Non-metal to Metal Transitions

the saga continues …

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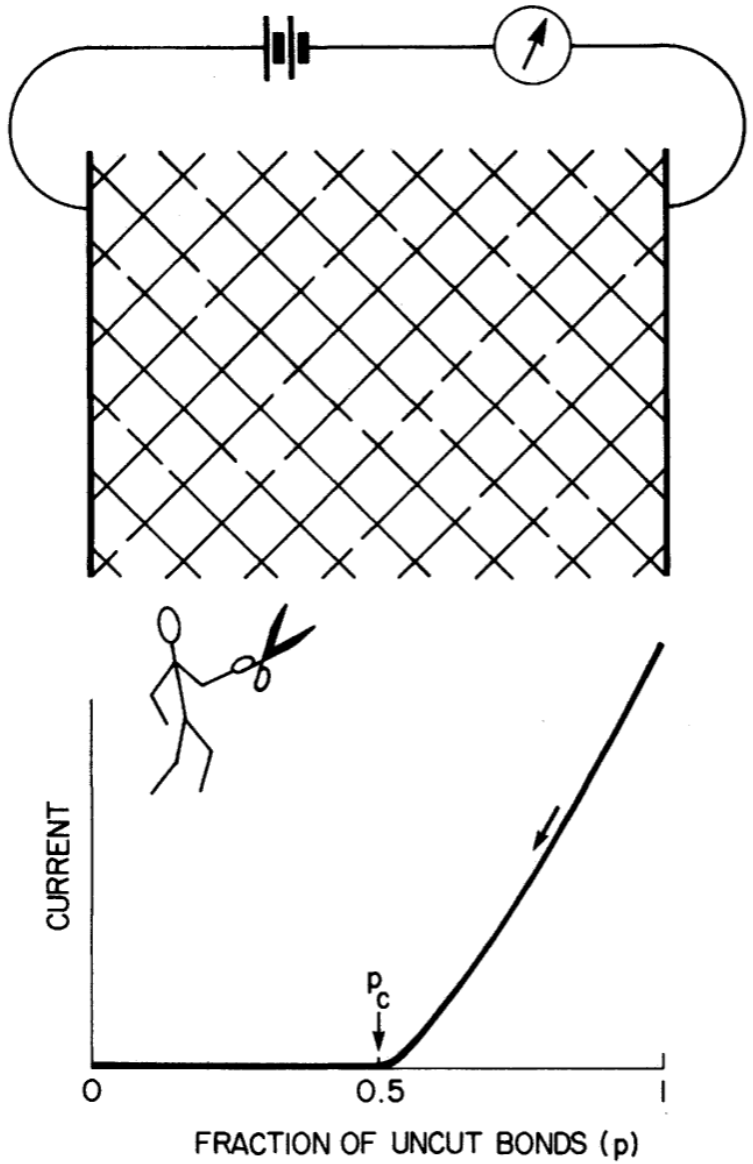
Percolation [Closely following the text by Zallen]



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.

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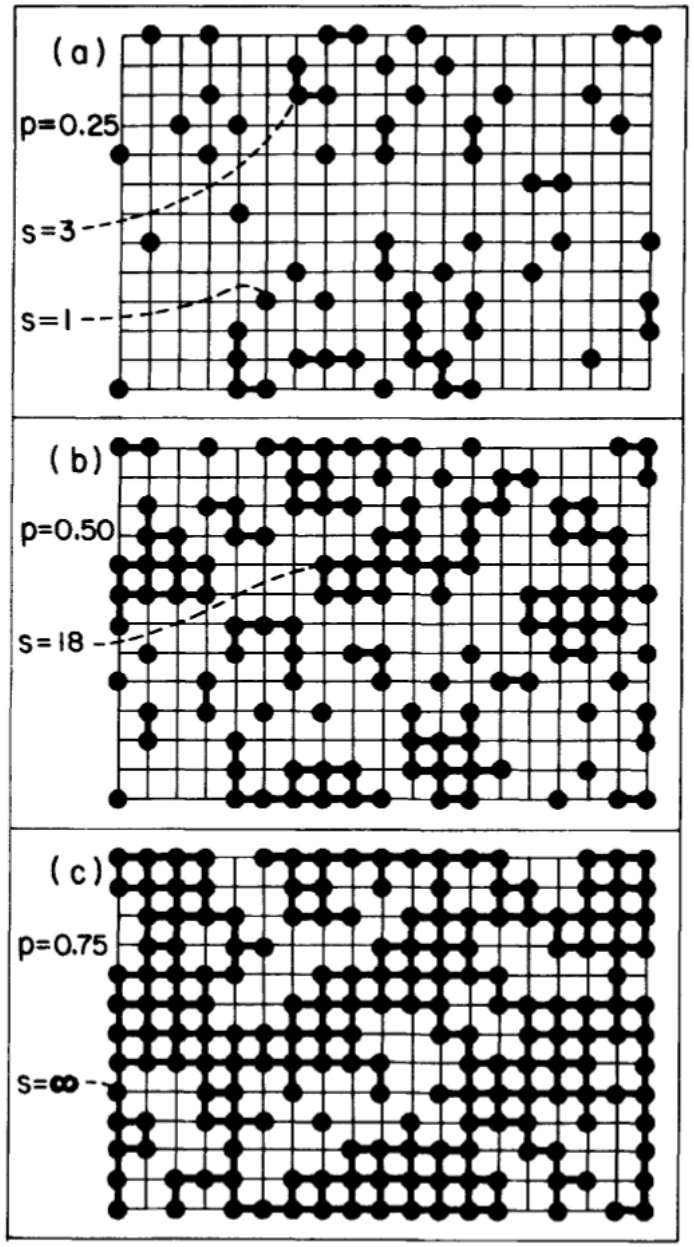
Percolation [Closely following the text by Zallen]



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.

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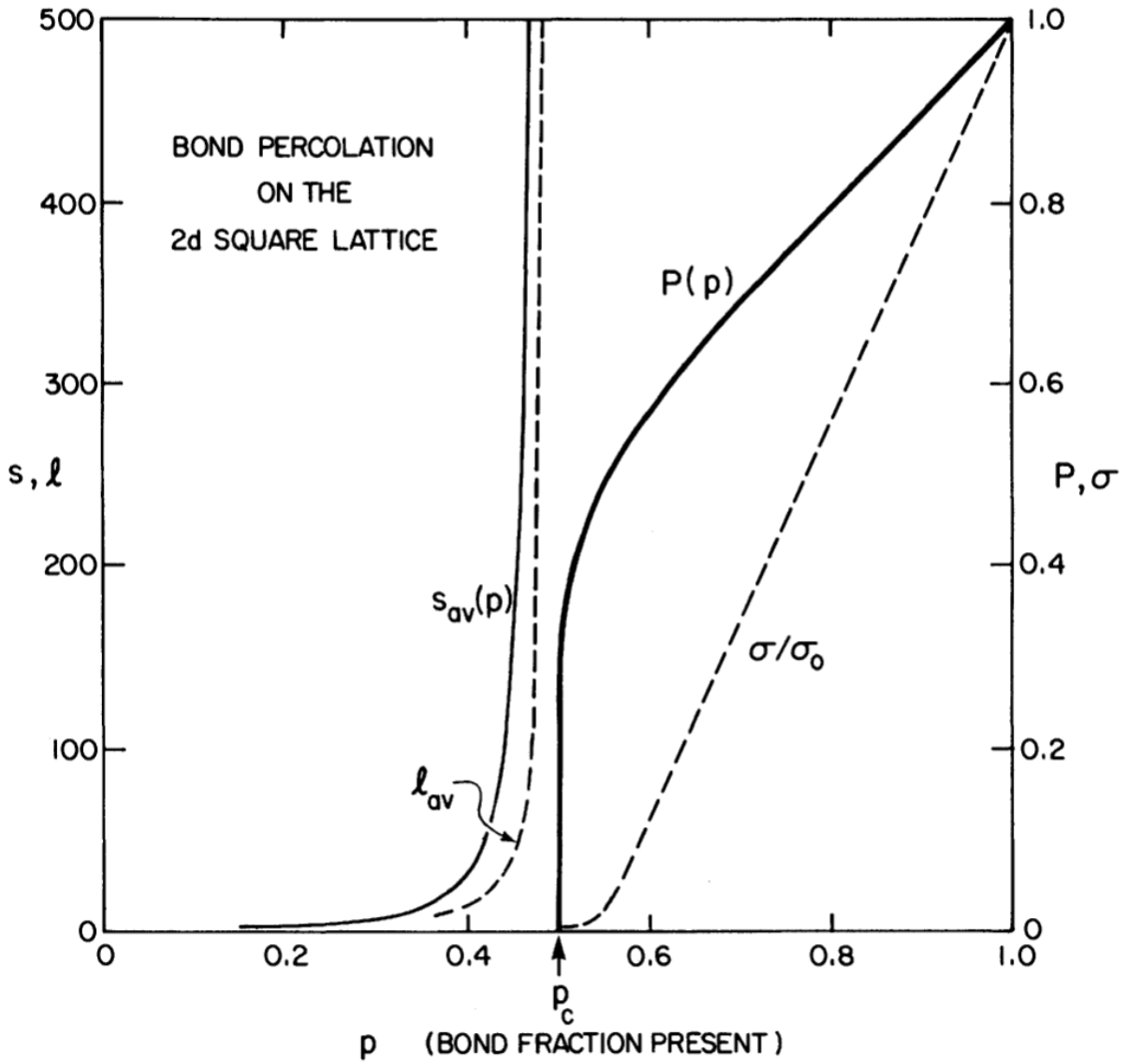
Percolation [Closely following the text by Zallen]



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.

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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.

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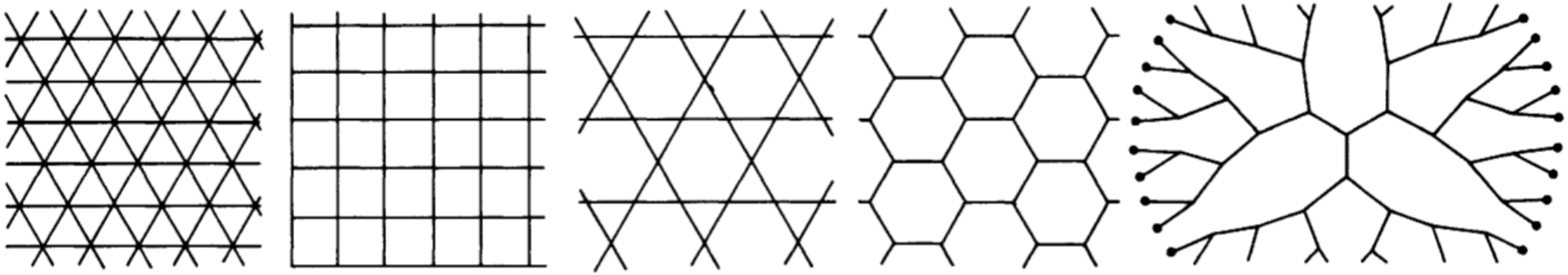
Different lattices:



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.

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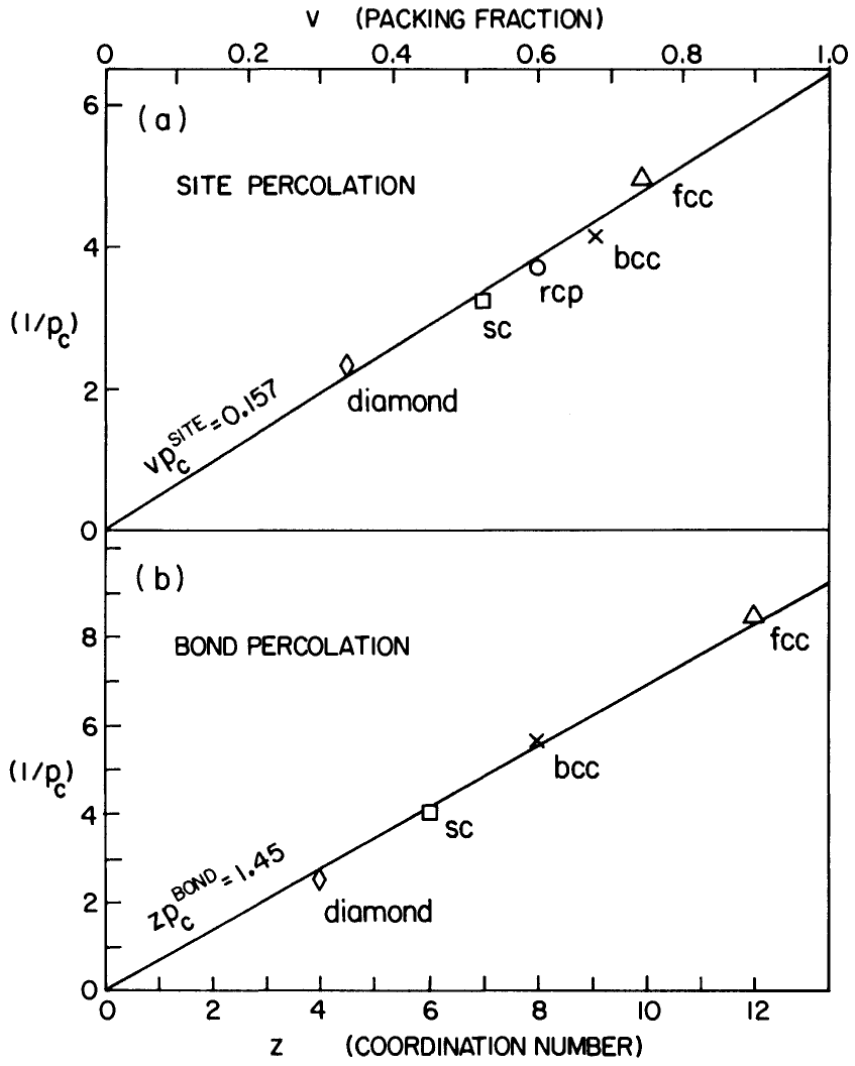
Percolation [Closely following the text by Zallen]

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

Page 170 of Zallen.

