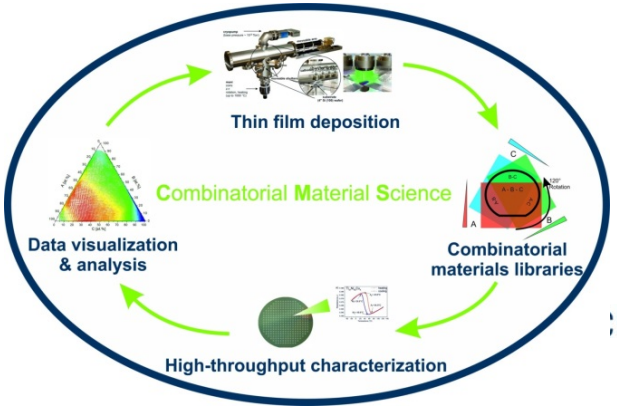
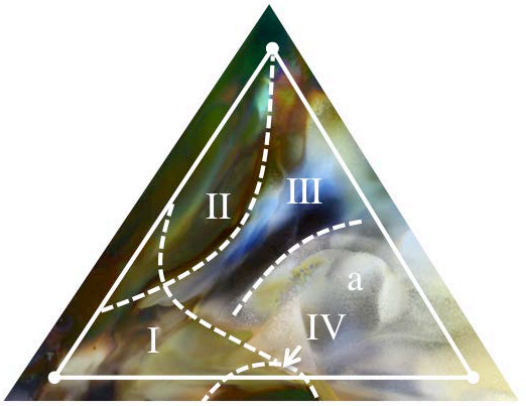
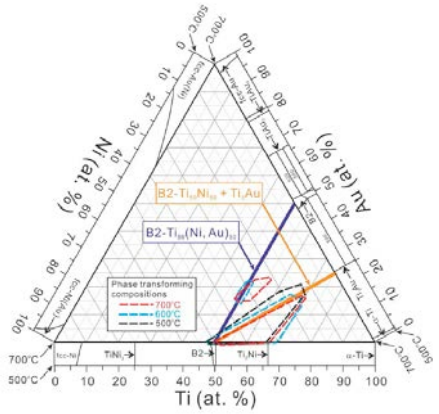






RUB

Fundamental Aspects of Materials Science and Engineering

Sommersemester 2020

Phase diagrams, intermetallic phases and combinatorial materials research

Prof. Dr.-Ing. Alfred Ludwig
Materials Discovery and Interfaces

Intermetallics:
Some past and present applications

Since approx.	Material or process	Phase	Application	Reference
2500 B. C.	cementation	Cu_3As	coating of bronze tools, etc. (Egypt, Anatolia, Britain)	Westbrook (1977)
100 B. C.	yellow brass	CuZn	coins, ornamental parts (Rome)	Gmelin-Institut (1955)
0	high tin bronze	$Cu_{31}Sn_8$	mirror (China)	Westbrook (1977)
600	amalgam	$Ag_2Hg_3 + Sn_6Hg$	dental restorative (China)	Westbrook (1977) Waterstrat (1990)
1500	amalgam	Cu_4Hg_3	dental restorative (Germany)	Paufler (1976), Westbrook (1977) Waterstrat (1990)
1505	amalgam	Sn_8Hg	mirror surface (Venice)	Westbrook (1977)
1540	type metal	SbSn	printing	Westbrook (1977)
1910	Acutal	$(Cu, Mn)_3Al$	fruit knife (Germany)	Heusler (1989)
1921	Permalloy	Ni_3Fe	high permeability magnetic alloy	Bozorth (1951)
1926	Permendur	FeCo(−2V)	soft magnetic alloy	Bozorth (1951), Chen (1961)
1931	Alnico	NiAl–Fe–Co	permanent magnet material	De Vos (1969)
1935	Sendust	$Fe_3(Si, Al)$	magnetic head material	Yamamoto (1980)
1938	Cu–Zn–Al Cu–Al–Ni	CuZn–Al $(Cu, Ni)_3Al$	shape memory alloys	Hodgson (1990)
1950	pack aluminide coating	NiAl, CoAl	surface coating for protection from environment	Nicholls and Stephenson (1991)
1956	Kanthal Super, Mosilit	$MoSi_2$	electric heating elements	Fitzer and Rubisch (1958)
1961	A 15 compound	Nb_3Sn	superconductors	Westbrook (1977), Geballe and Hulm (1986)
1962	Nitinol	NiTi	shape memory alloy	Delacy et al. (1974) Hodgson (1990)
1967	Co–Sm magnets	Co_5Sm	permanent magnets	Stadelmaier et al. (1991), Westbrook (1977),

Source: Sauthoff 1989

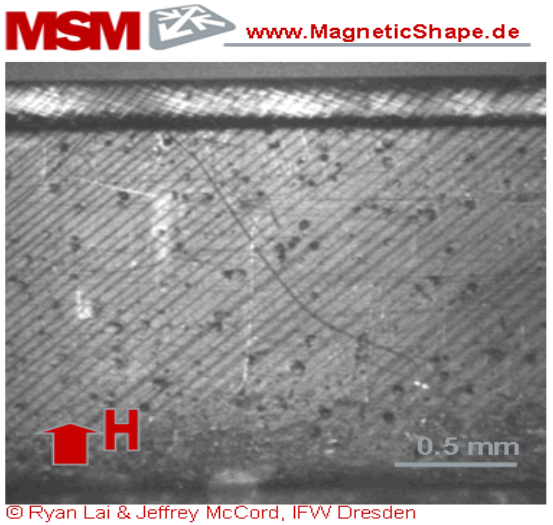
Examples of interesting intermetallics

for structural and functional applications

shape memory alloys
NiTi (B2)

Ni-based superalloys
(Ni)+Ni_3Al

ferromagnetic shape memory alloys
Ni_2MnGa (Heusler)



Source:www.magneticshape.de/

permanent magnets
$Nd_2Fe_{14}B$

Intermetallic compounds: Issues of plastic deformation

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Problem: brittleness

Plastic deformation:
Ususally more difficult than in pure metals
due to more complex crystal structures

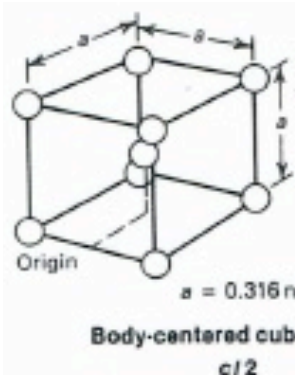
From experience:
brittleness increases with decreasing lattice symmetry and
increasing unit cell size

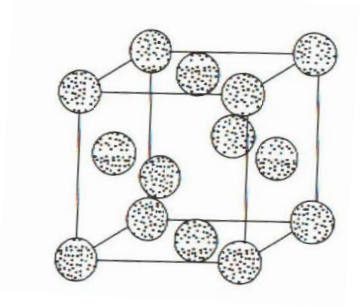
Therefore, intermetallics with high crystal symmetry and
small unit cells are preferred for developing structural materials

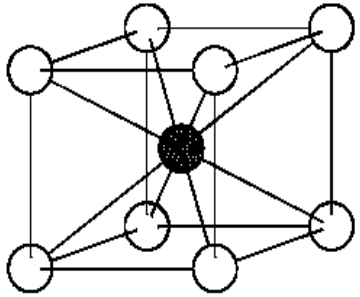
Crystal structures: “Cubic” systems

from fcc, bcc to

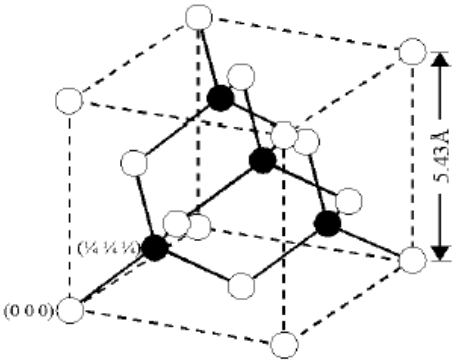
B2, diamond, Si, wurtzite, Heusler, Perovskite phases



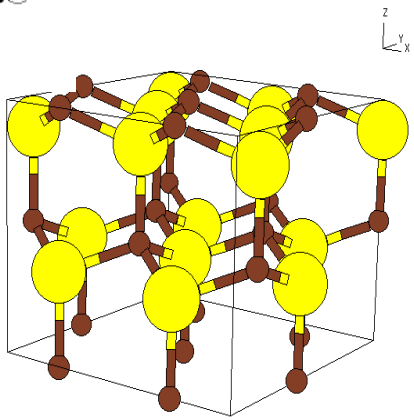




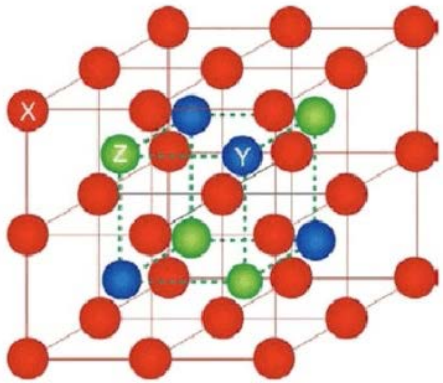
B2



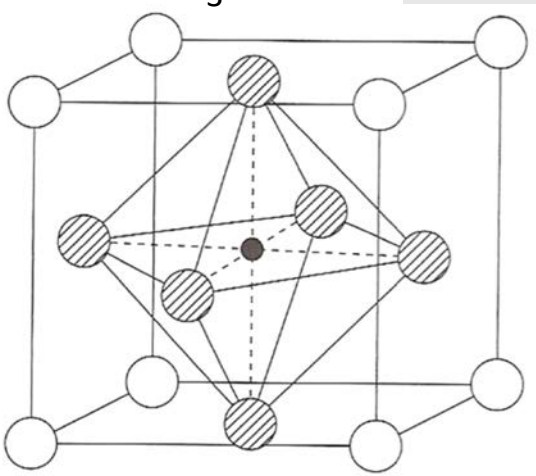
diamond
and
wurtzite



$L2_1$-type X_2YZ



Perovskite,
ABO_3



Crystal structures: derivations

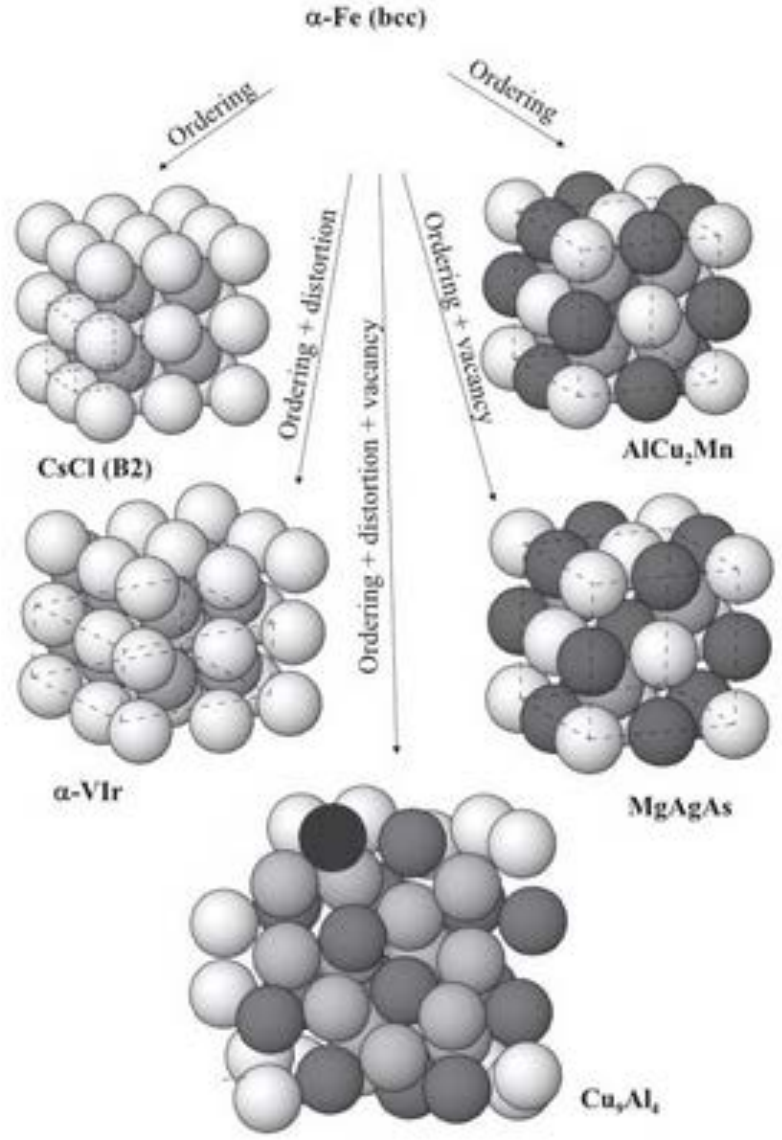


Fig. 2.16 Formation of structural patterns derived from the bcc packing.

crystal structure motifs

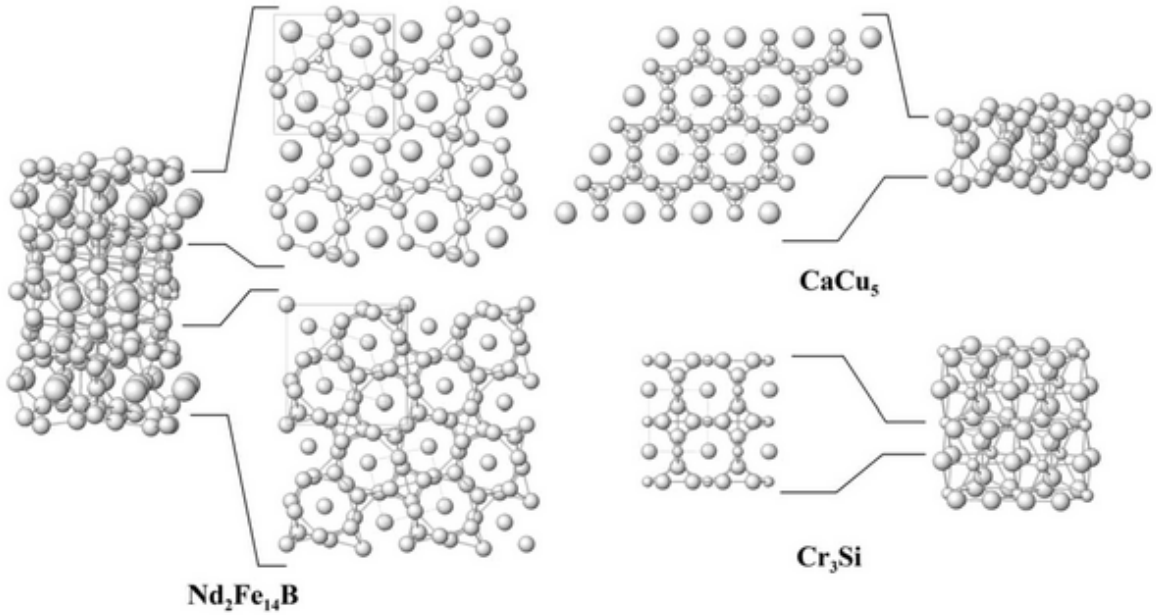


Fig. 2.21 The crystal structure of the hard magnetic material $Nd_2Fe_{14}B$ as a derivative of the crystal structure motifs of $CaCu_5$ and Cr_3Si.

Names of phases: Mineral names, trivial names

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Mineral names:
diamond, zinc blende, wurtzite,
quartz, rutil, pyrite, ilmenite, …

naming after prototype structures

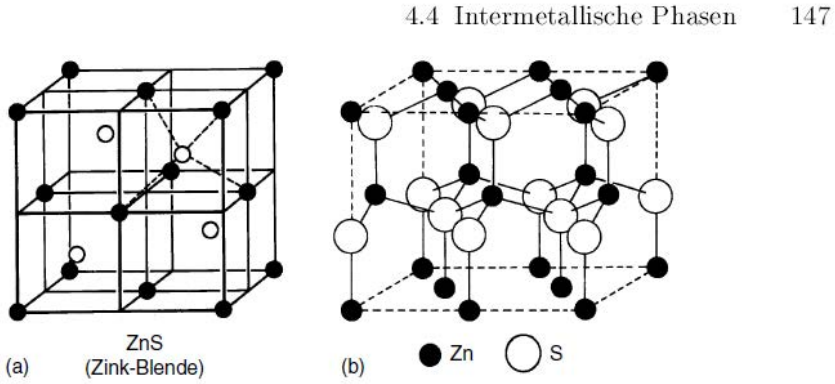


Abbildung 4.45. (a) Elementarzelle der Zinkblende-Struktur; (b) Elementarzelle des Wurtzitgitters.

γ : γ-brass type or similar structures
ε : Mg type
ζ : Mg type
η : W_3Fe_3C or Ti_2Ni type
μ : W_6Fe_7 type
σ : σ phase or σ-CrFe type
χ : α-Mn or Ti_5Re_{24} type
ω : ω_2-(Cr, Ti) type (similar to the AlB_2 type)
E : $PbCl_2$ or $CoSi_2$ type
G : G phase, Th_6Mn_{23} or $Cu_{16}Mg_6Si_7$
P : P phase or P-(Cr, Mo, Ni)
R : R phase or R-(Co, Cr, Mo)
T_1: W_5Si_3 type
T_2: Cr_5B_3 type

rt: room-temperature modification
ht: high-temperature modification
lt: low-temperature modification

Source: Gottstein, Cahn, Haasen, Cramer, Vol.1

Names from Strukturbericht

letter, number, number

Strukturbericht	Type
A	unaries
B	binaries AB
C	binaries AB_2
D	$A_m B_n$ compounds
E, F, …, K	complex compounds
L	alloys
O	organic compounds
S	Silicates

Examples

A1: cF4-Cu

A2: cI2-W

B2: cP2-CsCl

$L1_0$: tP2-AuCu

$L1_2$: cP4-$AuCu_3$

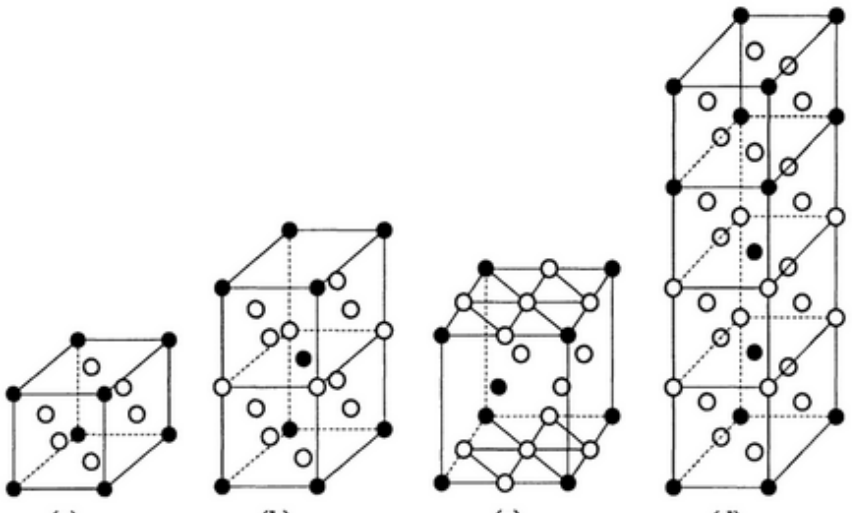


Fig.1 The unit cell of (a) $L1_2$, (b) $D0_{22}$, (c) $D0_{19}$ and (d) $D0_{23}$ structures.

Source: Cahn, Haasen, Cramer, Vol.1, Liu 92

Intermetallic phases named by scientists

Frank-Kasper phases

- Laves phases, e.g. hP12-$MgZn_2$, cF24-Cu_2Mg, hP24-Ni_2Mg
- σ phases, e.g. tP30
- other phases

Hume-Rothery phases

- electron compounds, VEC (valence electron concentration), same structural types for same VEC in well-definded ranges, e.g. in brass (Cu-Zn)

Heusler phases

- cF16-$MnCu_2Al$ (a derivative of the CsCl-type)

Zintl phases

- polar, salt-like phases, e.g. Zintl boundary in Periodic Table (alkali-, alkaline elements)+main group (>4) elements

Hägg phases

- interstitial phases based on occupancy of interstices in close-packed structure of transition metals by small non-metals (H,B,C,N)

Nowotny phases, Chevrel phases, …

also: martensite, austenite, …

Descriptors for intermetallic phases

- chemical composition and existence range (p, T)
- structure type
  (crystal system, space group, number of atoms per unit cell, list of occupied atomic positions)

non-stoichiometric phases:
formula denotes: „ideal composition“

variable composition,
e.g. for solid solution (Ni, Cu) or Ni_xCu_{1-x}
(0…1)

Crystal systems and Bravais lattices

Single crystals: chemically and structurally homogeneous materials with anisotropic properties

7 crystal systems:

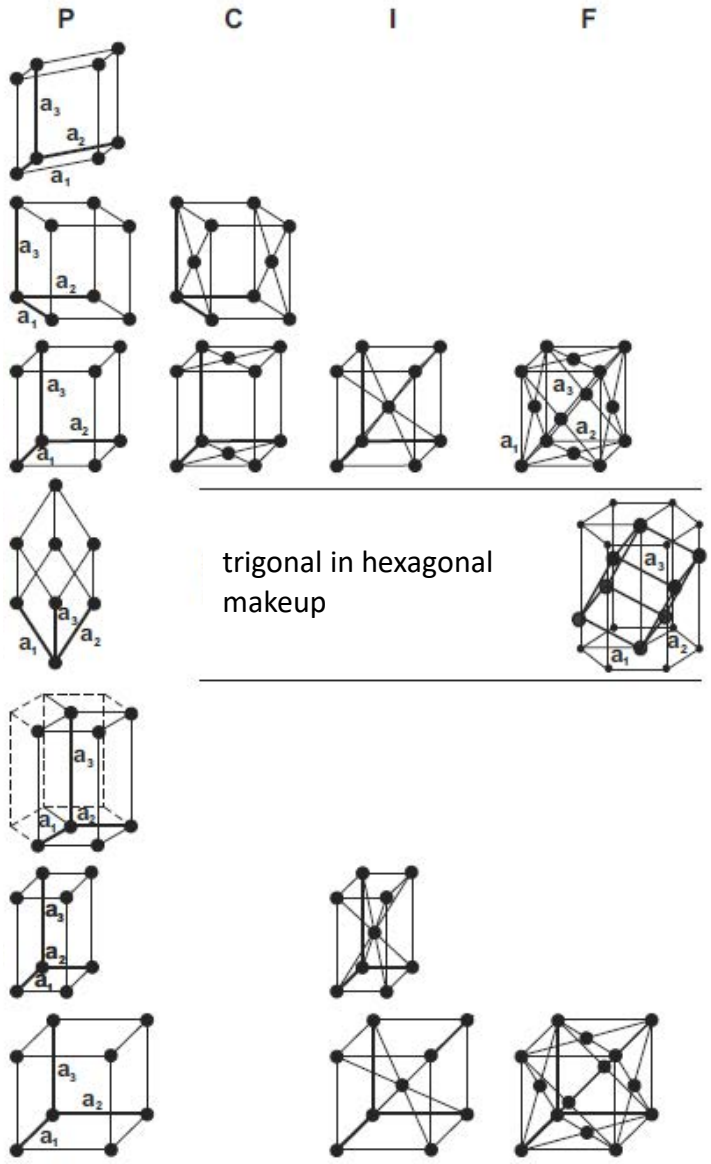
(fundamental point lattices from crystal morphology)

- triclinic (anorthic) a
- monoclinic m
- orthorhombic o
- trigonal (rhombohedral) r
- hexagonal h
- tetragonal t
- cubic c

14 Bravais lattices:

7 from centering translations, i.e. lattice points in interior of primitive cell

- primitive P
- side centered C
- body centered I
- face centered F



L. Spieß, G. Teichert, R. Schwarzer, Moderne Röntgenbeugung, Vieweg+Teubner, 2009

Crystal structures: Pearson symbols

consist of:
system symbol (small), lattice symbol (capital), number of atoms in unit cell

system symbol

- triclinic (anorthic) **a**
- monoclinic **m**
- orthorhombic **o**
- tetragonal **t**
- hexagonal (trigonal, rhombohedral) **h**
- cubic **c**

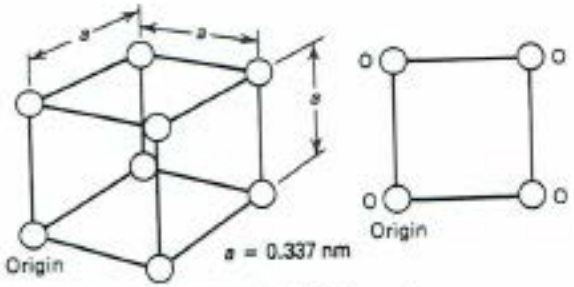
lattice symbol

P primitive
I body centered
F all face centered
C side face centered
R rhombohedral

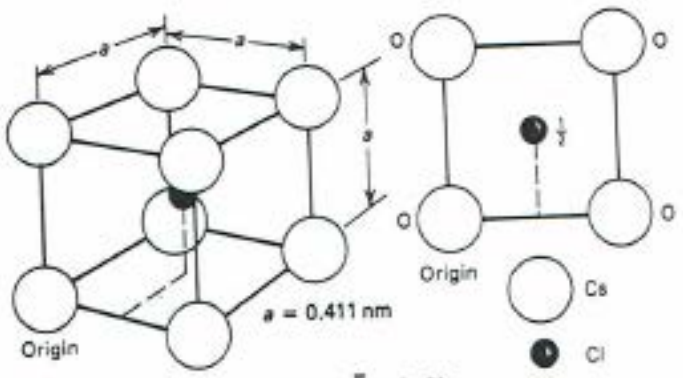
e.g.:
cI2 (α–Fe)
tP2 ($L1_0$ FePt)

Examples of cubic crystal structures

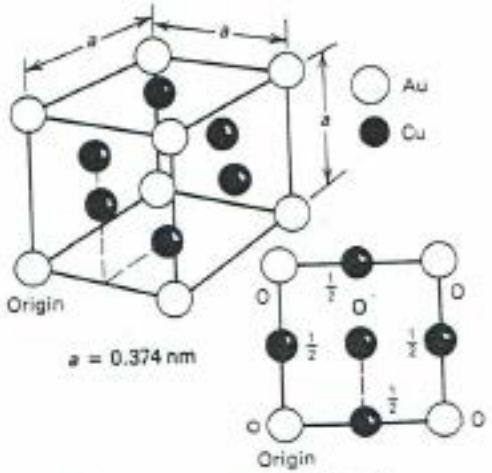
Schematic drawings of the unit cells and atom positions for some metal crystals,
Pearson symbol, space lattice, crystal system, space-group notation, prototype, lattice parameters of prototype crystal



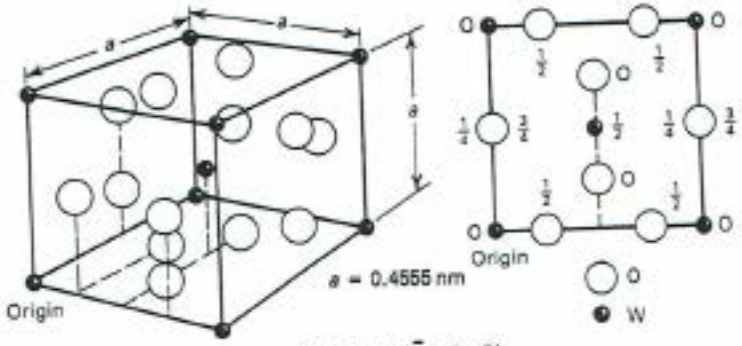
Primitive cubic: $Pm\bar{3}m$, α Po
$cP1$



