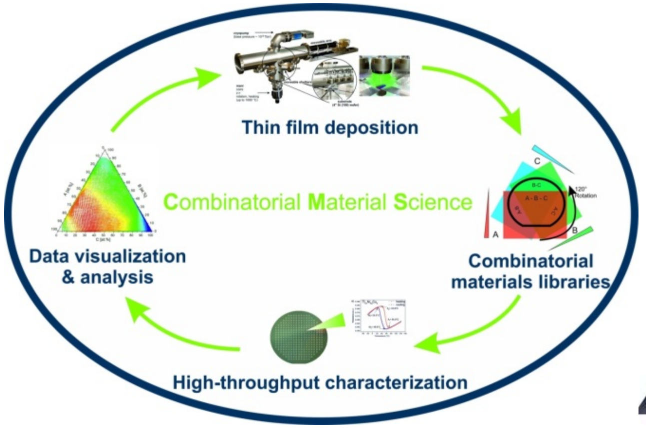
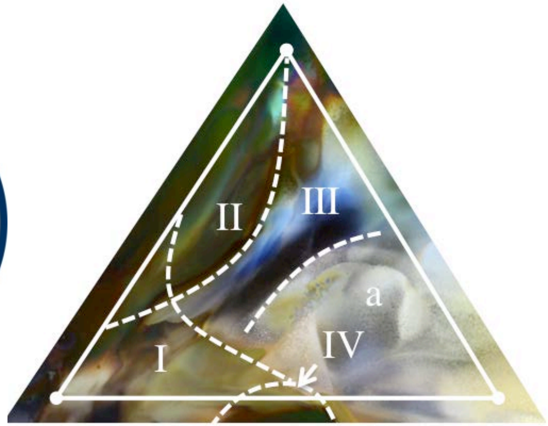
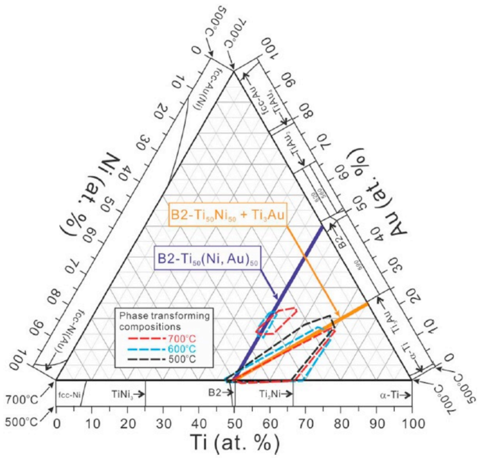






RUHR-UNIVERSITÄT BOCHUM

Fundamental Aspects of Materials Science and Engineering

Summer term 2020

Prof. Dr.-Ing. Alfred Ludwig
Chair for Materials Discovery and Interfaces
Institute for Materials

Lecture overview:

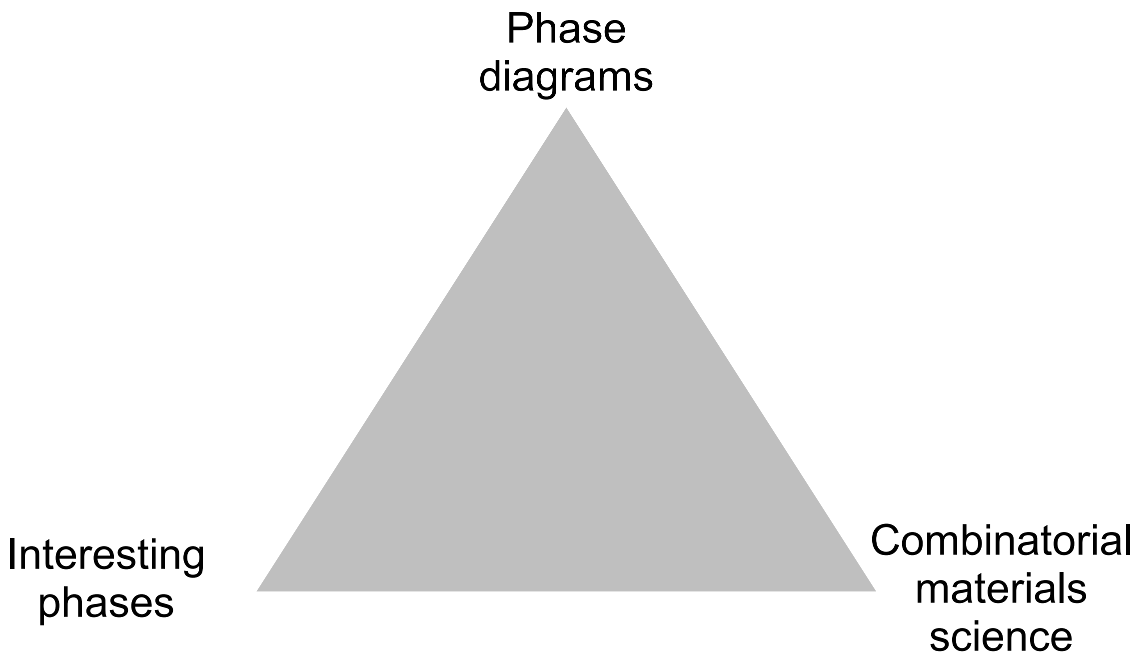
RUB

Binary and ternary phase diagrams

Intermetallic compounds

Combinatorial materials science

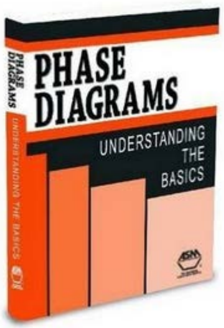
Exercises (Dr. Dennis Naujoks)

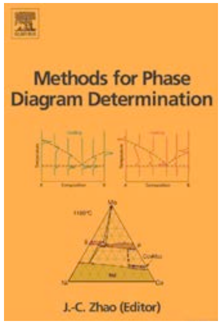


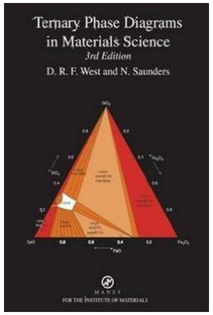
Literature

Text books

Lecture slides are based mainly on the following textbooks and databases. Slides are your personal copies and it is not allowed to distribute them further.

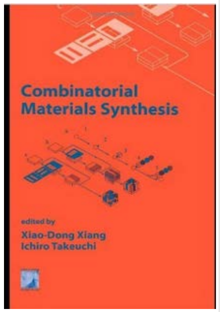






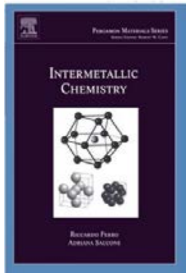
Phase diagrams

- F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012 (ISBN: 1615039864)
- J.-C. Zhao, Methods for Phase Diagram Determination, Elsevier 2011 (ISBN: 0080549969)
- D. R. F. West and N. Saunders, Ternary Phase Diagrams in Materials Science, Maney Publishing 2002 (ISBN:1902653521)



Combinatorial materials science

- X.-D. Xiang and I. Takeuchi, Combinatorial Materials Synthesis, Marcel Dekker Inc 2003 (ISBN: 0824741196)



Intermetallic compounds

- R. Ferro and A. Saccone, Intermetallic Chemistry, Pergamon 2008 (ISBN: 0080440991)
- G. Sauthoff, Intermetallics, Wiley-VCH 1995 (ISBN: 3527293205)

Chapters in many textbooks: Haasen, Gottstein, Eggeler, …

Literature

Examples of scientific journals

<u>Phase diagrams</u>

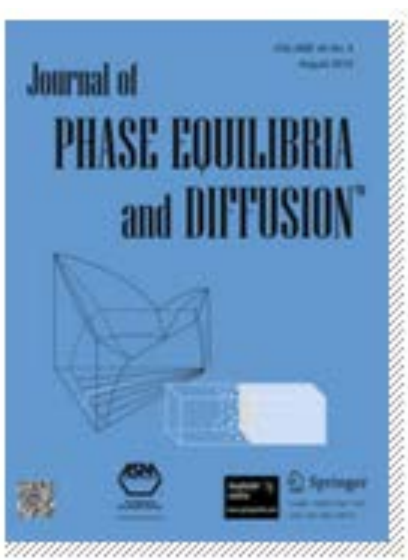
- Journal of Phase Equilibria and Diffusion, ASM International (ISSN: 1863-7345)

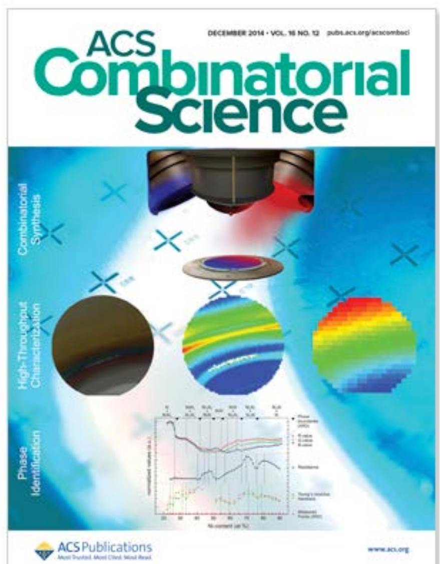
<u>Combinatorial materials science</u>

- ACS Combinatorial Science, American Chemical Society (ISSN: 2156-8952)

<u>Intermetallic compounds</u>

- Intermetallics, Elsevier (ISSN: 0966-9795)

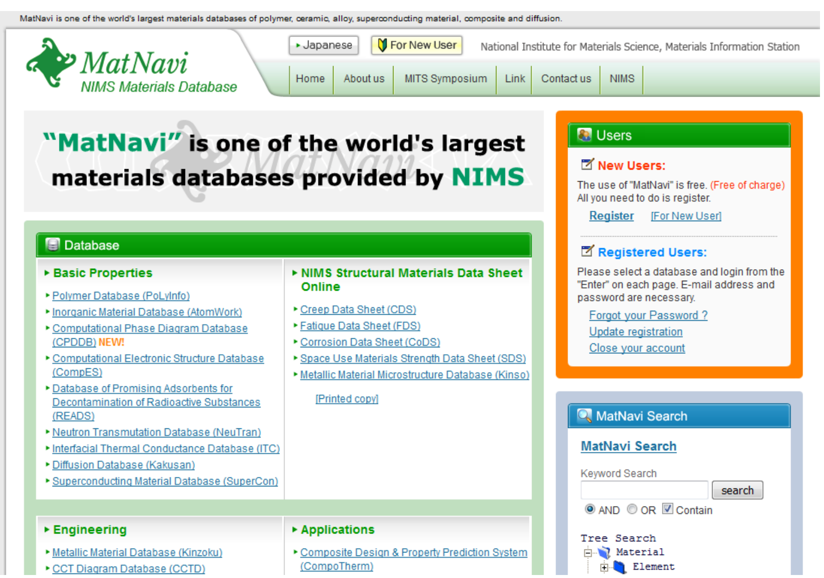


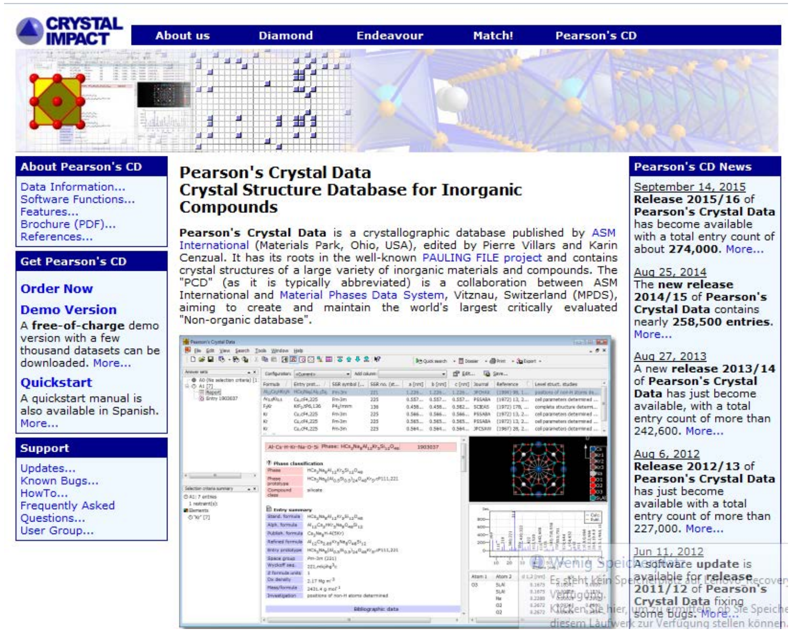


Open access article on phase diagrams:
http://link.springer.com/article/10.1007/s11669-014-0343-5/fulltext.html

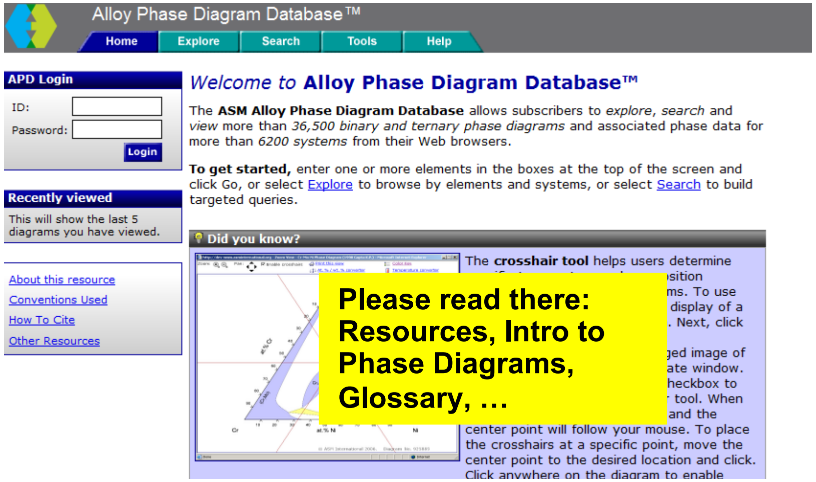
Introduction
Materials Databases: which materials exist?

- MatNavi: http://mits.nims.go.jp/index_en.html
- Pearson's Crystal Database: http://www.crystalimpact.com/pcd/
- Alloy Phase Diagram Database: http://www1.asminternational.org/asmenterprise/APD/default.aspx
- Computational Materials Repository: https://cmr.fysik.dtu.dk/
- The Materials Project: https://materialsproject.org/
- The Pauling file https://paulingfile.com/



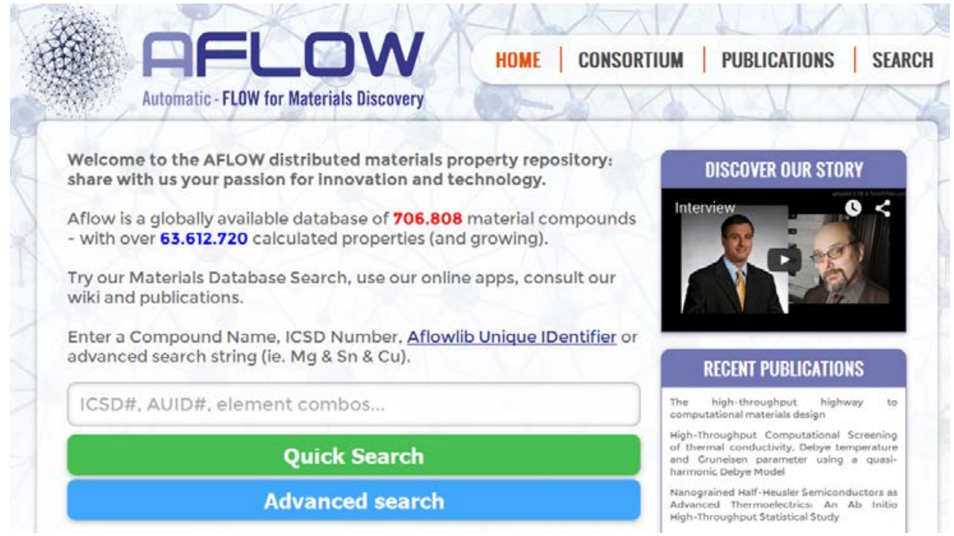


Phase diagrams, intermetallic phases and combinatorial materials research

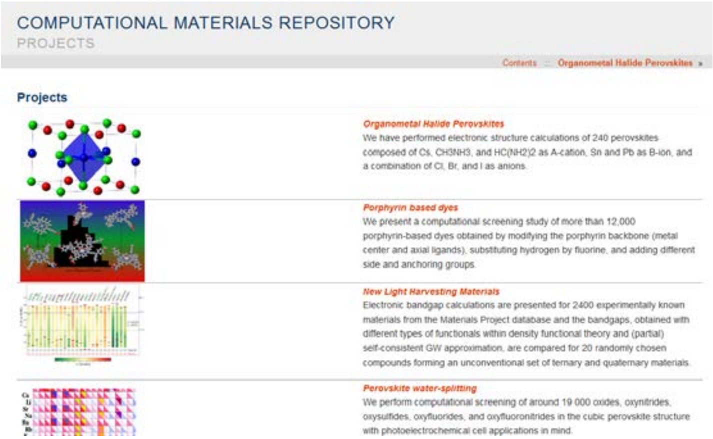


Please read there: Resources, Intro to Phase Diagrams, Glossary, …

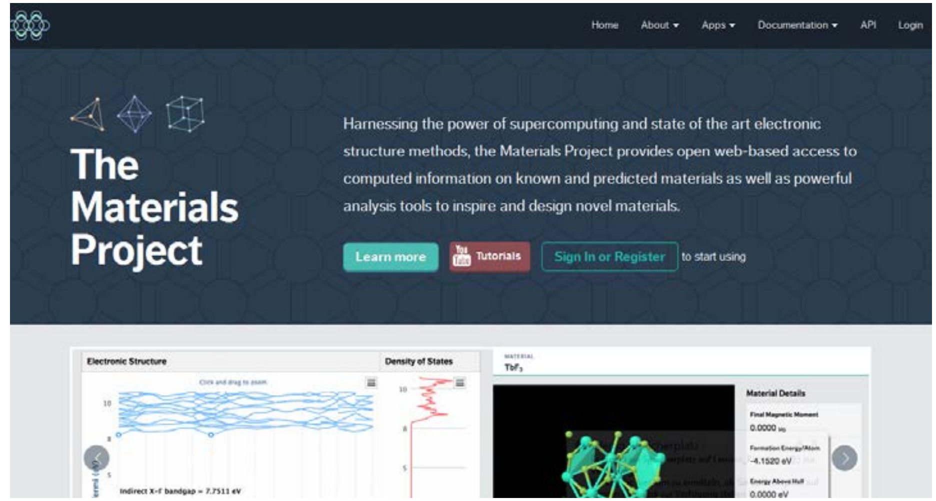
https://www.asminternational.org/



http://aflowlib.org/



https://cmr.fysik.dtu.dk/



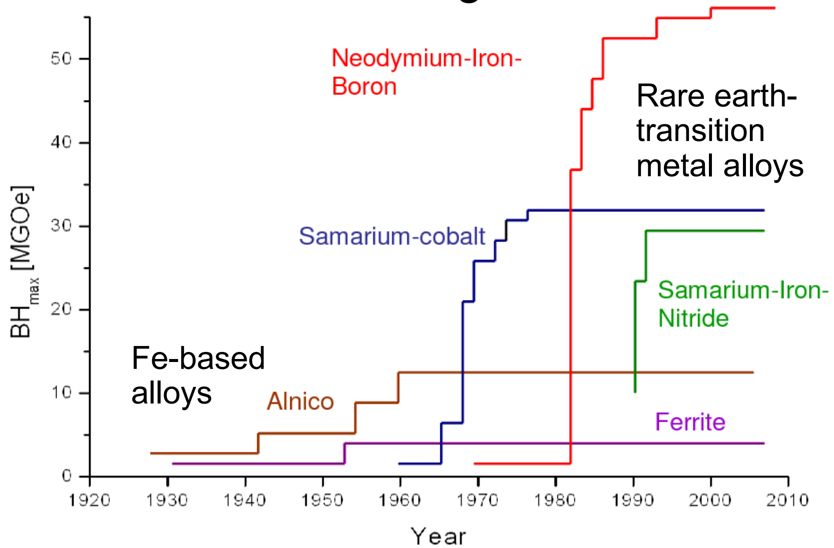
https://materialsproject.org/

Introduction

Development of new materials frequently based on new phases

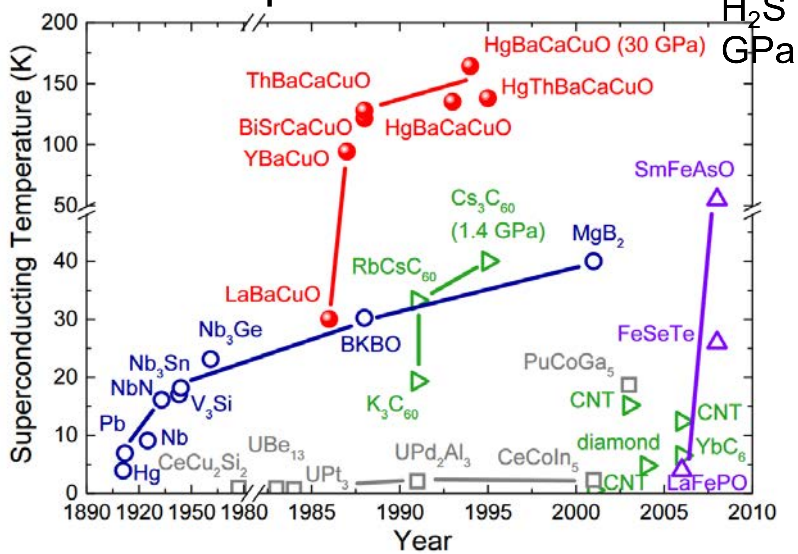
RUB

hard magnets

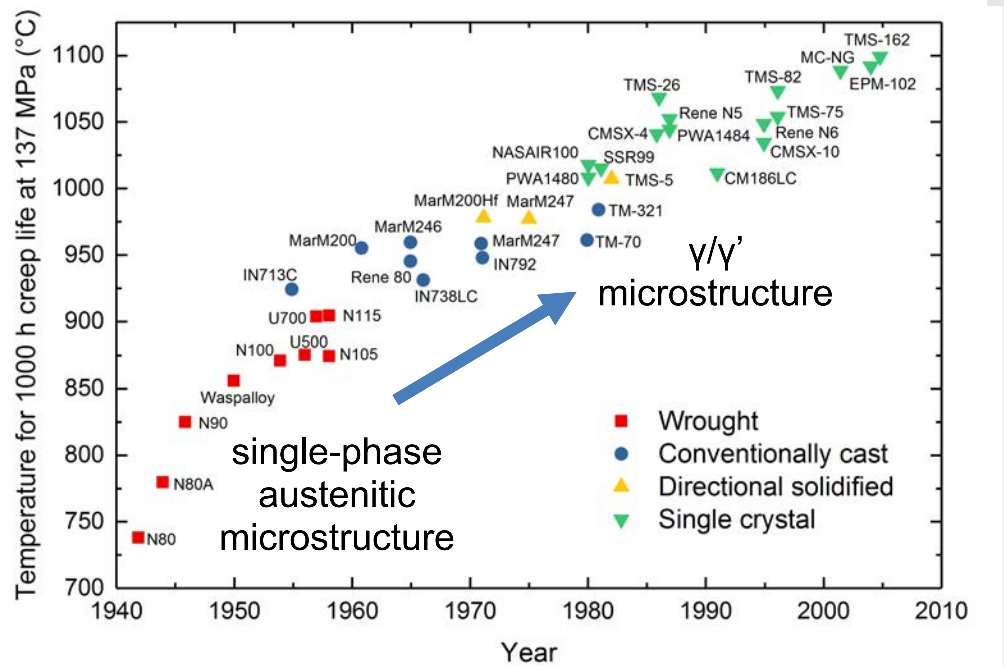


superconductors

H_2S @ 150 GPa



superalloys

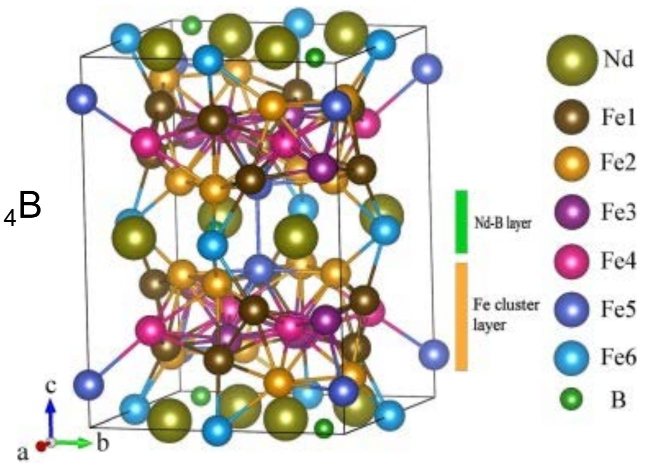


Introduction

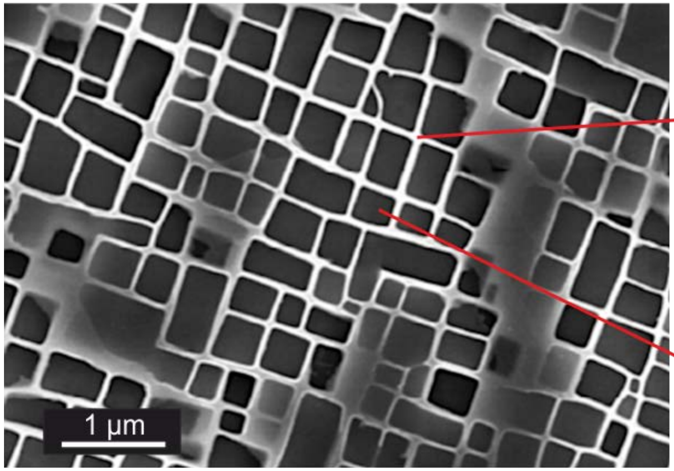
Examples of phases: alloys and compounds

hard magnets

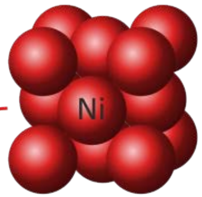
$Nd_2Fe_{14}B$



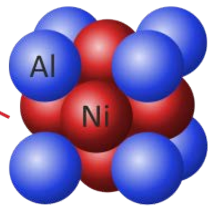
superalloys



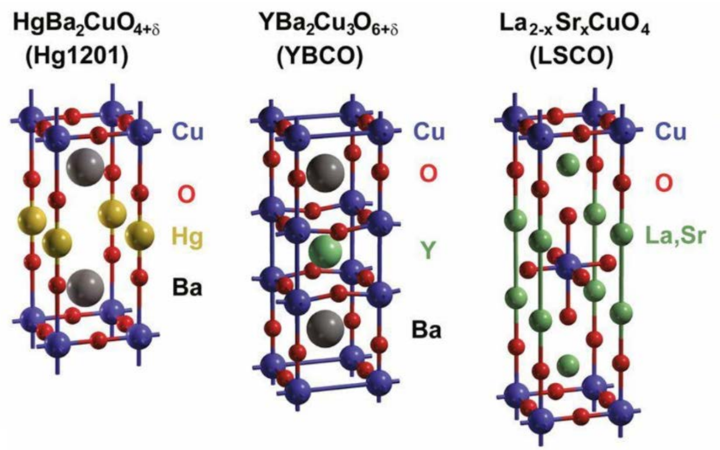
γ - A1 (fcc)



γ′ - $L1_2$



superconductors



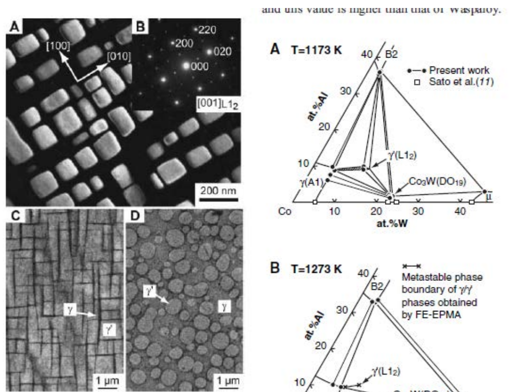


Fig. 1. Electron micrographs of Co-9Al-7.5W alloy annealed at 1173 K for 72 hours. (**A**) Dark-field image. (**B**) Selected area diffraction pattern. (**C** and **D**) Field emission scanning electron micrographs of Co-8.8Al-9.8W-2Ta (C) and Co-8.8Al-9.8W-2Mo (D) annealed at 1273 K for 1 week.

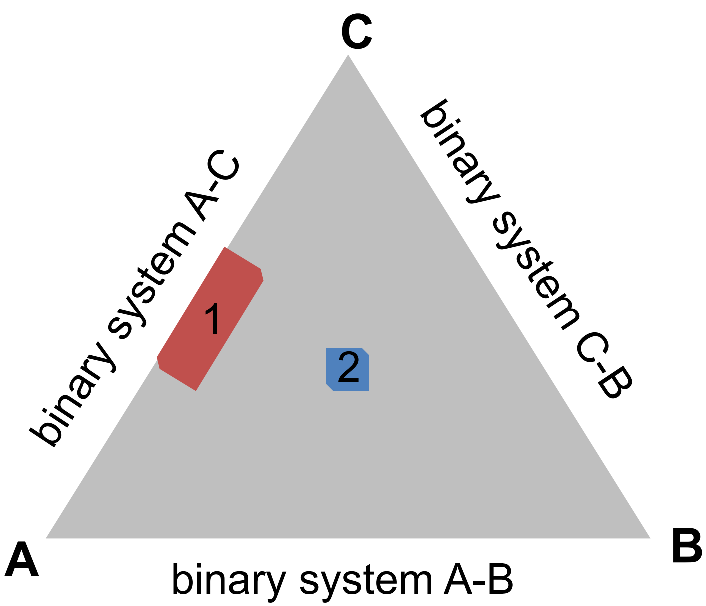
Fig. 2. Isothermal section diagrams of the Co-Al-W ternary system in the Co-rich portion at (**A**) 1173 K and (**B**) 1273 K.

2006 VOL 312 **SCIENCE** www.sciencemag.org

Introduction
Phase diagrams and existence diagrams

Visualizations of existence ranges of phases:

- **phase diagrams**: thermodynamic stable phases
- **existence diagrams**: metastable phases



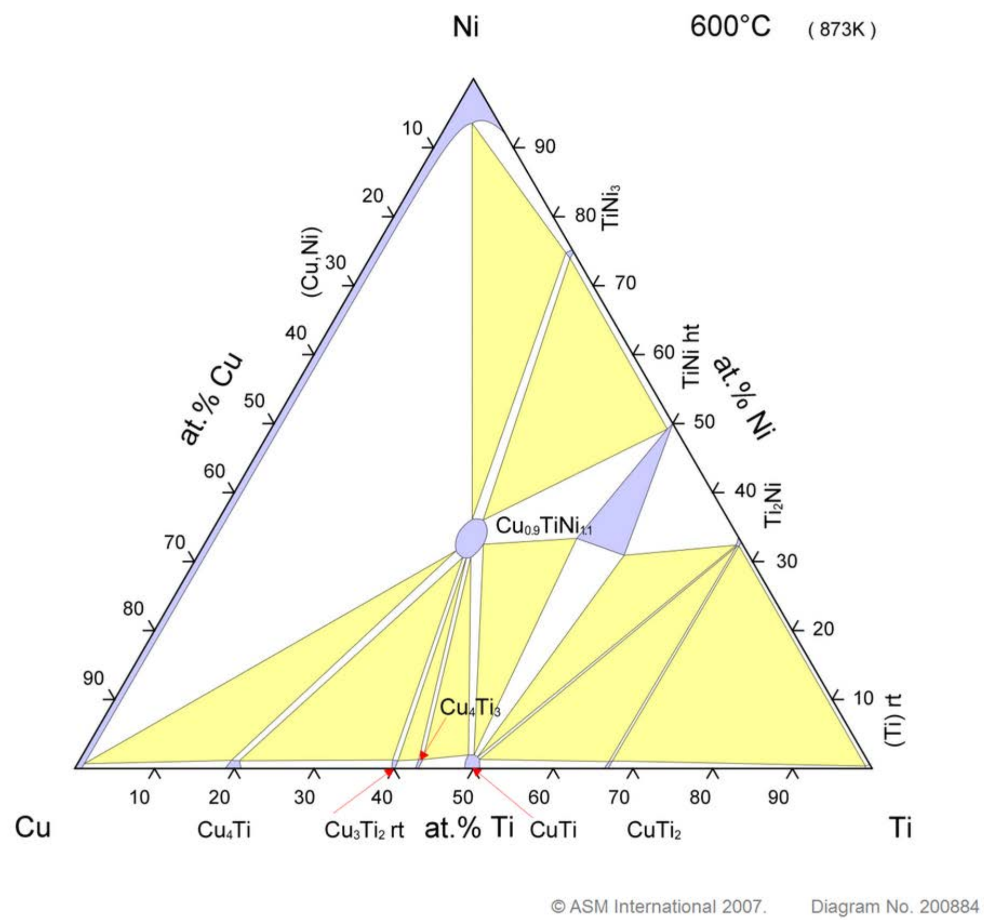
1: binary phase with solubility of 3rd component

2: „real“ ternary phase

composition-processing-structure-maps

Processing: temperature, pressure
Structure:
crystallographic structure (phase) and phase constitution (single or multiple phases)

Introduction
Example of a phase diagram



binary phase with solubility of 3rd phase

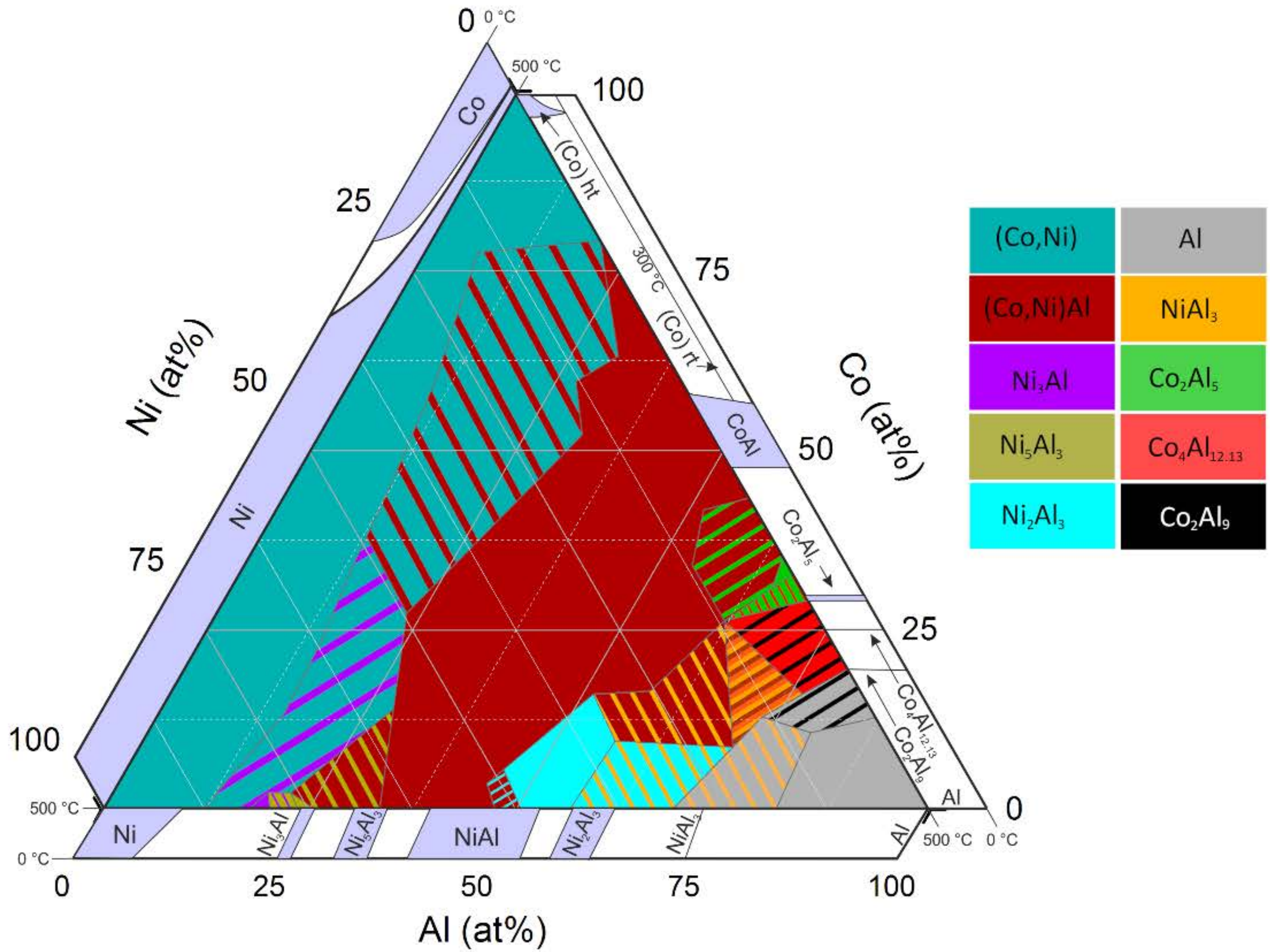
„real“ ternary phase

composition-processing-structure-maps

<u>Processing</u>: temperature, pressure
<u>Structure</u>:
crystallographic structure (phase)
and phase constitution
(single or multiple phases)

Introduction

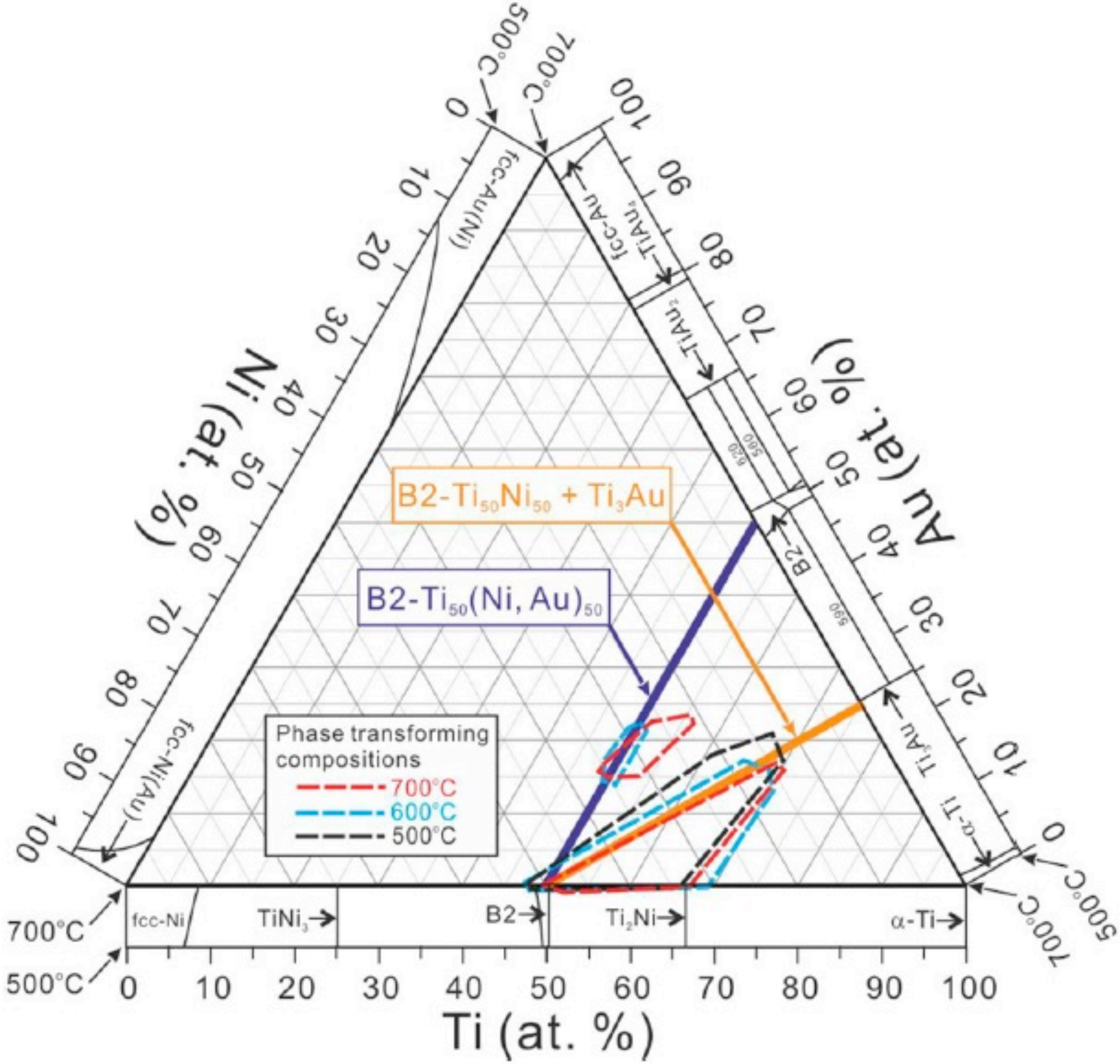
Assessment of phase diagrams by combinatorial materials science



D. Naujoks, J. Richert, P. Decker, M. Weiser, S. Virtanen, A. Ludwig (2016): Phase Formation and Oxidation Behavior at 500°C in a Ni-Co-Al Thin film Materials Library, ACS combinatorial science 18 (2016) 575–582.

Introduction

Assessment of phase diagrams by combinatorial materials science



P.J.S. Buenconsejo, A. Ludwig (2014) *Composition-Structure-Function diagrams of Ti-Ni-Au thin film shape memory alloys,* ACS Comb. Sci. 16, 678–685

Introduction
Combinatorial Materials Science

Number of combinations of n=50 elements

(n/k) = n!/(k!(n-k)!)

Binaries: 1225

Ternaries:
19600
(information on 7380 systems)

Quaternaries: 230000

1 H																	2 He
3 Li	4 Be											**5 B**	**6 C**	**7 N**	**8 O**	9 F	10 Ne
11 Na	**12 Mg**											**13 Al**	**14 Si**	15 P	16 S	17 Cl	**18 Ar**
19 K	20 Ca	**21 Sc**	**22 Ti**	**23 V**	**24 Cr**	**25 Mn**	**26 Fe**	**27 Co**	**28 Ni**	**29 Cu**	**30 Zn**	**31 Ga**	**32 Ge**	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	**39 Y**	**40 Zr**	**41 Nb**	**42 Mo**	43 Tc	44 Ru	45 Rh	**46 Pd**	**47 Ag**	48 Cd	**49 In**	**50 Sn**	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		**72 Hf**	**73 Ta**	**74 W**	**75 Re**	76 Os	77 Ir	**78 Pt**	**79 Au**	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Lanthanoide	57 La	58 Ce	59 Pr	**60 Nd**	61 Pm	**62 Sm**	63 Eu	**64 Gd**	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinoide	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Check databases for existing materials

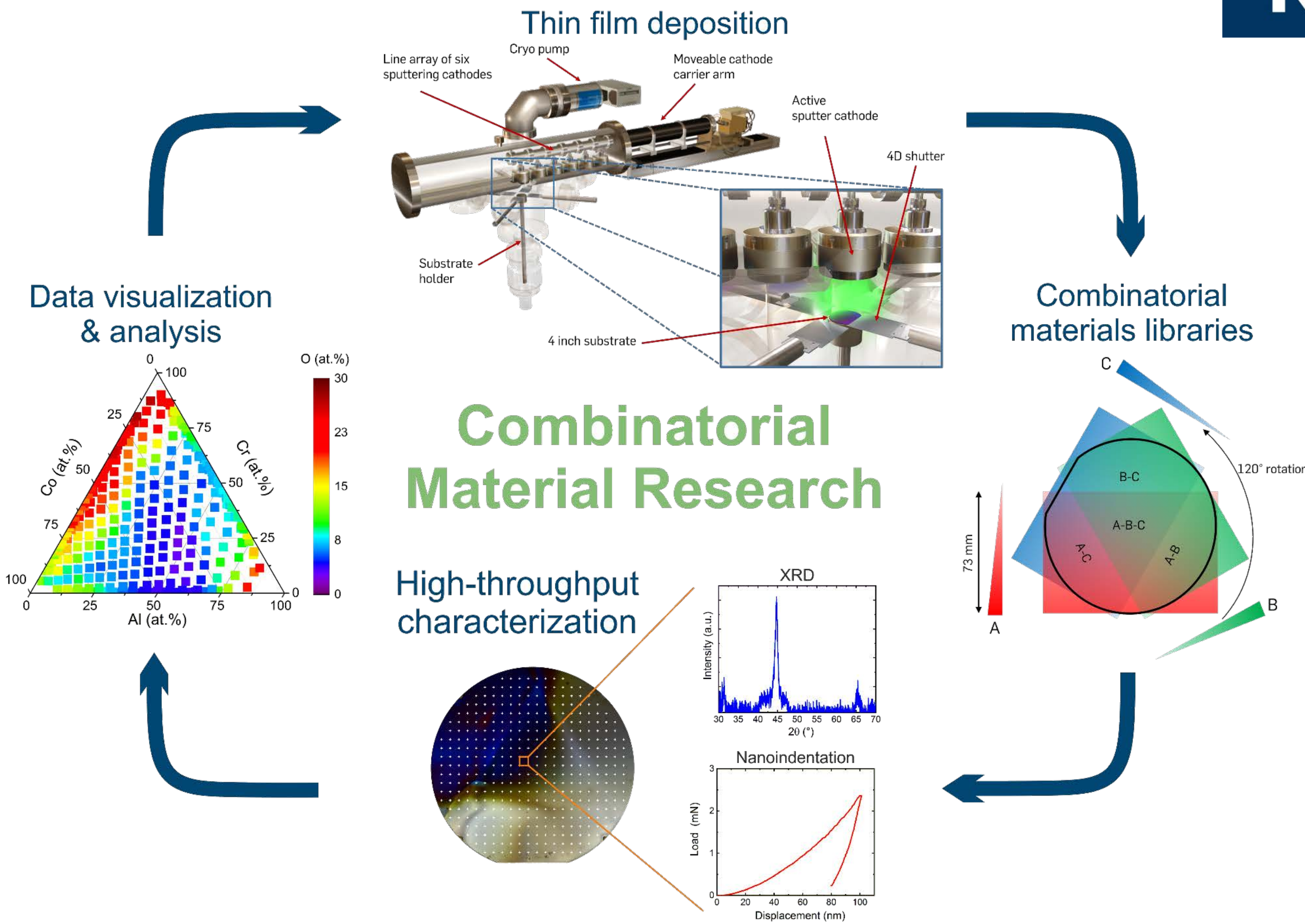
+ compositional and structural diversity (processing)

A_1B_{99} to $A_{99}B_1$

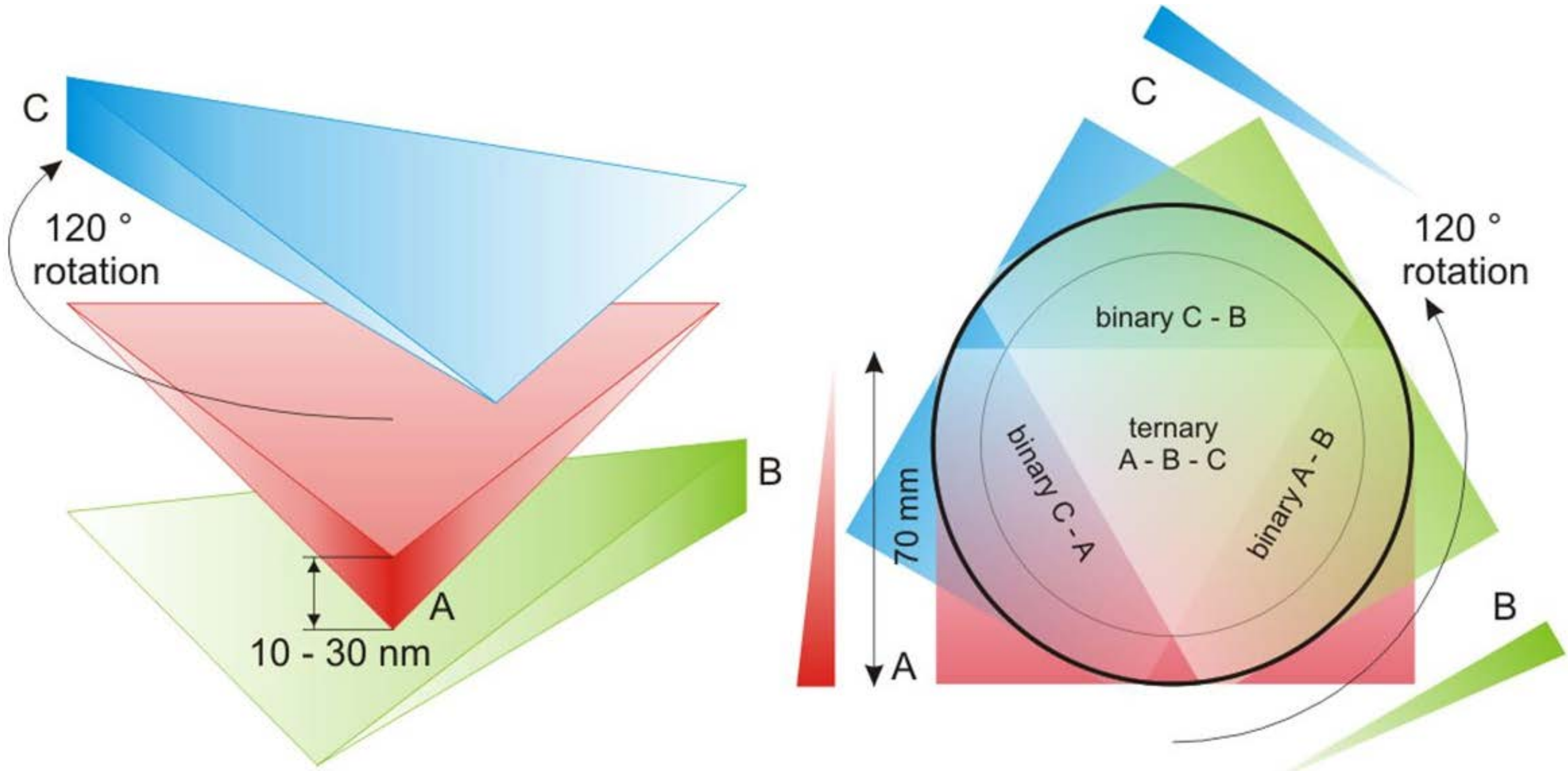
$A_{50}B_{50}$(bulk) ≠ $A_{50}B_{50}$ (thin film)

Introduction

Combinatorial materials science



Introduction
Combinatorial materials science:
Synthesis of complete binary and ternary thin film materials libraries by magnetron sputtering



Introduction
Combinatorial materials science

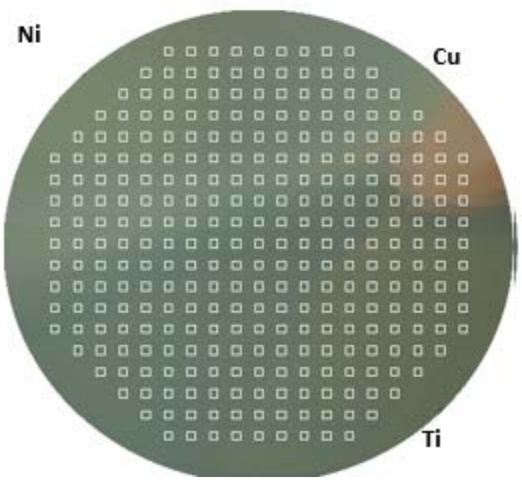
Establish

Composition-Structure-Property Correlation Maps

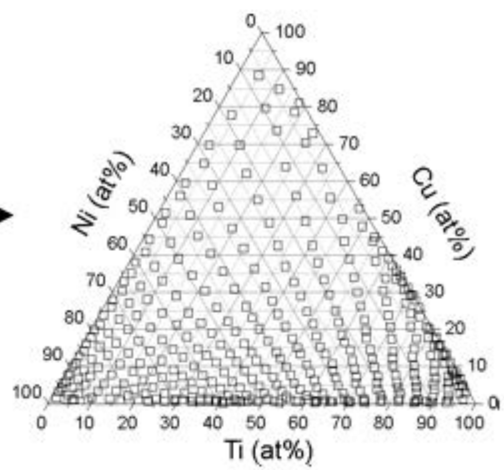
Trendlines: Property = f(composition)

Hits: compositions with unique properties

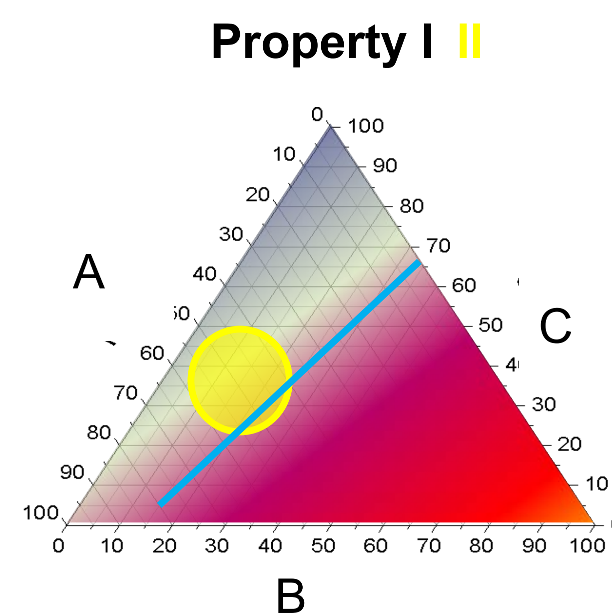
Composition: automated <u>E</u>nergy <u>D</u>ispersive <u>X</u>-ray analysis (EDX)
- over-night measurements (90-120 s/point – # of points 301)
- spacing in x-, y- direction 4.5 mm



Fabricate materials library

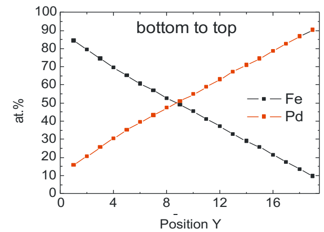
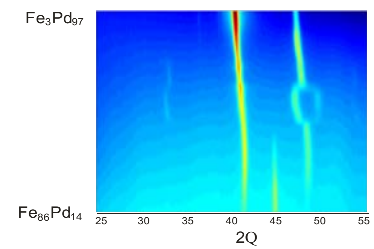
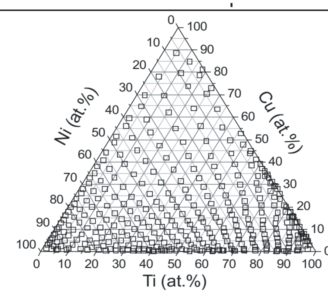
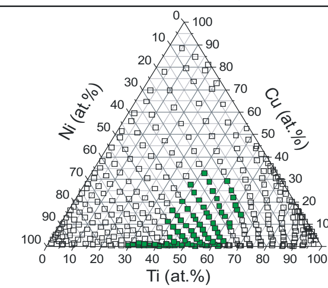
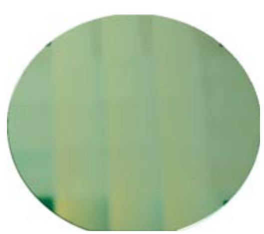
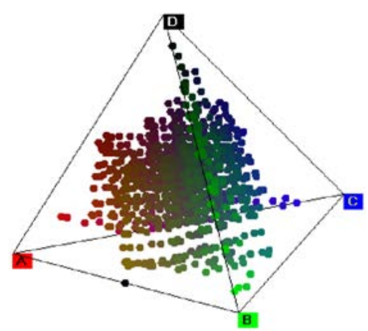
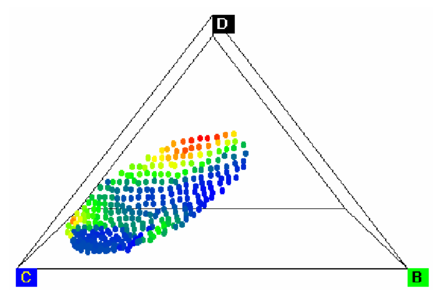


High-throughput characterization



S. Thienhaus, S. Hamann, A. Ludwig (2011), *Modular high-throughput test-stand for versatile screening of thin-film materials libraries*, Sci. Technol. Adv. Mater. 12 054206

Introduction
Combinatorial materials science

<table>
<tr><th rowspan="2">Type of materials library</th><th rowspan="2">Wafer appearance</th><th colspan="2">Screening results / Visualization</th></tr>
<tr><th>Composition (EDX)</th><th>Crystallinity (XRD) Functional Properties</th></tr>
<tr><td>Binary composition spread</td><td></td><td>
</td><td>
</td></tr>
<tr><td>Ternary composition spread</td><td></td><td>
</td><td>
</td></tr>
<tr><td>Quaternary composition spread</td><td></td><td>
</td><td>

A-content: 47— 64 at.%, $2\theta = 43.35 \pm 0.05$, color-code: intensity</td></tr>
</table>

Introduction

Aim of the lecture

Questions and tasks (examples):

- What are phases and phase diagrams?
- Define solid solutions, alloys and compounds.
- What are phase transformations?
- What are polymorphism and allotropy?
- How are phase diagrams determined / assessed?
- How can I calculate the fractions and compositions of phases in multi-phase regions?
- Apply the phase rule in a ternary system for different equilibria.
- Deduce isothermal and vertical sections from ternary phase diagrams.
- Know rules for formation of different classes of intermediate phases.
- Understand crystal structure and properties of important intermetallics.
- Why are many intermetallics brittle?
- Explain an example of the fabrication of a materials library.
- How is compositional and structural data acquired on materials libraries?

