Transition Metal Oxides

A. J. Millis
Department of Physics
Columbia University

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Outline

1. Introduction: History

2. Overview: Phenomena

3. Basic Chemistry and Electronic Structure

4. Theory--General

5. Dynamical Mean Field Theory and Oxides

6. Applications and Prospects

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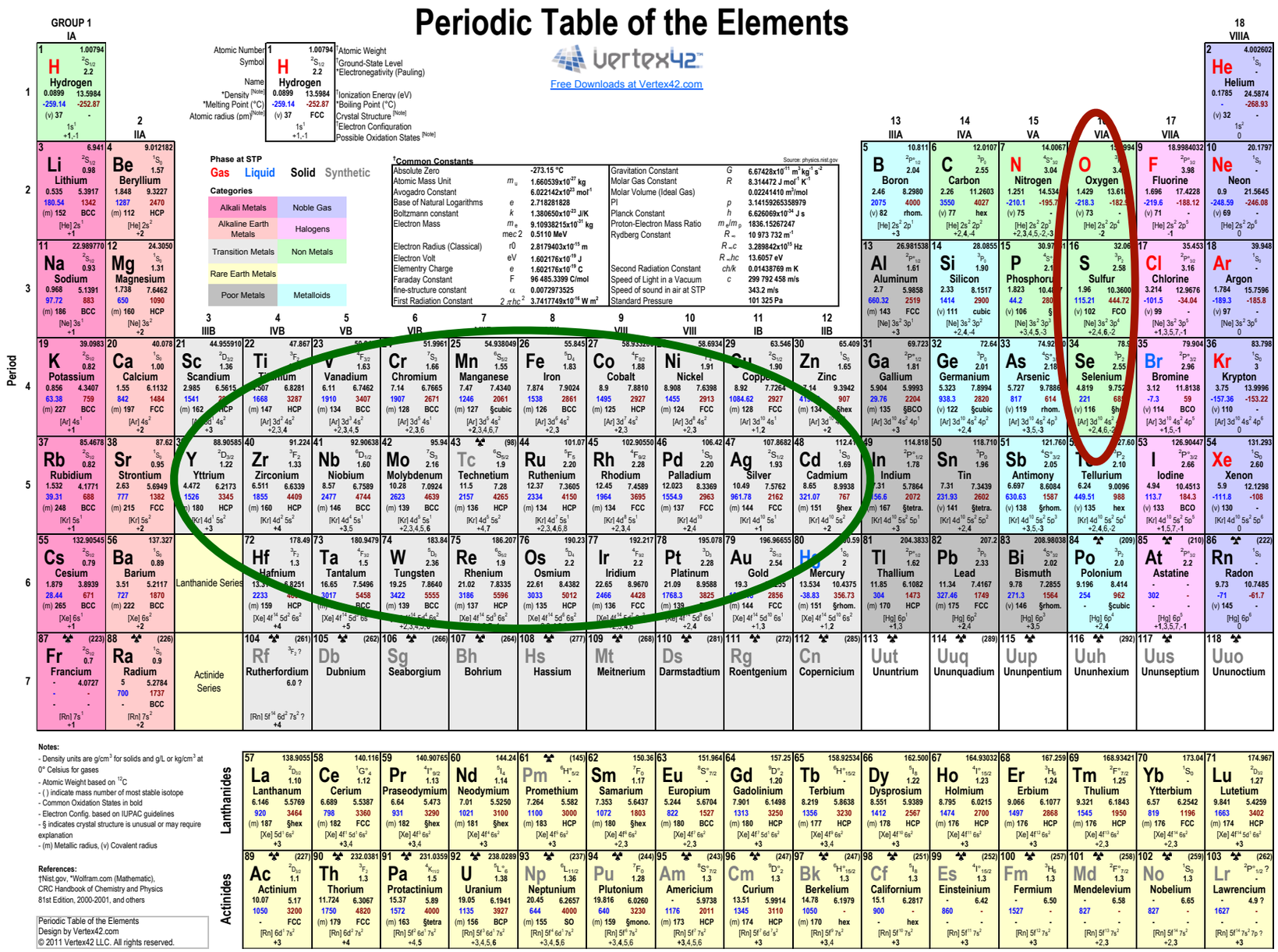
Transition metal ``oxides”



1 (or more) from transition metal group

1 (or more) from group VIA (O, or S, Se)

Plus other atoms (playing mainly structural role)

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Some jargon

Transition metal series: fill d-shell

`Early' (left side)

`Late' (right side)

3d

4d

5d

4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB
22 47.867	23 50.9415	24 51.9961	25 54.938049	26 55.845	27 58.933200	28 58.6934	29 63.546	30 65.409
Ti $^3F_2$ 1.54	V $^4F_{3/2}$ 1.63	Cr $^7S_3$ 1.66	Mn $^6S_{5/2}$ 1.55	Fe $^5D_4$ 1.83	Co $^4F_{9/2}$ 1.88	Ni $^3F_4$ 1.91	Cu $^2S_{1/2}$ 1.90	Zn $^1S_0$ 1.65
Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
4.507 6.8281	6.11 6.7462	7.14 6.7665	7.47 7.4340	7.874 7.9024	8.9 7.8810	8.908 7.6398	8.92 7.7264	7.14 9.3942
1668 3287	1910 3407	1907 2671	1246 2061	1538 2861	1495 2927	1455 2913	1084.62 2927	419.53 907
(m) 147 HCP	(m) 134 BCC	(m) 128 BCC	(m) 127 §cubic	(m) 126 BCC	(m) 125 HCP	(m) 124 FCC	(m) 128 FCC	(m) 134 §hex
[Ar] $3d^2 4s^2$ +2,3,4	[Ar] $3d^3 4s^2$ +2,3,4,5	[Ar] $3d^5 4s^1$ +2,3,6	[Ar] $3d^5 4s^2$ +2,3,4,6,7	[Ar] $3d^6 4s^2$ +2,3	[Ar] $3d^7 4s^2$ +2,3	[Ar] $3d^8 4s^2$ +2,3	[Ar] $3d^{10} 4s^1$ +1,2	[Ar] $3d^{10} 4s^2$ +2
40 91.224	41 92.90638	42 95.94	43 ☢ (98)	44 101.07	45 102.90550	46 106.42	47 107.8682	48 112.411
Zr $^3F_2$ 1.33	Nb $^6D_{1/2}$ 1.60	Mo $^7S_3$ 2.16	Tc $^6S_{5/2}$ 1.9	Ru $^5F_5$ 2.20	Rh $^4F_{9/2}$ 2.28	Pd $^1S_0$ 2.20	Ag $^2S_{1/2}$ 1.93	Cd $^1S_0$ 1.69
Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium
6.511 6.6339	8.57 6.7589	10.28 7.0924	11.5 7.28	12.37 7.3605	12.45 7.4589	12.023 8.3369	10.49 7.5762	8.65 8.9938
1855 4409	2477 4744	2623 4639	2157 4265	2334 4150	1964 3695	1554.9 2963	961.78 2162	321.07 767
(m) 160 HCP	(m) 146 BCC	(m) 139 BCC	(m) 136 HCP	(m) 134 HCP	(m) 134 FCC	(m) 137 FCC	(m) 144 FCC	(m) 151 §hex
[Kr] $4d^2 5s^2$ +4	[Kr] $4d^4 5s^1$ +3,5	[Kr] $4d^5 5s^1$ +2,3,4,5,6	[Kr] $4d^5 5s^2$ +4,7	[Kr] $4d^7 5s^1$ +2,3,4,6,8	[Kr] $4d^8 5s^1$ +2,3,4	[Kr] $4d^{10}$ +2,4	[Kr] $4d^{10} 5s^1$ +1	[Kr] $4d^{10} 5s^2$ +2
72 178.49	73 180.9479	74 183.84	75 186.207	76 190.23	77 192.217	78 195.078	79 196.96655	80 200.59
Hf $^3F_2$ 1.3	Ta $^4F_{3/2}$ 1.5	W $^5D_0$ 2.36	Re $^6S_{5/2}$ 1.9	Os $^5D_4$ 2.2	Ir $^4F_{9/2}$ 2.2	Pt $^3D_3$ 2.28	Au $^2S_{1/2}$ 2.54	Hg $^1S_0$ 2
Hafnium	Tantalum	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury
13.31 6.8251	16.65 7.5496	19.25 7.8640	21.02 7.8335	22.61 8.4382	22.65 8.9670	21.09 8.9588	19.3 9.2255	13.534 10.4375
2233 4603	3017 5458	3422 5555	3186 5596	3033 5012	2466 4428	1768.3 3825	1064.18 2856	-38.83 356.73
(m) 159 HCP	(m) 146 BCC	(m) 139 BCC	(m) 137 HCP	(m) 135 HCP	(m) 136 FCC	(m) 139 FCC	(m) 144 FCC	(m) 151 §rhom.
[Xe] $4f^{14} 5d^2 6s^2$ +4	[Xe] $4f^{14} 5d^3 6s^2$ +5	[Xe] $4f^{14} 5d^4 6s^2$ +2,3,4,5,6	[Xe] $4f^{14} 5d^5 6s^2$ +2,4,6,7,-1	[Xe] $4f^{14} 5d^6 6s^2$ +2,3,4,6,8	[Xe] $4f^{14} 5d^7 6s^2$ +2,3,4,6	[Xe] $4f^{14} 5d^9 6s^1$ +2,4	[Xe] $4f^{14} 5d^{10} 6s^1$ +1,3	[Xe] $4f^{14} 5d^{10} 6s^2$ +1,2

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Long history in condensed matter physics

Frederich Wohler 1823

WO_3: insulator (dull black)

add sodium

Na_xWO_3:
shiny metal

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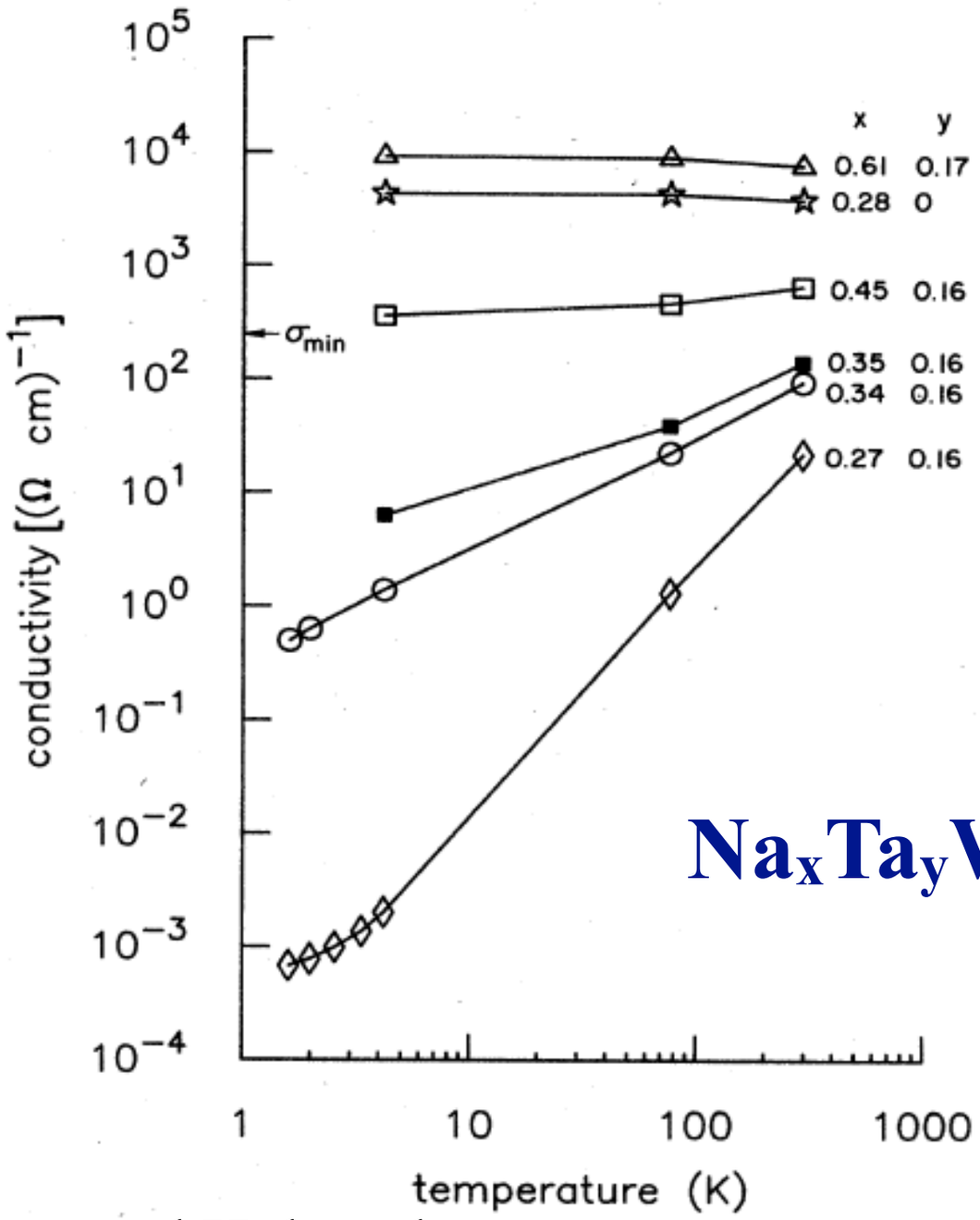
In modern terms: doping-driven metal insulator transition



$Na_xTa_yWO_3$: # added electrons=x-y

Dubson and Holcomb,
Phys. Rev. B32 1955 (1985)

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More history

1897: J.J. Thompson discovers electron.

Natural inference: transport and optical properties largely determined by electrons

1900: Drude--classical model of electronic conduction

Classical mechanics: mean velocity ~ $T^{1/2}$
idea: conduction should cease as T->0

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More history

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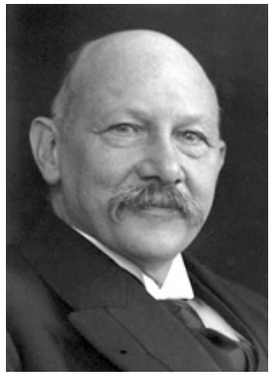
idea: conduction should cease as T->0

This idea motivated Kamerlingh-Onnes to investigate properties of metals at very low T



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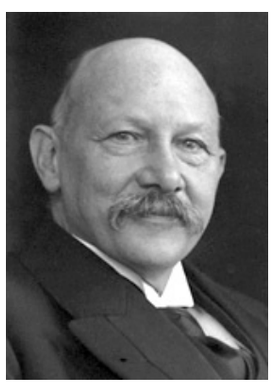
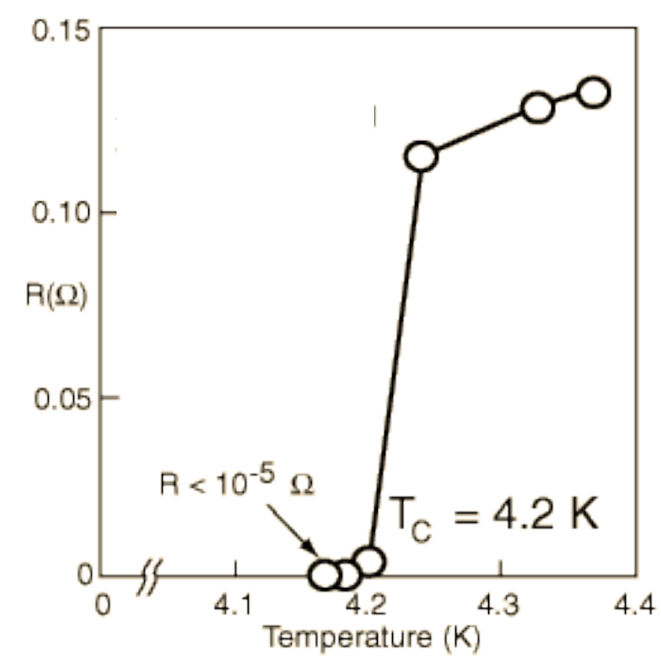


=>superconductivity!!



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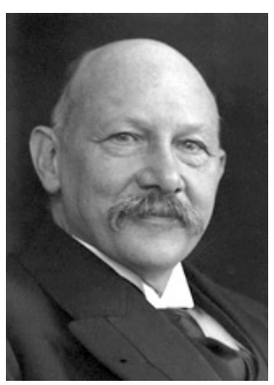
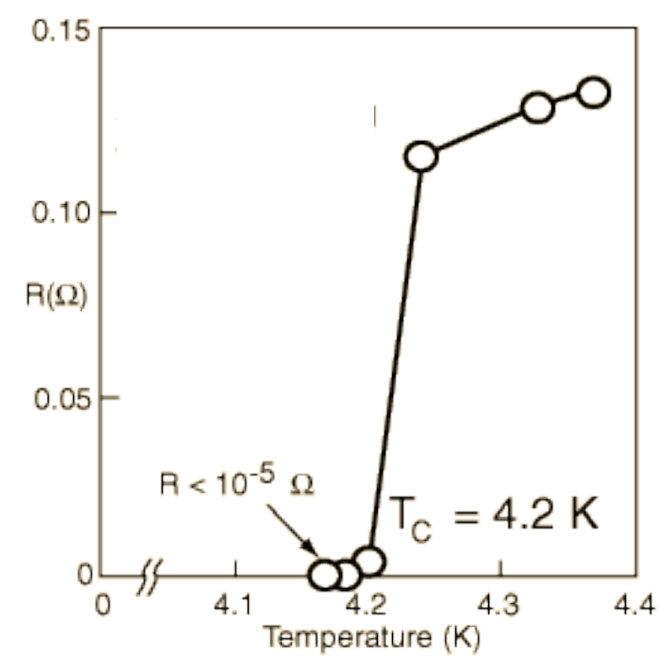


=>superconductivity!!



Importance of theory (even if wrong or incomplete) in motivating experiment

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More history

1920s: Sommerfeld, Peierls, Bloch--quantum theory

Fermi statistics=> non-zero electron velocity even at T=0

Neglect electron-electron interactions =>basic equation:

$$\mathbf{H} = -\sum_{\mathbf{i}} \frac{\nabla_{\mathbf{i}}^{2}}{2\mathbf{m}} + \mathbf{V}_{\mathbf{lattice}}(\mathbf{r}_{\mathbf{i}})$$

eigenfunctions: $\psi_{\mathbf{nk}}(\mathbf{r}) = \mathbf{e}^{\mathbf{ik}\cdot\mathbf{r}}\mathbf{u}_{\mathbf{nk}}(\mathbf{r})$

modulated plane wave, extended throughout solid; propagates at nonzero group velocity=>theory of metallic conduction

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1931: Enter A. H. Wilson

The Master and Fellows of Trinity College Cambridge; taken from http://www.computerhistory.org/semiconductor/timeline/1931-The-Theory.html

Bloch's theory had in fact proved too much. Before his paper appeared it was difficult to understand the existence of metals. Afterwards it was the existence of insulators that required explanation. This problem had been by-passed because it had been taken for granted that insulators were merely bad conductors rather than non-conductors, the difference between metals and insulators being a quantitative and not a qualitative one. This concept I now challenged.

Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 371, No. 1744, The Beginnings of Solid State Physics (Jun. 10, 1980), 39-48.

Note: first sharp statement
metal and insulator distinct phases

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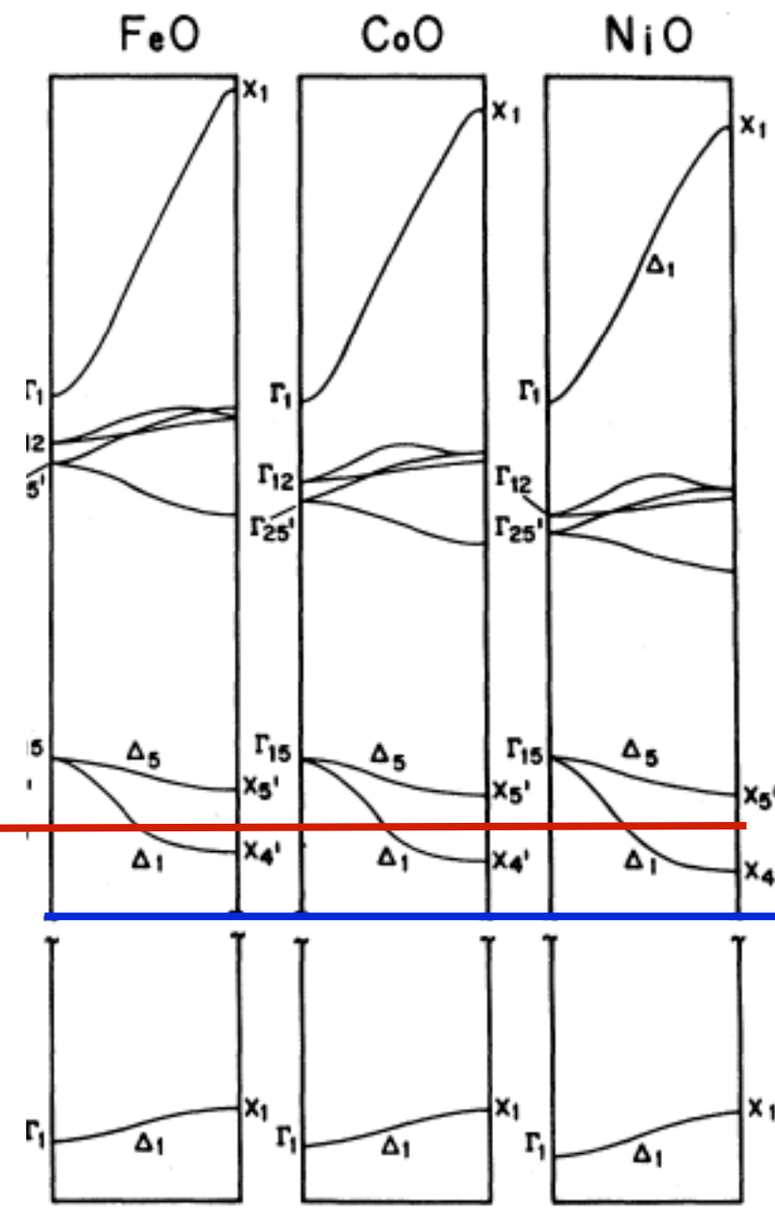
Key role of energy gap=>
sharp distinction, metal vs insulator

$$\mathbf{H} = -\sum_{\mathbf{i}} \frac{\nabla_{\mathbf{i}}^2}{2\mathbf{m}} + \mathbf{V_{lattice}(r_i)}$$



Mattheis, PRB5 290 (1972)

μ in bands: metal

μ in gap: insulator

In this theory, insulator possible only if even # electrons per cell

FeO, CoO and NiO: predicted to be metals

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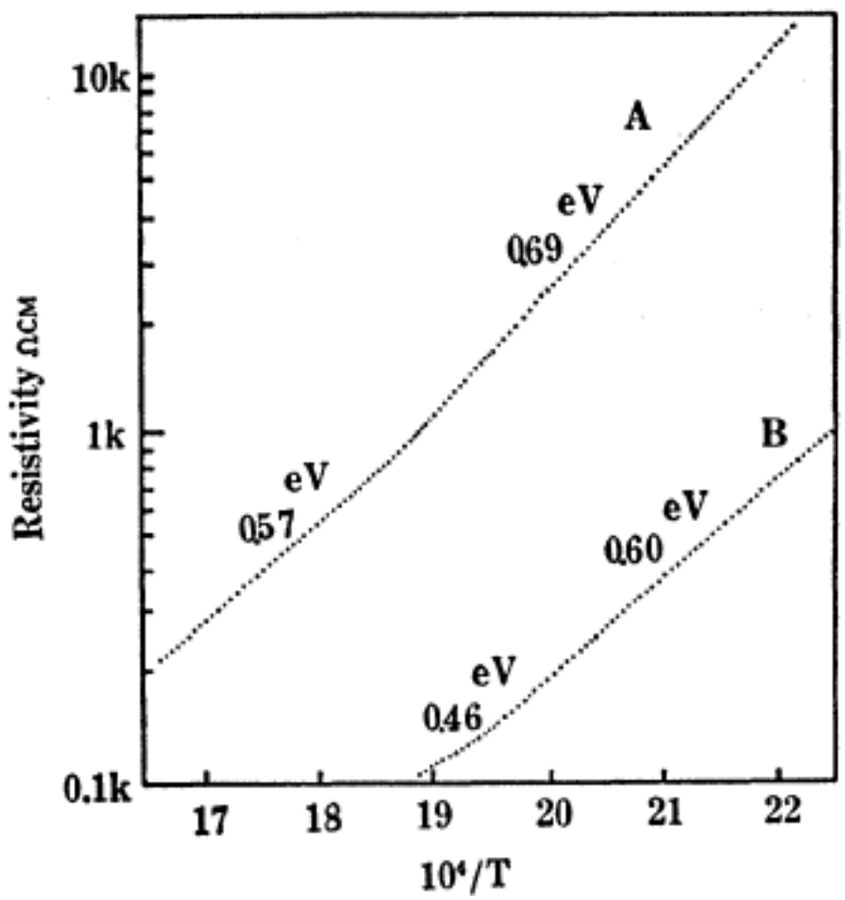
NiO is a very good insulator



Yamaka and Sawamoto PR 112 1861 1958

Discussion of the paper by de Boer and Verwey, reported by N. F. Mott with the help of some notes of R. Peierls 1937

Prof. Peierls agreed with Dr de Boer that the existence of semi-conductors with incomplete *d*-bands could not be understood merely by considering the low transparency of the potential barrier. This transparency could be perhaps 10^{-2} or 10^{-3} less than for ordinary metal but not 10^{-10}. He suggested that a rather drastic modification of the present electron theory of metals would be necessary in order to take these facts into account. The solution of the problem would probably be as follows: if the transparency of the potential barriers is low, it is quite possible that the electrostatic interaction between the electrons prevents them from moving at all. At low temperatures the majority of the electrons are in their proper places in the ions. The minority which have happened to cross the potential barrier find therefore all the other atoms occupied, and in order to get through the lattice have to spend a long time in ions already occupied by other electrons. This needs a considerable addition of energy and so is extremely improbable at low temperatures.

Peierls: Importance of electron-electron interactions in partially filled transition metal d-shell. Fundamental modification of usual ``band" picture. Need for real-space view of the physics.

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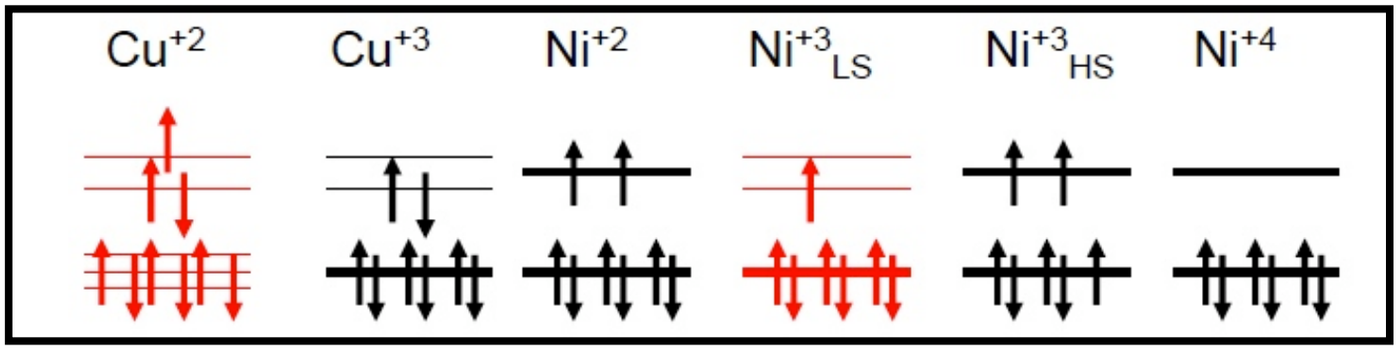
Electronic configuration of atoms complicated basic concept: 'Hubbard U'

Number of electrons on ion n_d



configuration: label by n_d, other (L,S) quantum numbers

Charging energy U:

$$E[n_d] = \frac{U}{2} n_d (n_d - 1)$$

$$U = E[d^{n_d+1}] + E[d^{n_d-1}] - 2E[d^{n_d}]$$

In transition metal oxides: U_{dd} big because d wave function small (esp in '3d' series)

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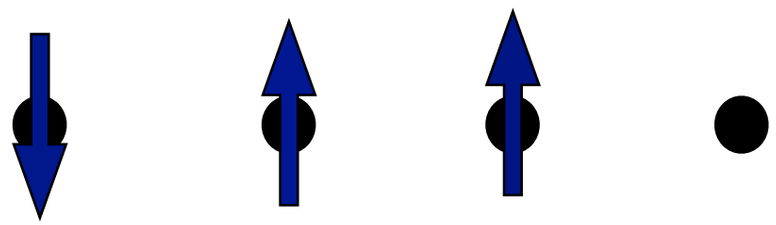
Consequence of ‘Charging energy’: Mott “blocking” effect



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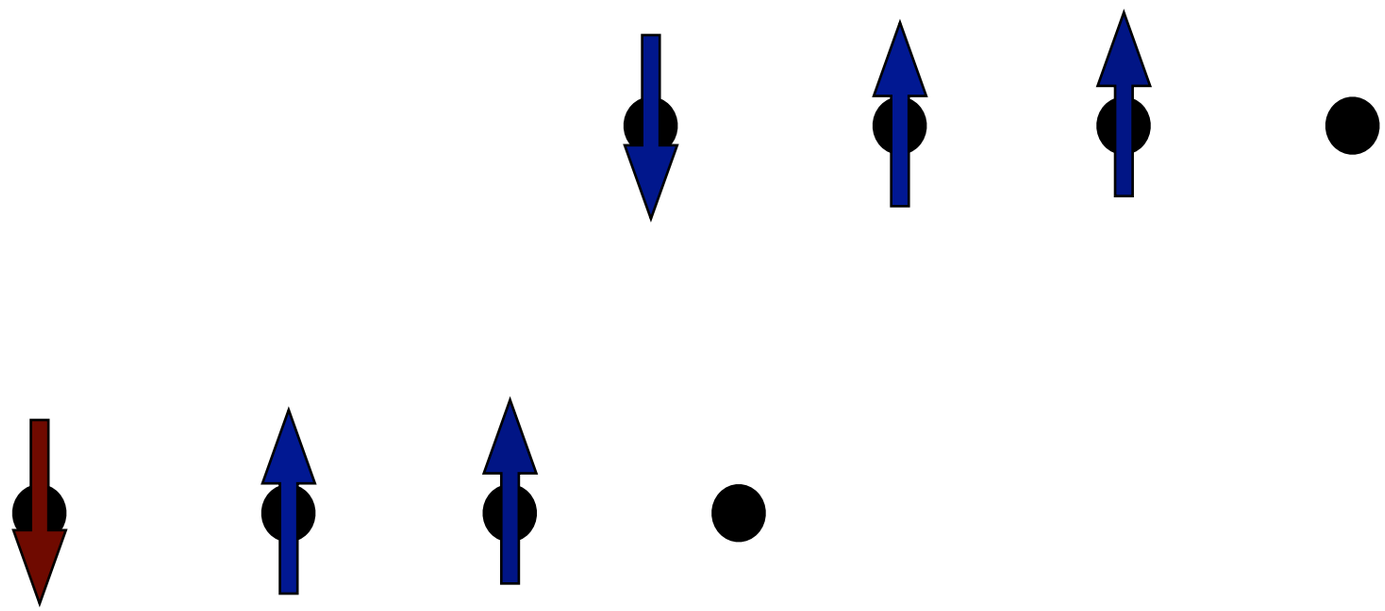

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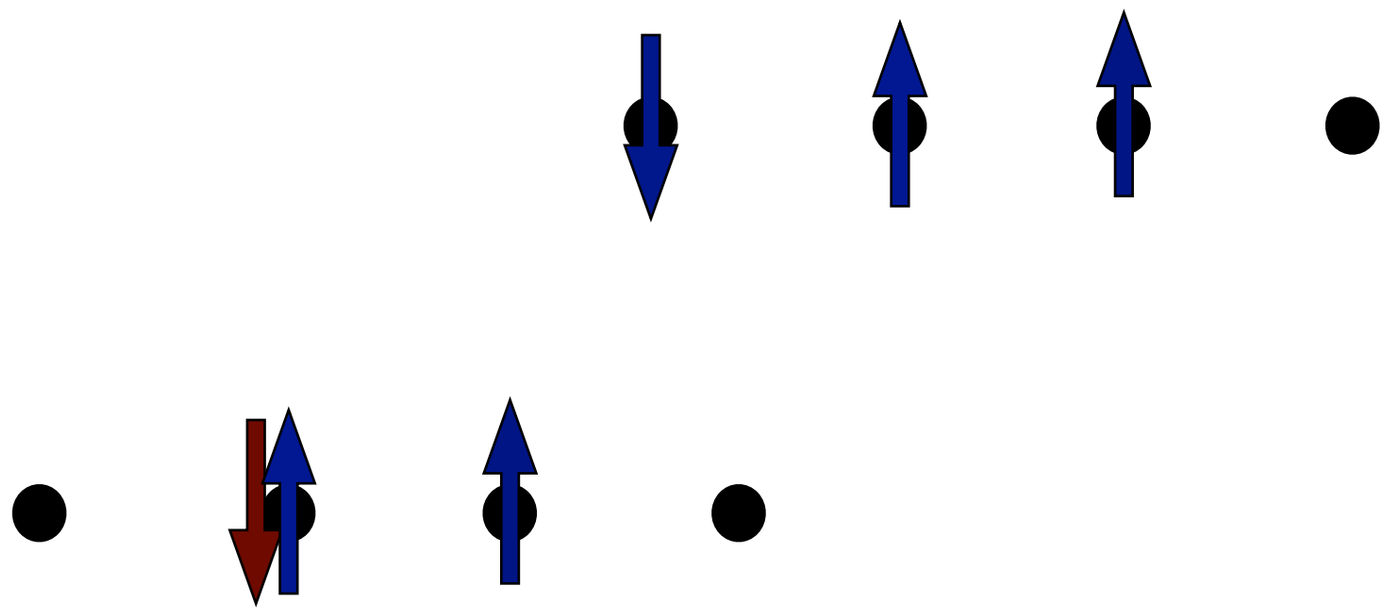

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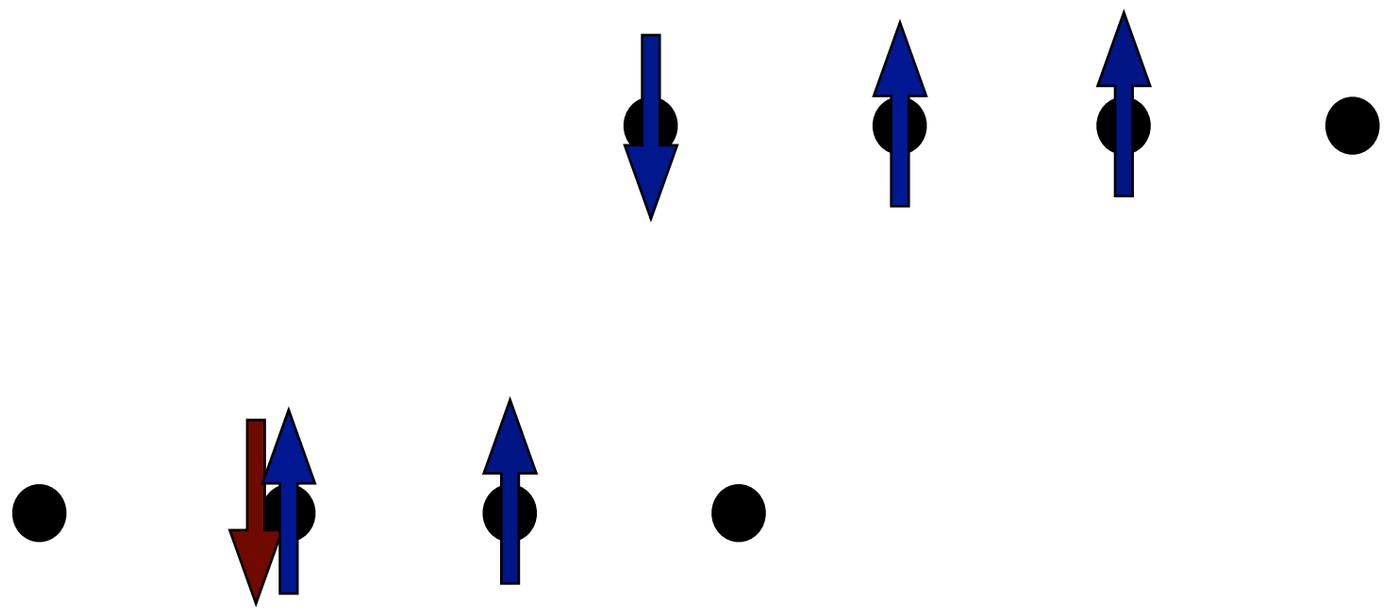

