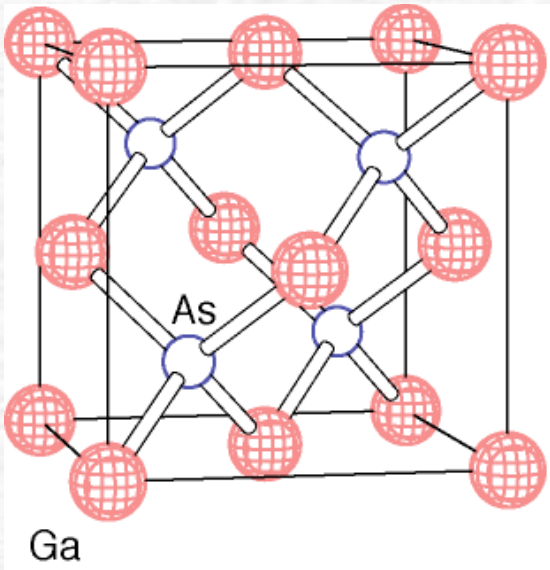
KKR-CPA method tutorial (MACHIKANEYAMA2002)

The 35th CMD workshop at Osaka Univ. Toyonaka Campus

Material design: application of machikaneyama

- Spintronics materials
  - Design of ZB-type half-metals (CrAs etc.)
  - Design of half-metallic half-Heusler alloy
  - Design of dilute magnetic semiconductors (DMS)
  - Design of full-Heusler alloy (effect of disorder)
- Li-ion battery electrode
  - $LiCoO_2$
  - Design of positive electrode material
- Hydrogen Storage material
  - Design of MgH_2 based materials

Half-metallic CrAs

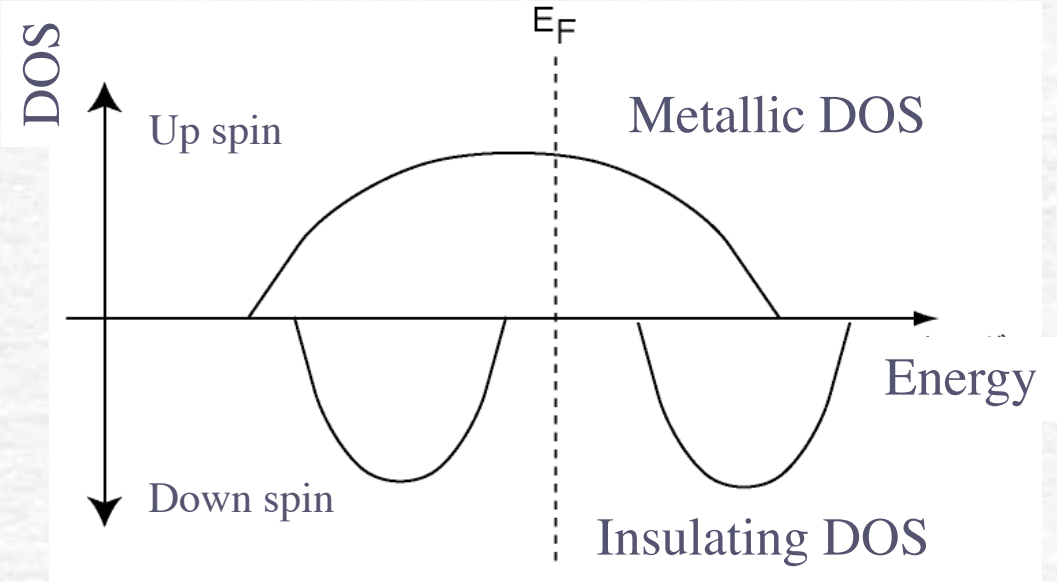


Zinc blende structure

GaP, GaAs, GaSb,
ZnS, ZnSe, ZnTe

Shirai et al. predicted zinc-blende CrAs is half-metallic ferromagnet From first-principles calculations. Akinaga et al. confirmed this prediction experimentally later.
(Jpn. J. Appl. Phys. 39 (2000) L1118)

Half-metallic ferromagnet



100 % spin polarization at the Fermi level.
Expected as a spin polarizer for semiconductor spintronics.

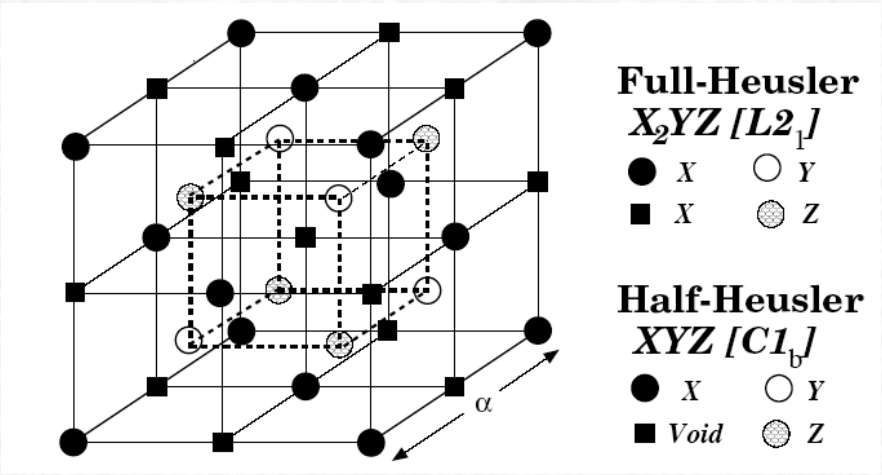
Explore half-metallic ferromagnets

1. CrAs
   - DOS, magnetic moment, half-metallicity, T_C
2. With transition metals other than Cr (such as V, Mn …)
3. With anions other than As (such as N, P, Sb, S, Se, Te …)
4. How large T_C values are expected ?
5. Lattice constant dependence ?
   - Suppose different substrate
   - Calculate theoretical lattice constant. Half-metallic ?

