Slater-(Koster)-Pauling State and Half-Metallic Heusler Alloys

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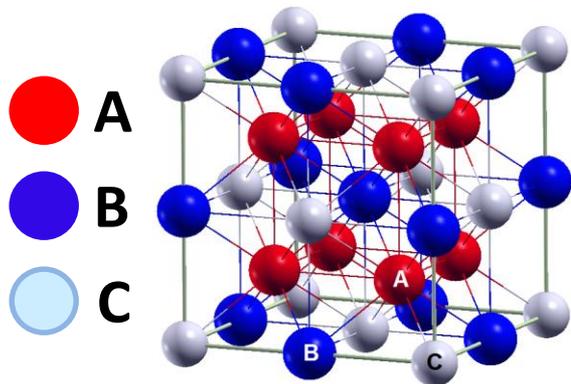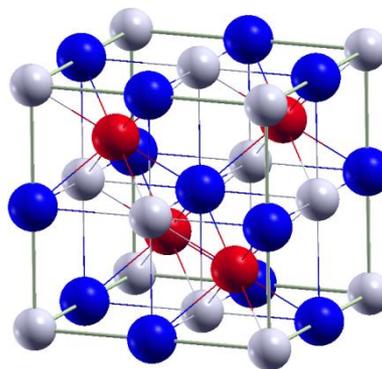CENTER FOR MATERIALS FOR INFORMATION TECHNOLOGY

Outline

- Heusler Survey

- Heusler Website

- Slater-Koster-Pauling State

- Co-authors and Collaborators

full, half, and inverse Heusler alloys

- A A
- B B
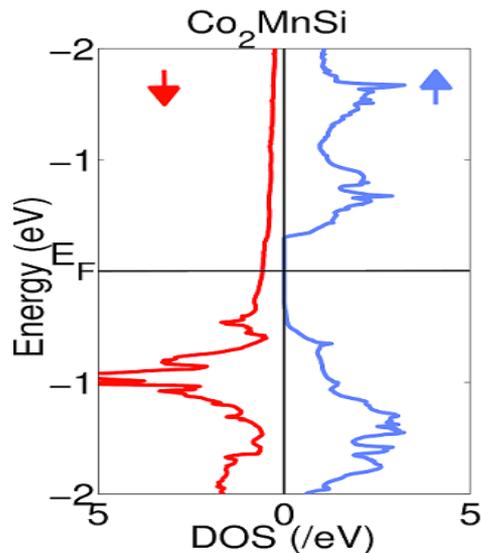- C C

A Full Heusler L2$_1$　　　**1b. Half Heusler C1$_b$**　　　**1c. Inverse Heusler XA**
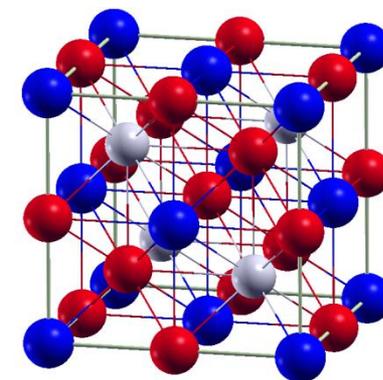
Tendency to form half-metals

Co$_2$MnSi

Heusler Survey
- **180 L2$_1$ (full) Heusler A$_2$BC.**
- **405 XA (inverse) Heusler ABAC.**
- **380 C1$_b$ (half) Heusler ABC**
- **http://heusleralloys.mint.ua.edu**

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Full-Heusler Alloys

A (red)
B (blue)
C (light)

Full Heusler (A$_2$BC)
A – Cr, Mn, Fe and Co
B – Ti, V, Cr, Mn and Fe
C – Al, Ga, In, Si, Ge, Sn, P, As and Sb

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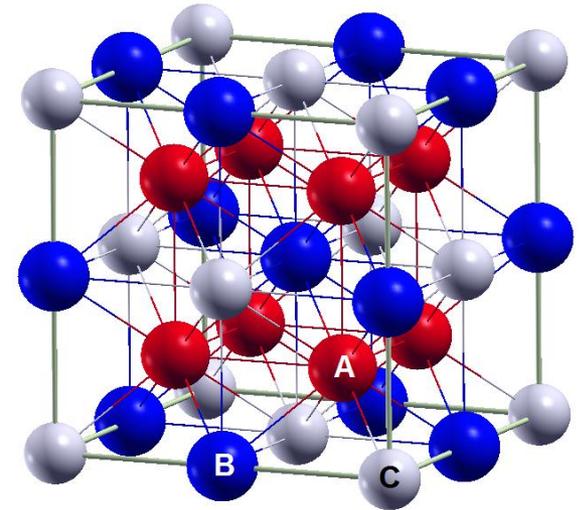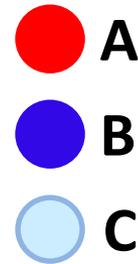
Half-Heusler Alloys

● A
● B
○ C
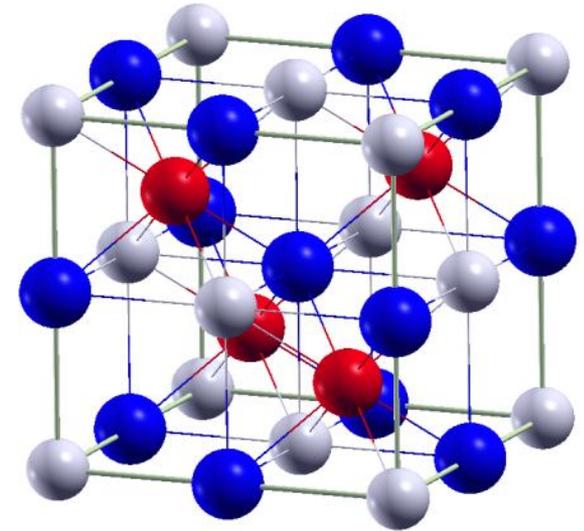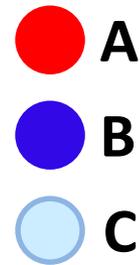
Half Heusler (A-BC)
A – Cr, Mn, Fe, Ru, Co, Rh and Ni
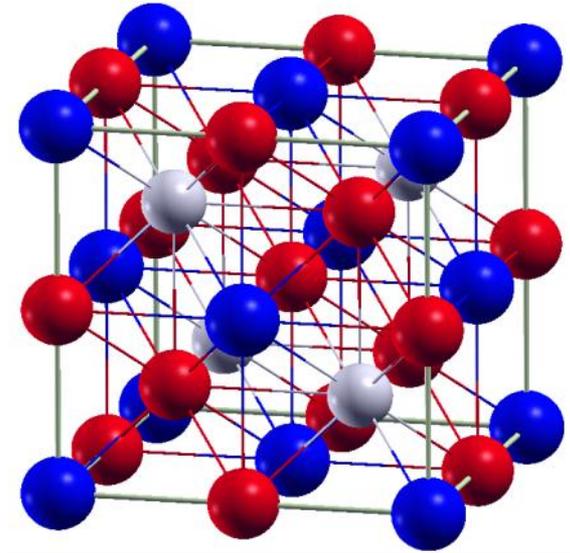B – Ti, V, Cr, Mn, Fe and Ni
C - Al, Ga, In, Si, Ge, Sn, P, As and Sb

