ICOSAHEDRAL ORDER:
The Link between Quasicrystals and Metallic Glasses

S. RANGANATHAN

Department of Materials Engineering
Indian Institute of Science
Bangalore, India

School on Glass Formers and Glasses
JNCASR, Bangalore
January 19, 2010

OUTLINE

- ❖THE SIZE FACTOR
- ❖PETTIFOR STRUCTURE MAPS
- ❖QUASICRYSTALS
- ❖THE SUPERTETRAHEDRON
- ❖EFFICIENT CLUSTER PACKING
- ❖BULK METALLIC GLASSES

INTERMETALLICS

- Zintl Phases
- Hume-Rothery Phases
- Frank-Kasper Phases

  - Chemical Compounds
  - Electron Compounds
  - Size factor Compounds

- **Where do Quasicrystals & Bulk Metallic Glasses fit in?**

Atomic Parameters in Phase Stability

W Hume-Rothery, 1926

1 SIZE

2 ELECTRONEGATIVITY

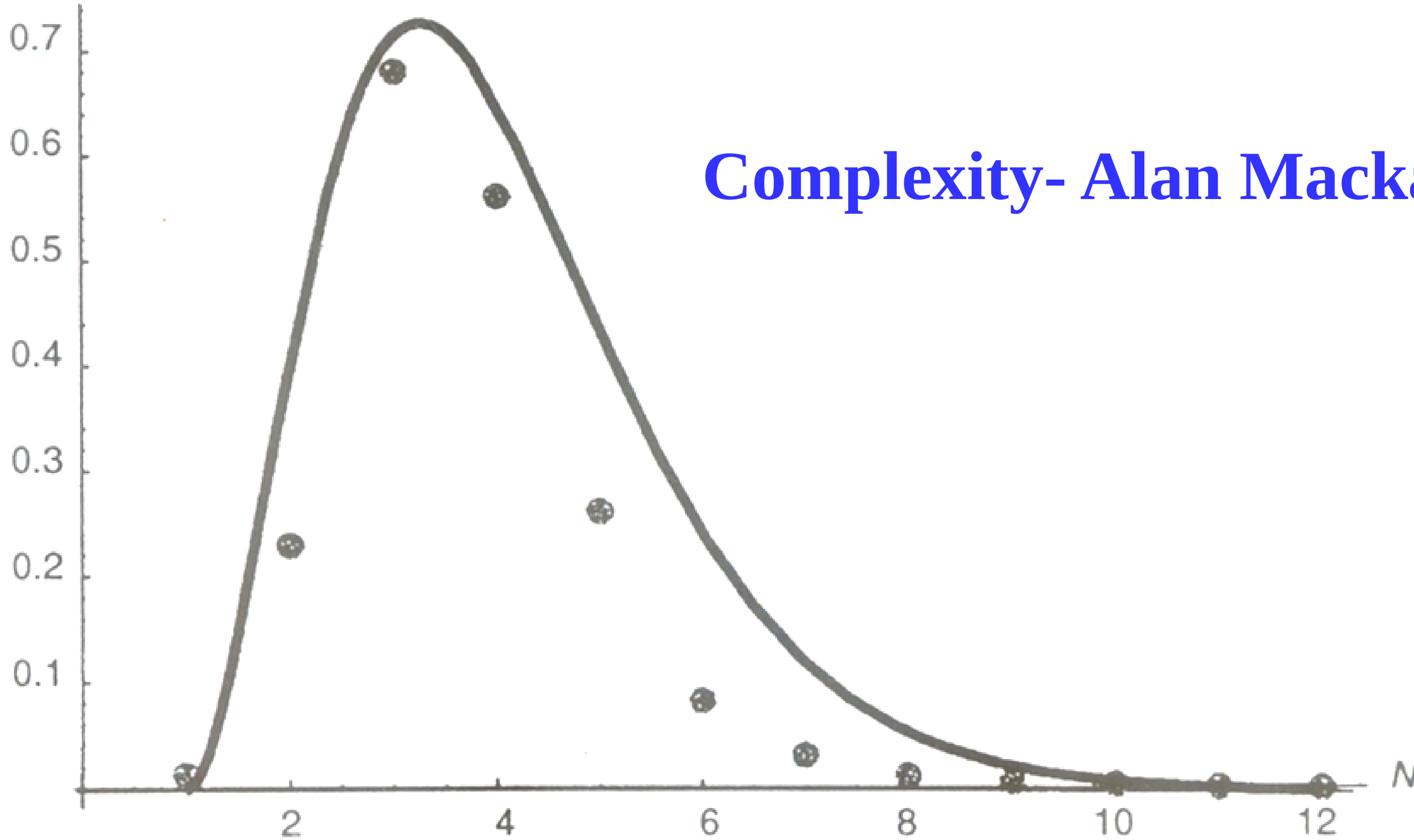
3 VALENCE ELECTRON CONCENTRATION

D Pettifor, 1984

4 BOND ORBITALS (s, p, d, f- orbitals)

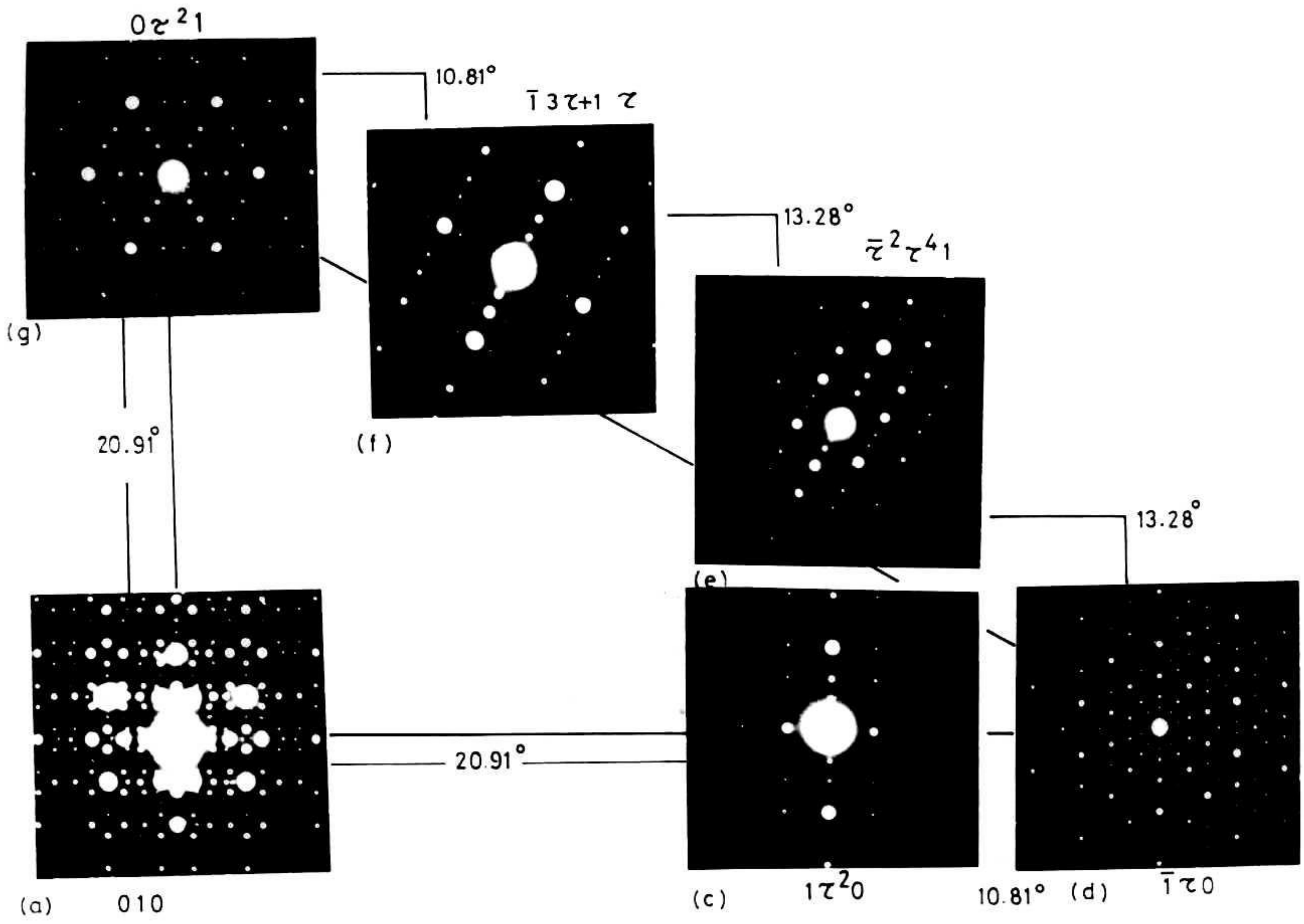
Distribution of Chemical Systems

Systems	Experimentally Known	Percent Known	Maximum Number
Unaries	100	100%	100
Binaries	4,000	81%	4,950
Ternaries	8,000	5%	161,700
Quaternaries	1,000	<1%	3,921,225



Complexity- Alan Mackay

Frequency distribution of inorganic crystal structures having N different elements



Electron diffraction patterns from a rapidly solidified Al-Mn alloy revealing Icosahedral symmetry

THE SIZE FACTOR

"My own view is that simple geometry…
. . atomic sizes. . . will prove to be the main criterion that in various subtle ways incorporates the others."

A. l. Greer & R.W. Cahn, 1991

- **Close packing of spheres of the same size**

- **Kepler's Conjecture in 1609**
- **David Hilbert highlighted efficient packing in a list of problems to guide mathematics in the 20th century**
- **Hales solution in 1997**

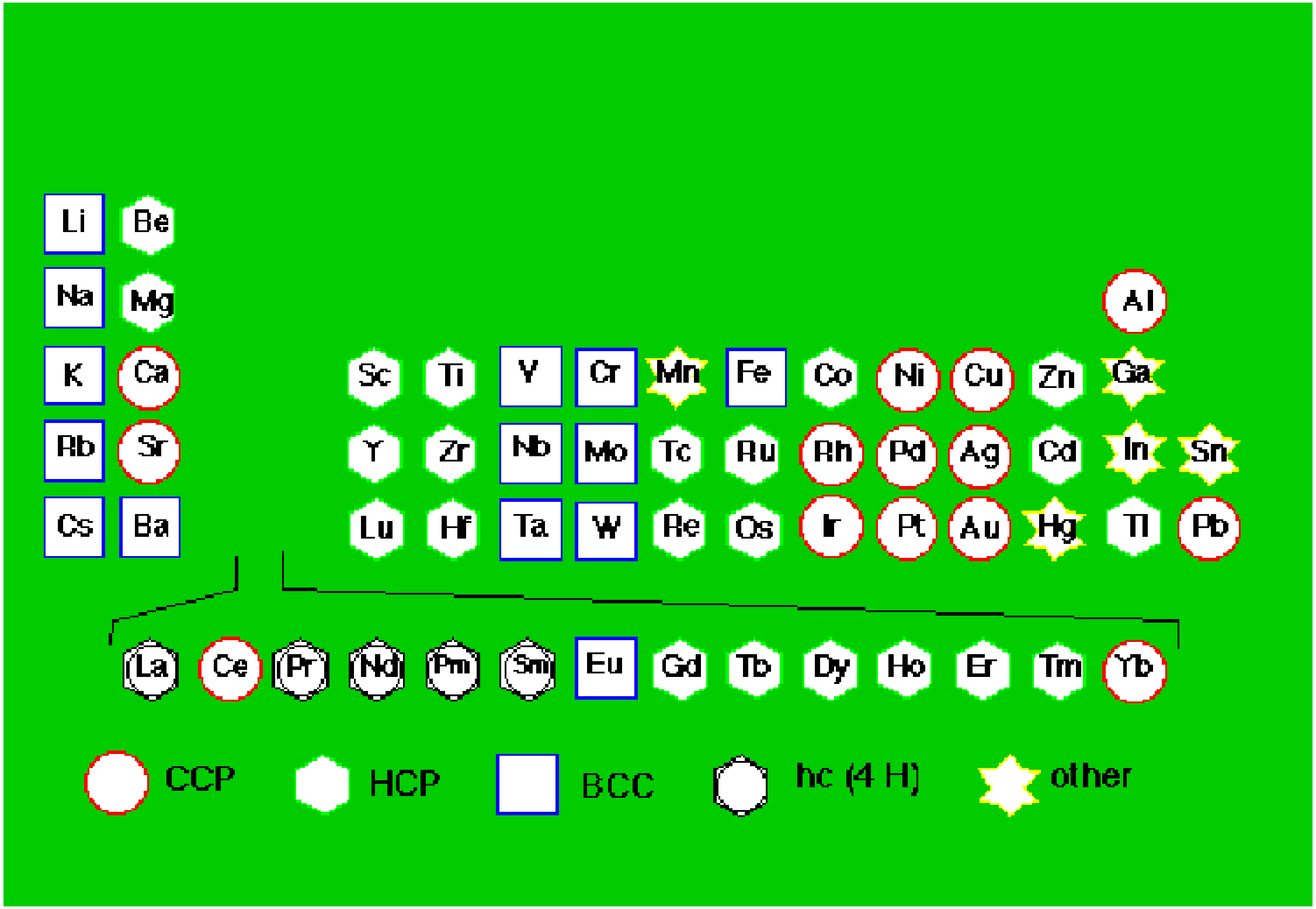
Spheres of Different Sizes

A major challenge

Structure of
Topologically close packed intermetallics
Quasicrystalline intermetallics
Metallic glasses
Bulk metallic glasses
Eutectic liquid compositions
Clusters
Colloidal Crystals
Nanosuperlattices

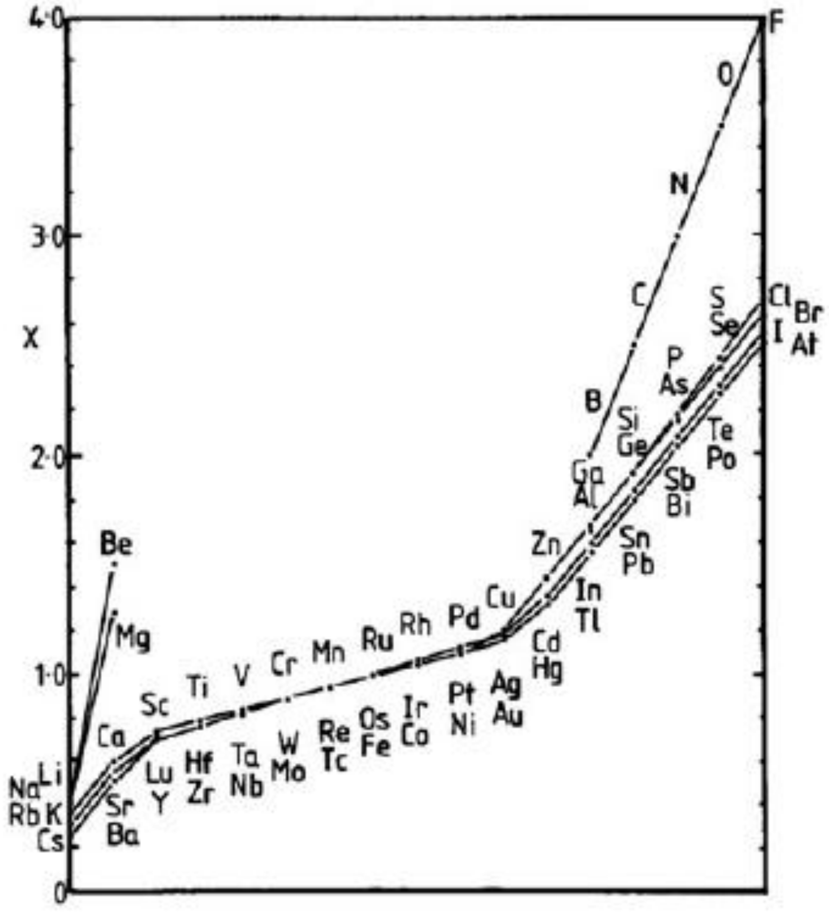
Frank 1952, Bernal 1959, Kasper 1959, Mackay 1977, Gaskell 1978, Egami 1984, Miracle 2003, Ma 2006