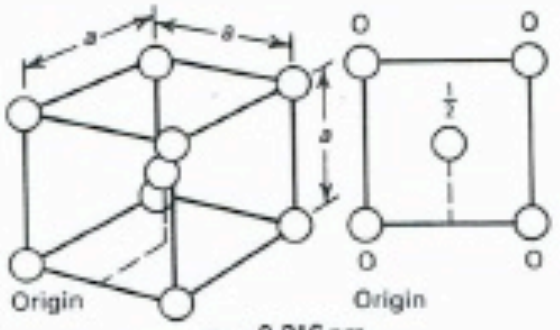
Cubic: $Pm\bar{3}m$, CsCl
$cP2$



Cubic superlattice: $Pm\bar{3}m$, $AuCu_3$
$cP4$



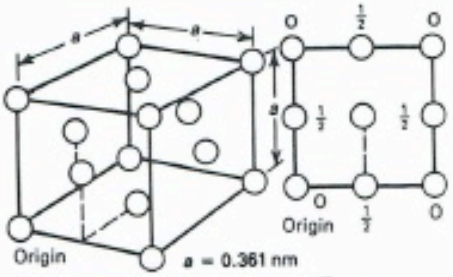
Cubic: $Pm\bar{3}n$, Cr_3Si
$cP8$



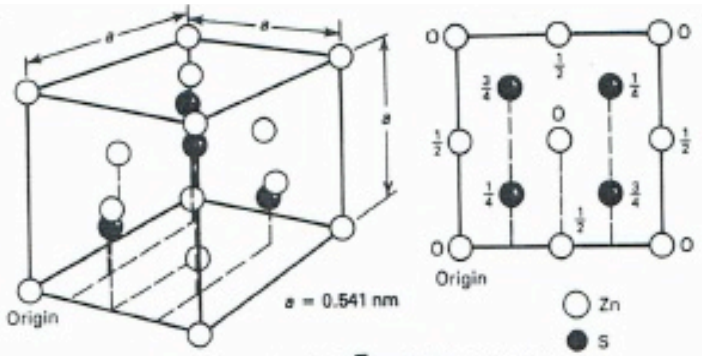
Body-centered cubic: $Im\bar{3}m$, W
$cI2$

Face-centered cubic crystal structures

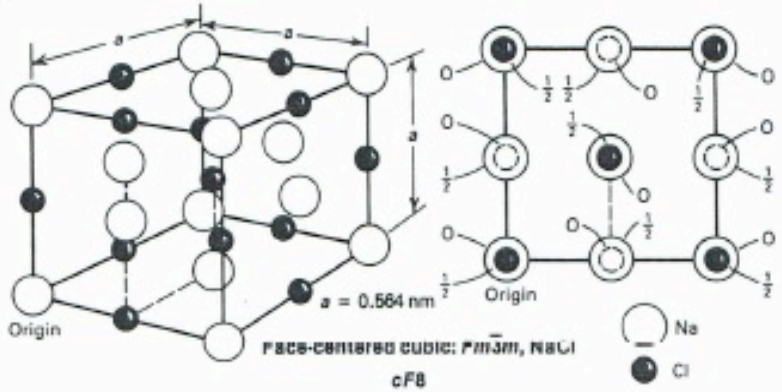
Schematic drawings of the unit cells and atom positions for some metal crystals, Pearson symbol, space lattice, crystal system, space-group notation, prototype, lattice parameters of prototype crystal



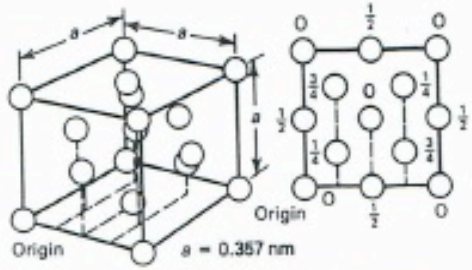
Face-centered cubic: $Fm\bar{3}m$, Cu
cF4



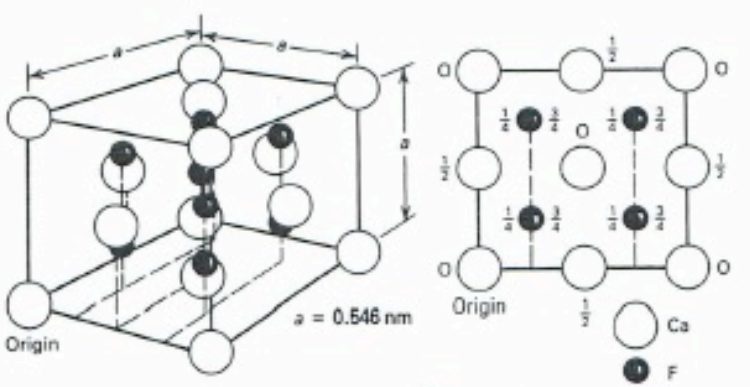
Face-centered cubic: $F\bar{4}3m$, ZnS (sphalerite)
cF8



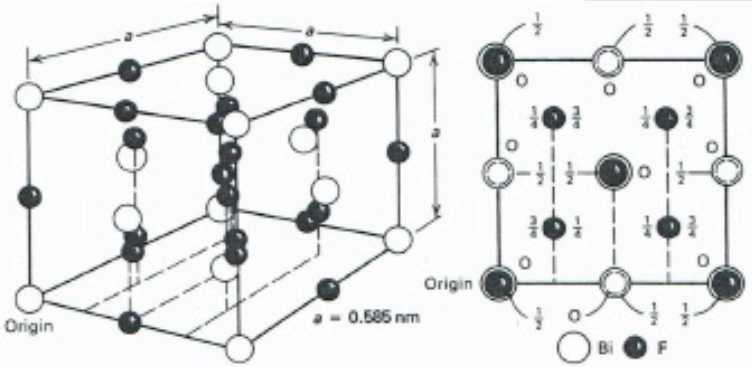
Face-centered cubic: $Fm\bar{3}m$, NaCl
cF8



Face-centered cubic: $Fd\bar{3}m$, C (diamond)
cF8



Face-centered cubic: $Fm\bar{3}m$, CaF_2 (fluorite)
cF12

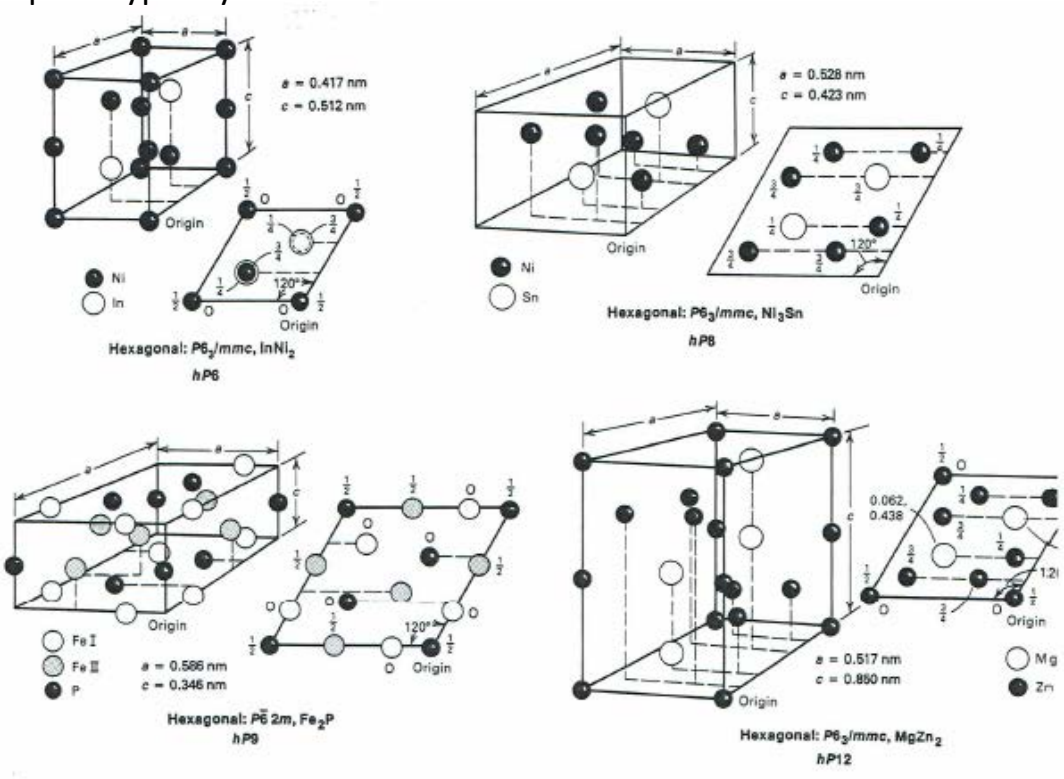


Face-centered cubic: superlattice: $Fm\bar{3}m$, BiF_3
cF16

Source: ASM Handbook, Vol3.

Examples of intermetallic crystal structures

Schematic drawings of the unit cells and atom positions for some metal crystals,
Pearson symbol, space lattice, crystal system, space-group notation, prototype, lattice parameters of prototype crystal



Source: ASM Handbook, Vol3.

Crystal structures: point groups

32 crystallographic point groups

point symmetry operations

- identity operation 1
- rotations 2, 3, 4, 6 (-fold)
  polar and non-polar rotation axes

proper rotations N

(transform an object congruently)

rotations through angles $\frac{2\pi}{N}$

improper rotations $\bar{N}$

rotoinversion axis $\bar{1}$

mirror plane $\bar{2}$ = m

$\bar{3}$

$\bar{4}$

$\bar{6}$ = 3/m

- at least 1 point invariant
- 32 point groups are compatible with 3D point lattices

Source: Cahn, Haasen, Cramer, Vol.1

32 crystallographic point groups

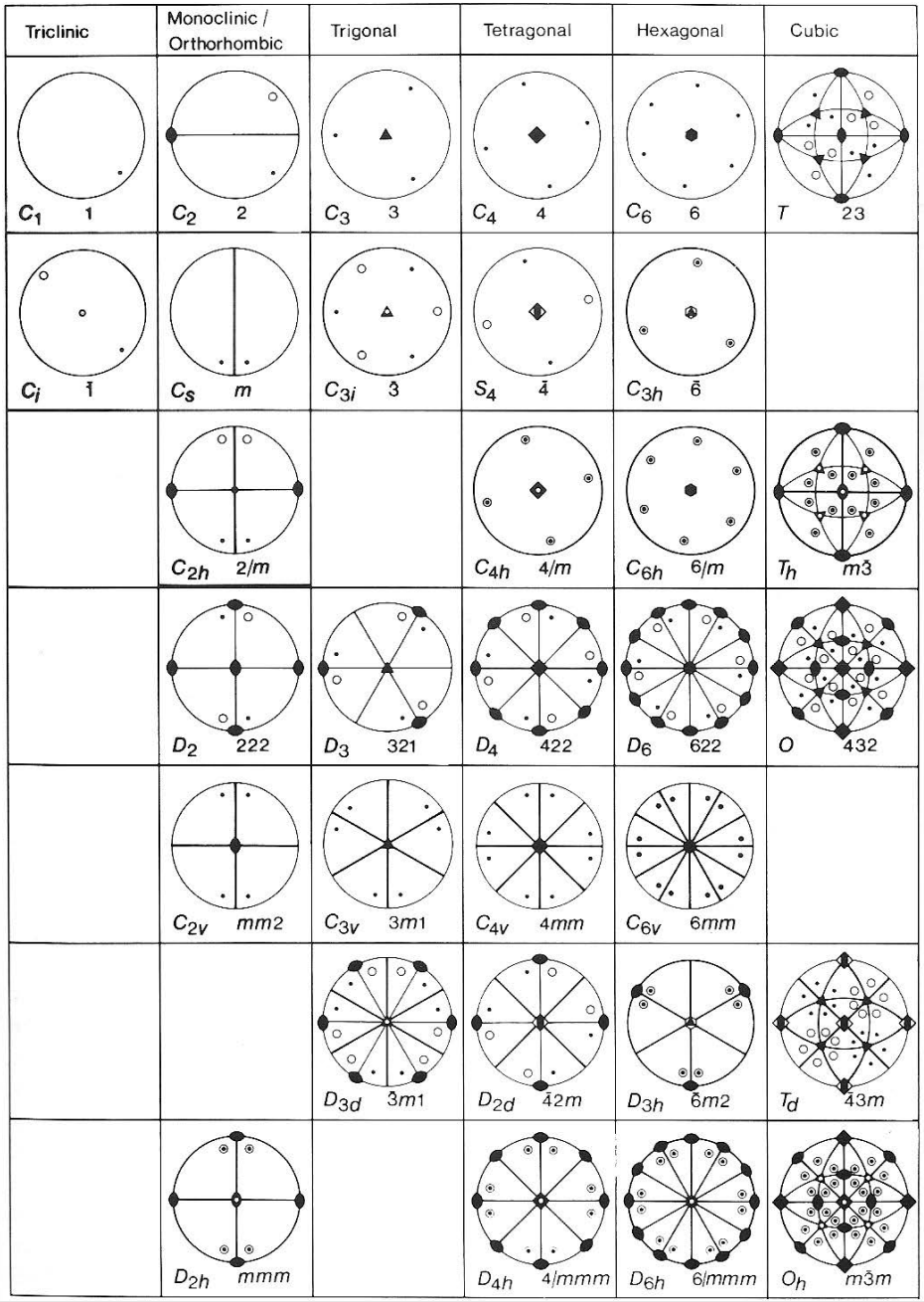


Figure 1-30. Stereographic projections of the 32 crystallographic point groups arranged in columns according to which of the 7 crystal systems they belong to. The order of the point groups increases from top to bottom. Both the Schoenflies and the Hermann–Mauguin (international) symbols are given. Rotation axes *N* are marked by black graphical symbols with *N*-fold rotation symmetry, rotoinversion axes by a white and black symbol with *N*-fold rotation symmetry, the inversion center by an open circle or a white dot when sited on a rotation axis; in-plane mirror planes are indicated by bold limiting circles on the stereographic projection, when normal to the plane they are marked by bold lines. Polar rotation axes parallel to the projection plane are marked by one graphical symbol only. The action of the symmetry operations on a pole (filled circle when above the paper plane, open circle when below) is shown also.

Schoenflies:

C_n:	cyclic	n=1,2,3,4,6
D_n:	dihedral	s, v, h: mirror planes
T:	tetrahedral	i: inversion center
O:	octahedral	

International (Herrmann-Mauguin):

e.g.: 2/m („two over m“)
= a twofold rotation axis
is perpendicular to a mirror plane

Source: Cahn, Haasen, Cramer, Vol.1

Crystal structures: 230 space groups

space groups
describe **spatial symmetry**
of a crystal on an atomic level

230 space groups
all regular crystal structures belong to one of the 230 space groups

space groups are associated with:
- a given point group
- a Bravais space lattice
- the action of the point group on the lattice

- screw axes
- glide planes

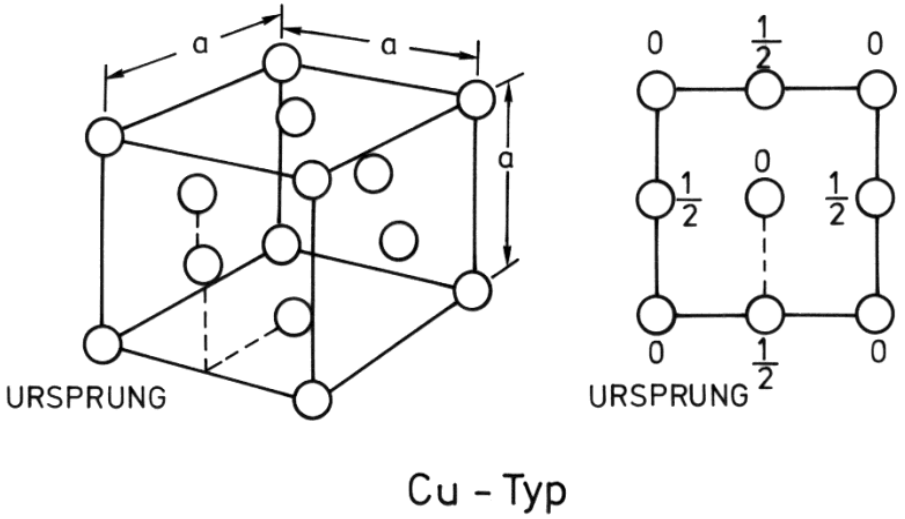
Wyckoff positions (Punktlage):
"a point belonging to a set of points for which site symmetry groups are conjugate subgroups of the space group"

each atom of a crystal structure can be assigned to a particular Wyckoff position with a given site symmetry

Source: Cahn, Haasen, Cramer, Vol.1
L. Kantorovich, Quantum Theory of the Solid State: An Introduction, 2004, Springer

Order and disorder in crystal structures

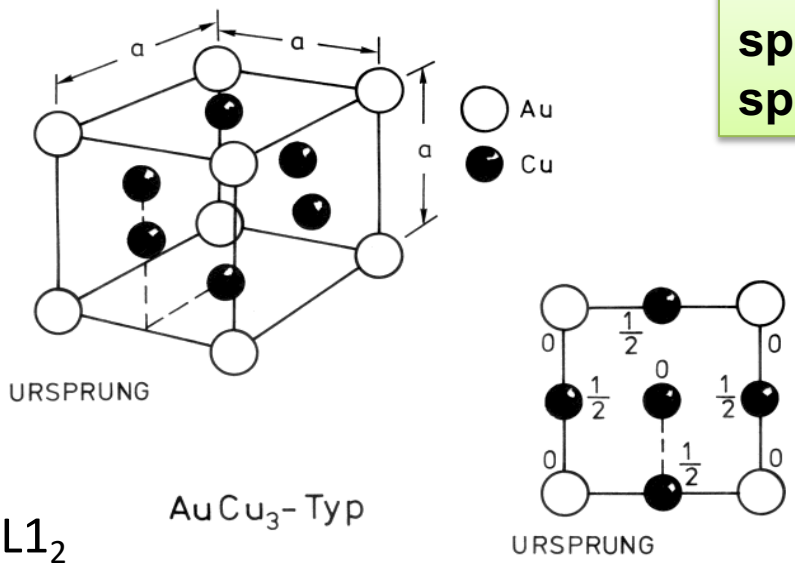
face centered cubic (fcc), Cu-type, A1, cF4



Cu - Typ

e.g.: Cu, Ni, γ-Fe, Al, …

ordered fcc, $L1_2$, cP4



$L1_2$

$AuCu_3$ - Typ

in ordered crystals, specific atoms occupy specific lattice sites

technologically important: Ni_3Al

Order and disorder in crystal structures

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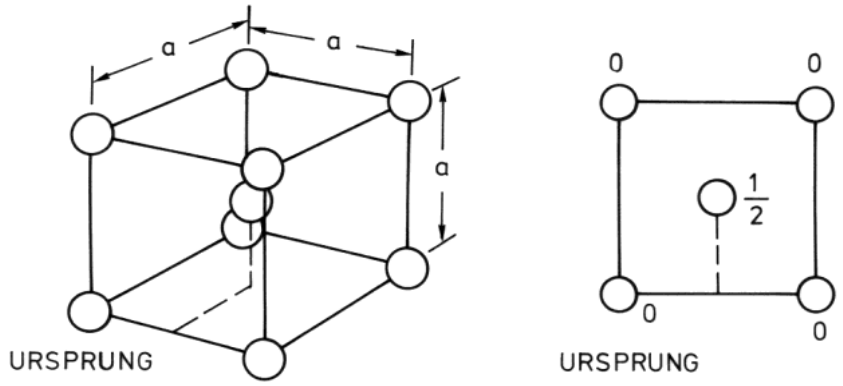
body centered cubic (bcc), W-type, A2, cI2

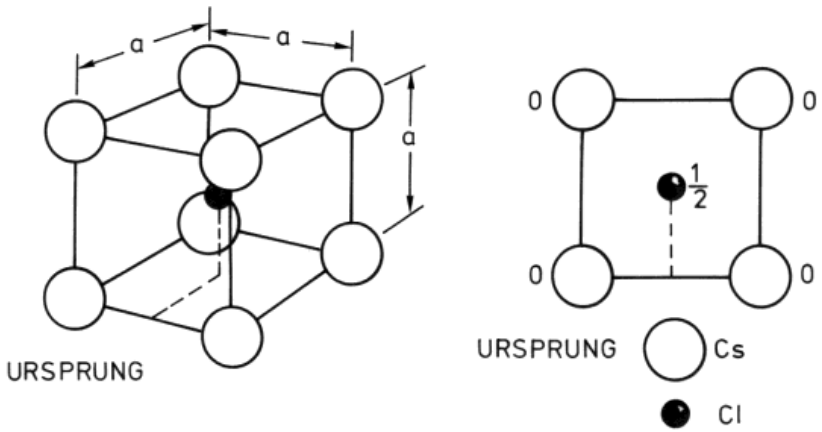


W- Typ

e.g.: W, α-Fe,
δ-Fe, Mo, V, Cr

ordered bcc (B2, CsCl-type, cP2)

e.g.: NiTi, NiAl,



Cs Cl - Typ

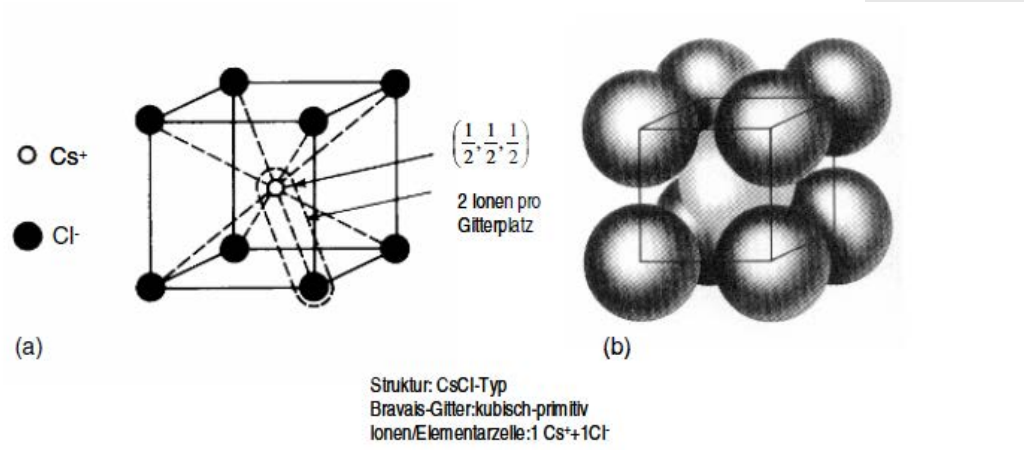
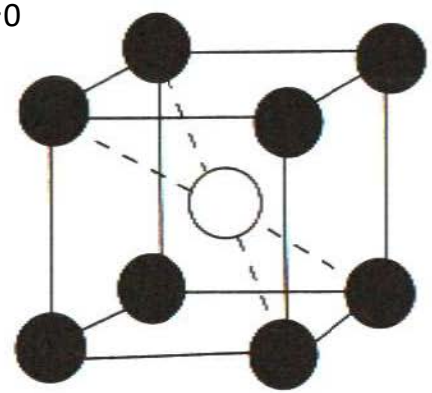


Abbildung 2.20. Elementarzelle von Cäsiumchlorid (CsCl); (a) Lage der Atome im Gitter; (b) Modell der harten Kugeln.

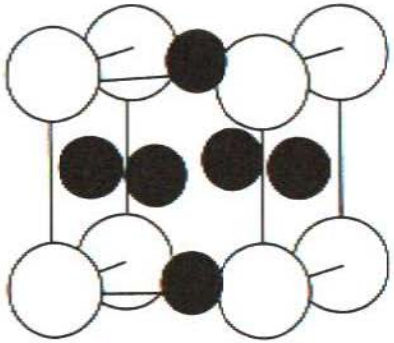
Ordered crystal structures

$L2_0$



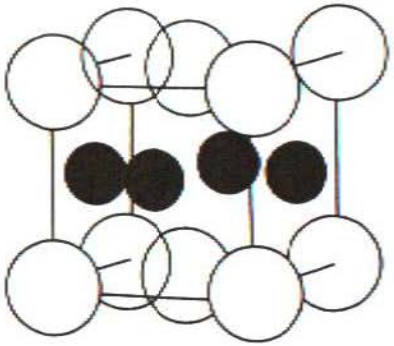
(a) Cu Zn

$L1_2$



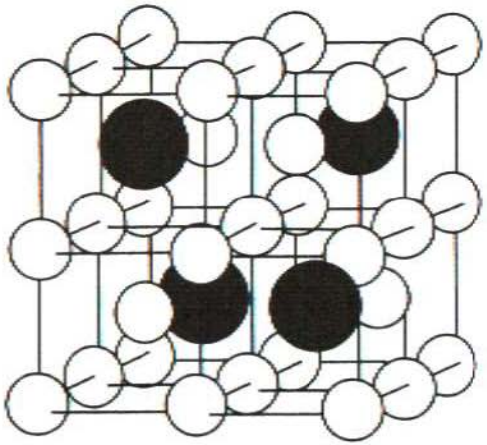
(b) Cu Au

$L1_0$

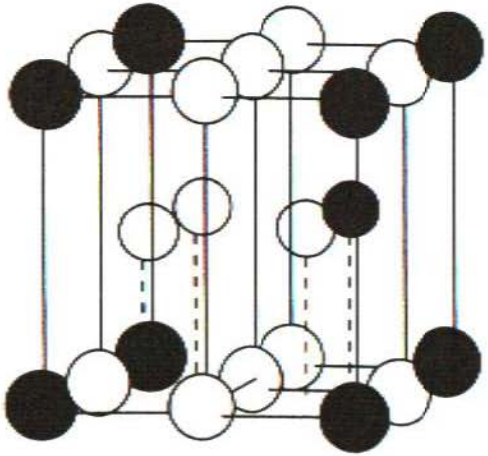


(c) Cu Au

$D0_3$



(d) Al Fe



(e) Cd Mg

$D0_{19}$

Order and disorder in alloys

equiatomic AB alloy

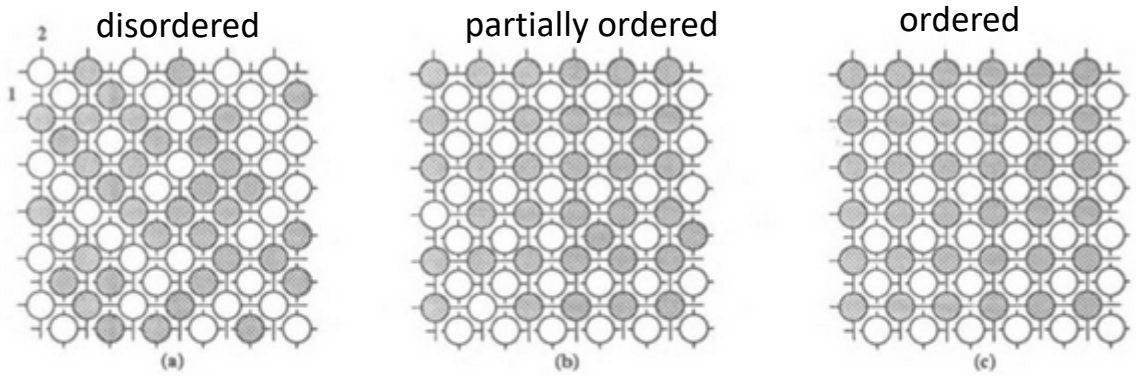


Figure 1: Two dimensional depiction of an equiatomic AB alloy. We have identified two sublattices (1,2) and two atomic species ($A \equiv$ unshaded; $B \equiv$ shaded), *(a)* disordered $A_{0.5}B_{0.5}$ solid solution for which the long range order parameter $\eta = 0$, *(b)* a partially ordered alloy $0 \leq \eta \leq 1$ *(c)* ordered AB intermetallic compound $\eta = 1$.