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

Percolation [Closely following the text by Zallen]

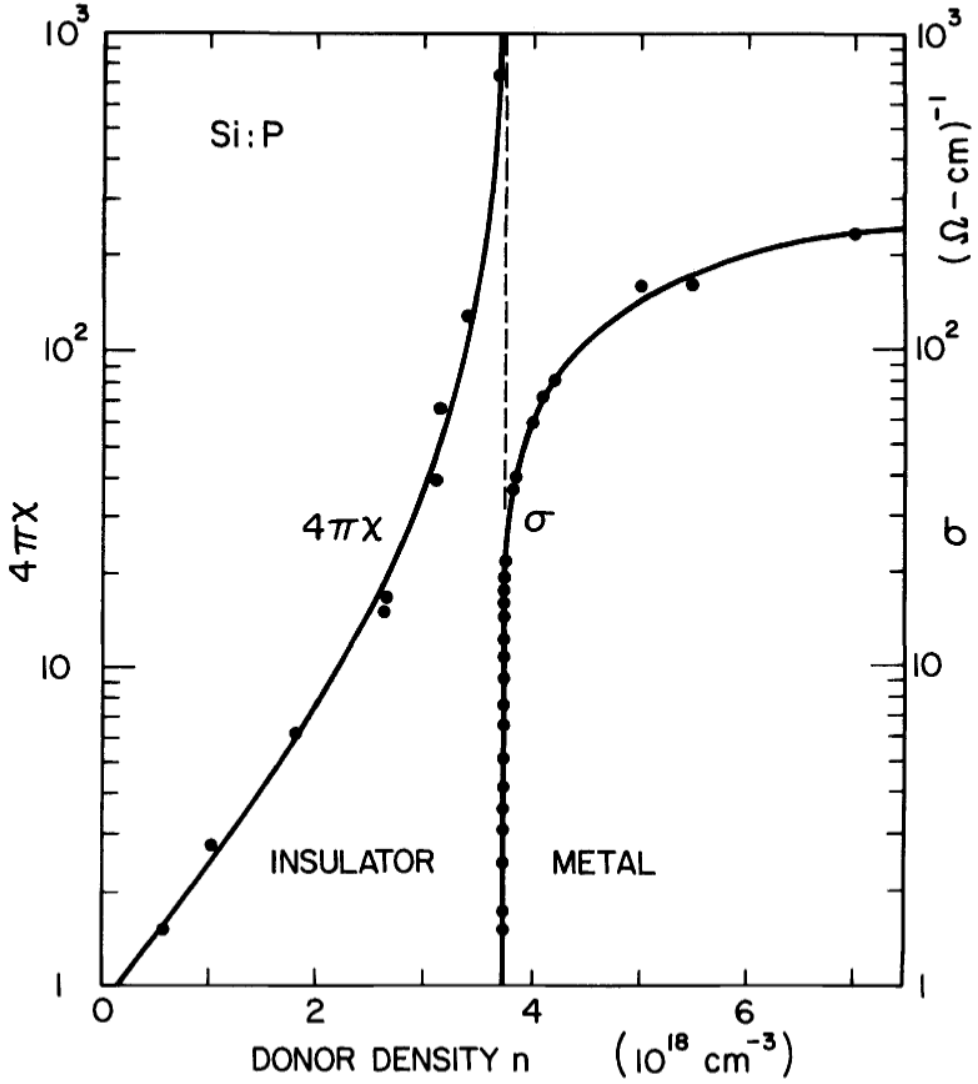


This figure is from page 187 of Zallen.

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.

Percolation [Closely following the text by 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.

This of the percolation, not of atoms but of Bohr radii.

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

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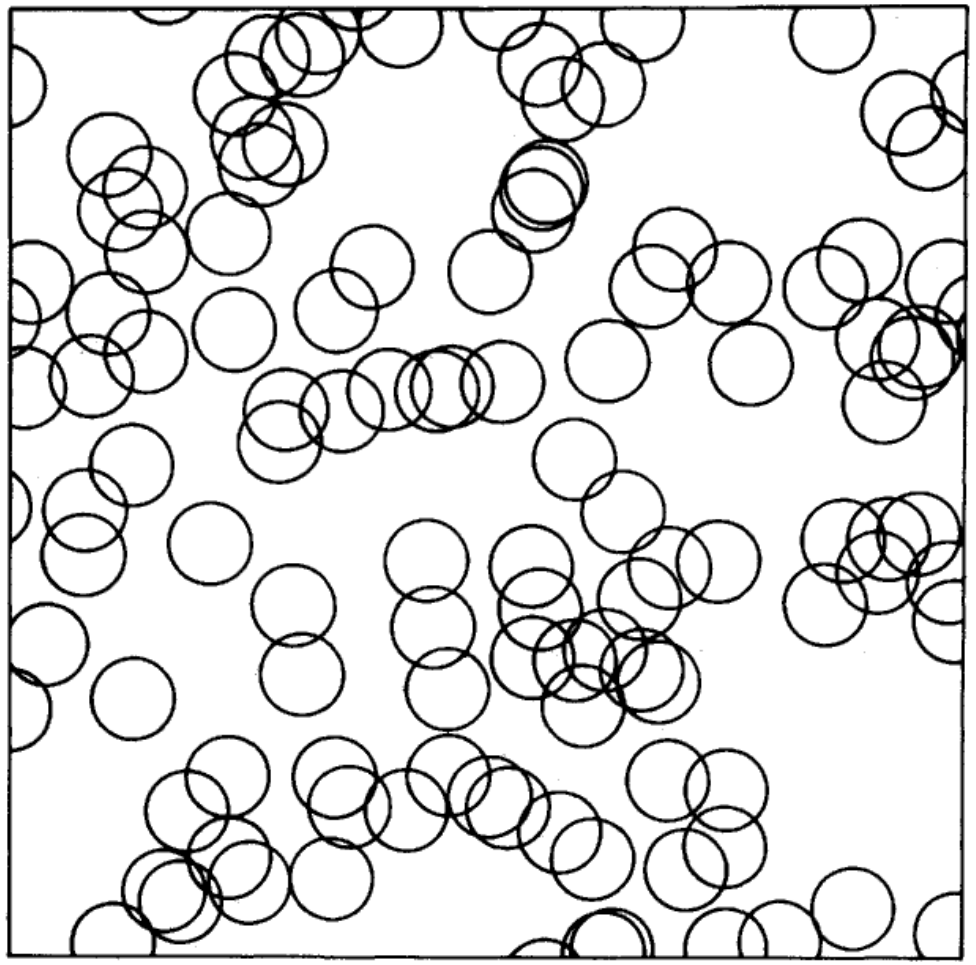
Percolation [Closely following the text by Zallen]



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.

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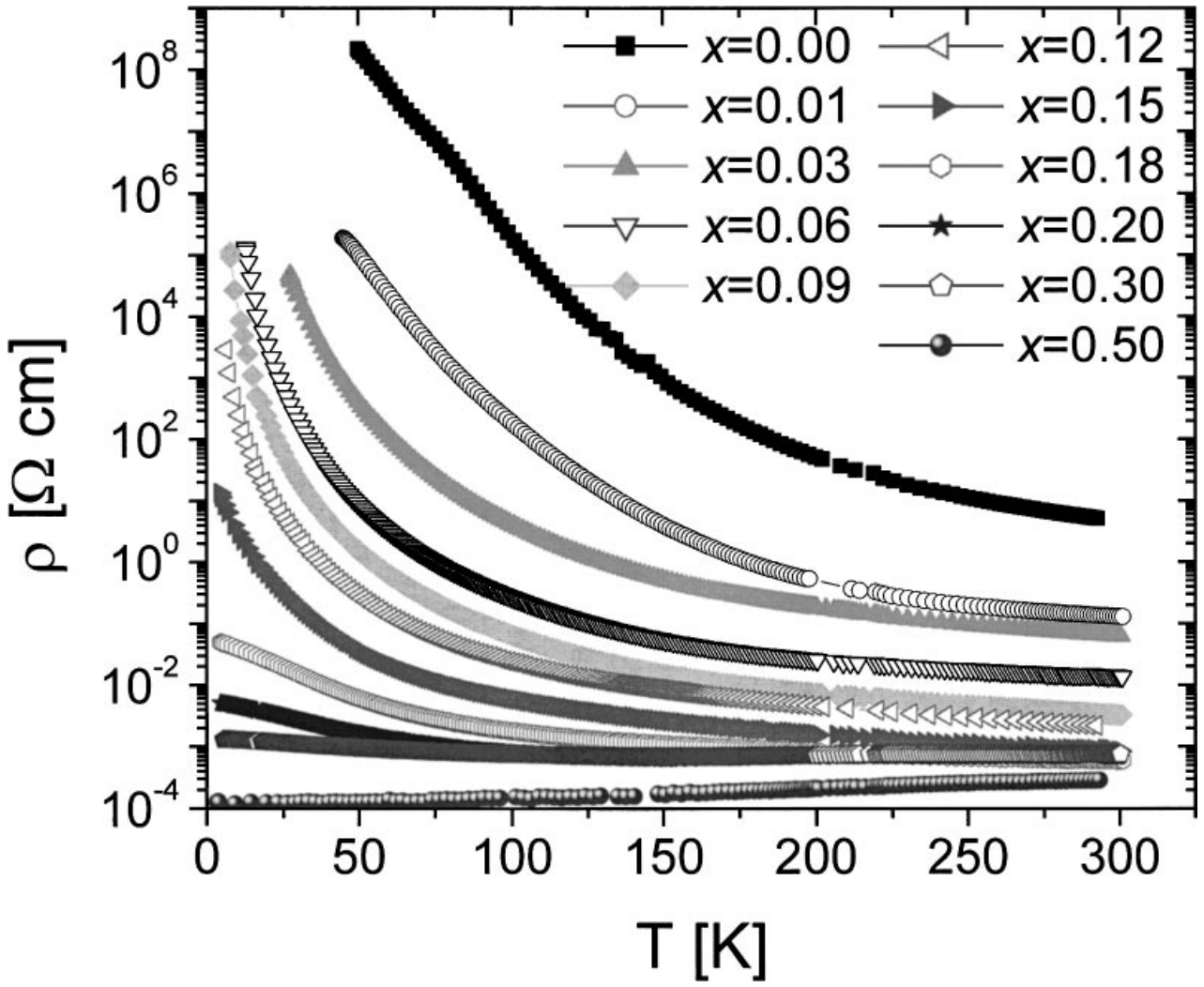
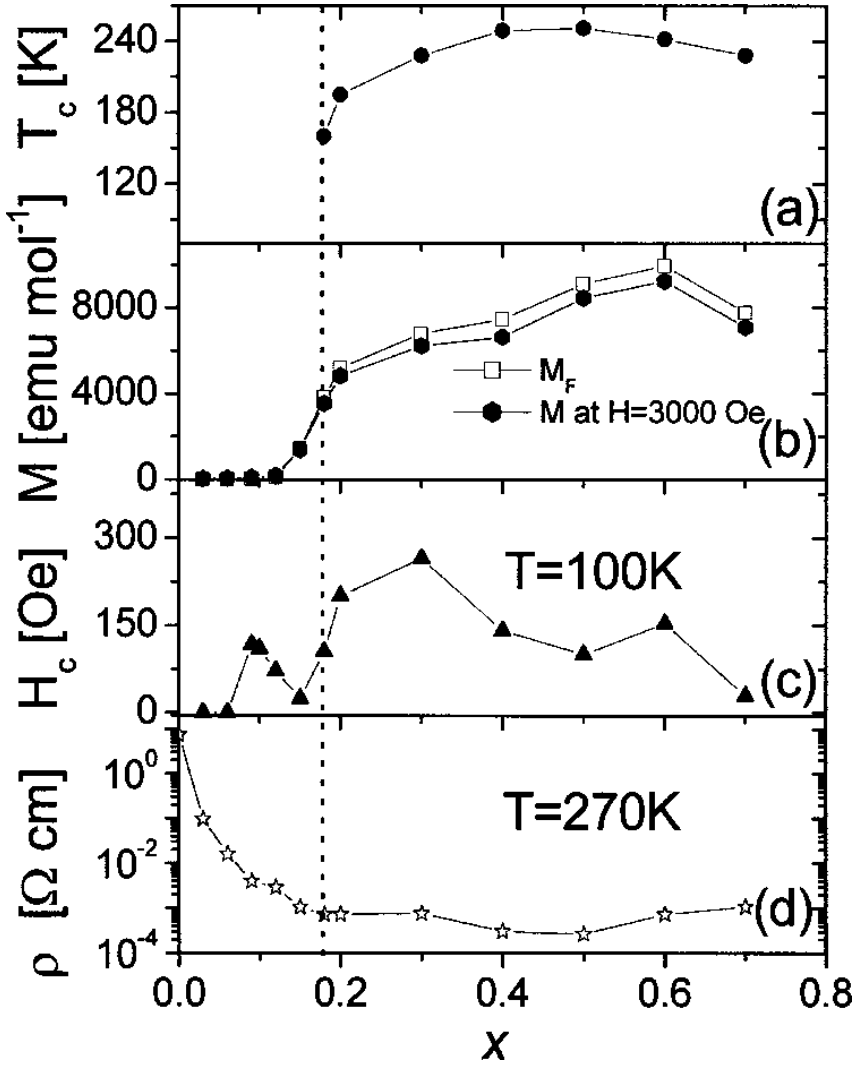
$La_{1-x}Sr_xCoO_3$



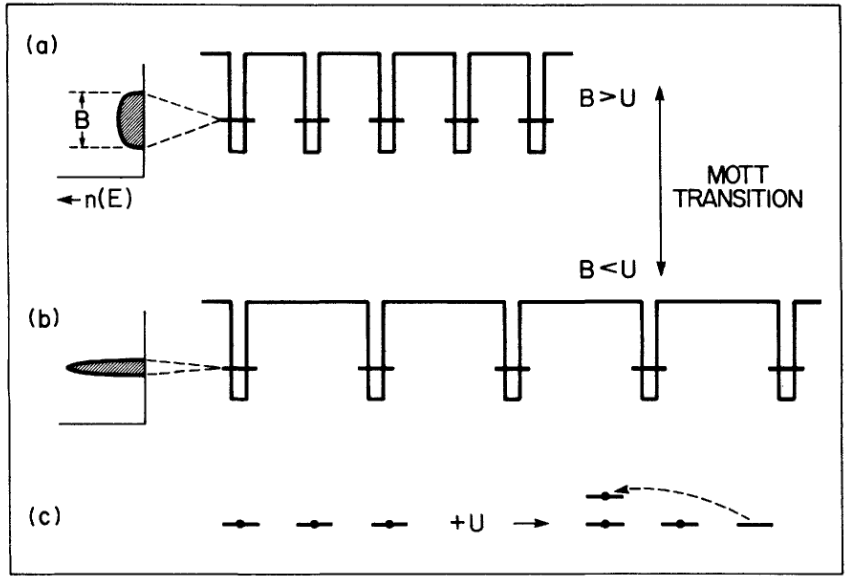
Wu, Leighton, *Phys. Rev. B* **67** (2003) 174408.

