQUARE	KAGOMÉ	HONEYCOMB	BETHE LATTICE
$z=6$	$z=4$	$z=4$	$z=3$	$z=3$
$p_c^{BOND}=0.3473$	$p_c^{BOND}=0.5000$	$p_c^{BOND}=0.45$	$p_c^{BOND}=0.6527$	$p_c^{BOND}=0.5000$
$p_c^{SITE}=0.5000$	$p_c^{SITE}=0.59$	$p_c^{SITE}=0.6527$	$p_c^{SITE}=0.70$	$p_c^{SITE}=0.5000$

This table is from page 168 of Zallen.

R. Zallen, *The Physics of Amorphous Solids*,
Wiley-VCH, 2004.

seshadri@mrl.ucsb.edu

Percolation *etc.* [Closely following the text by R. Zallen]

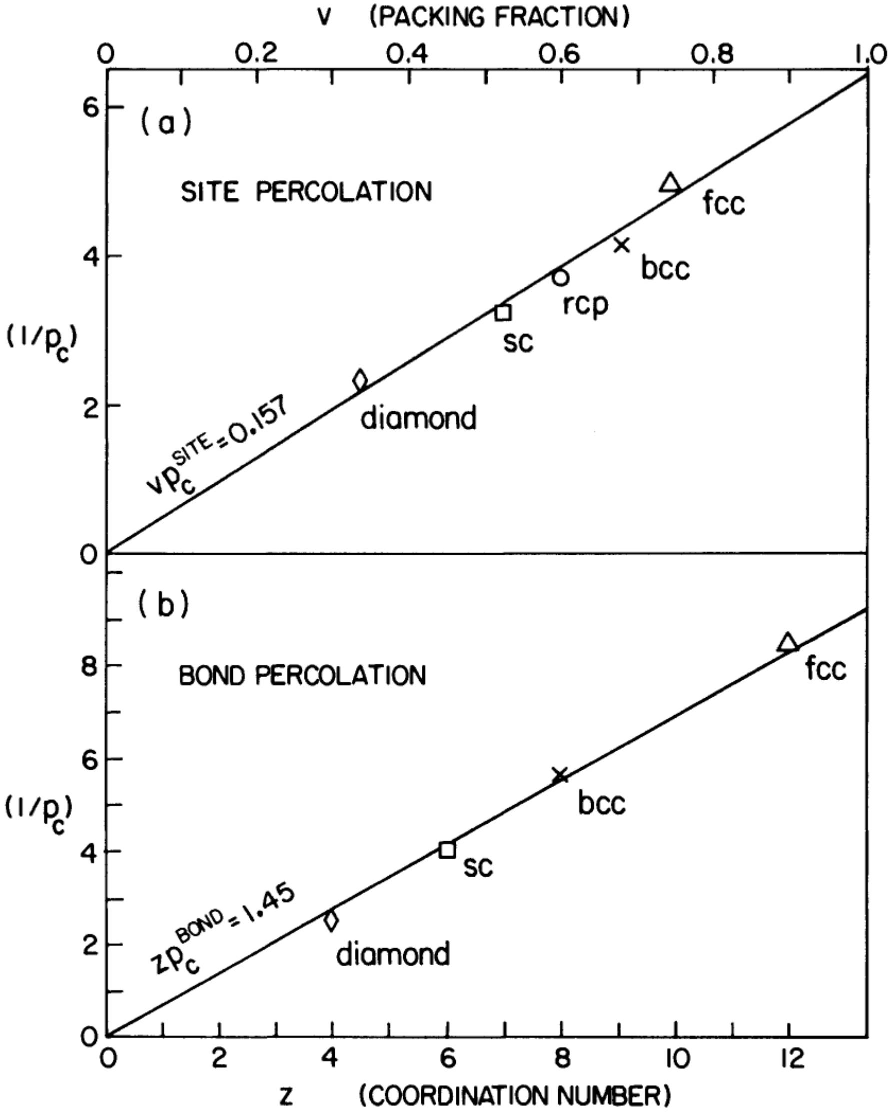


Dimensionality d	Lattice or Structure	p_c^{bond}	p_c^{site}	Coordination z	Filling Factor v	zp_c^{bond}	$vp_c^{site} \equiv \phi_c$
1	Chain	1	1	2	1	2	1
2	Triangular	0.3473	0.5000	6	0.9069	2.08	0.45
2	Square	0.5000	0.593	4	0.7854	2.00	0.47
