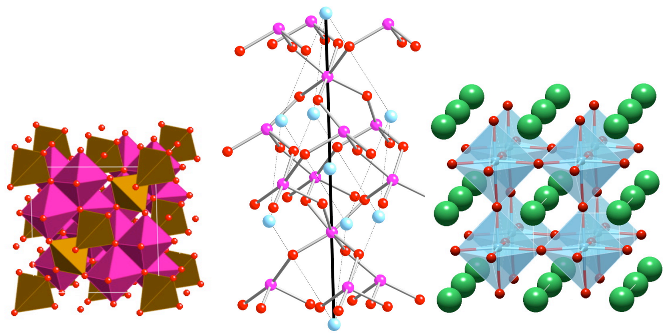
Cornell University

"I would found an institution where any person can find instruction in any study." – Ezra Cornell, 1868

Competing Ferroic Orders

The magnetoelectric effect

Craig J. Fennie
School of Applied and Engineering Physics
fennie@cornell.edu



Basic Training in Condensed Matter Theory 2009

Module Outline

1. Overview and Background
   - Ferro ordering, the magnetoelectric effect
2. ME revisited, and basic oxide physics
   - ME effect revisited: Toroidal moments
   - Complex oxides basics: Types of insulators (i.e., ZSA classifications), Coordination chemistry

The linear magnetoelectric effect

- Symmetry properties: broken time T and space I inversion, but the combination TI can be symmetry operation

$$\mathcal{F}_{ME} = \alpha_{ij} E_i H_j$$

$$\alpha_{ij} = \underbrace{\frac{1}{3}\alpha^0\delta_{ij}}_{\text{Pseudo scalar}} + \underbrace{\epsilon_{ijk}\tau_k}_{\text{Pseudo vector}} + \underbrace{[\frac{1}{2}(\alpha_{ij}+\alpha_{ji}) - \frac{1}{3}\alpha_0\delta_{ij}]}_{\text{Rank 2 traceless, symmetric}}$$

$\alpha^0 = \alpha_{ii}$

Pseudo scalar: $\sim \frac{\theta e^2}{2\pi h}\delta_{ij}$

Pseudo vector: Toroidal moment $\tau_k \equiv \epsilon_{ijk}\alpha_{ij}$

Rank 2 traceless, symmetric: Don't know, may be worth thinking about

From Joel Moore's talk yesterday I learned this is related to "axion electrodynamics," 3-d topological insulators, and Berry phase (or if your from Rutgers: Vanderbilt) theory of polarization

Cr_2O_3 ME effect

JETP LETTERS VOLUME 69, NUMBER 4 25 FEB. 1999

Magnetic-field-induced toroidal moment in the magnetoelectric Cr_2O_3

Yu. F. Popov,* A. M. Kadomtseva, D. V. Belov, and G. P. Vorob'ev
M. V. Lomonosov Moscow State University, 119899 Moscow, Russia
A. K. Zvezdin
Institute of General Physics, Russian Academy of Sciences, 117942 Moscow, Russia

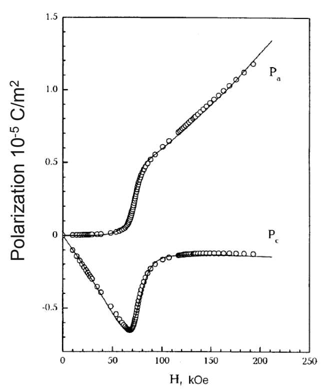


FIG. 2. Field dependence of the electric polarization P_i along the $a(x)$ and $c(z)$ axes for $\theta = -5°$ at a temperature of 150 K (solid lines — experiment, circlets — theory).

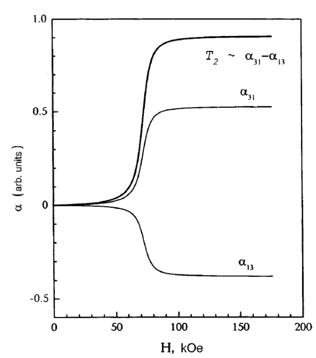


FIG. 3. Magnetic field dependence of the components of the ME susceptibility tensor α_{13}, α_{31}, and $T_z \sim \alpha_{31} - \alpha_{13}$ in arbitrary units at a temperature of 150 K.