$2d^n \Rightarrow d^{n-1}d^{n+1}$ E~U

process suppressed

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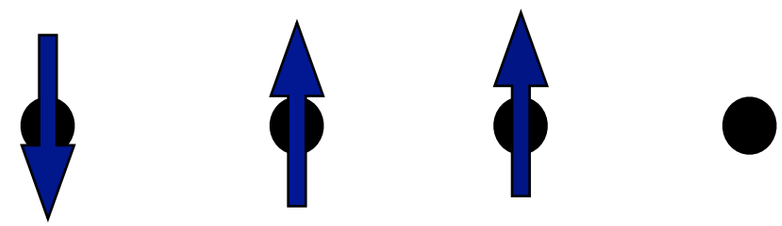
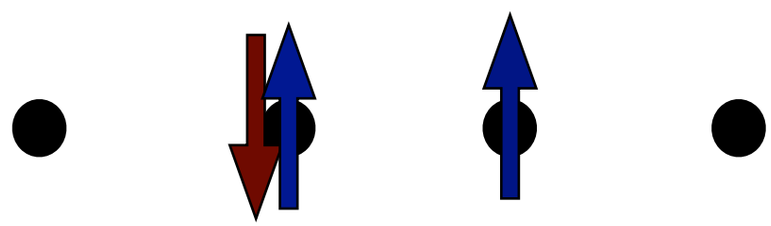
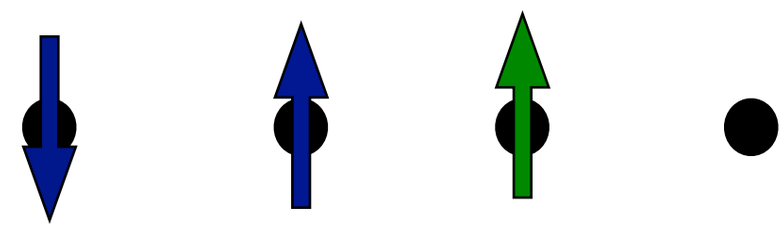
Consequence of ‘Charging energy’: Mott “blocking” effect







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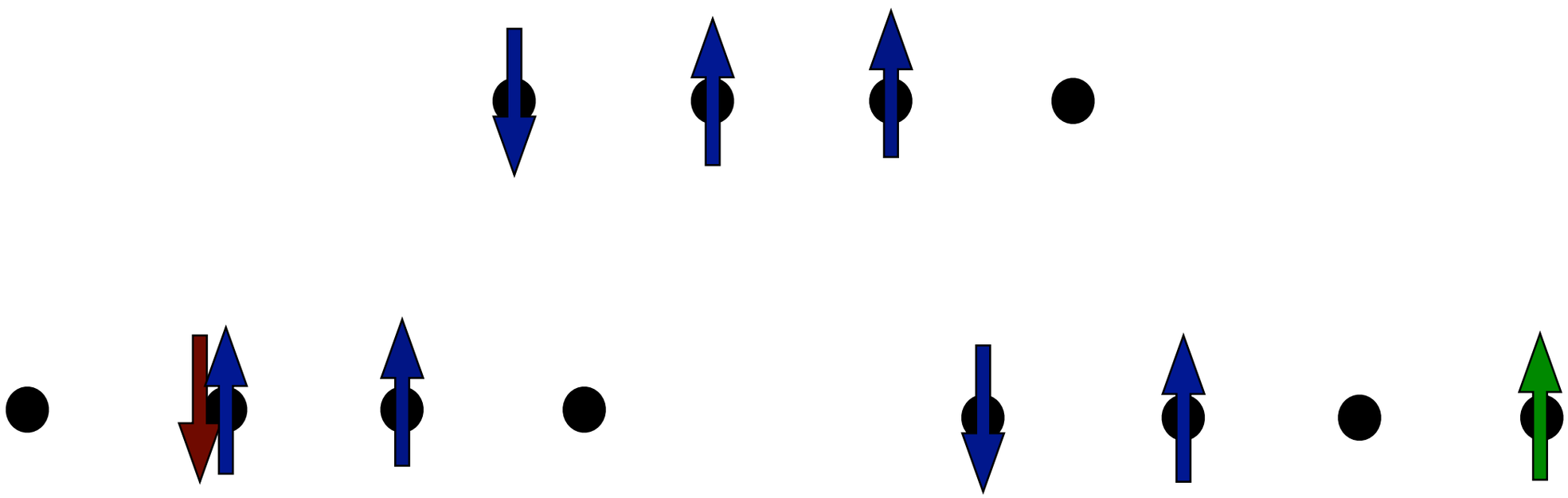

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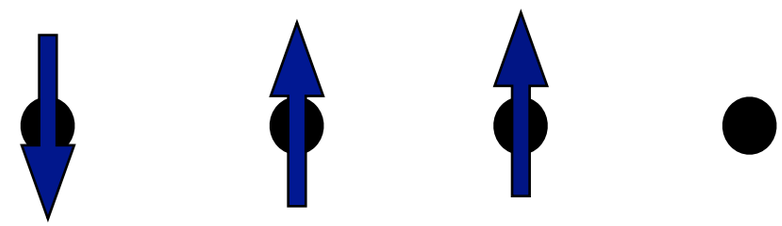
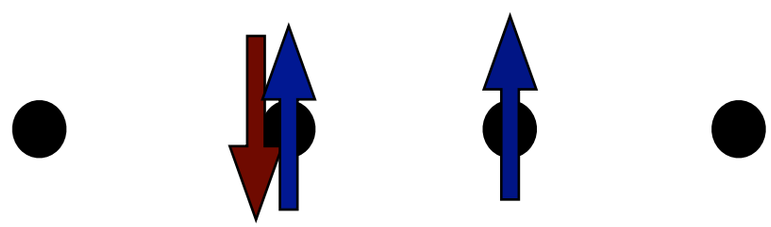
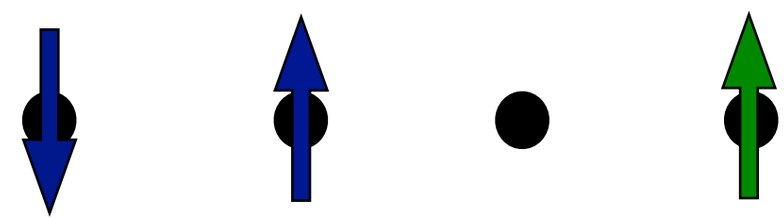




$2d^n \Rightarrow d^{n-1}d^{n+1}$ E~U
process suppressed



$d^n d^{n-1} \Rightarrow d^{n-1}d^n$
process allowed

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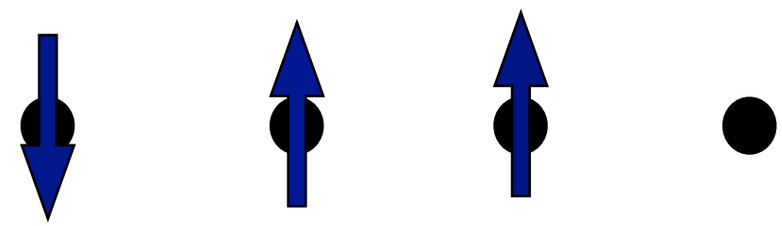
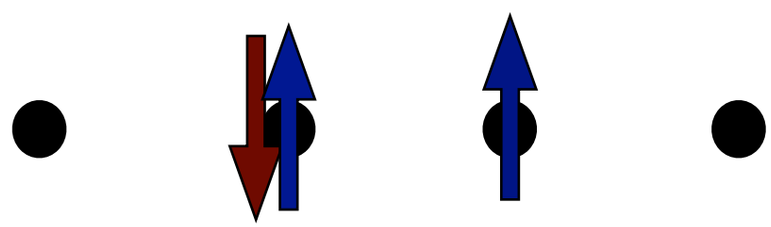
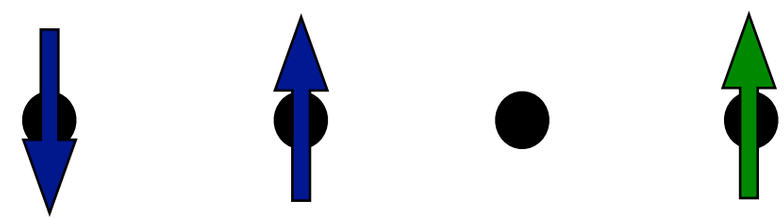
Consequence of 'Charging energy': Mott "blocking" effect





$2d^n \Rightarrow d^{n-1}d^{n+1}$ $E \sim U$

process suppressed



$d^n d^{n-1} \Rightarrow d^{n-1}d^n$

process allowed

If U large enough, only holes (or doubly occupied sites) can move=> if integer number of electrons per site: Mott insulator

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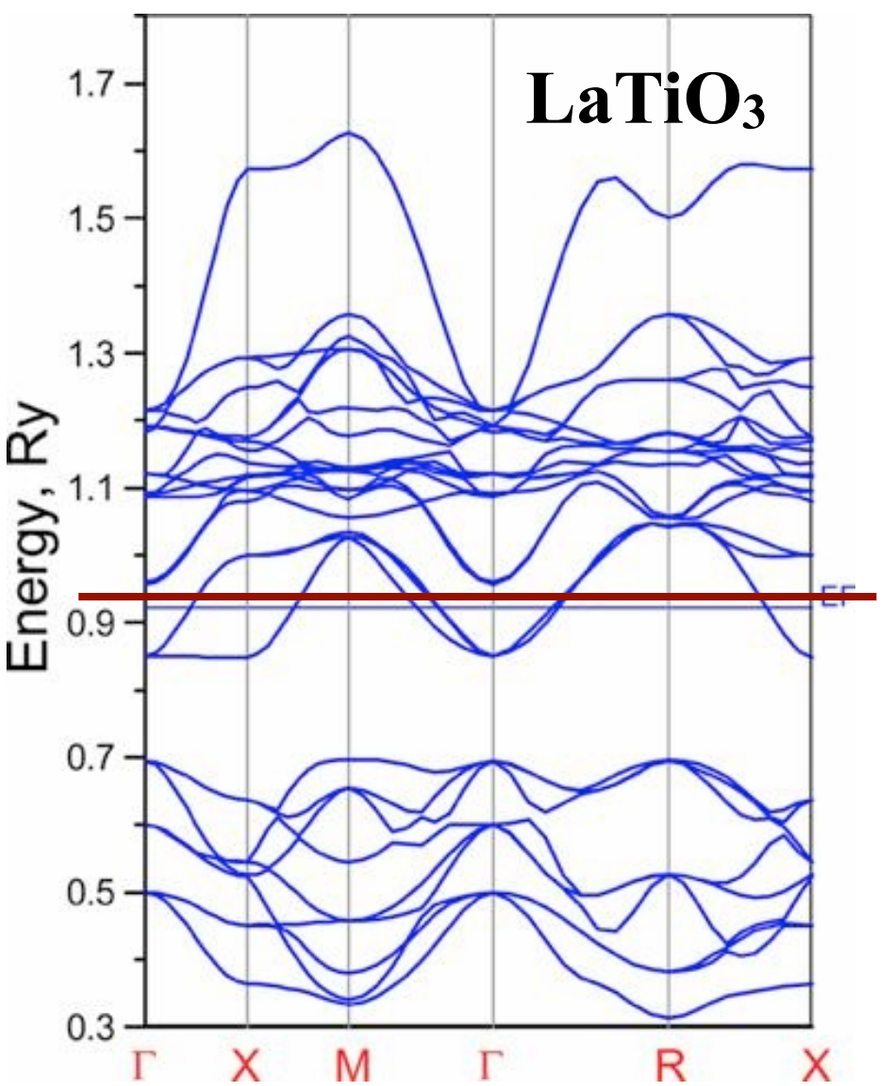
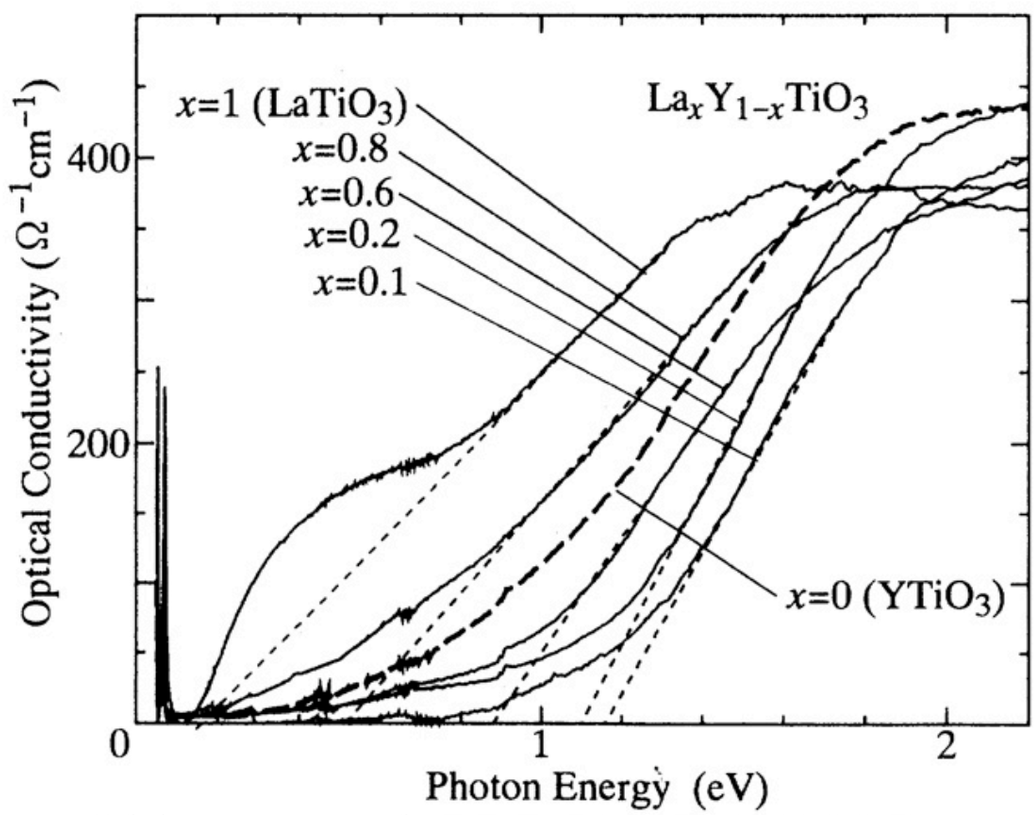
Something like this actually occurs



http://dmft.rutgers.edu/LDA/lmto/lmto_run.htm

$LaTiO_3$:

- **# electrons/unit cell is odd**
- **material is insulating!**
- **$YTiO_3$ even more insulating**



Okimoto et al. PRB51 9581 (1995)

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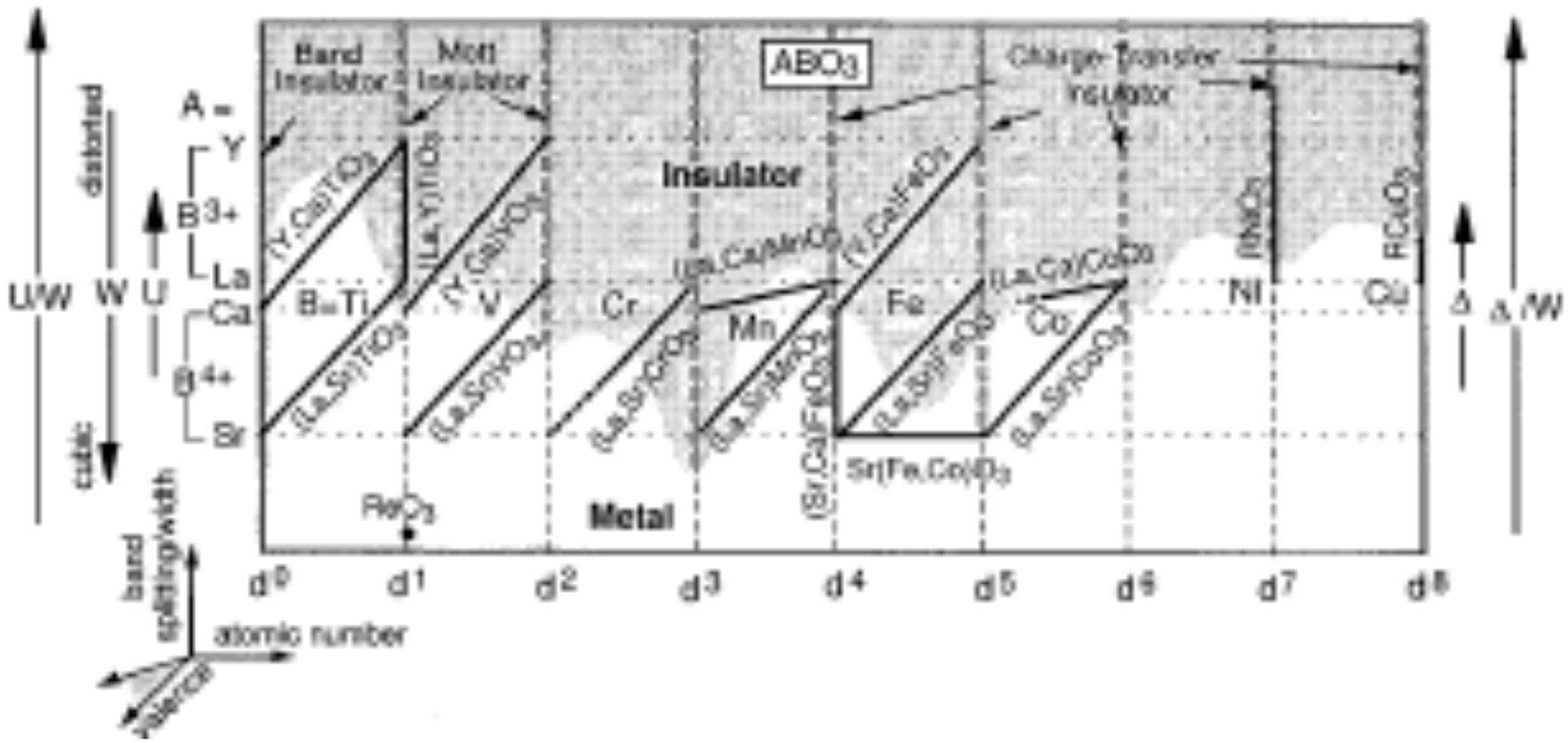
`Mott' insulator: fundamental paradigm for oxides



But be careful: in many cases ``Mott" is not the controlling physics

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Basic properties of transition metals and their oxides

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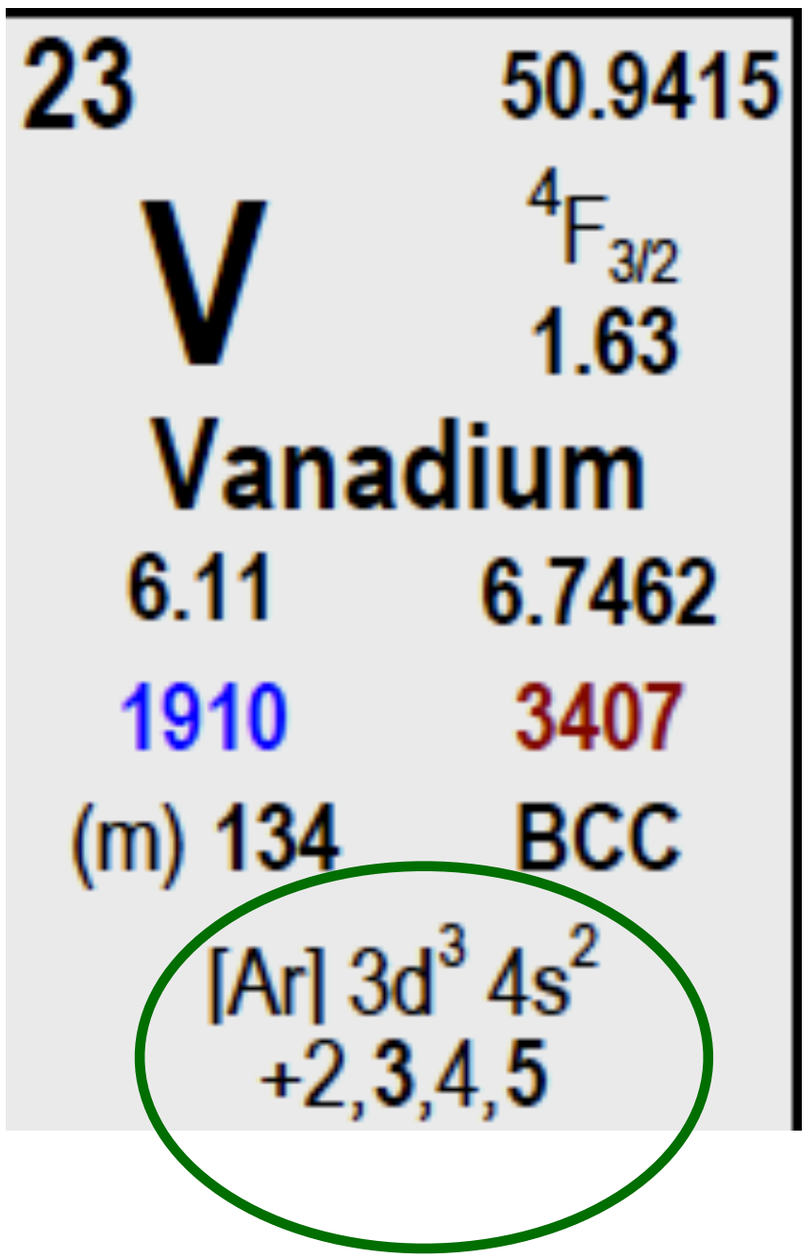
Transition metal ion: many accessible valence states



***Partly filled d-shell =>spin and orbital degrees of freedom active**

***Multiple valence states=>many electronic configurations, many bonding modalities easily available**

***energies of different transition metal valences compatible with energies of different oxygen charge states =>tunability of materials properties**

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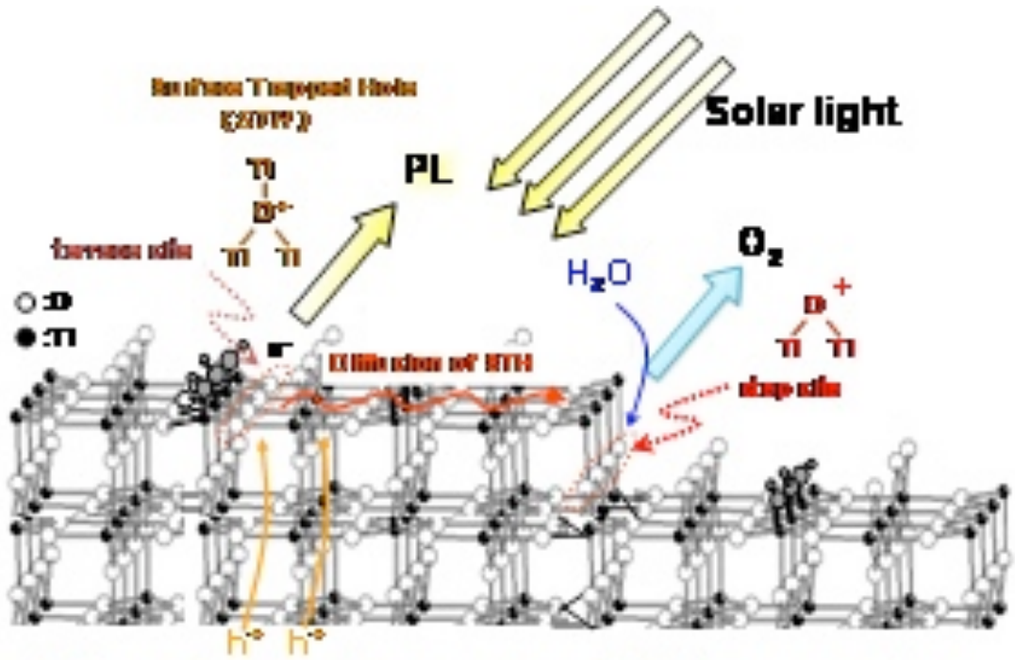
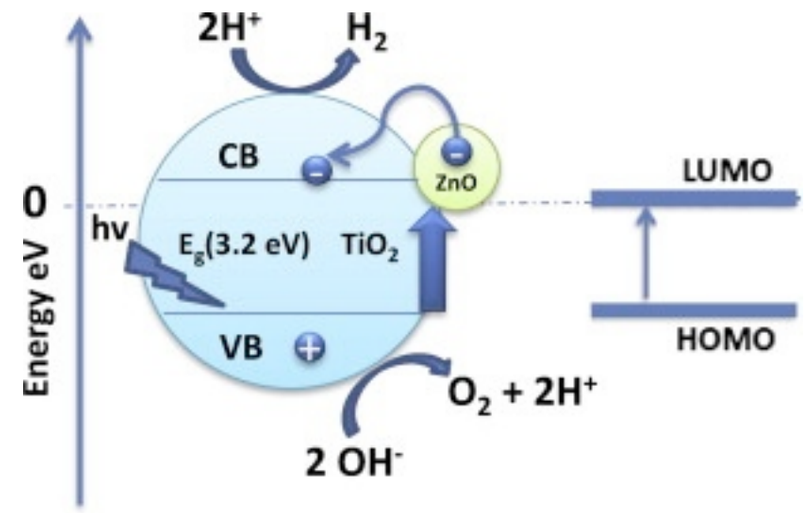
Application: Catalysis
(ex: photon-induced water splitting)



Photon-induced water splitting reaction mechanism on TiO_2 electrode

spigse.chem.es.osaka-u.ac.jp



sciencedirect.com

Works, in essence, because of multiple d-valence: it is easy to transfer electrons back and forth between free oxygen and transition metal ions.

Goal: manipulate band-gap to match solar spectrum

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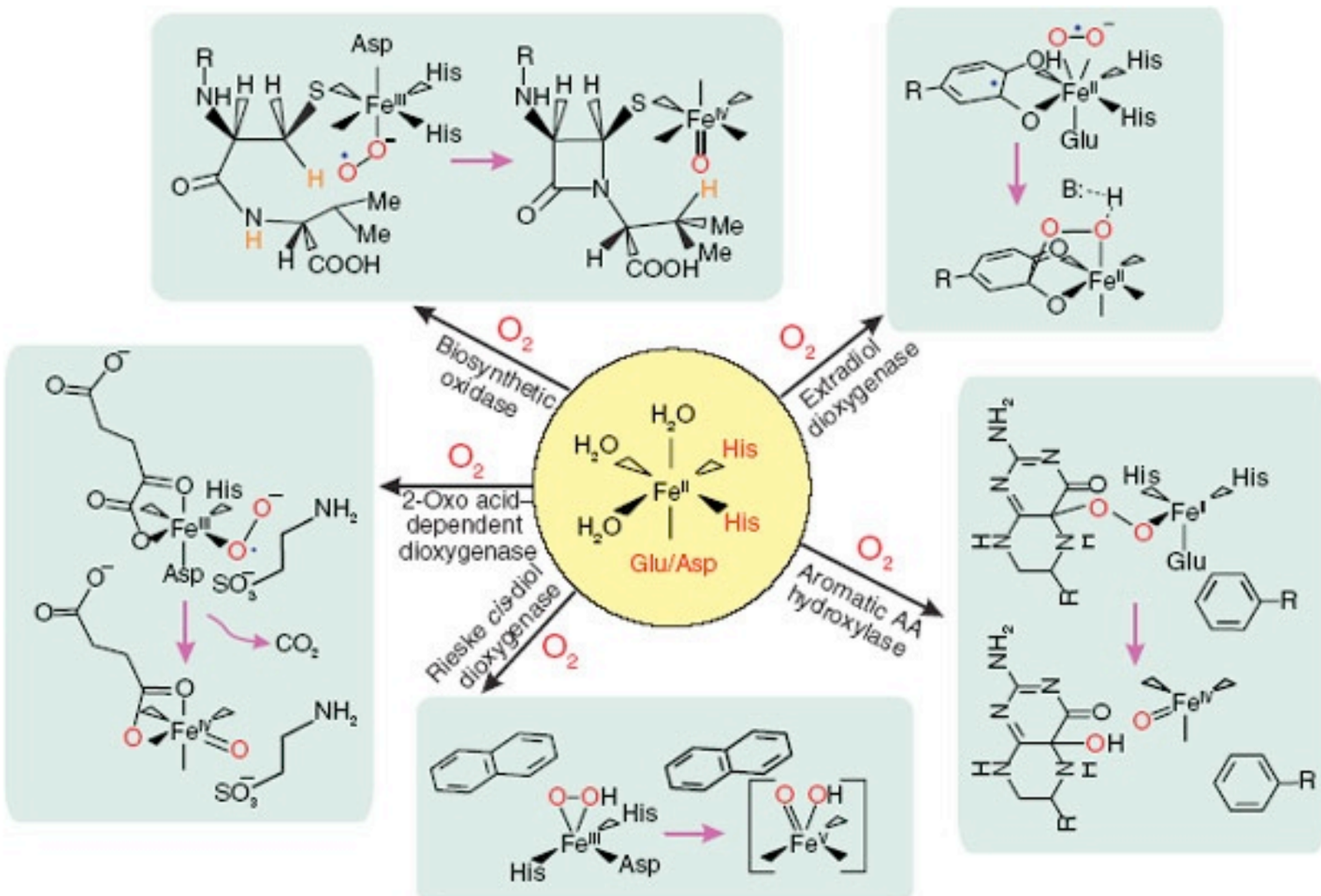
Application: Respiration etc in biochemistry



From the following article
Versatility of biological non-heme Fe(II) centers in oxygen activation reactions
Elena G Kovaleva & John D Lipscomb
Nature Chemical Biology **4**, 186 - 193 (2008)

Works, in essence, because of multiple d-valence: it is easy to transfer electrons back and forth between free oxygen and Fe complex.

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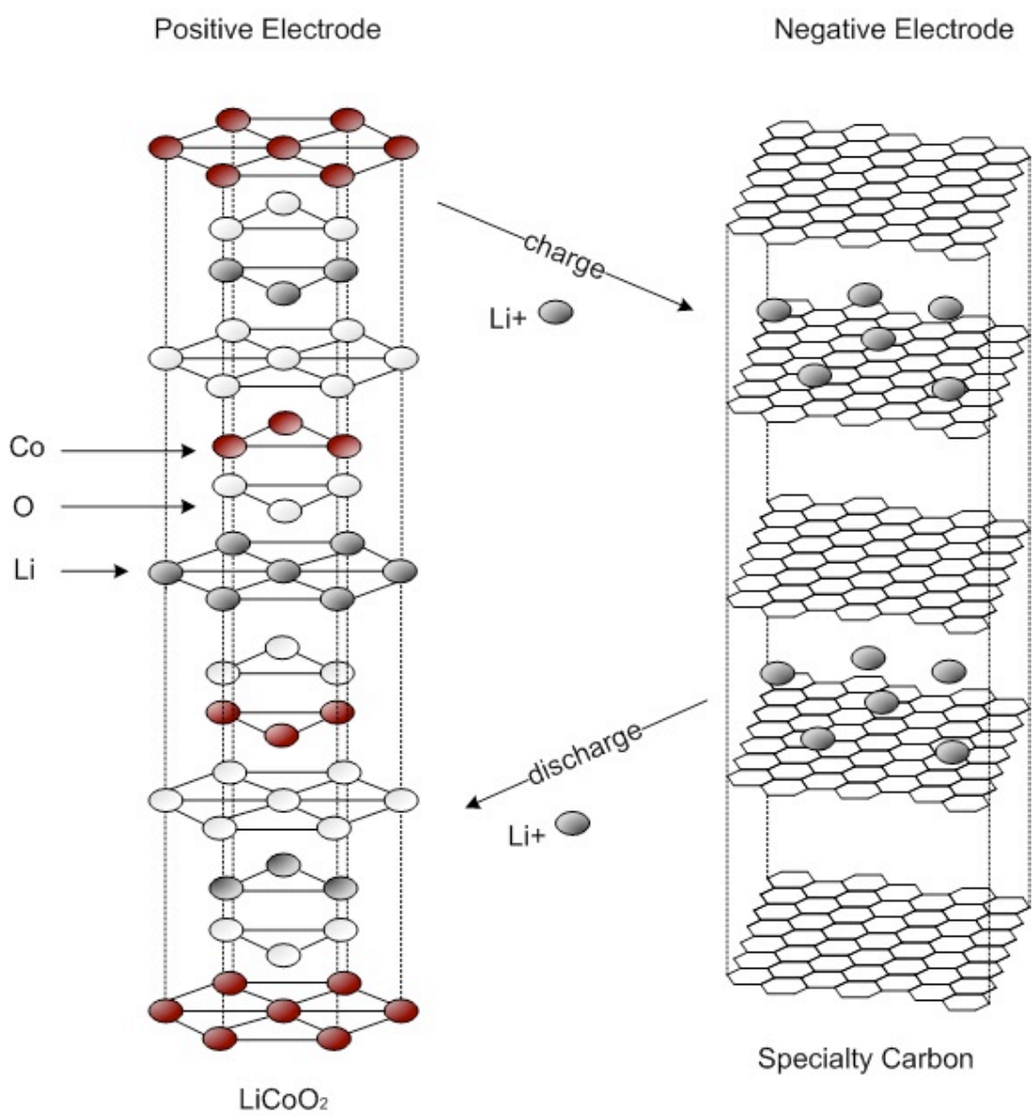
Application: Batteries



http://www.electronics-lab.com/articles/Li_Ion_reconstruct/

Works, in essence, because of multiple d-valence: it is easy to transfer electrons into and out of CoO_2 complex