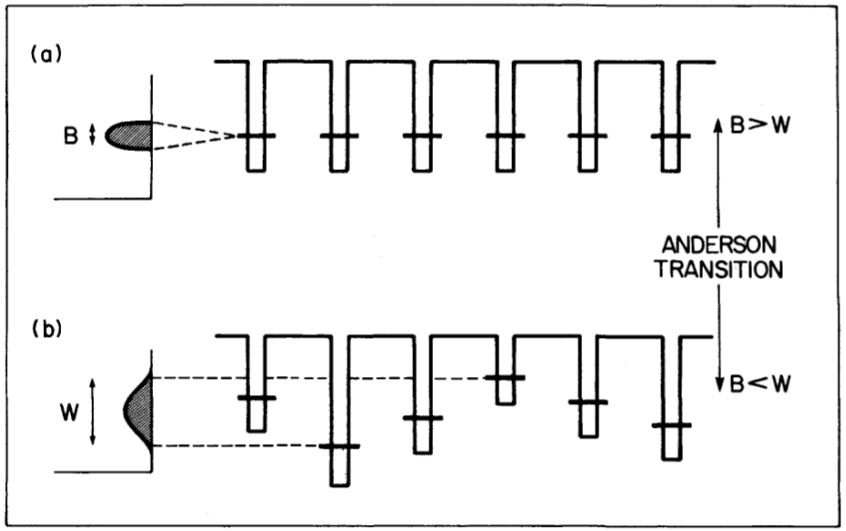
$La_{1-x}Sr_xCoO_3$



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

Anderson localization and the mobility edge [Closely following the text by Zallen]





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.

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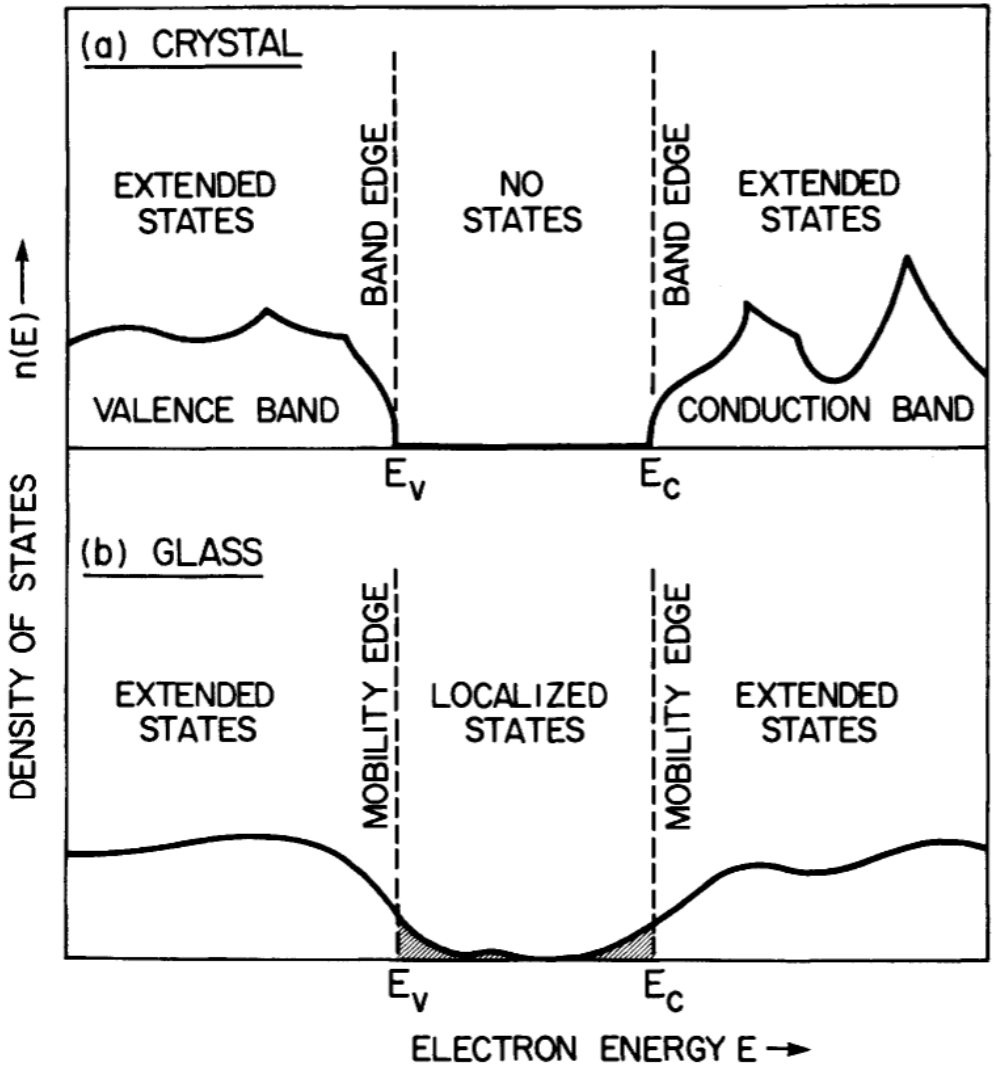
Anderson localization and the mobility edge [Closely following the text by Zallen]



This figure is from page 235 of Zallen.

The notion of the mobility edge.

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

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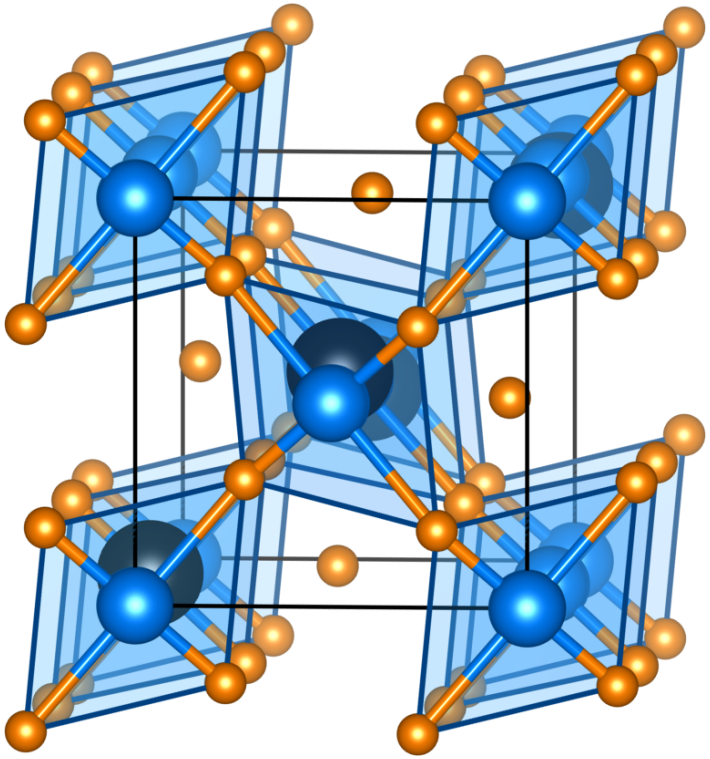
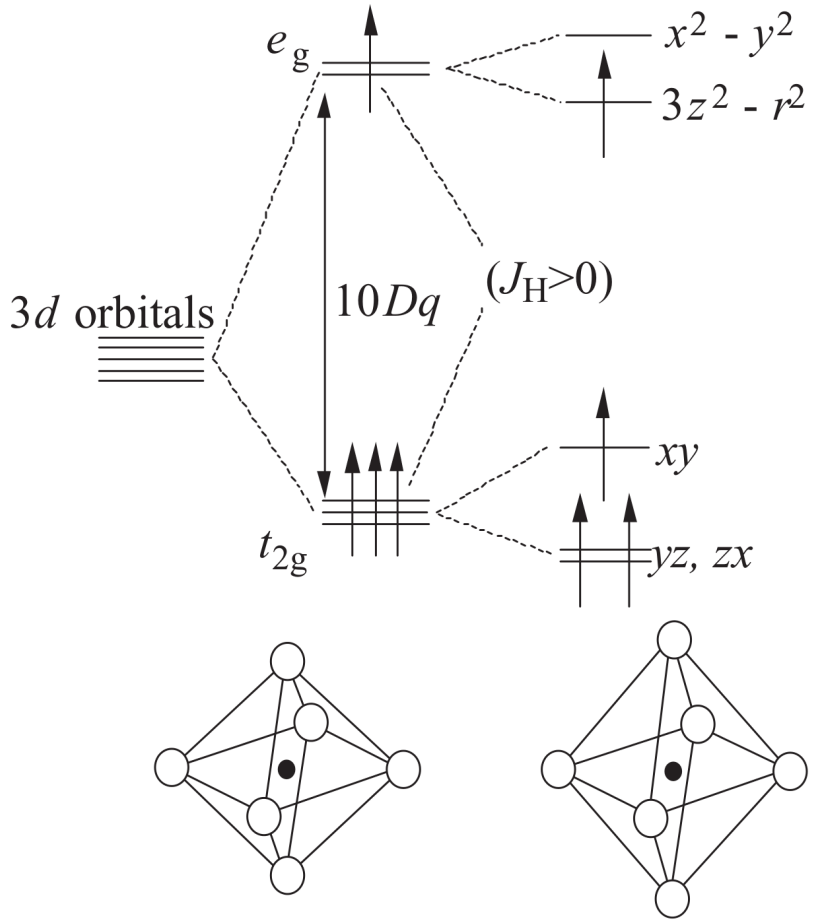
Correlation and the Hubbard model: $LaMnO_3$



Jahn-Teller distorted orthorhombic perovskite (space group *Pnma*)



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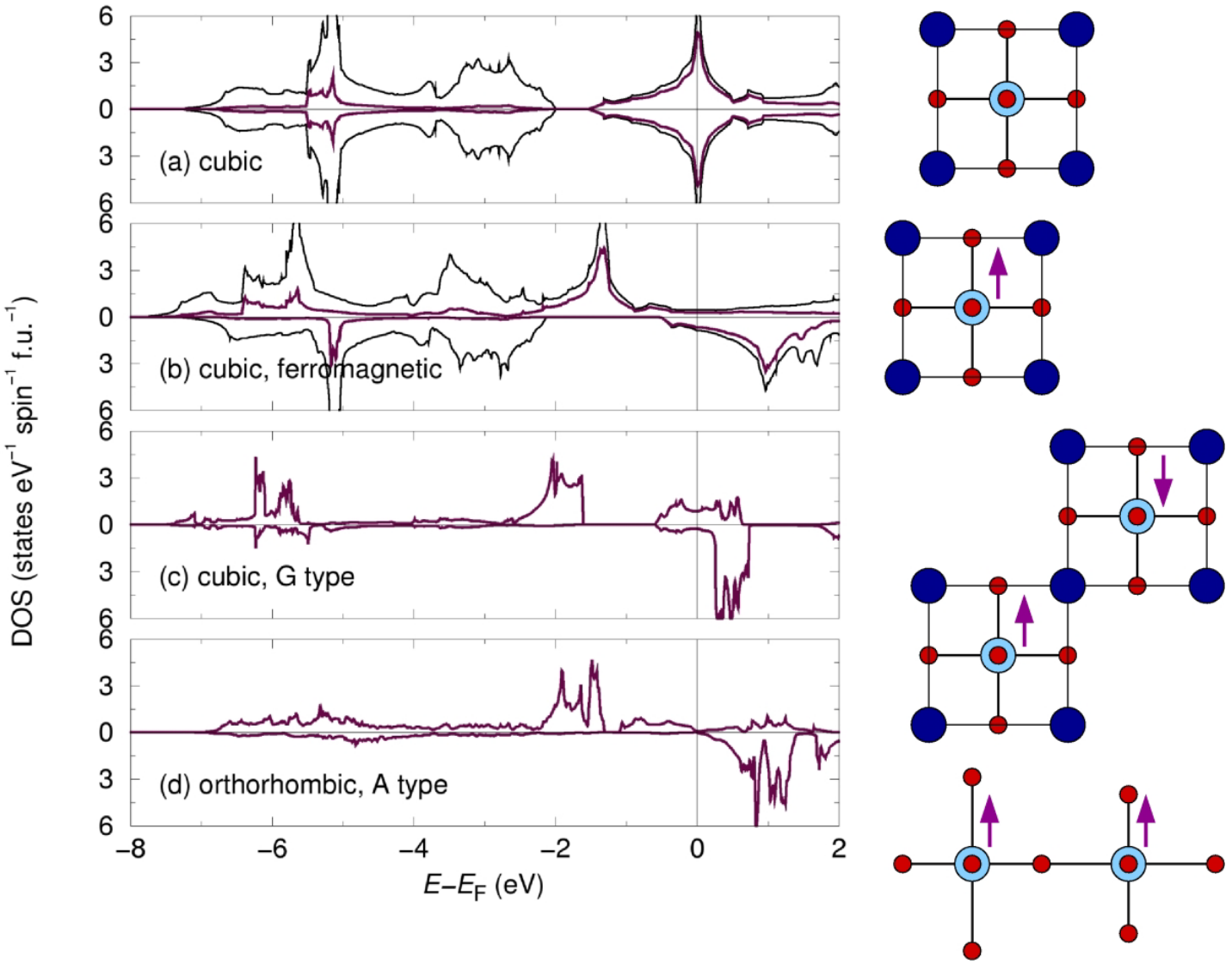
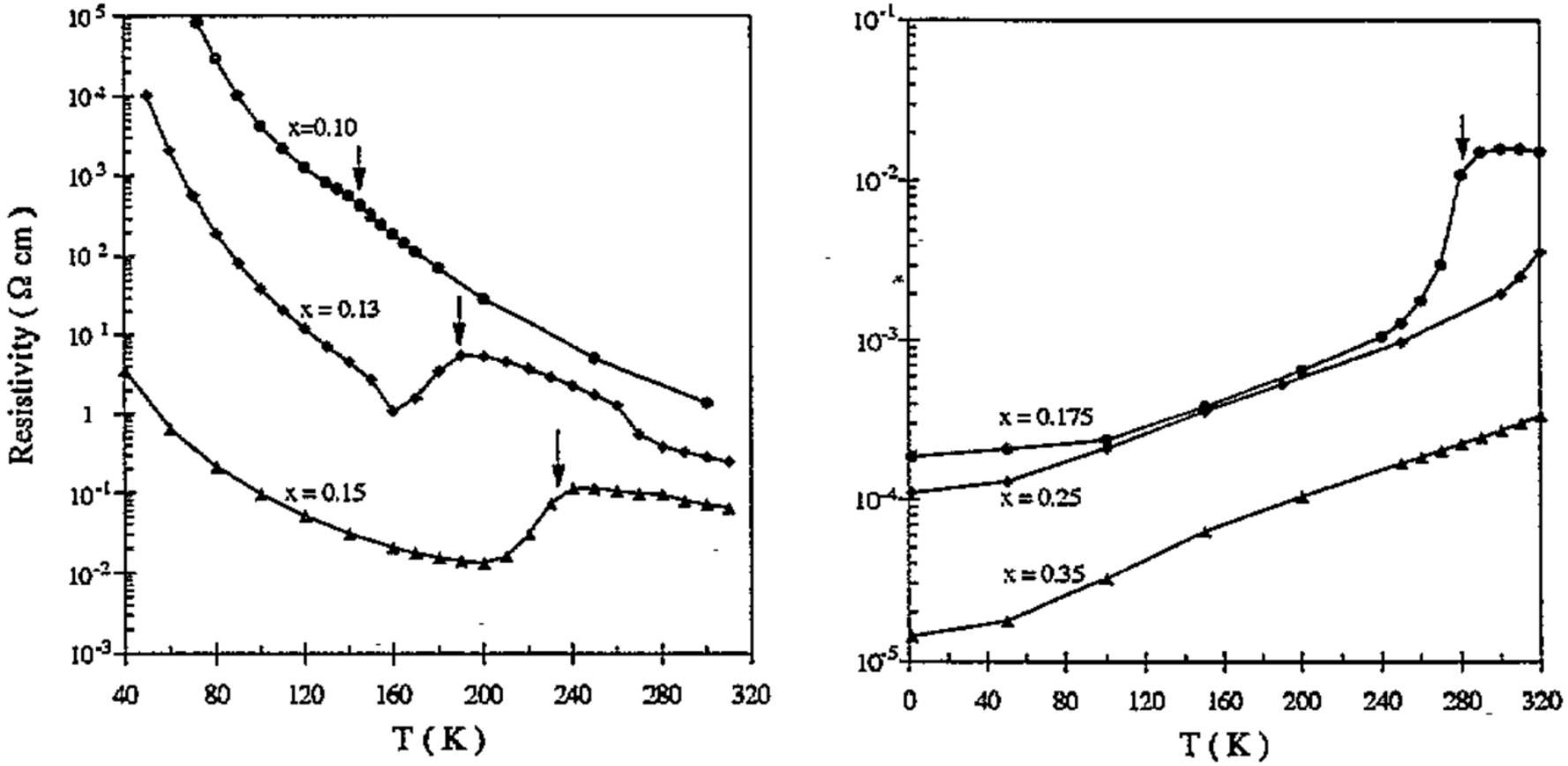
Correlation and the Hubbard model: $LaMnO_3$