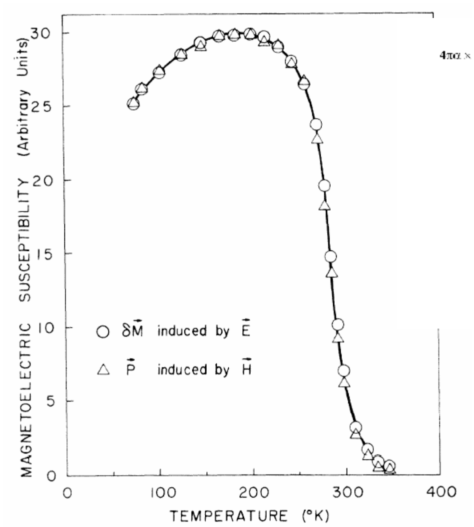
1 Telsa = 10 kOe

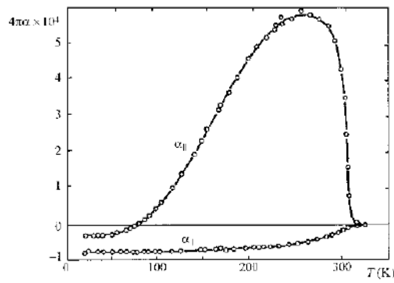
From Max Mostovoy

Linear magnetoelectric effect

Cr_2O_3

*I. E. Dzyaloshinskii JETP **10** 628 (1959),*
*D. N. Astrov, JETP **11** 708 (1960)*



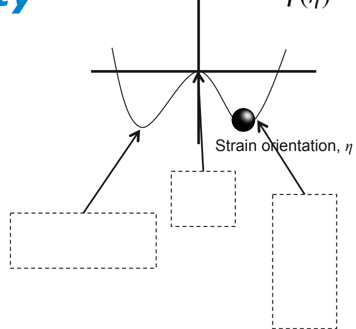


*G.T. Rado PRL **13** 335 (1964)*

Ferroelasticity

Ordering of long wavelength lattice modes→ spontaneous strain

$\mathcal{F}(\eta) = \alpha\eta^2 + \beta\eta^4 - \eta\sigma$



Spontaneous symmetry breaking

Symmetry properties

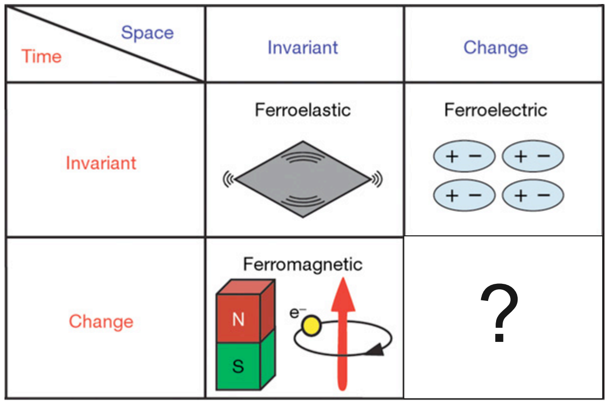
$\eta(-t) = +\eta(t)$

$\eta(-x) = +\eta(x)$

Actually a rank 2 polar tensor*

**polar tensor transforms like a product of coordinate under rotations or rotations-inversions.*

Ferro recap



Nature 449, 702-705 (11 October 2007)
Observation of ferrotoroidic domains
Bas B. Van Aken et al.

Missing "Ferro"-icity?

- What would this missing "ferro"-icity require?

	OP	Coupling Field	Interaction energy
Ferromagnetism:	M	H	F~ -M·H
Ferroelectricty:	P	E	F~ -P·E
Ferroelasticity	η	σ	F~ -η·σ

Can we construct what this missing invariant should look like?

(don't take this seriously, just a lot of hand waving)
- Must be odd under space inversion
- Must be odd under time inversion

} Sounds like the Magnetoelectric tensor

- Symmetry properties: broken time T and space I inversion, but the combination TI can be symmetry operation

$$\mathcal{F}_{ME} = \alpha_{ij} E_i H_j \qquad \tau_k \equiv \epsilon_{ijk}\alpha_{ij}$$