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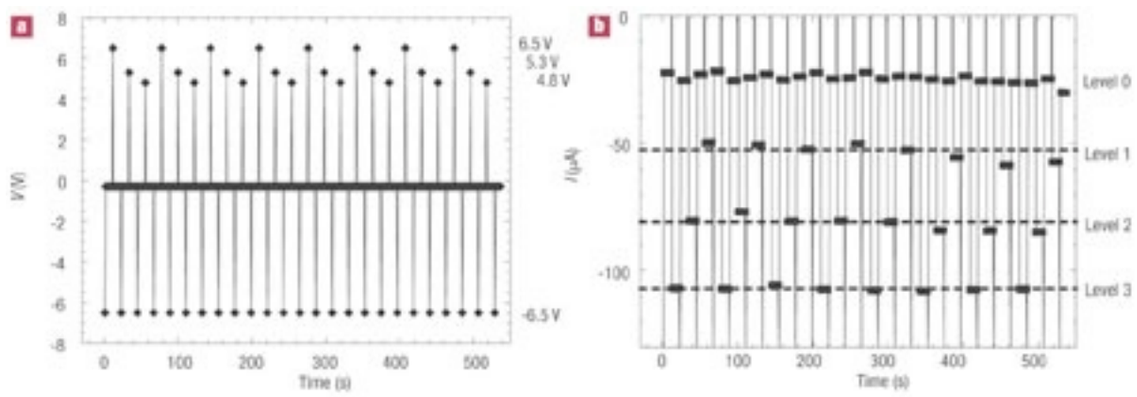
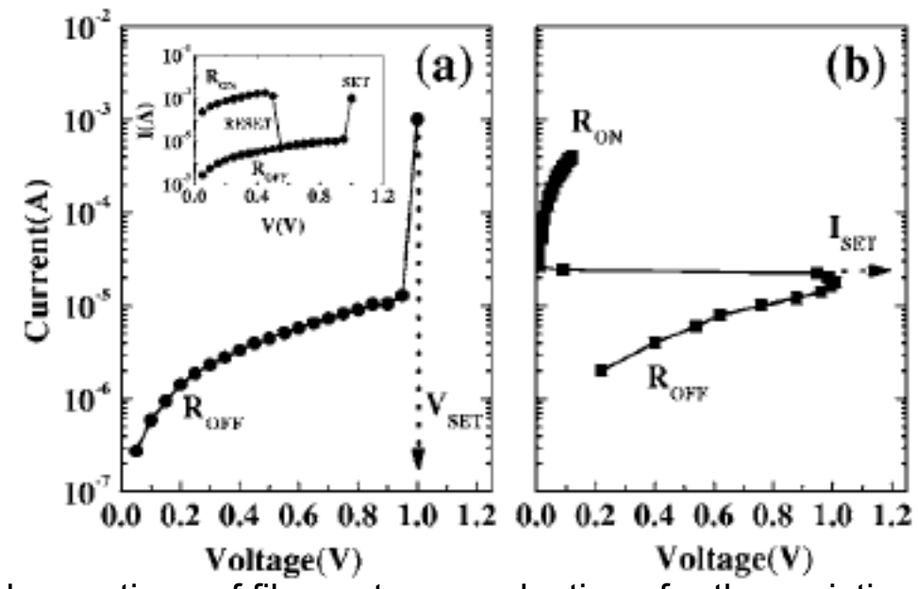
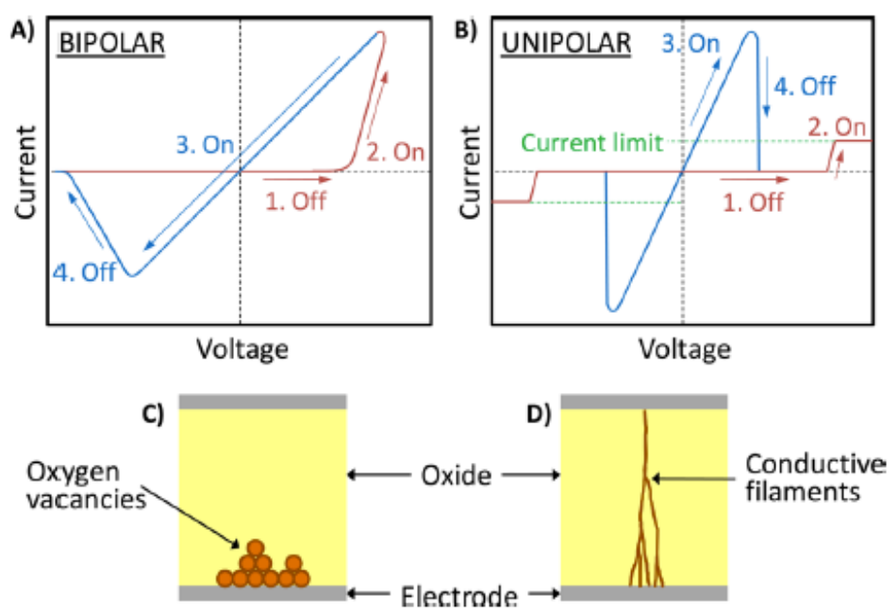
Application: ``Memristor”

Nature **453**, 80-83 (2008)





Electrical observations of filamentary conductions for the resistive memory switching in NiO films D. C. Kim, S. Seo, S. E. Ahn, D.-S. Suh, M. J. Lee et al. Appl. Phys. Lett. 88, 202102 (2006)



In oxides works, in essence, because of multiple d-valence: it is easy to transfer electrons into and out of NiO complex

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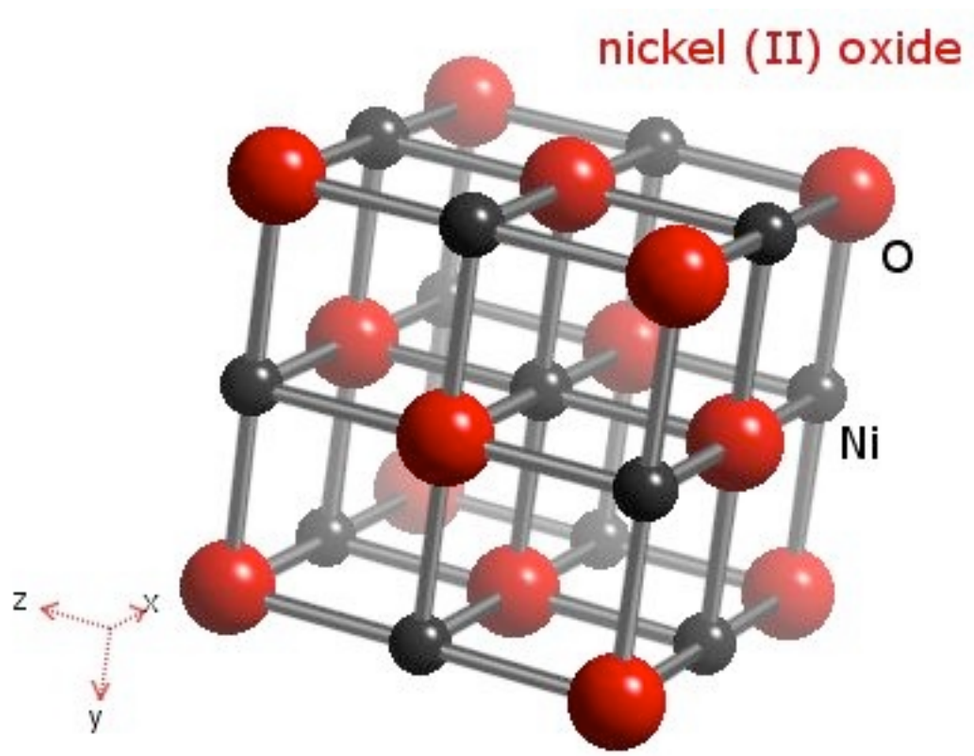
Many structures possible

Monoxide (e.g NiO): rocksalt structure



http://www.webelements.com/compounds/nickel/nickel_oxide.html

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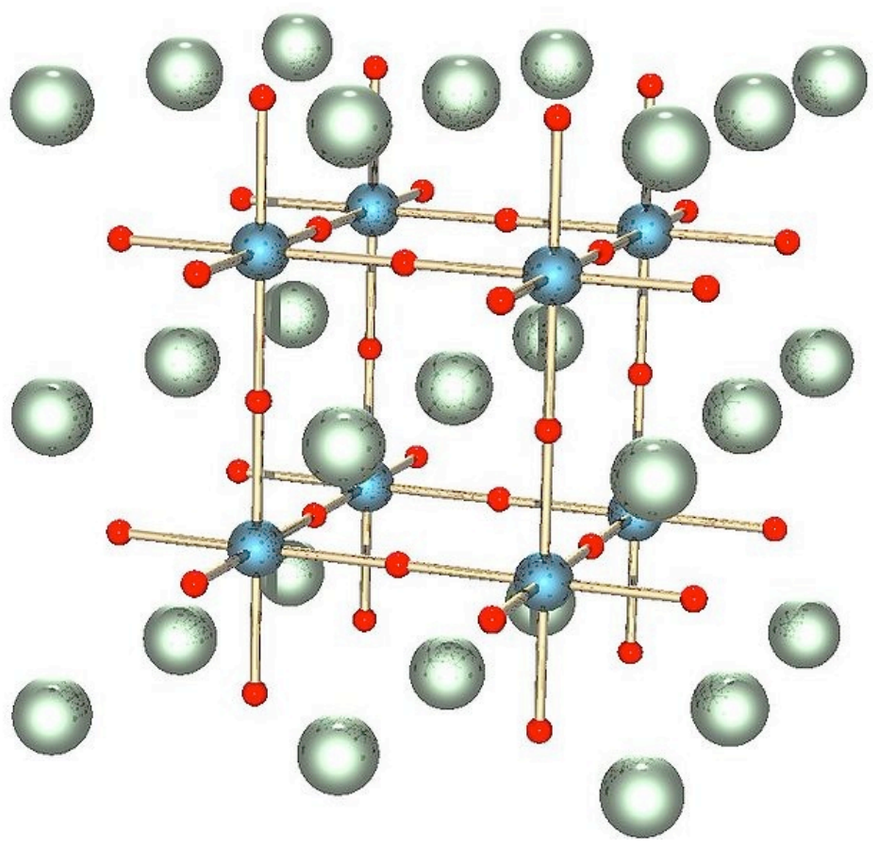
Many structures possible

ABO_3 Perovskite (e.g $LaNiO_3$):
A and B sites: 2 interpenetrating cubic lattices



A-site. Typically electrically inert

B-site: in our case, transition metal

dont forget oxygen!

Fundamental motif: BO_6 octahedron

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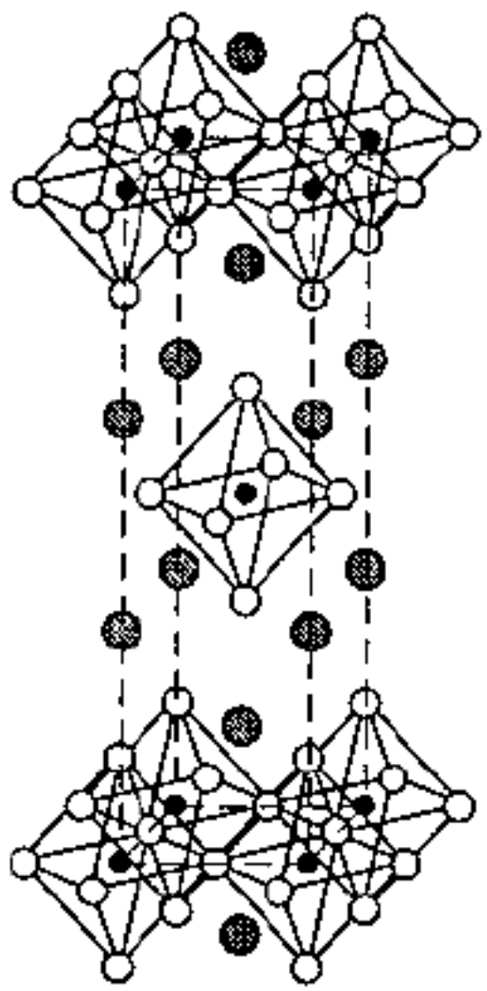
Many structures possible

A_2BO_4 Perovskite (e.g La_2CuO_4): Layered structure



Octahedra as in perovskite but now organized two dimensionally, with weak interplane coupling

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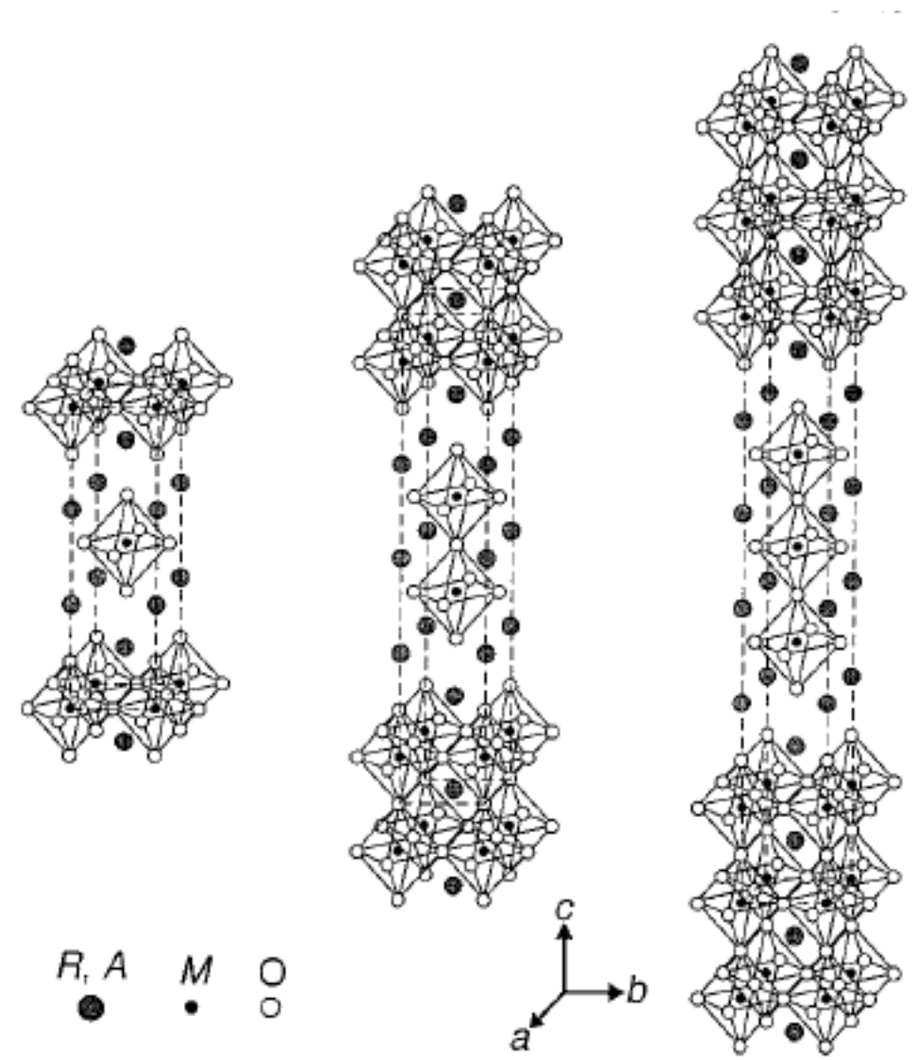
Many structures possible

Ruddlesden-Popper series $A_{n+1}B_nO_{3n+1}$
(e.g Sr_2RuO_4->$Sr_3Ru_2O_7$->$Sr_4Ru_3O_{10}$->$SrRuO_3$)

Interpolates between 2 and 3 dimensional coordination



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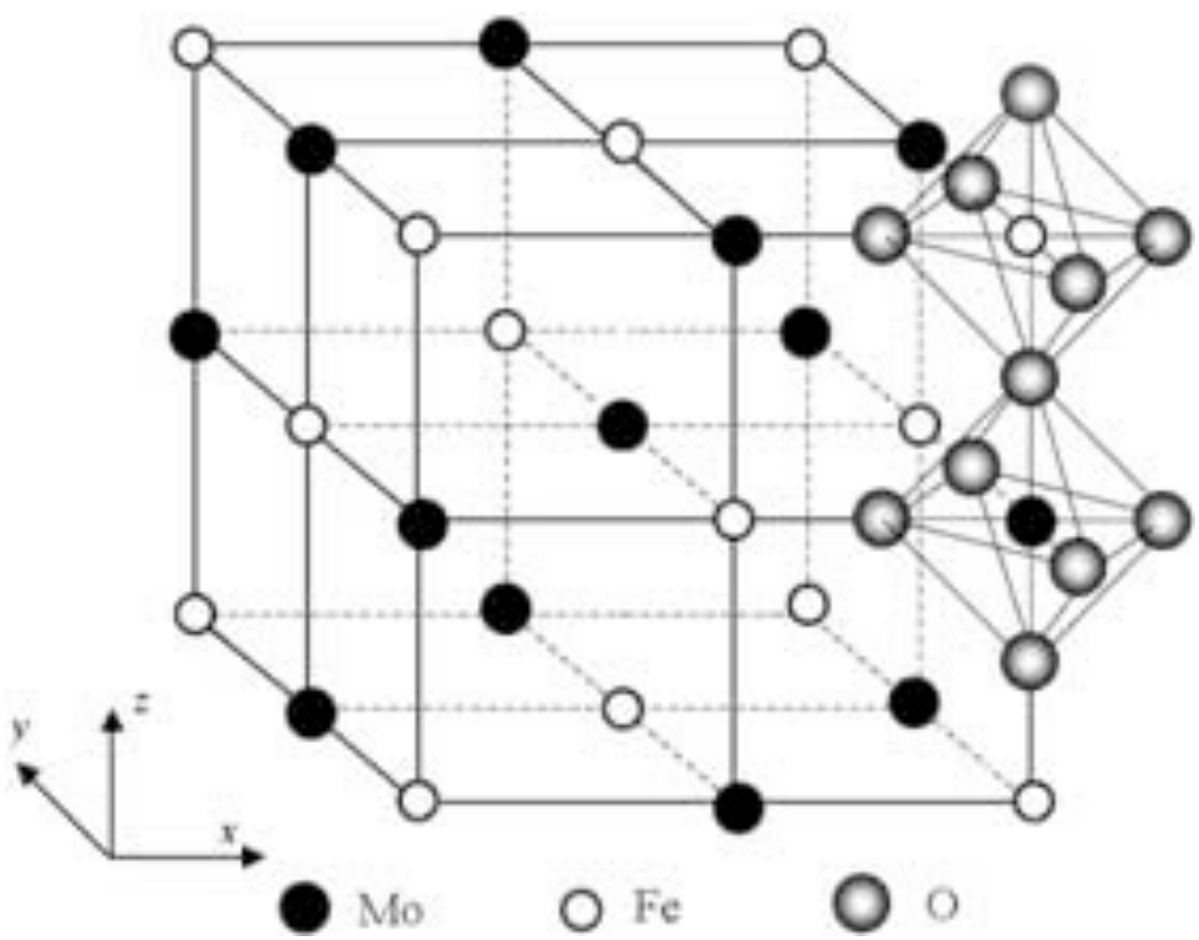
Many structures possible

Double perovskite AA'BB'O_6

Sr_2FeMoO_6



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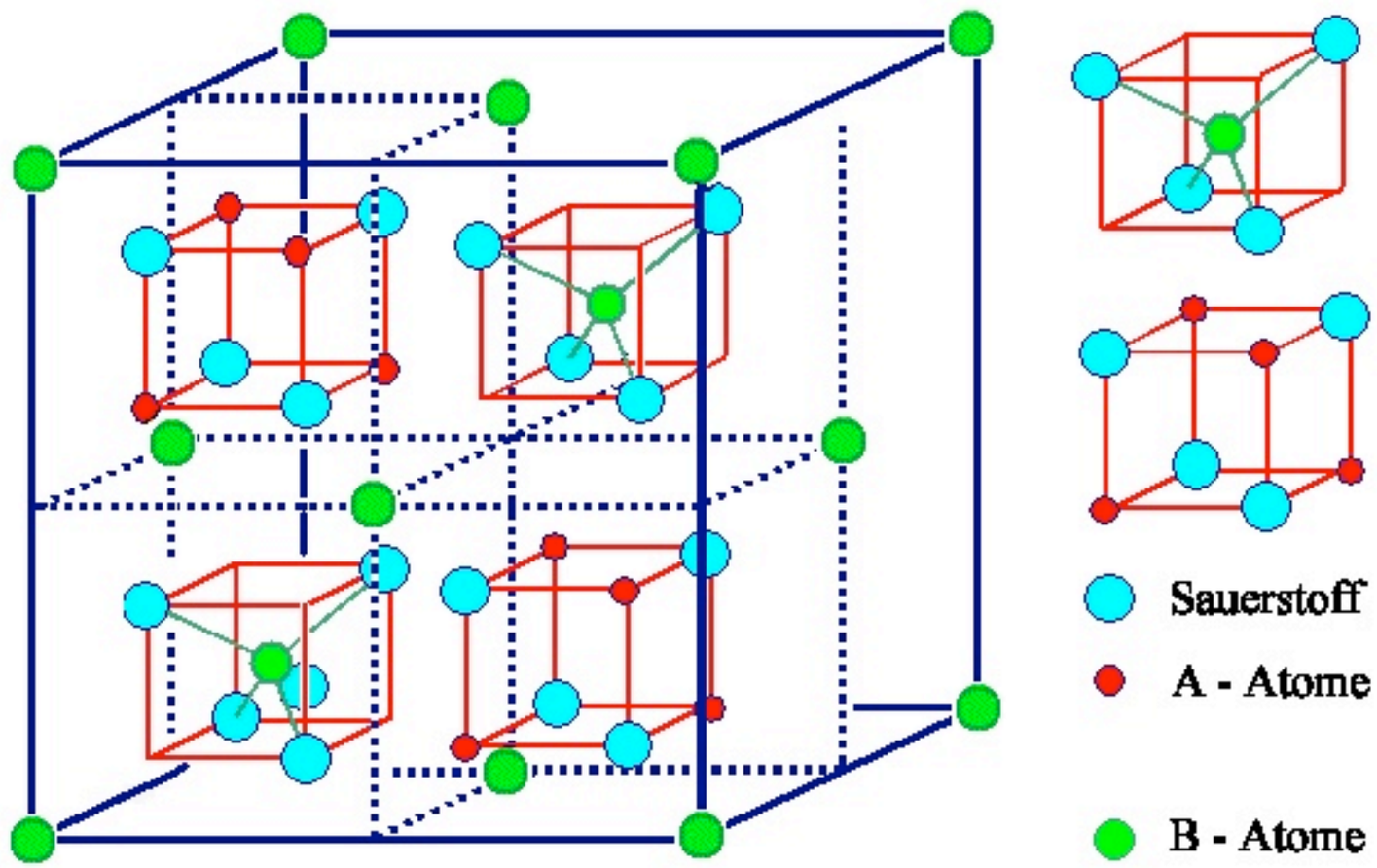
Many structures possible

Other structures: spinel (2 inequivalent sites: one rocksalt and one tetrahedrally bonded



AB_2O_4 Spinell Die roten "Würfel" sind auch im hinterenTeil des Kristalls

tf.uni-kiel.de

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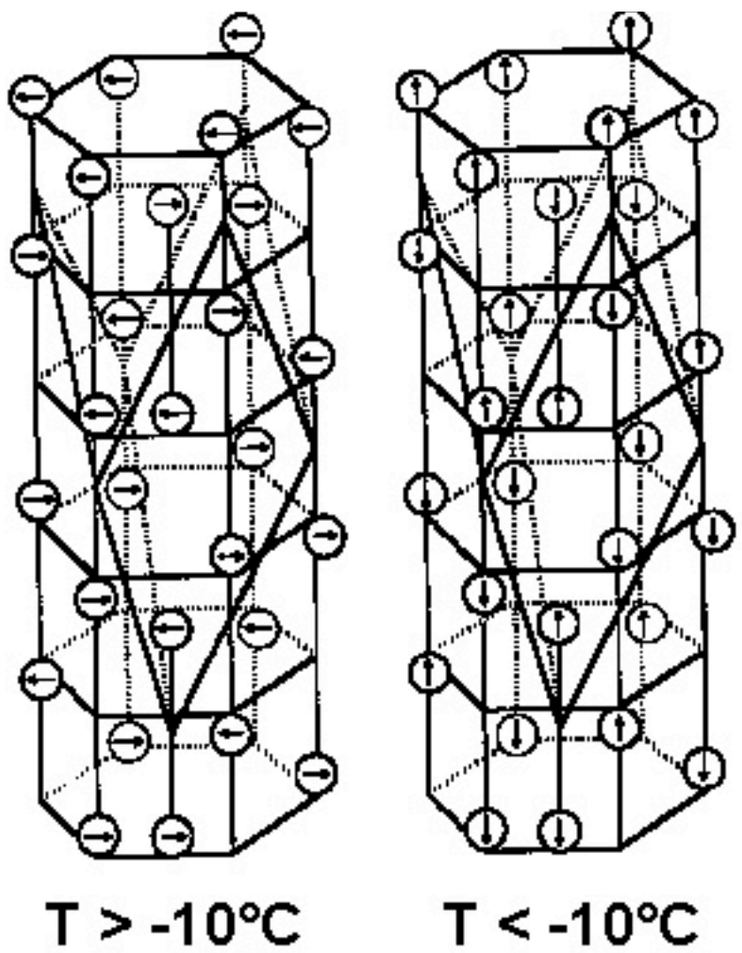
Many structures possible

Corundum structure: V2O3; hematite....



after Fuller (1987)

Here, only transition metal ions are shown

http://www.irm.umn.edu/hg2m/hg2m_b/hg2m_b.html

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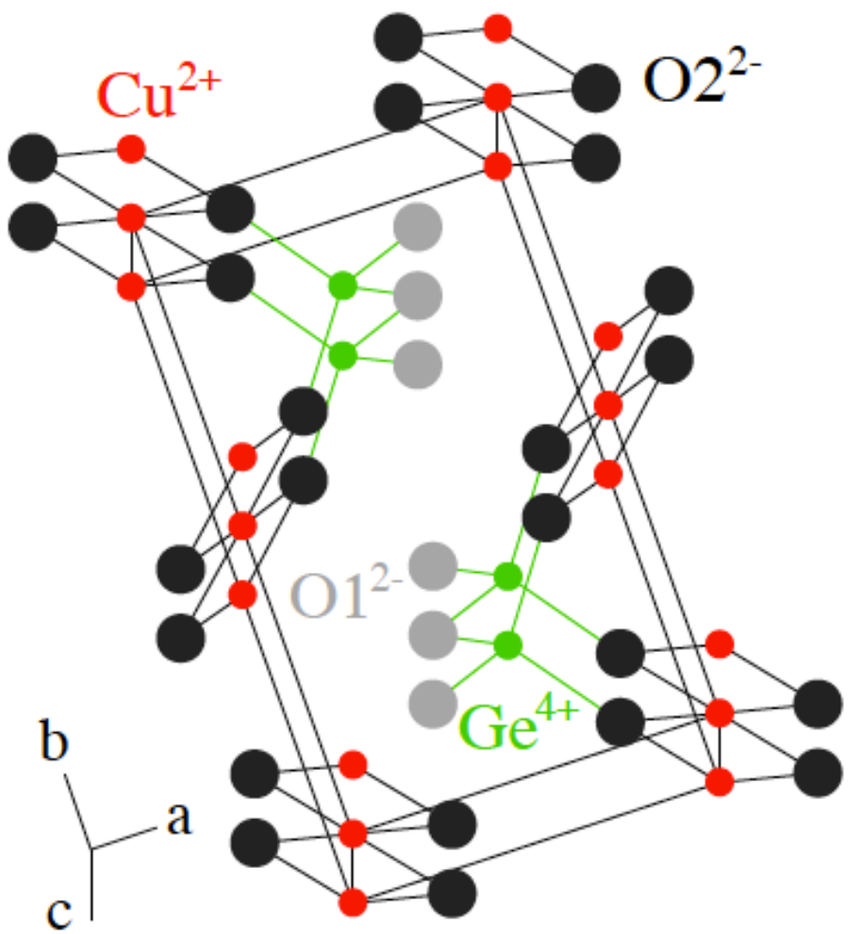
Many structures possible

Many other structures: for example quasi one dimensional arrays of transition metal ions (e.g. $CuGeO_3$ below),



Basic point: multiple configurations of transition metal=>multiple structures possible.

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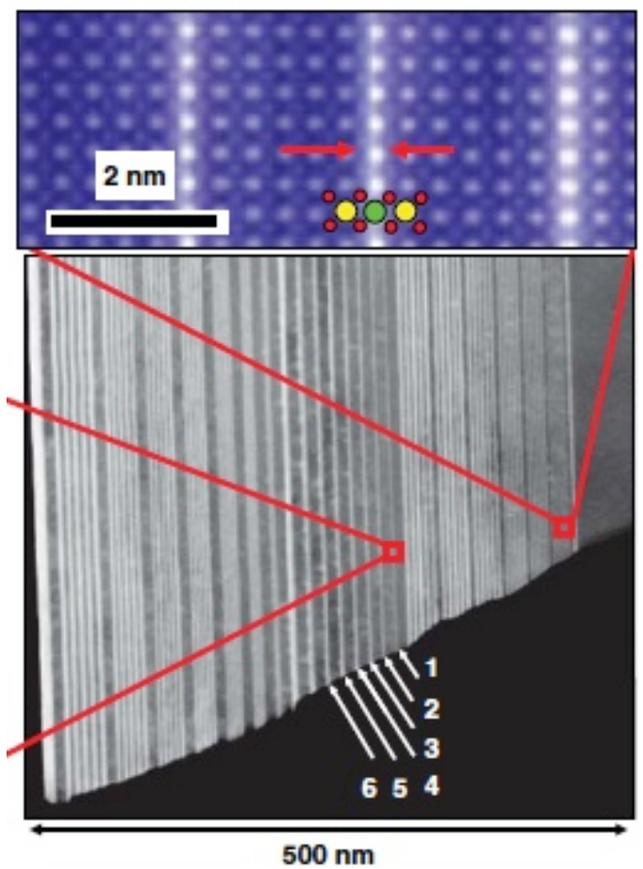
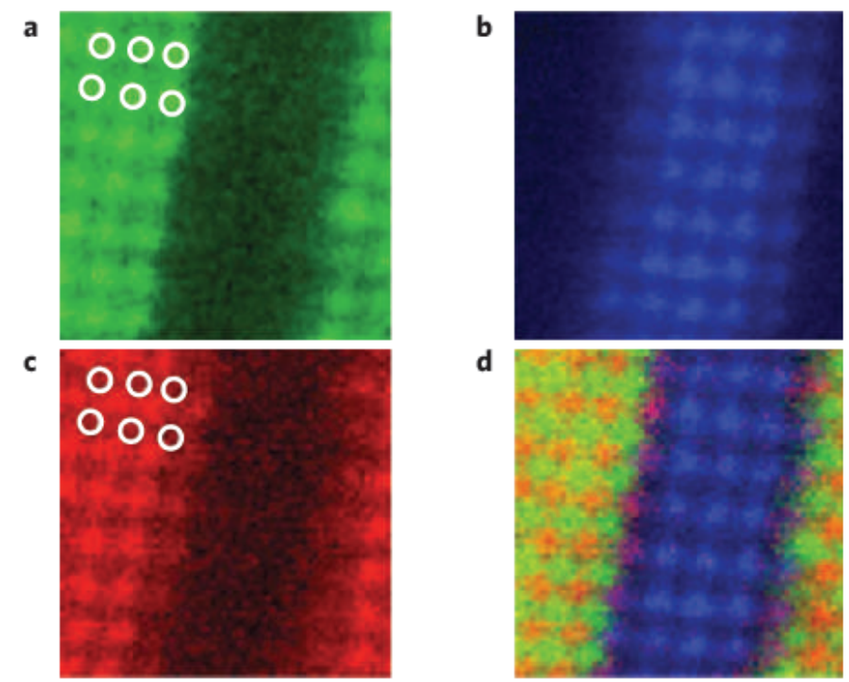
New development: artificially constructed superlattices

$LaTiO_3/SrTiO_3$



A. Ohtomo, D. A. Muller, J. L. Grazul and H. Hwang, Nature **419** 378 (2002)

$LaMnO_3/SrTiO_3$



(a): La (b) Ti
(c) Mn (d) composite

D. Muller Nat. Mat. 9 263 (2009)

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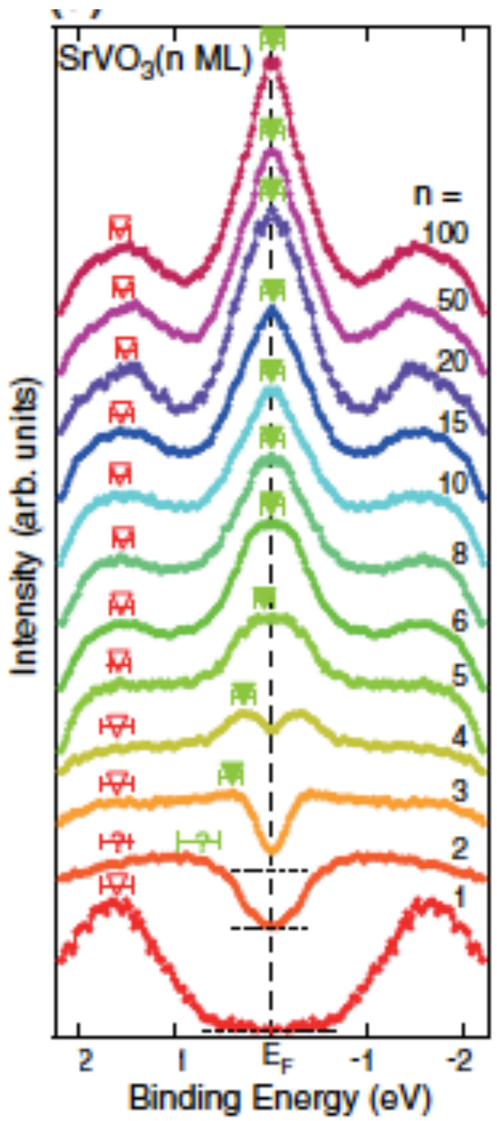
New window onto basic questions

PRL 104, 147601 (2010) PHYSICAL REVIEW LETTERS week ending 9 APRIL 2010

Dimensional-Crossover-Driven Metal-Insulator Transition in $SrVO_3$ Ultrathin Films

K. Yoshimatsu,[1] T. Okabe,[1] H. Kumigashira,[1,2,3,*] S. Okamoto,[4] S. Aizaki,[5] A. Fujimori,[5] and M. Oshima[1,3,6]



Photoemission (many-body density of states--here symmetrized) for n layers of $SrVO_3$ (paramagnetic metal) embedded in $SrTiO_3$ (insulator)

As SrVO3 becomes thinner, gap opens

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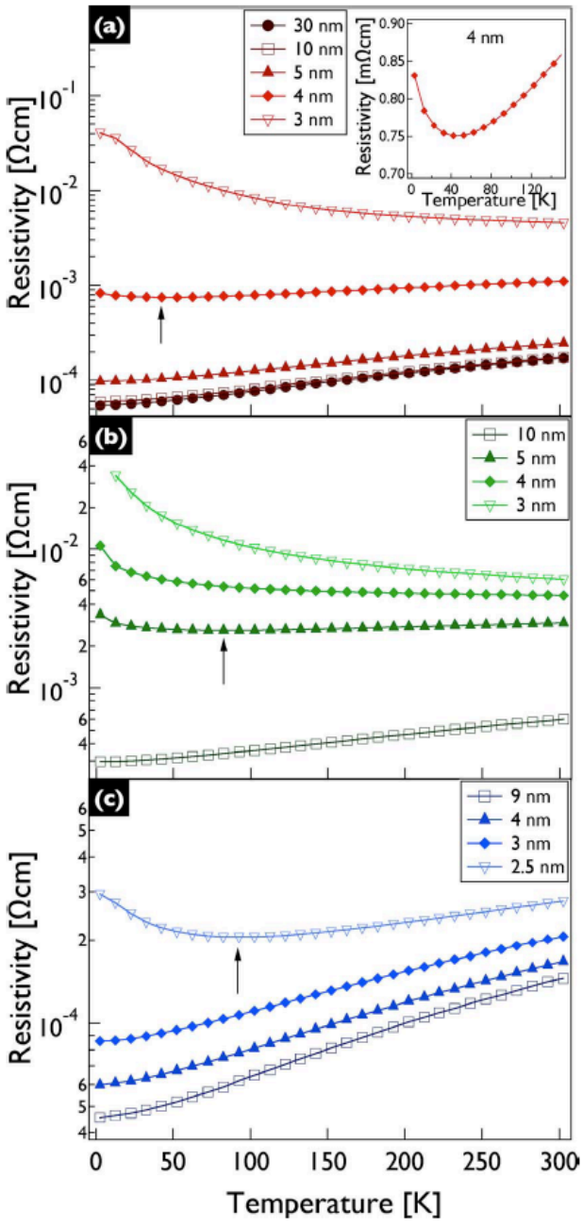
Columbia University

Strain control of metal-insulator transition in $LaNiO_3$

Son et al Appl. Phys. Lett. 96 062114 (2010)



LAO: 1.3% compressive strain
LSAT: 0.8% tensile strain
DSO: 2.5% tensile strain

Critical thickness for metal-insulator transition depends on magnitude and sign of strain

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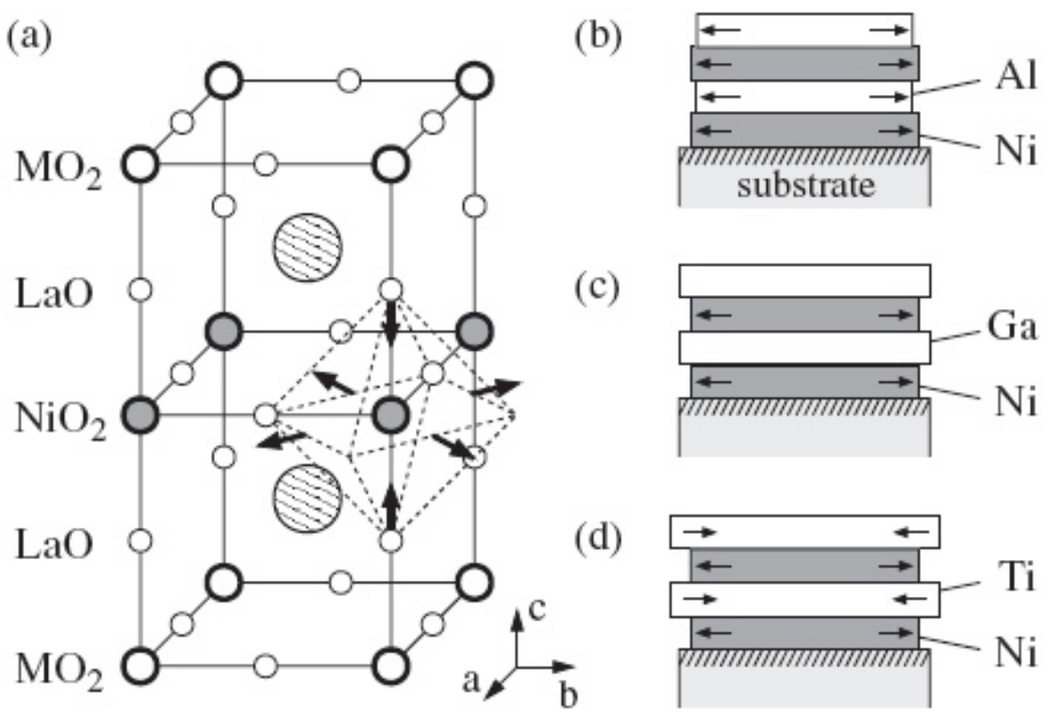
More exotic: ``design in new properties”

e.g. Chaloupka/Khalliulin: ?New high-T_c superconductor?



