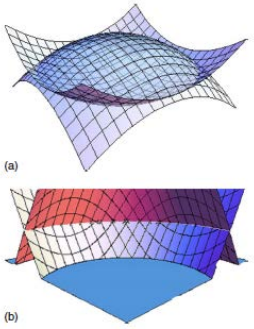
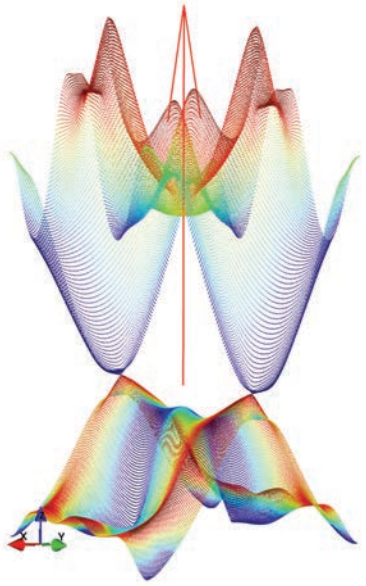
Materials Design: Perspectives, Challenges, Selected Case Studies Mostly from Correlated Materials

MagLab Winter Theory School
January 2017

Warren Pickett, UC Davis





Acknowledgments:
Y. Quan, Beijing Normal University
V. Pardo, Santiago de Compostela
K-H Ahn, K-W Lee, Korea University
R. Pentcheva, Univ. of Duisburg-Essen

U.S. DEPARTMENT OF ENERGY | Office of Science

Supported by U.S. DOE/BES

Supported by U.S. NSF/DMREF

THE U.S. MATERIALS GENOME INITIATIVE

"...to discover, develop, and deploy new materials twice as fast, we're launching what we call the Materials Genome Initiative"
–President Obama, 2011

Meeting Societal Needs

Advanced materials are at the heart of innovation, economic opportunities, and global competitiveness. They are the foundation for new capabilities, tools, and technologies that meet urgent societal needs including clean energy, human welfare, and national security.

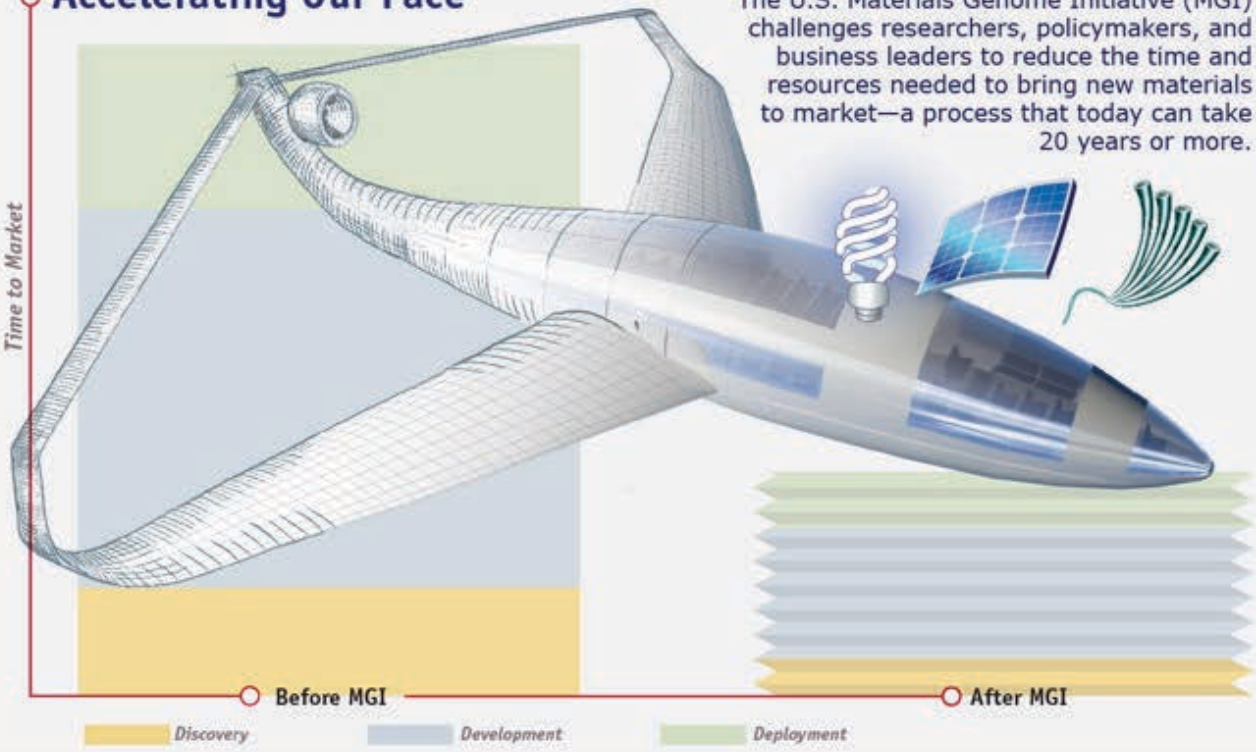
Clean Energy

Human Welfare

National Security

Accelerating Our Pace

The U.S. Materials Genome Initiative (MGI) challenges researchers, policymakers, and business leaders to reduce the time and resources needed to bring new materials to market—a process that today can take 20 years or more.



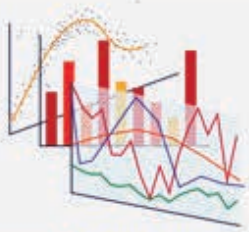
Building Infrastructure for Success

The MGI is a multi-agency initiative to renew investments in infrastructure designed for performance, and to foster a more open, collaborative approach to developing advanced materials, helping U.S. Institutions accelerate their time-to-market.

Computational tools

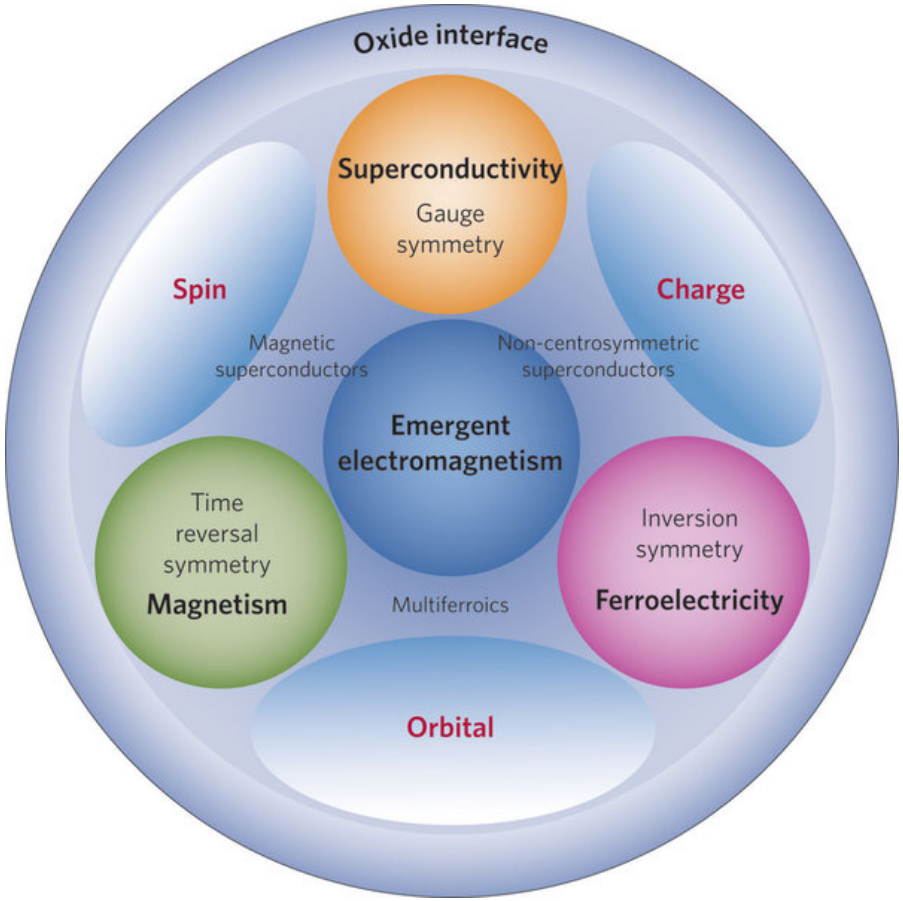
Experimental tools

Collaborative networks



Digital data

Strongly Correlated Electron Systems



Oxide Nanostructures: The Attraction

Emergent Phenomena at Oxide Interfaces
Hwang, Iwasa, Kawasaki, Keimer, Nagaosa, Tokura,
Nature Materials 2012

Areas of interest

- Charge/spin transport
- Spontaneous order
- Symmetry breaking
- Thermal anomalies
- External field probes
- Competing phases
- Coexisting phases
- Topological character
- ……

3

Title and cmmentary from a previous talk

Spin-Orbit Coupling, Strong Interactions, and Topological Character: By Design & By Serendipity

"Serendipity"

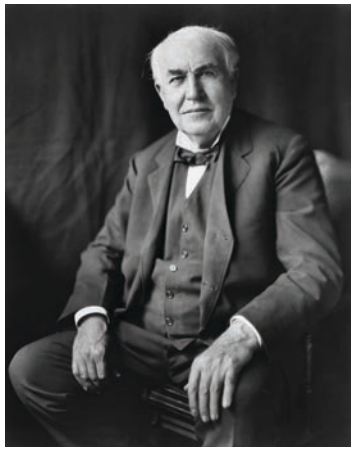
Horace Walpole (1754)

"This discovery I made by a talisman ... by which I find everything I want ... wherever I dip for it. This discovery, indeed, is almost of that kind which I call Serendipity, a very expressive word."

Walpole formed the word on an old name for Sri Lanka, *Serendip.* He explained that this name was part of the title of *"a silly fairy tale, called* The Three Princes of Serendip: *as their highnesses traveled, they were always making discoveries, by accidents and sagacity, of things which they were not in quest of...."*

Talisman: object thought to have magical powers

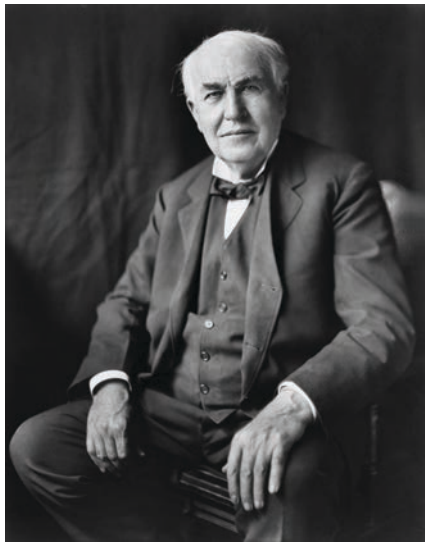
Edisonian Discovery and Invention;
not trial and error.
ref. historian Thomas Hughes, 1977



- In formulating problem-solving ideas, he was inventing;
  -in developing inventions, his approach was akin to engineering;
  -in looking after financing and manufacturing and other post-invention and development activities, he was innovating.
- Edison "adroitly chose" problems that made use of what he already knew.
- Edison's method was to invent **systems** rather than components of systems. Edison did not just invent a light bulb, he invented an economically viable system of lighting including its generators, cables, metering and so on.
- Edison invented by repeatedly trying devices in more complex environments to progressively approximate their final use conditions.
- Edison blended invention with economics. His electric lighting system was designed to be an economic competitor with gas lighting.

Edison was much cleverer than "trial and error."

Edison on *Reading the Literature, Performing and Executing a Plan*



"When I want to discover something, I begin by reading up everything that has been done along that line in the past – that's what all these books in the library are for. I see what has been accomplished at great labor and expense in the past. I gather data of many thousands of experiments as a starting point, and then I make thousands more."

Edison	created/consulted databases (of known results) performed data mining (such as was possible) extended to high throughput (in his manner)

When did identifiable materials design begin?

Rocksalt MoN as a high temperature superconductor: T_C = 30K.
Papaconstantopoulos, Klein, Boyer, WEP, Nature 1982
Unfortunately, a few years later was shown to have a negative elastic constant.

(Ba,K)BiO_3: should be better superconductor than Ba(PbBi)O_3 [T_c=13K]
Len Mattheiss and experimental coworkers (1988)
Huge success: BKBO has T_c=34K. The pairing mechanism is still unclear.

There must be many examples of such predictions.
But what about design in the modern (MGI) sense?

Modern Design & Discovery:
Selected Examples

Predicting Crystal Structures with Data Mining of Quantum Calculations

PRL 2003

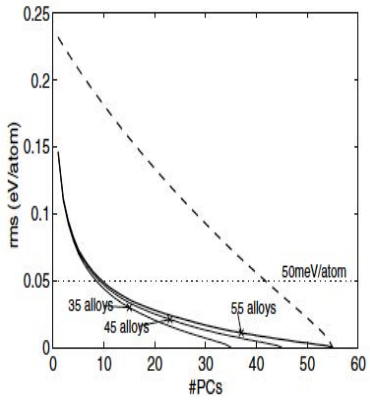
Stefano Curtarolo,[1] Dane Morgan,[1] Kristin Persson,[1] John Rodgers,[2] and Gerbrand Ceder[1,*]

Predicting and characterizing the crystal structure of materials is a key problem in materials research and development. It is typically addressed with highly accurate quantum mechanical computations on a small set of candidate structures, or with empirical rules that have been extracted from a large amount of experimental information, but have limited predictive power. In this Letter, we transfer the concept of heuristic rule extraction to a large library of *ab initio* calculated information, and we demonstrate that this can be developed into a tool for crystal structure prediction.

DMQC approach: data mining of quantum calculations

They used a principal component analysis (PCA) on over 6000 ab initio energy calculations

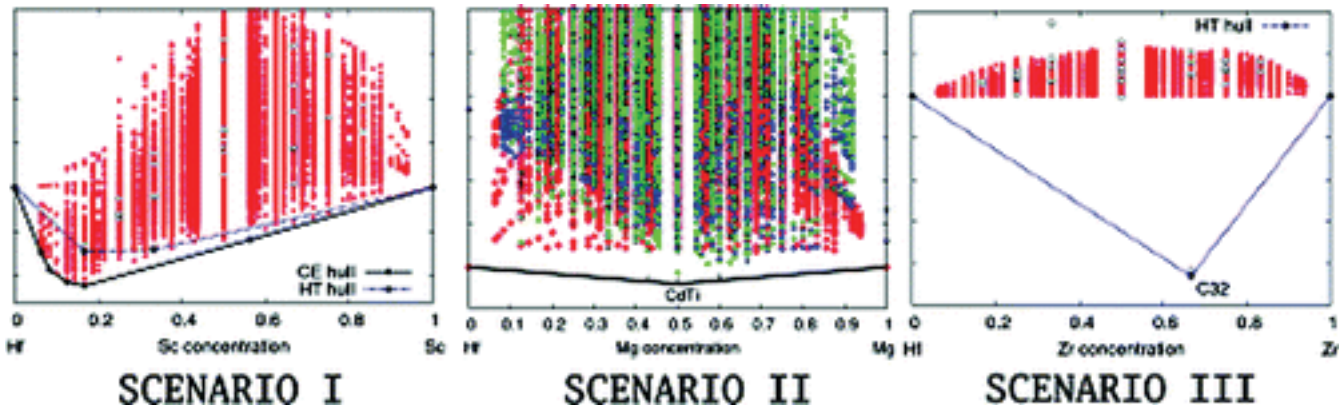
Used 114 different crystal structures in each of 55 binary metallic alloys.



Uncovering Compounds by Synergy of Cluster Expansion and High-Throughput Methods

C. Levy. G. W. L. Hart, and S. Curtarolo, JACS 2010

Evolutionary algorithms have been recently introduced to search for stable off-lattice structures at fixed mixture compositions. We present an integrated approach of CE and high-throughput ab initio calculations (HT) applicable to the full range of compositions in binary systems where the constituent elements or the intermediate ordered structures have different lattice types. The HT methodreplaces the search algorithms by direct calculation of a moderate number of naturally occurring prototypes



Predicting from first-principles calculations whether mixed metallic elements phase-separate or form ordered structures is a major challenge of current materials research.