Inverse Heusler Alloys
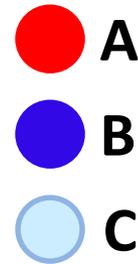
Inverse Heusler (AB-AC)

A – Cu, Ni, Co, Fe, Mn, Cr, V, Ti and Sc

B – Zn, Cu, Ni, Co, Fe, Mn, Cr, V and Ti

C - Al, Ga, In, Si, Ge, Sn, P, As and Sb

Consistent and Accessible set of calculations

– Facilitate search for trends
– "consistent" calculations of nearly 1000 Heusler alloys

- VASP (all parameters needed to reproduce our calculations)
- 520 eV cut-off energy to facilitate interphase energy comparisons
- Formation energies
- Tetragonal distortions considered
- VASP parameters and reference energies consistent with oqmd database (Wolverton Group)

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"Low-throughput" study of Heusler alloys

Select A and B from transitional metals and C from group III, IV or V

For each alloy, calculate E(a) for multiple initial moment configurations

Relaxation: Check for tetragonal distortion

Find minimum Energy configuration

Cubic study CoMnAl
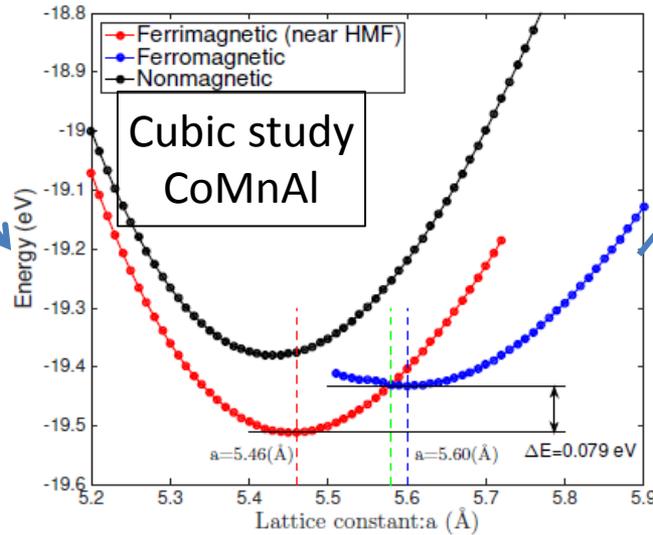
Calculate magnetic moment Formation energy DOS, bands, etc.

Identify promising candidates And Check against other binary And ternary phases (www.oqmd.org)

Suggest candidates to experimentalist

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heusleralloys.mint.ua.edu

- http://heusleralloys.mint.ua.edu
  - "consistent" calculations of nearly 1000 Heusler alloys
  - Easily accessible to all
  - Suggestions for improvements are solicited
  - Currently in β-phase with only full-Heusler data uploaded

Cautions

- Nature is smarter than me and you
  - e. g. in minimizing the system energy in a way you didn't think of
- And often not very cooperative
  - Even when we figure out the correct ground state, kinetic effects may make it difficult to get the system into it.
- Even if your Heusler alloy shows a negative enthalpy of formation and there are no lower free energy phases in the oqmd database – this is "indicative" rather than sufficient.

To do list for: heusleralloys.mint.ua.edu

- Upload Half-Heusler alloy data (2 weeks)
- Upload Inverse Heusler alloy data (4 weeks)
- Add data for Heusler phase (e.g. $L2_1$ or $C1_b$ even when it is not the ground state)
- Additional References (theory and experiment, please help)
- Add ordering energies (e.g. full Heusler vs Inverse Heusler)
- Add commentaries (please help – e.g. often it is important to know what was tried and didn't work)

Why are Heusler Alloys so seductive?

