RUB

Neue Materialien
und Grenzflächen

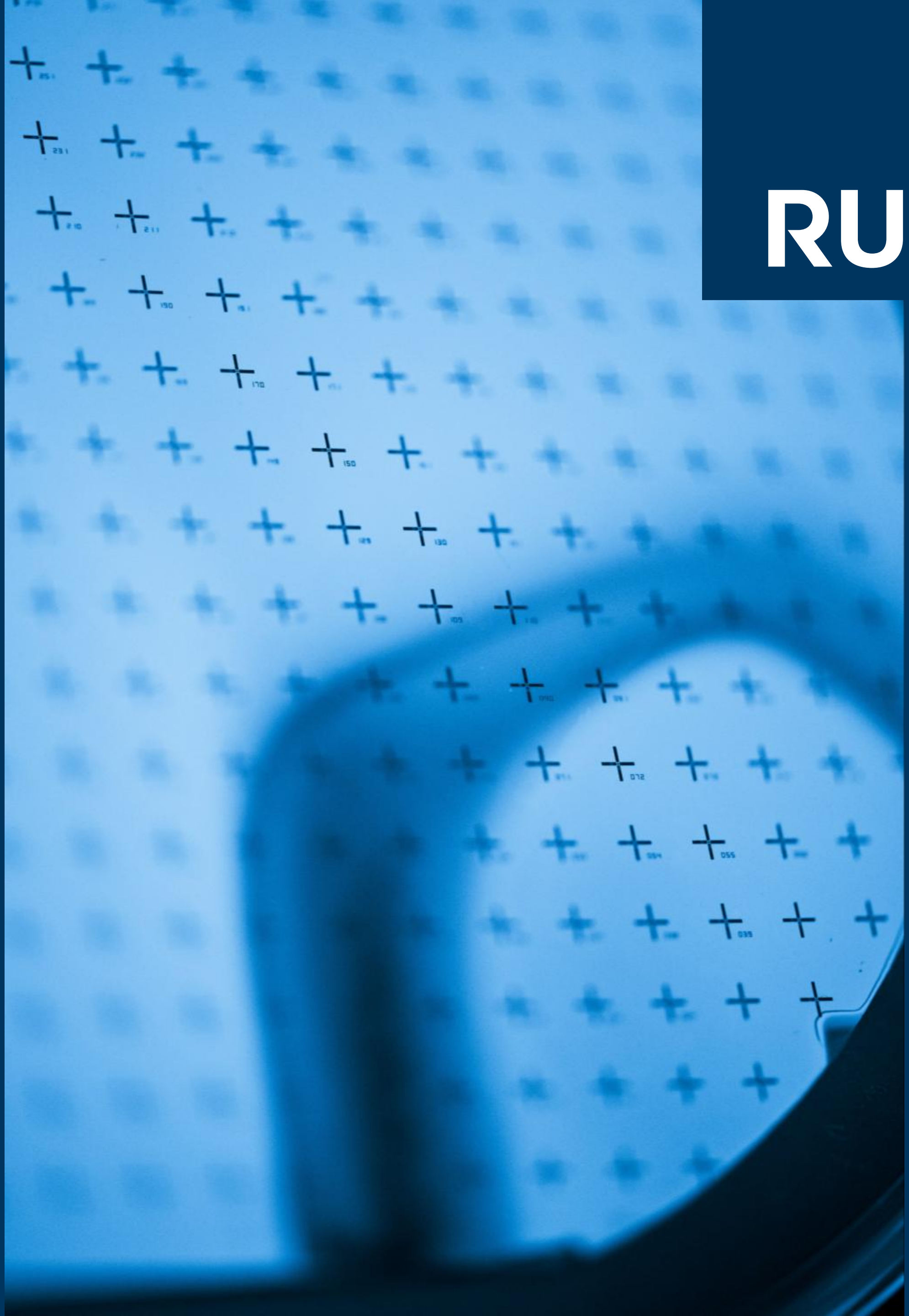
RUHR-UNIVERSITÄT BOCHUM

Fundamental Aspects of Materials Science and Engineering

Exercise 3

15.07.2025

Recap & Exercise

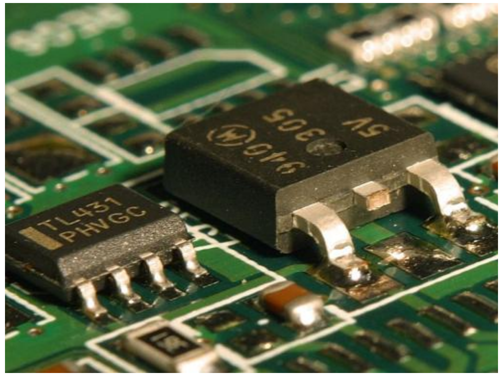


Phase diagrams

Why are phase diagrams important?

- Display of thermodynamic data
- Show information on existing phases and existence ranges
- Starting points for **materials design** and **process optimization**

1)

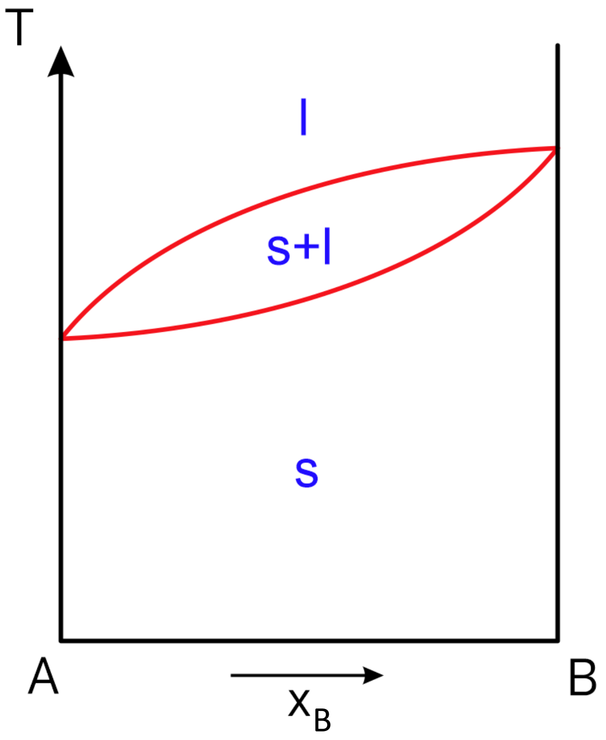


2)

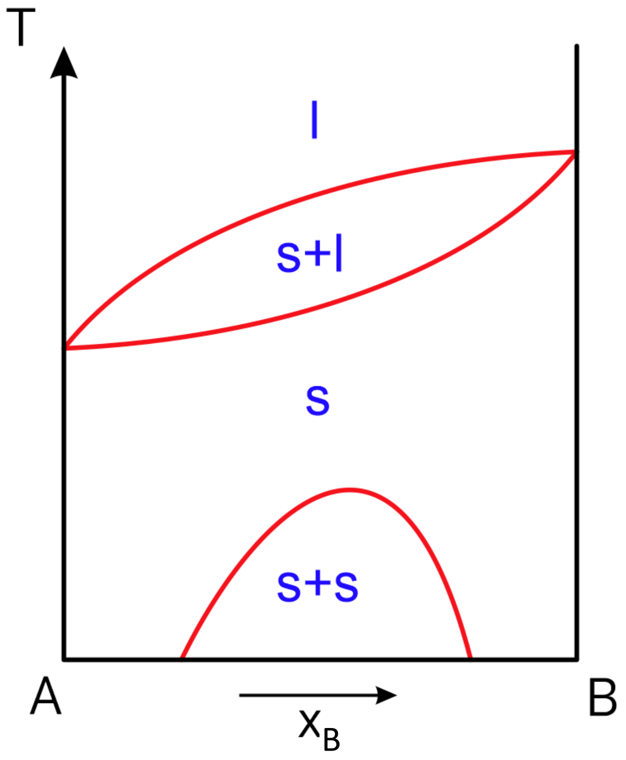
1) https://www.skf.com/uk/products/rolling-bearings/ball-bearings/deep-groove-ball-bearings
2) Public Domain

