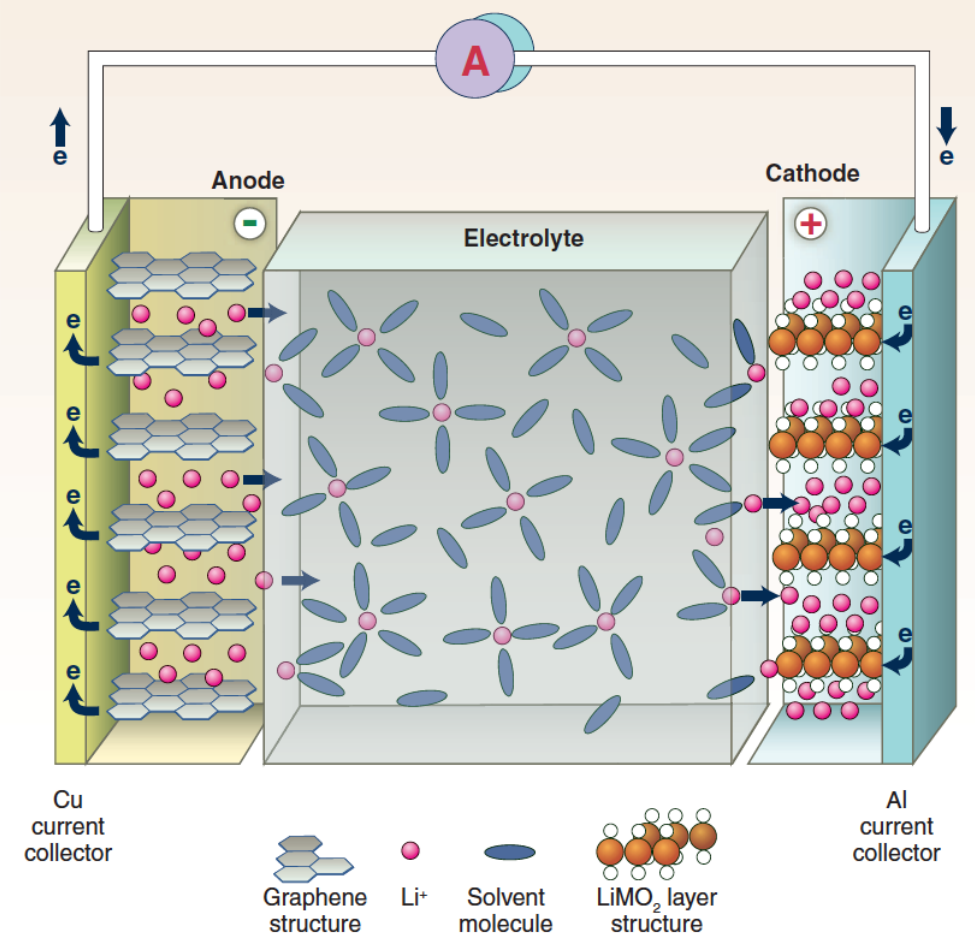
HiLAPW – Advanced Course 1

- **Target: Evaluation of electromotive force (voltage) for secondary battery**

Anode
$Li \rightarrow Li^+ + e^-$



Cathode
$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

Characteristics of Battery

- Electromotive Force (Voltage) V
  - Gibbs free energy difference of reactant and product (ΔG) per transferred charges (Z) as $V = \Delta G/Z$ [V]
- Capacity Q
  - Amount of electrical charge stored by Faraday's law
  - Theoretical capacity $Q = FZ/M$ [Ah/kg] with Faraday constant (F), transferred charges (Z), and mass of cathode material (M)
- Specific Energy (Energy Density) QV [Wh/kg]