Slater-Pauling State

Slater-(Koster)-Pauling States

- Slater-Pauling State: Solution to the non-relativistic DFT equations with 3 electrons per atom in one of the spin-channels
  - Gap in the DOS of at least one of the spin channels with 3 valence electron states per atom below the gap
  - Fermi energy in the gap
- "nearly" Slater-Pauling states, e.g.
  - Pseudogap instead of gap
  - Gap, but Fermi energy is very near, but not in gap ("near half-metal")
- Slater-Pauling or "nearly" Slater-Pauling state is almost always present in the systems in our database
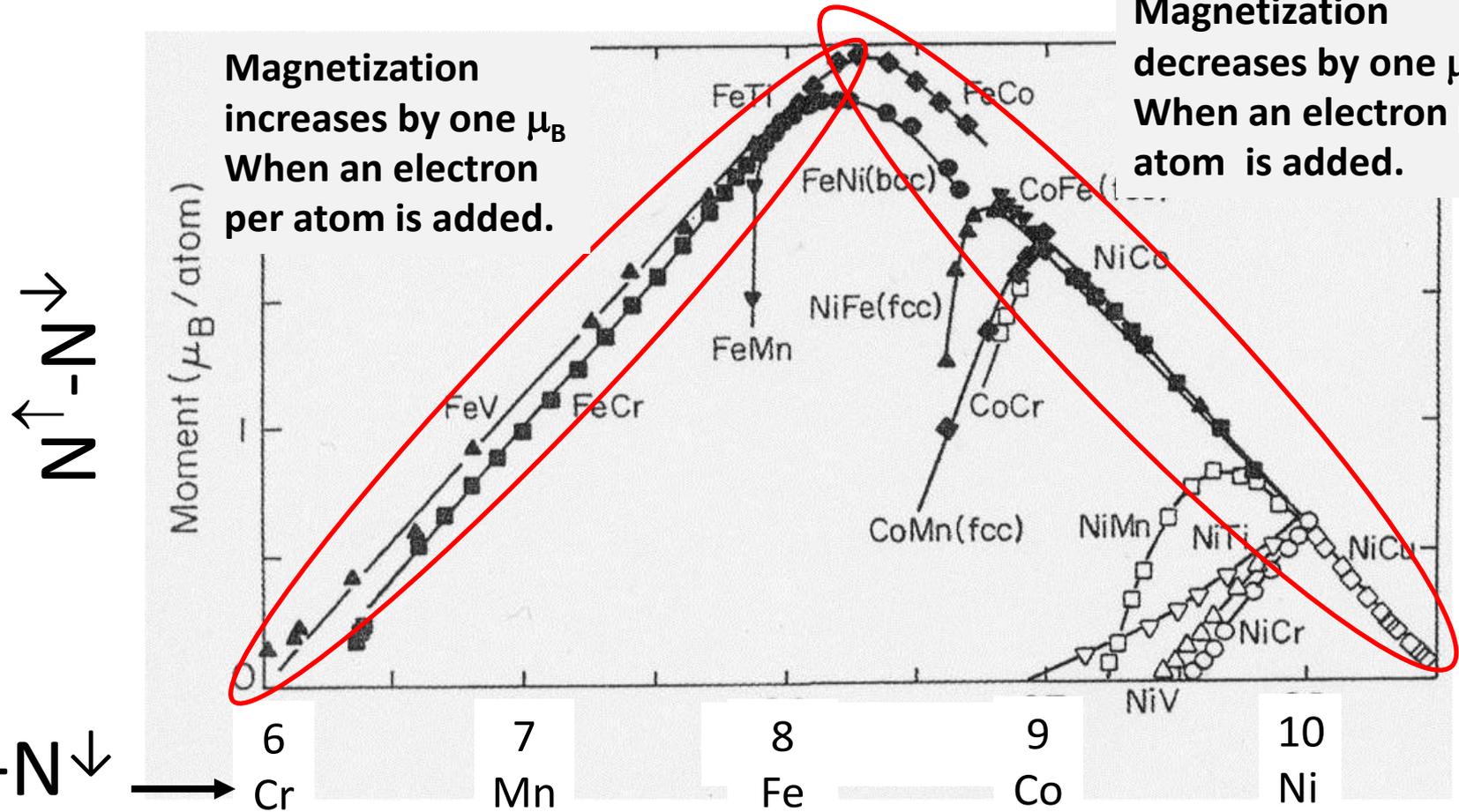
If God did not want us to do spintronics he would not have given us the ….

Slater-Pauling Curve

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On the Right (fcc) Side of the Slater-Pauling Curve $N^\uparrow$ is constant.

	$N^\uparrow + N^\downarrow$	$N^\uparrow - N^\downarrow$	$N^\uparrow$	$N^\downarrow$
Cu	11	0	5.5	5.5
Ni	10	0.6	5.3	4.7
Co	9	1.6	5.3	3.7
fcc Fe	8	2.6	5.3	2.7
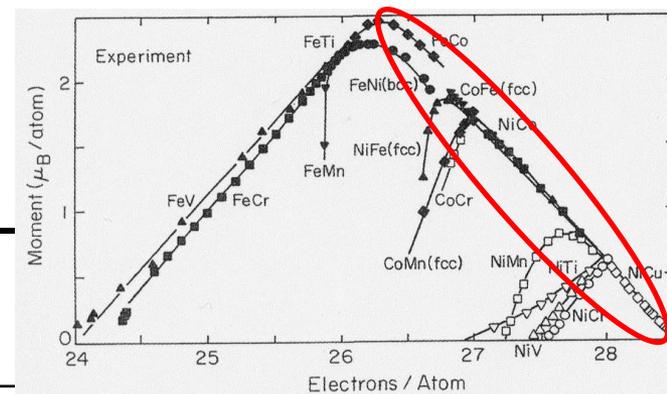
These materials were the basis of the GMR sensors developed in the 1990s.

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For fcc magnetic alloys, the majority d-band is filled because of Hund's rule and relatively narrow d-bands. Additional electrons go into minority band.