Binary phase diagrams

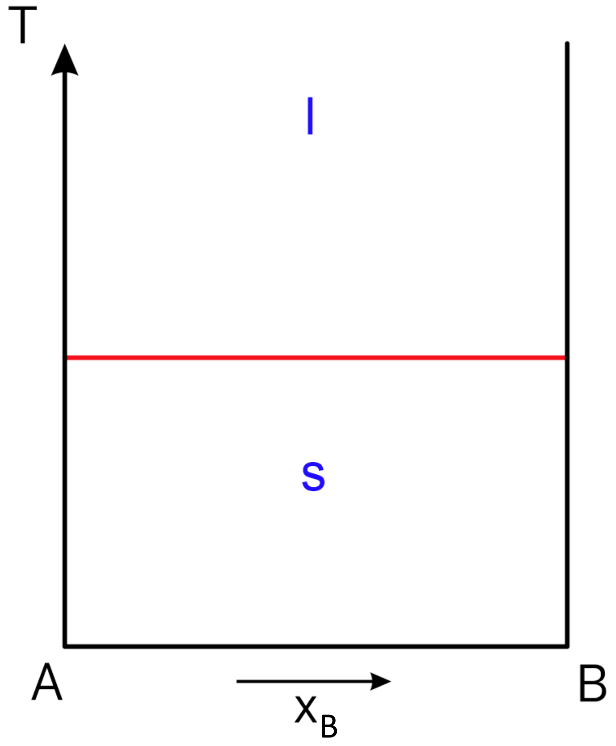
- **full miscibility**



- **limited solubility**

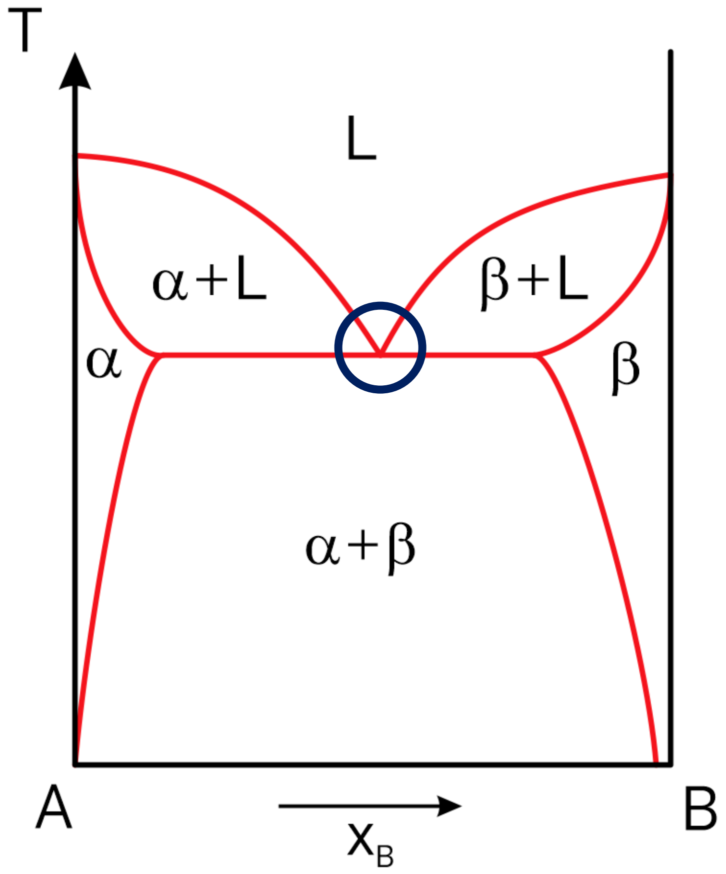


- **full immiscibility**

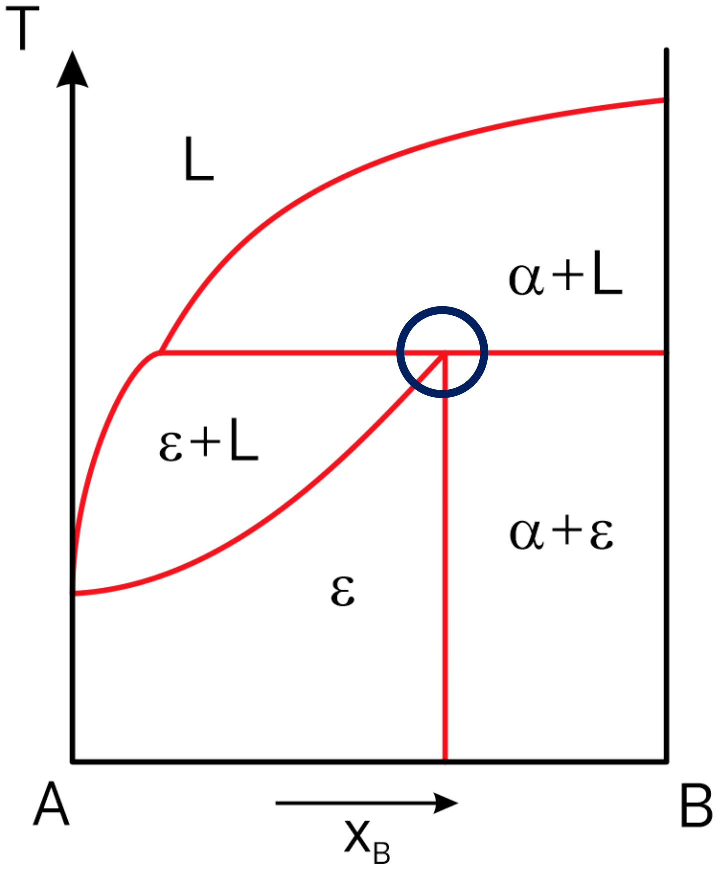


Binary phase diagrams

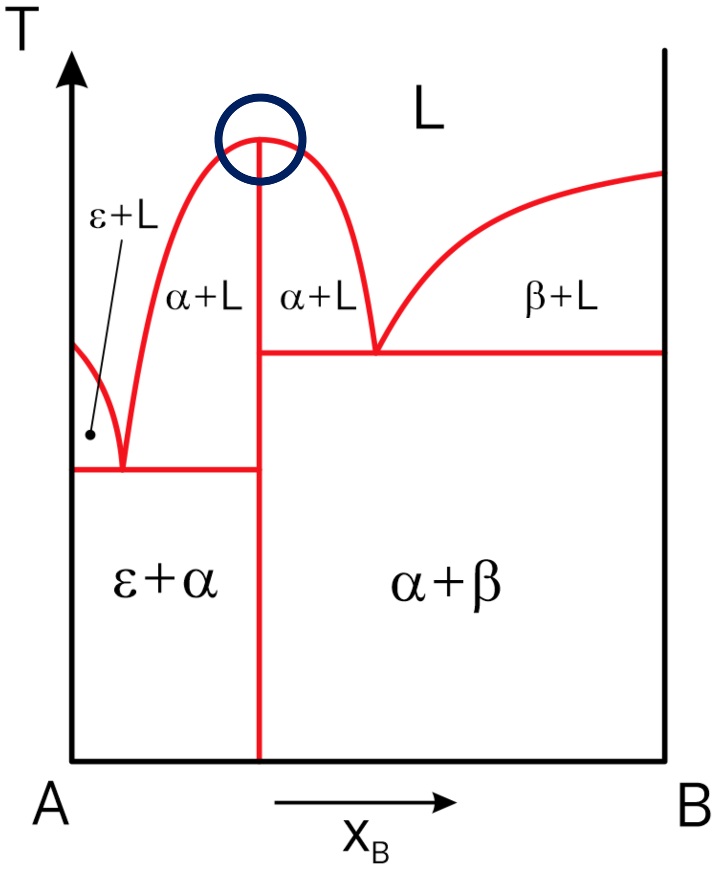
- **eutectic**



- **peritectic**



- **congruent**

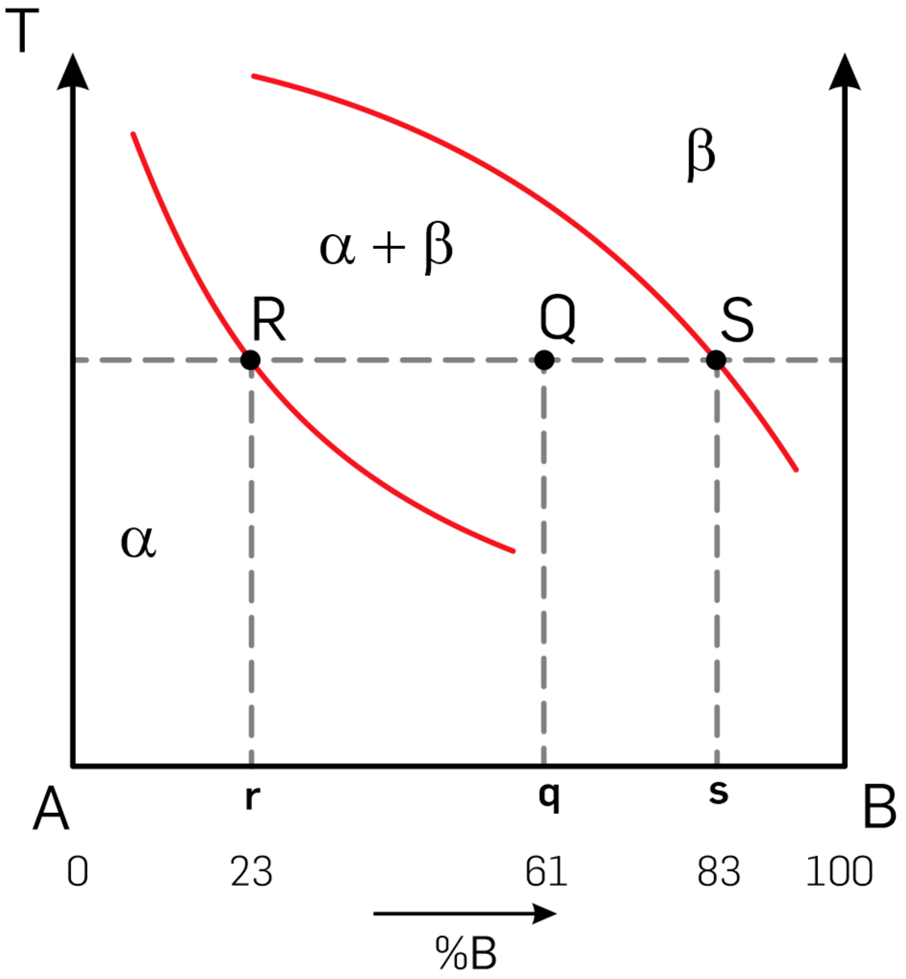


Binary phase diagrams

Lever rule

$$x_\alpha^q = 1 - x_\beta^q \qquad m_\alpha^q = x_\alpha^q \cdot m_q$$

$$x_\alpha^q = \frac{\overline{QS}}{\overline{QS} + \overline{RS}} \qquad x_\beta^q = \frac{\overline{RQ}}{\overline{RQ} + \overline{QS}}$$



Vegard‘s law

Definition:

Vegard‘s law:

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

- a_A, a_B : lattice constants of elements A and B
- x_A : concentration of A in solid solution
- allows determination of lattice constants in a solid solution in dependence of composition

Prerequisites for solid solutions:

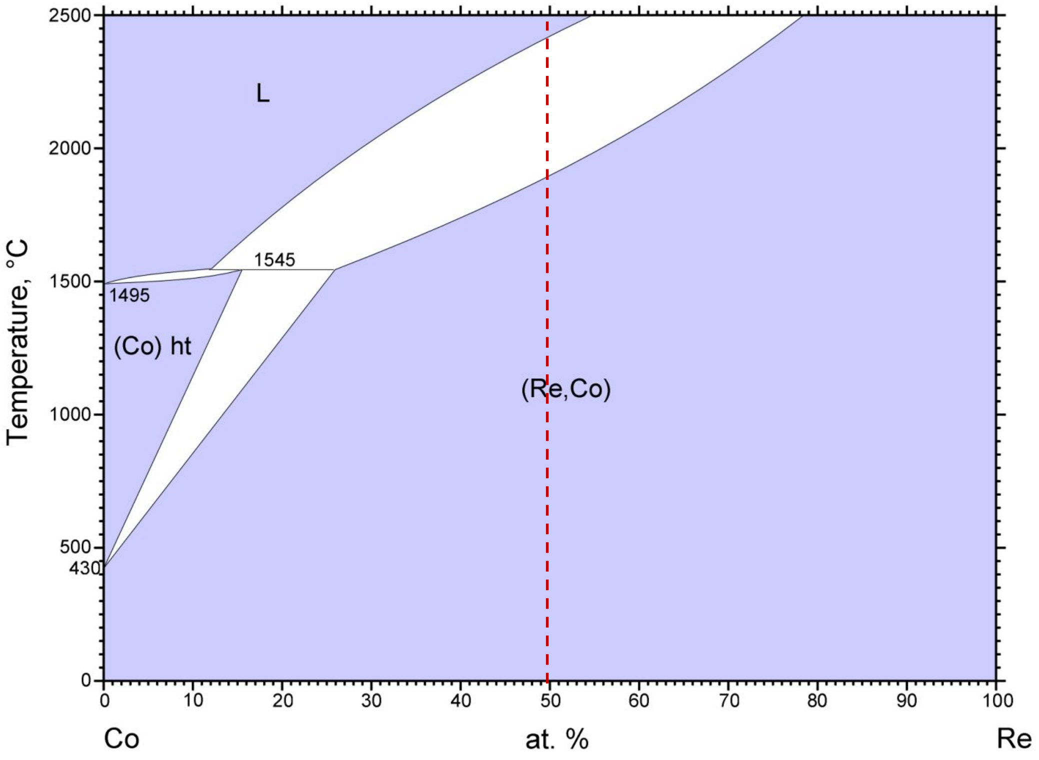
- same structure types of A and B
- similar atom/ion radius (Δ < 15%)
- similar electronegativity
- chemical similarity

Vegard‘s law

We have a binary Co-Re system and want to determine the lattice parameter of the solid solution at X_{Co} = 0.5 and X_{Re} = 0.5

- Lattice parameters:
  - Re*: a = 0.251 nm, c = 0.407 nm
  - Co*: a = 0.276 nm, c = 0.440 nm

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



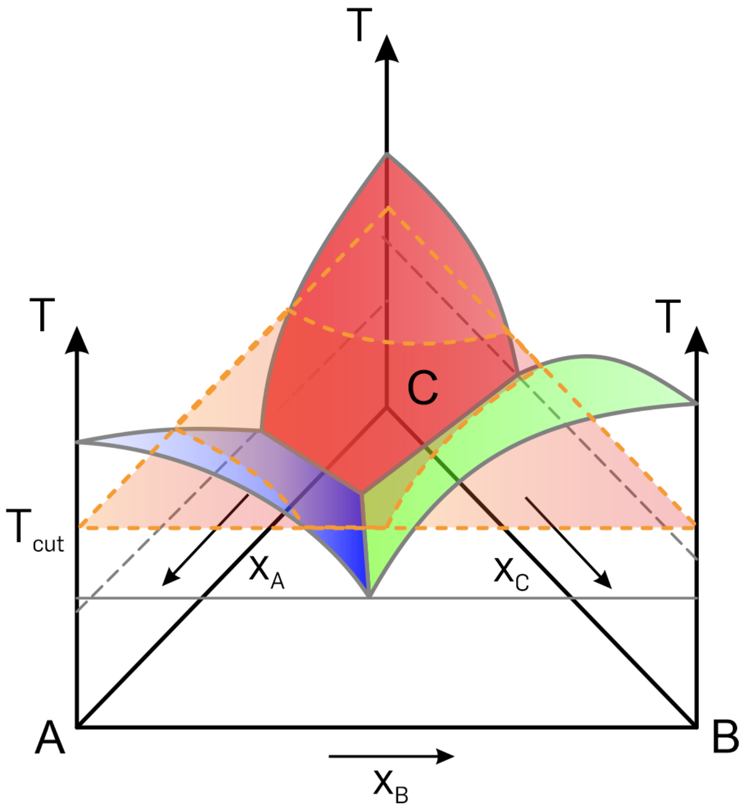
$Co_{0.5}Re_{0.5}$: a = 0.264 nm, c = 0.428 nm [1]

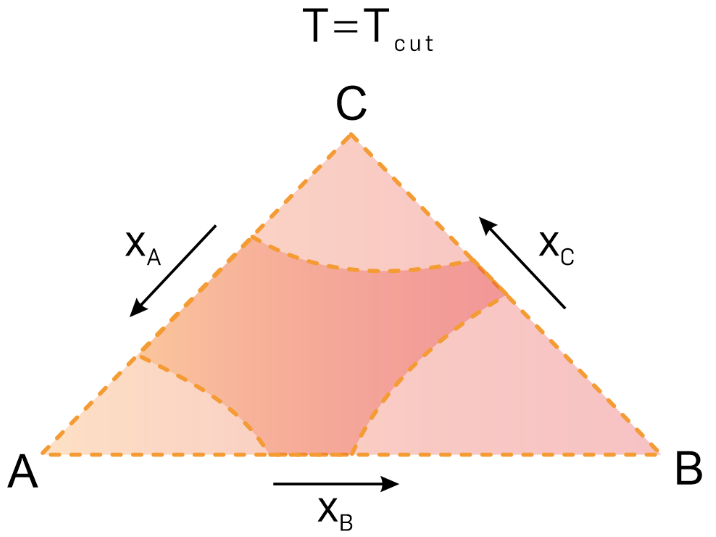
*Space group of Co (rt) and Re: $P6_3/mmc$

[1] Köster W., and Horn E., Zustandsbild und Gitterkonstanten der Legierungen des Kobalts mit Rhenium, Ruthenium, Osmium, Rhodium und Iridium, Z. Metallkd., Vol. 43, 1952, p 444-449

Ternary phase diagrams

- Usually as isothermal cuts through temperature-composistion-space
- Beware:
  - Side faces are binaries
  - Points become channels
  - Lines become areas
  - Areas become spaces





Ternary phase diagrams

cut a:

