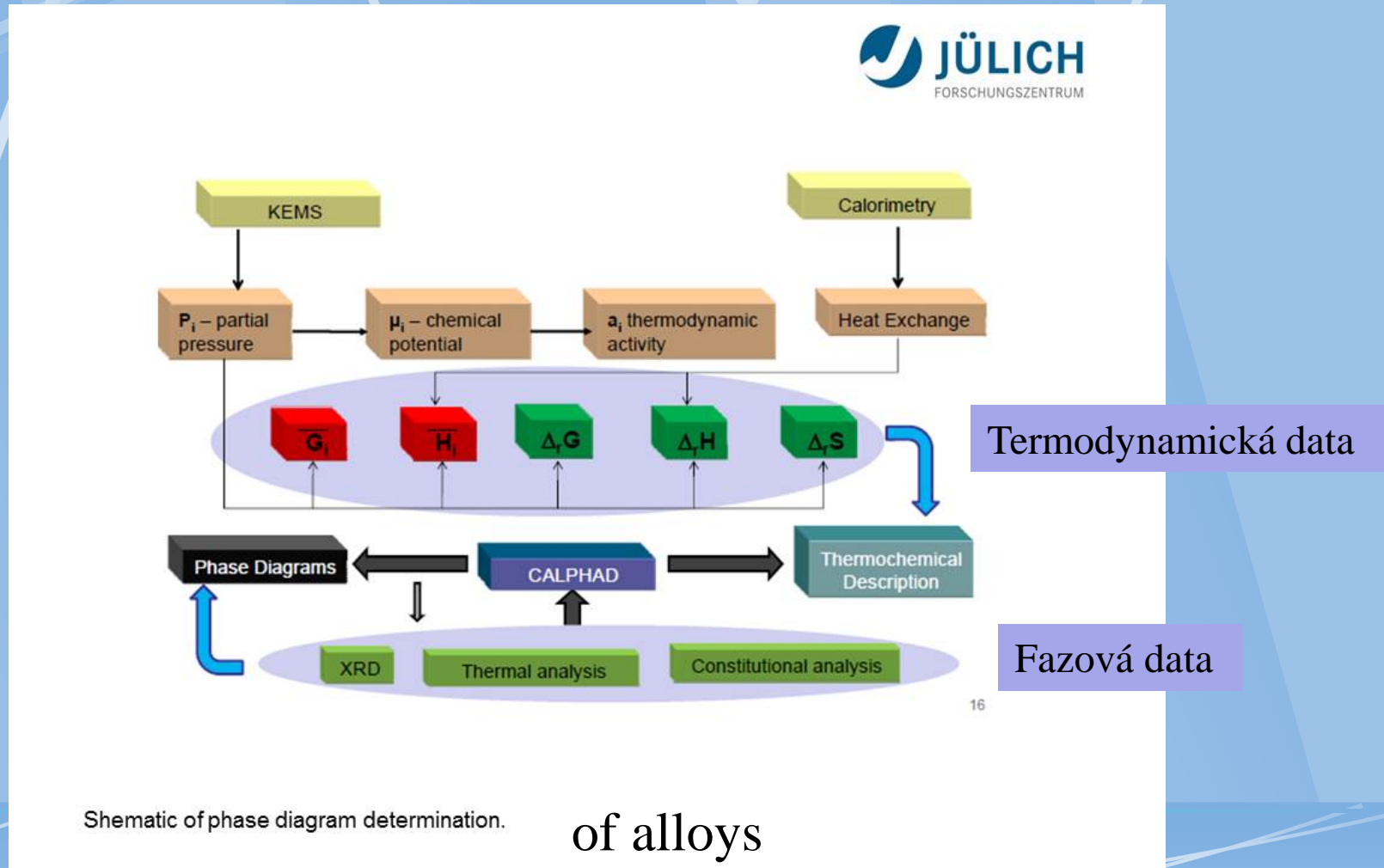


# Experimentální metody studia FR

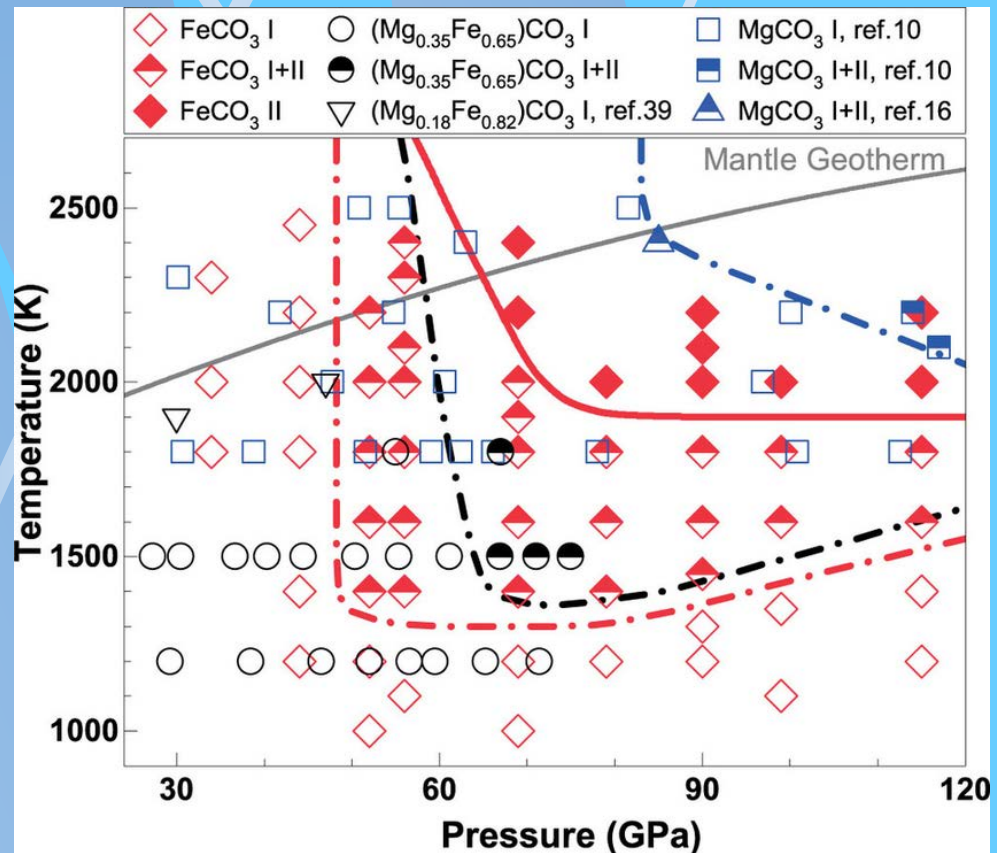


# Experiment

## Měření fázových dat

## Měření termodynamických dat