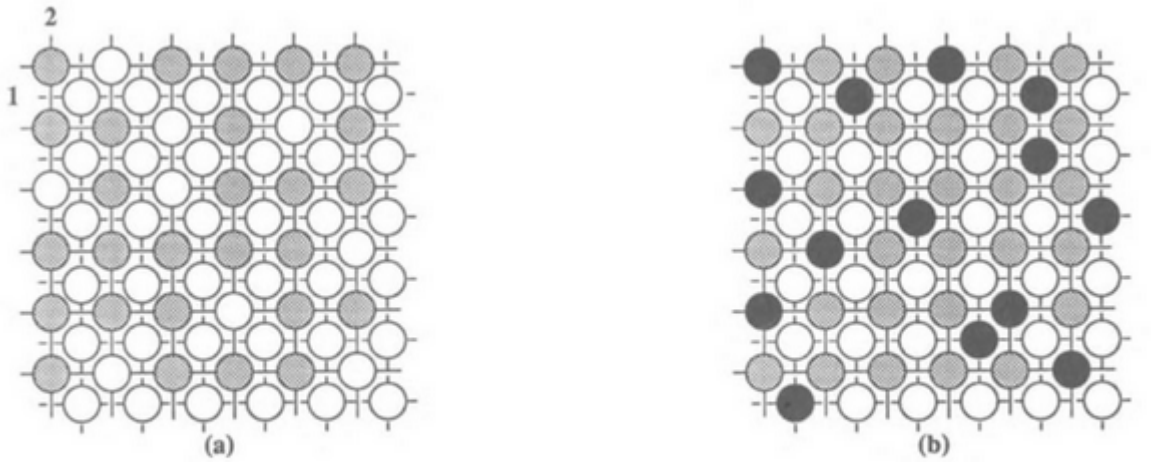


Figure 2: Two dimensional depiction of *(a)* off-stoichiometric AB ordered intermetallic, *(b)* ternary addition to binary AB ordered intermetallic

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C. T. Liu et al. (eds.), Ordered Intermetallics – Physical Metallurgy and Mechanical Behaviour,
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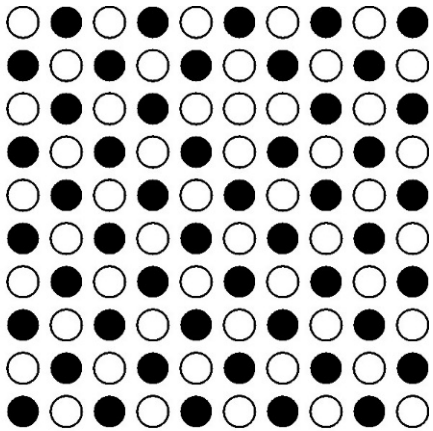
Order and disorder reactions

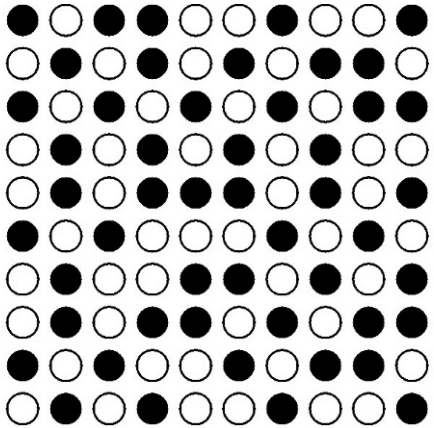
order

disorder



order reaction

disorder reaction



e.g. in the systems
Cu-Au, Cu-Zn

superlattice structures

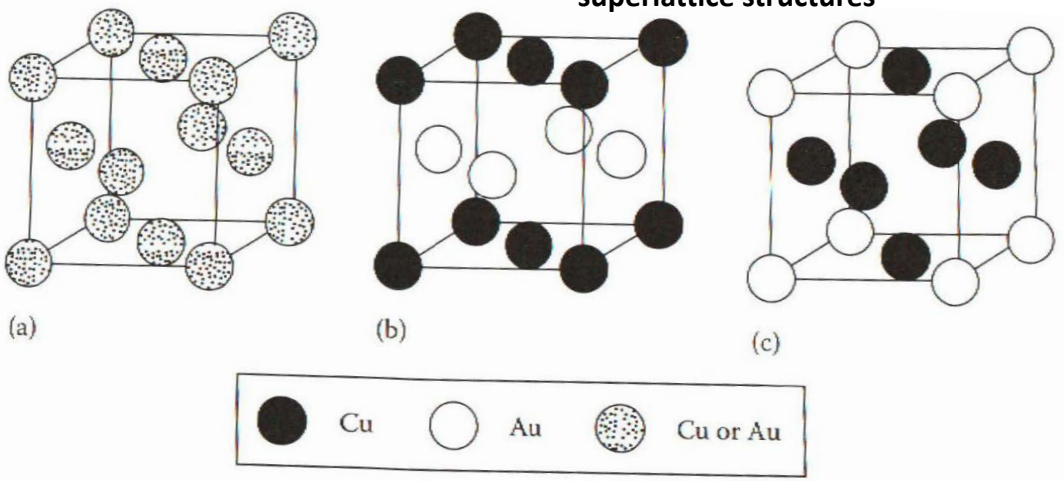
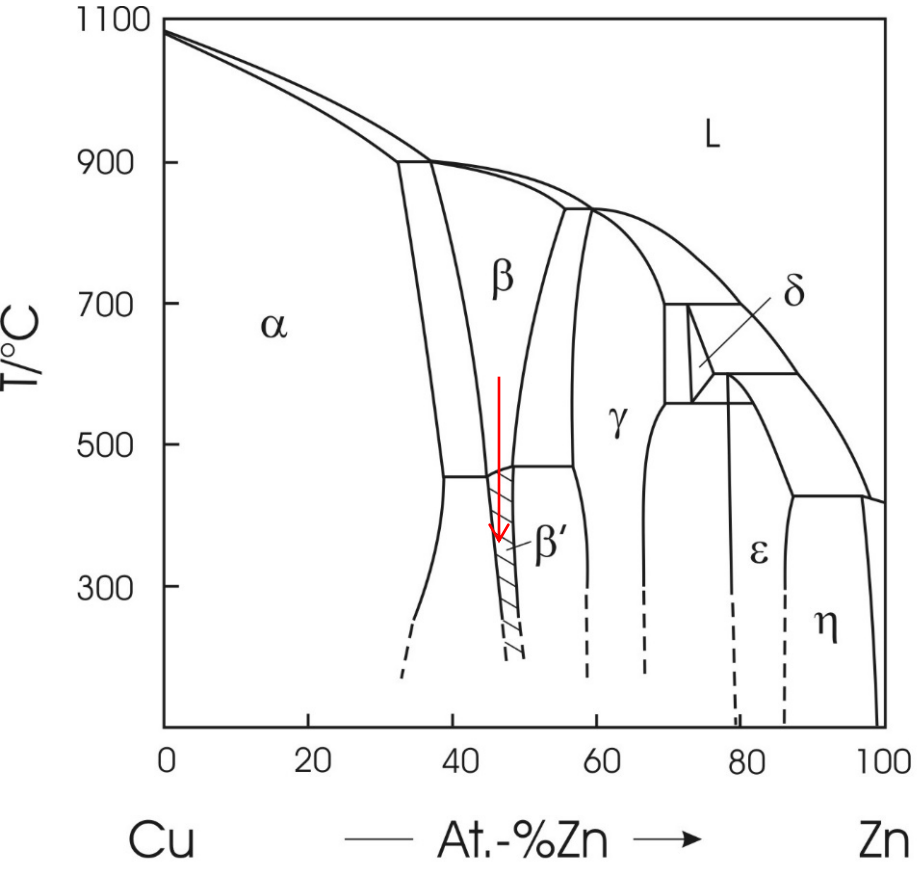
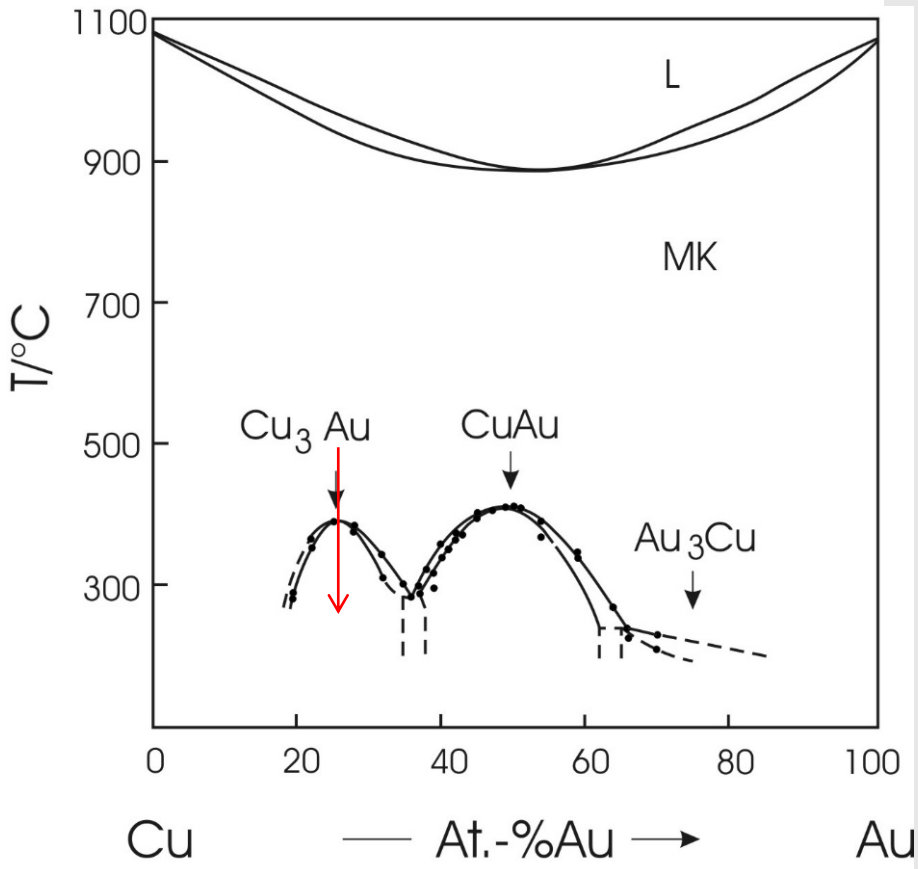


FIGURE 1.20
Ordered substitutional structures in the Cu-Au system: (a) high-temperature disordered structure, (b) CuAu superlattice, (c) Cu_3Au superlattice.

Order and disorder reactions in phase diagrams



order reaction:
β -> β‘



order reaction:
solid solution -> Cu_3Au

Quantifying order

RUB

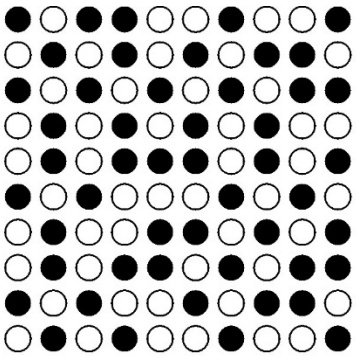
Order parameter p (Bragg/Williams):

system: AB
fully ordered state: all A-atoms on α-sites, all B-atoms on β-sites

q: fraction of A-atoms on α-sites
1-q: fraction of A-atoms on β-sites

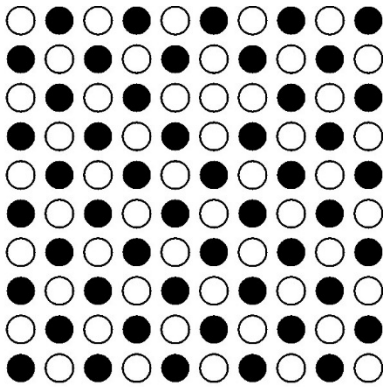
$$p = 2 \cdot q - 1$$

fully disordered



q=0.5
p=0

fully ordered



q=1
p=1

Quantifying order

intermetallic compound A_mB_n

i.e. m atoms of A and n atoms of B

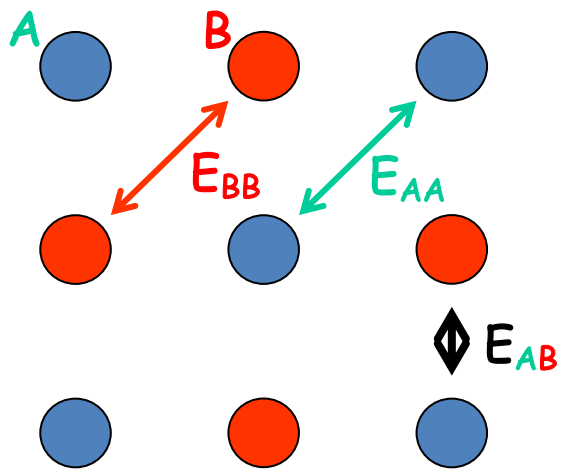
p_α – fractions of A atoms on A-places,
p_β – fraction of B atoms on B-places,
x_A=m/(m+n),
x_B=n/(m+n)

order parameter:

$$p = \frac{p_\alpha - x_A}{1 - x_A} = \frac{p_\beta - x_B}{1 - x_B}$$

For order/disorder reactions the interaction W between atoms plays an important role:

$$W = E_{AB} - 1/2 \cdot (E_{AA} + E_{BB})$$



Cu-Au

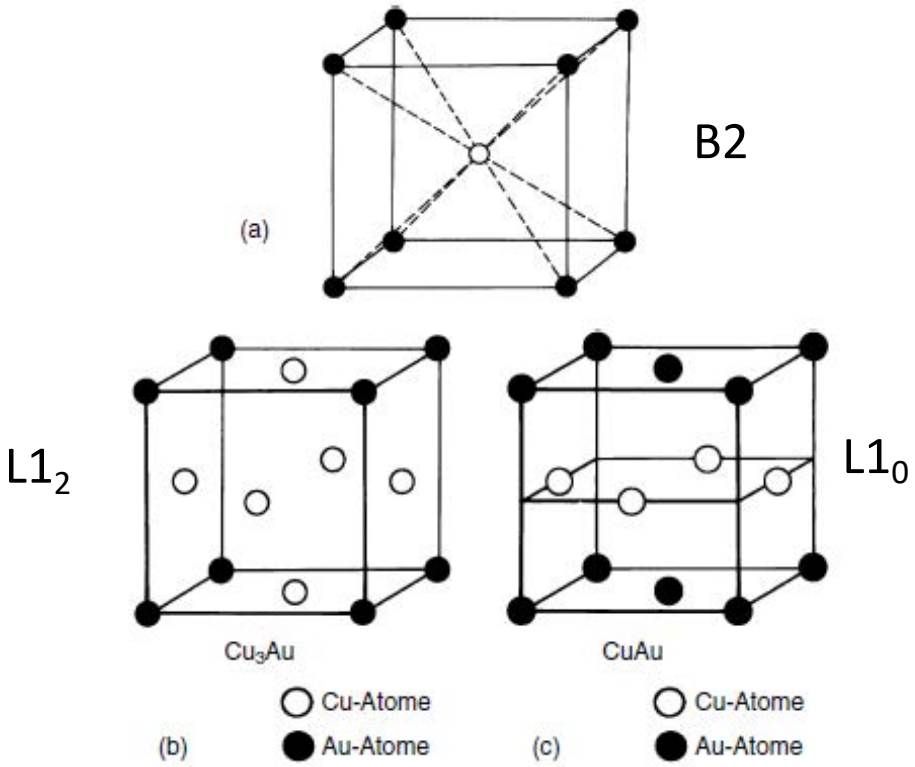


Abbildung 4.33. Geordnete Atomverteilungen vom Typ AB lassen sich im CsCl-Gitter (a) (B2-Struktur), solche vom Typ AB_3 im Cu_3Au-Gitter (b) ($L1_2$-Struktur) verwirklichen, die mit einem krz bzw. kfz Mischkristall bei regelloser Atomverteilung verträglich sind. Ein kubisch flächenzentrierter Mischkristall vom Typ AB (c) kann nicht ordnen ohne seine kubische Struktur zu verlieren. Bei einer Unterteilung des kfz Gitters in je zwei Untergitter für A und B kommt es zur Schichtenbildung und damit wegen der unterschiedlichen Atomradien A und B zu einer tetragonalen Kristallstruktur.

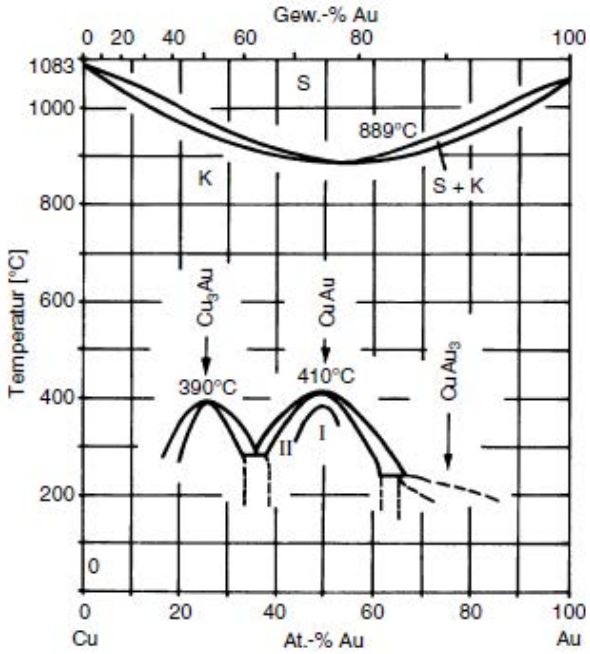


Abbildung 4.34. Zustandsdiagramm des Systems Cu-Au, das bei tieferen Temperaturen verschiedene geordnete Phasen im festen Zustand bildet, die aber bereits weit unterhalb des Schmelzpunktes wieder in eine regellose Verteilung übergehen [4.1].

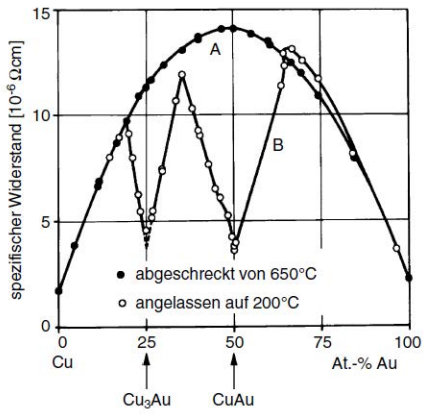


Abbildung 4.39. Das Auftreten von Überstrukturen führt zur starken Verringerung des elektrischen Widerstandes, bspw. für Cu_3Au und CuAu (nach [4.6]).

Gottstein, pp. 134

Temperature-dependence of order

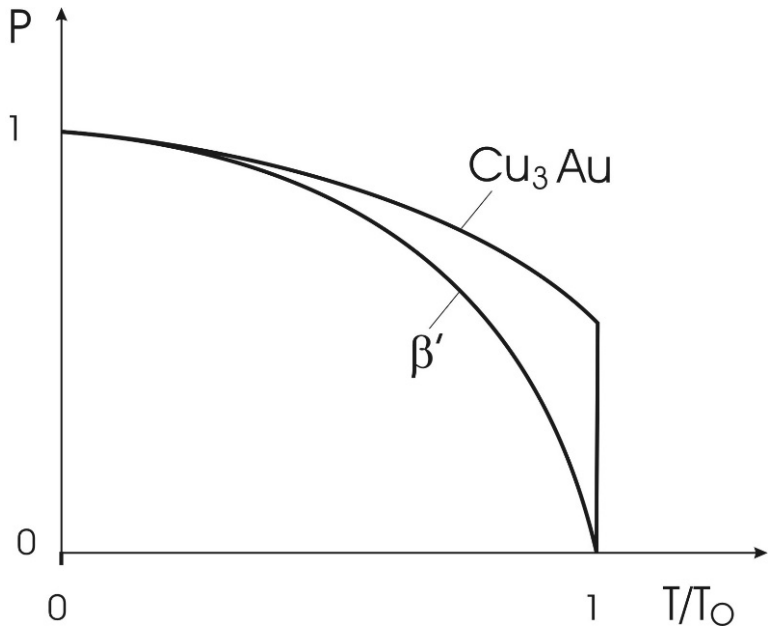
(1) critical temperature T_O

$T < T_O$ system is ordered

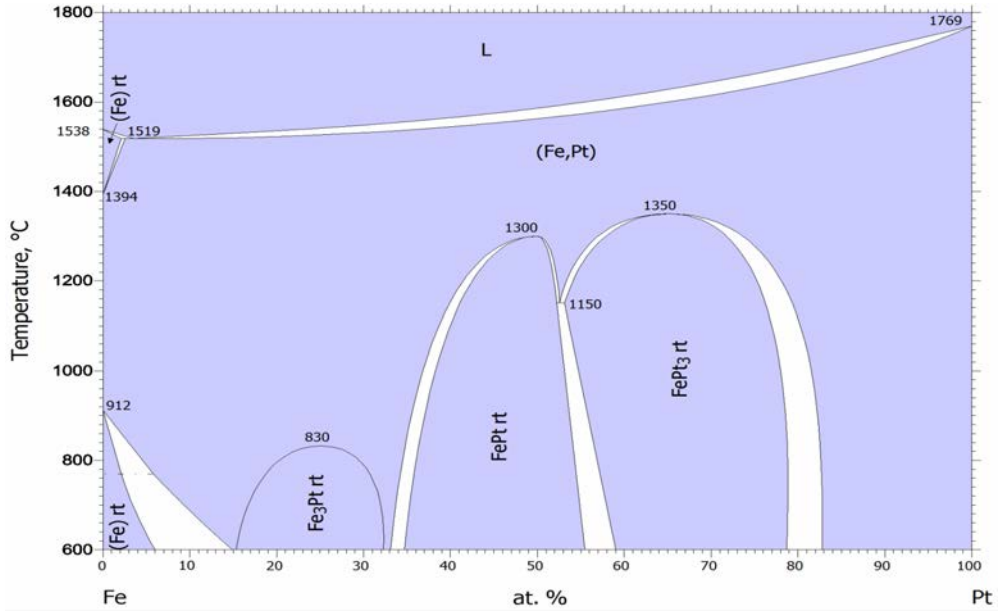
$T > T_O$ system is not ordered

(2) order parameter p is temperature-dependent

- up to 0.3 T_0 order is maintained
- aproaching T_0, order decreases
- T_O is proportional to interaction energy W



The Fe-Pt system



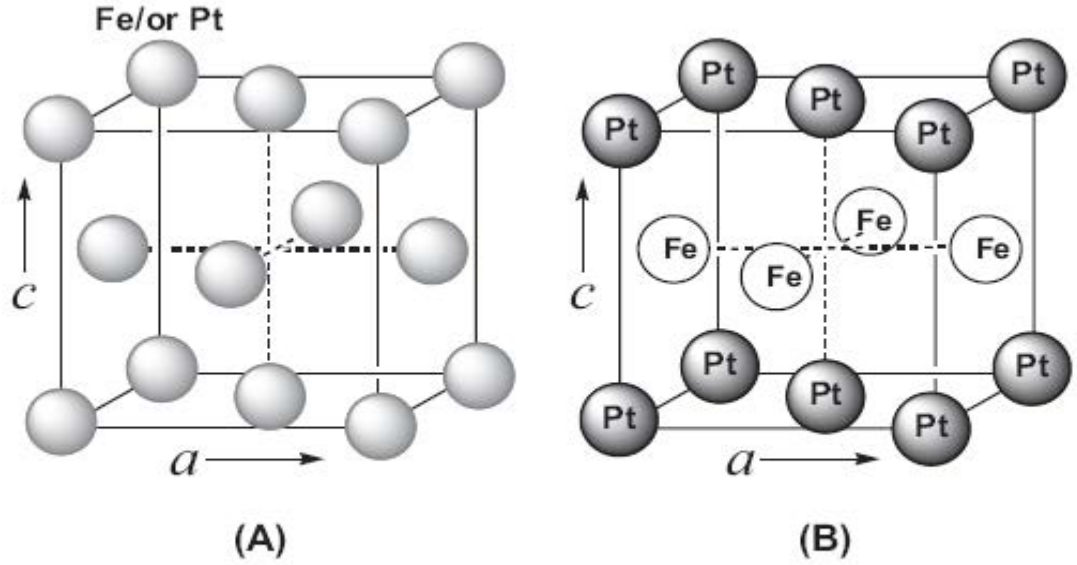


Figure 2. Schematic illustration of the unit cell of A) chemically disordered fcc and B) chemically ordered fct FePt.