PERIODIC TABLE OF METAL STRUCTURE



Issue :Combination of topological and chemical identities

THE CHEMICAL SCALE



From David Pettifor (1984)
Note anomaly in places for Be & Mg

PETTIFOR MAP

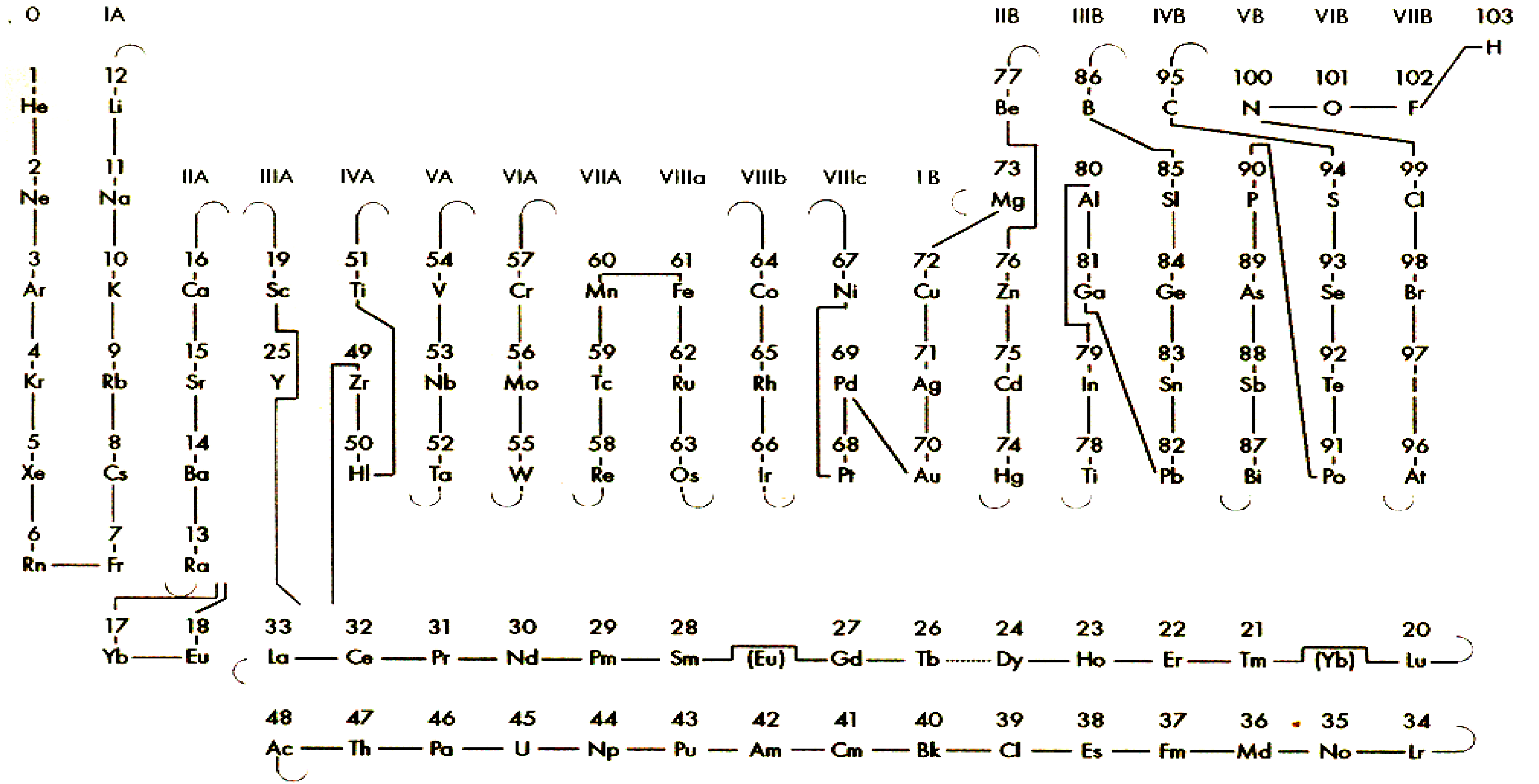
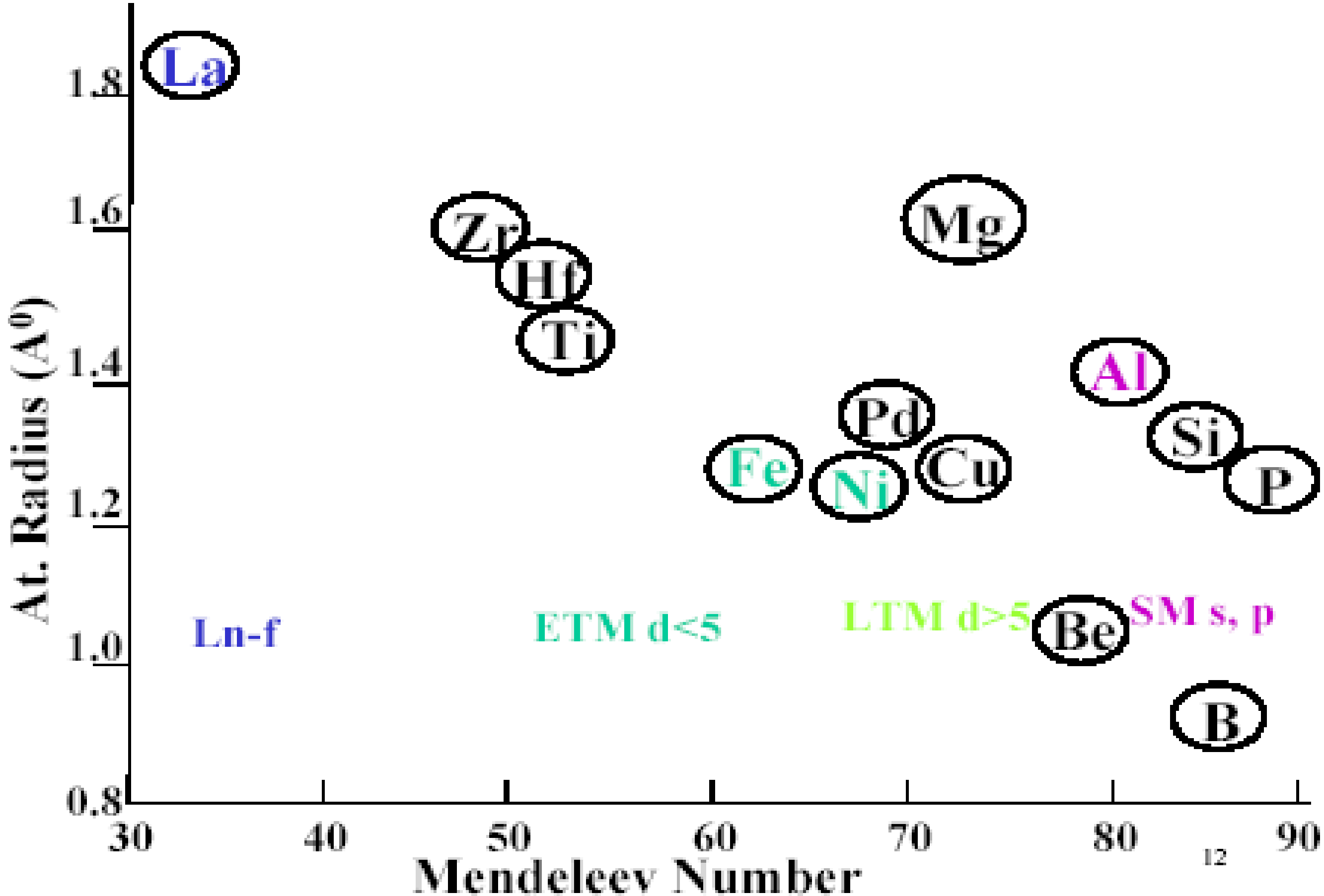


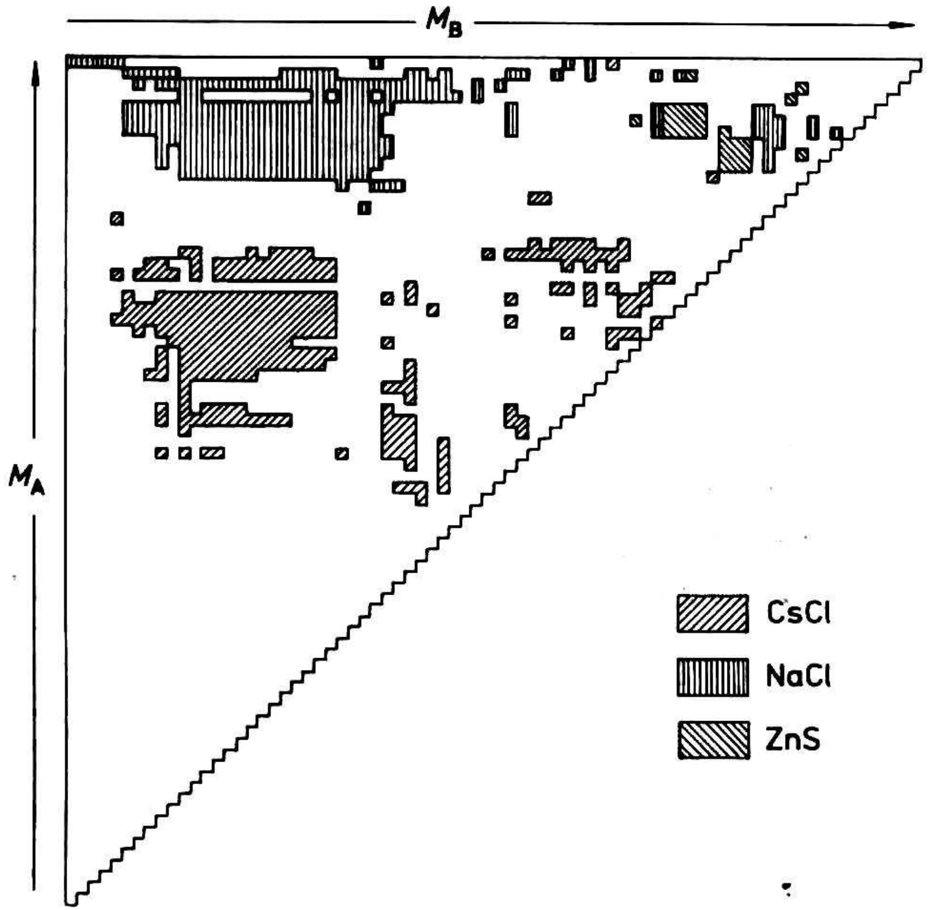
Figure 5: The string running through this modified periodic table puts all the elements in sequential order, thereby defining their Mendeleev number

Pettifor assignment of Mendeleev numbers to elements by using a string through the modified Periodic Table

Size versus Mendeleev Number



•



Pettifor map with Mendeleev number as the discriminator for AB type binary compounds

AB STRUCTURE MAP

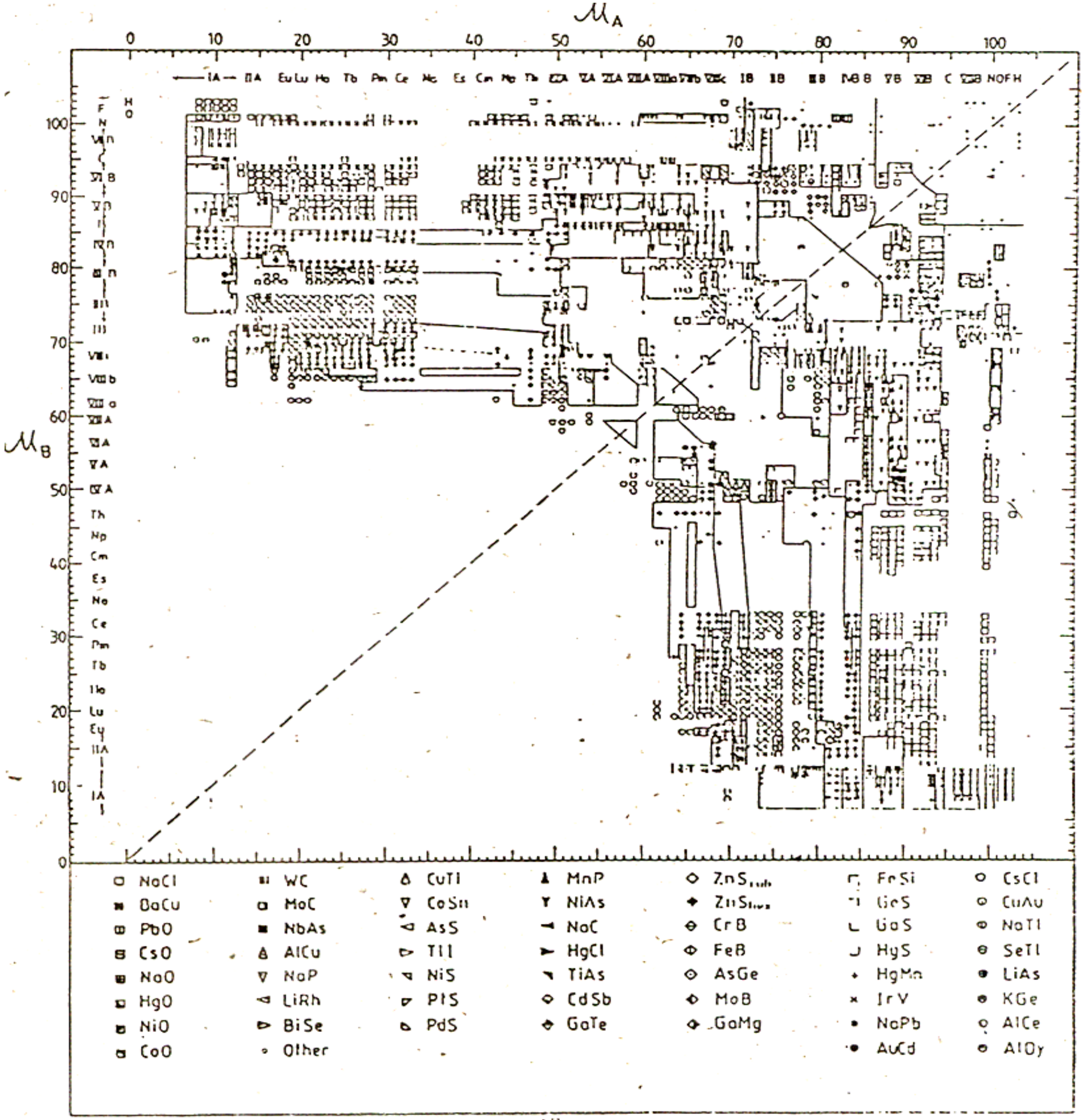


Figure 2-2. The AB structure map (Pettifor, 1988a).

Pseudo-Binary Intermetallics

If Ax By is considered as the binary alloy, a quaternary alloy with constituent atoms as A, B, C and D may be treated as a pseudo-binary

$(A_x C_{1-x})(B_y D_{1-y})$.

The average Mendeleev numbers M^*_A and M^*_B are given by

$$M^*_A = x M_A + (1-x) M_C$$

$$M^*_B = y M_B + (1-y) M_D.$$

Successfully applied so far only to AB and AB_3 compounds.
Our analysis extend to
to A_2B_3, A_5B_2 AB_2 and AB_6 stoichiometry and related quasicrystals and Laves Phases

CLASSIFICATION OF QUASICRYSTALS :

Majority Component versus Large Atom

Alloy	Discovery	Year	Majority Component	Large Atom
Al-Mn 14	Shechtman	1984 (1982)	Aluminium	Aluminium
Mg 36-Zn38-Al25	*Ramachandra Rao*	*1985*	*Zinc*	*Magnesium*
Mg38-Zn15-Cu5-Al42	*Ranganathan*	*1985*	*Aluminium*	*Magnesium*
Ti-V-Ni	Kuo	1985	Titanium	Titanium
Ga-Mn	Tartas	1985	Gallium	Gallium
Al60-Li30-Cu10	*Audier*	*1986*	*Aluminium*	*Lithium*
Ti40-Zr40-Ni20	Molokanov	1990	Zirconium	Zirconium
Zn60-Mg30-RE10	*Luo*	*1993*	*Zinc*	*Rare Earth*
Zr-Ni-Cu-Al	Koester	1996	Zirconium	Zirconium
Hf-Ni-Cu-Al	Inoue	2000	Hafnium	Hafnium
Cd65-Mg20-RE15	*Tsai*	*2000*	*Cadmium*	*Rare Earth*
Cd-Yb	*Tsai*	*2000*	*Cadmium*	*Ytterbium*
Zn80-Mg5-Sc15	*Ishimasa*	*2001*	*Zinc*	*Scandium*
Cu48-Ga34-Mg3-Sc15	*Ishimasa*	*2001*	*Copper*	*Scandium*
Ag38-In38-Mg8-Ca16	*Tsai*	*2001*	*Silver-Indium*	*Calcium*