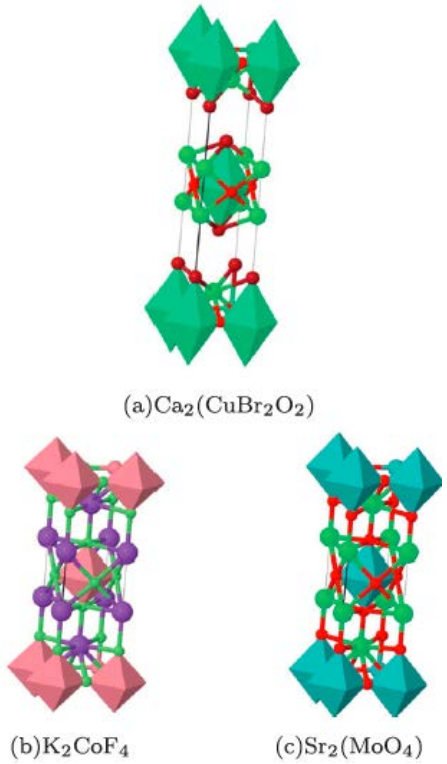
Possible high-temperature superconductors predicted from electronic structure and data-filtering algorithms

M. Klintenberg, O. Eriksson, Comp. Matl. Sci. 2013

…(calculation) of the electronic structure of the majority of the known stoichiometric inorganic compounds, as listed in the Inorganic Crystal Structure Data-base (ICSD). We make a detailed comparison of the electronic structure, crystal geometry and chemical bonding of cuprate high temperature superconductors, with the *calculated over 60,000 electronic structures*.

- Data-base
- Data-filtering
- Accelerated DFT calculations

New layered compounds



Pre-Modern Design & Discovery: Selected Examples

Principles and Applications of Complementary Computing

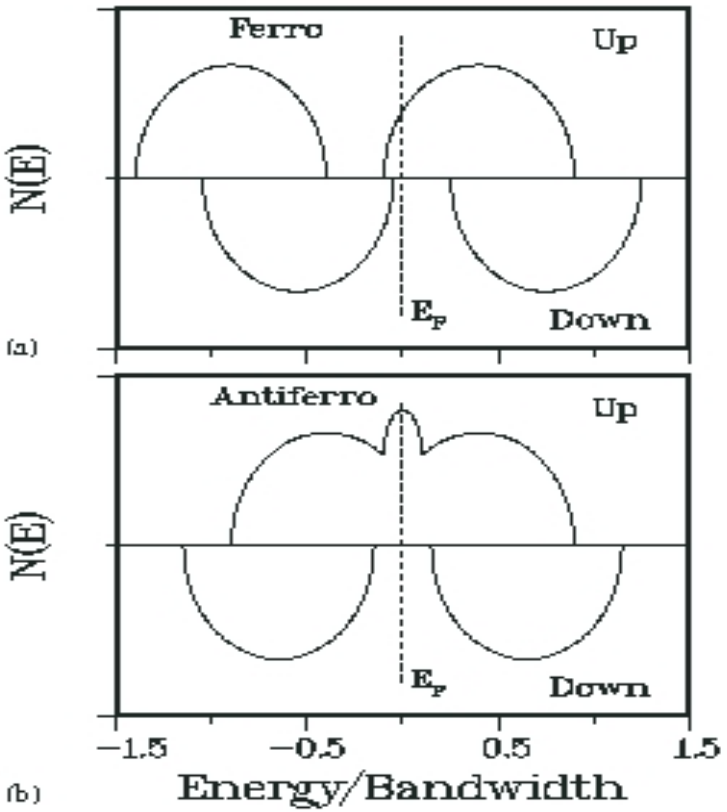
Eric Horvitz *, Microsoft Research*

I will describe several examples of collaborative problem-solving between people and computing systems that demonstrate how we can leverage the complementarity of humans and machines in tackling challenging problems.

Pre-Modern Design & Discovery: Selected Examples

Materials Design of Half Metallic Antiferromagnets: 1998 style

Half metallic FM: metallic in one spin channel, gapped in the other
Spin magnetic moment must be an integer K (filled bands)
Compensated: K=0. FM symmetry but no macroscopic moment



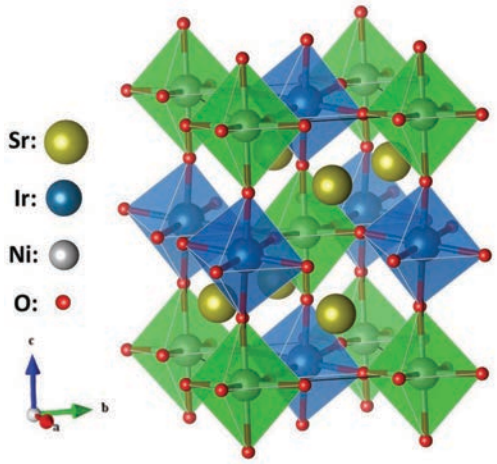
Ferromagnetic symmetry:
up is different from down spin

No net moment, no macroscipic magnetic field.

Yet fully spin-polaried carriers

Provides a platform for a novel type of single spin superconductor

Spin-density-functional-based search for half-metallic antiferromagnets



WEP, PRB 1998

Combinatorics of $A'A''M'M''O_6$

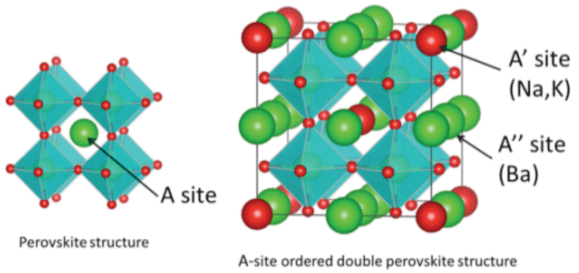
Double perovskite crystal structure

$$25 \times 2^2 \times \frac{18 \times 17}{2} \approx 15\,000$$ candidates

A'=A"

9 d^n configurations, 3d and 4d elements
with ~2 charge states each.
Cation A chosen from ~25 2+ and 3+ ions

With distinct A',A" ions, **2×10^5 candidates**

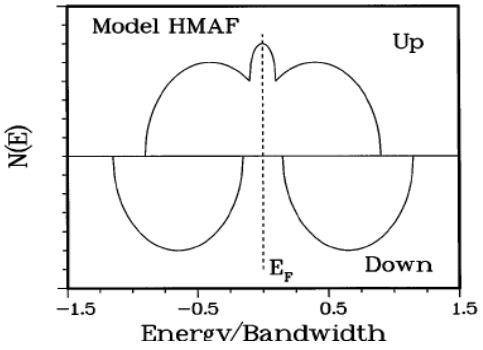


A Case Study of an early Materials Design

Design of a half metallic antiferromagnet?

First: what is a half metallic antiferromagnet?

HM AFM: a half metallic magnetic material
with opposing & cancelling magnetic moments.
It is "ferromagnetic" but with no macroscopic B field.

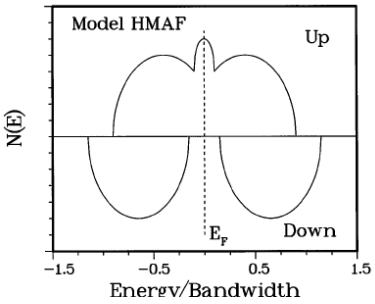


1st: magnetic with ferromagnetic spin symmetry (but NOT FM)
2nd: half metallic: gap in one spin channel, metallic in other
3rd: up and down magnetic moments must cancel each other
4th: FM alignment must be favorable compared to AFM
5th: must be ground state structure, and (meta)stable

6th: magnetic ordering temperature should be high
7th: the desired phase must be synthesizable
8th: the material must be integratable into an existing system
9th: (there will be more, don't doubt it)

Spin-density-functional-based search for half-metallic antiferromagnets
Single Spin Superconductivity

WEP, PRB 1998



Preselection before computation

Narrowing the candidates:

- valence counting→ d^n configurations
- choose size of moments wanted
- spin of d^n ion in octahedral field
- antiligned spins: check energy differences
- is it half metallic??

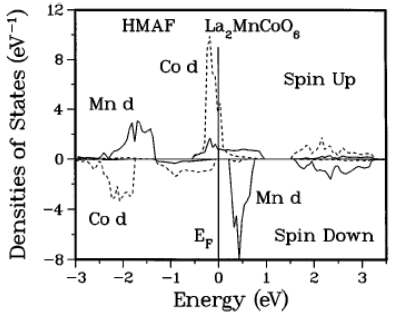
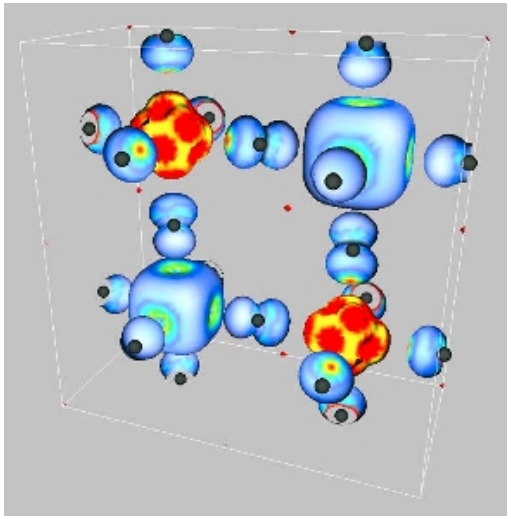


TABLE I. Nominal charge states, Hund's rule magnetic moments m (μ_B), and crystal field moments m (μ_B), for AMO_3 compounds. Ions in parentheses are uncommon. As discussed in the text, Hund's rule will not be followed if the crystal field splitting is comparable to the intra-atomic exchange splitting. "cf" and "no cf" indicates atomic moments with a normal crystal field for the perovskite structure, or negligible crystal field (Hund's rule), respectively (see text).

Compound	Ion	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
$A^{4+}M^{2+}O_3$	M^{2+}	(Sc)	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
	m (no cf)	1	2	3	4	5	4	3	2	1
	m (cf)	1	2	3	4	5	0	1	2	1
$A^{3+}M^{3+}O_3$	M^{3+}	Ti	V	Cr	Mn	Fe	Co	Ni	(Cu)	
	m (no cf)	1	2	3	4	5	4	3	2	
	m (cf)	1	2	3	4	3	0	1	2	
$A^{2+}M^{4+}O_3$	M^{4+}	V	Cr	Mn	Fe	Co	(Ni)			
	m (no cf)	1	2	3	4	5	4			
	m (cf)	1	2	3	4	3	0			

Isosurface plot of the Spin density of $La_2V^{4+}Cu^{2+}O_6$. (Cu: red; blue: V)



Likely candidates amongst $La_2BB'O_6$:

S=1/2: $La_2V^{4+}Cu^{2+}O_6$.

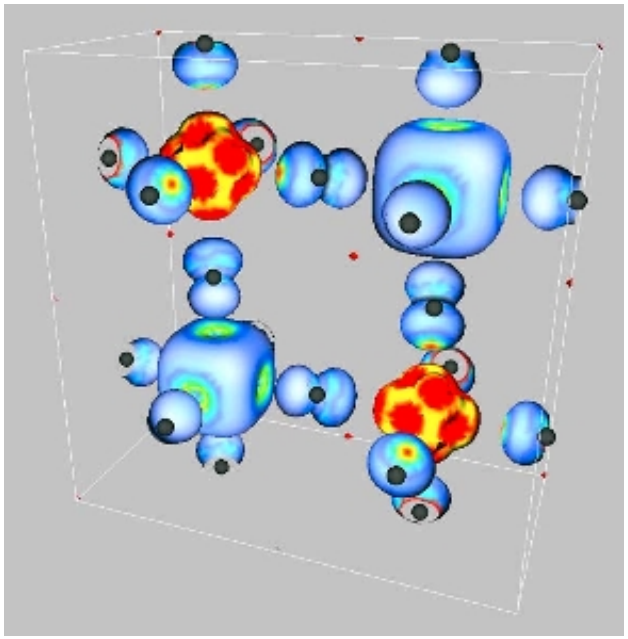
Experimental attempts obtained disordered V, Cu

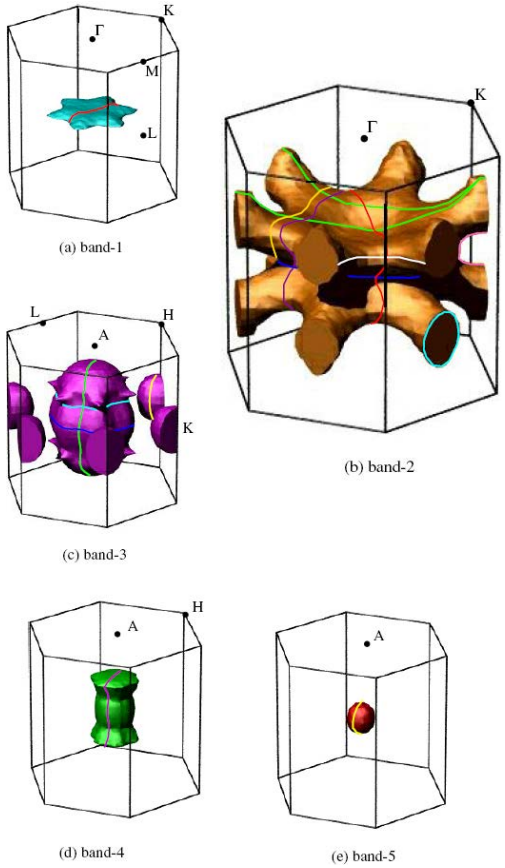
S=2: $La_2Mn^{3+}Co^{3+}O_6$ (actually, a close call)

Not aware of experimental work

This should be considered a preliminary, unfinished design study.

Electronic Structure Methods:
an overview of past, present, (future)

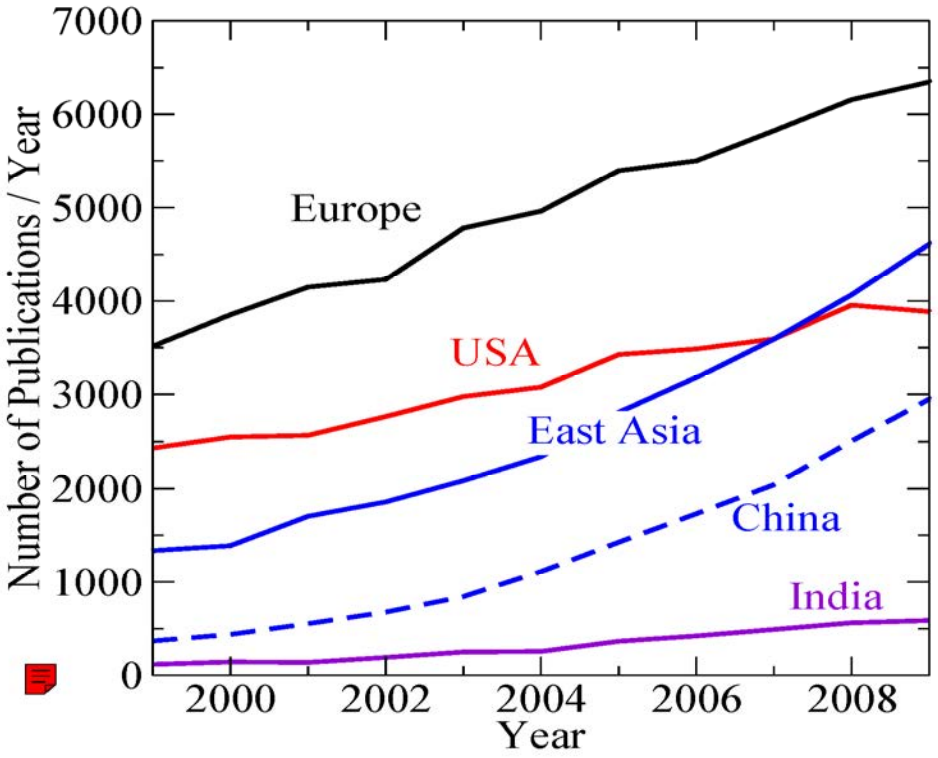




DFT Citation History

P. Dederichs, Psi-k Newsletter 2010

Web of Science search, linking
"ab initio" or
"first principles" or
"density functional"
to country of address of authors



Can observe:
- overall rapid rise
- Europe faster than USA
- rapid relative increase in East Asis, esp. China

Can make this a wake-up call for USA researchers in this field

Can simply note the incredible total numbers: 14,300 in 2009 on this chart

Robust, Supported DFT Crystal Codes

- Wien2k LAPW Austria
- CRYSTAL LO Italy/UK
- Abinit PWpp Belgium
- pwSCF/Quantum Espresso PWpp Italy
- VASP PAW Austria
- SIESTA LO Spain
- FPLO LO Germany
- MindLab LMTO US / Germany
- FLEUR LAPW Germany
- EXCITING/ELK LAPW Austria
- Aims LO Germany
- etc., etc.