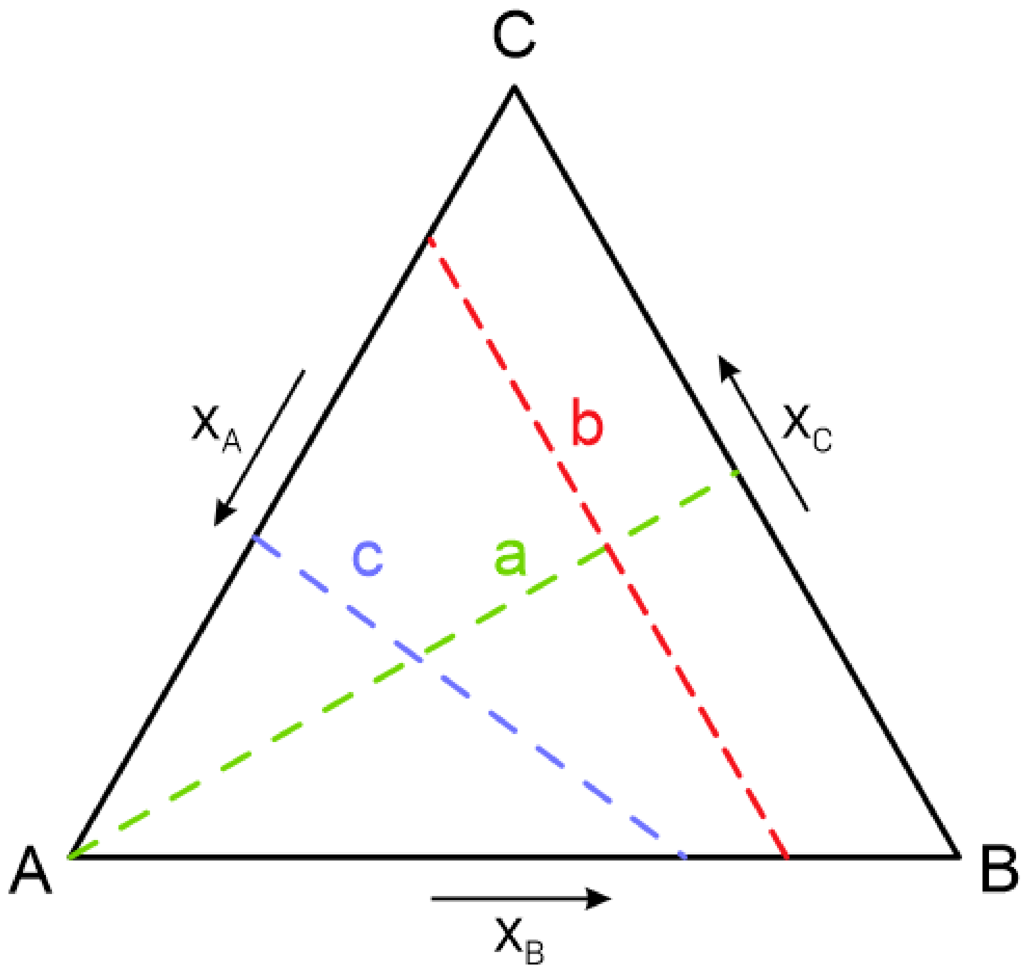
- ratio of x_B: x_C stays constant

cut b:

- x_A stays constant

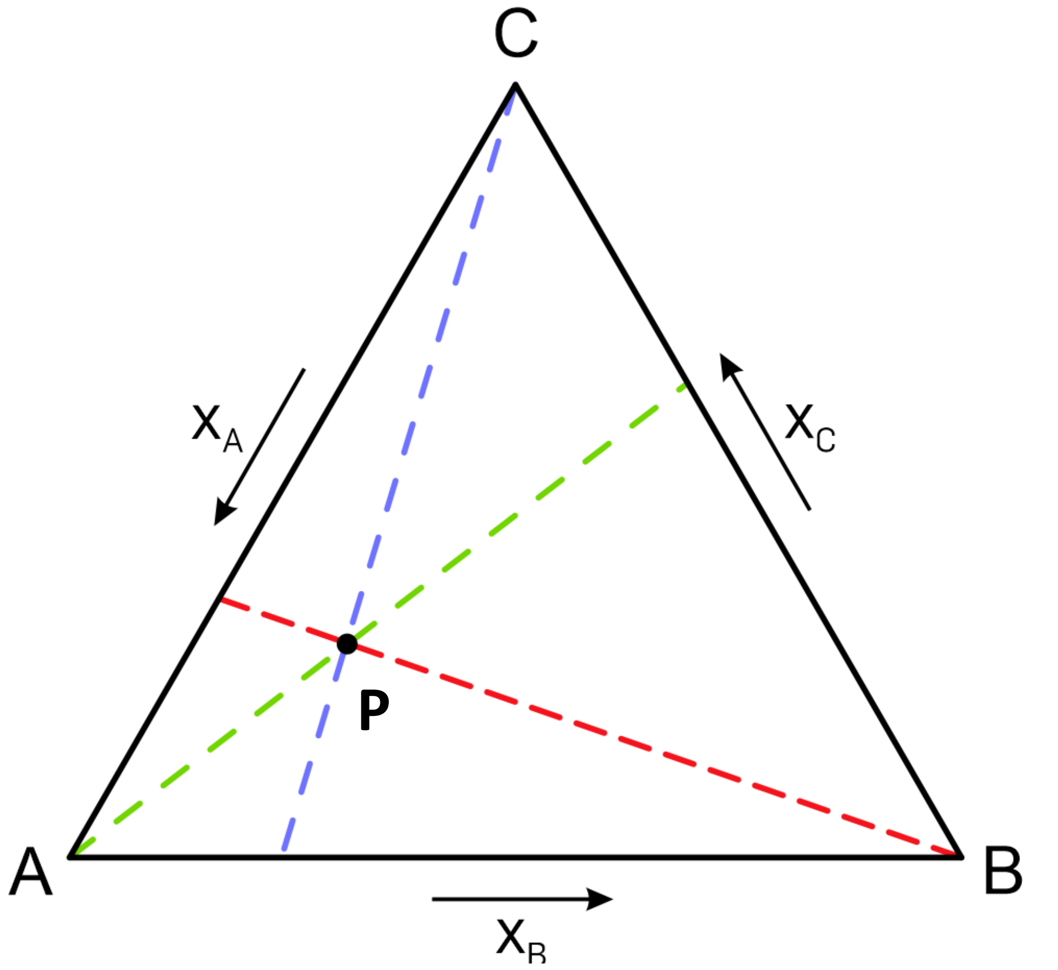
cut c:

- rarely seen; only useful for some special cases



Ternary phase diagrams

Intersection method:

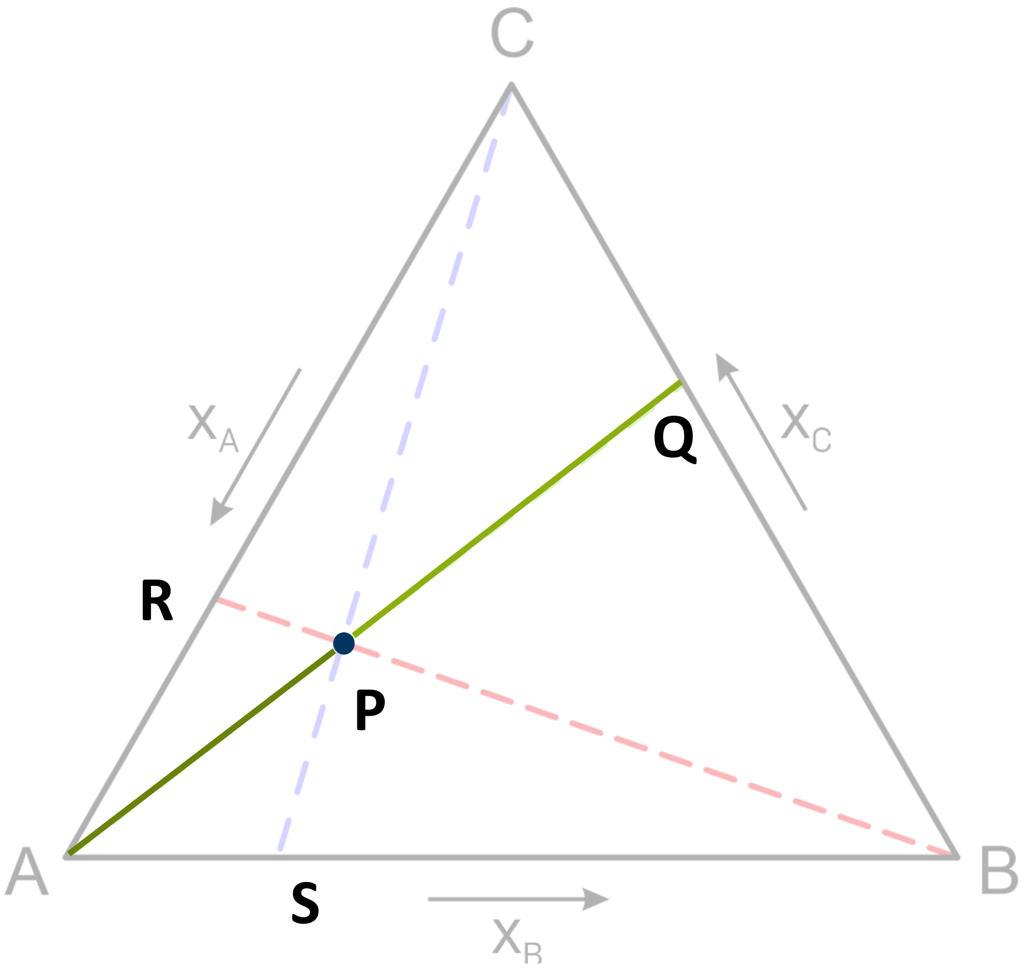


Ternary phase diagrams

Intersection method:

$$x_A = \frac{\overline{PQ}}{\overline{AP} + \overline{PQ}}$$

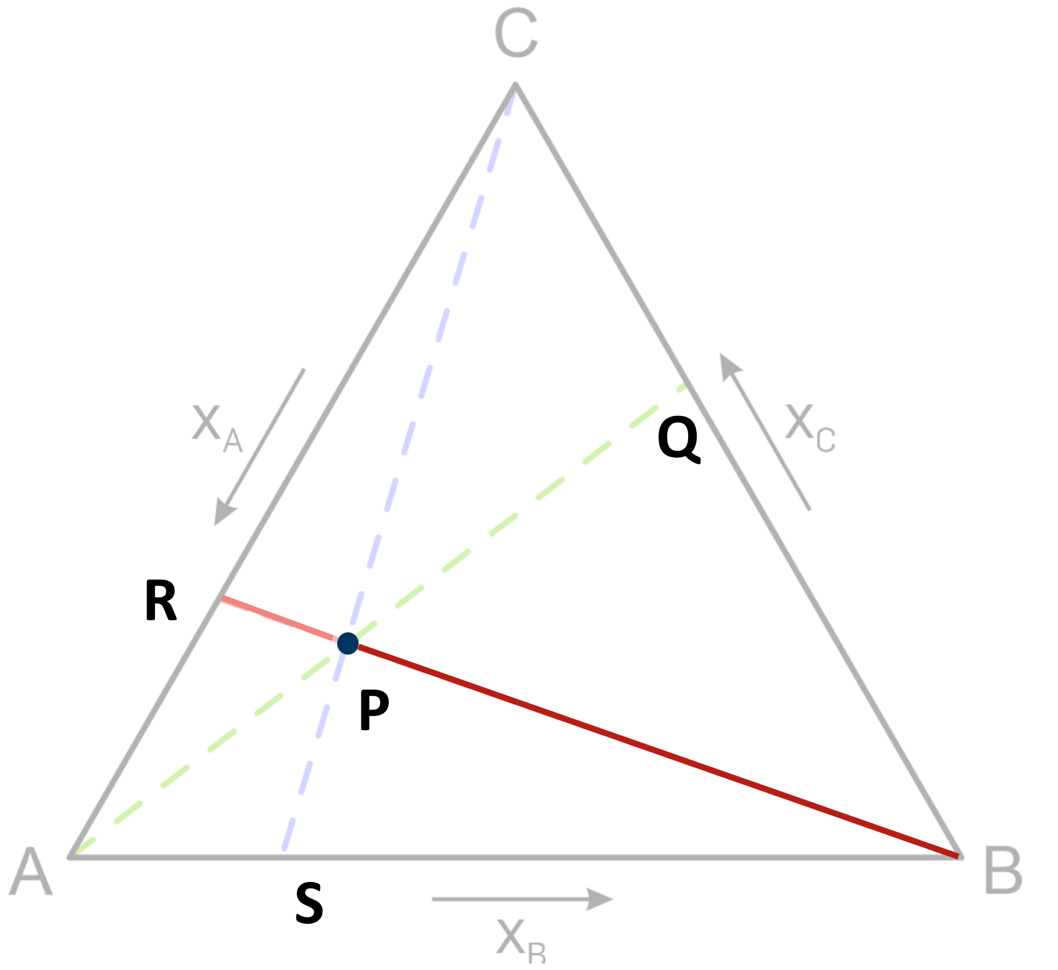
$$x_A = \frac{7.3}{5.9 + 7.3} = 0.55$$



Intersection method:

$$x_A = \frac{\overline{PQ}}{\overline{AP} + \overline{PQ}} \qquad x_A = \frac{7.3}{5.9 + 7.3} = 0.55$$

$$x_B = \frac{\overline{RP}}{\overline{RP} + \overline{PB}} \qquad x_B = \frac{2.3}{2.3 + 11.1} = 0.17$$



