

Integrating Data and Modeling In Materials Design

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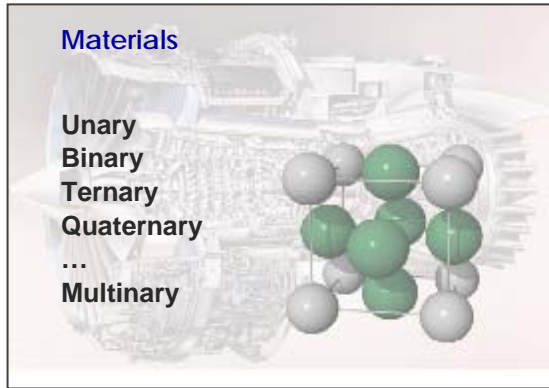
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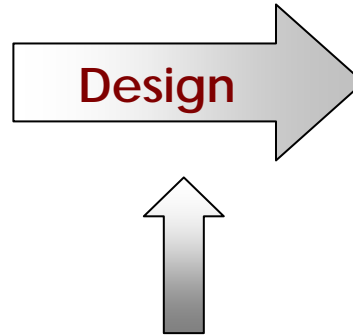
Outline

- I. Introduction: materials design
- II. Approach
 - Data-driven approach: data mining
 - Modeling-driven approaches
 - Data/Modeling-driven approach
- III. Examples
 - Structural map: empirical, computational
 - Discovery of new H-storage materials
 - 1st principles calculation of phase diagram
- IV. Summary

I. Introduction: Materials Design



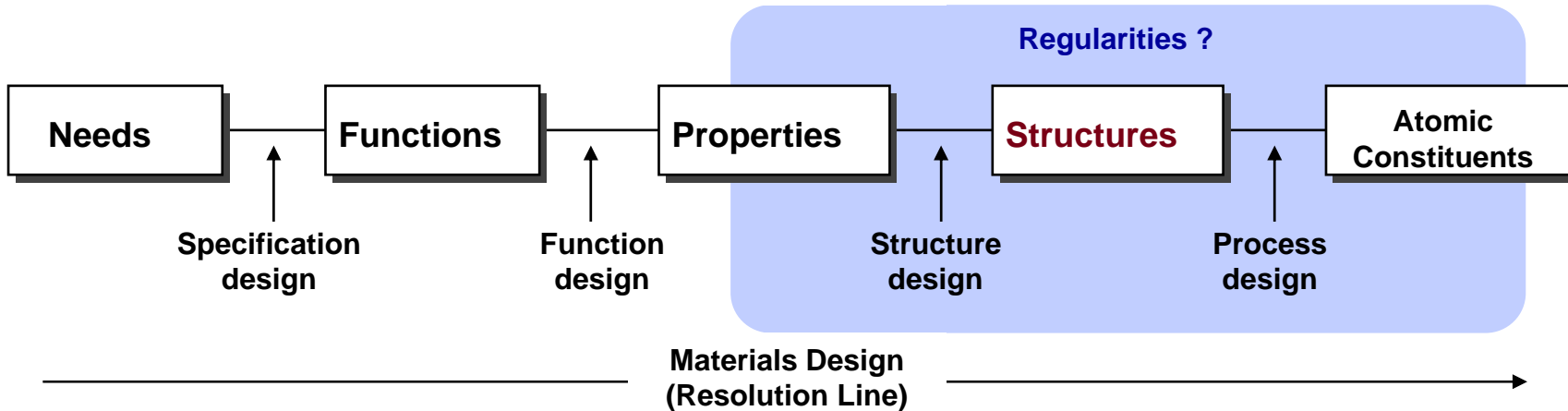
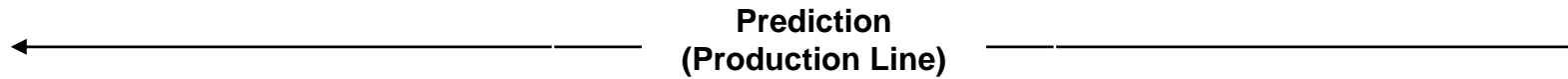
Too many Possibilities...?



Periodic Table of the Elements

Showing: Atomic weight

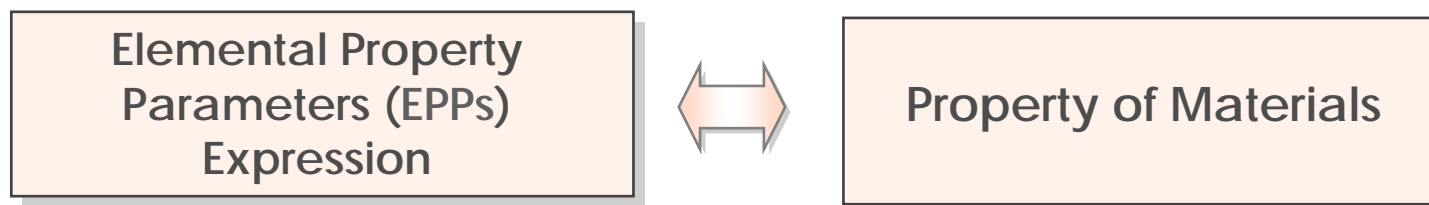
IA	Periodic Table of the Elements																VIIA	Ho
H																	He	4.0026
Li	Be											B	C	N	O	F	Ne	
6.94	9.0121											10.81	12.011	14.0064	16.0000	18.9984	20.1798	
Na	Mg	Al	Si	P	S	Cl	Ar									Kr		
22.98976928	24.304	26.9815386	28.0855	30.973762	32.06	35.453	39.948									78.96		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
39.0983	40.078	44.955912	47.867	50.9415	51.99616	54.938044	55.845	58.933195	58.933195	63.546	65.38	69.723	72.64	74.9216	78.96	79.904	83.80	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
85.4678	87.62	88.906124	91.224	92.90638	95.94	98.90625	101.07	101.07	106.365	107.8682	112.411	114.818	118.710	121.757	127.60	126.905	131.29	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
132.90545196	137.327	138.90547	178.49	180.948	183.84	186.207	188.906	192.222	195.084	196.966569	200.59	204.38	207.2	208.9804	209	210	222	
Fr	Ra	Ac	Unq	Unp	Uns	Uno	Unn											
(223)	(226)	(227)	(251)	(262)	(263)	(264)	(265)	(266)	(267)	(268)	(269)	(270)	(271)	(272)				
Lanthanide Series																		
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
140.12	140.90768	144.24	(145)	150.4	151.964	157.25	162.50	164.93032	167.259	173.054688	174.967	175.0474	174.967					
Actinide Series																		
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					
232.037724	231.036888	238.02891	237.048173	244.04094	247.071251	251.079014	257.10371	261.108888	265.1078	269.10974	270.1063	270.1063	270.1063					



II. Approaches: Data-Driven Approach

Basic Idea

- Based on the comprehensive **materials database** to reveal **regularities**:
 - **Formation** of compound in a given binary system
 - **Composition** of stable compounds in “compound formers”
 - **Structures** of a given compound
 - **Properties** of a given compound
- **Postulation**



- **Tool: Materials Databases: Pauling File**

II. Approaches: Data-Driven Approach

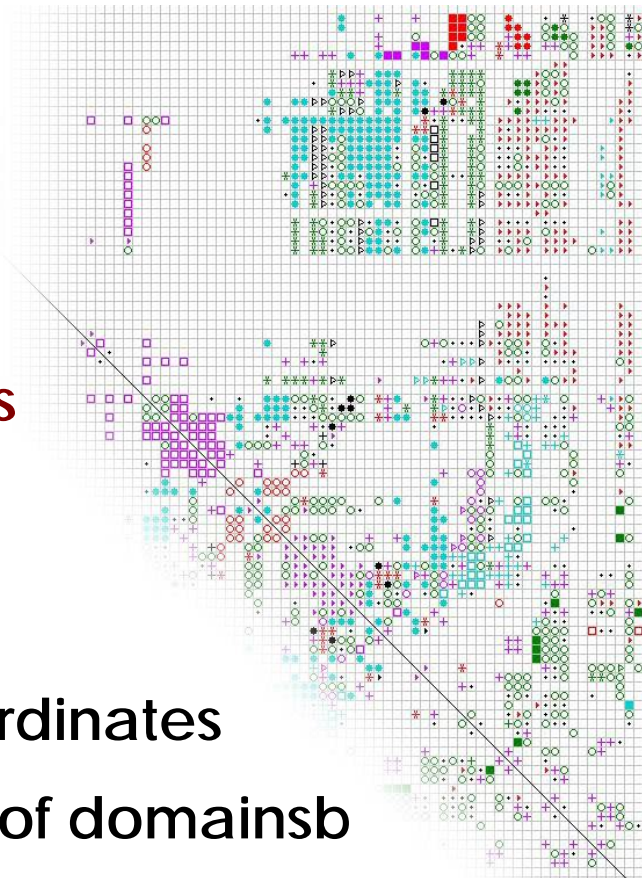
Mapping

- Purpose of Mapping

Proper **Elemental Properties** as **Axes**



Substances in same/similar
structure/properties → **Groups**



- Two key points in mapping

Characterization: To find optimal coordinates

Classification: To define meaning of domains

II. Approaches: Modeling-Driven Approach

Calculations based on various physical models provide:

- **Complement** to empirical data, provide **new** data;
- **Further screening** and prediction of hypothesis;
- Understanding of **insight** into the origin;
- **Prediction** of materials with required properties.

II. Approaches: Modeling-Driven Approach

Theoretical Approaches

- First Principles Electronic Structures (FLAPW, Wien)
- Car-Parrinello Molecular Dynamics (CPMD, VASP)
- Cluster Expansion Method (CEM)
- Cluster Variation Method (CVM)
- Phase Field Method (PPM)
- Classical Molecular Dynamics (MD)
-

II. Approaches: Data/Modeling-Driven Approach

Materials

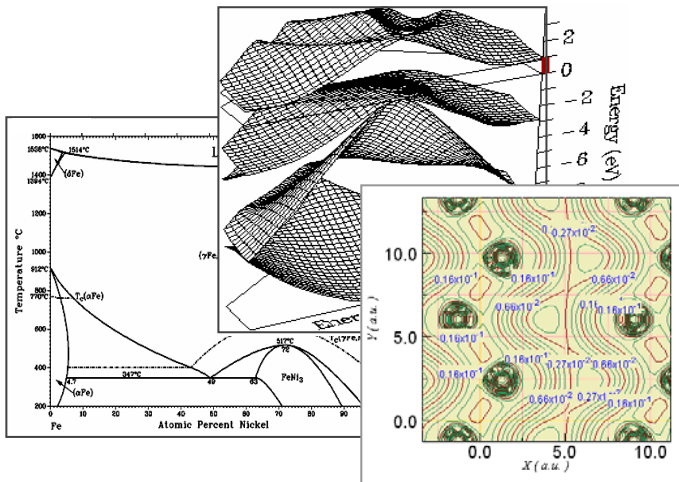
Unary
Binary
Ternary
Quaternary
...
Multinary

Too many
Possibilities...?