2	Kagomé	0.45	0.6527	4	0.6802	1.80	0.44
2	Honeycomb	0.6527	0.698	3	0.6046	1.96	0.42
						2.0 ± 0.2	0.45 ± 0.03
3	fcc	0.119	0.198	12	0.7405	1.43	0.147
3	bcc	0.179	0.245	8	0.6802	1.43	0.167
3	sc	0.247	0.311	6	0.5236	1.48	0.163
3	Diamond	0.388	0.428	4	0.3401	1.55	0.146
3	rcp		[0.27][b]		0.637 [0.6][b]		[0.16][b]
						1.5 ± 0.1	0.16 ± 0.02
4	sc	0.160	0.197	8	0.3084	1.3	0.061
4	fcc		0.098	24	0.6169		0.060
5	sc	0.118	0.141	10	0.1645	1.2	0.023
5	fcc		0.054	40	0.4653		0.025
6	sc	0.094	0.107	12	0.0807	1.1	0.009

R. Zallen, *The Physics of Amorphous Solids*, Wiley-VCH, 2004.

Page 170 of Zallen.

Percolation *etc*. [Closely following the text by R. Zallen]



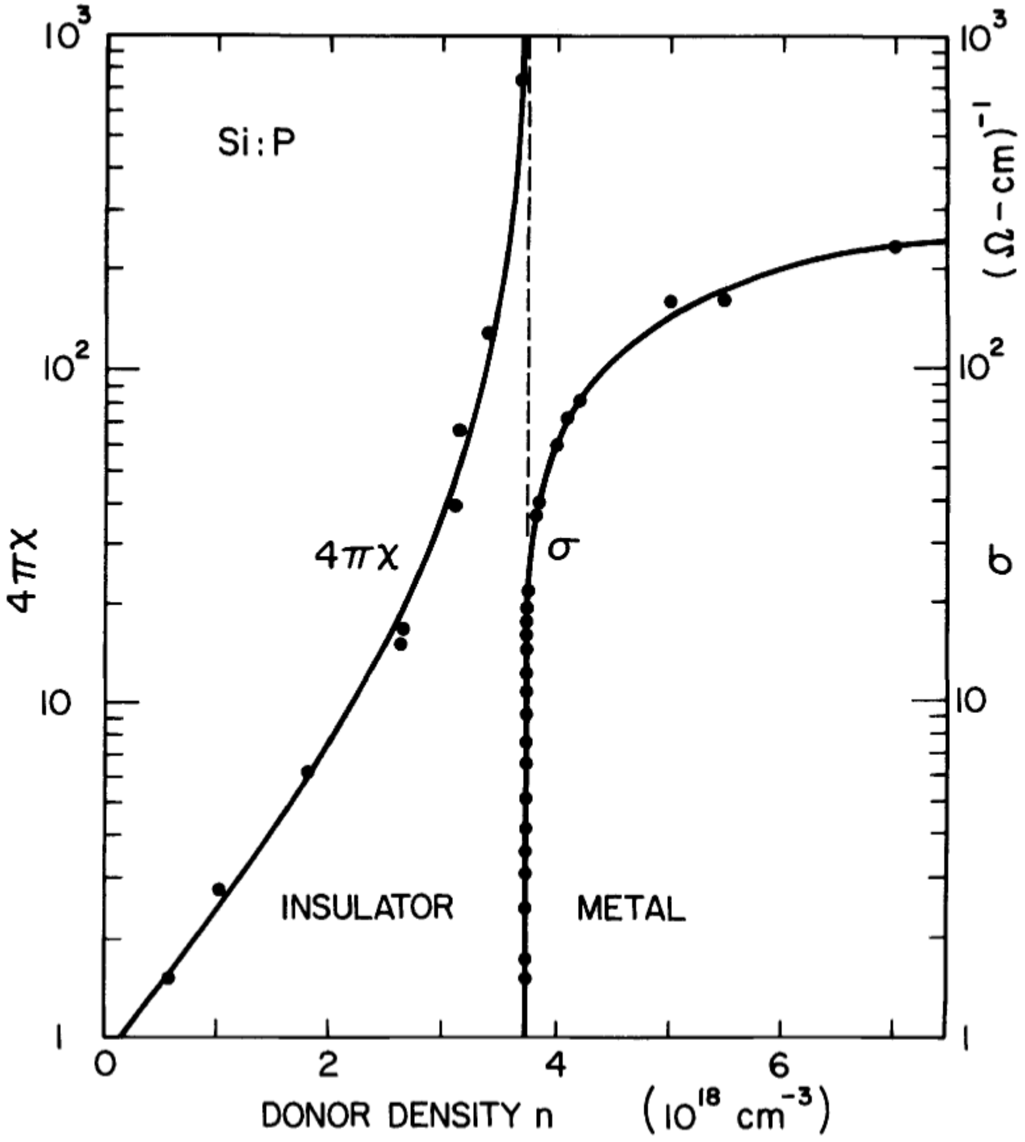
This figure is from page 187 of Zallen.