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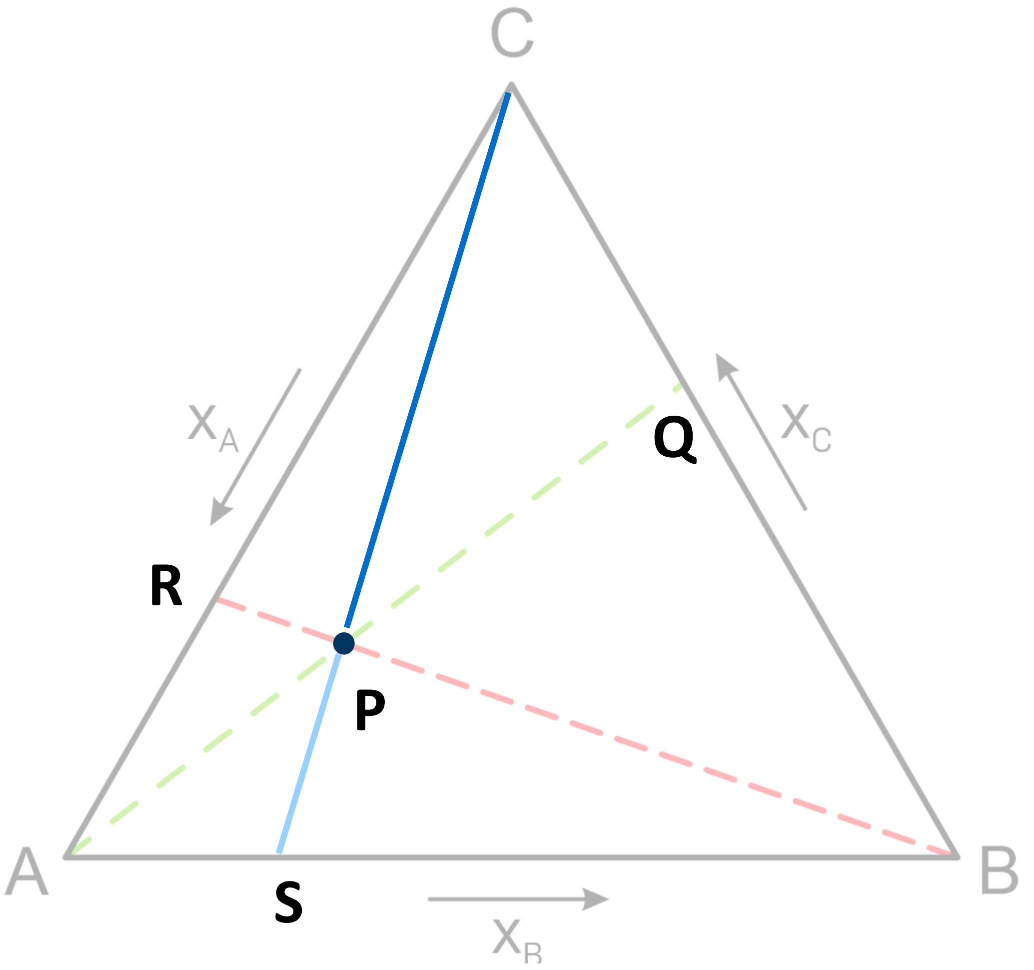
$$x_B = \frac{2.3}{2.3 + 11.1} = 0.17$$

$$x_C = \frac{\overline{PS}}{\overline{PS} + \overline{PC}}$$

$$x_C = \frac{3.8}{3.8 + 10} = 0.28$$



Ternary phase diagrams

Intersection method:

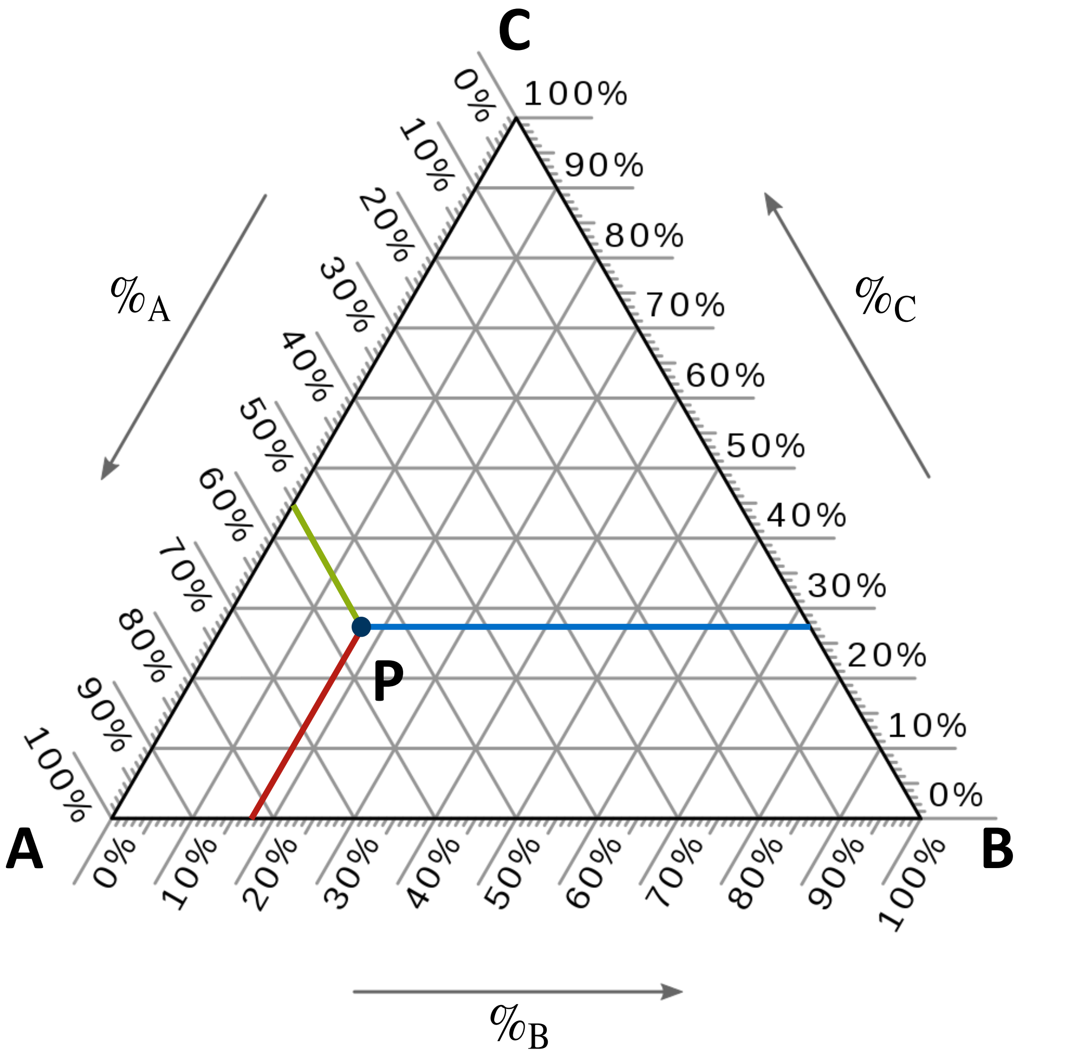
- The composition of alloy P is

  55 % A

  17 % B

  28 % C

- This method is based on the ratios in the equilateral triangle
- $x_A + x_B + x_C = 1$



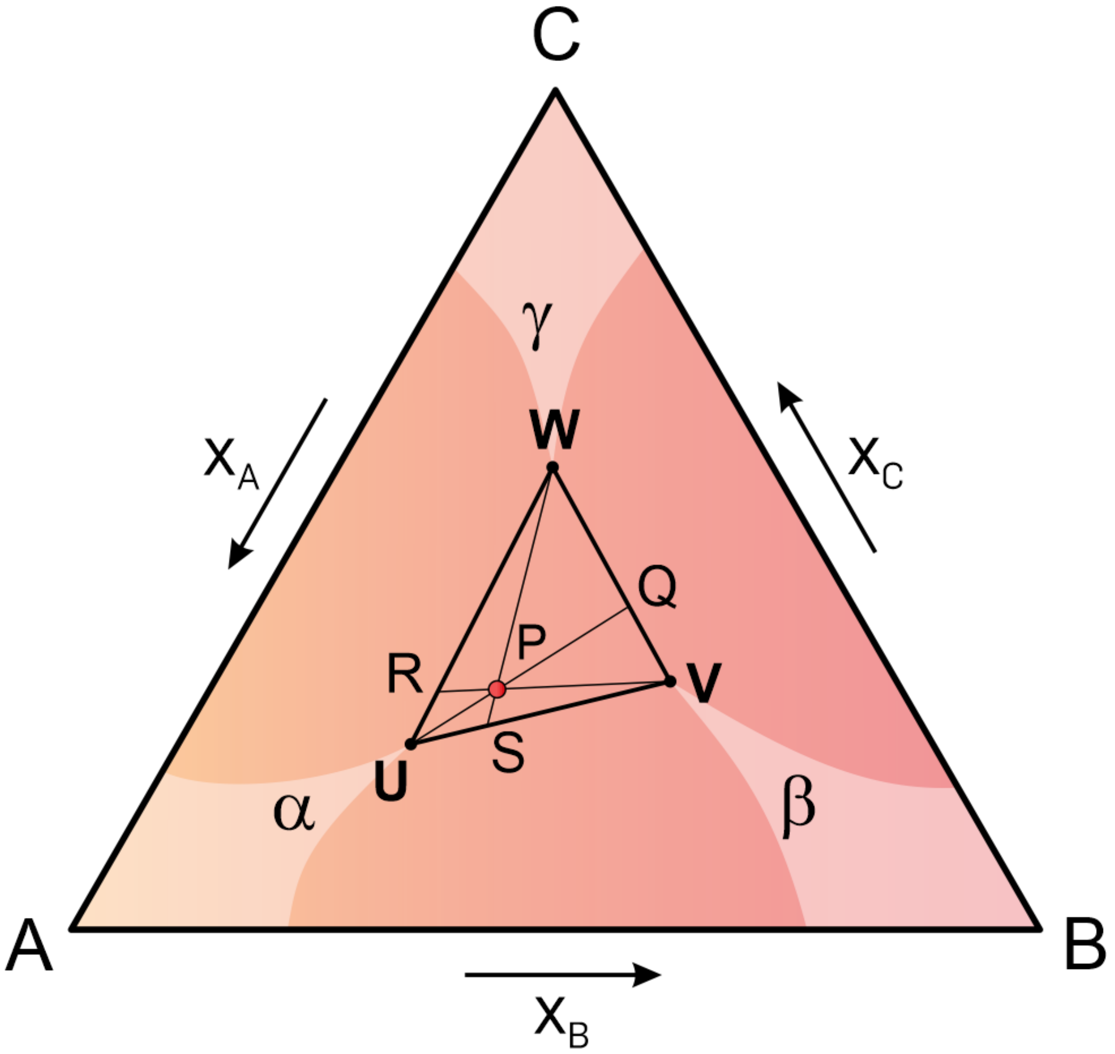
Ternary phase diagrams

Three coexisting phases:

- Application of lever rule to determine phase fractions
- $x_\alpha + x_\beta + x_\gamma = 1$

$$x_\alpha^P = \frac{\overline{PQ}}{\overline{UQ}} \qquad x_\beta^P = \frac{\overline{PR}}{\overline{VR}} \qquad x_\gamma^P = \frac{\overline{PS}}{\overline{WS}}$$

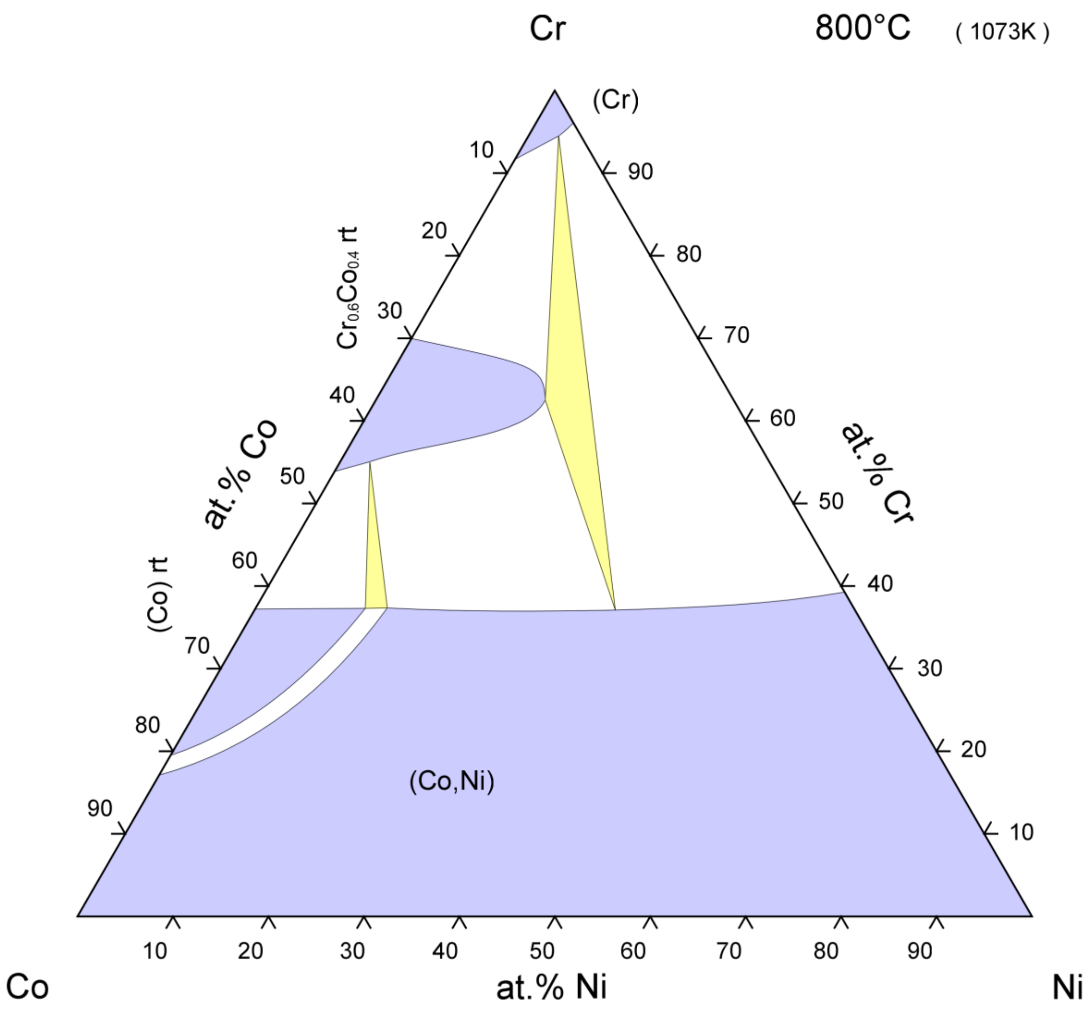
- Determine composition of phases (X_A, X_B, X_C) with intersection method on points U, V and W



B. Predel – *Heterogene Gleichgewichte*, Grundlagen und Anwendungen, Heidelberg 1982

Ternary phase diagrams

In the phase diagram, highlight a single-phase field, a two-phase field, and a three-phase field.