Structure and magnetism do not explain the insulating behavior.

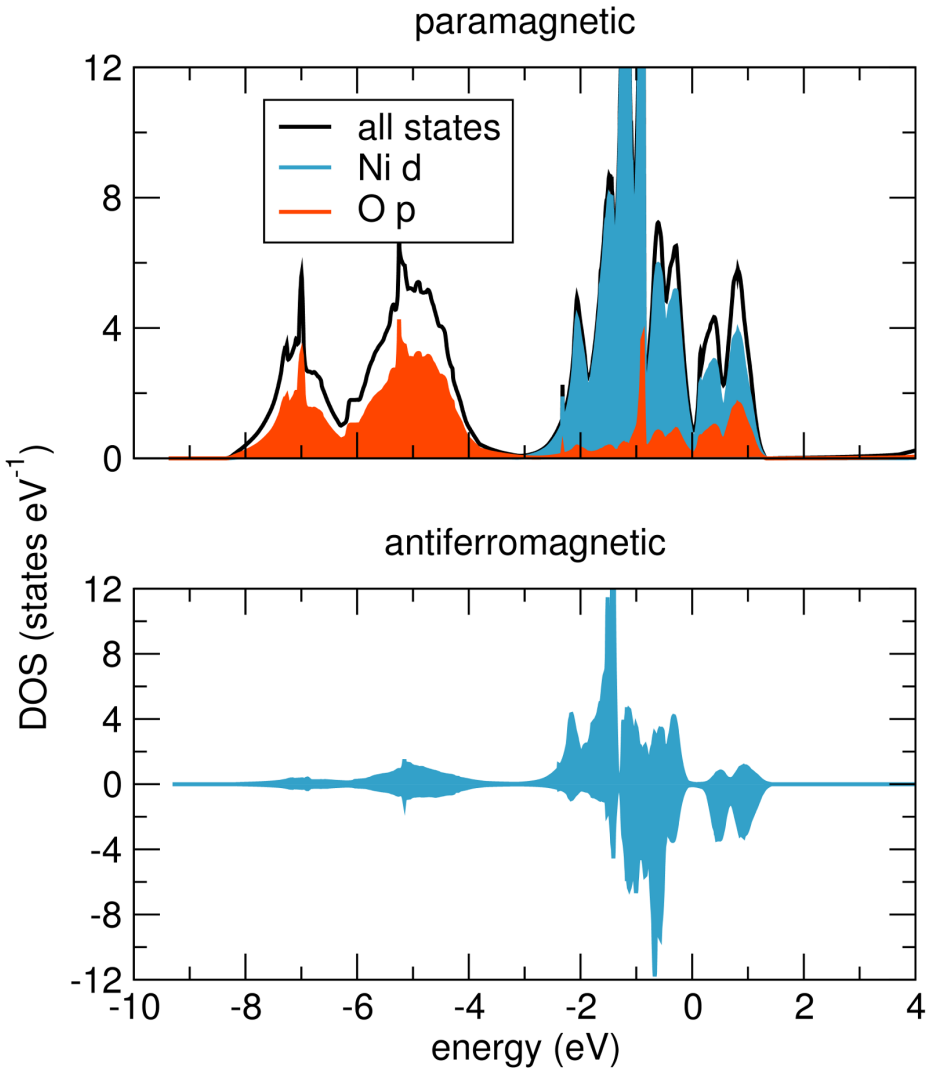
Correlation and the Hubbard model: $LaMnO_3$

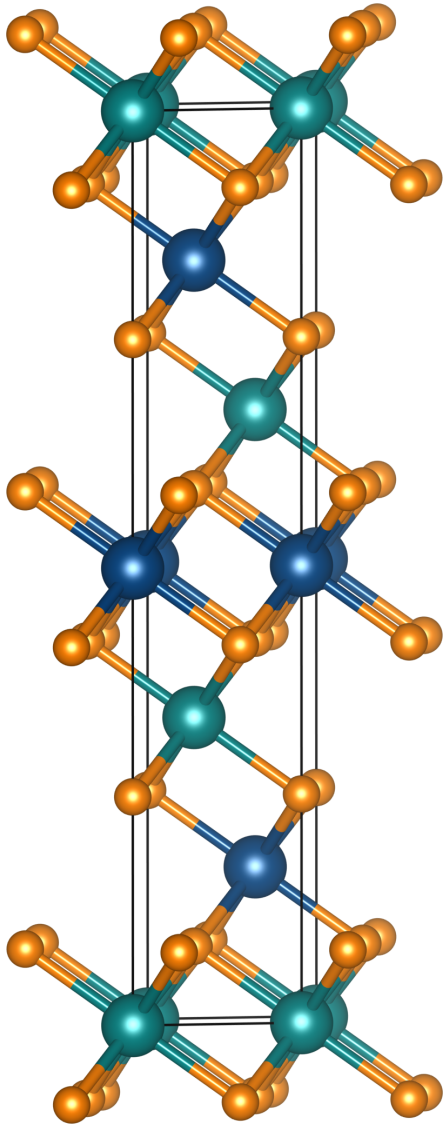


Electrical resistivity behavior in $La_{1-x}Sr_xMnO_3$

Anane, Dupast, Dang, Renard, Veillet, de Leon Guevare, Millot, Pinsard, Revcolevschi, *J. Phys.: Condens. Matter* **7** (1995) 7015-7021.

Correlation and the Hubbard model: NiO





NiO displays the color of isolated Ni^{2+} in solution, with similar spectra.

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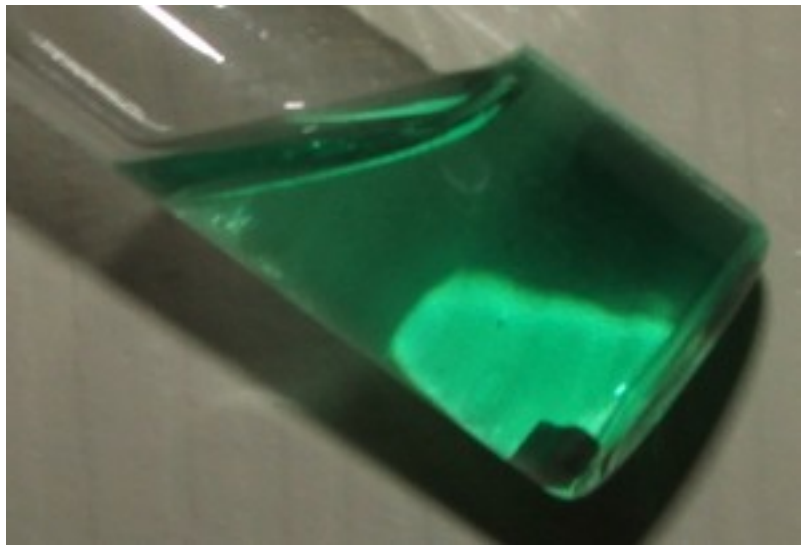
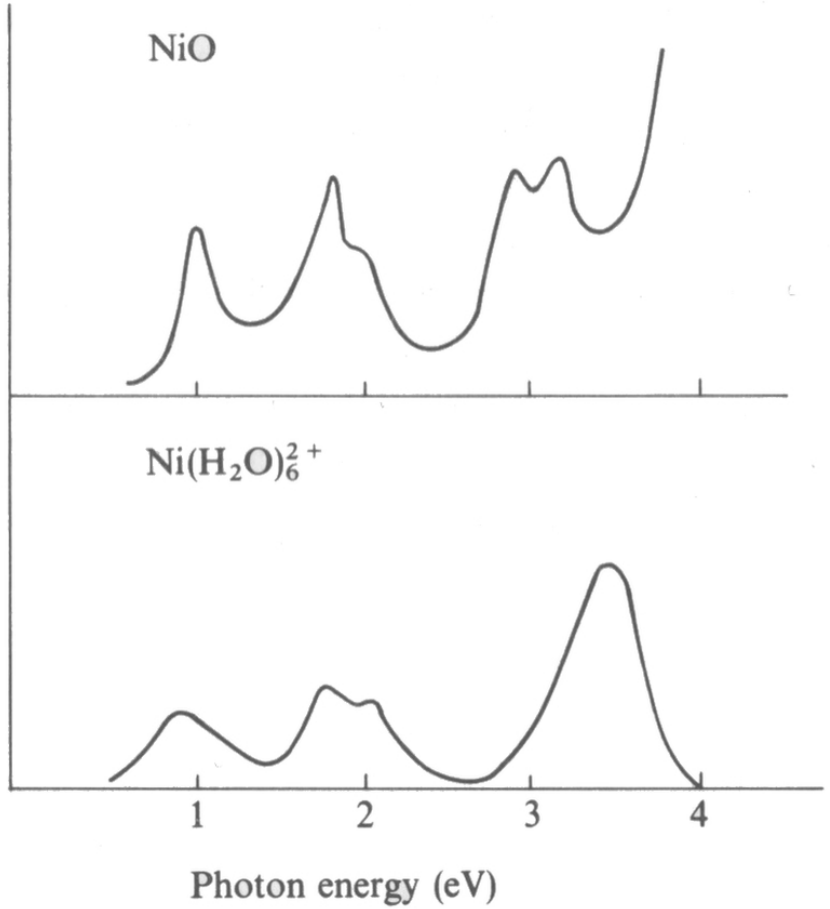
Correlation and the Hubbard model: NiO