There is a simple scaling in 3D, between both the site and bond percolation thresholds, with the packing fraction and coordination number, and the percolation thresholds.

R. Zallen, *The Physics of Amorphous Solids*, Wiley-VCH, 2004.

seshadri@mrl.ucsb.edu

Percolation *etc.* [Closely following the text by R. Zallen]



This figure is from page 243 of Zallen.

The non-metal to metal transition on Si:P.

$4\pi\chi$ is the dielectric sucseptibility.

Note the similarity with percolation (the third slide in this set of slides).

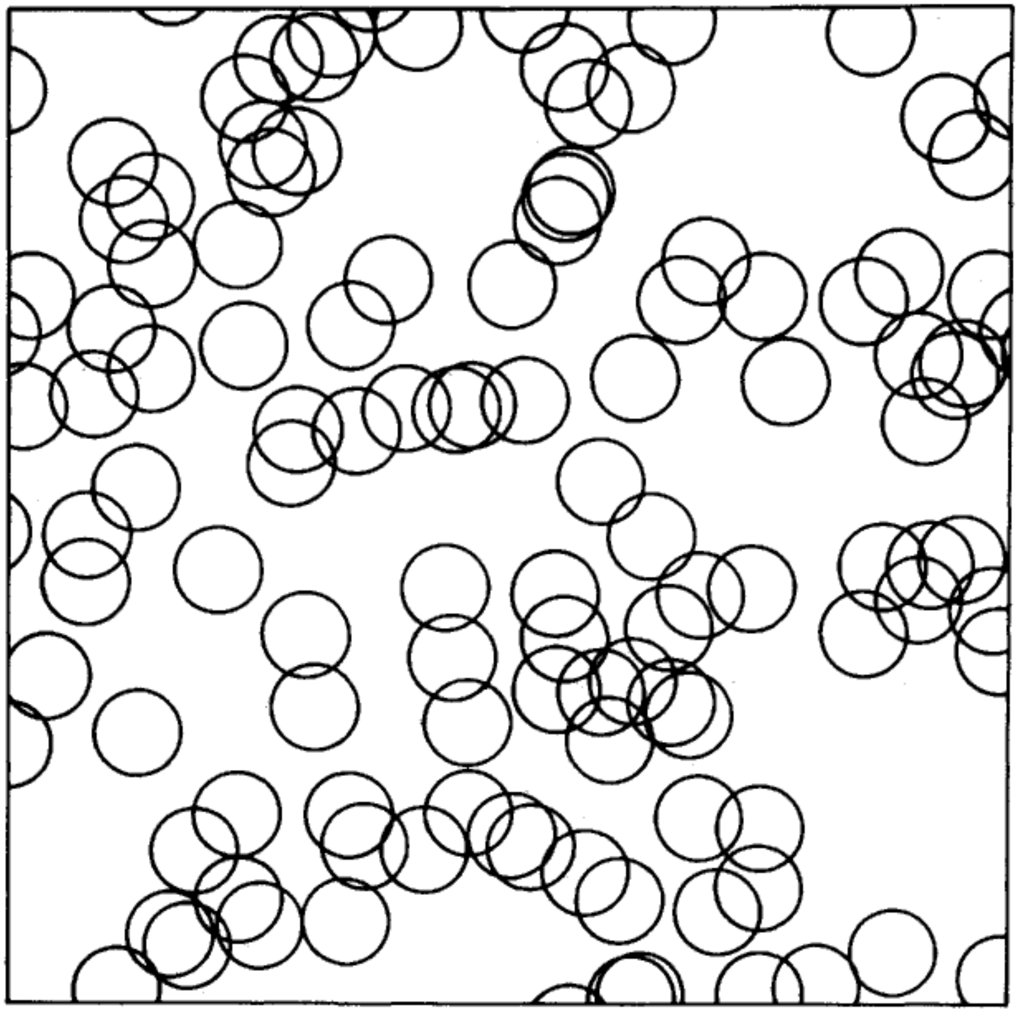
Measurements by Rosenbaum and others at 10 mK.