$L1_0$

unique magnetic properties

Rules for formation of intermetallic phases

Intermediate and intermetallic phases

RUB

for a lot of intermetallic phases *simple valence concepts are not applicable*, some compounds have a broad existence range, others not

Some examples of intermetallics:
- Valence compounds
- NiAs-compounds
- Hume-Rothery phases
- Laves-phases (AB_2)
- Zintl-phases
- TCP phases: topologically close packed phases

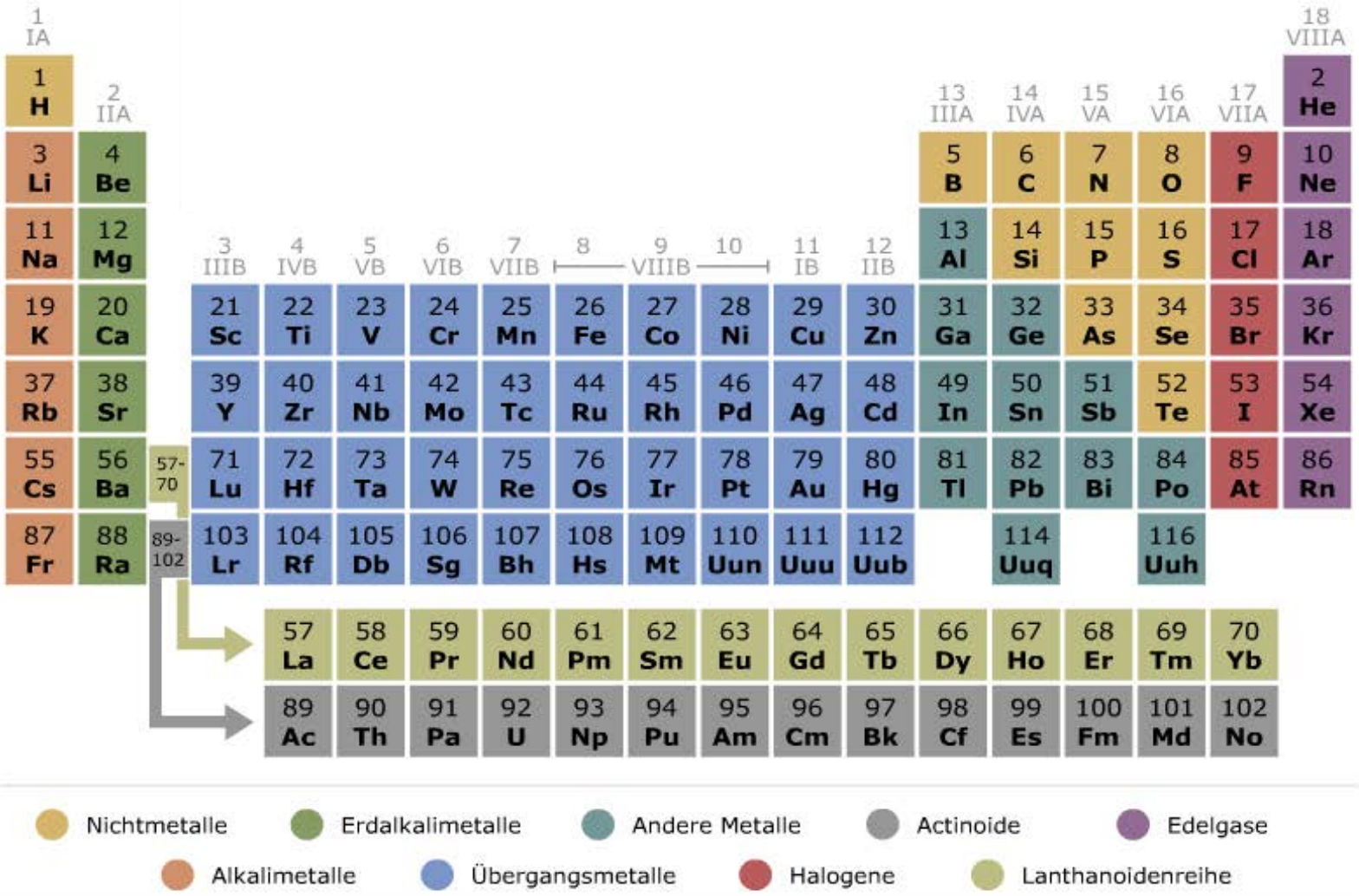
- constituents A, B tend to form a compound, if properties are different (size, electronegativity, valence electron concentration, (electro)chemical properties, …)
- from supersaturated solid solutions over intermediate phases to stoichiometric compounds
- binding can be a mixture of metallic, covalent, ionic binding; the higher the degree of covalent and ionic bonding, the higher is ususally brittleness and resistivity (non-metallic properties)

Periodic tables of elements

Periods

increasing ionisation energy, increasing electronegativity

Groups: elements with similar chemical behavior: similar outer electron configuration, same number of valenc electrons



Intermetallic phases

About 2/3 of elements are metals

Furthermore, alloys (based on metals): intermetallic phases (alloys, compounds) as well as metal-oxides, -nitrides, -carbides, hydrides, ...
Different groups of intermetallics

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

metals

electropositive metals

transition metals
(similar radii and electronegativity, different number of valence electrons)

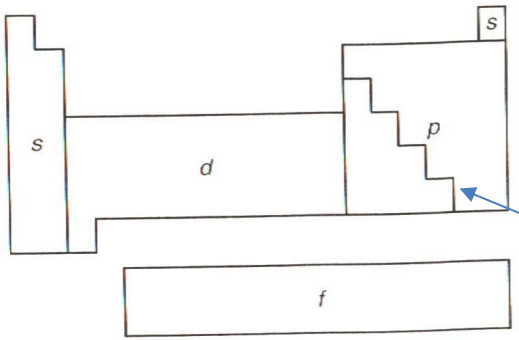
meta-metals

semi-metals

very small overlap between bottom of conduction band and top of valence band. Semimetal has no band gap and a negligible density of states at the Fermi level.

half-metals: act as conductor to electrons of one spin orientation, but as an insulator or semiconductor to those of the opposite orientation. Although all half-metals are ferromagnetic (or ferrimagnetic), most ferromagnets are not half-metals. Many of the known examples of half-metals are oxides, sulfides, or Heusler alloys.

Periodic tables of elements



valence electrons in orbitals
s, d, p, f

Zintl line between d (semi-metals) and p (non-metals)

form easily **anions** (negative)

form easily **cations** (positive)

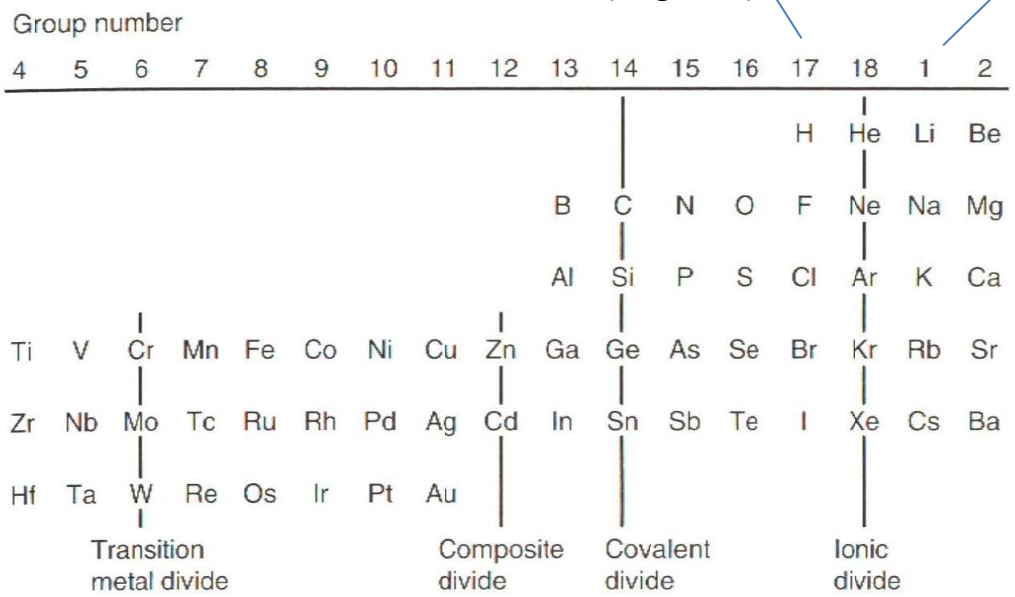


Figure 4.7. The metallurgist's Periodic Table showing the four 'divides' proposed by Stone (1979) Notice that the position of the different groups has been shifted, in comparison with the conventional presentation of the Table, in order to give special emphasis to the ionic divide.

Source: Intermet. Chemistry

Electronegativity

RUB

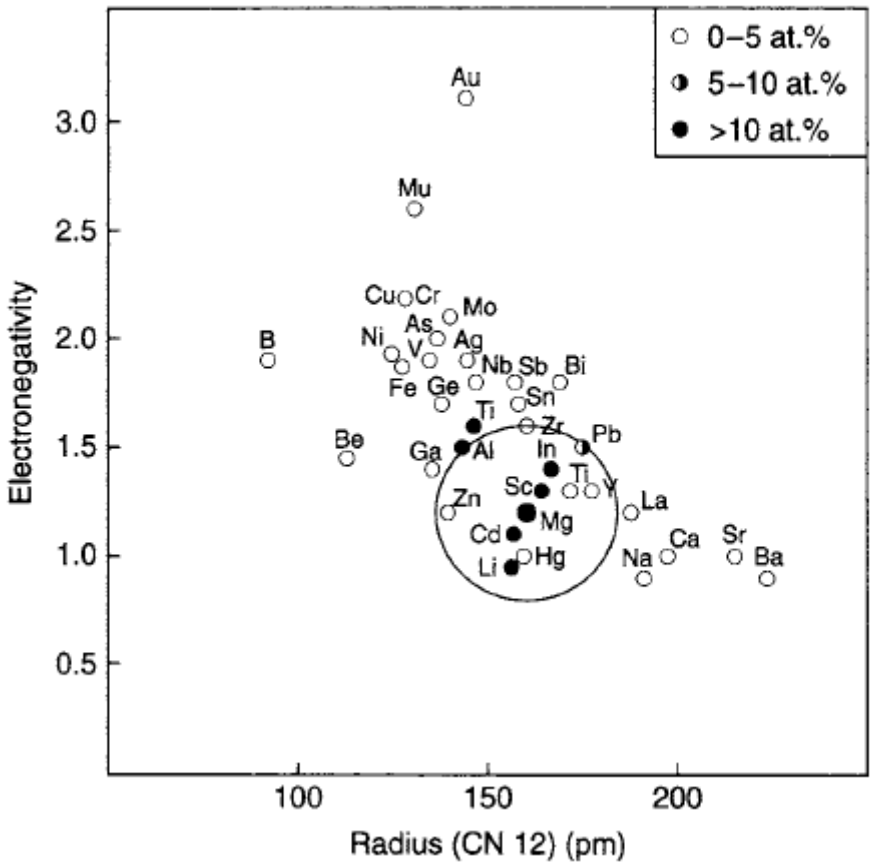
Table 2.1. The electronegative scale as reported by Pauling (1967).

H																	
2.1																	
Li	Be	B												C	N	O	F
1.0	1.5	2.0												2.5	3.0	3.5	4.0
Na	Mg	Al												Si	P	S	Cl
0.9	1.2	1.5												1.8	2.1	2.5	3.0
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	
0.8	1.0	1.3	1.4	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5	
Cs	Ba	La–Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	
0.7	0.9	1.1–1.2	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2	
Fr	Ra	Ac	Th	Pa	U	Np–No											
0.7	0.9	1.1	1.3	1.5	1.7	1.3											

electronegativity:
„the power of an atom in a material to attract electrons to itself“

Solubility: Darken and Gurry diagram

Darken and Gurry proposed rules for elemental solubility in 1953.
An ellipsoid is drawn around an element (e.g. Mg) showing the elements with a maximum variance of 15% atomic size and 0.3 electronegativity.
Elements inside the ellipsoid usually have a higher solubility in the respective element indicated by the color of the dots in the figure.



L. S. Darken, R. W. Gurry, Physical Chemistry of Metals, McGraw-Hill Book Company, 1953

Mutual solubility in binary alloys of transition metals (X-Y)

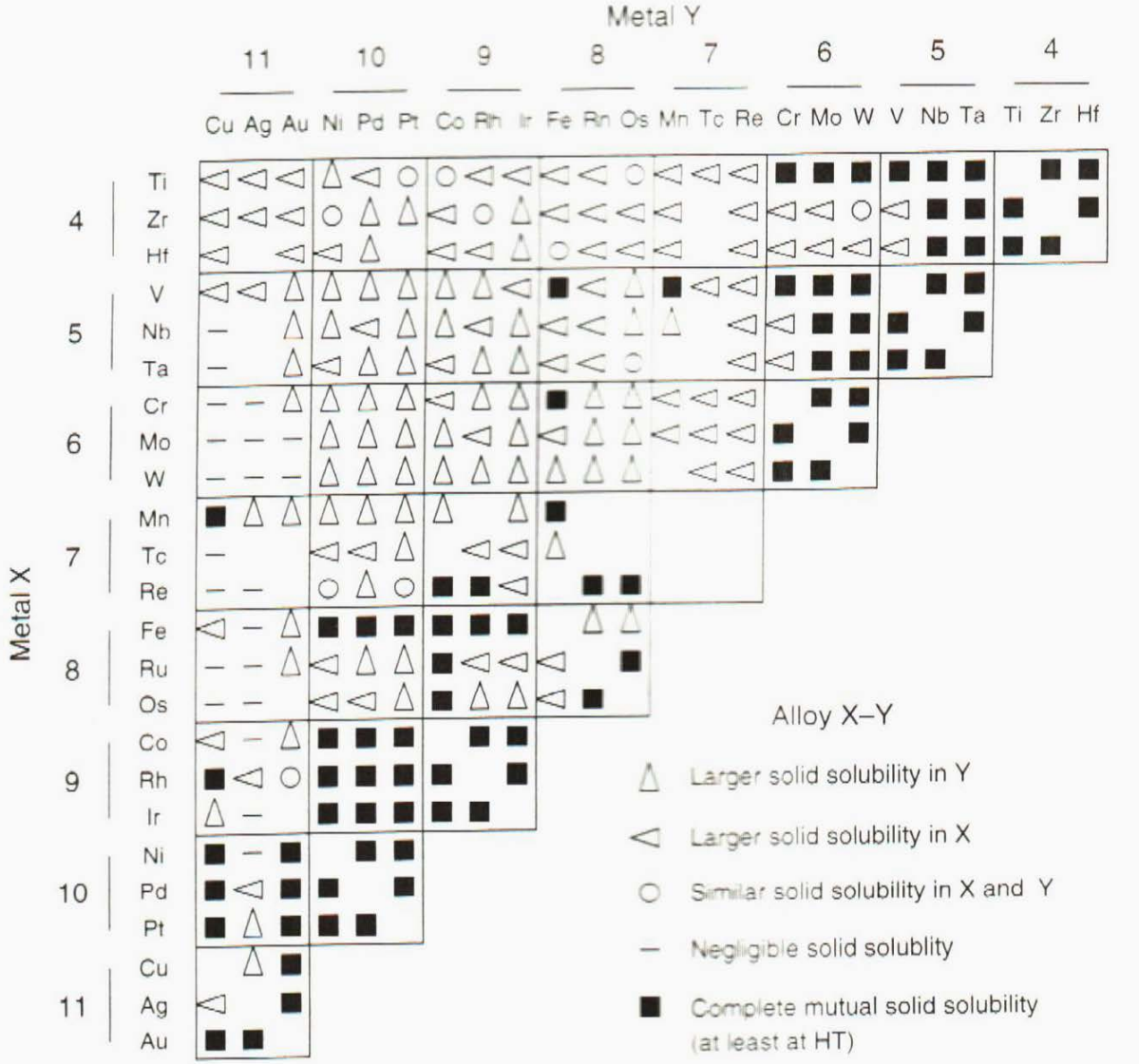


Figure 2.15. Relative extent of the mutual solid solubility in binary alloys of transition metals, ordered according to their group number in the Periodic Table. The group number is reported on the left and on the top of the figure.

Source: Intermetallic chemistry

Mutual solubility: Mendeleev number

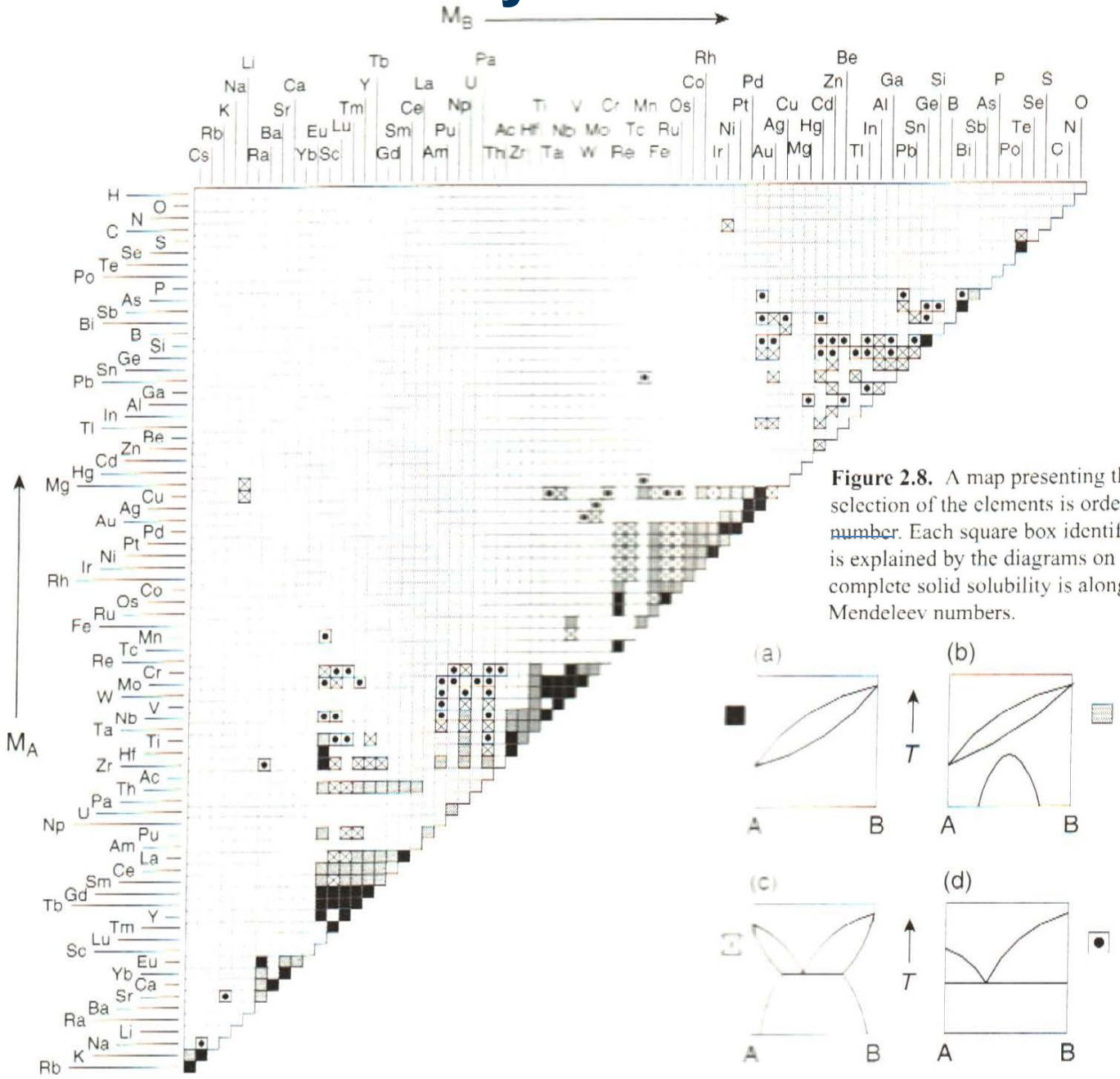


Figure 2.8. A map presenting the mutual solubility in the solid state of the different metals. A selection of the elements is ordered along the two axes according to their values of the Mendeleev number. Each square box identifies a metal pair. The meaning of the codes inserted in the boxes is explained by the diagrams on the right. Notice that the crowding of the metal pairs showing complete solid solubility is along the diagonal of the figure corresponding to close values of their Mendeleev numbers.

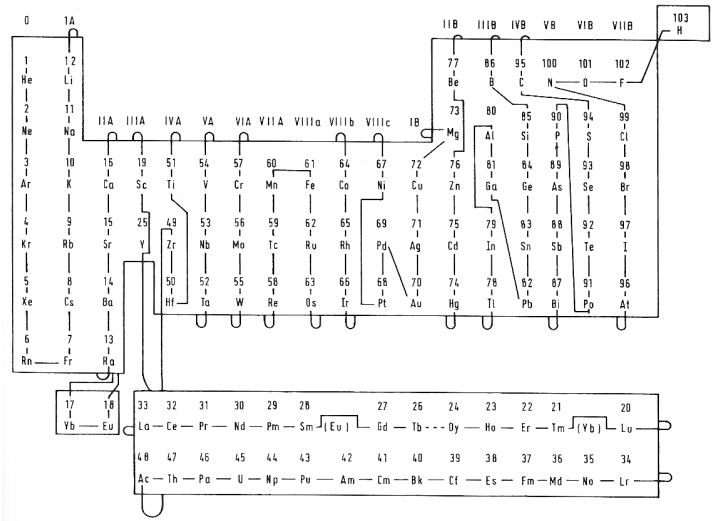
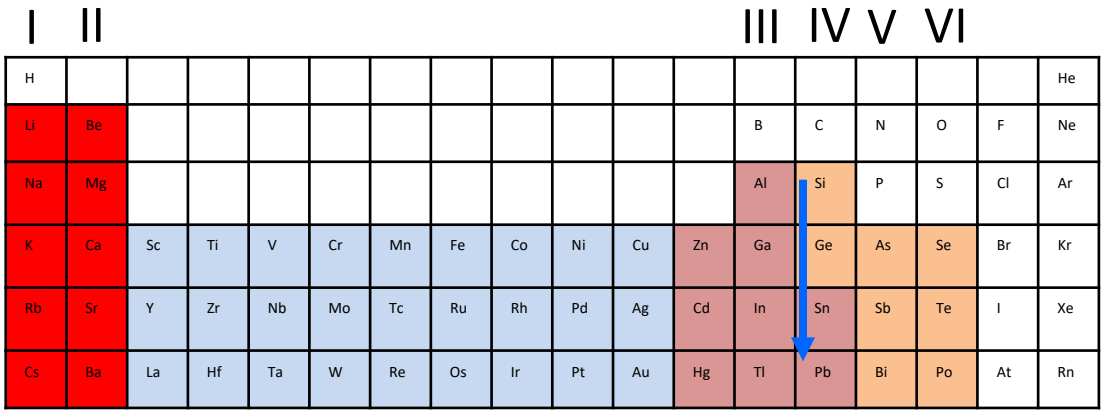


Figure 2-1. The string running through this modified periodic table puts all the elements in sequential order according to the Mendeleev number. (Pettifor, 1988a). Note that group IIA elements Be and Mg have been grouped with IIB, divalent rare earths have been separated from trivalent, and Y has been slotted between Tb and Dy.

Source: Intermet. chemistry

Intermetallic compounds: Valence compounds



metals from groups I, IV, V, VI

e.g.:

Mg_2Si – T_S = 1085°C
Mg_2Ge – T_S= 1115°C
Mg_2Sn – T_S= 778°C
Mg_2Pb – T_S= 550°C

decreasing electronegativity

Intermetallic phases: Hume-Rothery Phases

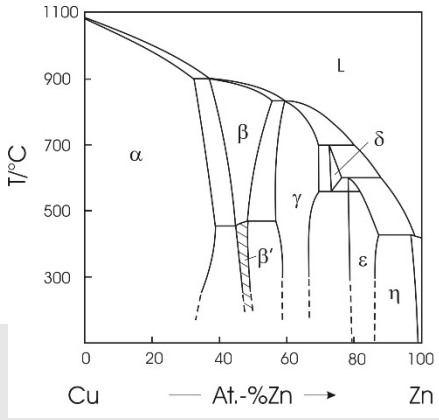
Hume-Rothery rule:
„electron phases“

compare rules for solid solution formation

similar structures for similar <u>valence electron concentration</u> (VEC)

VEC = number of VE/atom of the phase, also (e/a) ratio

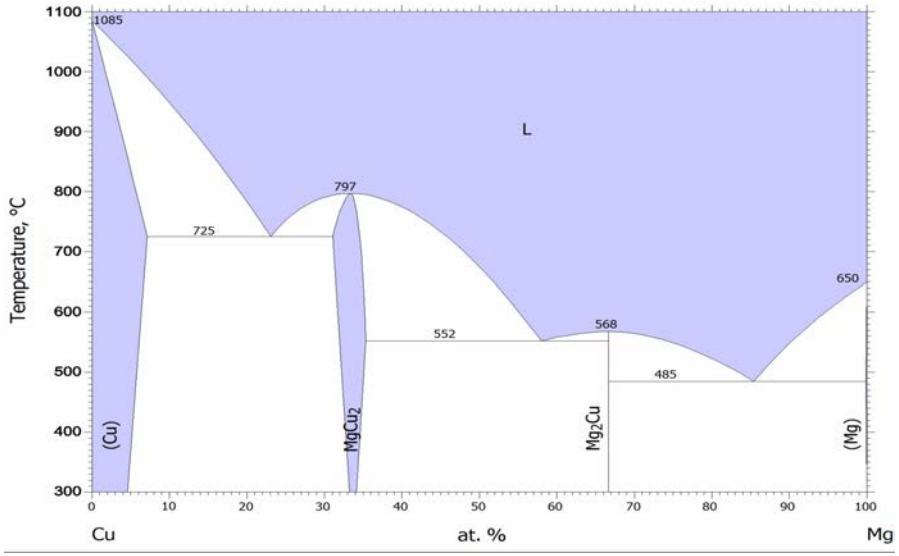
VEC = 3/2 (21/14): „bcc“, β structures	**e.g.: CuZn, CuBe, NiAl, …**
VEC = 21/13: γ structures	**e.g.: Cu_5Zn_8, Cu_9Al_4, …**
VEC = 7/4 (21/12): „hex“ ε structures	**e.g.: $CuZn_3$, $CuSn_3$, …**



Laves phases (AB_2)

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

frequently Laves-phases and related phases (e.g. $MgCu_2$, $NbFe_2$, $TiFe_2$, $TbFe_2$)



Laves-phases:

determined by ratio of atom radii

e.g. 1/1.225 -> AB_2- compounds

densely packed (e.g. 0.71) (bcc 0.682)

- usually hard, brittle
- undesired in superalloys
- interesting magnetic material ($TbFe_2$)

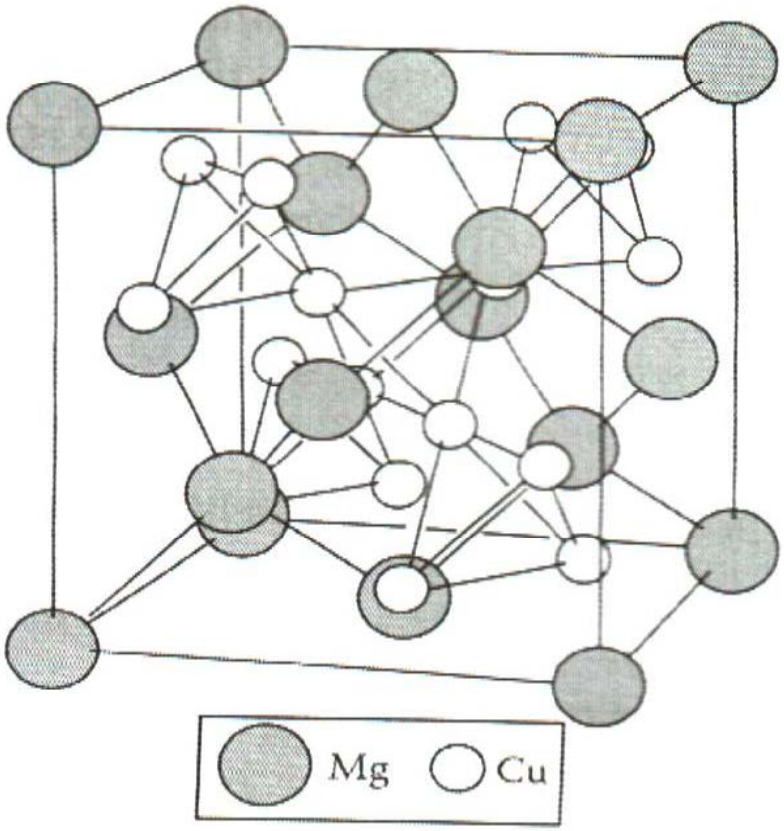
Intermetallic compounds: Laves-Phases

determined by the ratio of atom radii of components

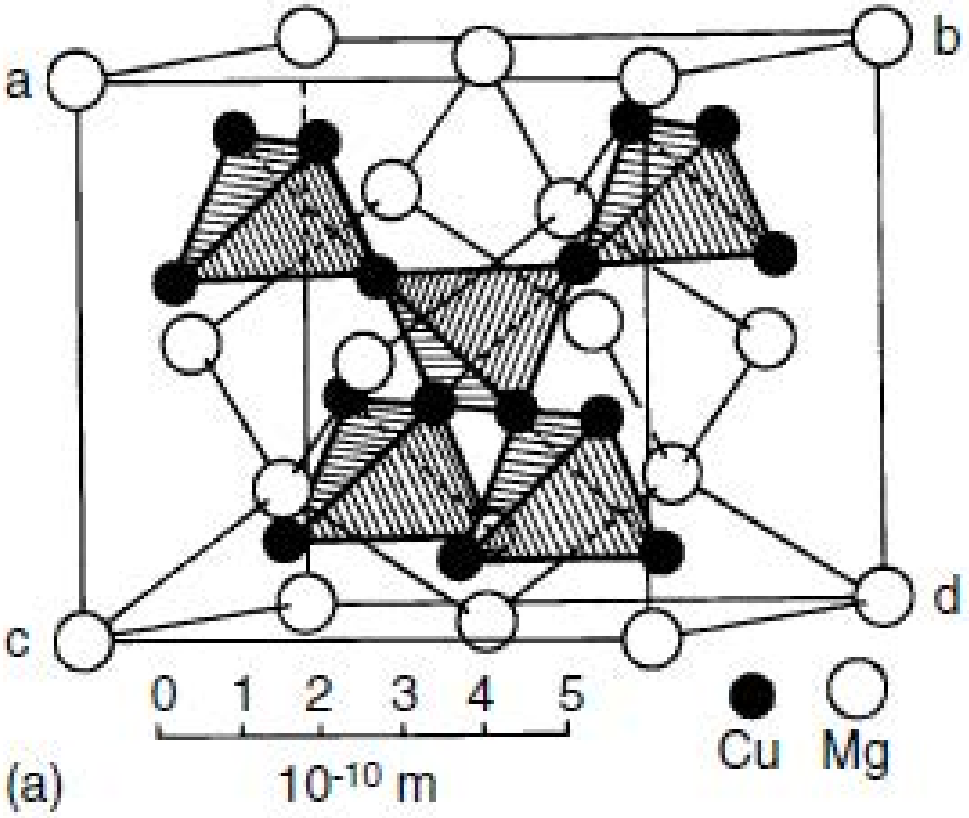
e.g. radii ratio 1/1.225 -> AB_2-compounds