Becomes, slightly more illuminating if we write our free energy in terms the dynamic variables that order:

$$\mathcal{F}_{ME} = \gamma_{ijk} L_k P_i M_j$$

The antisymmetric part

$$\gamma_{ijk} L_k \rightarrow \tilde{t}_k \epsilon_{kij}$$

t ≡ Toroidal moment

Whatever this toroidal moment is it seems to be related to antiferromagnetism

Toroidal moment

$$\langle \boldsymbol{A}(\boldsymbol{R})\rangle = \frac{1}{c}\int \mathrm{d}^3x \frac{\langle \boldsymbol{j}(\boldsymbol{x})\rangle}{|\boldsymbol{R}-\boldsymbol{x}|} = \frac{1}{c}\left\langle \sum_\alpha \frac{e_\alpha \cdot \dot{\boldsymbol{r}}_\alpha}{|\boldsymbol{R}-\boldsymbol{r}_\alpha|}\right\rangle$$

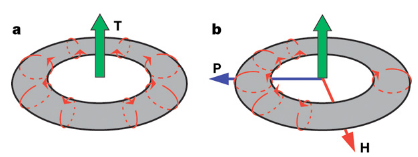
$$\langle \boldsymbol{A}\rangle^{(2)}_{\text{toroidal}} = \nabla(\boldsymbol{t}\cdot\nabla)\frac{1}{R} + 4\pi \boldsymbol{t}\delta(\boldsymbol{R}),$$

$$\boldsymbol{t} = \frac{1}{6c}\left\langle \sum_\alpha e_\alpha [\boldsymbol{r}_\alpha \times [\boldsymbol{r}_\alpha \times \dot{\boldsymbol{r}}_\alpha]]\right\rangle = -\frac{1}{4c}\left\langle \sum_\alpha e_\alpha r_\alpha^2 \dot{\boldsymbol{r}}_\alpha\right\rangle = -\frac{1}{4c}\left\langle \int \mathrm{d}^3r\, r^2 \boldsymbol{j}(\boldsymbol{r})\right\rangle$$

$$\boldsymbol{t} = \frac{1}{10c}\left\langle \sum_\alpha \left(\boldsymbol{r}_\alpha(\boldsymbol{r}_\alpha\cdot \boldsymbol{j}_\alpha) - 2r_\alpha^2 \boldsymbol{j}_\alpha\right)\right\rangle,$$

The toroidal moment in condensed-matter physics and its relation to the magnetoelectric effect*

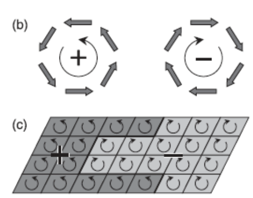
Nicola A Spaldin[1], Manfred Fiebig[2] and Maxim Mostovoy[3]



a Torus with an even number of current windings forming a toroidic moment, T. **b**, The magnetoelectric effect is illustrated by the current loops being shifted by the magnetic field (H), thus inducing an electric polarization (P). By rotating the figure by 90°, the asymmetry ($_{ij}$ = -$_{ji}$) *becomes obvious. Note that* $_{ij}$ *corresponds to a toroidal moment* T_k *(i j k).*

For localized spins

$$\boldsymbol{t} = \frac{g\mu_B}{2}\left\langle \sum_\alpha [\boldsymbol{r}_\alpha \times \boldsymbol{S}_\alpha]\right\rangle = \frac{1}{2}\left\langle \sum_\alpha [\boldsymbol{r}_\alpha \times \boldsymbol{m}_\alpha]\right\rangle.$$



$$H_{\text{int}} = -\boldsymbol{m}\cdot\boldsymbol{H}(0) - a(\nabla\cdot\boldsymbol{H})_{r=0} - \boldsymbol{t}\cdot[\nabla\times\boldsymbol{H}]_{r=0} - q_{ij}\left(\partial_i H_j + \partial_j H_i\right)_{r=0}.$$

Ferrotoroidicity

Nature 449, 702-705 (11 October 2007)
Observation of ferrotoroidic domains
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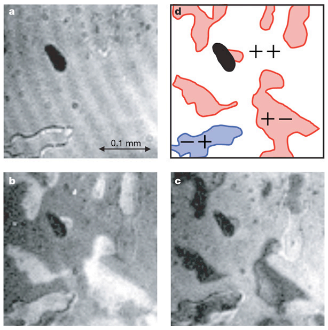
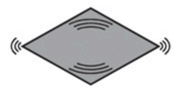
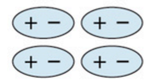
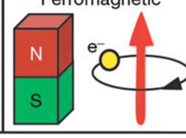
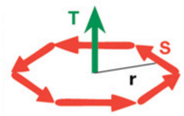
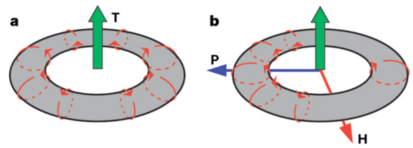
Used SHG to map out ferrotoroidic domains in $LiCoPO_4$