Material design of half-metallic compounds with zinc-blende structure

	4.98 Å (InN)	5.45 Å (GaP)	5.65 Å (GaAs)	5.87 Å (InP)	6.06 Å (InAs)	6.10 Å (GaSb)	6.48 Å (InSb)
CrP							
CrAs							
CrSb							
MnP							
MnAs							
MnSb							
VP							
VAs							
VSb							

Heusler alloy



Composed with FCC sub-lattices (similar to the zinc blende structure)

- Full Heusler
  - Co_2MnSi …
  - Half-metallic, T_C=985 K
- Half Heusler
  - NiMnSb (a = 5.93 Å)
  - Half-metallic, T_C=730 K

Various combinations of transition metals.
Systematic study on the electronic structure, magnetic moment, T_C

Slater-Pauling curve of Half-Heusler alloy

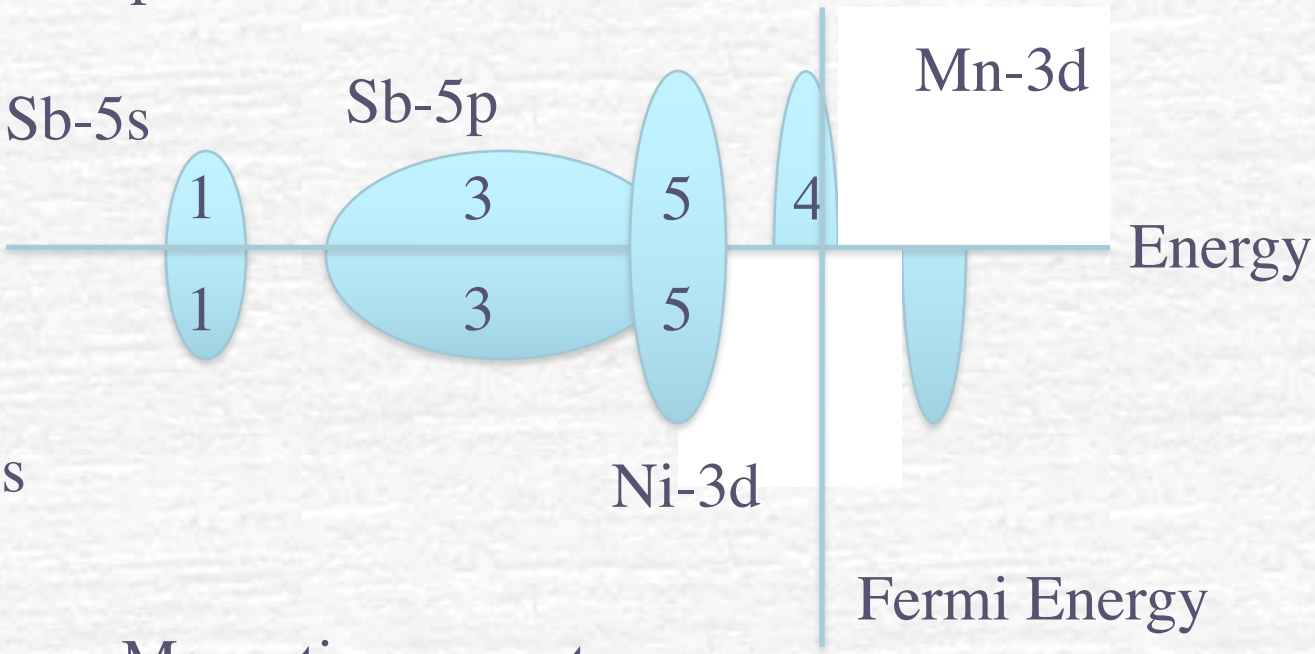
1. NiMnSb、CoMnSb、FeMnSb
   - DOS, magnetic moment, half-metallicity
   - Estimate T_C
2. Magnetic moment vs. total valence electron number
   - Slater-Pauling curve,
   - Guess how large magnetic moment is expected for different combinations
   - Confirm the above expectation by ab-initio calculation.
   - Is it also true in ,e.g., $(Ni_{1-x}Co_x)MnSb$?
3. New ferromagnets based on semiconducting Half-Heusler alloy
   - Predict semiconducting Half-Heusler alloy based on the
   - Dope magnetic impurities Co(Ti, Mn)Sb

Half-metallic half-Heusler alloy

XYSn (50)		Element at site Y			
		Ti (22)	V (23)	Cr (24)	Mn(25)
X	Ni(28)				
	Co(27)				
	Fe(26)				
	Pd(46)				
	Rh(45)				
	Ru(44)				