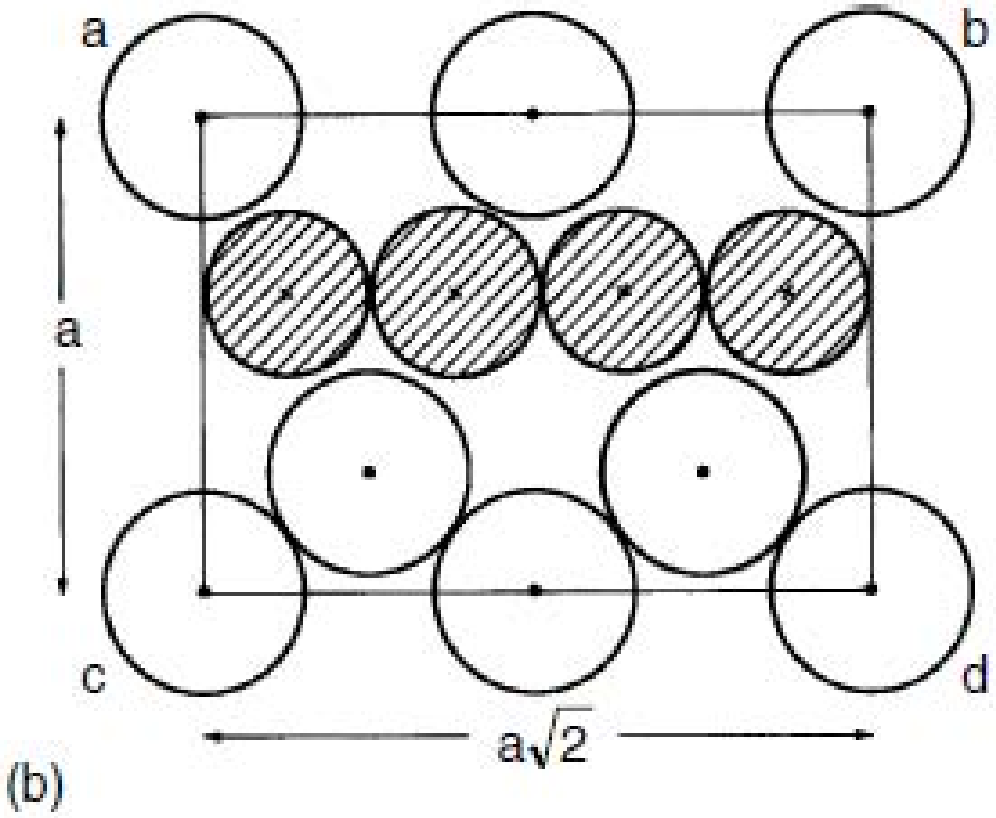
more densly packed (e.g. 0.71) than bcc (e.g. 0.682)

$MgCu_2$



Unit cell of the Laves phase $MgCu_2$

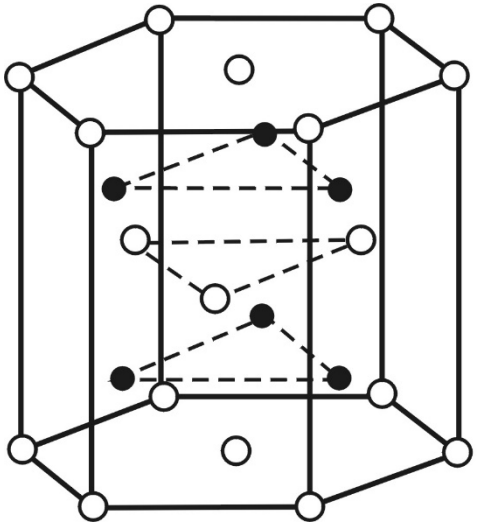




(110) plane

Intermetallic compounds: NiAs-compounds

H																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn



○ As

● Ni

Compounds of: Se, Te, Sn, Sb, As, Bi

and transition metals: Fe, Cr, Co, Ni, Mn

NiAs:

As-atoms form densest packed partial lattice

Ni occupies octahedral sites

Mendeleev number

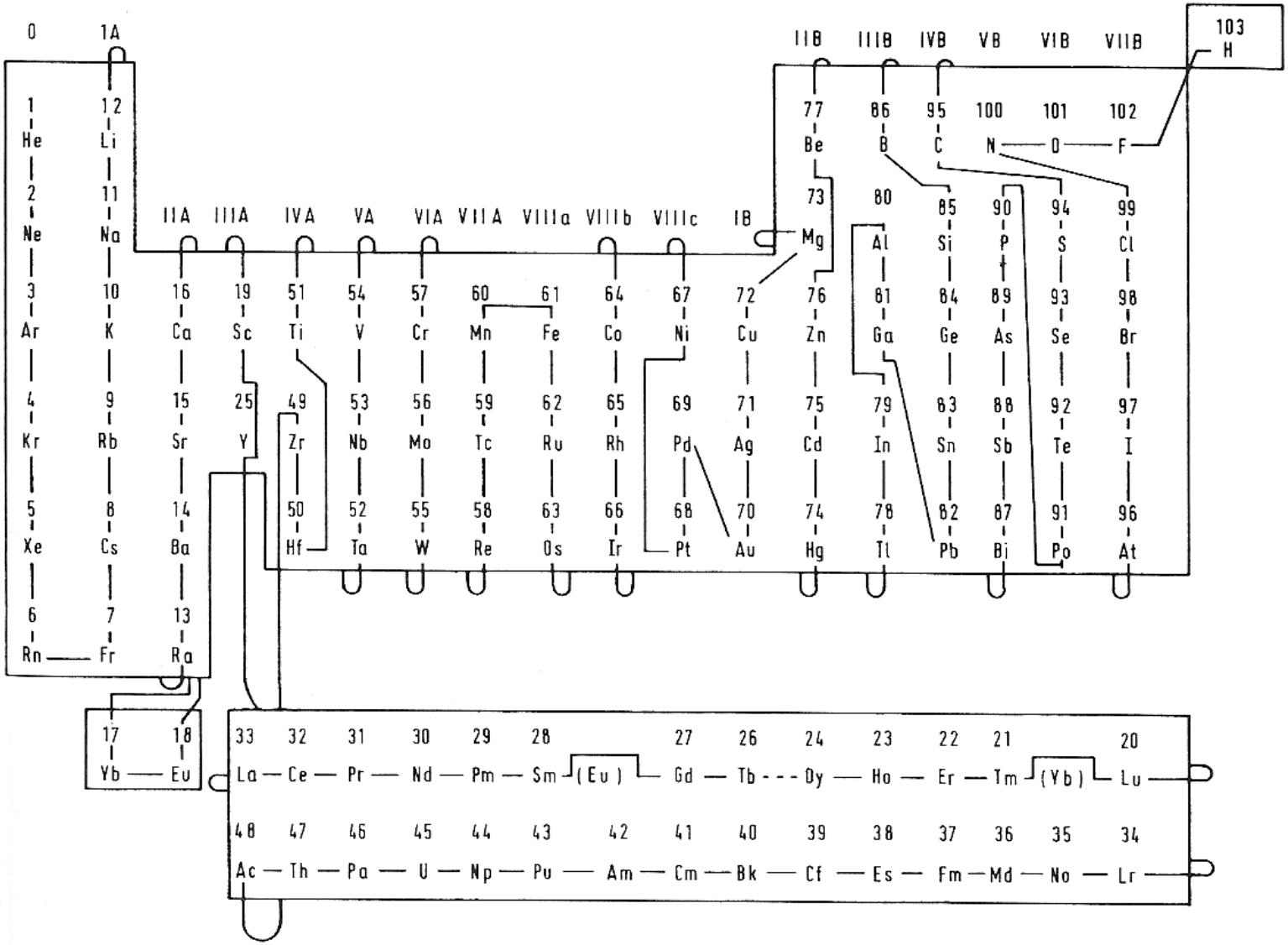
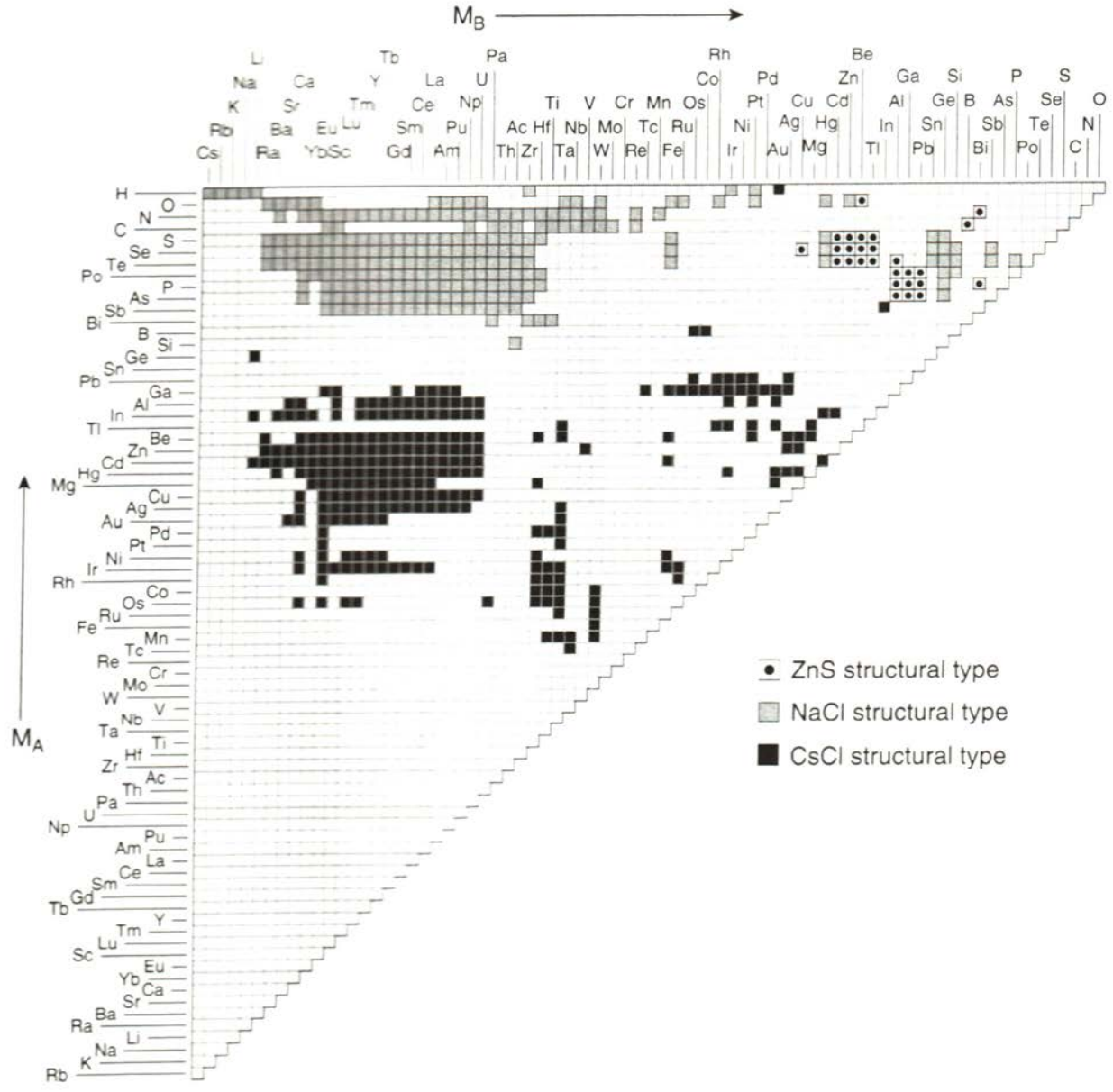


Figure 2-1. The string running through this modified periodic table puts all the elements in sequential order according to the Mendeleev number. (Pettifor, 1988 a). Note that group II A elements Be and Mg have been grouped with II B, divalent rare earths have been separated from trivalent, and Y has been slotted between Tb and Dy.

Source: Cahn Haasen (Pettifor)

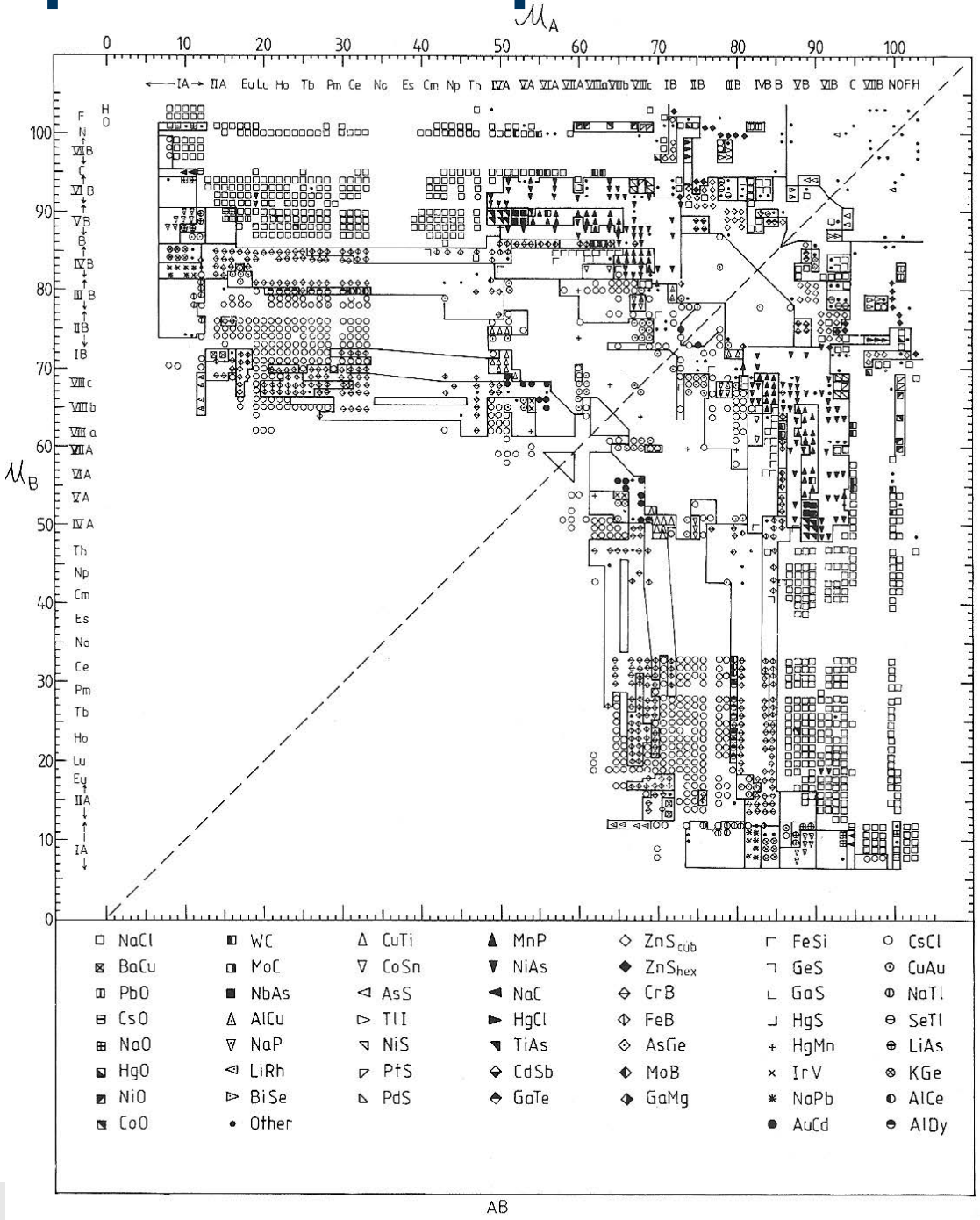
Simplified version of Pettifor's map for AB compounds



Source: Intermetallic Chemistry

Pettifor's map for AB compounds

AB structure map
(Pettifor 1988)



Source: Cahn Haasen

Pettifor's map for AB_2 and AB_3 compounds

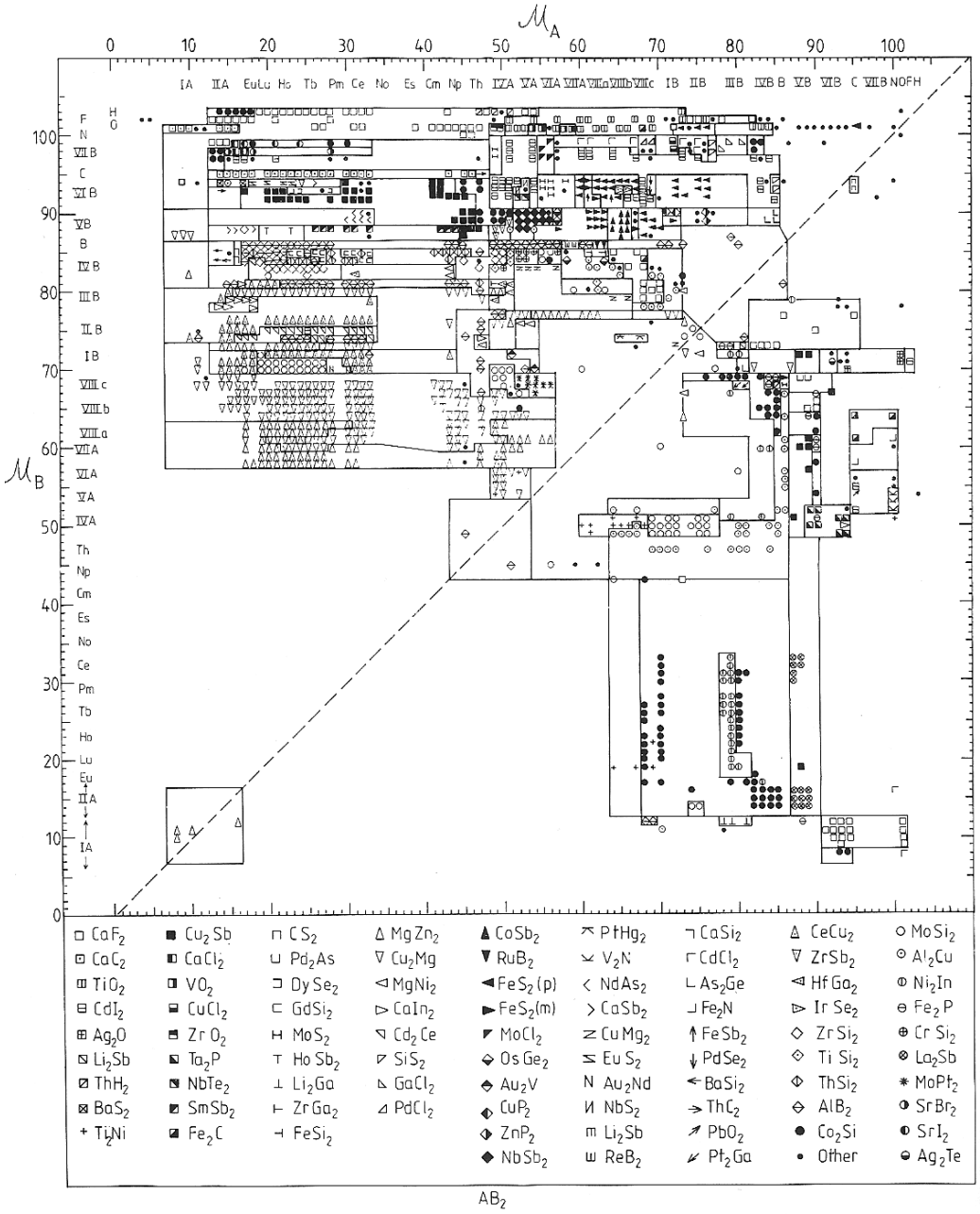


Figure 2-4. The AB_2 structure map (Pettifor, 1988 a).

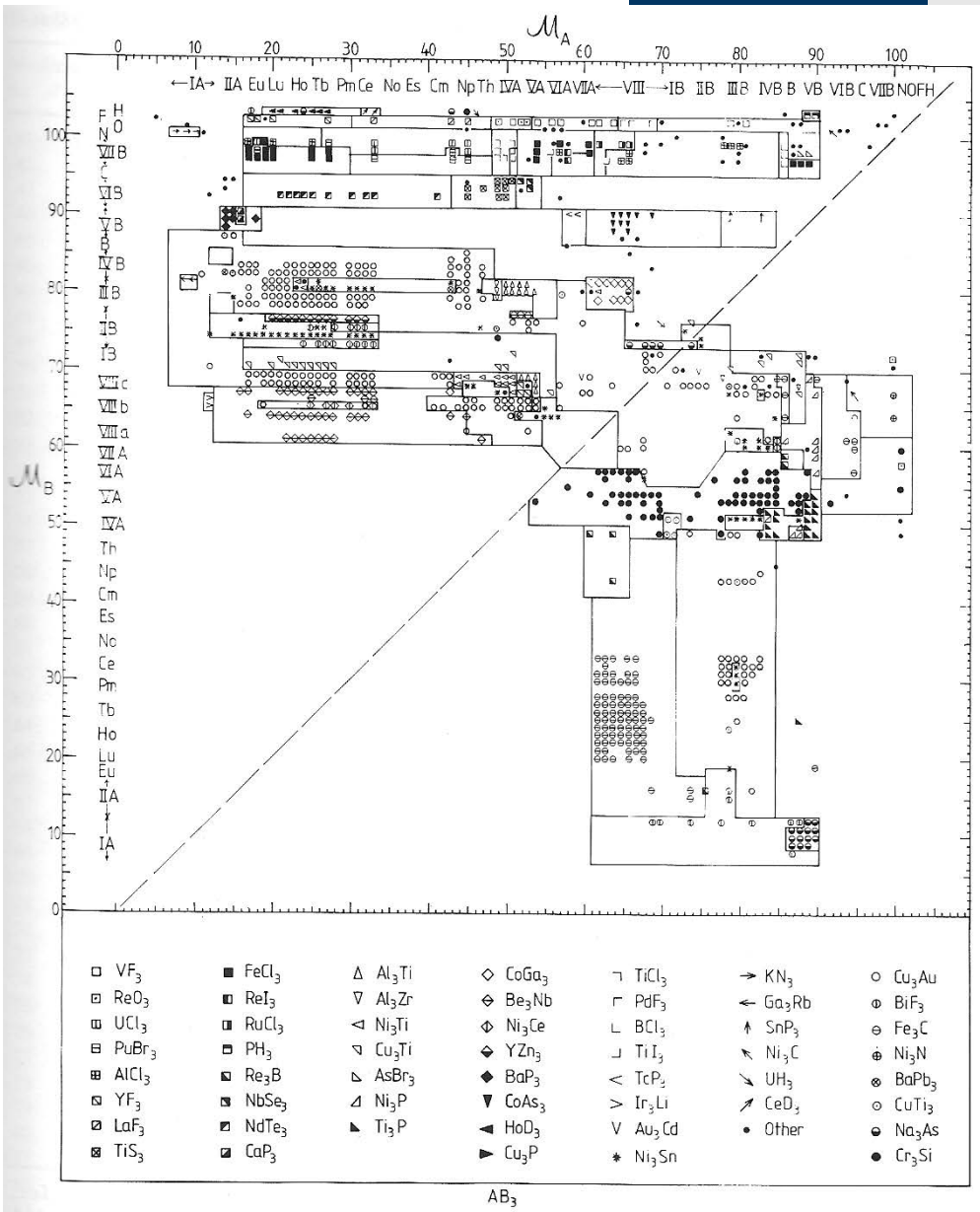
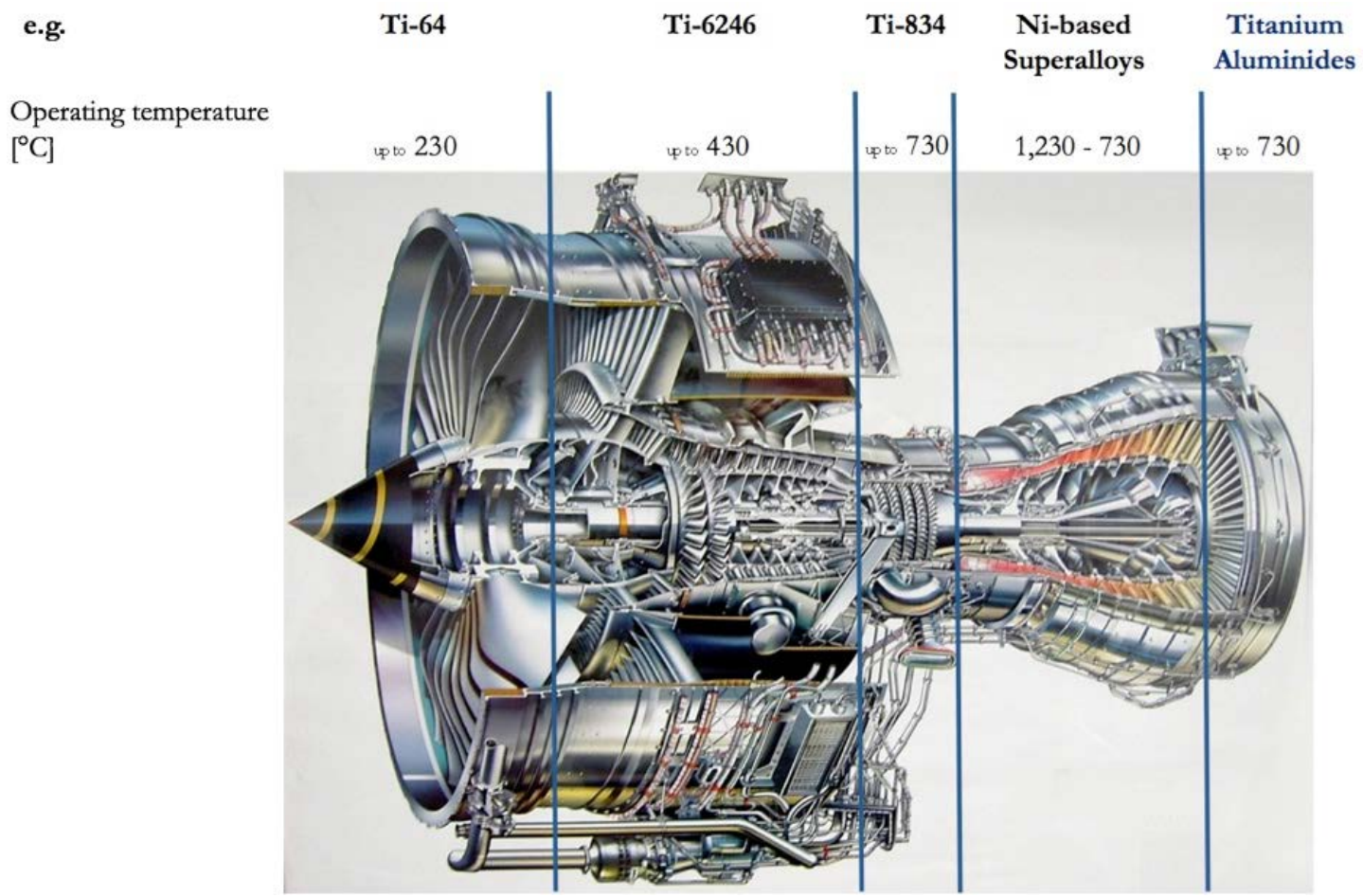