For a longer list, see http://dft.sandia.gov/codes_list.html

Electronic Structure and Density Functional Theory (DFT)

W. Kohn & colleagues; many others

Hamiltonian for electrons interacting with nuclei (huge many-problem):

$$\hat{H}\Psi = \left[\hat{T} + \hat{V} + \hat{U}\right]\Psi = \left[\sum_i^N -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_i^N V(\vec{r}_i) + \sum_{i<j}^N U(\vec{r}_i, \vec{r}_j)\right]\Psi = E\Psi$$

Density functional viewpoint: consider energy as functional of electron density

$$E[\rho] = T_s[\rho] + \int d\mathbf{r}\; v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + V_H[\rho] + E_{\text{xc}}[\rho], \qquad \rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2.$$

Kinetic energy functional: $T_s[\rho] = \sum_{i=1}^N \int d\mathbf{r}\; \phi_i^*(\mathbf{r})\left(-\frac{\hbar^2}{2m}\nabla^2\right)\phi_i(\mathbf{r}),$

Hartree Energy Functional $V_H = \frac{e^2}{2}\int d\mathbf{r}\int d\mathbf{r}'\;\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},$

Exchange & correlation effects $v_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}$

Total energy in terms of Kohn-Sham eigenvalues (band structure) $E = \sum_i^N \varepsilon_i - V_H[\rho] + E_{\text{xc}}[\rho] - \int \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}\rho(\mathbf{r})d\mathbf{r}$

Kohn-Sham Hamiltonian for electron states

$h_{KS} = p^2/2m + V$; $h_{KS}\,\phi_k = \varepsilon_k\,\phi_{k,}$ $\phi_k = e^{ik*r}\,u_k$

With V from DFT, this is the "band structure problem."

e^{ik*r} factor is known and can be eliminated:

$e^{ik*r}\,h_{KS}\,e^{-ik*r} = h_{k,}$ $h_k\,u_k = \varepsilon_k\,u_k$

$h_k = (p+k)^2/2m + V$

Exchange-correlation functional: the rub

[connections to kinetic energy functional]

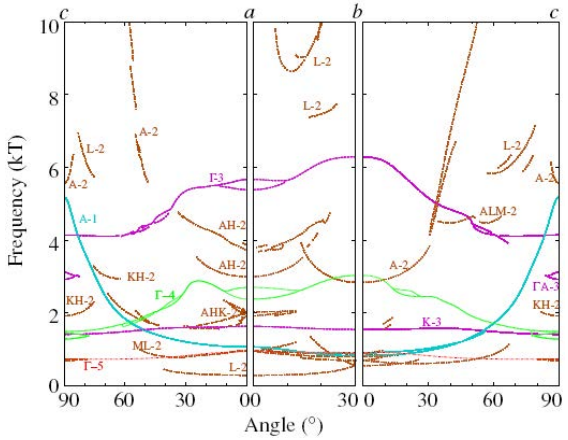
- LDA (local density approximation)
- GGA (generalized gradient approximation)
- meta-GGA: dependence on orbital kinetic energy
- normal density+pairing density for superconductors
- density-polarization functional for ferroelectrics
- hybrid functional: x LDA exchange, 1-x Hartree-Fock
- LDA+U: (atomic) orbital-dependent functionals
  for strongly correlated insulators
- non-local functionals to treat van der Waals systems
- etc. etc.

Pretty impressive. Still, we have no single great functional for everything.
There is plenty of work to do.

Many, many impressive successes
of the local density approxiamtion

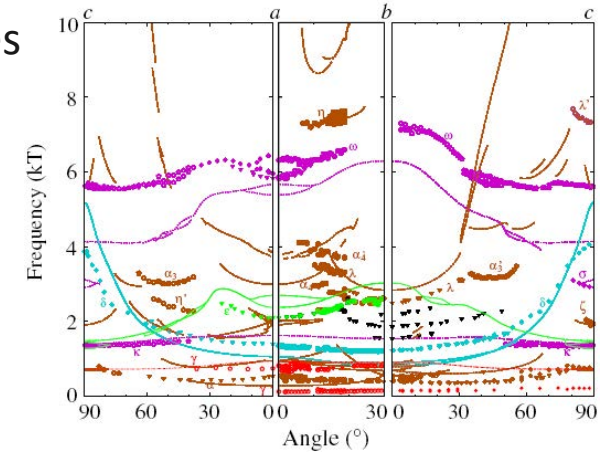
UPt_3 is a heavy fermion metal,
is superconducting below 0.5K,
is a very strongly correlated matal

Heavy fermion UPt_3 metal:
very impressive elucidation
of a very complex Fermi surface
by LDA calculation



LDA

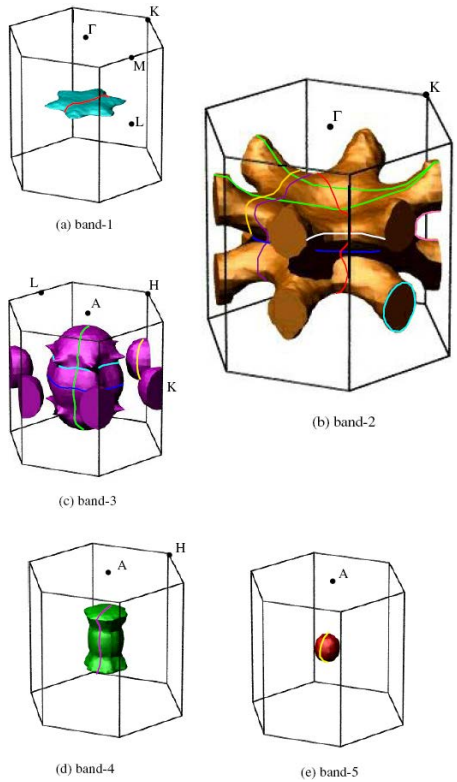
dHvA
frequencies



Expt.

G. McMullan et al., NJP (2008)

[NRL-LANL-ANL collaboration in mid-80s
already had obtained very surprising agreement]



Band Theory of Strong Correlated Electrons

Approximate DFT with correlation corrections
for strong intra-atomic repuslsion "LDA+U"

Generically referred to also as DFT+U

LSDA+U
Double Counting
Correction Functionals

[Ylvisaker, Koepernik, Pickett PRB 2008)

On top of LDA/GGA: $\Delta E = E_I - E_{\rm dc}$

$$E_I = \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} W^{\sigma\sigma'}_{mm'} n_{m\sigma} n_{m'\sigma'}$$

$$W^{\sigma\sigma'}_{mm'} = (U_{mm'} - J_{mm'}\delta_{\sigma,\sigma'}).$$

LDA+U Functional	E_{dc}	=	E_{dc} (rewritten)	DFT XC Functional
Fl-nS	$\frac{1}{2}UN^2 - \frac{U+2lJ}{2l+1}\frac{1}{4}N^2$	=	$\frac{1}{2}UN^2 - \frac{U+2lJ}{2l+1}\frac{1}{2}\sum_\sigma(\frac{N}{2})^2$	LDA
Fl-S (AMF)	$\frac{1}{2}UN^2 - \frac{U+2lJ}{2l+1}\frac{1}{2}\sum_\sigma N_\sigma^2$	=	$\frac{1}{2}UN^2 - \frac{U+2lJ}{2l+1}\frac{1}{2}\sum_\sigma N_\sigma^2$	LSDA
FLL	$\frac{1}{2}UN(N-1) - \frac{1}{2}J\sum_\sigma N_\sigma(N_\sigma - 1)$	=	$\frac{1}{2}UN(N-1) - \frac{1}{2}J\sum_\sigma(N_\sigma^2 - N_\sigma)$	LSDA
FLL-nS	$\frac{1}{2}UN(N-1) - \frac{1}{4}JN(N-2)$	=	$\frac{1}{2}UN(N-1) - \frac{1}{2}J\sum_\sigma((\frac{N}{2})^2 - N_\sigma)$	LDA

"Fluctuation forms" of the functional

(Anisimov, Zaanen,Andersen, ca. 1992)

$$\Delta E^{Fl-nS} = \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} W^{\sigma\sigma'}_{mm'} (n_{m\sigma} - \bar{n})(n_{m'\sigma'} - \bar{n}).$$

$$\Delta E^{Fl-S} = \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} W^{\sigma\sigma'}_{mm} (n_{m\sigma} - \bar{n}_\sigma)(n_{m'\sigma'} - \bar{n}_{\sigma'})$$

FLL
w
fluctu

Aspects of the LDA+U Method

LDA+U for diagonal $\{n_{m\sigma}\}$: Energetics

Site Occupations $\{n_{m\sigma}\}; N_\sigma = \sum_m n_{m\sigma}, N = \sum_\sigma N_\sigma$

$$
\begin{aligned}
E_U &= \frac{1}{2} \sum_{m\sigma \neq m'\sigma'} (U - J\delta_{\sigma\sigma'}) n_{m\sigma} n_{m'\sigma'} - E_U^{dc} \\
&= \frac{1}{2} U N^2 \quad \text{inhibits charge order} \\
&\quad -\frac{1}{2} J \sum_\sigma N_\sigma^2 \quad \text{promotes exchange splitting} \\
&\quad -\frac{1}{2}(U - J) \sum_{m\sigma} n_{m\sigma}^2 \quad \text{promotes orbital polarization}
\end{aligned}
$$

"Orbital polarization" means $n_{m\sigma} = 0$ or $n_{m\sigma} = 1$.

"Fully Localized" Orbital-dependent Potential

$$\Delta v_{m\sigma} = -(U - J) \left(n_{m\sigma} - \tfrac{1}{2}\right)$$

Appropriate values of U and J? Constrained DFT. (not discussed today)

Open shell in spherical environment:

f^2 as an example: 7 orbitals x 2 spins

f^2 configuration: 91 states (configuration = one specific occupation of available states)

Result: each one of the 7 energies $^1S_0$, ... can be expressed in terms of only 4 constants E_0, E_1, E_2, E_3

[Also, four Slater integrals F_0,F_1,F_2,F_3]

- # of configurations: 14!/(14-N)!N!
- N=7: 3432 configurations

- G. Racah, PR 76, 1352 (1949)

In LDA/GGA one never thinks about these details, because the occupation numbers are not evident

LSDA+U Hund's rules:
including spin-orbti coupling

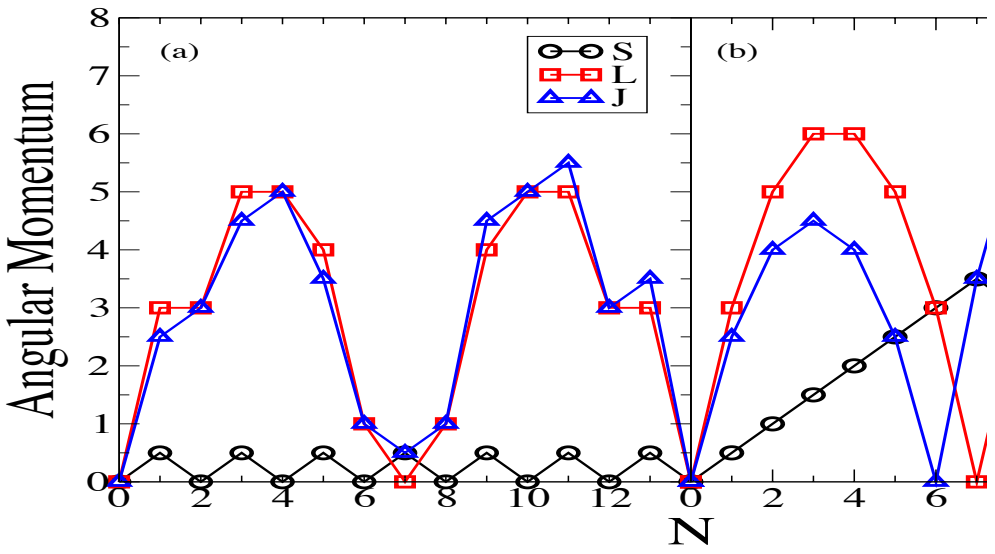
1. Maximize S.
2. Maximize L, subject to #1.
3. J=|S-L|, less than half filled;
   J=S+L, more than half filled

Prediction of the lowest energy configuration

$$\Delta E = E_l[\{n_{ms}\}] - E_{dc}[N,M] + \lambda L_z S_z$$

- **AMF *minimizes* spin**
- **FLL gets Hund's rules**
- **FLL encourages high spin states**
- **z-projections only**

AMF FLL



FLL vs. AMF state ordering, all f^N configurations for N=7

$$\Delta E = E_I[\{n_{ms}\}] - E_{dc}[N,M] + \lambda L_z S_z$$

- U = 8 J = 1 I = 1
- AMF state ordering from left to right
- FLL state ordering from bottom to top
- AMF opposes magnetism

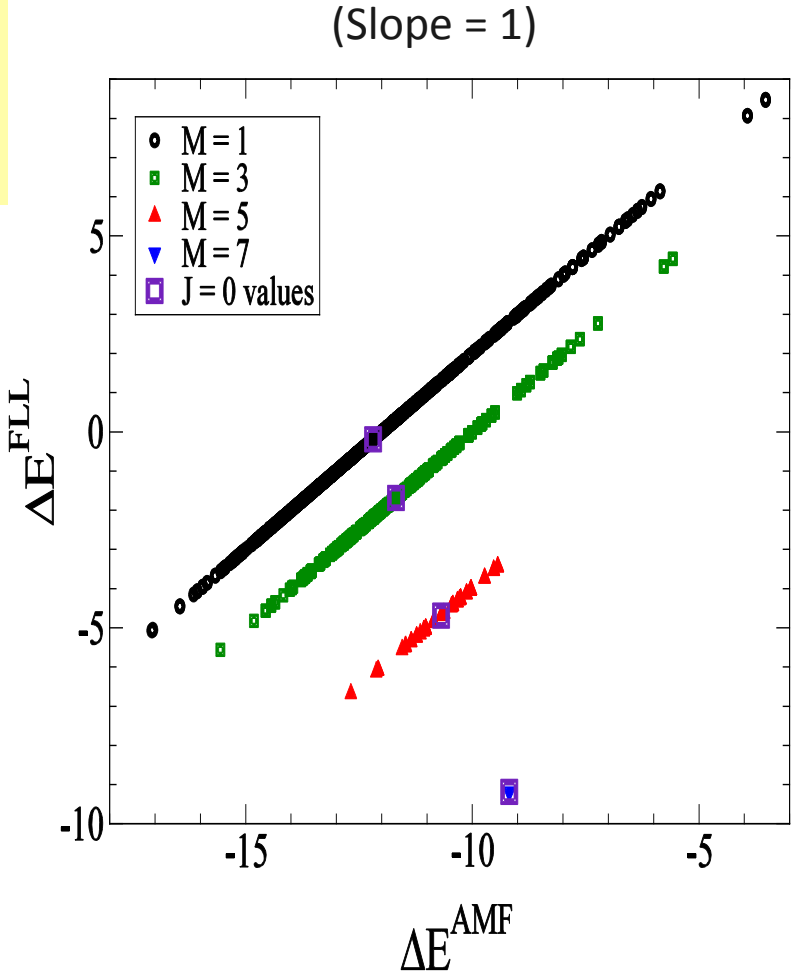
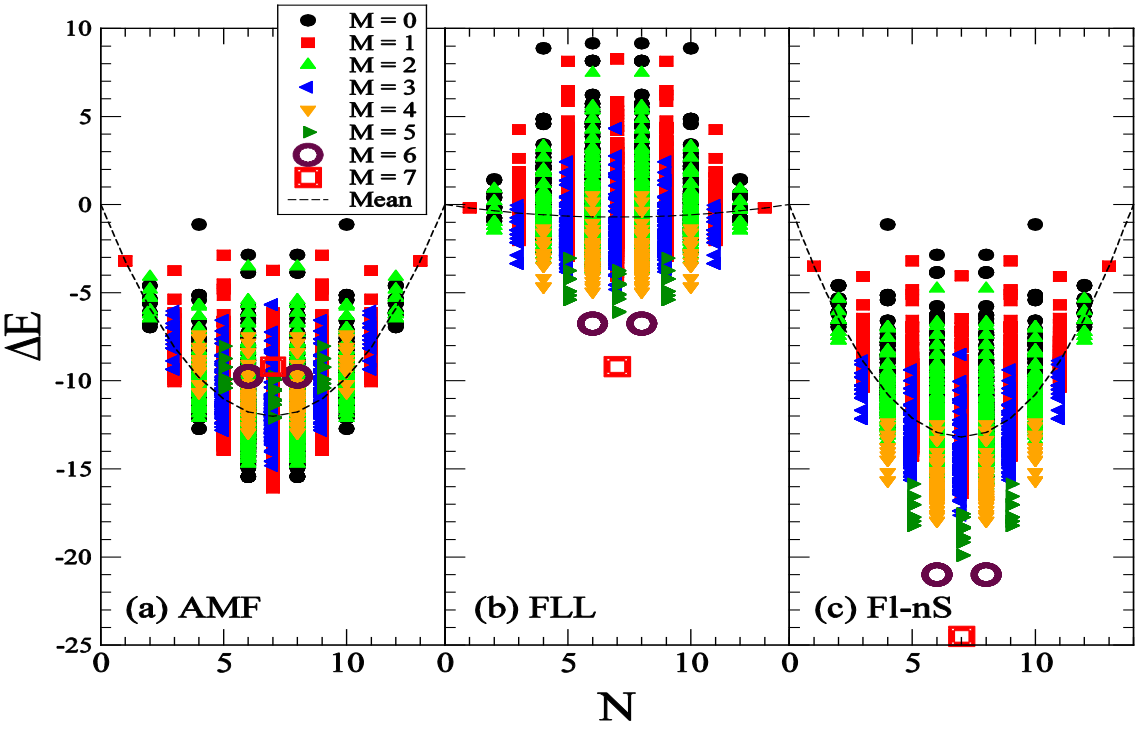


FIG. 2. (Color online) Shown here is ΔE^{FLL} plotted vs $\Delta E^{Fl\text{-}S}$ for each of the 3432 configurations of $N=7$ electrons using $U=8, J=1, I=0.75$, all in eV. The ordering of states is shown for Fl-S by counting from left to right and for FLL by counting from bottom to top. Open squares show values for $U=7$ and $J=0$.