DOS For fcc Ni, Co, Fe
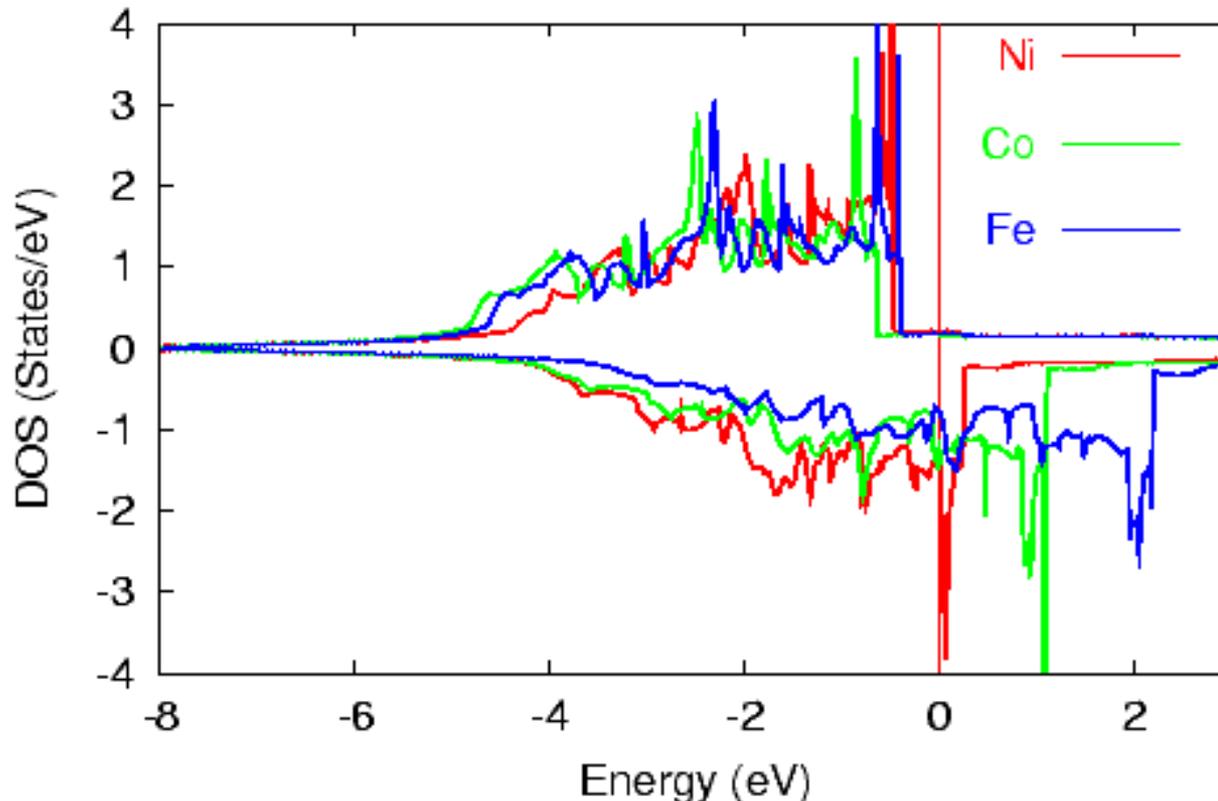
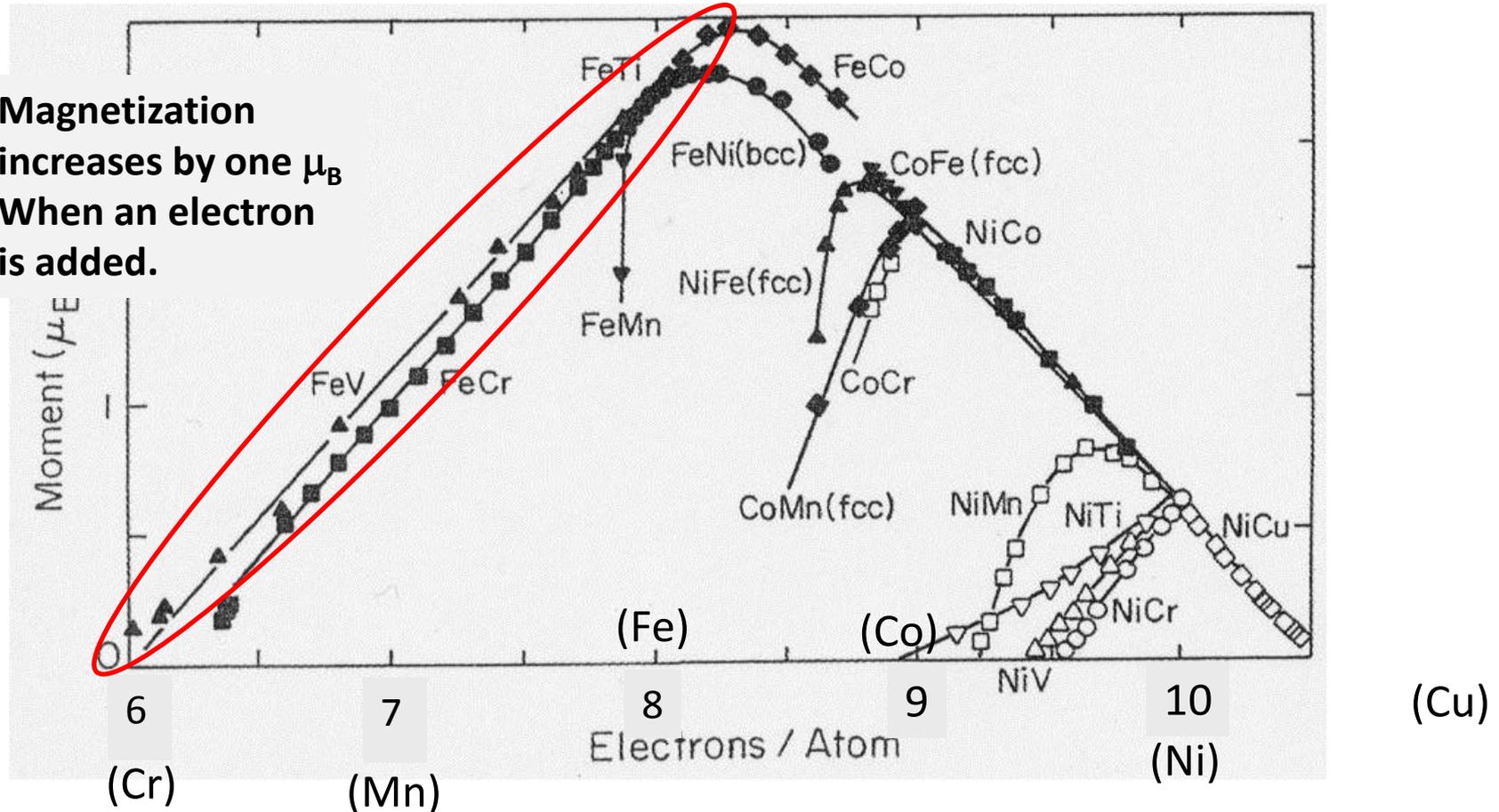Majority channel electrons see (approx.) the same potential on all sites also approx. the same as Cu.

There is a tendency for atoms to adjust their moments to improve the matching. (Delocalization energy)

This matching allowed development of GMR sensors.

What about the left-hand side?

Slater-Pauling Curve

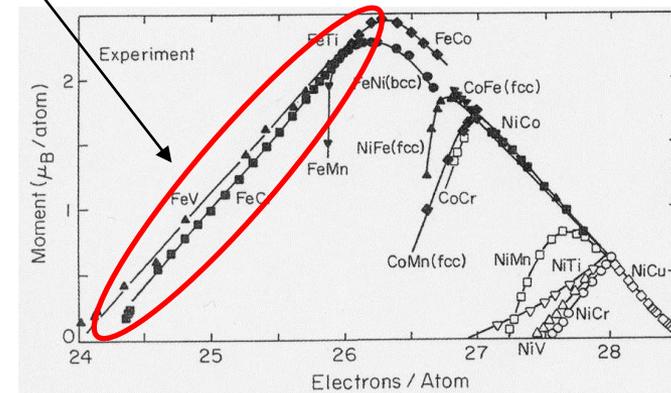Magnetization increases by one μ_B When an electron is added.

Left (bcc) side of Slater-Pauling Curve

- Note that $N^{\downarrow}$ remains approximately 3 electrons/atom on lhs of Slater-Pauling

	$N^{\uparrow}+N^{\downarrow}$	$N^{\uparrow}-N^{\downarrow}$	$N^{\uparrow}$	$N^{\downarrow}$	
Cr	6	0	3	3	
CrMn	6.5	0.3	3.4	3.1	
Mn	7	0.53	3.8	3.2	
MnFe	7.5	1.6	4.6	2.9	
Fe	8	2.2	5.1	2.9	
FeCo	8.5	2.25	5.4	3.1	

This matching of electronic structures led to the discovery of GMR in 1988

It is also closely related to the formation of $L2_1$ structure half-metals.