Rational Approximants to Quasicrystals

The Colouring Problem

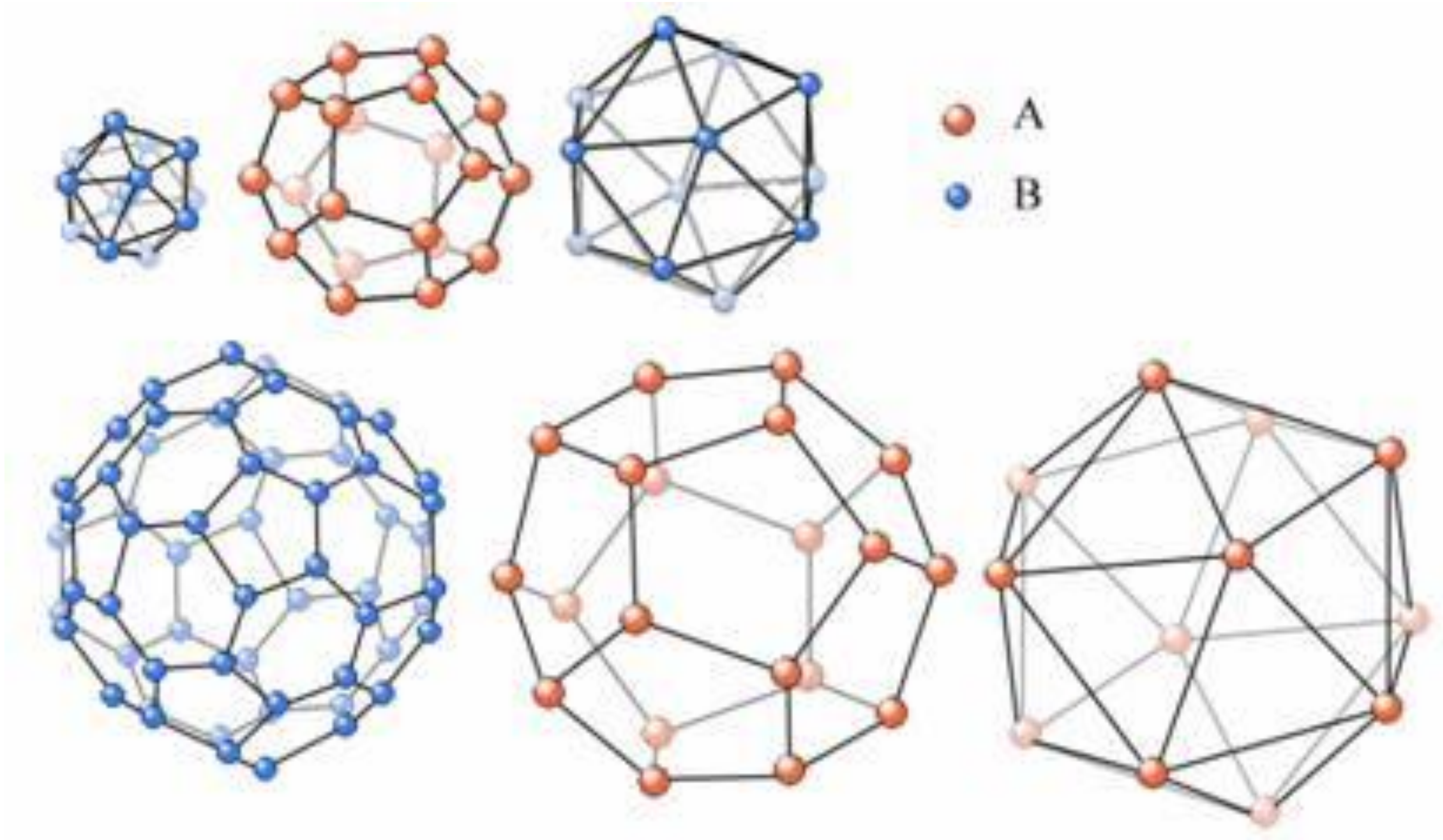
1. Bergman Approximant - Li, Mg

2 Mackay Approximant - Al. Ga

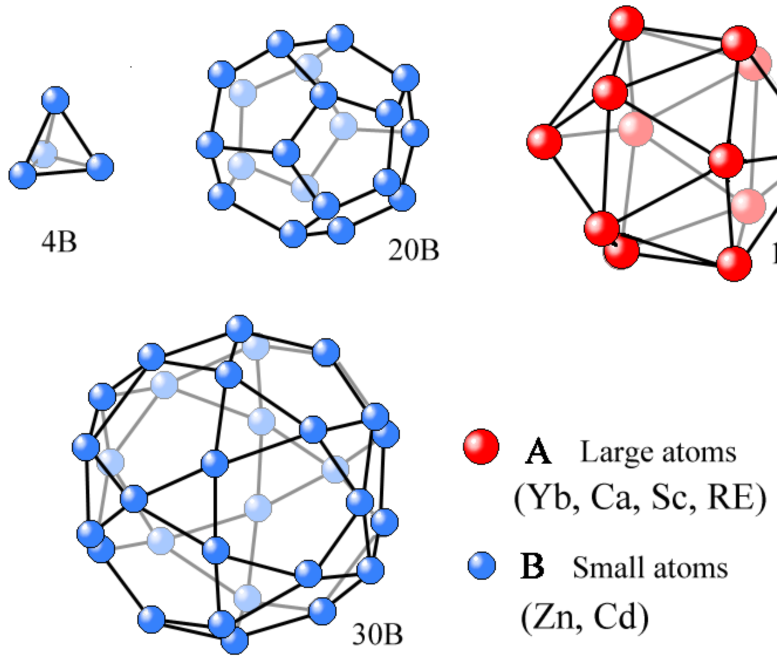
3 Kuo Approximant- Ti, Zr, Hf

4 Tsai Approximant- RE, Ca, Sc,

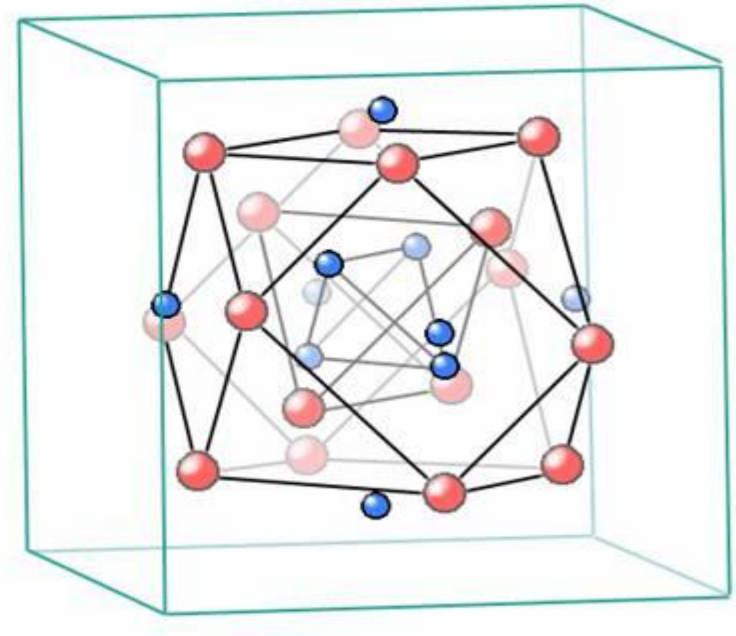
Bergman cluster



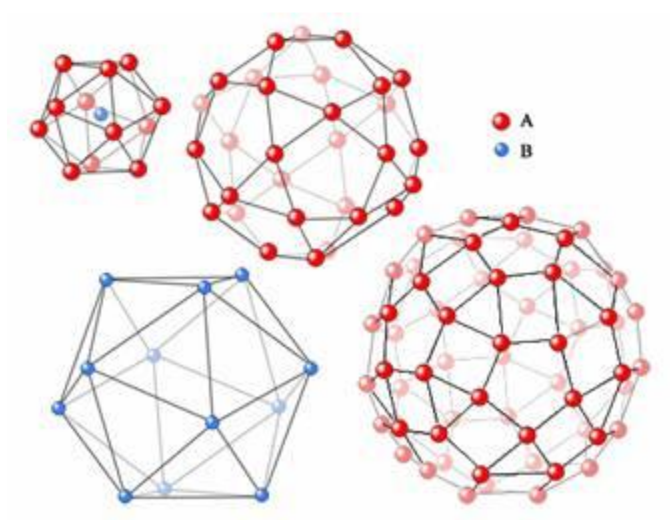
The Bergman Cluster with seven shells (117 atoms):
a central atom, surrounded by an icosahedron (12 atoms),
a dodecahedron (20 atoms), a second icosahedron (12 atoms),
a truncated icosahedron (60 atoms),
a dodecahedron (20 atoms) and an icosahedron (12 atoms).



Tsai

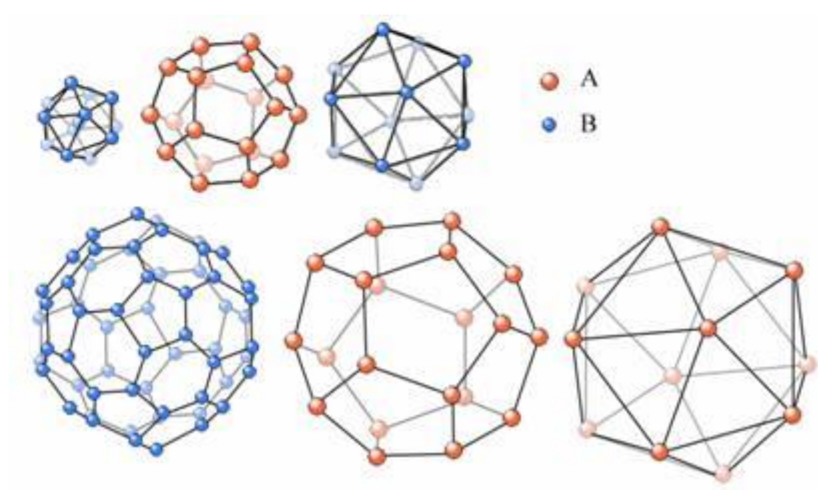


Kuo



Mackay

Acta Materialia, 2006



Bergman

QUASICRYSTALS
AS PSEUDO-BINARY INTERMETALLICS

	Bergman Class	Mackay Class	Kuo Class	Tsai Class
Binary	**---**	**Al-Mn**	**Ti-Ni, Zr-Pd**	**Cd-Yb, Cd-Ca**
Ternary	**Mg-(Zn, Al)** **Mg(Cu, Al)** **Mg(Zn, Ga)** **Li-(Cu,Al)**	**Al-(Cu,Fe)** **Al(Pd, Mn)**	**Ti-Zr-Ni** **Ti-Hf-Ni**	**Cd-Mg-RE** **Zn-Mg-RE** **Zn-Mg-Sc**
Quaternary	**Mg-(Cu,Zn, Al)** **Mg-(Zn, Al, Ga)** **(Li,Mg)-(Zn,Al)**	**(Al,Ga)-(Pd, Mn)** **Al-(Pd, V,Co)**	**Ti-Zr-Ni-Cu**	**Cu-Ga-Mg-Sc** **Ag-In-Mg-Cd** **(Zn, Mg)-(RE1,RE2)**

1: 2 Stoichiometry
& R ` 1.225

Laves Phase AB_2

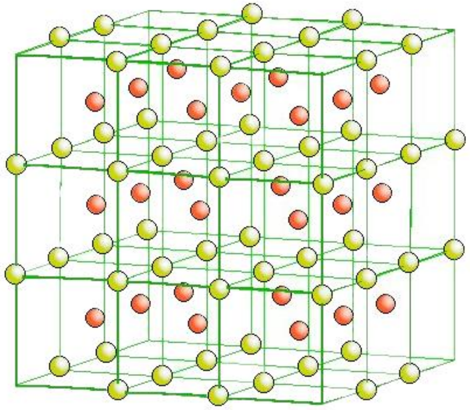
Anti-Laves Phase A_2B (Giessen glasses)

Atomic environment Laves phase CN 16 and CN12
anti-Laves phase CN 15 and 10

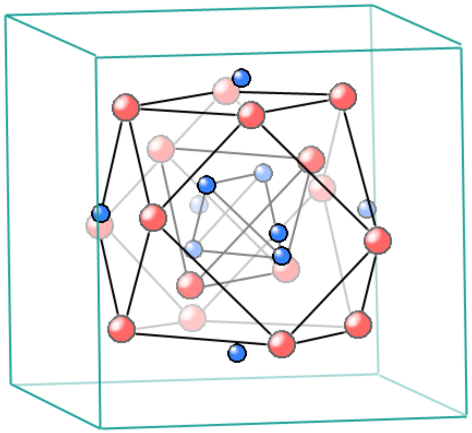
Average coordination number of both is 13.33!

The supertetrahedron as a common building block
Dong -2004

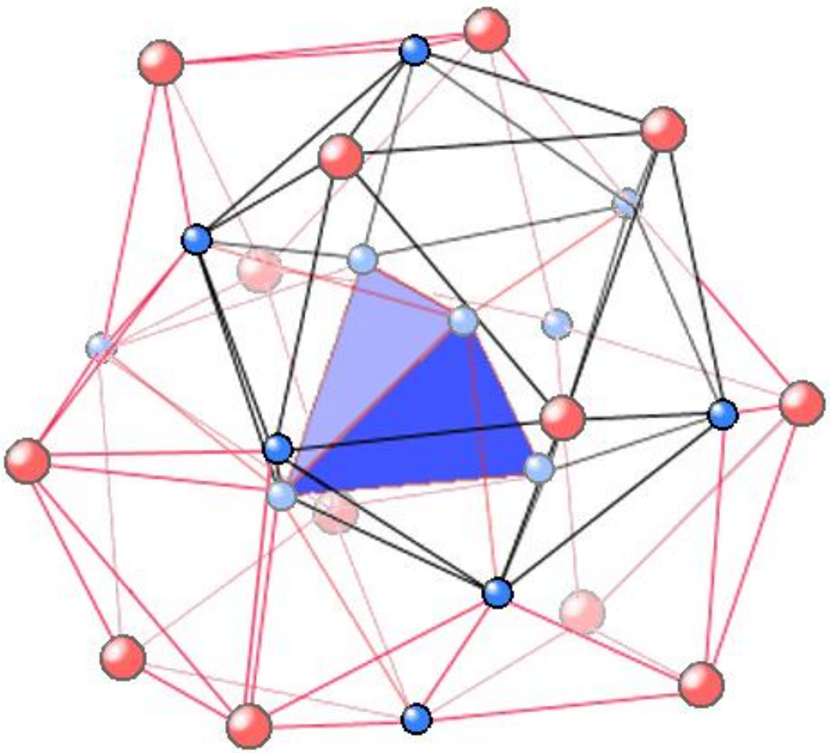
Gamma brass



1928 Bradley & Thewlis
Modified B2

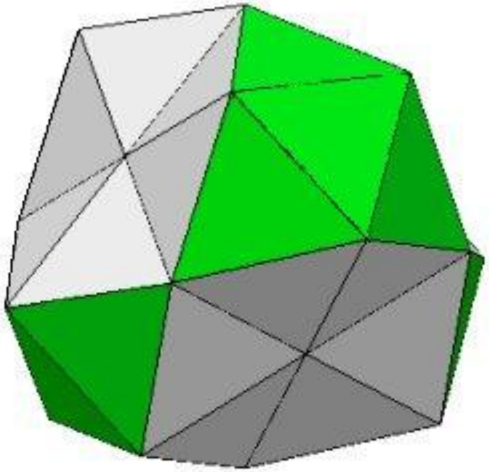


1933 Bradley & Jones
Nested polyhedra

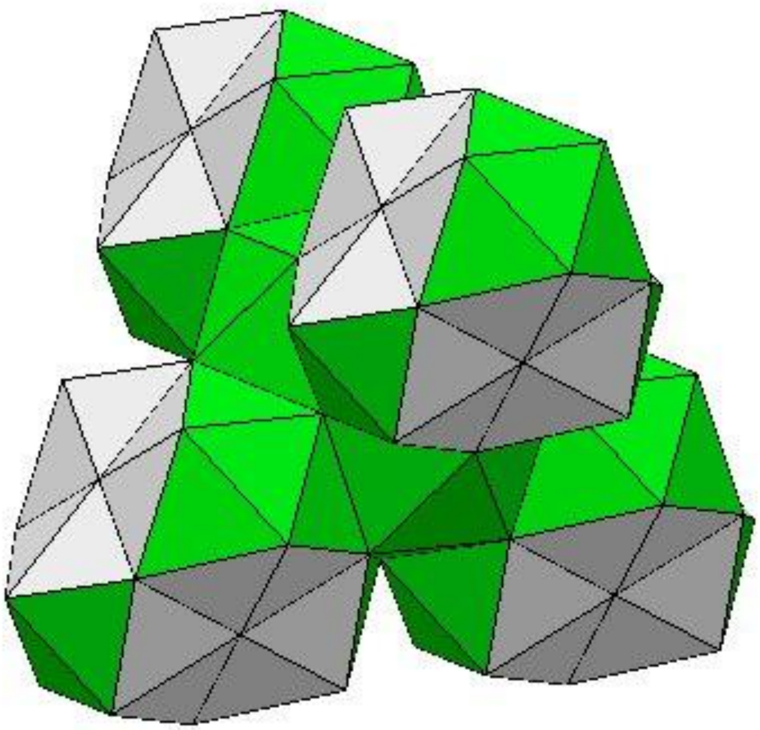


Supertetrahedron
Four interpenetrating icosahedra

Anti-Laves phase



A_2B (Ti_2Ni, Zr_2Ni etc)