Scatter plot of LSDA+U energies (all configurations)

particle-hole symmetric

- **AMF high M states in center of distribution**
-
- **Stoner $IM^2/4$ used for AMF and FLL**
- **U=8, J=1, I=0.75**



AMF (Fl-S) FFL Fl-nS

Fpr AMF, low-spin states (black&red)

Issues to Recognize about LSDA+U

Results depend on which functional you choose.

Results depend on values of U, J you choose.
Values of U depend on the number of bands/states kept in calculating it..

Results depend on the **method/code** you use.
n_{ms} is specified differently depending on code.
{recall, LSDA+U drives n_{ms} --> 0 or 1.
may need to compensate by choice of U, J

Don't use $U_{eff} = U-J$, $J_{eff} = 0$. Results are different in general, and if they are, then they are wrong.

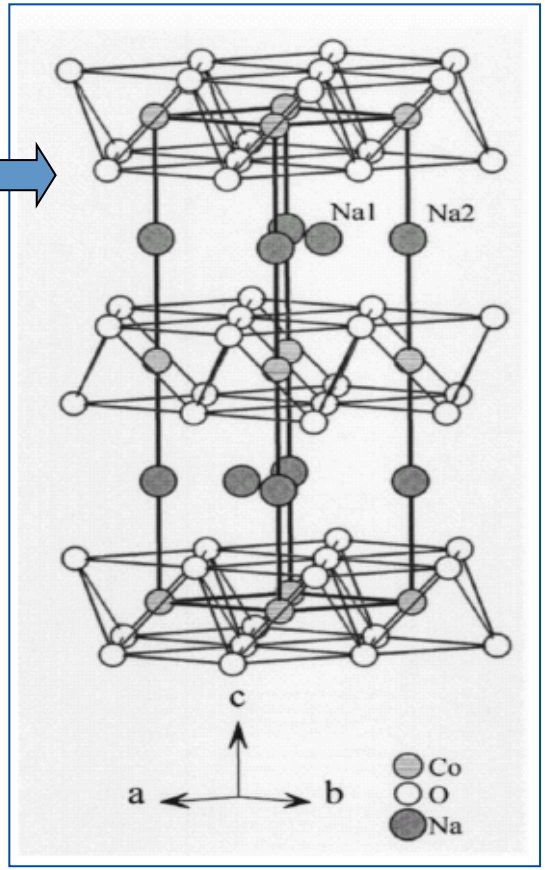
Examples of the effects of including U in open d shells

Na_xCoO_2, the Dehydrated Superconductor
Just add water!

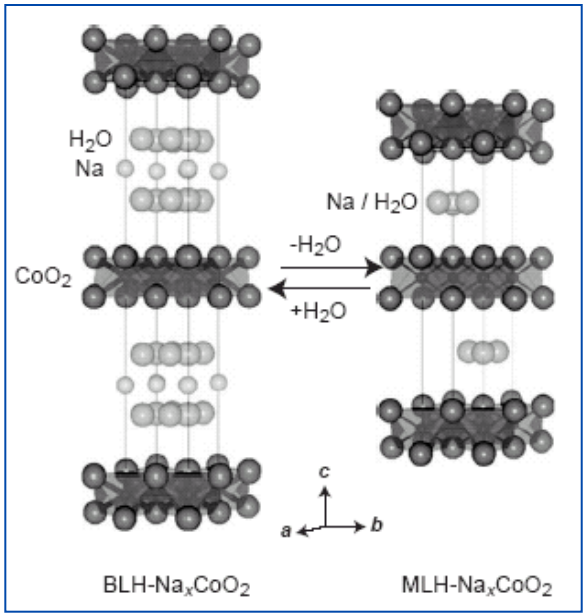
Edge-sharing CoO6 Octahedra

By the trigonal symmetry of the Co site:

$t_{2g} \Rightarrow e'_g + a_g$



Water



J.D. Jorgensen et al. (ANL)

Phys. Rev. B 68, 214517 (2003)

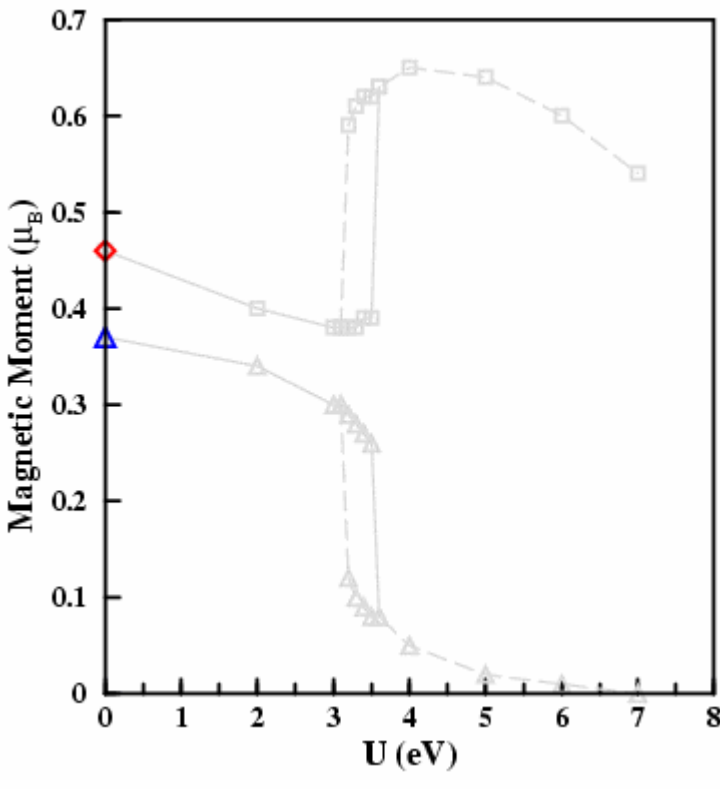
K. Takada et al. (Japan), Nature 422, 53 (2003);

Adv. Mater. 16, 1901 (2004)

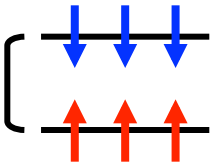
Cobalt Ion

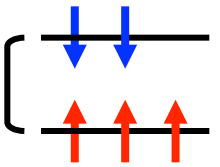
Cobalt moment vs. U in LDA+U : FM (x=1/2)

Na_xCoO_2



- xCo^{3+} : **(S=0) nonmagnetic**
- $(1-x)Co^{4+}$: **(S=1/2) magnetic**

$Co^{3+}(3d^6): t_{2g}$ 

$Co^{4+}(3d^5): t_{2g}$ 

d Charge on Co ions

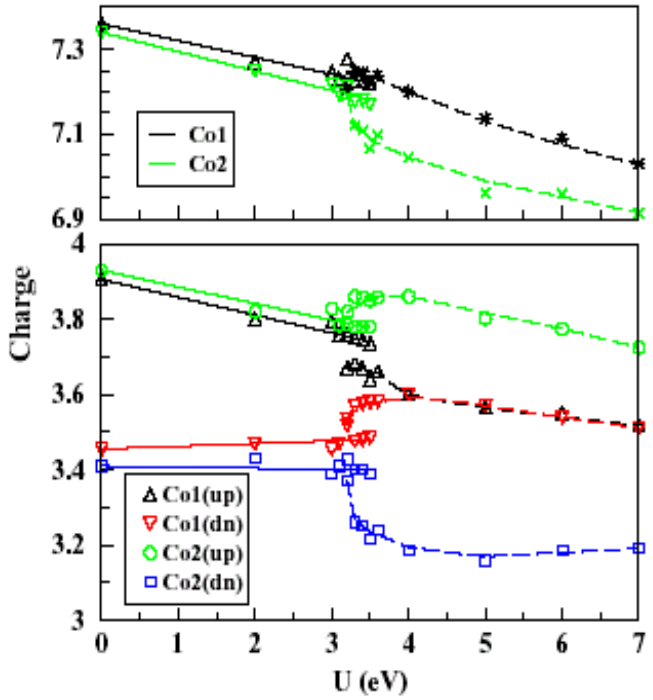


FIG. 2: Change with U of d charge for the two Co ions. *Upper panel*: change of total $3d$ charge (the charge is transferred to O ions). *Lower panel*: changes of the majority and minority separately.

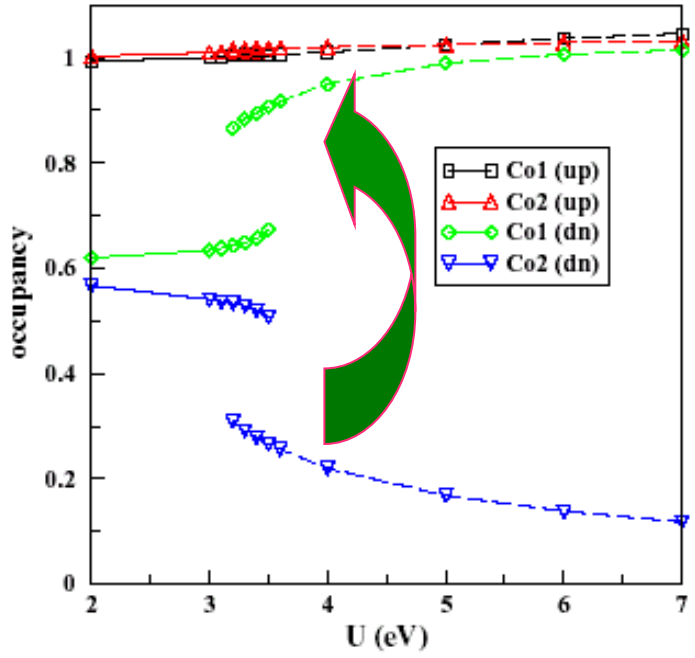
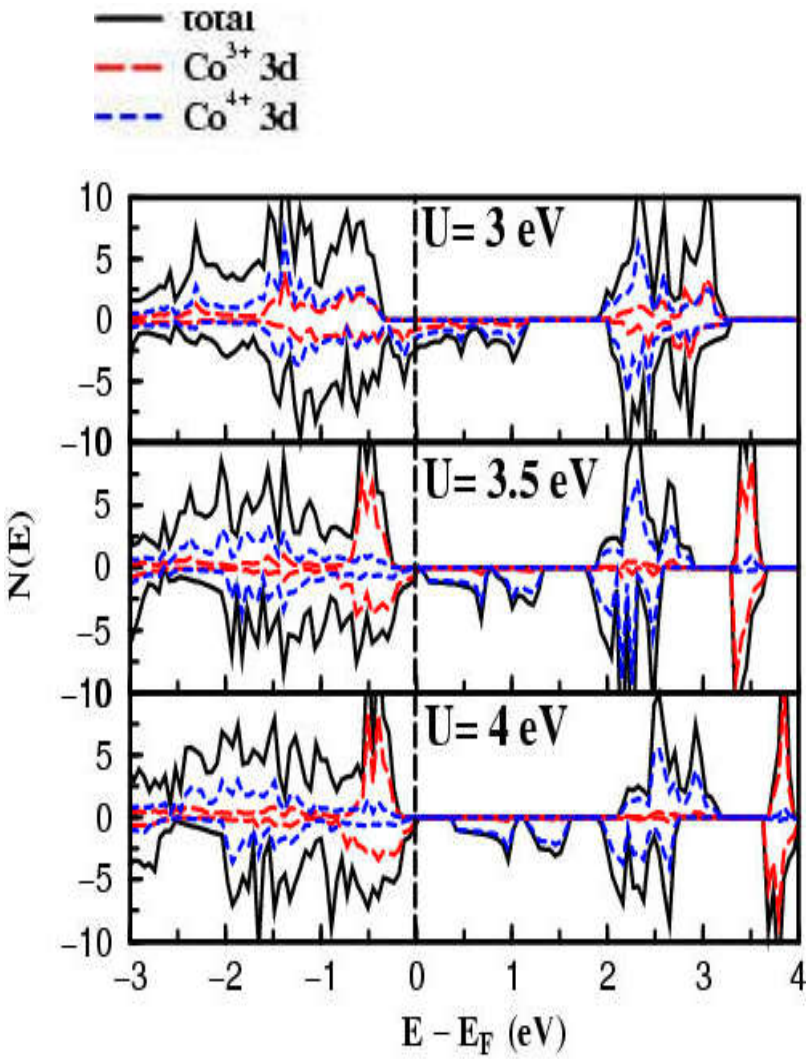
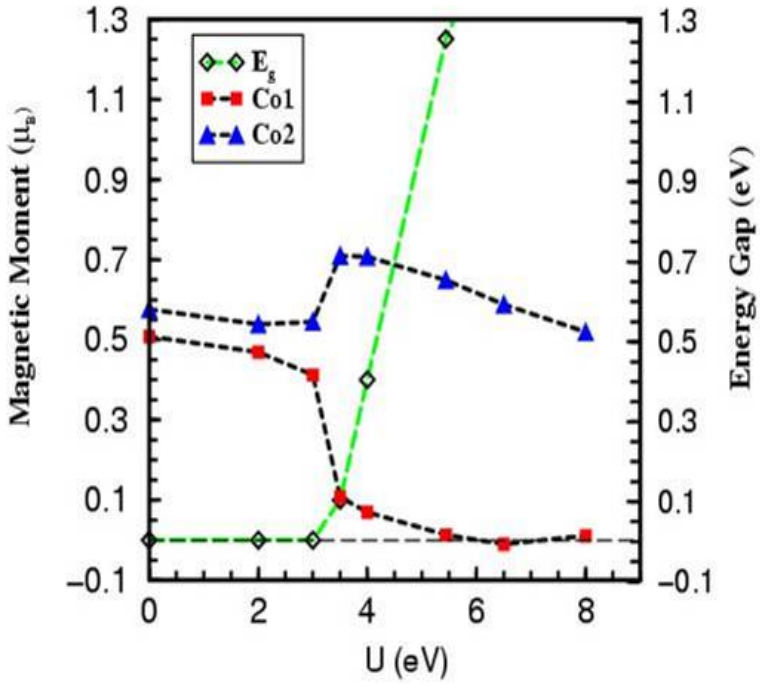


FIG. 3: Change of the occupancy n_{a_g} of the a_g state versus U, which reveals the strong a_g charge disproportionation at the transition. Majority orbitals of both Co ions are fully occupied regardless of U. At $U = U_c$, the occupancy of the minority decreases for Co2 and increases for Co1 by 0.23 e.

Gap, Moment vs. U in LDA+U : FM (x=1/3)





- **Below Uc= 3eV, Co moments are nearly equal to LDA values.**
- **Above Uc: CD into one Co^{3+} and two Co^{4+} with MI transition.**
- **dEg/dU = 0.6**

LDA+U (aka DFT+U)

LDA(GGA)+U is beyond LDA(GGA) as it can describe
-Mott insulating states (open d shell, yet insulating)
-charge disproportionation, separate spin states
-orbital ordering: breaking of real space symmetry

Typically a 1st order transition as U is varied

LDA+U+SOC + crystal fields, especially for lanthaide compounds, results in very “interesting” behavior.

A change of topic

Why the great emphasis on
acceleration of
design and discovery?

Seems like a silly question,
but an example can be illuminating.

A history of (topological) nodal ring semimetals

A nodal loop semimetal is a crystalline material
that has a closed ring (loop) of dgeneracies of 2 bands.

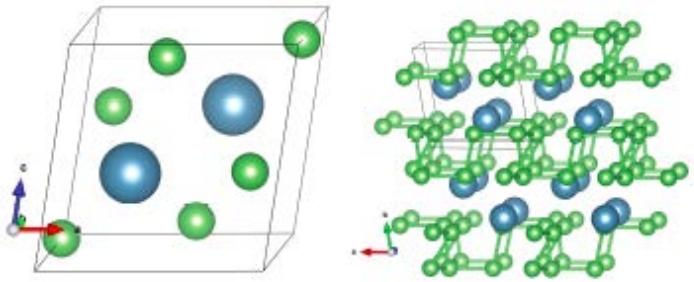
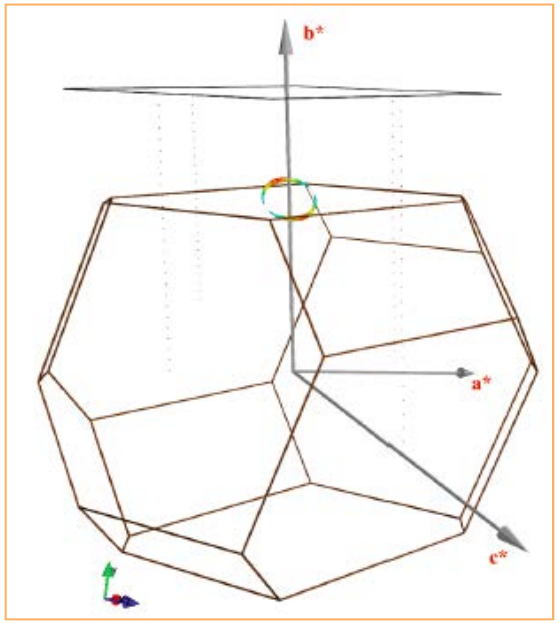


FIG. 1: Left: Unit cell of $CaAs_3$. Blue spheres: Ca atoms. Green spheres: As atoms. Right: 2x2x2 supercell with As-As bonds (cutoff is 3Å) shown.