Time \ Space	Invariant	Change
Invariant	Ferroelastic 	Ferroelectric 
Change	Ferromagnetic 	Ferrotoroidic 



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Ferroelectricty:	P	E	F~ -P·E
Ferroelasticity	η	σ	F~ -η·σ
FerroToroidicty	T	∇×H	F~ -T·(∇×H)

T≡ Toroidization

Honest recap on FerroToroidicty

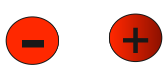
Presented a relatively new (or rediscovered) ferro-toroidal ordering. What is this? Don't know yet, here is what I know: Electromagnetism allows the existence of some moment referred to as a toroidal moment (toroidal because it has the symmetry of of toroidal solenoid). Expanding the interaction energy between energy the magnetic density and the magnetic field, one arrives at a coupling between the toroidal moment and the field which has the same symmetry as the antisymmetrical component of the magnetoelectric tensor, i.e., a toroidal moment would lead to an antisymmetric ME effect. That's it, that is all I presently understand. Questions are plentiful.

Multifunctional multiferroics

Multiferroic: combine more than one "ferro" ***property***:
Ferroelectricity, ferroelasticity, and/or magnetism

(Hans Schmid, 1973)

Polarization, P

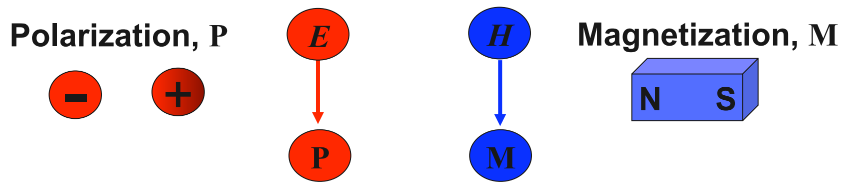


Magnetization, M

e.g., ferroelectric ferromagnet

Multifunctional multiferroics

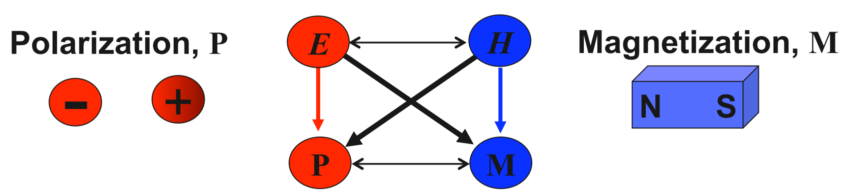
Multifunctional: response to more than one external ***perturbation***: Electric and magnetic fields



e.g., ferroelectric ferromagnet

Multifunctional magnetoelectrics

(Generalized) **Magnetoelectric**: cross coupled response to electric and magnetic fields

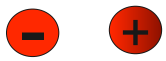


i.e. control of the magnetic $\mathbf{M}$ (electric $\mathbf{P}$) phase with an applied electric E (magnetic H) field

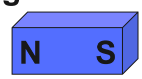
Multiferrroic and the Linear ME effect

Magnetic-ferroelectrics

Polarization, P



Magnetization, M



Symmetry in some cases then *allows* a Linear Magnetoelectric effect, $E_{int} = \gamma$ E H

$$P = \gamma \mathbf{H}$$

$$M = \gamma \mathbf{E}$$

$\gamma \equiv$ linear magnetoelectric coefficient*

But… intrinsic γ small

*Landau and Lifshitz, "Electrodynamics of continuous media"; Dzyaloshinskii, JETP 1957; Astrov JETP 1960 -> Cr_2O_3

Why mutiferroics and magnetoelectric effet

$$\mathcal{F}(E,H) = \frac{1}{2}\epsilon_{ij}E_iE_j + \frac{1}{2}\mu_{ij}H_iH_j + \alpha_{ij}E_iH_j +$$

$$4\pi\alpha_{ij} \leq \sqrt{\epsilon_{ij}\mu_{ij}}$$

We are we going?