Gibbs Free Energy Difference

- **Can be estimated approximately from a DFT total energy difference for a reaction formula assumed such as**

$$Li + CoO_2 \rightarrow LiCoO_2$$

$$V = \Delta G/Z = - [E(LiCoO_2) - E(Li) - E(CoO_2)]/Z$$

Anode: $Li \rightarrow Li^+ + e^-$

Cathode: $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

Transfered Charge: $Z = 1$

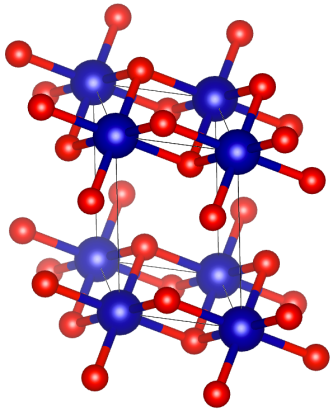
G. Cedar, *et al*., Comput. Mater. Sci. 8, 161 (1997).

Reactant and Product Materials

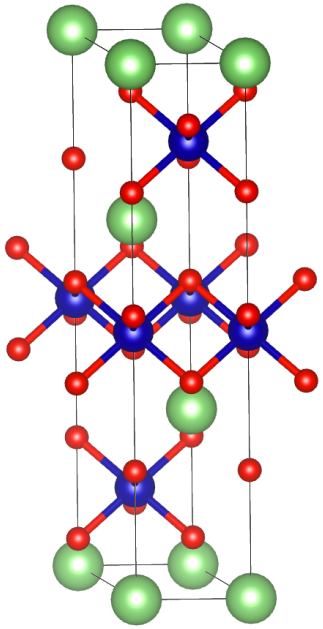
- Li: Im-3m, a=3.491Å
- CoO_2: P-3m1, a = 2.8208Å, c = 4.2403Å, z(O) = 0.21
- $LiCoO_2$: R-3m, a = 2.815Å, c = 14.0516Å, z(O) = 0.2397

  $a_r = (a^2/3 + c^2/9)^{1/2} = 4.95782Å$

  $\alpha = \cos^{-1} (-3a^2+2c^2)/(6a^2+2c^2) = 32.98559^o$



CoO_2

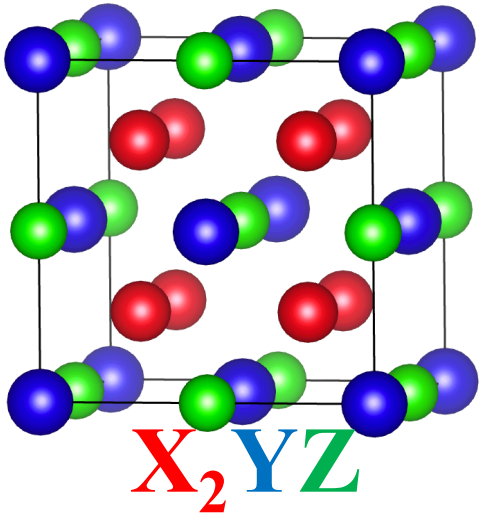


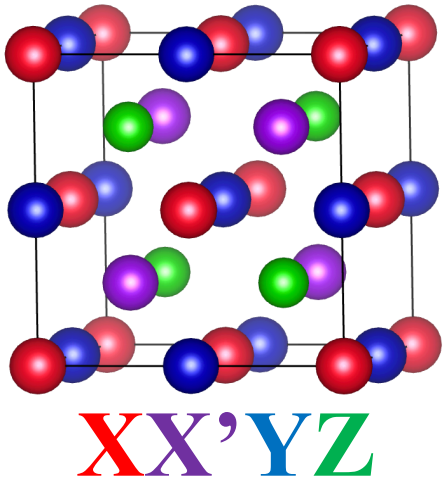
$LiCoO_2$

HiLAPW – Advanced Course 2

- **Target: Evaluation of energy difference of Heusler alloys X_2YZ between $L2_1$ and Xa structures**

$L2_1$ regular





Xa Inverse

Structure Stability

Mn_2YGa (Y= Transition metal)