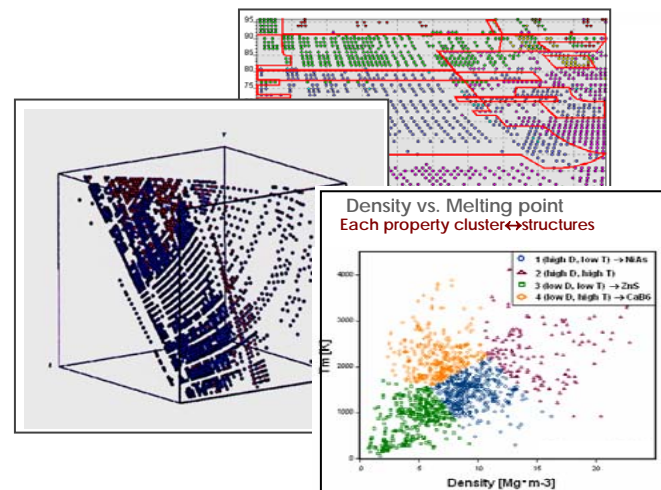


Regularities

Periodic Table of the Elements

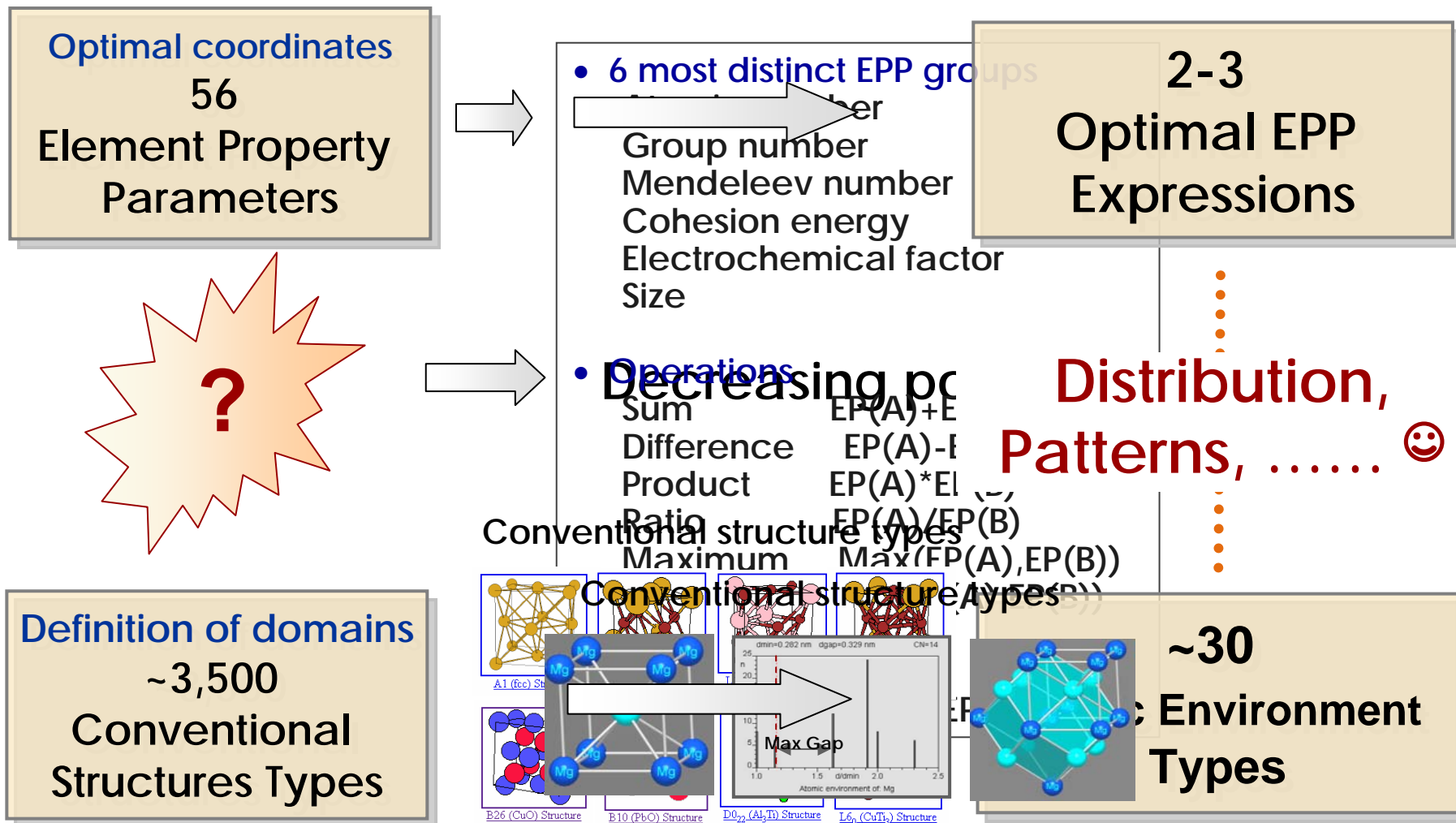


Model-Driven Approach → Origin



Data-Drive Approach → Discovery

Purpose: Regularity between Crystal structure & Element properties

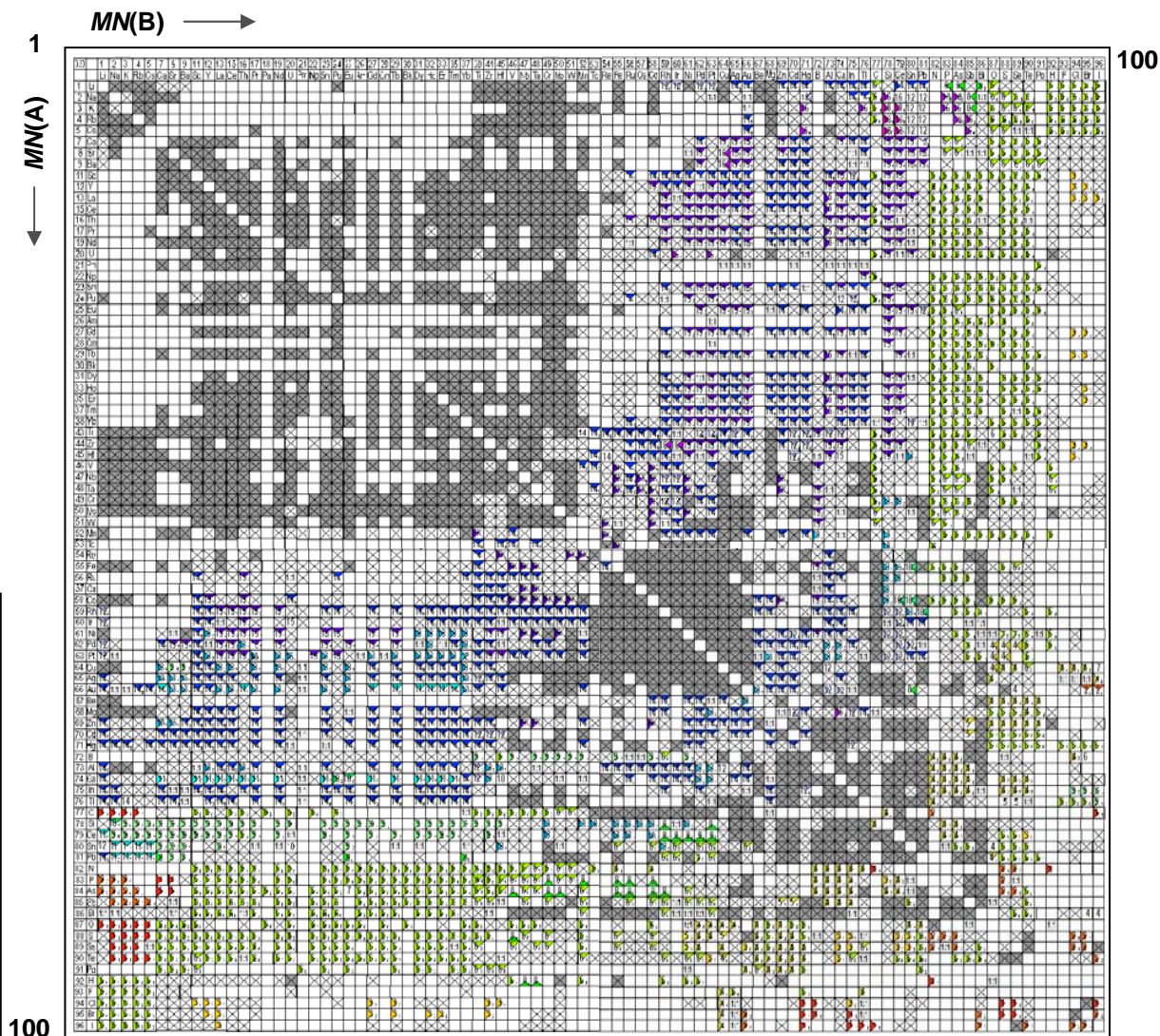


MN(A) vs. MN(B) Map for 1:1 Binary Compounds (RT)

- CN 1-3
- CN
- CN 6 (-11)
- CN 12 (-13)
- CN 14(-18)
- Non-former
- Former (no 1:1)

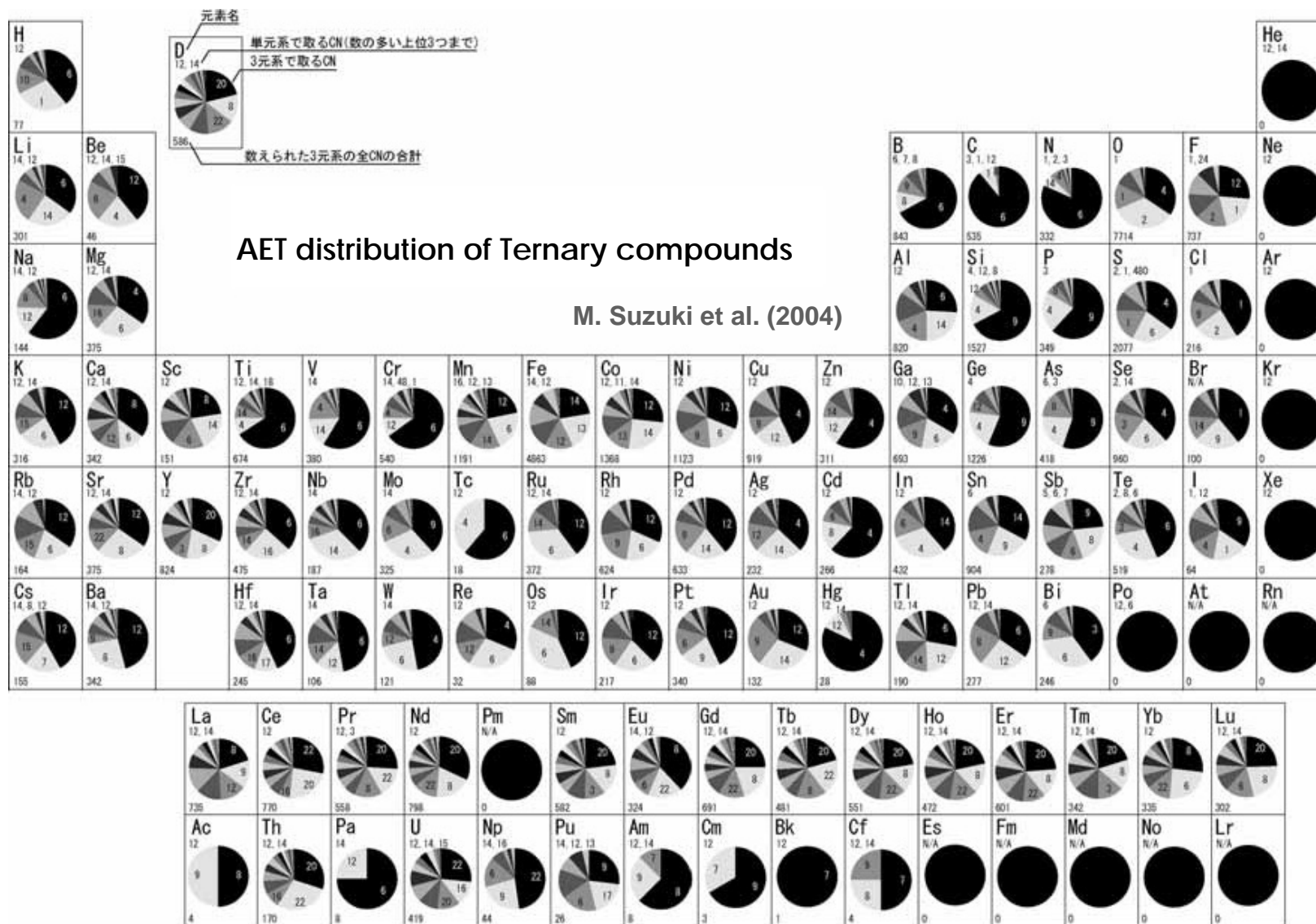
Mendeleev Number MN1

																92	98																	
Li 3	Be 4															B 5	C 6	N 7	O 8	F 9	Ne 10													
1	7															72	77	82	87	93	99													
Na 11	Mg 12															Al 13	Si 14	P 15	S 16	Cl 17	Ar 18													
3	9															73	78	83	88	94	100													
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36																	
1	11	13	45	48	51	54	57	60	63	66	69	74	79	84	89	95	101																	
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54																	
4	10	14	46	49	52	55	58	61	64	67	70	75	80	85	90	96	102																	
Cs 55	Ba 56	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86																		
5	1	47	50	53	56	59	62	65	68	71	76	81	86	91	97	103																		
Fr 87	Ra 88																																	
6	12																																	
																La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71				
																15	17	19	21	23	25	27	29	31	33	35	37	39	41	43				
																Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103				
																16	18	20	22	24	26	28	30	32	34	36	38	40	42	44				