- although symmetry allows the existence of a ME effect, it tells us nothing about its size. This is not a question of optimizing parameters to increase the magnitude of the effect in e.g., Cr_2O_3, but requires entirely new physical ideas.
- An idea that is prevalent in materials physics today (some would argue throughout nature) is the idea where the competition between different ordered ground states leads to new emergent phenomena (sometimes the adjective "colossal" is attached the observed effect).
- What if we have a system where ferroelectricity and (anti)ferromagnetism compete with each other, will it lead to "colossal" ME effects. Note this doesn't mean we simply add ferroelectricity and magnetism, i.e., multiferroics, we need to think of microscopic mechanisms that would COUPLE the two order parameters in a nontrivial way .
- Can we provide this coupling through the lattice? So in the remainder of this module we will
  - Understand the origin of ferroelectricity and how it couples to the lattice
  - Understand the origin of (anti)ferromagnetism and how it couples to the lattice
  - Combine these ideas to produce the stated goal.

But first, perovskites are ubiquitous materials that display an amazing variety of different phenomena, lets focus on them

Emergence of new macroscopic phenomena

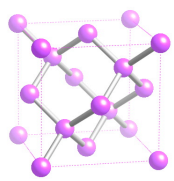
Where do we look for new phenomena and why do we look there?

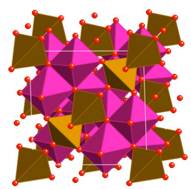
Emergence of new macroscopic phenomena

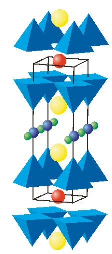
"More is Different," Phil Anderson, Science 1972

As the complexity of the crystalline motif increase, new properties have the potential to emerge!

	Elements	binary	tertiary	Quaternary		Life
	100	10,000	1,000,000	100,000,000	≀≀	
Elements/ unit cell	1	2	3	4		~10
	Si Fe Hg	GeTe	$ZnCr_2O_4$ $BiFeO_3$	YBCO		





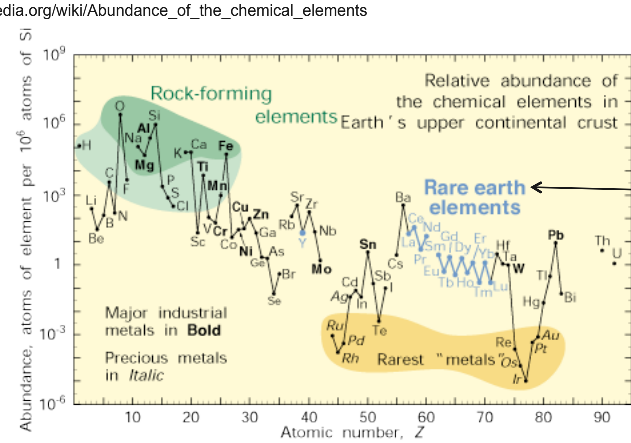


Based on a talk at Rutgers by P. Coleman

Oxides oh plenty!

- Except for the core, most of the earth is made of oxides

http://en.wikipedia.org/wiki/Abundance_of_the_chemical_elements



Note, Rare earth's arent so "rare", why the name?

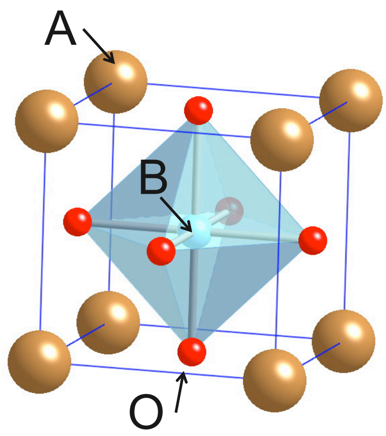
- Also, the chemistry obeys "goldilock" theorm: not too ionic, not too colavent