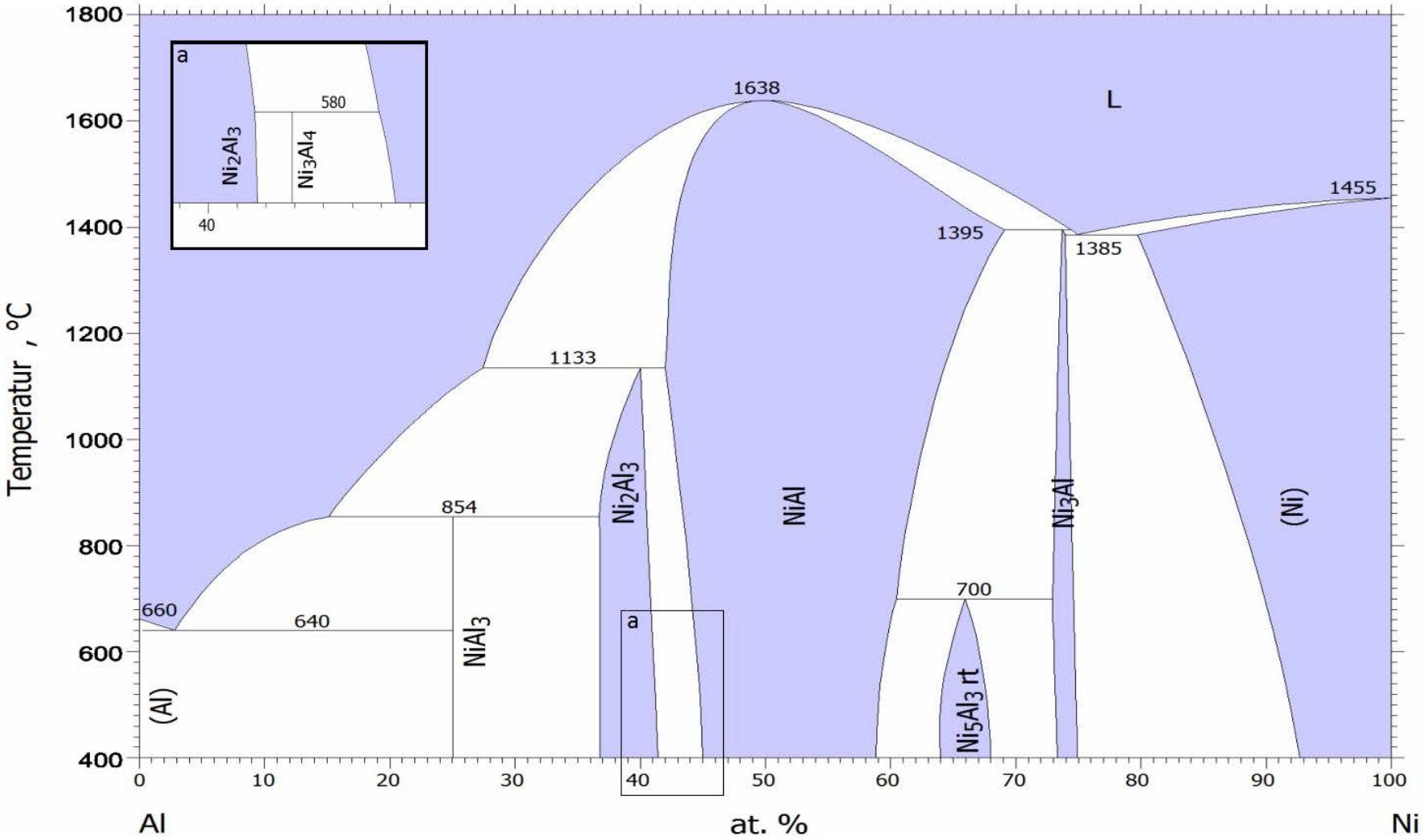
Figure 2-5. The AB_3 structure map (Pettifor, 1988 a).

Source: Cahn Haasen

Aluminides: Intermetallic phases for application in turbines



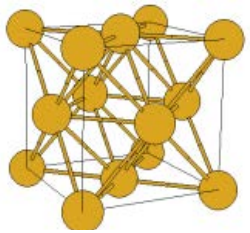
Intermetallic phases: Nickel aluminides



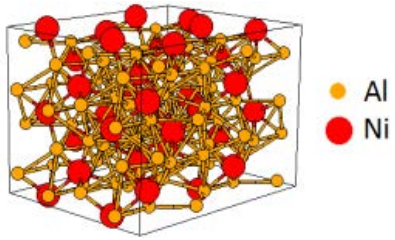
Intermetallic phases: Nickel aluminides

RUB

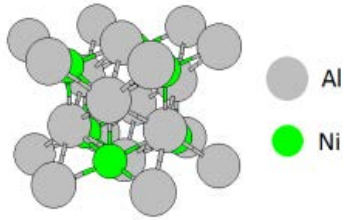
Crystal structures in the system Ni-Al



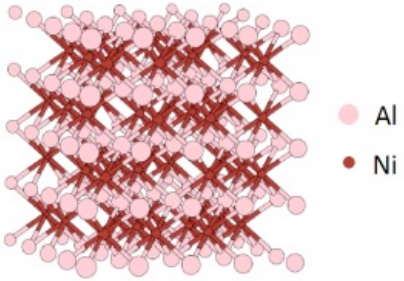
Ni/Al: face-centered cubic Fm3m (225)



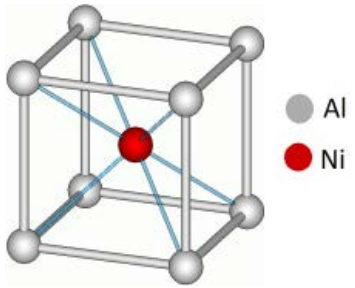
$NiAl_3$: orthorombic Pnma (62)



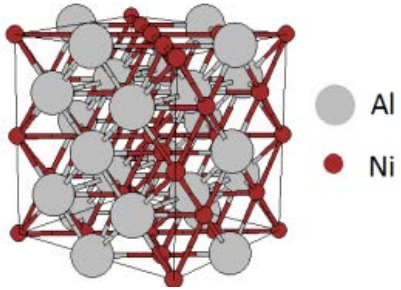
Ni_2Al_3: trigonal P3m1 (164)



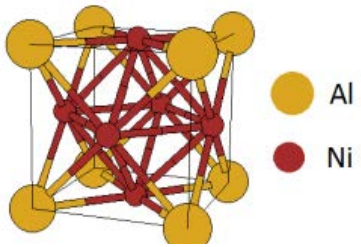
Ni_3Al_4: cubic Ia3d (230)



NiAl: body-centered cubic Pm-3m (221)



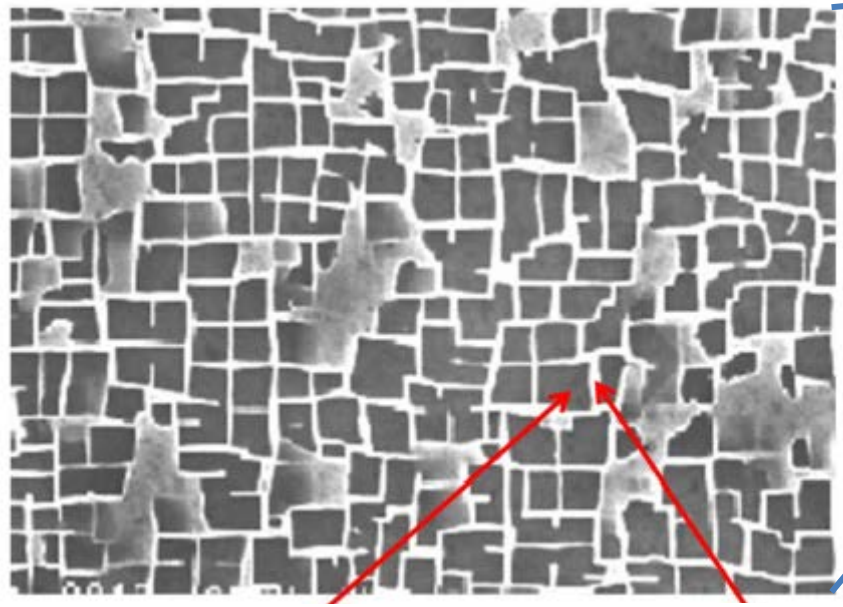
Ni_5Al_3: orthorombic Cmmm (65)

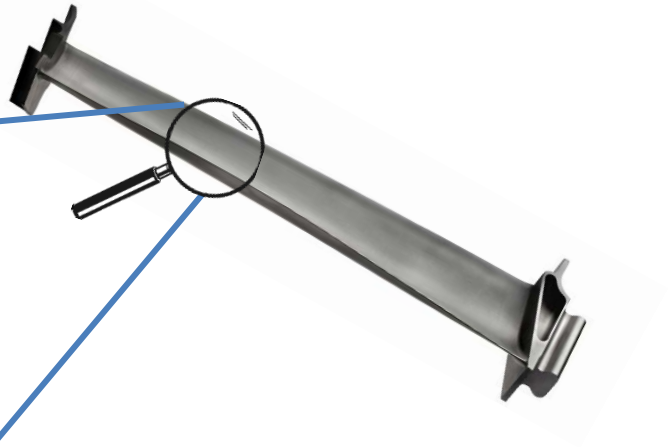


Ni_3Al: face-centered cubic Pm-3m (221)

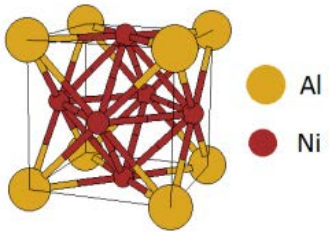
Intermetallic compounds: Nickel aluminides

application: Ni-based superalloys



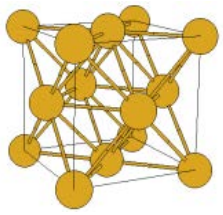


γ‘-precipitate



Ni_3Al: face-centered cubic Pm-3m (221)

γ-matrix

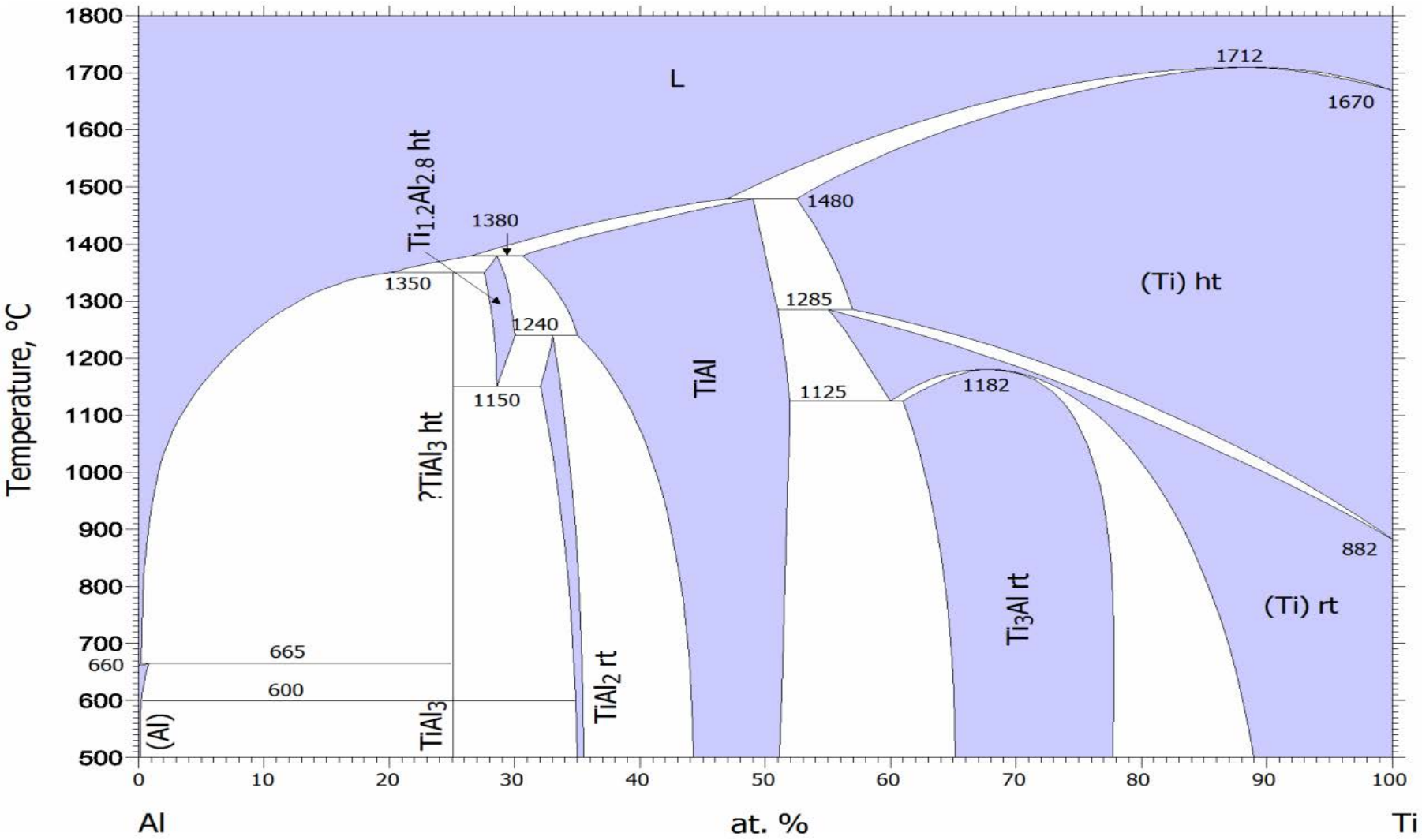


Ni/Al: face-centered cubic Fm3m (225)

Intermetallic compounds: Titanium aluminides

RUB

Phase diagram of the system Ti-Al



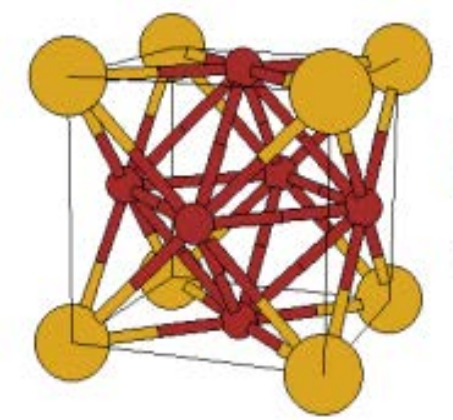
Source: Pauling file

Intermetallic phases: Titanium aluminides

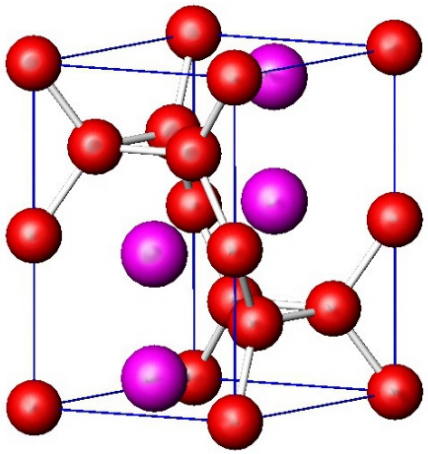
Phases in the system Ti-Al

- Most important for applications: TiAl and Ti_3Al

- other phases are not used in commercial alloys

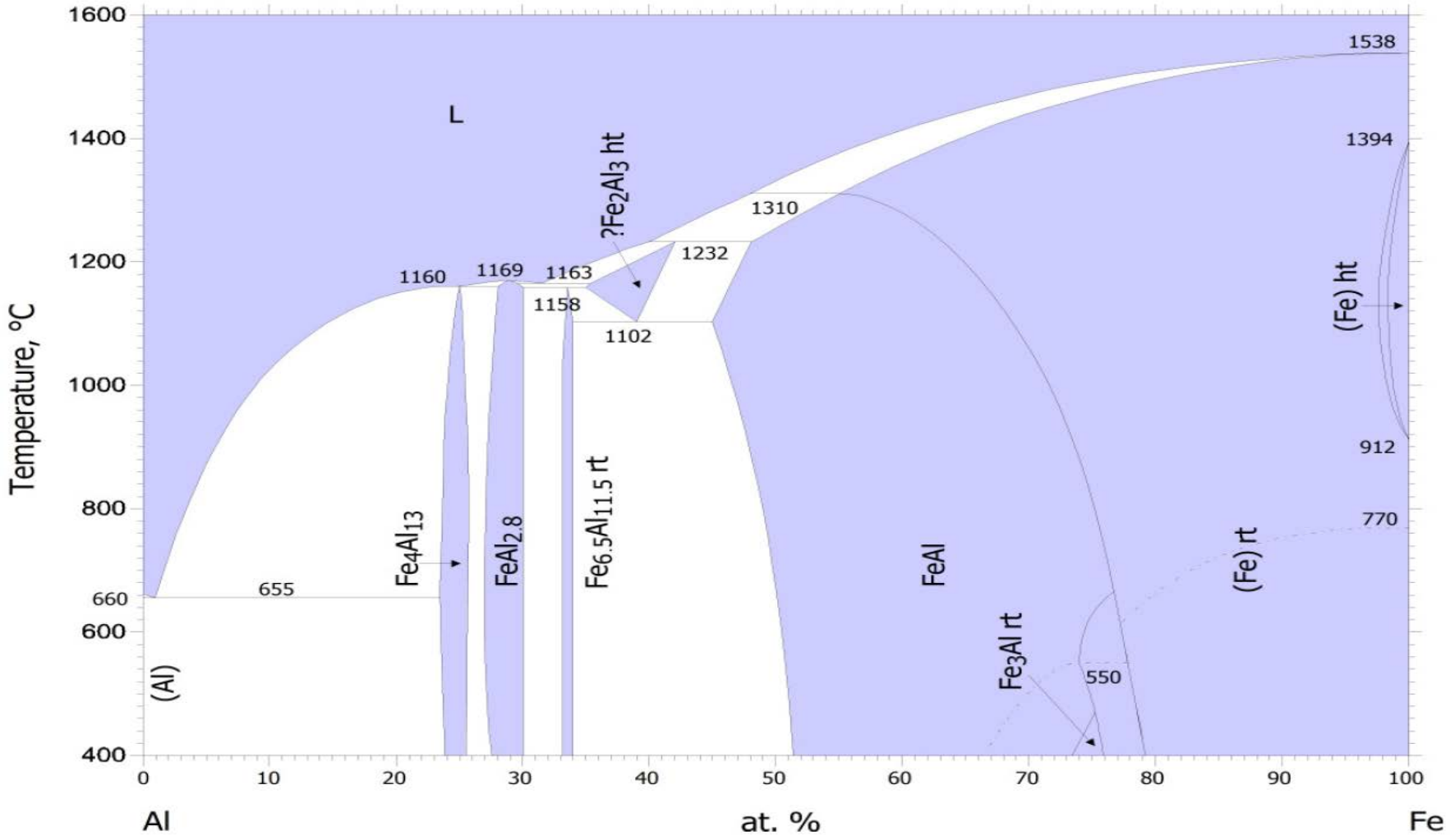


γ - TiAl (tetragonal)

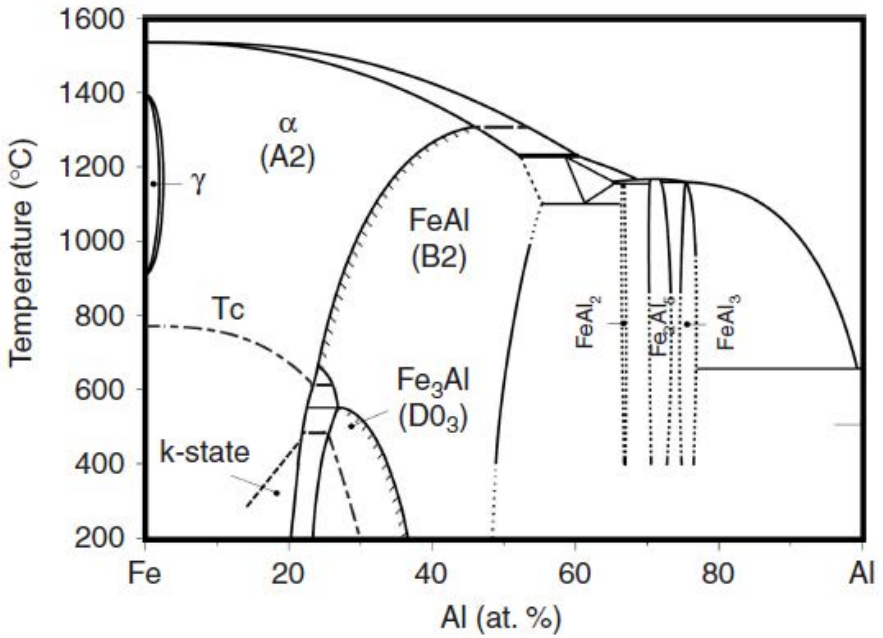


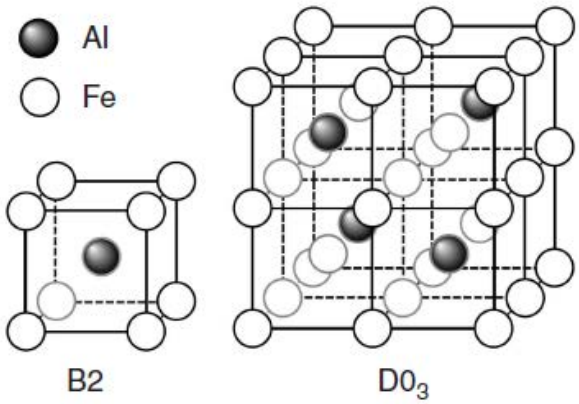
α_2 Ti_3Al (cubic)

Intermetallic phases: Iron aluminides



Intermetallic phases: Iron aluminides





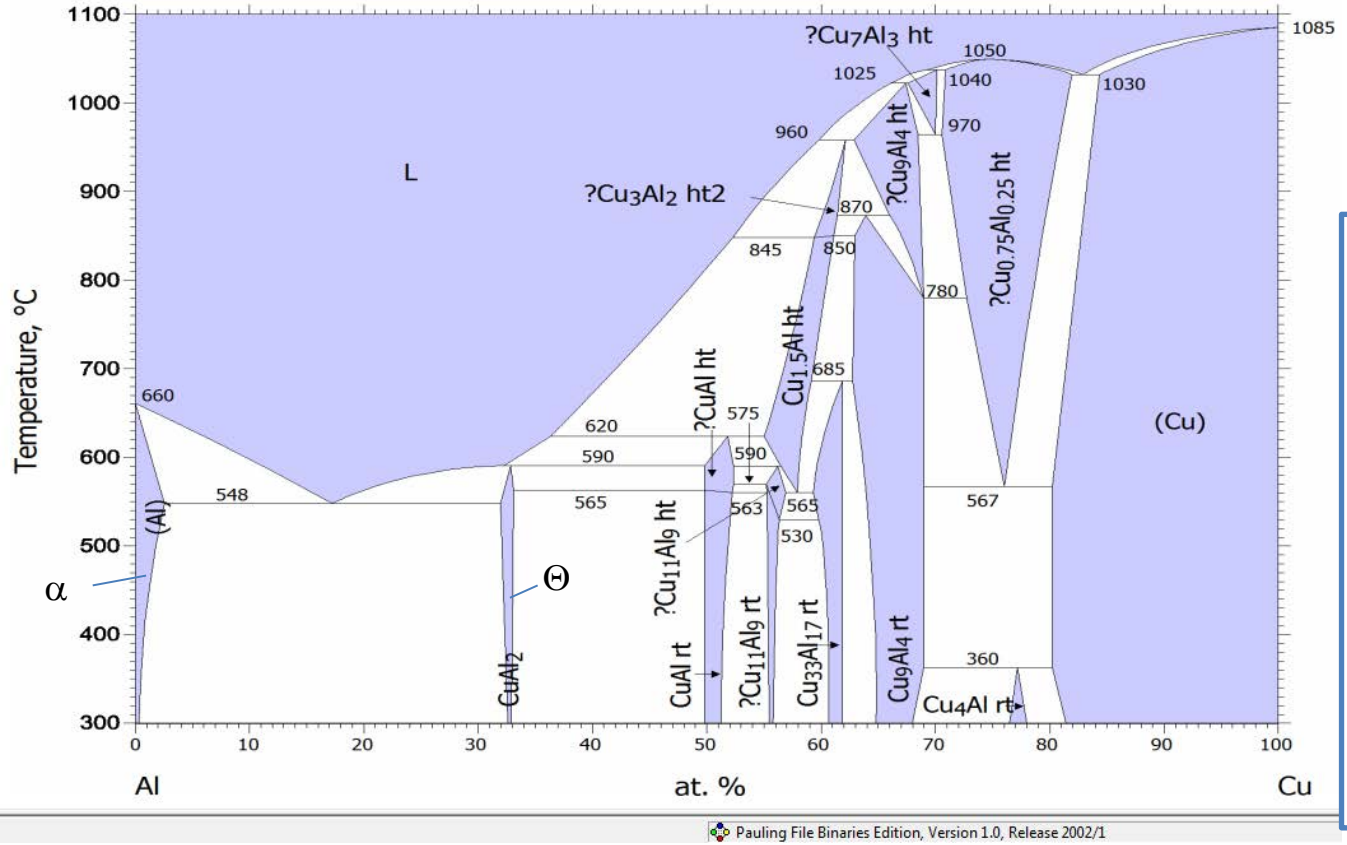
Fe–Al binary phase diagram and crystal structures of B2 and $D0_3$ [24].