Phys. Rev. Lett. **100** 016404 (2008)

Idea:

Bulk $LaNiO_3$ Ni $[d]^7$ (1 electron in two degenerate e_g bands).

In correctly chosen structure, split e_g bands, get 1 electron in 1 band--”like” copper-oxide high-Tc

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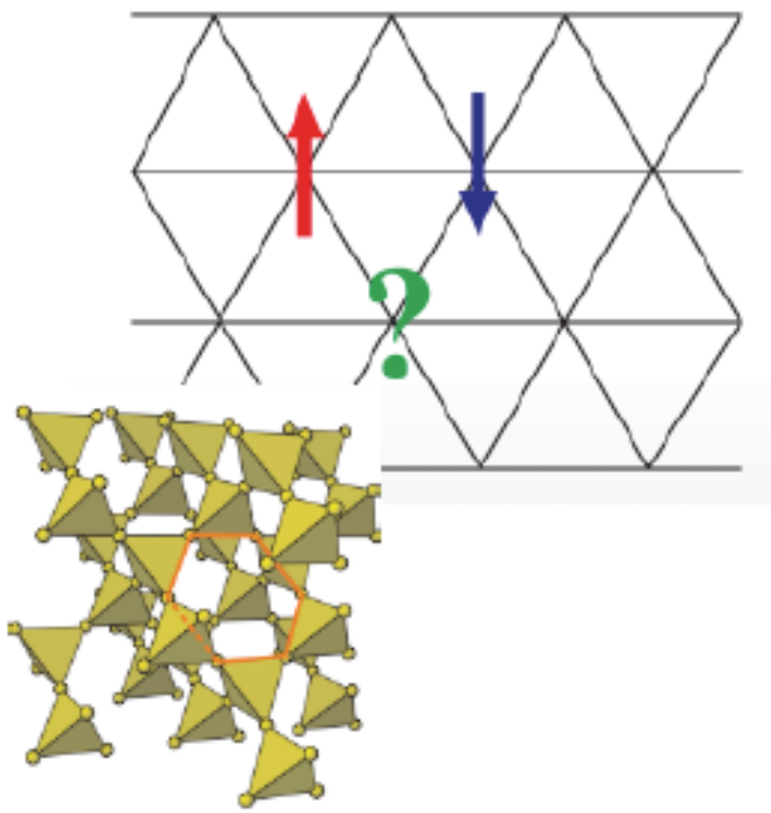
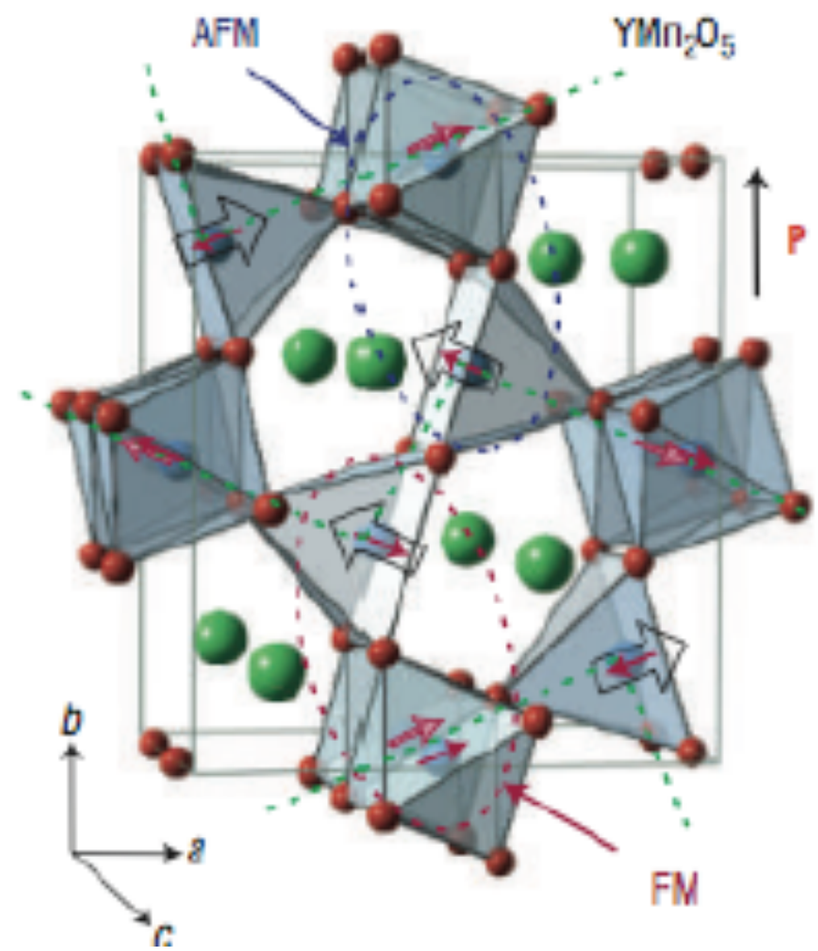
Structure =>interesting behavior

Spins on geometrically frustrated lattices



Multiferroics



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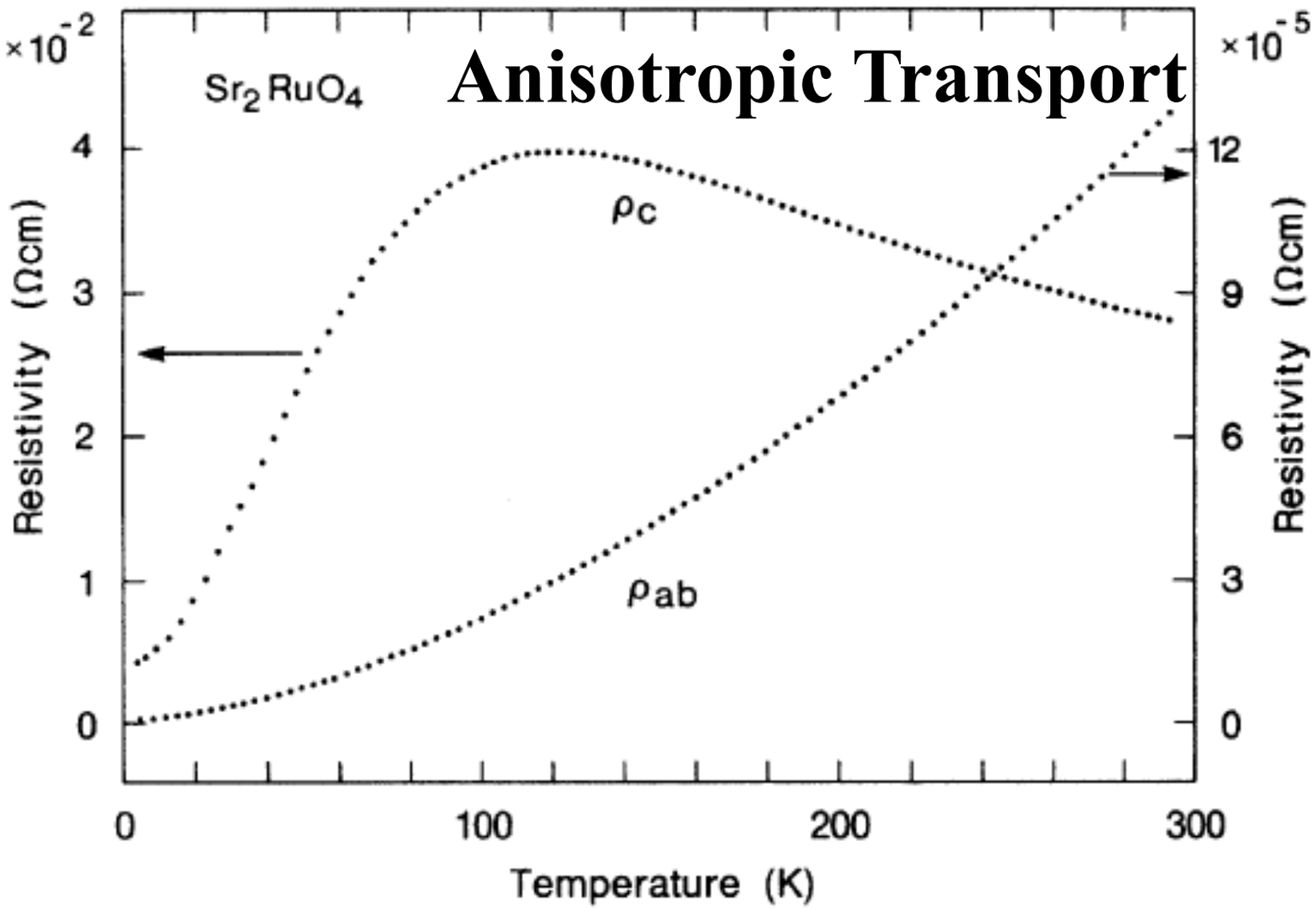
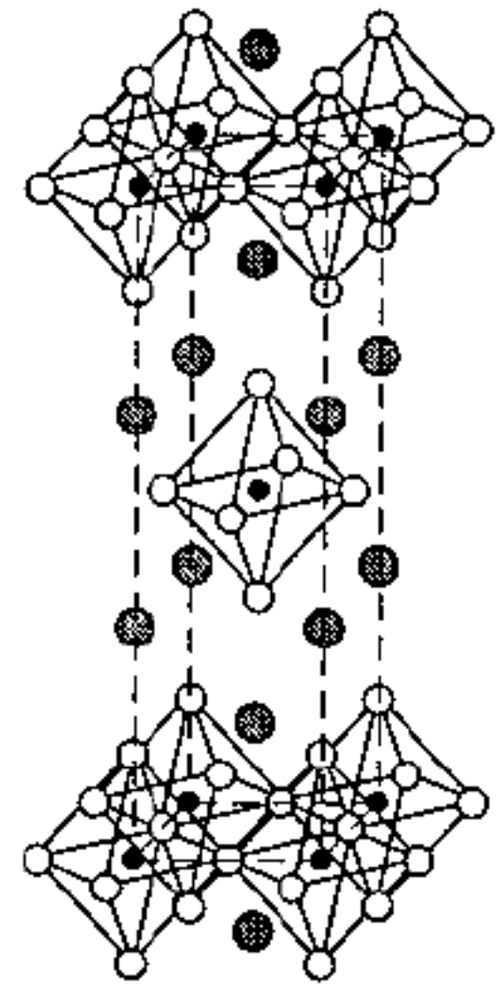
Structure =>interesting behavior





F. Lichtenberg / Progress in Solid State Chemistry 30 (2002) 103–131

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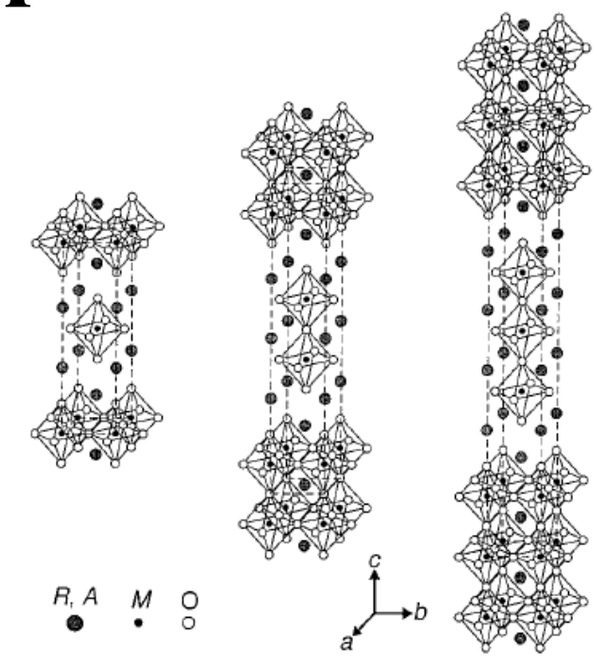
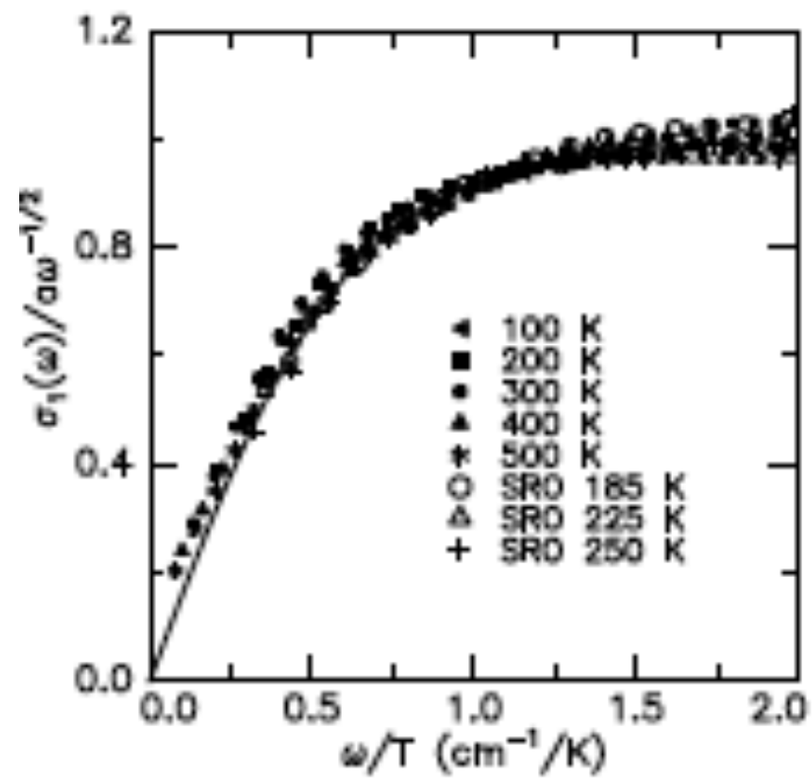
Structure =>interesting behavior



Sr_2RuO_4: p-wave superconductor

$Sr_3Ru_2O_7$: almost ferromagnetic (100x susceptibility enhancement).

$SrRuO_3$: Ferromagnetic (T_c ~150K). Power-law conductivity. $CaRuO_3$: no fm, but power law



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Important property of transition oxides: partially filled d-shells

Hund's first rule (maximize total spin)

=>magnetism

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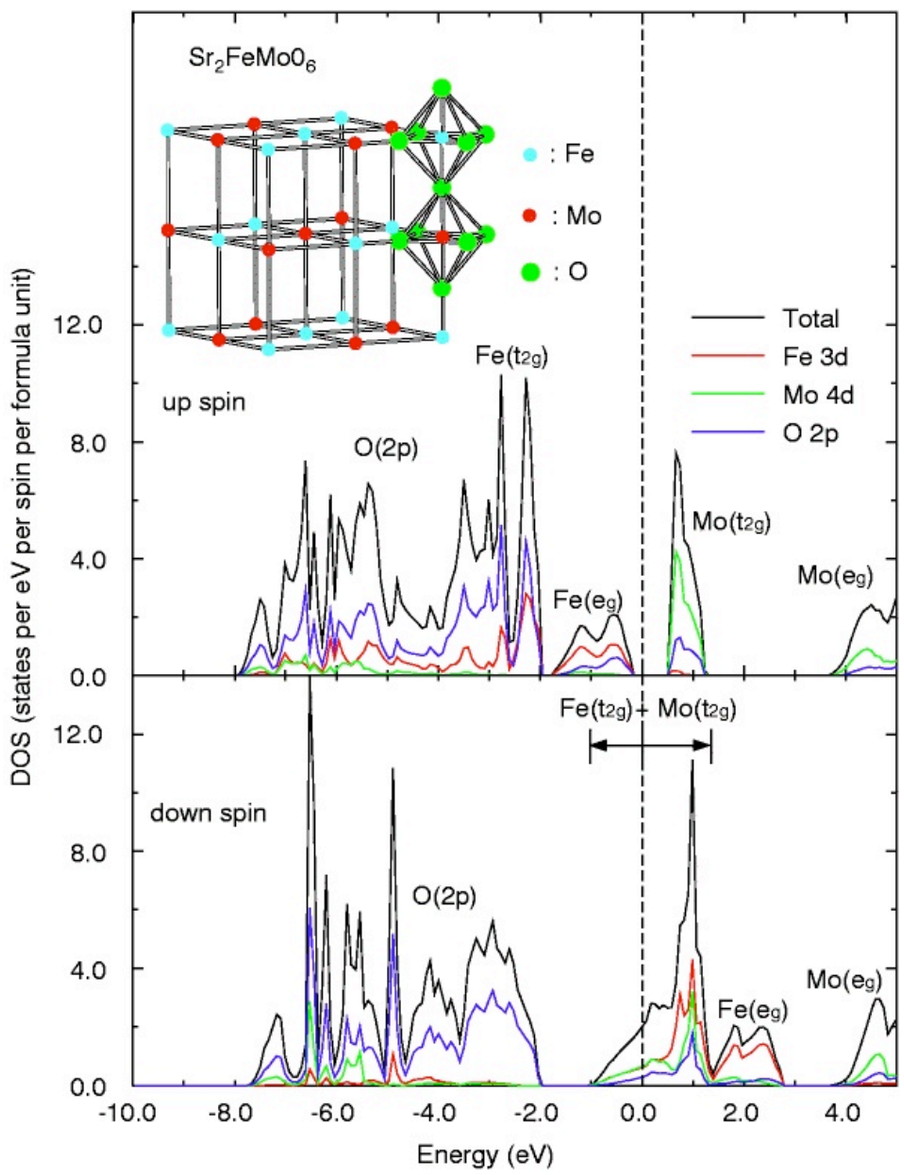
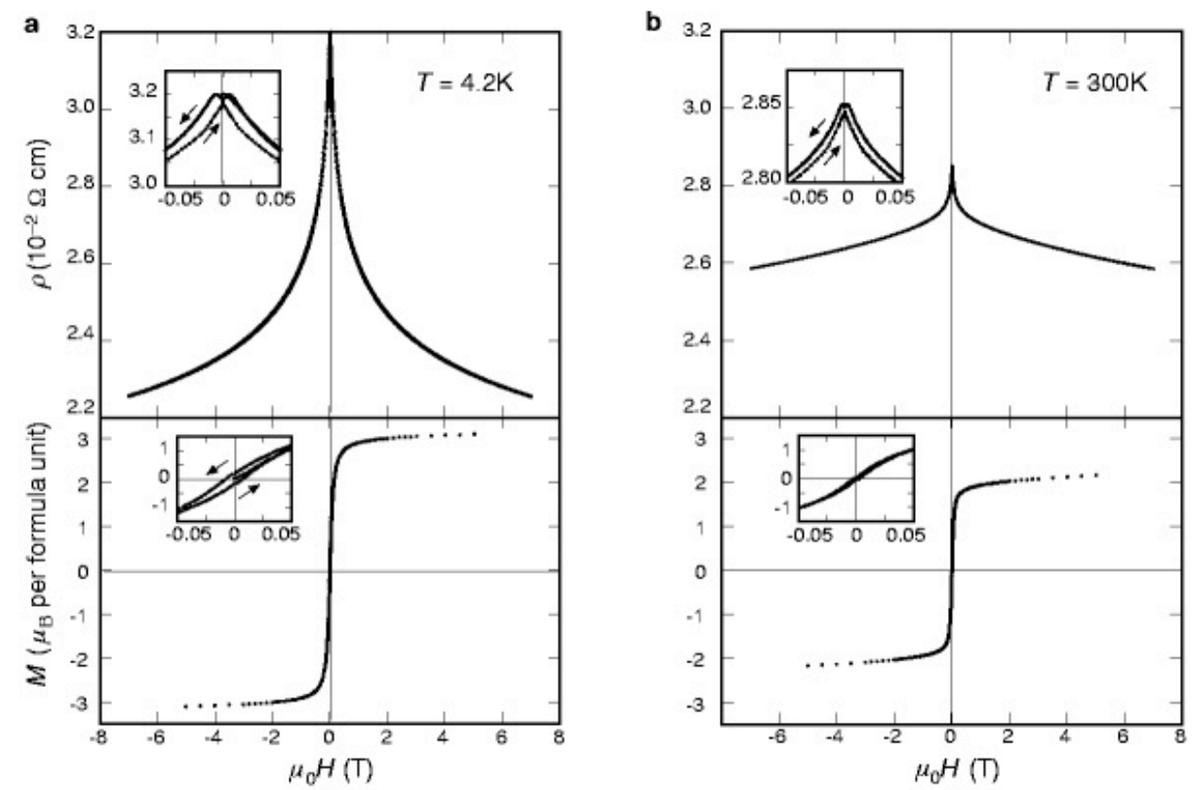
Magnetism and full spin polarization at temperatures above room T





Nature **395**, 677-680
(15 October 1998)

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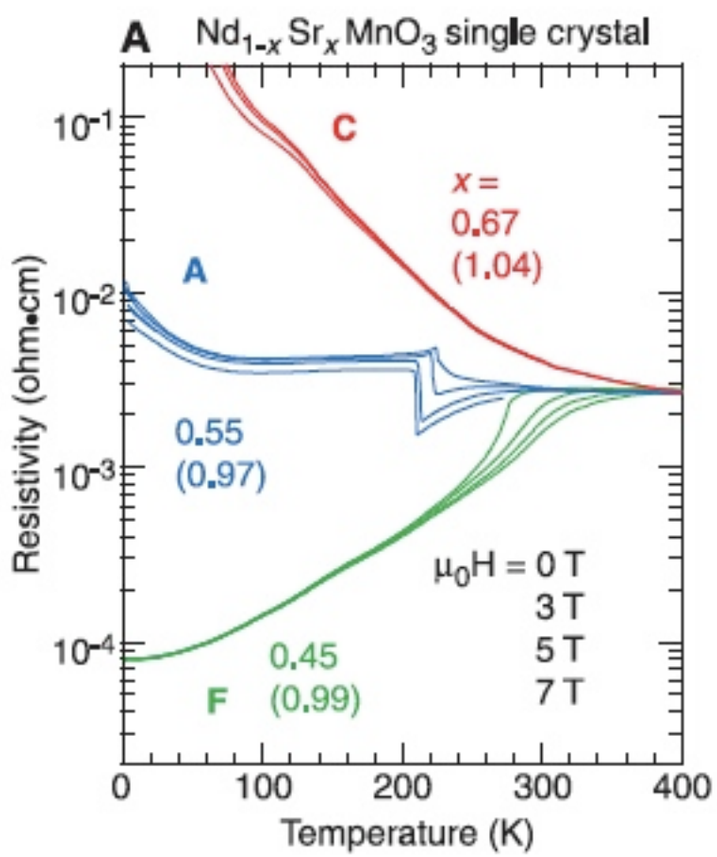
Columbia University

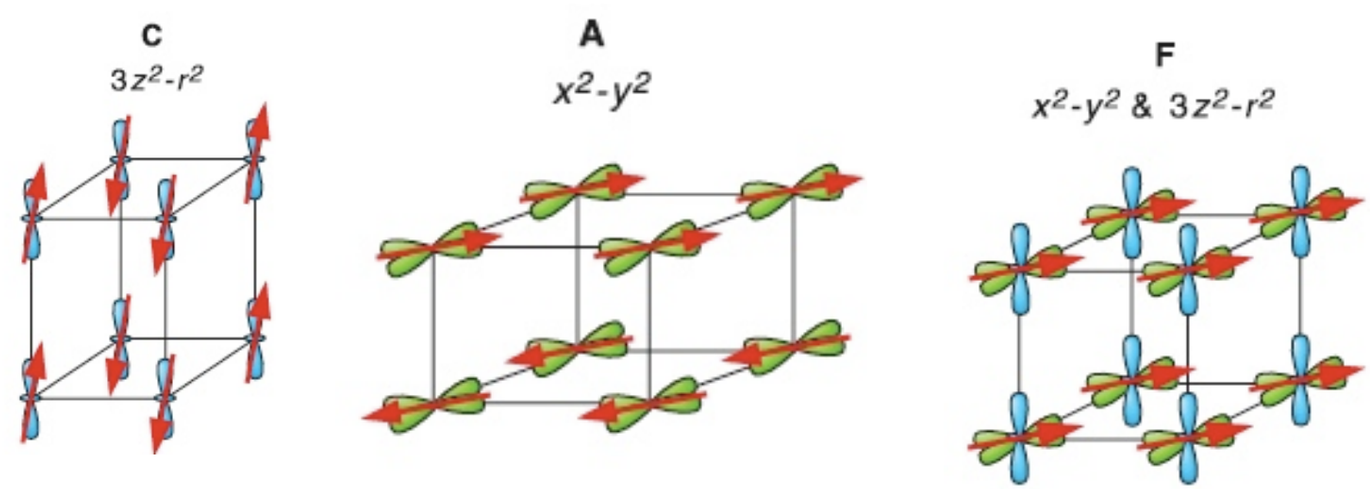
Hunds second rule:
maximize orbital angular momentum

In solid state context: occupy a subset of d-orbitals

<=> ``orbital order”=>anisotropic transport

Ex: Manganese perovskites band filling x controls orbital ordering=>conductivity





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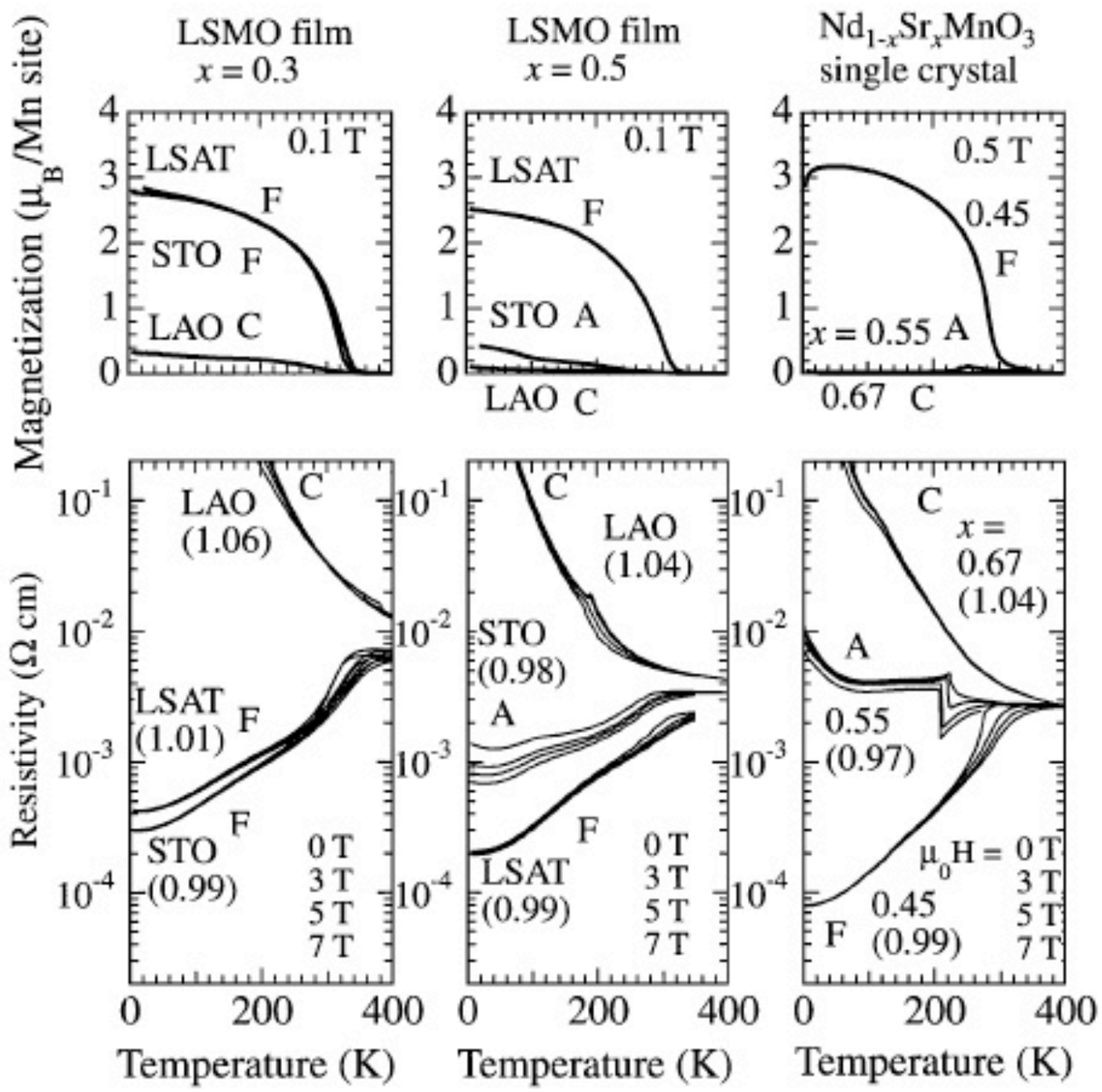
Nagaosa/Tokura Science **288** 462

These effects can be induced by strain



Konishi et al , J. Phys Soc. Jpn **68** 3790

Ex: CMR films--substrate-induced strain=>(putative) orbital ordering=> conductivity.

Mechanism: 'orbital ordering' triggered by strain

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Proximity (in energy) of several spin and charge configurations=> interesting and potentially useful transport properties

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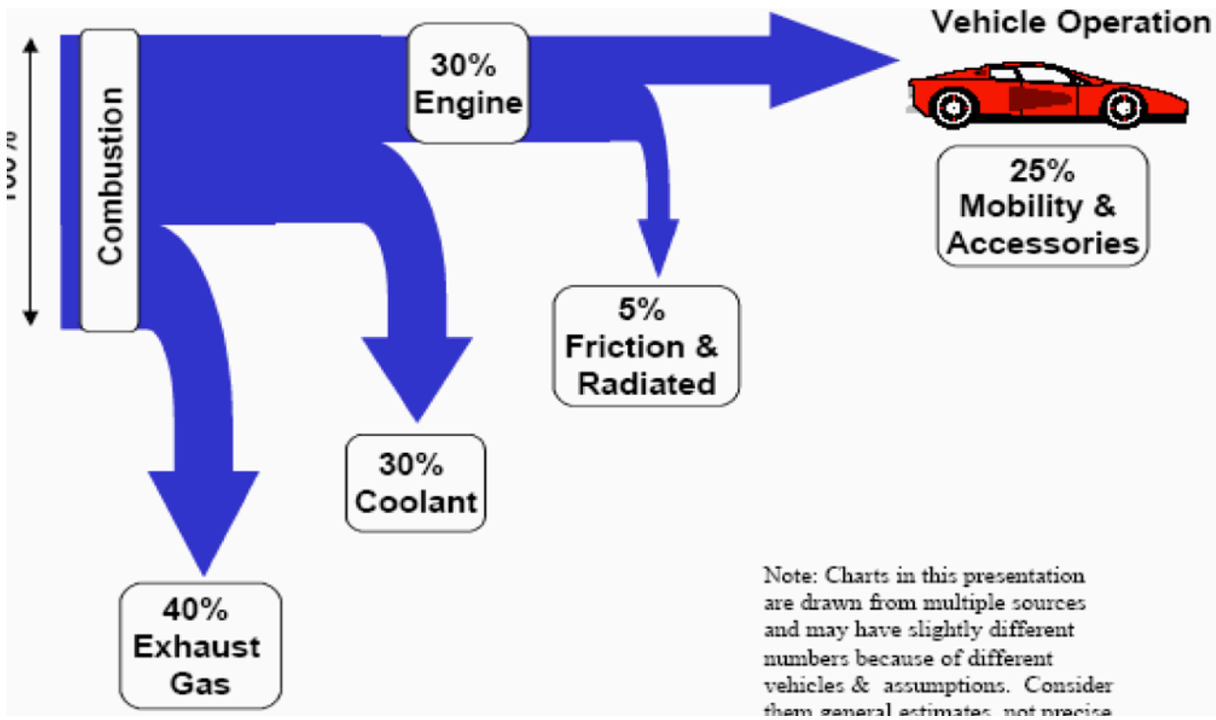
Thermoelectric effects

Lots of waste heat in the world:



A.Maignan, APs tutorial 2010

Thermal conductivity

$$S = \frac{\Delta V}{\Delta T}$$

=>from temperature difference, can get voltage=>current

=>recapture some energy

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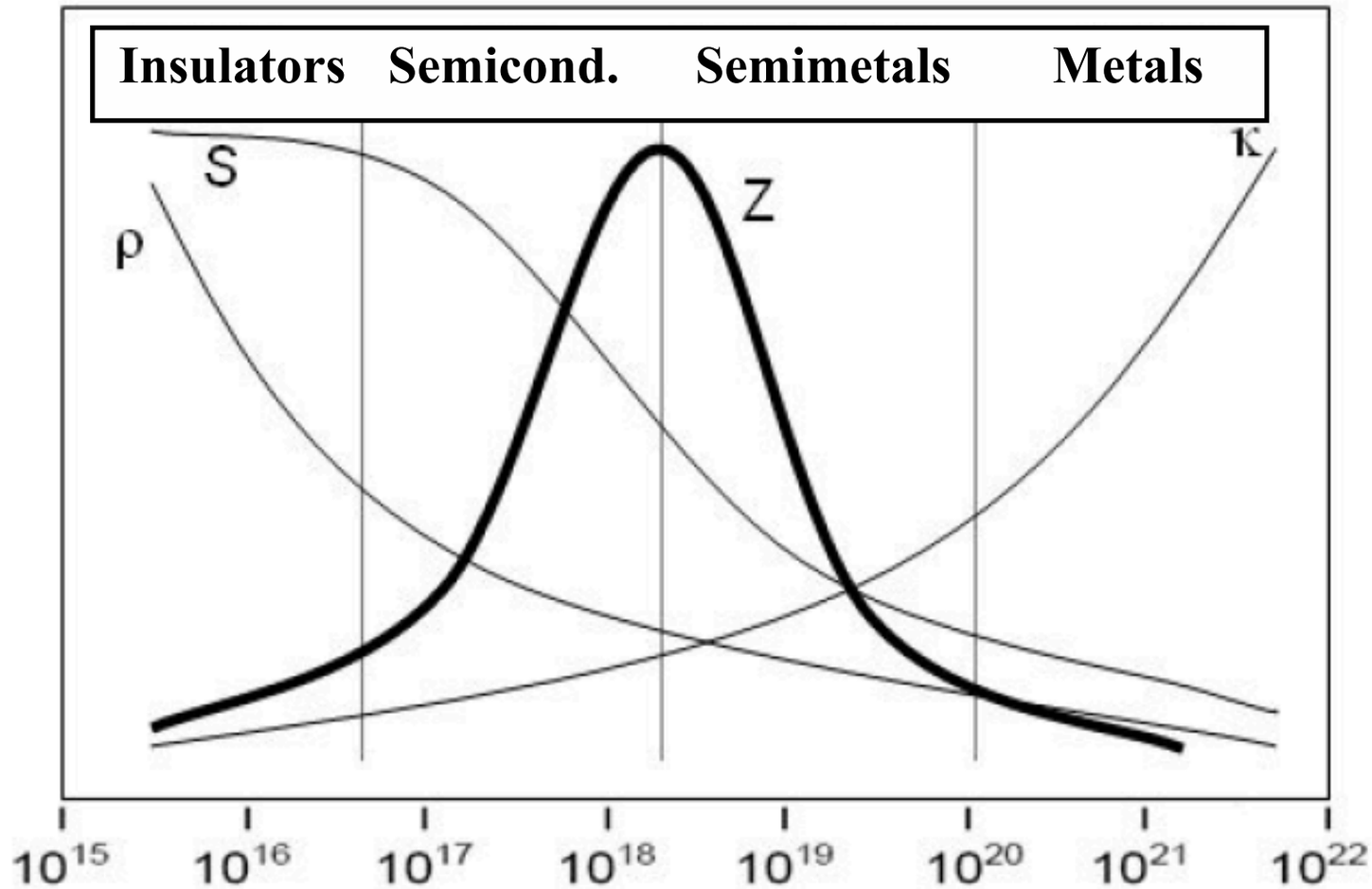
Thermoelectric figure of merit