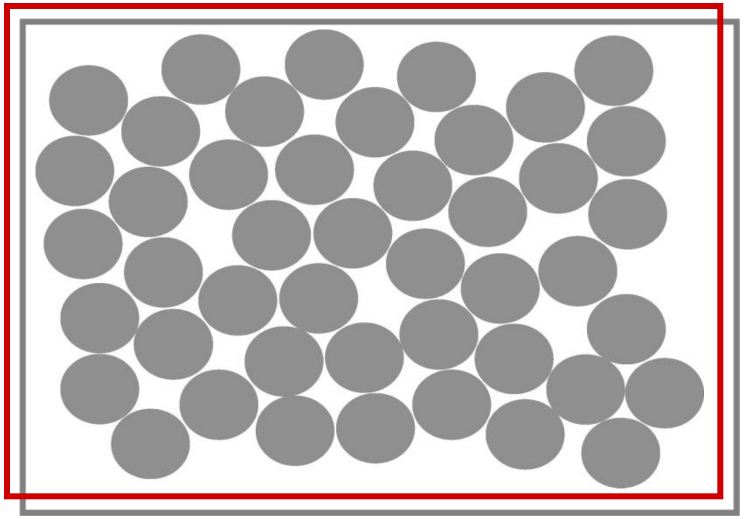


Supertetrahedra sharing atoms to form a 'diamond-type' network

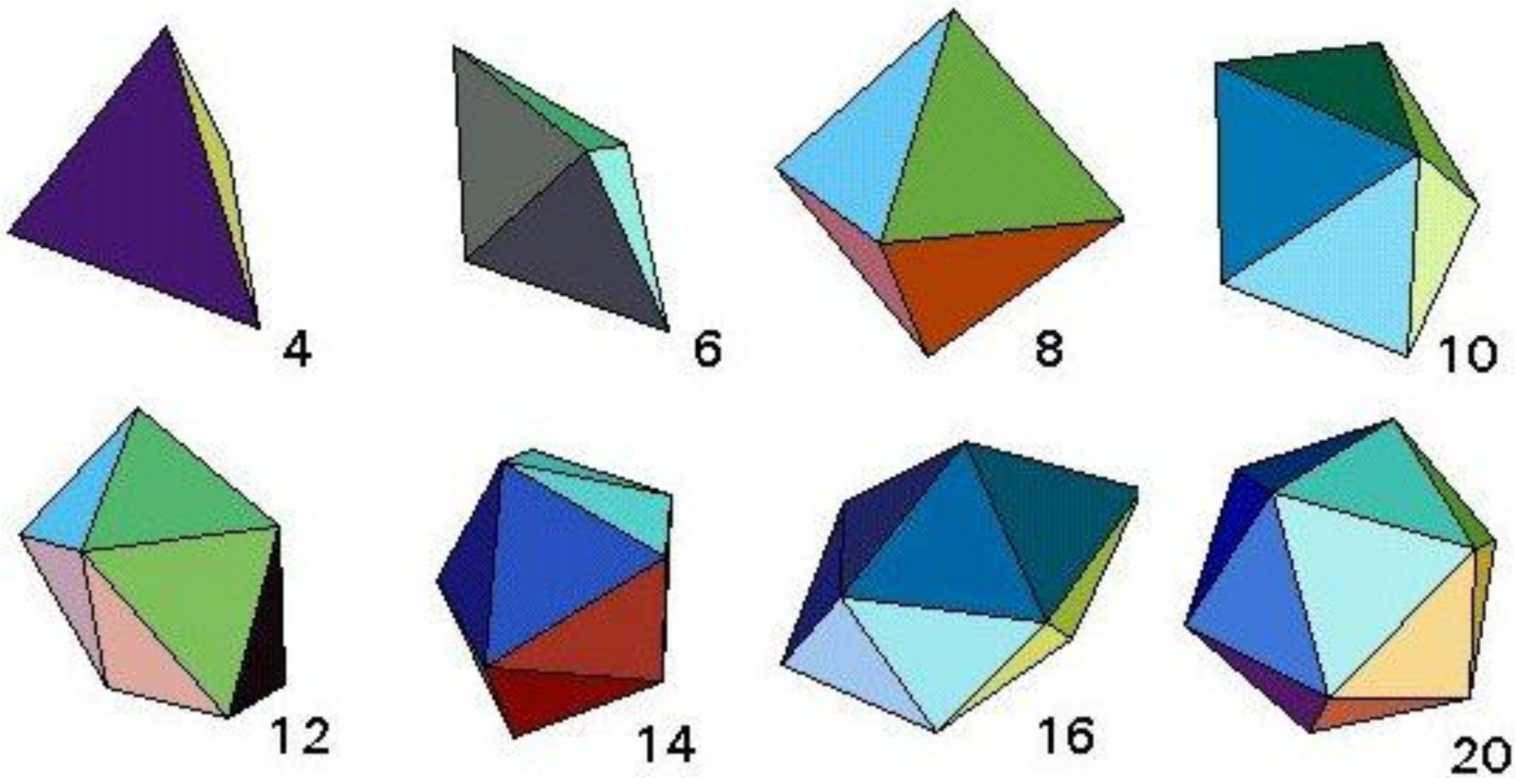
DENSE RANDOM PACKING

A Statistical Model

- A dense random packed structure of equal-sized spheres is characterized by:
  - a packing fraction of 0.6366
  - frequently observed specific local atomic clusters
    - tetrahedra, half-octahedra, trigonal prisms, Archimedian antiprisms, tetragonal dodecahedron
  - the absence of medium-and long-range order



Miracle 2004

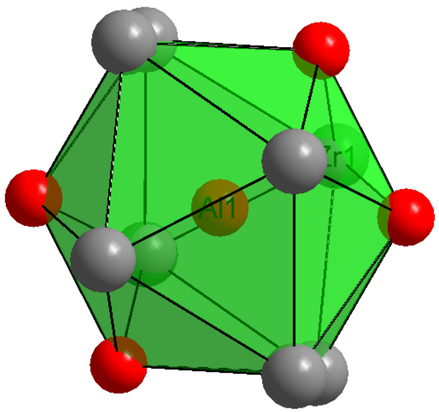


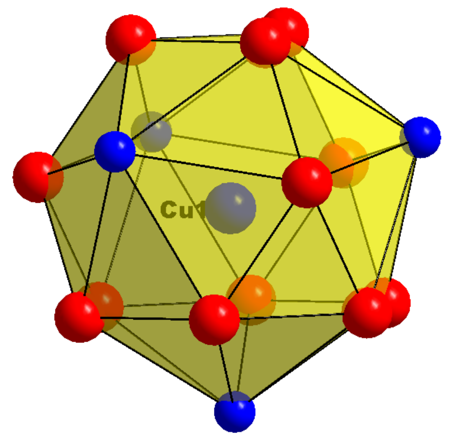
The eight Bernal convex deltahedra

Bernal; *Nature*, **185**, (1959)

FRANK-KASPER PHASES

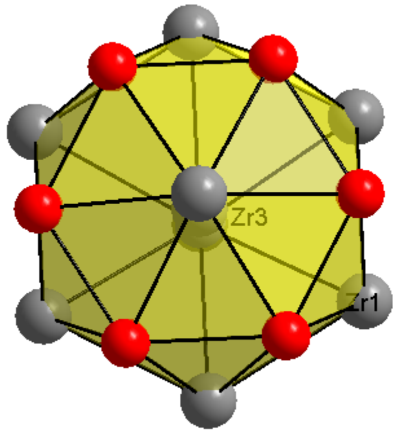
CN 12

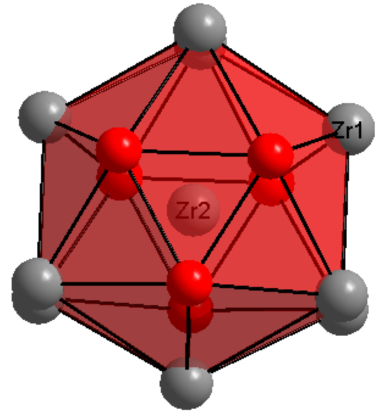




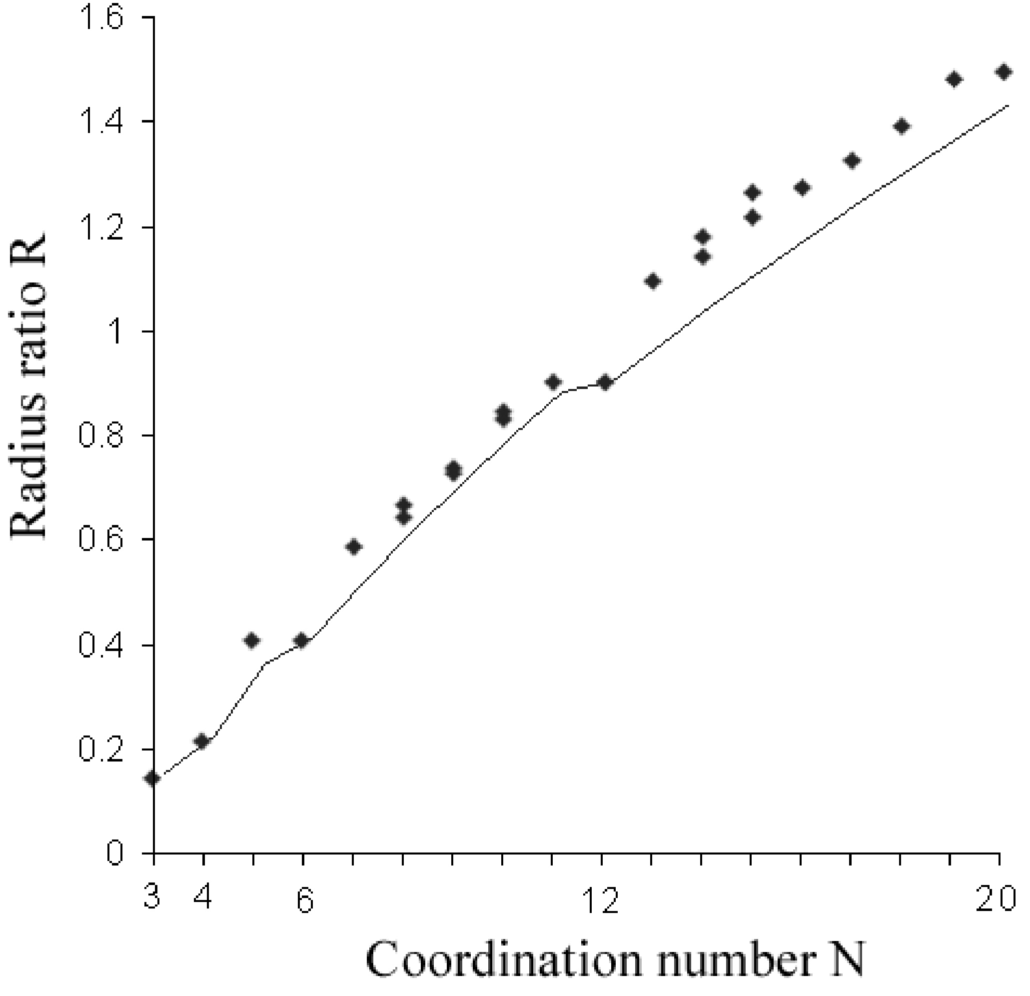
CN 16

CN 14



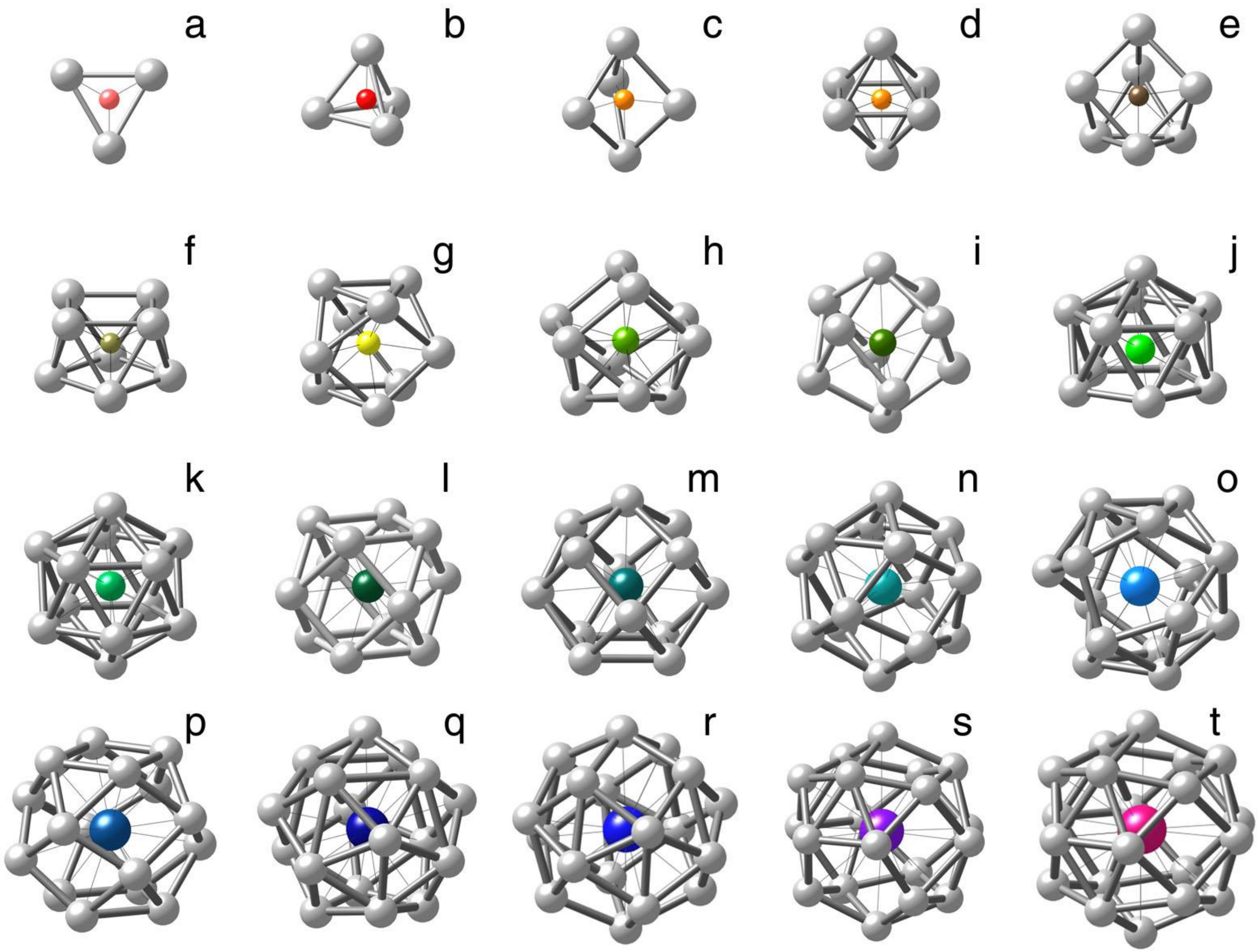


CN 15



Radius ratios of hard sphere clusters with $3 \leq N \leq 20$
The solid line is an idealized relation from Miracle et al (2003) shown for comparison

CANDIDATE EFFICIENTLY PACKED ATOMIC CLUSTERS



Miracle, Lord and Ranganathan; *"Candidate Atomic Cluster Configurations in Metallic Glass Structures"*

STRUCTURAL MODELS

□ β and γ solutes form efficiently packed clusters with Ω atoms only in the 1st coordination shell

- these clusters overlap with α clusters in the 1st coordination shell
- β and γ clusters form regular arrays within the DCP structure

Miracle, D. B. *Nature Mater.* **3**, 697−702 (2004).

<12-10-9> Glass

<17-12-10> Glass

ISMANAM2006
August 27-31, 2006

Analysis of Composition Dependence of Formation of Ternary Bulk Metallic Glasses from Crystallographic Data on Ternary Compounds

A. Takeuchi [a], **S. Ranganathan** [b], **B.S. Murty** [c] **and A. Inoue** [a]

[a] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

[b] Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India

[c] Dept. Metal. Mater. Eng., Indian Institute of Technology, Madras, Chennai 600 036, India

Audience Hall, Bulk Metallic Glasses (1), August 28, 2006, 10:15~10:30

Outline

1. Introduction

1-1. Early studies on stabilization of glassy phase, bulk metallic glasses (BMGs)

1-2. Purpose

2. Methods

2-1. Seven classes of BMGs (C-1~C-7): chemical species

2-2. Three types of BMGs (L-,M-,S-type): relative atomic size of the main constituent (**L**arge, inter**M**ediate, **S**mall) in ternary alloys

2-3. **L-M-S composition diagram**

2-4. Data source

3. Results and Discussion

3-1. L-M-S composition diagram for ternary compounds

3-2. Representative compounds

3-3. L-M-S composition diagram for BMGs and representative compounds

4. Summary

(2) Stabilization of glassy phase ← stoichiometory of compounds

- W. Hume-Rothery and E. Anderson, Phil. Mag., 5 (1960), 383-405.

  A:B = 1:6, 1:3, 1:2, 2:3 ← **eutectic compositions** ← binary phase diagram by Hansen (1958))

  $A_{12}B$ ← Frank **icosahedral** unit

- R.St. Amand and B.C. Giessen, Scripta Metall., 12 (1978) 1021-1026.