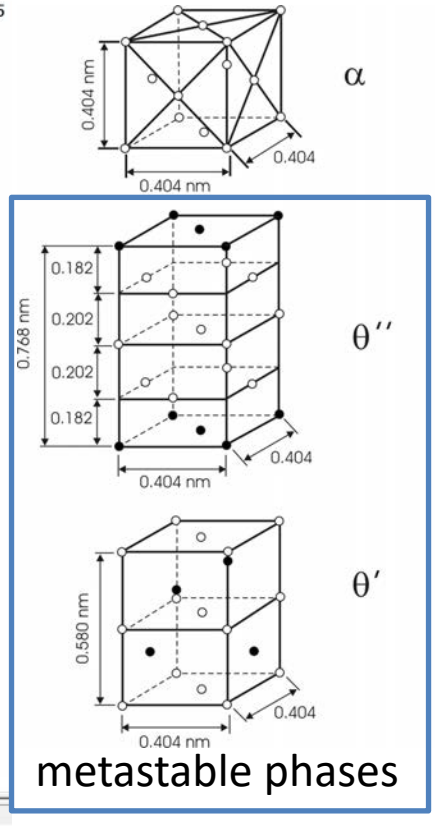
Phases in Fe-Al

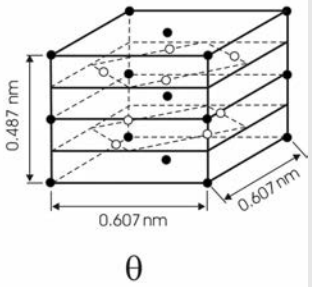
- most important: Fe_3Al and FeAl
- high electrical resistance and good corrosion resistance
- applications: e.g. heating elements
- problem: brittleness

[S.C. Deevi, V.K. Sikka: Nickel and iron aluminides: an overview on properties, processing, and applications]

From metastability to stability: Precipitation strengthening in the system Al-Cu by age hardening



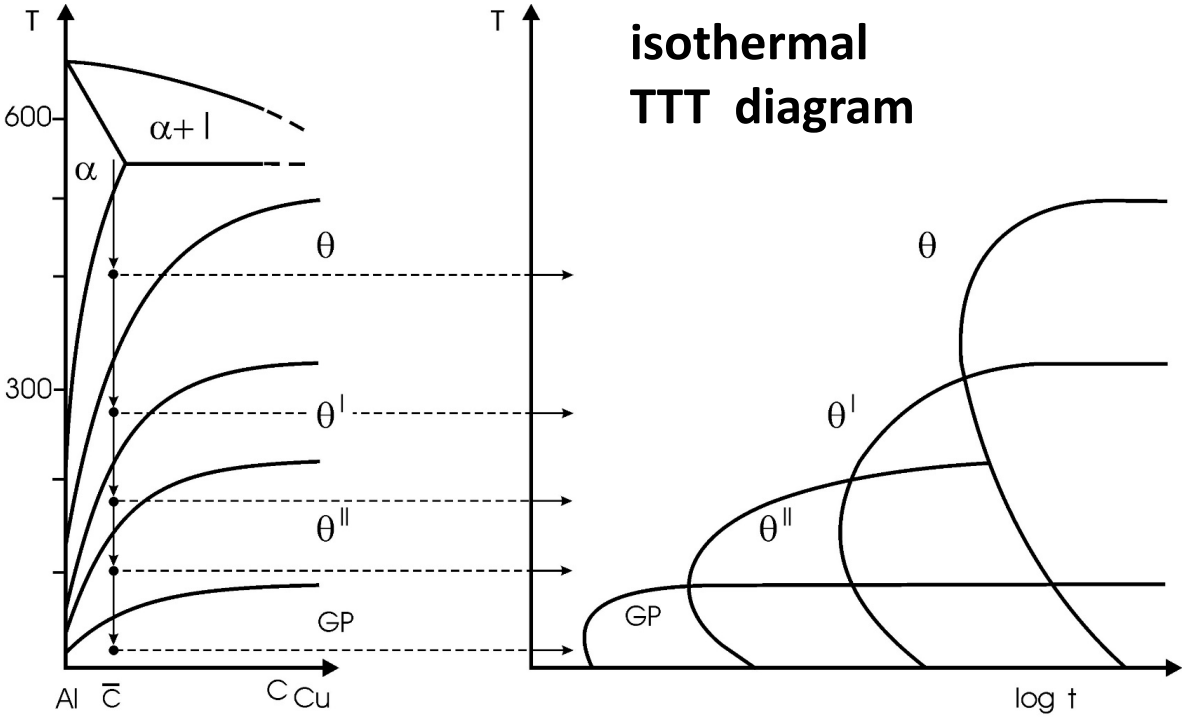




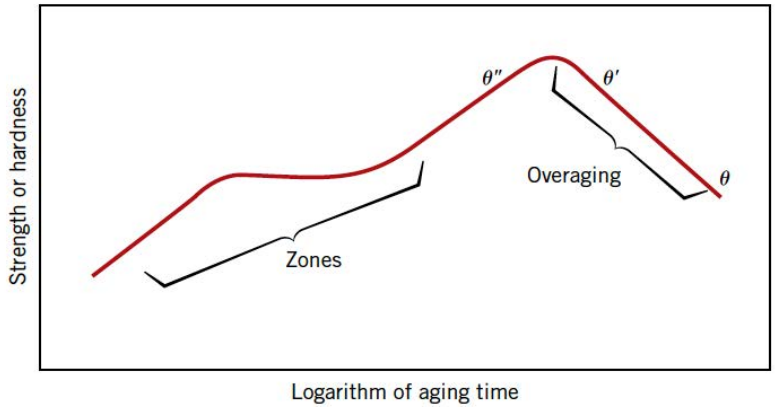
Important for lightweight constructions, e.g. aerospace, high strength Al-alloys

Source: Pauling file, Eggeler

From metastability to stability: Precipitation strengthening in the system Al-Cu



(a) (b)

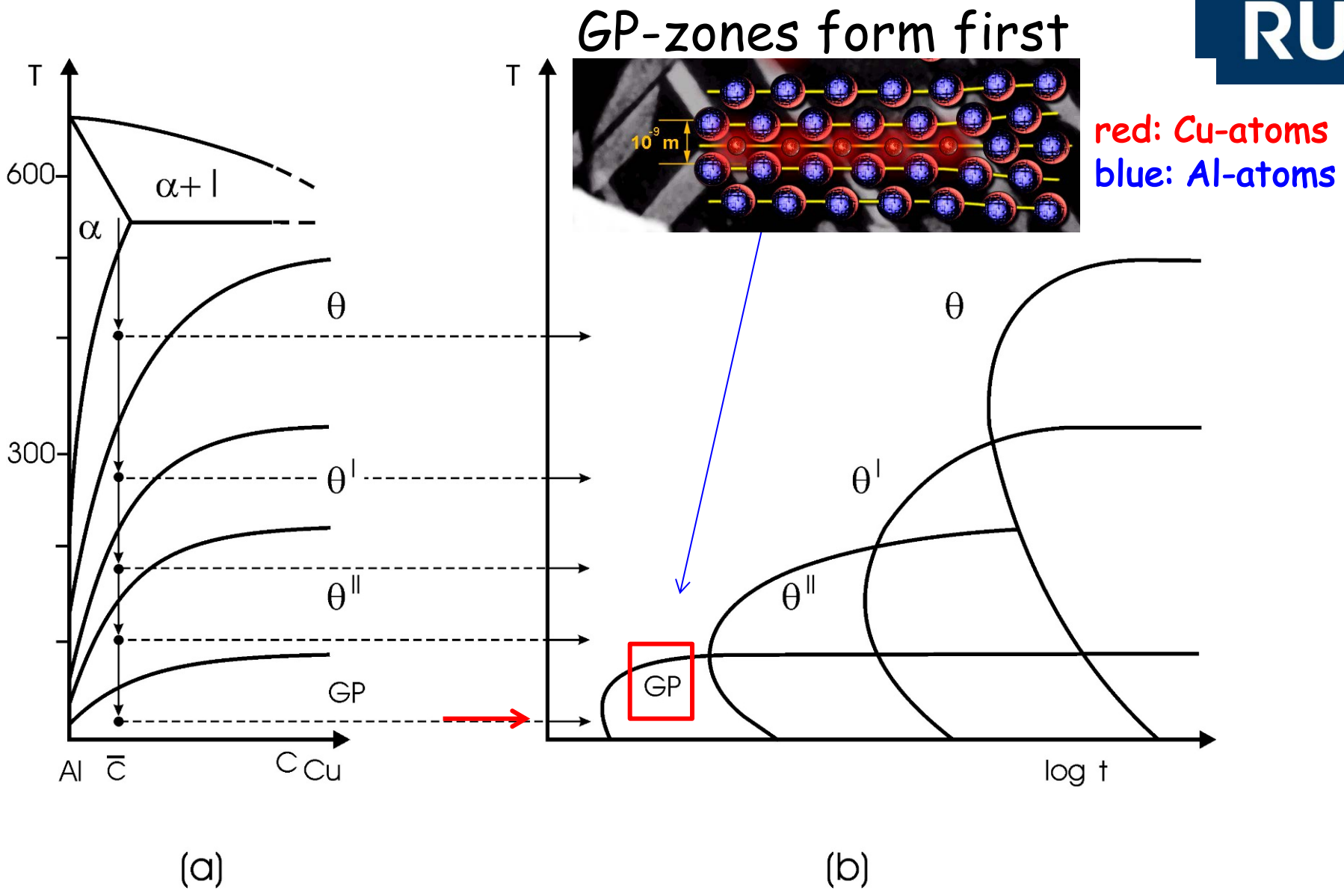


Phase diagram with cooling/holding steps

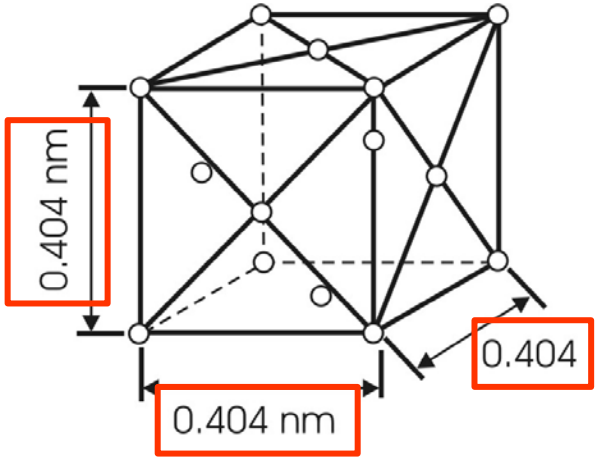
what fits best
(from a point of view of the
lattices of the parent and the product phase)
forms first
GP: Guinier-Preston zones

Source: Callister, Eggeler

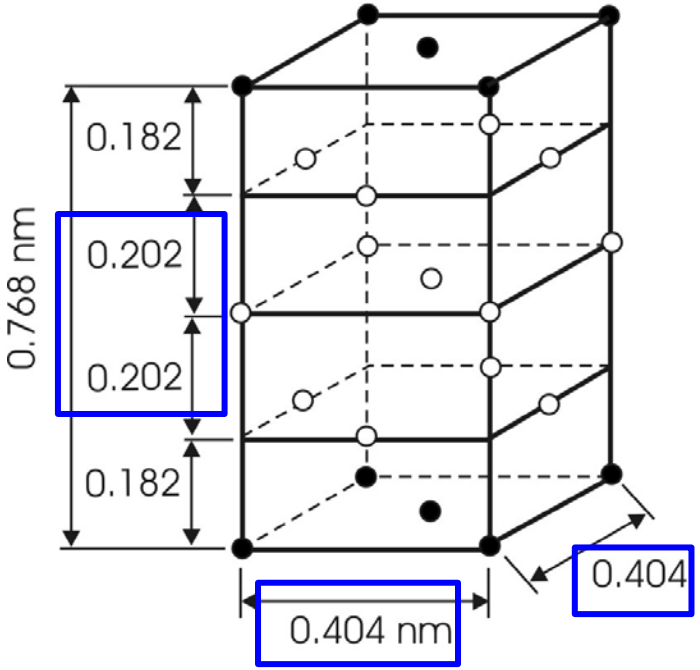
Early stage of nucleation



Al and θ''



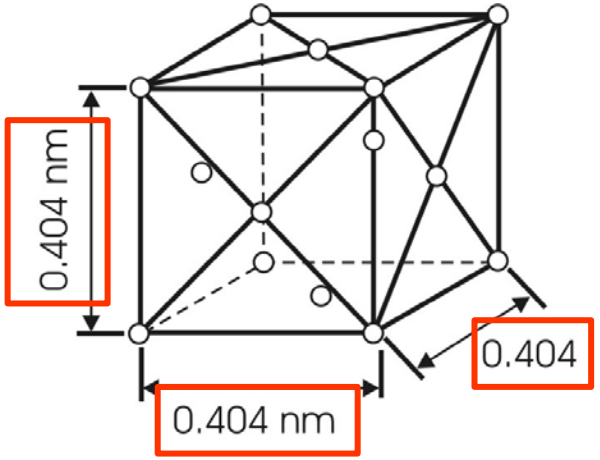
α



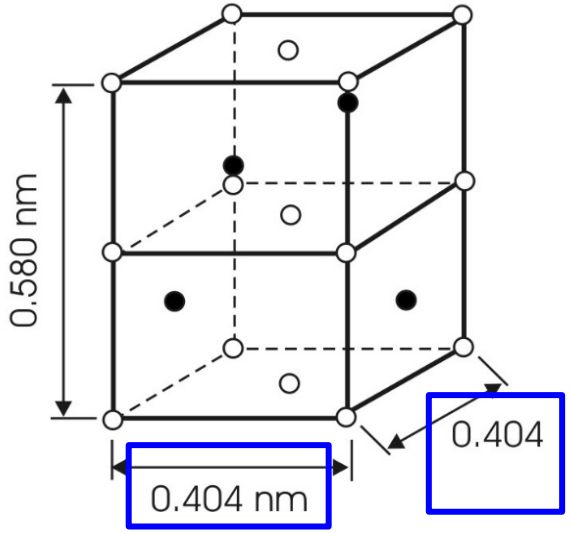
θ''

lattice fits very well into Al-lattice

Al and θ'



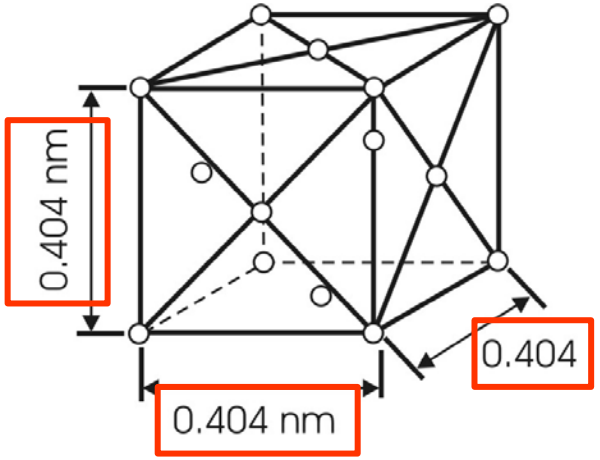
α



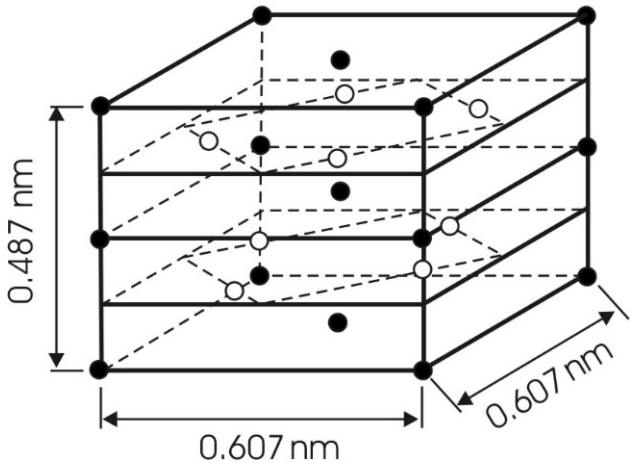
θ′

Θ‘ still fits rather well

Al and θ



α



θ

crystal lattice of equilibrium phase Θ does not fit well

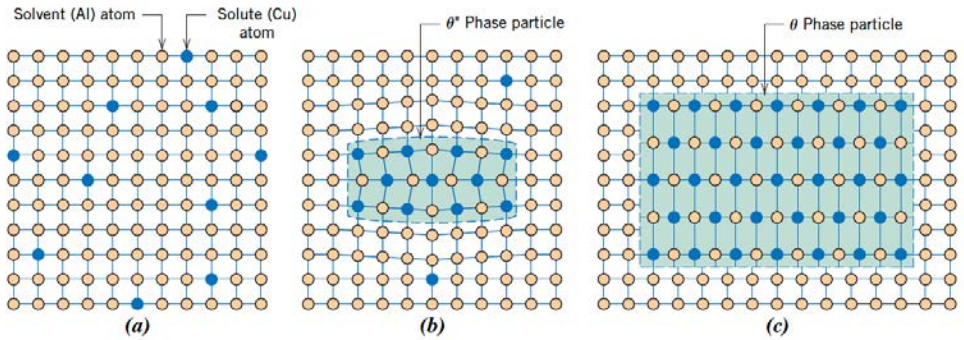
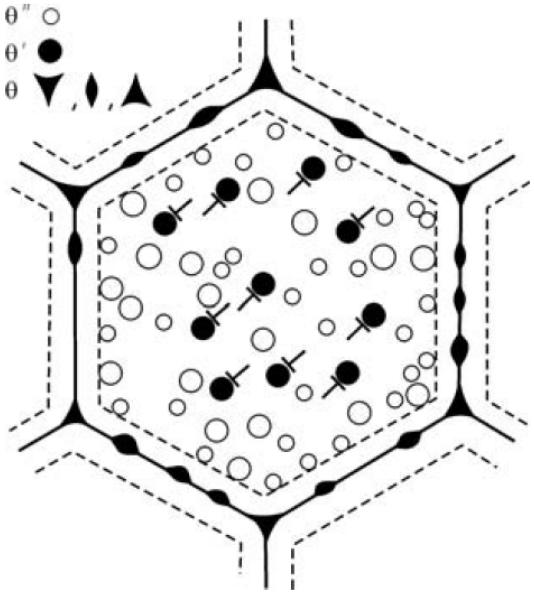


Figure 11.26 Schematic depiction of several stages in the formation of the equilibrium precipitate (θ) phase. (a) A supersaturated α solid solution. (b) A transition, θ″, precipitate phase. (c) The equilibrium θ phase, within the α-matrix phase.



Source: Callister, Eggeler

Heusler phases

- discovered by Heusler in 1903
- ferromagnetism in a ternary phase of non-ferromagnetic components

Heusler discovered that an alloy of the non-ferromagnetic elements Cu, Mn and Al shows ferromagnetism (Cu_2MnAl)

Über magnetische Manganlegierungen;
von Fr. Heusler.

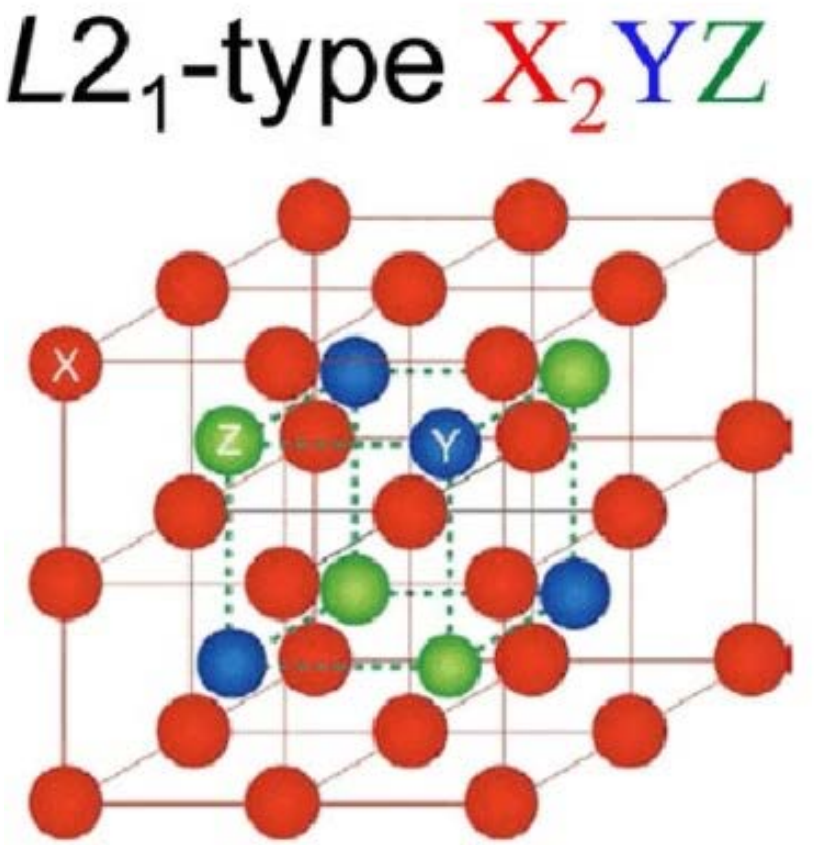
(Niedergelegt im Archiv der Deutschen Physikalischen Gesellschaft am 18. Juni 1901, der Öffentlichkeit übergeben in der Sitzung vom 12. Juni 1903.)

(Vgl. oben S. 217.)

Ich habe gefunden, daß im Gegensatz zu den unmagnetischen Eigenschaften des Manganmetalles sowie des Mangankupfers gewisse andere Legierungen des Mangans stark magnetisierbar sind und diese Eigenschaft auch behalten, wenn man den Legierungen Kupfer und andere an sich unmagnetische Metalle zusetzt. Die

Source: Fr. Heusler, Verhandlungen der DPG (1903)

Heusler phases



X, Y transition metals
Z element of main groups

4 overlapping fcc lattices
X: (0,0,0) und (½, ½, ½)
Y: (¼, ¼, ¼)
Z: (¾, ¾, ¾)

full Heusler structure
(„combine two different B2 cells“)

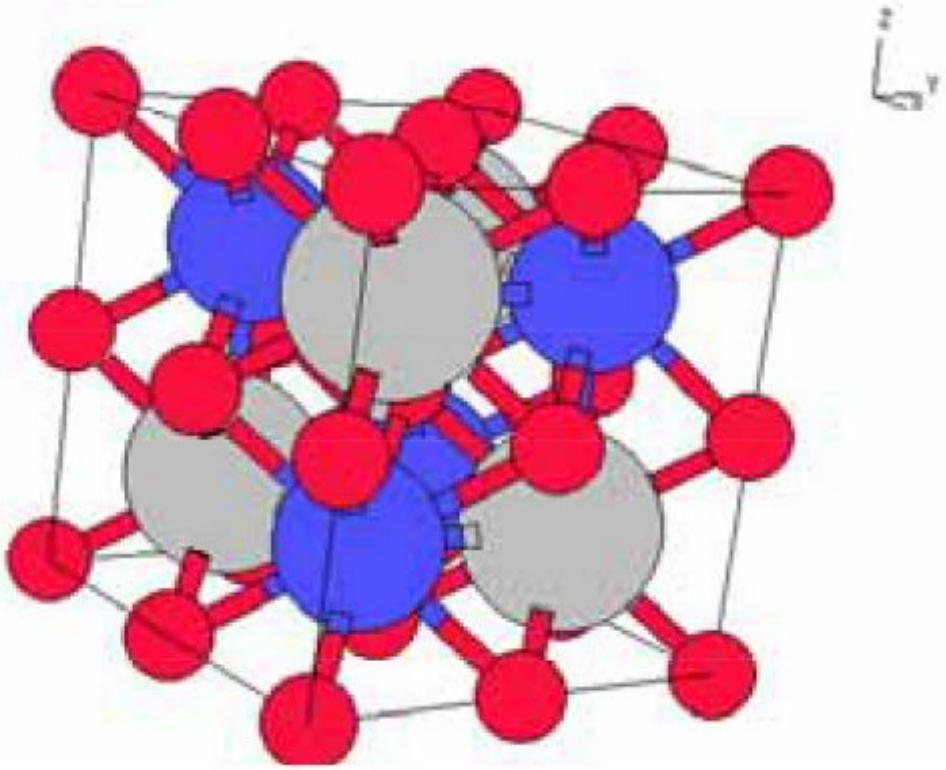
The ferromagnetic shape memory alloy Ni_2MnGa

RUB

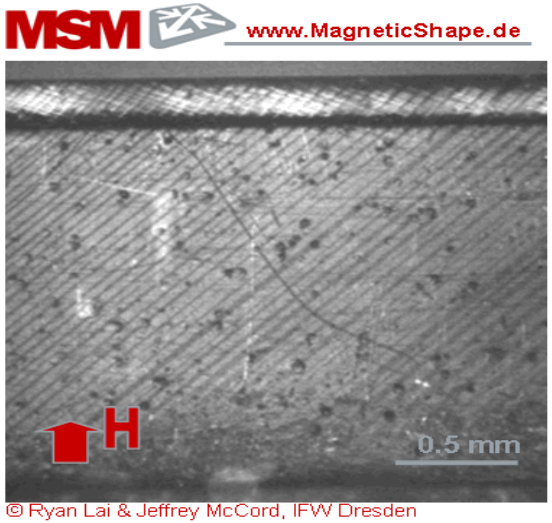
Ni_2MnGa: Heusler phase

martensitic transformation:

„fcc“ austenite to tetragonal martensite



$L2_1$ (austenite)