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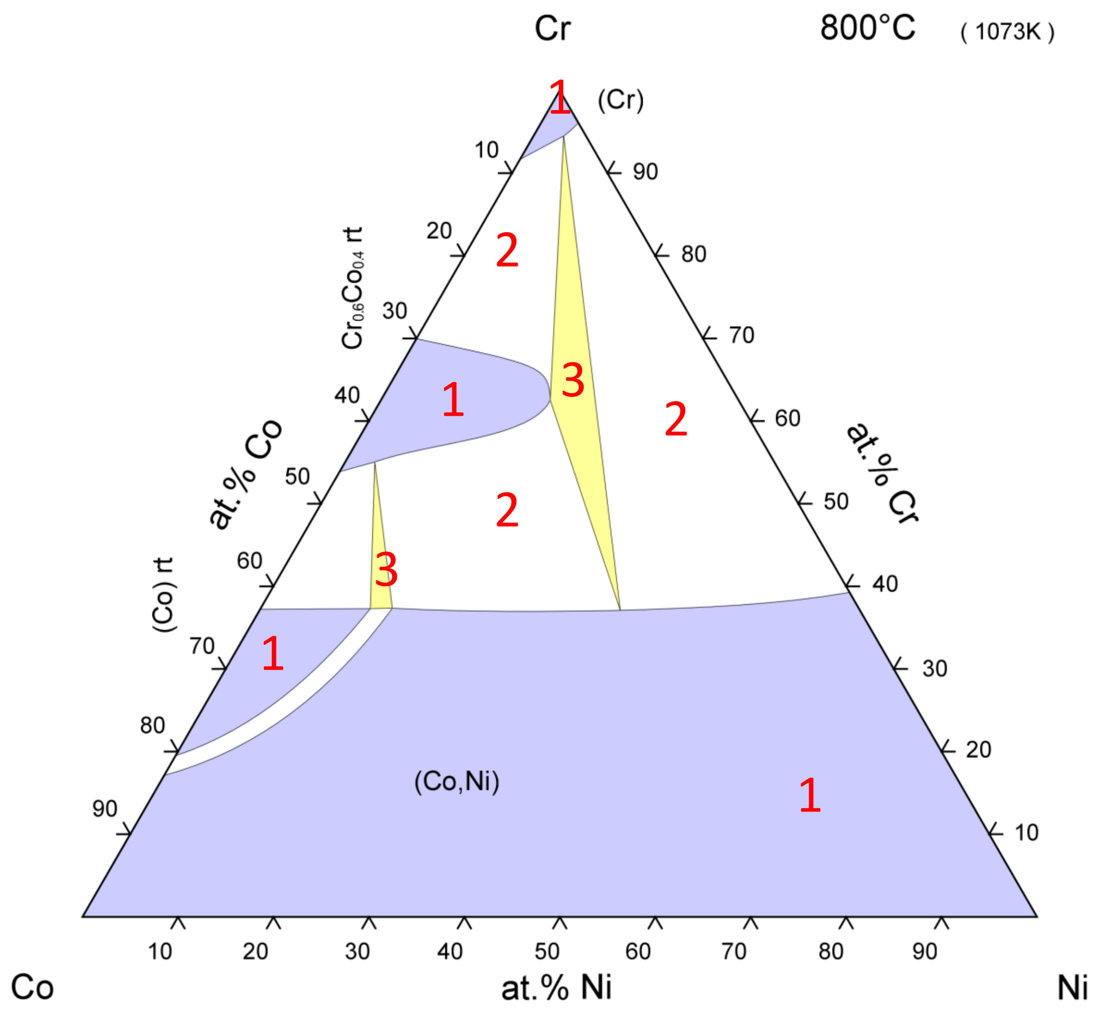
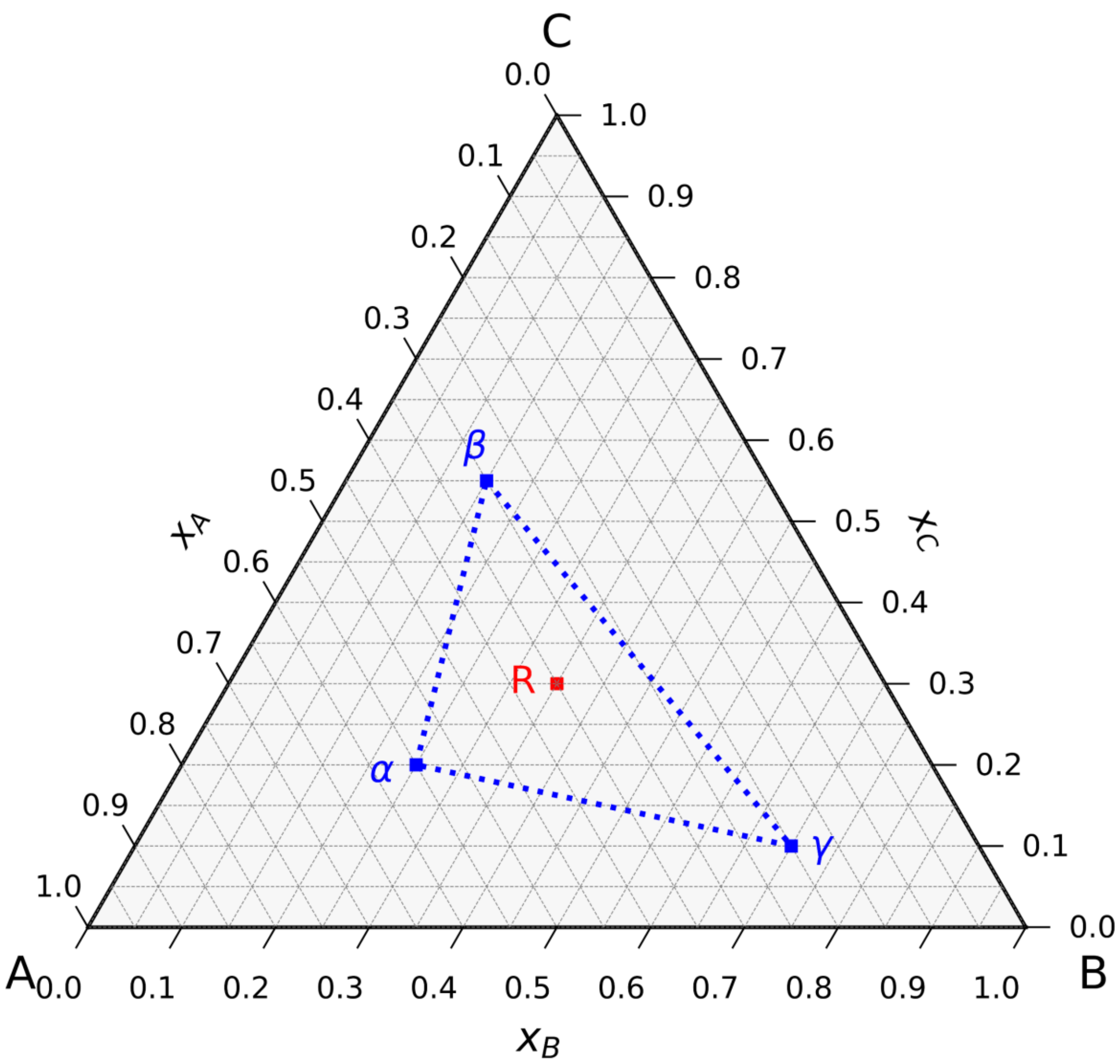


Ternary phase diagrams

a) The points α, β and γ mark the compositions of three different phases. Write down their compositions.

b) Calculate the phase fractions of all three phases at position point R in the ternary phase diagram.

c) Draw in the ternary diagram lines of constant elemental ratios: for A/B = 1/3 and $x_A = 0.5$



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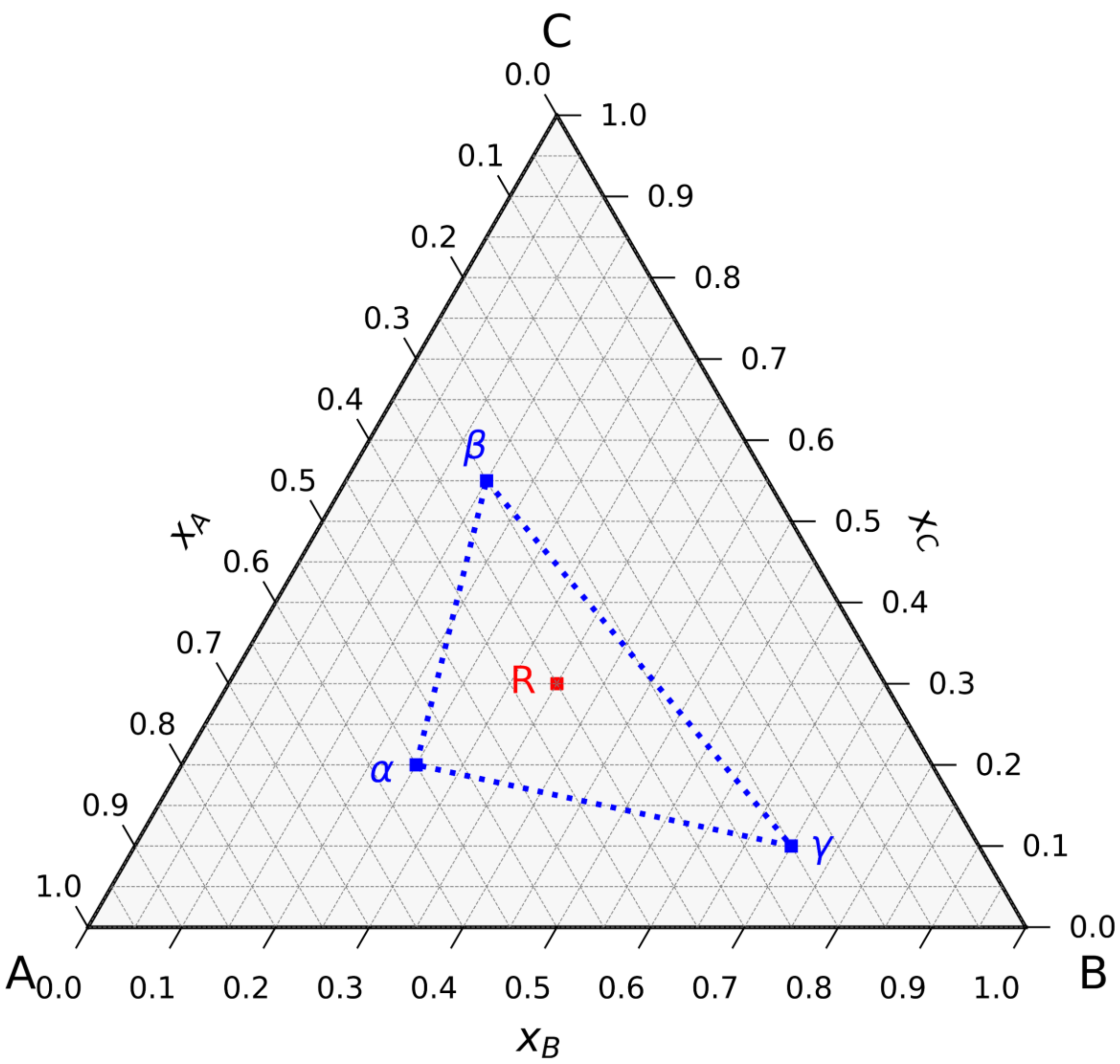