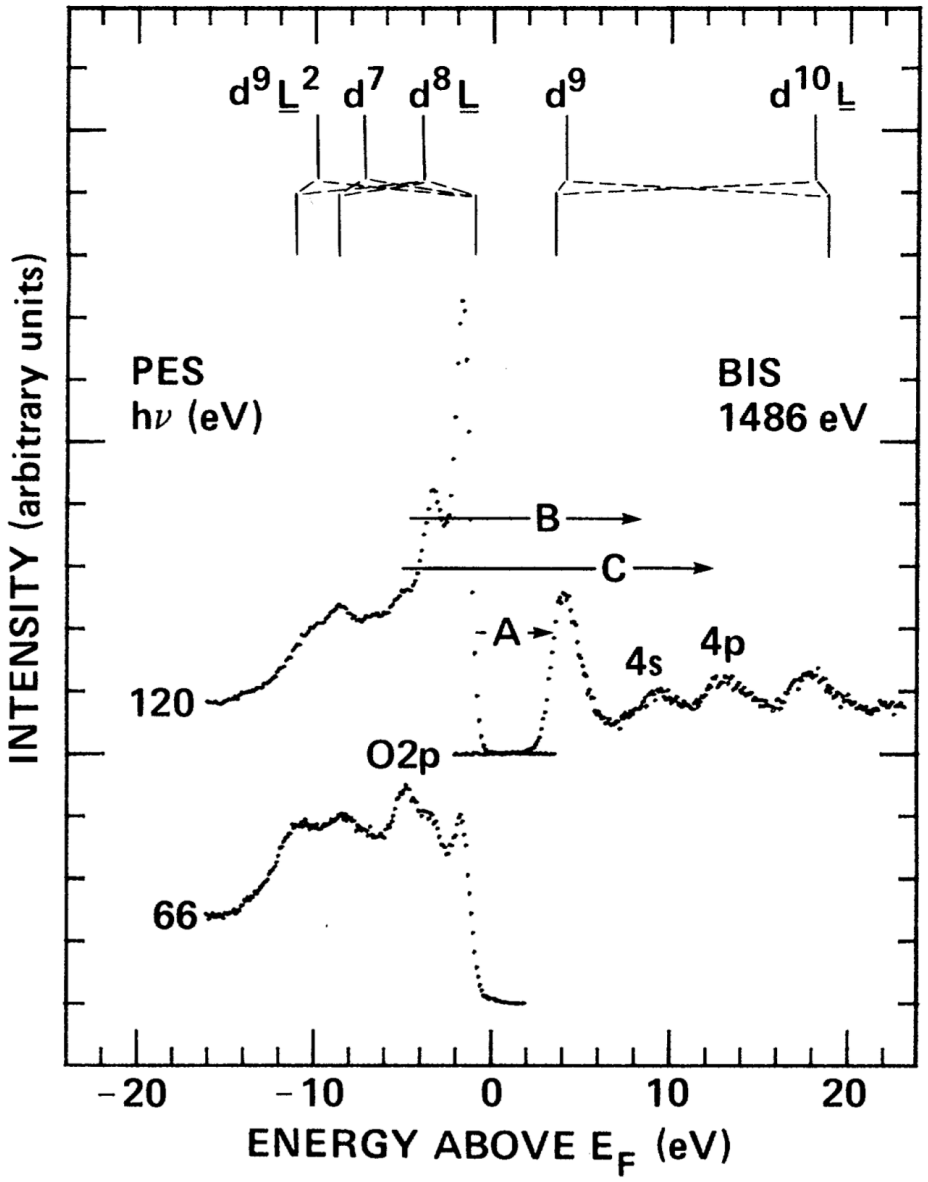
NiO displays the color of isolated Ni^{2+} in solution, with similar





From the Cox The Electronic Structure and Chemistry of Solids (Oxford Science Publications) 1st Edition, page 151

Correlation and the Hubbard model: NiO



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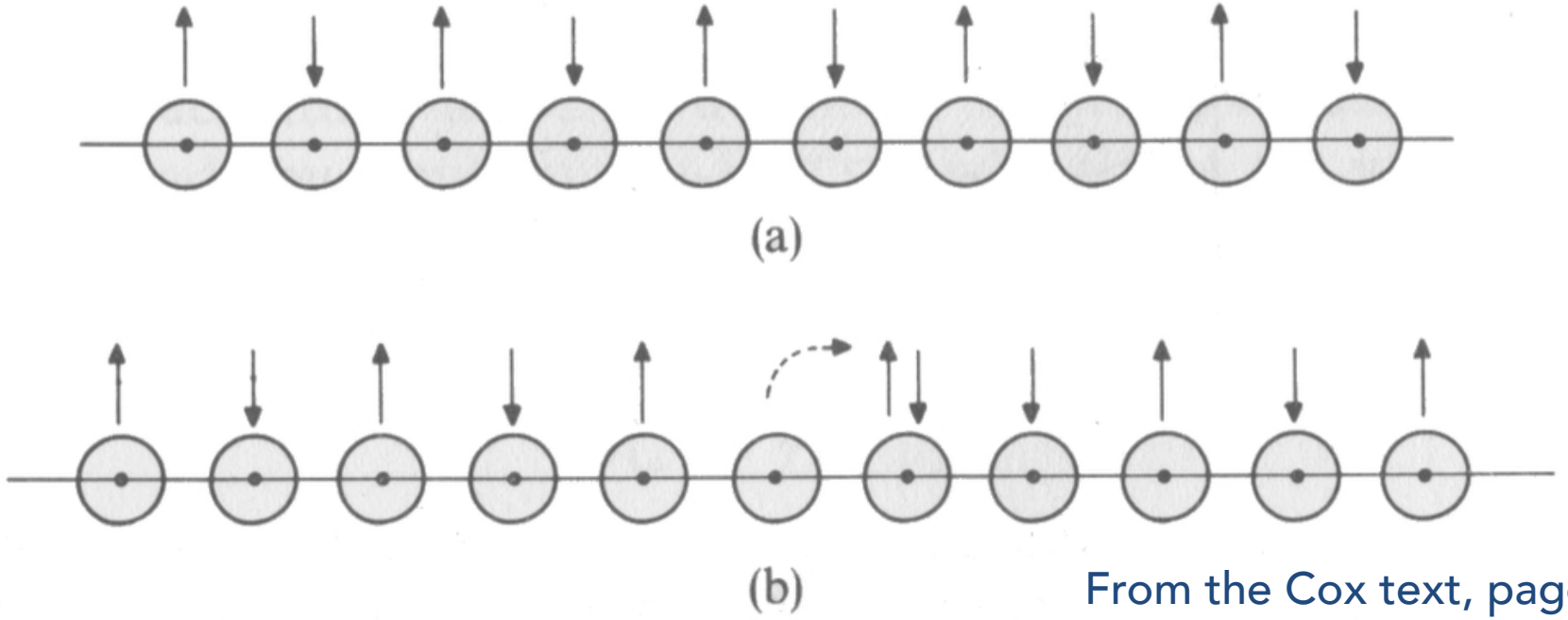
Correlation and the Hubbard model: NiO



From the Cox text, page 135

Consider a chain of orbitals, each with one electron. To hop an electron, an orbital has to be ionized at cost I, which is compensated a little by the electron affinity A.

$U = I - A$

For H atoms, I = 13.6 eV and A = 0.8 eV, meaning U = 12.8 eV. However, this does not account for some screening (due to the dielectric not being vacuum).

Correlation and the Hubbard model: The Hamiltonian

$$H = -t \sum_{<i,j>,\sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + c^{\dagger}_{j,\sigma} c_{i,\sigma}) + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow}$$

hopping or tight-binding (LCAO) part

double-occupancy cost or on-site repulsion

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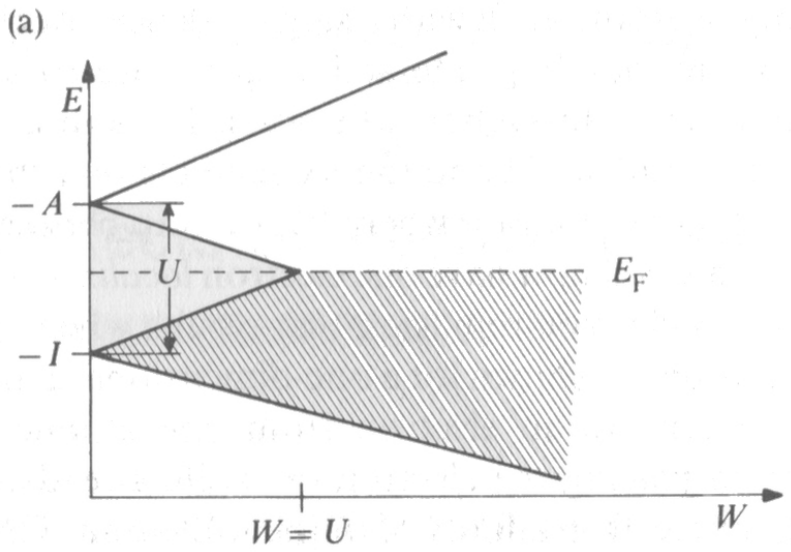
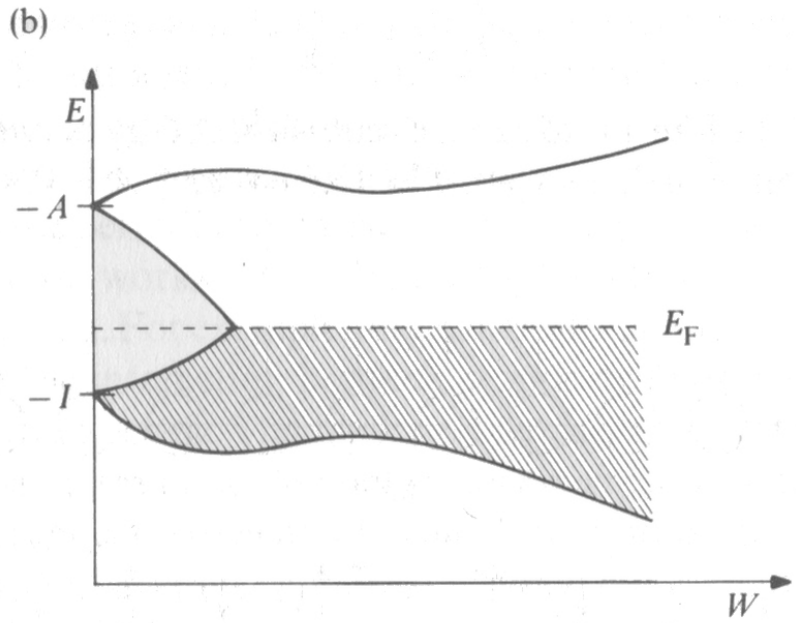
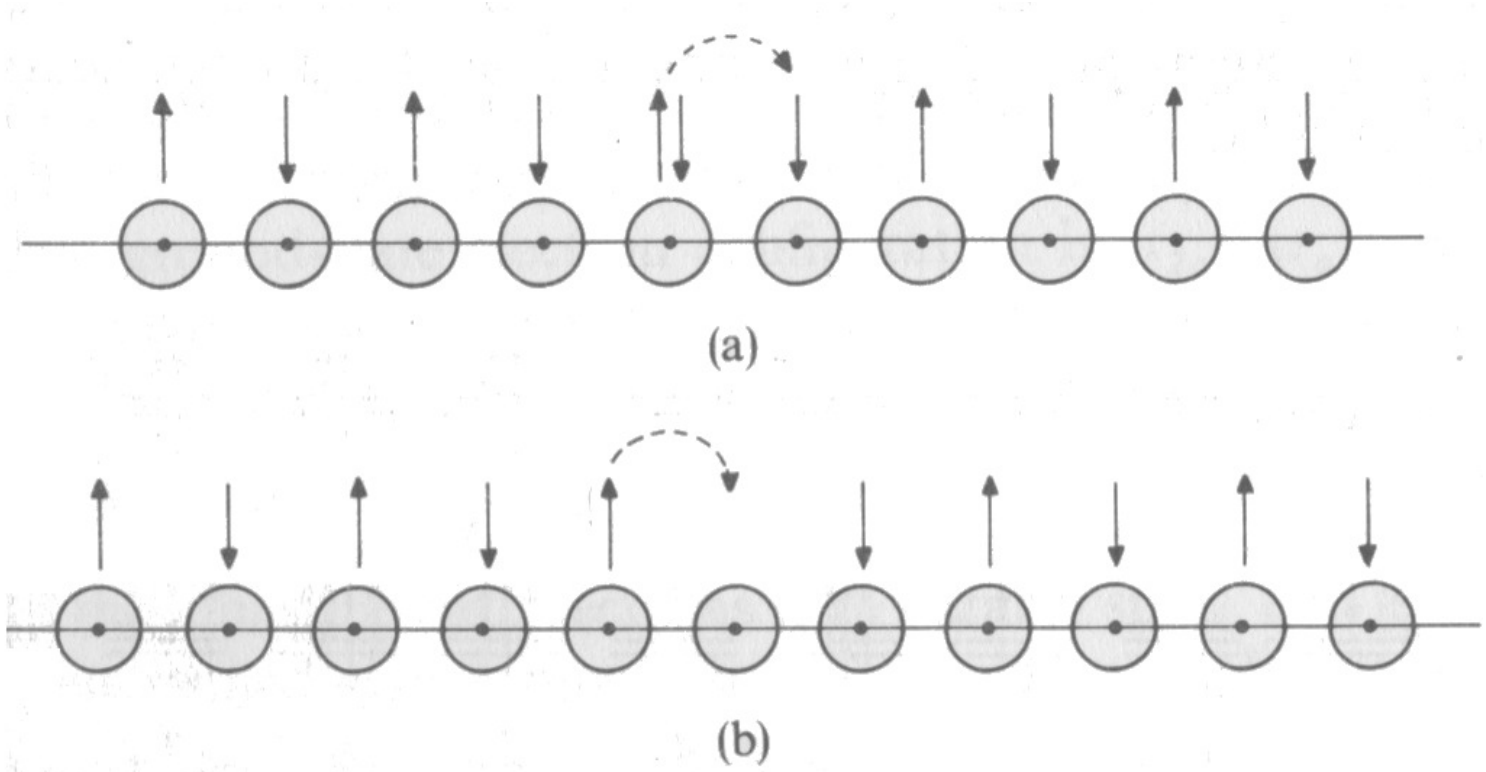
Correlation and the Hubbard model





As the bandwidth is increased, (or as the atoms approach closer) the gap can close.