  Ca-based metallic glasses: ← **anti-Laves composition** ← **A_2B** (Laves phase)

Absence of systematic researches on the formation of ternary **BMGs** based on crystallographic data

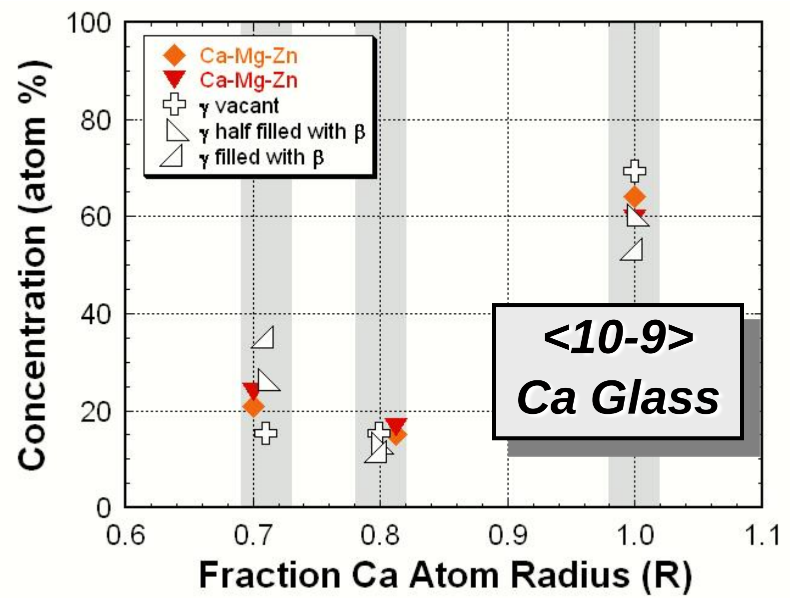
Crystallographic data on ternary compounds ← **Ternary phase diagram**

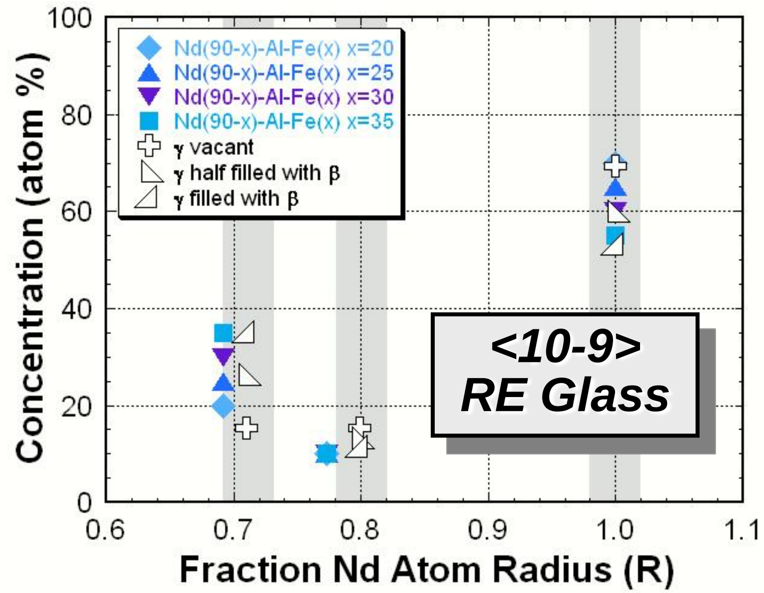
- crystalline structure (local atomic arrangements of BMGs)
- stoichiometry of compounds

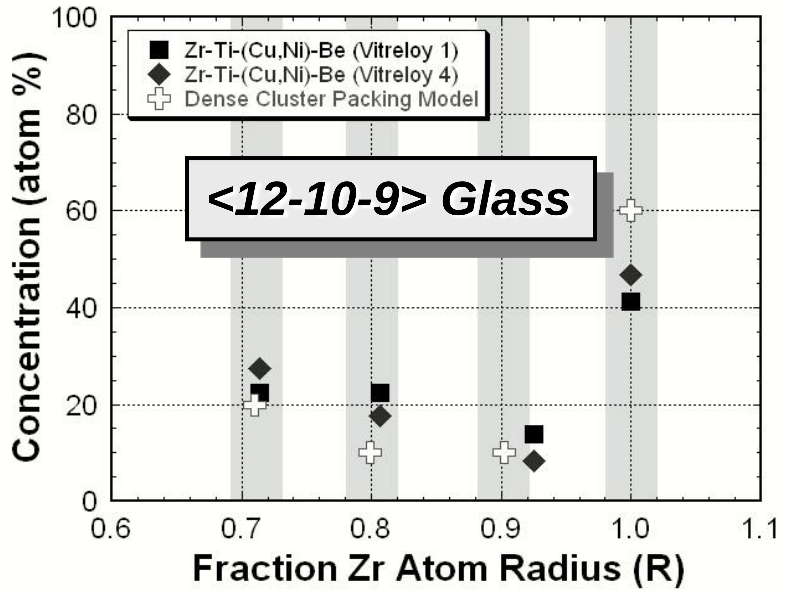
↓ ← Classification of BMGs: 2-1, 2-2

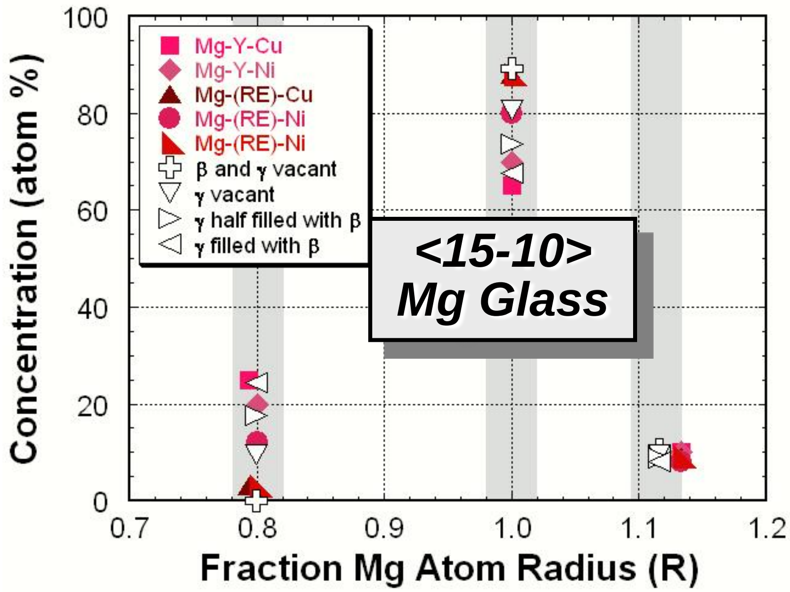
To identify **general trends** of composition dependence of formation of ternary **BMGs**

ALLOY COMPOSITIONS
Ca, RE, Zr, Mg *Glasses*

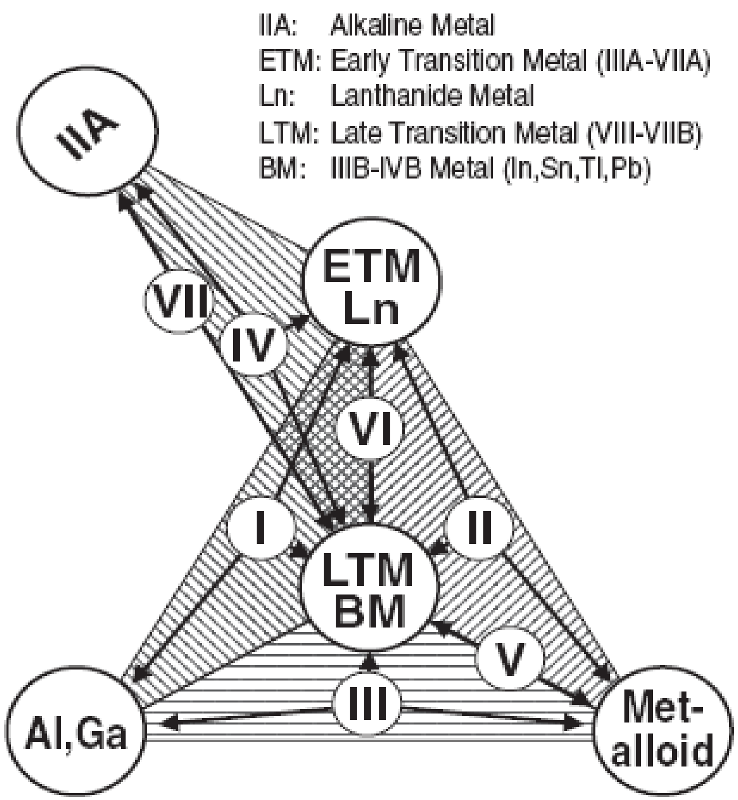








Classification of Bulk Metallic Glasses



I	Zr-Al-Ni, Ln-Al-Ni
	Zr-Al-Cu, Ln-Al-Cu
	Zr-Al-Ni-Cu, Ln-Al-Ni-Cu
	Zr-Ti-Al-Ni-Cu
	Zr-Ga-Ni, Ln-Ga-Ni Ln-Ga-Cu
II	Fe-Zr-B, Fe-Hf-B
	Fe-Zr-Hf-B
	Fe-Co-Ln-B
	Co-Zr-Nb-B
	Co-Fe-Ta-B
III	Fe-(Al,Ga)-Metalloid
IV	Mg-Ln-Ni, Mg-Ln-Cu
	Zr-Ti-Be-Ni-Cu
	Ti-Cu-Ni-Sn-Be
	Ti-Cu-Ni-Sn-Be-Zr
V	Pd-Ni-P
	Pd-Cu-Ni-P
	Pt-Ni-P
VI	Cu-Zr-Ti
	Ni-Nb-Ta, Ni-Nb-Sn
	Ti-Zr-Cu-Ni
	Ti-Ni-Cu-Sn
	Ti-Cu-Ni-Mo-Fe
VII	Ca-Mg-Cu
	Ca-Mg-Zn

A Inoue Acta Mater 2001

Five chemical types, Five ternary groups

A Takeuchi & A Inoue Mater Trans 2005

Five slightly different chemical types, Seven groups

2．Methods

2-1. Seven classes of BMGs (C-1~C-7)* : combinations of class of constituents

Class of BMGs

*A. Takeuchi and A. Inoue: Mater. Trans., 46 (2006), 2817-2829.

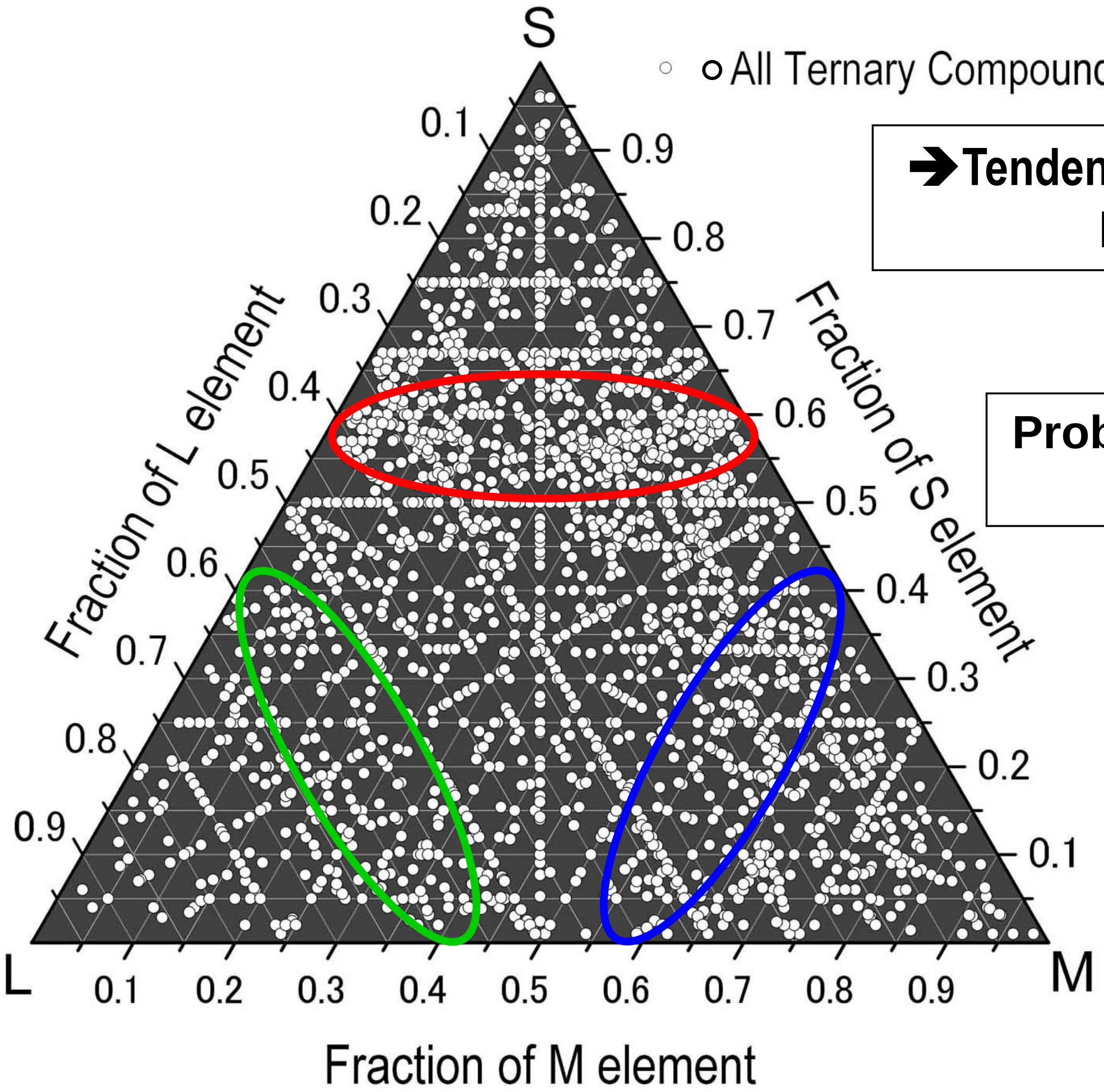
Class	Representative alloy system	Combinations of class of constituents
C-1	**La**-Al-Ni, **Zr**-Al-Ni	(ETM,Ln)-(Al,Ga)-(LTM,BM)
C-2	**Fe**-Zr-B	(LTM,BM)-(ETM,Ln)-(Metalloid)
C-3	Fe-(Al,Ga)-Metalloid	(LTM,BM)-(Al,Ga)-(Metalloid)
C-4	**Mg**-Cu-Y	(IIA)-(LTM,BM)-(ETM,Ln)
C-5	**Pd**-Ni-P	(LTM,BM)-(Metalloid)
C-6	**Cu**-Zr-Ti	(LTM,BM)-(ETM,Ln)
C-7	**Ca**-Mg-Cu	(IIA)-(LTM,BM)

Class of constituents

IIA:	Alkaline Earth Metal	(Be,Mg,Ca)
ETM:	Early Transition Metal (IIIA-VIIA)	(Zr,Ti,Nb,…)
Ln:	Rare Earth Metal	(La,Nd,Gd,…)
LTM:	Late Transition Metal (VIII-VIIB)	(Fe,Co,Ni,…)
BM:	B-group Metal(IIIB-IVB)	(In,Sn,Pb,…)
Metalloid:		(P,C,B,Si,Ge)
Al,Ga:		

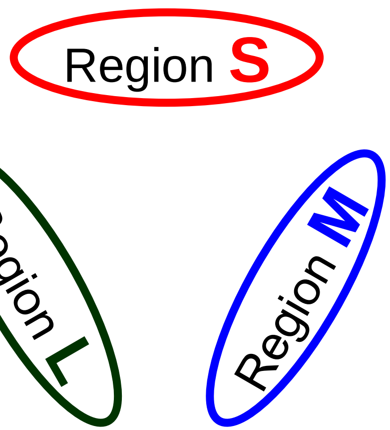
3．Results and discussion

3-1. L-M-S composition diagram for ternary compounds

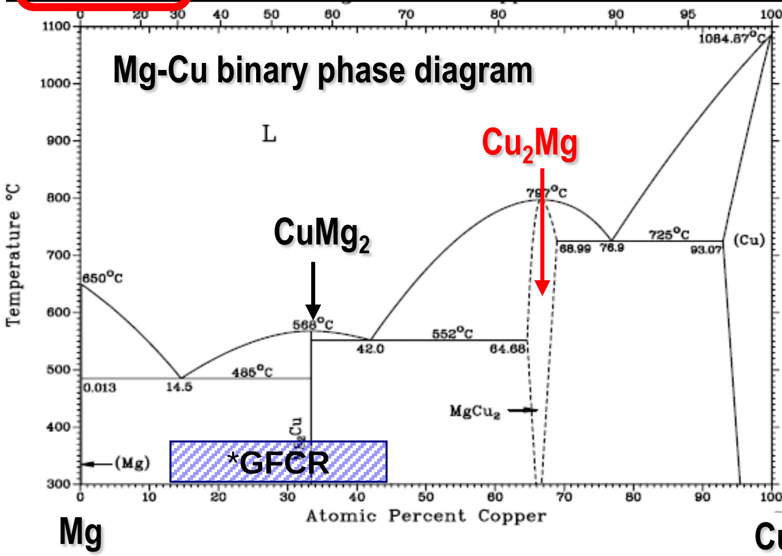


➔Tendency to form <u>ternary compounds</u>
Region: L < M < S

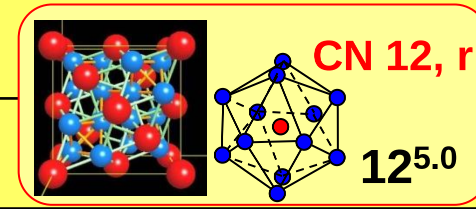
Probability to form <u>glassy phase</u>
Region: L > M > S



Cu_2Mg: Laves /Anti-Laves relationship



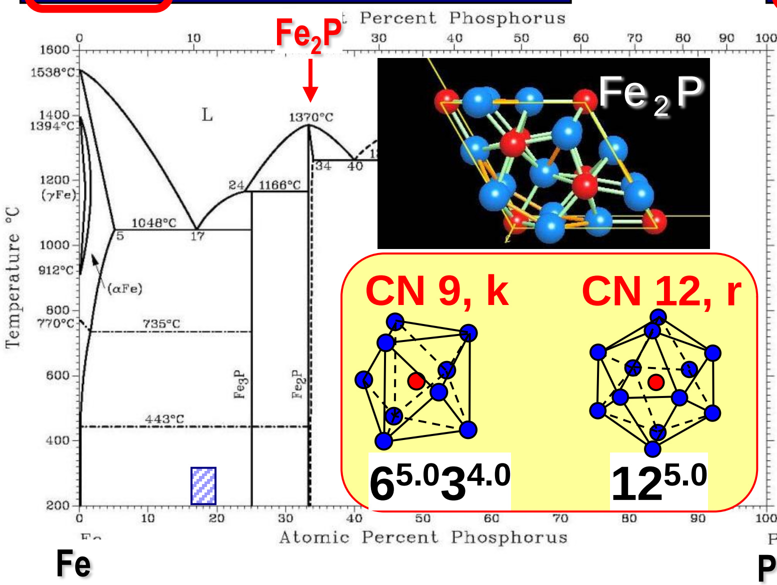
Compound	$CuMg_2$	Cu_2Mg
Crystal structure, Feature	Orthorombic	A prototype of Cubic **Laves-phase**, High melting temp.
GFCR*	**Inside**	Outside
The No. comp. in ternary system	5	474
Description with atomic size**	SL_2	S_2L



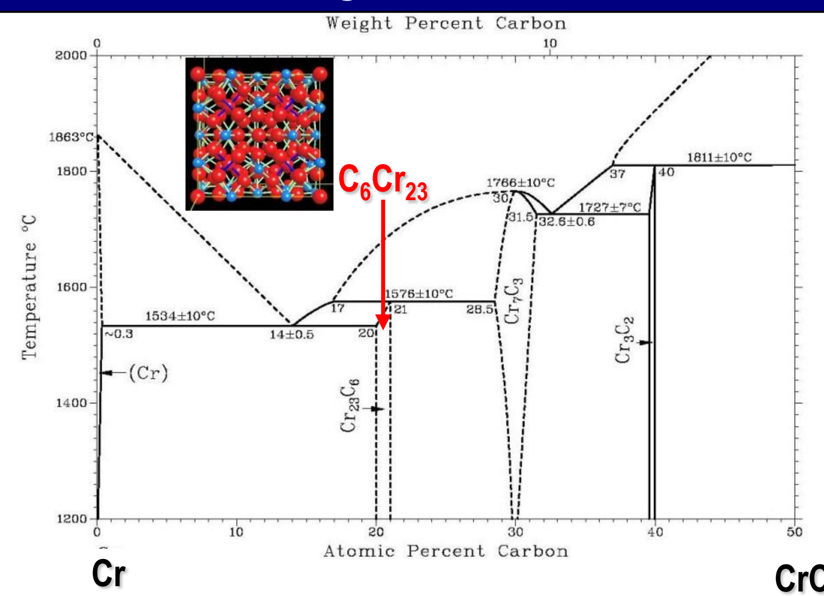
*GFCR from "Guide for amorphous alloy formation", eds. U. Mizutani, Agne Tech. Center （1987）.