Schematic density of state of half-Heusler alloy

18 electrons are needed
to fill up the valence band



NiMnSb

Valence electrons
Sb: 5
Ni: 10
Mn: 7
Total: 22

Magnetic moment
= total valence electron number – 18
=22-18 = 4

Carrier induced ferromagnetism in DMS

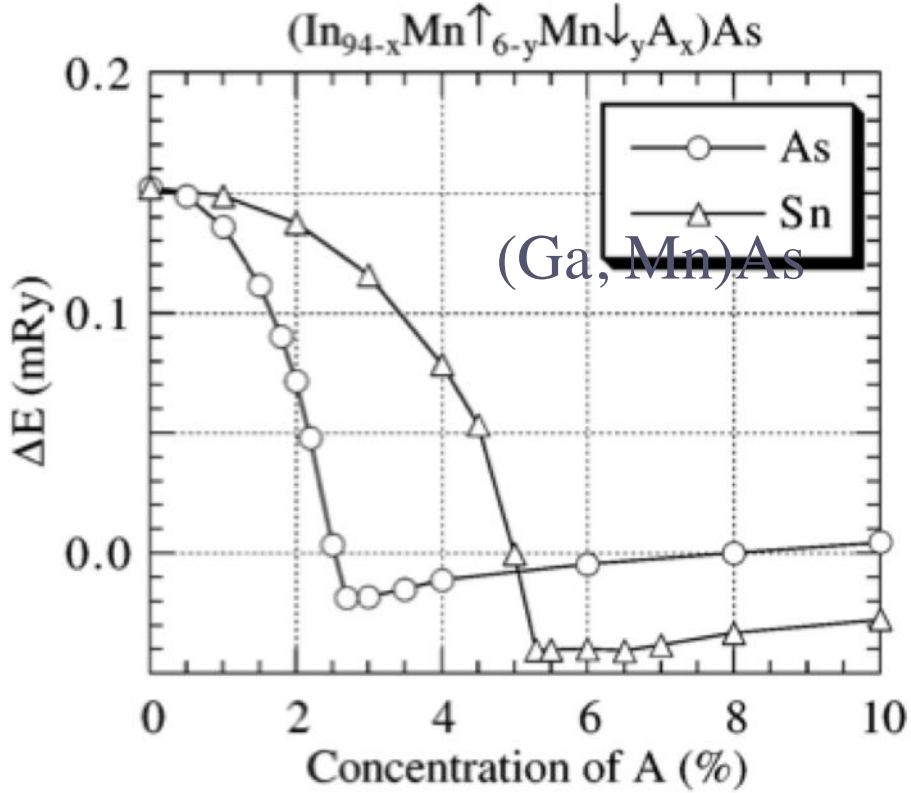


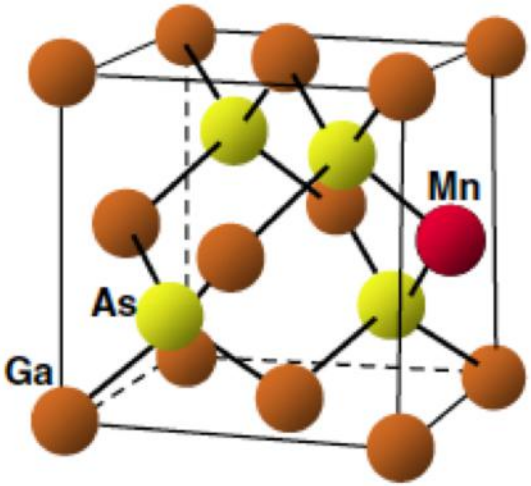
FIG. 3. The difference $\Delta E = E_{LMD} - E_{ferro}$ in the total energy between $(In_{0.94-x}Mn\uparrow_{0.03}Mn\downarrow_{0.03}A_x)As$ and $(In_{0.94-x} \times Mn\uparrow_{0.06}Mn\downarrow_0A_x)As$ as a function of the concentration x of A = As or Sn at the antisite.

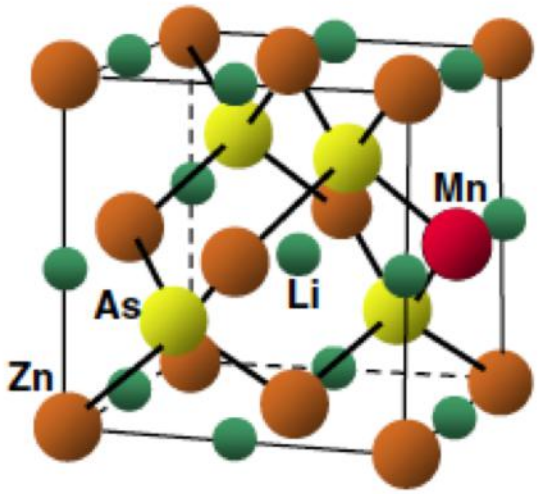
- Dilute magnetic semiconductors (DMS)
  - (Ga, Mn)As, (In, Mn)As ..
  - Ferromagnetic material
  - Ferromagnetism controllable by changing carrier density
  - Semiconductor spintronics
- High-Tc DMS necessary
  - High concentration doping crucial
- Material design

H. Ohno, JMMM 200 (1999) 110.
H. Akai, PRL 81 (1998) 3002
Nature 408 (2000) 944. Nature 402 (1999) 790.

Filled tetrahedral semiconductors LiZnAs

Masek et al., PRL 98 (2007) 067202





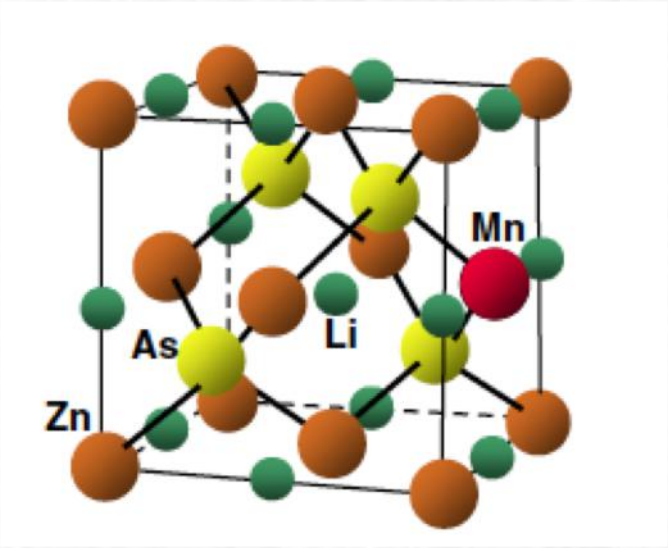
- Zinc blende structure + interstitial Li (Half-Heusler)
- $Ga^{3+}As^{3-}$

  $\Rightarrow$ $Zn^{2+}As^{3-}$ + Li^{1+}
- $Zn^{2+} \Rightarrow Mn^{2+}$: High solubility
  - $E_{Form}(Mn_{Zn}$ in LiZnAs)=~ -3 (eV)
  - $E_{Form}(Mn_{Ga}$ in GaAs)=~ +1 (eV)

  Mahadevan et al., PRB 68 (2003) 075202.
- Carrier control by Li addition (removal)

Juza et al., Angew. Chem. 7 (1968) 360
v. G. Achenbach et al., Z. Anorg. Allg. Chem. 476 (1981) 9.