Monoclinic
$CaAs_3$
Space group #2

A nodal loop
semimetal

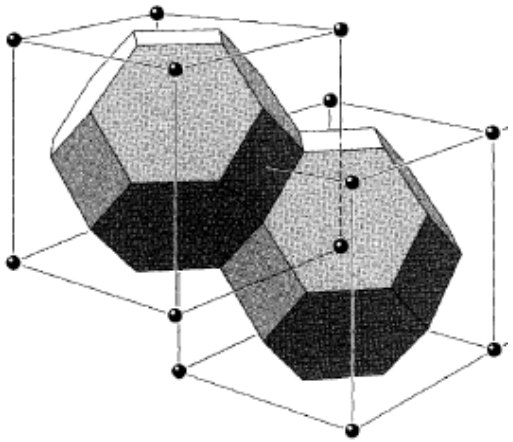


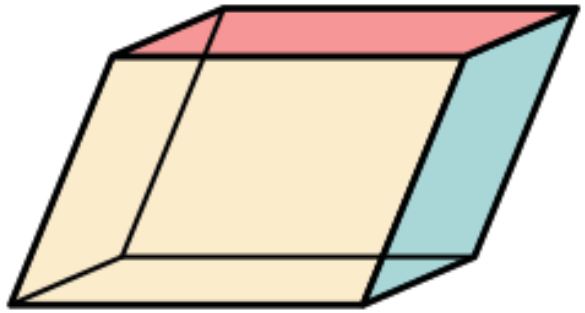
Everyone in the field knows that the topic of NLSs began with the PRB 2011 paper of **Burkov, Hook, Balents**

That is not quite the whole story…

Periodicity: in r space and in k space

Periodic cells
In k space

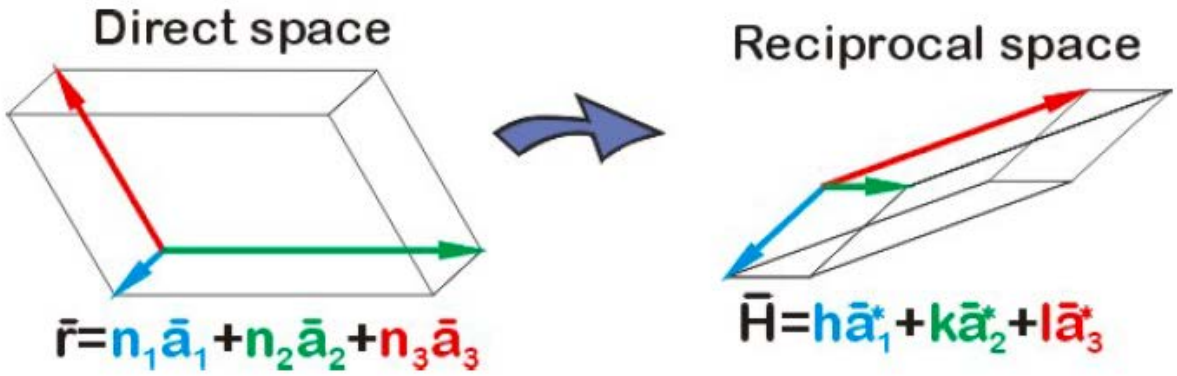




Periodically
Repeated
parallelapiped:
Brillouin zone

$$\vec{G}_{mnp} = m\vec{G}_1 + n\vec{G}_2 + p\vec{G}_3$$

Direct space to reciprocal space



Periodicity: in r space and in k space

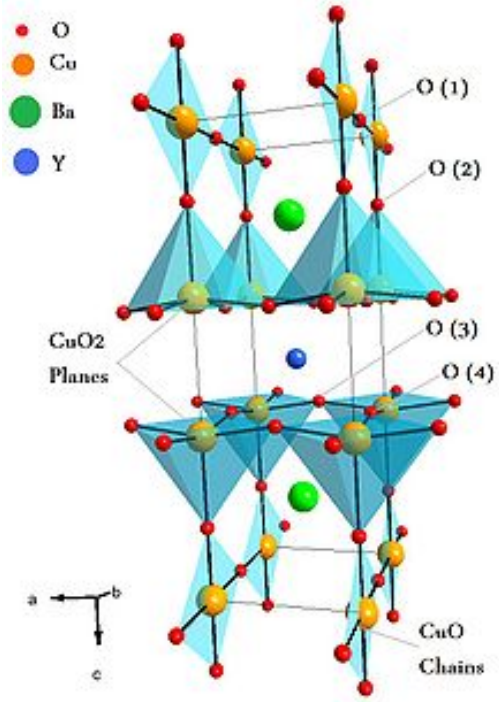
Bloch's Theorem (1928)

$$\psi_k(r) = e^{ik\cdot r} u_k(r)$$

1 $u_k(r + R_{mnp}) = u_k(r)$

2 $u_{k+G_{mnp}}(r) = u_k(r)$

3 $E_{k+G_{mnp}} = E_k$



YBa2Cu3O7

Bloch Hamiltonian for u_k

$$H_k u_k = \left[\frac{(p+\hbar k)^2}{2m} + V(r)\right] u_k = E_k u_k$$

$$H_k = H(k_x, k_y . k_z)$$

A Hamiltonian with three 'parameters' that can wander around periodic k-space.

Adiabatic changes of $\vec{k} \rightarrow$ what implications for the crystal?

$$\left[\nabla_k H_k - \nabla_k E_k\right] u_k + \left[H_k - E_k\right] \nabla_k u_k = 0$$

Matrix elements will involve a "vector potential-like" Berry connection:

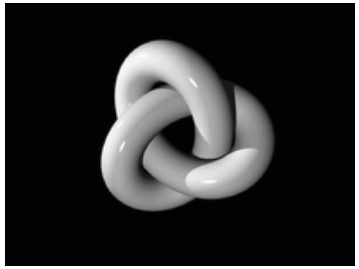
$$\vec{A}_{kn} = -i < u_{kn} | \nabla_k | u_{kn} >$$

$$u_{kn} = |u_{kn}| e^{i\theta_{kn}}$$

$$Z_n = \frac{1}{2\pi} \oint d\vec{\ell} \cdot A_{kn} = \frac{1}{2\pi} \oint d\vec{\ell} \cdot \nabla_k \theta_{kn}$$

The integral over certain closed contours gives a quantized topological invariant Z.

Z is a "winding number" equal to 0 or 1,
Z=0: simple (trivial); Z=1: topological.



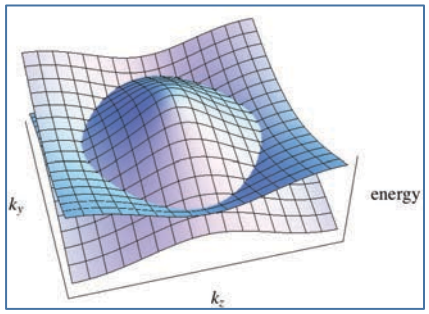
The first modern publication on a topic…

Topological Nodal Semimetals

(Weyl and **nodal loop** semimetals)

A closed loop of degeneracies in BZ

before consideration of spin-orbit coupling

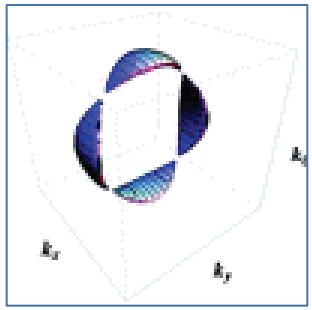


Intersection of energy surfaces, without SOC

Burkov, Hook, Balents PRB 2011

Murakami NJP 2007

Including SOC



- Loops need not lie in a plane, maybe not even close
- Loops need not cut at the Fermi energy; if they do span E_F there are two Fermi points (w/o SOC), or an even number
- SOC may open up a Fermi surface something like that at left, with compensating el & hole surfaces
- In bulk, slightly unusual semimetals (with special cases)
- they are **topological**, and produce **Fermi arcs**.

First: a comment on degeneracies in band structures

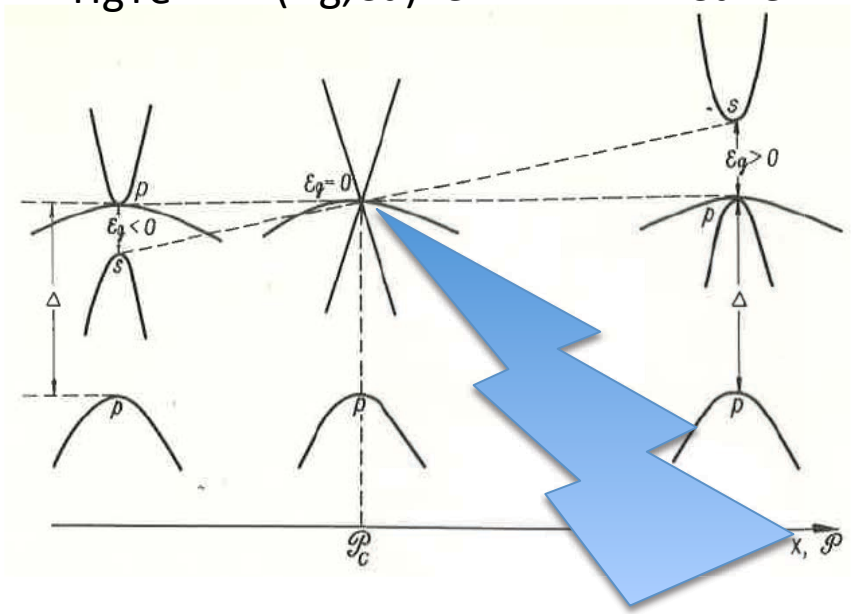
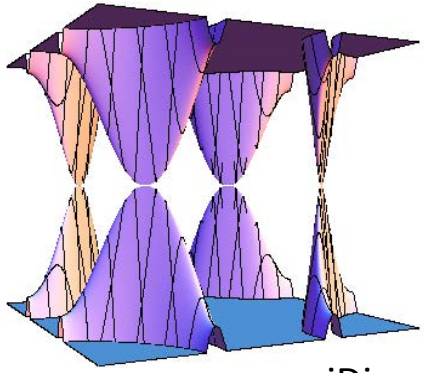


Figure from book
"Gapless Semiconductors"
I M Tsidilkovski, 1988

Eigensystem becomes non-analytic at a degeneracy.

Non-analyticity is the source of topological character.



semiDirac
Pardo & WEP
PRL 2009

Types of degeneracies in Band Structures

POINTS: Dirac; semi-Dirac; Weyl; quadratic band touching
LINES: "nodal loops" are closed lines of degeneracies in the BZ
SURFACES: no way

On the Behavior of Eigenvalues in Adiabatic Processes

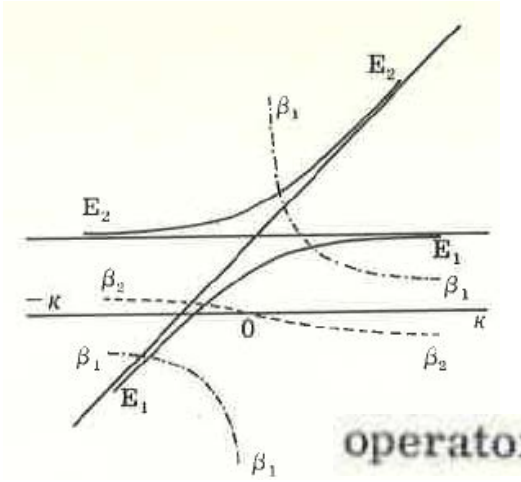
J. von Neumann and E. Wigner

Physikalische Zeitschrift, **30**, 467–470 (1929)

Requirement for degeneracy to occur:

Hermitian matrix: 3 parameters

Real Hamiltonian: 2 parameters



operator $H + \kappa V$ for increasing κ,

Translated and reprinted in:

SYMMETRY

IN

THE SOLID STATE

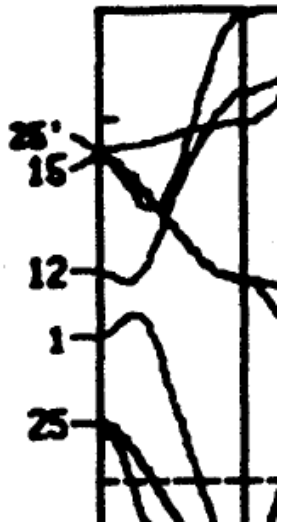
ALBERT GOLD

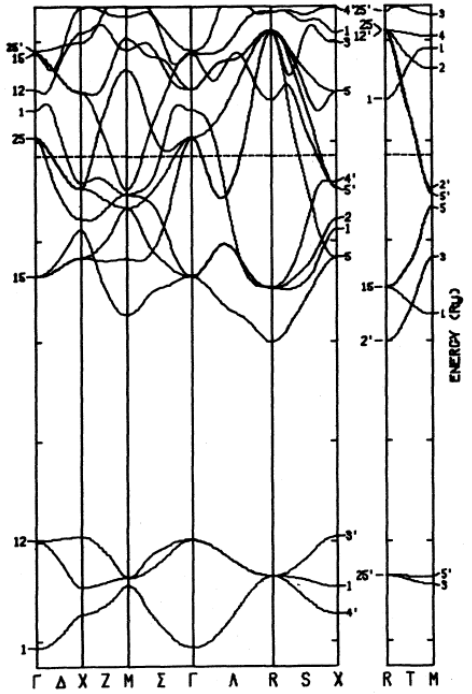
ROBERT S. KNOX

Theory of Brillouin Zones and Symmetry Properties of Wave Functions in Crystals
L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936)

Symmetry-determined degeneracies in electronic structures
from the viewpoint of group theory

Symmetry labeling
of band points and lines





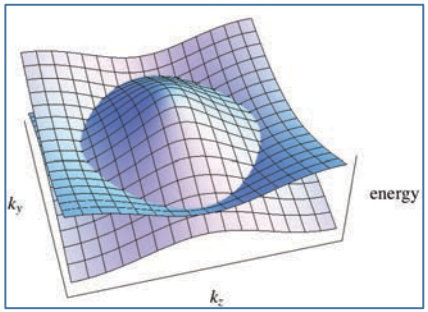
Band structure of Bi_3Sr
Papaconstantopoulos,
Klein, Boyer, Connolly
PRB 1982

"Conyers: go learn what sorts of accidental degeneracies can occur in crystalline energy bands."
Eugene Wigner, ca. 1935

AUGUST 15, 1937 PHYSICAL REVIEW VOLUME 52

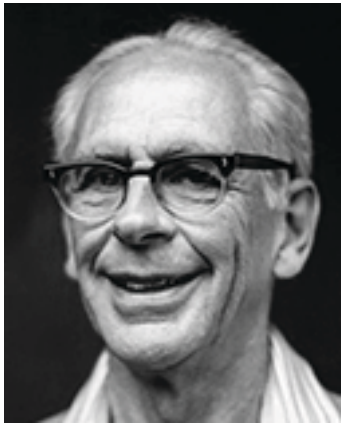
Accidental Degeneracy in the Energy Bands of Crystals