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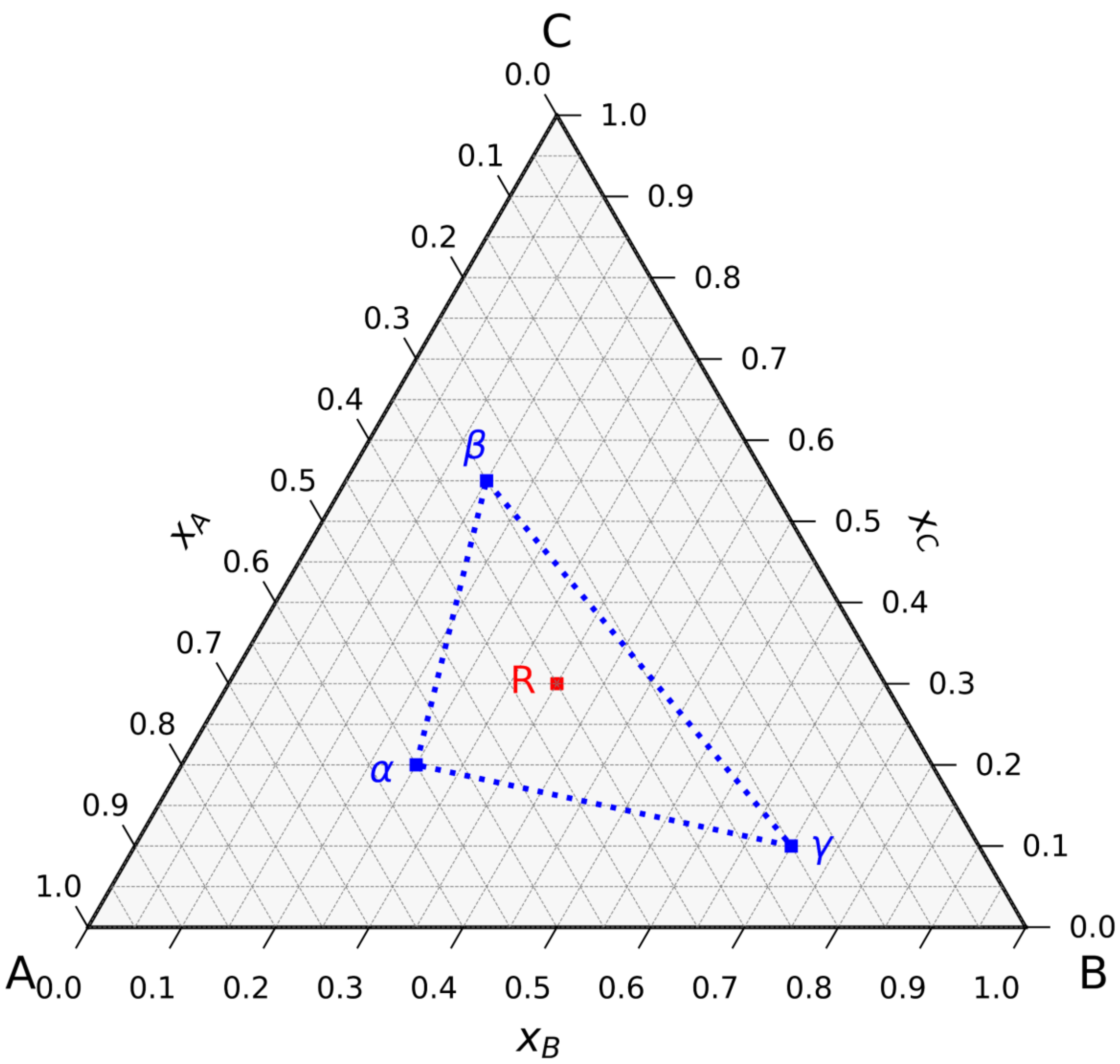
	A [%]	B [%]	C [%]
α	55	25	20
β	30	15	55
γ	20	70	10



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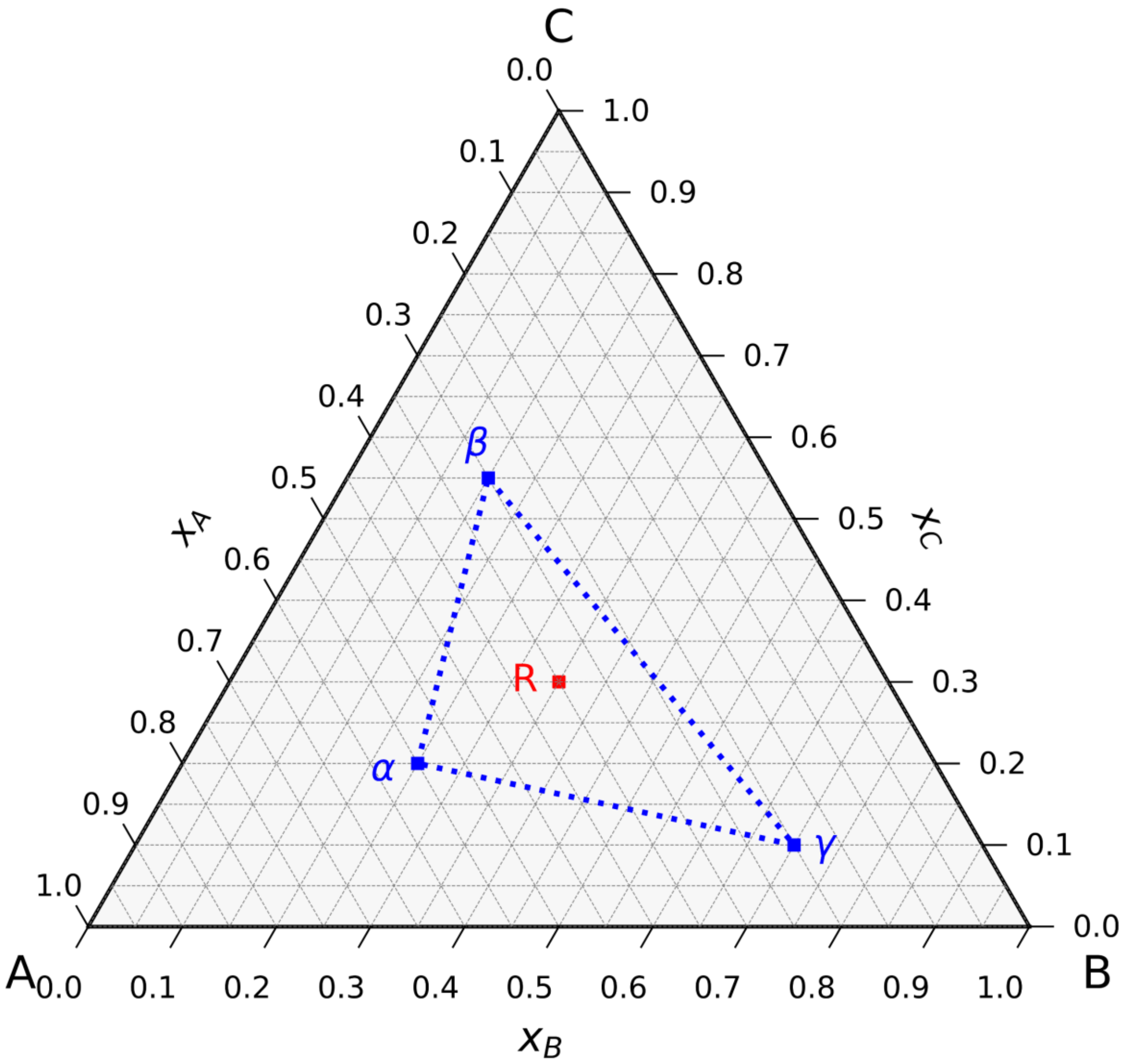

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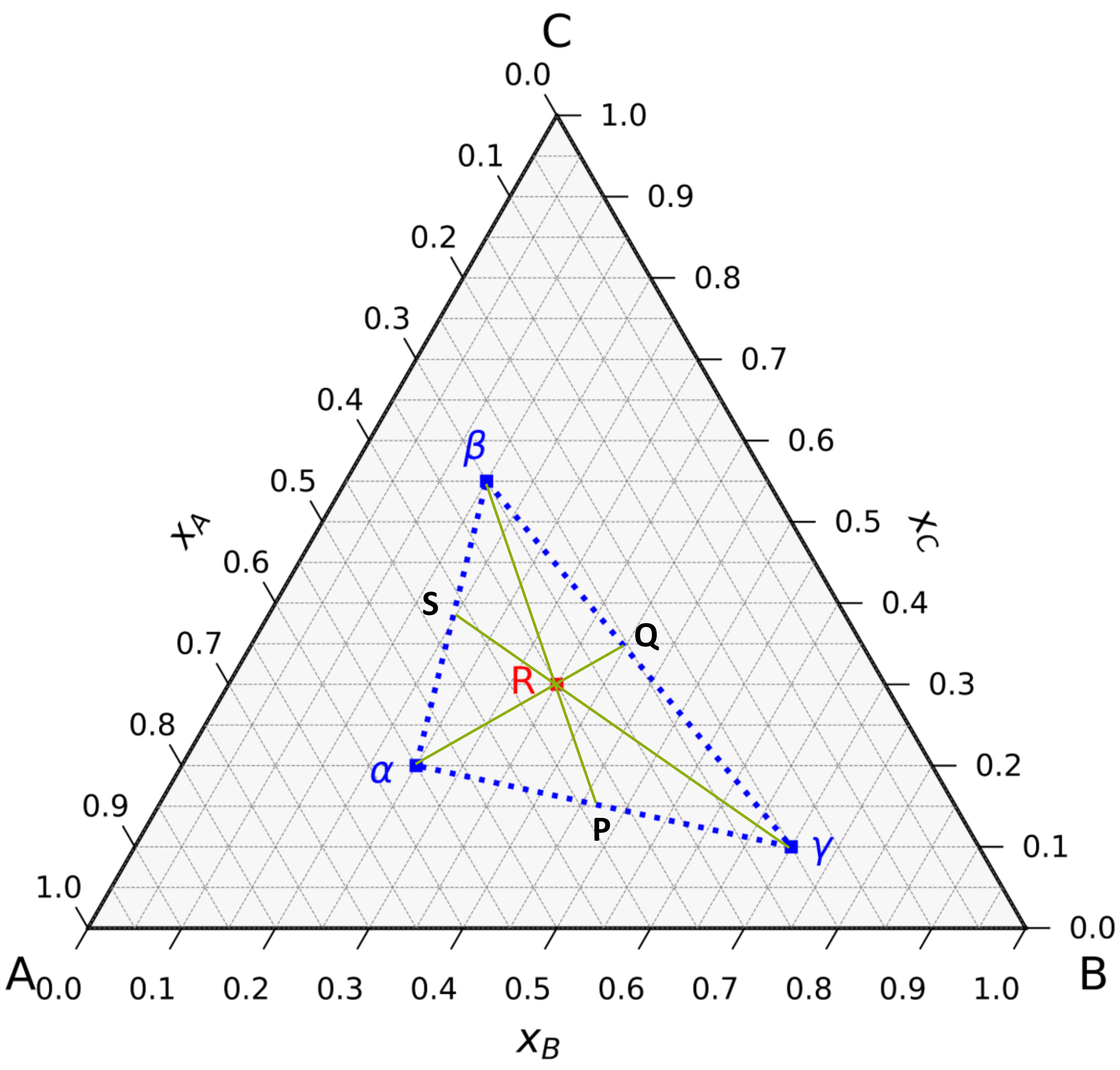

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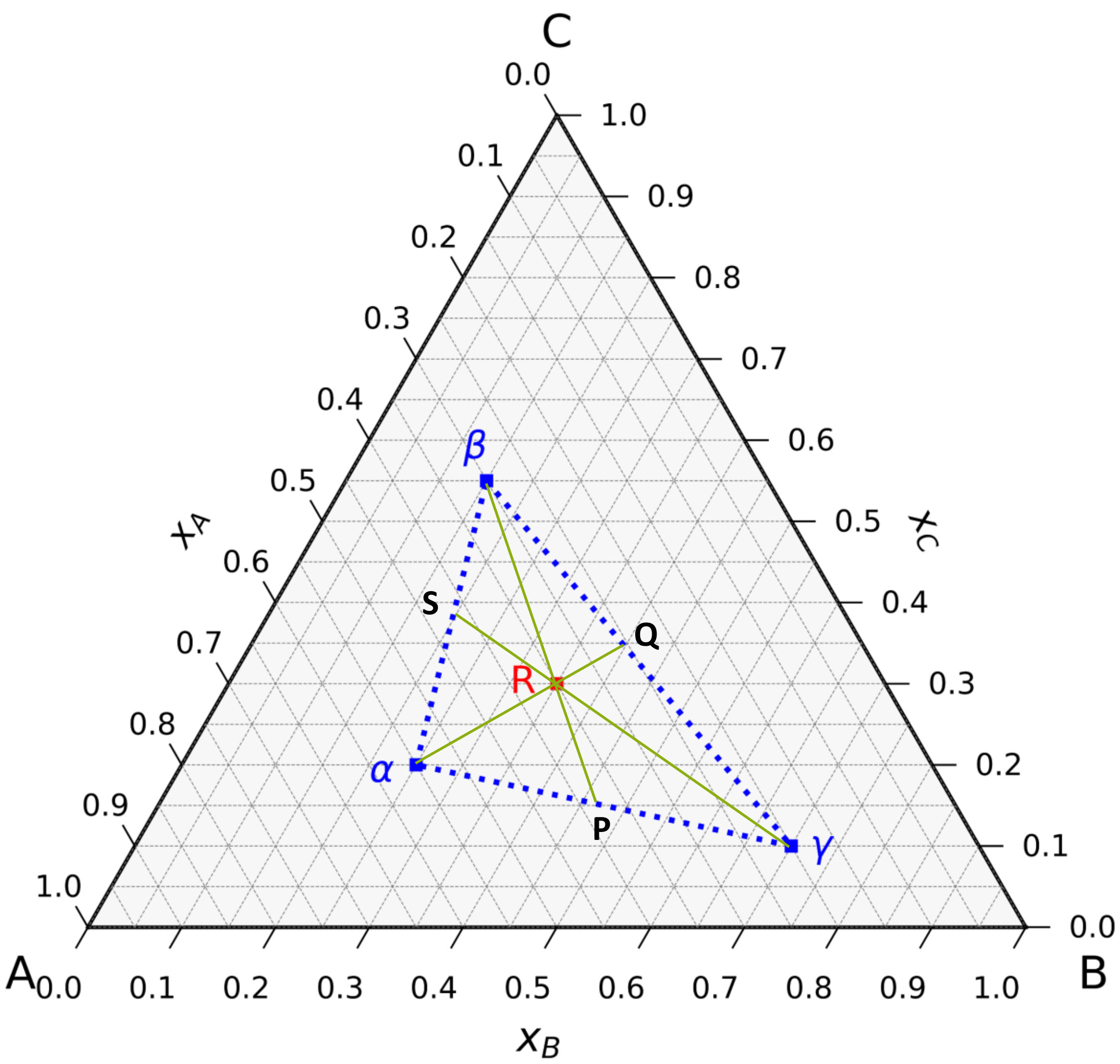
$$X_\alpha^P = \frac{\overline{RQ}}{\overline{\alpha Q}} = \frac{1{,}1\ cm}{3{,}4\ cm} = 0.3235$$