A.Maignan, APs tutorial 2010

$$\mathbf{ZT} = \frac{\mathbf{S^2T}}{\rho\left(\kappa_{\mathbf{el}} + \kappa_{\mathbf{lattice}}\right)}$$

Want: high thermal conductivity, low electrical resistance, low thermal resistance



Carrier density (simple band picture)

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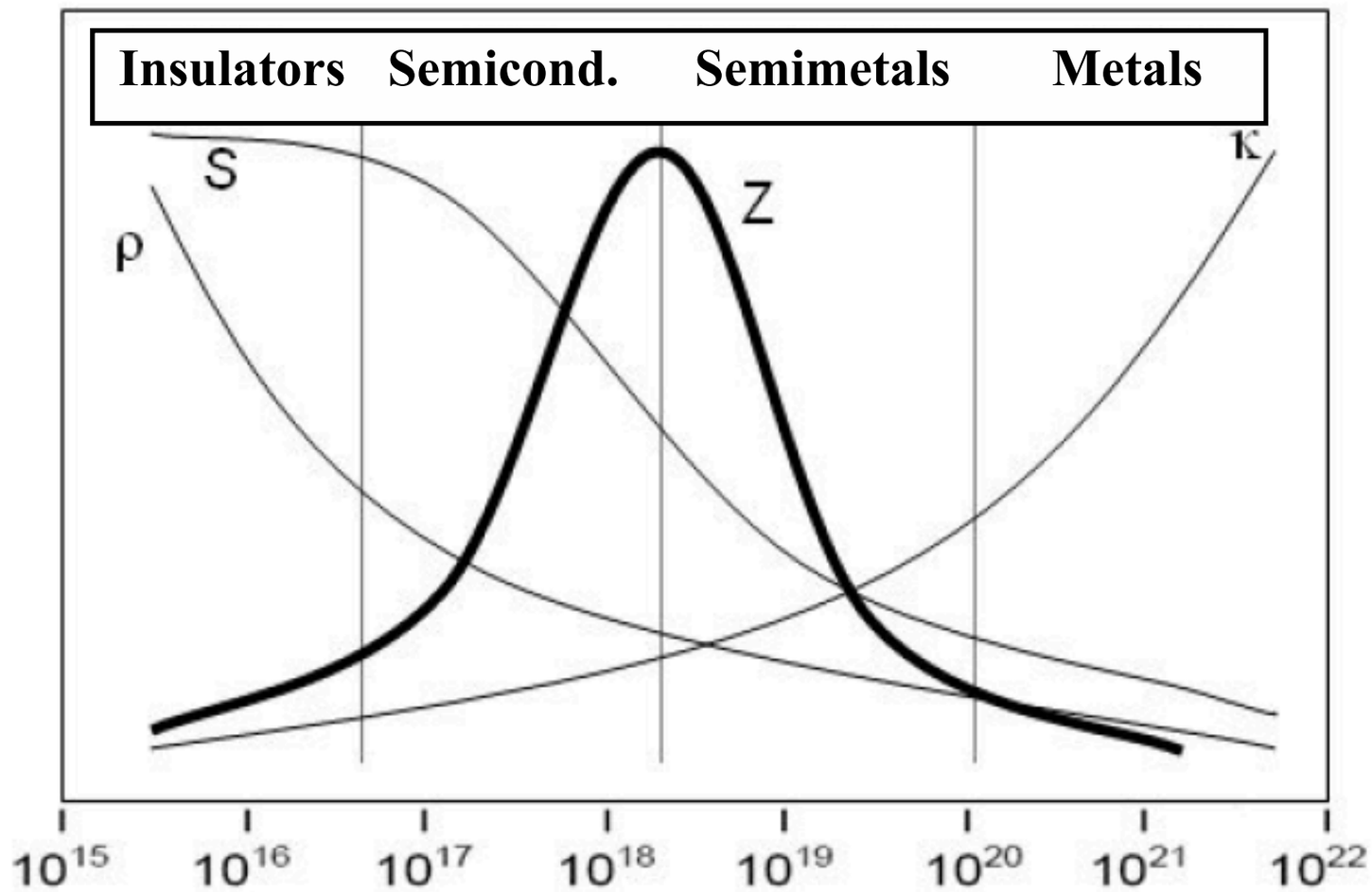
(Over)simplification of physics

$$\mathbf{F = Energy - T \times Entropy}$$

Temperature gradient drives carriers by coupling to entropy

Insulator: no carriers

Metal: entropy per carrier is very small



Carrier density (simple band picture)

Transition metal oxide: partially filled d-shell=>high density of nearly localized carriers, high spin=>high entropy/carrier

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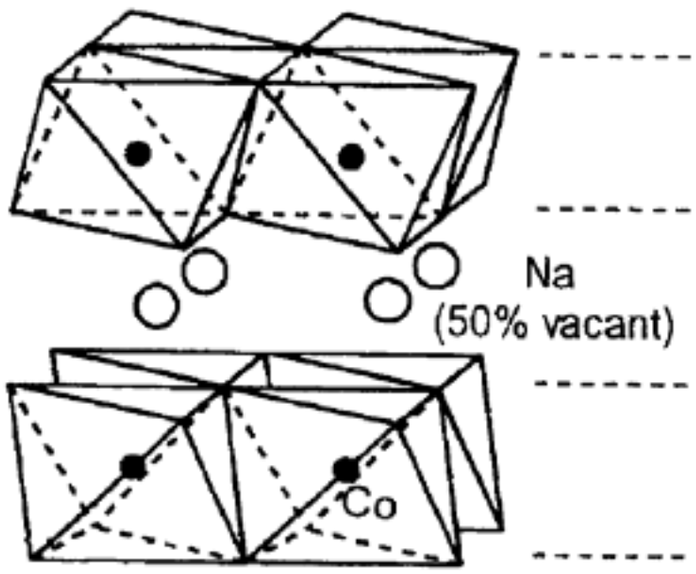
$NaCo_2O_4$ ‘ *Phonon Glass / Electron crystal* ’

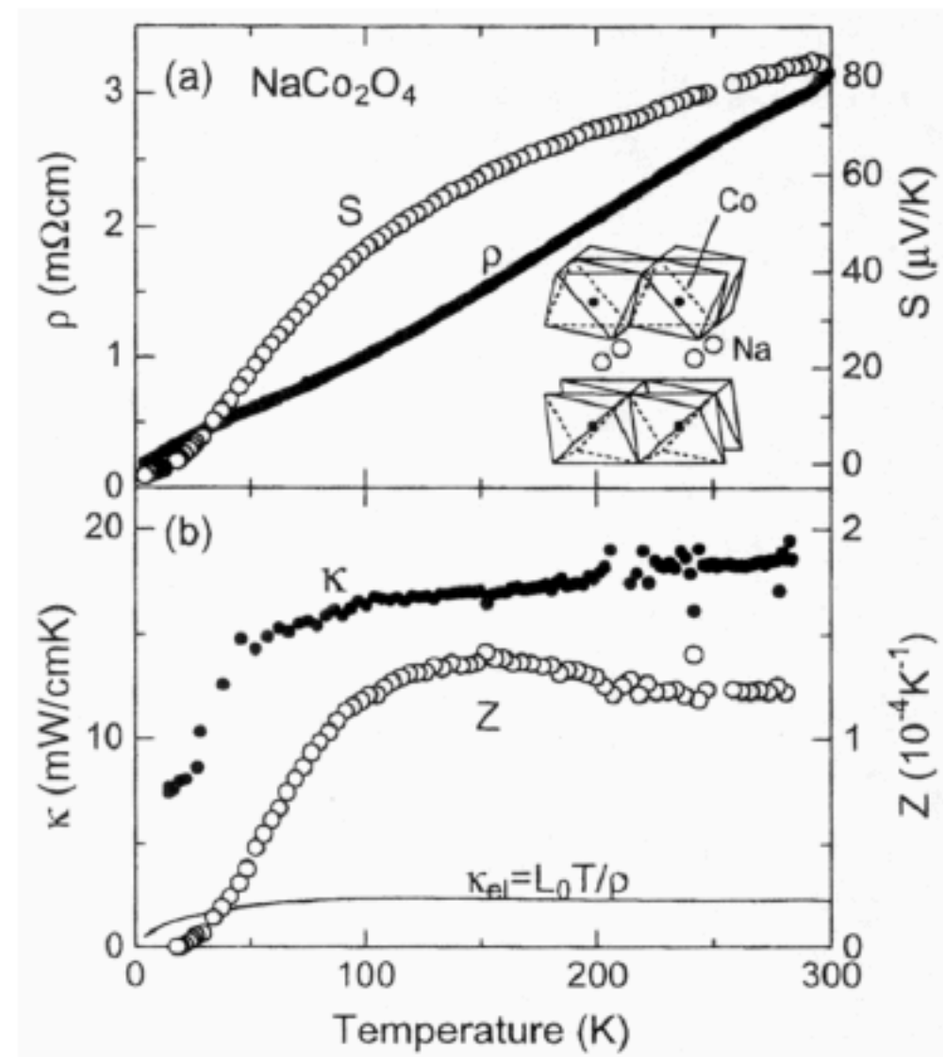
I. Terasaki et al., Phys. Rev. B 56, R12685 (1997)

Na_xCoO_2 : $Na^+_xCo^{3+}_xCo^{4+}_{1-x}O_2$



Co^{3+} ($3d^6$) / Co^{4+} ($3d^5$)

Measurements on polycrystals



At 300K

Metallicity (crystals) $\rho \sim 0.2\ m\Omega\ cm$

Large S $S \sim +80\ \mu V/K$

Small κ (polycrystals) $\kappa \sim 2 Wm^{-1}K^{-1}$

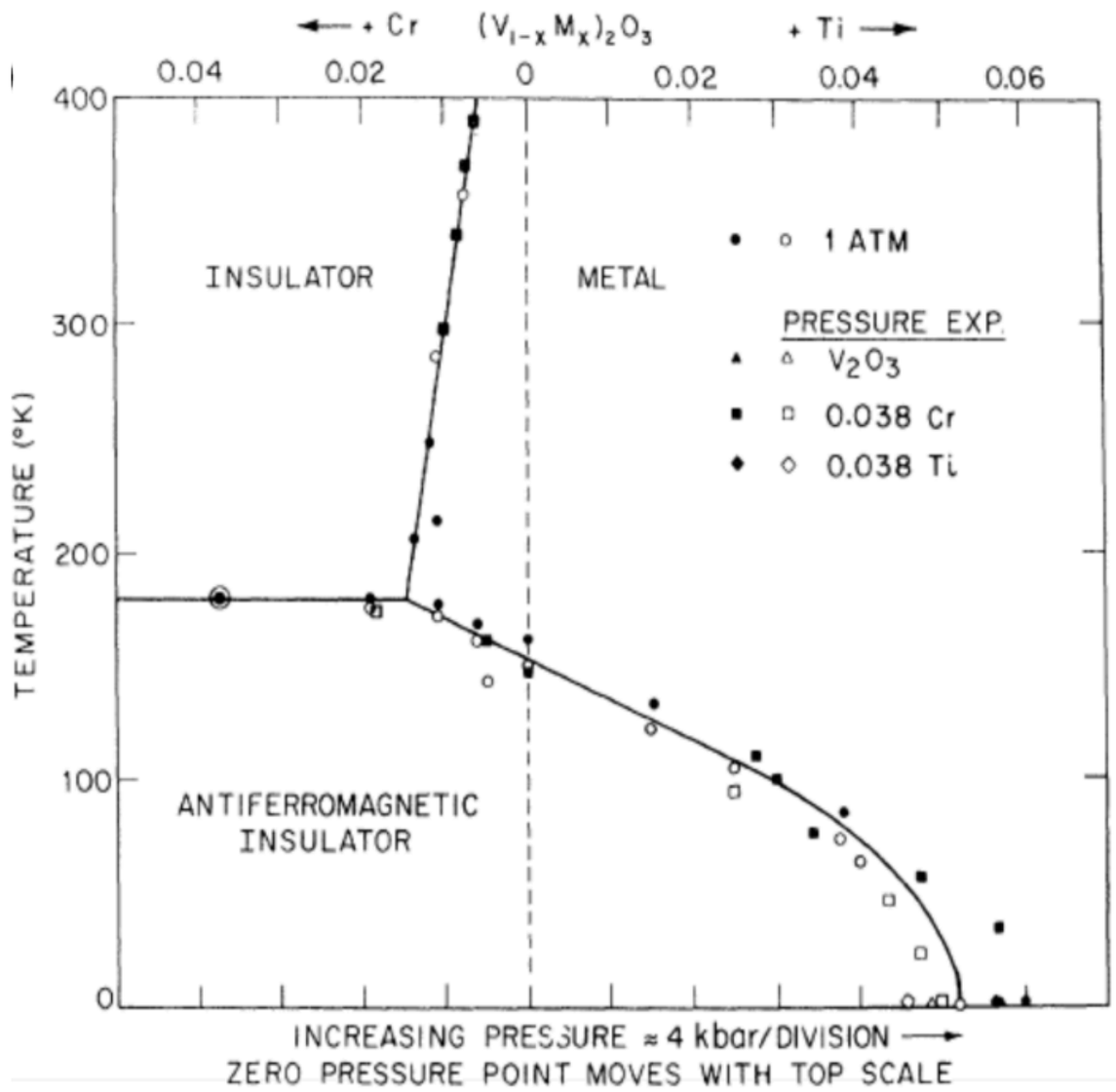
(crystals) $\kappa \sim 5 Wm^{-1}K^{-1}$

A.Maignan, APs tutorial 2010

Copyright A. J. Millis 2013

More extreme transport anomaly: ``Mott" transition

V_2O_3--and other oxides--can be switched from metallic to insulating behavior by modest changes in temperature and pressure.



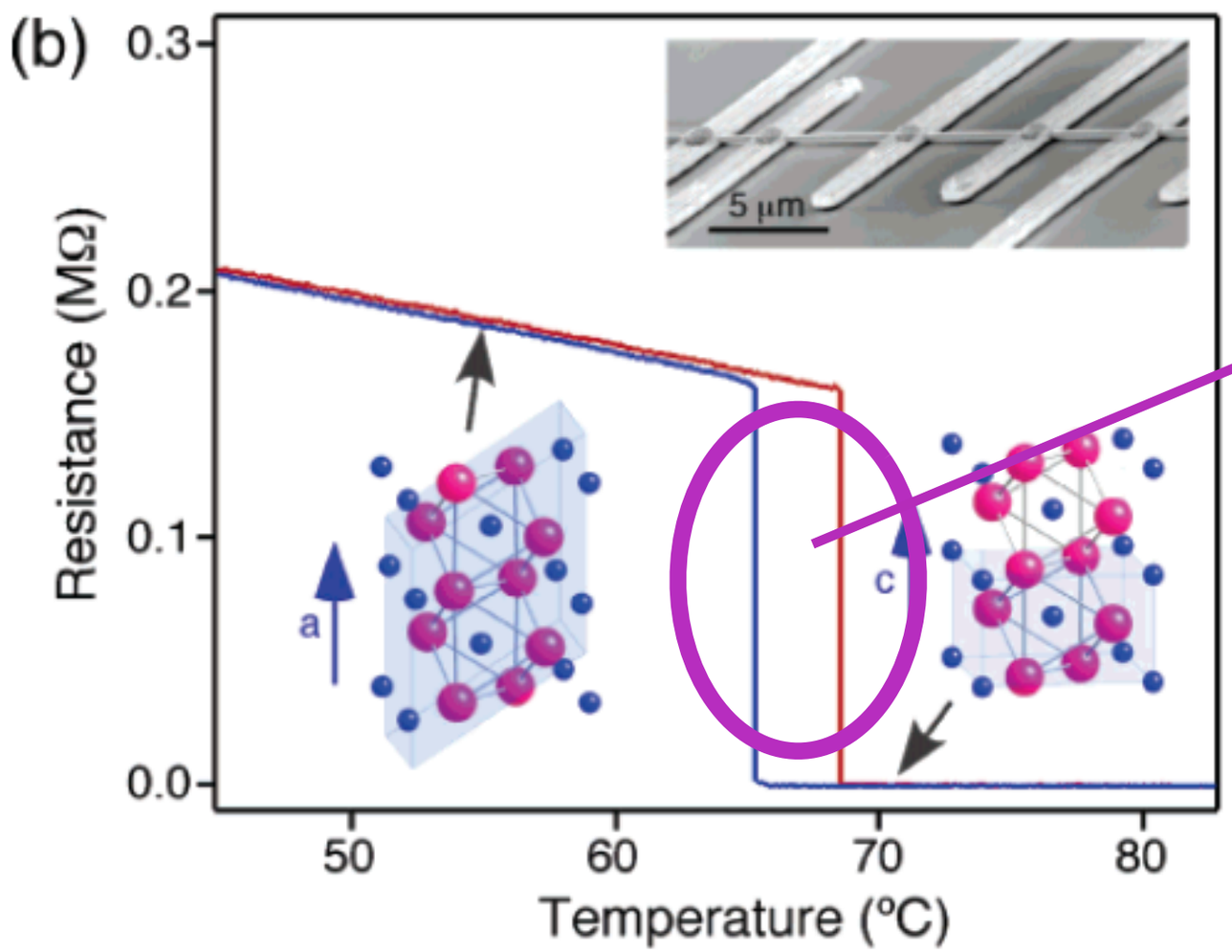
McWhan et al,PRL 27 941 (1971)

Note! Transitions are first order

Copyright A. J. Millis 2013

Device Application: bolometer

VO_2: thermally driven metal-insulator transition



Wu et al, Nanoletters 6 2313 (2006)

Tune device to critical temperature. Small amount of absorbed heat=>large change in resistance

Copyright A. J. Millis 2013

VO_2 proposed for actual use

(12) **United States Patent**
Grossman et al.

(10) **Patent No.: US 6,323,486 B1**
(45) **Date of Patent: Nov. 27, 2001**

(54) **METHOD AND APPARATUS FOR BIAS AND READOUT OF BOLOMETERS OPERATED ON A HYSTERETIC METAL-INSULATOR TRANSITION**

(75) Inventors: **Erich N. Grossman**, Boulder; **Carl D. Reintsema**, Nederland, both of CO (US)

(73) Assignee: **The United States of America as represented by the Secretary of Commerce**, Washington, DC (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/365,113**

OTHER PUBLICATIONS

DeNatale, J.F. et al., "Formation and characterization of grain–oriented VO_2 thin films," (1989) *J. Appl. Phys.* 66(12):5844–5850.

(List continued on next page.)

Primary Examiner—Constantine Hannaher
Assistant Examiner—Albert Gagliardi
(74) *Attorney, Agent, or Firm*—Greenlee, Winner and Sullivan, P.C.

(57) **ABSTRACT**

This invention consists of a bias and readout scheme for resistive bolometers. It is chiefly intended for use with bolometer materials which exhibit a phase transition that is hysteretic. A preferred bolometer material is vanadium dioxide, which has a metal-semiconductor phase transition at 68° C. and a hysteresis of typically 5° C., depending on material preparation. The existence of hysteresis precludes

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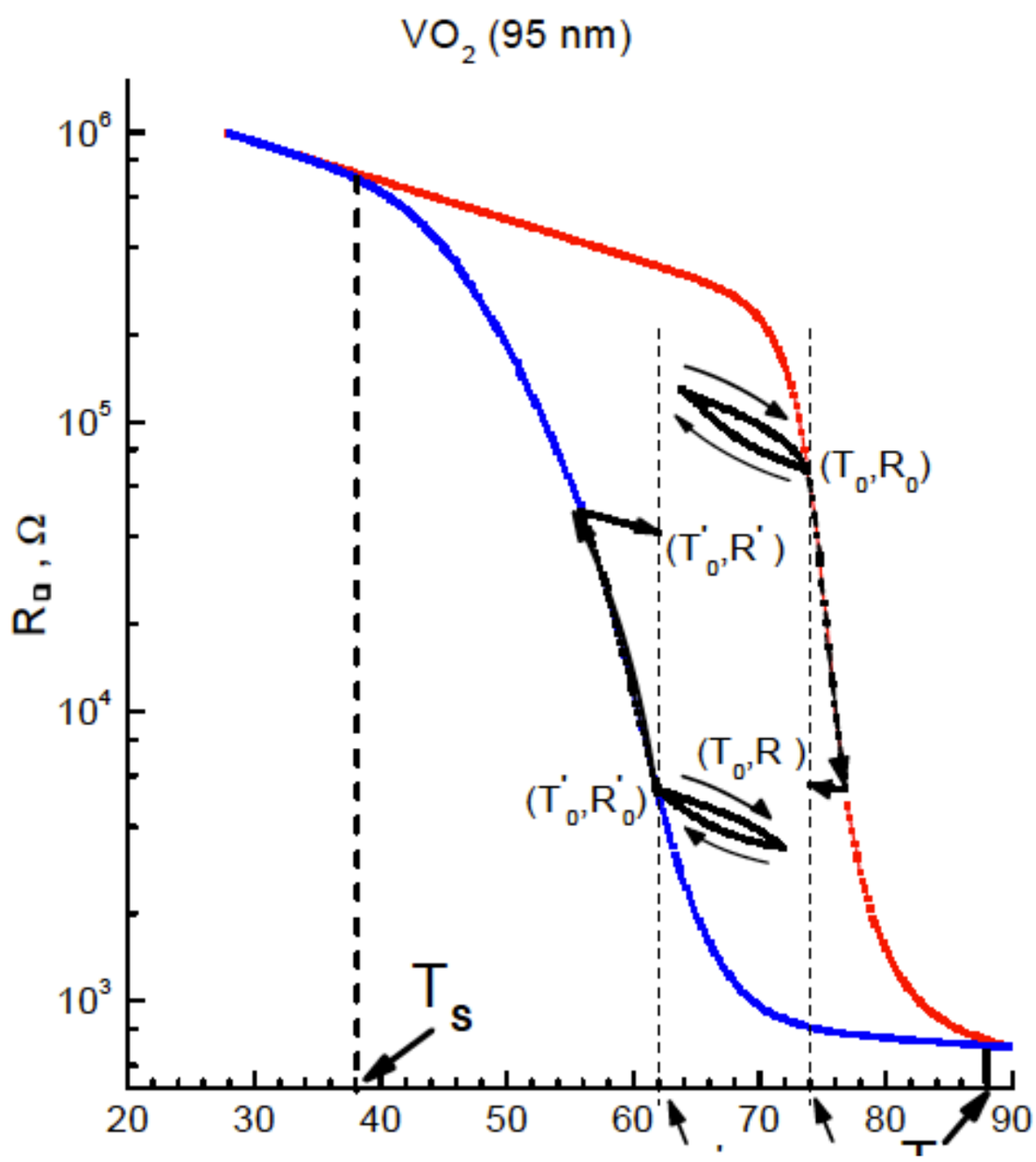
Hysteresis is a problem



hard to 'reset' after initial temperature pulse

Gurvitch et al http://www.ee.sunysb.edu/~serge/234.pdf

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Partially filled d-shell: ``emergent'' electronic properties

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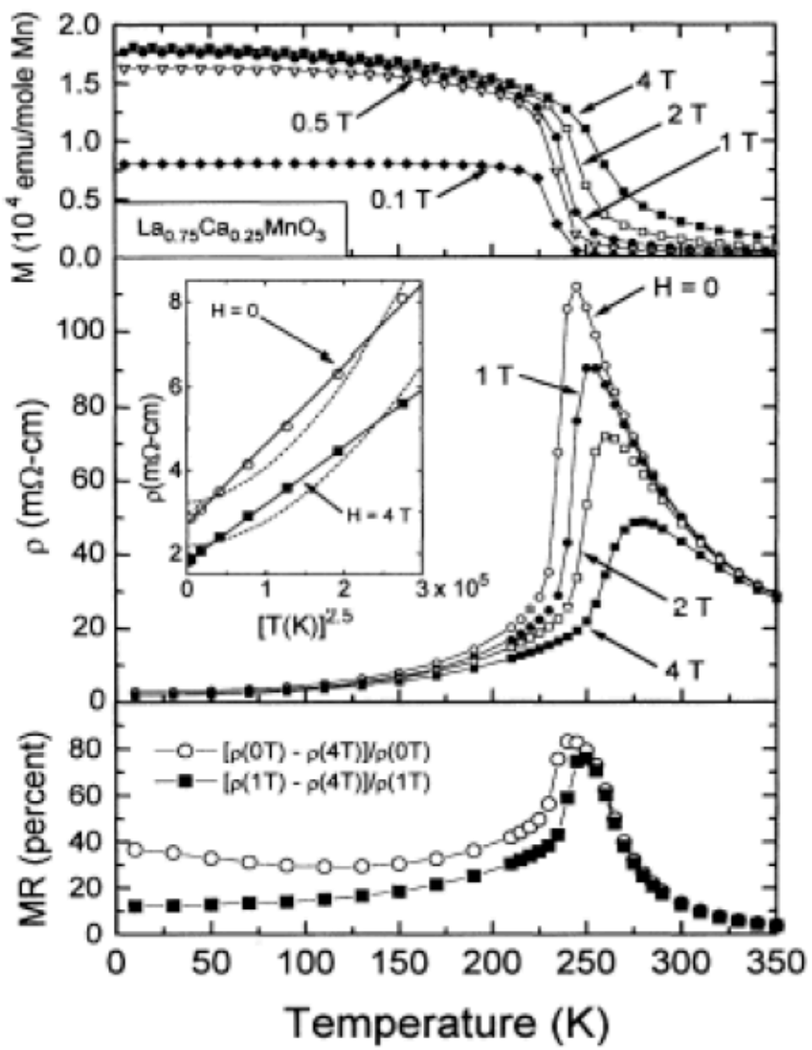
Emergent electronic properties

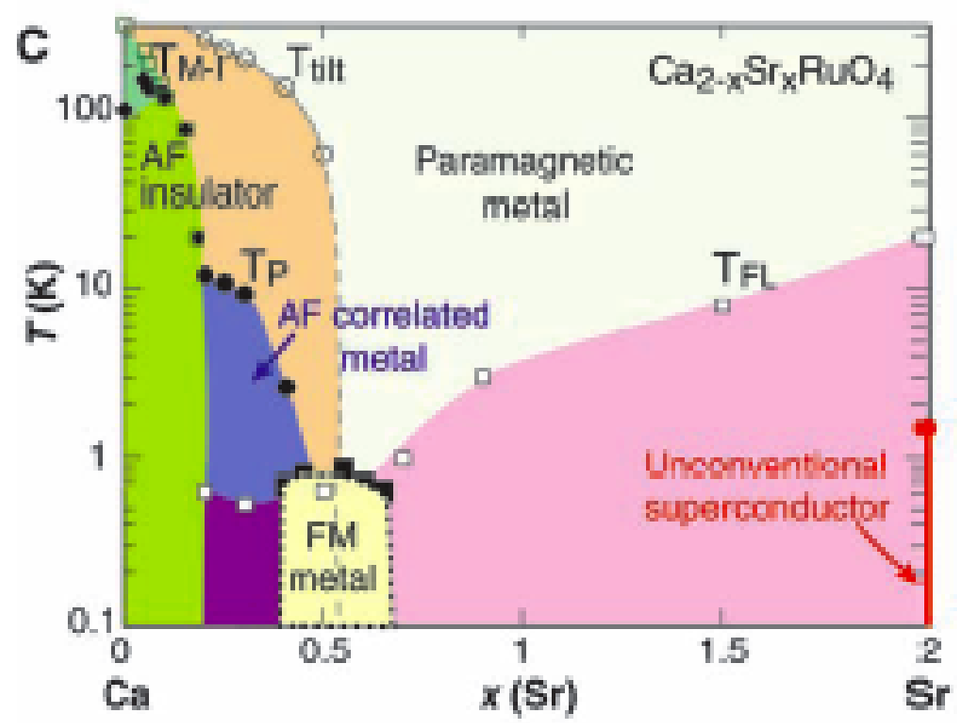
``Colossal" Magnetoresistance

$La_{1-x}Ca_xMnO_3$



Ramirez et al PRL 75 1336

p-wave superconductivity (and many other phases)



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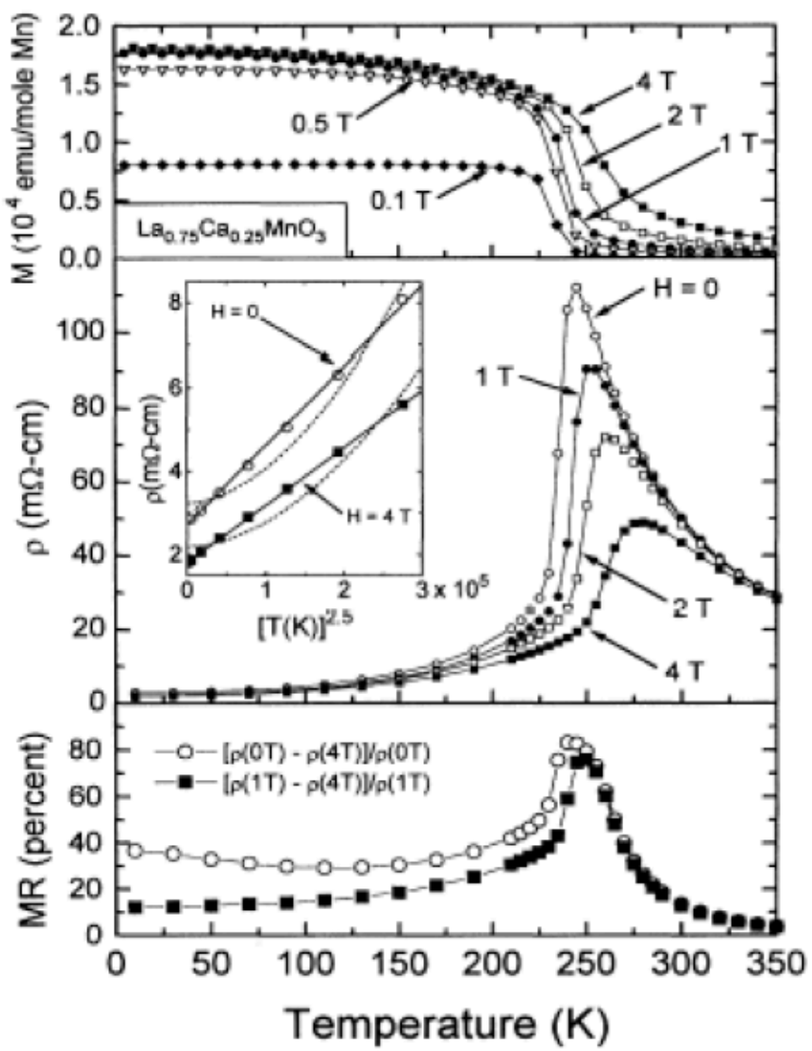
Colossal Magnetoresistance: Phase competition

$La_{1-x}Ca_xMnO_3$



Ramirez et al PRL 75 1336

High T phase: ``insulating" (resistivity large and increasing as T is decreased)

Low T phase metallic and ferromagnetic

Transition appears more or less continuous, and for many years was thought to be second order.

BUT.....