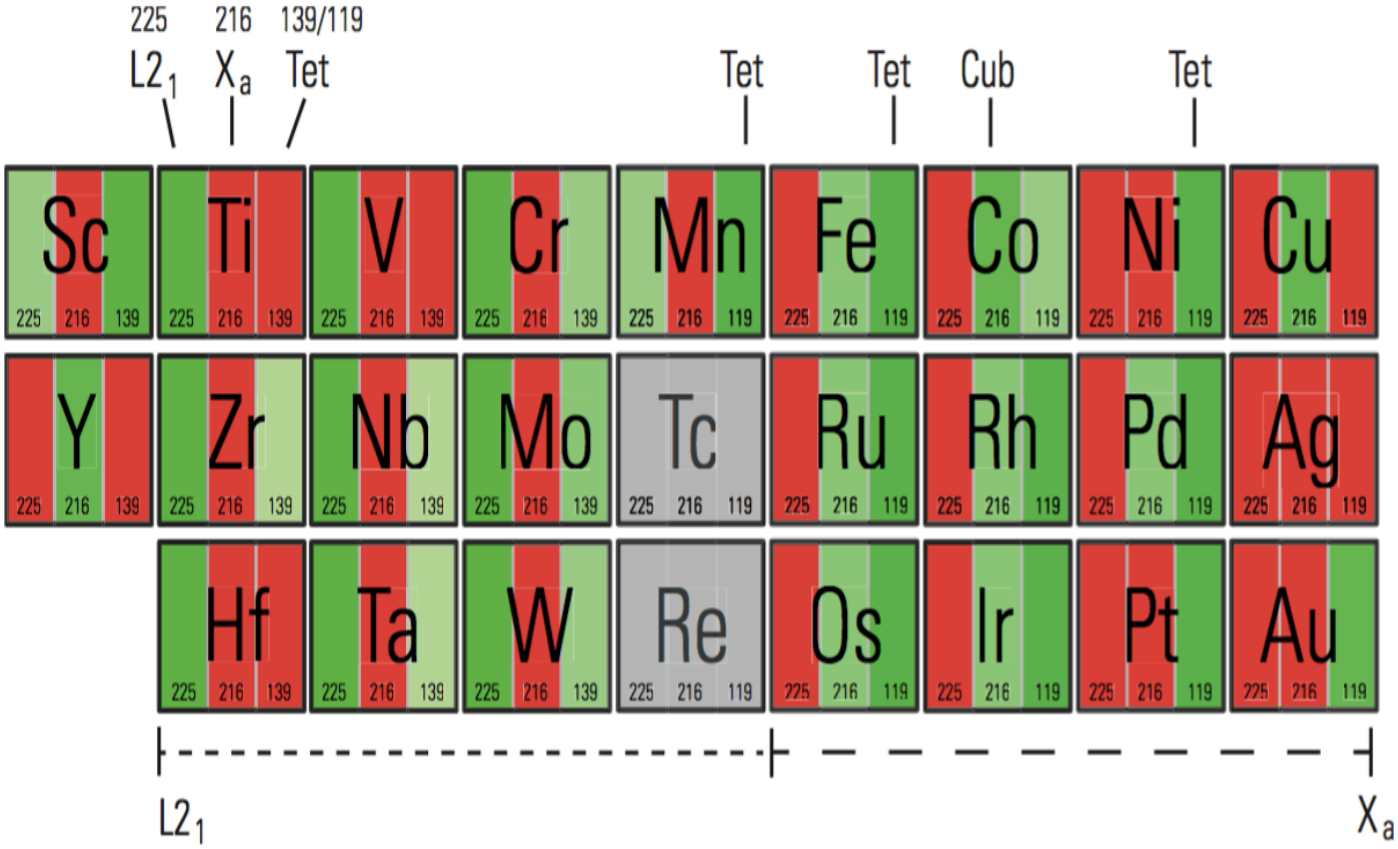


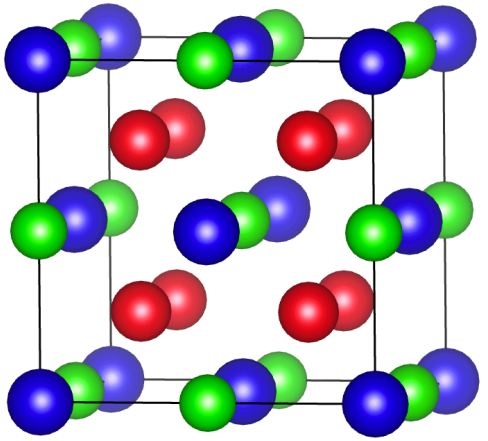
FIG. 4. (Color online) Schematic overview of the preferred site occupancy and crystal structure of Mn_2YGa Heusler compounds. Stable, metastable, and instable lattices are marked by dark-green, light-green, and red subcells, respectively.

Wollmann, *et al.*, Phys. Rev. B 92, 064417 (2015)