$$X_\beta^P = \frac{\overline{RP}}{\overline{\beta P}} = \frac{1{,}85\ cm}{4{,}85\ cm} = 0.3814$$

$$X_\gamma^P = \frac{\overline{RS}}{\overline{\gamma S}} = \frac{1{,}8\ cm}{5{,}85\ cm} = 0.3076$$

$$X_\alpha^P + X_\beta^P + X_\gamma^P \stackrel{!}{=} 100$$

	R [%]
α	32.4
β	38.1
γ	30.8
total	101.3



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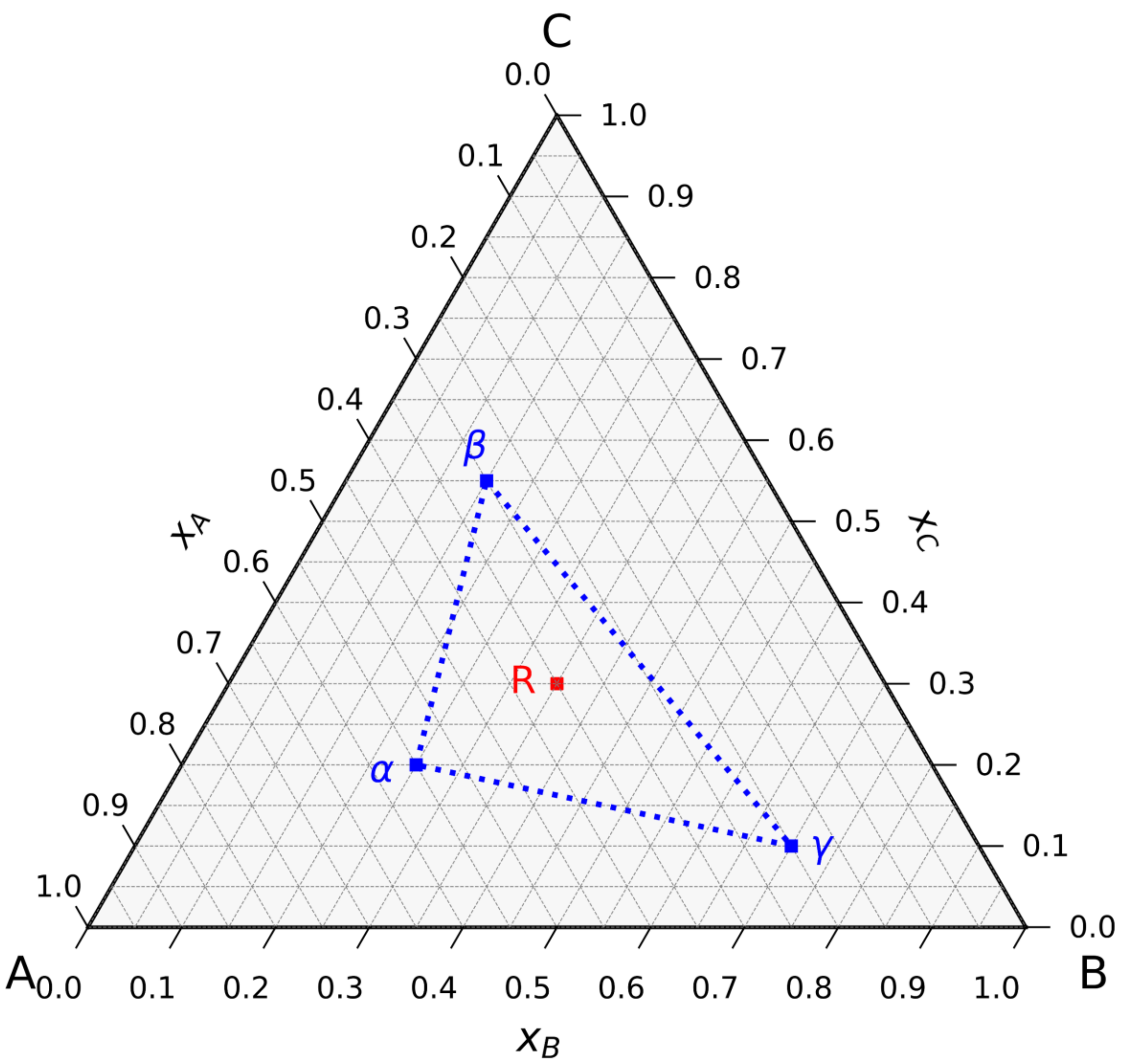

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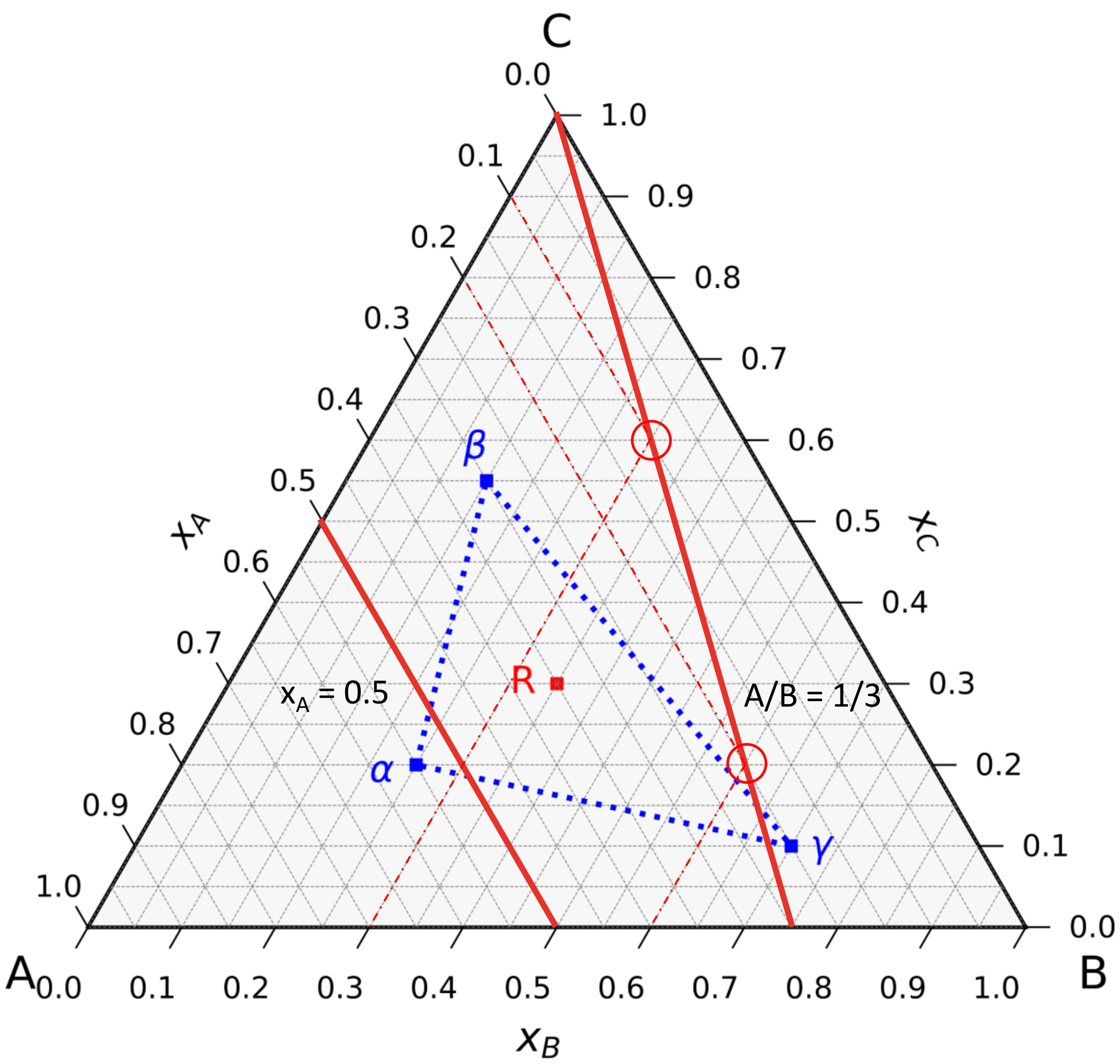
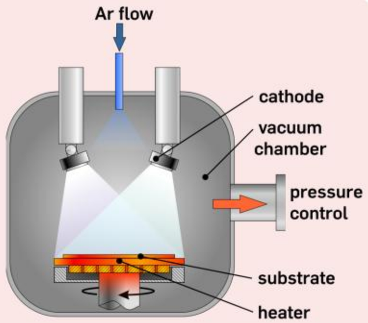
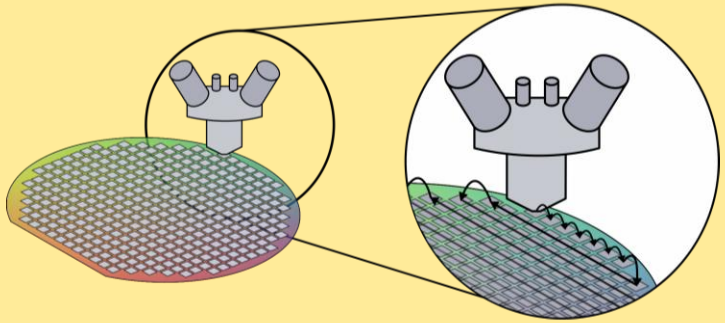


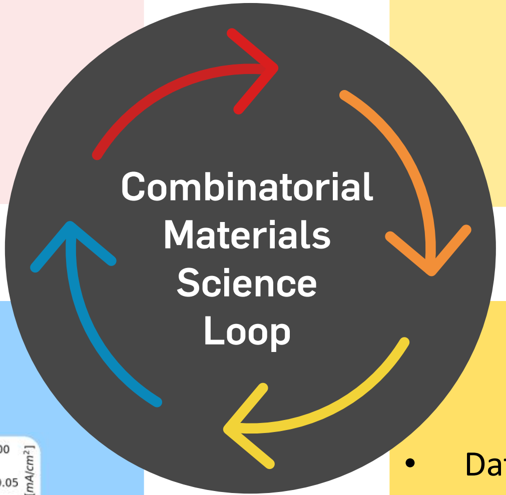
Combinatorial Material Science

Synthesis of materials libraries



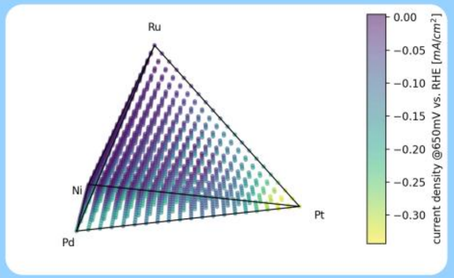
High-throughput characterization





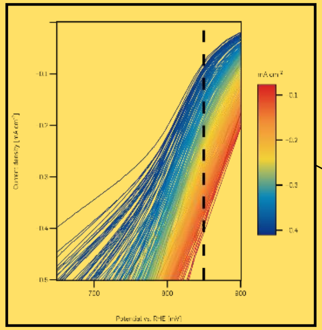
Planning of next experiment

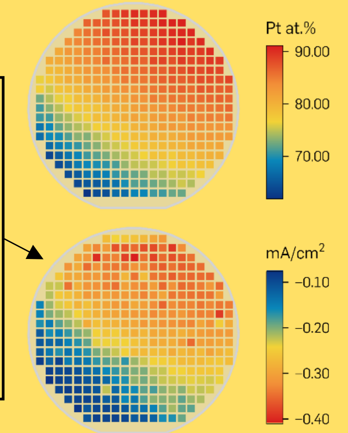
- May be guided by machine learning, to predict optimal region for next experiment
- May also be guided by researchers expertise, knowledge or intuition