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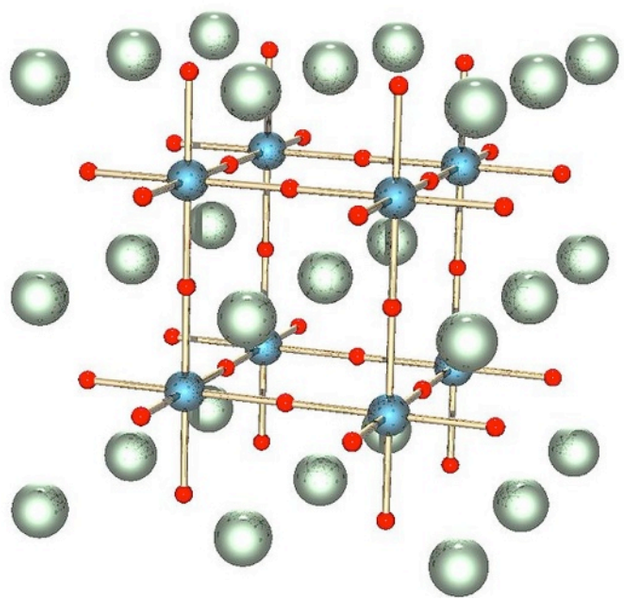
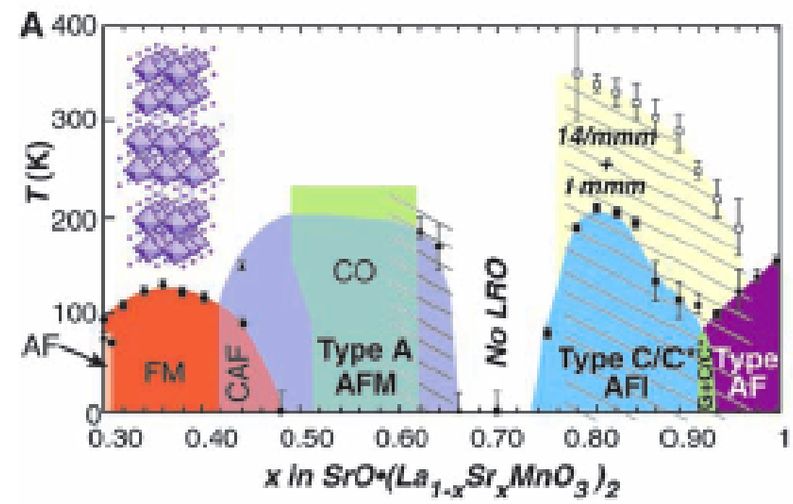
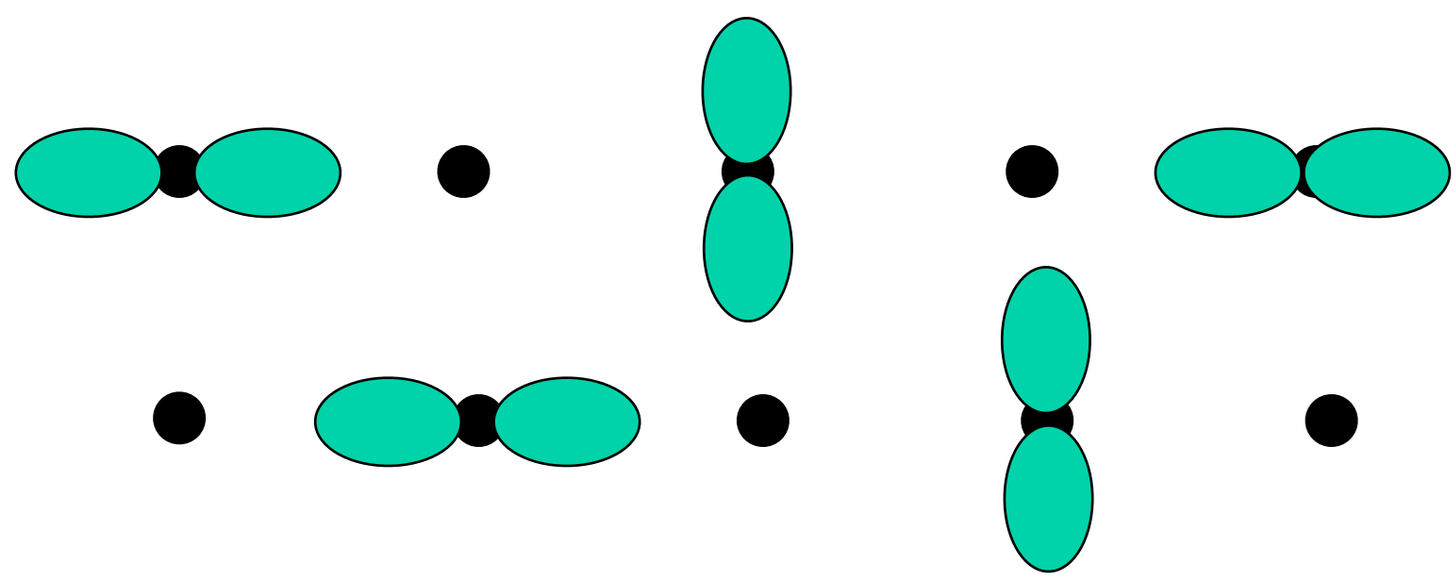
Manganese perovskites

Average high-T structure cubic perovskite



Many low-T phases





``charge/orbital order"
(2d slice shown).
Note 4 unit cell period

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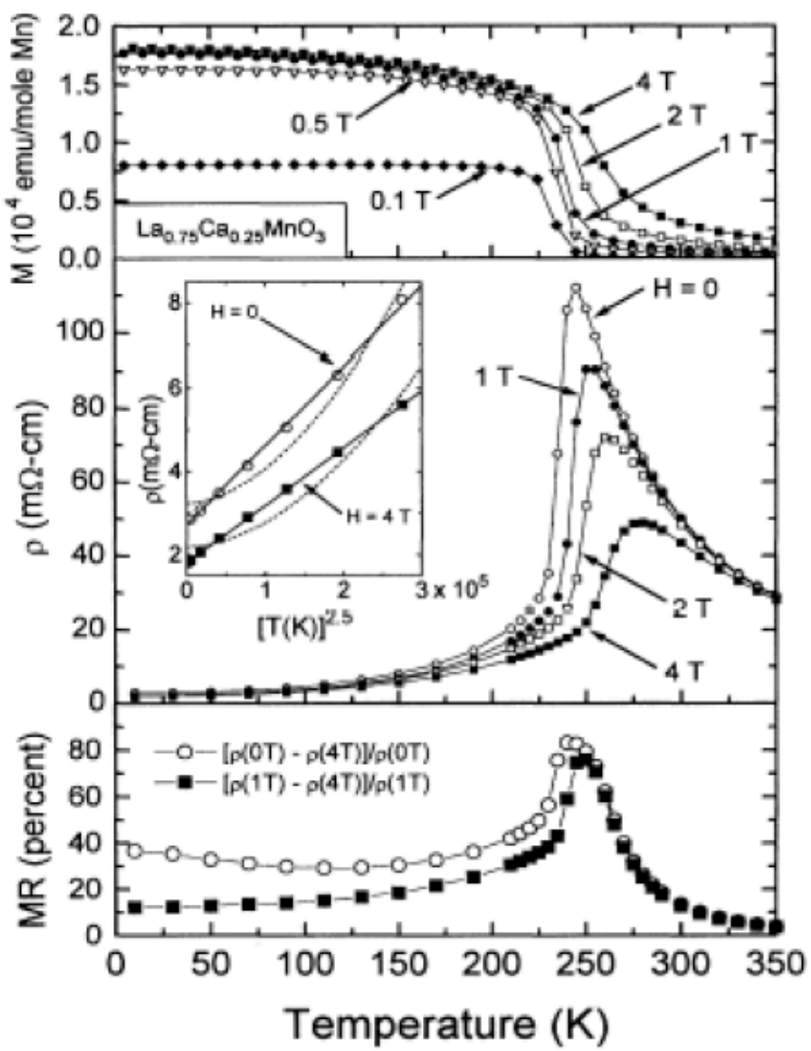
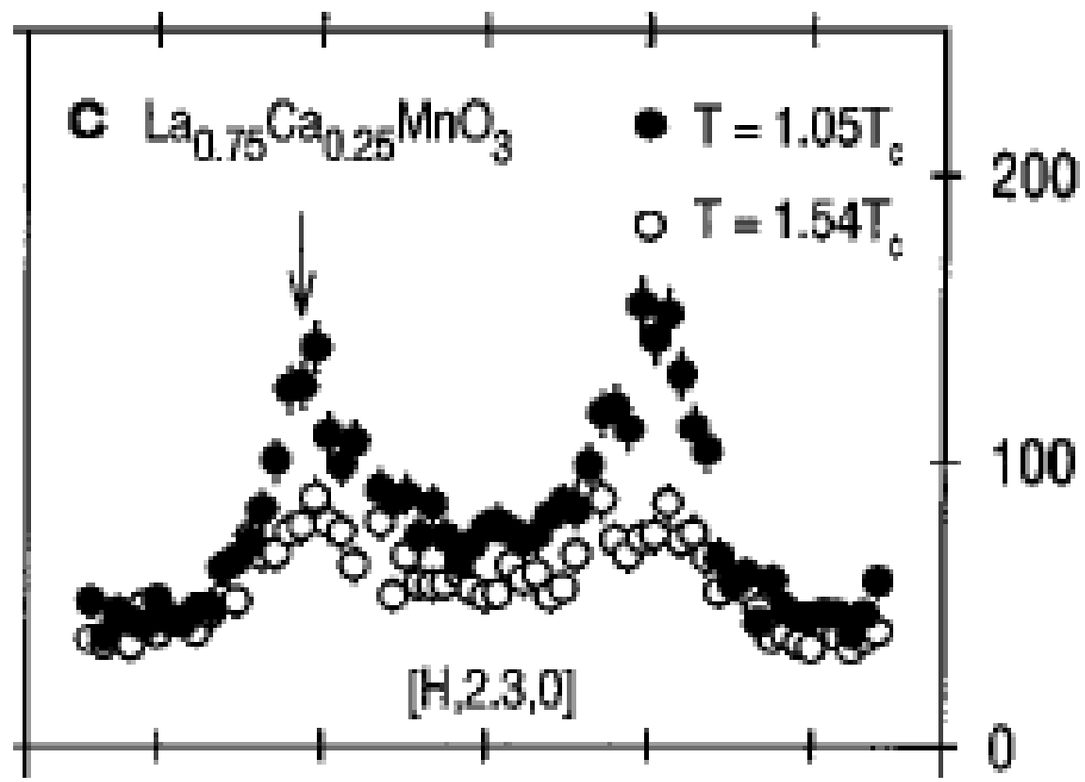
Transition is first order

$La_{1-x}Ca_xMnO_3$



Ramirez et al PRL 75 1336

High T phase has period 4 ordering



Adams et al PRL 85 2553 and 3954 2000

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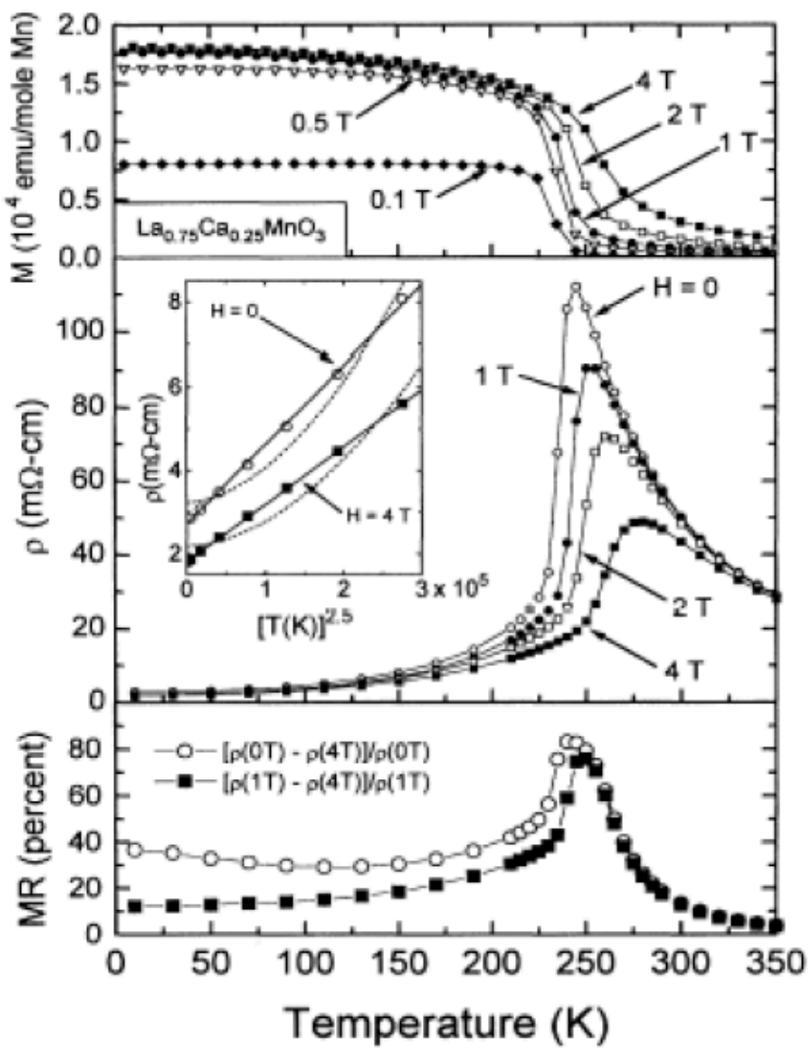
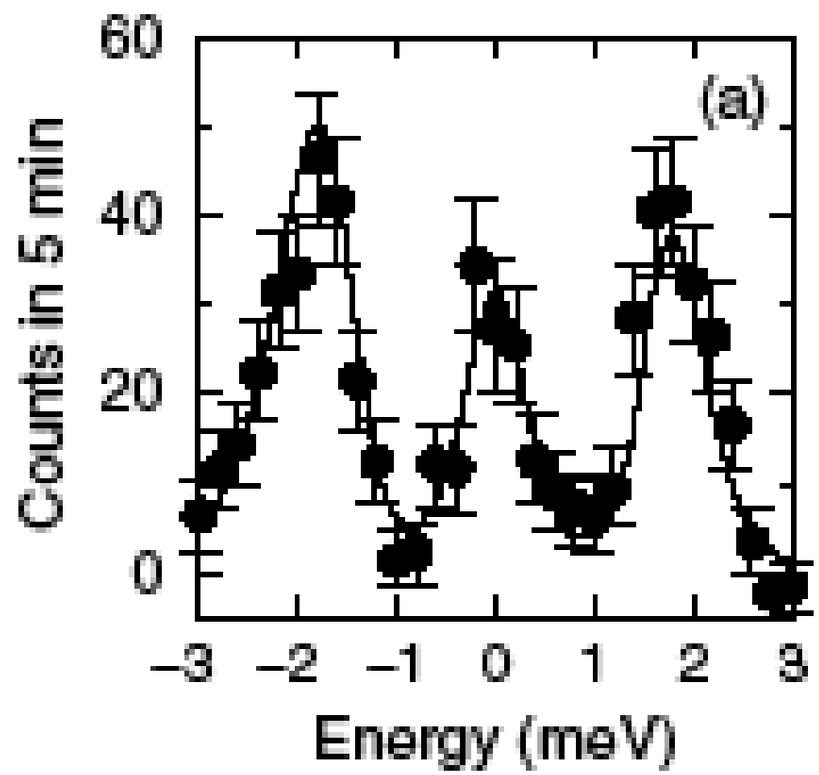
Transition is first order

$La_{1-x}Ca_xMnO_3$



Ramirez et al PRL 75 1336

Low T phase: ferromagnetic.
Well defined spin stiffness T phase has period 4 ordering



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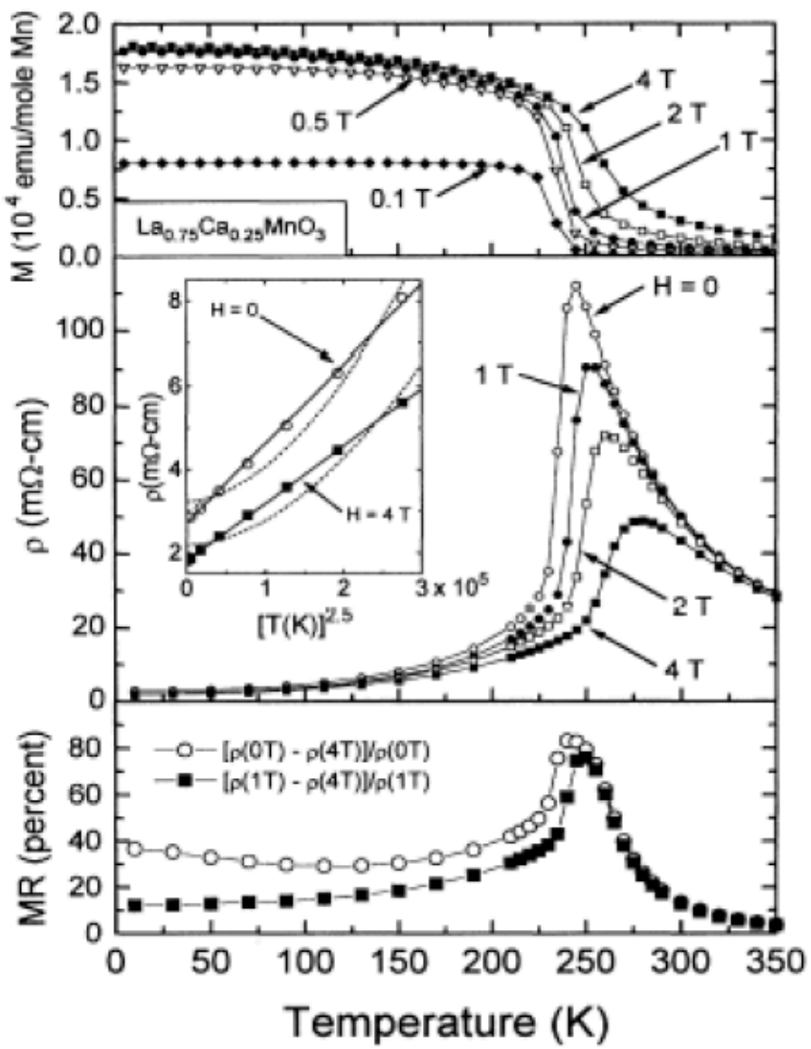
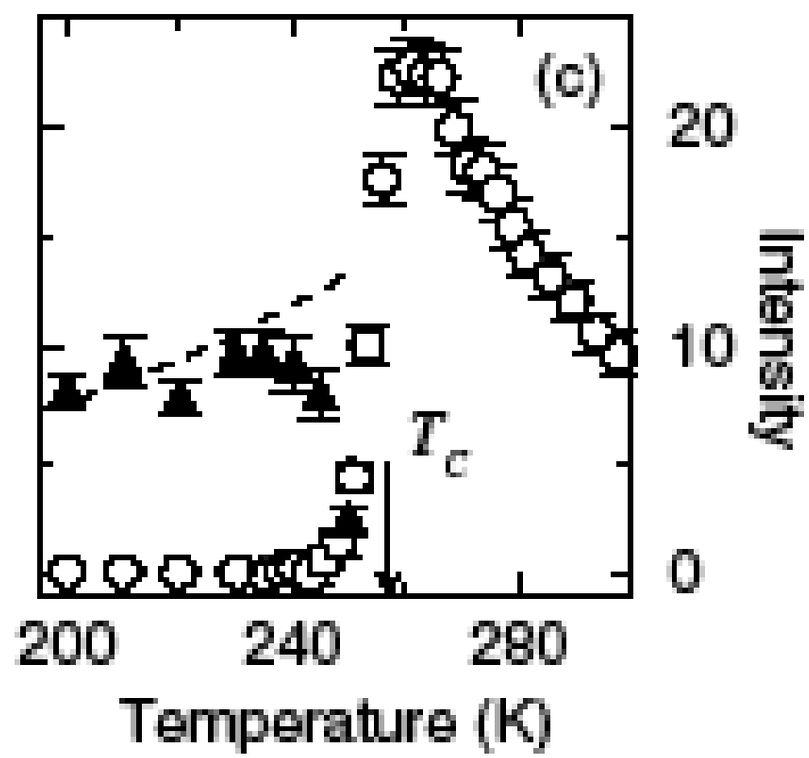
Transition is first order

$La_{1-x}Ca_xMnO_3$



Ramirez et al PRL 75 1336

Spin stiffness jumps discontinuously as does 1/4,0,0 intensity



Morals:

--Unusual high T behavior <=>short ranged order

--First order transitions (may be hard to see)

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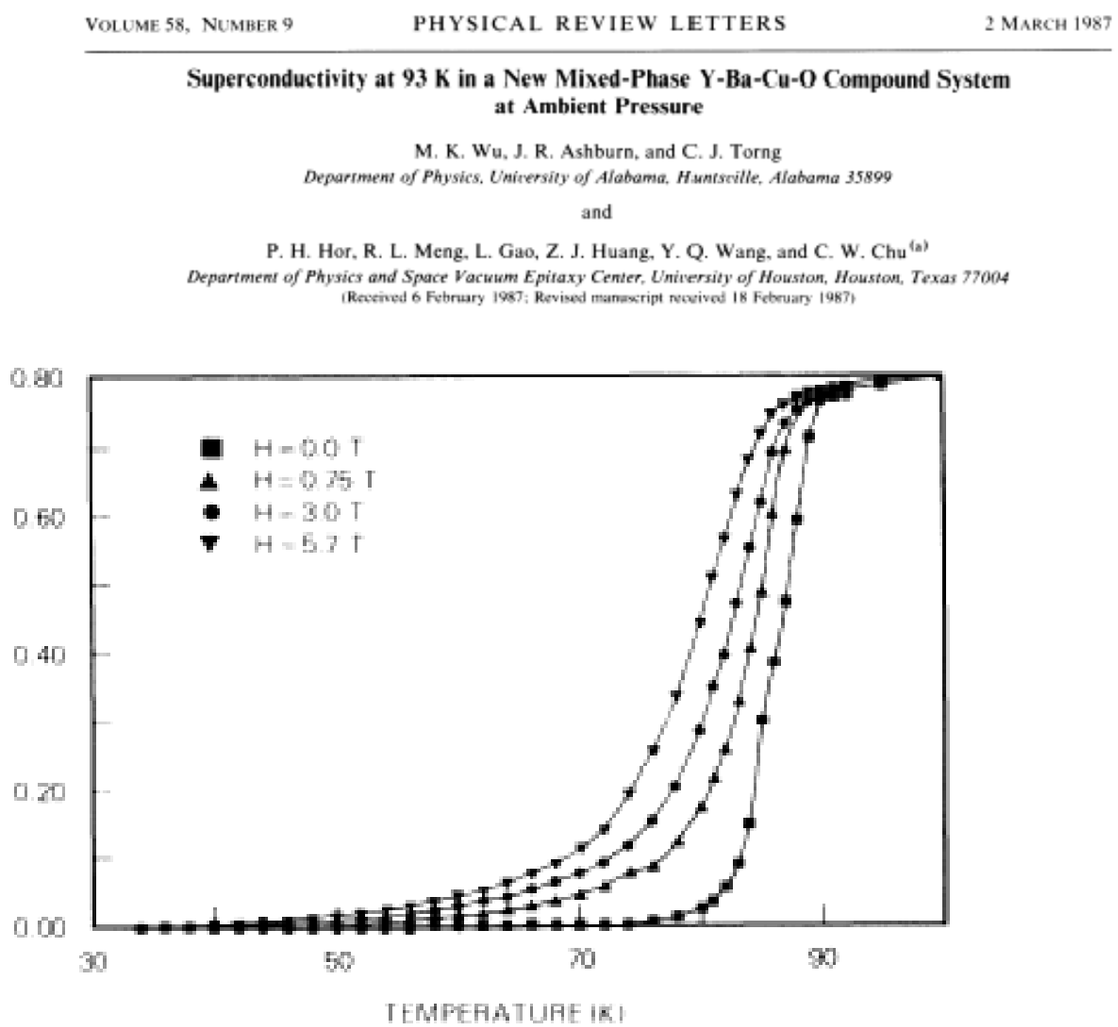
Emergent electronic properties

High Tc Superconductivity: in copper oxide and iron arsenide superconductors



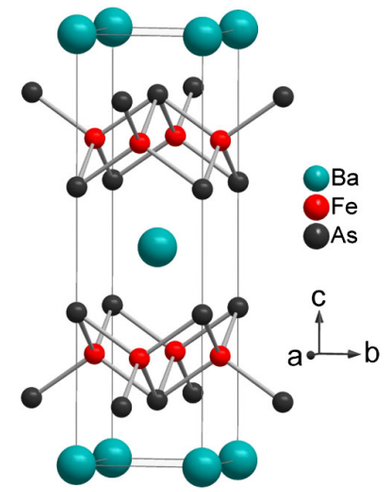
VOLUME 58, NUMBER 9 PHYSICAL REVIEW LETTERS 2 MARCH 1987

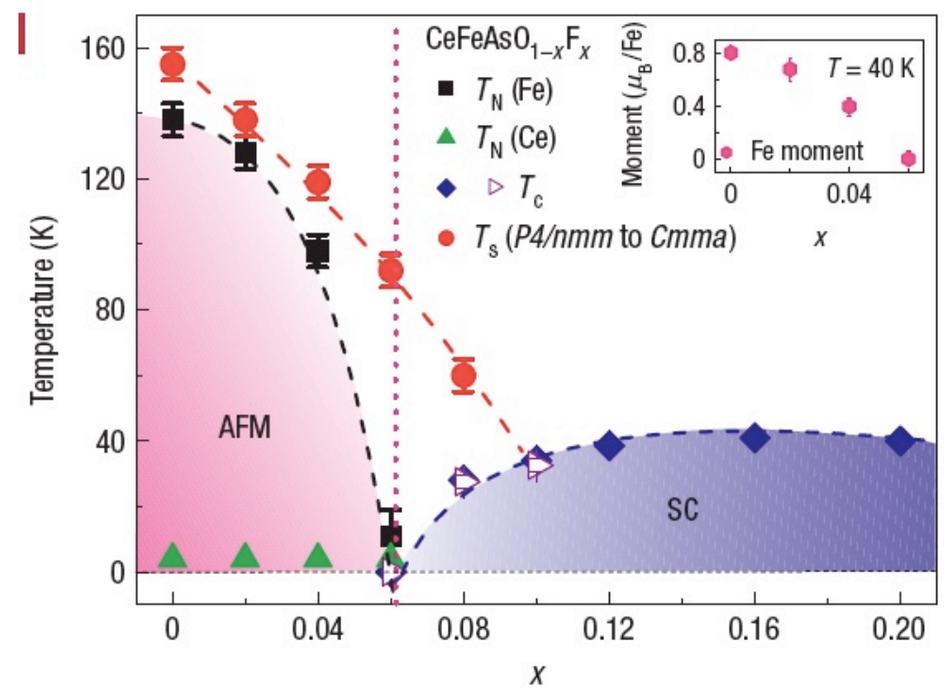
Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure

M. K. Wu, J. R. Ashburn, and C. J. Torng
Department of Physics, University of Alabama, Huntsville, Alabama 35899

and

P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu[a]
Department of Physics and Space Vacuum Epitaxy Center, University of Houston, Houston, Texas 77004
(Received 6 February 1987; Revised manuscript received 18 February 1987)





010 825

J.Zhao, et.al, Nature Mater. 7, 953(2008)

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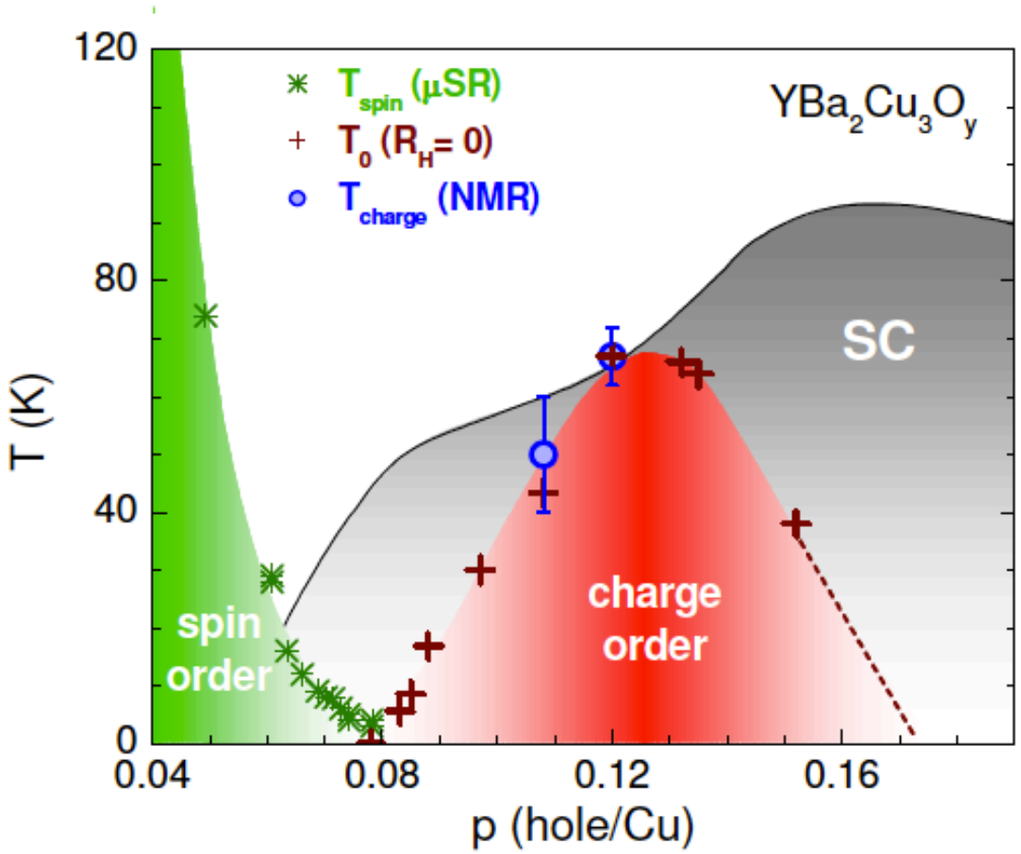
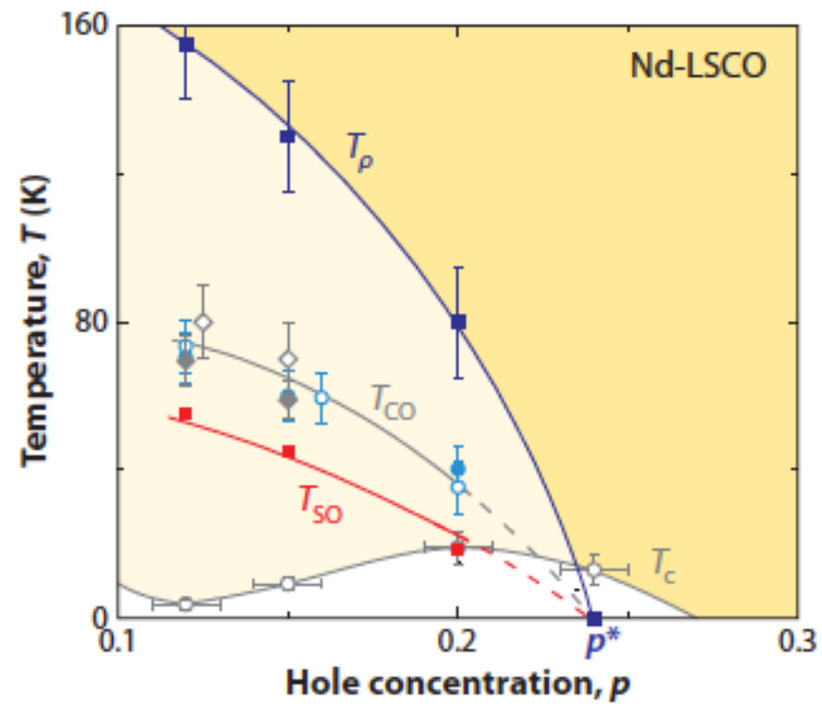
Copper-oxide high T_c:
again competing density-wave phases





Louis Taillefer

Wu et al Nature 477 7363 2011

Annu. Rev. Condens. Matter Phys. 2010. 1:51–70

Open question: how much of the physics of oxide superconductivity arises from competing phases

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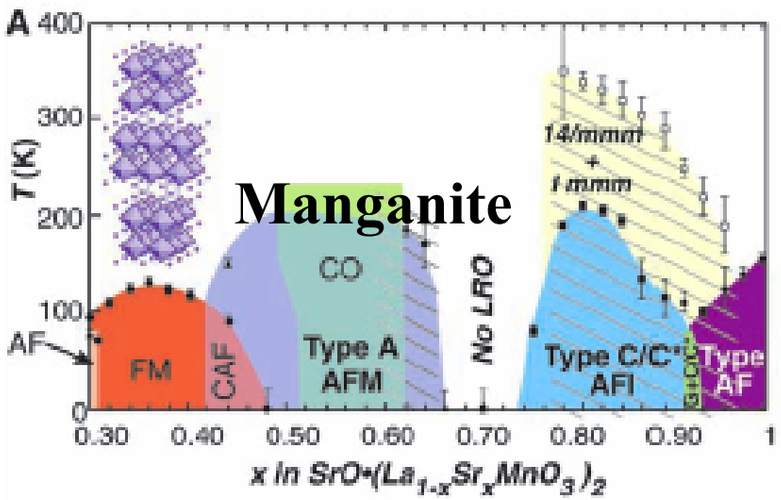
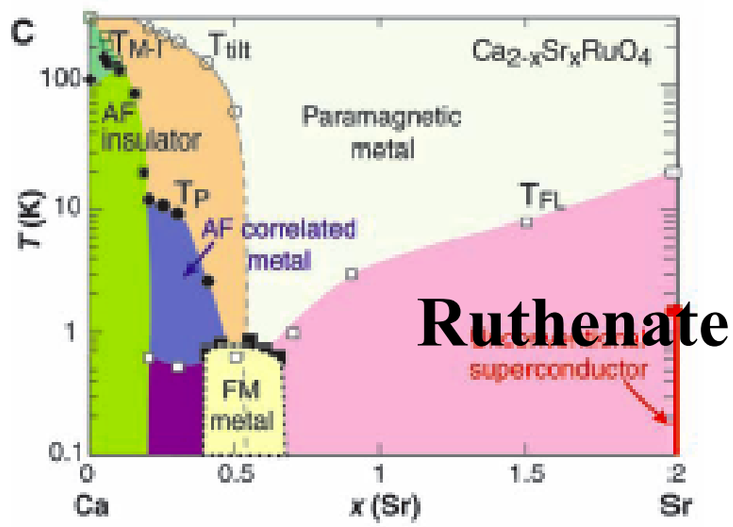
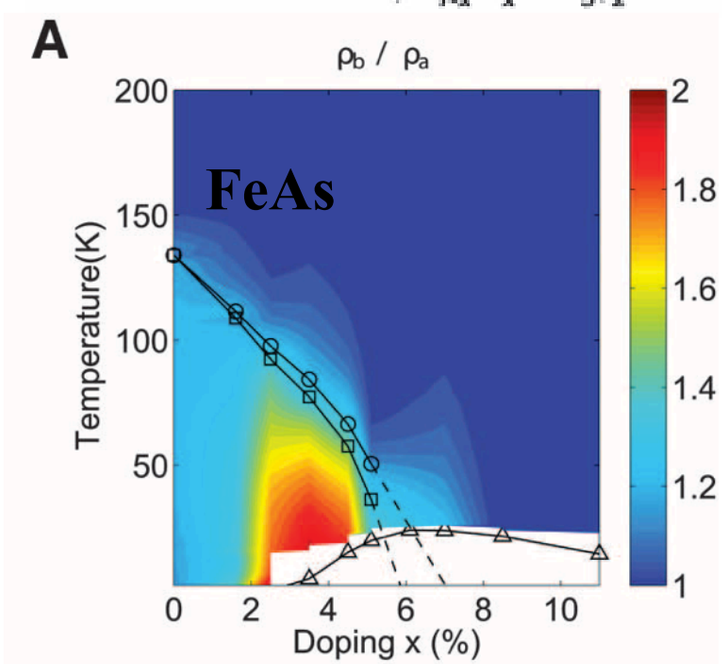
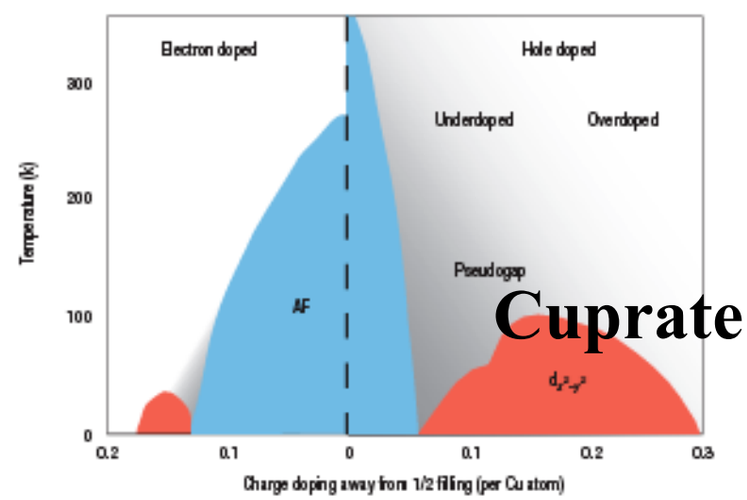
summary:
profusion of emergent electronic phases









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Key Features of Transition Metal Oxides

- **Multiple d configurations (both valence and spin/orbital configuration at fixed valence)**
- **``Easy" charge exchange with other ions (esp O)**
- **Multiple bonding modalities <=> many possible structures**
- **Unusual transport: high carrier density but low coherence scales**
- **Multiple electronic phases (some, unexpected)**

All of these properties stem from electron-electron interactions in the partly filled transition metal d-shell

The question: relate crystal structure, chemistry to material properties

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Periodic Table to Properties: Stereotypical Theorist's View

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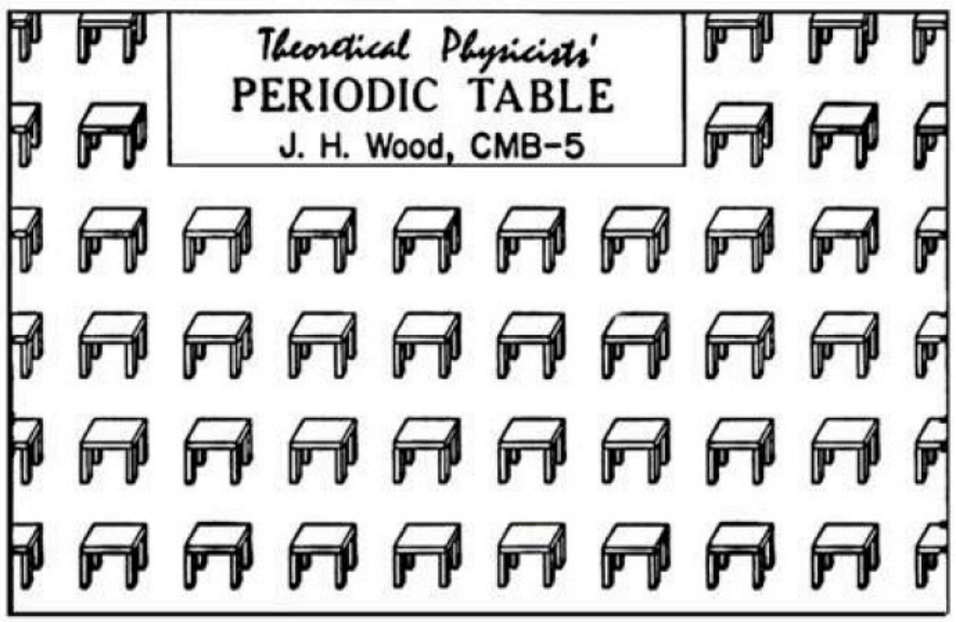
Periodic Table to Properties: Stereotypical Theorist's View