Aim:
You should be able to answer important scientific and technical questions regarding these topics.

RUB

Phase diagrams

Phase diagrams
Definition of a phase

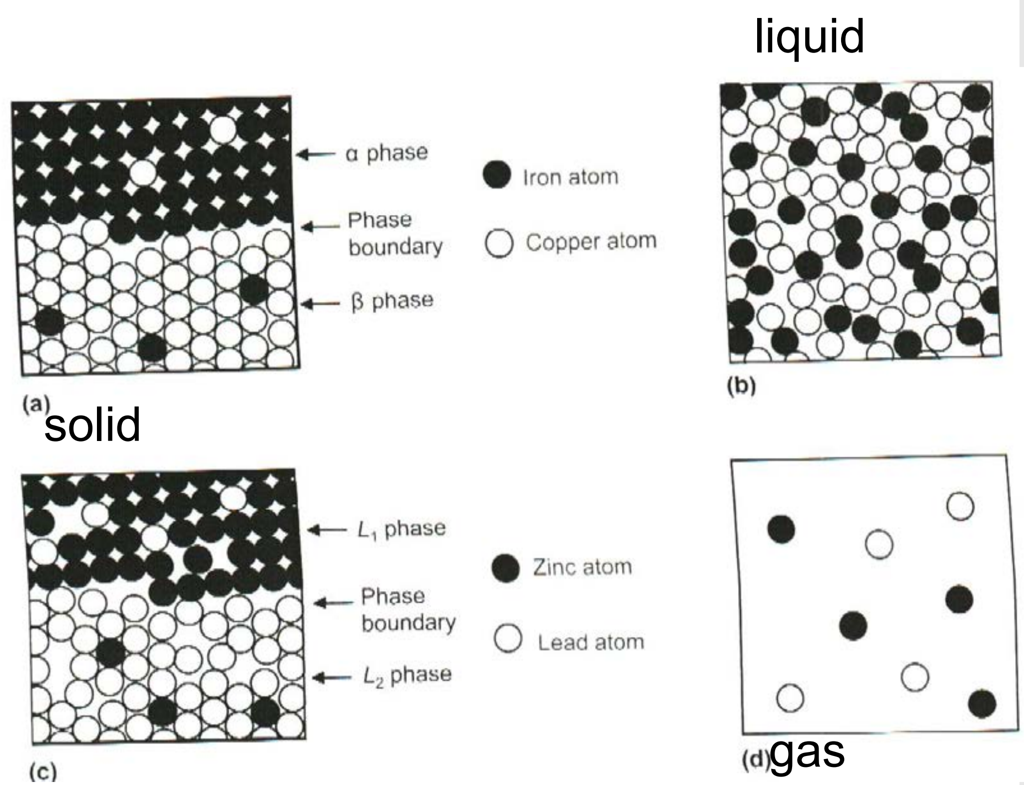
RUB

A phase is:
- a homogeneous part of a system, consisting of components
- a physically homogenous state of matter with a given chemical composition and structure
- different phases have different arrangement of atoms
- phases have phase boundaries

States of matter:
solid, liquid, gaseous

State variables:
composition, temperature, pressure, …

Examples of solid phases:
- solid solution
- line compound
- intermetallic phase
- alloy



Source: Campbell

Phase diagrams

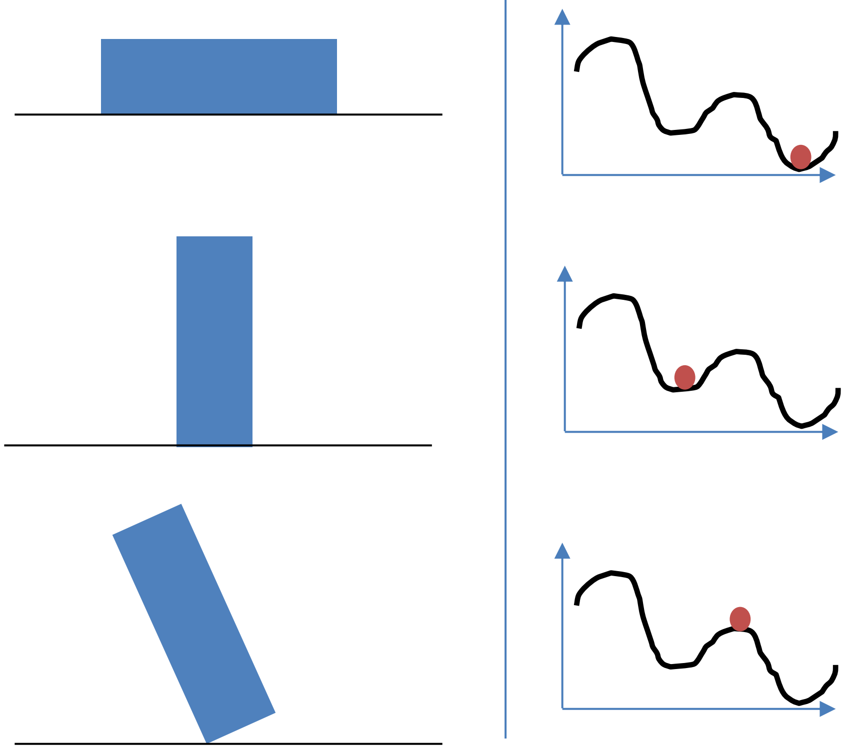
Phase diagrams are:

- important and useful as „tools“ in materials science, physical chemistry, geosciences, …
- graphical representations of possible phases and phase changes
- showing information on existing phases and their existence ranges
- visualizing material behavior and phase constitution,
  often: during heating/cooling, under equilibriunm conditions
- showing occuring material reactions
- displaying thermodynamic data
- give guidance on microstructures forming at different conditions
  (e.g. on cooling from melt, during heat treatment)
- shows constitution information: type of phases, composition of phases, fraction of phases
- roadmaps to understand conditions for phase formation or transformation caused by a change of state variables
- starting points for materials design and process optimization
- …

also called: *constitutional diagram*, *equilibrium diagram*,
in case of non-equilibrium conditions also: *existence diagram*

Phase equilibrium
Three types of equilibria

mechanical interpretation | energy „landscape“



- **stable** — exists when an object is in its <u>lowest energy condition</u>
- **metastable** — exists when additional energy must be introduced before the object can reach true stability
- **unstable** — unstable equilibrium exists when no additional energy is needed before reaching metastability or stability

Although true stable equilibrium conditions seldom exist, the study of equilibrium systems is valuable, because it constitutes a limiting condition from which actual conditions can be estimated. Phase diagrams can help elucidating the path from metastable states to stable states.

Source: Alloy Phase Diagram Database, ASM International

Phase equilibrium
Phase rule

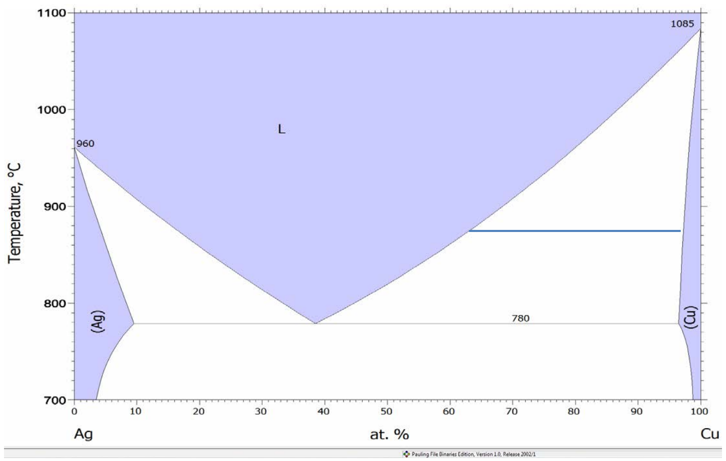
F + P = C + 2

For p=const.: F+P=C+1

F: degrees of freedom (e.g. temperature T, composition c, pressure p)
C: number of components (unary = 1, binary = 2, ternary = 3, …)
P: number of phases

Invariant equilibrium: 0 degrees of freedom
Univariant equilibrium: 1 degrees of freedom
Bivariant equilibrium: 2 degrees of freedom

Example of binary eutectic system (C=2) at constant pressure



PAULING FILE, Binaries Edition, ASM International, 2002

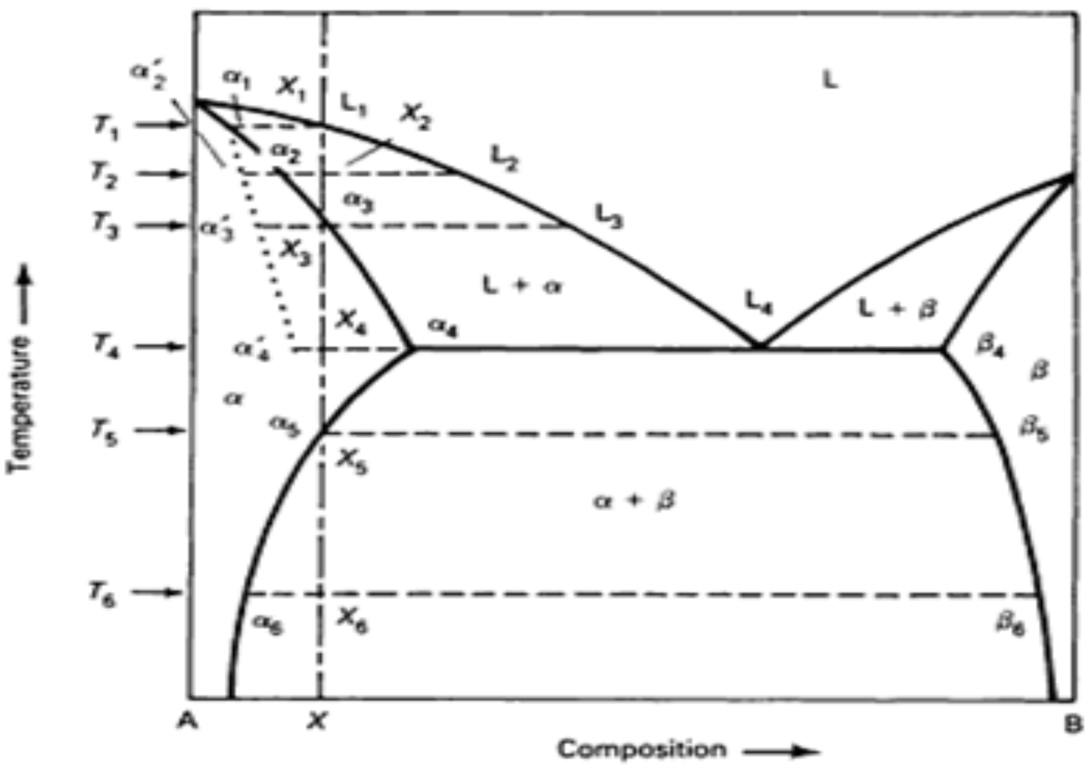
F+P=3
Single phase field: F=2
Two-phase field: F=1
Three phases in equilibirum: F=0

Gibbs phase rule can be used to analyze nonequilibrium conditions. E.g., a microstructure for a binary alloy that developed over a range of temperatures and consists of three phases is a nonequilibrium one; under these circumstances, three phases exist only at a single temperature.

W. D. Callister, D. G Rethwisch: Materials Science and Engineering An Introduction, 8th edition, 2009
F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012
Alloy Phase Diagram Database, ASM International

Phase equilibrium
Effects of heating/cooling rate

Binary phase diagram:
Illustration of the effect of cooling rate on an alloy lying outside the equilibrium eutectic-transformation line.
Rapid solidification into a terminal phase field can result in some eutectic structure being formed;
homogenization at temperatures in the single-phase field will eliminate the eutectic structure;
β phase will precipitate out of solution upon slow cooling into the a + β field.

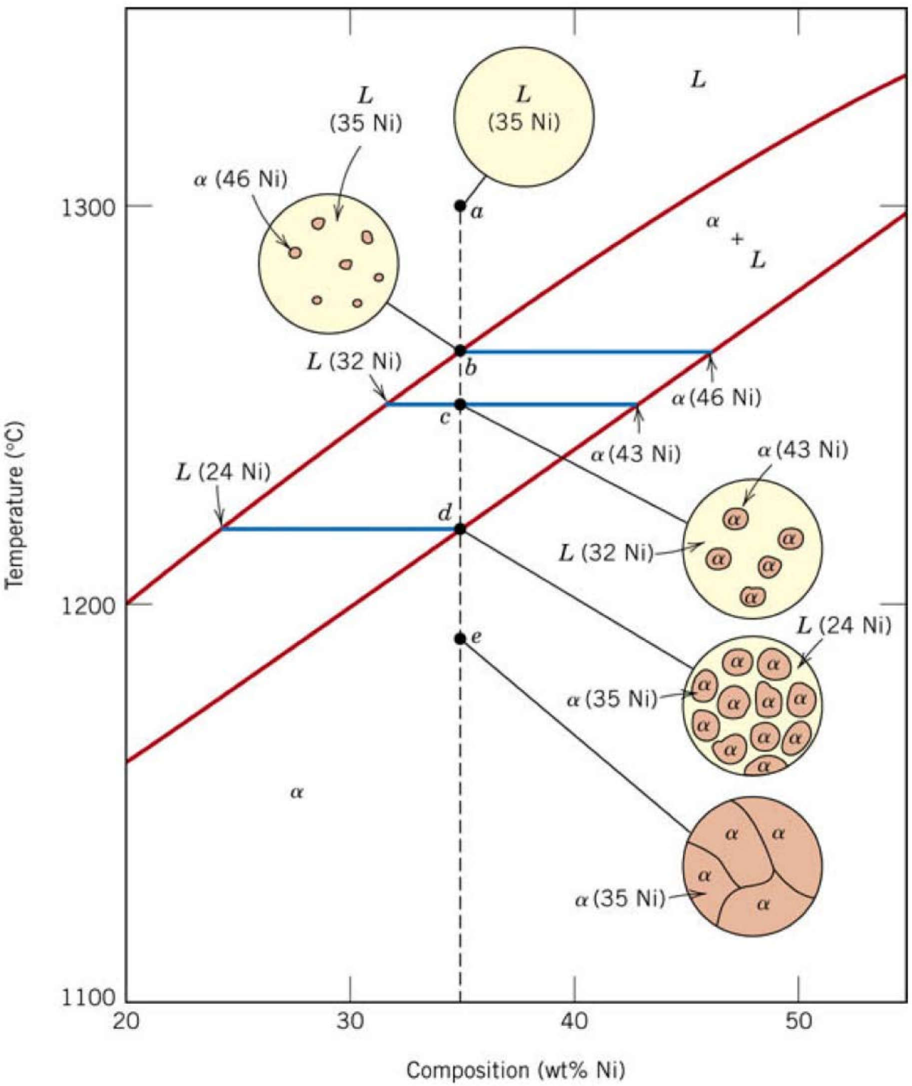


F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012
Alloy Phase Diagram Database, ASM International

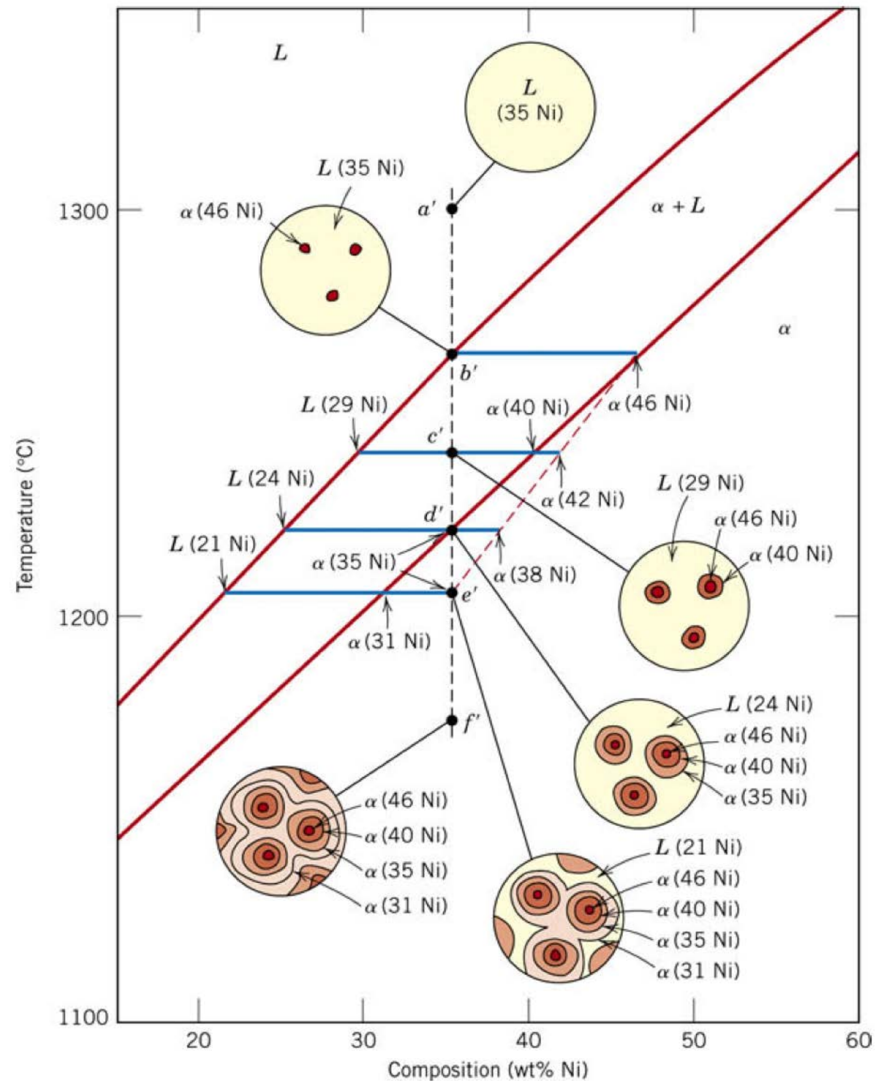
Phase equilibrium
Effects of heating/cooling rate

RUB

Equilibrium solidification



Non-equilibrium solidification



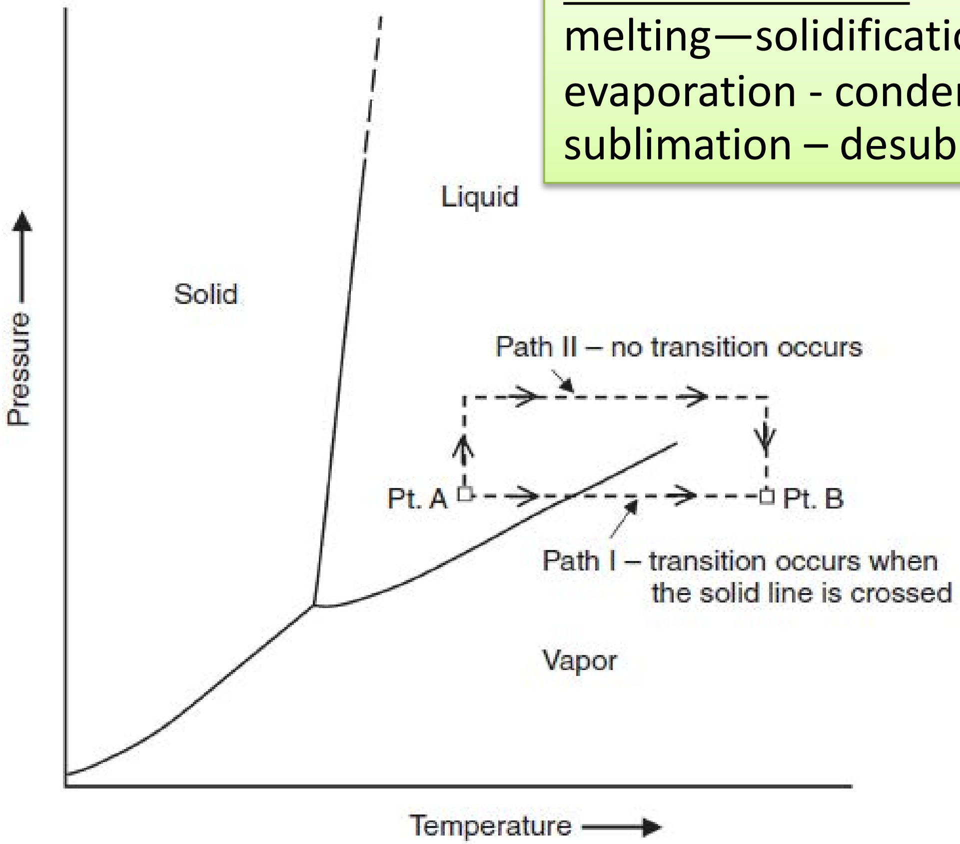
Coring
due to non-equilibrium solidification

W. D. Callister, D. G Rethwisch: Materials Science and Engineering An Introduction, 8th edition, 2009

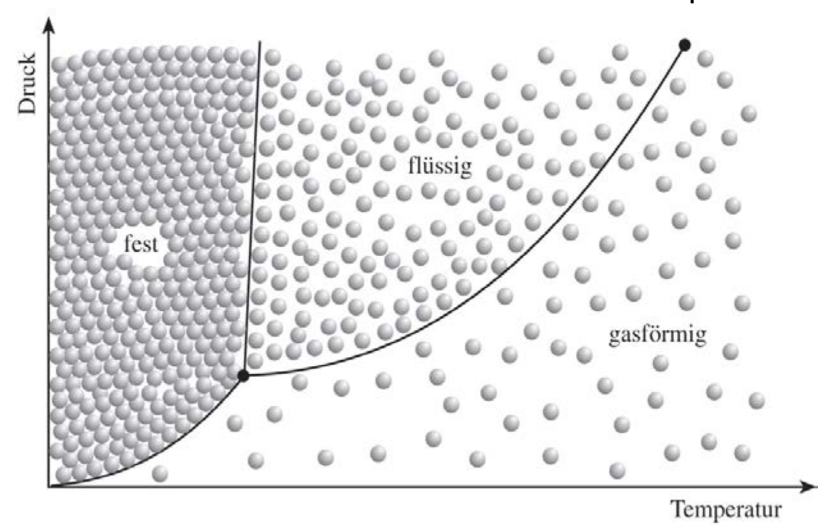
Unary phase diagrams (schematic)

Which phases and phase transitions can occur in a unary system?

<u>Phase transitions:</u>
melting—solidification
evaporation - condensation
sublimation – desublimation (deposition)



critical point



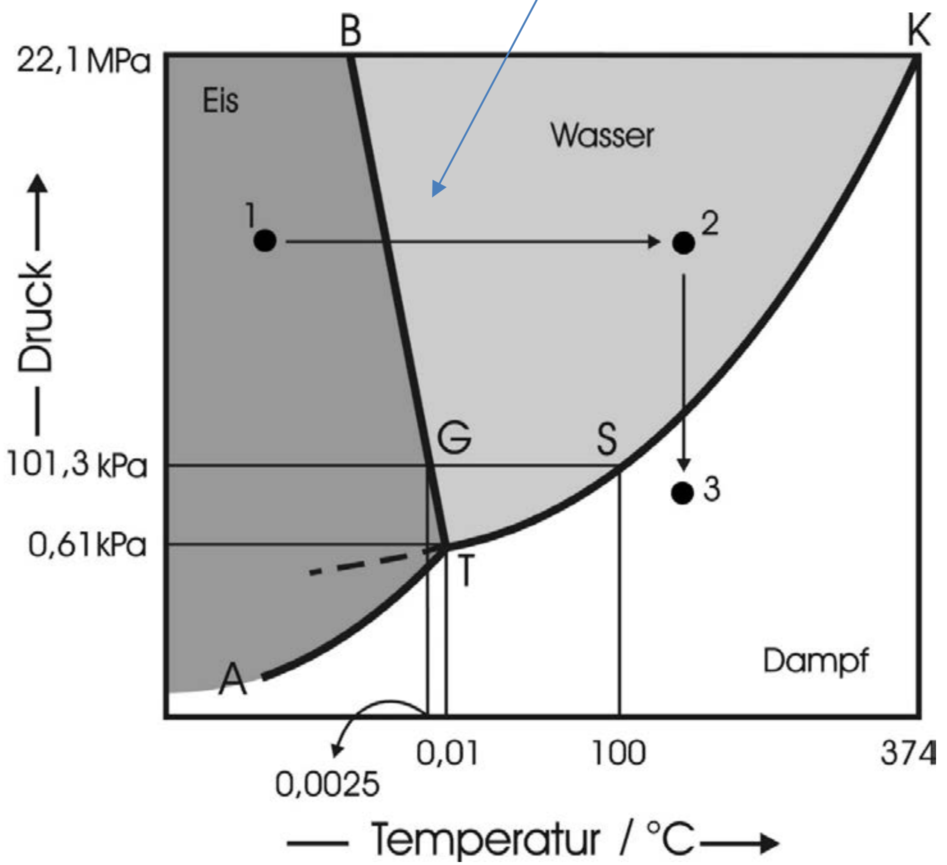
invariant point (F=0): triple point

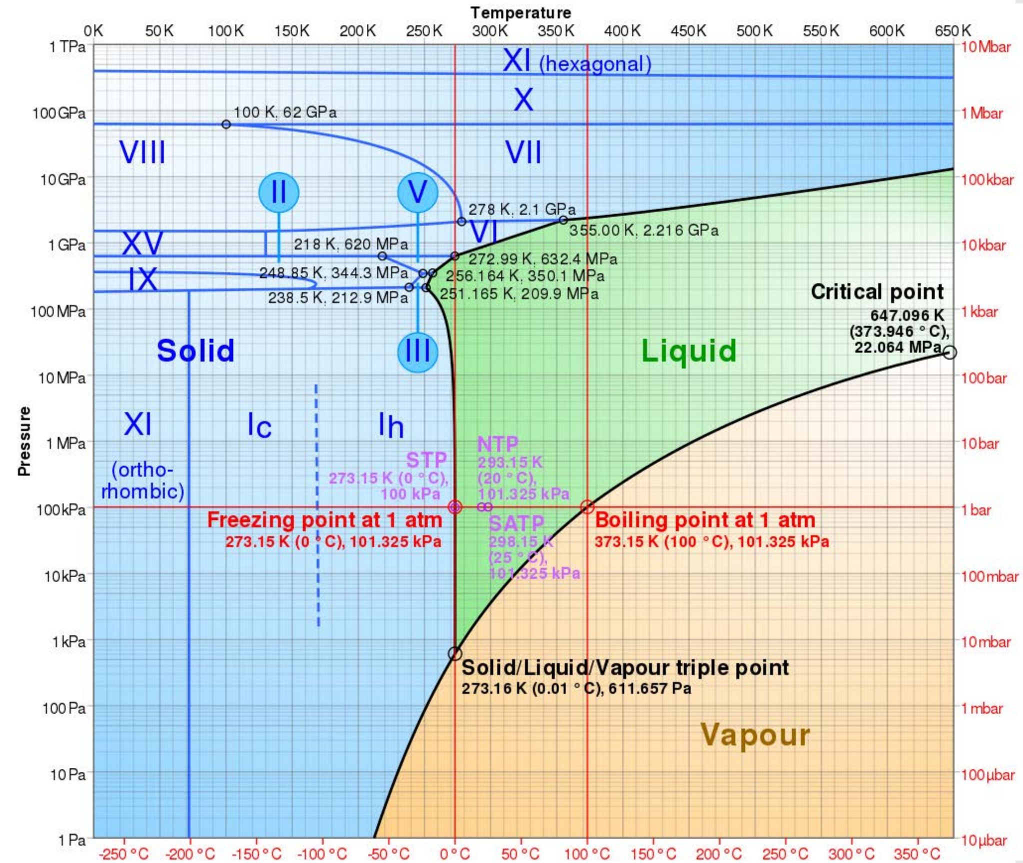
On <u>phase boundaries</u> (in the phase diagram), phases coexist

Unary phase diagrams
Phase diagram of molecules (H_2O)

RUB

- The decrease of T_M with increasing pressure is special for water



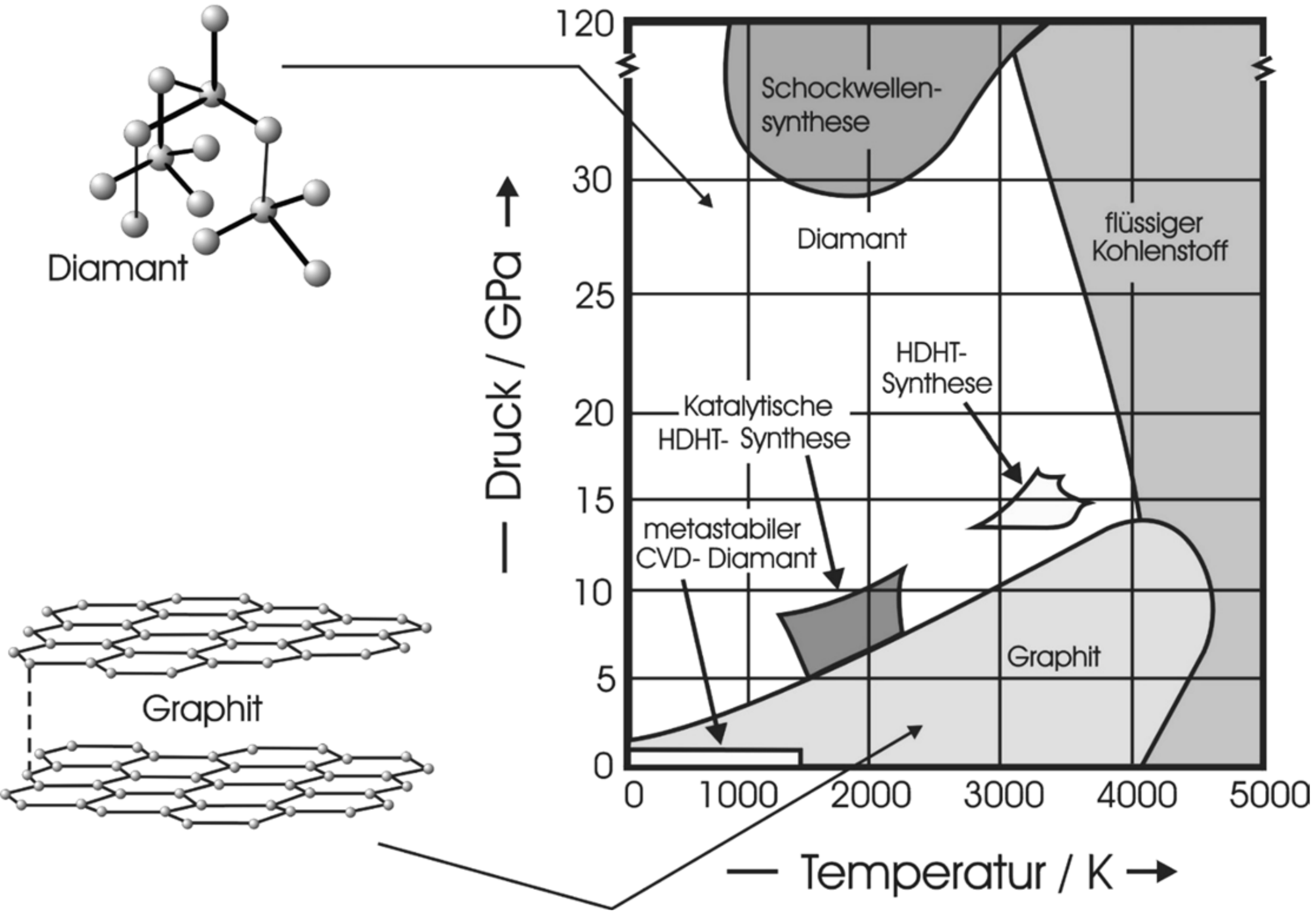


Log-lin pressure–temperature phase diagram of water

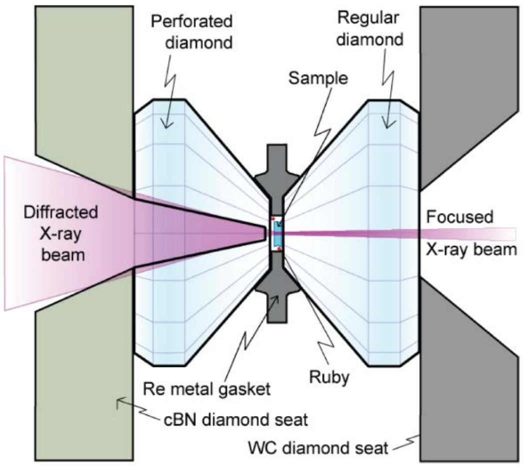
https://commons.wikimedia.org/wiki/File:Phase_diagram_of_water.svg

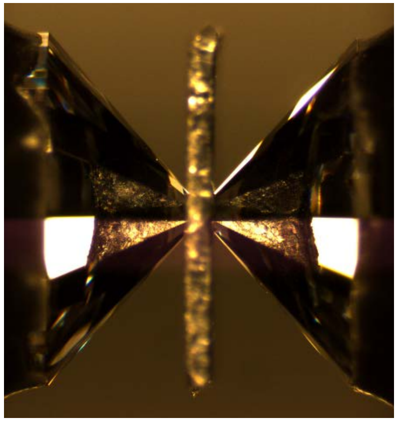
Unary phase diagrams and allotropy of elements

Examples: Carbon (different allotropes)



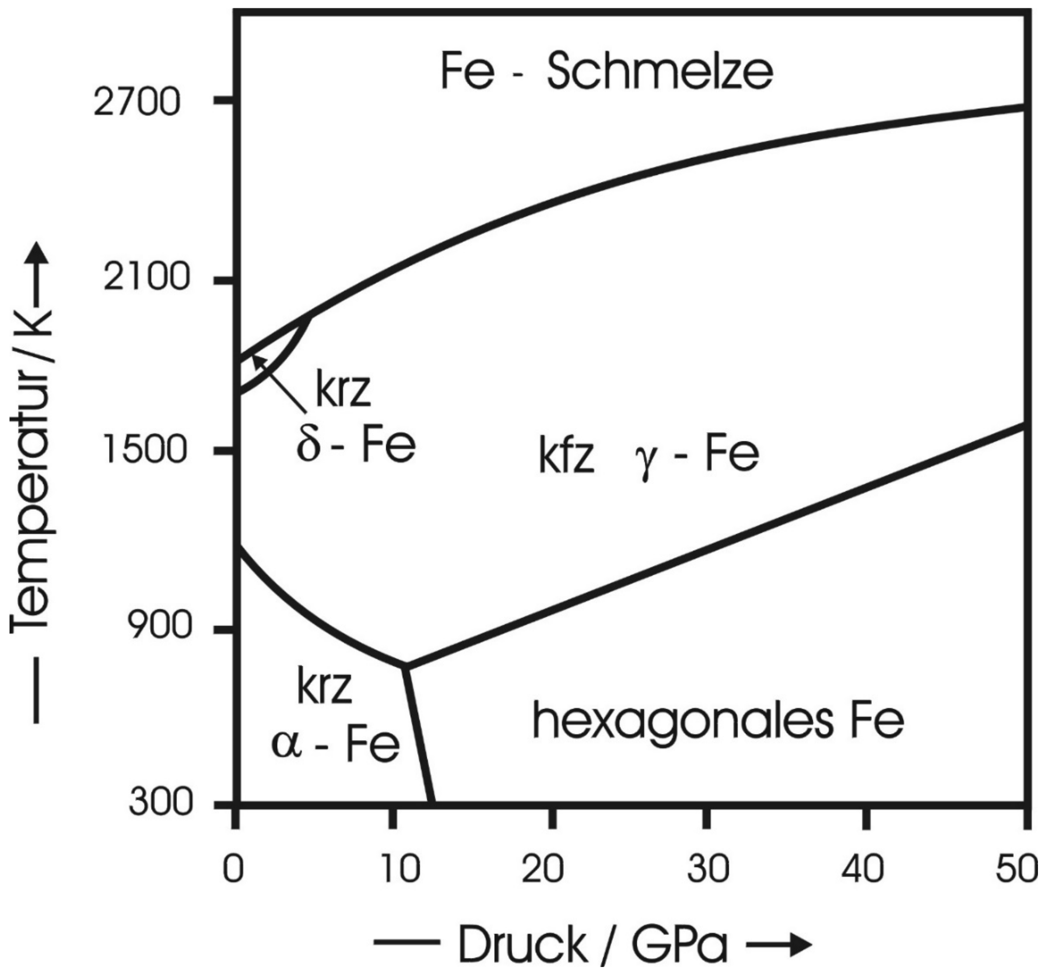
DAC:
diamond anvil cell



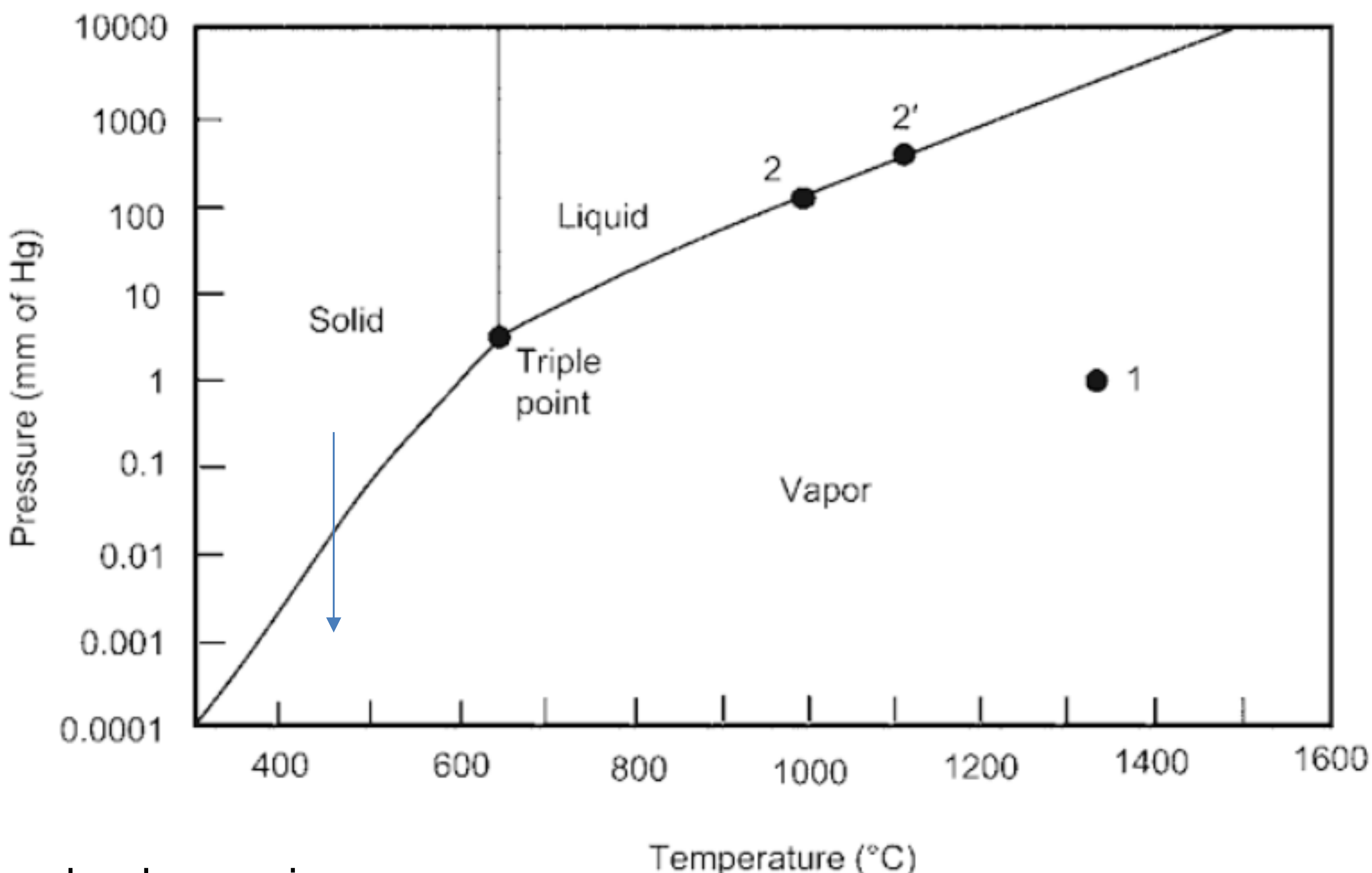


Unary phase diagrams and allotropy of elements

Examples: Fe



Unary phase diagrams
Examples: Mg (effect of low pressure)

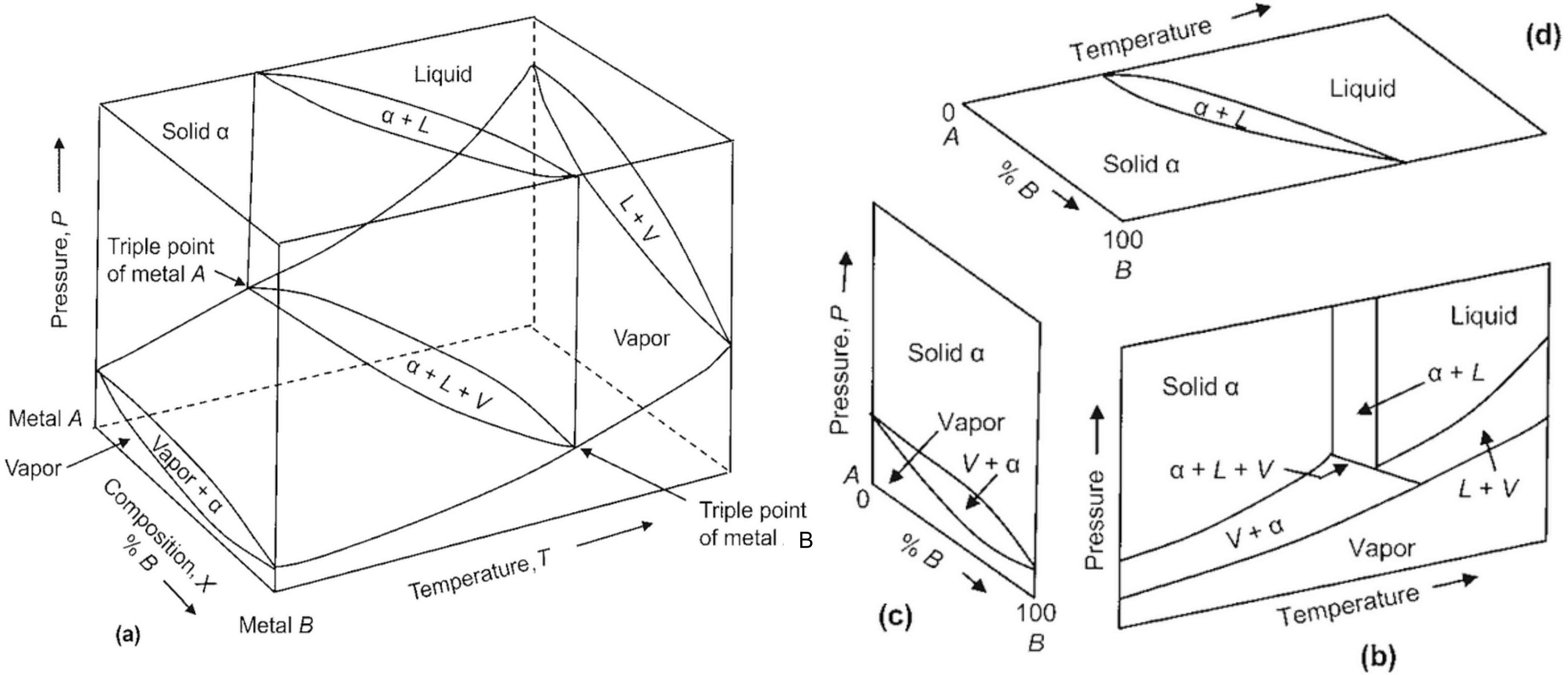


by decreasing pressure,
a solid can sublimate

F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

General example of a phase diagram (P-T-X): binary system with complete miscibility

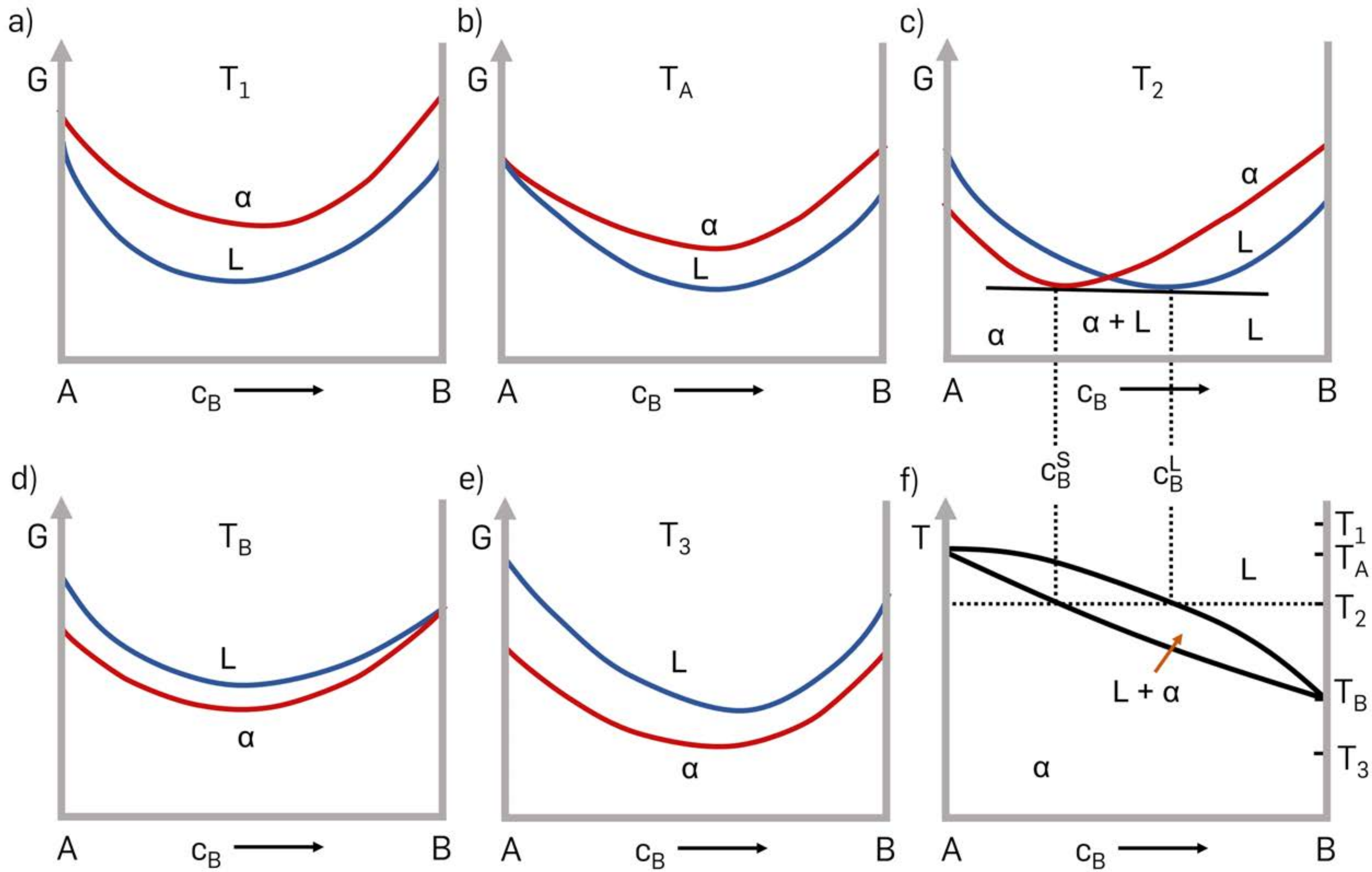
- materials science (especially metallurgy): isobaric phase diagrams (d) most common



F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012, Fig. 4.1

Phase diagram determination
Construction based on thermodynamics

Use **Gibbs energy (G) curves** to construct a binary phase diagram that shows miscibility in both liquid and solid

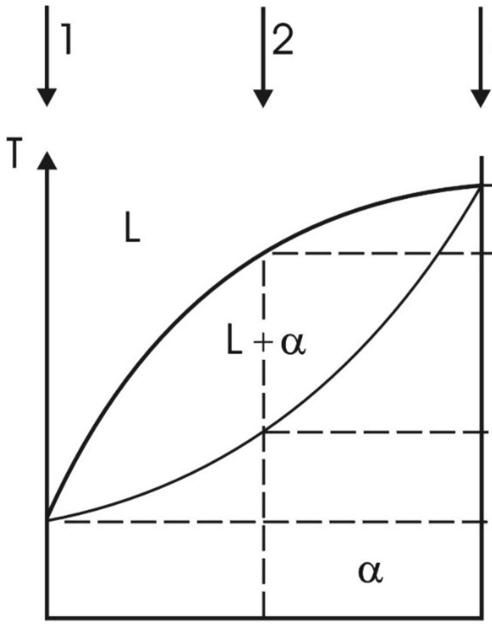


Alloy Phase Diagram Database, ASM International
Gottstein, Günter : Physical Foundations of Materials Science

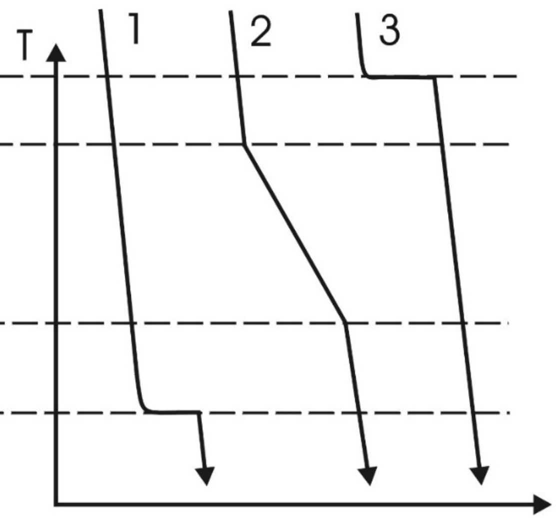
Phase diagram determination
Complete miscibility (solid solutions)

RUB

a system bordered by two components (A, B)



isobaric phase diagram



- cooling curves

F+P=C+1,
p= e.g. atmospheric pressure

Examples of binaries with complete miscibility

Au-Ag	Co-Re	α-Fe-V	Ni-Pd
Ag-Pd	Co-Rh	γ-Fe-Co	Ni-Pt
As-Sb	Co-Ru	α-Fe-Ni	Pd-Rh
Au-Cu	Cr-α-Fe	α-Fe-Pd	Pd-Pt
Au-Ni	Cr-Mo	γ-Fe-Pt	Pt-Rh
Au-Pd	Cr-Ti	Hf-Zr	Se-Te
Au-Pt	Cr-W	Ir-Pt	Si-Ge
Bi-Sb	Cs-K	K-Rb	Ta-β-Ti
Ca-Sr	Cs-Rb	Mn-Ni	Ta-W
Co-Ir	Cu-Mn	Mo-Ta	Ti-Mo
Co-Ni	Cu-Ni	Mo-W	Ti-Nb
Co-Os	Cu-Pd	Nb-Ta	Ti-V
Co-Pd	Cu-Pt	Nb-Mo	Ti-Zr
Co-Pt	Cu-Rh	Nb-W	