DOS for bcc Fe

Majority

5.1 electrons

'+dos.total'

Calculated moment
2.21μ_B

2.9 electrons

Note Fermi energy near
minimum of minority DOS

Minority

DOS (States/eV)

Energy (eV)

- Simplest explanation is based on rigid band model.
- Something more interesting may be going on.
- Something observed by Slater and Koster in 1954
    - Hence "Slater-Koster-Pauling" rule

(Every atom the same)   DOS for PM bcc Cr

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DOS for PM and AFM bcc Cr

Energy decrease: PM→AFM
0.064 eV

B2-AFM
bcc-Para

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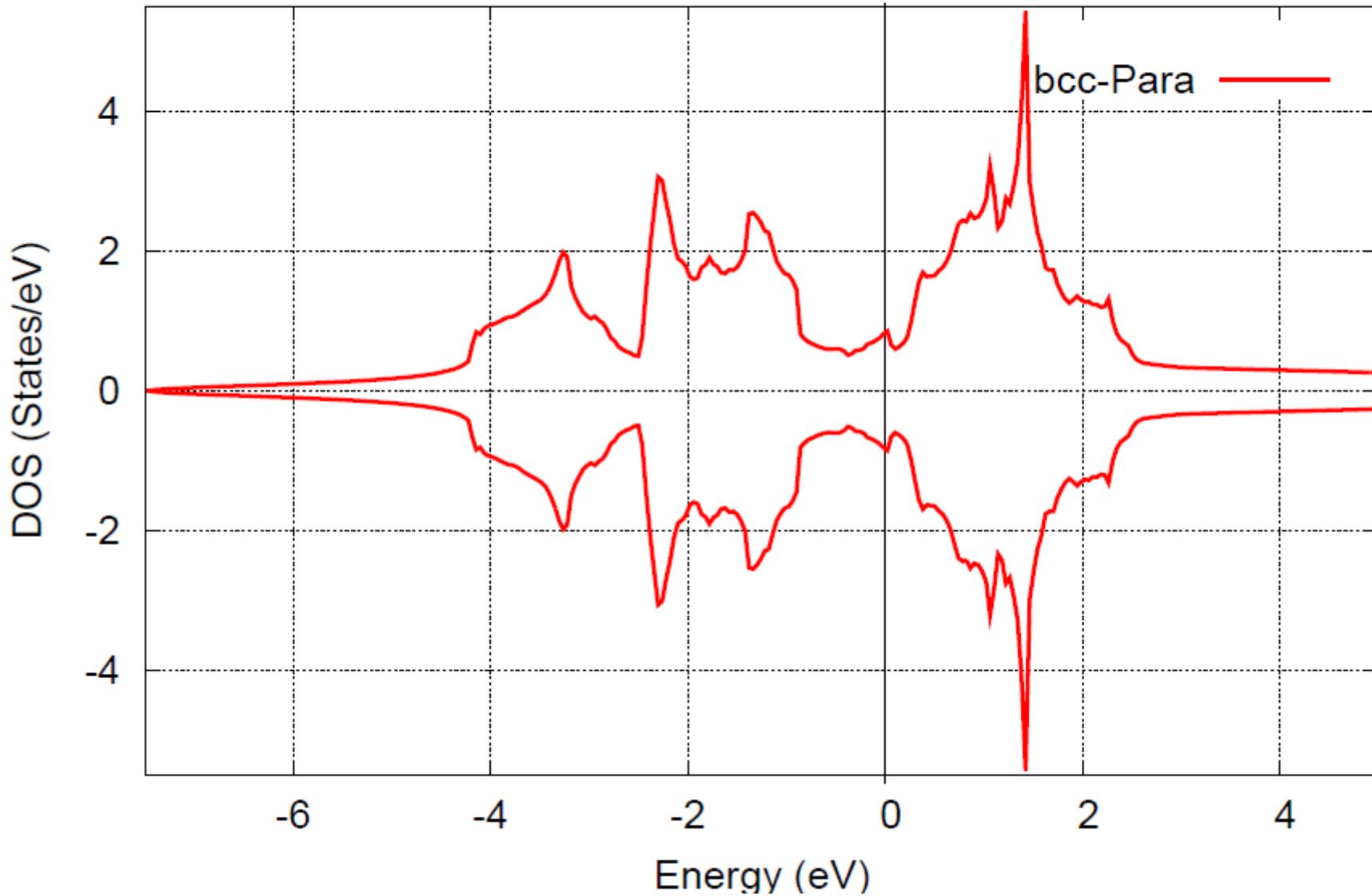
Cr-Cr alloy