CONYERS HERRING
Princeton University, Princeton, New Jersey



$$u_n(\vec{k},\vec{r}) = \exp(-i\vec{k}\cdot\vec{r})\psi_n(\vec{k},\vec{r})$$

$$\mathcal{H}(\vec{k}) = (\vec{p}+\hbar\vec{k})^2/2m + V(\vec{r}).$$

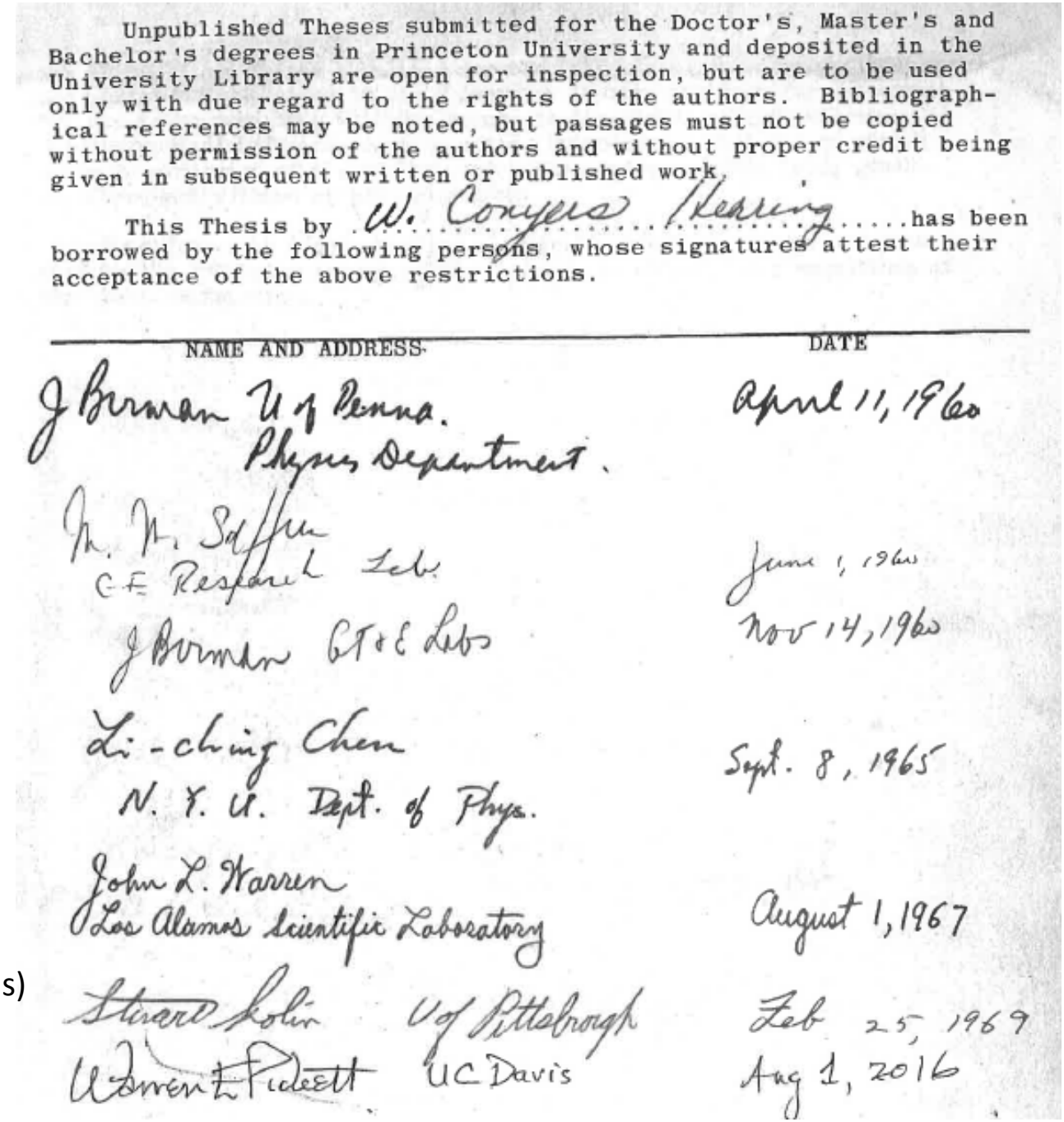


For crystals with an inversion center, contacts of equivalent manifolds $M^i(\mathbf{k})$, $M^j(\mathbf{k})$ may occur at all points $\mathbf{k}$ of an endless curve, or of a number of such curves, in $\mathbf{k}$-space. These contact curves cannot be destroyed or broken by any infinitesimal change in the potential V which preserves the inversional symmetry. It is vanishingly improbable for such curves to lie in planes of symmetry in the B-Z; however a contact curve may pass through a symmetry axis at a point where necessary degeneracy or contact of inequivalent manifolds occurs.

...refer to my thesis...

Signout sheet
for the thesis (1937) of
W. Conyers Herring.

Princeton Univ. Library



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J Birman U of Penna. Physics Department.		April 11, 1960
M. M. Saffren G E Research Lab.		June 1, 1960
J Birman GT&E Labs		Nov 14, 1960
Li-ching Chen N. Y. U. Dept. of Phys.		Sept. 8, 1965
John L. Warren Los Alamos Scientific Laboratory		August 1, 1967
Stuart Golin	U of Pittsburgh	Feb 25, 1969
Warren E Pickett	UC Davis	Aug 1, 2016

1960 J Birman (Penn)
1960 M M Saffron (GE)
1960 J Birman (GT&E)
1965 Li-ching Chen (NYU)
1967 John L Warren (LASL)
1969 Stuart Golin (Pittsburgh)
2016 Warren E Pickett (UCDavis)

ASPECTS OF DEGENERACY

M. V. Berry, 1984

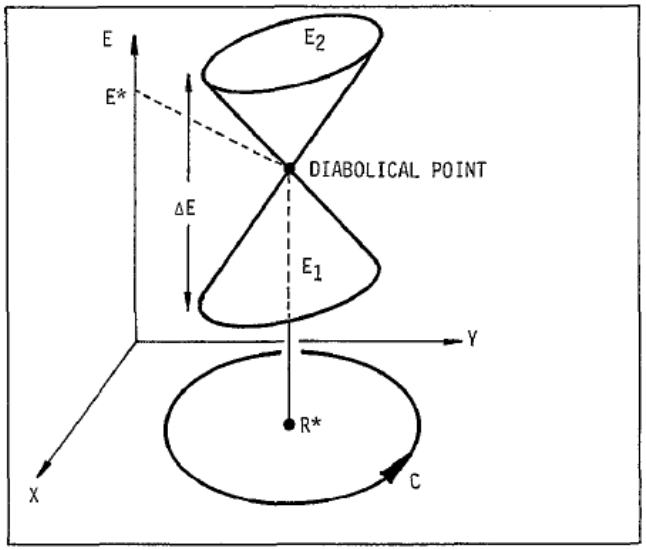


Fig.1. Geometry and notation near a diabolical point.

Evolution of H(X,Y,Z) under adiabatic variation of X,Y,Z

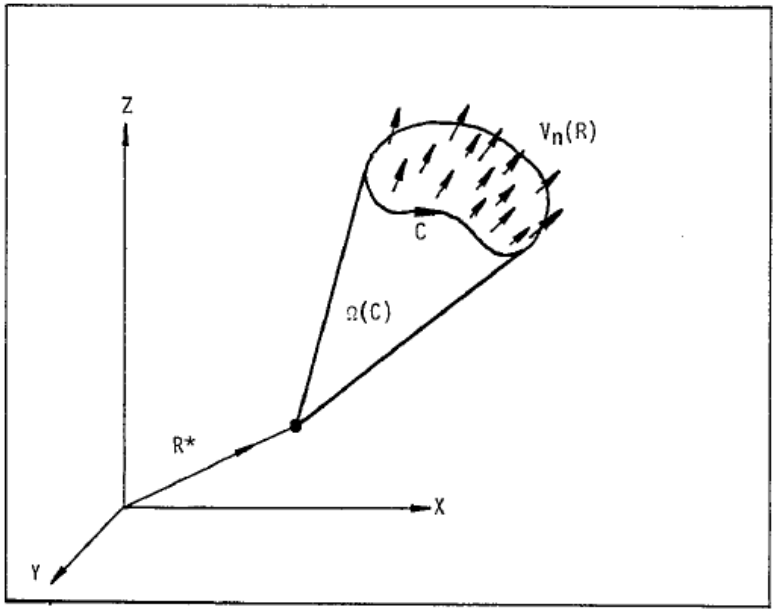
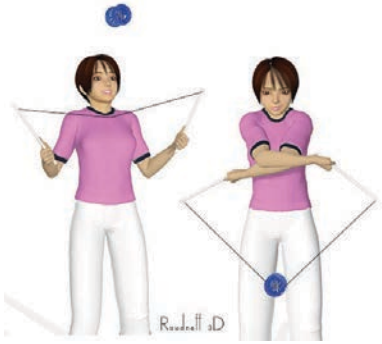


Fig.4 Circuit C near degeneracy R* in R=(X,Y,Z) parameter space

The diabolical point in parameter space (degeneracy)

G. Volovik, several papers

Diabolo → diabolical point



Close up view

Large diablo

Diablo juggling

Three Diablo shuffle

What happens to geometric phase when spin-orbit interactions lift band degeneracy?

$$\mathcal{H}_{\rm eff} = \begin{pmatrix} \hbar\vec{k}\cdot\vec{v}_a\hat{1} & \hbar\vec{k}\cdot\vec{v}_b\hat{1} - i\vec{\xi}\cdot\vec{\sigma} \\ \hbar\vec{k}\cdot\vec{v}_b\hat{1} + i\vec{\xi}\cdot\vec{\sigma} & -\hbar\vec{k}\cdot\vec{v}_a\hat{1} \end{pmatrix}$$

P. B. Allen, arXiv:0709.1457, Sept 2007 (unpublished, probably never cited)

Spin-orbit coupling destroys the degeneracy of the loop, but does not destroy the singularity associated with the loop.

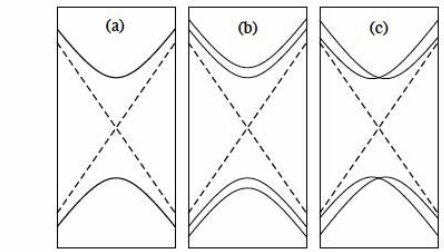


FIG. 1: Energy *versus* $|\vec{k}|$ near the degeneracy point, for (a) no magnetic field, (b) field parallel to $\vec{\xi}$, and (c) field perpendicular to $\vec{\xi}$. The dashed lines are for $\xi = 0$ and $b = 0$; solid lines in panel (a) are $\pm\lambda$, which becomes $\pm\xi$ at the degeneracy point $\vec{k} = 0$.

His acknowledgment:

I thank A. G. Abanov and M. S. Hybertsen for help. **I thank the students of Phy556 who were subjected to preliminary versions of this work.** This work was supported in part by NSF grant no. NIRT-0304122.

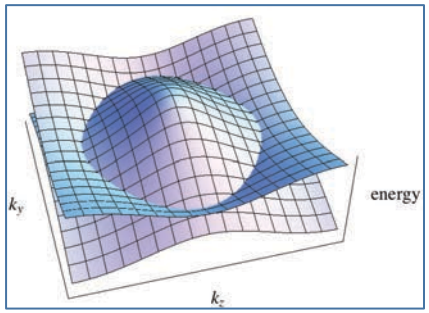
The first modern publication on a …

Topological nodal semimetals

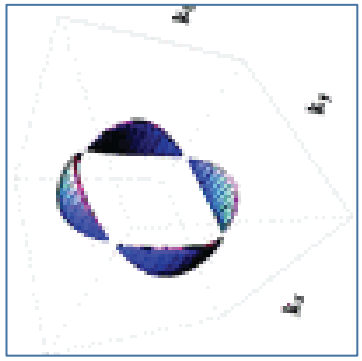
(Weyl and nodal loop/line semimetals)

A closed loop of degeneracies in BZ
before consideration of spin-orbit coupling

Burkov, Hook, Balents PRB 2011
Murakami NJP 2007



Including SOC



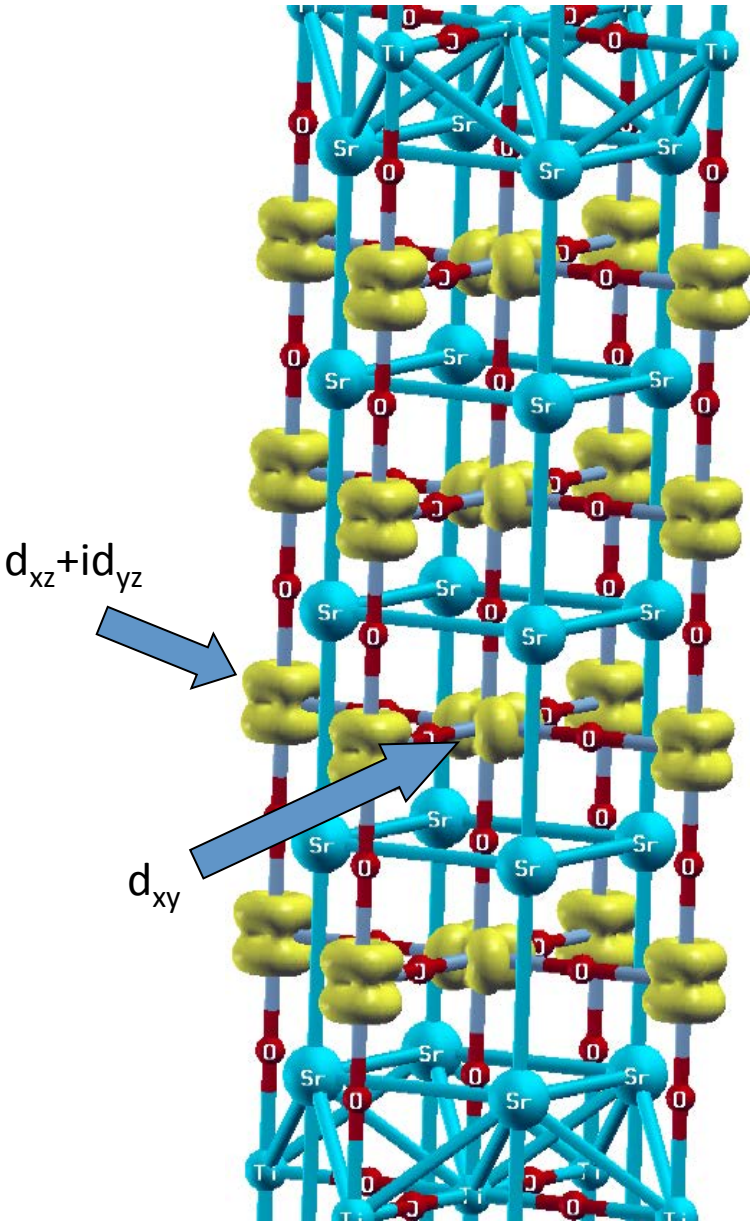
Accumulated Facts

- **Inversion symmetry alone** is sufficient for a nodal loop
- Loops **will not lie in a plane**, maybe not even close
- Loops **need not cut at the Fermi energy**; if they do span E_F there are two Fermi points (w/o SOC), (or an even number; see figure at left)
- **SOC will split** the nodal degeneracy (subj. to symmetry)
- In bulk, may be somewhat unusual semimetals
- they are **topological**, and produce boundary **Fermi lines** and **Fermi arcs**

A nodal loop discovered computationally in $SrVO_3$ nanolayers, 2009

STO/m$SrVO_3$/STO(001) system

Pardo & Pickett, PRB 2009



Bulk SVO: correlated metal

No polar discontinuity

Insulator-metal transition at m=4-5, in agreement with Kim et al (2000)

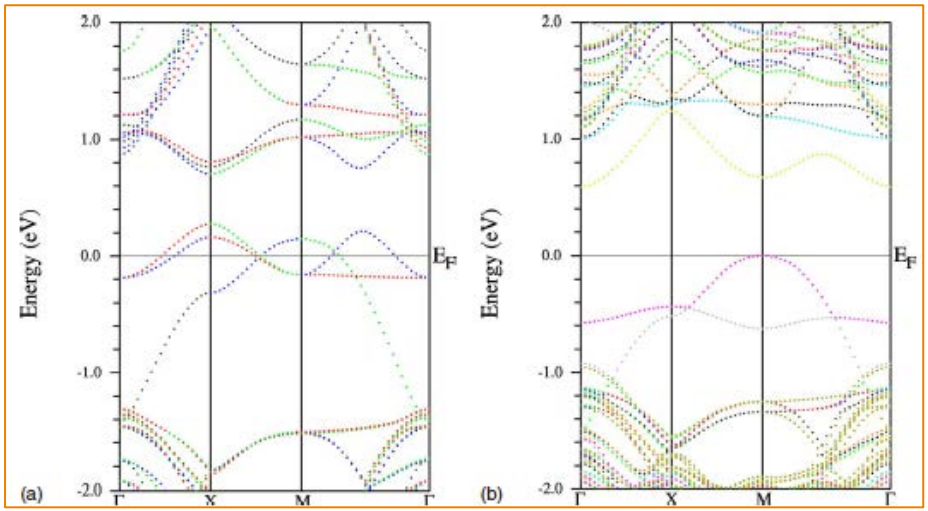
Insulator-metal transition through **unusual semimetal phase**