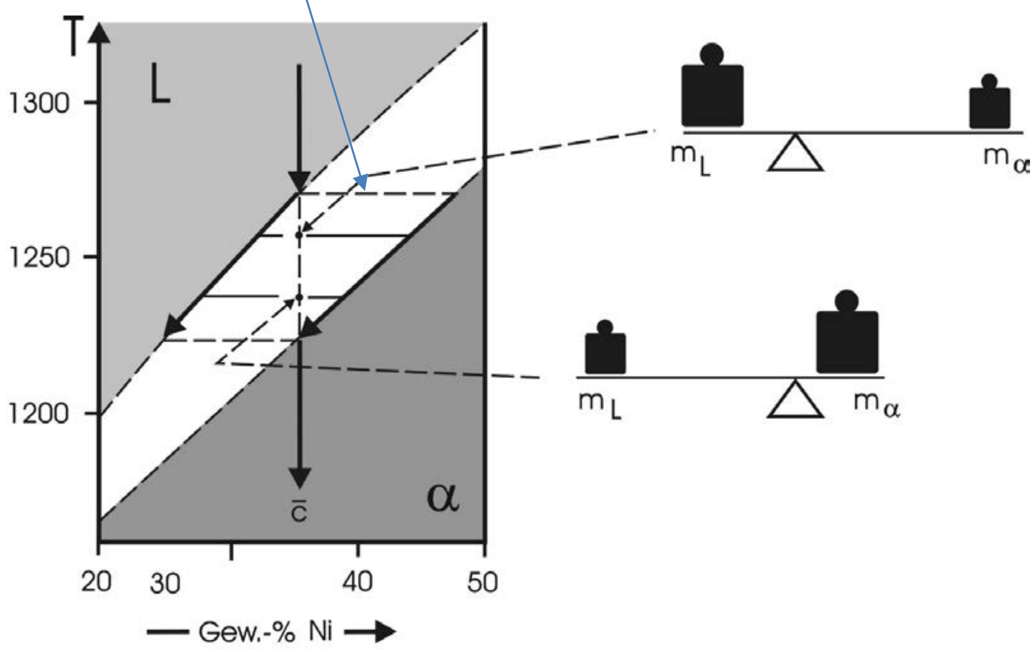
Formation of solid solutions
(at least at higher temperatures)

G. Gottstein, Physikalische Grundlagen der Materialkunde, Springer Verlag, 2013
E. Hornbogen, G. Eggeler, E. Werner, Werkstoffe: Aufbau und Eigenschaften… , Springer Verlag, 2017

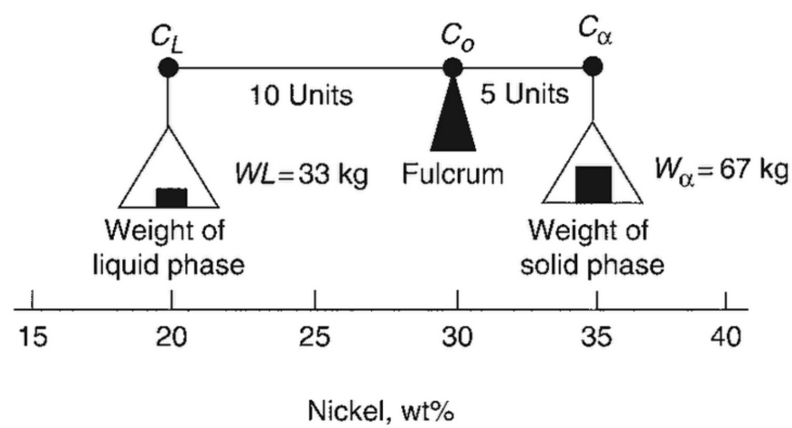
Binary phase diagrams
Lever rule

tie line

tie lines connect concentrations in equilibrium



(a) (b)



$$\text{wt\% } L = \frac{C_\alpha - C_o}{C_\alpha - C_L} = \frac{35-30}{35-20} \approx 0.33, \text{ or } 33\%$$

$$\text{wt\% } S = \frac{C_o - C_L}{C_\alpha - C_L} = \frac{30-20}{35-20} \approx 0.67, \text{ or } 67\%$$

$$m_L \cdot (\bar{c} - c_L) = m_\alpha \cdot (c_\alpha - \bar{c})$$

F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012
E. Hornbogen, G. Eggeler, E. Werner, Werkstoffe: Aufbau und Eigenschaften… , Springer Verlag, 2017

Phase diagram determination
Vegard‘s law

- Vegard‘s law allows determination of lattice constants in a solid solution in dependence of composition

$$a_{AB} = x_A \cdot a_A + (1 - x_A) \cdot a_B$$

  - a_A, a_B: lattice constants of elements A and B
  - x_A: concentration of A in solid solution

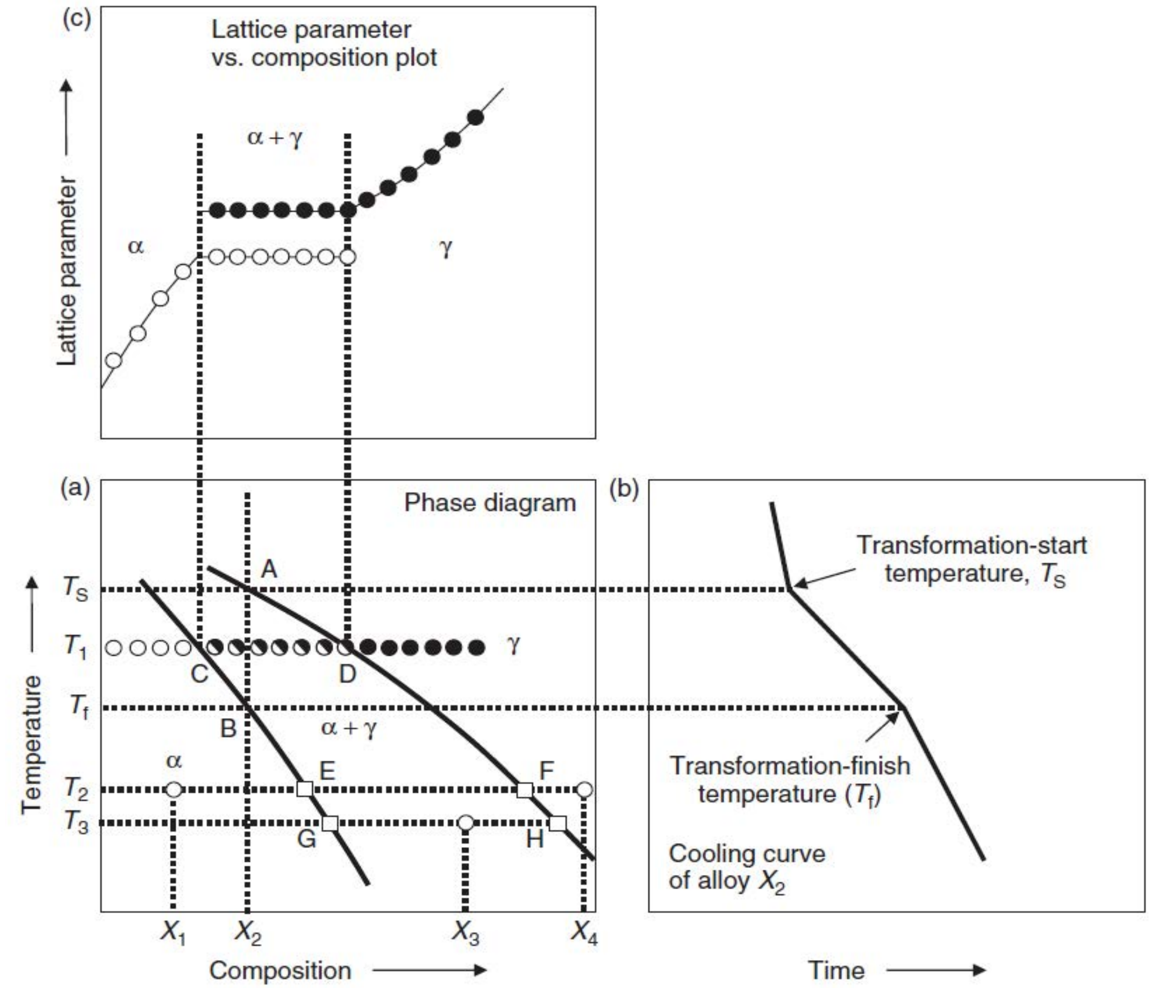


Figure 2.1 Schematic diagram showing two methods for the determination of phase diagrams: (a) schematic phase diagram; (b) the schematic cooling curve of a specific alloy X_2; and (c) schematic plot of lattice parameters vs. composition.

J.-C. Zhao, Methods for Phase Diagram Determination, Elsevier 2011

Binaries: Mixtures, solid solutions, alloys, compounds, intermediate phases, …

What can happen if we bring two materials A and B together?

- Mixing of elements: Formation of mixtures, solid solutions,
- Reactions: Formation of alloys, compounds, intermediate phases
- A-B compositions: Influence on T_M
- A-B compositions: Influence on crystal structure

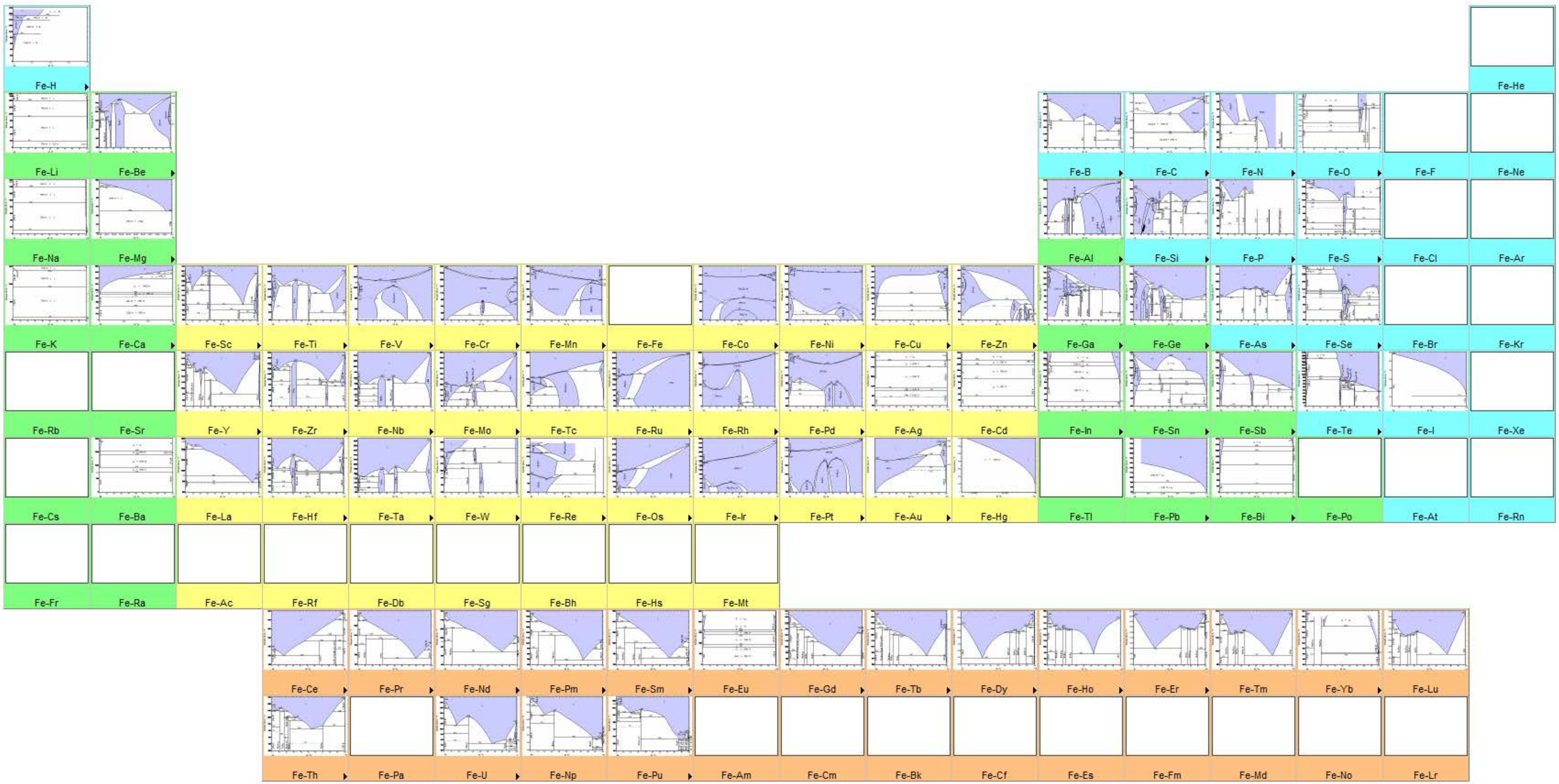
<u>Doping</u>

Doping is very important in semiconductor physics,
a very small amount of B in A, typical << 1 at.% (ppm)

e.g. B or P in Si

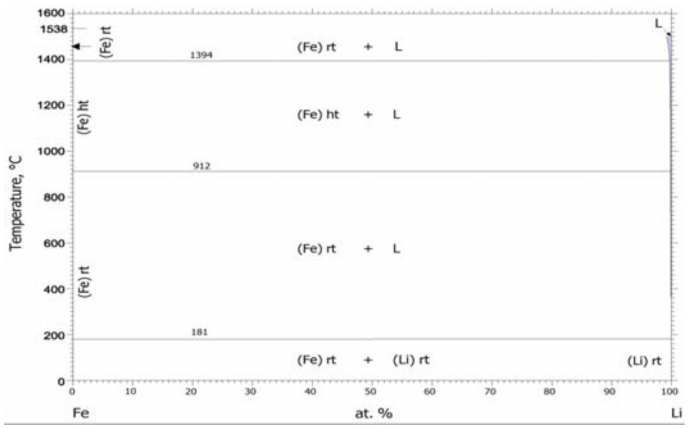
Binary phase diagrams

Overview of all Fe-X phase diagrams

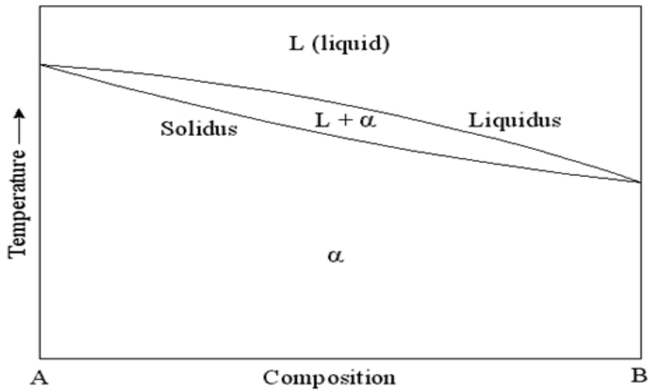


PAULING FILE, Binaries Edition, ASM International, 2002

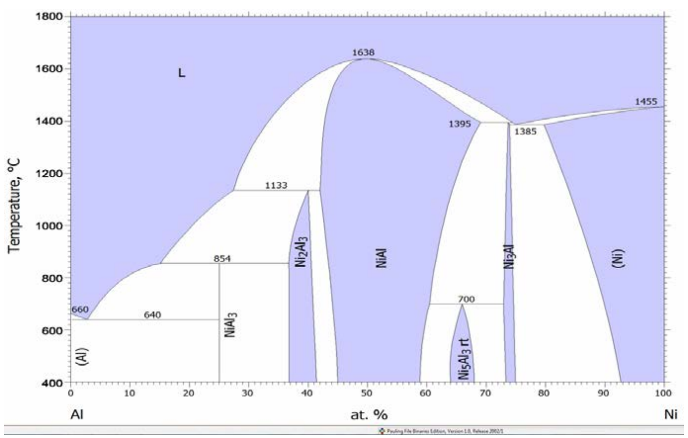
Types of binary materials diagrams



non-compound forming system

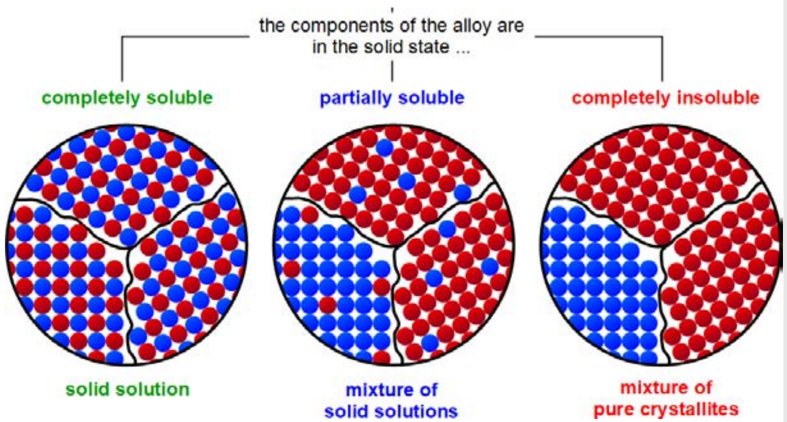


only solid solution(s)



compound forming system

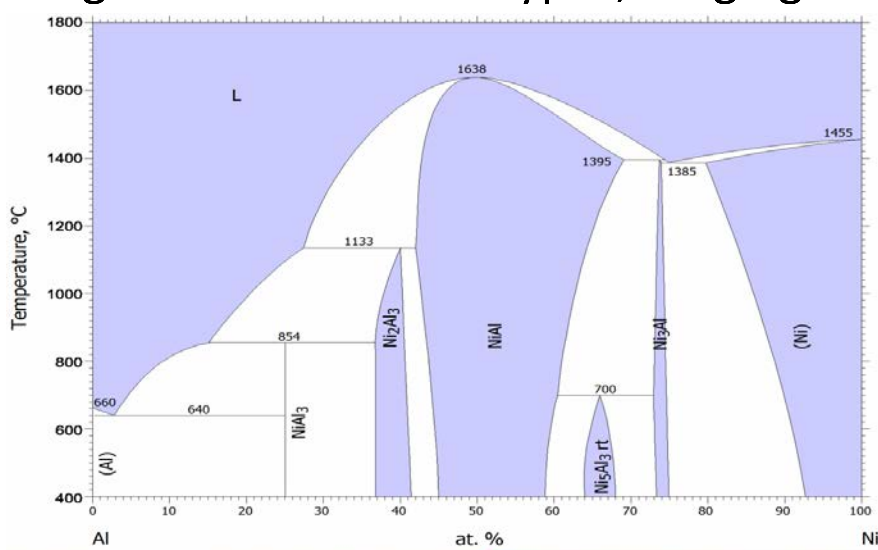
Types of alloys



PAULING FILE, Binaries Edition, ASM International, 2002
https://www.tec-science.com/material-science/alloys/typs-of-alloys/

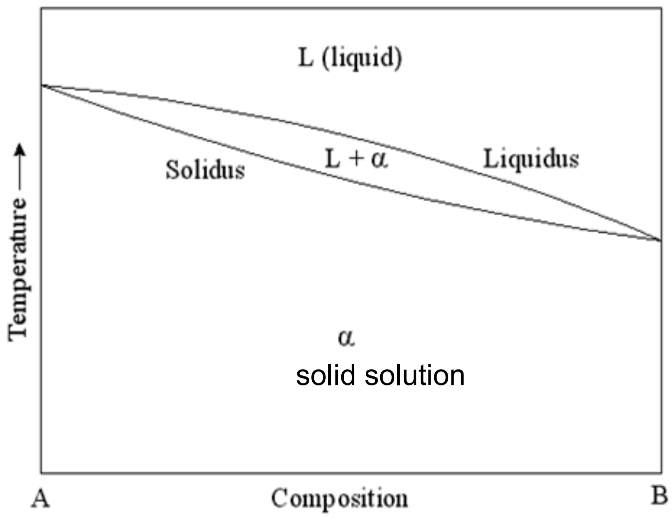
Definitions of alloys and compounds

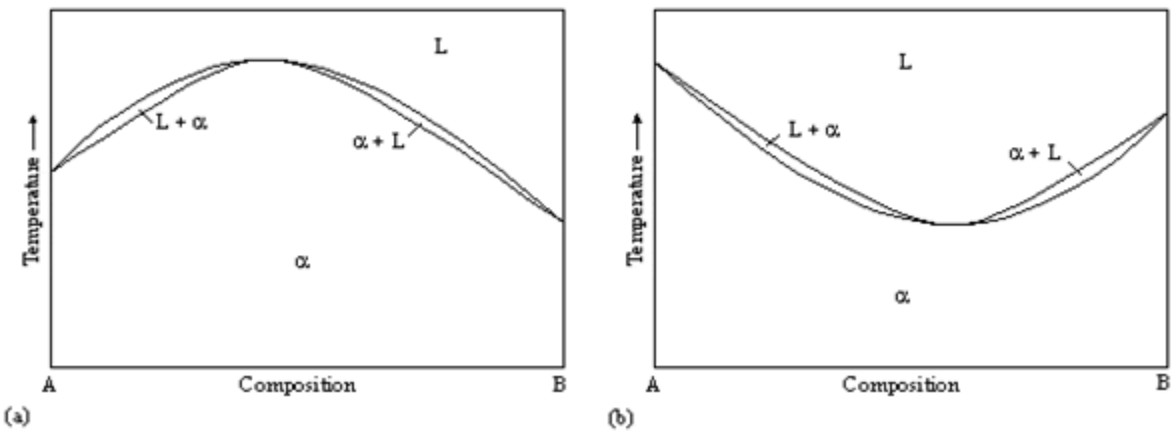
- **Alloy**: A substance having metallic properties and being composed of two or more chemical elements of which at least one is a metal
- **Intermediate phase**: In an alloy or a chemical system, a distinguishable homogeneous phase whose composition range does not extend to any of the pure components of the system
- **Intermetallic phase**: A compound or intermediate solid solution, containing two or more metals, which usually has a composition, characteristic properties, and crystal structure different from those of the pure components of the system
- **Intermetallic compound**: An intermediate phase in an alloy system, having a narrow range of homogeneity and relatively simple stoichiometric proportions; the nature of the atomic binding can be of various types, ranging from metallic to ionic



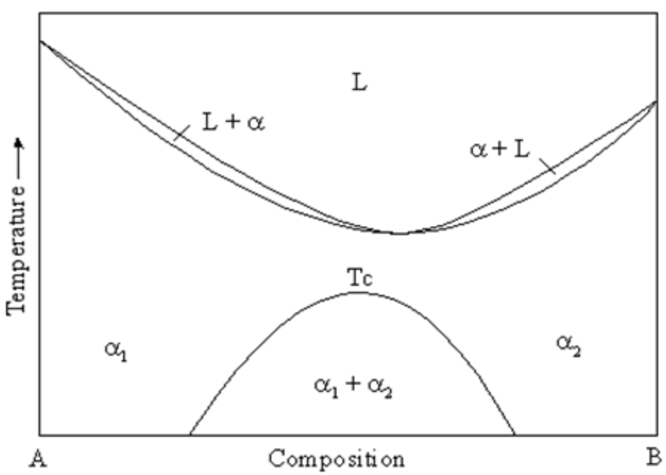
Alloy Phase Diagram Database, ASM International

Binary phase diagrams

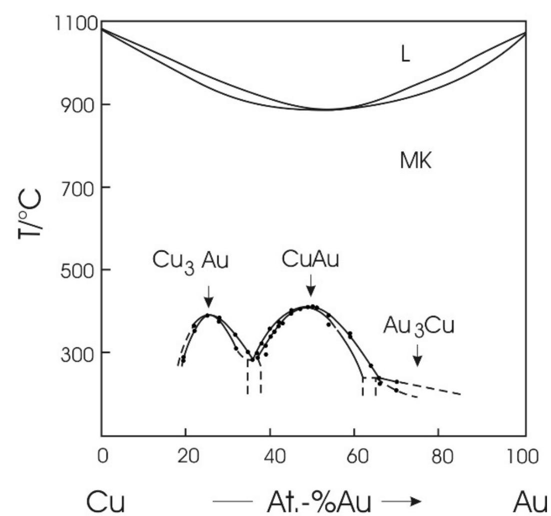




Schematic binary phase diagrams with solid state miscibility where the liquidus shows a maximum and a minimum



*Schematic binary phase diagram with **miscibility gap** in a single-phase field*



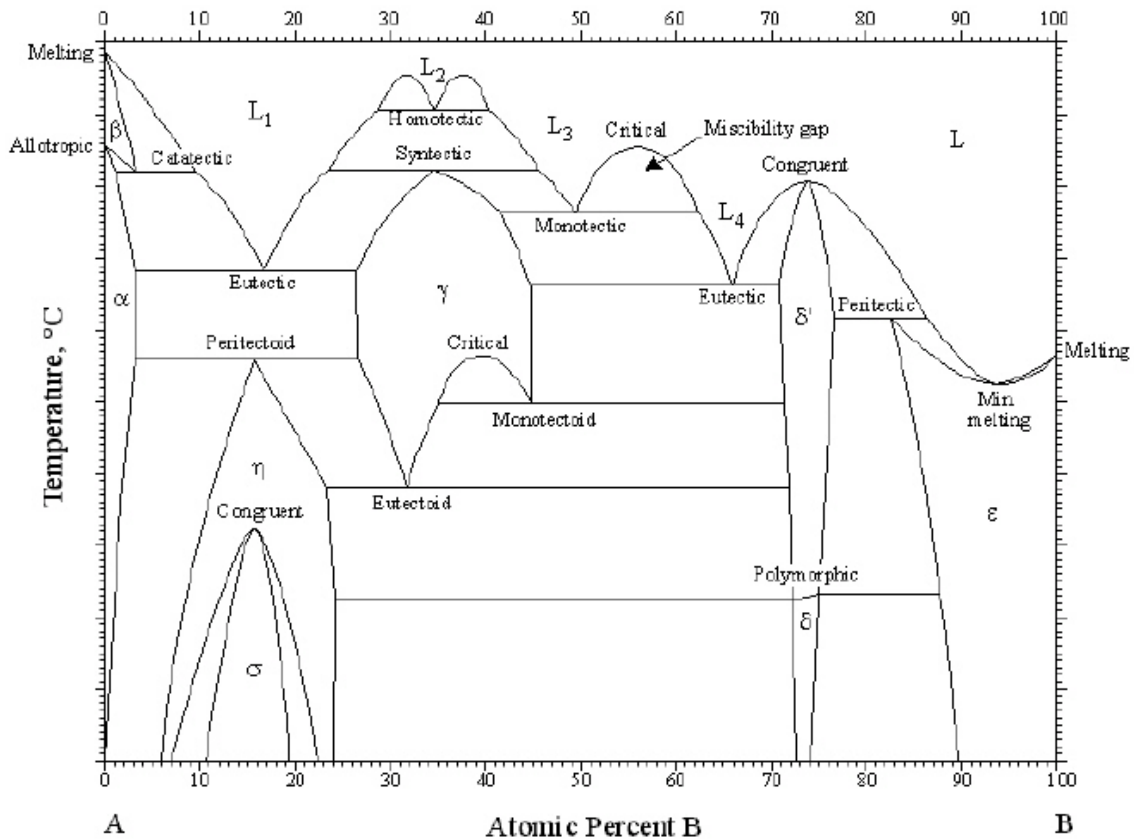
<u>increase of Tm with increasing element B</u> corresponds to stronger bonding, and tends to the formation of intermediate phases

<u>decrease of Tm with increasing element B</u> corresponds to weaker bonding, and tends to decomposition

G. Gottstein, Physikalische Grundlagen der Materialkunde, Springer Verlag, 2013
Alloy Phase Diagram Database, ASM International

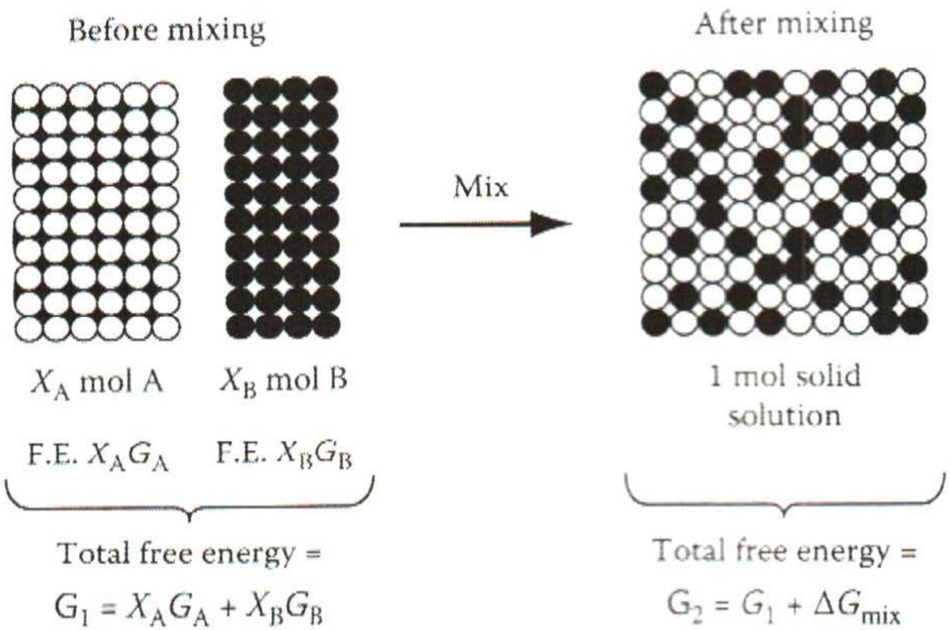
Phase equilibria in binary systems

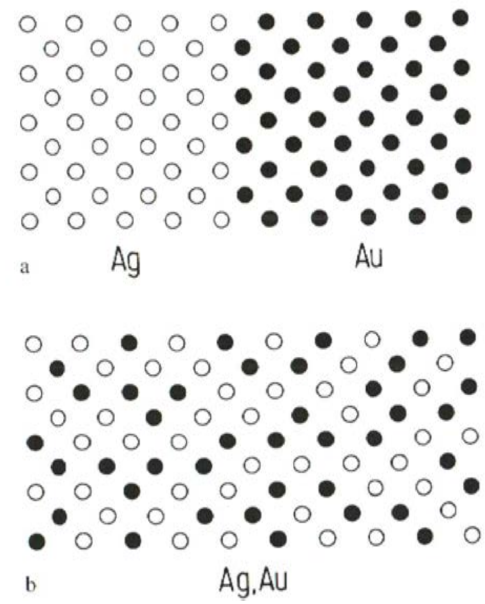
Name of reaction	Phase equilibrium	Schematic representation
Eutectic	$L \leftrightarrow s_1 + s_2$	$s_1 >$ $s_1 + L$ | L | $L + s_2$ $< s_2$; $s_1 + s_2$
Peritectic	$s_1 + L \leftrightarrow s_2$	$s_1 >$ $s_1 + L$ $< L$; $s_1 + s_2$ | s_2 | $s_2 + L$
Monotectic	$L_1 \leftrightarrow s_1 + L_2$	$s_1 >$ $s_1 + L$ | L_1 | $L_1 + L_2$ $< L_2$; $L + s_2$
Eutectoid	$s_1 \leftrightarrow s_2 + s_3$	$s_2 >$ $s_2 + s_1$ | s_1 | $s_1 + s_3$ $< s_3$; $s_2 + s_3$
Peritectoid	$s_1 + s_2 \leftrightarrow s_3$	$s_1 >$ $s_1 + s_2$ $< s_2$; $s_1 + s_3$ | s_3 | $s_3 + s_2$
Monotectoid	$s_{1a} \leftrightarrow s_{1b} + s_2$	$s_{1b} >$ $s_{1b} + s_{1a}$ | s_{1a} | $s_{1a} + s_2$ $< s_2$; $s_{1b} + s_2$
Metatectic	$s_1 \leftrightarrow s_2 + L$	$s_2 >$ $s_2 + s_1$ | s_1 | $s_1 + L$ $< L$; $s_2 + L$
Syntectic	$L_1 + L_2 \leftrightarrow s$	$L_1 >$ $L_1 + L_2$ $< L_2$; $L_1 + s$ | s | $s + L_2$



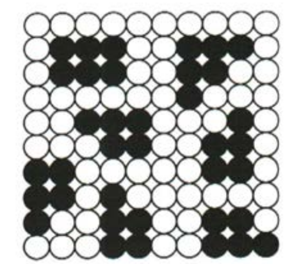
J.-C. Zhao, Methods for Phase Diagram Determination, Elsevier 2011
PAULING FILE, Binaries Edition, ASM International, 2002

Solid solutions



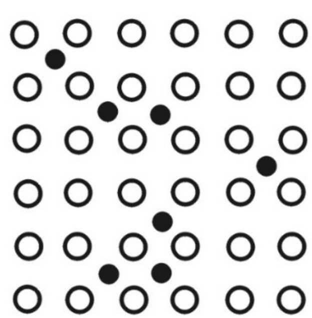


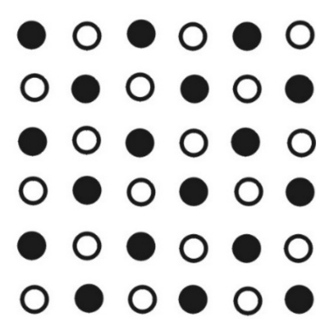
clustered solid solution



substitutional solid solutions

interstitial solid solutions (typical: H, B, C, N)





ordered solid solution

D. A. Porter, K. E. Easterling, Phase Transformations in Metals and Alloys, CRC Press, 1992
P. Haasen, Physikalische Metallkunde, Springer Verlag, 2013

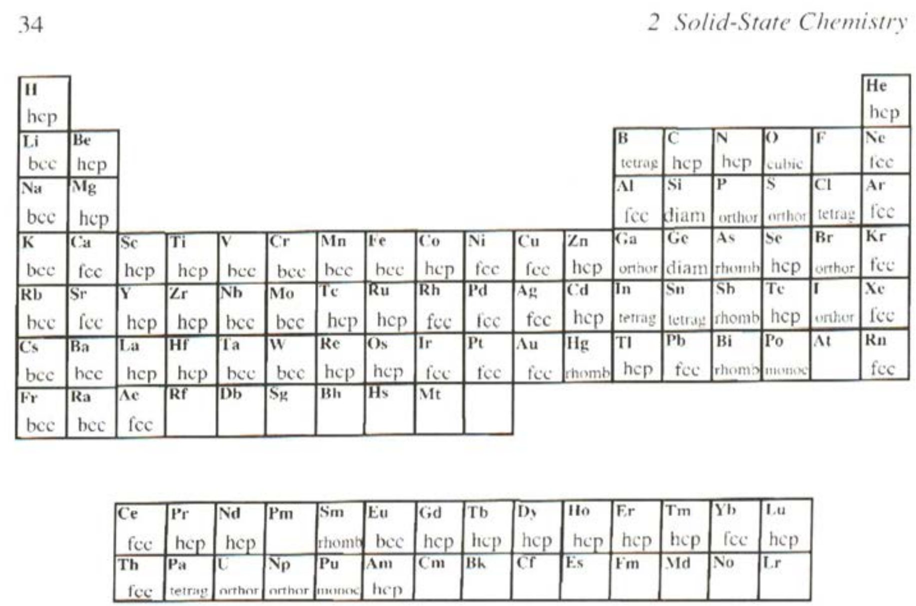
Solid solutions

When do they form?

RUB

solid solutions can form,
if components have:

- similar size (< 15%)
- same crystal structure
- similar electronegativity



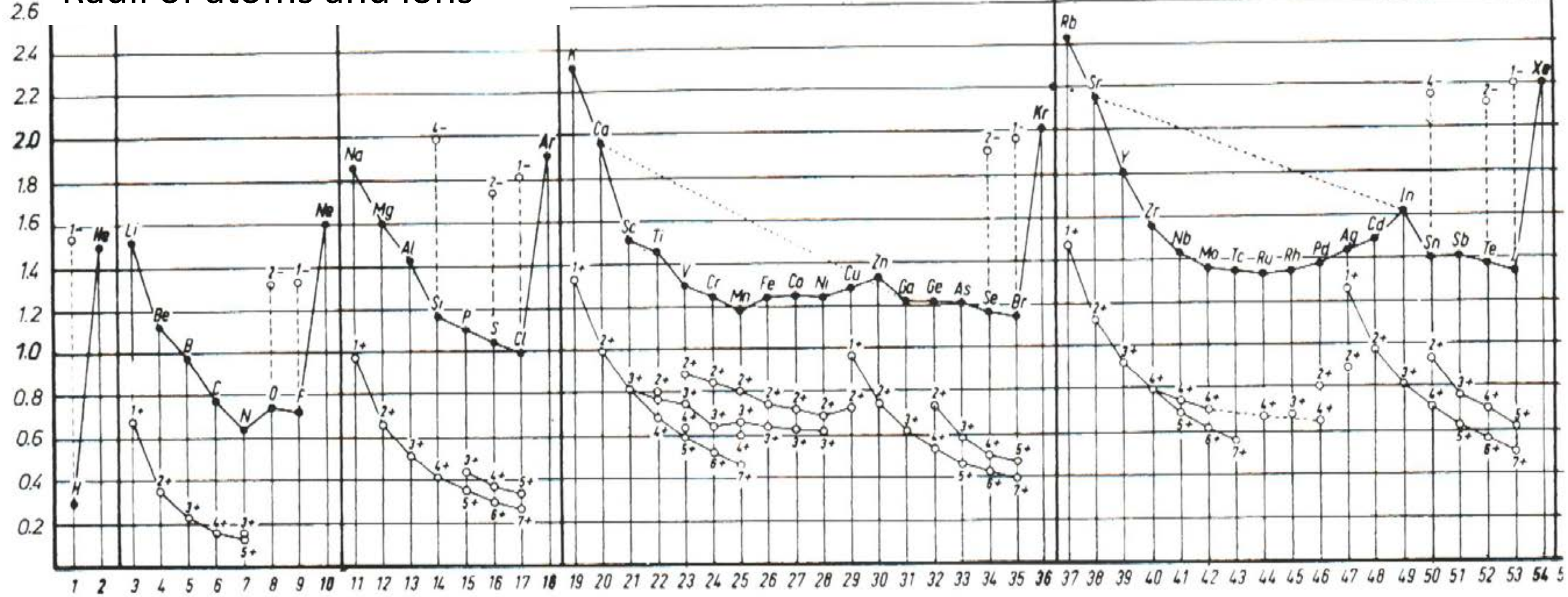
34 — 2 Solid-State Chemistry

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

Ce fcc	Pr hcp	Nd hcp	Pm	Sm rhomb	Eu bcc	Gd hcp	Tb hcp	Dy hcp	Ho hcp	Er hcp	Tm hcp	Yb fcc	Lu hcp
Th fcc	Pa tetrag	U orthor	Np orthor	Pu monoc	Am hcp	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 2.13. *Preferred* crystal structures of the elements. Shown are the ordinary forms of each element

Radii of atoms and ions



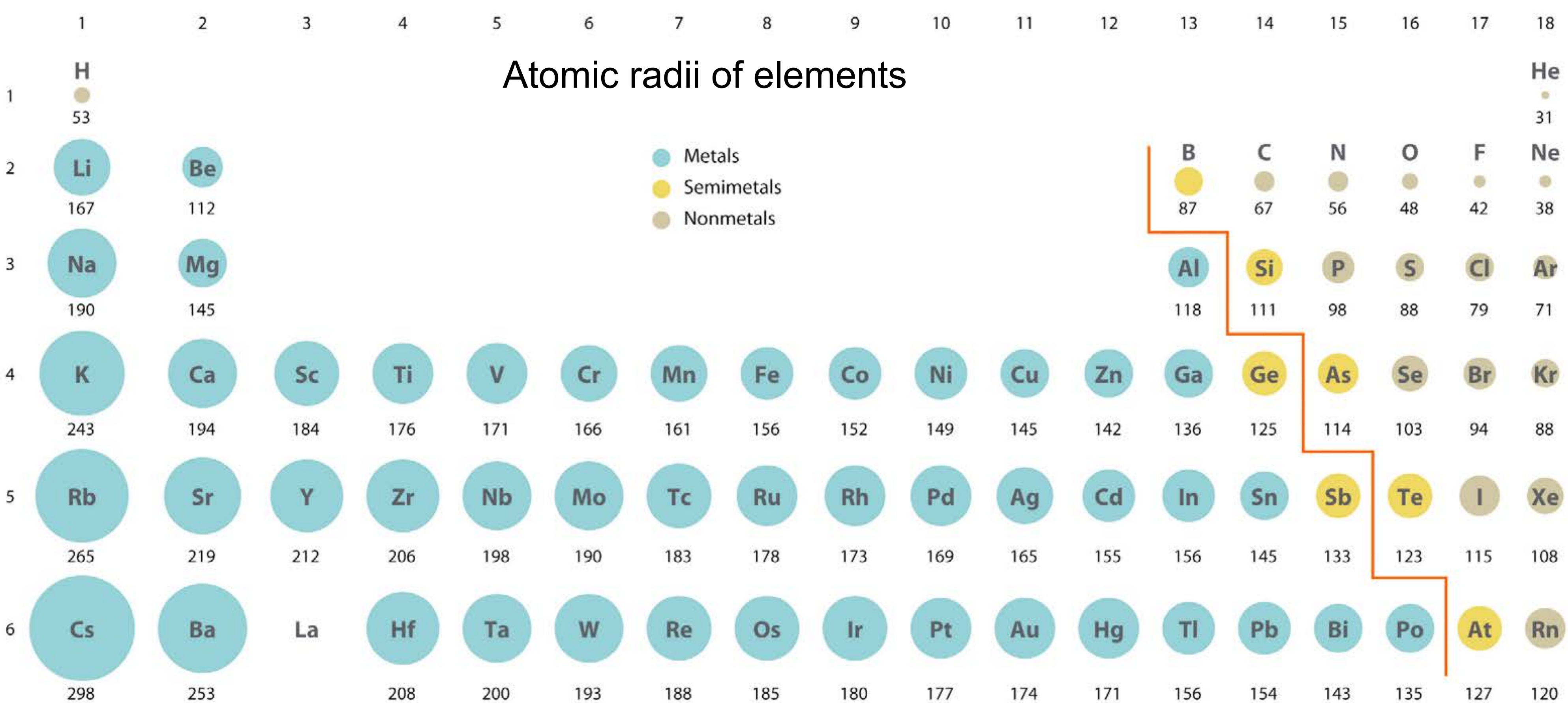
bb. 12.7 Atom- und Ionenradien in Abhängigkeit von der Ordnungszahl, nach Ramdohr u. Strunz [35]

Solid solutions

When do they form?

Solid solutions can form, if components have:

- similar size (< 15%)



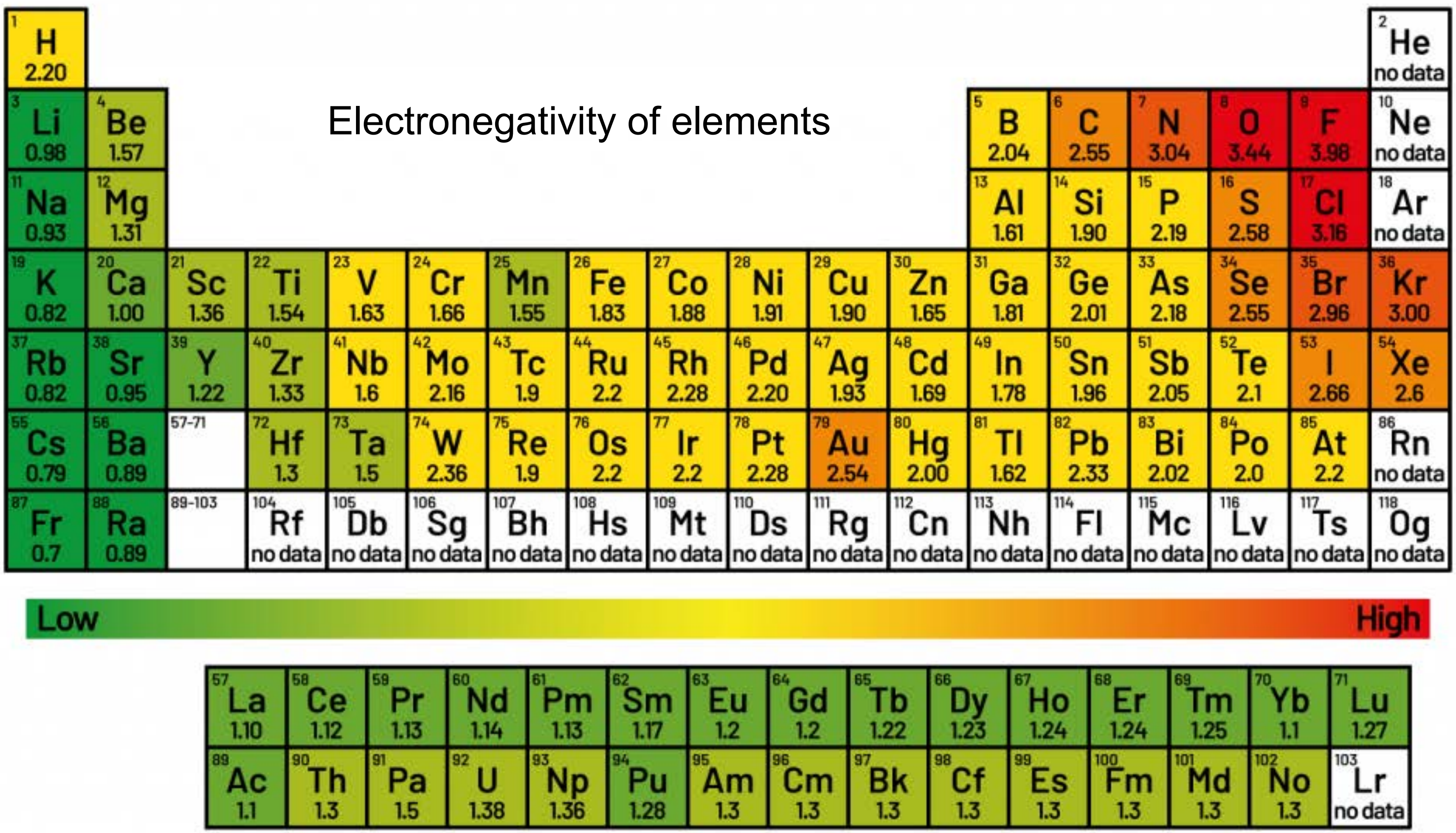
http://sayrechem.weebly.com/atomic-radii.html

Solid solutions

When do they form?

Solid solutions can form, if components have:

- similar electronegativity



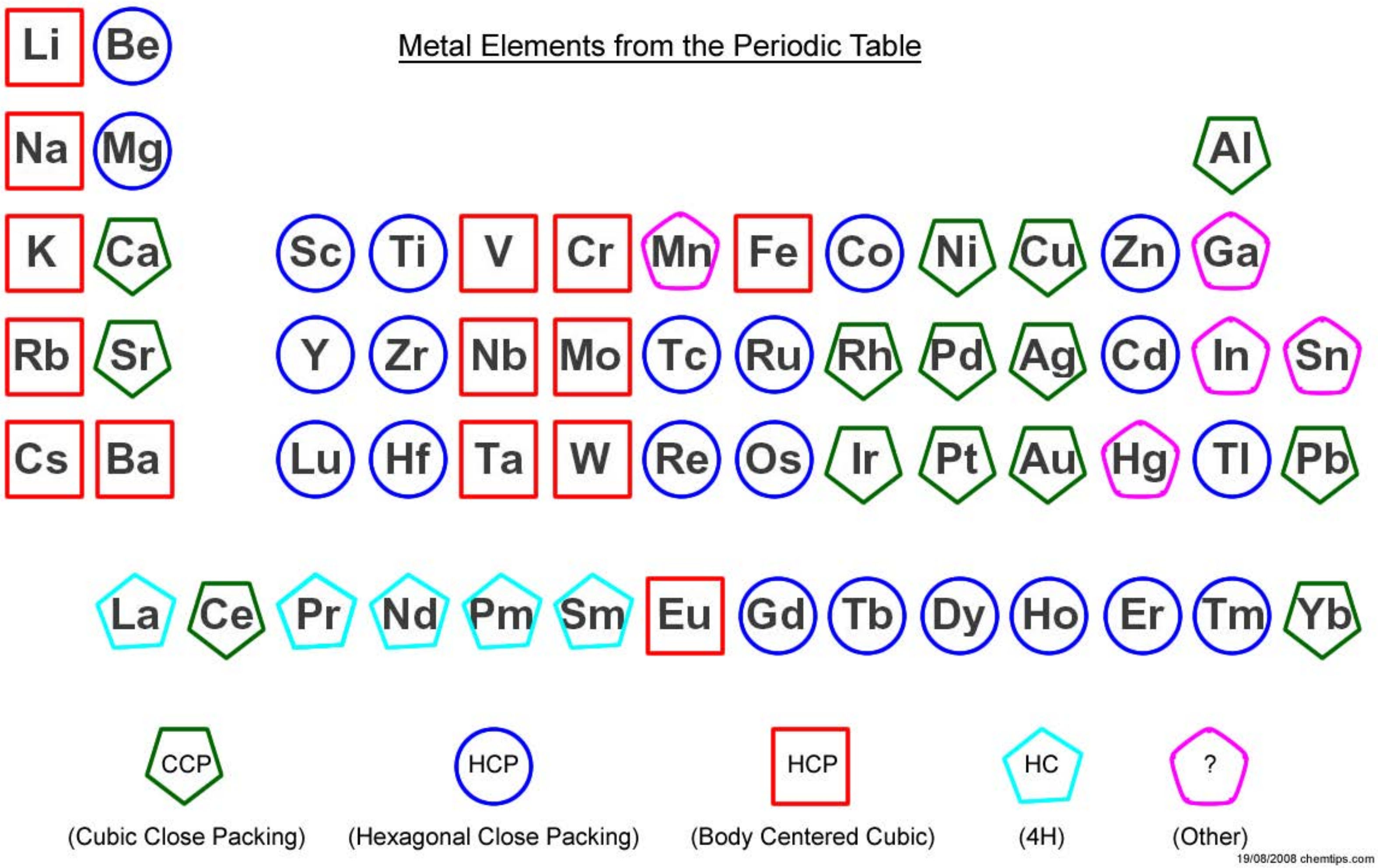
https://sciencenotes.org/electronegativity-definition-and-trend/

Solid solutions

When do they form?