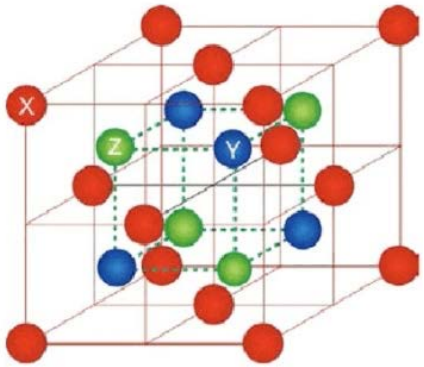


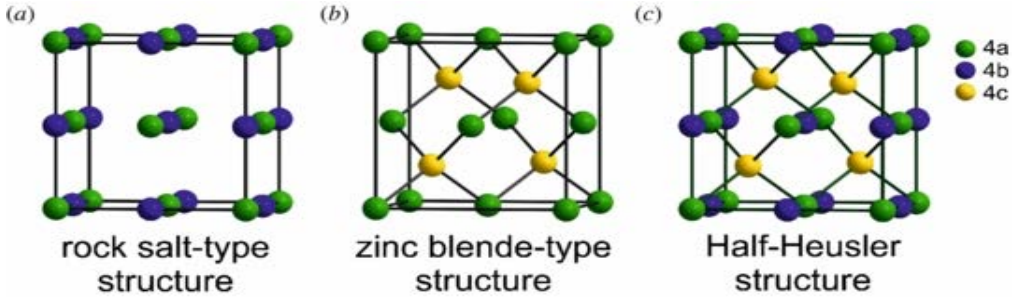
Source:www.magneticshape.de/

Half-Heusler phases

Half-Heusler-structure = Full-Heusler-structure with unoccupied sub-lattice

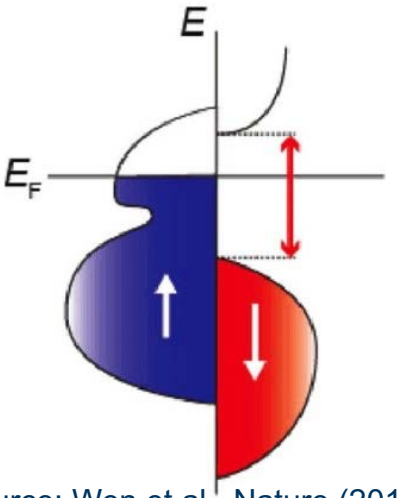
$C1_b$-type XYZ





Casper et al., Semicond. Sci. Technol. (2012)

thermoelectric half-Heusler phase NiTiSn

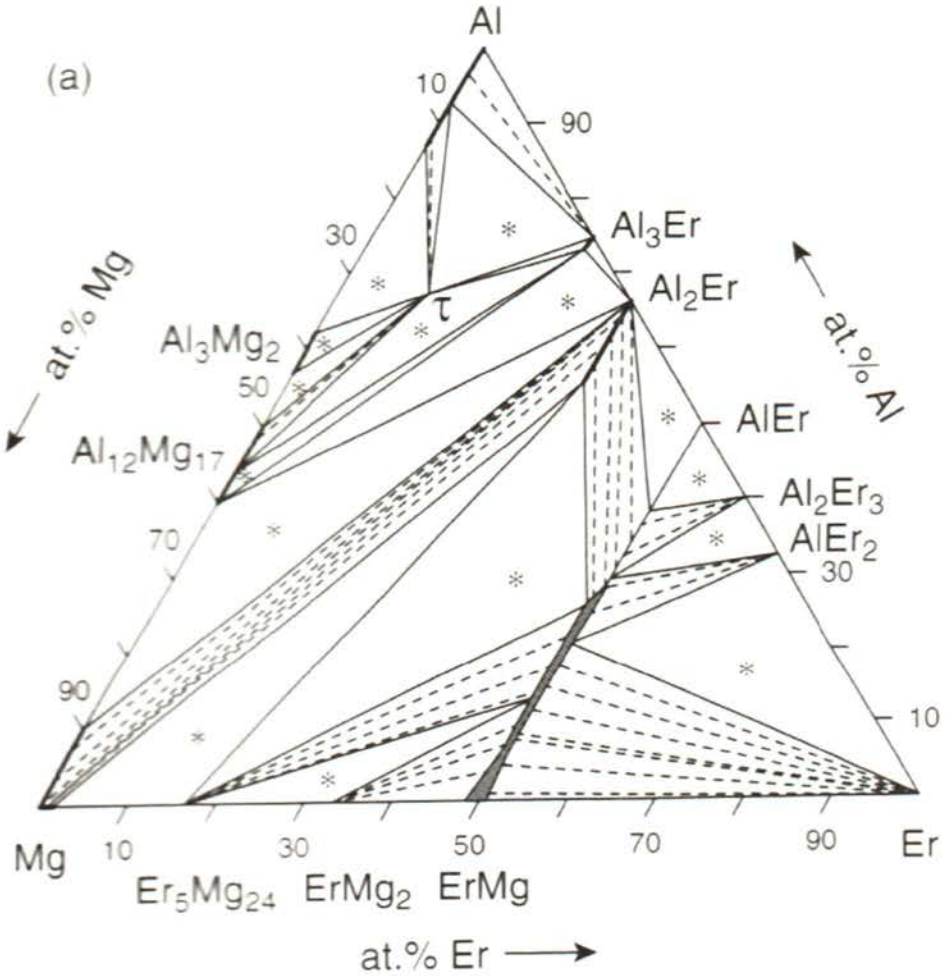


band gap

semiconducting if VEC (valence electron count) is 18

Source: Wen et al., Nature (2015)

Isothermal sections of ternary phase diagrams



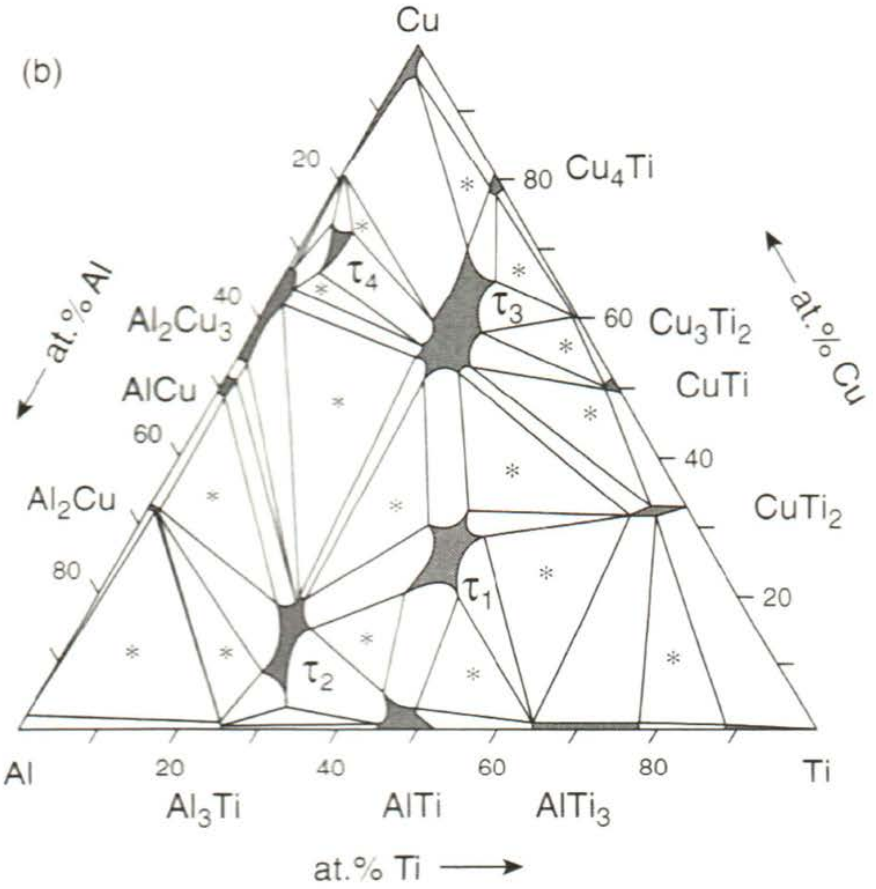
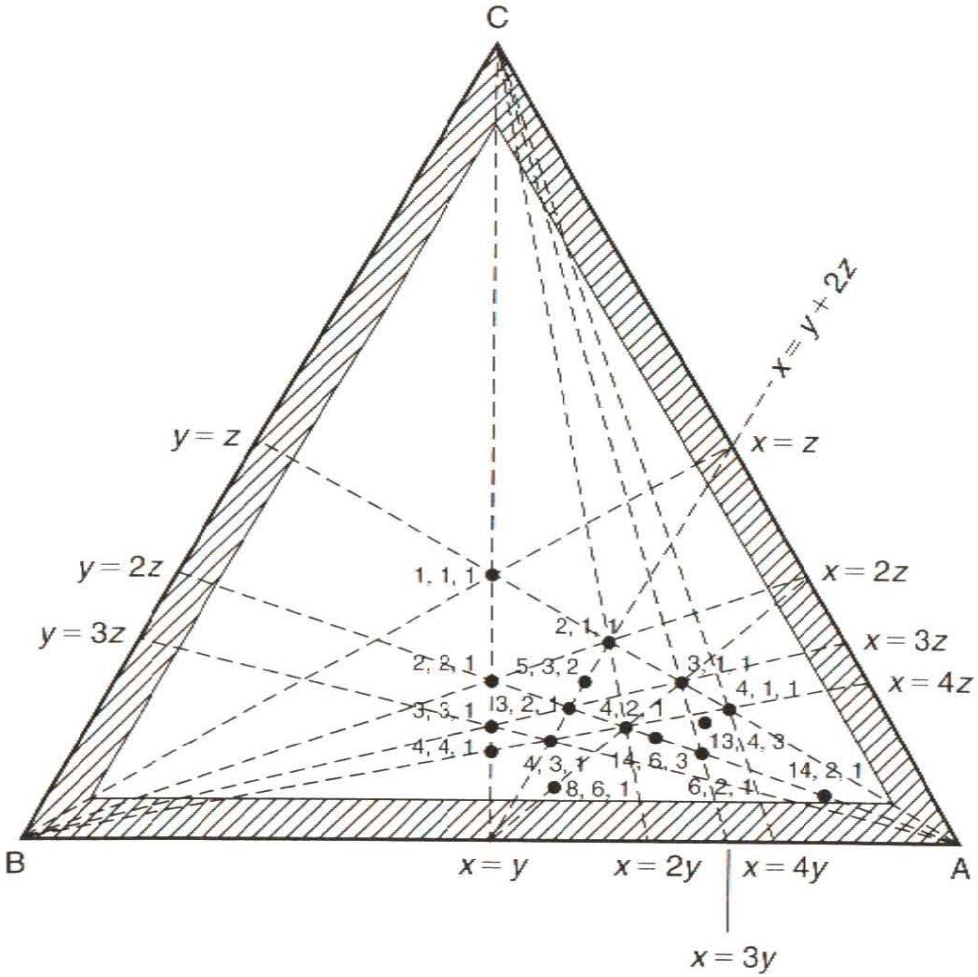


Figure 2.29. Isothermal sections of ternary phase diagrams: (a) Al–Er–Mg system at 400°C, Saccone *et al.* (2002) and, (b) Al–Cu–Ti system at 540°C from Villars *et al.* (1995). A number of single-phase regions (dark grey) may be noticed, both extending from binary compounds and as ternary intermediate phases (τ) in the Al–Er–Mg system and the four phases τ_1 τ_2 τ_3 and τ_4 in the Al–Cu–Ti system. The three-phase fields are marked by an asterisk, in the Al–Er–Mg system a few tie-lines are indicated in the two-phase fields.

Source: Intermetallic chemistry

Ternary intermetallic phases



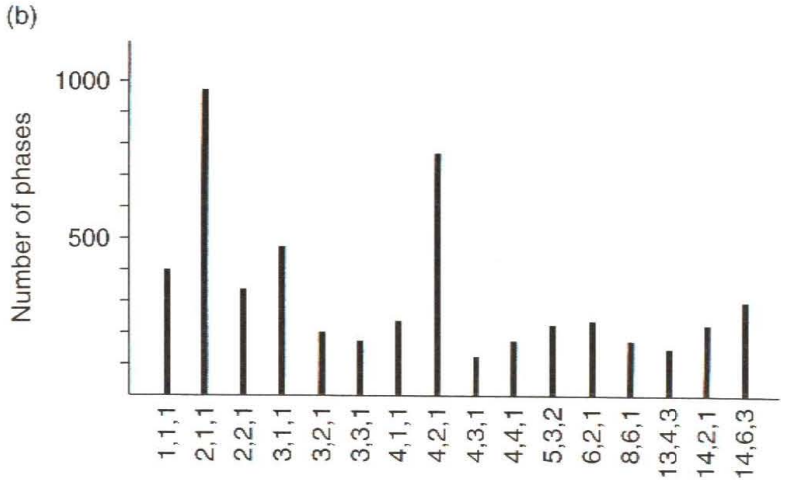


Figure 7.2. Distribution of the more common ternary intermetallic phases according to their stoichiometry. (a) Shows the position of $A_xB_yC_z$ phases in a representative portion of a general composition triangle. The hatched region corresponds to composition values for which in general ternary compounds are very seldom observed. (b) An indication is given about the number of phases reported by Rodgers and Villars (1993) for different typical stoichiometries.

Source: Intermetallic chemistry, p. 621

Hydrides, carbides, borides, nitrides

Metal hydrides:
e.g. Mg-H, TiH_2

Metal borides:
e.g. MgB_2

Metal nitrides:
e.g. TiN

Metal carbides
e.g. TiC, WC, Fe_3C

Interstitial compounds:
transition metals + H,C,B,N
very hard, very high T_m

$c > c_{solv}$:
small atoms are still in interstitial positions
but overall crystal structure changes

Carbides

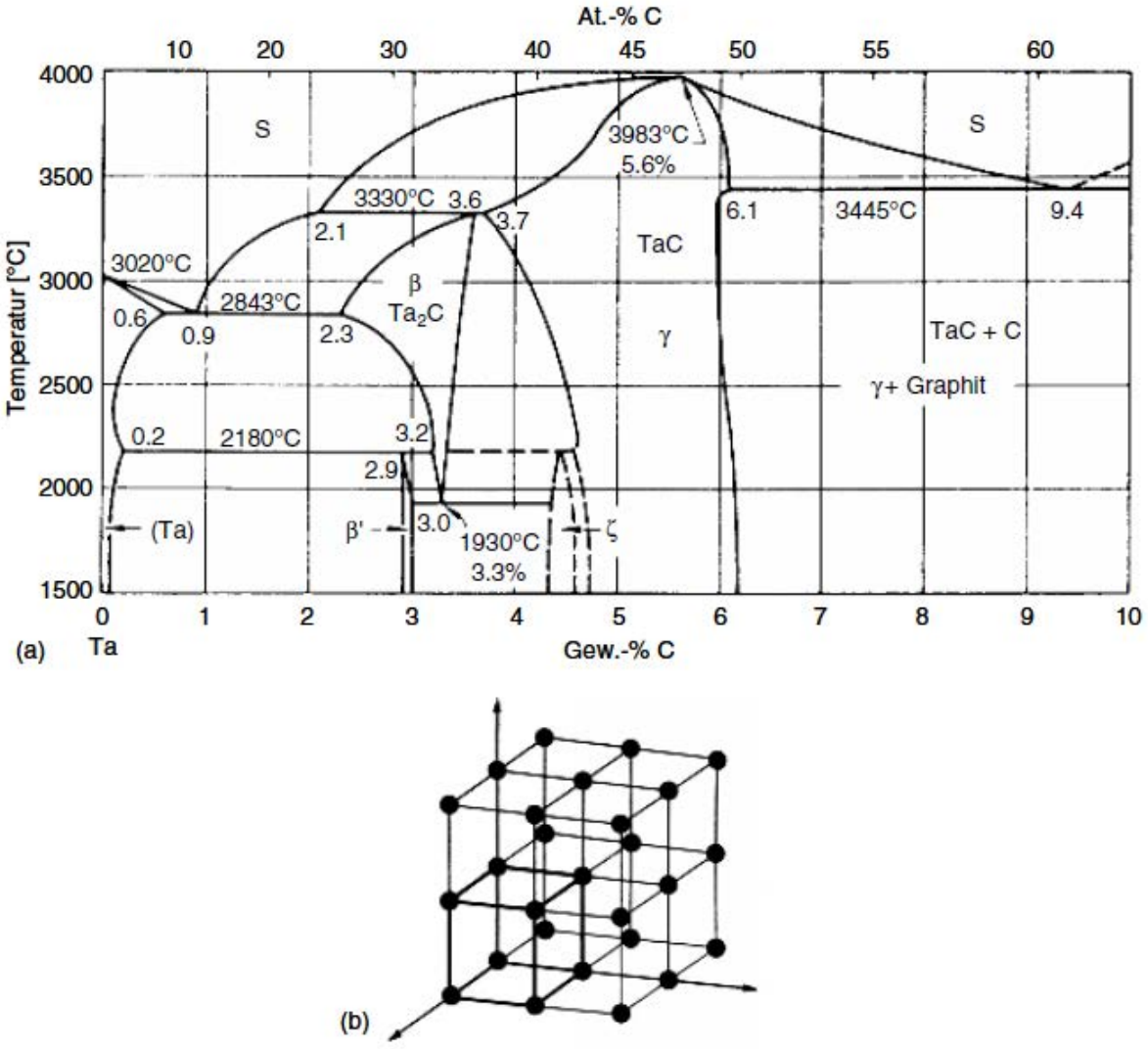


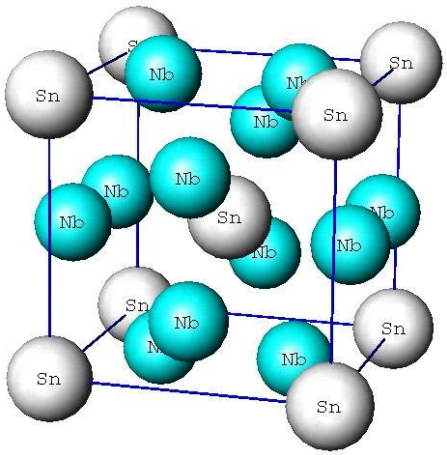
Abbildung 4.47. (a) Zustandsdiagramm des Systems Ta-C mit den Hägg-Phasen TaC (kfz) und Ta_2C (hexagonal). (b) Gitter des TaC; die C-Atome sitzen auf allen oktaedrischen Zwischengitterplätzen im kfz Gitter (NaCl-Struktur) [4.1].

Hägg-phases

here: TaC (fcc)
Ta_2C (h)

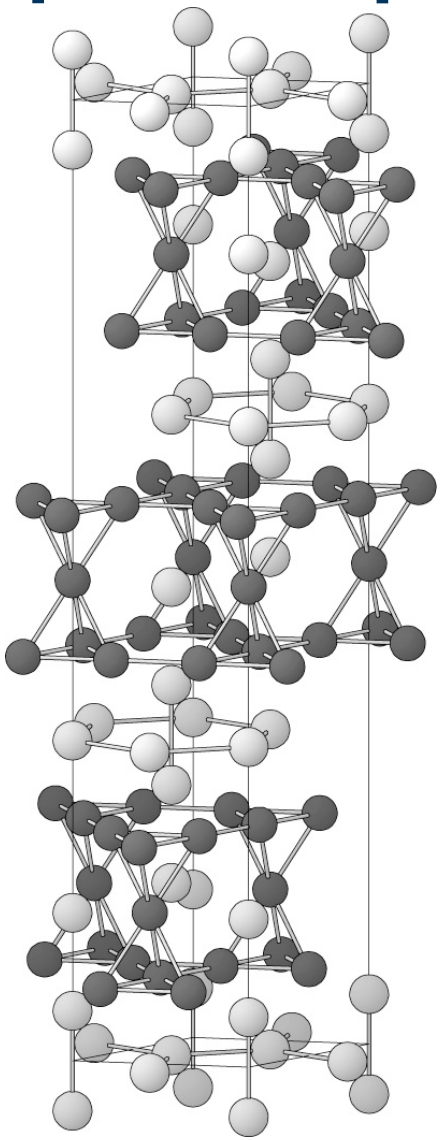
Topologically close packed (TCP) phases: A15

- complex cubic structure derived from A2 with 8 atoms in unit cell
- Typical example for TCP, which result from stacking of polyhedra of various shapes to accomodate atoms of different sizes
- Laves phases (C14, C15, C36) can be derived from A15 by crystallographic operations
- Important superconductors: Nb_3Sn, Nb_3Ge
- Problem: brittleness



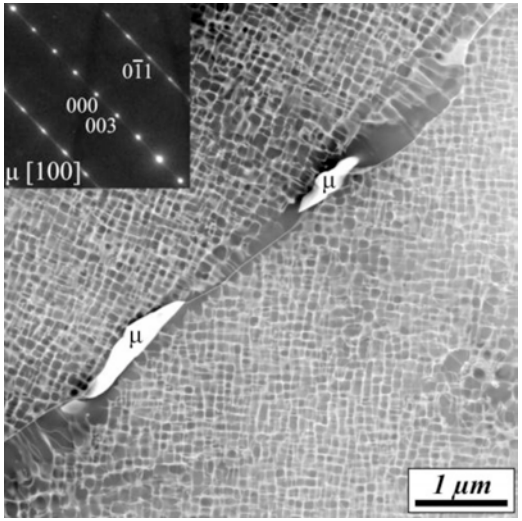
- TCP structures allow closer stacking of atoms with different sizes than geometrically close packed structures (A1, A3)
- intermetallic phases with TCP structure: Frank-Kaspar phases

Topologically close packed (TCP) phases: μ-phase



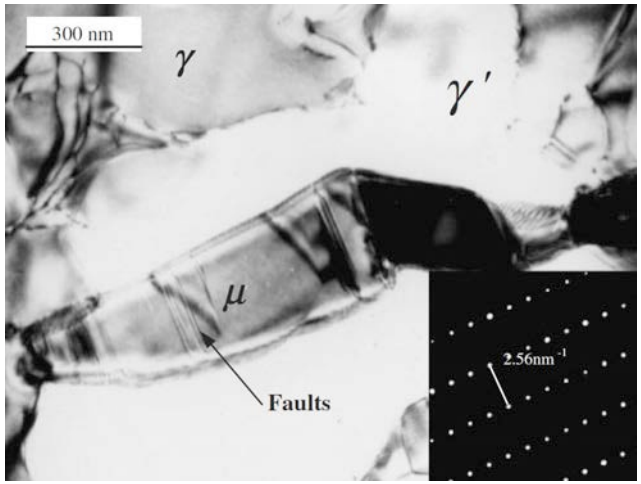
P. Villars, K. Cenzua: *Structure Types*, Springer-Verlag Berlin Heidelberg 2007

μ-phase in CMSX-4 Ni-base superalloy produced by selective electron beam melting



Alireza B. Parsa, Markus Ramsperger, Aleksander Kostka, Christoph Somsen, Carolin Körner and Gunther Eggeler: *Transmission Electron Microscopy of a CMSX-4 Ni-Base Superalloy Produced by Selective Electron Beam Melting*, *Metals* 2016, *6*(11), 258

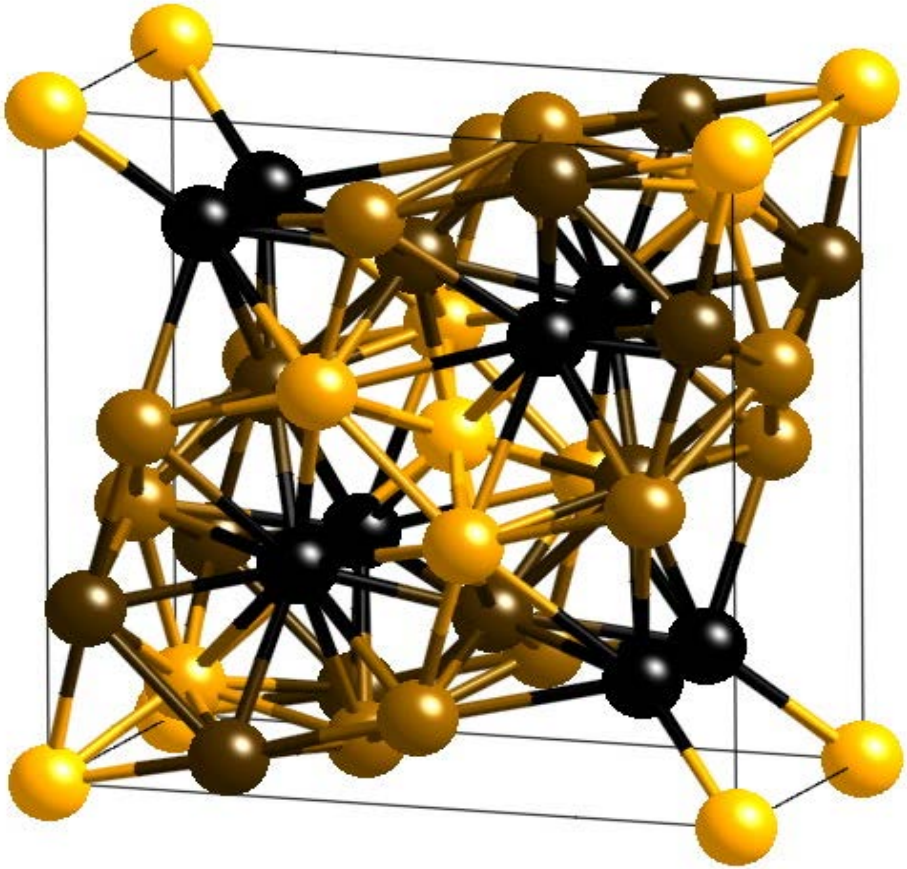
μ-phase in a Ni-base directionally solidified alloy



K. Zhao, Y. H. Ma, L. H. Lou and Z. Q. Hu: *Phase in a Nickel Base Directionally Solidified Alloy, Materials Transactions*, Vol. 46, No. 1 (2005) pp. 54 to 58

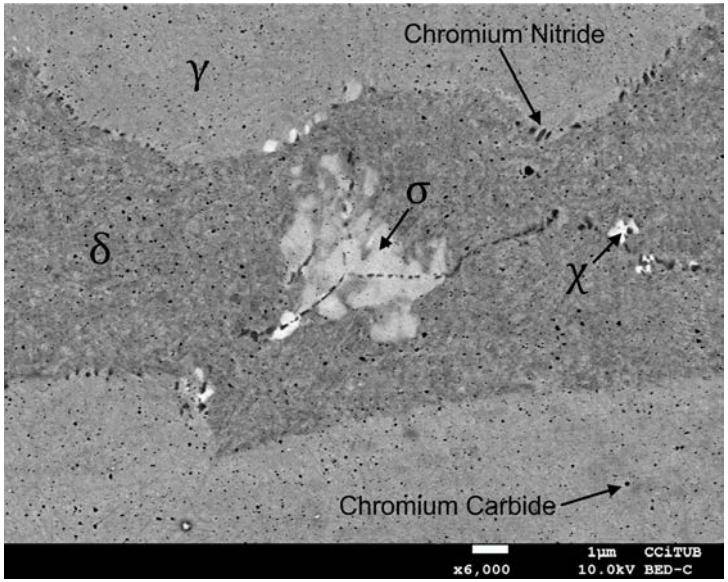
- hexagonal system
- typically forms in superalloys from Co and W → W_6Co_7

Topologically close packed (TCP) phases: σ-phase



http://som.web.cmu.edu

σ-phase phase in duplex stainless steels



Núria Llorca-Isern, Héctor López-Luque, Isabel López-Jiménez, Maria Victoria Biezma:
Identification of sigma and chi phases in duplex stainless steels, Materials Characterization
Volume 112, February 2016, Pages 20-29

- tetragonal system
- typically forms in stainless steel and superalloys from Fe and Cr → FeCr

Questions

(1) Define the terms solid solution, alloy and compound. Discuss the stoichiometry and the compositional existence range.

(2) What is allotropy?

(3) What do the abbreviations rt, ht and lt mean?

(4) What is the difference between alloying and doping?

(5) Explain the difference between an interstitial and a substitutional element.

(6) Why are intermetallic compounds frequently brittle?

(7) Name the intermetallic compound with the highest technical relevance in the Ni-Al system. What is its crystal structure?

(8) What is a Heusler phase? Sketch a unit cell.

(9) Cu_2MnAl was the first Heusler phase to be discovered. What special property does it have?

(10) What is the structural difference between a half Heusler and a (full) Heusler phase?

(11) What is a Pettifor map?

(12) Name two important intermetallic compounds in the Fe-Al materials system. Where and why are they applied?

(13) What does the abbreviation TCP mean?

(14) What is the purple plague?

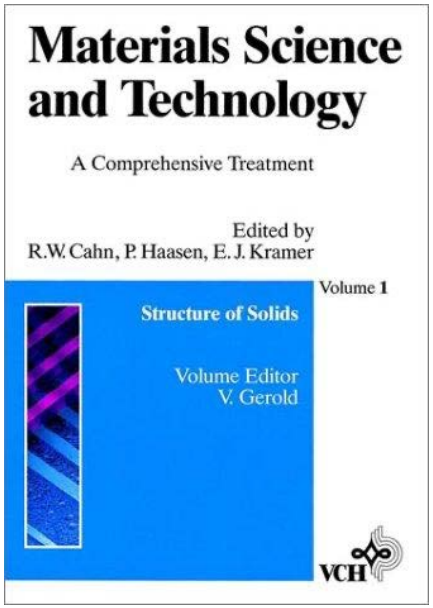
(15) Name a Laves phase with magnetostrictive behavior.

(16) Name an intermetallic compound in the Ni-Ti system frequently used in application. What property makes this compound valuable?

(17) What is a Guinier-Preston zone?

(18) What is an interstitial compound? Give two examples.

Literatur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