Materials design of LiZnAs-DMS



- Atomic position
  - Zn: (0,0,0)
  - As: (0.25, 0.25, 0.25)
  - Li: (0.5, 0.5, 0.5)
  - Vc: (0.75, 0.75, 0.75)
  - Lattice constant a = 4.955 Å

- Carrier doping
  - Hole: Li vacancy
  - Electron Li interstitial
  - Calculate DOS

- Mn doping
  - DOS
  - Curie temperature
  - Carrier concentration dependence

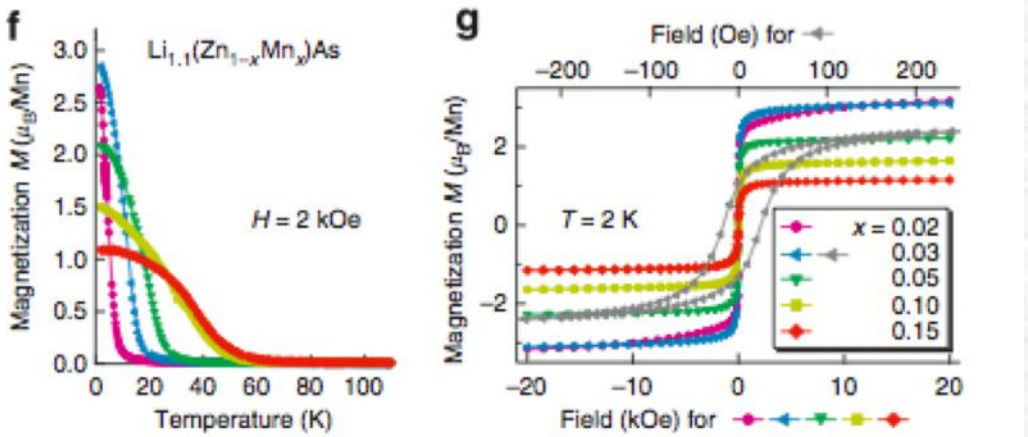
Carrier induced ferromagnetism in Li(Zn, Mn)As

Hole doping		0%	5%	10%	15%	20%	25%
Mn conc.	5%						
	10%						
	15%						
	20%						

Electron doping		0%	5%	10%	15%	20%	25%
Mn conc.	5%						
	10%						
	15%						
	20%						

Recent experiment

Z. Deng et al., Nature Commun. 2:422, (2011, Aug.) 1-5.



- Solid-state reaction
- XRD
- dc-magnetization, μSR
- Hall effect ⇒ *p*-type
  - Li at Zn substitutional site

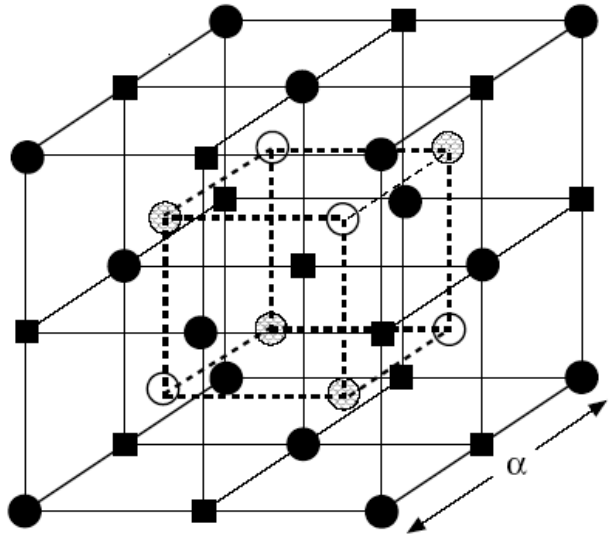
Table 1 | Ferromagnetic transition temperature and ordered moment size.

Li concentration	1.05		1.1		1.2	
	T_c (K)	M (T=2K)	T_c (K)	M (T=2K)	T_c (K)	M (T=2K)
Mn concentration						
0.03			17	2.9		
0.05			29	2.1	14	1.8
0.1	22	0.6	49	1.5	22	1.4
0.15	38	0.5	50	1.1	23	0.7

M (Bohr magneton per Mn).

The values of T_c and the average ordered moment size M per Mn of $Li_{1-y}(Zn_{1-x}Mn_x)As$ at T=2K and H=2 kOe derived from magnetization measurements for several combinations of Li and Mn concentrations.

Atomic Disorder in full Heusler alloys



Full-Heusler
X_2YZ $[L2_1]$
X Y
X Z

Half-Heusler
XYZ $[C1_b]$
X Y
Void Z

$$Polarization = \frac{DOS^{\uparrow}(E_F) - DOS^{\downarrow}(E_F)}{DOS^{\uparrow}(E_F) + DOS^{\downarrow}(E_F)}$$

- Co_2CrAl
- Cr⇄Al disorder
- Cr⇄Co disorder
  - Half-metallicity
  - Magnetic moment
  - Spin polarization
  - Total energy

$$Polarization = \frac{DOS^{\uparrow}(E_F) - DOS^{\downarrow}(E_F)}{DOS^{\uparrow}(E_F) + DOS^{\downarrow}(E_F)}$$

$Co_2(Cr_{1-y}Al_y)(Al_{1-y}Cr_y)$

y	Total energy (Ry)	Moment	Polarization
0			
0.05			
0.1			
0.15			
0.2			
0.25			
0.3			
0.35			
0.4			
0.45			
0.50			