PeriodicTable



Periodic table from J H Wood; quoted in Z Fisk 2010 KITP talk

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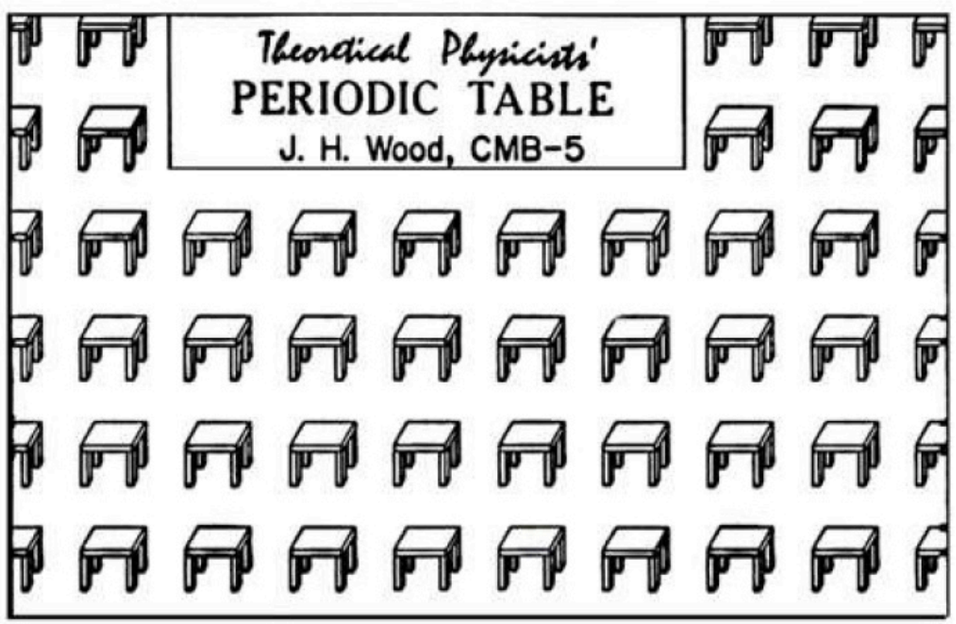
Periodic Table to Properties: Stereotypical Theorist's View

PeriodicTable



Ignore details: write Quantum Field Theory

$$\Rightarrow \quad \frac{\kappa}{2}\epsilon^{\mu\nu\lambda}\mathbf{A}_\mu\partial_\nu\mathbf{A}_\lambda + \ldots$$

Periodic table from J H Wood; quoted in Z Fisk 2010 KITP talk

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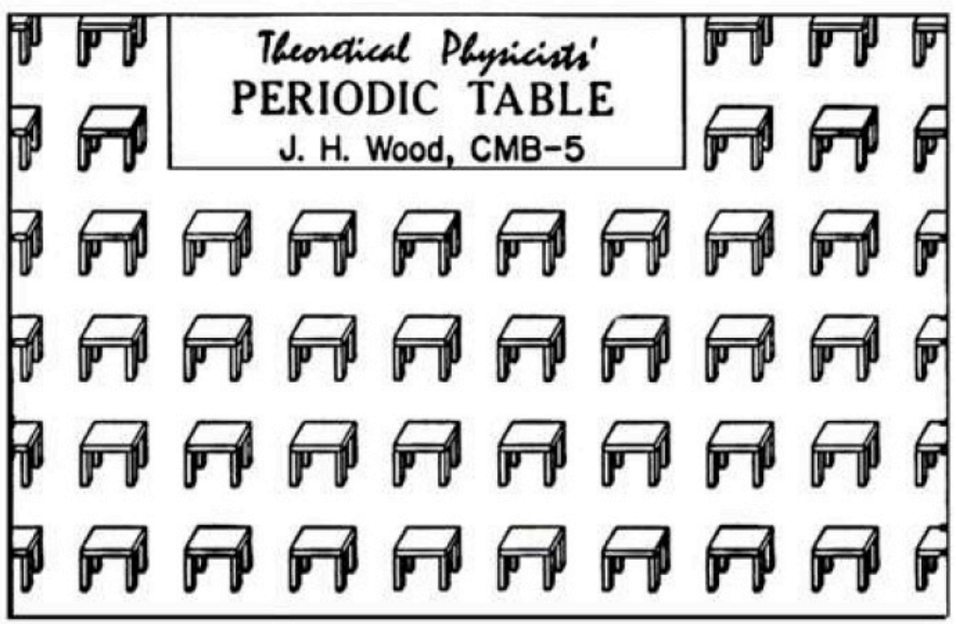
Periodic Table to Properties: Stereotypical Theorist's View

PeriodicTable



Ignore details: write Quantum Field Theory

$$\Rightarrow \quad \frac{\kappa}{2}\epsilon^{\mu\nu\lambda}\mathbf{A}_\mu\partial_\nu\mathbf{A}_\lambda + \ldots$$

These lectures--where we are on attempts to do better:

Periodic table from J H Wood; quoted in Z Fisk 2010 KITP talk

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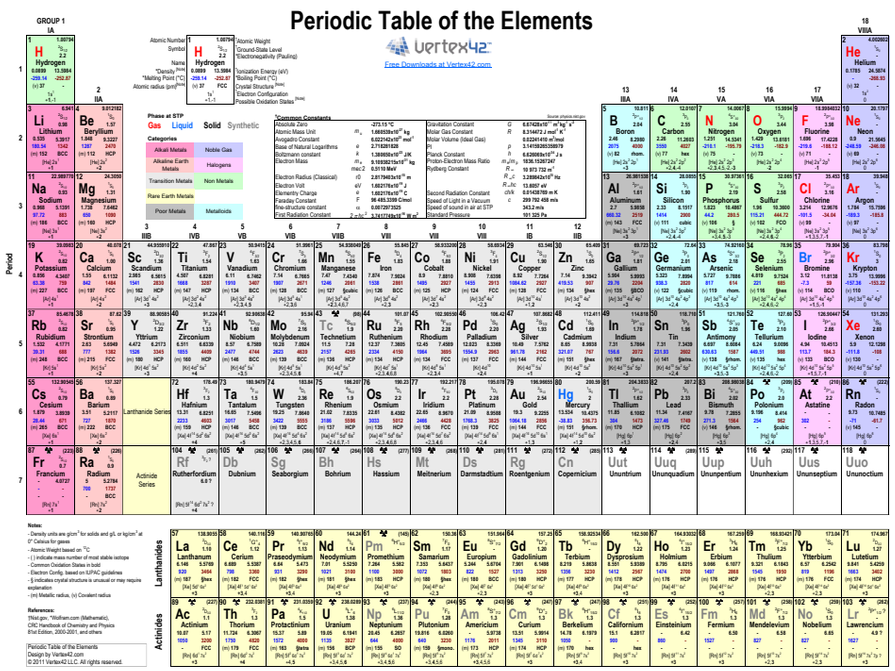
Periodic Table to Properties: Stereotypical Theorist's View

PeriodicTable



Richer Description of Properties

Understand and control what situations give which properties

These lectures--where we are on attempts to do better:

Periodic table from J H Wood; quoted in Z Fisk 2010 KITP talk

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Basic chemistry and physics

- **Crystal type and nominal valence**
- **Crystal structure and level ordering**
- **Energetics**
  - **Interactions**
  - **Charge transfer**
  - **Hybridization**
- **Classification and Summary**

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Crystal type and nominal valence

Basic idea

--Oxygen: very electronegative.

In vacuum: $1s^2 2s^2 2p^4$

In solid: oxygen ``wants`` to fill up p-shell

(O^{2-}: $1s^2 2s^2 2p^6$)

--Transition metal: less electronegative

In vacuum: $[Ar]d^n 4s^2$

In solid: ``wants`` to lose 4s electrons, change # d =>$[Ar]d^{n+m}$

By controlling number of oxygen per transition metal, and number and electronegativity of other elements, can control filling of d-shell

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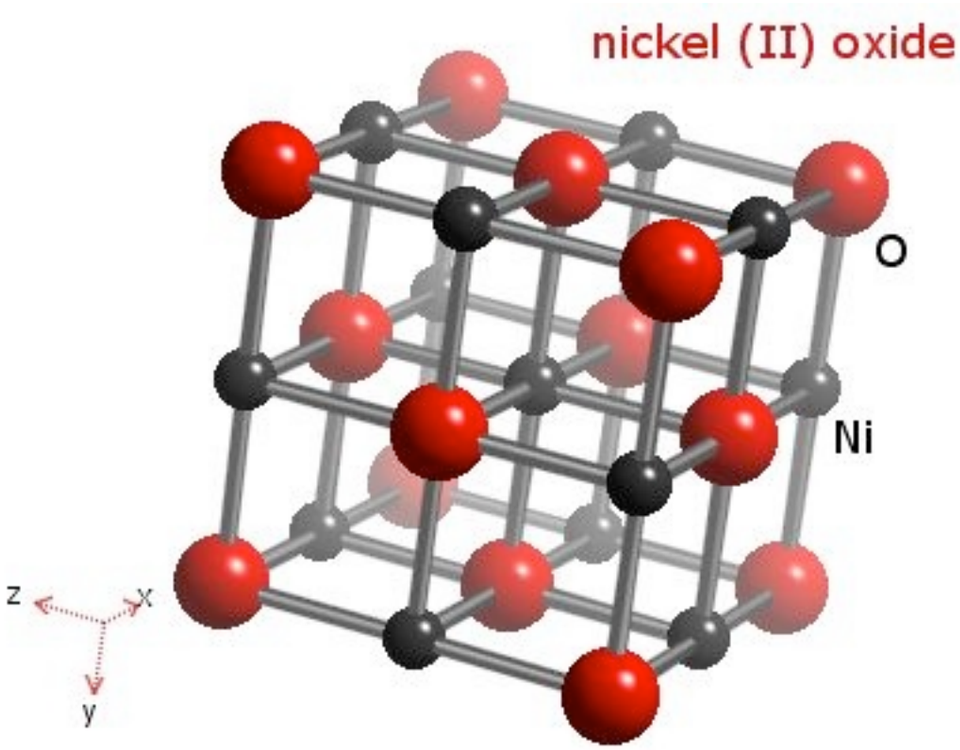
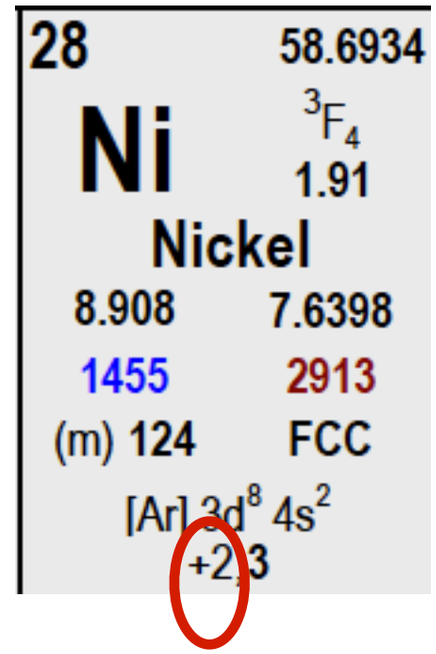
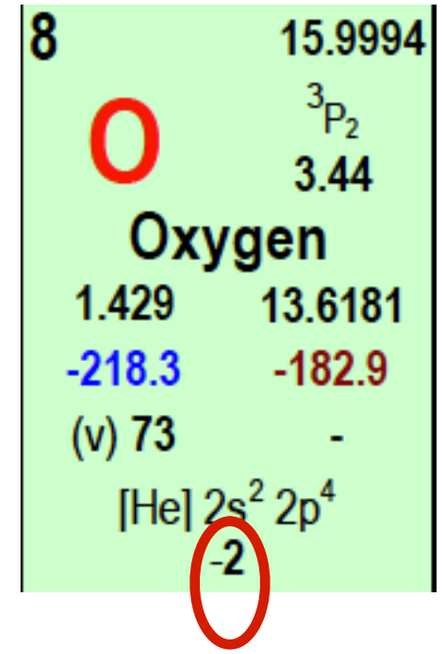
Crystal type and nominal valence

Monoxide: rocksalt structure



http://www.webelements.com/compounds/nickel/nickel_oxide.html





Simple picture: removal energy of Ni 4s low; electron affinity of O 2p high
=>
Ni: [Ar]$3d^8$ O: [He]$2s^2 2p^6$

Complication: Ni-O hybridization

Ni: [Ar]$3d^{8+x}$ O: [He]$2s^2 2p^{6-x}$

??how big is x??

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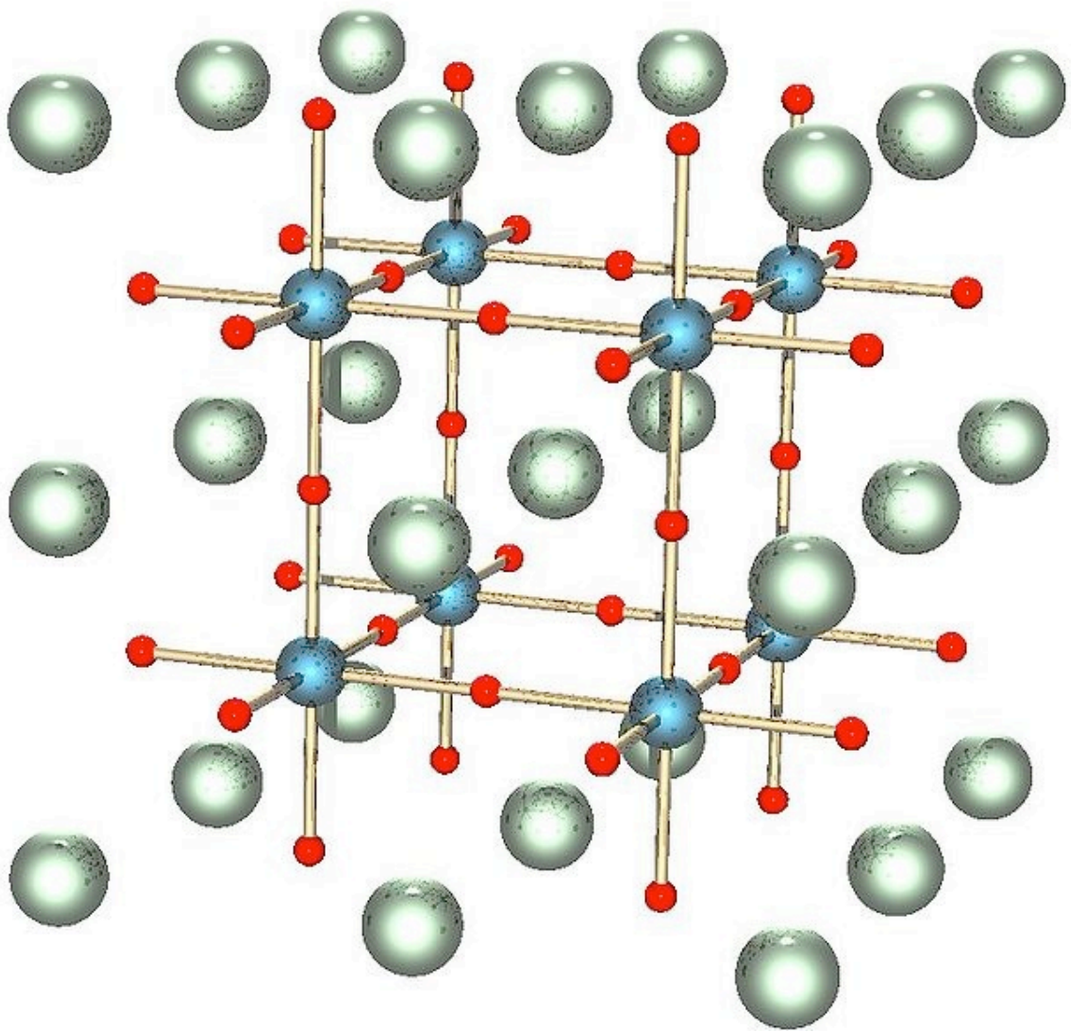
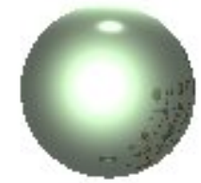
Crystal type and nominal valence

ABO_3 perovskite, cubic phase





A-site. Typically electrically inert; choice of A ion controls valence of B site

B-site: in our case, transition metal with partly filled d-shell

dont forget oxygen!

http://en.wikipedia.org/wiki/File:Perovskite.jpg

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Crystal type and nominal valence

ABO_3: Presence of A-site ion stabilizes different valence

57	138.9055
La	$^2D_{3/2}$ 1.10
Lanthanum	
6.146	5.5769
920	3464
(m) 187	§hex
[Xe] $5d^1\ 6s^2$	
+3	

23	50.9415
V	$^4F_{3/2}$ 1.63
Vanadium	
6.11	6.7462
1910	3407
(m) 134	BCC
[Ar] $3d^3\ 4s^2$	
+2,3,4,5	

8	15.9994
O	$^3P_2$ 3.44
Oxygen	
1.429	13.6181
-218.3	-182.9
(v) 73	-
[He] $2s^2\ 2p^4$	
-2	

Simple picture: removal energies of La 5d, 6s V 4s, 3d low; electron affinity of O2p high

=>$LaVO_3$

La^{3+} [Xe] V^{3+}: [Ar]$3d^2$ O^{2-}: [He]$2s^2 2p^6$

Complication: V-O hybridization

V: [Ar]$3d^{2+3x}$ O: [He]$2s^2 2p^{6-x}$

??how big is x??

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Crystal type and nominal valence

Vary A-site ion: change valence

38	87.62
Sr	$^1S_0$ 0.95
Strontium	
2.63	5.6949
777	1382
(m) 215	FCC
[Kr] $5s^2$	
+2	

57	138.9055
La	$^2D_{3/2}$ 1.10
Lanthanum	
6.146	5.5769
920	3464
(m) 187	§hex
[Xe] $5d^1$ $6s^2$	
+3	

23	50.9415
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1910	3407
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[Ar] $3d^3$ $4s^2$	
+2,3,4,5	

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O	$^3P_2$ 3.44
Oxygen	
1.429	13.6181
-218.3	-182.9
(v) 73	-
[He] $2s^2$ $2p^4$	
-2	

Simple picture: removal energies of La 5d, 6s V 4s, 3d low; electron affinity of O2p high
=>$SrVO_3$
V^{4+}: [Ar]$3d^{1+3x}$ O^{2-}: [He]$2s^2 2p^{6-x}$

Simple picture: removal energies of La 5d, 6s V 4s, 3d low; electron affinity of O2p high
=>$LaVO_3$
La^{3+} [Xe] V^{3+}: [Ar]$3d^2$ O^{2-}: [He]$2s^2 2p^6$

Complication: V-O hybridization

V: [Ar]$3d^{2+3x}$ O: [He]$2s^2 2p^{6-x}$

??how big is x??

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Crystal structure and level ordering

Basic idea

--d-levels degenerate in free space.
--Solid state: local environment breaks the symmetry

By controlling the local (point) symmetry of the transition metal ion, can control which orbitals are occupied.

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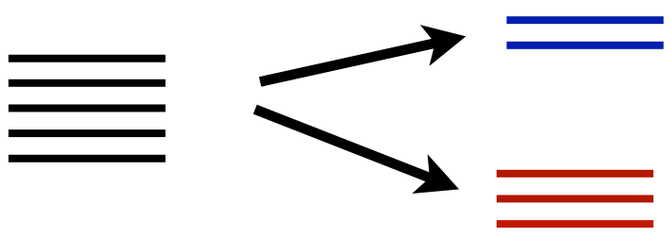
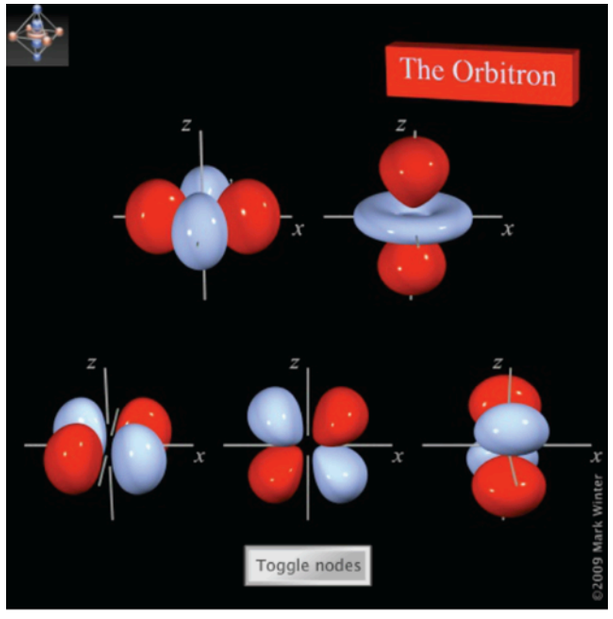
Symmetry breaking: Group Theory

Simplest example: nearly cubic environment

	Free space (no spin orb)	Cubic
group:	$O(3)$	O_h
representation	$L=2$ →	e_g t_{2g}
		x^2-y^2; $3z^2-r^2$ xy; xz; yz
picture		



http://winter.group.shef.ac.uk/orbitron/AOs/3d/index.html

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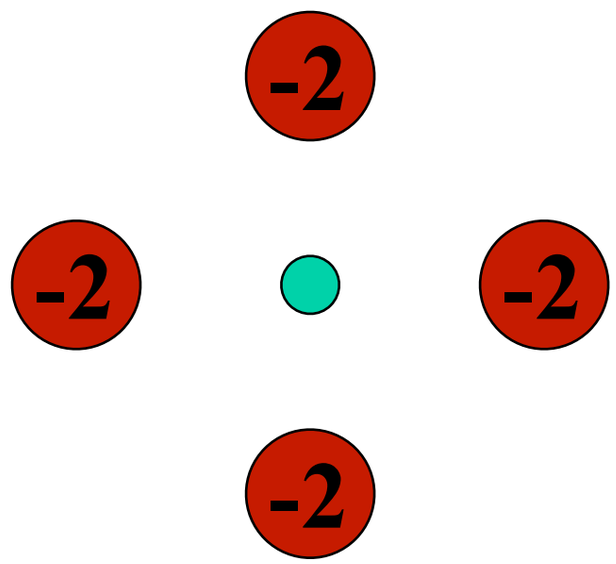
Electrostatic contribution to crystal field splitting small

Simple estimate: point charge model:
O charge -2 at distance R_O~2A; ``size" of d orbital R_d~0.5A



$$\mathbf{V}(\vec{r}) = \sum_{\mathbf{i=1\ldots6}} \frac{\mathbf{4e^2}}{|\vec{\mathbf{r}} - \vec{\mathbf{R}}_i|}$$

Level splitting: expand for small r. First deviation from spherical symmetry is quadrupole term

$$\mathbf{V_{quad}} \sim \frac{\mathbf{4e^2}}{\mathbf{R_O}} \left(\frac{\mathbf{R_d}}{\mathbf{R_O}}\right)^{\mathbf{4}} \sim \mathbf{0.1eV}$$

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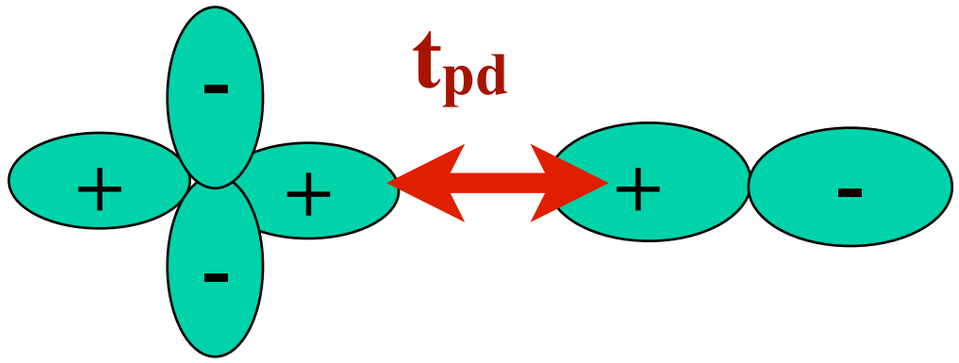
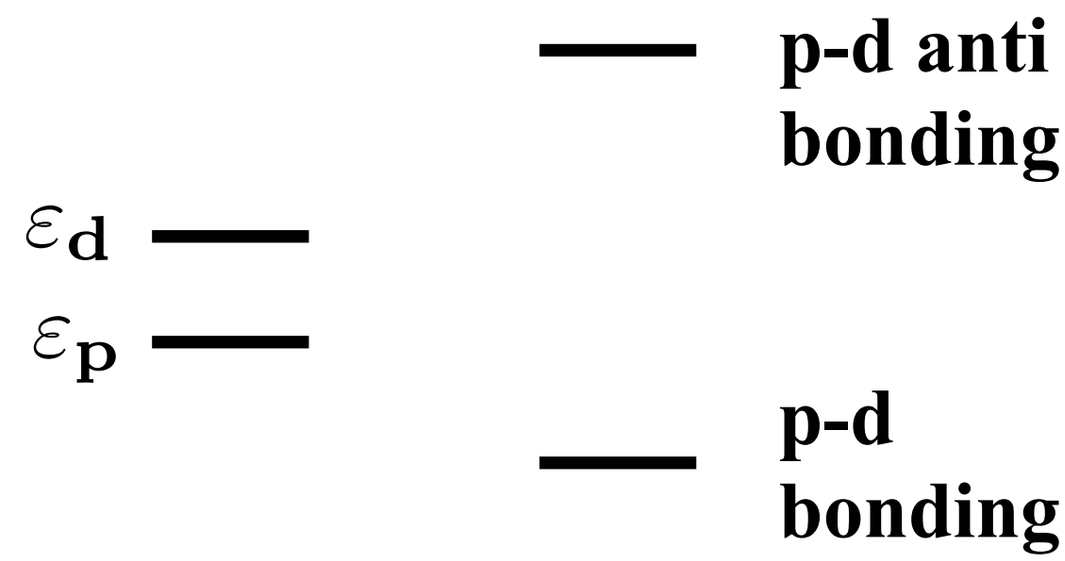
Dominant contribution: hybridization to ligand (oxygen)



$d_{x^2-y^2}$ p_σ



In almost all transition metal oxides, the near-fermi surface states are p-d ANTIBONDING states.
Question: how much d and how much p character

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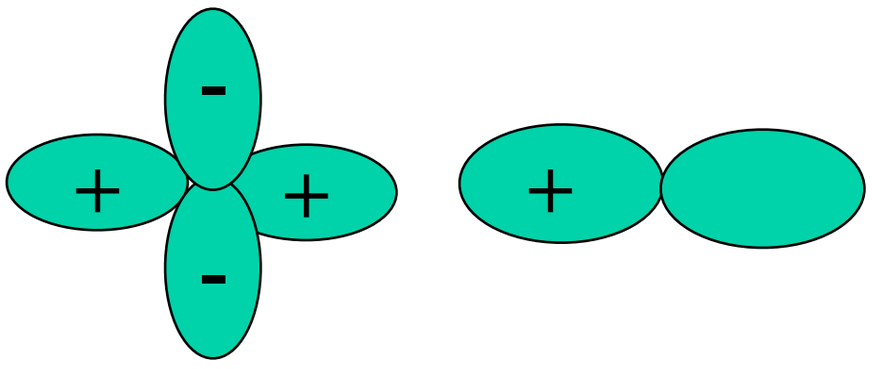
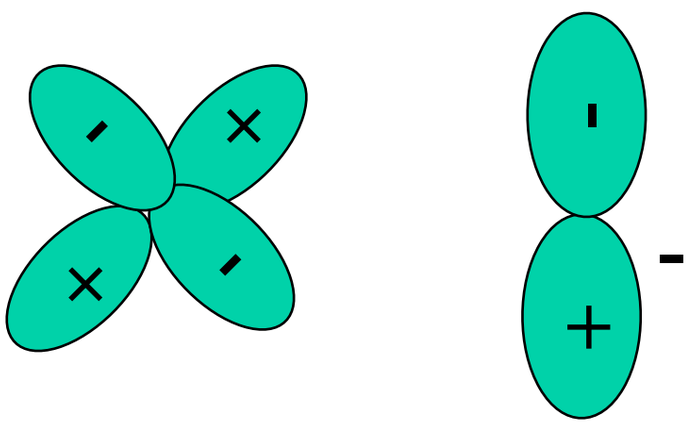
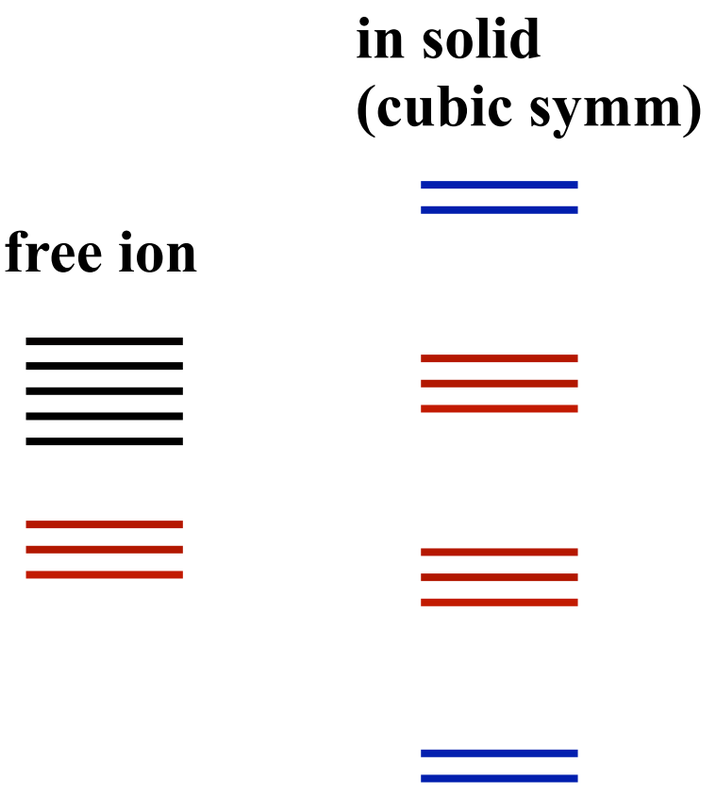
d-p overlap stronger for e_g than t_{2g}



$d_{x^2-y^2}$ p_σ



d_{xy} p_π



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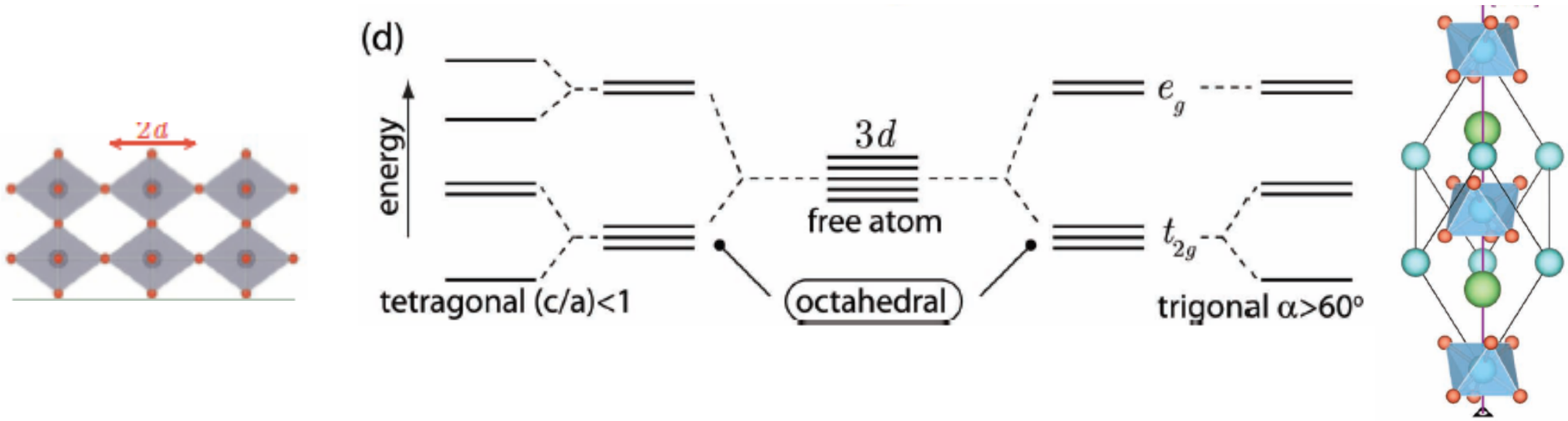
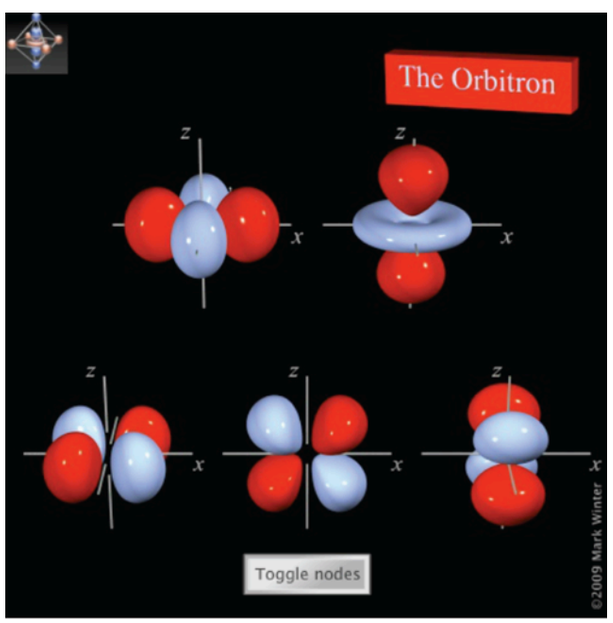
Lower than cubic symmetry

Rondinelli and Spaldin, Adv. Mater. **23** 3363 (2011)





(Recall! what is depicted are the p-d antibonding bands)

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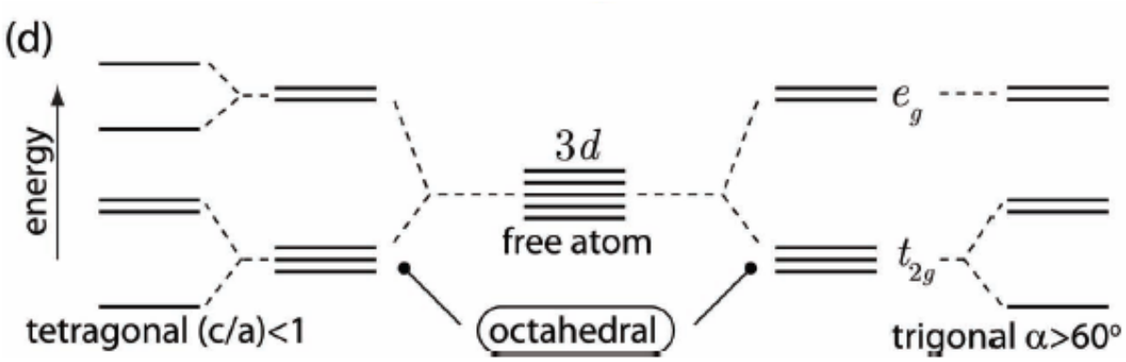
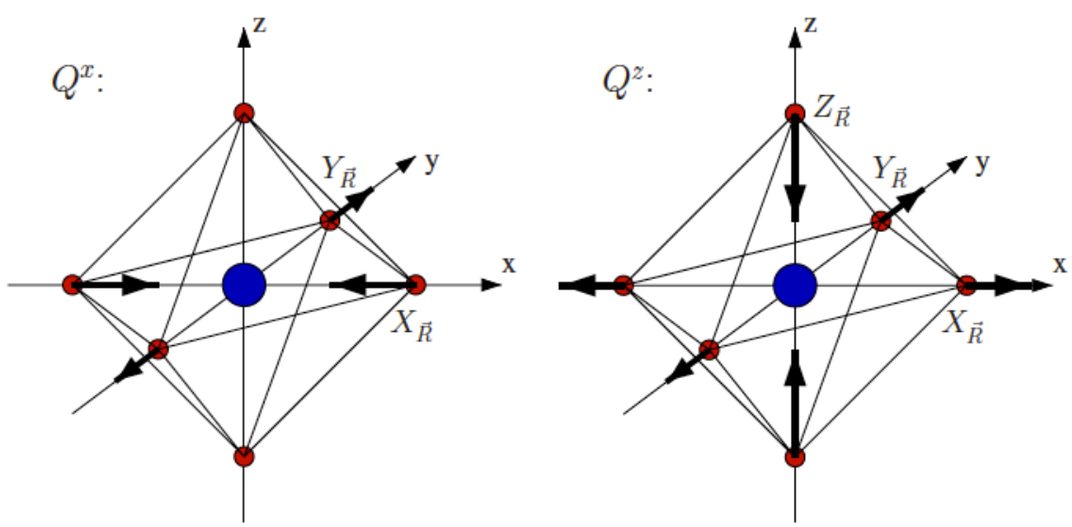
Jahn-Teller (cubic-tetragonal) distortion