Crystal Structure

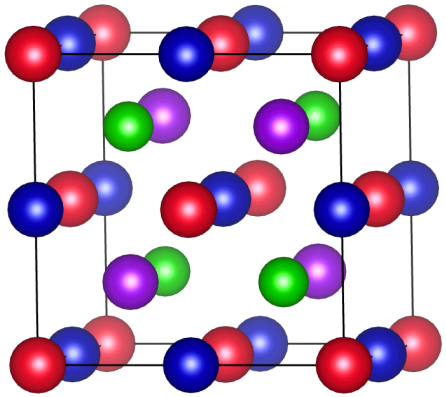
- $L2_1$ type Cu_2MnAl Fm-3m

X_2YZ



- Xa type Hg_2CuTi F-43m

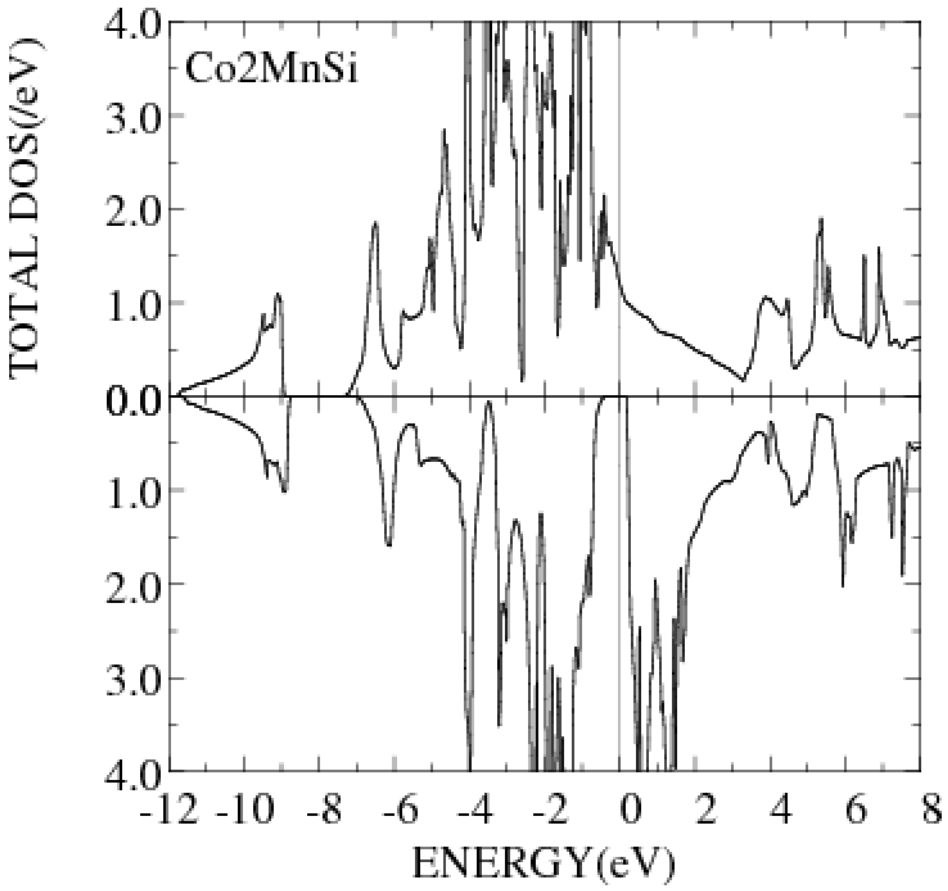
XX'YZ

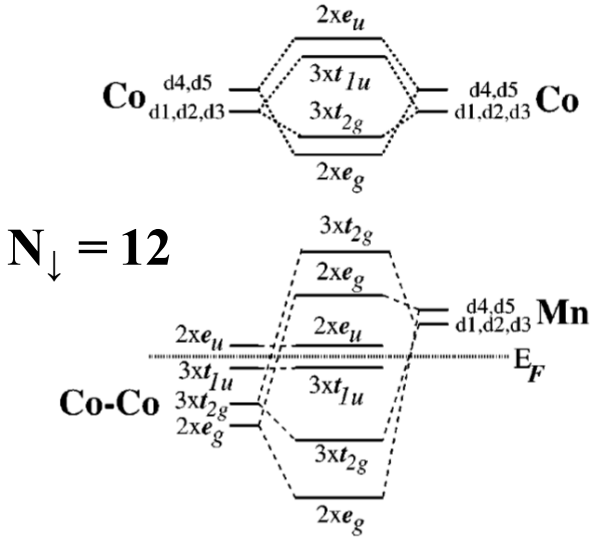


	(0, 0, 0)	(1/2, 1/2, 1/2)	(1/4, 1/4, 1/4)	(3/4, 3/4, 3/4)