Solid solutions can form, if components have:

- same crystal structure



https://biochem.co/wp-content/uploads/2008/08/metal-elements-periodic-table-structures.png

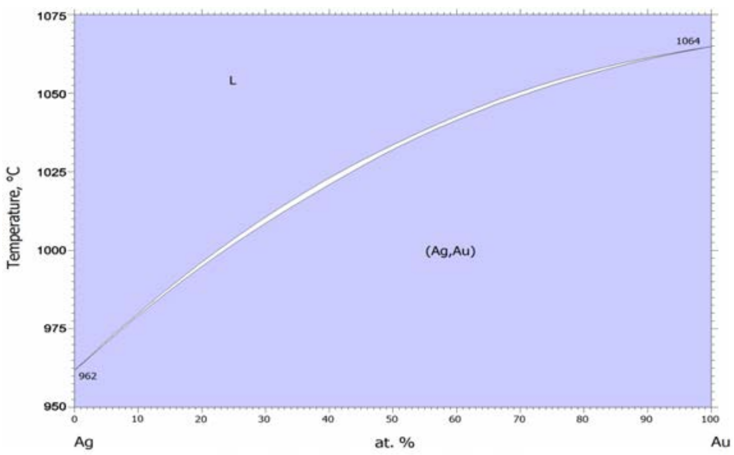
Binary phase diagrams

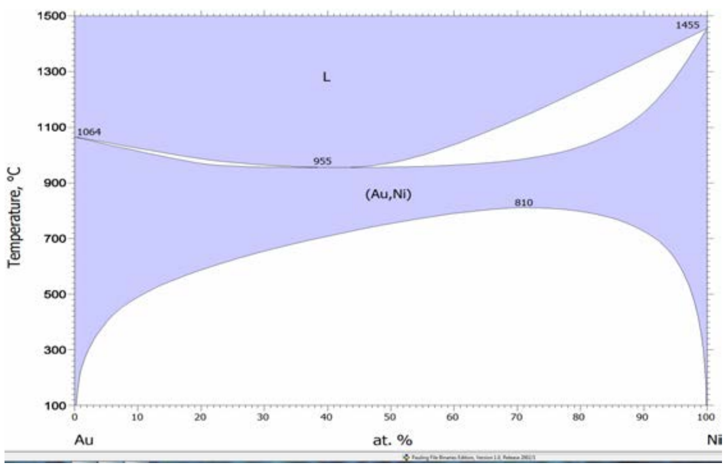
Comparison of the systems

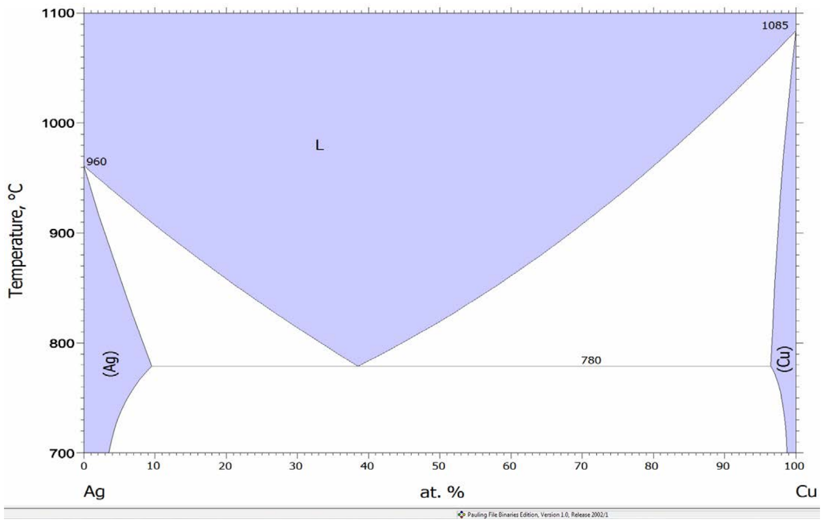
Cu-Au, Cu-Ag, Cu-Ni, Ag-Au

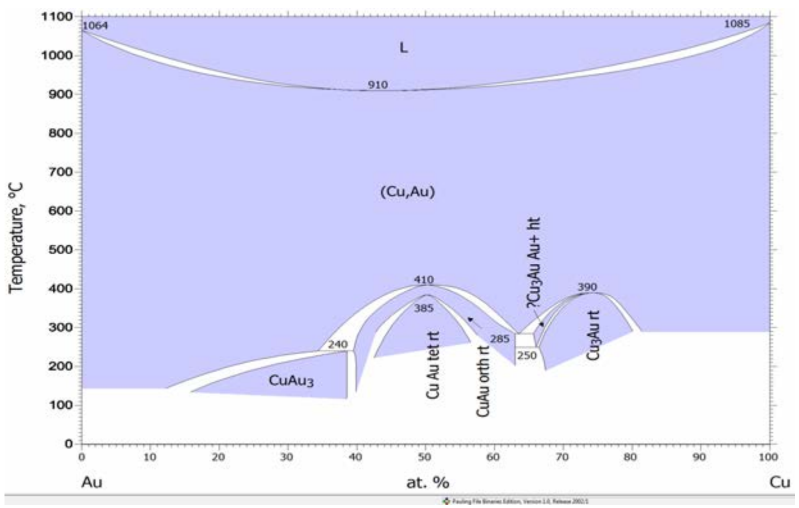
Au, Ag, Cu, Ni: fcc

a_{Ag}= 0.40863 nm
a_{Au}= 0.40786 nm
a_{Ni}= 0.38411 nm
a_{Cu}= 0.36148 nm





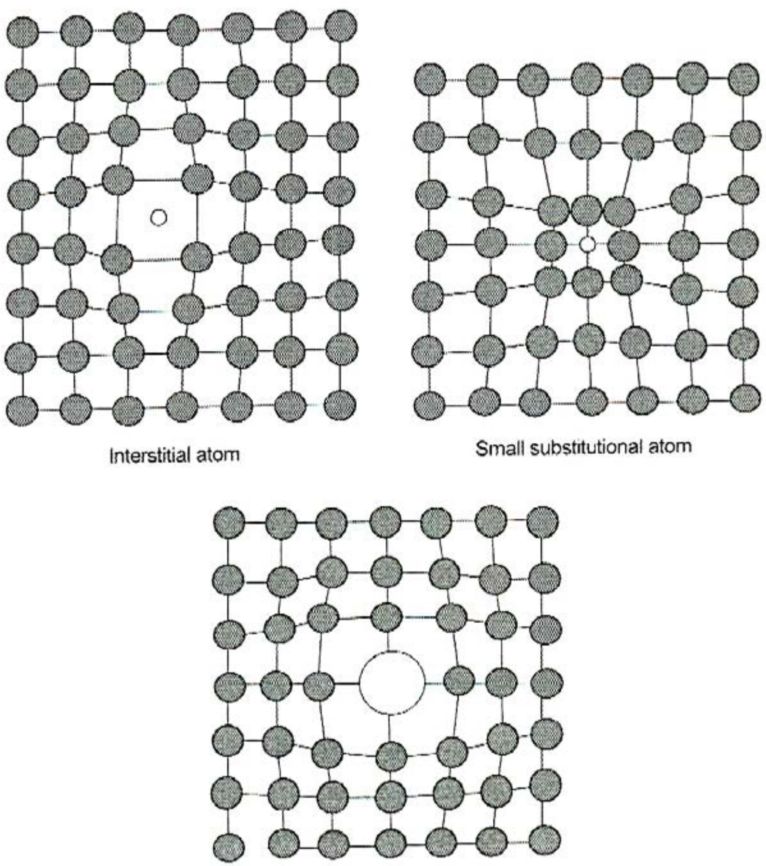




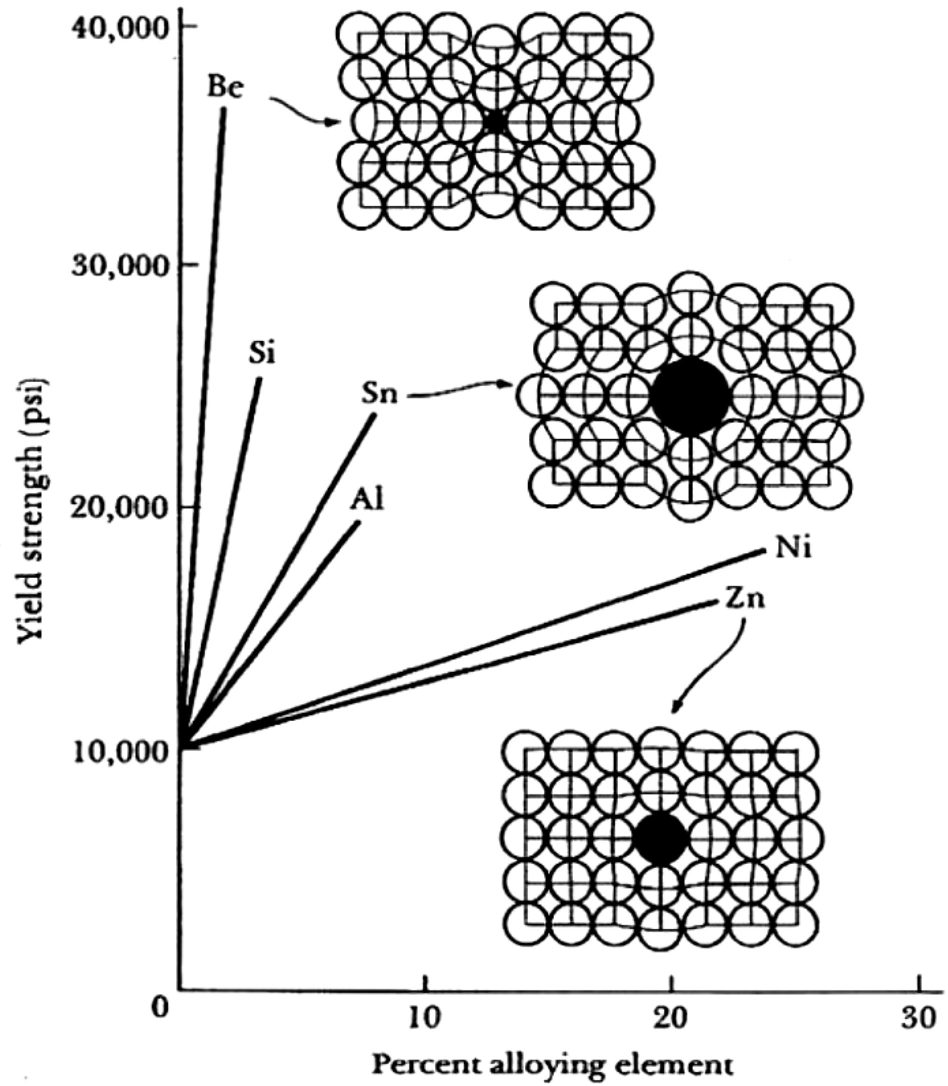
PAULING FILE, Binaries Edition, ASM International, 2002

Solid solutions
Mechanical properties

- soluble atoms add lattice distortions depending on position in the lattice
- distortions affect mechanical properties



Effects of alloying elements on the yield strength of Cu



F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

Dependence of physical properties on composition for binary systems with complete miscibility

electrical resistivity

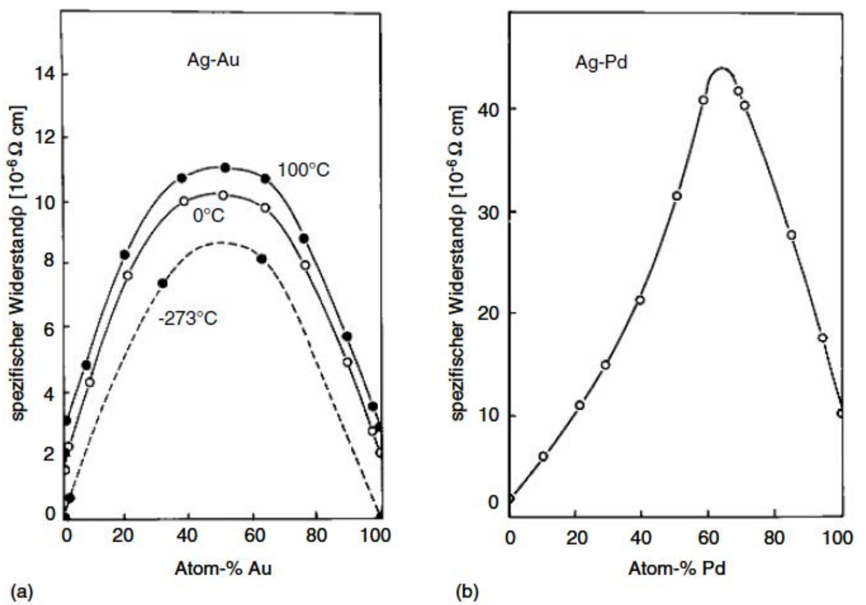


Abbildung 10.22. Spezifischer elektrischer Widerstand bei Raumtemperatur in Abhängigkeit von der Legierungskonzentration bei den lückenlos mischbaren Legierungen Ag-Au (a) und Ag-Pd (b) (nach [10.13]).

mechanical properties

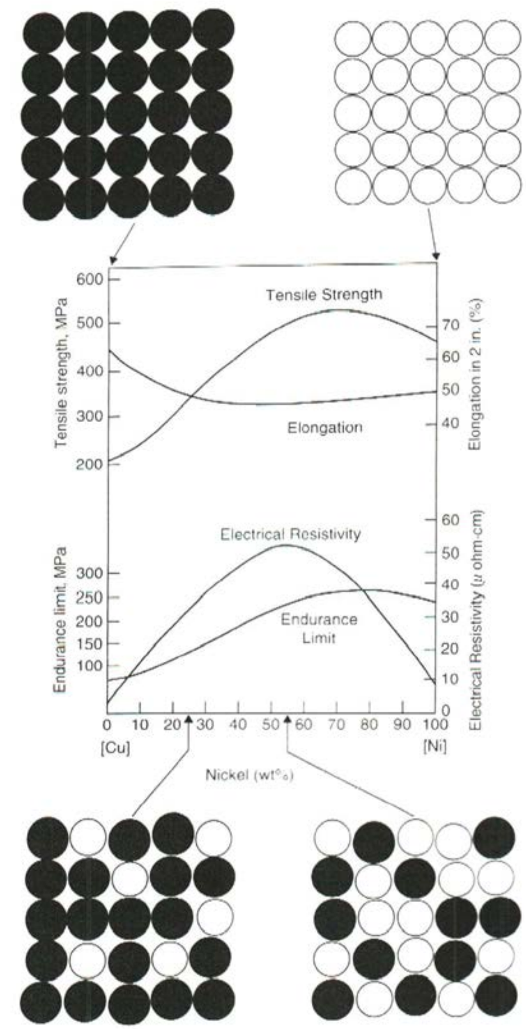
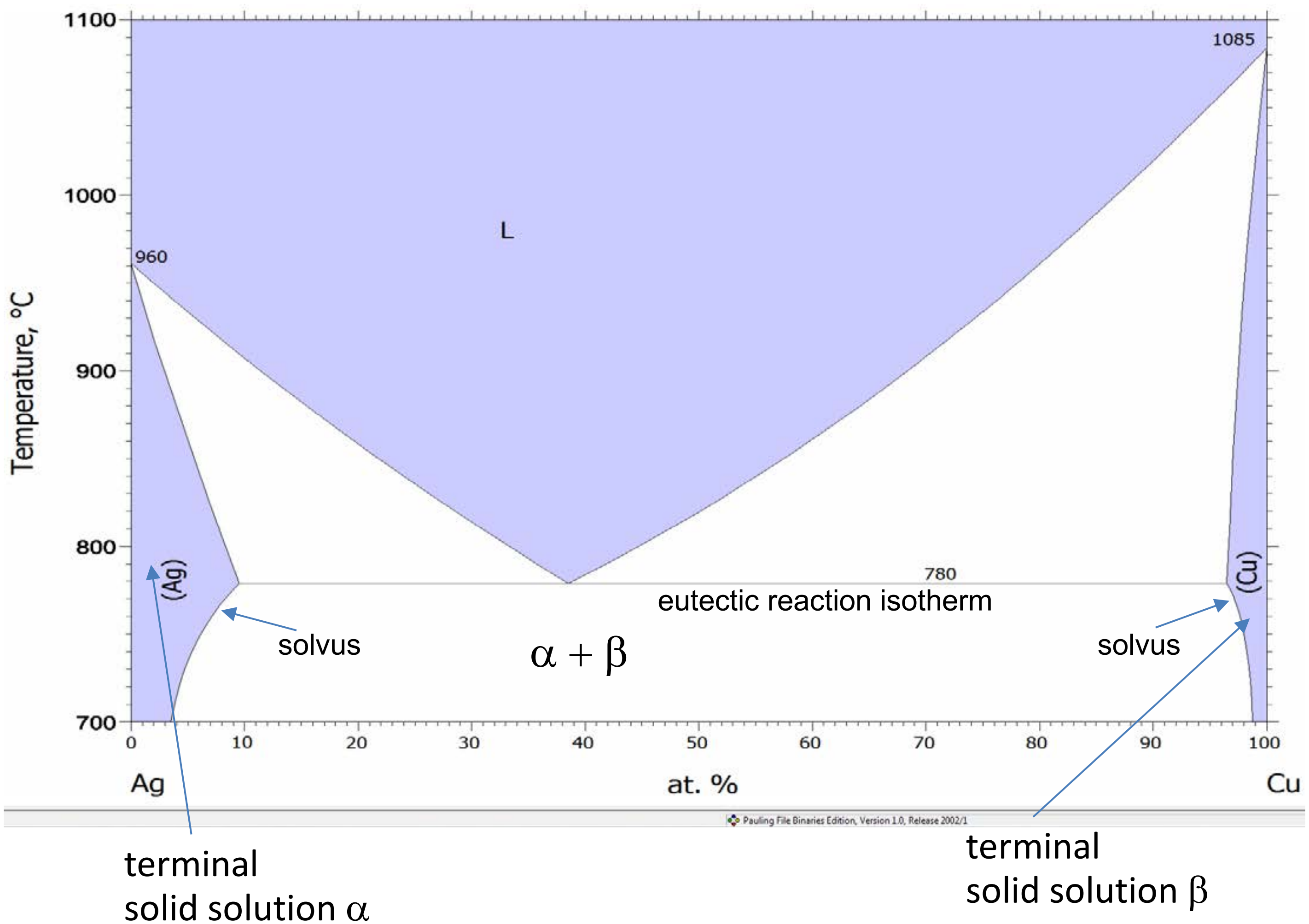


Fig. 4.6 Typical property variations in copper-nickel system. Source: Ref 4.2 as published in Ref 4.3

F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

Eutectic phase diagrams
Systems with limited solubility



Indicate single-phase and two-phase field(s)

What is the solubility of Cu in Ag at 700°C?

What is the solubility of Ag in Cu at 700°C?

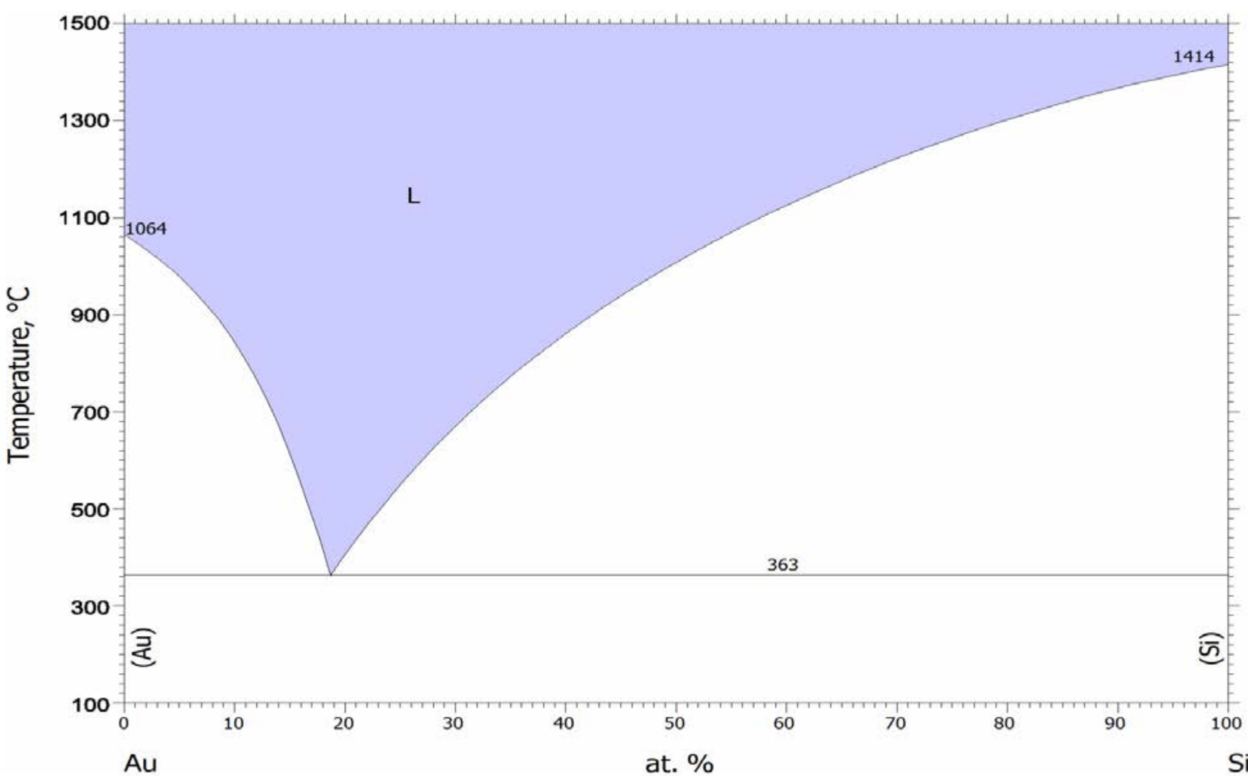
Write down the eutectic reaction.

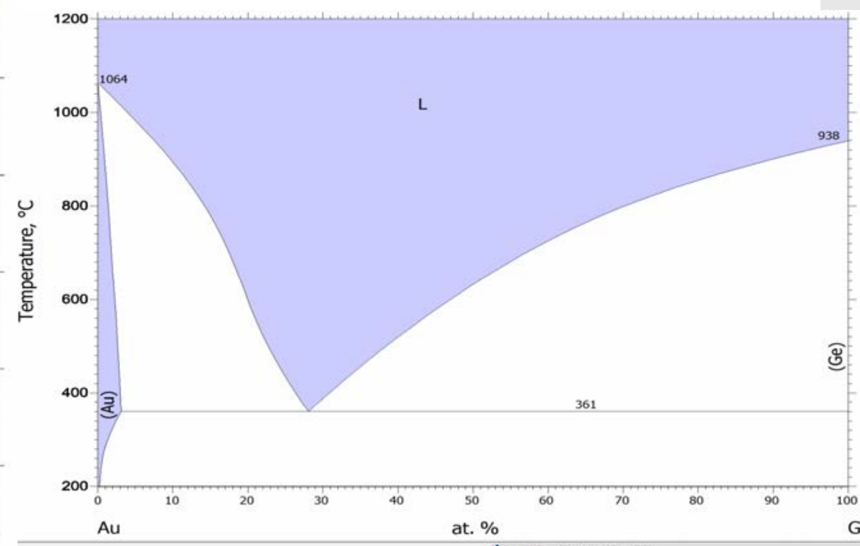
Where do we find maximum solubility?

PAULING FILE, Binaries Edition, ASM International, 2002

Eutectic phase diagrams
Examples

- Interesting phase diagrams:
  high melting point of components, low eutectic temperature



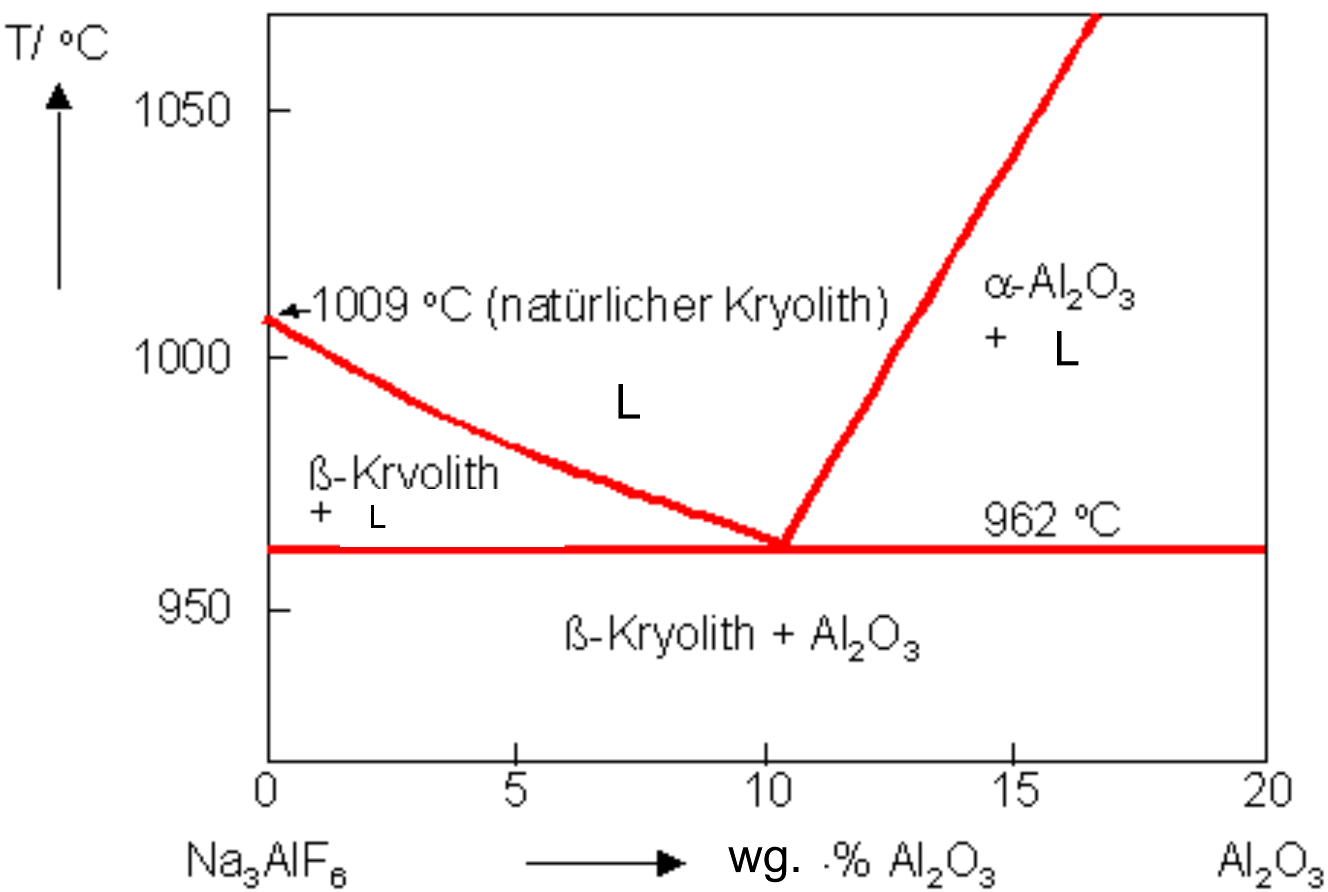


Au-Si eutecticum is used in MEMS
as bonding material

PAULING FILE, Binaries Edition, ASM International, 2002

Eutectic phase diagrams

Application example Al production: Lowering process temperatures by mixing of two components

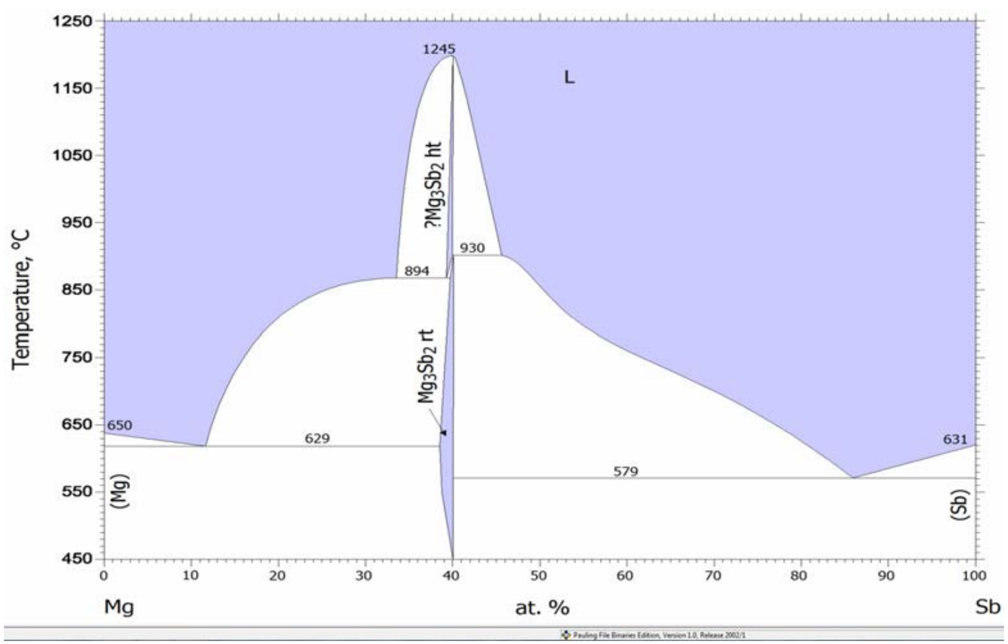


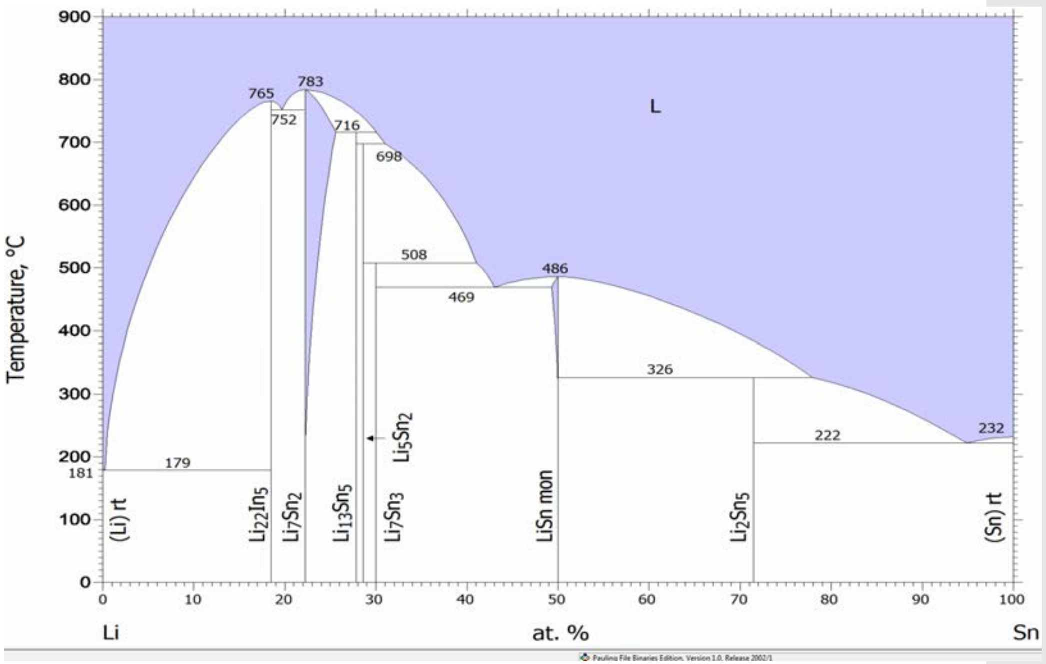
melt electrolysis process
Tm of Al_2O_3: 2000°C

U. Schubert, N. Hüsing, Synthesis of Inorganic Materials, John Wiley & Sons, 2012

Examples of interesting phase diagrams

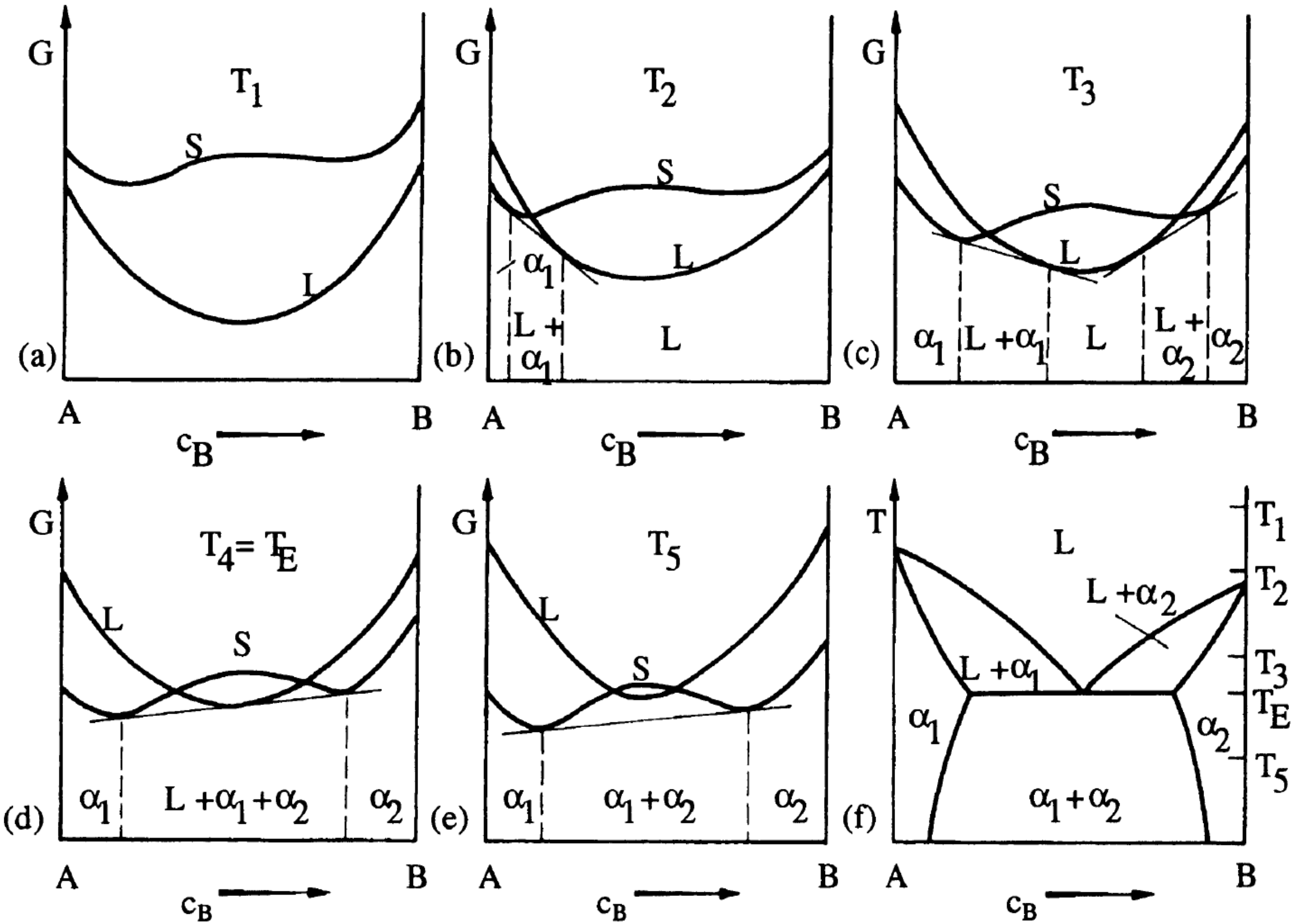
low melting point of components, high melting temperature of compound





PAULING FILE, Binaries Edition, ASM International, 2002

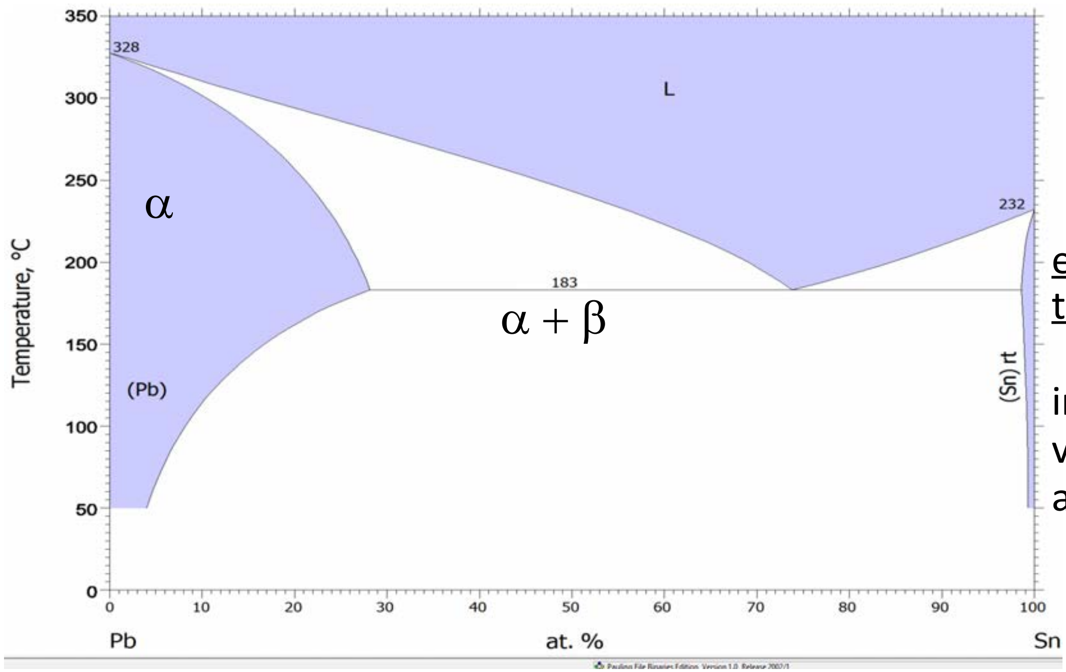
Eutectic phase diagrams
Thermodynamic evaluation



Gottstein, Günter : Physical Foundations of Materials Science

What are reasons for limited solid solubility?

RUB



size of atoms
crystal structure of components
electronegativity of components

extent of solid solution increases with temperature for both phases

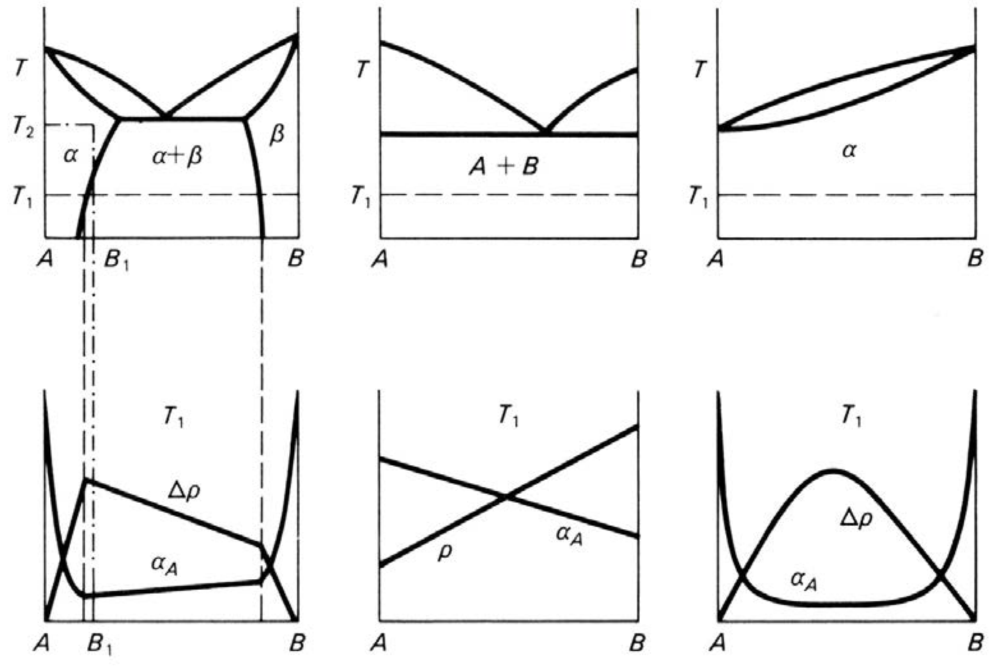
increasing temperature leads to greater atomic vibrations, allowing more flexibility in accommodation of foreign atoms

β phase has same crystal structure as pure Sn,
Pb atoms are distributed at random within the Sn crystal as defects.

Extent of solid solution in α phase is much greater than that in β phase, as smaller Sn atoms are more readily accommodated in the structure of the large Pb atoms, than are Pb atoms in the Sn structure.

PAULING FILE, Binaries Edition, ASM International, 2002
R. J. D. Tilley, Understanding Solids: The Science of Materials, John Wiley & Sons, 2013

Examples of the dependence of electrical properties of binary systems on the composition and type of phase diagram



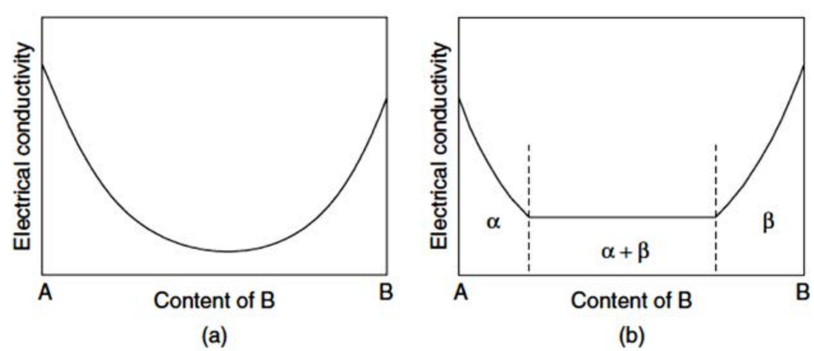
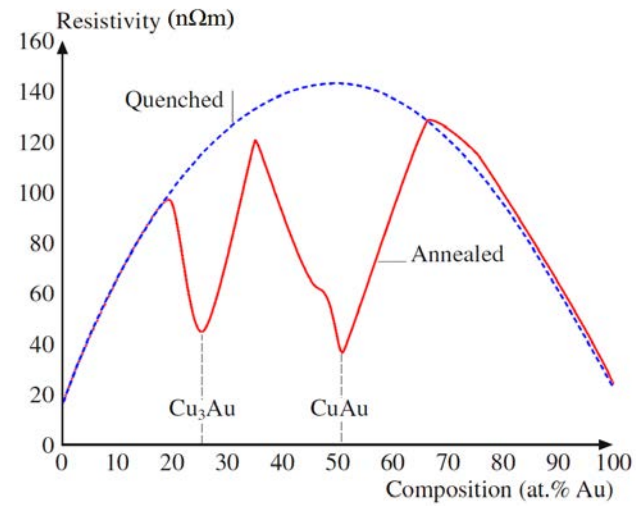


Figure 4.7 Variation of electrical conductivity with composition for (a) a continuous solid solution and (b) a binary eutectic system.



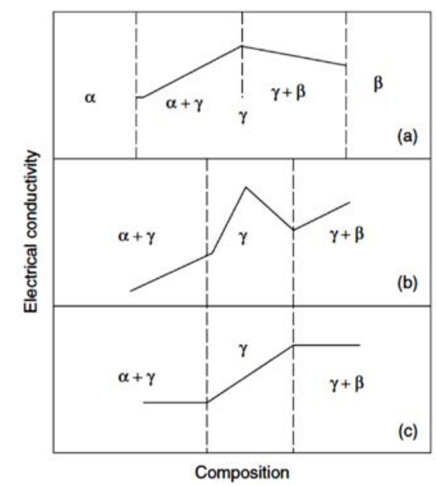


Figure 4.8 Different kinds of electrical conductivity vs. composition curve for binary systems with intermetallic phase γ [4]: (a) stoichiometric compound (γ), (b) ordered compound γ with wide homogeneity range, and (c) disordered compound with wide homogeneity range.

J.-C. Zhao, Methods for Phase Diagram Determination, Elsevier 2011

Temperature-dependent resistivity measurements indicate phase transformations

Fe

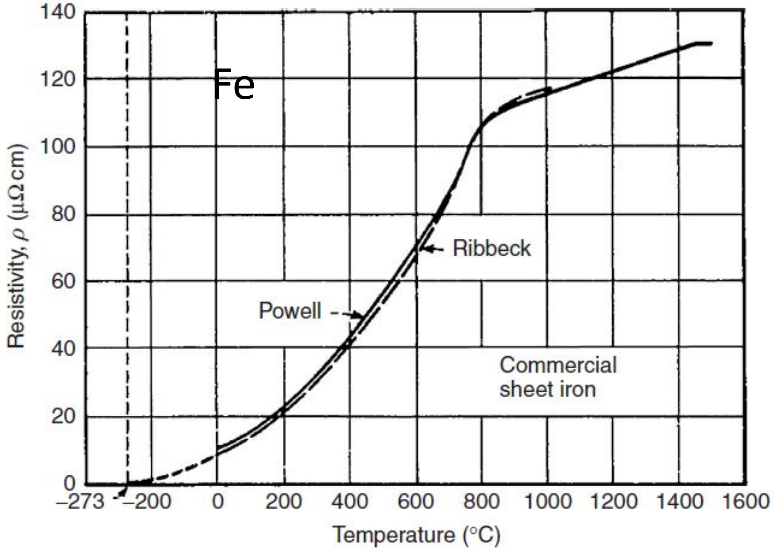


Figure 12.6 Temperature dependence of the
From Ref. [7].

FeCo

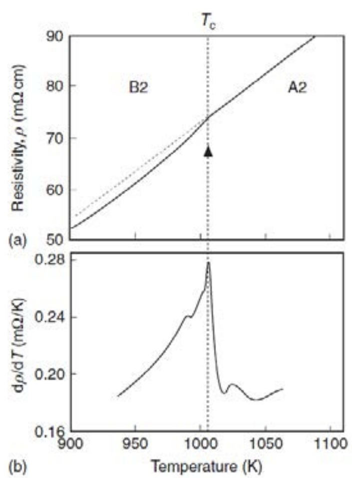


Figure 11.2 Electrical resistance curve (a) and its differential (b) showing a 2O-OD transition of a Fe–50 at.% Co alloy reported by Seehra and Silinsky [4]. The behavior of electrical resistance is similar to that in the 1O-OD transition.

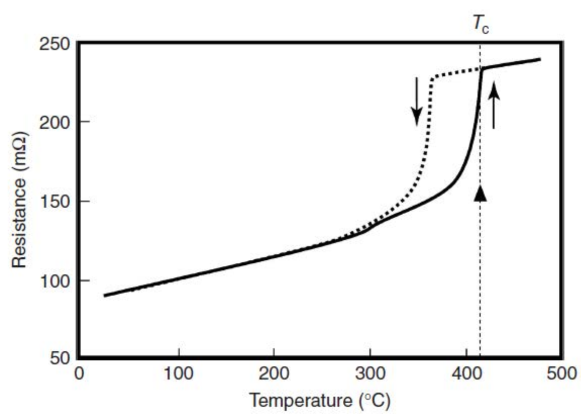
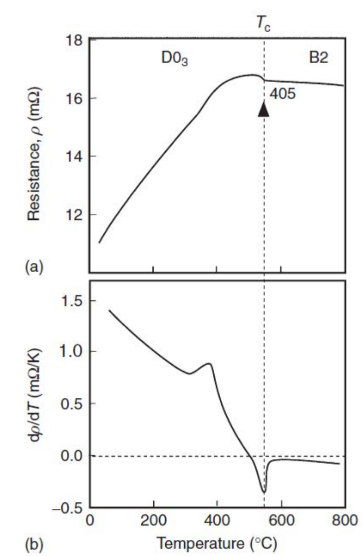


Figure 11.1 Electrical resistance curves showing the 1O-OD transition of a Au–50 at.% Cu alloy reported by Sprusil and Pfeiler [2]. The T_c is defined as the temperature with the maximal gradient in the heating curve.

364 Ryosuke Kainuma, Ikuo Ohnuma and Kiyohito Ishida

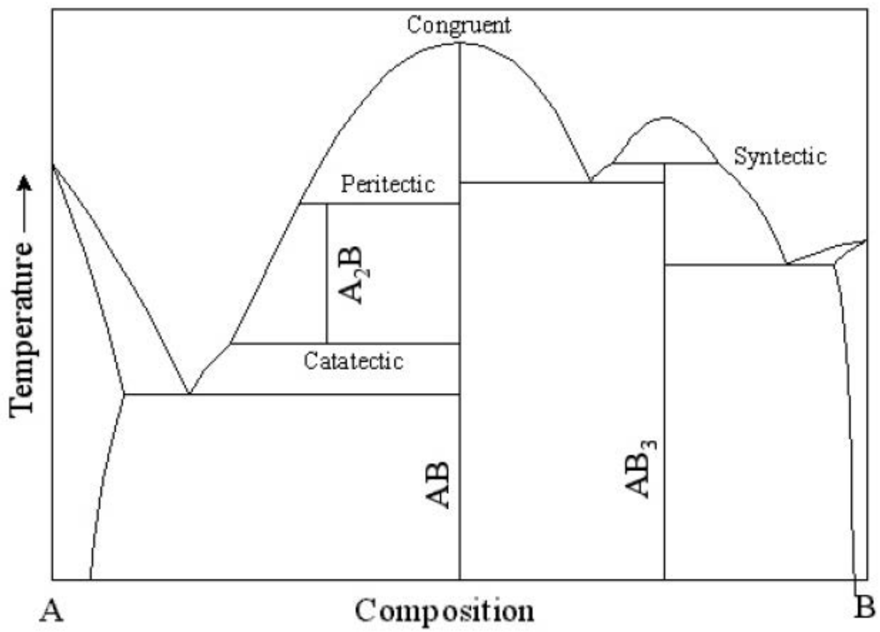


Fe-Al

Figure 11.3 Electrical resistance curve (a) and its differential (b) showing a 2O-OD transition of Fe–27 at.% Al alloy reported by Sprusil and Pfeiler [5]. While a small and broad peak appears in the temperature region below T_c, the T_c is defined as the temperature at the minimum point of the negative peak in the differential curve.

J.-C. Zhao, Methods for Phase Diagram Determination, Elsevier 2011

Schematic binary phase diagram with intermetallic line compounds and different melting reactions



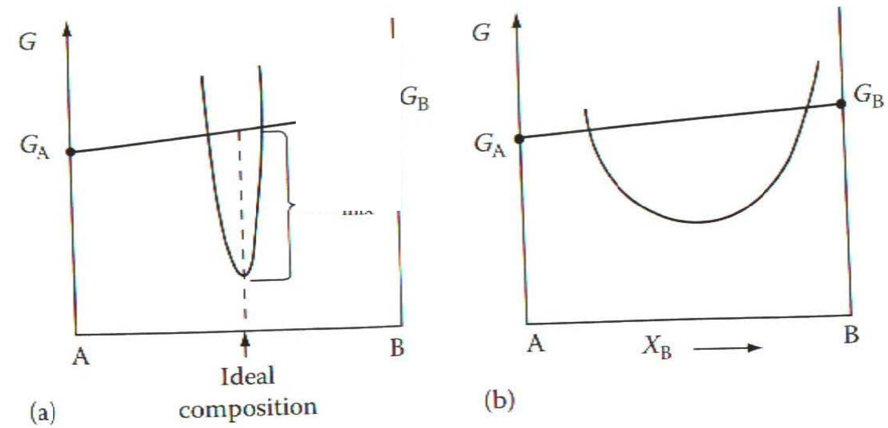


FIGURE 1.23
Free energy curves for intermediate phases: (a) for an intermetallic compound with a very narrow stability range, (b) for an intermediate phase with a wide stability range.

line compounds have stoichiometric compositions: AB, A_2B, AB_3, …

frequently intermediate phases have compositional existence ranges

PAULING FILE, Binaries Edition, ASM International, 2002
D. A. Porter, K. E. Easterling, Phase Transformations in Metals and Alloys, CRC Press, 1992

Peritectic phase reactions

Not all intermediate compounds show congruent melting.
Many intermediate phases transform into a liquid at a peritectic point. On heating through a peritectic point, a solid transforms to a liquid plus another solid of a different composition.

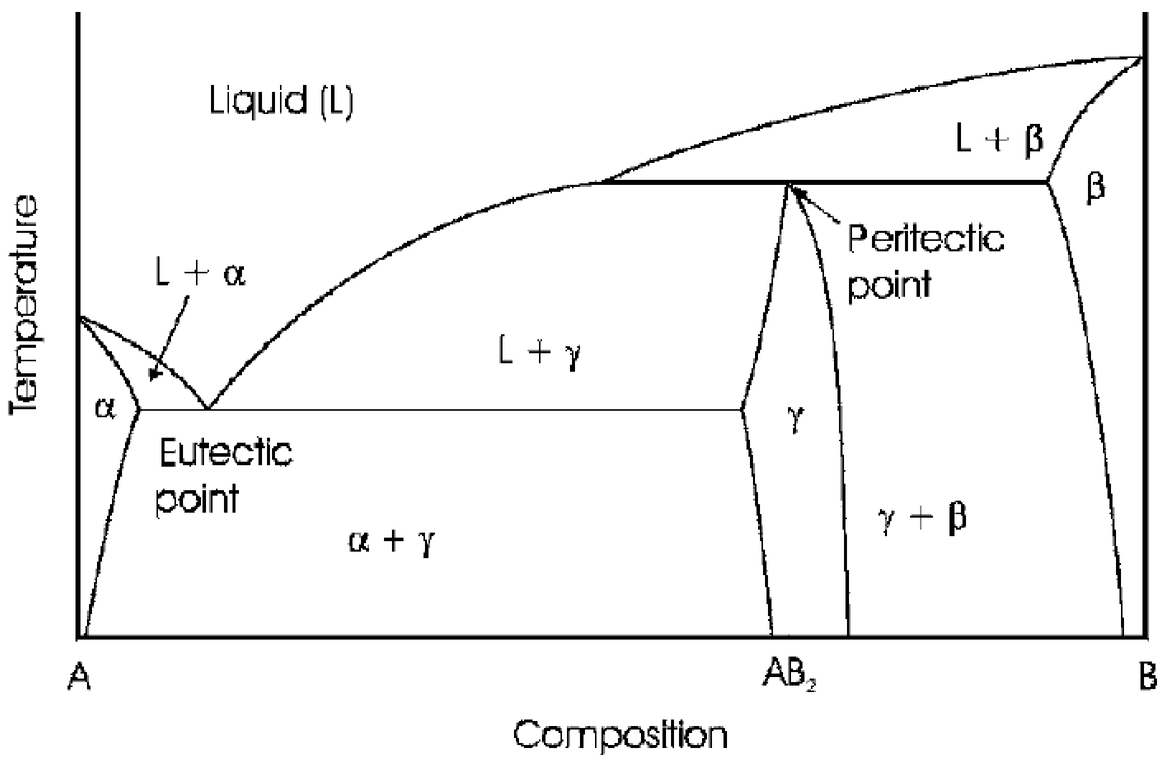
The solid melts “incongruently”.