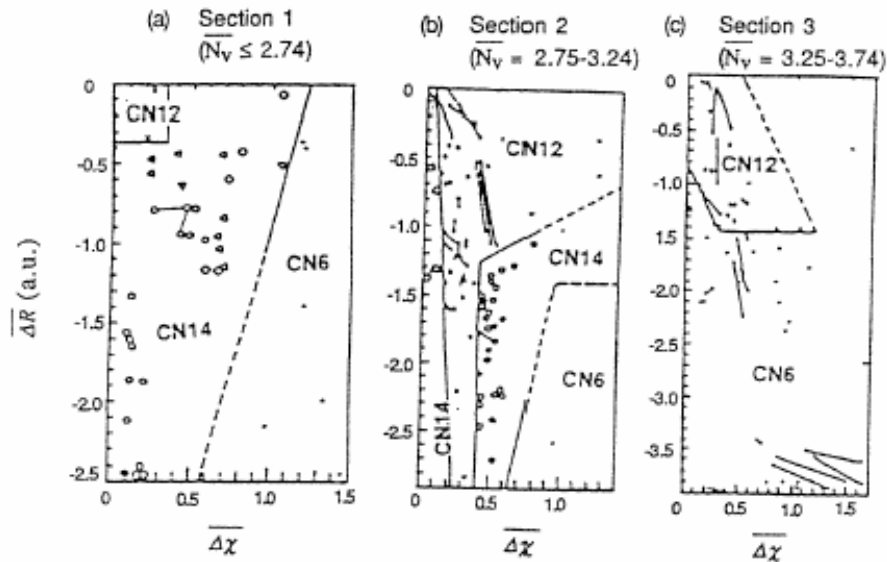


P. Villars, Y. Chen et al. (2004)

III-1 AET distribution of Ternary compounds

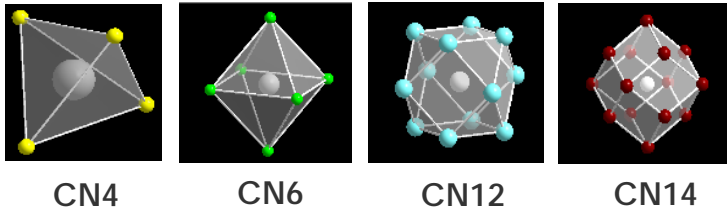


Successfully separated ~2,500 intermetallic compounds with single AET



x: difference of Zunger's radii
 y: difference of M-B electronegativity
 z: sum of valence electrons number

4 most popular AETs



P. Villars et al. (1983)

Problems

- Microscopic mechanism ?
- Uncompleted separation



Theoretical Modeling:
 Calculated map

Model Systems

AB intermetallic compound

- $Nv < 3.5$, s-s, s-p, p-d
- Martynov-Batsanov's electronegativity χ

$$\overline{\Delta\chi} = \chi_A - \chi_B$$

→ Atomic valence electronic energy level $\{\varepsilon_i\}$

$$\Delta E = E_A - E_B$$

- Pseudopotential radii's sum $R = r_s + r_p$

→ Bond length d

Calculation Approaches

Tight-binding approach $E_{tot} = E_{bond} + E_{rep}$

E_{bond} - attractive bond energy: $E_{bond} = \sum_k^{occ.} q_k \varepsilon_k$

$$H = \sum_{i\alpha} \varepsilon_{i\alpha} |i\alpha\rangle\langle i\alpha| + \sum_{i\alpha j\beta} h_{i\alpha j\beta} |i\alpha\rangle\langle j\beta| + |j\beta\rangle\langle i\alpha|$$

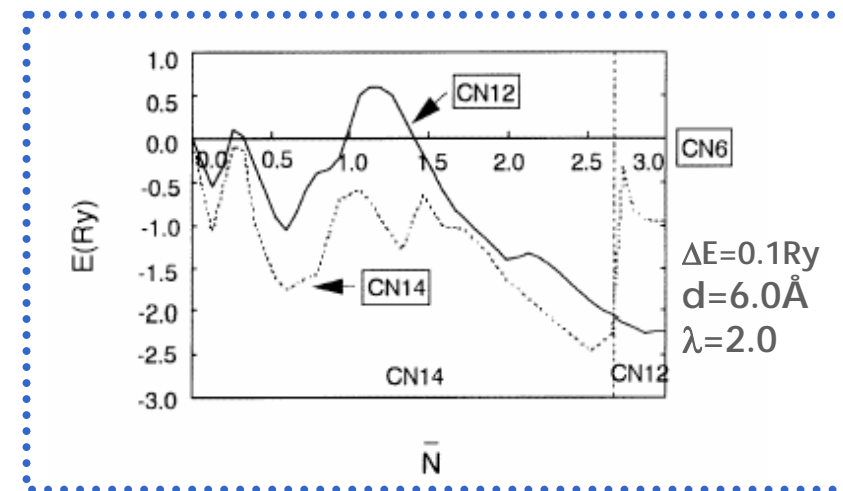
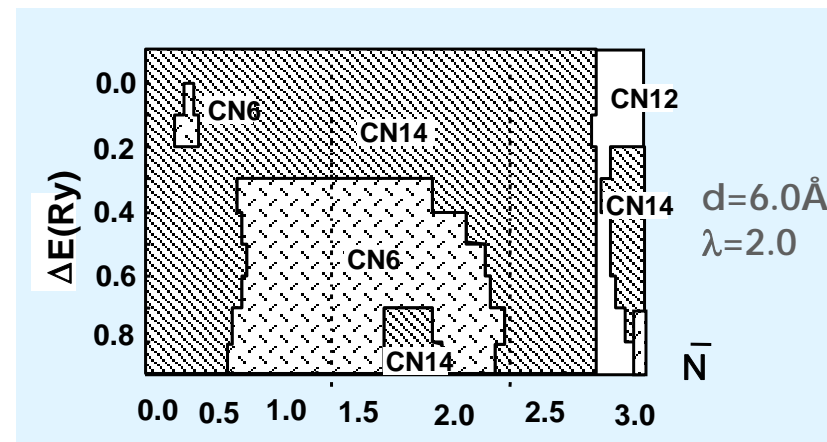
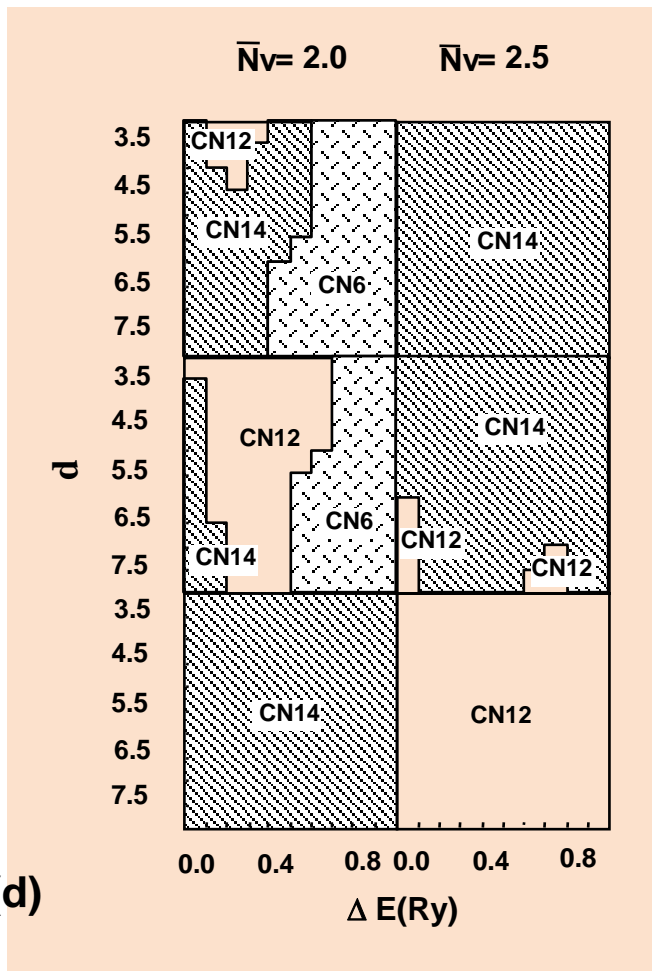
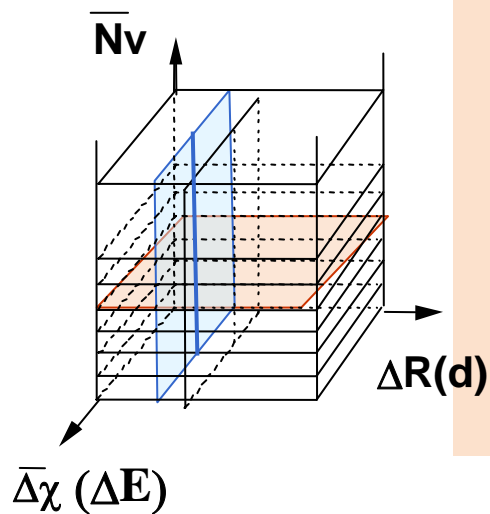
$$h_{\alpha\beta\gamma}(d) = \eta_{\alpha\beta\gamma} \frac{h}{md^2}$$