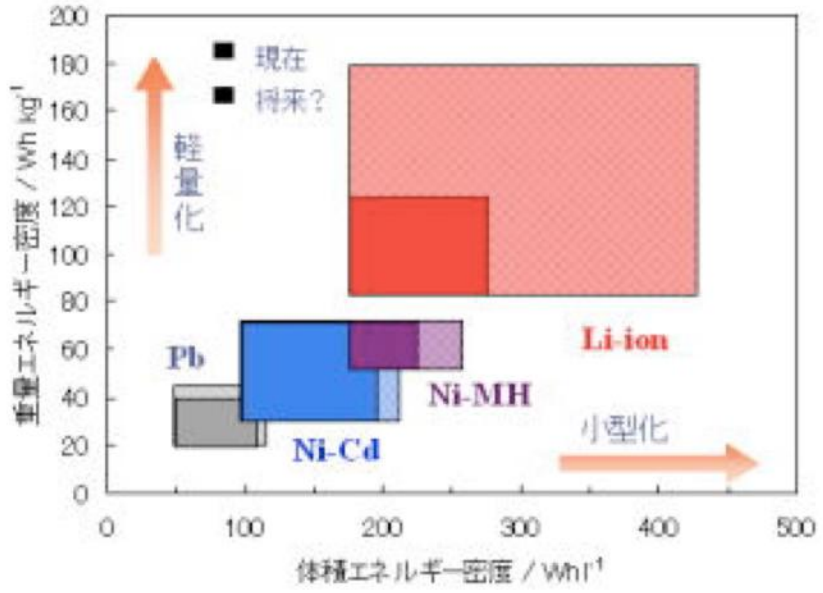
$$Polarization = \frac{DOS^{\uparrow}(E_F) - DOS^{\downarrow}(E_F)}{DOS^{\uparrow}(E_F) + DOS^{\downarrow}(E_F)}$$

$(Co_{1-x/2}Cr_{x/2})_2(Cr_{1-x}Co_x)Al$

x	Total energy (Ry)	Moment	Polarization
0			
0.05			
0.1			
0.15			
0.2			
0.25			
0.3			
0.35			
0.4			
0.45			
0.47			
0.50			

Lithium-ion rechargeable battery

1. Rechargeable battery
   - Chargeable, usable repeatedly
   - Lead battery, Ni-Cd battery
   - Li-ion battery, Ni-H battery (large energy density)

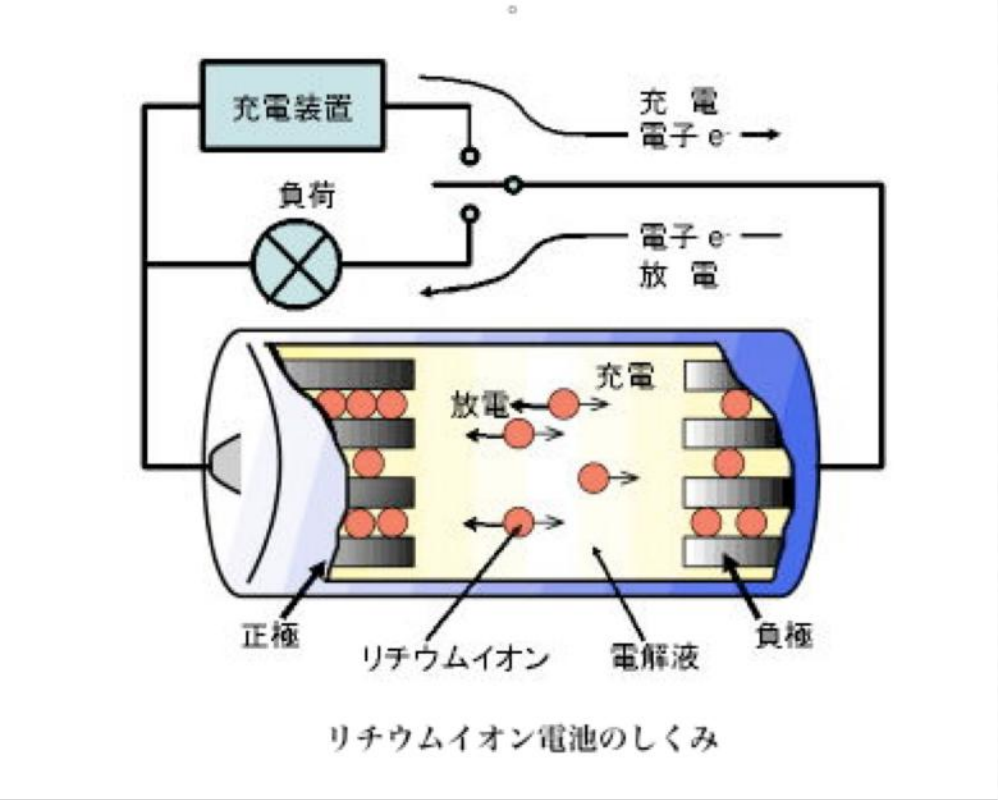


リチウムイオン電池と各種電池の比較

Design of positive and negative electrodes for more effective rechargeable battery