R. Zallen, *The Physics of Amorphous Solids*, Wiley-VCH, 2004.

seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Percolation *etc.* [Closely following the text by R. Zallen]



This figure is from page 244 of Zallen.

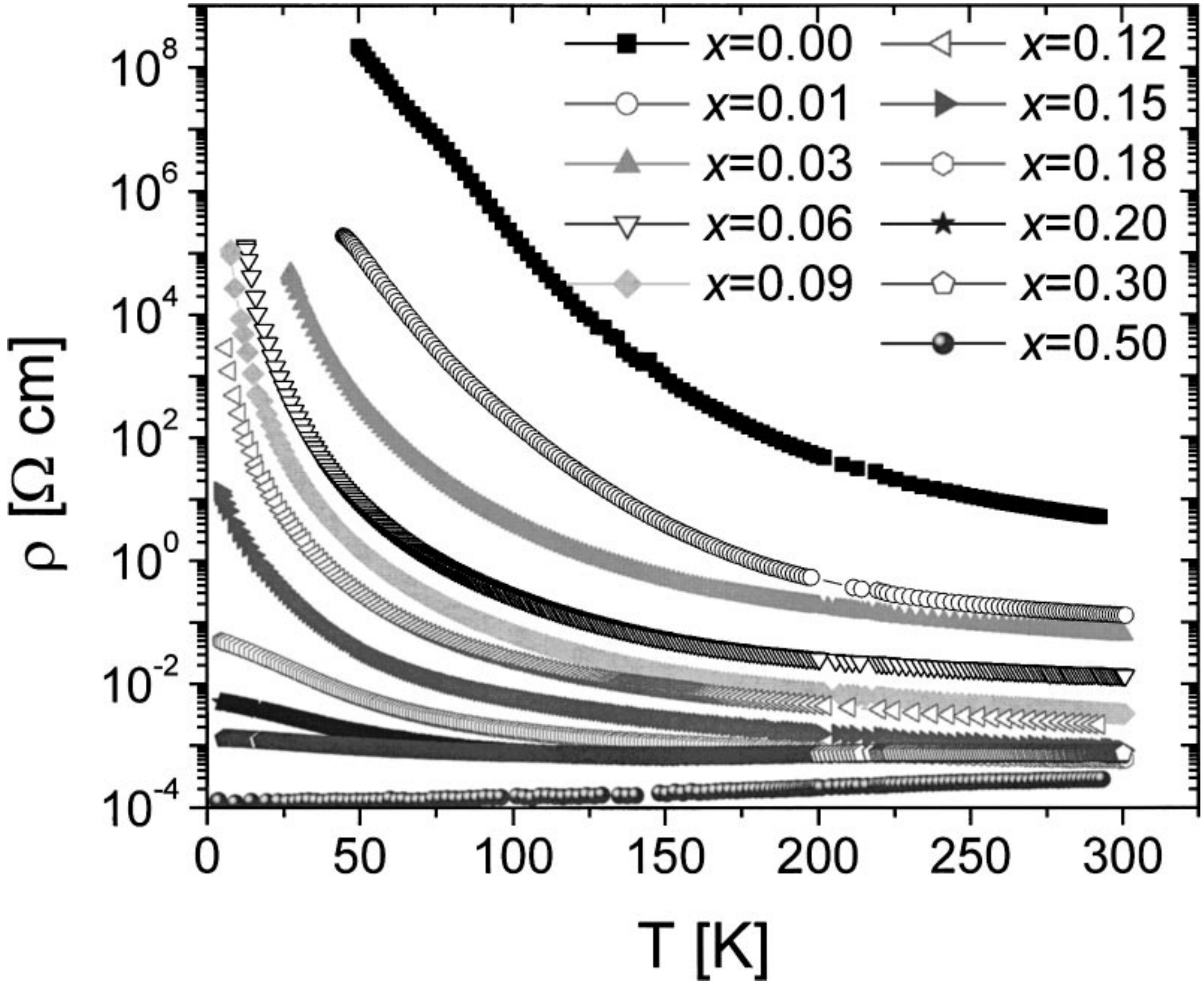
Showing the percolation of hydrogenic wave-functions around the phosphorus donor atoms (much larger than the interatomic spacing).