E_{rep} - pairwise repulsive contribution

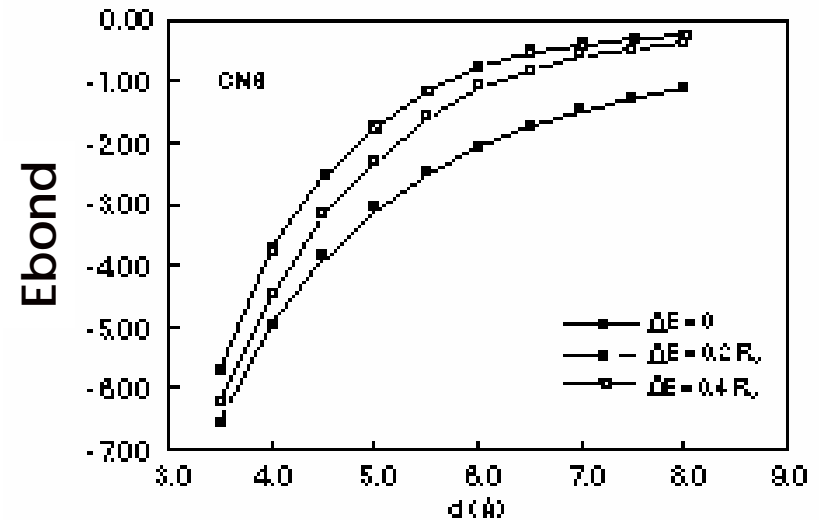
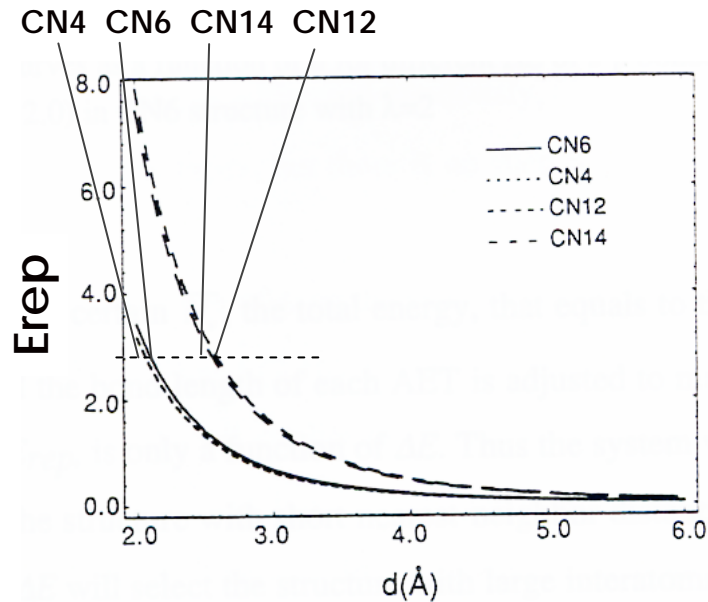
$$E_{rep} = \frac{1}{2N} \sum_{i,j} \Phi(R_{ij}) \quad \Phi_{AA}(\mathbf{R}) = \mathbf{h}^\lambda(\mathbf{R})$$

Structural energy difference theorem

$$\Delta E_{tot} = (\Delta E_{bond})_{\Delta E_{rep}=0}$$



Investigate Origin of structural preference



Influence of ΔE : large $\Delta E \rightarrow$ small $d \rightarrow$ CN4 and CN6
 \rightarrow CN4 requires very large ΔE , no in low N_V .

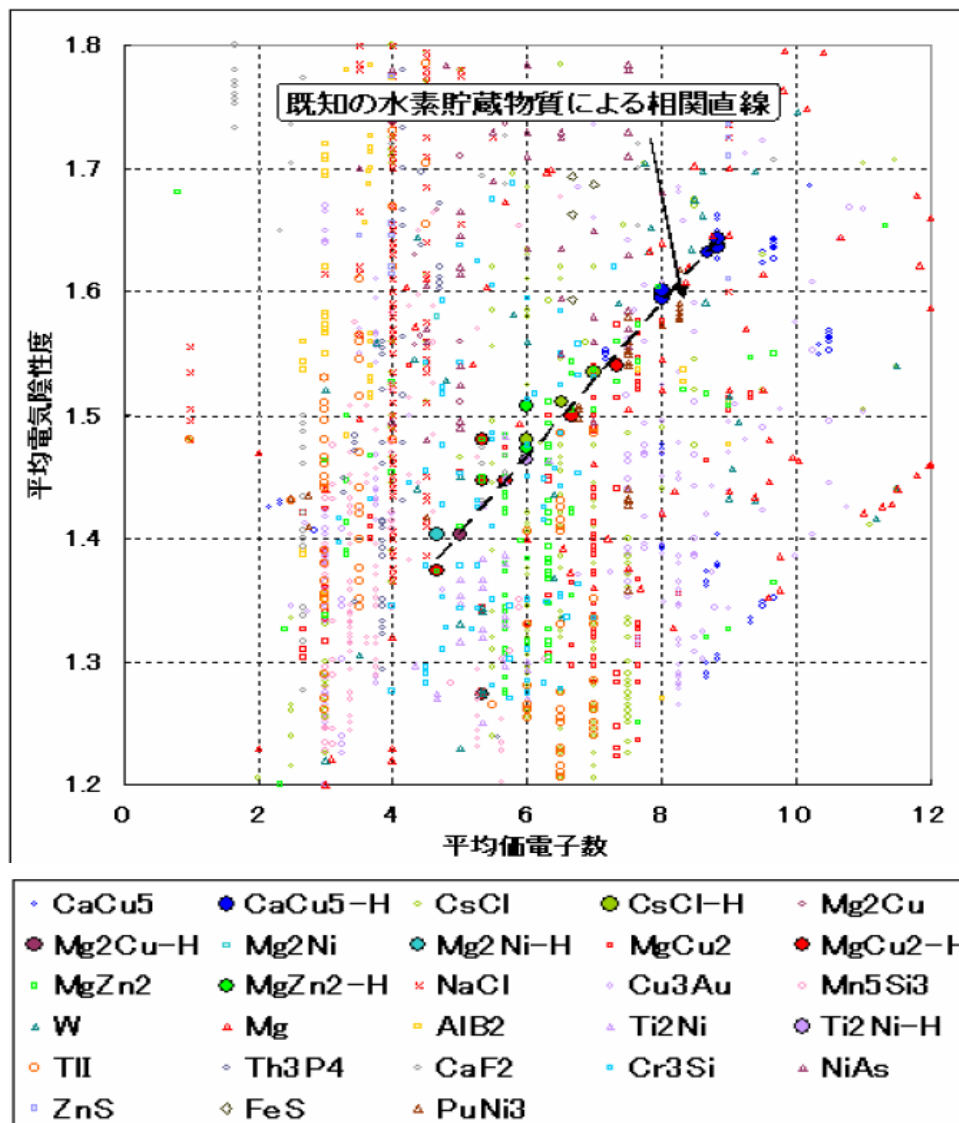
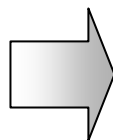
Influence of λ : higher $\lambda \rightarrow$ higher CN: CN12, CN14