* **GFCR**: **G**lass-**F**orming **C**omposition **R**egion
**Atomic radius ： Mg(0.160 nm),Cu(0.128 nm), "Metal Databook", Marzen（2004）

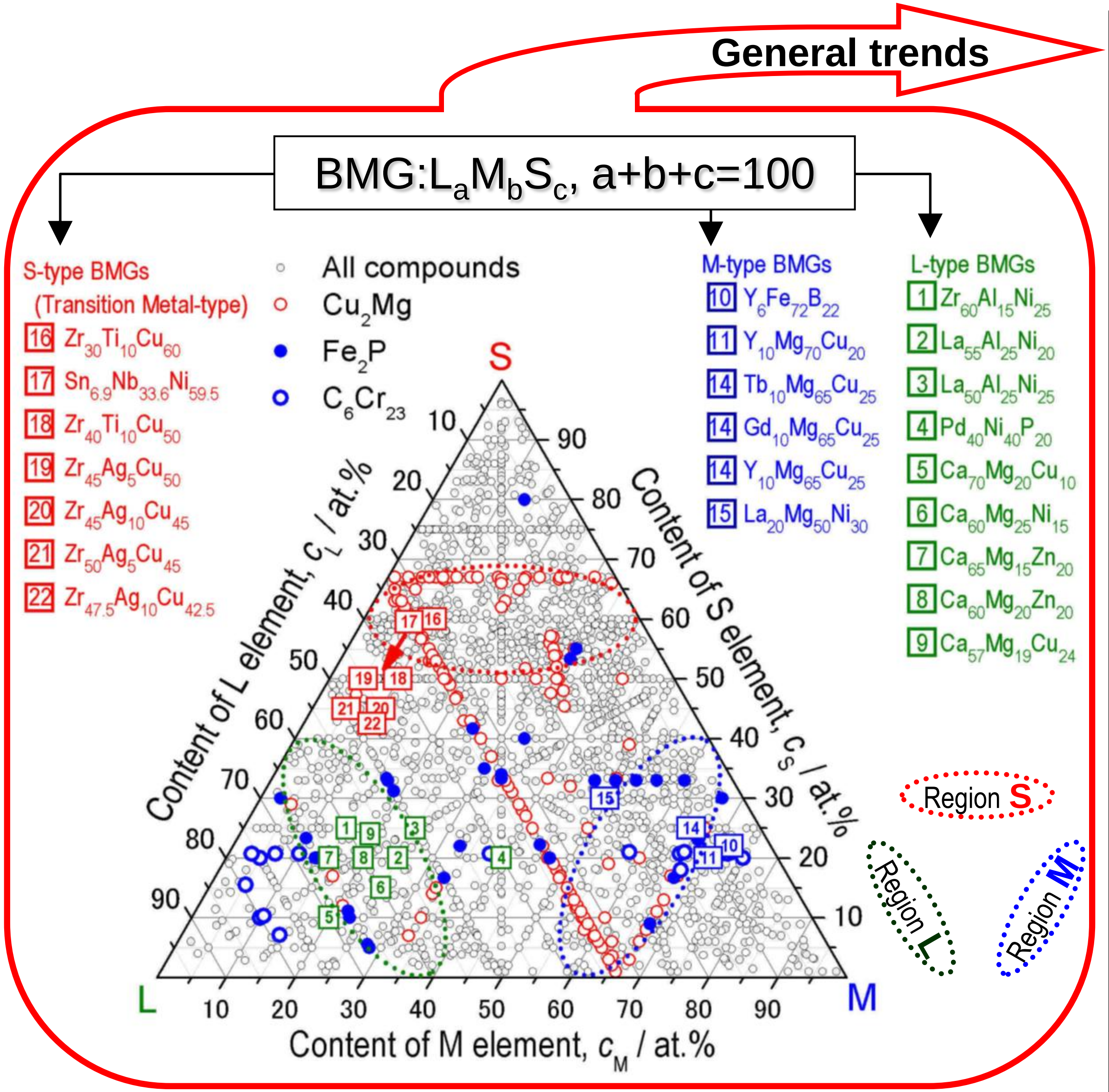
Fe_2P: Metal-Metalloid



C_6Cr_{23}: local atomic arrangements for Fe-based BMGs



3-3. L-M-S composition diagram for BMGs and representative compounds



(1) Ternary BMGs compositions

L-,M-type BMGs [□□]

➔ Independent to Cu_2Mg [○]

➔ BMGs content: c_S ~ 20 at.%

L-type BMGs [□]

➔ Formation: **Region L~ $L_{60}M_{20}S_{20}$**

➔ **anti-Laves relation** to Cu_2Mg

M-type BMGs [□]

➔ relate to Fe_2P,C_6Cr_{23} [●○]

➔ Formation: edge of **Region M**, M-S side (~$L_{10}M_{70}S_{20}$)

S-type BMGs [□]

➔ **[16,17] overlap with Cu_2Mg [○] in Region S**

→ low glass-forming ability (GFA)

➔ shift of main constituent

(from S-[16,17] to L-[18-22]-rich side)*

→ increase in GFA

➔ Formation: **Region S, c_M ~ 10 at. %**

(2) Ternary compounds compositions

Fe_2P,C_6Cr_{23} [●○] at around Region L

➔ Influence to L-type BMG formation

4. Summary

1. Introduction: Stabilization of glassy phase ← eutectic reaction
   ← **local atomic arrangements**, **stoichiometory** of compounds
2. Methods: Seven classes of BMGs (**C-1~C-7**) and three types of BMGs (**L-,M-,S-type**),
   L-M-S composition diagram, Crystallographic data from ternary phase diagrams

3. Resulsts and Discussion

3-1. **L-M-S composition diagram** for **ternary compounds**

→ **ternary compounds** tend to form in **S-rich corner (Region S)**

3-2. **Representative compounds** → (1)$\mathbf{Cu_2Mg}$, (2)$\mathbf{Fe_2P}$ and (3)$\mathbf{C_6Cr_{23}}$

3-3. **L-M-S composition diagram for BMGs and representative compounds**

S-type (transition metal) BMGs: (ex: Cu-based BMGs)
→ influenced by Cu_2Mg → **low-glass forming ability**
→ shift of **main constituent** in atomic size from **S to L**
→ Formation: **Region S, L-S side (c_M ~ 10 at. %)**

M-type BMGs: (ex: Fe- and Mg-based BMGs)
→ independent to Cu_2Mg, influenced by Fe_2P and C_6Cr_{23}
→ Formation: edge of **Region M**: **M-S side** ($\mathbf{\sim L_{10}M_{70}S_{20}}$)

L-type BMGs:most stable BMGs (ex: La-,Zr-,and Ca-based BMGs)
→(1) **anti-Laves** relationship to Cu_2Mg
→(2) ternary compounds in **Region L: infrequent**
→ somewhat affected by Fe_2P and C_6Cr_{23}
→ Formation: **Region L**: around $\mathbf{L_{60}M_{20}S_{20}}$)

$Pd_{40}NI_{40}P_{20}$ $\mathbf{c_S}$**~20at. %**

Chemical identity on the basis of Mendeleev Numbers

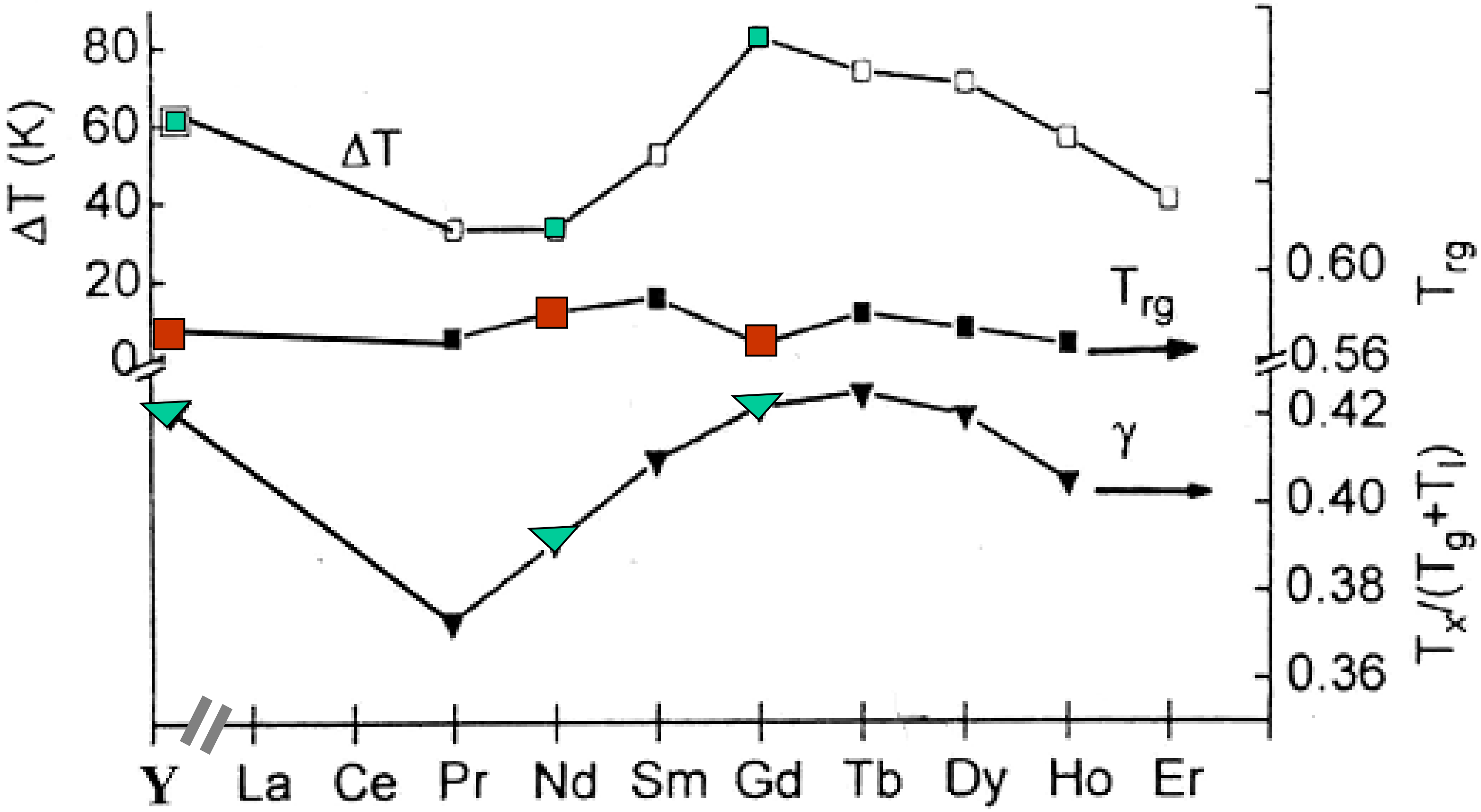
6 types based on orbitals and MN

New types	Metal (MN)	Takeuchi &Inoue
f electrons	Ca (16), Sc(19)	
	Lu (20).. Dy(24), Y (25)	Ln
	Gd(27), Ce(32), La (33)	
		+
d electrons (ETM)	Zr(49), Hf(50), Ti(51), Ta(52), Nb(53)	ETM
d electrons (LTM)	Fe(61), Co(64), Ni(67), Pt(68), Pd(69)	LTM + Sn
	Au(70), Ag(71), Cu(72)	
Mg (73), Zn(76), Be (77)		Be, Mg, Ca
sp electrons metallic	Al (80), Ga (81), Sn (83)	Al,Ga
sp electrons metalloid	Ge (84), Si (85), B (86), P (90), C (95)	Metalloid

Takeuchi & Inoue ANMM Sept 2005

Ranganathan, Murty, Inoue & Takeuchi , 2006 in progress

$Mg_{65}Cu_{25}RE_{10}$

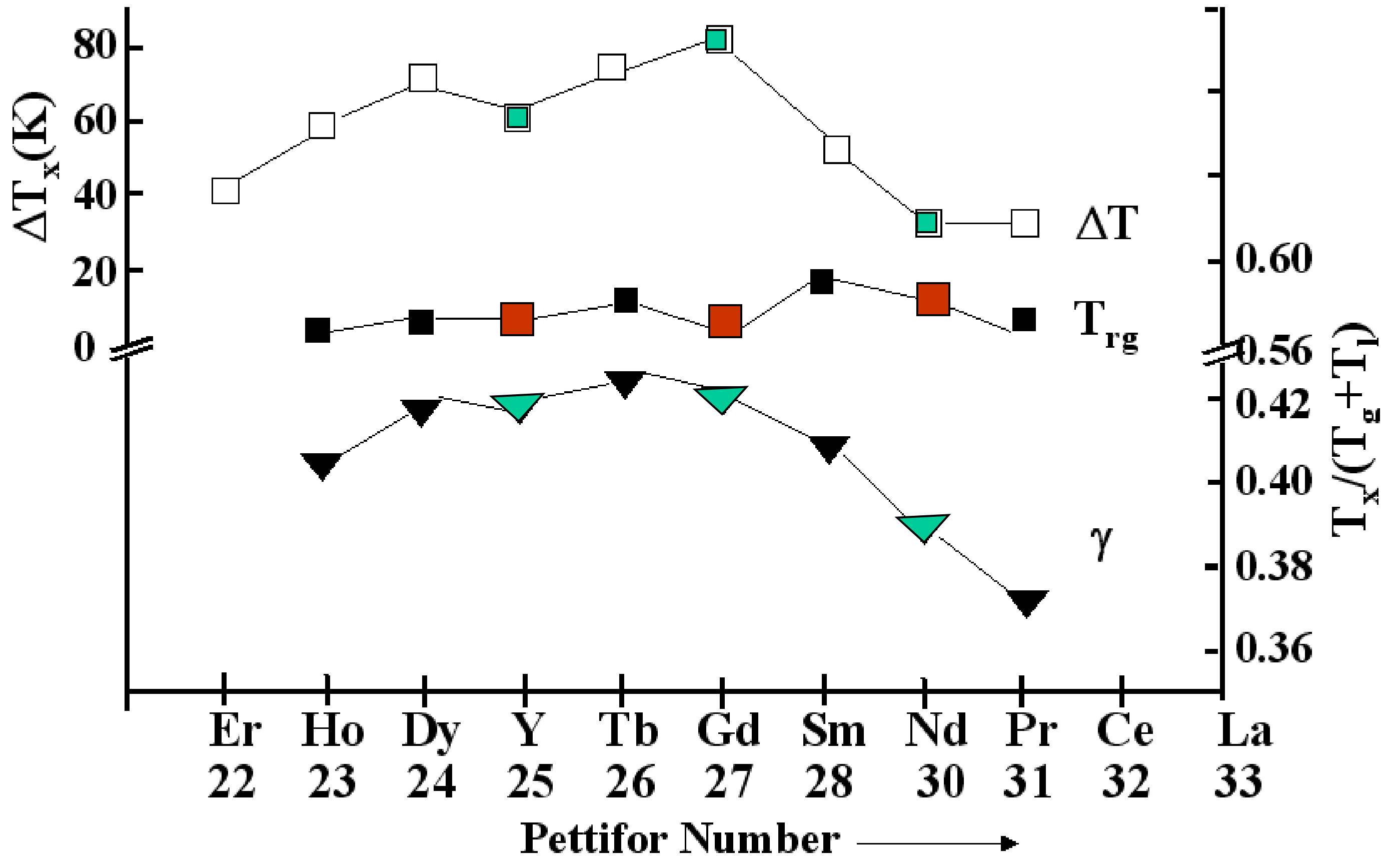


GFA parameters of the $Mg_{65}Cu_{25}RE_{10}$ alloys: super cooled liquid region ($\Delta T = T_x - T_g$), reduced glass transition temprature ($T_{rg} = T_g/T_l$) and γ ($T_x/(T_g + T_l)$)