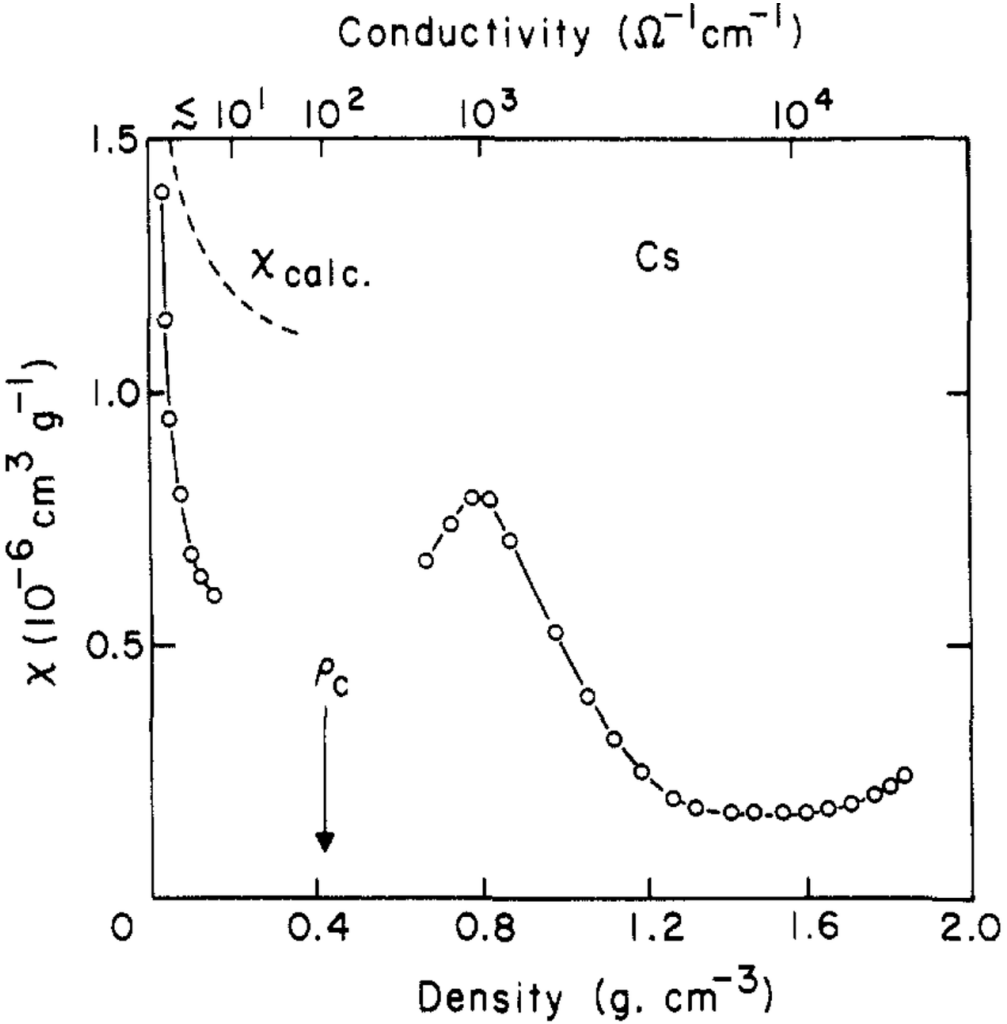
From the Cox text, page 137



Doping of holes (removal of electrons) as in (b) makes hopping much easier, with the on-site repulsion having been removed.

From the Cox text, page 149

Correlation and the Hubbard model: Magnetism



On the insulating side of the M–I transition, magnetism of some sort (usually antiferromagnetism) manifests.

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In the limit that *U* >> *t*, the Hubbard model:

$$H = -t \sum_{<i,j>,\sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + c^{\dagger}_{j,\sigma} c_{i,\sigma}) + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow}$$

Can be reduced to the Heisenberg Hamiltonian:

$$H = J \sum_{<ij>} \vec{S_1} \vec{S_2} \quad \text{where} \quad J = \frac{4t^2}{U}$$

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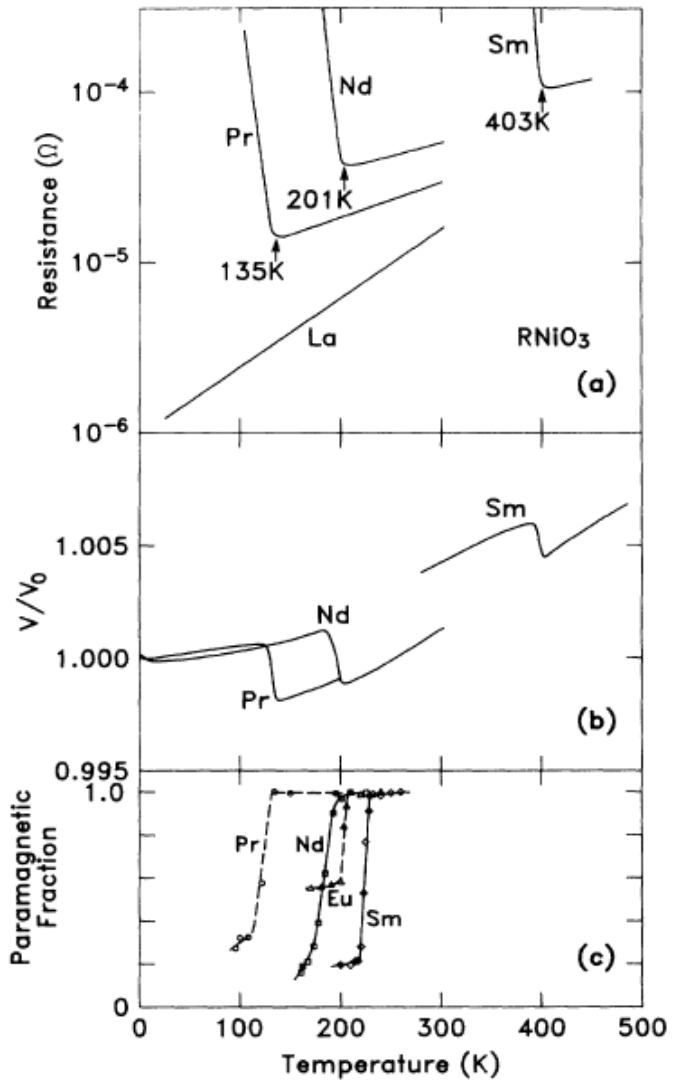
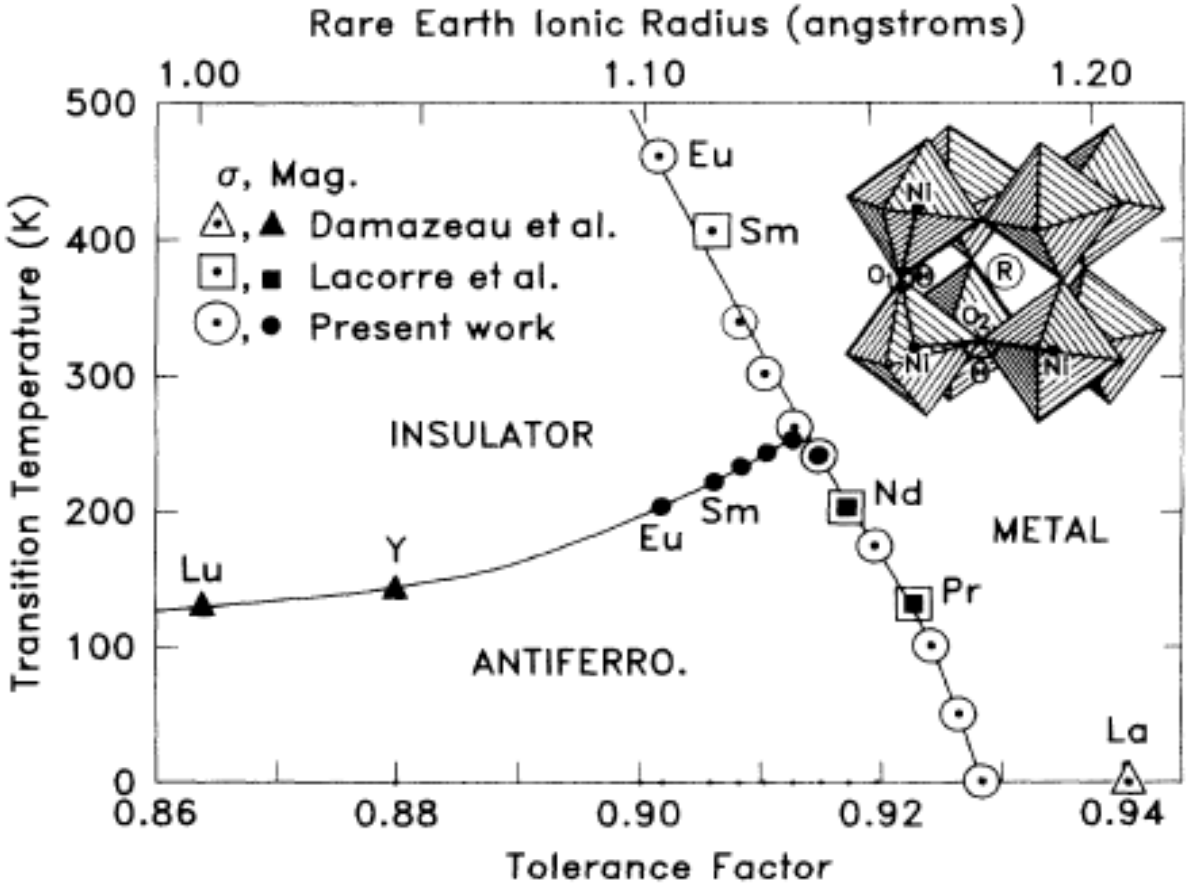
Correlation and the Hubbard model: The rare-earth nickel oxide perovskites

The example of $LnNiO_3$, *Ln* = La, Pr, Nd, Sm:

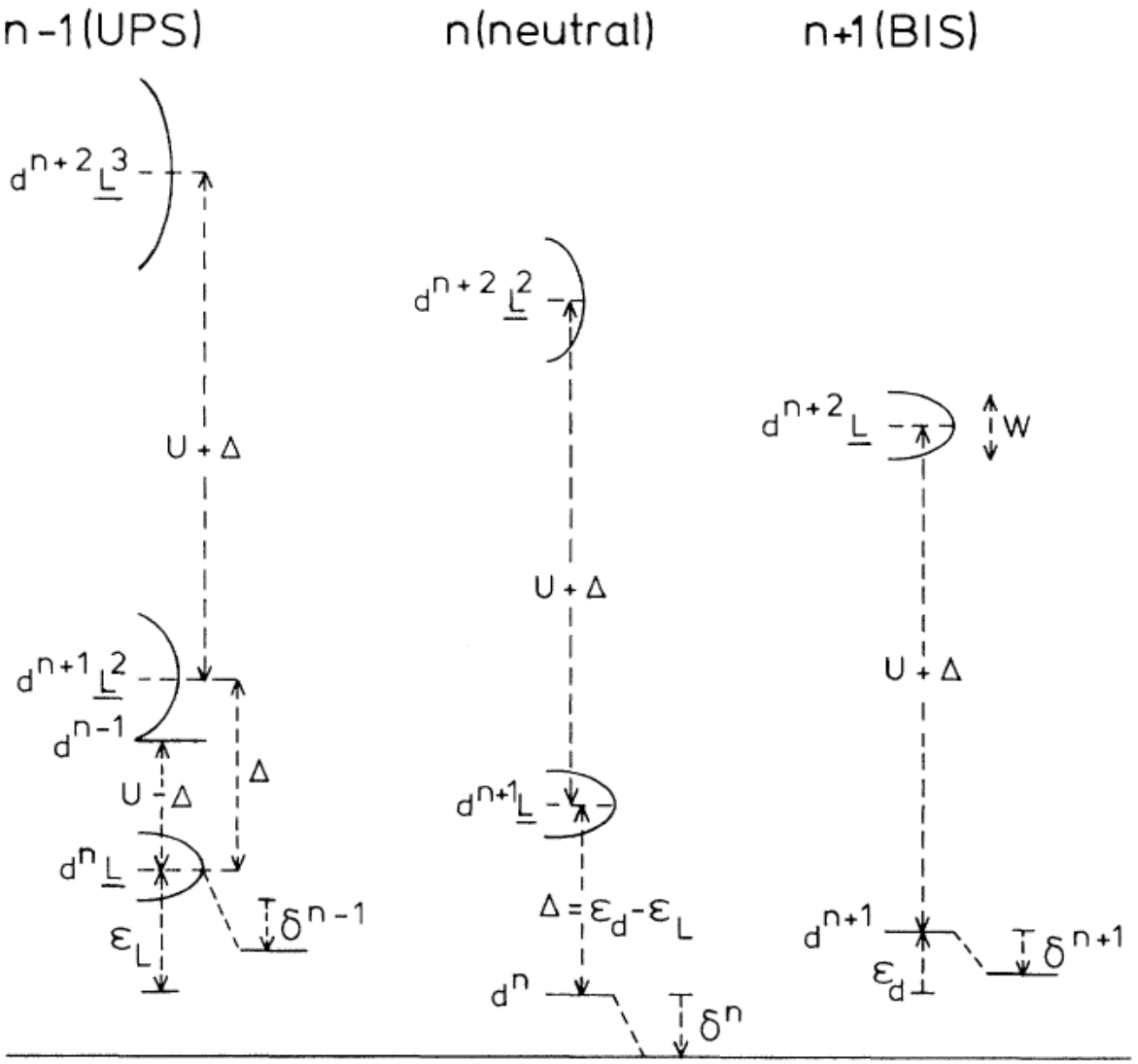




Torrance, Lacorre, Nazzal, Ansaldo, Niedermayer, *Phys. Rev. B.* **45** (1992) 8209–8212.

The Zaanen-Sawatzky-Allen phase diagram

The position of transition metal d-states *vs.* anion p states:



Zaanen, Sawatzky, Allen, *Phys. Rev. Lett.* **55** (1985) 418–421.