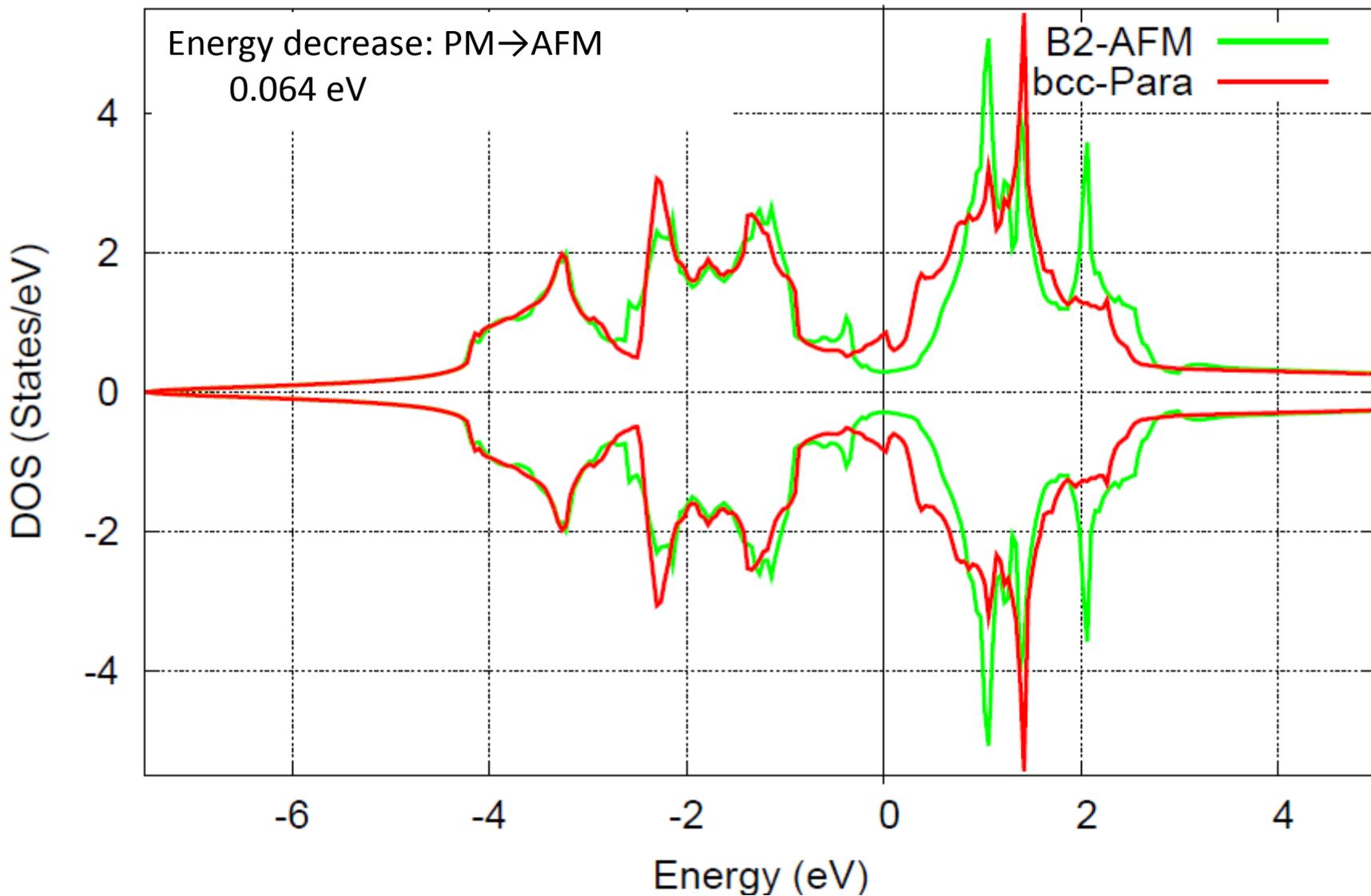CrA (3.75 $\uparrow$ electrons 2.25 $\downarrow$ electrons)

CrB (2.25 $\uparrow$ electrons 3.75 $\downarrow$ electrons)

We restricted Cr to having B2 magnetic structure
(everyother atom is the same).

Reality is slightly more complicated.

Note that this model generates a spin density wave with period a.

$\uparrow$ $\downarrow$ $\uparrow$ $\downarrow$ $\uparrow$ $\downarrow$

This picture of an antiferromagnetic Cr is approximately correct,
but the period of the spin density wave is not exactly a.

The Cr spin-density wave was important for the discovery of GMR

CrA

CrA

CrA

CrB

a

CrA

CrA

a

CrA

a

CrA

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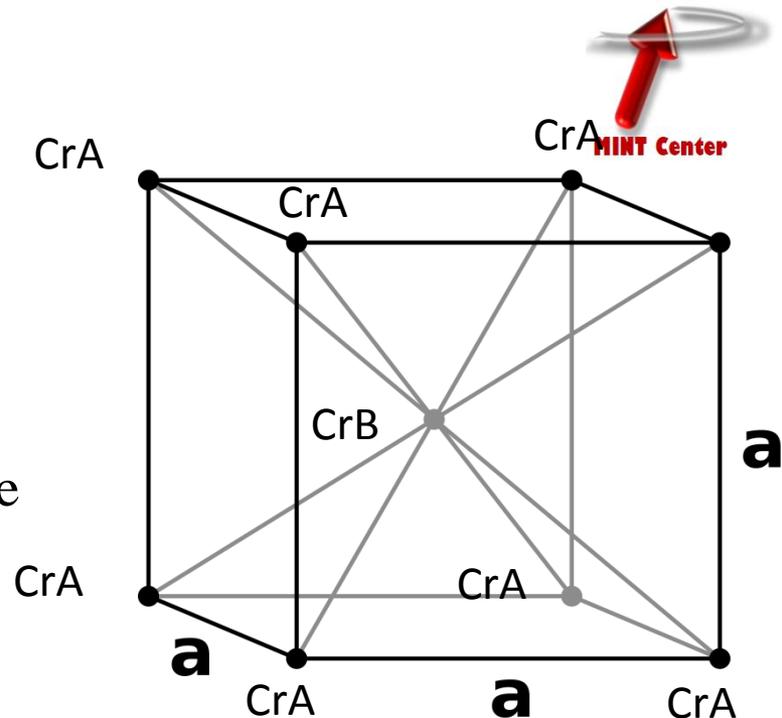
Gaps and Pseudogaps at Half-Filling

- Slater and Koster 1954: B2 alloy with only d-orbitals and only nn interactions has-

  - Gap at half filling of the d-band
  - Gap extends from E_d^A to E_d^B
  - If three center interactions are included gap is minimum of $E_d^A - E_d^B$

Beyond d-orbitals

- S-K : gap at the center of the d-band if only d-orbitals and nn interactions.

- What about s-orbitals?
  - s-orbitals have very large dispersion (strong s-d interactions compared to d-d)
  - They hybridize with the d-states and split between bottom and top of the d-bands
  - So – ignoring nnn interactions, B2 TM alloys would (often) have a gap at the center of the s-d band.