III. Example-2: Discovery of New H-Storage Materials

Starting point

32 Already known
H-storage alloys (HAS)

結晶構造	水素貯蔵物質
CaCu ₅	LaNi ₅ , LaCo ₅ , CaNi ₅ , CeCo ₅ , CeNi ₅ , GdCo ₅ , GdNi ₅ , NdCo ₅ , NdNi ₅ , PrCo ₅ , PrNi ₅ , YNi ₅ , YCo ₅ , ThCo ₅ , YbNi ₅ , SmNi ₅ , SmCo ₅
CsCl	TiFe, TiNi, TiCo
Mg ₂ Cu	Mg ₂ Cu
Mg ₂ Ni	Mg ₂ Ni
MgCu ₂	ZrV ₂ , ZrCo ₂ , ZrMo ₂ , ZrFe ₂ , ZrCr ₂ , TiCr ₂ , Ti ₂ Co
MgZn ₂	ZrMn ₂ , TiMn ₂
Ti ₂ Ni	Ti ₂ Ni



Surprising

linear relation for known HSAs
Average valence electrons

VS.

Average electronegativity

M. Ono et al. (2005)

III-2. Discovery of New H-Storage Materials

linear relation for known HSAs → Candidates of new HSAs

From small **distance** To the straight line

化学式	結晶構造	L	化学式	結晶構造	L
ErNi5	CaCu5,hP6,191	0.000	Nd5Sb3	Mn5Si3,hP16,193	0.001
ThNi5	CaCu5,hP6,191	0.000	Pr5Sb3	Mn5Si3,hP16,193	0.001
TmNi5	CaCu5,hP6,191	0.000	Sm5Sb3	Mn5Si3,hP16,193	0.001
TaFe2	MgZn2,hP12,194	0.000	Ce5Sb3	Mn5Si3,hP16,193	0.001
TaCo2	MgCu2,cF24,227	0.000	Yb5Sb3	Mn5Si3,hP16,193	0.001
La5Si3	Mn5Si3,hP16,193	0.000	HoFe5	CaCu5,hP6,191	0.001
NpFe2	MgCu2,cF24,227	0.001	Mn3Rh	Cu3Au,cP4,221	0.001
PuFe2	MgCu2,cF24,227	0.001	WFe2	MgZn2,hP12,194	0.001
UFe2	MgCu2,cF24,227	0.001	ScCo2	MgCu2,cF24,227	0.001
NdFe5	CaCu5,hP6,191	0.001	ErIn	CsCl,cP2,221	0.001
DyNi5	CaCu5,hP6,191	0.001	GdIn	CsCl,cP2,221	0.001
HoNi5	CaCu5,hP6,191	0.001	TmIn	CsCl,cP2,221	0.001
TbNi5	CaCu5,hP6,191	0.001	YIn	CsCl,cP2,221	0.001
HfMn2	MgZn2,hP12,194	0.001	LuNi5	CaCu5,hP6,191	0.001
CeBi	CsCl,cP2,221	0.001	Sc5Pb3	Mn5Si3,hP16,193	0.001
BaPo	NaCl,cF8,225	0.001	DyCo5	CaCu5,hP6,191	0.001
CeBi	NaCl,cF8,225	0.001	HoCo5	CaCu5,hP6,191	0.001
AmNi2	MgCu2,cF24,227	0.001	TbCo5	CaCu5,hP6,191	0.001
NpNi2	MgCu2,cF24,227	0.001	RuAl	CsCl,cP2,221	0.001
PuNi2	MgCu2,cF24,227	0.001	GdFe5	CaCu5,hP6,191	0.001
UNi2	MgZn2,hP12,194	0.001	ThFe5	CaCu5,hP6,191	0.001
NpCo2	MgCu2,cF24,227	0.001	ScFe2	MgCu2,cF24,227	0.001
PuCo2	MgCu2,cF24,227	0.001	ScFe2	MgZn2,hP12,194	0.001
UCo2	MgCu2,cF24,227	0.001			

Further screening by large **unfilled volume**

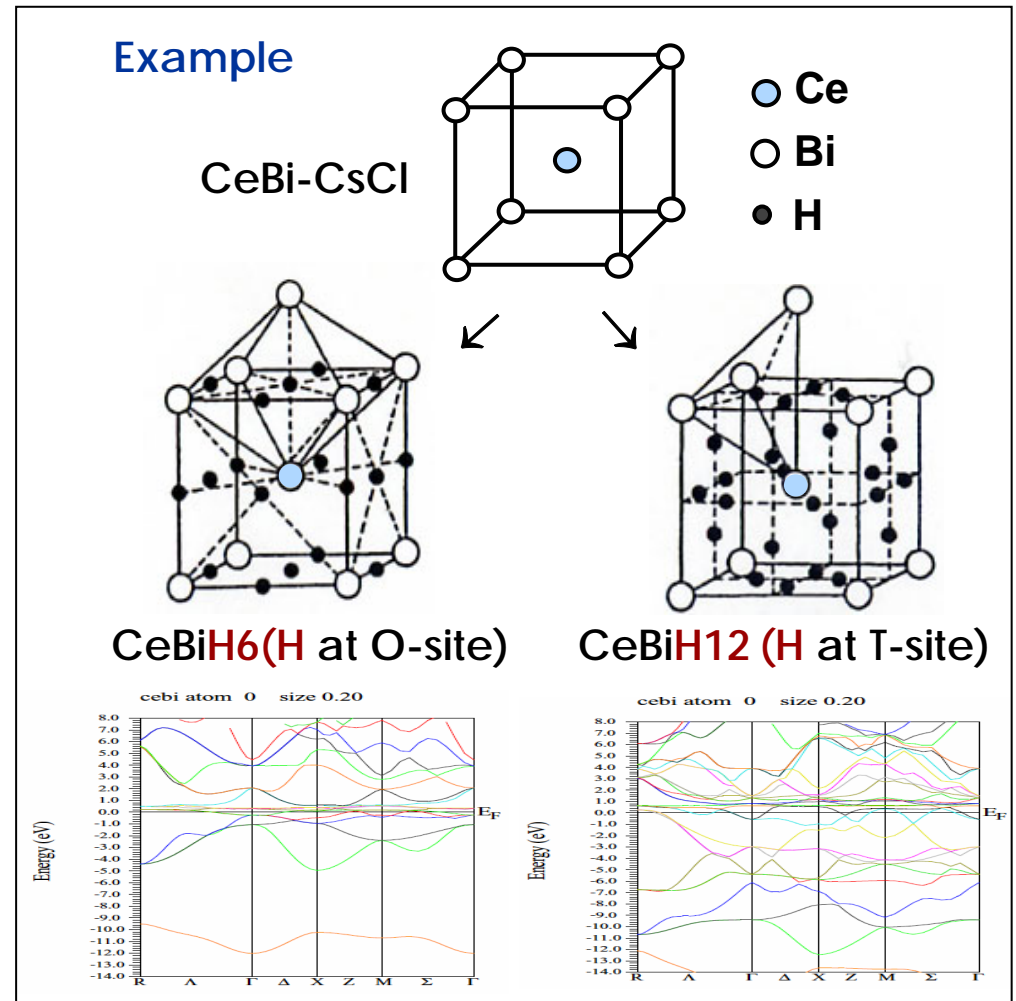
	結晶構造	隙間の体積 [Å ³ Atom ⁻¹]	直線との 距離
PuCo ₃	PuNi ₃	4.36	0.0157
PuNi ₃	PuNi ₃	4.30	0.0120
ThFe ₃	PuNi ₃	4.12	0.0120
HfV ₂	MgCu ₂	4.37	0.0037
NpFe ₂	MgCu ₂	4.41	0.0108
NpNi ₂	MgCu ₂	4.25	0.0076
PuFe ₂	MgCu ₂	4.20	0.0120
PuNi ₂	MgCu ₂	4.23	0.0105

III-2. Discovery of New H-Storage Materials

First Principles Calculation: A_nB_m , $A_nB_mH_q$

- Possible H sites, structures
- stability
- Interstitial volume, Storage capacity
- Electronic structure, binding
- Formation energy, Dissociation pressure

→ Candidates of New H-storage alloys !