Peritectic reaction:
usually for systems where the components have very different T_M

At the peritectic point:

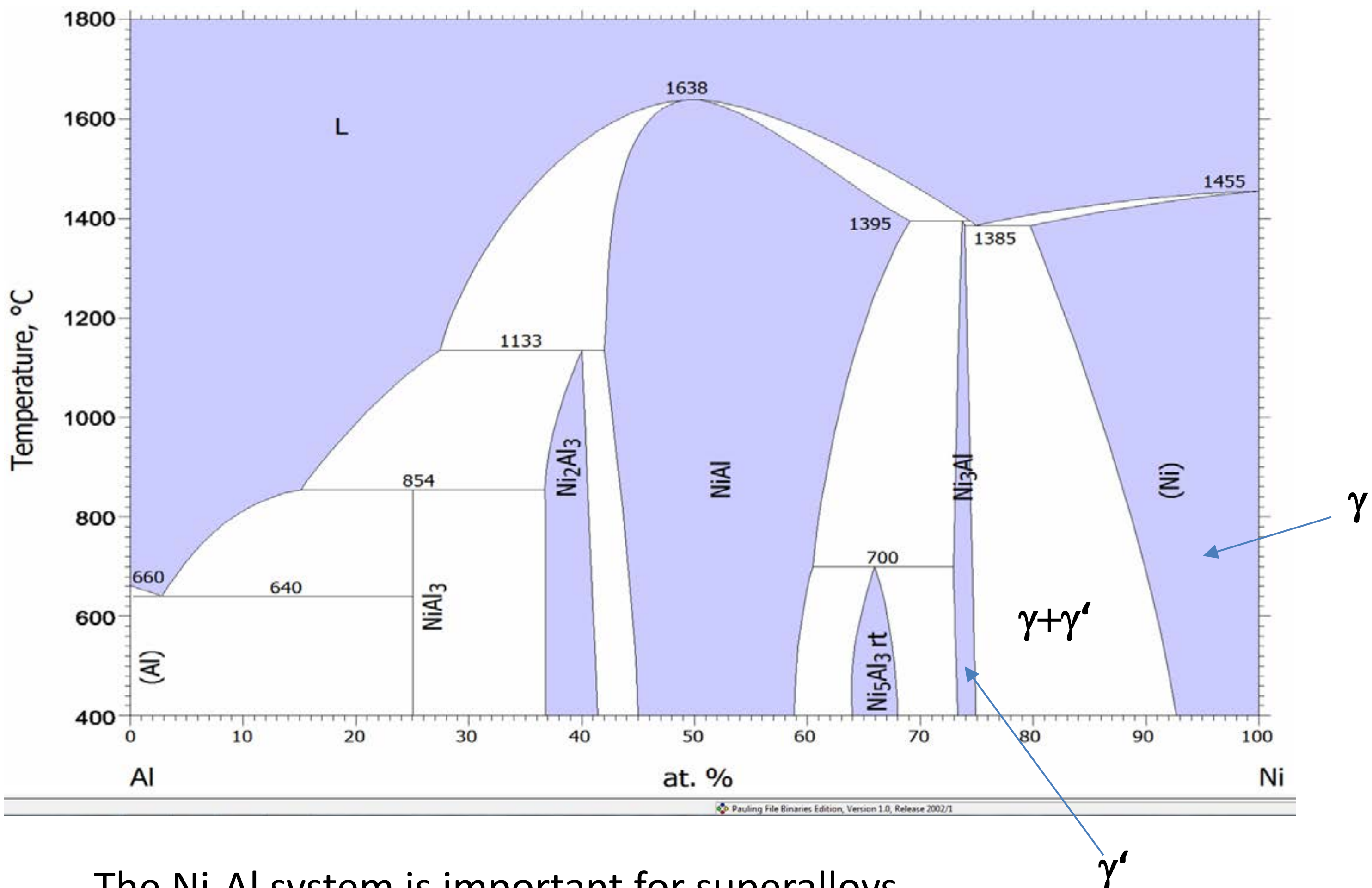
On cooling: L+ $\beta \rightarrow \gamma$

On heating: $\gamma \rightarrow$ L+ β



R. J. D. Tilley, Understanding Solids: The Science of Materials, John Wiley & Sons, 2013

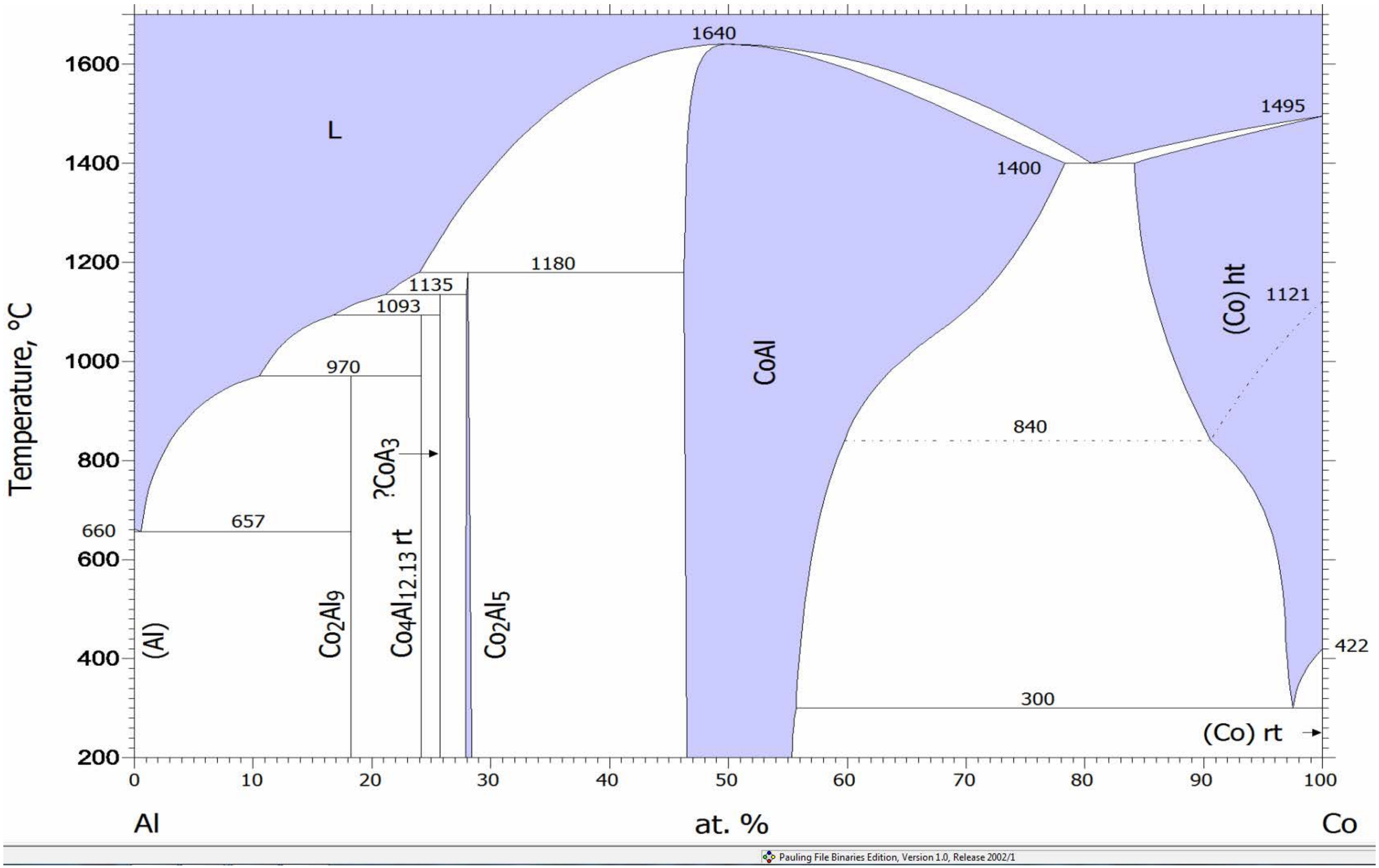
Binary system with limited mutual solubility, line compounds and alloys with existence range



The Ni-Al system is important for superalloys

PAULING FILE, Binaries Edition, ASM International, 2002

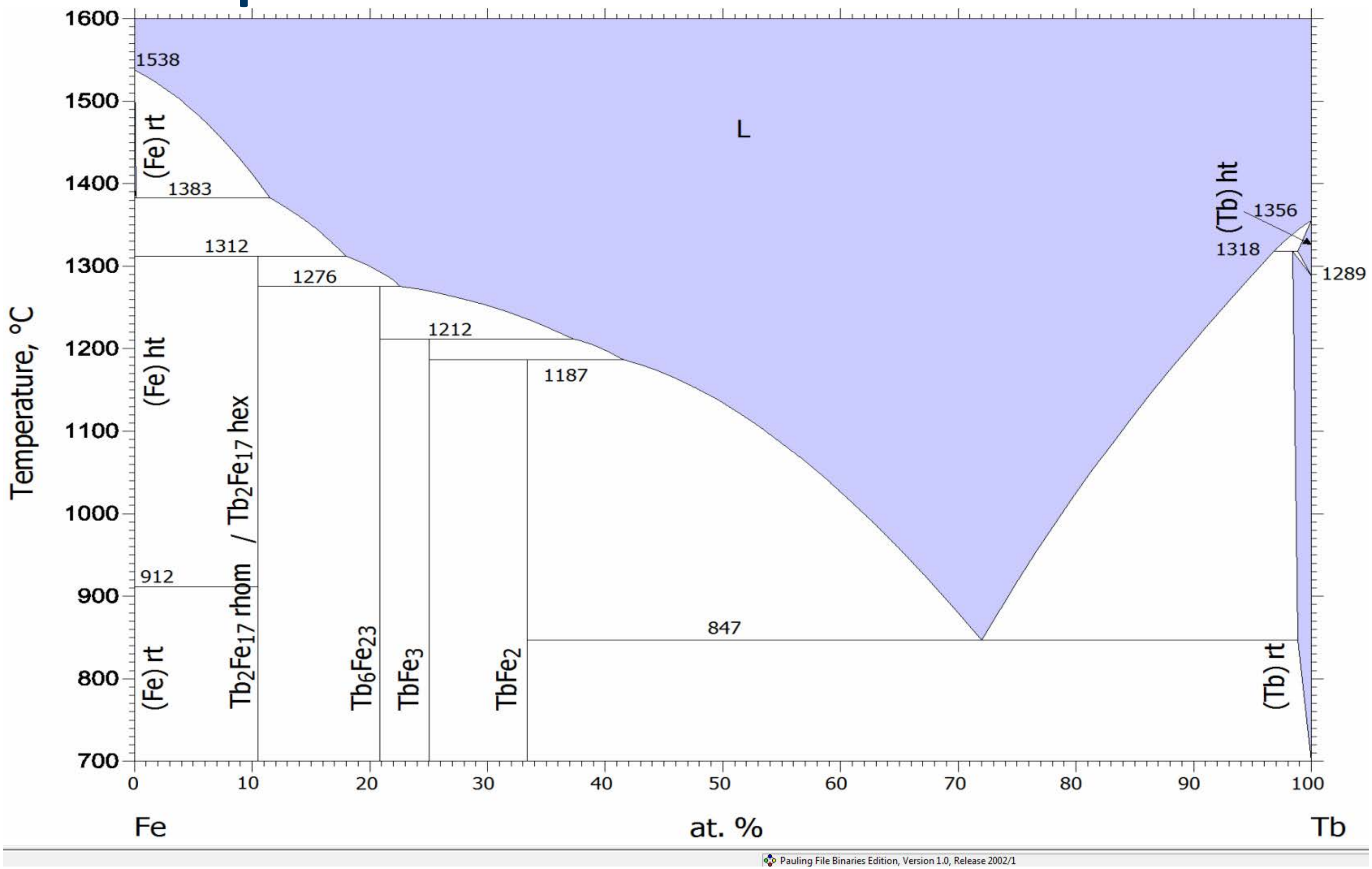
Binary system with limited mutual solubility, line compounds and alloys with existence range



The Co-Al system is important for superalloys

PAULING FILE, Binaries Edition, ASM International, 2002

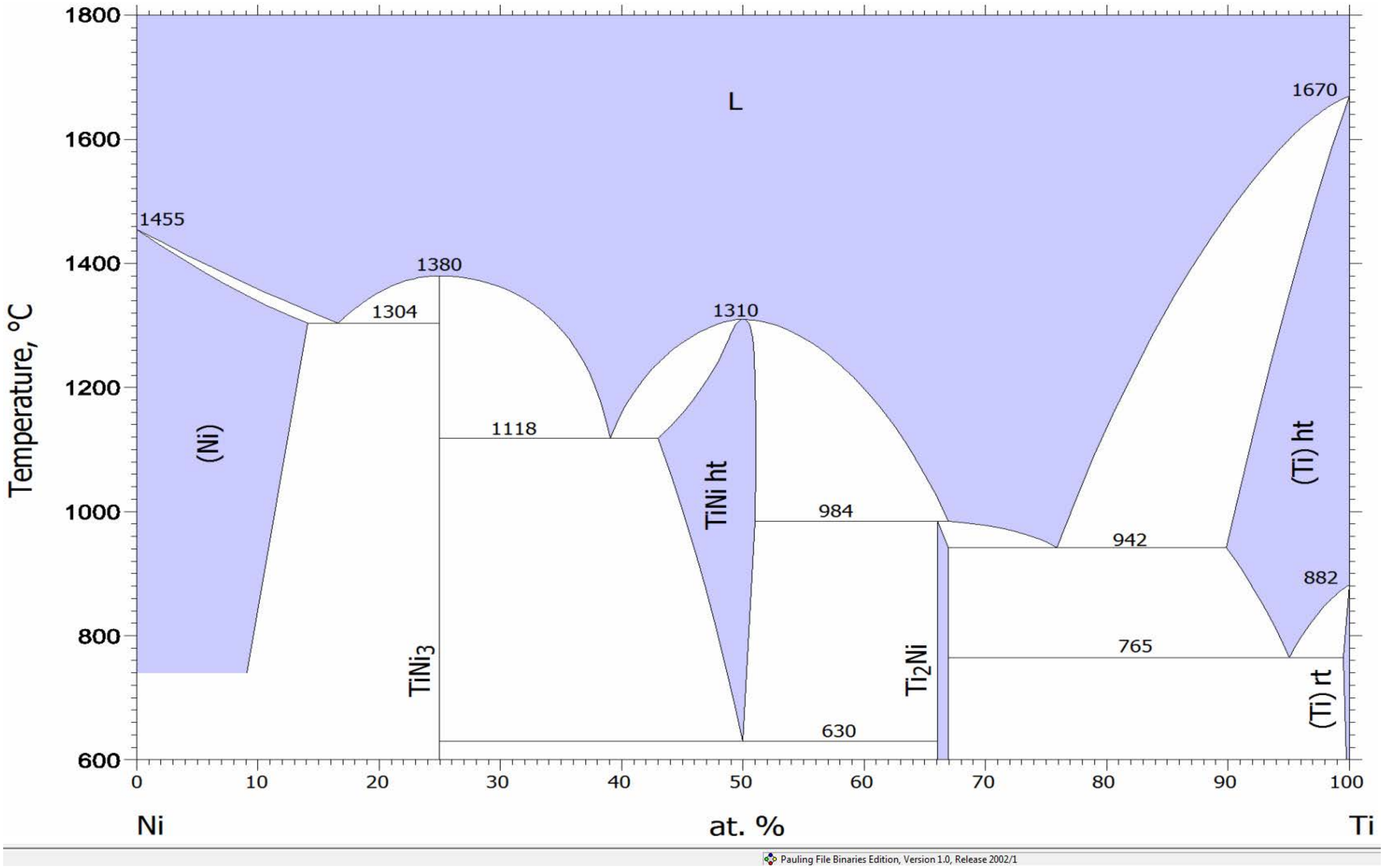
Example of a binary system with intermetallic line compounds



Laves phase: $TbFe_2$ (magnetostriction)

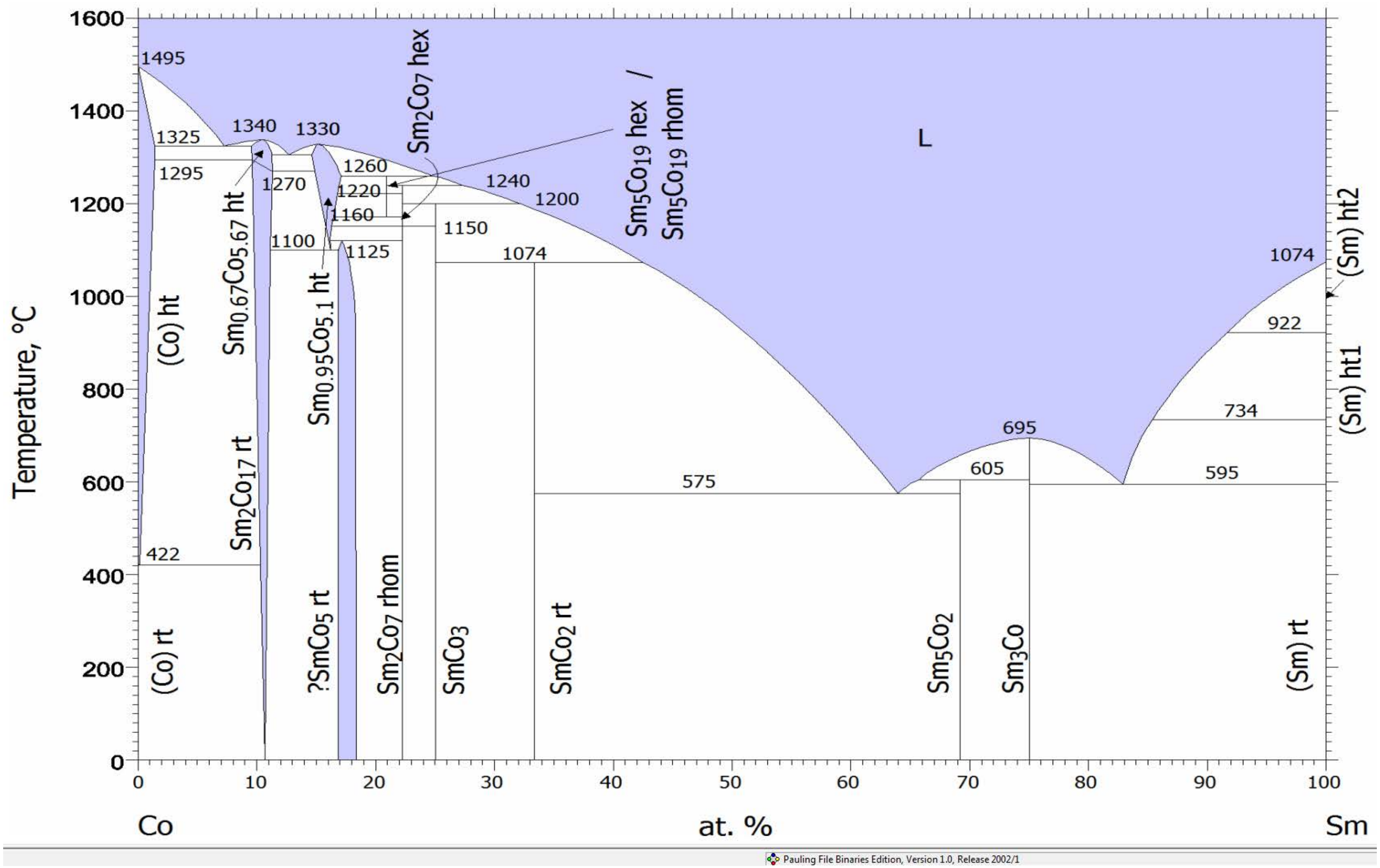
PAULING FILE, Binaries Edition, ASM International, 2002

Example of a binary system with intermetallic phases



B2 phase: TiNi, shape memory alloys

Example of a binary system with intermetallic phases: hard magnets



The phases $SmCo_5$ and Sm_2Co_{17} are important for hard magnets

PAULING FILE, Binaries Edition, ASM International, 2002

Example of a binary system with intermetallic phases: hard magnets

$SmCo_5$: hexagonal

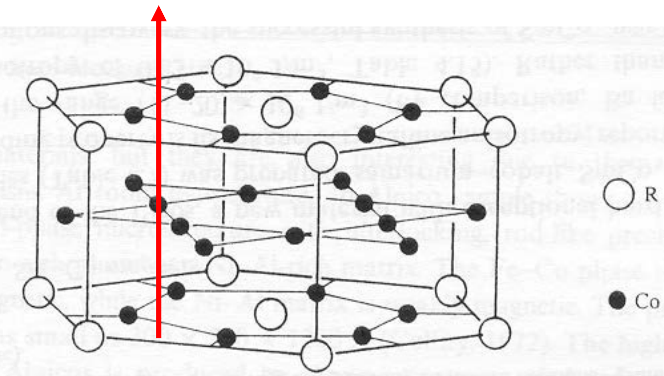


Fig. 6.28. The hexagonal unit cell of $SmCo_5$ ($CaCu_5$ type).

Sm_2Co_{17}: hexagonal, rhomboedric,

$Sm(Co_{0.67}Fe_{0.23}Cu_{0.08}Zr_{0.02})_{8.35}$

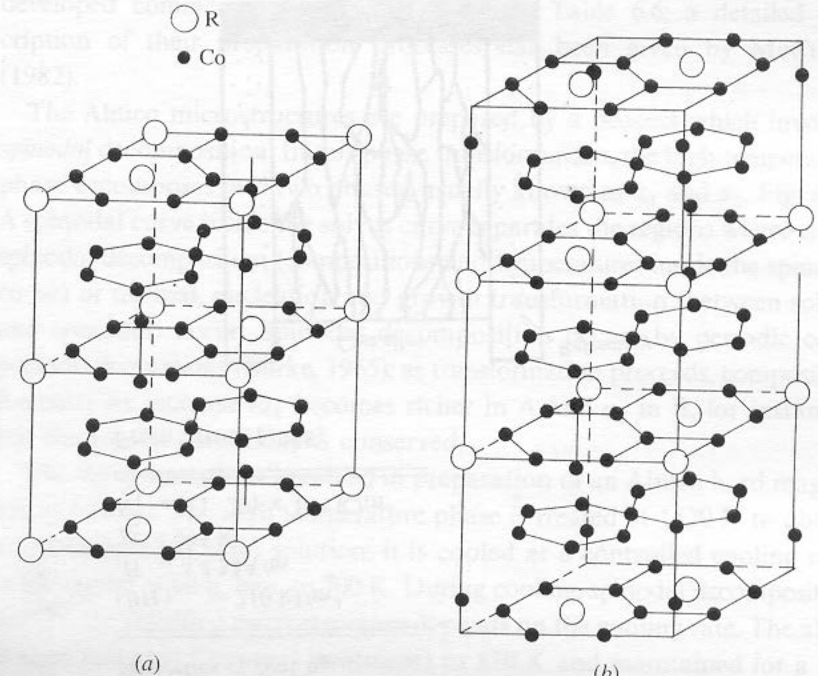
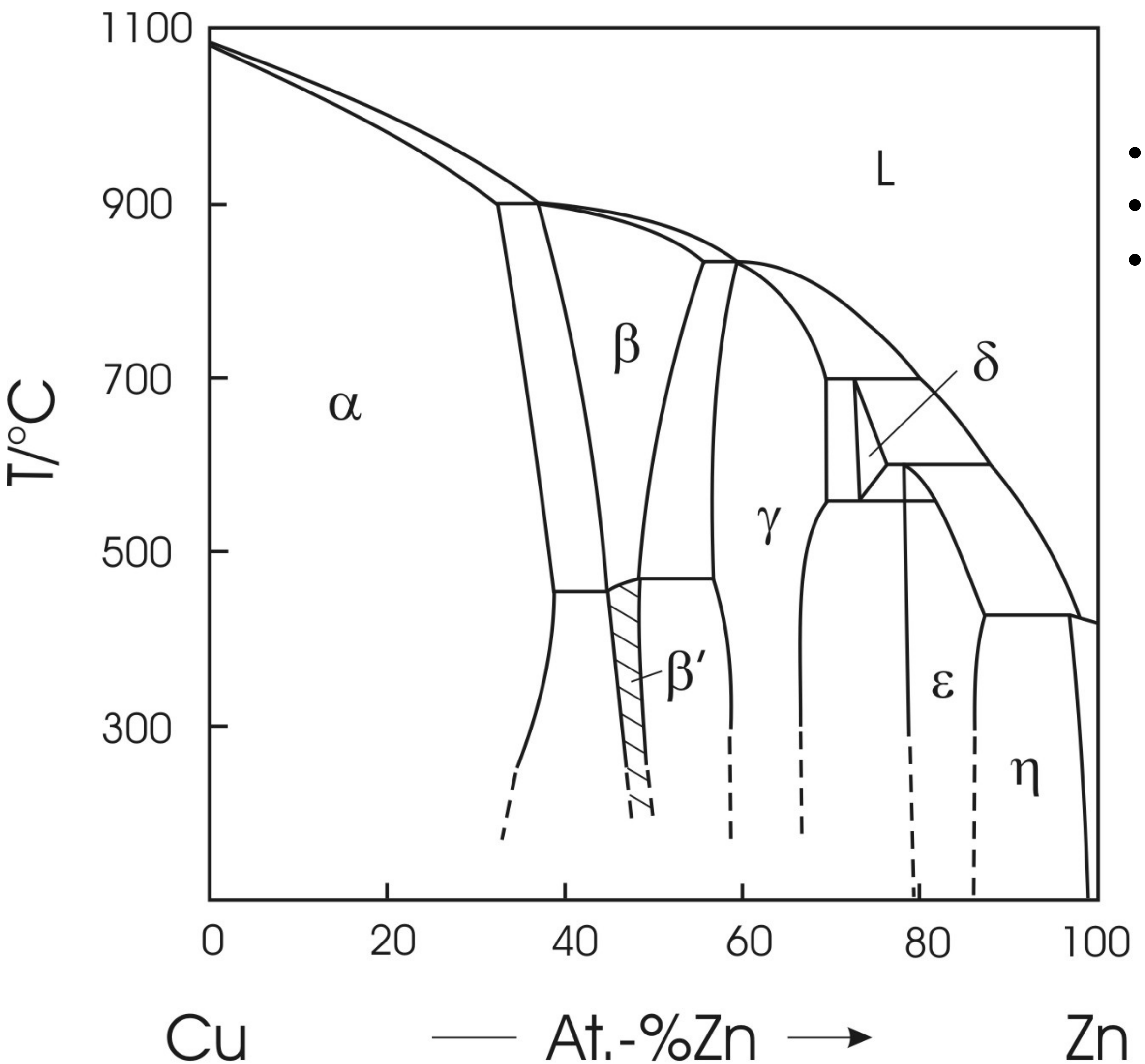


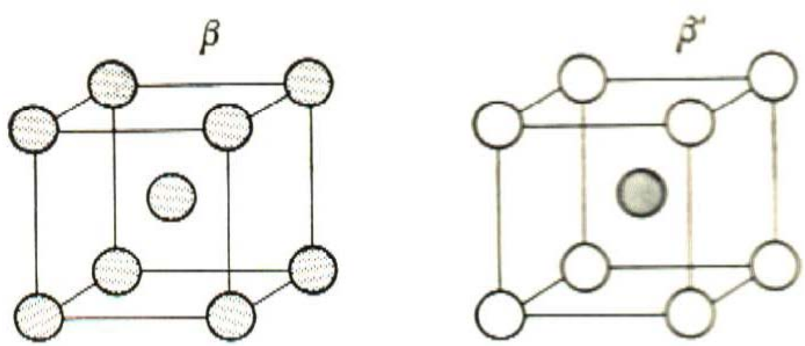
Fig. 6.29. (a) Hexagonal and (b) rhombohedral structures of Sm_2Co_{17} compounds.

Hume-Rothery phases in the Cu-Zn system

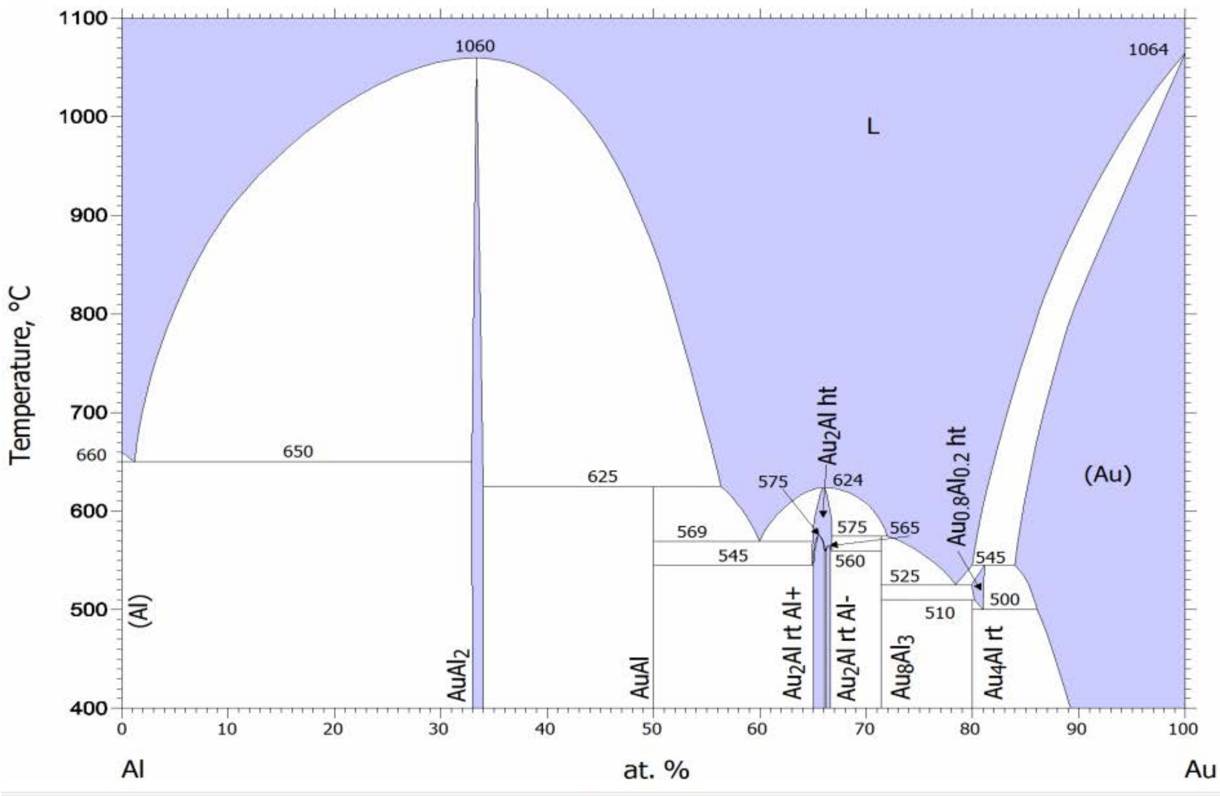
(valence electron phases)



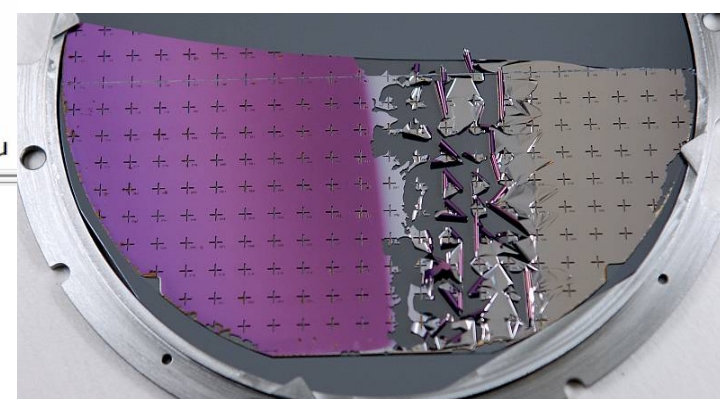
- a series of peritectic reactions
- phases are named consecuetively
- order transformation (β, β')



“Purple plague” in the Au-Al system



- „purple plague“ $AuAl_2$
- “white plague“ Au_5Al_2
- further phases $AuAl$, Au_2Al, Au_4Al



PAULING FILE, Binaries Edition, ASM International, 2002

Gas metal systems

Gas metal systems:

- during processing
- during service
- high-temperature oxidation
- hot-gas corrosion

Metal hydrogen systems
(e.g. Pd-H, Mg-H)

Nitrides

Oxides

Determination of Phase Diagrams for Hydrogen-Containing Systems 461

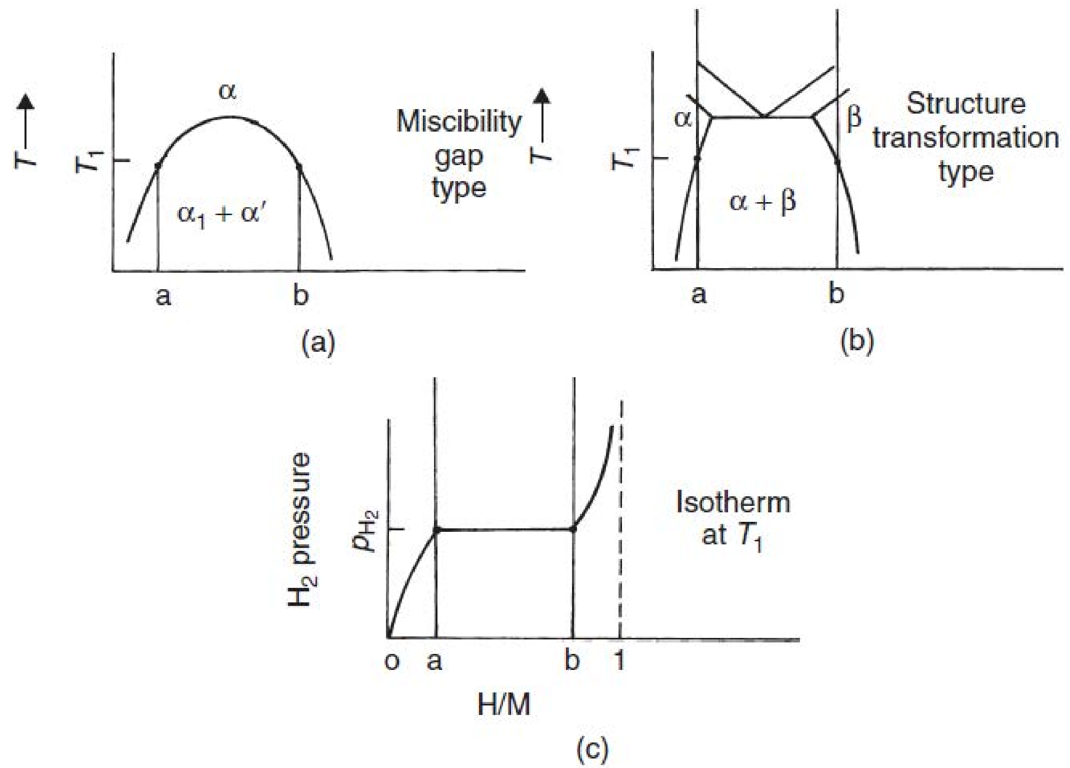
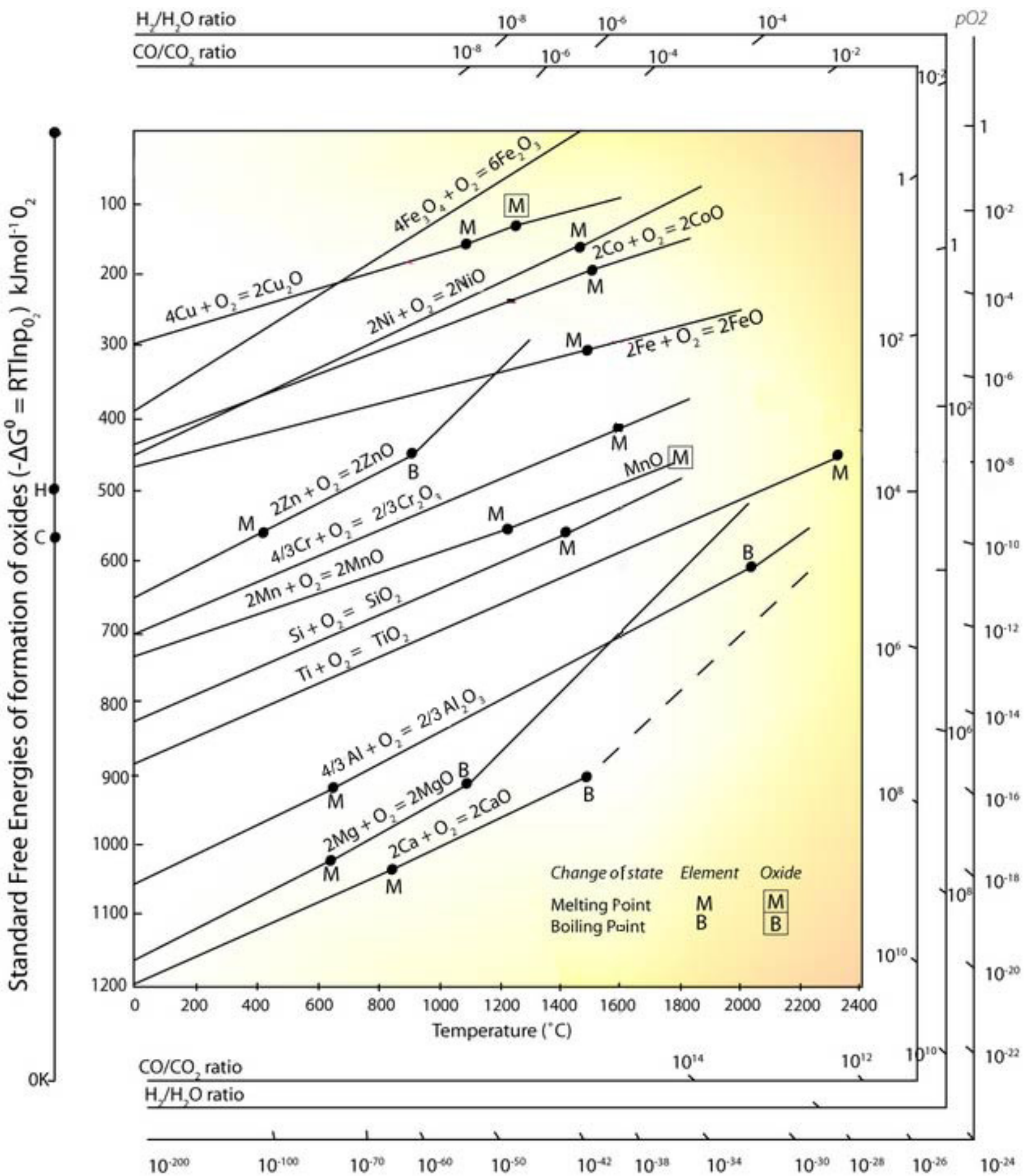


Figure 15.1 Schematic diagrams showing (a) a miscibility gap system, (b) a structural transformation system and (c) an isotherm corresponding either to (a) or (b) at temperature T_1 [8].

J.-C. Zhao, Methods for Phase Diagram Determination, Elsevier 2011

Gas metal systems: Ellingham diagram for oxidation of metals



Gibbs energy ΔG – temperature T diagram for metals in equilibrium with their oxides

$$xM + \frac{y}{2} O_2 = M_x O_y$$

$$\Delta G^0 = \frac{y}{2} RT ln p O_2$$

Used for:

- „ease“ of oxidation/reduction
  (but only thermodynamics, no kinetics)
- Determine partial pressure of oxygen in equilibrium with metal oxide at given T
- Determine ratio of reducing gas mixtures (CO, H_2)
- Determine which metal can reduce which metal oxide(s)
  - E.g. Mg can reduce TiO_2

http://web.mit.edu/2.813/www/readings/Ellingham_diagrams.pdf

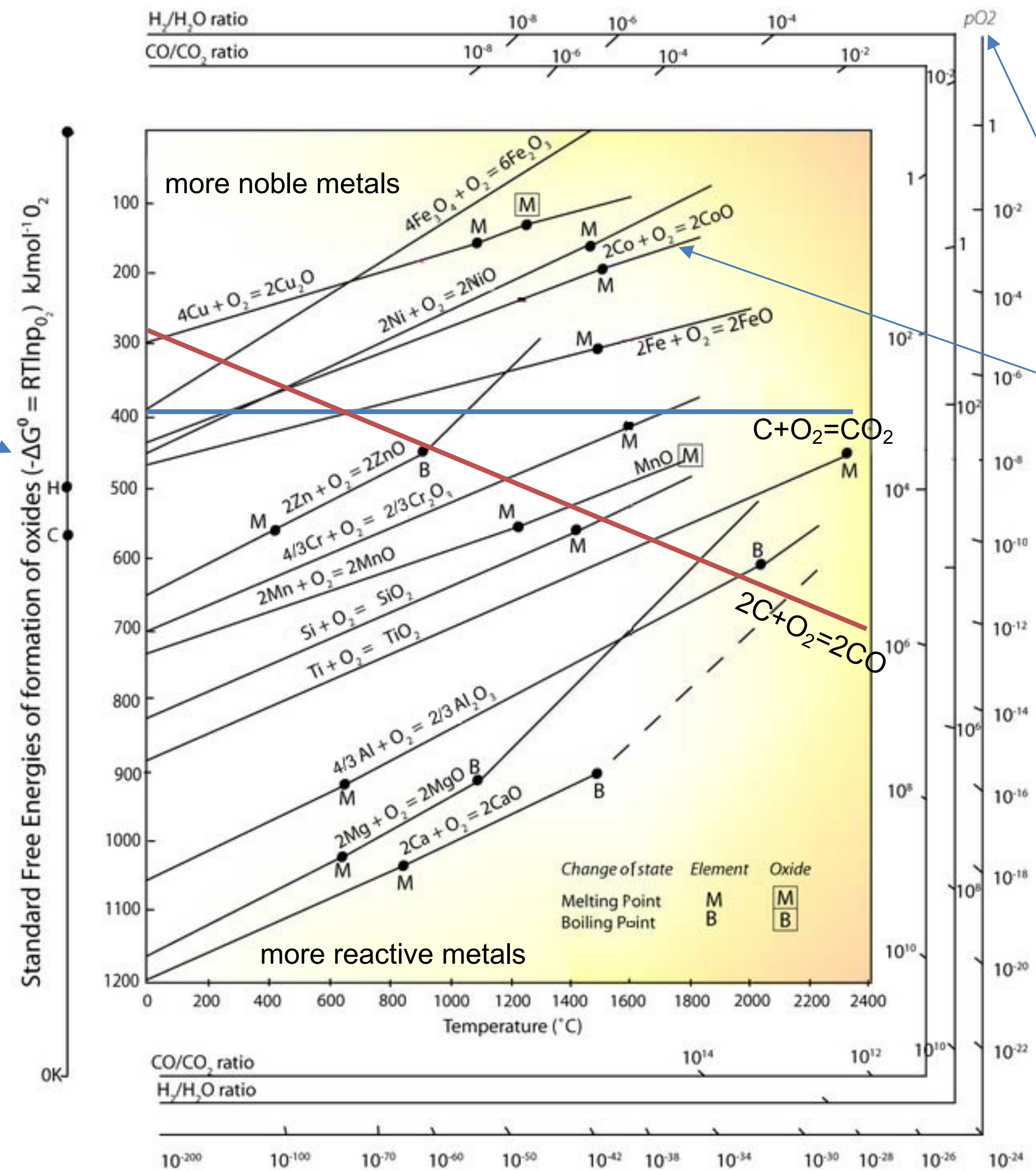
Picture: https://www.doitpoms.ac.uk/tlplib/ellingham_diagrams/ellingham.php
Publication: Ellingham H. J. T., J Soc Chem Ind (London) **63** 125 (1944)

Gas metal systems: Ellingham diagram for oxidation of metals

RUB

Free energy of formation is negative for most metal oxides

The lower the position of a metal's line, the greater is the stability of its oxide.



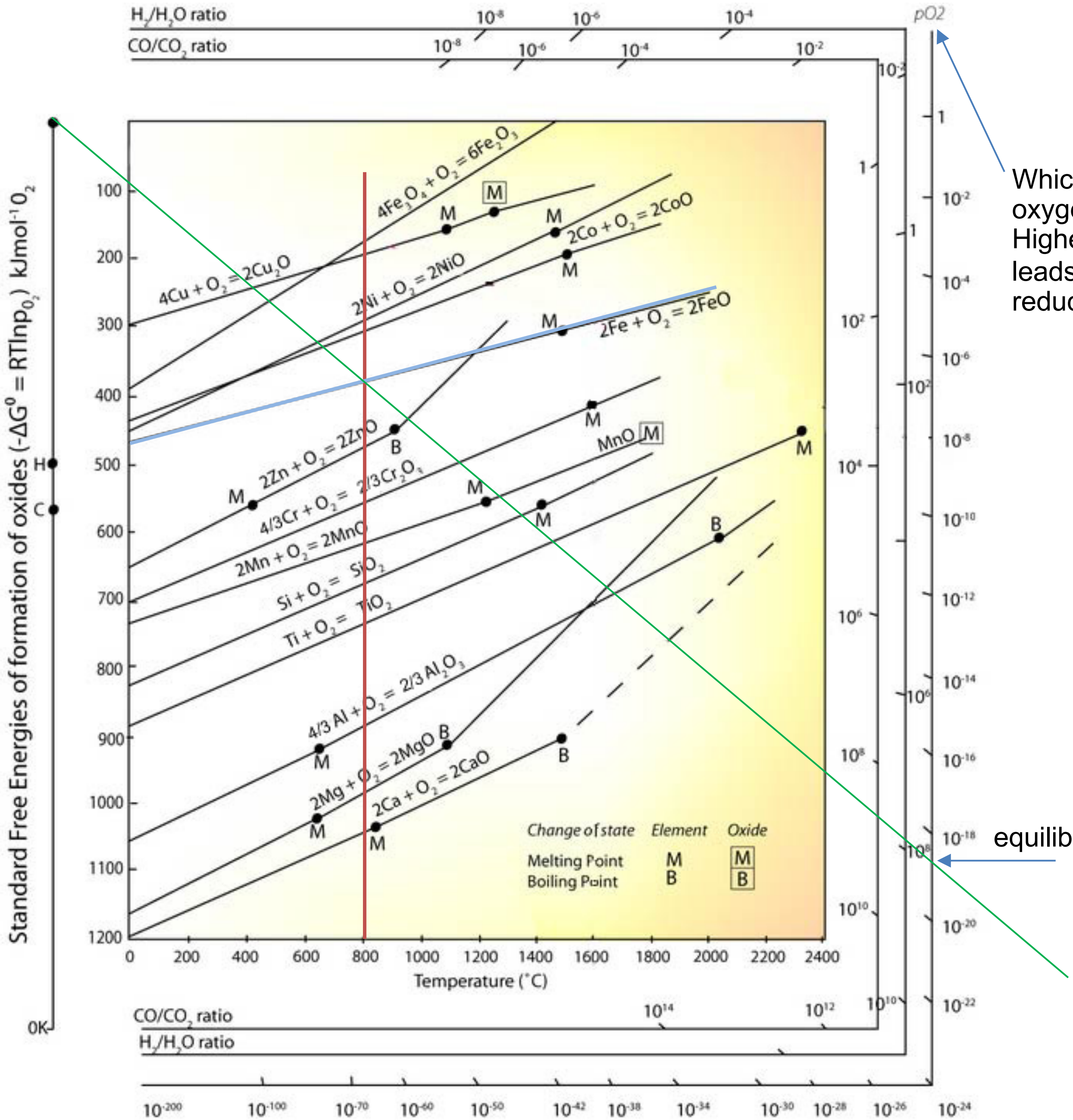
Which partial pressure of oxygen is in equilibrium? Higher pO2 than equilibrium leads to oxidation, lower to reduction.

Positive slopes for metal + gas = solid as entropy is reduced

Carbon is an important reducing agent

Picture: https://www.doitpoms.ac.uk/tlplib/ellingham_diagrams/ellingham.php
Publication: Ellingham H. J. T., J Soc Chem Ind (London) **63** 125 (1944)

Gas metal systems: Ellingham diagram for oxidation of metals



Which partial pressure of oxygen is in equilibrium? Higher pO2 than equilibirum leads to oxidation, lower to reduction.

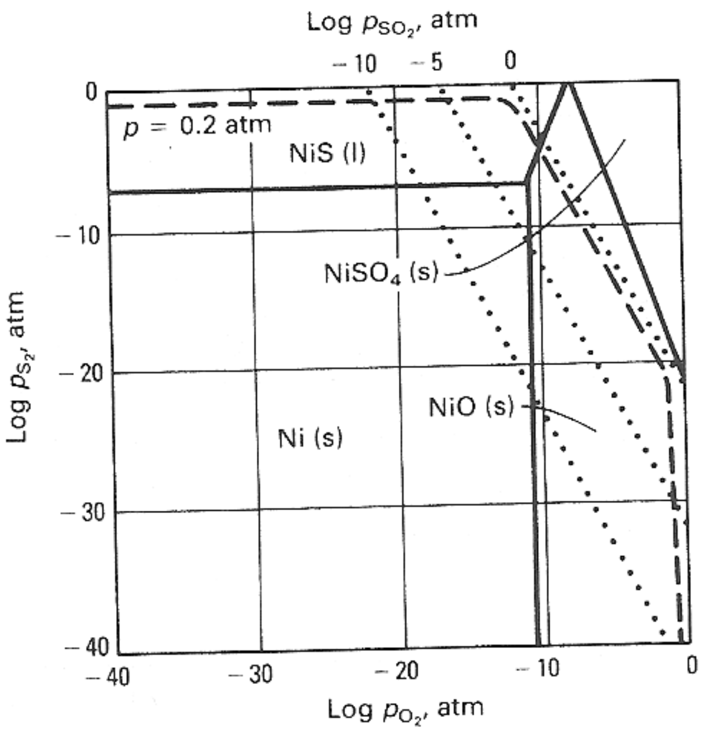
equilibrium partial pressure

Picture: https://www.doitpoms.ac.uk/tlplib/ellingham_diagrams/ellingham.php
Publication: Ellingham H. J. T., J Soc Chem Ind (London) **63** 125 (1944)

Gas metal systems: isothermal stability diagrams

a metal and two gases

alloys and gas(es)



The Ni-O-S system at 977 °C (1790 °F). Source: Ref 11.3 as published in Ref 11.2

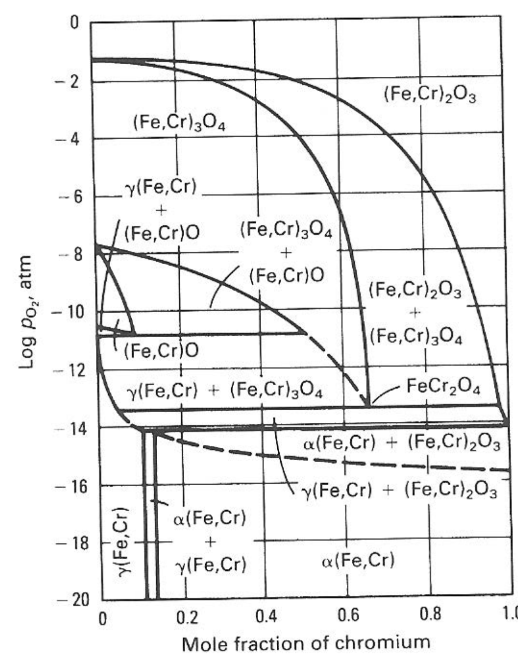
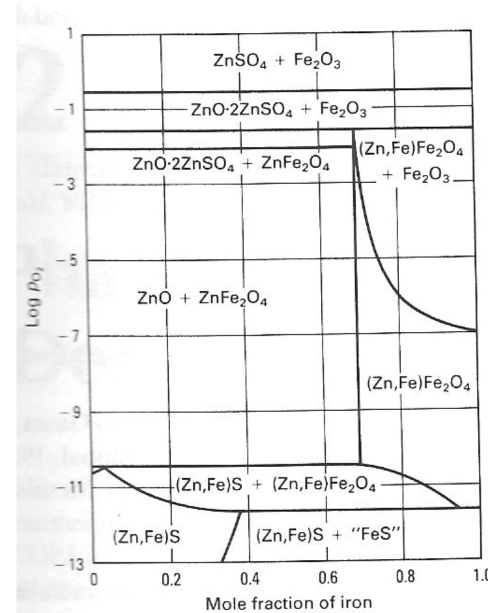


Fig. 11.3 Stability diagram for the Fe-Cr-O system at 1300 °C
Source: Ref 11.2



The Fe-Zn-S-O system for p = 1 atm at 890 °C (1635 °F). Source: Ref 11.4 as published in Ref 11.2

p_{SO_2}= const.

also: Kellog diagram

<u>predominance diagram</u>: phase fields show predominant phase, other phases may also be present

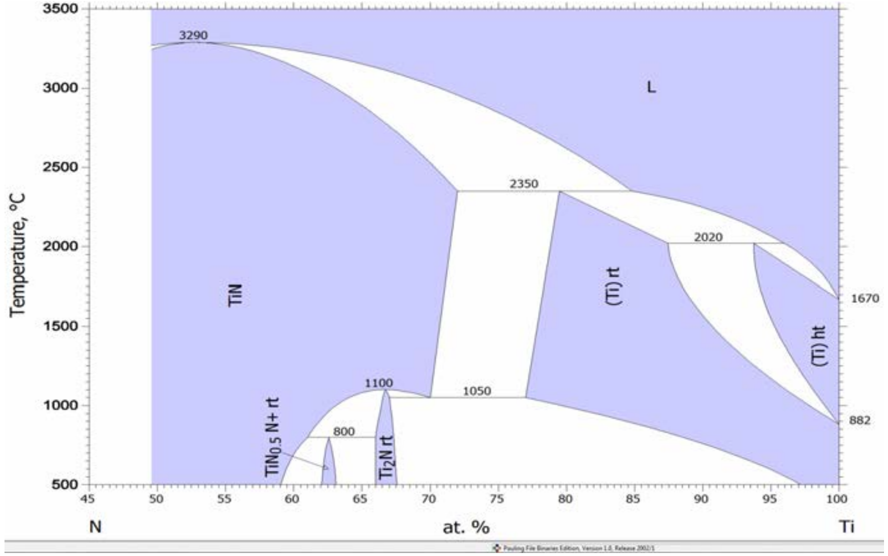
F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