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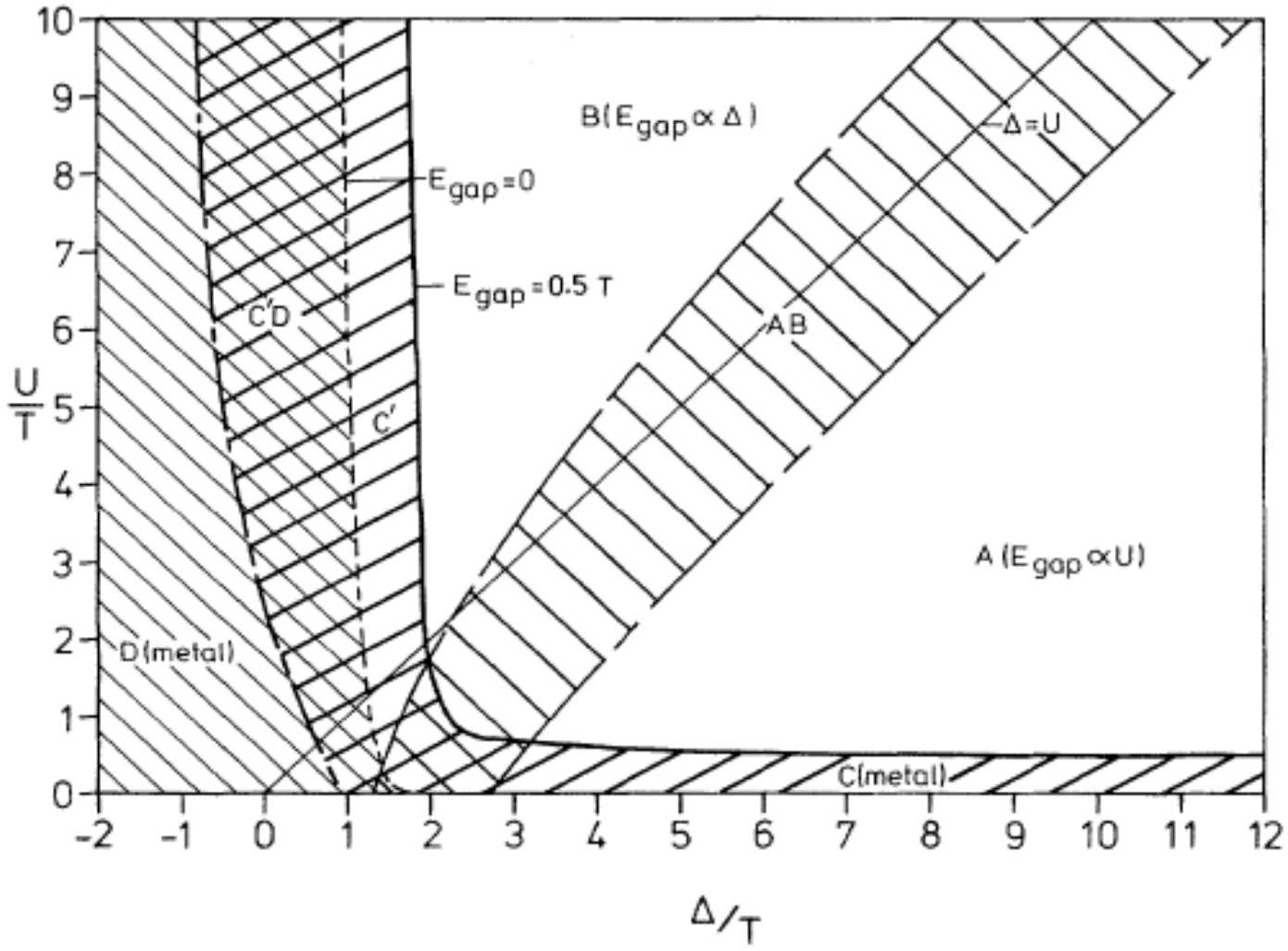
The Zaanen-Sawatzky-Allen phase diagram

The actual diagram. Note that *T* is what we have been calling *W*, and *W* is proportional to *t* in the Hubbard Model.



Zaanen, Sawatzky, Allen, *Phys. Rev. Lett.* **55** (1985) 418–421.

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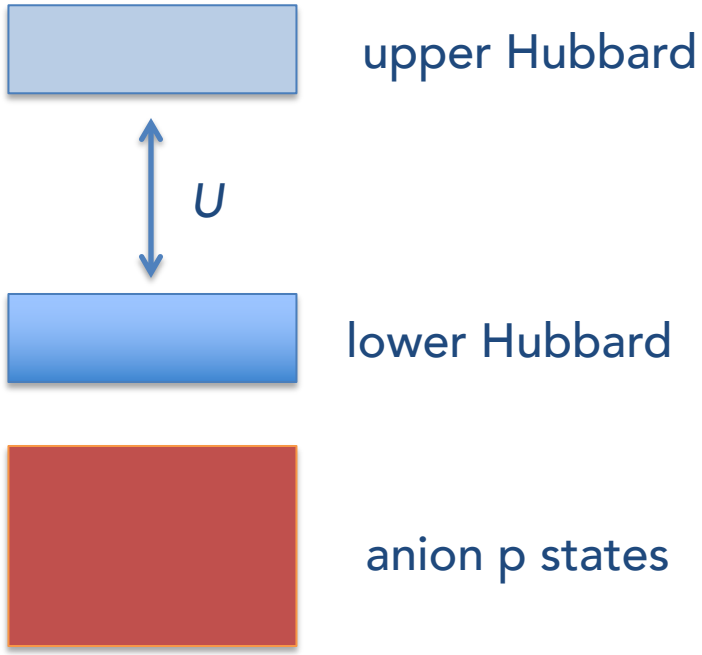
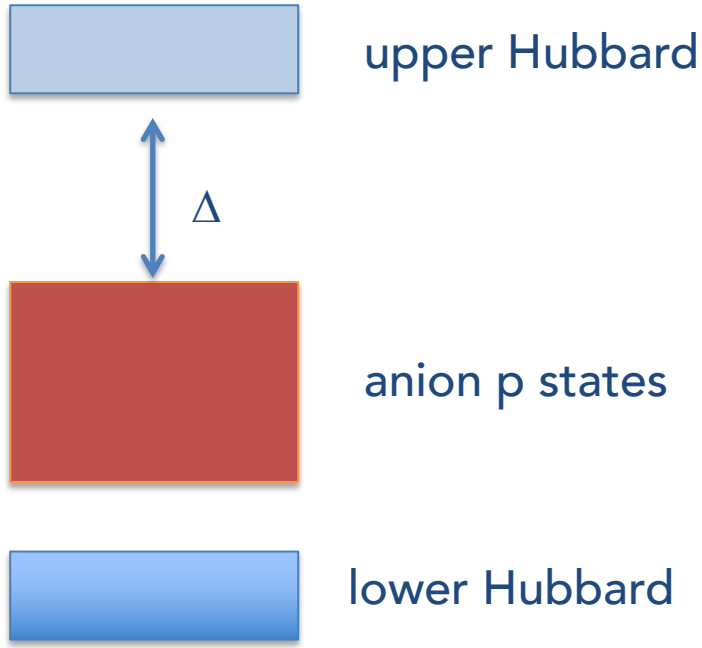
The Zaanen-Sawatzky-Allen phase diagram

A simplified view: In the language of ZSA:

Mott-Hubbard insulators:



Charge-transfer insulators:



Zaanen, Sawatzky, Allen, *Phys. Rev. Lett.* **55** (1985) 418–421.

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The Zaanen-Sawatzky-Allen phase diagram

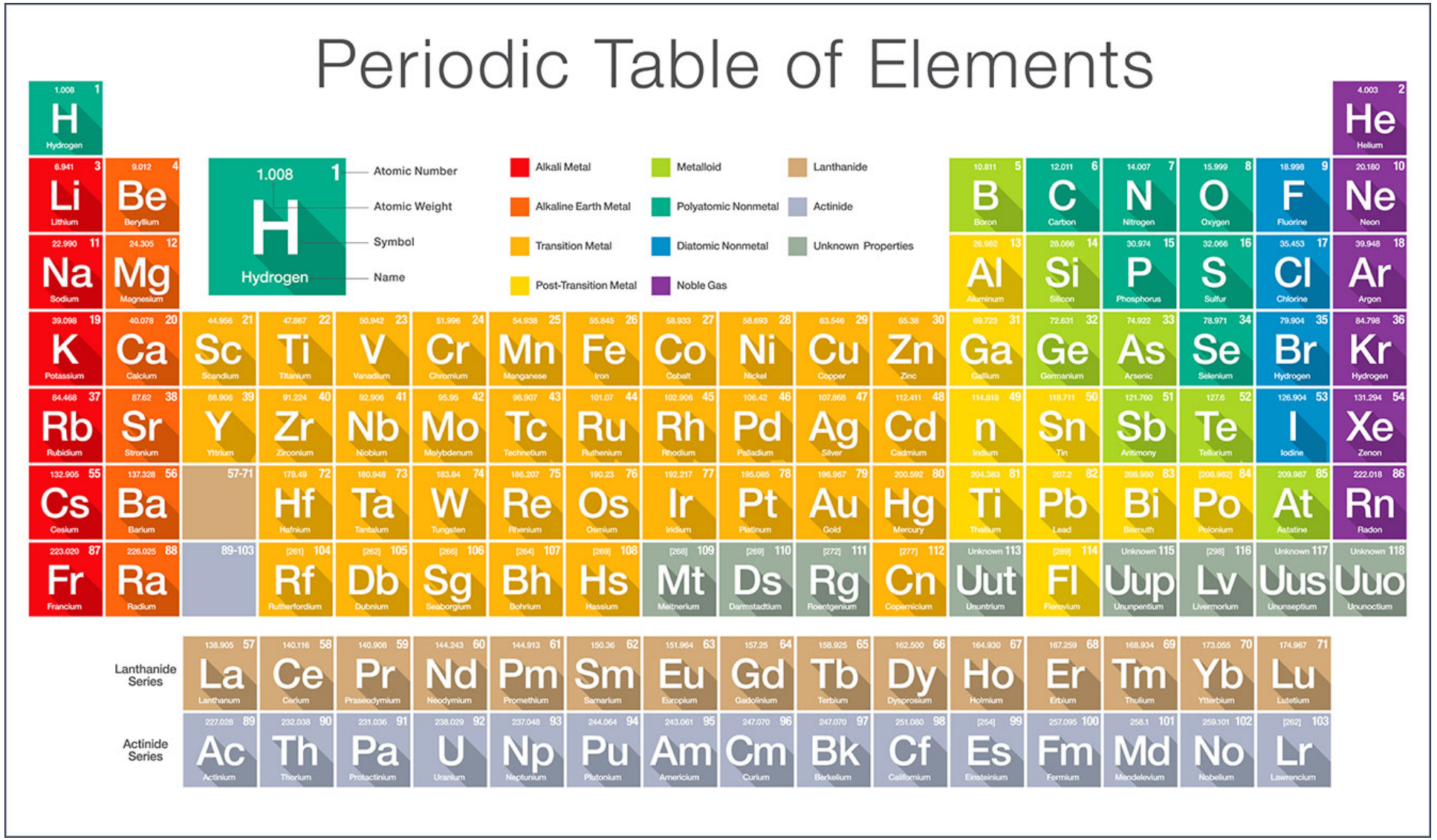
Examples of Mott-Hubbard: V_2O_3, Ti_2O_3, and most halides. Early transition metals, and lower oxidation states. Interestingly, these display T-dependent M–I transitions.

Examples of Charge-transfer: CuO, $NiCl_2$, NiS, *etc.* Later transition metals and higher oxidation states. CuO and $NiCl_2$ are always insulating.

Zaanen, Sawatzky, Allen, *Phys. Rev. Lett.* **55** (1985) 418–421.

seshadri@mrl.ucsb.edu

The Zaanen-Sawatzky-Allen phase diagram. Periodic trends



Zaanen, Sawatzky, Allen, *Phys. Rev. Lett.* **55** (1985) 418–421.

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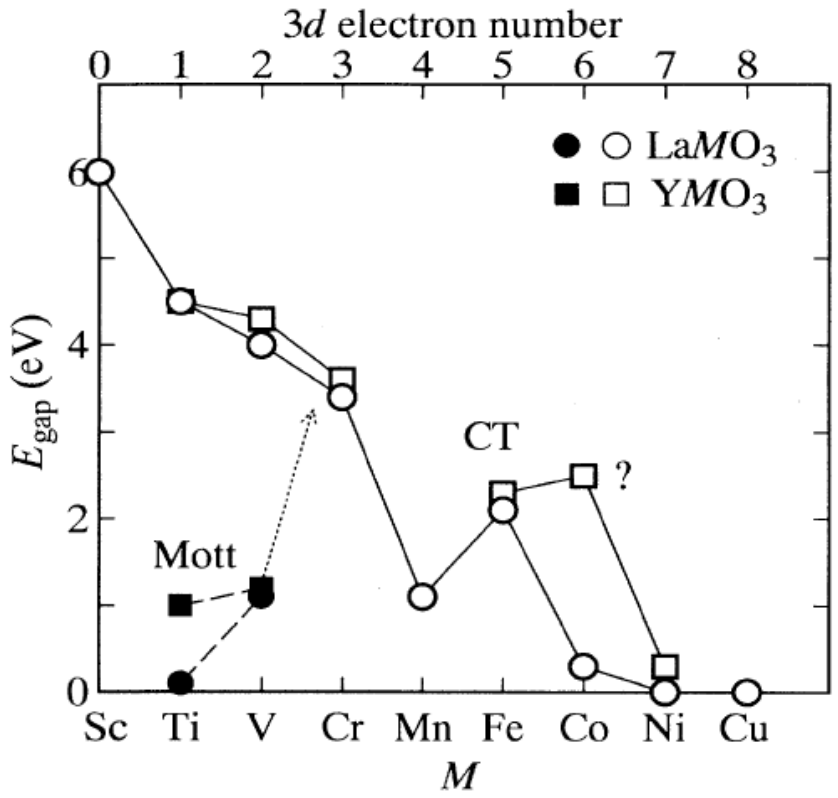
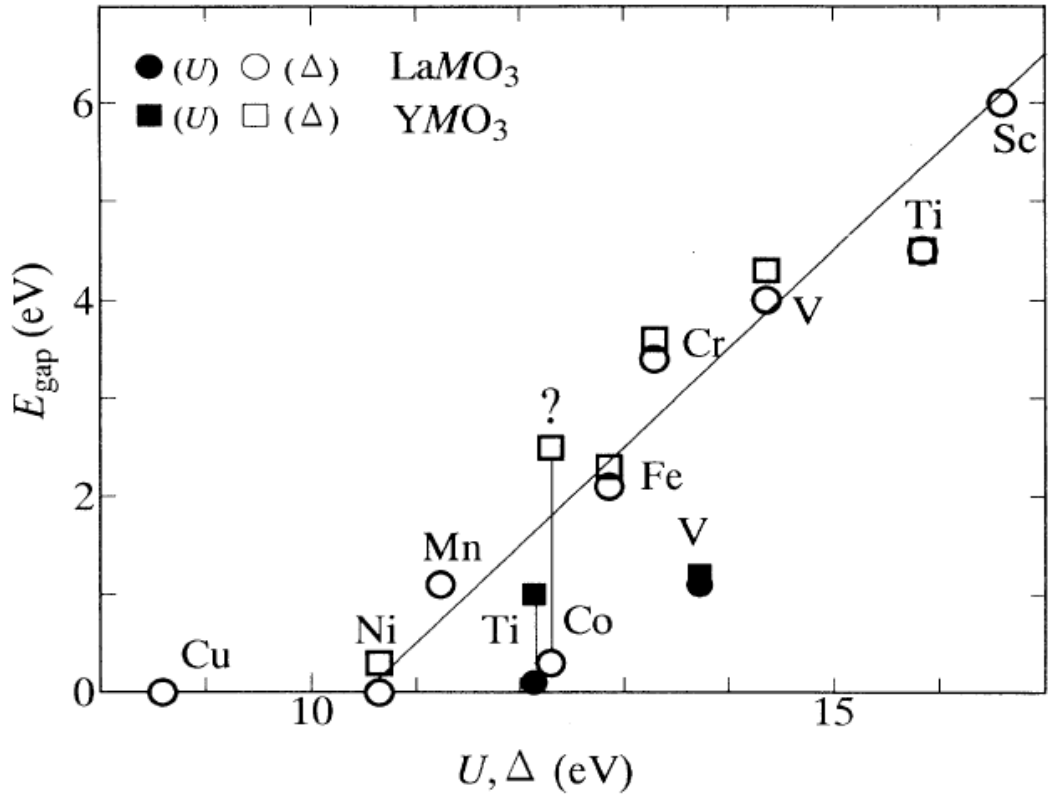
The Zaanen-Sawatzky-Allen phase diagram and perovskites

Optical studies of band gaps: Distinguishing d–d and p–d character:





Zaanen, Sawatzky, Allen, *Phys. Rev. Lett.* **55** (1985) 418–421.