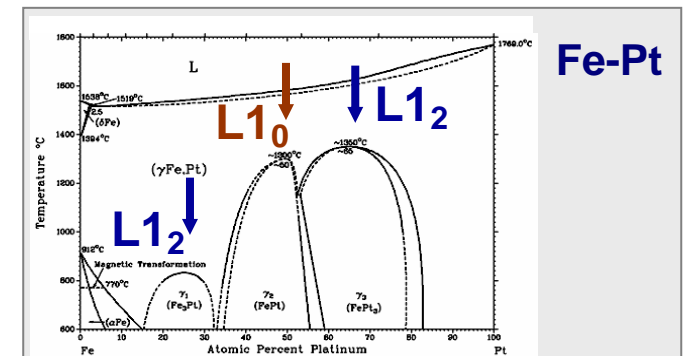
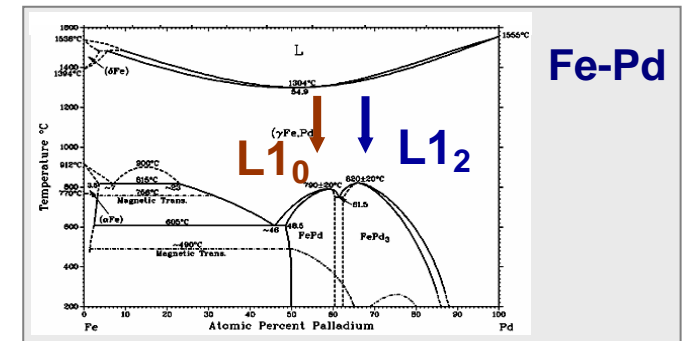
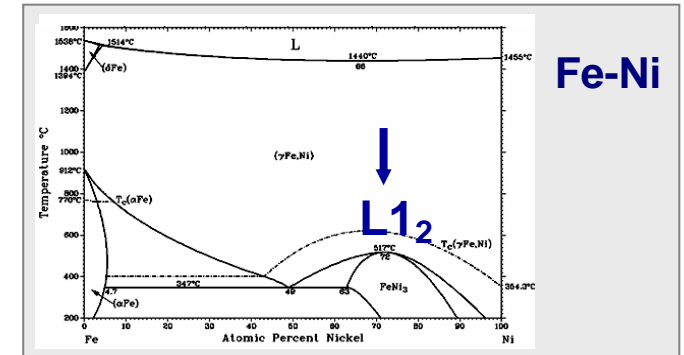


III-3 Phase Equilibrium of Fe-Pt, Pd, Ni

Periodic Table of the Elements

IA																		VIII																					
1																	2																			10			
H																	He																			4.0026			
3	4																		10																				18
Li	Be																		Ne																				20.17
6.94	9.0121																		18.998																				39.948
11	12																		18																				39.948
Na	Mg																		Ar																				39.948
22.989	24.305																		39.948																				39.948
19	20		IIIA		IVA		VA		VIA		VIIA		VIII		IB		IIB																				39.948		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																			39.948			
39.098	40.08	44.956	47.90	50.941	51.996	54.938	55.847	58.933	58.71	63.546	65.38	69.723	72.64	74.921	78.96	79.904	83.80																			39.948			
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																			39.948			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																			39.948			
85.467	87.62	88.906	91.22	92.906	95.94	98.906	101.07	102.90	105.4	107.86	112.41	114.82	118.66	121.76	127.60	129.90	131.30																			39.948			
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86																			39.948			
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																			39.948			
132.90	137.33	138.90	178.49	180.94	183.84	186.20	190.2	192.22	195.08	196.96	200.59	204.37	207.2	208.98	(209)	(210)	(222)																			39.948			
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118																			39.948			
Fr	Ra	Ac	Unq	Unp	Unh	Uno	Une	Unn	Unn	Unn	Unn	Unn	Unn	Unn	Unn	Unn	Unn																			39.948			
(223)	(226.02)	(227)	(261)	(262)	(263)	(262)	(265)	(266)	(272)																											39.948			

Lanthanide Series													
58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.90	144.24	(145)	150.4	151.96	157.25	158.92	162.50	164.93	167.26	168.93	173.04	174.96
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.03	231.03	238.02	237.04	(244)	(243)	(247)	(247)	(251)	(254)	(257)	(258)	(259)	(260)
Actinide Series													



Fe-Ni, Pd, Pt

- Systematic variation of phase stability
- L1₀: Mechanical, Magnetic properties

Objectives

- Phase stability: Reproducing, Origin?

Y. Chen, T. MOhri (2002-2005)

III. Example 3: First Principles Cal. of Phase Diagram

Atomic Information

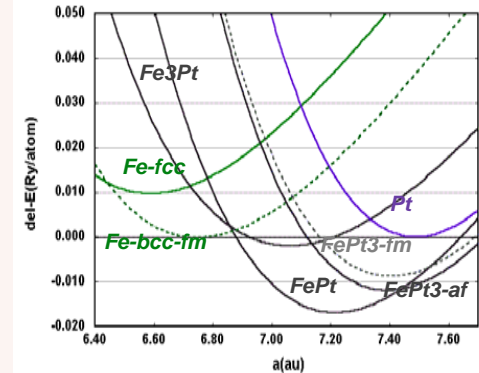
Internal Energy (First principles):

E

Cluster Expansion Method (CEM)

$$E^{(k)}(r) = \sum_{i=1}^m v_i(r) \cdot \xi_i^k$$

$$v_i = \sum_{k=0}^{m-1} \left\{ \xi_j^k \right\}^{-1} \cdot E^{(k)}$$



Thermodynamics: $F = E - T \cdot S$

$$F(T, V(r), \{\xi_i\}) = \sum_j v_j(V(r), \{\xi_i\}, T) - T \cdot S(\{\xi_i\})$$

Cluster Variation Method (CVM): S

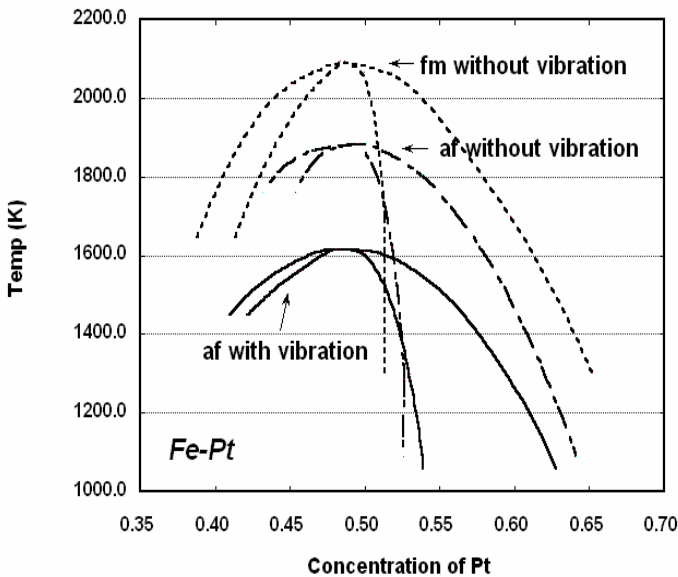
$$S = k_B \cdot \ln \frac{\prod_{i,j} \{N y_{ij}!\}^6 \cdot \{N!\}}{\prod_i \{N x_i!\}^5 \cdot \prod_{i,j,k,l} \{N w_{ijkl}!\}^2}$$