中山将伸氏ホームページより

Lithium-ion rechargeable battery



リチウムイオン電池のしくみ

A. 'good' battery
   1. High voltage
   2. Large capacity
   3. Low cost
   4. Light weight
   5. safety

Positive electrode：

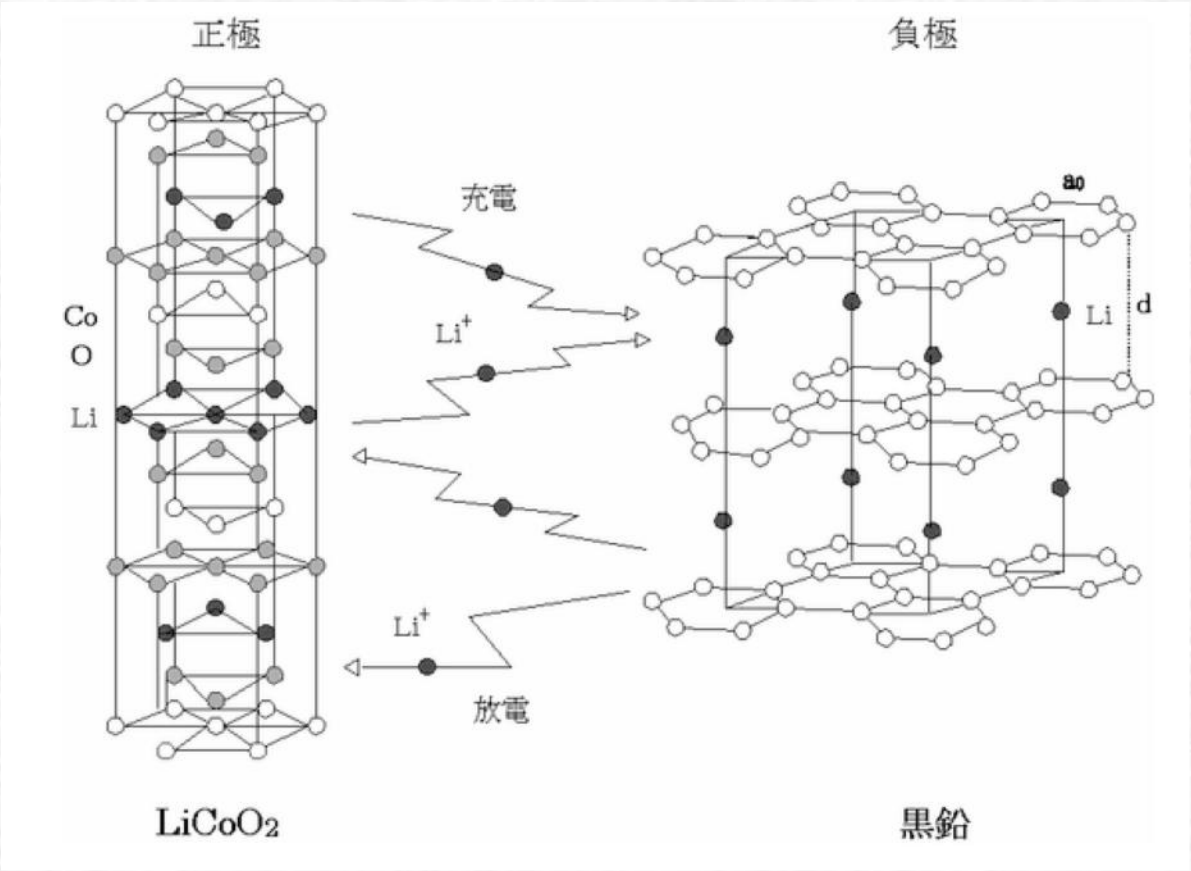
$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$$

Negative electrode：

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

Total（discharging reaction）：$CoO_2 + Li \rightarrow LiCoO_2$

Positive electrode: $LiCoO_2$



1. Estimation of battery voltage
2. Negative electrode ：Li metal
3. No lattice relaxation

Rhombohedral

R (TM): (0,0,0)
M (Li): (1/2, ½, ½)
O: (u, u,u), (-u, -u, -u)

$$-V = TE(LiCoO_2) - TE(CoO_2) - TE(Li)$$

Positive electrode: $LiCoO_2$

Co is very expensive → use the other transition metals for electrodes

	Ti	V	Cr	Mn	Fe	Co	Ni
¥/kg	2000	6000	400	310	30-90	8000	2000
toxicity	—	×	×	—	—	—	—

- Chemical trend of the battery voltage on TM ions
  $LiTMO_2$, TM=Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al

- Alloying works? Use much cheaper TM metals
  $Li(Co, Al)O_2$, $Li(Co, Zn)O_2$, $Li(Co, Cu)O_2$
  $Li(Ni, Mn)O_2$
  $Li(Ni, Mn, Co)O_2$

Try to design positive electrode

TM	Tl(22)	V(23)	Cr(24)	Mn(25)	Fe(26)	Co(27)	Ni(28)
a (a.u.)	9.458	9.764	9.638	9.081	9.227	9.373	9.486
Alpha (deg)	34.64	31.90	33.12	35.37	34.17	32.97	33.37
Voltage (V)							

Metal	Cu(29)	Zn(30)	Al(13)	Sc(21)	B(5)
a (a.u.)	8.664	8.767	9.460		
alpha	38.85	39.04	32.48	(34.64)	
Voltage					

TM conc. = 10 %, 100%

Suppose u=0.26

Hydrogen strage material
水素吸蔵材料

Hydrogen energy system
水素エネルギーシステム

- Decomposition of H_2O by using solar energy → H_2
- Energy storage and transfer in the form of H_2
- Taking out electricity by using fuel cell

→ 'Greener' energy cycle　（環境に優しいエネルギーサイクル）

→ Hydrogen strage material（水素吸蔵材料）

Design of hydrogen storage materials

Metal hydrates (inorganic hydrogen storage materials)
無機系水素貯蔵材料（金属水素化物）

- High H concentration（高い水素含有量）
- Low price
- Too stable 高温で水素を放出（安定すぎる）

Metal hydrates	H concentration (weight%)	Formation enthalpy (kJ/mol)
LiH	12.7	-91
NaH	4.2	-56
KH	2.5	-58
MgH_2	7.6	-76
CaH_2	4.8	-186