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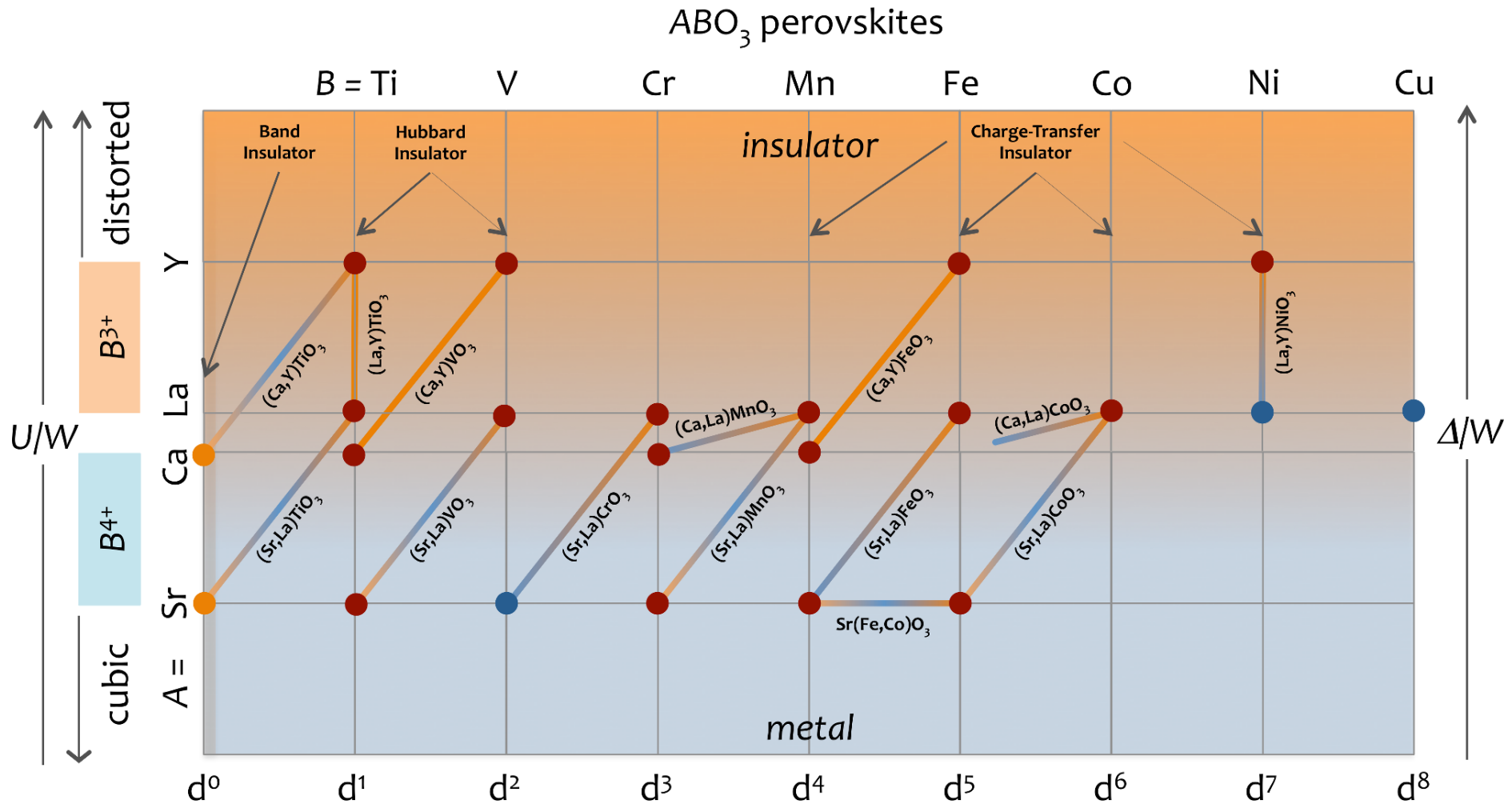
The Zaanen-Sawatzky-Allen phase diagram and perovskites



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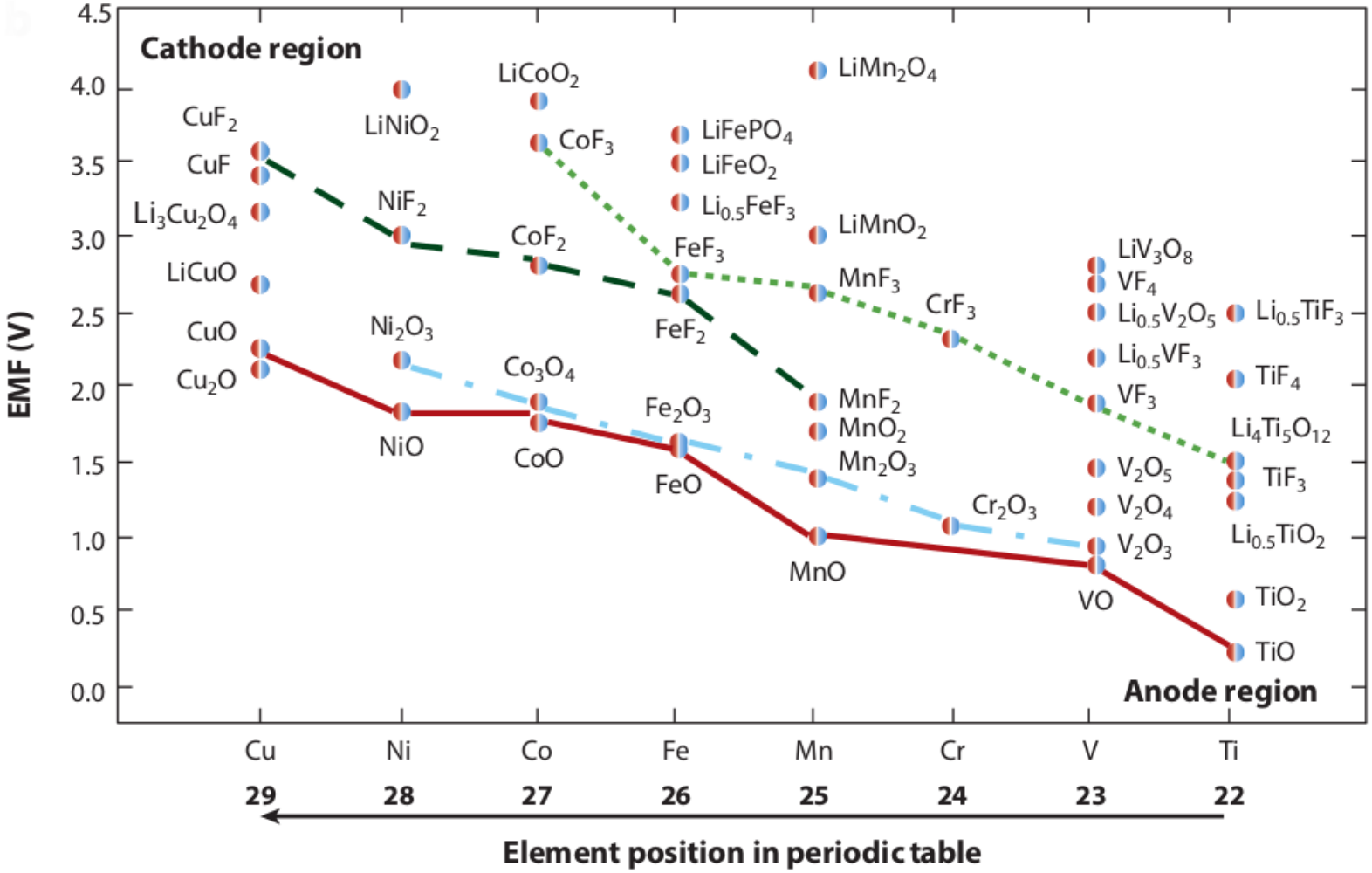
The Zaanen-Sawatzky-Allen phase diagram and batteries

The transition metal d and anion p levels manifest in Li-battery electrochemistry.



Hayner, Zhao, Kung, *Annu. Rev. Chem. Biomolec. Eng.* **3** (2012) 445–471.

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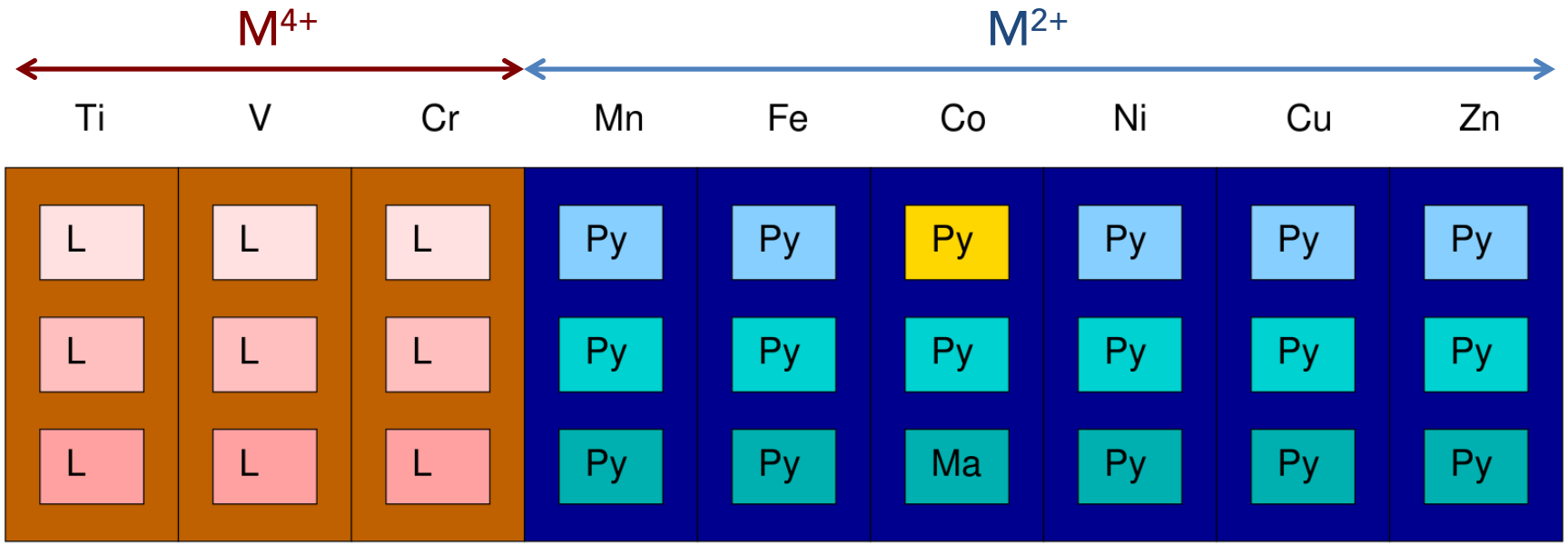
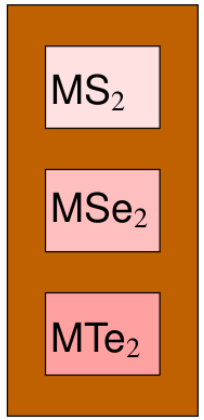
The Zaanen-Sawatzky-Allen phase diagram and redox competition



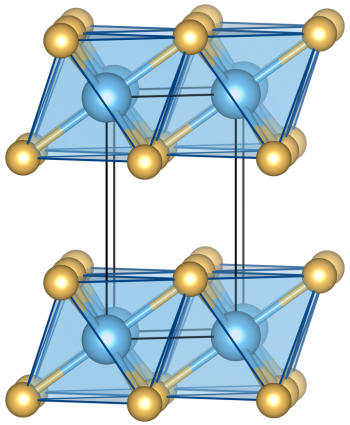


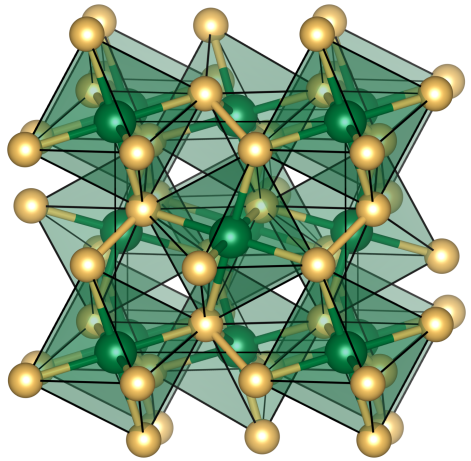
Py = pyrite

Ma = marcasite

L = layered

Py ferromagnetic





Ideas of Goodenough, Rouxel *etc.*

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