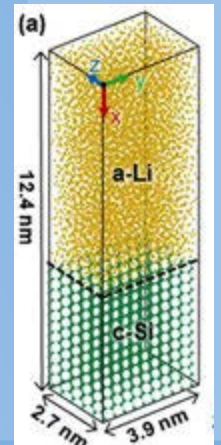
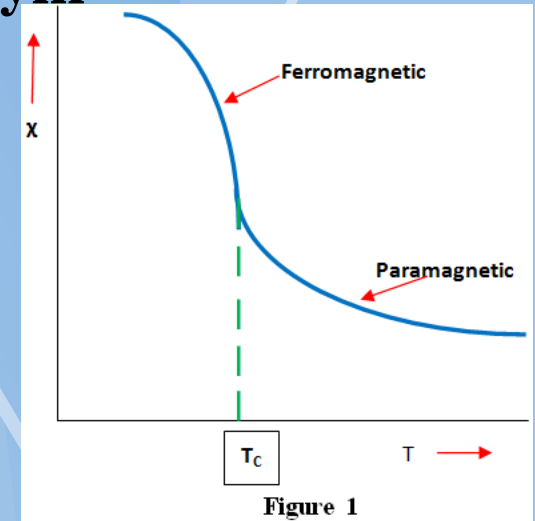
Viz data získaná řešením  
fázové rovnováhy v  
uzavřené soustavě  
nacházející se v  
termodynamické  
rovnováze