→Un-stabilize the metal hydrates by doping transition metal impurities

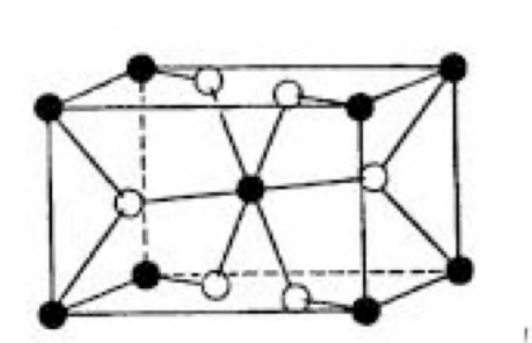
M. Tsuda et al., Thin Solid Films 509 (2006) 157

Formation energy of MgH_2

$$\Delta E = TE(MgH_2 : rutile) - TE(Mg : hcp) - 2 \times TE(H)$$

1. Instead of TE(H_2 molecule), we use TE(H: FCC) to be in consistent with MT approximaion. TE(H)=-1.076 Ry
2. Lattice constants of MgH_2, Mg → experimental value
3. No-lattice relaxation

- Calculate how largely we can destabilize MgH_2 by introducing transition metal impurities.
- Which TM is the most effective ?



●：Ti，○：O

図 1. 29　ルチル型構造

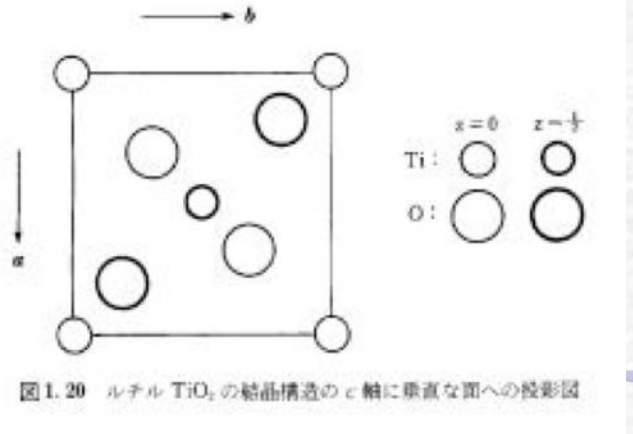


図 1. 20　ルチル TiO_2 の結晶構造の c 軸に垂直な面への投影図

MgH_2 :
a= 4.501 A,
c=3.01 A,
u= 0.304

Mg :
a= 3.20936 A,
c=5.2112A,

Formation energy of MgH_2 with transition metal impurities

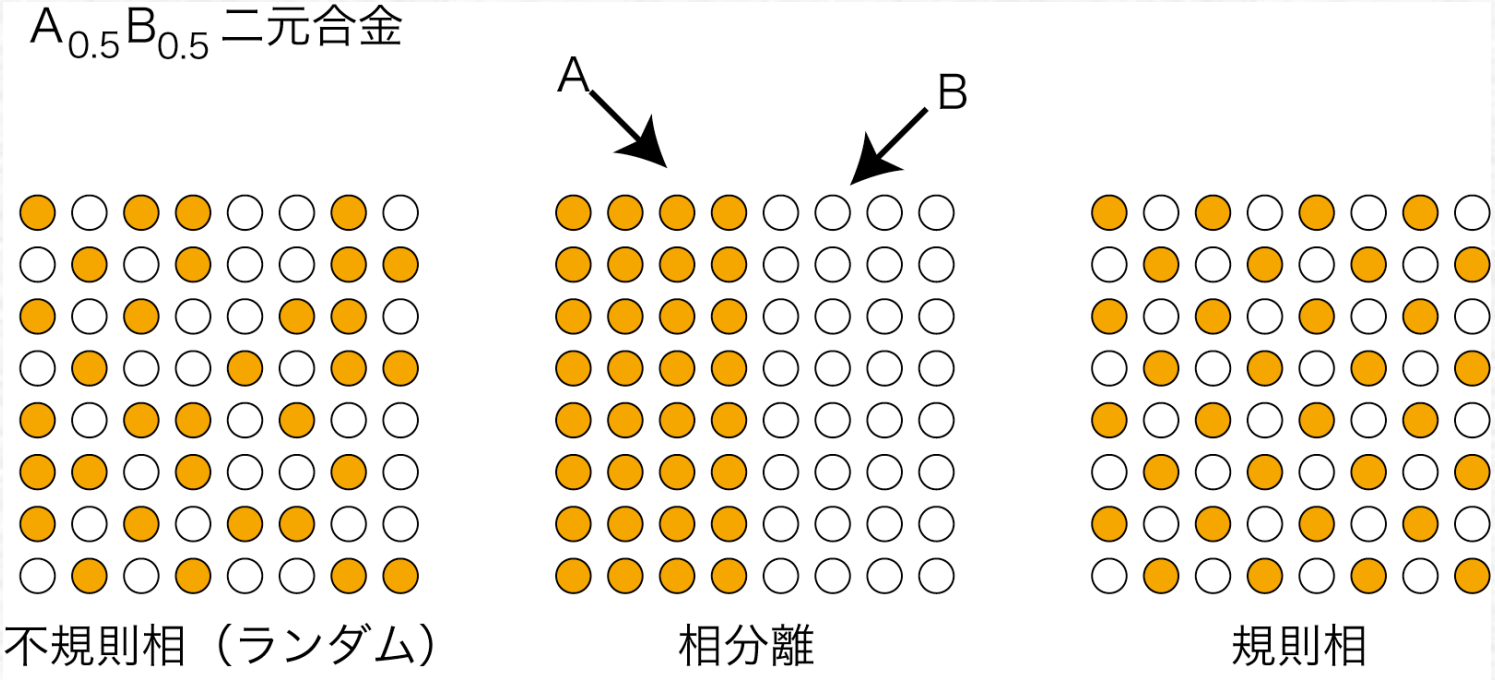
$$\Delta E = TE(Mg_{1-x}TM_xH_2 : rutile)$$
$$-TE(Mg_{1-x}TM_x : hcp) - 2 \times TE(H)$$