Regular	Y	Z	X	X
Inverse	X	Y	Z	X'
LiMgPdSn	X	X'	Y	Z

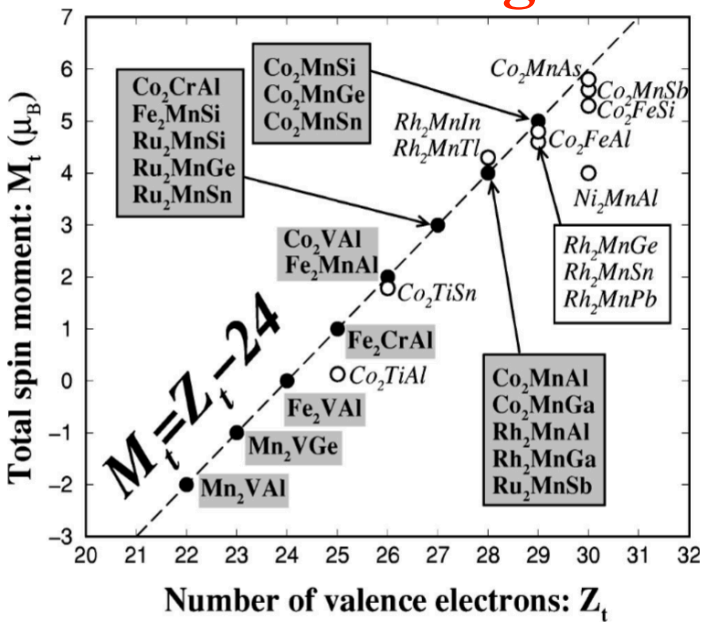
Half Metals

- $L2_1$ type Co_2MnSi





Slater-Pauling rule



$Z_t = N_\uparrow + N_\downarrow$

$M_t = N_\uparrow - N_\downarrow$

$M_t = Z - 2N_\downarrow$