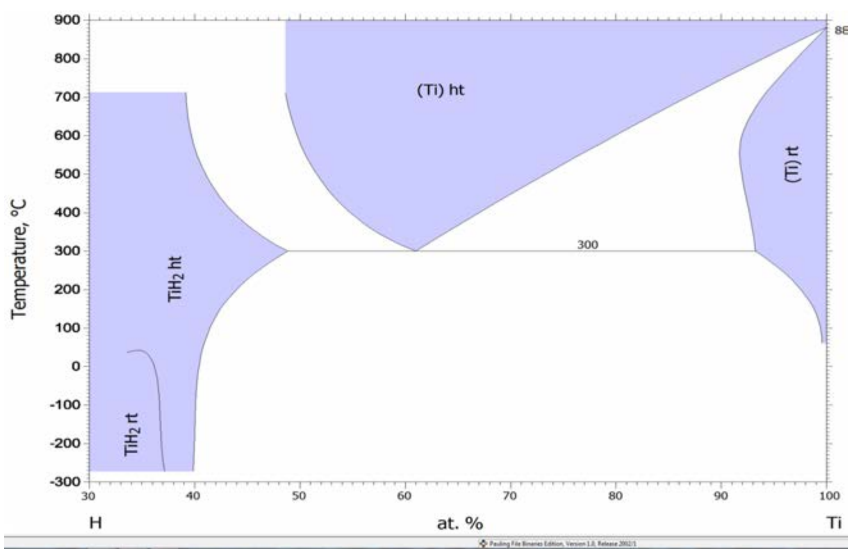
Gas metal systems: Ti systems

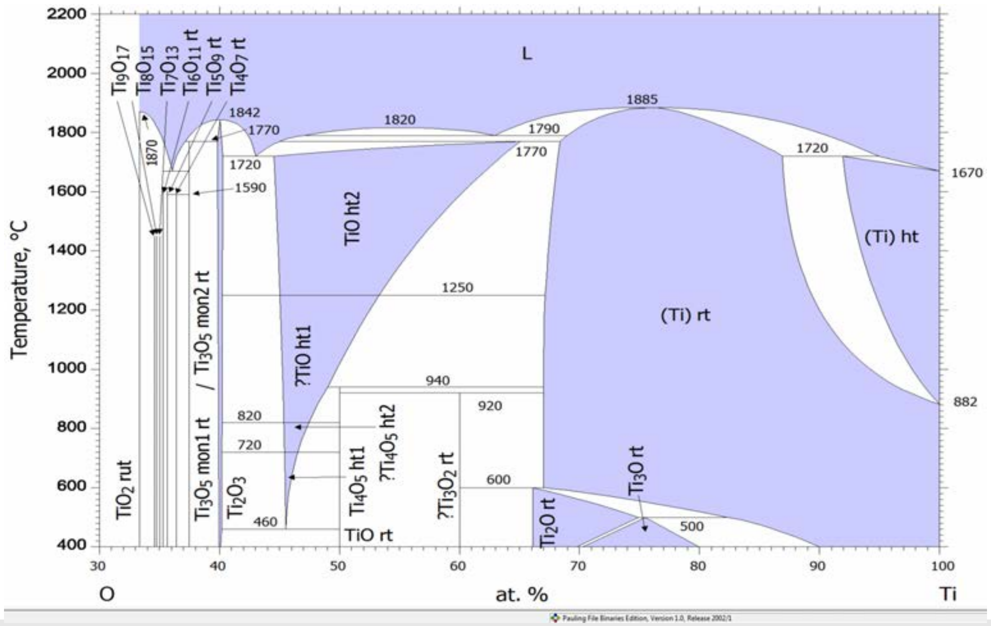
TiN: hard coating material

TiO_2: numerous applications, e.g. catalyst

TiH_2: hydrogen storage

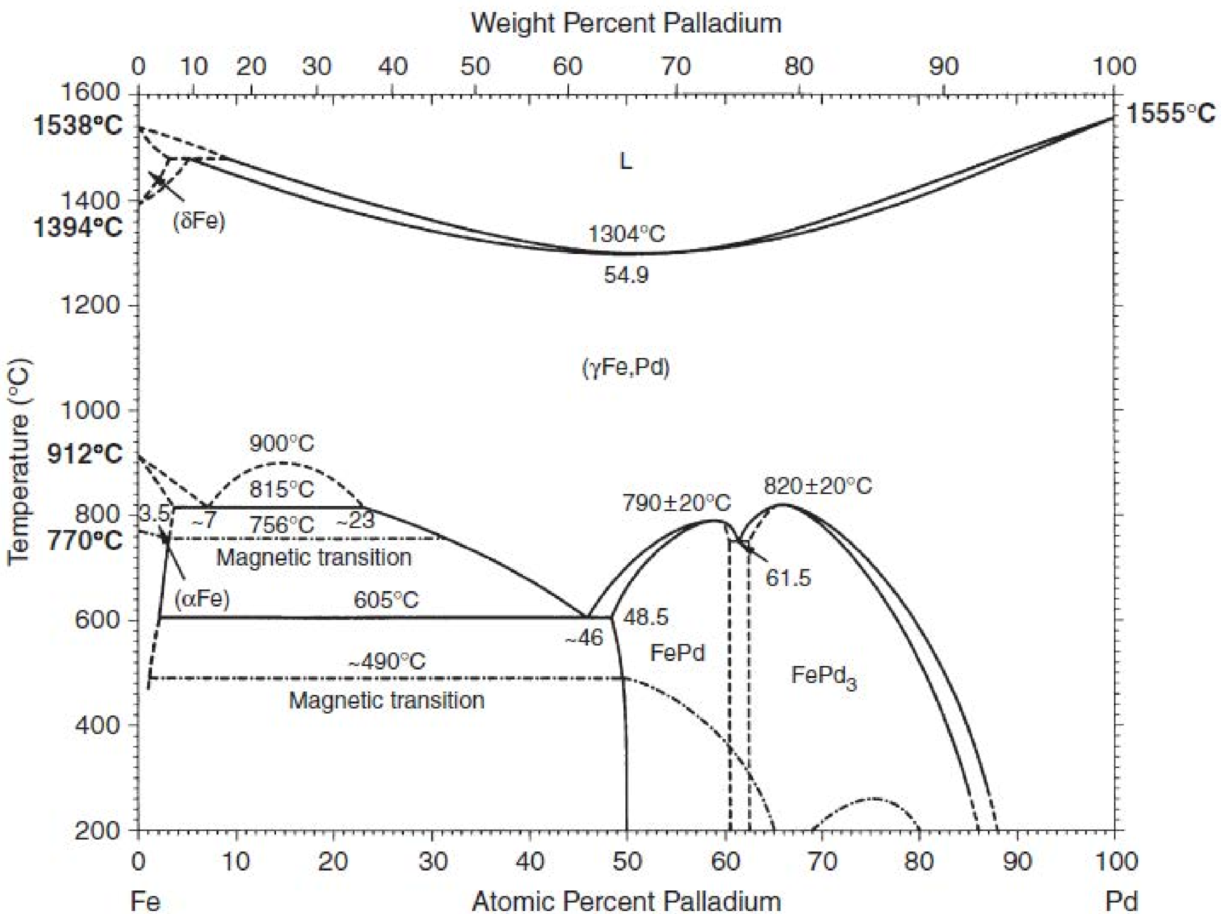






PAULING FILE, Binaries Edition, ASM International, 2002

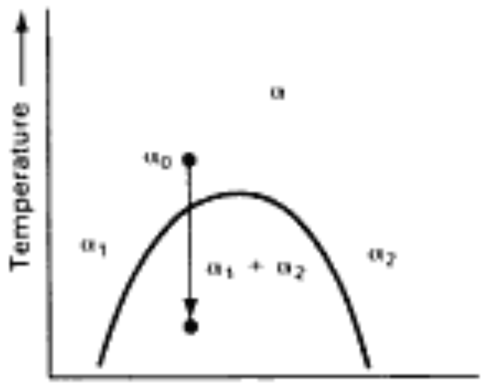
Further information in phase diagrams: magnetic transitions



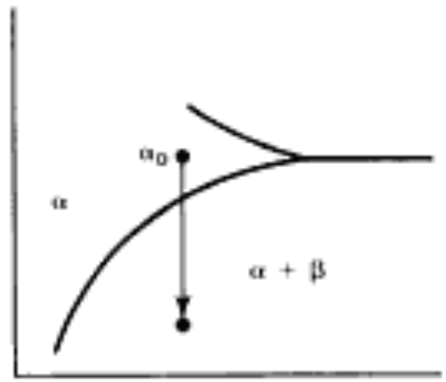
metastable $Fe_{70}Pd_{30}$: ferromagnetic shape memory alloy

J.-C. Zhao, Methods for Phase Diagram Determination, Elsevier 2011

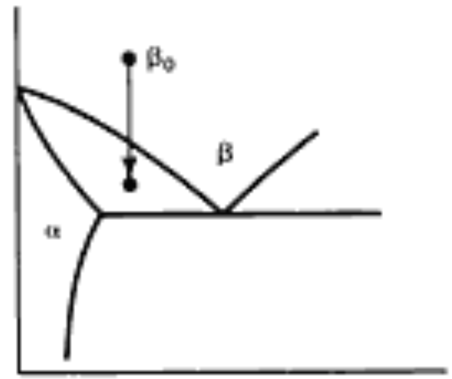
Examples of binary phase diagrams that give rise to precipitation reactions



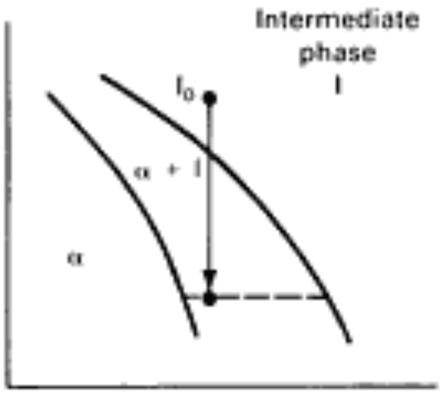
Miscibility gap
$\alpha_0 \rightarrow \alpha_1 + \alpha_2$



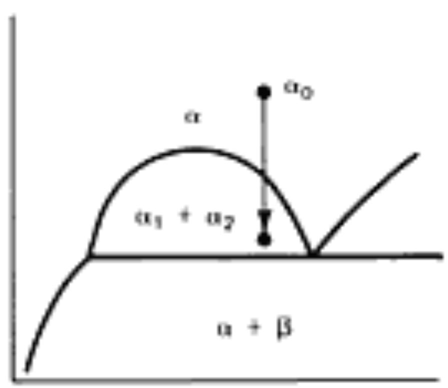
Sloping solvus: decreasing solid solubility with decreasing temperature
$\alpha_0 \rightarrow \alpha + \beta$



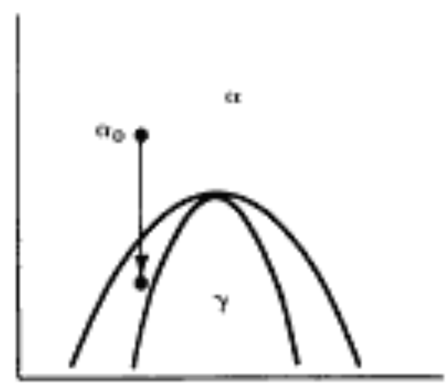
Proeutectoid reaction
$\beta_0 \rightarrow \alpha + \beta$



Intermediate phase
$I_0 \rightarrow I + \alpha$



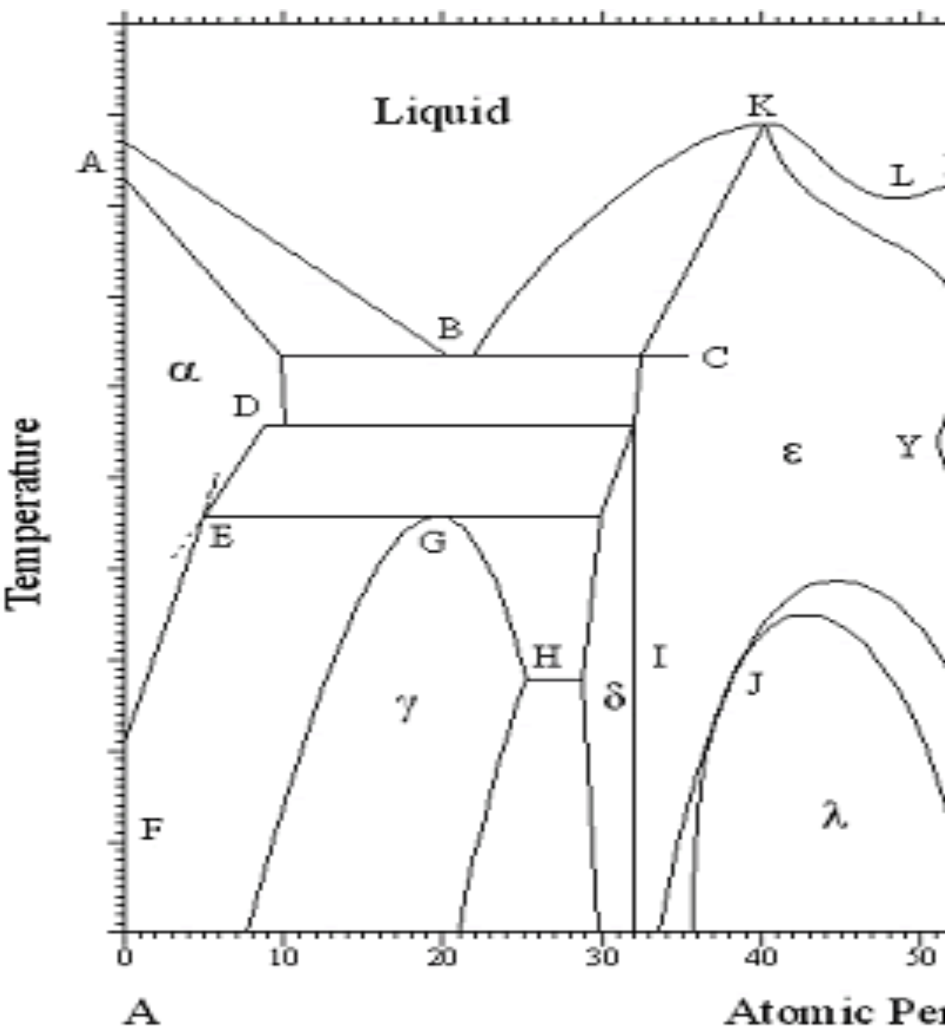
Promonotectoid; similar to miscibility gap
$\alpha_0 \rightarrow \alpha_1 + \alpha_2$



Heterogeneous ordering; γ is an ordered phase
$\alpha_0 \rightarrow \alpha + \gamma$

: http://mio.asminternational.org/apd/index.aspx

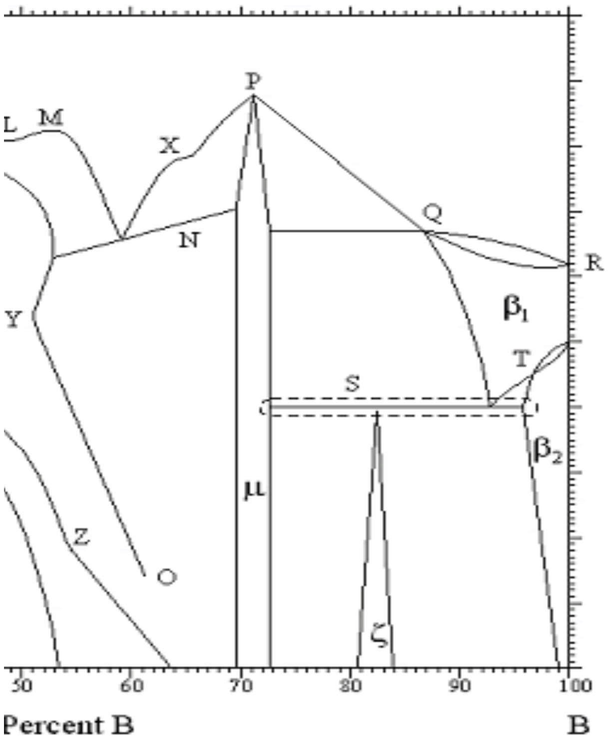
Summary of impossible phase relationships in published phase diagrams



A: The liquidus and solidus must meet at the melting point of the pure element.
B: Two liquidus curves must meet at one composition at a eutectic temperature.
C: A tie line must terminate at a phase boundary.
D: Two solvus boundaries (or two liquidus, or two solidus, or a solidus and a solvus) of the same phase must intersect at one composition at an invariant temperature.
E: A phase boundary must extrapolate into a two-phase field after crossing an invariant point.
F: A two-phase field cannot be extended to a pure element end.
G: Two boundaries of g must not be continuous at the invariant temperature. They must cross one another.
H: An invariant temperature line should involve equilibrium among three phases.
I: There should be a two-phase field between two single phase fields.
J: When two phase boundaries touch at a point, they should touch at an extremity of temperature.
K: A touching liquidus and solidus (or any two touching boundaries) must have a horizontal common tangent at the congruent point. In this case, the slope of the solidus appears to be discontinuous at the melting point.
L: A local minimum point in the lower part of a single-phase field cannot be drawn without an additional boundary in contact with it (minimum congruent point or monotectic reaction in this case).

: http://mio.asminternational.org/apd/index.aspx

Summary of impossible phase relationships in published phase diagrams



M: A local maximum point in the lower part of a single-phase field cannot be drawn without a monotectic, monotectoid, syntactic, and syntectoid reaction occurring at a lower temperature. Alternatively, a solidus curve must be drawn to touch the liquidus at point M. (If the maximum is not local, as in a miscibility gap, this is not a phase rule violation.)

N: The temperature of an invariant reaction must be constant. (The reaction line must be horizontal.)

O: A phase boundary cannot terminate within a phase field (except the case when the boundary is unknown beyond this point).

P: The liquidus should not have a discontinuous sharp peak at the melting point of a compound. (See exceptions below.)

Q: The compositions of all three phases at an invariant reaction must be different.

R: Temperatures of liquidus and solidus (or any two boundaries) must either increase or decrease together from one point on the pure element line as the content of a second element increases.

S: A four-phase equilibrium is not allowed in a binary system. (See exceptions below.)

T: Two separate phase boundaries that create a two-phase field between two phases in equilibrium should not cross one another.

Although phase rules are not violated, three additional unusual situations (X, Y, and Z) are also included in Fig. 27. These unlikely situations are discussed in the next section.

An additional problem, not shown in Fig. 27: would be a continuous solid solution phase between two phases with different crystal structures. For example, a fcc phase and a bcc phase cannot form a continuous phase. There must be a two-phase field between them.

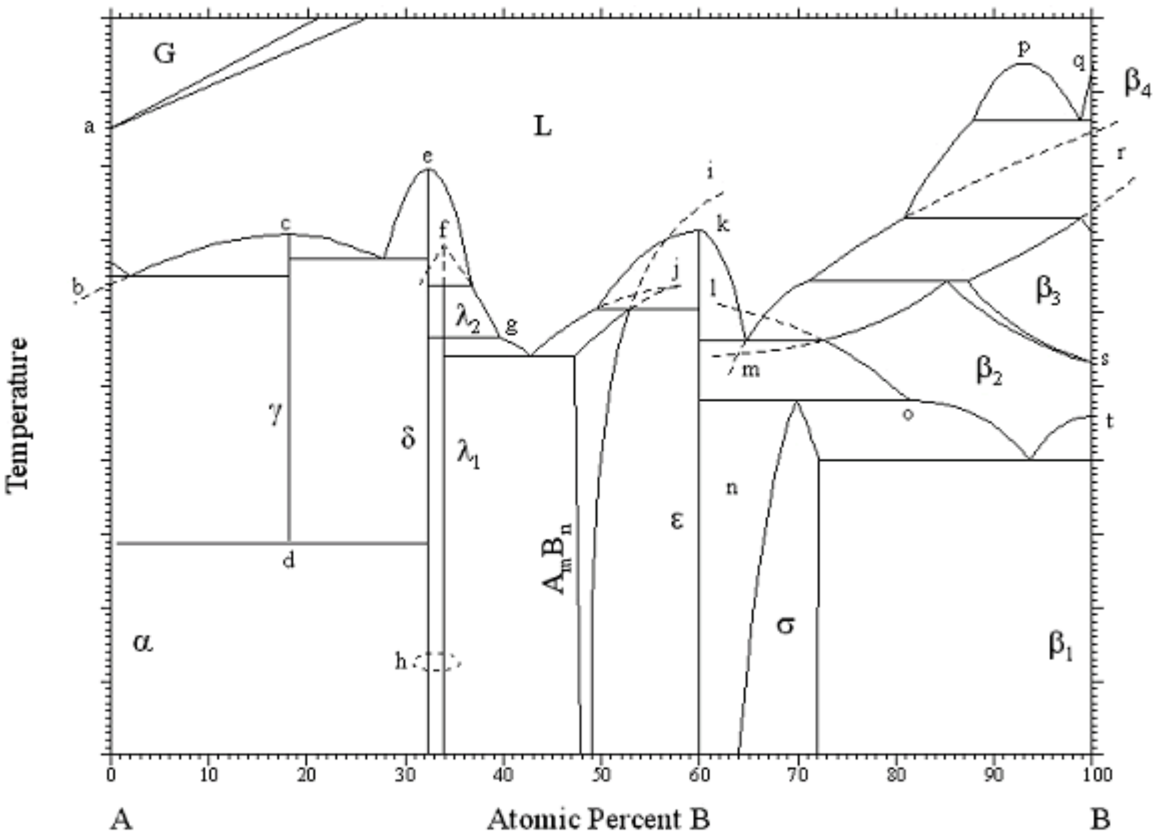
Exceptions

A four-phase reaction in appearance, as S in Fig. 27, may occur if temperatures of two invariant reactions with an overlapping composition range are very close to one another.

A sharp peak as P may occur if this phase exists in the same molecular state in the liquid phase as it does in the solid state. The apparent sharpness of the peak varies depending on the degree of association of the liquid molecules.

: http://mio.asminternational.org/apd/index.aspx

Types of improbable phase boundaries



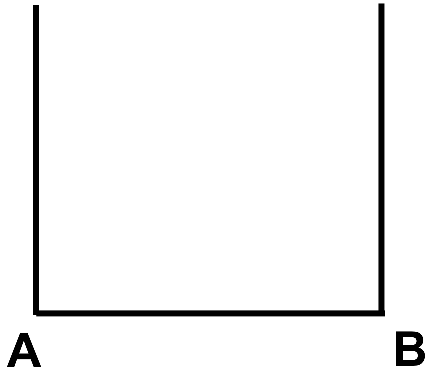
k: The liquidus is too asymmetric. According to the author's criterion, a liquidus is already too asymmetric if the liquidus width ratio to the left and right of a compound exceeds 2 to 3.
l: The transformation temperature of ε to β_2 should be higher than the melting point of ε. Otherwise, the β_2 phase is stable above point j.
m: Extrapolation of two boundaries of L + β_2 should not cross. Problem T of Fig. 27 occurs.
n: A two-phase field must be narrower at higher temperatures.
o: The slope is too flat to have a maximum point at the composition of ϕ.
p: The liquid miscibility gap is too close to the edge of a phase diagram.
q: The liquidus slope is too steep. The initial slope of a liquidus must conform to the van't Hoff relationship. If no solubility can be assumed for the solid phase, extrapolation of the initial liquidus should go through the horizontal axis at 0 K near approximately 110 at.%.
r: Extrapolation of two boundaries of L + β_3 should cross at the 100 at.% line, not at some composition exceeding 100 at.%. Problem A of Fig. 27.
s: Two phase boundaries should have different initial slopes.
t: The slopes of two phase boundaries are too far apart.

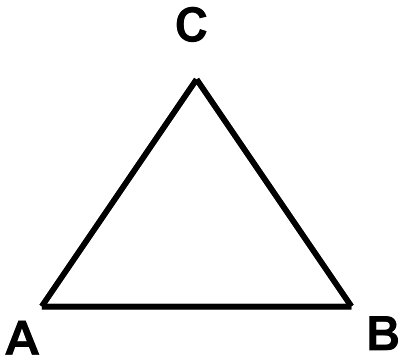
a: G + L two-phase field is too narrow. The opening angle of G + L at 0 at.% must be much larger because the heat of vaporization of an element is usually much greater than the heat of fusion.
b: Extrapolation of the liquidus should not cross the 0 at.% line. Otherwise, problem F of Fig. 27 occurs.
c: The liquidus of δat point c is too flat in comparison with the liquidus of δat point e. Problems c, d, and e are related. Because entropy of fusion of elements and compounds cannot differ much, curvatures of liquidus curves for compounds in a binary system must be similar. A phase with a sharper liquidus tends to decompose into two neighboring phases at low temperatures.
d: A compound with a flat liquidus is stable and will not decompose at low temperatures.
e: Liquidus at point e is too sharp in comparison with the liquidus at point c.
f: Extrapolation of the liquidus of λ_2 must have a peak at the composition of λ_2. Otherwise, problem P of Fig. 27 occurs.
g: Change of liquidus slope associated with an allotropic transformation must be small.
h: Two compounds having similar compositions cannot be stable over a wide temperature range.
i: A phase field of a compound cannot extend over a neighboring phase. Problem T of Fig. 27 occurs.
j: The congruent melting point of AmBn compound is too far away from its stoichiometric composition.

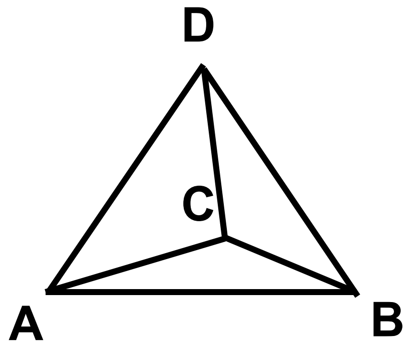
: http://mio.asminternational.org/apd/index.aspx

Multinary systems

Number of components	system
1	unary
2	binary
3	ternary
4	quaternary
5	quinary







Example of a phase diagram of ceramics with a quaternary line compound

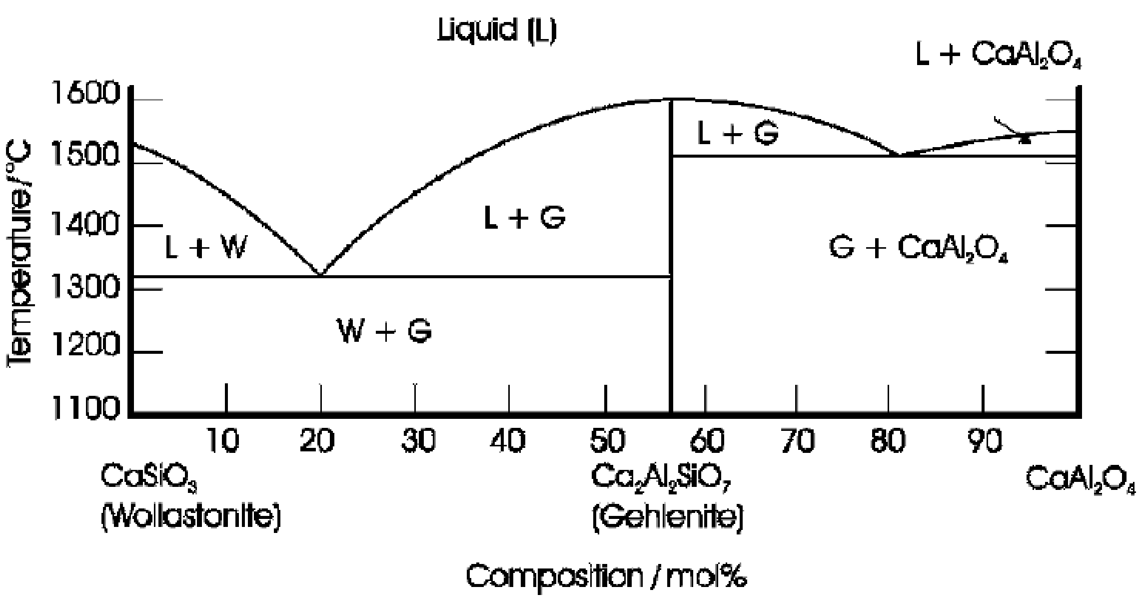


Figure 4.14 The wollastonite–calcium aluminate ($CaSiO_3$–$CaAl_2O_4$) phase diagram showing the intermediate phase gehlenite, $Ca_2Al_2SiO_7$

congruent melting

R. J. D. Tilley, Understanding Solids: The Science of Materials, John Wiley & Sons, 2013

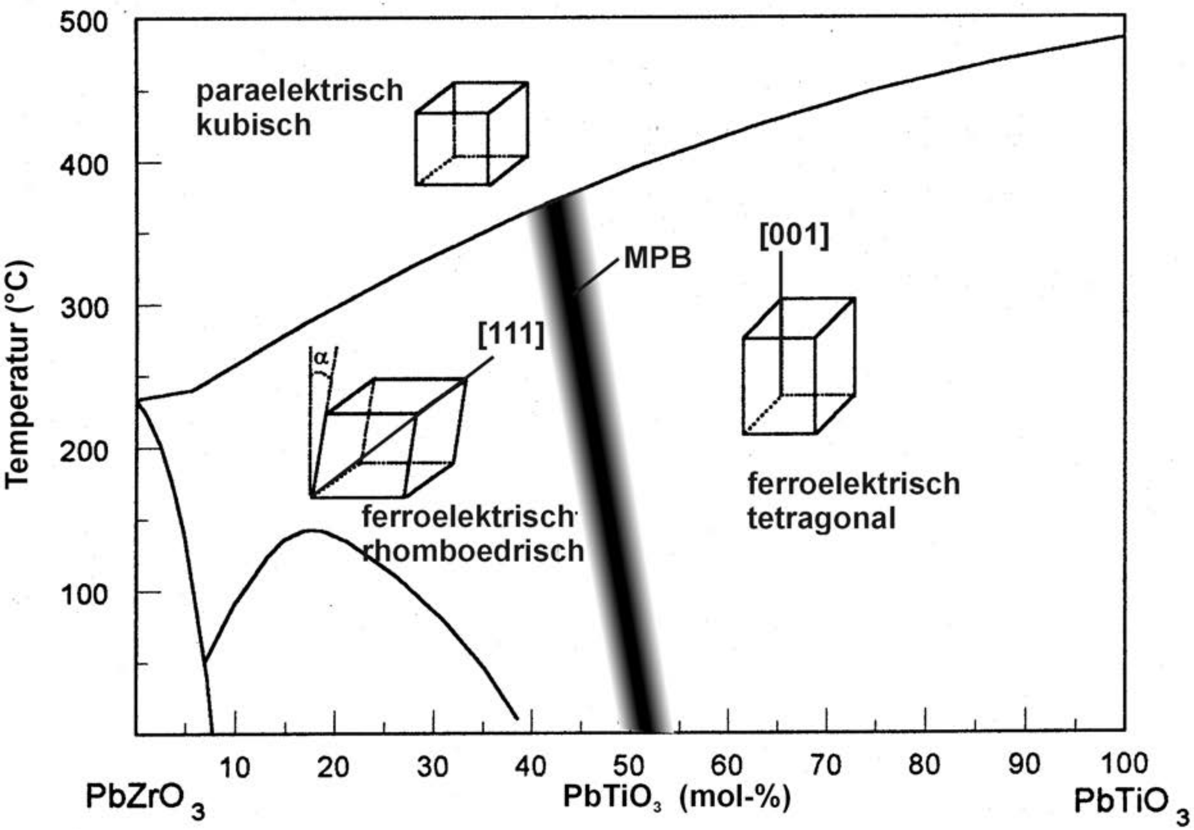
Phase diagram of functional ceramic PZT

solid solution of lead titanate and lead zirconate

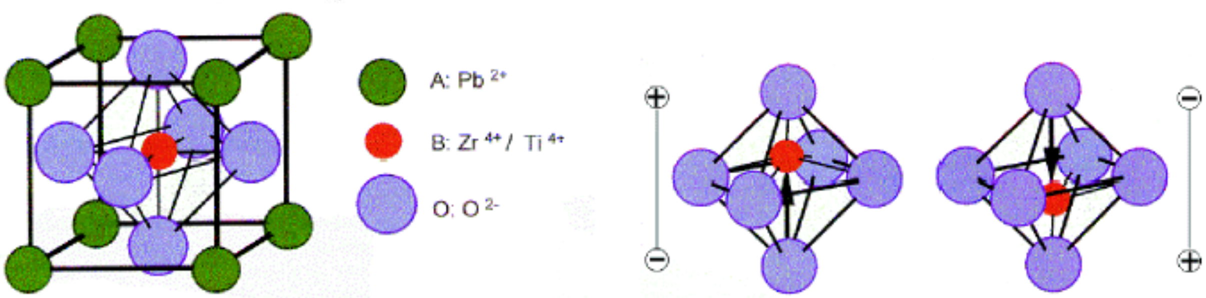
MPB:

morphotropic phase boundary

ferroelectric (piezoelectric) sensors and actuators (transducers)



phase transformation of perovskite structure

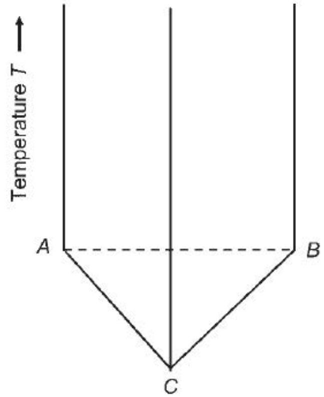


1.3 a: unpolar ($T > T_C$)

1.3 b: polar ($T < T_C$)

Ternary phase diagrams
Isothermal and isopleth sections

ternary: C=3,
shown in **equilateral triangle**
What about T and pressure?
most often: isobaric
equilateral prism



Space model for ternary phase diagrams

vertical section (isopleth)

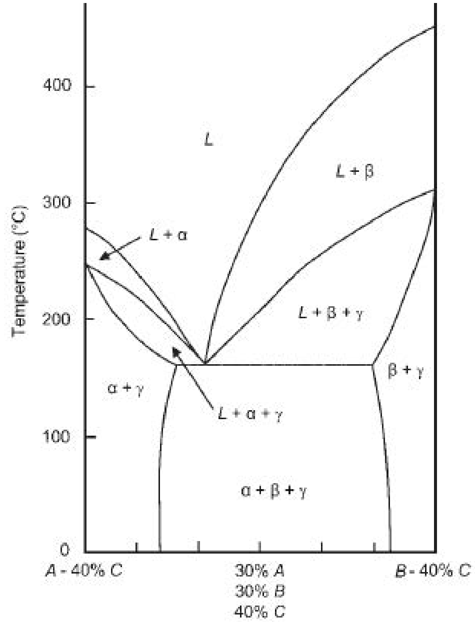
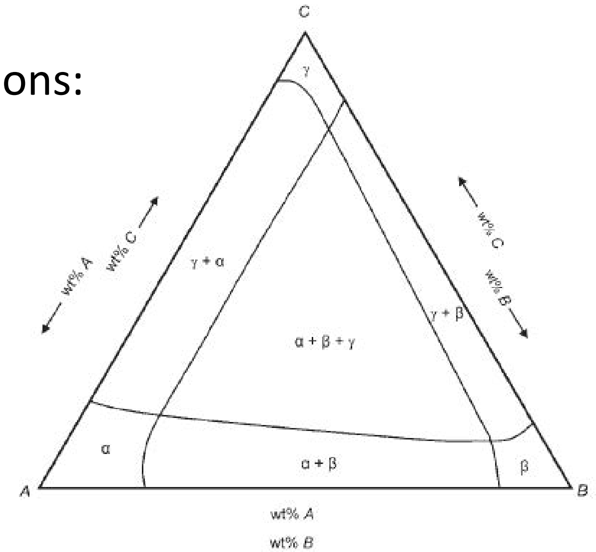
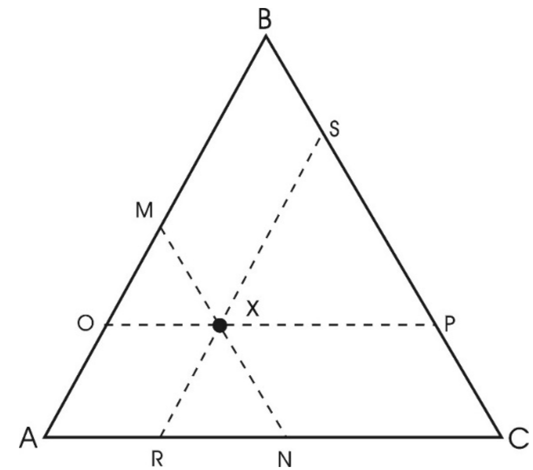


Fig. 10.5 Isopleth through hypothetical ternary phase diagram at a constant 40% C. Adapted from Ref 10.1

Isothermal sections:



phase fields



determining compositions

F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012
E. Hornbogen, G. Eggeler, E. Werner, Werkstoffe: Aufbau und Eigenschaften… , Springer Verlag, 2017

Free energies of a liquid and three solid phases of a ternary system

RUB

three binary eutectics

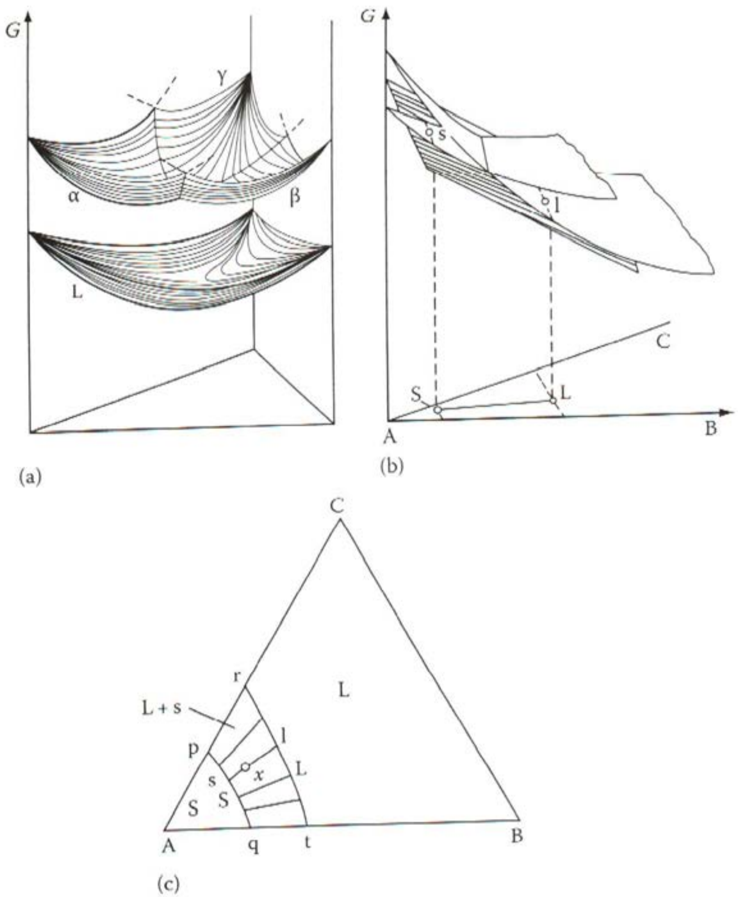
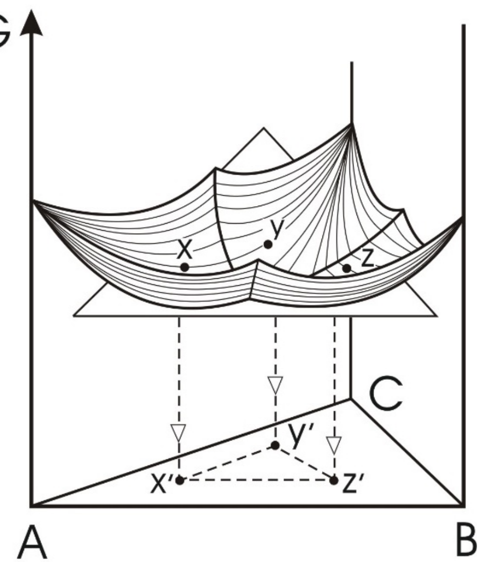
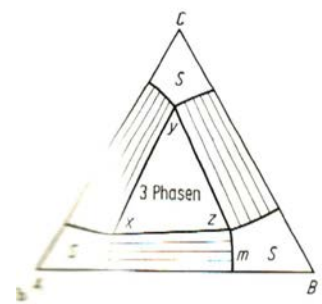


FIGURE 1.41
(a) Free energies of a liquid and three solid phases of a ternary system. (b) A tangential plane construction to the free energy surfaces defines equilibrium between *s* and *l* in the ternary system, (c) Isothermal section through a ternary phase diagram obtained in this way with a two-phase region (L1S) and various tie-lines. The amounts of *l* and *s* at point *x* are determined by the lever rule. (After P. Haasen, *Physical Metallurgy*, Cambridge University Press,



three phase equilibrium



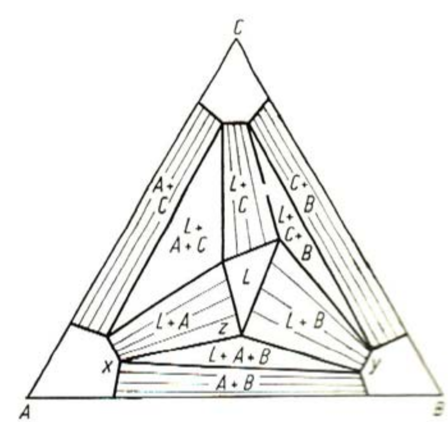


Abb. 5.23. Schnitt durch ternäres Zustandsdiagramm bei Temperatur oberhalb der ternären eutektischen, aber unterhalb aller binären T_E

D. A. Porter, K. E. Easterling, Phase Transformations in Metals and Alloys, CRC Press, 1992
P. Haasen, Physikalische Metallkunde, Springer Verlag, 2013

Ternary phase diagrams

for enlargements
of small composition ranges
the rectangular diagram is useful

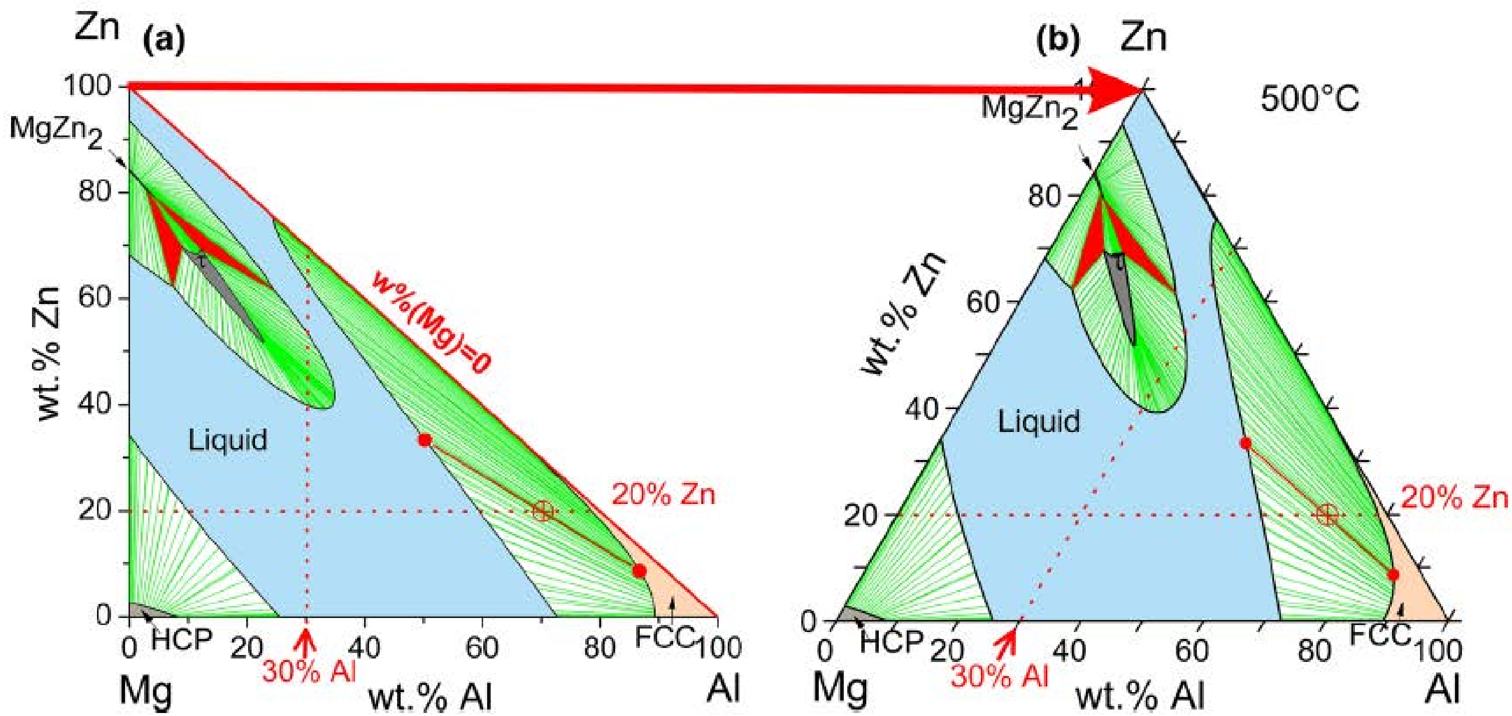
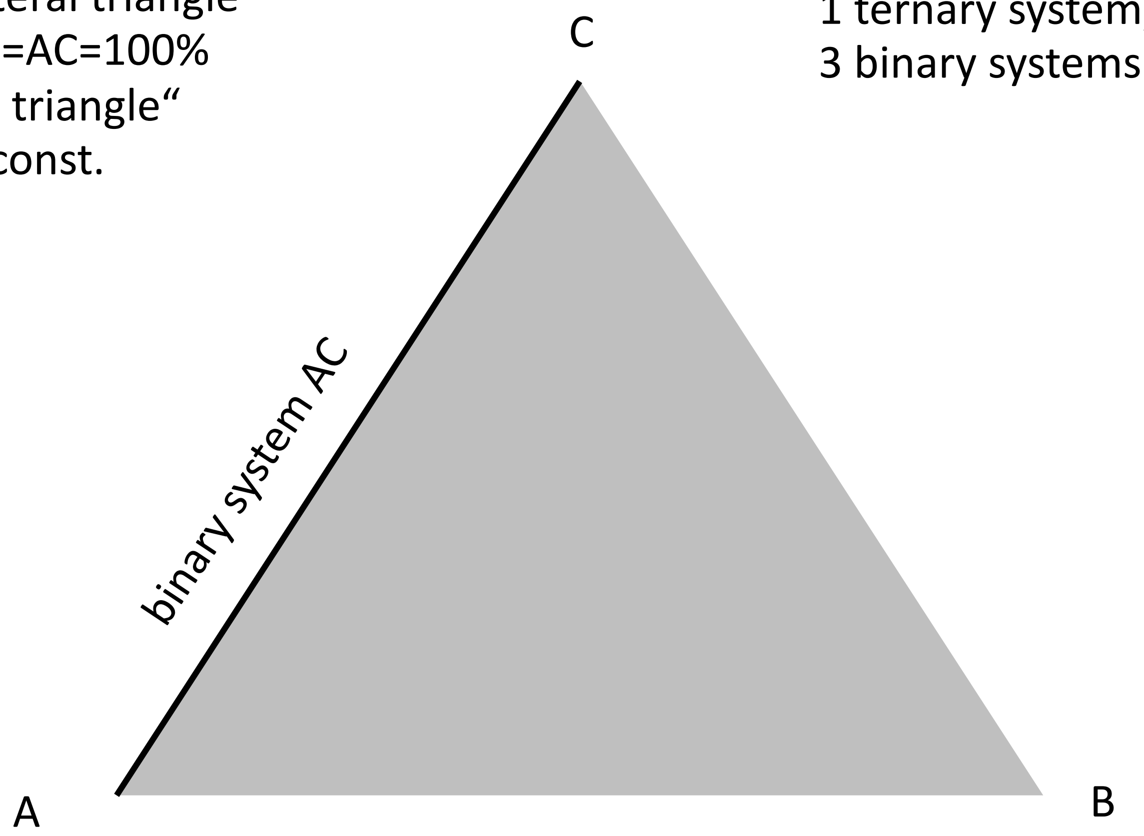


Fig. 7 Isothermal section of the Mg-Al-Zn phase diagram at 500 °C displayed in (a) rectangular coordinates, and (b) in the equilateral composition triangle. The L + FCC tie line passing through the state point of the alloy Mg10Al70Zn20 (wt.%) is highlighted

Schmid-Fetzer, R. J. Phase Equilib. Diffus. (2014) 35: 735

Ternary phase diagram (isobaric, isothermal)

equilateral triangle
AC=AB=AC=100%
„Gibbs triangle“
p, T = const.



1 ternary system, C=3 (A,B,C)
3 binary systems: A-B, A-C, B-C

Phase rule

F+P=C+2

p=const
F+P=C+1

Ternary phase diagrams: Determining compositions

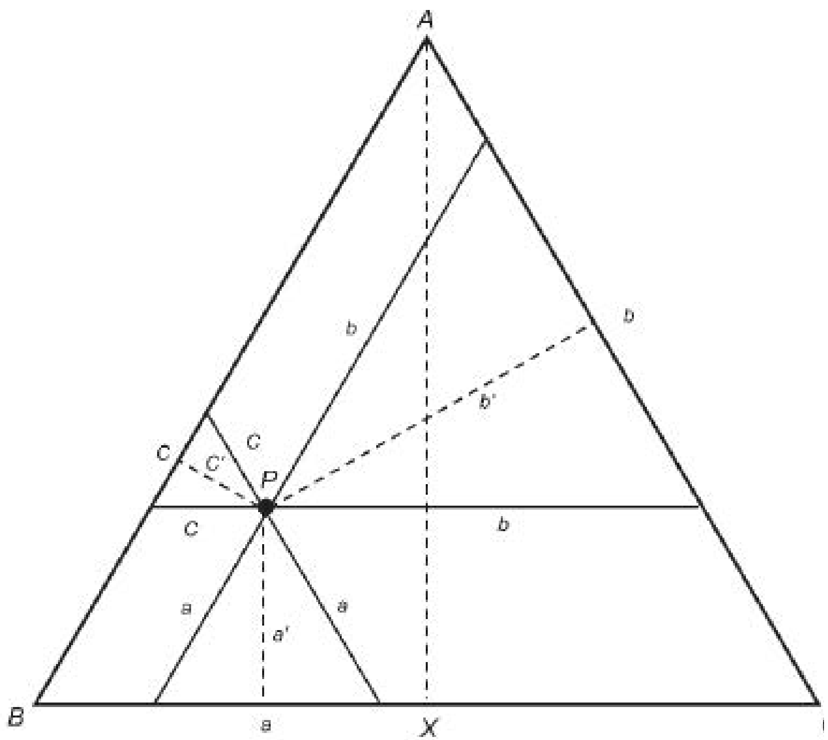
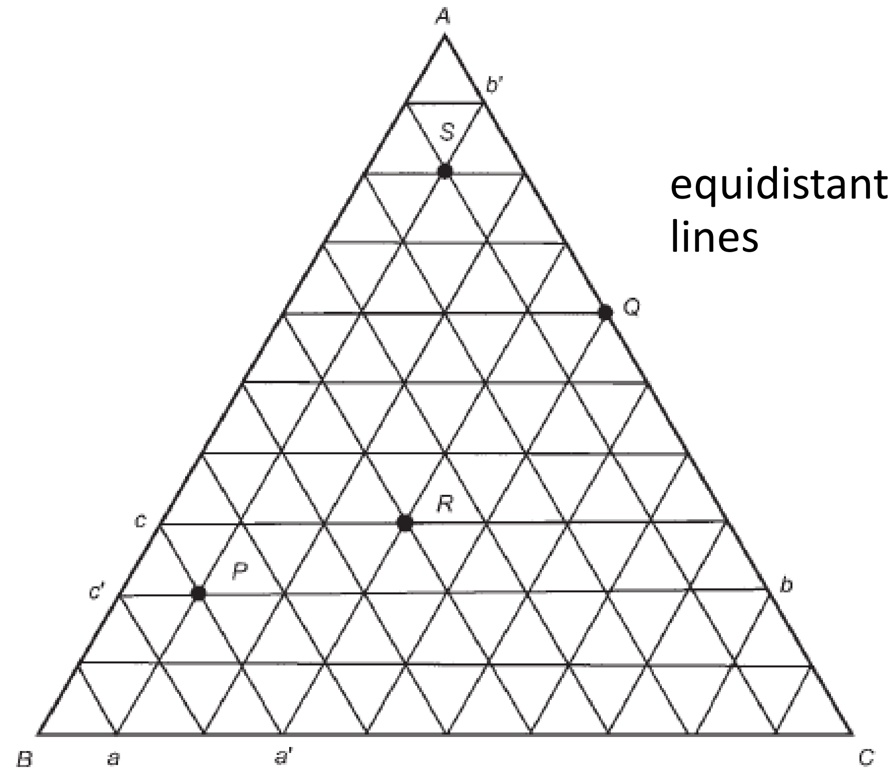


Fig. 10.7 The Gibbs triangle. Adapted from Ref 10.3



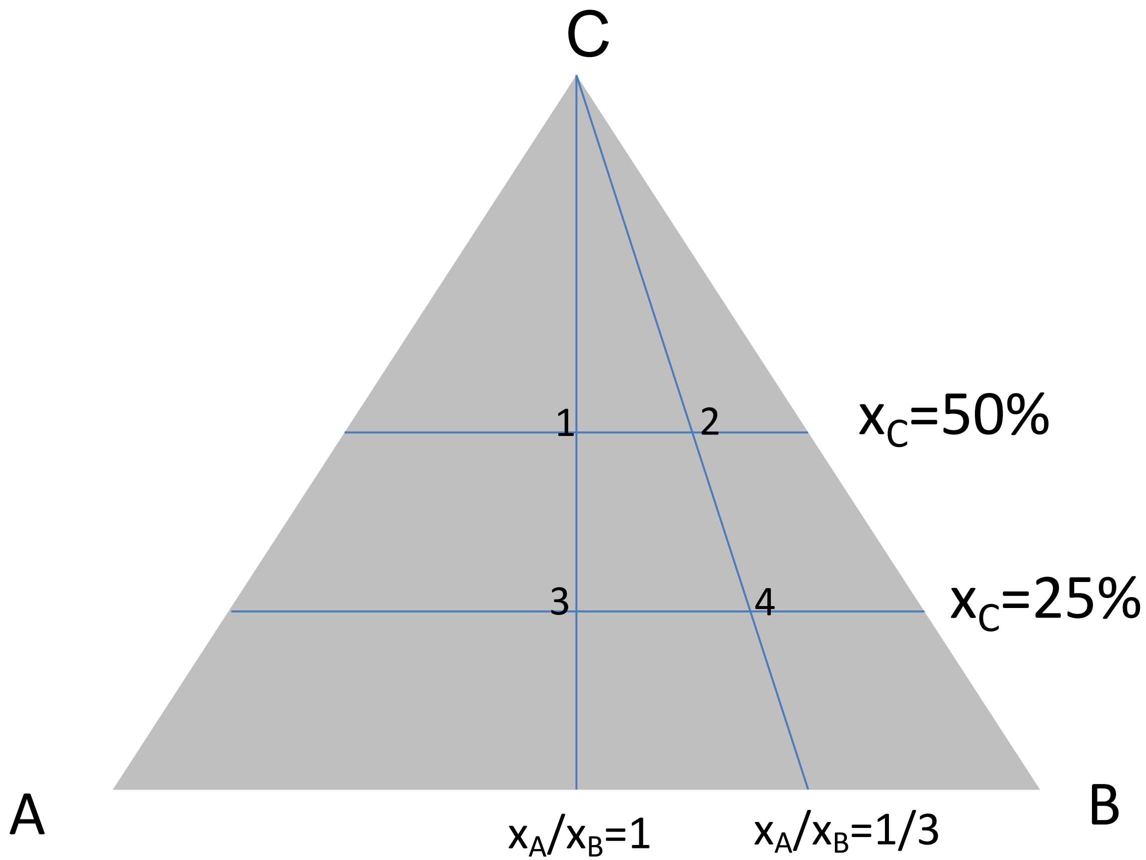
equidistant lines

Fig. 10.8 The Gibbs triangle with composition lines. Adapted from Ref 10.3

the percentage of *C* by the line *Pc* (or *Pc*′), 10 units long. Other examples shown in Fig. 10.8 are: Alloy *R* = 30% *A* + 40% *B* + 30% *C*, Alloy *S* = 80% *A* + 10% *B* + 10% *C*, and Alloy *Q* = 60% *A* + 0% *B* + 40% *C*.