Since P substitution is random, this is a problem of percolation in a random close packing.

R. Zallen, *The Physics of Amorphous Solids*, Wiley-VCH, 2004.

Percolation ?

$La_{1-x}Sr_xCoO_3$



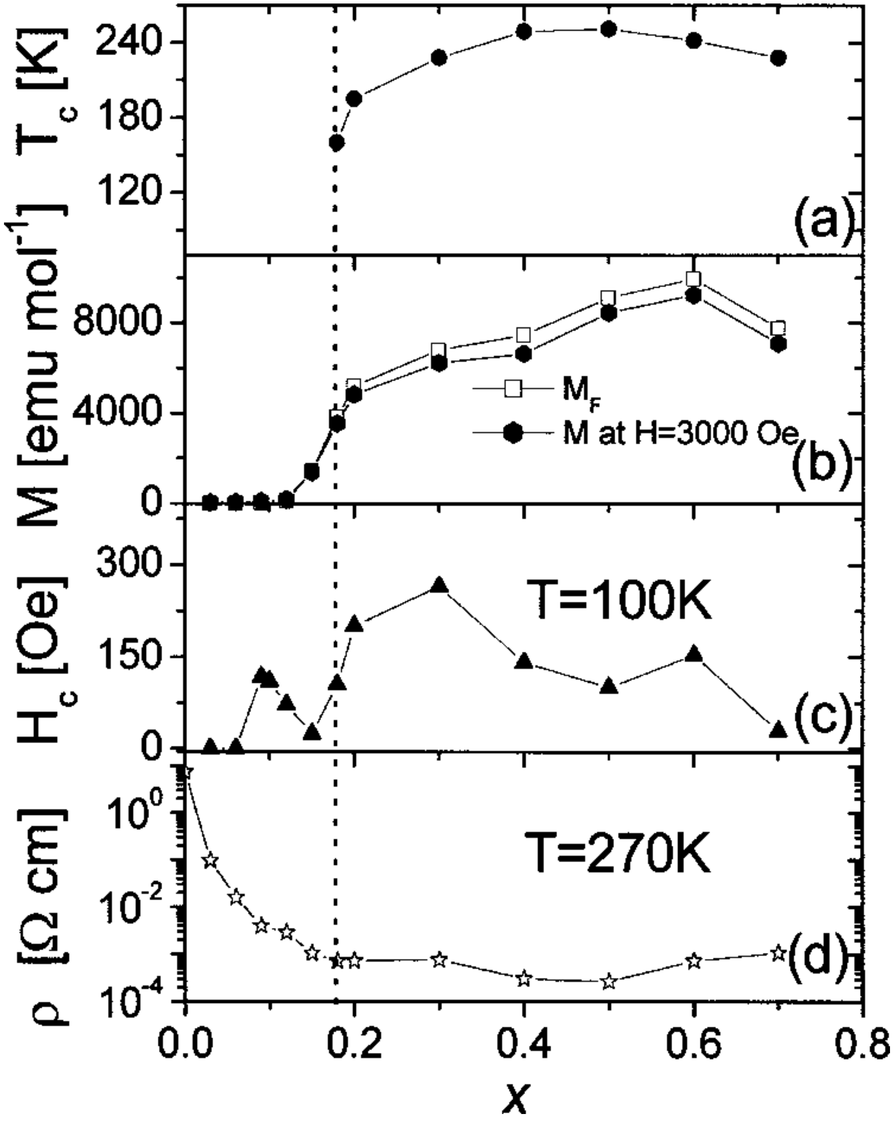
Wu, Leighton, *Phys. Rev. B* **67** (2003) 174408.

seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Percolation ?