Complex oxides: ABO_3 Perovskites

Nearly any physical property

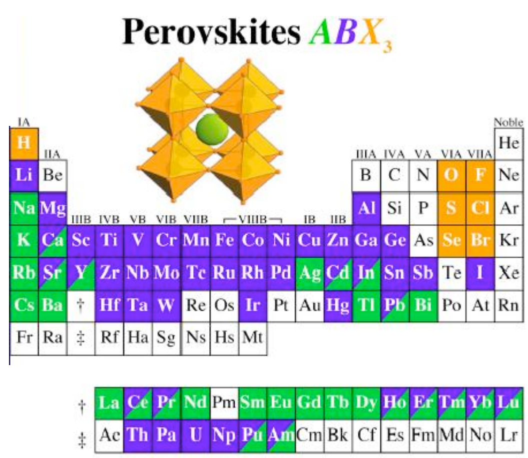
Same prototypical structure

Dielectric	$CaTiO_3$, $SrTiO_3$, $(CaCu_3)(Ti_4)(O_4)_3$
Ferroelectric	$BaTiO_3$, $LiNbO_3$, $PbTiO_3$
Magnetoelectric	$TbMnO_3$, $BiFeO_3$
Antiferroelectric	$PbZrO_3$
Piezoelectric	$PbZr_xTi_{1-x}O_3$
Antiferromagnetic	$LaMnO_3$
Ferromagnetic	$SrRuO_3$
Superconducting	doped-$SrTiO_3$
Colossal Magneto-resistance	$(La,Ca)MnO_3$



The most abundant mineral within the earth is a perovskite, which one?

Perovskites and the Period Table



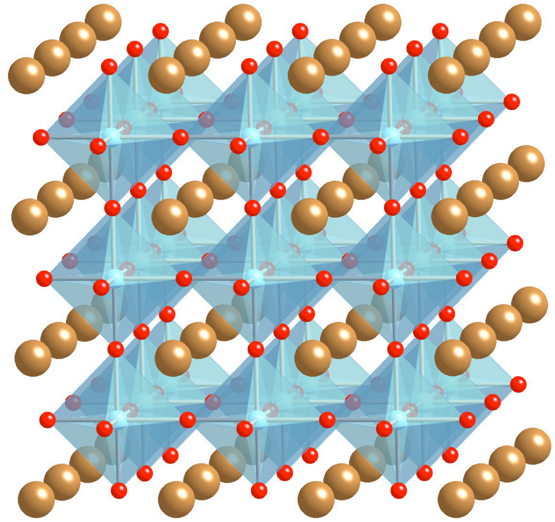
Substitutions on A, B or both

$(A_{1-x}A'_x)(B_{1-y}B'_y)O_3$

Random distribution or ordered

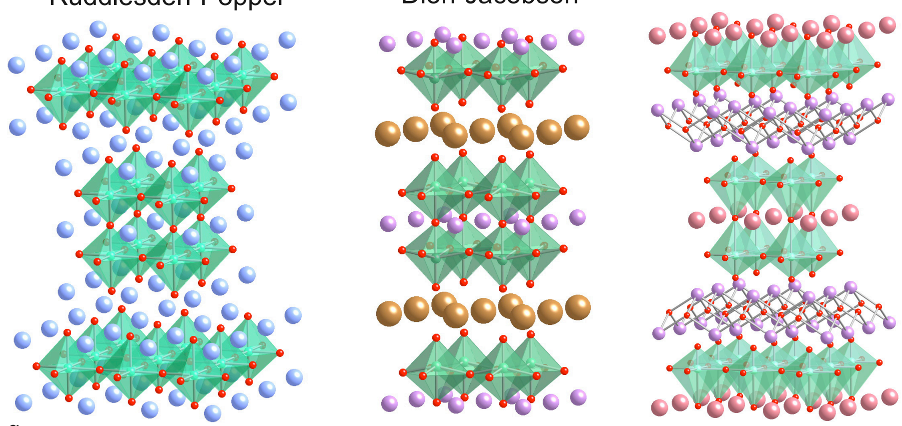
ABO_3 Perovskites

3-d network of corner shared octahedra



Layered Perovskites - Nature's superlattices

A_2 $[A'_{n-1}B_nO_{3n+1}]$	A $[A'_{n-1}B_nO_{3n+1}]$	Bi_2O_2 $[A'_{n-1}B_nO_{3n+1}]$
Ruddlesden-Popper	Dion-Jacobson	Aurivillius



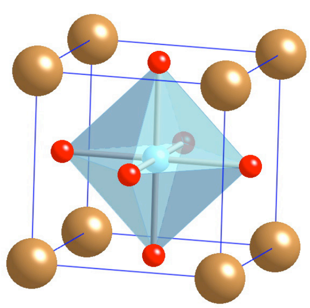
e.g., n=2	*$Sr_3Ru_2O_7$*	*$CsBiNb_2O_7$?*	*$SrBi_2Ta_2O_9$*