Define distortions



$$Q^x_{\vec{R}} = \frac{1}{\sqrt{2}}(X_{\vec{R}} - Y_{\vec{R}}),$$

$$Q^z_{\vec{R}} = \frac{1}{\sqrt{6}}(2Z_{\vec{R}} - X_{\vec{R}} - Y_{\vec{R}})$$

$$\hat{H}_{\mathrm{JT}} = -\lambda \sum_{\vec{R},\sigma} (Q^x_{\vec{R}} d^+_{\vec{R},\sigma} \tau^x d_{\vec{R},\sigma} + Q^z_{\vec{R}} d^+_{\vec{R},\sigma} \tau^z d_{\vec{R},\sigma}).$$

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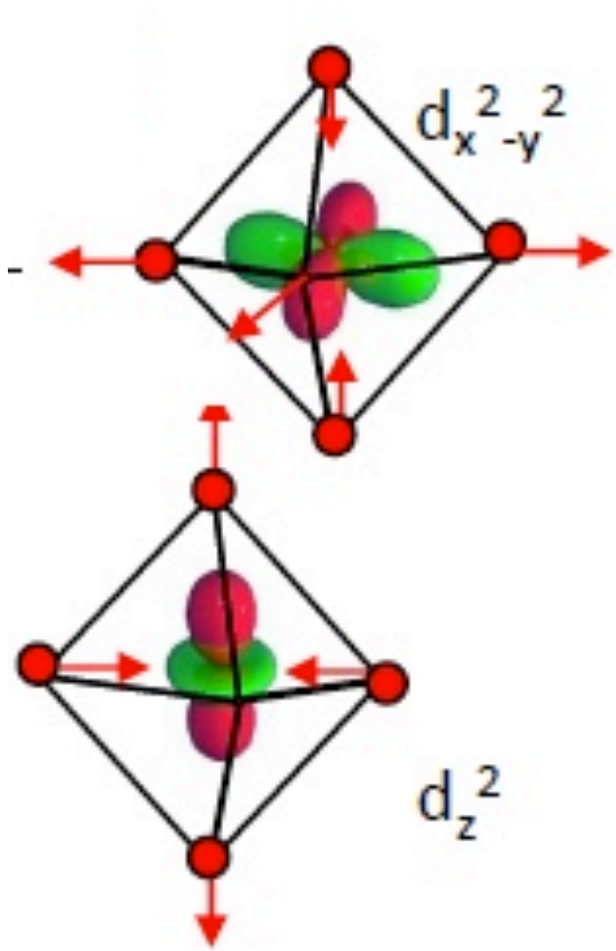
Consequence of structural distortion: change of hybridization

Jahn-Teller type: change Tm-O bond length

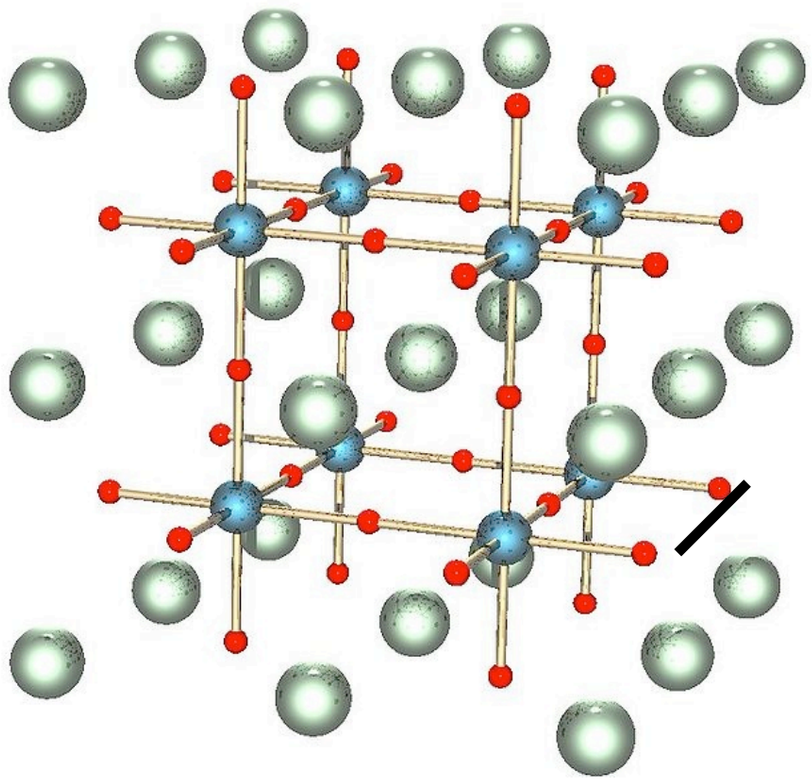


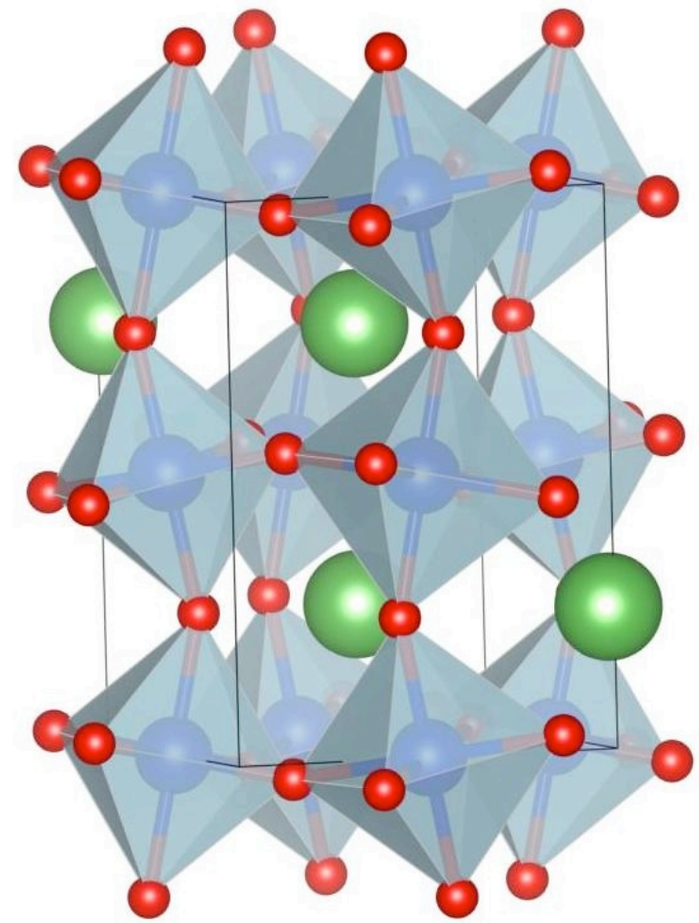
Change transition metal-oxygen distance: hybridization changes. =>shifts bonding-antibonding splitting

Columbia University

Alternative: $GdFeO_3$ distortion

Rotate octahedra about two axes





Induced by choice of A-site ion.
If $d_{AA}<2d_{BO}$ then B-O-B bond is under compressive strain.
B-O bond relatively rigid =>B-O-B bond buckles.
Angle can be as small as 140°
Change in bandwidth: 30%

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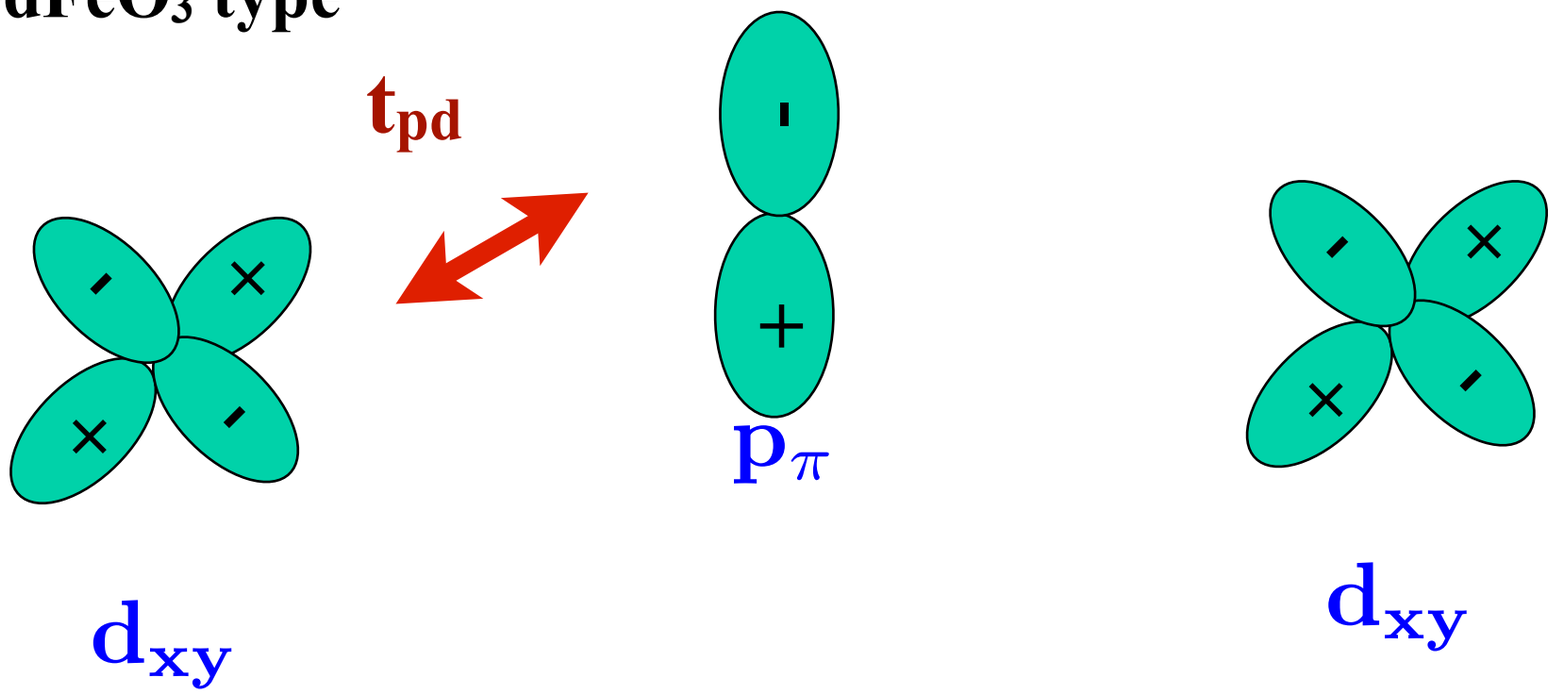
Consequence of structural distortion: change of hybridization

$GdFeO_3$ type



Move oxygen out of alignment: overlap decreases

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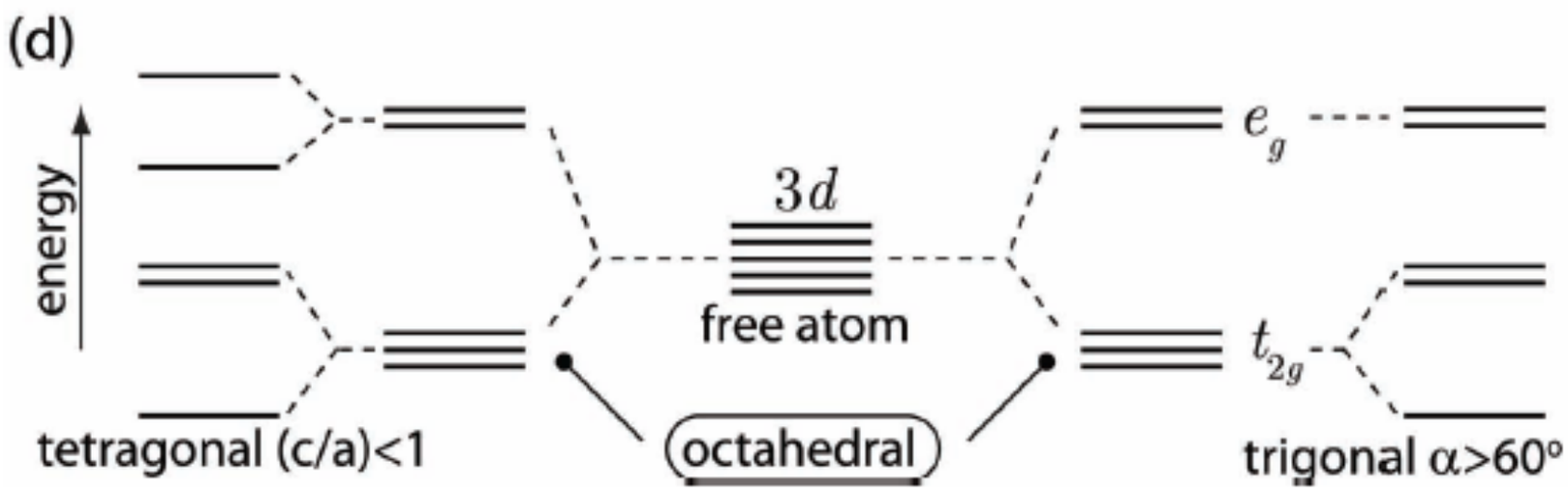
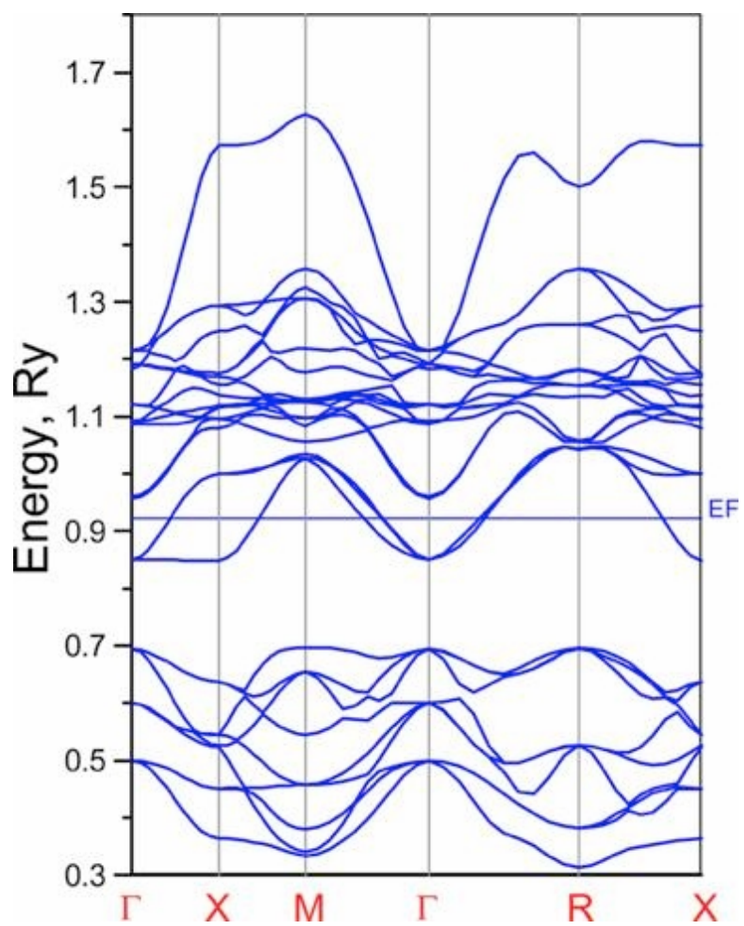
How big are these effects?





Cubic perovskite structure:
e_g-t_{2g} splitting ~2eV

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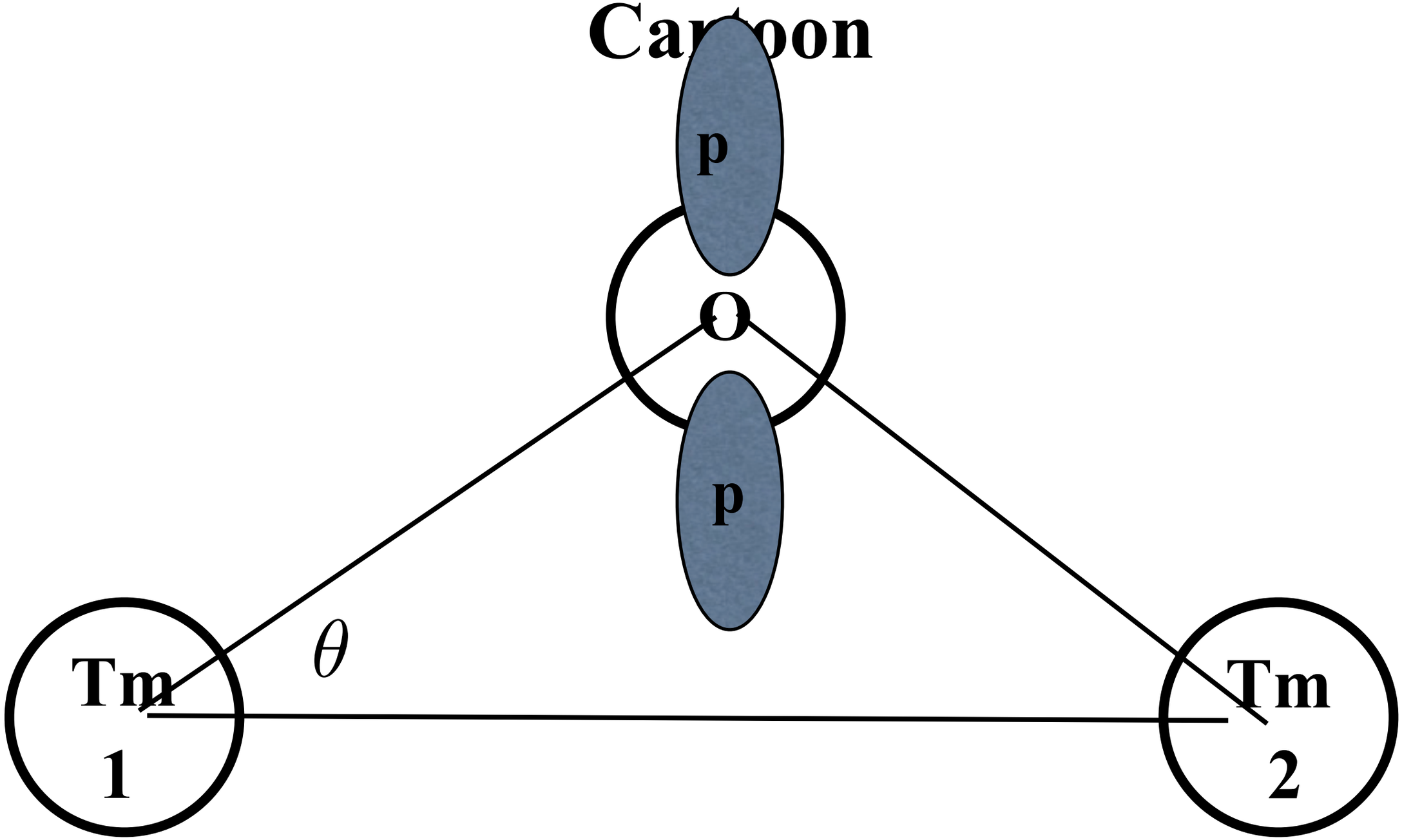
Cartoon



$\mathbf{t_{pd} \rightarrow t_{pd} \cos\,\theta}$ $\mathbf{Bandwidth \sim \cos^2\,\theta}$

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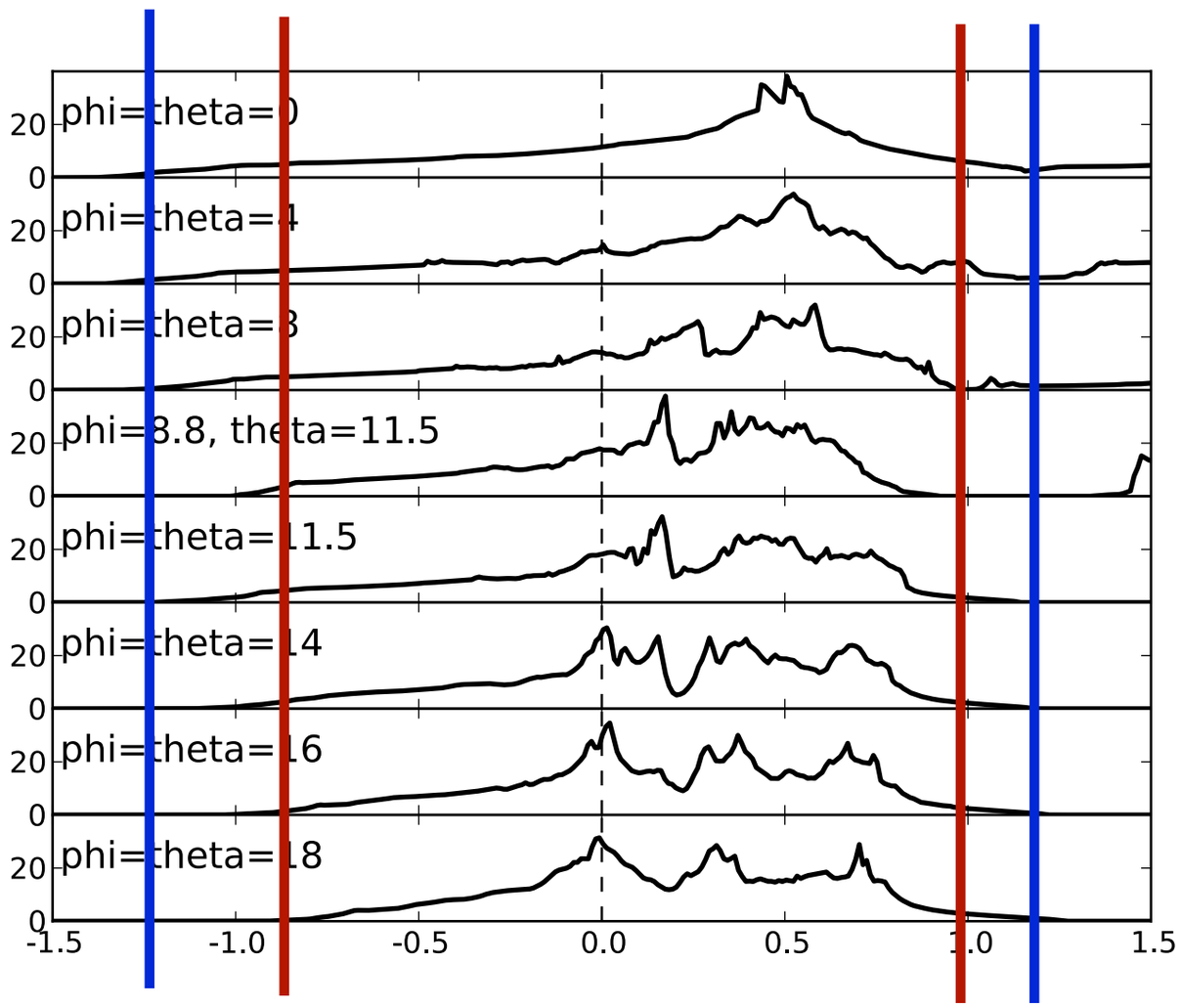
Density of states of t2g antibonding band as function of amplitude of GdFeO3 distortion: ``$LaVO_3$'' (H. T. Dang)



Bandwidth varies from ~2.5eV to ~1.6eV

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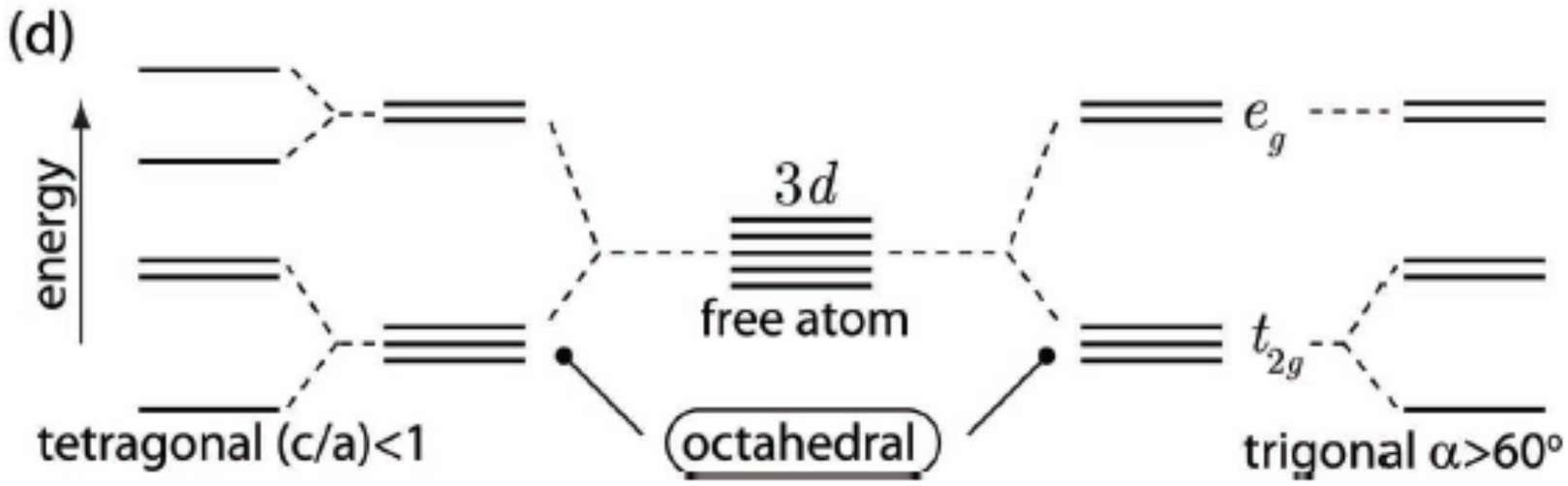
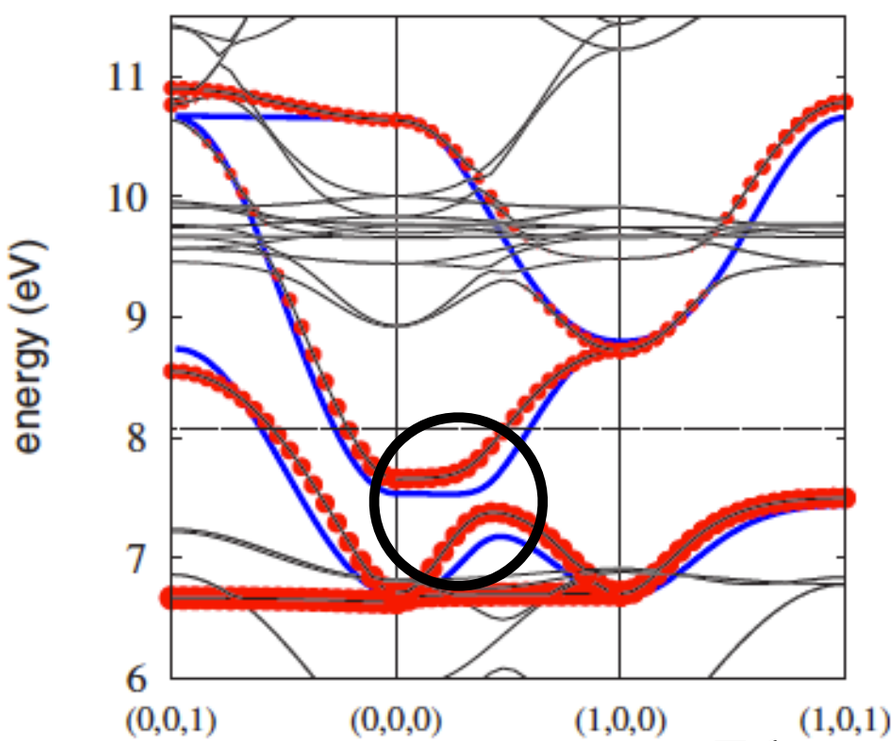
Jahn-Teller (cubic-tetragonal) distortion



Analyse band structure in distorted case



$$\hat{H}_{JT} = -\lambda \sum_{\vec{R},\sigma} \left(Q^x_{\vec{R}} d^+_{\vec{R},\sigma} \tau^x d_{\vec{R},\sigma} + Q^z_{\vec{R}} d^+_{\vec{R},\sigma} \tau^z d_{\vec{R},\sigma} \right).$$

$$\lambda : 2 - 3\mathrm{eV}/\mathrm{\AA}$$

Ederer and AJM, PRB 76 155105 (2007)
Popovic and Satpathy, PRL 84 1603 (2000)
Yin et al PRL 96 116405 (2006)

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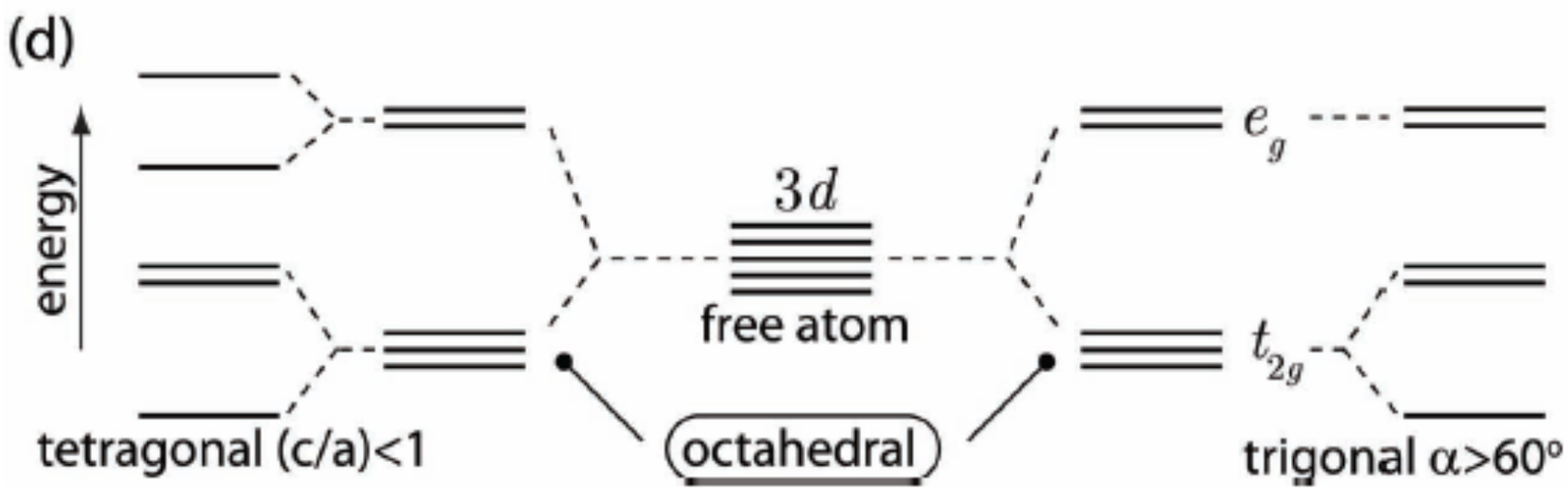
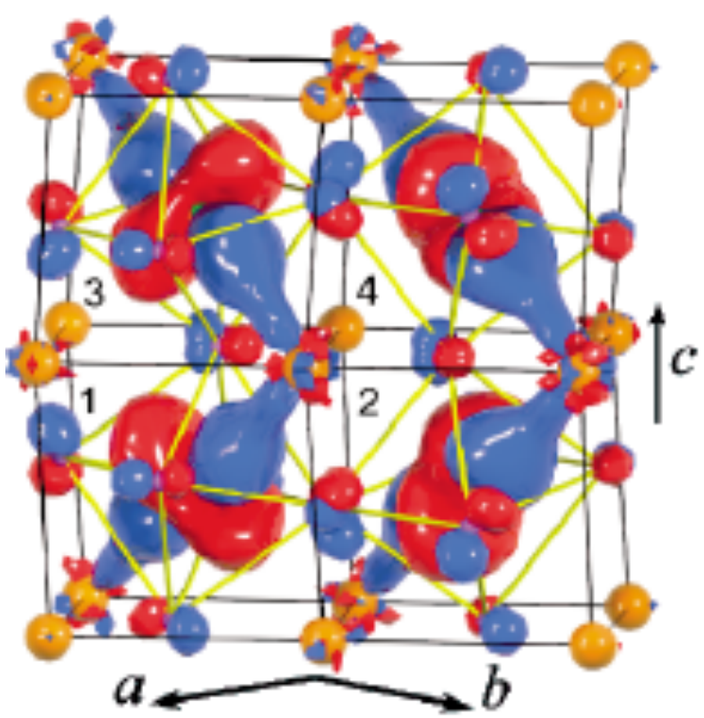
$GdFeO_3$ rotation (trigonal) distortion



Analyse band structure in distorted case

$\theta = 12^\circ$



Local basis rotated WRT mean crystal structure

$\theta = 12^\circ$ **Level splitting : 0.15eV**

$\theta = 20^\circ$ **Level splitting : 0.25eV**

Pavarini et al PRL 92 176403 (2004)

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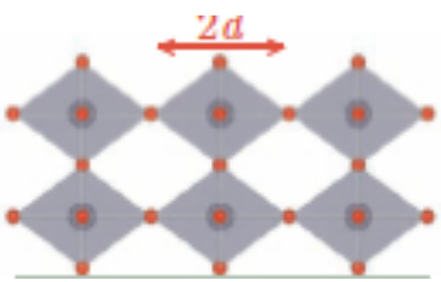
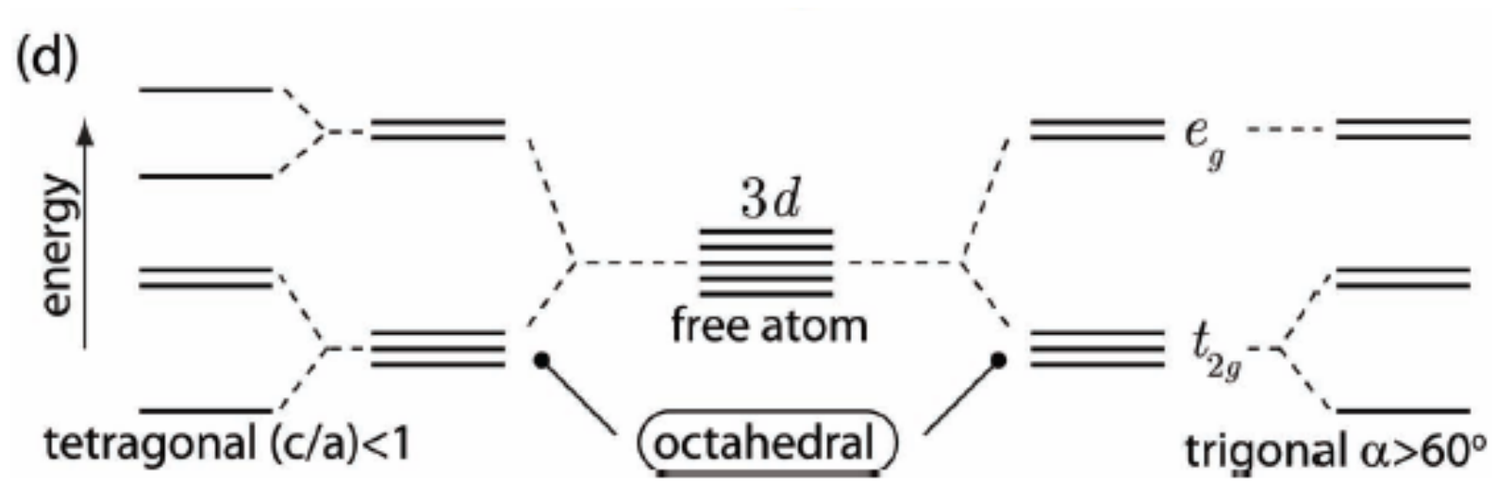
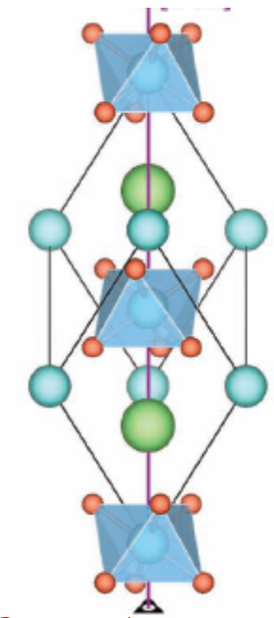
free-space d-orbital: 5-fold degenerate lattice effects lift degeneracy

Rondinelli and Spaldin, Adv. Mater. **23** 3363 (2011)







Jahn-Teller (0.1/AA: 0.2eV) **$GdFeO_3$ Rotations (15º: 0.2eV)**

Splittings from structural effects by themselves are typically small compared to bandwidths. Overall band-width renormalization important.

?Enhancement of splitting by many-body effects: orbital ordering?

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