(Xi et al, 2005, Intermetallics)

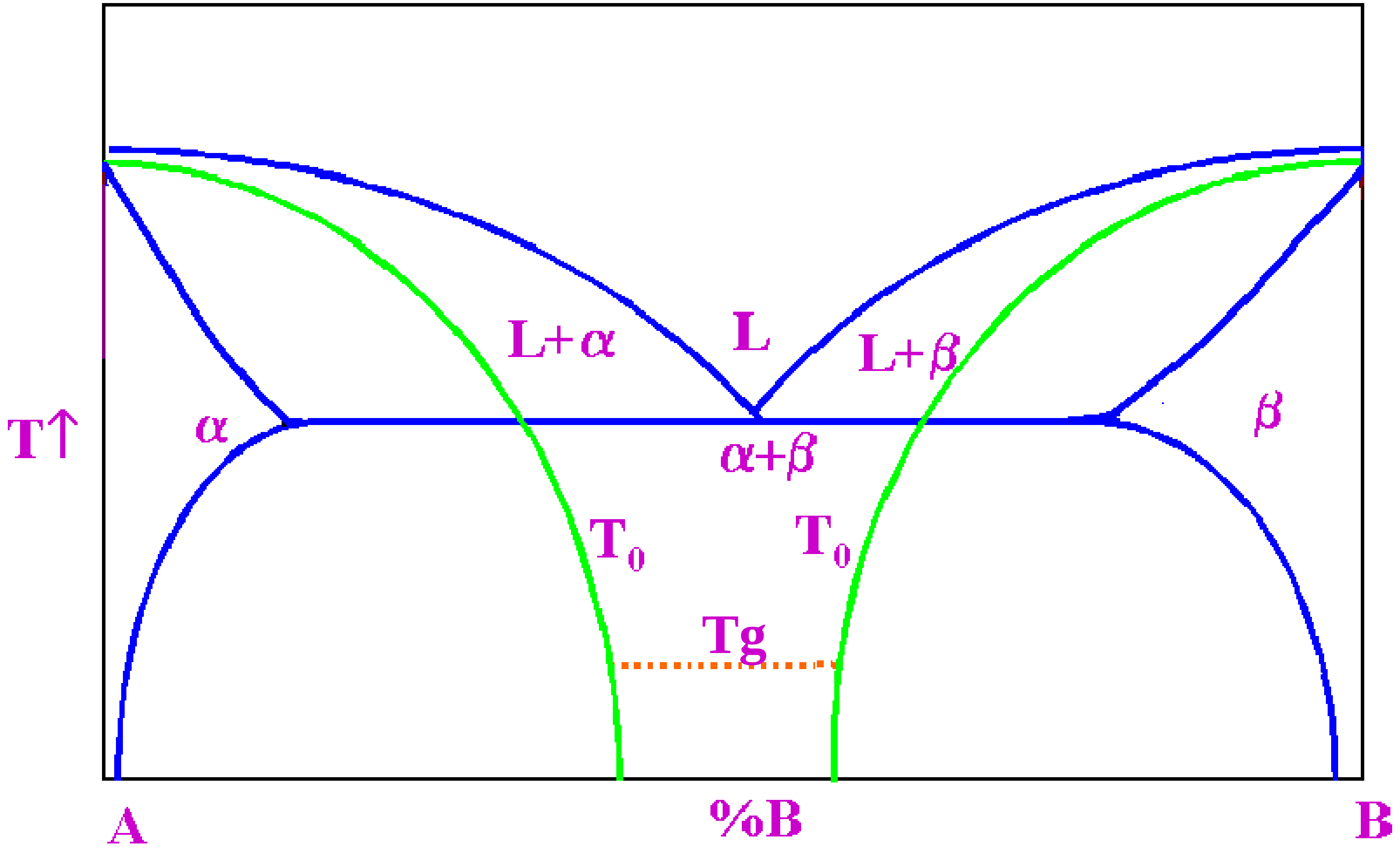
Coloured points: exp. data

$Mg_{65}Cu_{25}RE_{10}$



GFA parameters of the $Mg_{65}Cu_{25}RE_{10}$ alloys: super cooled liquid region ($\Delta T = T_x - T_g$), reduced glass transition temperature ($T_{rg} = T_g/T_l$) and γ ($T_x/(T_g + T_l)$)

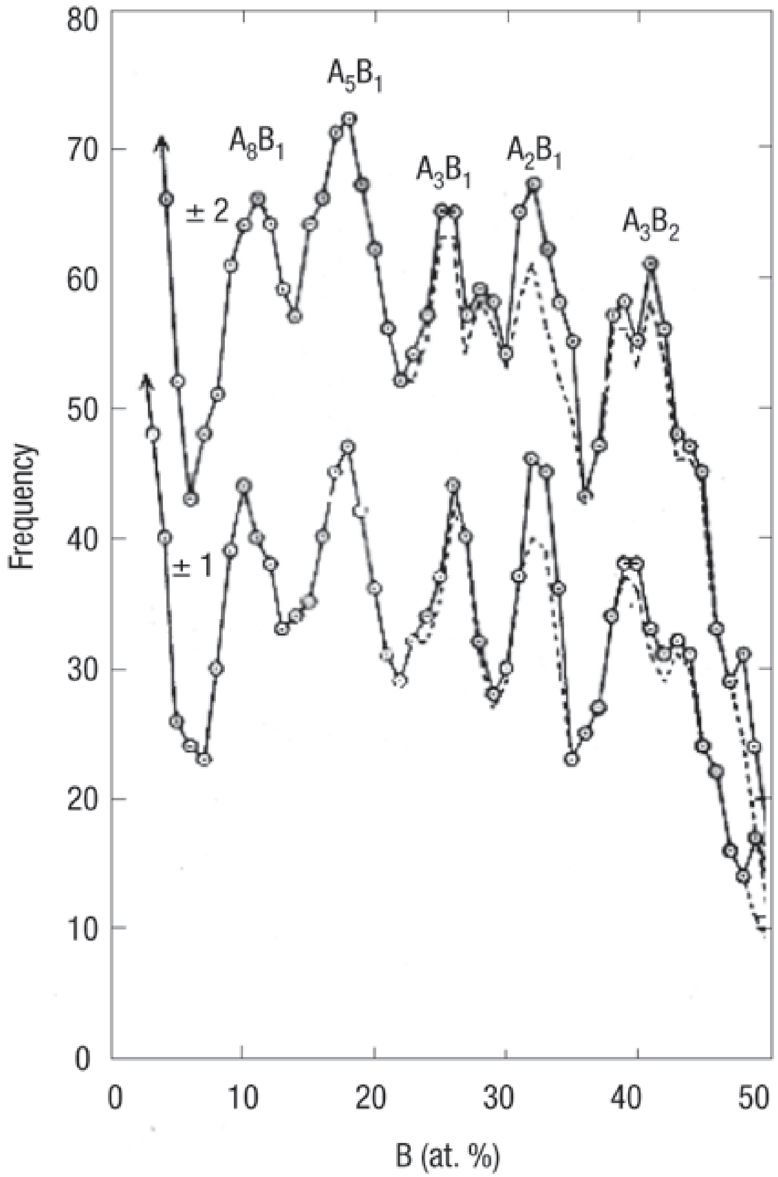
Coloured points: exp. data



→ BMG

Strict stoichiometry ?

EQUILIBRIUM PHASE DIAGRAM & POLYMORPHOUS PHASE DIAGRAM

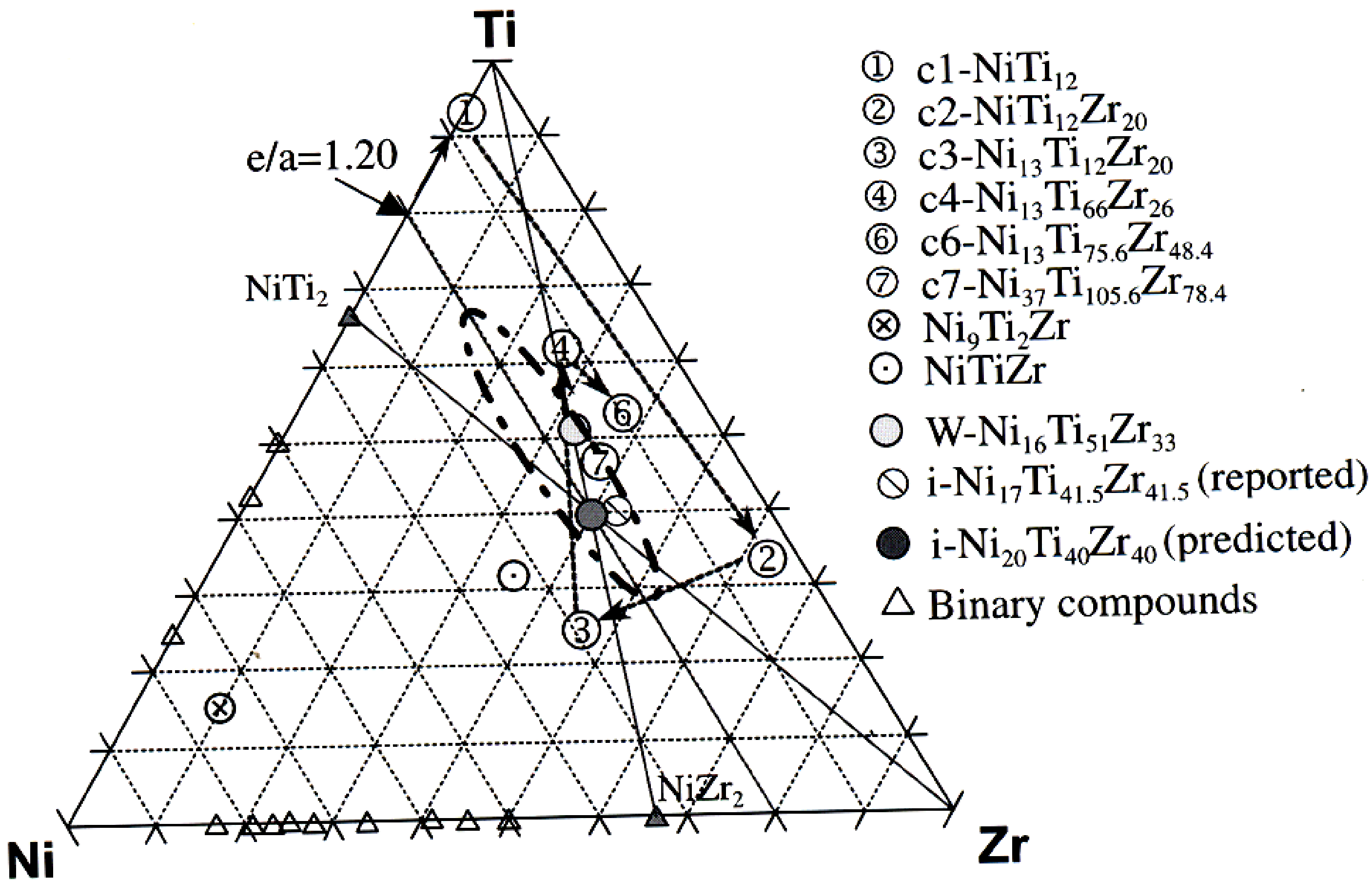


D. Stockdale,
Proc. Roy. Soc. A **152**, 81 (1935).
W. Hume-Rothery & E. Anderson, E.
Phil. Mag. **5**, 383−405 (1960).

A.R. Yavari,

Nature Materials, **4**, 2,3 (2005)

1. Binary eutectics by telescoping multinary eutectics-
Pseudobinary & ternary eutectics-
2. Hume-Rothery explanation of eutectic composition in terms of icosahedral clusters
S Ranganathan



J. Phys. D: Appl. Phys. 40 (2007) R273–R291
TOPICAL REVIEW
From clusters to phase diagrams:composition rules of quasicrystals and bulk metallic glasses
C Dong1, QWang, J B Qiang, Y M Wang, N Jiang, G Han, Y H Li, J Wu and J H Xia
State Key Laboratory for Materials Modification by Laser, Ion and Electron Beams, Dalian

EARLY TRANSITION METAL-
LATE TRANSITION METAL ALLOYS
Glass & Quasicrystal forming ability

Hf70-Cu30
Hf70-Cu20-Ag10
Hf70- Cu20-(Pt/Pd)10 a--qc
Hf73-Pd27 a-qc

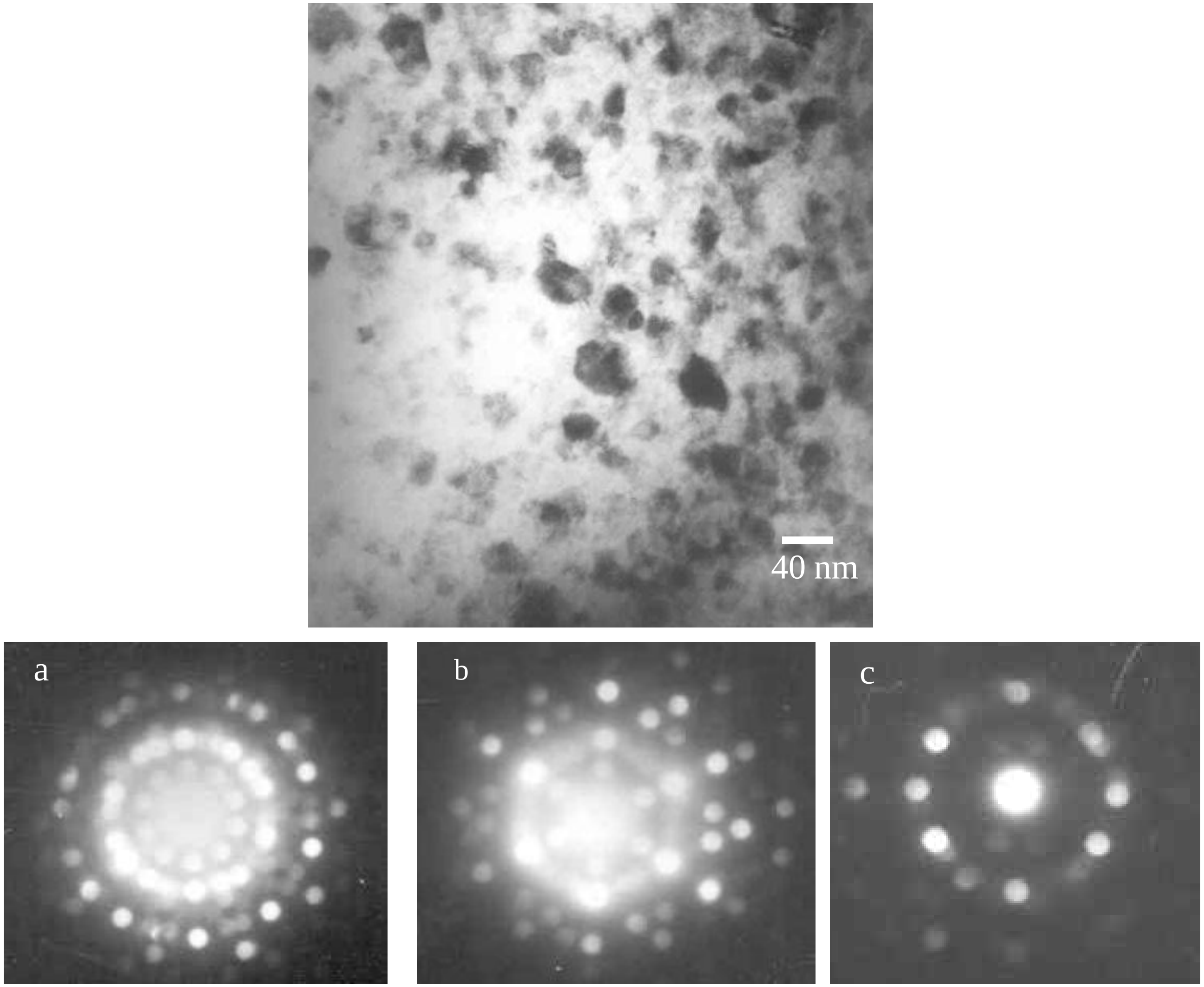
Li, Ranganathan & Inoue, Acta mater 2001

Zr41.5-Ti41.5-Ni17 a-- qc
Zr41.5-Hf41.5-Ni17
Basu, Louzguine, Inoue ,JNCS 2004

Ti40-Zr20- Hf20-(LTM= Ni/Pd/Pt)20
Nano qc
Chen, Louzguine,Kubota, Ranganathan & Inoue Scripta mater. 2005