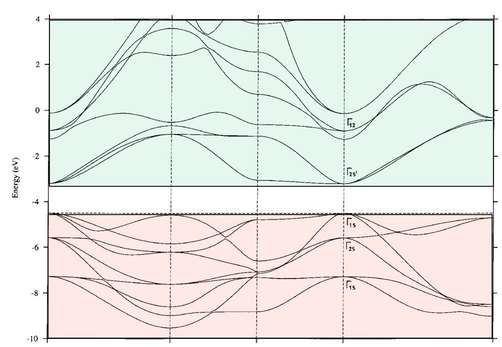
Two kinds of insulators *(that I'll be discussing)*

Band Insulator

Even # of electrons per site

Example Sr^{2+} Ti^{4+} O_3^{2-} Perovskite structure





Sr: [Kr] $4s^2$

Ti: [Ar] $3d^2\,4s^2$

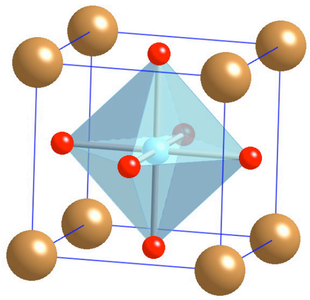
O: [He] $2s^2\,2p^4$

Even lda gets a gap

Band Insulator

Even # of electrons per site

Example Sr^{2+} Ti^{4+} O_3^{2-} Perovskite structure



What's the primary source of magnetism in insulating oxides?

Unpaired electrons

Ti^{4+}: [Ar] $3d^0\,4s^0$

Nominally empty d-shell*

Sr: [Kr] $4s^2$

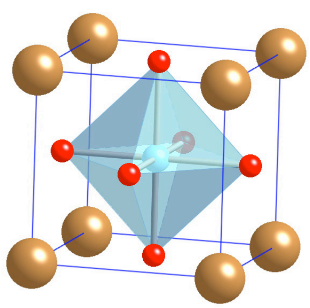
Ti: [Ar] $3d^2\,4s^2$

O: [He] $2s^2\,2p^4$

Mott Insulator

odd# of electrons per site

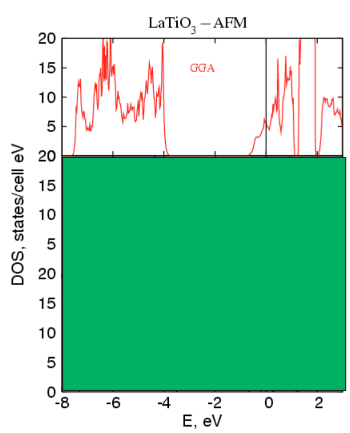
Example La^{3+} Ti^{3+} O_3^{2-} Perovskite structure



La: [Xe] $5d^1\,6s^2$

Ti: [Ar] $3d^2\,4s^2$

O: [He] $2s^2\,2p^4$



lda has finite DOS at E_F

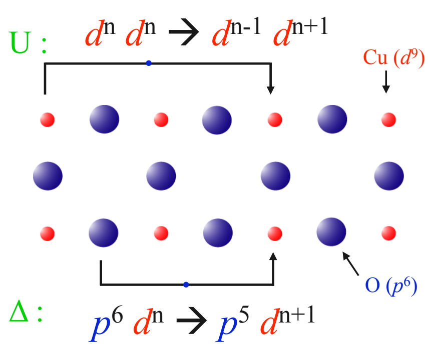
Lichtenstein Europhys lett 2005)

Not all Mott insulators are created equal

Hubbard model

Need model that includes hybridization of 3d with ligands (and also other 3d) and strong on-site Coulomb repulsion

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



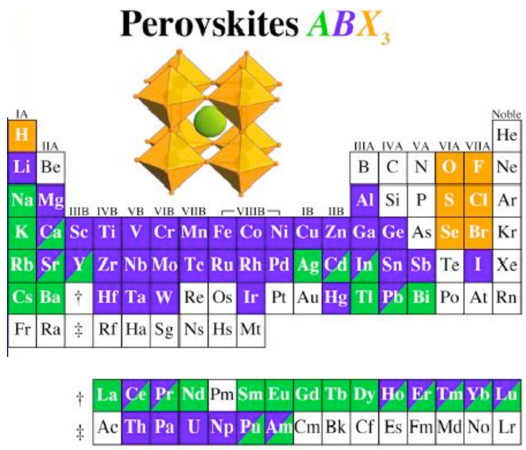
U = E(d^{n+1})+E(d^{n-1})-2E(d^n)