F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

Ternary phase diagrams: ternary stoichiometric phases and lines of constant binary ratios



1: ABC_2
2: AB_3C_4
3: $A_3B_3C_2$
4: $A_3B_9C_4$

A ternary system can comprise stoichiometric ternary phases, e.g. ABC_2 and/or areas with variable composition

Ternary phase diagrams

components of ternary systems can be also compounds

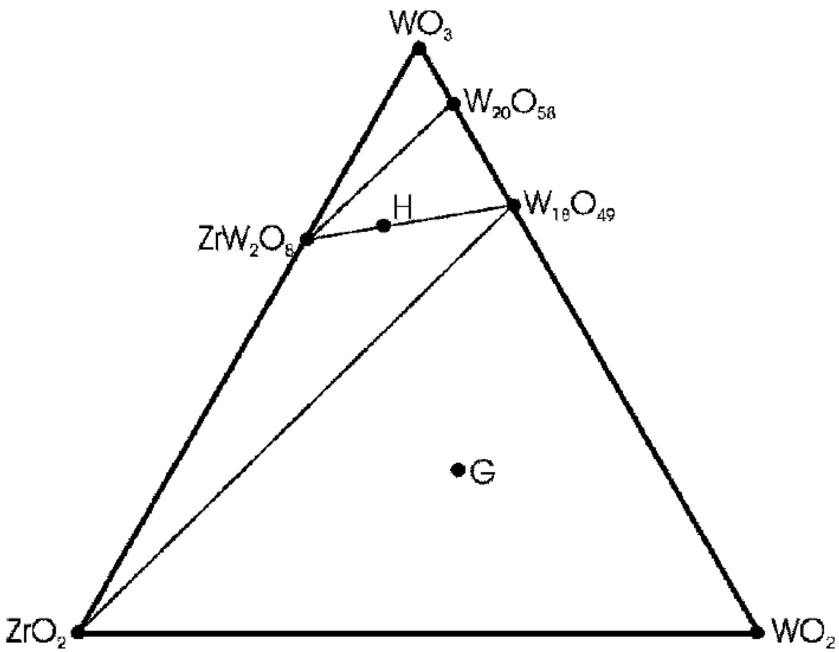


Figure 4.20 The simplified WO_3–WO_2–ZrO_2 phase diagram

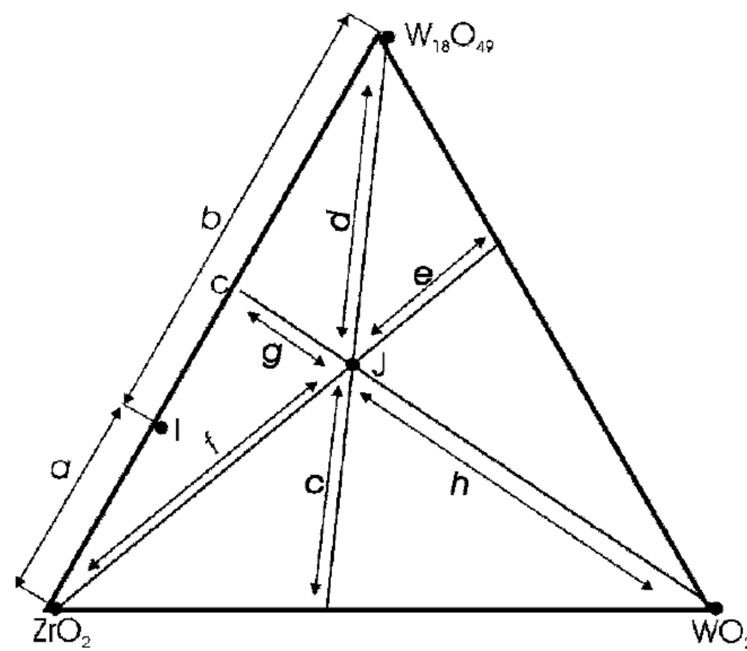


Figure 4.21 The method of determination of compositions on an isothermal phase diagram

tie lines and tie triangles

R. J. D. Tilley, Understanding Solids: The Science of Materials, John Wiley & Sons, 2013

Ternary phase diagrams: Tie lines, lever rules

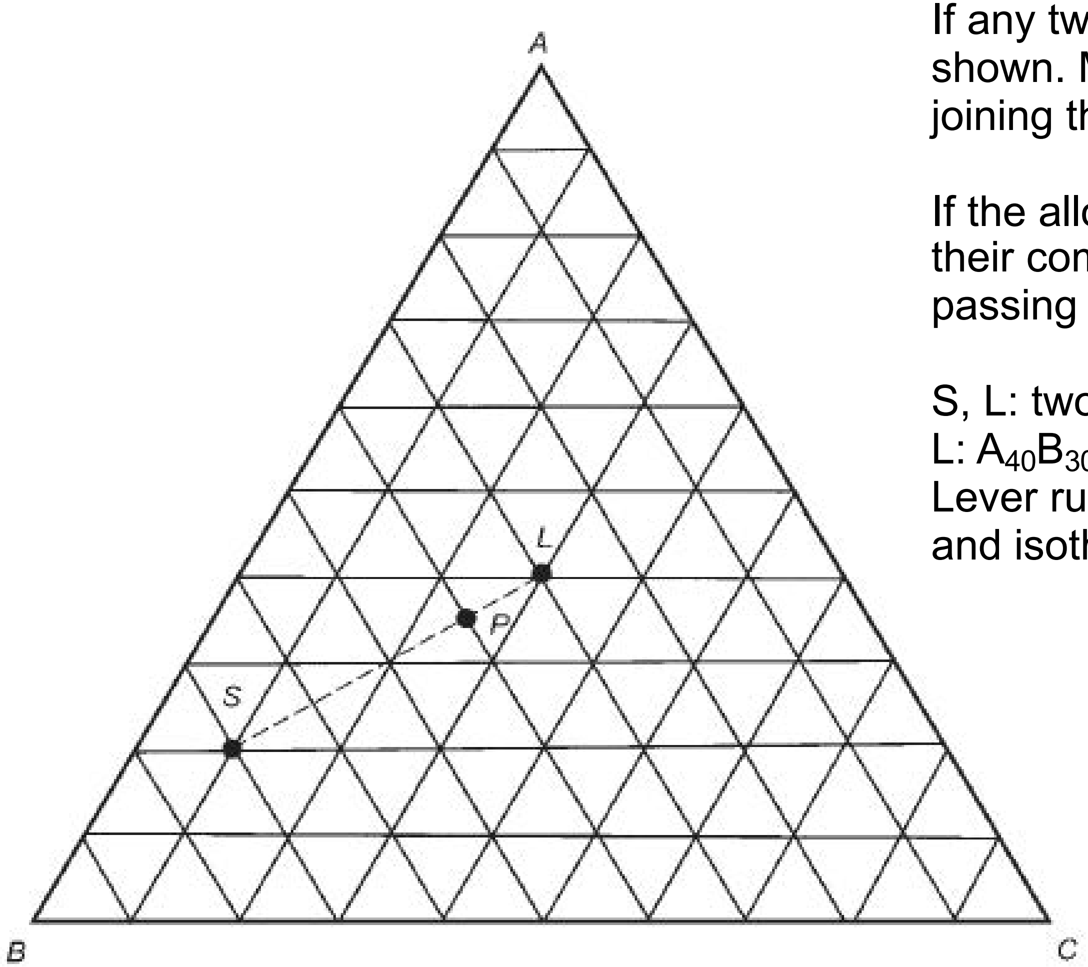


Fig. 10.9 The Gibbs triangle with tie line. Adapted from Ref 10.3

If any two ternary alloys are mixed tie lines can be shown. Mixture compositions will lie on a straight line joining the original compositions.

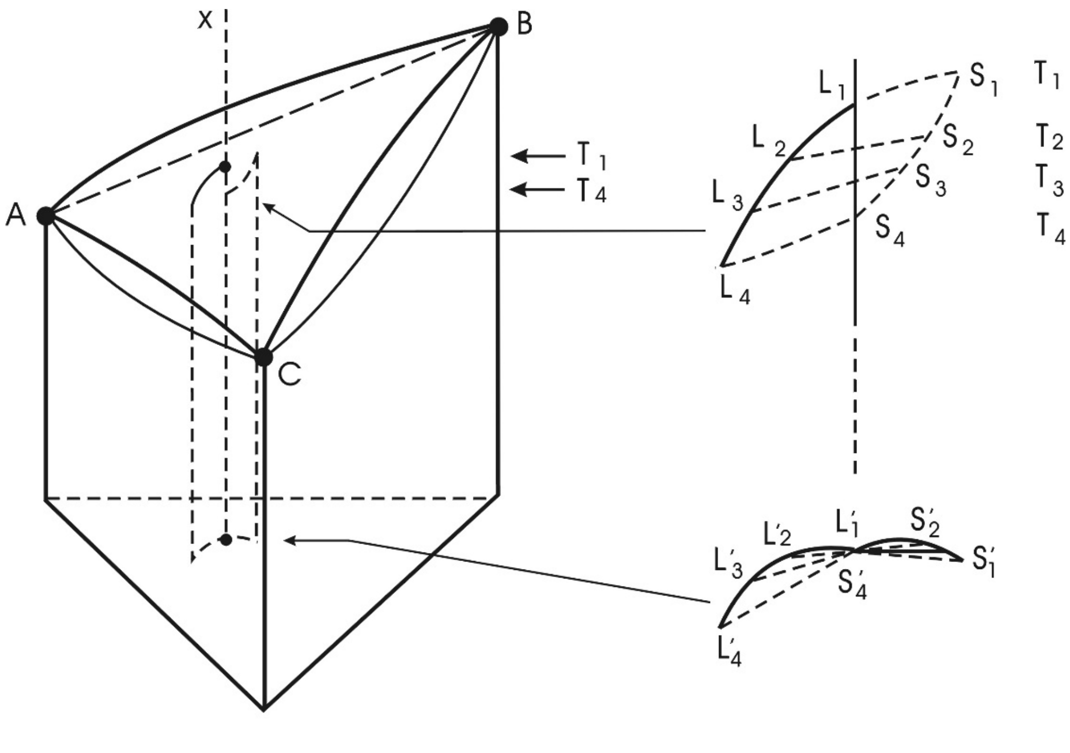
If the alloy decomposes in two fractions, ‘
their composition will lie on the ends of a straight line passing through the original composition.

S, L: two ternary alloys of composition $S=A_{20}B_{70}C_{10}$,
L: $A_{40}B_{30}C_{30}$. P: 25%S+75%L
Lever rule can be applied as the diagram is isobaric and isothermal.

$$\% S = \frac{PL}{SL} \times 100$$

$$\% L = \frac{SP}{SL} \times 100$$

Ternary isomorphous phase diagram: example of solidification of an alloy x

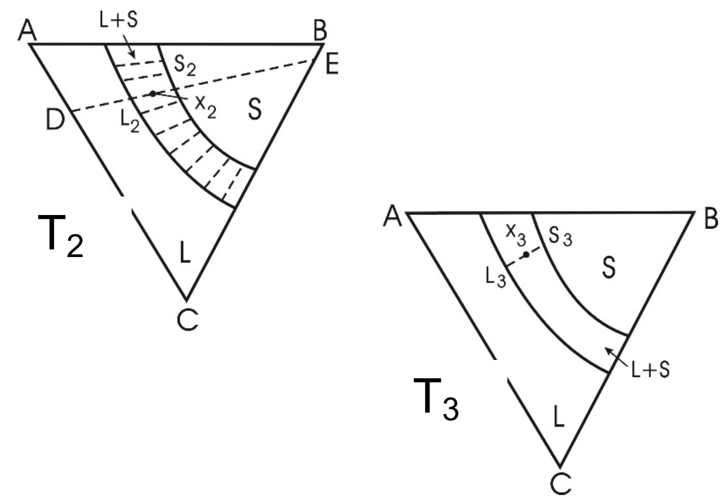


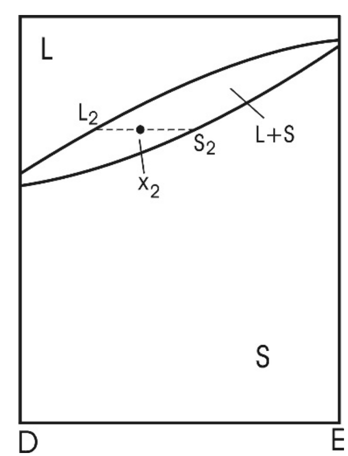
(a)

(b)

L1, L2, … on liquidus surface
S1, S2, … on solidus surface

isothermal cuts

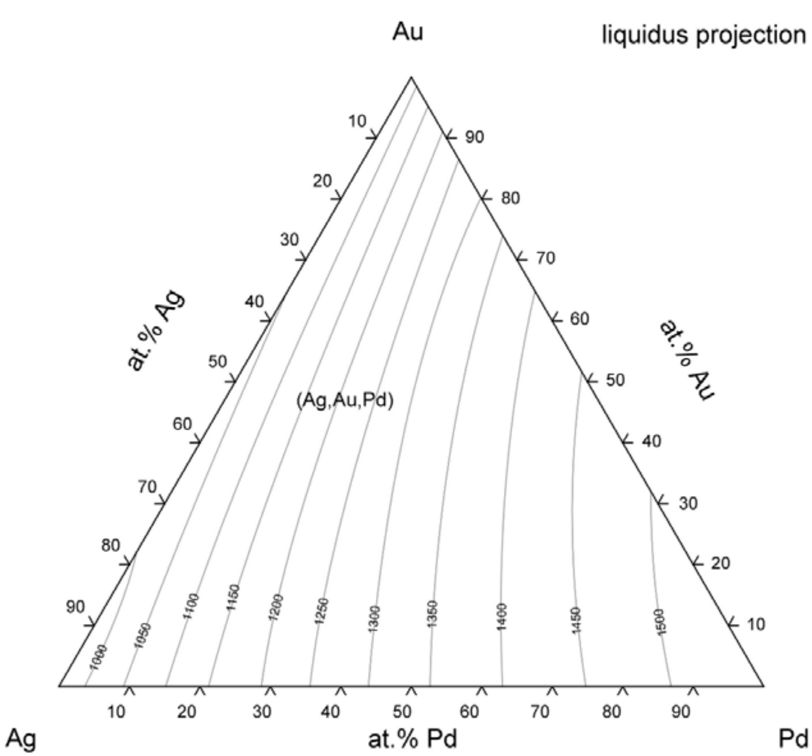


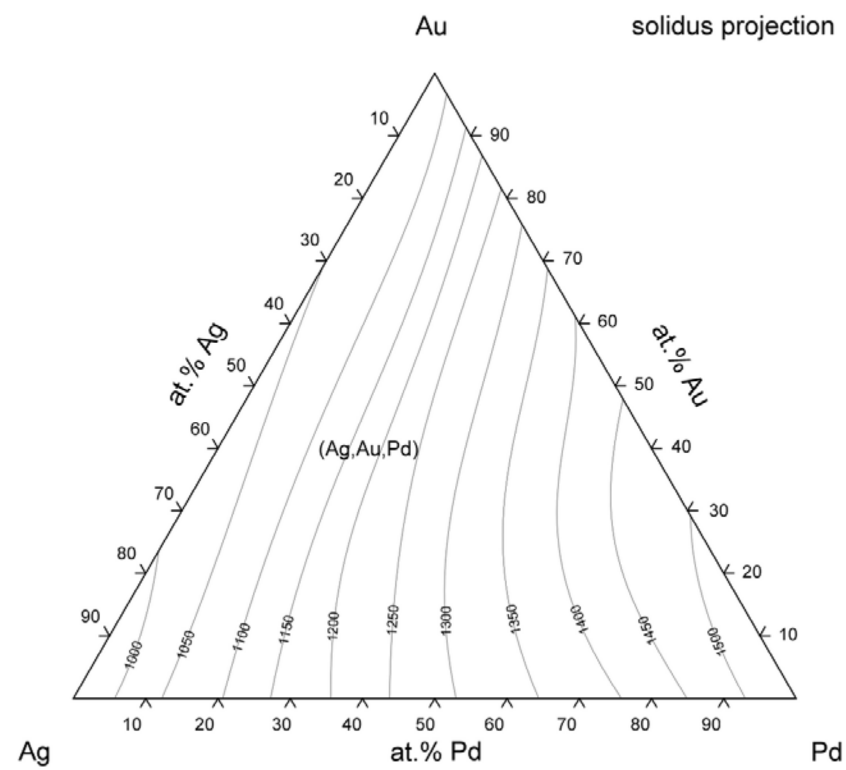


vertical section
=quasibinary cut
= isopleth

E. Hornbogen, G. Eggeler, E. Werner, Werkstoffe: Aufbau und Eigenschaften… , Springer Verlag, 2017

Ternary isomorphous phase diagram: projection of liquidus temperatures





all fcc

Alloy Phase Diagram Database: http://www1.asminternational.org/asmenterprise/APD/default.aspx

Three phase equilibrium in ternary systems: Tie triangle

Three phase equilibrium in ternary systems occurs over a temperature range (bivariant)

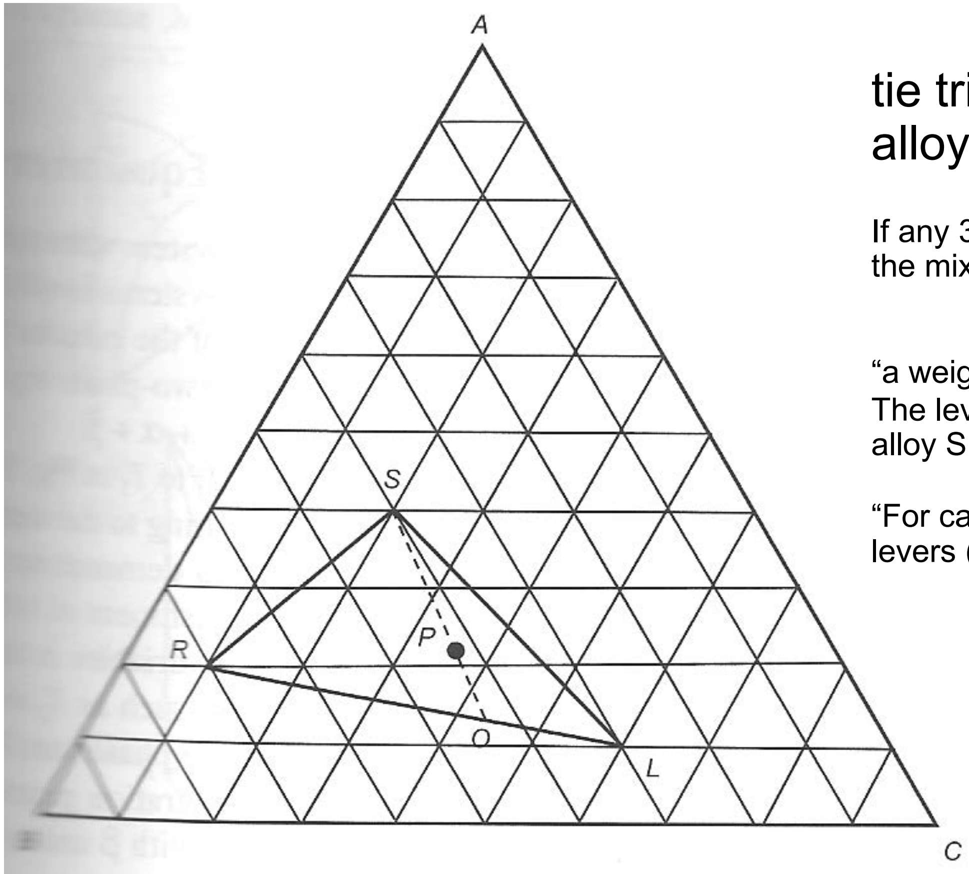


Fig. 10.19 Analysis of a tie triangle. Adapted from Ref 10.3

tie triangle:
alloys S, R, L in equilibrium

If any 3 alloys of a ternary system are mixed,
the mixture composition will lie within the triangle.

“a weightless plane triangle (here: RSL) supported on a point fulcrum at P” The lever plane balances: “if 20% of alloy R is placed on point R, 30% of alloy S and 50% of alloy L on point L”

“For calculation, it is convenient to resolve the planar lever into two linear levers (here SPO, ROL)”

F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012, pp. 208-210

Three phase equilibrium in a ternary system (I)

one isomorphous binary and two eutectic binaries

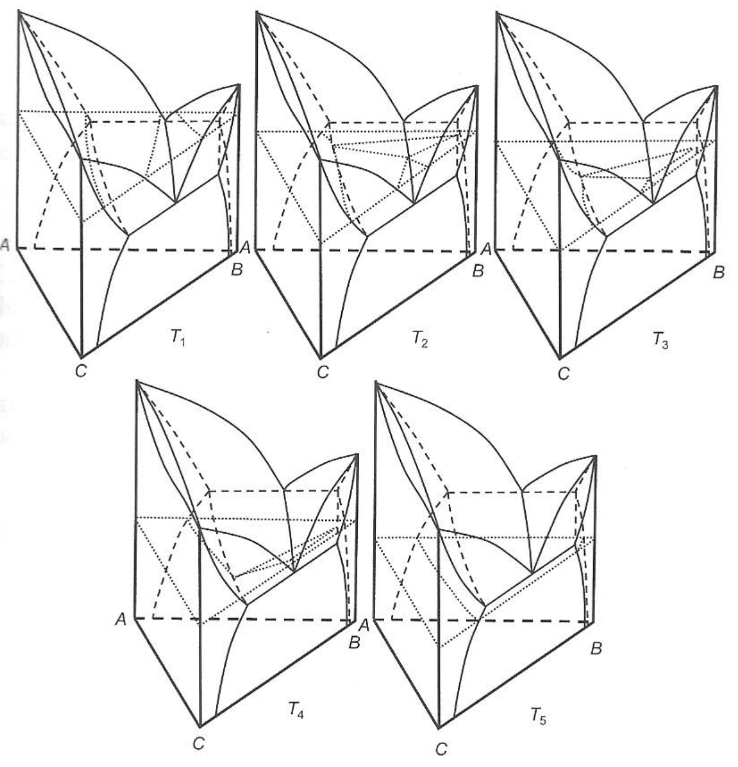


Fig. 10.21 Development of isotherms shown in Fig. 10.22. Adapted from Ref 10.3

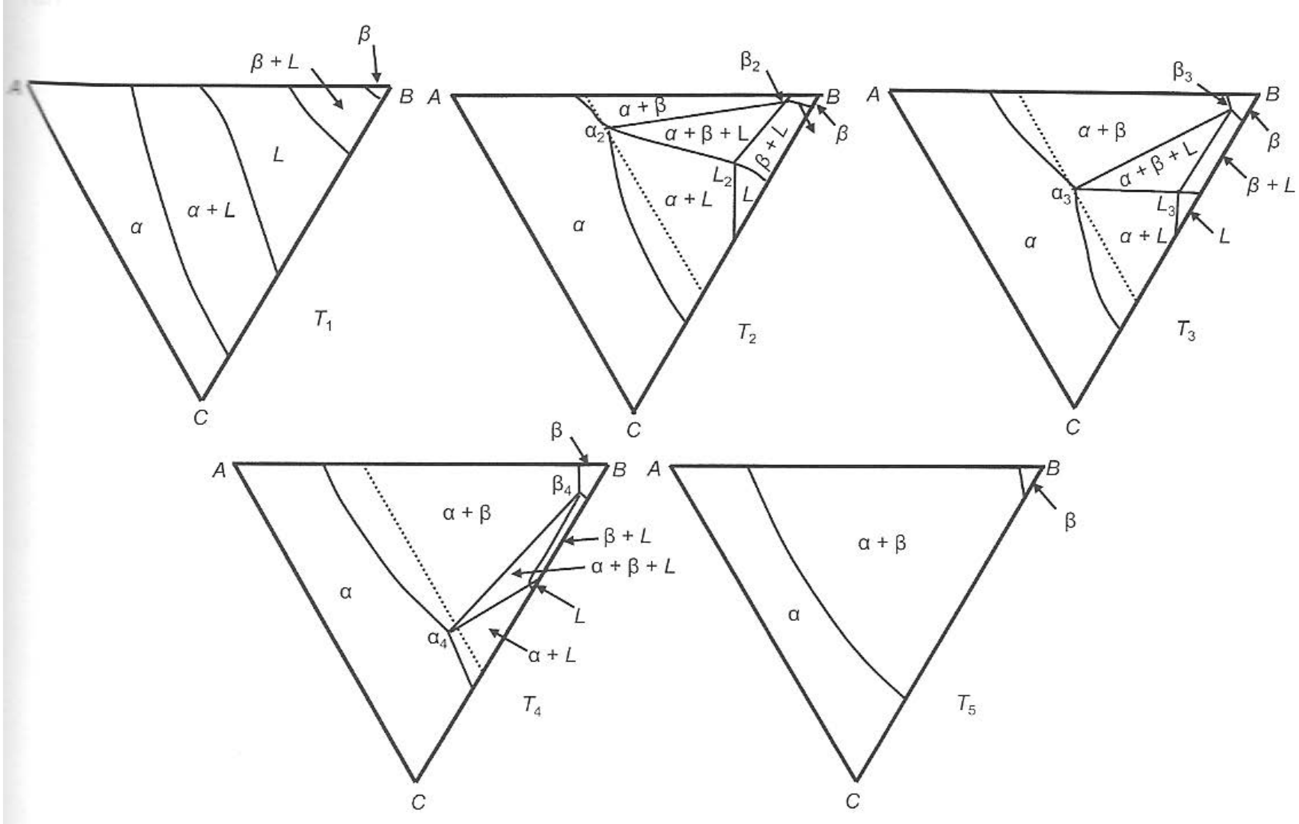


Fig. 10.22 Isotherms through the space diagrams of Fig. 10.21. Adapted from Ref 10.3

F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

Three phase equilibrium in a ternary system (II)

2 eutectic binaries, 1 isomorphous binary

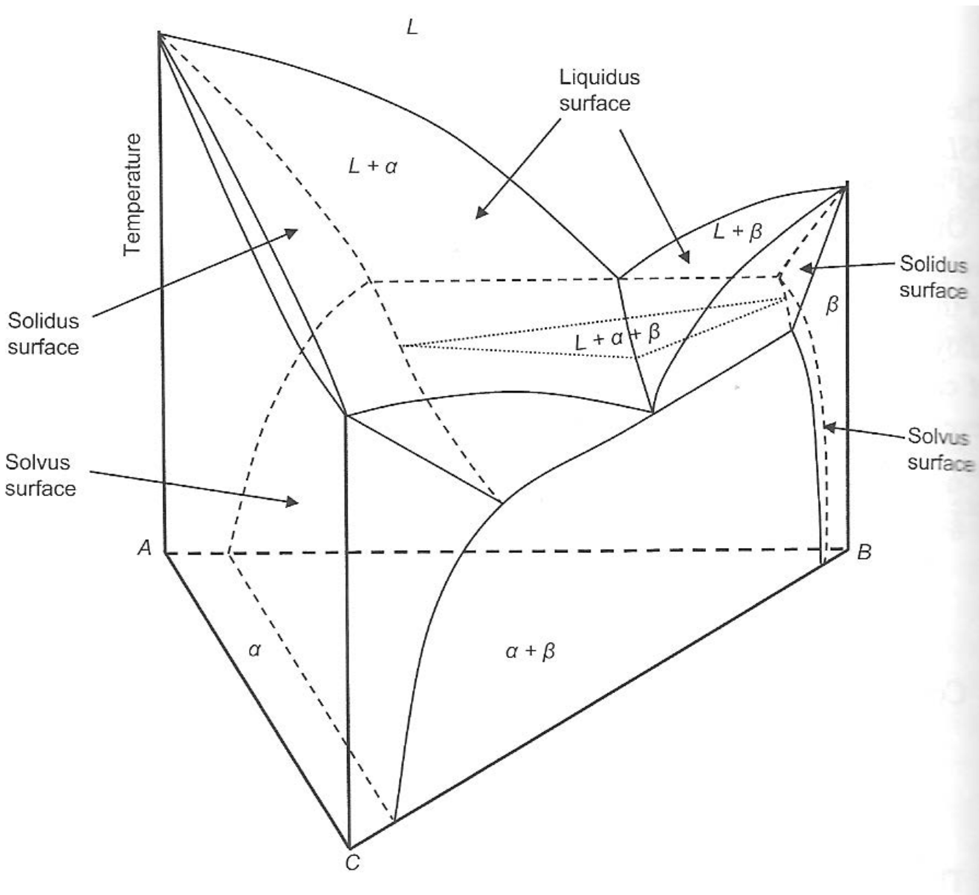
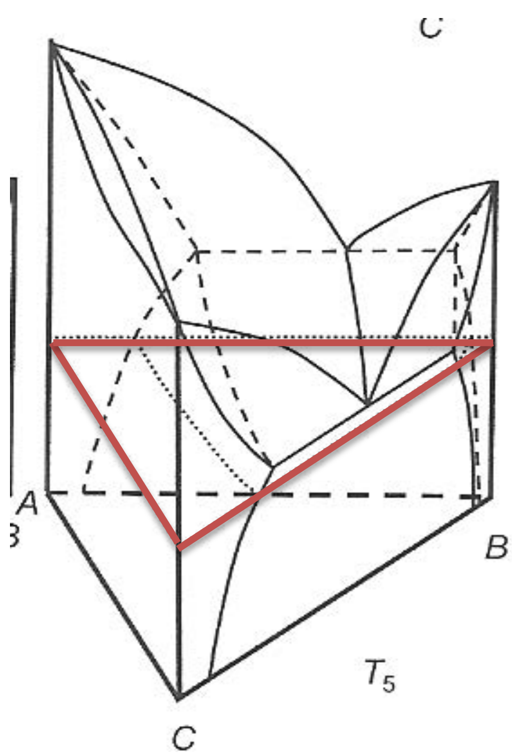
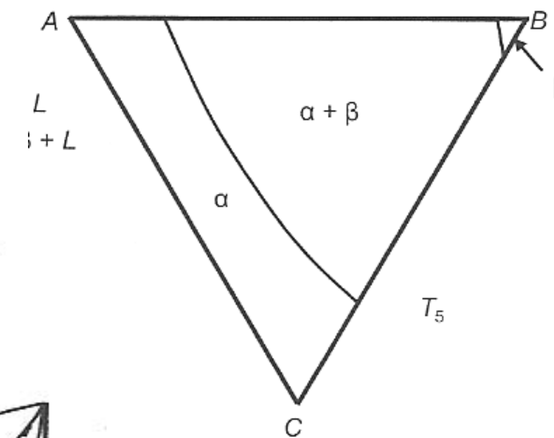


Fig. 10.20 Three-phase equilibria in a ternary system with a eutectic reaction. Adapted from Ref 10.3



isothermal section at T < $T_{solidus}$

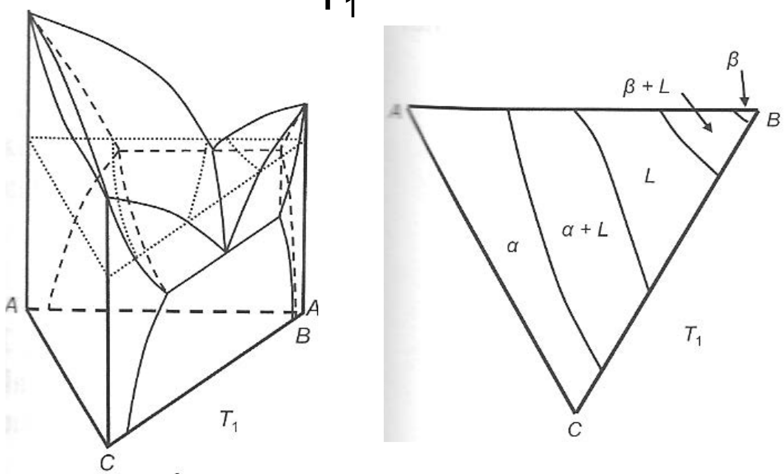


F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

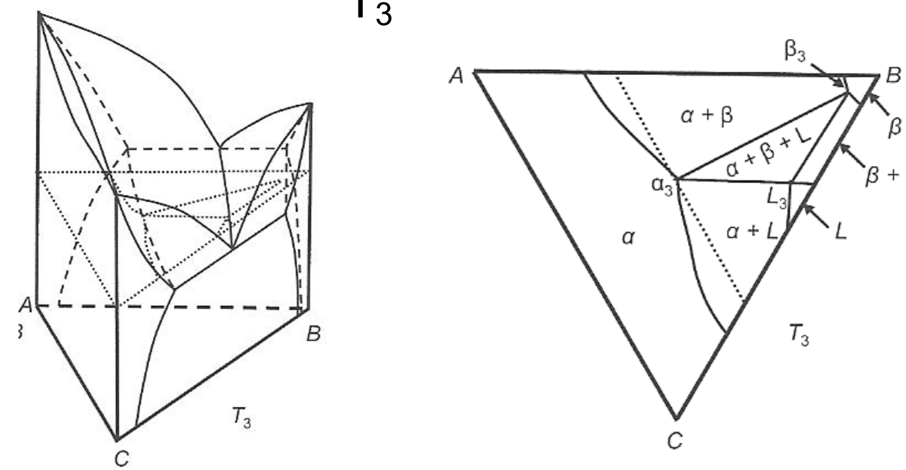
Three phase equilibrium in a ternary system (III)

$T_1 > T_2 > T_3 > T_4$

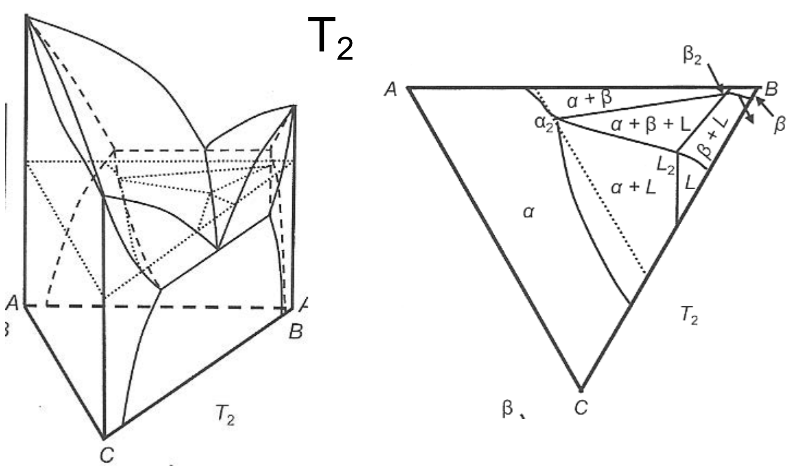
T_1



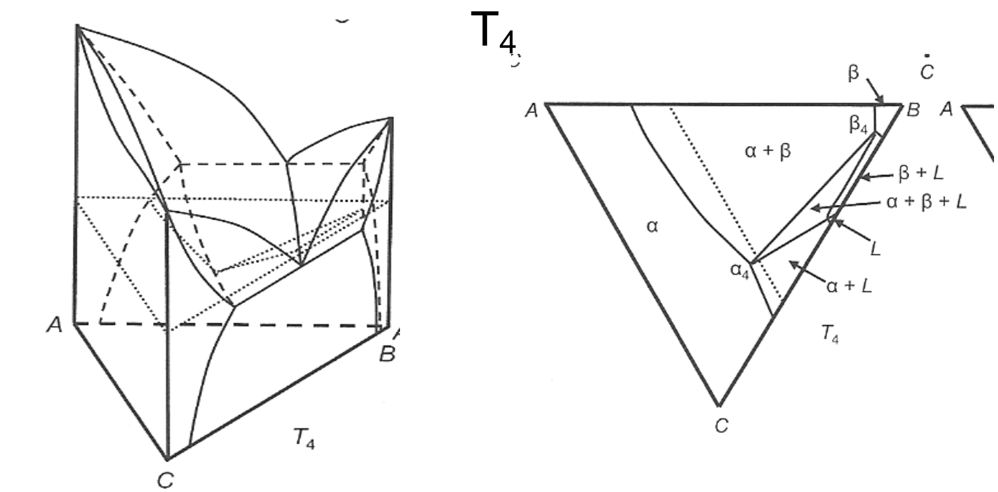
T_3



T_2



T_4



F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

Three phase equilibrium in a ternary system (IV)

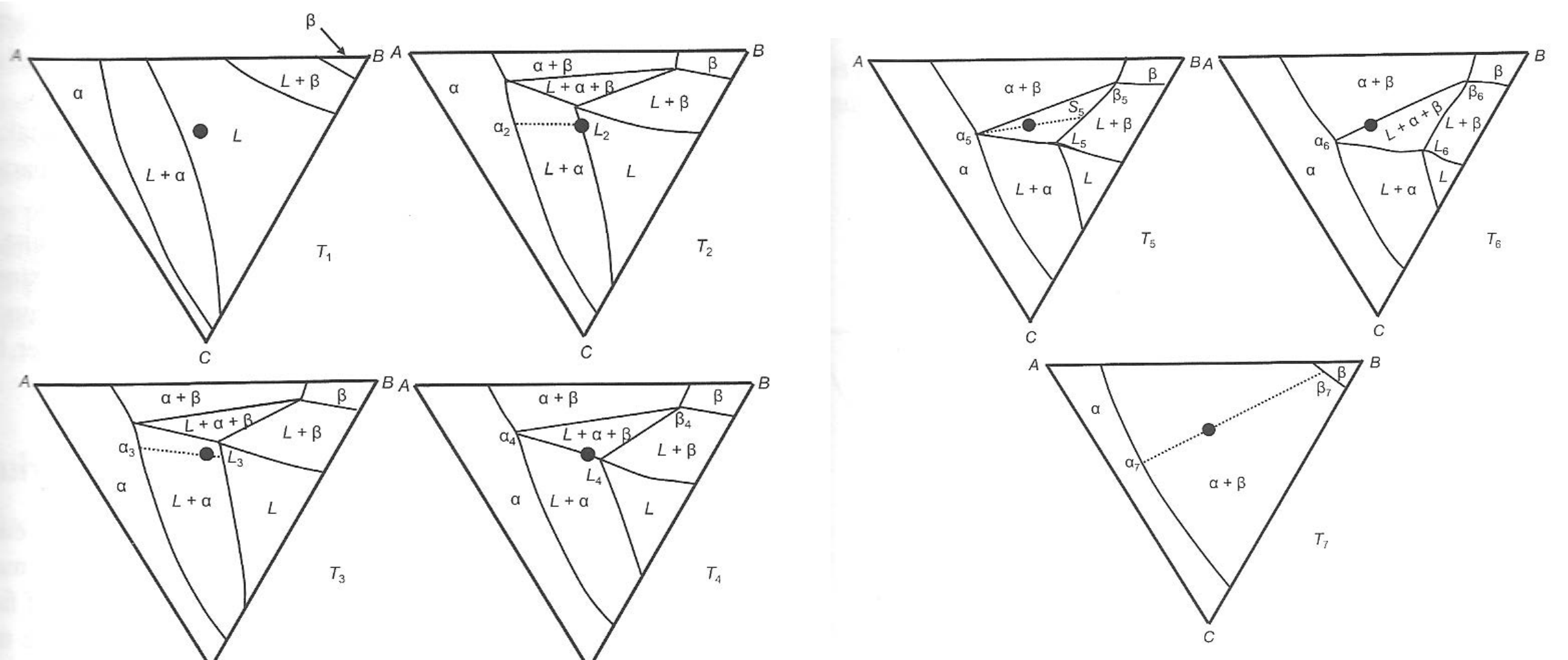


Fig. 10.23 Sequence of equilibria involved in freezing of an alloy, showing gross composition in each isotherm. Adapted from Ref 10.3

F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

Peritectic system with three-phase equilibrium

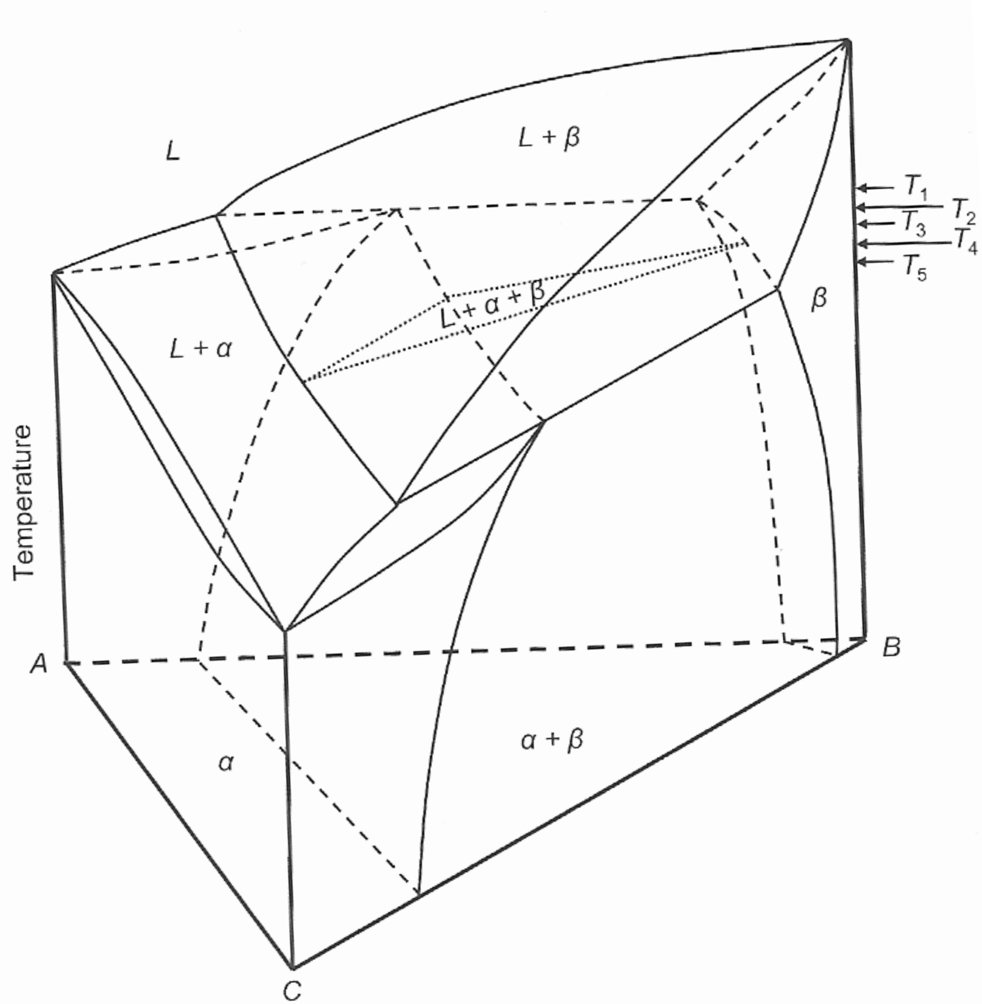


Fig. 10.24 Three-phase equilibria in a ternary system with a peritectic reaction. Adapted from Ref 10.3

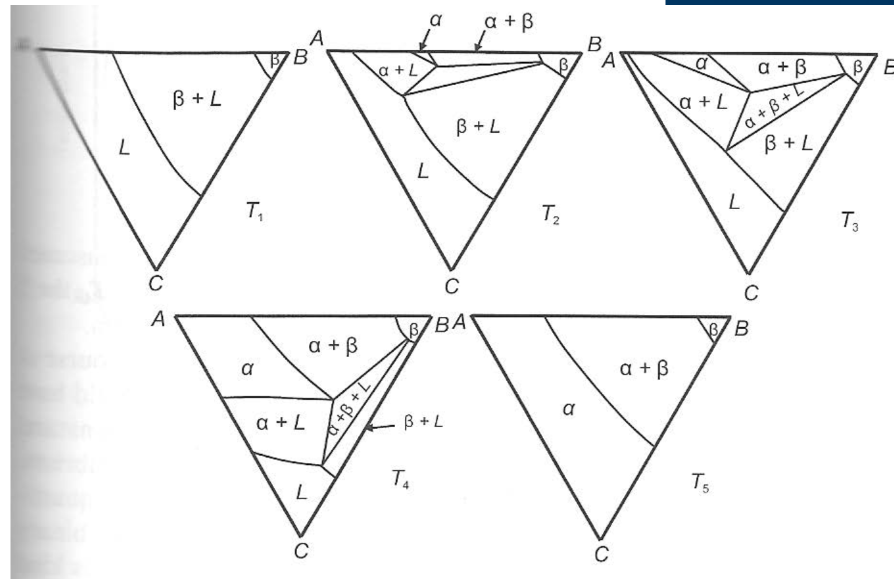


Fig. 10.25 Isotherms through the space diagram of Fig. 10.24. Adapted from Ref 10.3

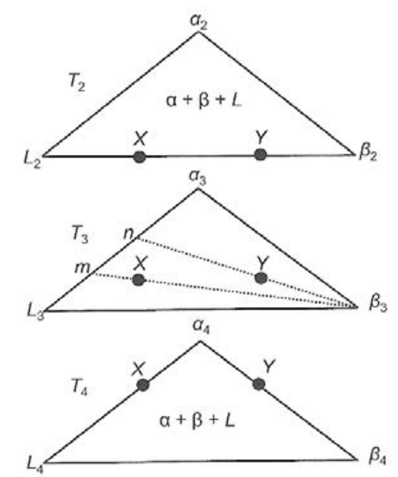
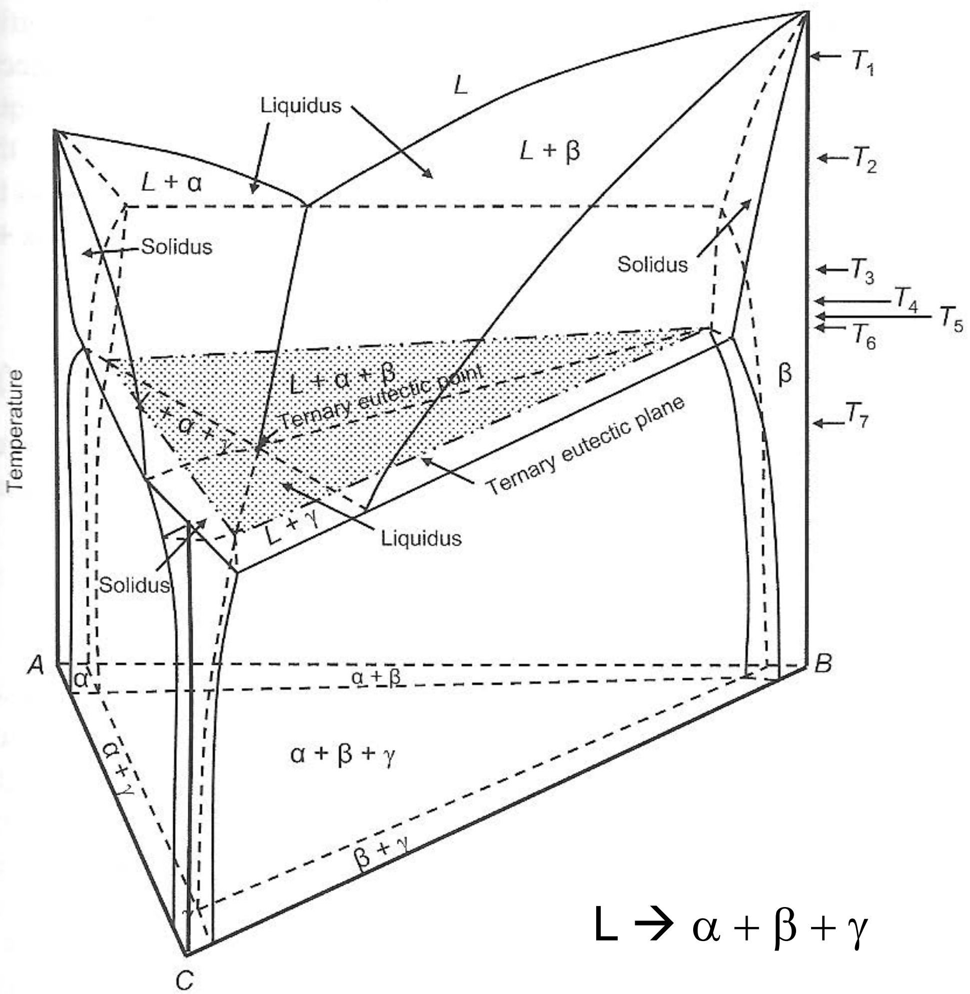


Fig. 10.26 Tie triangles at three different temperatures. Adapted from Ref 10.3

F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

Ternary four-phase equilibrium

$$F = C + 2 - P$$
$$F = 3 + 2 - 4 = 1$$



$$L \rightarrow \alpha + \beta + \gamma$$

Fig. 10.27 Temperature-composition space model of a ternary eutectic system with the reaction $L \rightarrow \alpha + \beta + \gamma$. Adapted from Ref 10.3

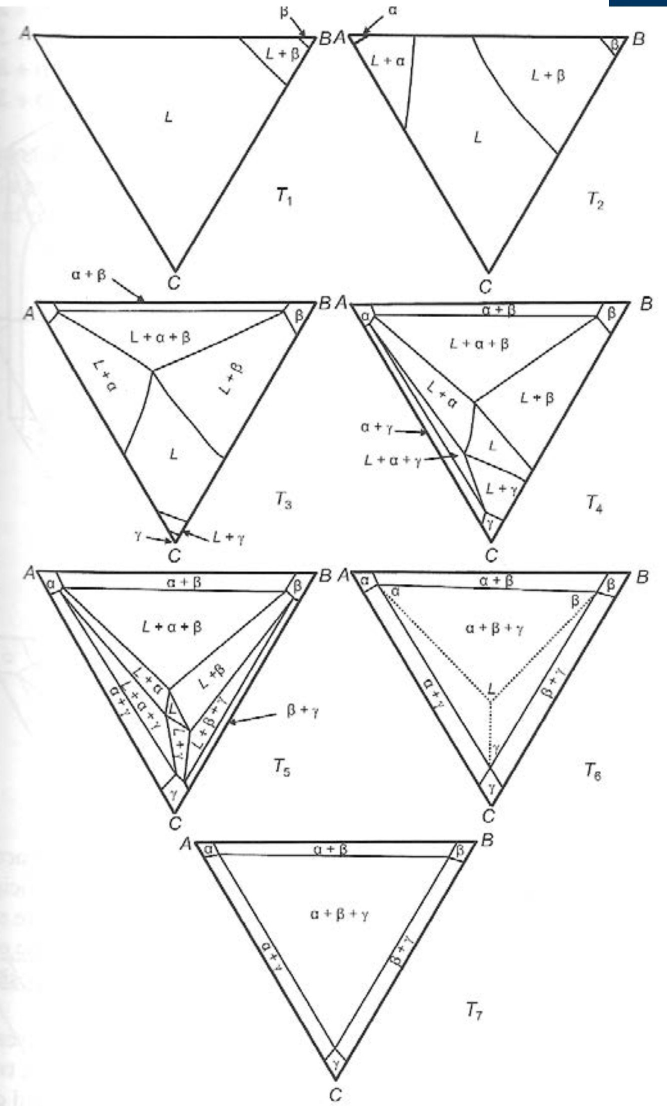


Fig. 10.28 Isotherms taken through space model in Fig. 10.27. Adapted from Ref 10.3

Ternary phase diagram (isobaric, eutectic)

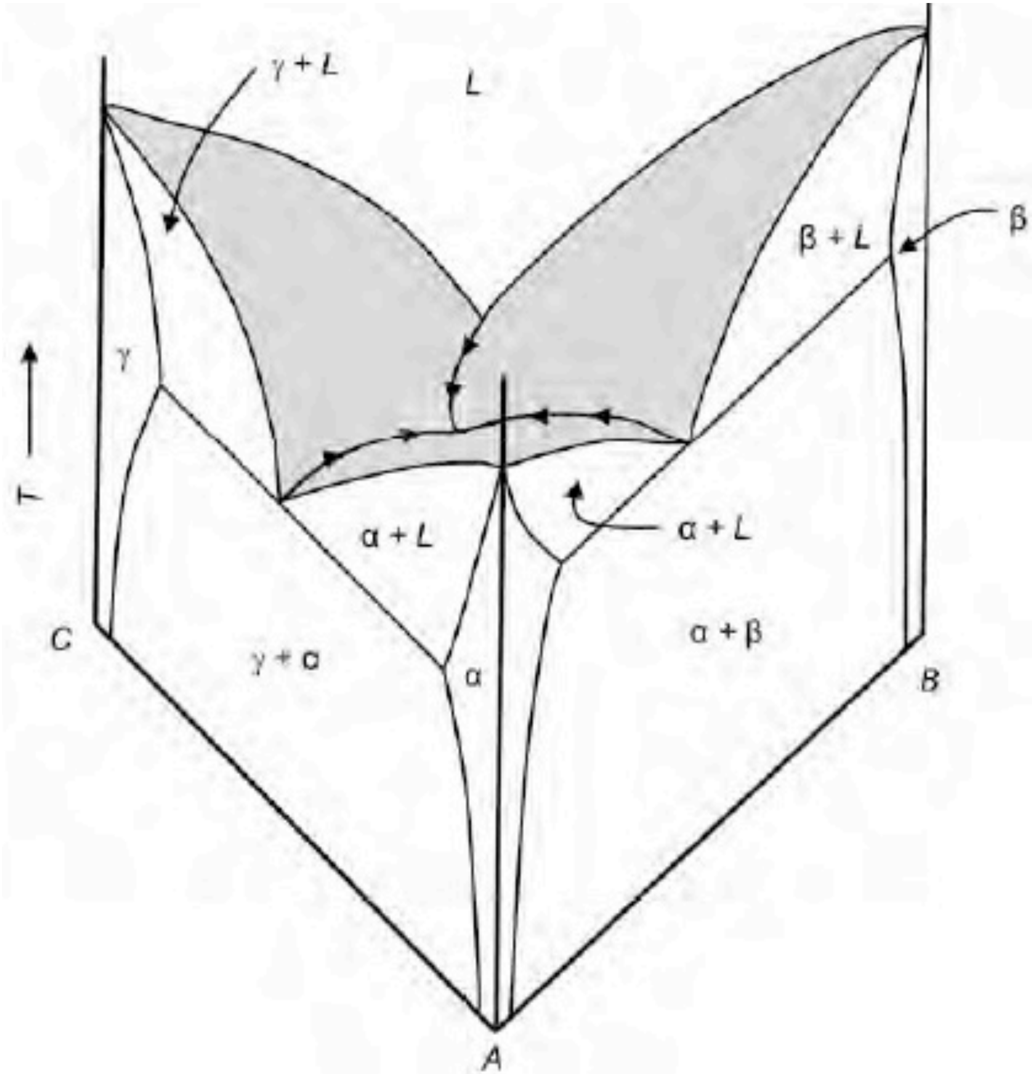


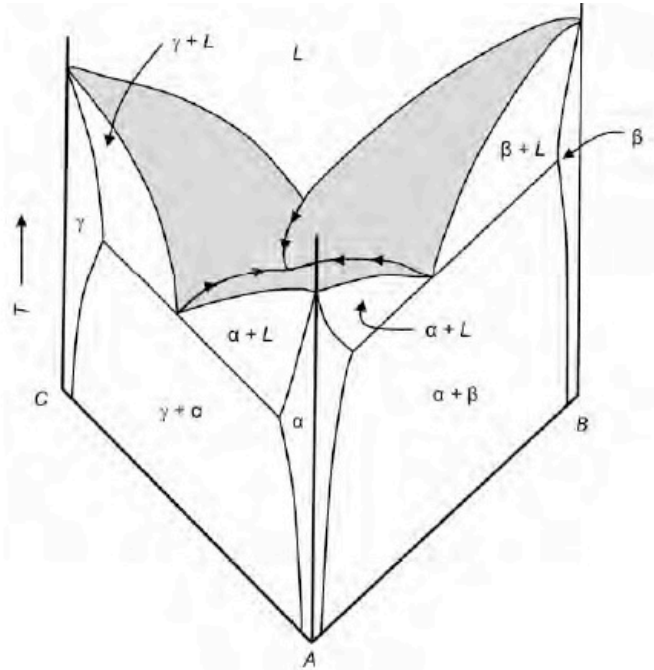
Fig. 10.2 Hypothetical ternary phase diagram. Binary phase diagrams are present along the three faces. Adapted from Ref 10.1

three eutectic binaries

ternary eutectic:
L = $\alpha + \beta + \gamma$

F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

Ternary phase diagram (isobaric, eutectic)