$La_{1-x}Sr_xCoO_3$

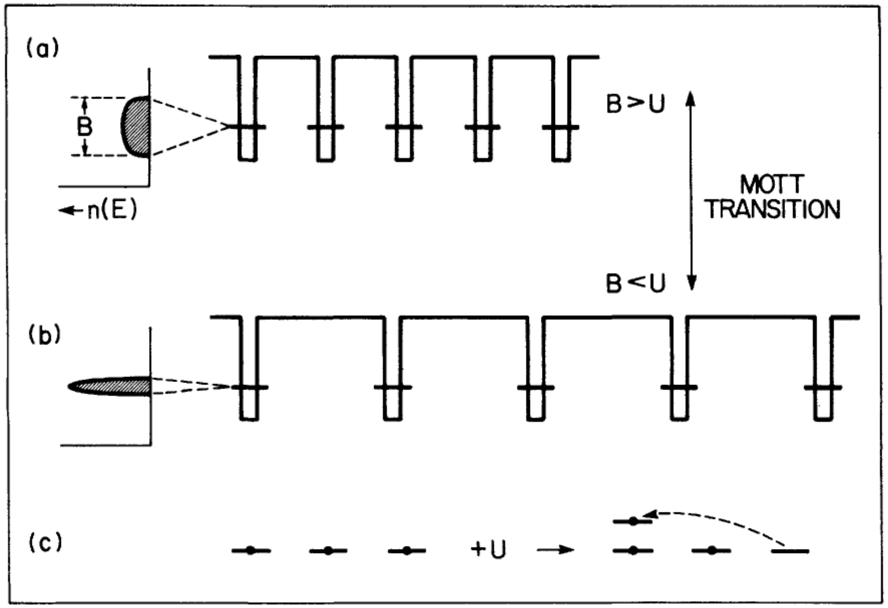


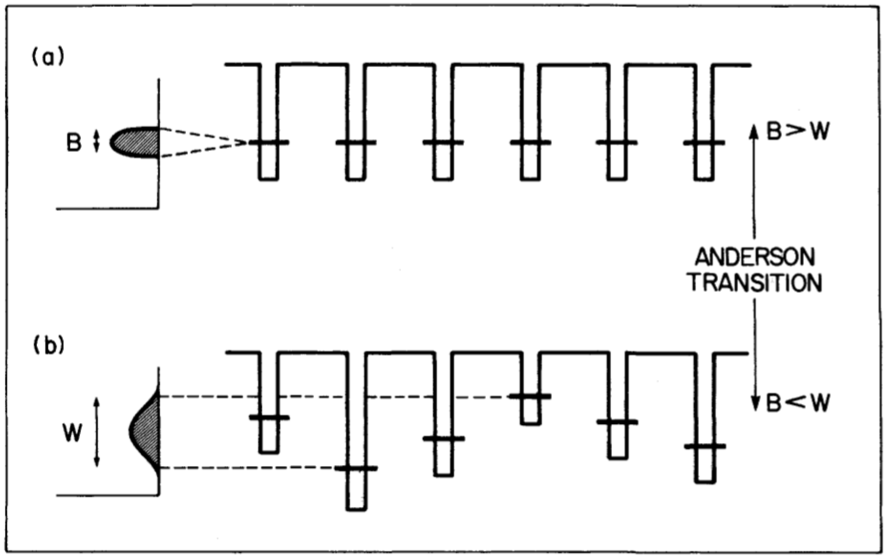
Wu, Leighton, *Phys. Rev. B* **67** (2003) 174408.

seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Anderson localization and the mobility edge





This figure is from pages 229 and 232 of Zallen.