Nominal
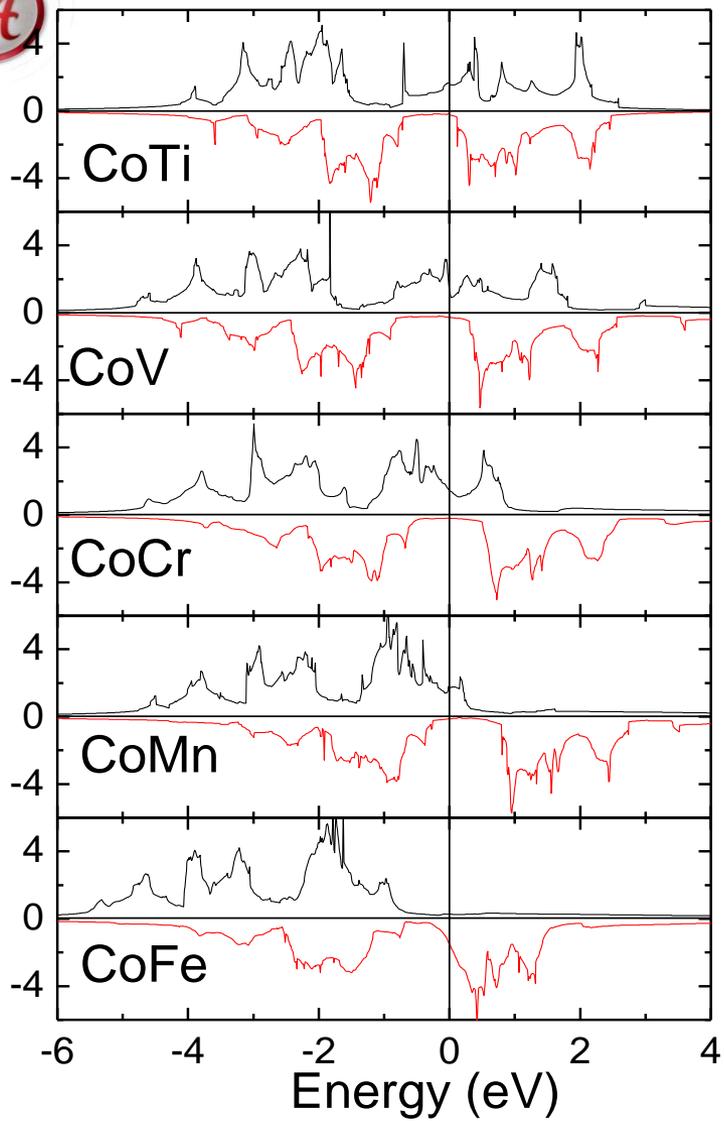
Co   Ti
5↑ 2↑
4↓ 2↓

Co   V
5↑ 3↑
4↓ 2↓

Co   Cr
5↑ 4↑
4↓ 2↓

Co   Mn
5↑ 5↑
4↓ 2↓

Co   Fe
5.3↑ 5.3↑
3.7↓ 2.7↓

Some B2 alloys with Co - now allowed to be magnetic

Note that the pseudogap tends to be wider and deeper, the greater the difference between the electron numbers.

Note that Fermi energy is attracted to pseudogap.

4-2 is not feasible here
Co   Fe
5↑   6↑
4↓   2↓

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- Co Mn Co Mn Co
  ↑ 5   5   5   5   5
  ↓ 4   2   4   2   4