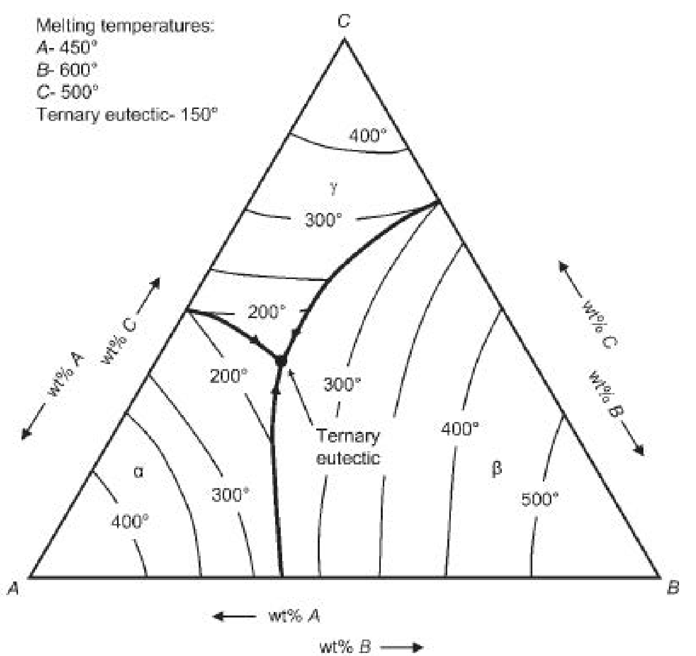
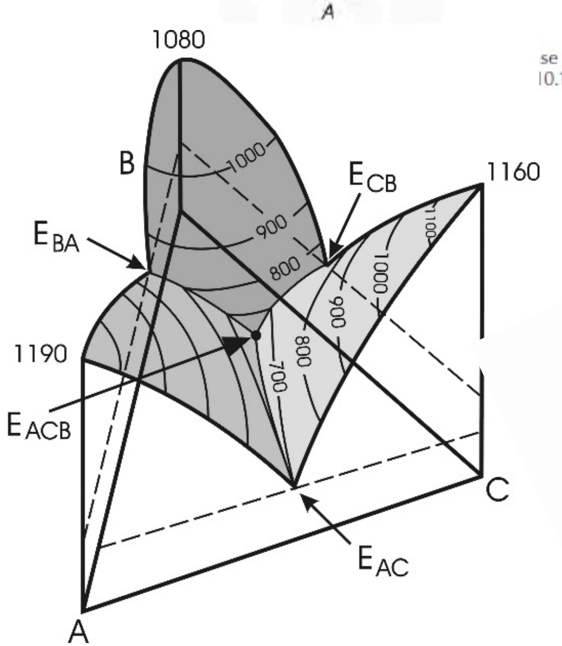
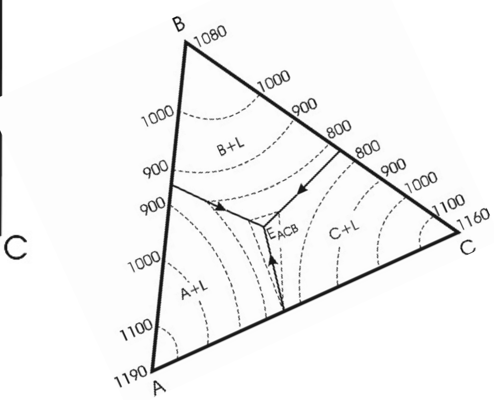
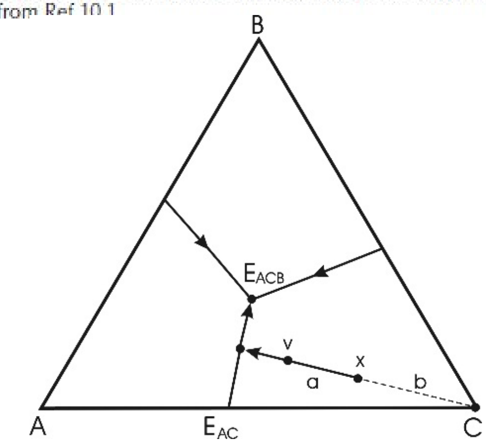


Fig. 10.3 Liquidus plot for hypothetical ternary phase diagram. Adapted from Ref 10.1



se diagrams are
10.1





F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

Example: Fe-Cr-Ni system

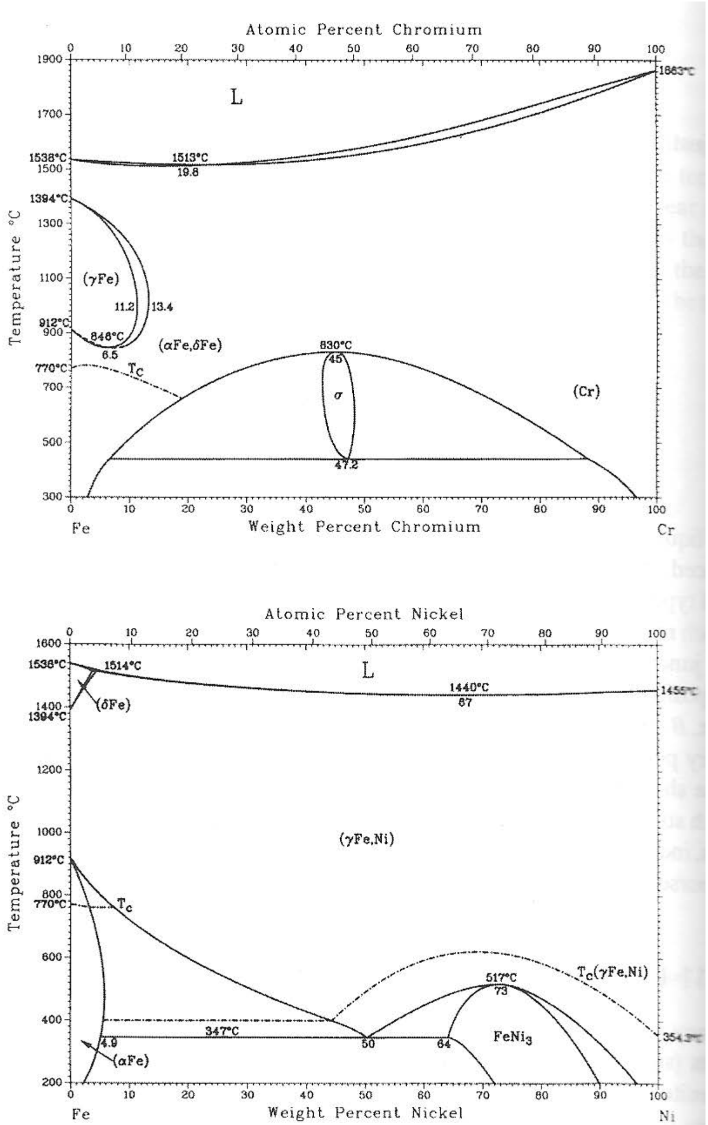


Fig. 10.37 Two representative binary iron phase diagrams, showing ferrite stabilization (iron-chromium) and austenite stabilization (iron-nickel). Source: Ref 10.4 as published in Ref 10.5

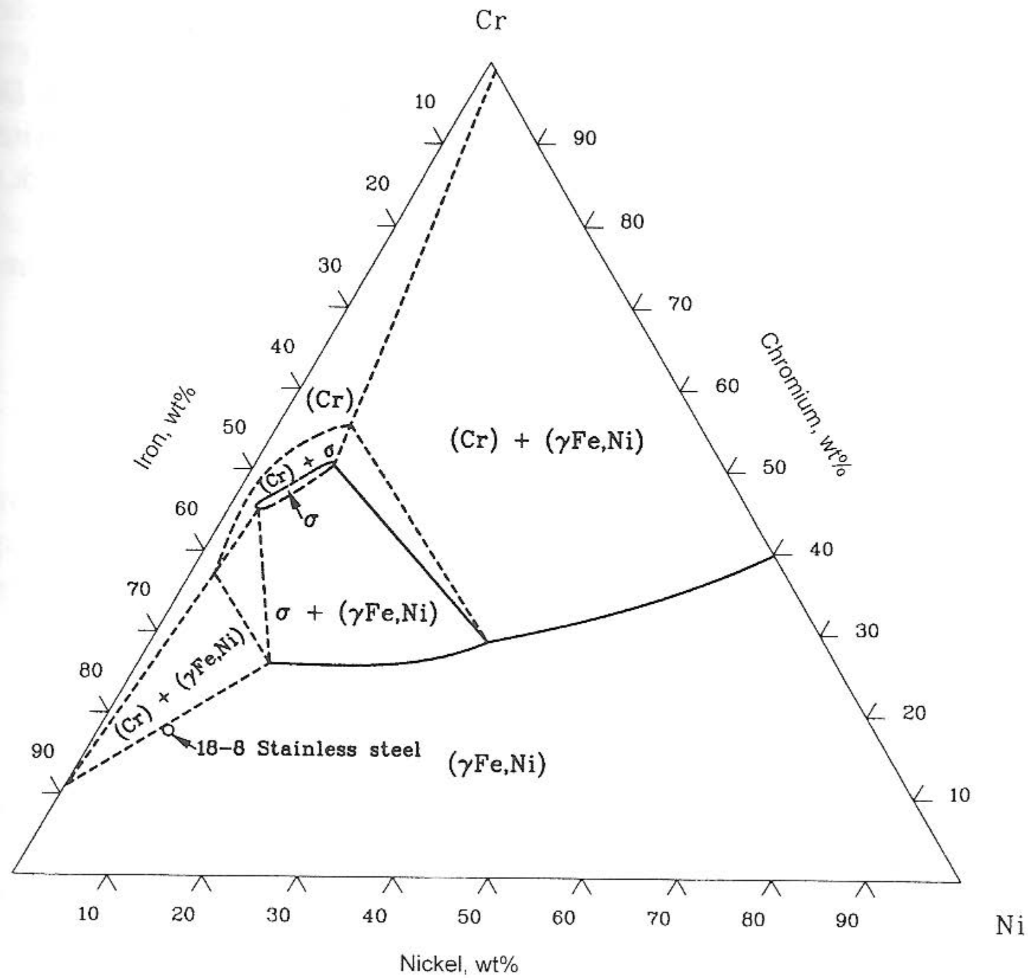
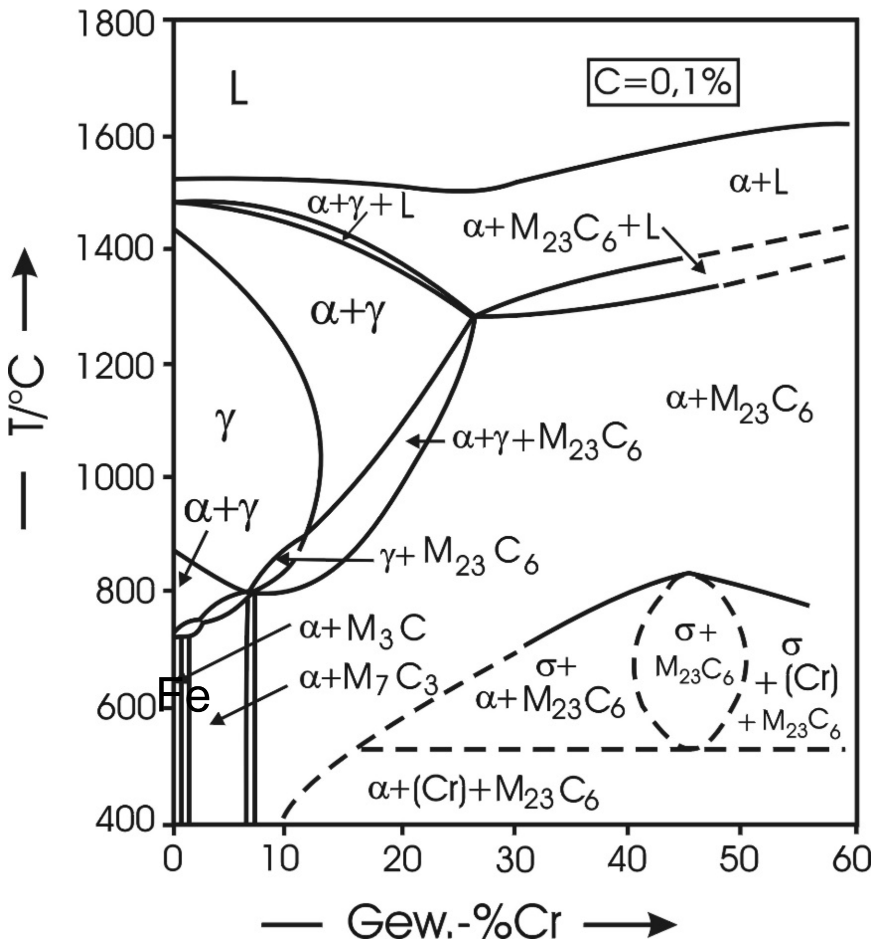


Fig. 10.38 The isothermal section at 900 °C (1652 °F) of the Fe-Cr-Ni ternary phase diagram, showing the nominal composition of 18-8 stainless steel. Source: Ref 10.6 as published in Ref 10.5

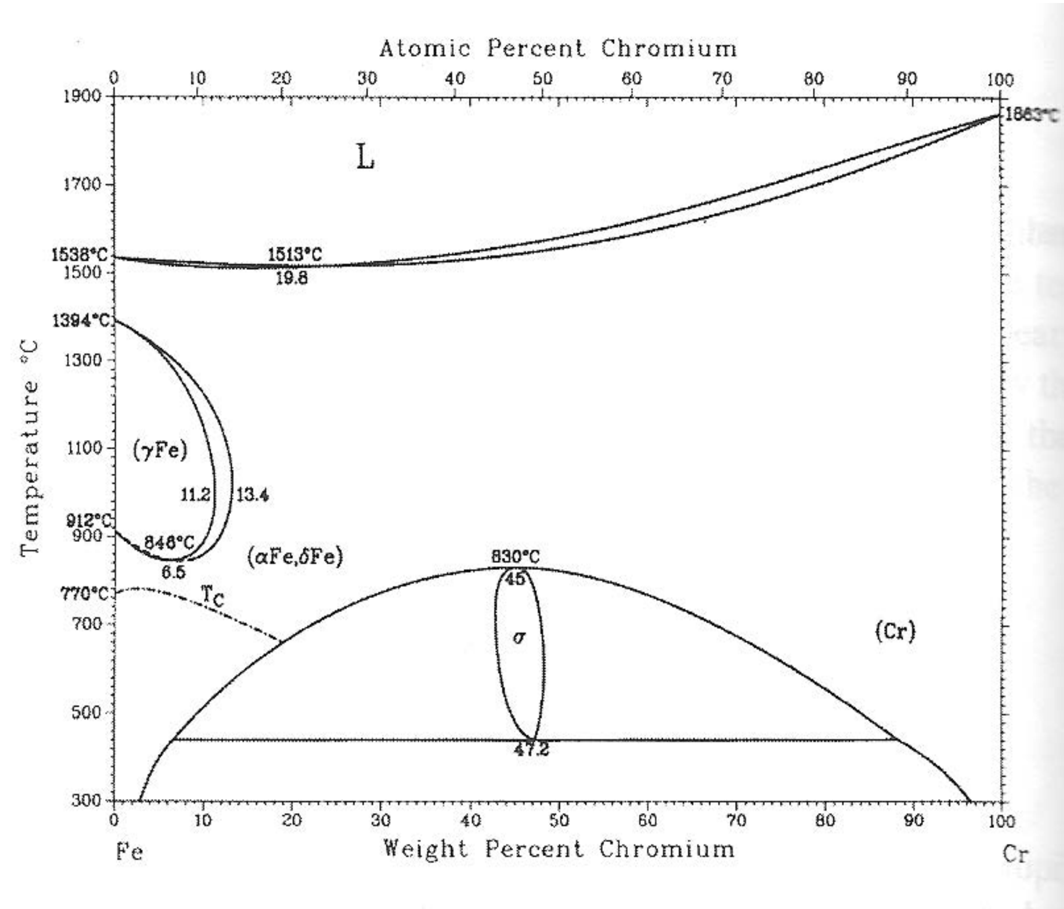
F. C. Campbell, Phase Diagrams: Understanding the Basics, ASM International, 2012

Ternary phase diagrams: quasibinary section

Fe-Cr-C



quasibinary cut



E. Hornbogen, G. Eggeler, E. Werner, Werkstoffe: Aufbau und Eigenschaften… , Springer Verlag, 2017

Quasi-ternary phase diagrams

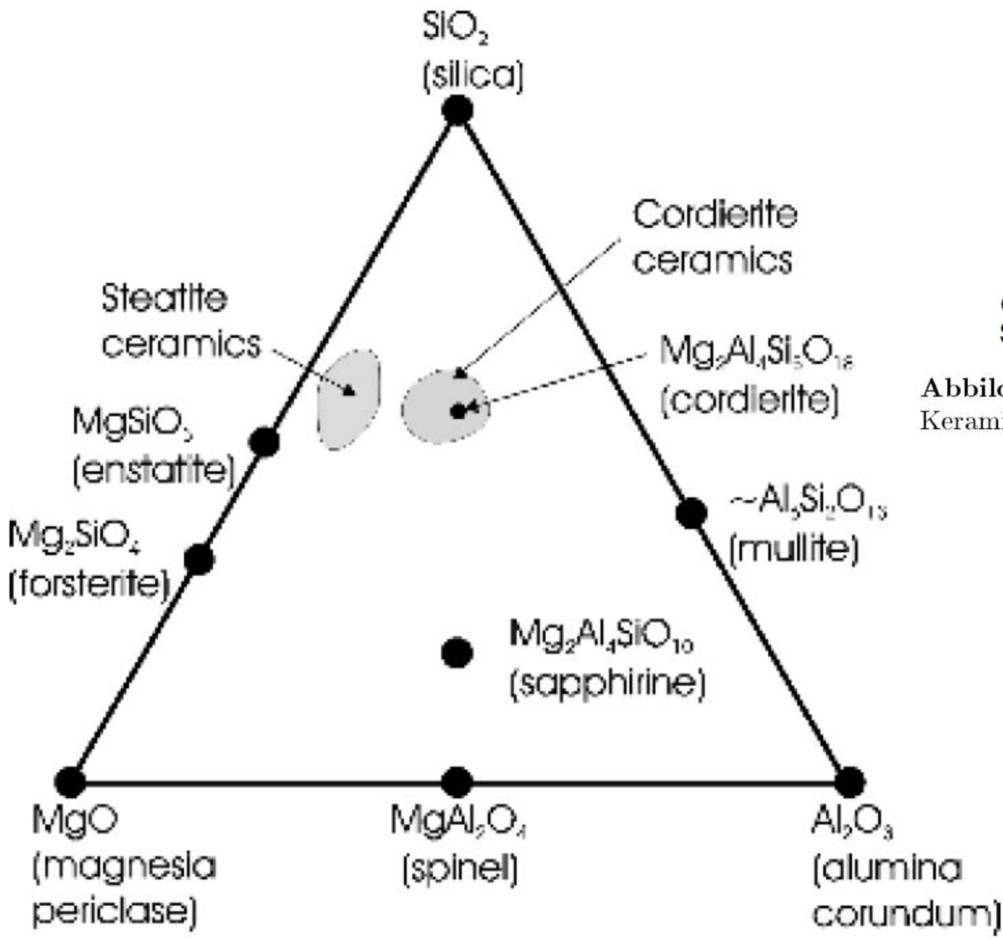
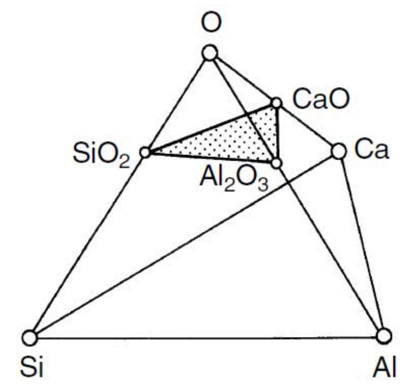
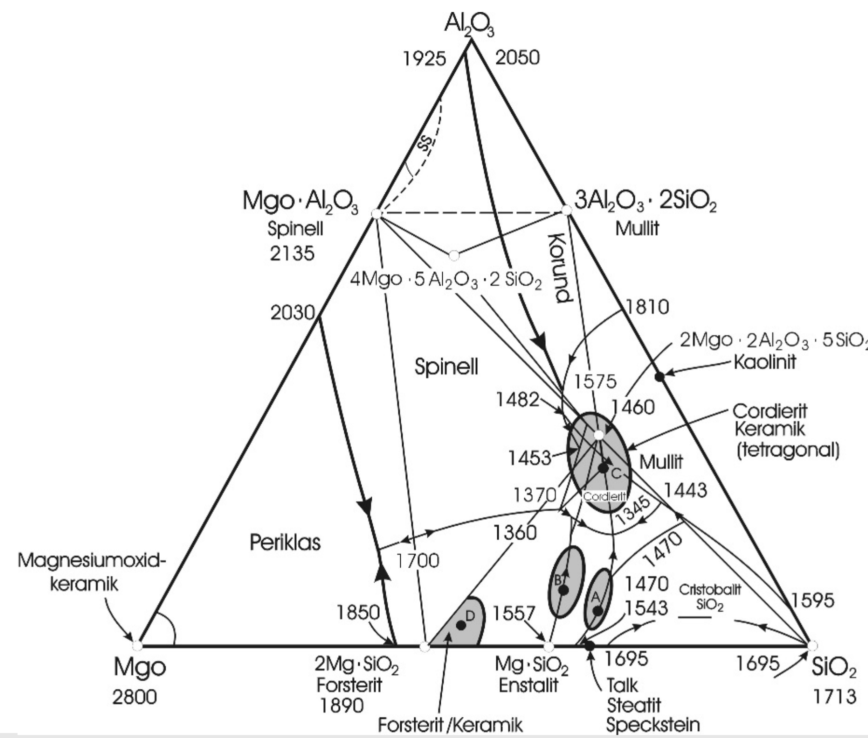


Figure 4.22 Schematic phase diagram for the MgO–Al_2O_3–SiO_2 system, which contains several important ceramic materials



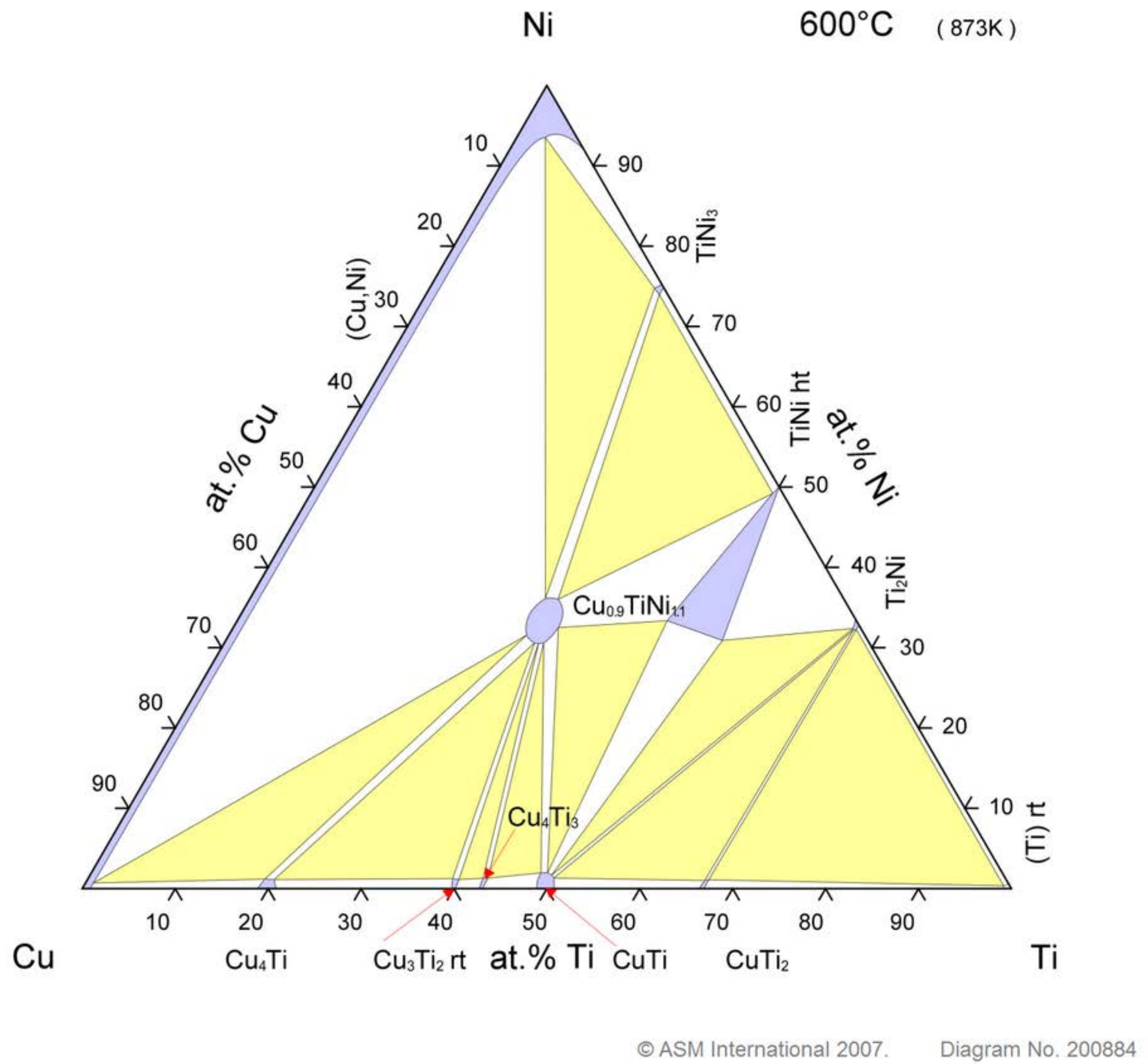
ternär 4
binär 6
Atomarten 4
} Randsysteme

Abbildung 4.51. Schematische Darstellung eines quasiternären Systems wichtiger Keramiken.



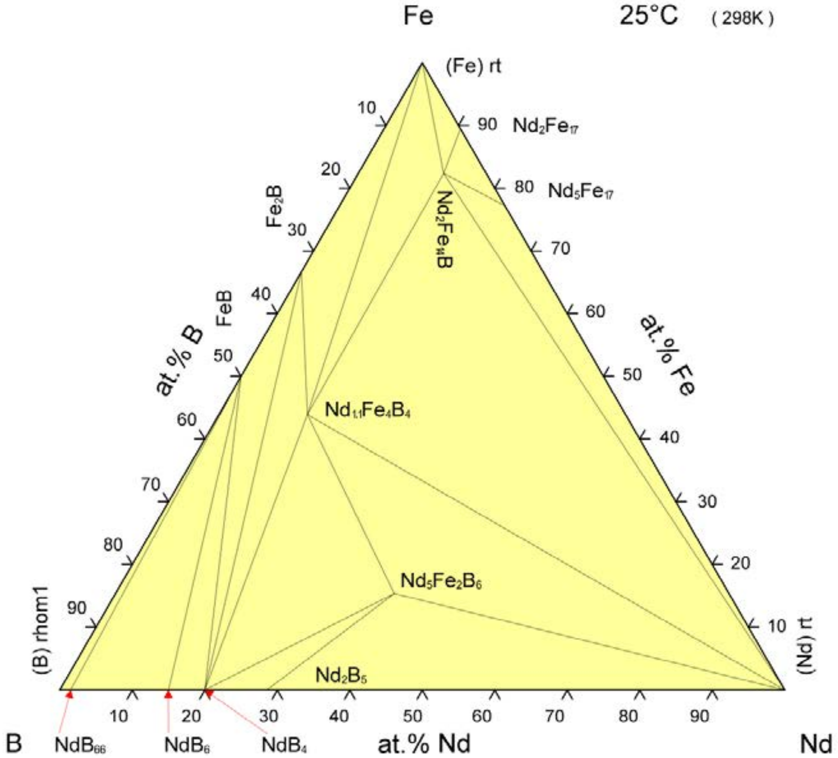
R. J. D. Tilley, Understanding Solids: The Science of Materials, John Wiley & Sons, 2013
G. Gottstein, Physikalische Grundlagen der Materialkunde, Springer Verlag, 2013

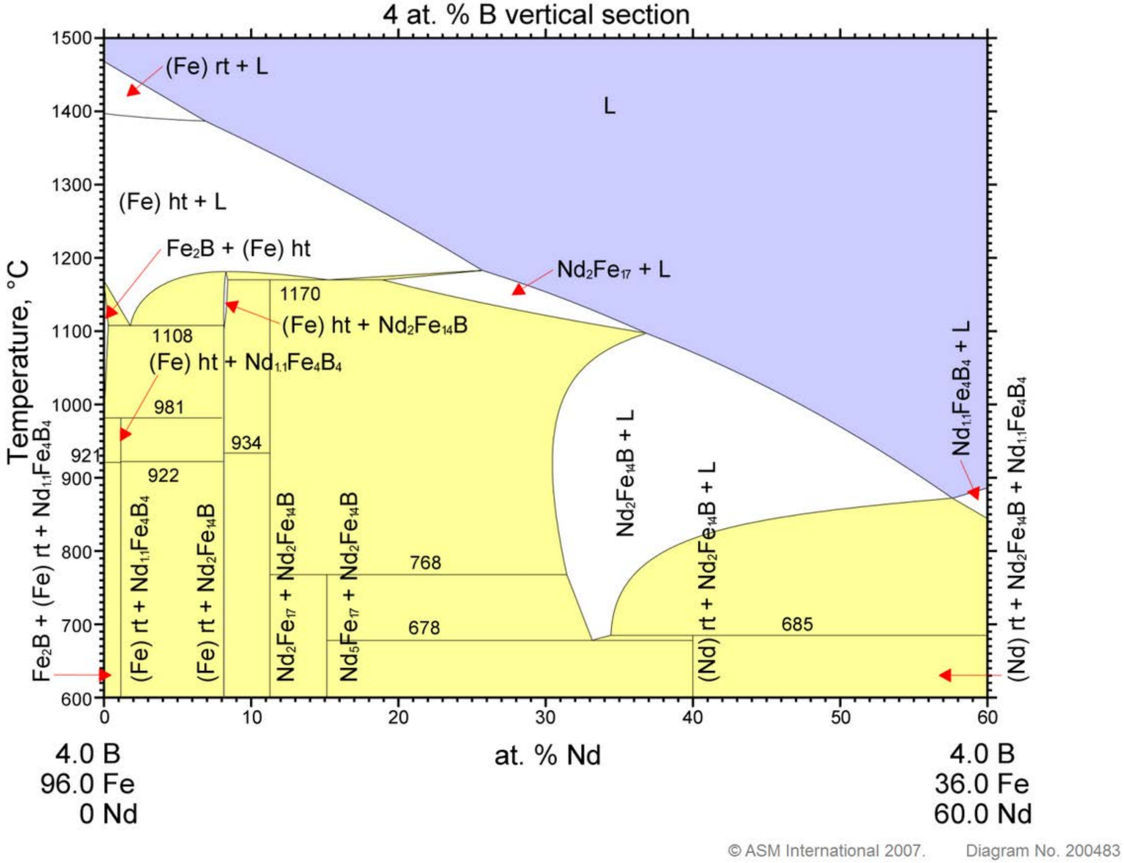
Ti-Ni-Cu



Alloy Phase Diagram Database: http://mio.asminternational.org/apd/index.aspx

Nd-Fe-B





Alloy Phase Diagram Database: http://www1.asminternational.org/asmenterprise/APD/default.aspx

RUB

$Nd_2Fe_{14}B$

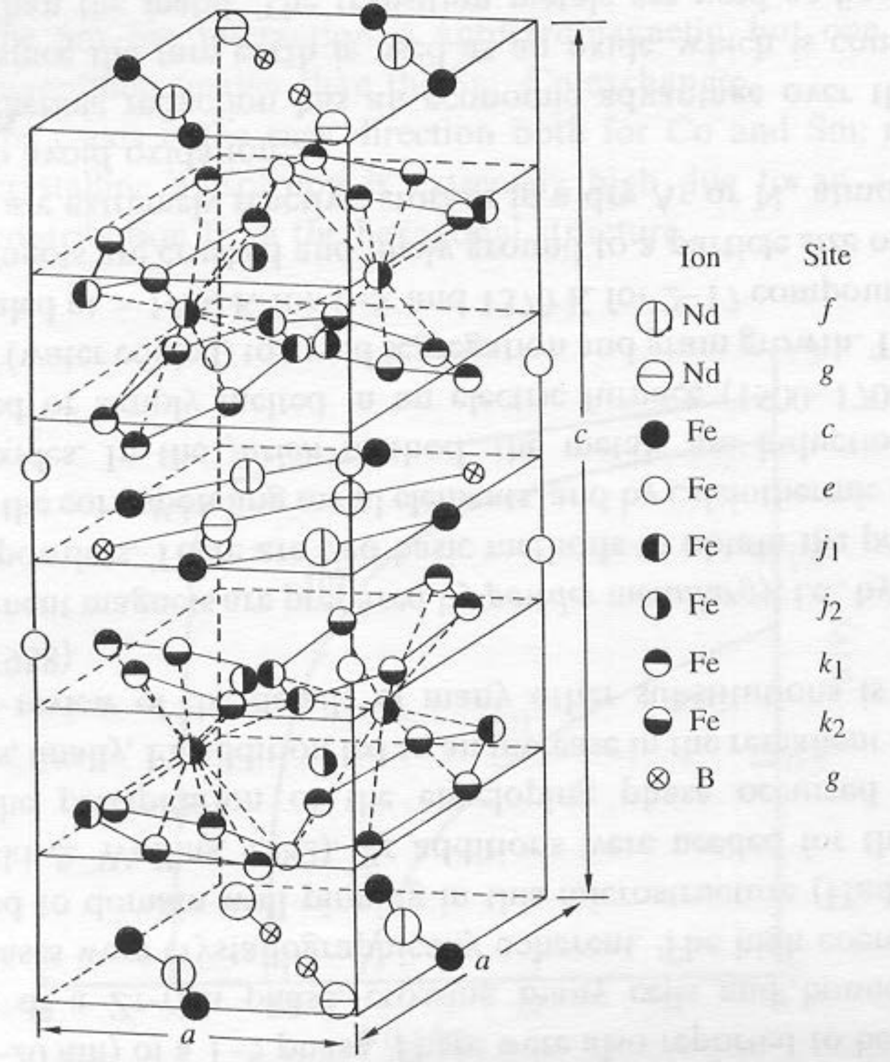
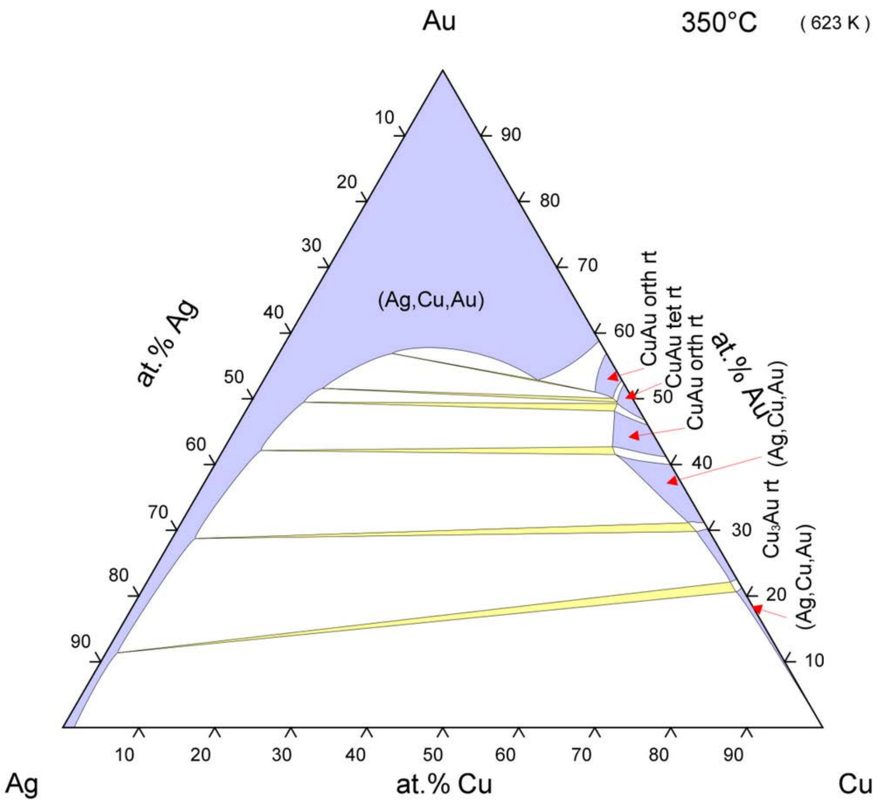
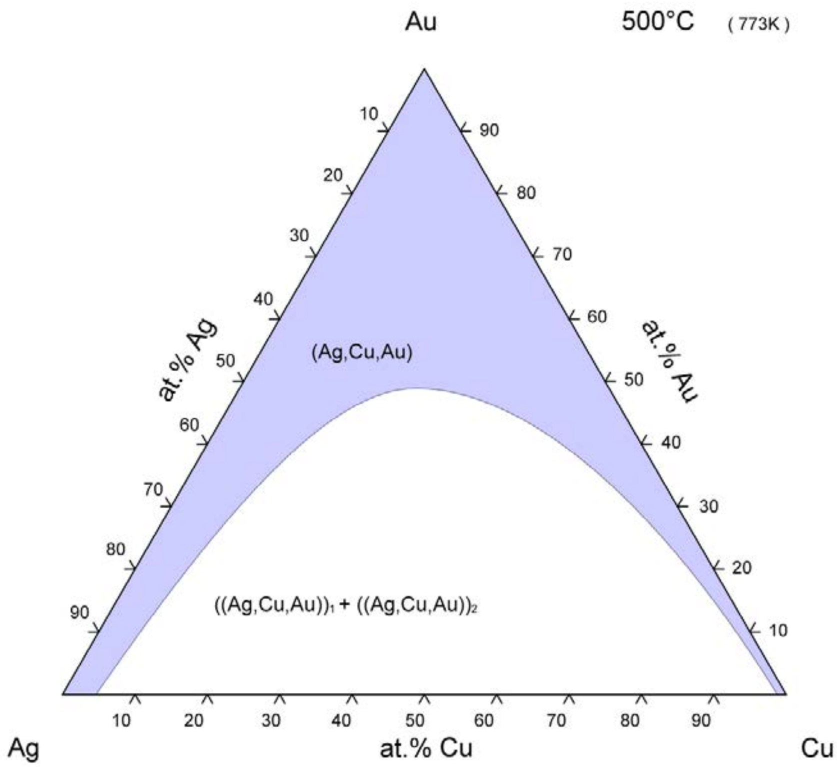


Fig. 6.30. The unit cell of $Nd_2Fe_{14}B$, showing the different Fe sites. (Adapted from Croat *et al.*, 1984)

J.J. Croat et al, Journal of Applied Physics **55**, 2078 (1984)

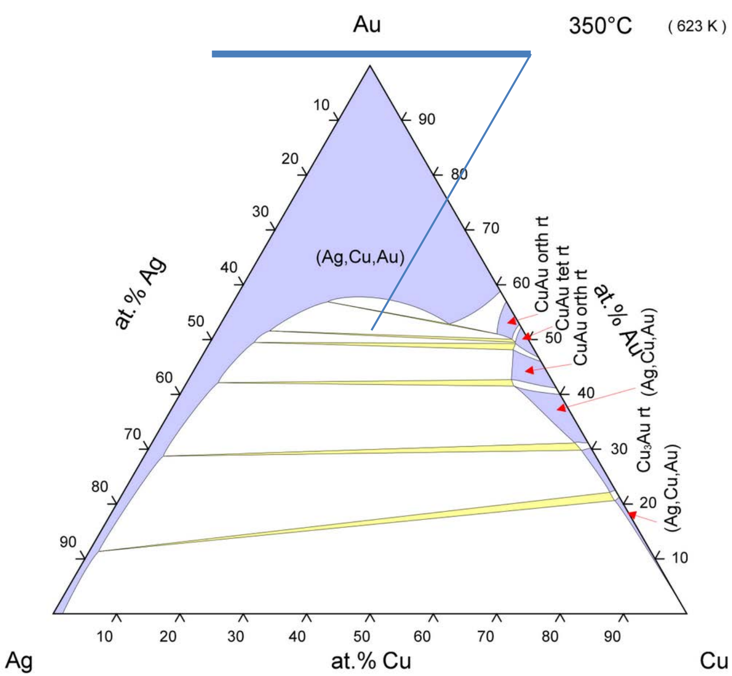
Ag-Au-Cu: isothermal diagrams

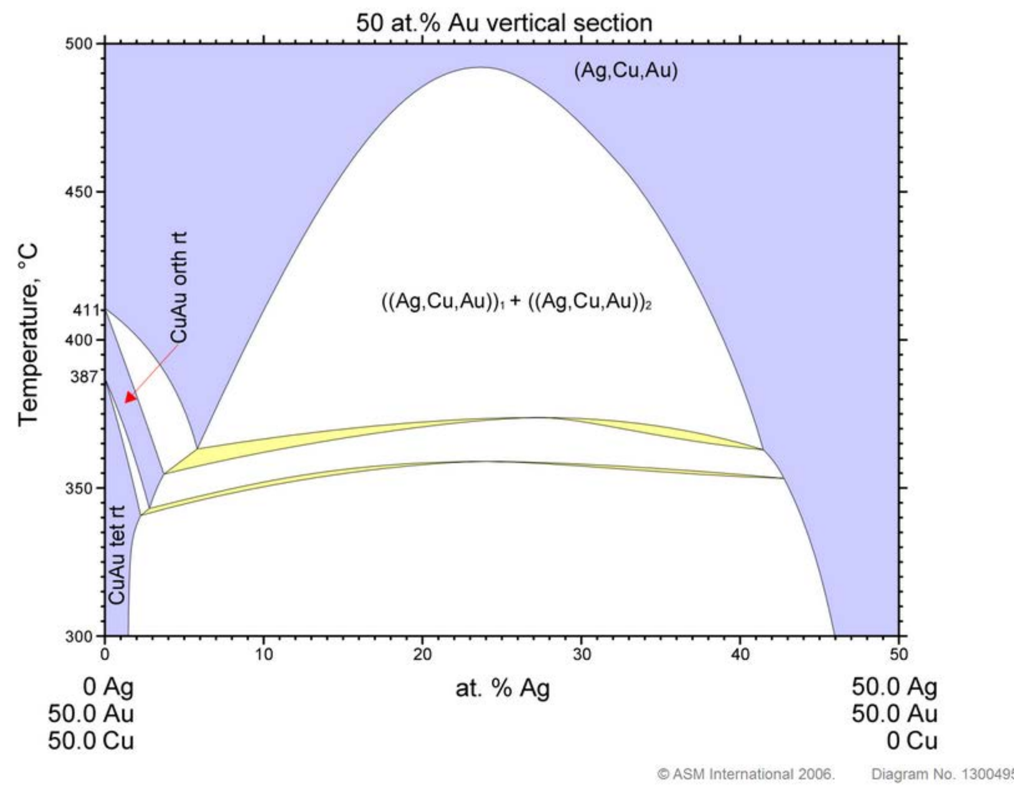




Alloy Phase Diagram Database: http://www1.asminternational.org/asmenterprise/APD/default.aspx

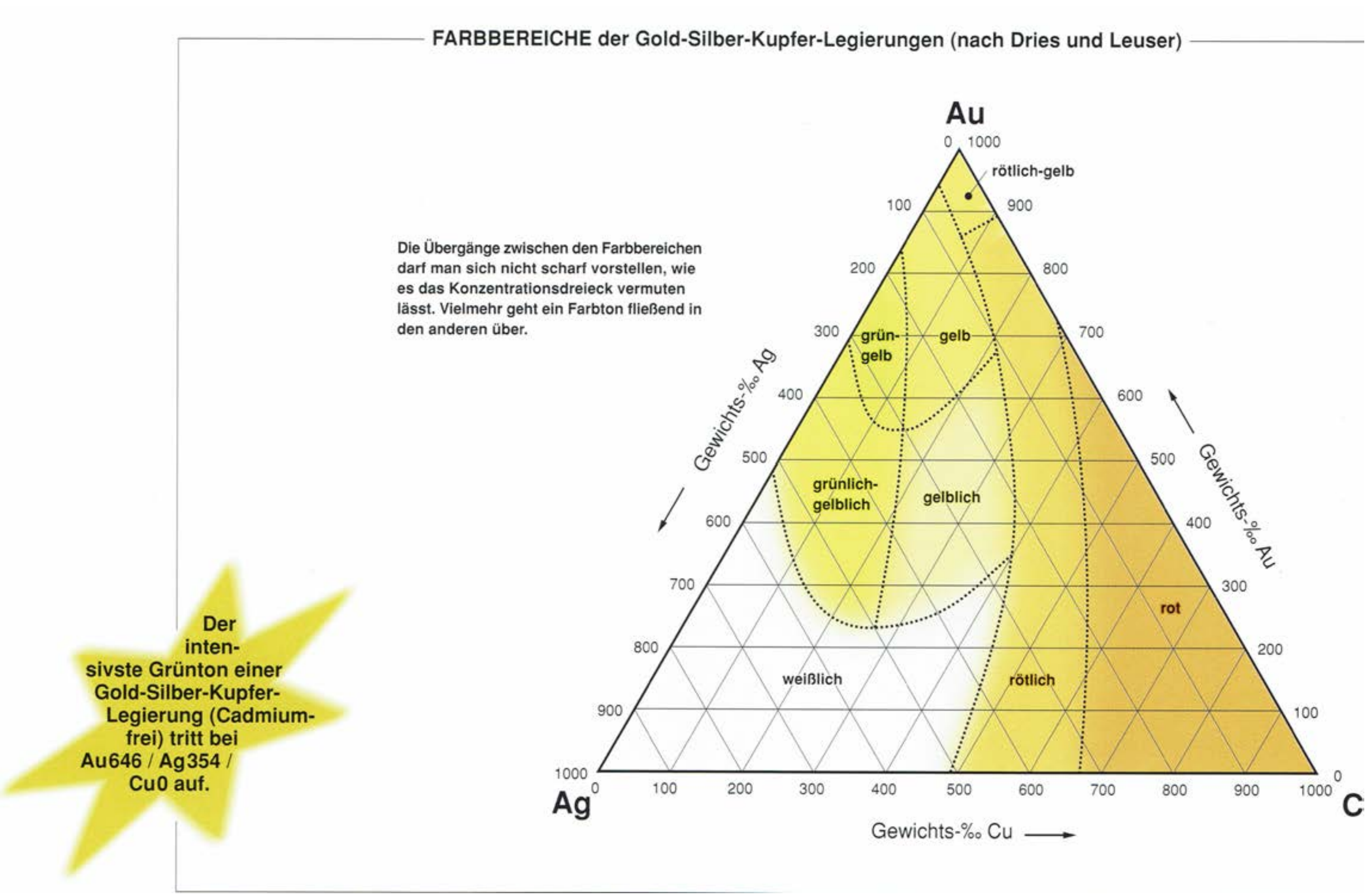
Ag-Au-Cu: vertical section





Alloy Phase Diagram Database: http://www1.asminternational.org/asmenterprise/APD/default.aspx

Ternary phase diagram of jewelry metals: color



Technisch wissenschaftliche Grundlagen des Goldschmiedens,
Teil 2 Werkstoffkunde der Edelmetallverarbeitung, Bielefelder Verlag, 2004

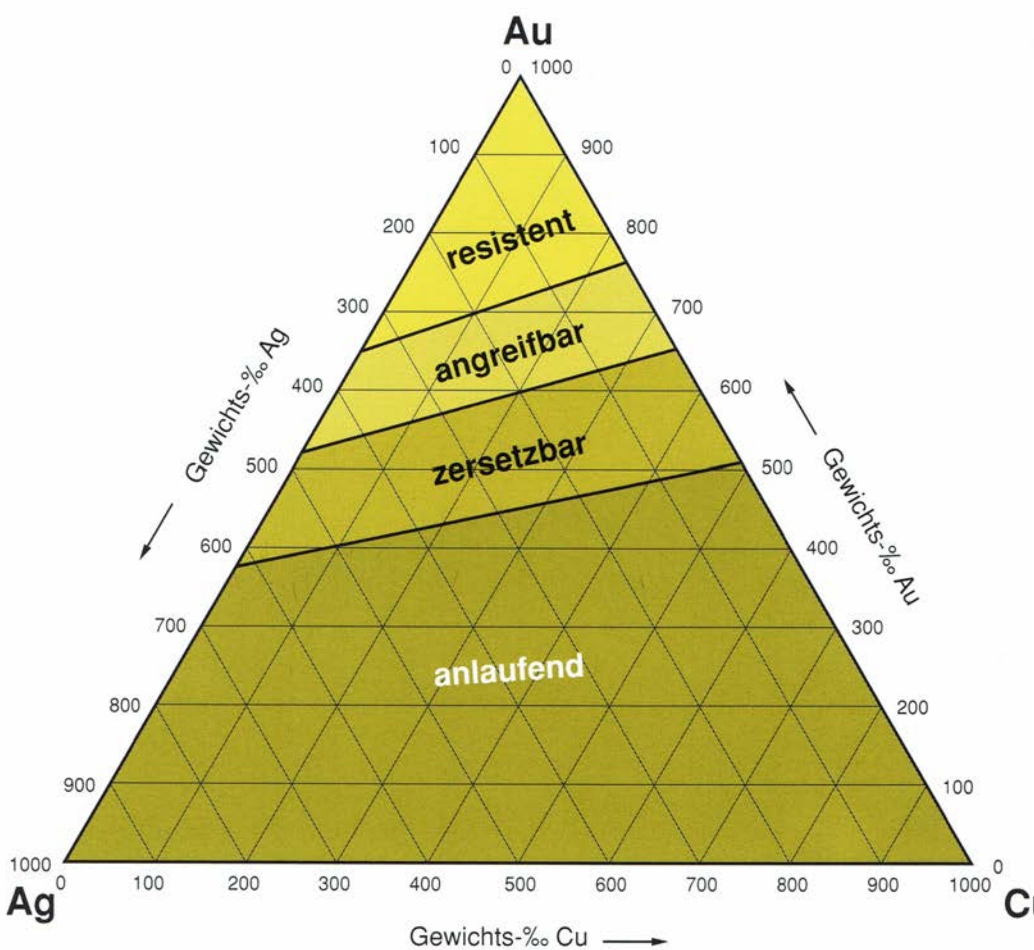
Ternary phase diagram of jewelry metals: chemical resistance

CHEMISCHE BESTÄNDIGKEIT der Gold-Silber-Kupfer-Legierungen (nach Tammann und Sterner-Rainer)

Folgende vier Bereiche chemischer Beständigkeit, die scharf gegeneinander abgegrenzt sind, lassen sich unterscheiden:

- Legierungen mit mehr als 50 Atom-% Gold (dies entspricht etwa 750 Gewichts-‰) sind gegen chemische Einflüsse vollkommen resistent und lassen sich nur in Königswasser lösen.
- Legierungen mit 37,5 bis 50 Atom-% Gold (ca. 650 bis 750 Gew.-%) werden von starken Säuren (z.B. Salpetersäure) angegriffen. Dabei lösen sich die Kupfer- und Silberanteile soweit auf, bis sich ein Goldanteil von 50 Atom-% gebildet hat Dies hat gleichzeitig eine Farbänderung ins Goldgelbe zur Folge.
- Legierungen mit Goldgehalten von 25 bis 37,5 Atom-% (ca. 530 bis 650 Gew.-‰) werden in starken Säuren völlig zersetzt, indem die Zusatzmetalle in Lösung gehen, das Gold jedoch als Bodensatz zurückbleibt.
- Legierungen, deren Goldanteil unter 25 Atom-% liegt (unter ca. 530 Gew.-‰), laufen unter dem Einfluss von Schwefel sowie an der Luft infolge des in der Atmosphäre vorhandenen Schwefelwasserstoffs leicht an.

Unabhängig vom Goldgehalt sind die blassen, also mehr silberhaltigen Legierungen beständiger als die rötlichen, mehr kupferhaltigen Legierungen mit gleichem Feingehalt, da das Edelmetall Silber neben dem Gold zur Beständigkeit mit beiträgt.



Technisch wissenschaftliche Grundlagen des Goldschmiedens,
Teil 2 Werkstoffkunde der Edelmetallverarbeitung, Bielefelder Verlag, 2004

Control questions I

See also aims of the lecture questions

RUB

(1) Give a definition for “phase”.

(2) What is an intermediate phase?

(3) What physical variable is kept constant in most of the phase diagrams used in materials science? Please explain why.

(4) Explain stability and metastability.

(5) Why is the metastable phase diagram for Fe used more frequently than the stable one? Which two compounds/elements define the composition axis?

(6) What is the triple point and in what type of phase diagrams can it be found?

(7) How many phases can occur in a unary system?

(8) What are the prerequisites for a solid solution?

(9) Sketch a peritectic, eutectic and eutectoid reaction.

(10) What is the lever rule? Write down and explain the formula.

(11) Explain Vegard’s law. For what type of phase is it applicable?

(12) What is a tie line?

(13) What are the liquidus and the solidus line?

(14) What is a liquidus projection?

(15) Draw a Gibbs triangle and indicate a line of constant composition ration A/B=1.

Technisch wissenschaftliche Grundlagen des Goldschmiedens,
Teil 2 Werkstoffkunde der Edelmetallverarbeitung, Bielefelder Verlag, 2004

Control questions II

(1) Name all polymorphs of pure Fe and the respective crystal structures.

(2) How can temperature-dependent phase transformations be determined?

(3) Give three examples for binaries with complete miscibility.

(4) Name a practical application for the eutectic point in the Au-Si system.

(5) Give three examples for prominent metal-gas system.

(6) Why does solubility generally increase in solid solutions with temperature?

(7) What is a congruent melting point?

(8) Determine phase compositions in a ternary system

(9) Apply the phase rule for a ternary system.

(10) How many phases exist in the eutectic point of an isobaric ternary system?

(11) What is an isopleth?

(12) Explain isothermal and isopleth cuts in a ternary system

(13) Indicate solidus and solvus surfaces in a three-dimensional ternary phase diagram

(14) What is a tie triangle?

(15) For what can you use an Ellingham diagram?

Technisch wissenschaftliche Grundlagen des Goldschmiedens,
Teil 2 Werkstoffkunde der Edelmetallverarbeitung, Bielefelder Verlag, 2004