Unexpected c(2x2) orbital ordering

d^1 orbital moment: 0.75 μ_B, strong cancellation of $M=M_{orb}+M_{spin}$

m layers of $SrVO_3$(001) encased in $SrTiO_3$

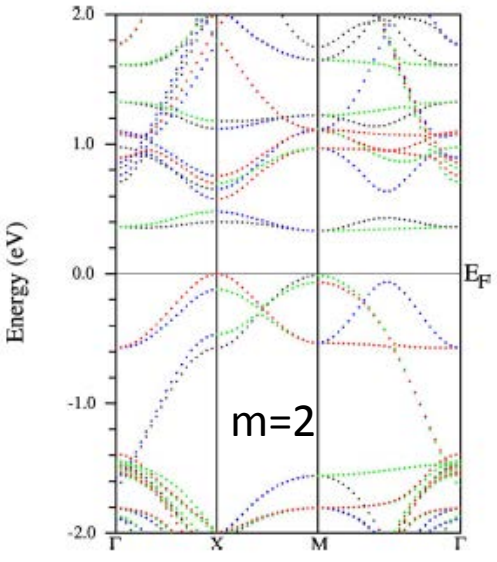
LDA+U: HM FM LDA+U+SOC: FM MI



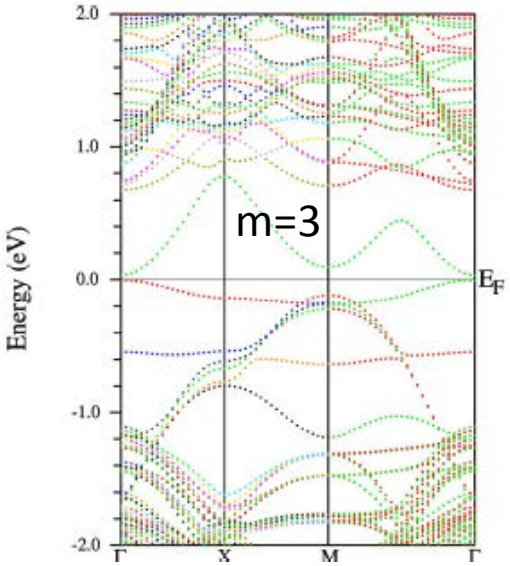
m=1

No polar discontinuity

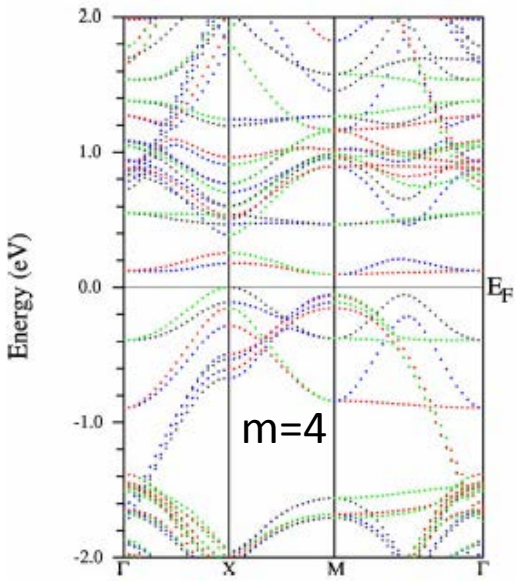
Ferromagnetic V^{4+}: d^1
Each layer adds 2 bands



AOO FM MI (w/o SOC)



up/dn/up FM layers

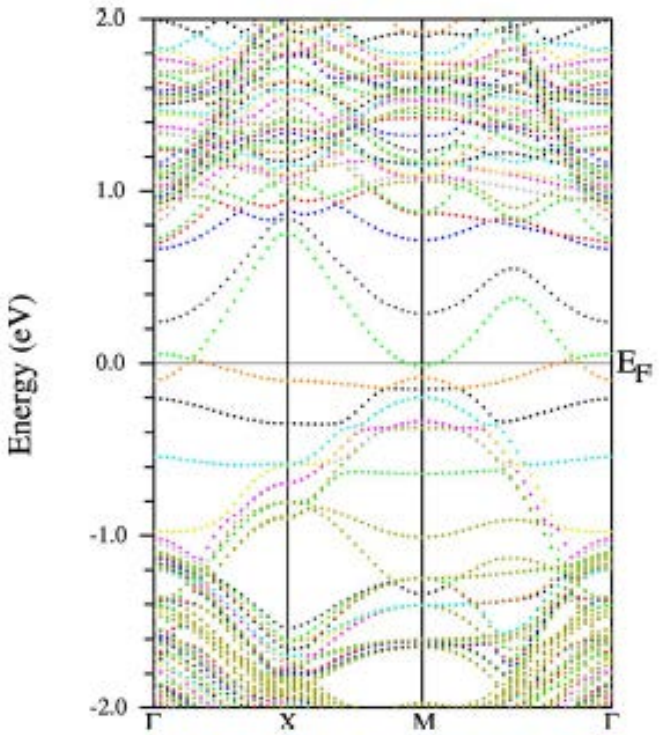


AOO FM MI (w/o SOC)

m=5 layers of $SrVO_3$(001) encased in $SrTiO_3$

Pardo & Pickett, PRB 2009

FM half semimetal. AOO within each layer.
Upper majority band overlaps conduction band, producing inverted bands at Γ.



Most of the zone is gapped.
(Neglect tiny pocket at M)

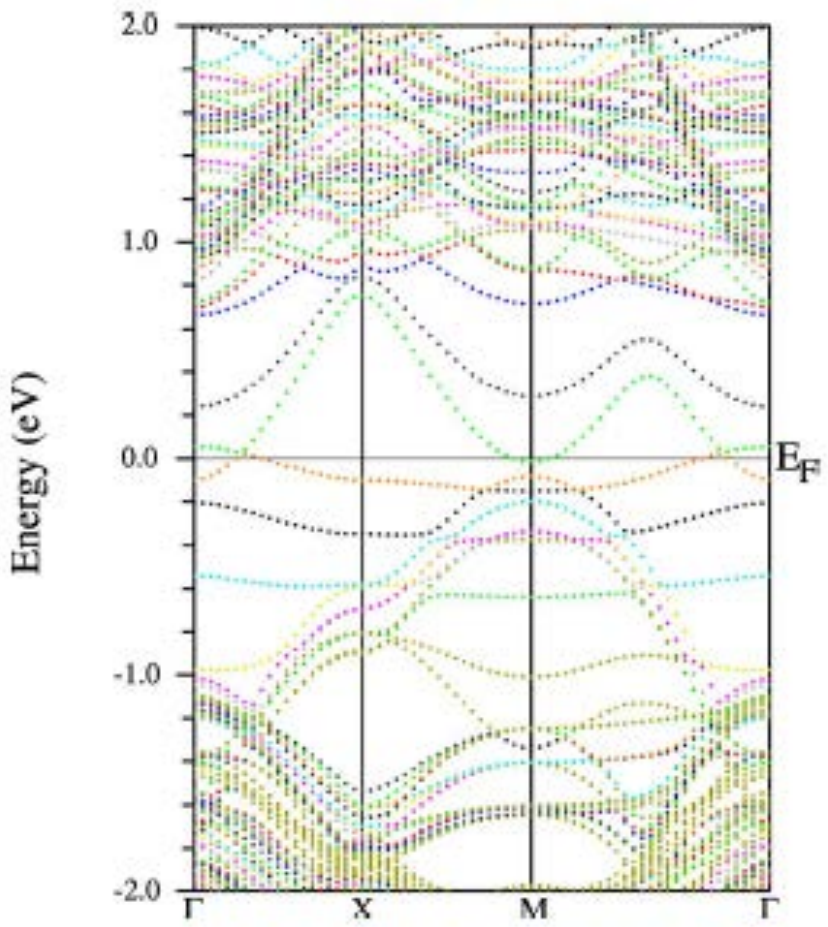
Apparent Dirac points at E_F along Γ-X and along Γ-M, pinning the Fermi energy.

In fact: there are two "degenerate" Fermi circles surrounding Γ:
Identical electron & hole FSs,
Because $n_e == n_h$.

Upon doping, an annulus around Γ containing the carriers.

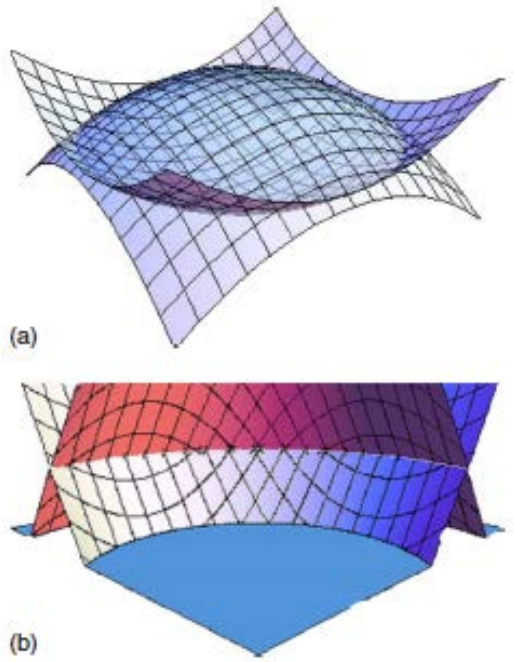
5 layers of $SrVO_3$(001) encased in $SrTiO_3$

Pardo & Pickett, PRB 2009



A ferromagnetic (!) 2D(!) nodal loop semimetal

$$\epsilon_k = \pm v(|\vec{k}| - k_F)$$



First nodal loop that I know of.

End of the History of Degeneracies in Crystals

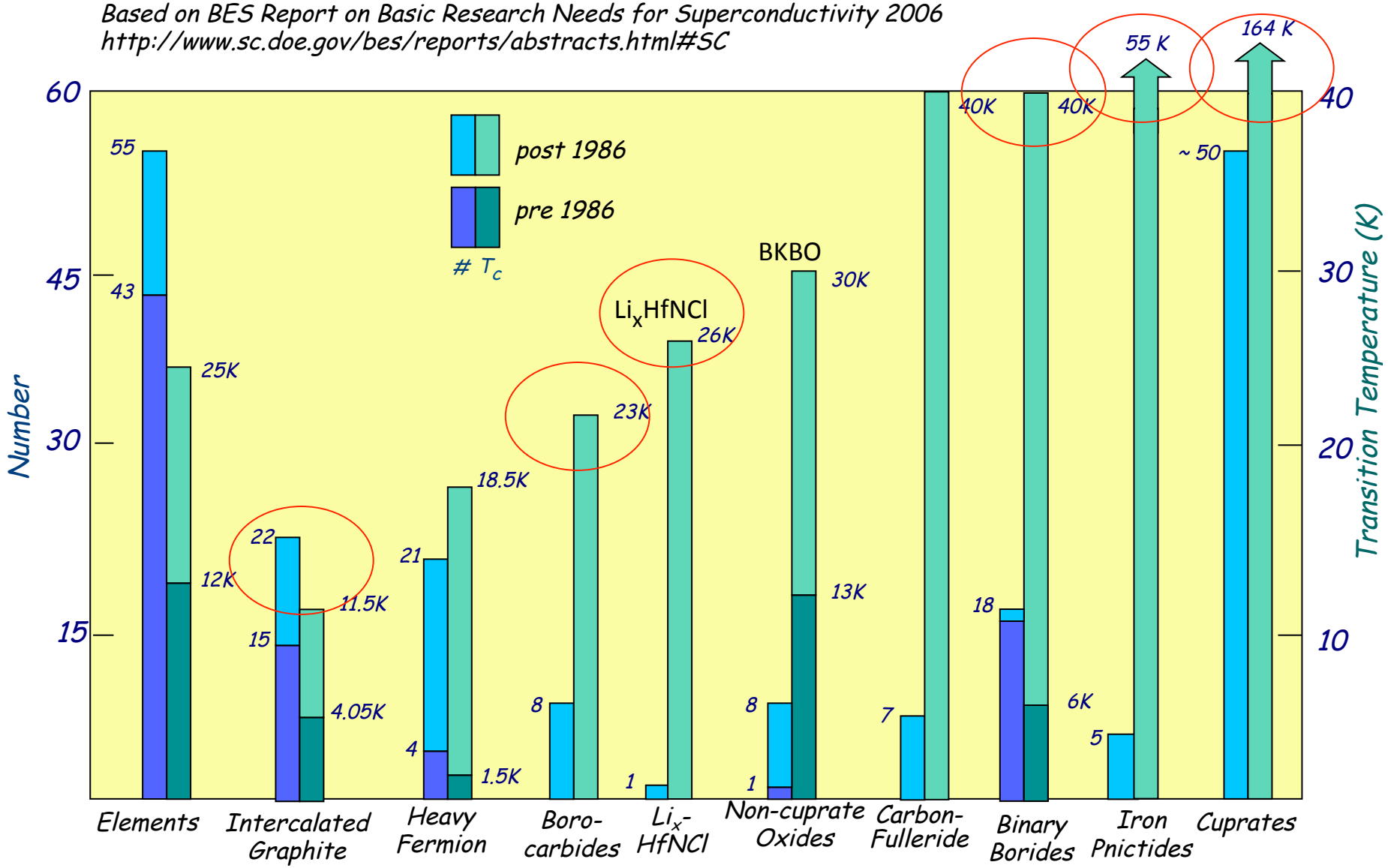
A very short overview of a remarkable discovery: the new and current highest T_c superconductor

New Materials:
Recent Superconductor Discoveries

Courtesy:
G. W. Crabtree

2D materials

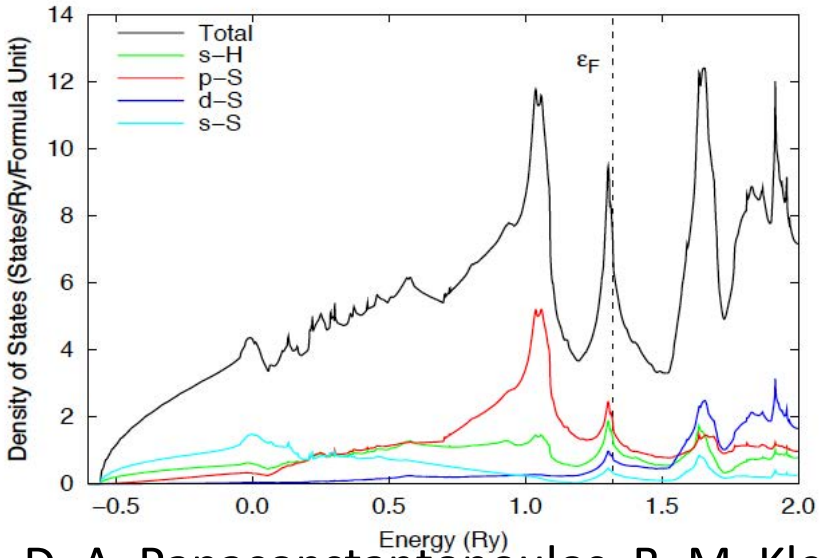
Based on BES Report on Basic Research Needs for Superconductivity 2006
http://www.sc.doe.gov/bes/reports/abstracts.html#SC

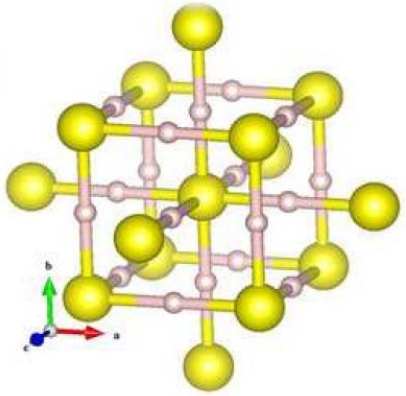


A ground-breaking discovery in the MGI spirit

Cubic H_3S around 200 GPa, T_c~200 K:
an atomic hydrogen superconductor stabilized by sulfur

Total & atom-projected
Density of states





Simple bcc structure of H_3S:
interleaved ReO_3 sublattices

D. A. Papaconstantopoulos, B. M. Klein, M. J. Mehl, W. E. Pickett, PRB 2015

The metallization and superconductivity of dense hydrogen sulfide

Yinwei Li,[1,a)] Jian Hao,[1] Hanyu Liu,[2] Yanling Li,[1] and Yanming Ma[3,b)]