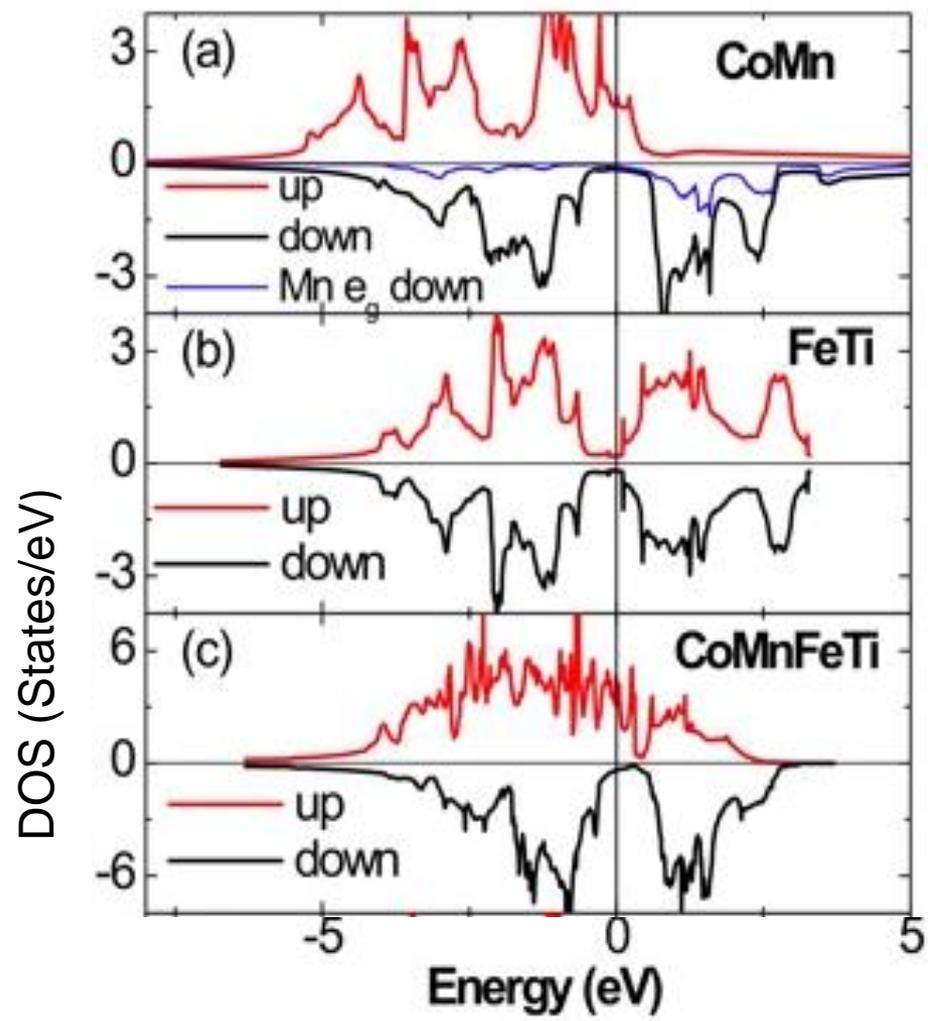- Fe Ti Fe Ti Fe
  ↑ 4   2   4   2   4
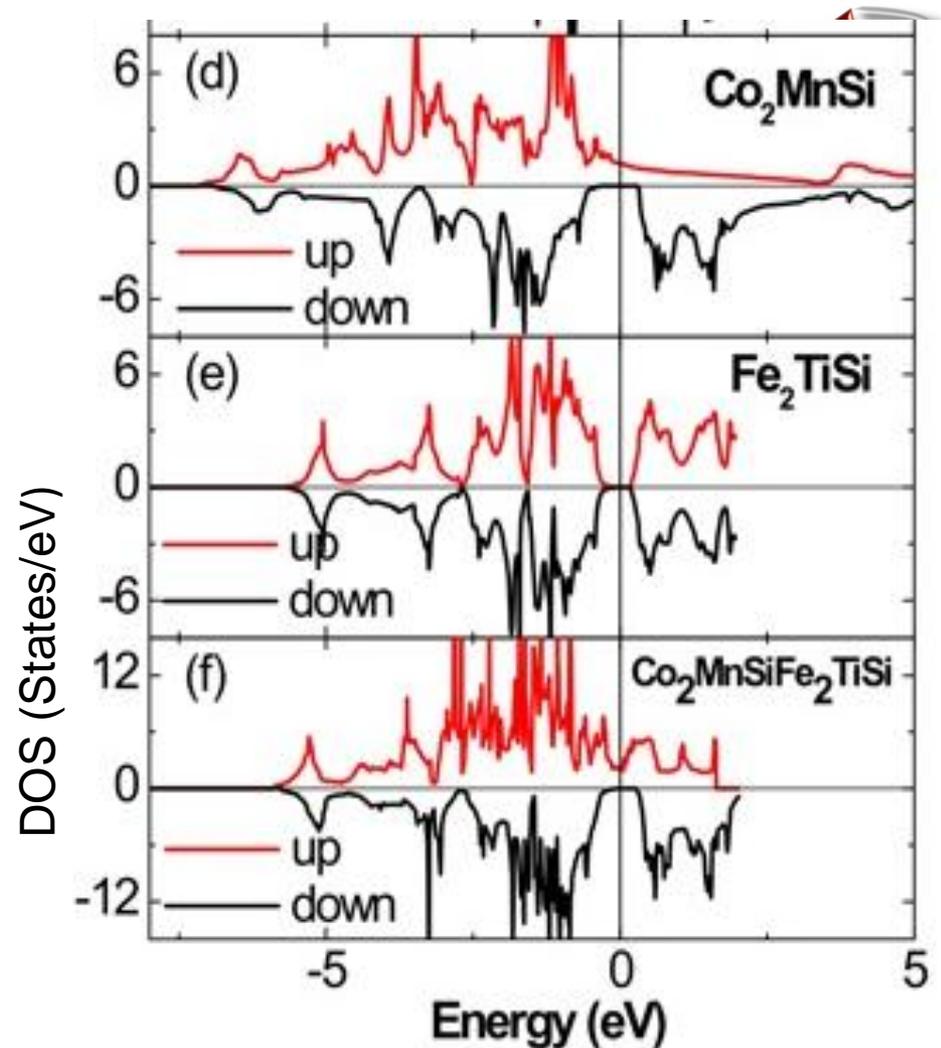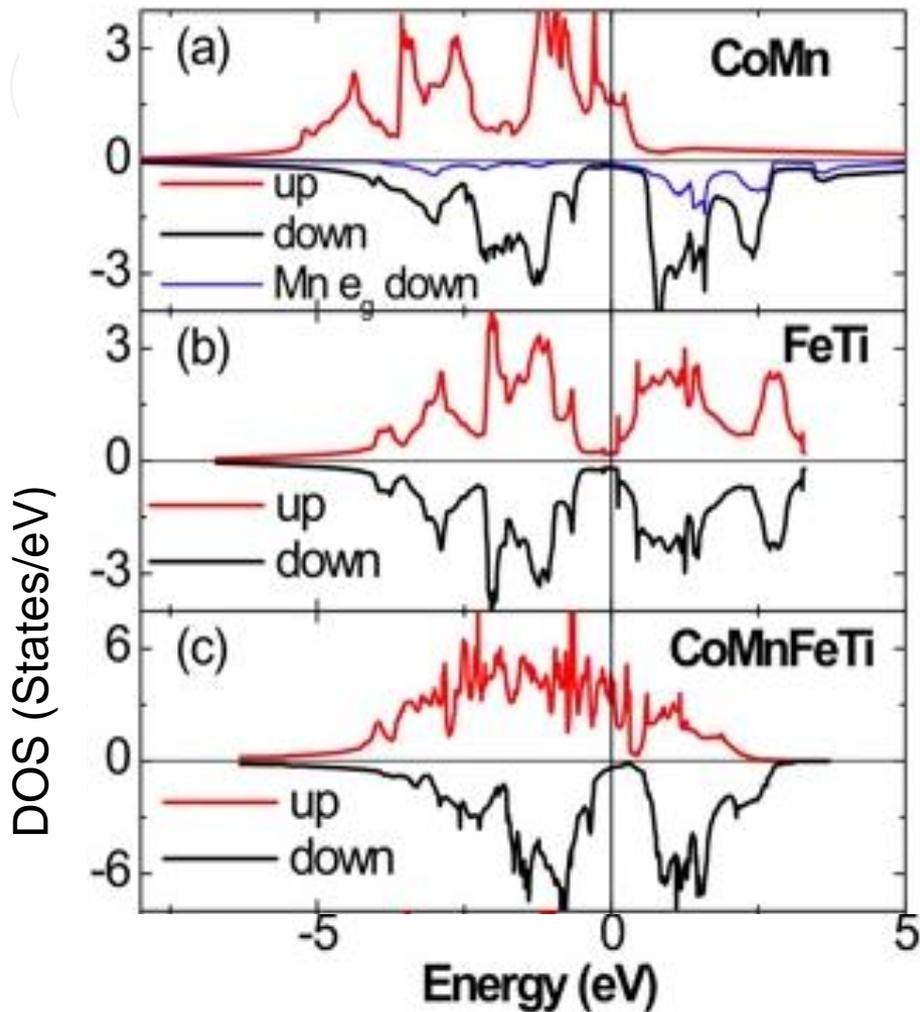 ↓ 4   2   4   2   4

- Co Mn Fe Ti Co
  ↑ 5   5   4   2   5
  ↓ 4   2   4   2   4

- By adding Si, we are reducing the "hybridization" between nnn Mn or Ti atoms without disturbing the number of ↓spin electrons.

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Major Findings

- Slater-Pauling State is usually present
  - Slater-Pauling state is one that has a gap or a pseudo-gap in one or both of the d-bands at half-filling.
    - This gap or pseudo-gap usually attracts the Fermi energy
    - It often competes with other phases
      - Not always the lowest energy phase
      - It provides a way to obtain an additional minimum in the energy landscape.
      - Possible route to multiple phases accessible with magnetic fields

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Magnetic Anisotropy

Choocka Sivakumar
Interfaces between Heuslers and GaAs

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Full Heuslers

Scripts for running calculations

Chris Lample

Inverse Heuslers and Initial Website

Leighton Wilson

Band Plotting Routines

David Mildebrath

Website

Thank You!