1. Calculate ΔE, when transition metal impurity TM (TM=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn,) are doped in MgH_2. Suppose x=0.1

$$\Delta E(MgH_2) = -1.376eV$$

TM	Sc (21)	Ti (22)	V (23)	Cr (24)	Mn (25)	Fe (26)	Co (27)	Ni (28)	Cu (29)	Zn (30)
ΔE (eV)										

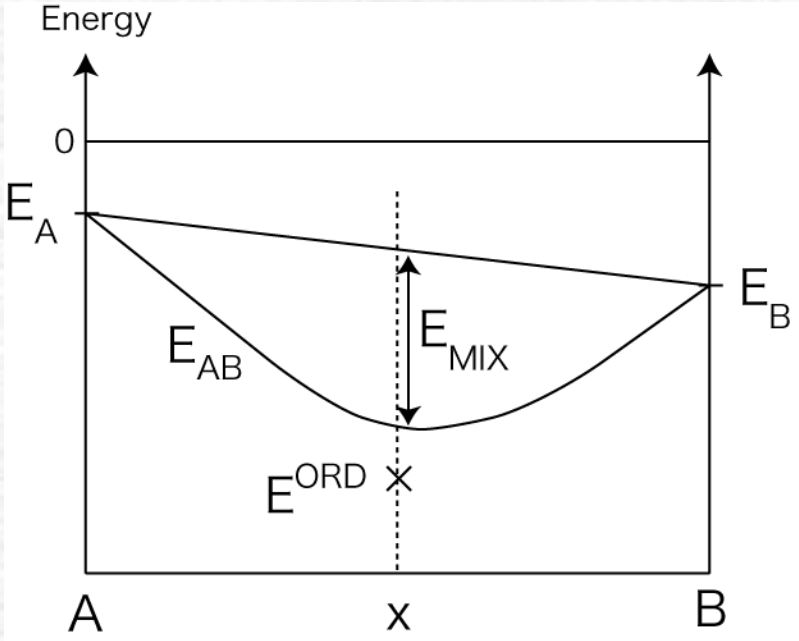
FCC two-component alloy



- Soluble
  - Ag-Au（），Ag-Pd（），Pd-Pt（），Au-Ni（）
- Phase separate
  - Cu-Ag（），Au-Pt（），Au-Rh（），Pd-Rh, Pt-Rh
- Ordered phase
  - Au-Pd, Au-Cu

By using the CPA, all phases (disordered, ordered) can be calcuated with in the same framework.

Calculation of mixing energy



E_A : Total energy of A

E_B : Total energy of B

E_{AB} : Total energy of disordered phase

E_{MIX}: Mixing energy

$= E_{AB} - (1-x)E_A - xE_B$

x: concentration of B

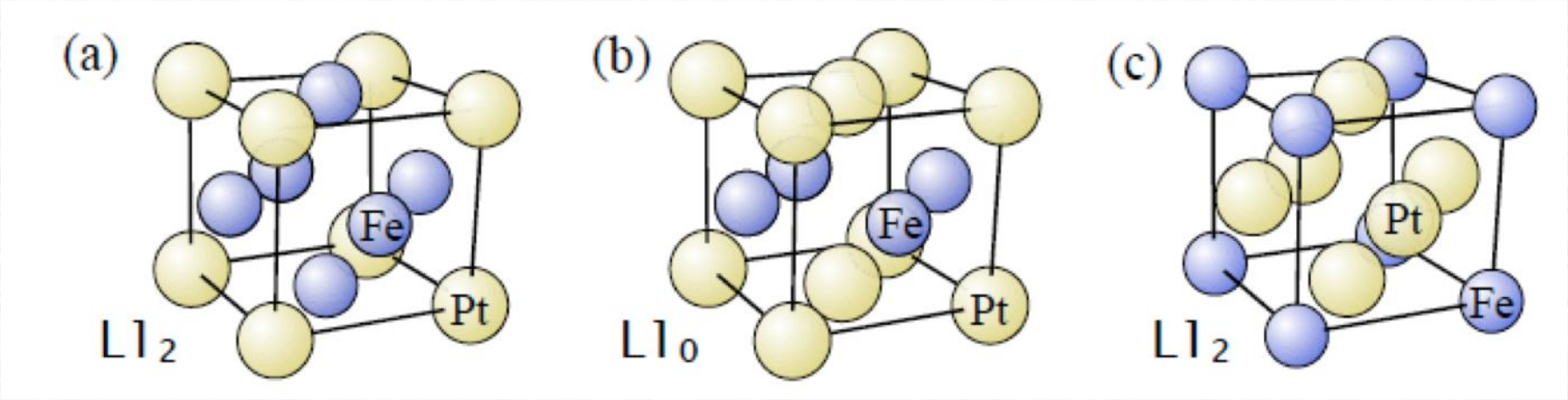
E_{AB}^{ORD}: Total energy of ordered phase

Assumption:
Lttice constants follow the Vegard's law.

x = 25, 50, 75 %

$$a(A_{1-x}B_x) = (1-x) \times a(A) + x \times a(B)$$

$L1_0$, $L1_2$ ordered state



SC
Pt: (0, 0, 0)
Fe: (1/2, ½, 0),
(1/2, 0, ½),
(0, ½, ½)

ST
Pt: (0, 0, 0),
(1/2, ½, 0),
Fe: (1/2, 0, ½),
(0, ½, ½)

SC
Fe: (0, 0, 0)
Pt: (1/2, ½, 0),
(1/2, 0, ½),
(0, ½, ½)

Assumption:
Lttice constants follow the Vegard's law.

$$a(A_{1-x}B_x) = (1-x) \times a(A) + x \times a(B)$$