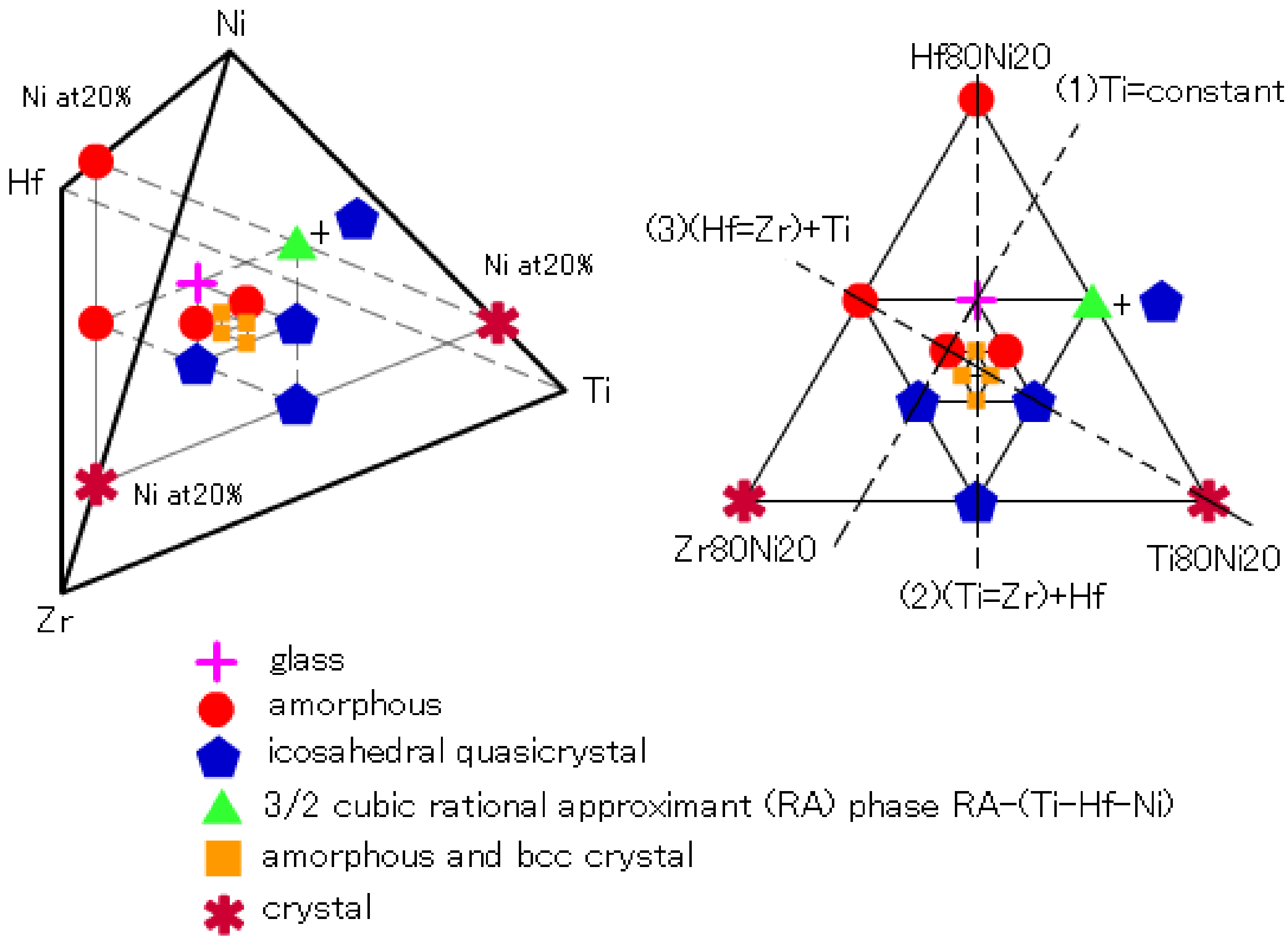
Zr-80Pt20
Zr70-(Cu/Ag/Au)10-Pt20
Zr70-Pd 30
Zr70-(Ag/Au)10-Pd20
Saida, Ranganathan & Inoue

Multicomponent alloys viewed as pseudo lower order alloys

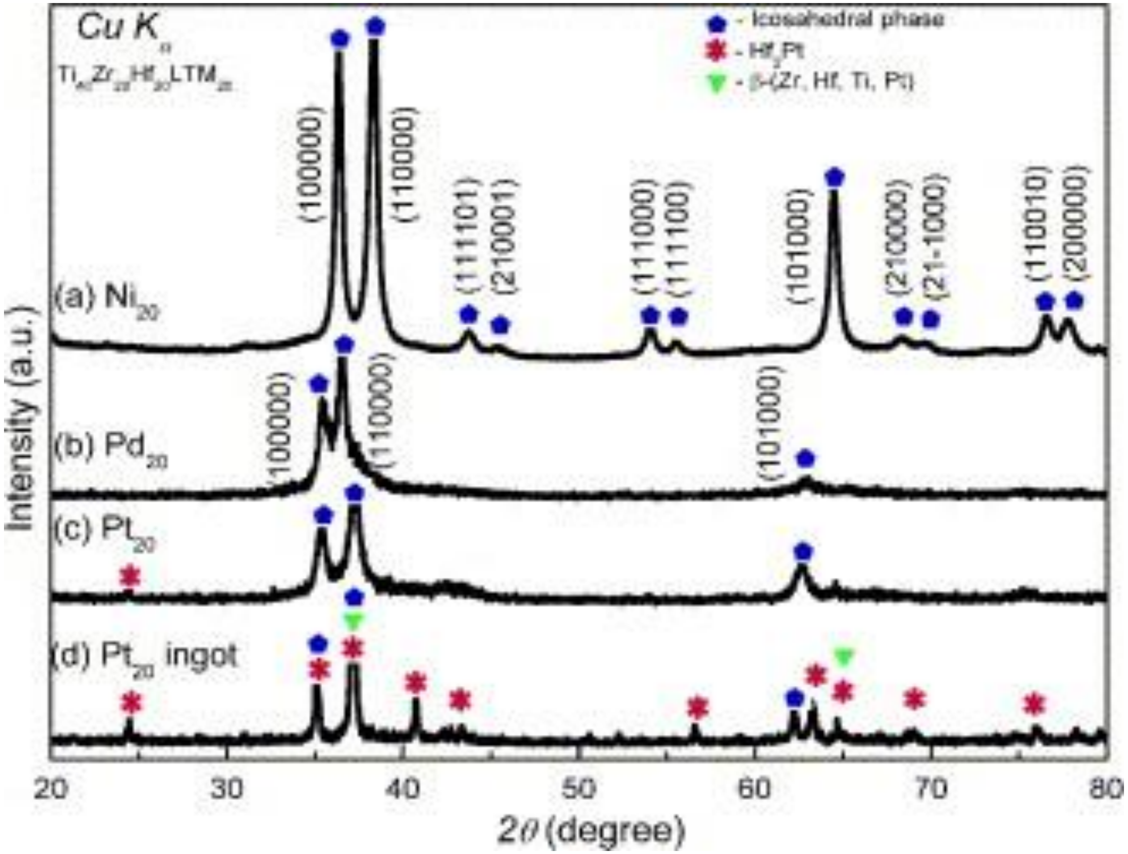


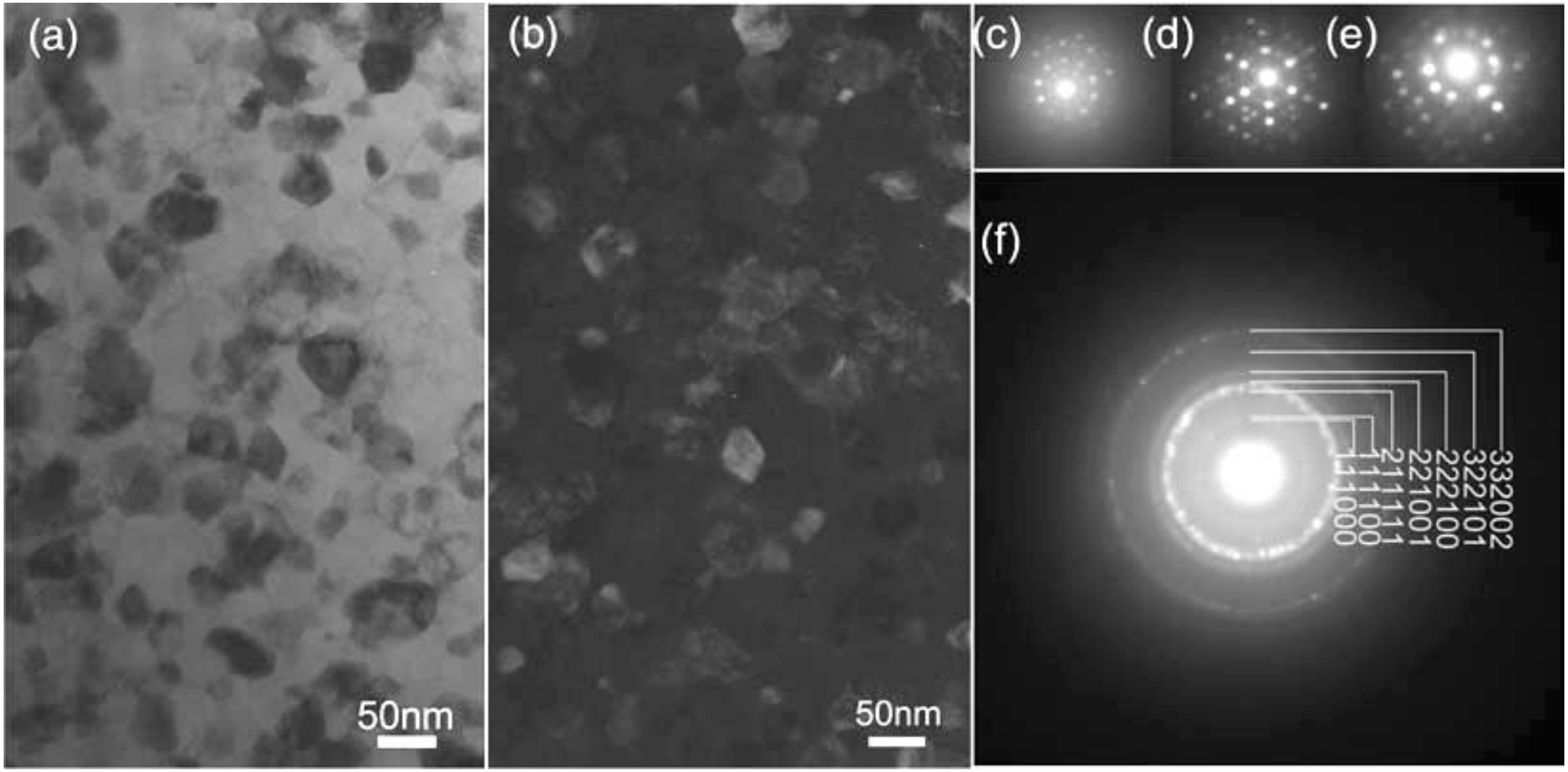
Bright field electron micrograph of a nanoquasicrystallised Zr-Ti-Ni alloy with nano beam electron diffraction pattern showing a) 5-fold b) 3-fold c) 2-fold symmetry

Phases in Melt-spun Alloys

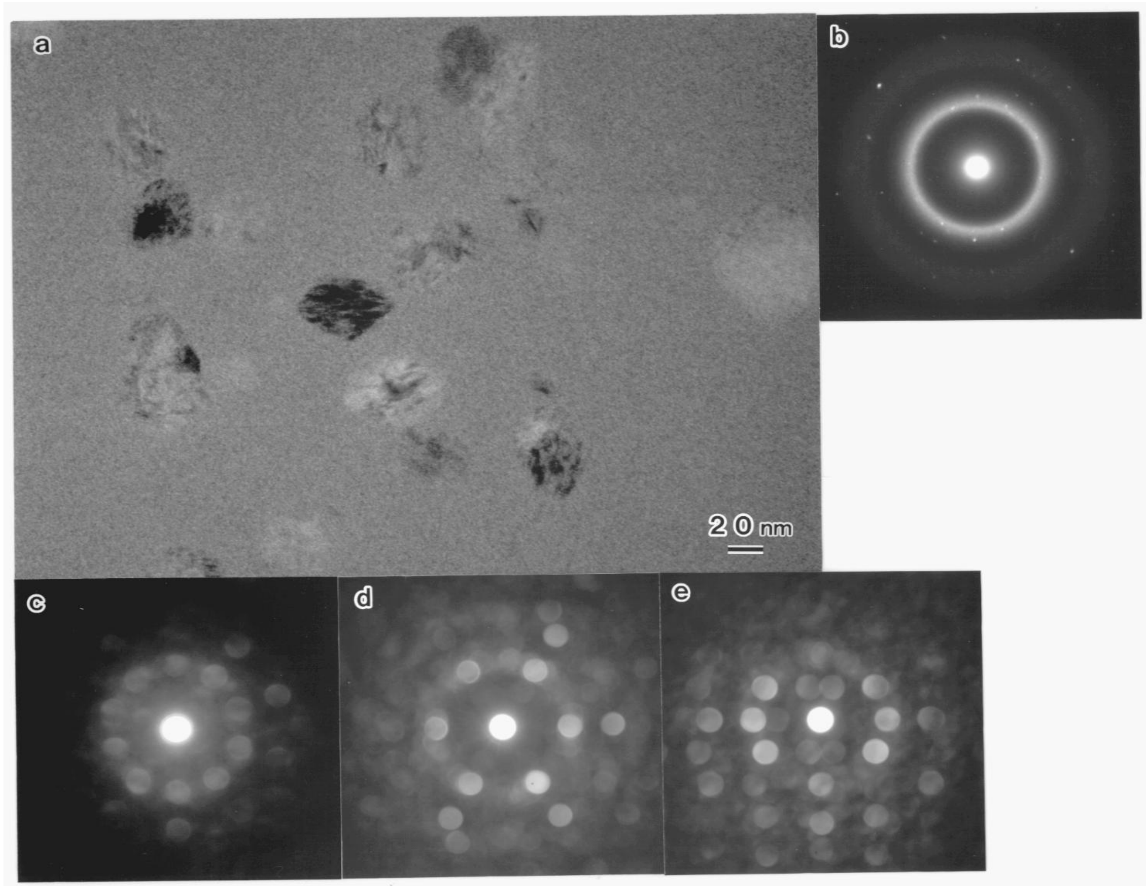


XRD patterns
(a) Ti40-Zr20-Hf20- Ni20 (b) Ti40-Zr20-Hf20-Pd 20
© Ti40 -Zr20-Hf20- Pt20 alloys
(d) Ti40- Zr20- Hf20- Pt 20 ingot





TEM of the melt-spun $Ti_{40}Zr_{20}Hf_{20}Ni_{20}$ alloy. (a) Dark-field (b) bright field image (c-e) nano beam diffraction patterns of five-, three- and twofold symmetry respectively and (f) selected-area electron diffraction pattern



Bright field TEM image (a), selected area diffraction pattern (b) and nanobeam electron diffraction patterns (c)-(e) of the rapidly solidified $Zr_{70}Au_{10}Pt_{20}$ alloy.
The beam diameter for electron diffraction is 1μm in (b) and is 2.4 nm in (c)-(e) (J. Saida, A. Inoue S. Ranganathan)

QUASICRYSTALS AND METALLIC GLASSES: A COMPARISON

Bond Orbital	Large Atom	Quasicrystal	Bulk Metallic Glass	
s-electrons	Li, Mg	Li-Cu-Al Mg-Zn-Al	(Mg-Cu-Y)	
p-electrons	Al, Ga	Al-Pd-Mn Ga-Cu-Co	Al-La-Ni (Al-rich marginal)	
d- electrons (ETM)	Zr, Hf, Ti	Zr-Ti-Ni Zr-Ti-Ni-Cu Zr-Pd-Cu	Zr-Ni-Al Zr-Ni-Cu-Al Zr-Ti-Ni-Cu-Be	
d- electrons (LTM)	Fe, Co, Ni Pd, Pt	-	Fe-Ni-P-B Pd-Ni-P-B	Fe-Zr-B
f-electrons	Ln	Ln-Zn-Mg Ln-Cd-Mg	La-Ni-Al (Mg-Cu-Y) (Al-Ni-La)	

CONCLUSIONS- I

- **The close packing of spheres of different sizes favours intrinsically polytetrahedral packings involving icosahedral order. This extends from atomic to micrometre dimensions .-e.g colloids**
- **Icosahedral order applies to crystalline and quasicrystalline intermetallics as well as bulk metallic glasses.**
- **The size ratio close to 1.225 is favoured for both large atom minority and majority compositions.**
- **The topological complexity in BMG s extends up to four components only (Miracle 2004).**

CONCLUSIONS- II

- **The chemical complexity for topologically close packed crystalline and quasicrystaline intermetallics extends to two**
- **The Pettifor structure mapping approach allows to consider both topology and chemistry together.**
- **For bulk metallic glasses the chemical complexity can be three or four. Binary BMGs are an exception .**
- **The composition of eutectics with strict stoichiometry mirrors that of resultant BMGs. There is a strong connection in the stoichiometry of higher order eutectics so that many appear to be psuedo binary or ternary.**

ACKNOWLEDGEMENTS

Collaboration with

Prof A Inoue, Prof A Takeuchi, Prof H Kimura,
Prof J Saida and Prof D Louzguine

Discussions with Dr Eric Lord and Dr Daniel
Miracle, Prof B S Murty

Comments from
Prof David Pettifor and Prof Alan Mackay

Sponsors
DRDO, India; AOARD, Tokyo