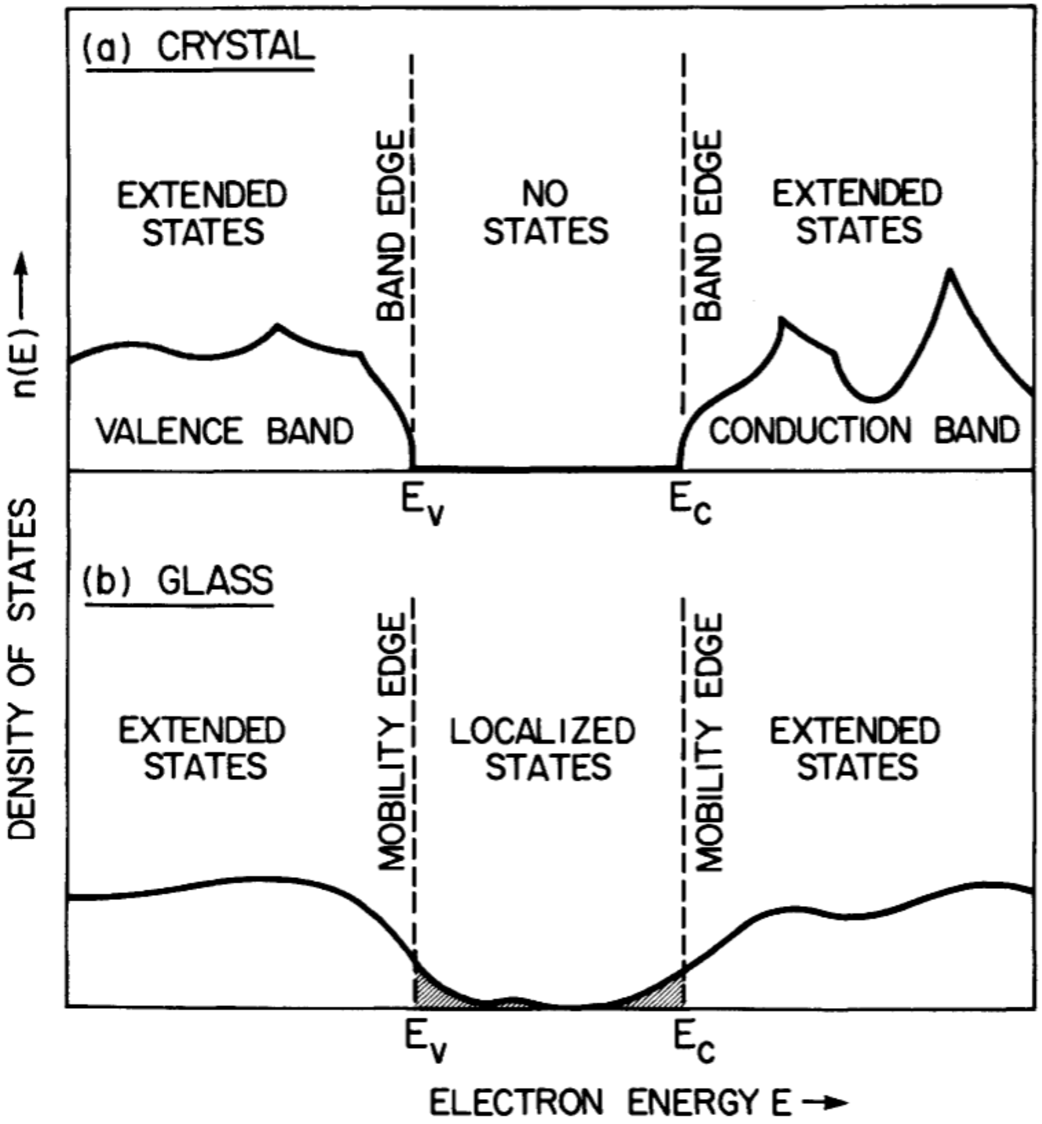
The Mott and Anderson transitions represented graphically in 1D.

R. Zallen, *The Physics of Amorphous Solids*, Wiley-VCH, 2004.

seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Anderson localization and the mobility edge



This figure is from page 235 of Zallen.

The notion of the mobility edge.

R. Zallen, *The Physics of Amorphous Solids*, Wiley-VCH, 2004.

seshadri@mrl.ucsb.edu