Data analysis

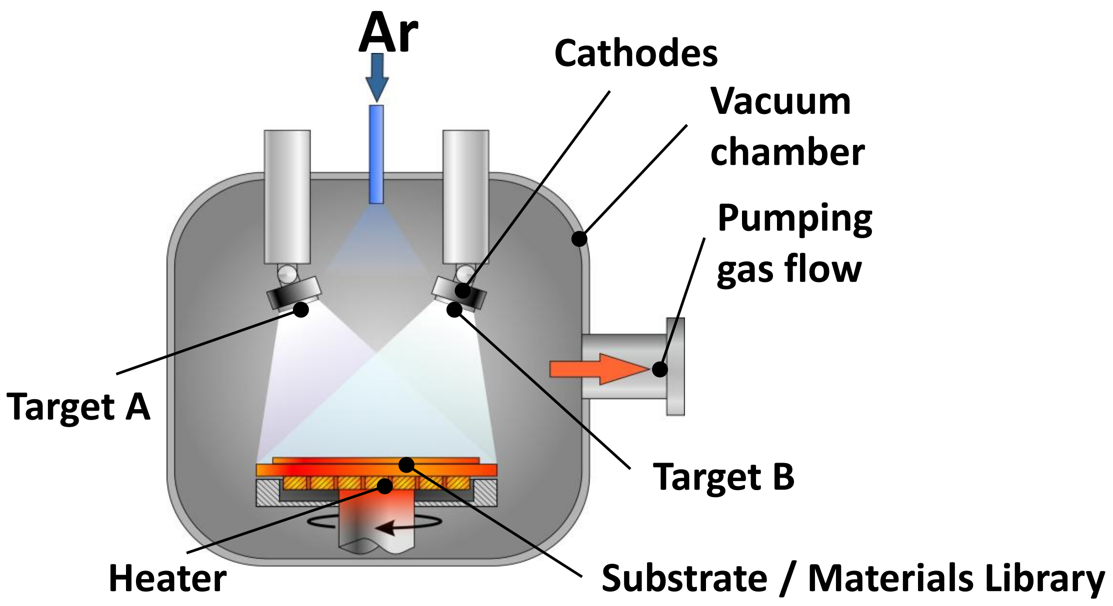
- Data is processed to identify trends, correlations
- Involves statistical tools, visualization techniques



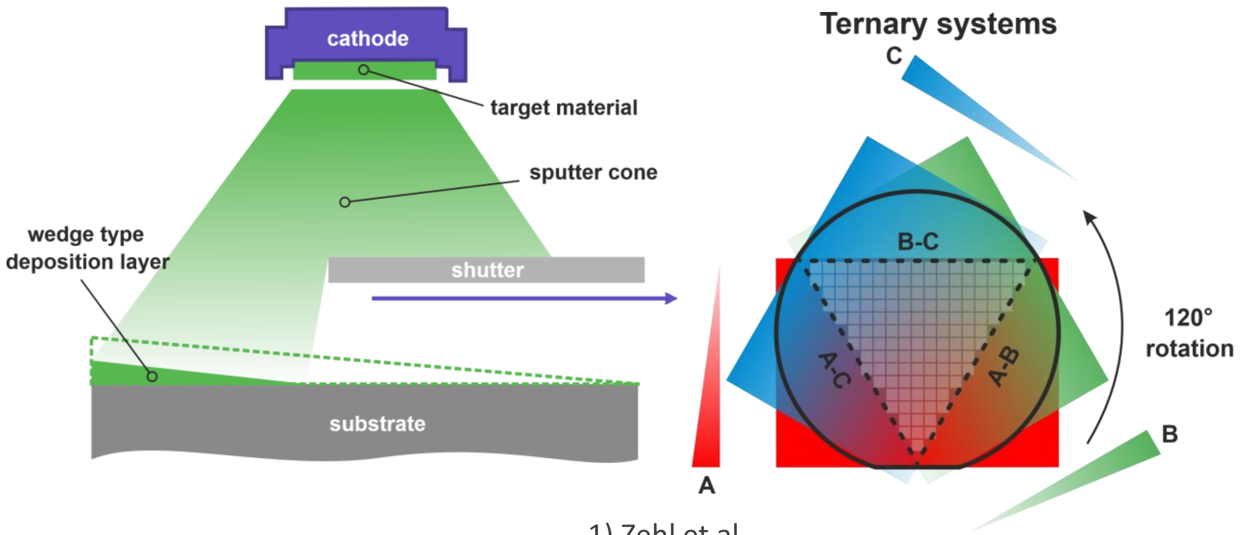


Synthesis - Sputtering

Cosputtering



Multi-layer deposition



1) Zehl et al.

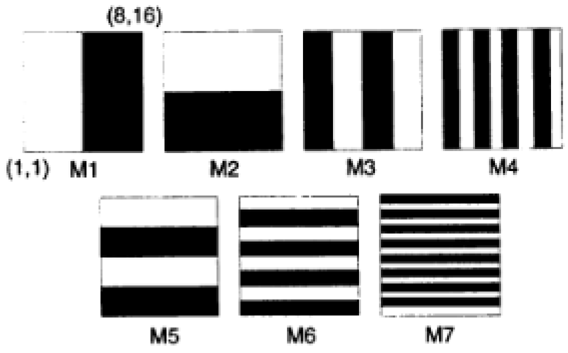
- Can not map an entire system with one materials library, due to parallel deposition
- Materials already mixed in the as-deposited state → can analyse metastable materials (e.g. solid solutions normally forming at high temperatures)

- Possibility of mapping an entire ternary system with just one materials library
- Necessity to anneal the materials library after the deposition process → only stable materials can be screened

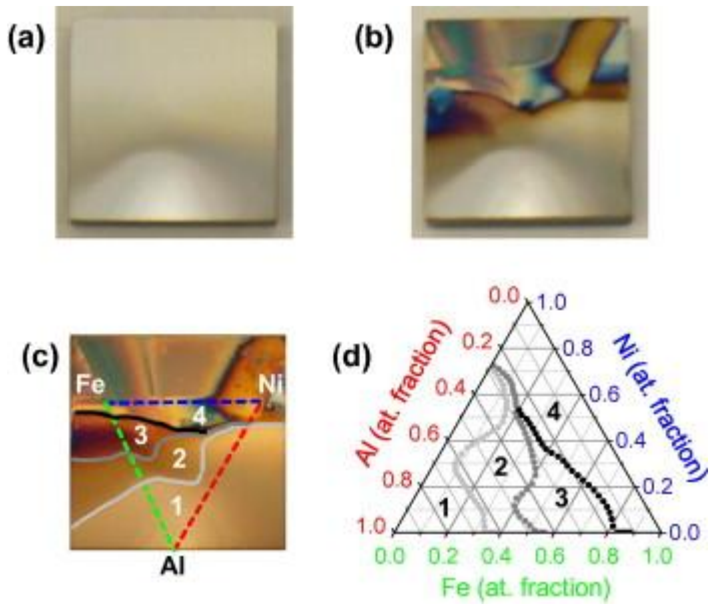
Materials library

Materials library: A well-defined set of materials (suitable for high-throughput characterization) produced in one experiment under identical conditions. Either continuous or discrete materials libraries can be synthesized.

1) Piotrowiak et al. : Continuous materials library of La-Co-Mn-Fe on a single crystal Al_2O_3-substrate (with a 100 mm diameter)



2) Xiang et al. : Discrete materials library of with MgO single crystal as substrate (each discrete site is 1x2 mm)



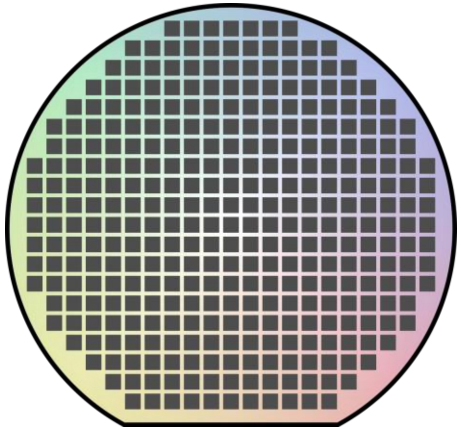
3) Payne et al.: Continuous materials library of $Al_xFe_yNi_{1-x-y}$ on a polycrystaline Mo-substrate (14x14x2.5 mm)

1) Piotrowiak et al. (2023), doi.org/10.1002/adem.202300437
2) Xiang et al. (1995), DOI: 10.1126/science.268.5218.1738
3) Payne et al. (2015), doi.org/10.1016/j.corsci.2014.10.034

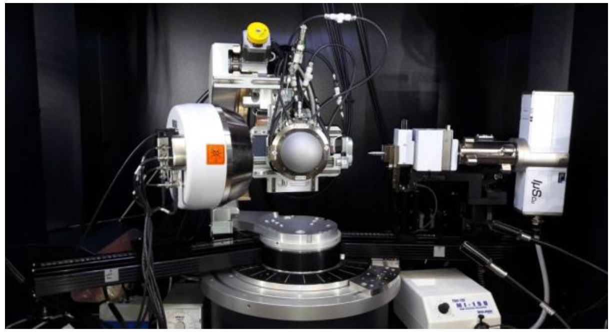
High-throughput characterization

Screening should be: automated, quick, quantitative, non-destructing.
It can be distinguished between parallel and sequential screening.

With parallel screening the entire materials library can be screened in one measurement (e.g. photo for optical analysis).
To sequentially screen a continuous materials library, measurement areas have to be defined. These are screened one after the other automatically (e.g. EDX, XRD, 4PP).

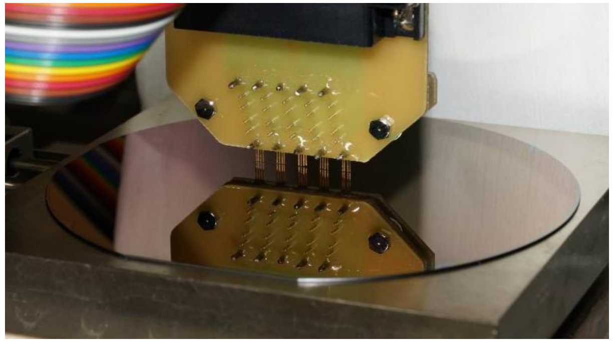


342 measurement areas on a materials library on a 4 inch wafer



XRD

EDX

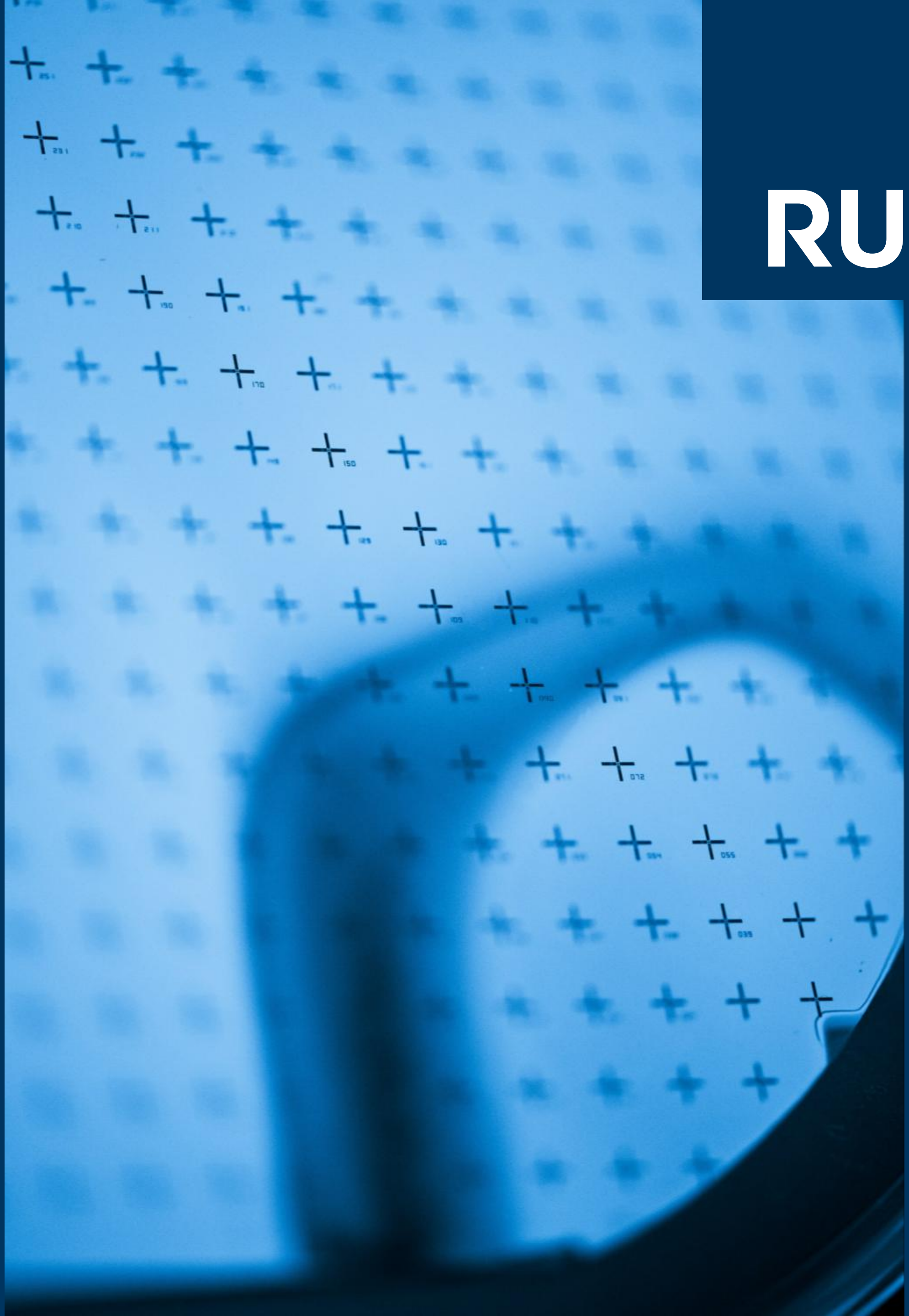


4PP

- **EDX** (Energy dispersive X-ray spectroscopy for chemical composition)
- **XRD** (X-ray diffraction for phase constitution)
- **4PP** (4-point-probe measurement for electrical resistance)
- **SDC** (Scanning droplet cell for electrochemical activity)
- **Photo** (for optical analysis)
- **Potential-Seebeck Microprobe** (for Seebeck coefficient)

………

Questions?



Contact

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