Δ = E(d^{n+1} L̥) – E(d^n)

L̥ hole on ligand

U/t >> 1	insulator
U/t << 1	metal

Perovskites and the Period Table

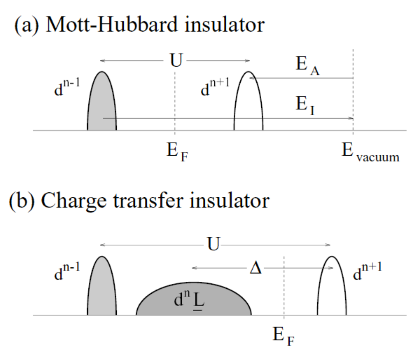


Transition metals: 3d
Rare earths: Eu,Gd

Tend to well localized
Small KE (t)
Larger U

U/t >> 1 insulator
U/t << 1 metal

Zaanen-Sawatzky-Allen model



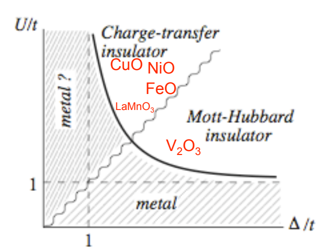


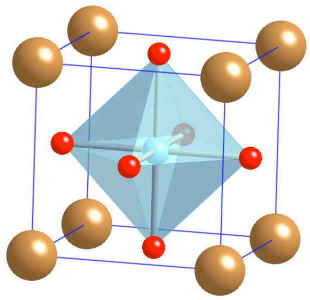
Fig. 5.16. Zaanen–Sawatzky–Allen diagram showing the regions of Mott–Hubbard ($\Delta > U$) and charge-transfer ($\Delta < U$) insulators

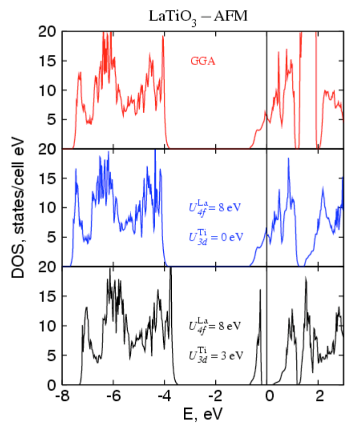
Why care? Many reasons, Critical to understand doping effects, understandind magnetic exchange etc.

Mott Insulator

odd# of electrons per site

Example La^{3+} Ti^{3+} O_3^{2-} Perovskite structure





La: [Xe] $5d^1$ $6s^2$

Ti: [Ar] $3d^2$ $4s^2$

O: [He] $2s^2$ $2p^4$

Lda +U opens Gap

Lichtenstein Europhys lett 2005)

Crystal Field Effects

Local ionic model: assume properties are not to different than isolated atoms, i.e., consider formal valances (reasonable in oxides, why?)

Crystal field splitting of d-levels

- *Hund's rule modified*

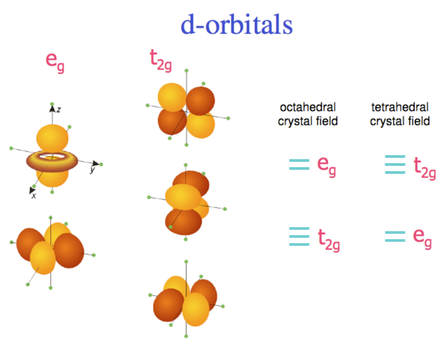
(reminder, Hund's rule:
Max spin, max L, J= |L-S| or |L+S|)

High Spin vs Low spin

For example: d^6 transition metal
If crystal field splitting is large

High spin (Hund's Rule) could have higher energy than

Low Spin



If energies close you could imagine tuning between HS and LS states, for example $LaCoO_3$

Jahn-Teller

- Orbital degenercy spontaneously lifted by crystal distortion

For example Mn^{3+} in an octahedral environment

$LaMnO_3$

Mn^{3+} 3d4 4s0

Next time

Understand the origin of ferroelectricity and how it couples to the lattice

- Soft mode theory, lattice dynamics, group theoretic methods
- Competing lattice instabilities
- microscopic mechanisms, improper FE
- Modern theory of polarization (Berry Phase)