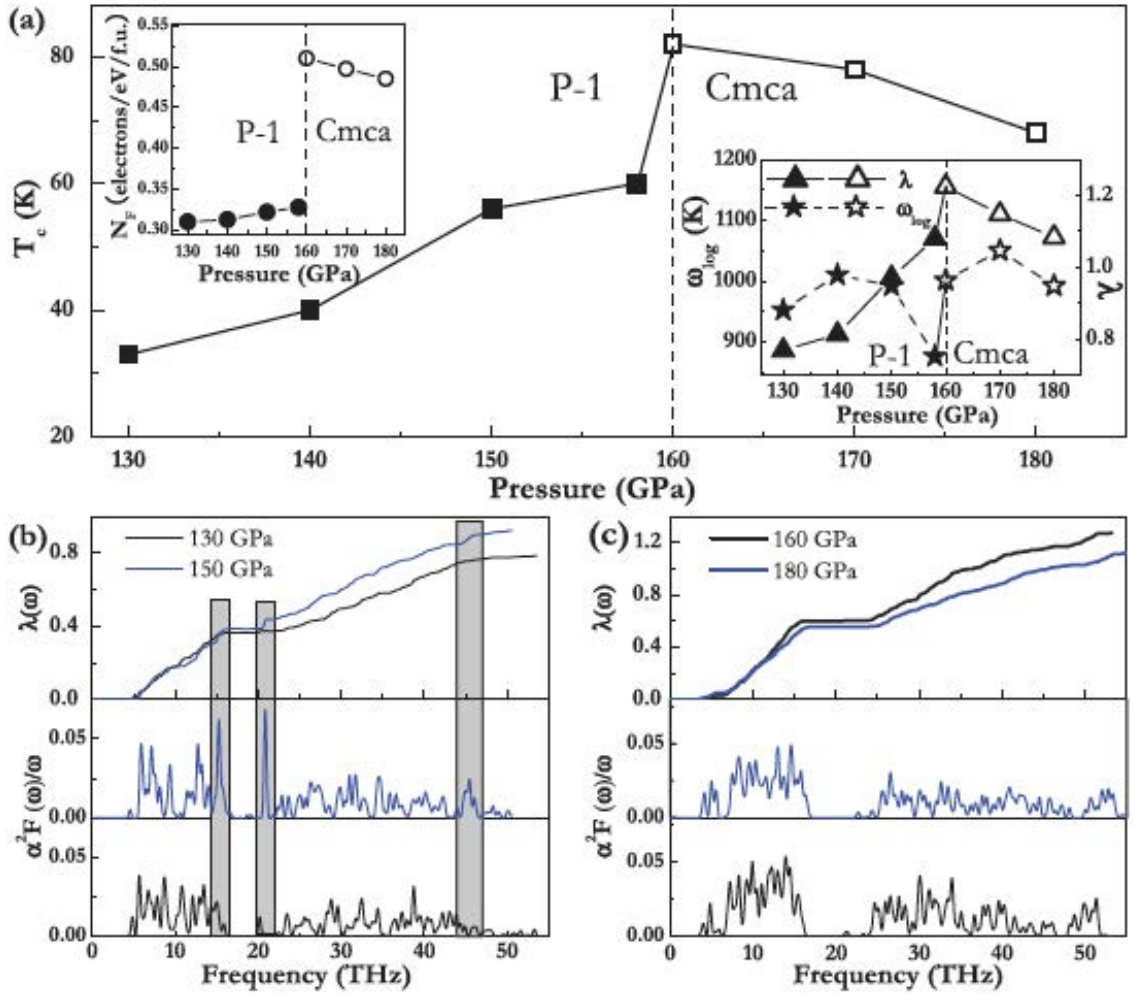
J. Chem. Phys., May 2014

2014

H_2S

Critical temperature in predicted stable phase of H_2S versus pressure, up to 80 K (!)

Spectral function versus frequency, for two phases



Pressure-induced metallization of dense $(H_2S)_2H_2$ with high-T_c superconductivity

Defang Duan[1,2], Yunxian Liu[1], Fubo Tian[1], Da Li[1], Xiaoli Huang[1], Zhonglong Zhao[1], Hongyu Yu[1], Bingbing Liu[1], Wenjing Tian[2] & Tian Cui[1]

Sci. Rep., Nov. 2014

H_3S

λ=2.1

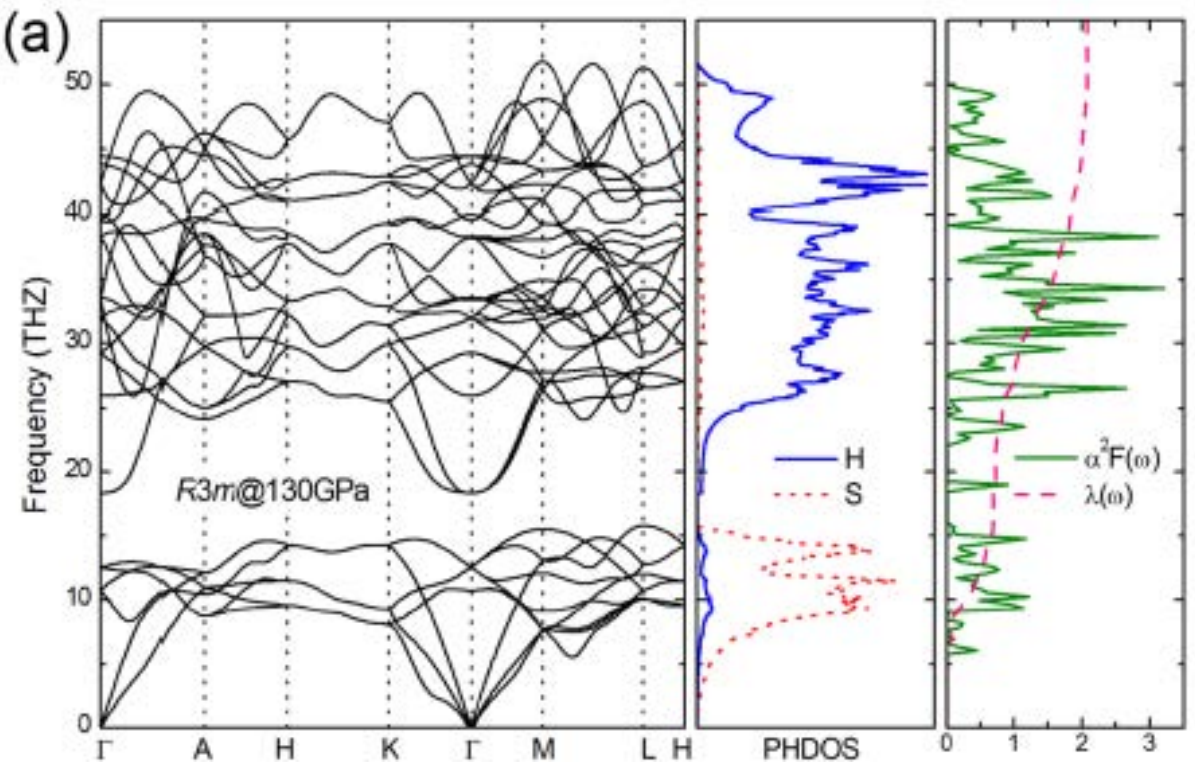
ω_{log} =1125 K

T_c = 160 K

at

P=130 Gpa

rhombo. H_3S



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H_3S

λ=2.2

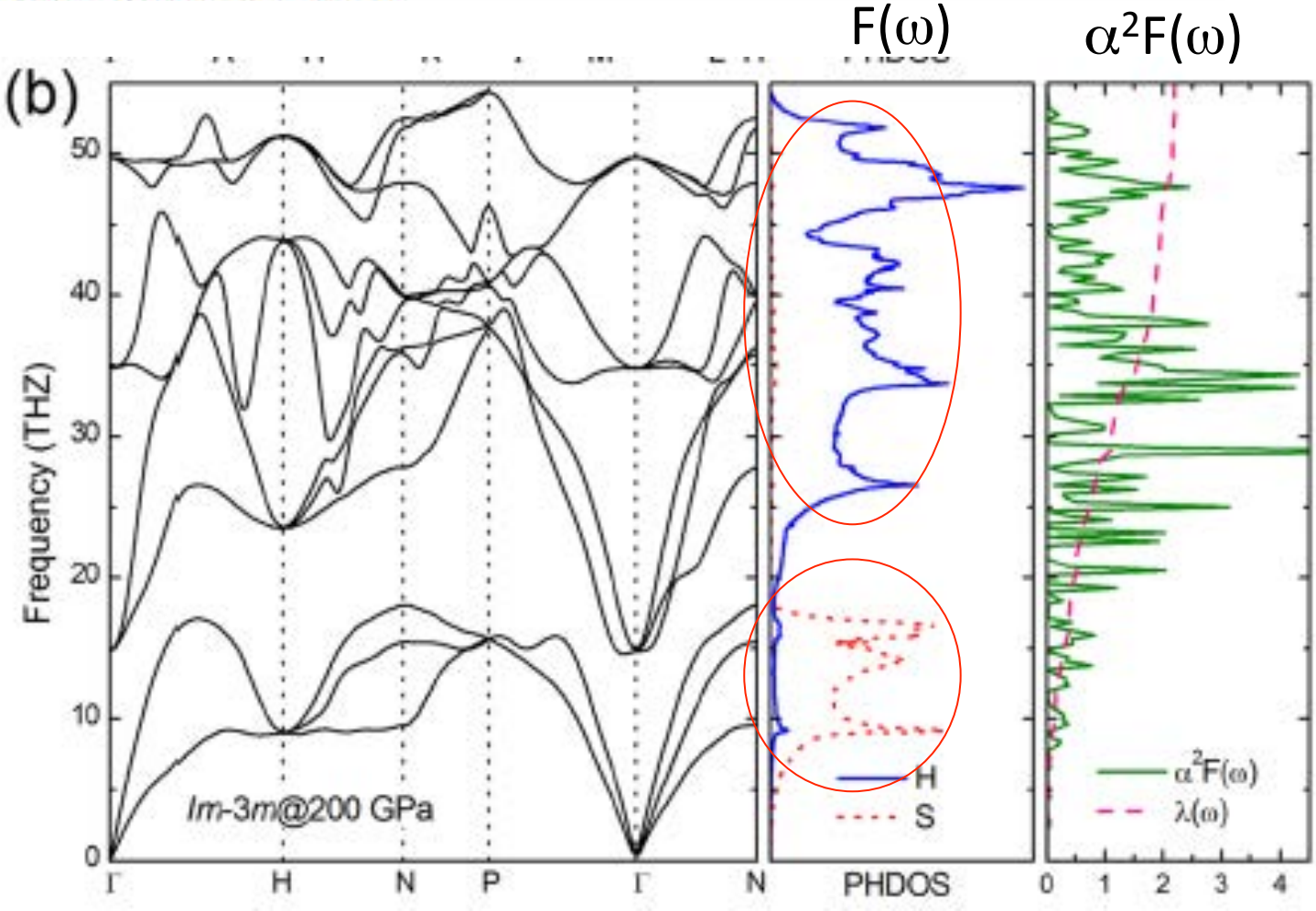
ω_{log}=1334 K

T_c = 200 K

at

P=200 GPa

bcc H_3S



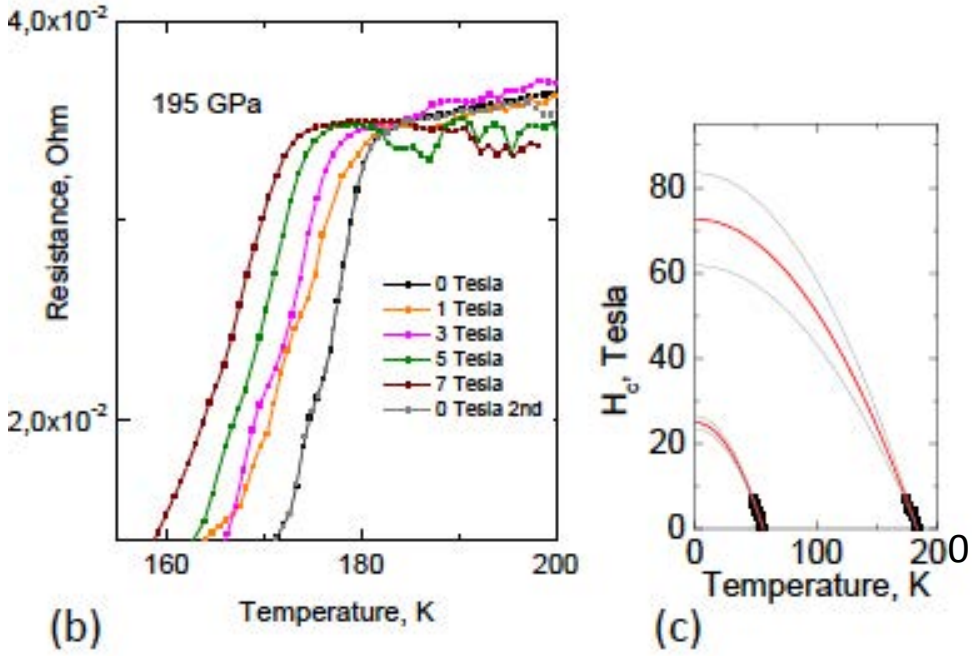
Experimental breakthrough, announced in December 2014

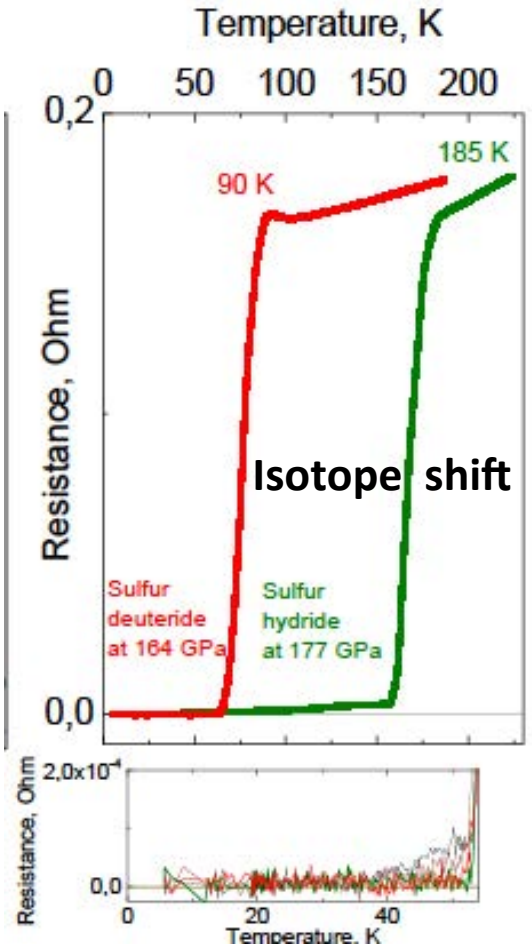
Conventional superconductivity at 190 K at high pressures

A.P. Drozdov, M. I. Eremets*, I. A. Troyan

Max-Planck Institut fur Chemie, Chemistry and Physics at High Pressures Group

Dihydrogen sulfide H_2S loaded into DAC





Superconductivity ~190 K around 180-190 GPa

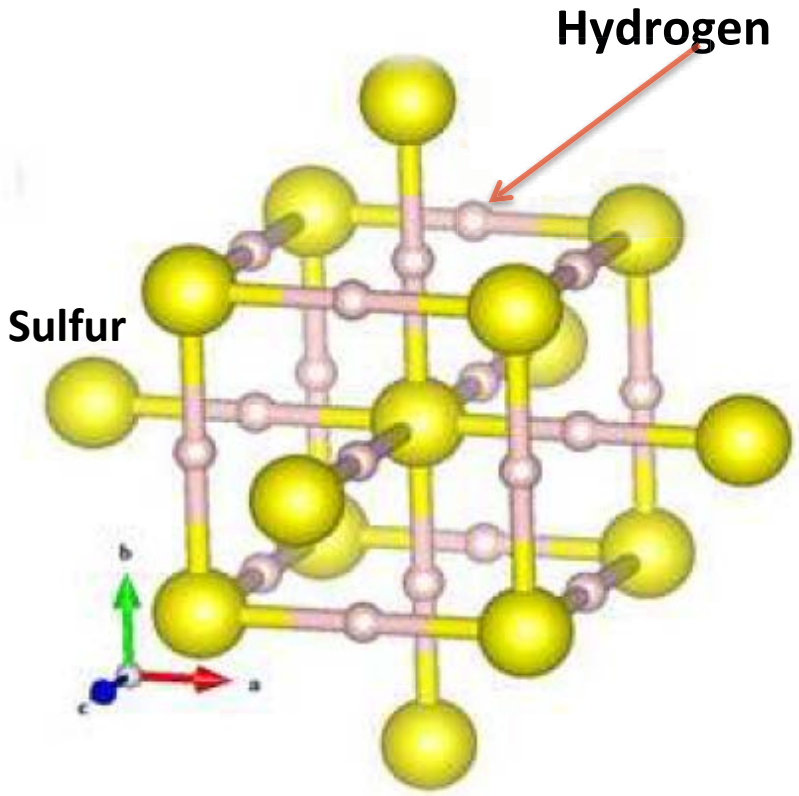
DFT studies of stable high P phases

Li et al. 2014
Duan et al. 2014
Berstein et al. 2015
Papaconstantopoulos et al. 2015
Flores-Livas et al 2015
Errea et al. 2015
… more theory …

The experimental discovery paper cited 7 theory papaers explaining rhe origin of pairing and size of Tc

Theory predicted an amazing property, experiment discovered & verified, stimulating further theory.

Primitive type of DMREF llop.



Summary: superconducting H_3S

MGI-like: Theory led experiment, predicted much higher T_c

- H_2S predicted to have high T_c~90K at high pressure (Ma group)
- experimental group began high pressure efforts (Eremets group)
- H_3S predicted to have high T_c~200K at high pressure (Cui group)
- experimental discovery of T_c~200 K in H3S (Eremets group)

Theory → experiment ; theory → theory; experiment → theory.
A crude example of the DMREF design & discover loop.