Phase
Equilibria,
Thermo-
dynamic
properties

III-3 Phase Equilibrium of Fe-Pt, Pd, Ni

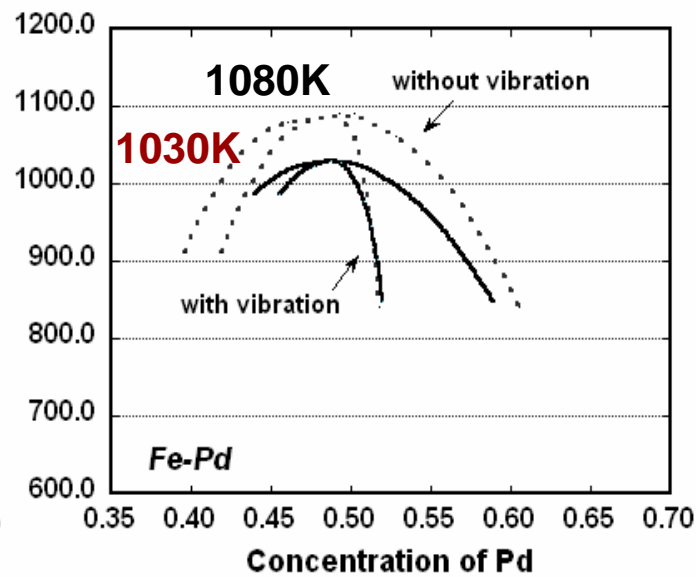
Phase Diagram: L10-disorder, Phase Separation

Fe-Pt



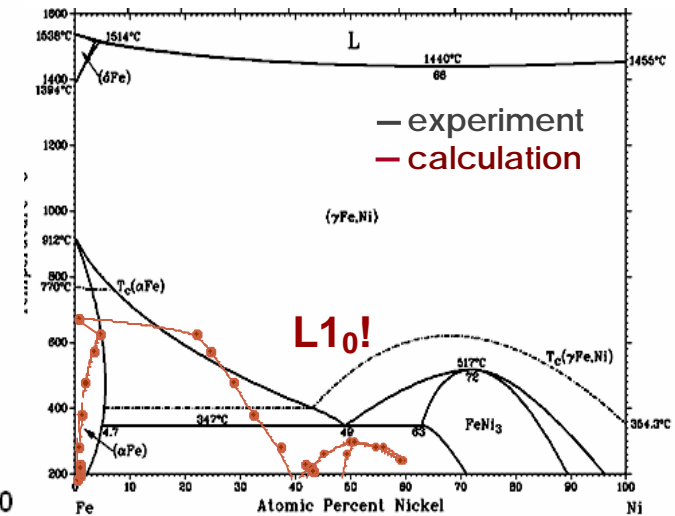
Experiment
1600K

Fe-Pd



Experiment
1023K

Fe-Ni



No L10 in exp. Phase diagram: Stable L10?
Exp.(1962), MC(1996): 590K~775K
Ohuma et al. ASM meeting 2004

IV. Summary

Interaction of Data & Modeling

Data Mining
→ Regularity

Modeling
→ Physical Origin





Thank you very much !

Element Properties (56 properties, ...182 data sets)

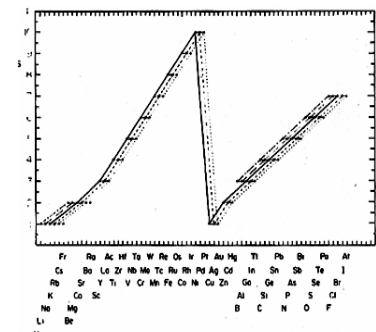
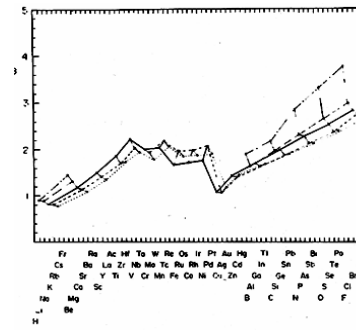
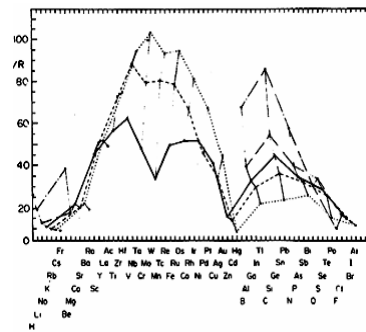
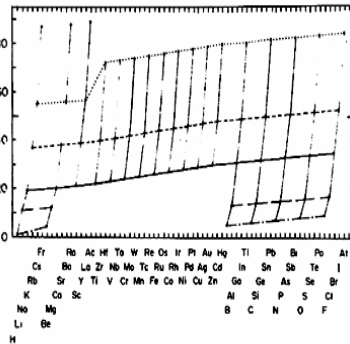
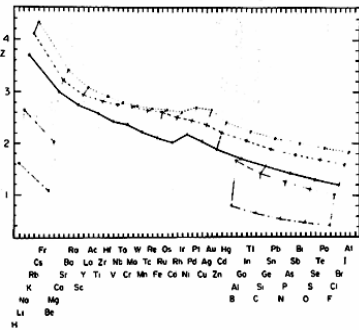
atomic number
atomic weight
density
molar volume
atomic energy level (Herman-Skillman)
valence electron number
atomic radius
Van der Waals radius
covalent radius
first ionic radius
second ionic radius
third ionic radius
metallic radius
Zunger pseudo-potential radius
Pauling electronegativity
Alfred-Rochow electronegativity
Martynov-Batsanov electronegativity
absolute electronegativity
first ionization energy
second ionization energy
third ionization energy
molar electronic affinity

Young's modulus
rigidity modulus
bulk modulus
Poisson's ratio
mineral hardness
Brinell hardness
melting temperature
Vickers hardness
boiling temperature
Debye temperature
thermal conductivity
molar heat capacity
coefficient of linear thermal expansion
atomization enthalpy
fusion enthalpy
vaporization enthalpy
electrical resistance
magnetic susceptibility
reflectivity
refractive index
...

**Optimal coordinate
for certain problem?**

Element property vs. Atomic number

- 5 Patterns
- 5 Element property groups
- 1 representative for 1 group



Size factor

Atomic No. factor

Cohesive energy factor

Electro-chemical factor

Valence electron factor

Zunger's pseudopotential radii (r_s, r_p, \dots)

Atomic No.

Atomization energy

Electro-negativity

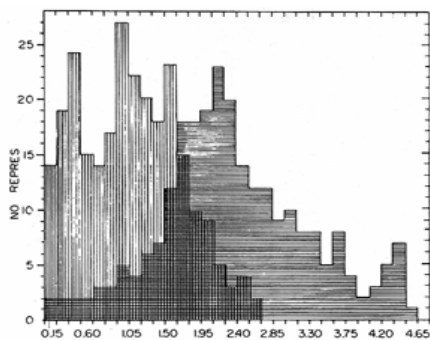
valence electron

Expression of compound property by element property

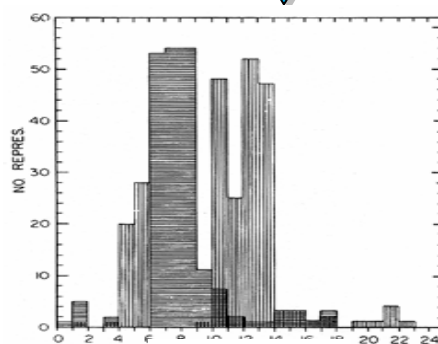
$$EP(\text{tot}) = EP(A) \text{ op } EP(B)$$

Operations		
	Sum	$EP(A)+EP(B)$
	Difference	$EP(A)-EP(B)$
	Product	$EP(A)*EP(B)$
	Ratio	$EP(A)/EP(B)$
	Maximum	$\text{Max}(EP(A),EP(B))$
	Minimum	$\text{Min}(EP(A),EP(B))$

Test separating capacity
for NaCl-type and CsCl-type structures

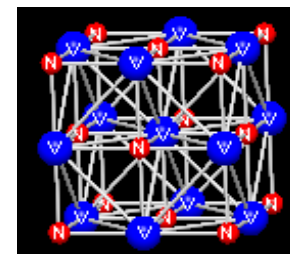


EP1(tot)

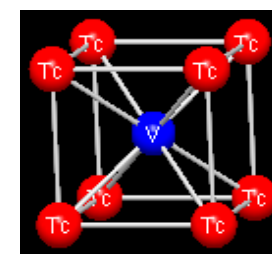


(c) EP2(tot)

 NaCl



 CsCl



31 Most common Atomic Environment Types (AETs)