**Při experimentu měníme teplotu, (tlak), složení.**

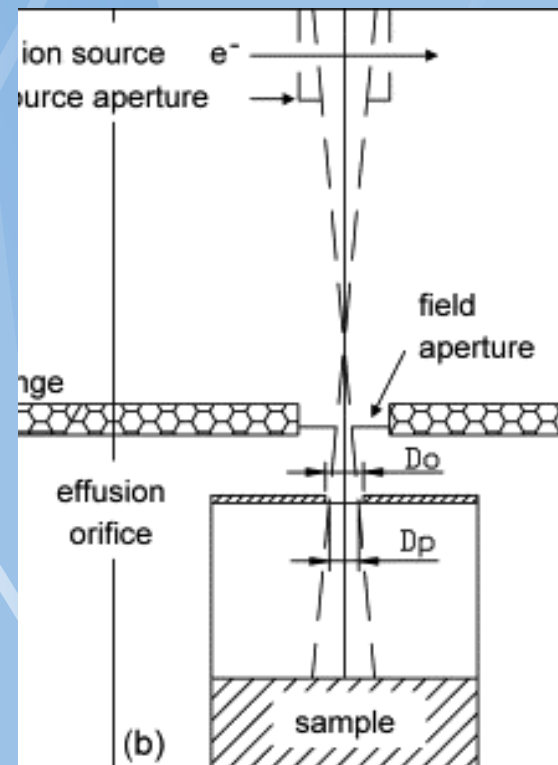
# Měření fázových dat

- **Neisotermální metody (pro soustavy s rychlým ustavením termodynamické rovnováhy)**
  - Termická analýza (TA, DSC, DTA,...)
  - Měření chemických potenciálů
  - Měření magnetické susceptibility
  - Měření vodivosti
  - Dilatometrie
- **Isotermické metody (Equilibration)**
  - Metalografie , difrakce (XRD) – fázové podíly
  - Mikroanalytické metody (WDX, EDX, Laserová ablace, ...) – složení koexistujících fází
  - Studium difúzních párů a multivrstev
  - **Aplikace analytické chemie na anorganické, organické, či polymerní směsi** (destilace na koloně, extrakce,

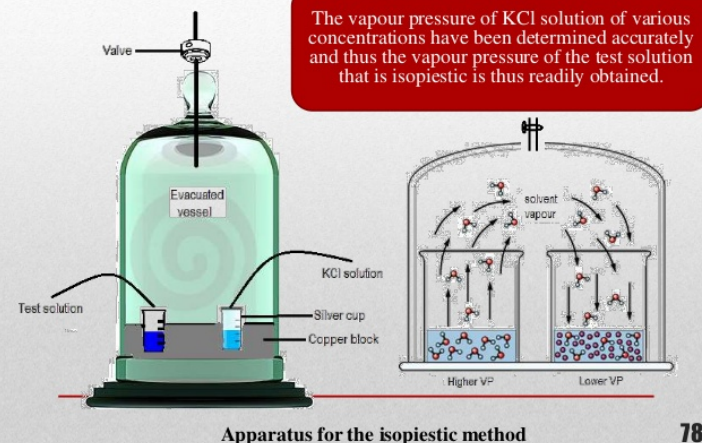


# Měření termodynamických dat

- **Kalorimetrické metody**
  - Měření entalpií a tepelných kapacit
  - Měření entalpii fázových transformací
- **Temperace s plynnou fází**
  - Statické metody měření tenzí par (aktivity složek)
  - Kondenzační metody a neisotermické isopiestické metody
  - Knudsenova efúzní metoda
- **Měření elektromotorických napětí ( $\Delta G$ )**



Isopiestic method is used for precise determination of vapour pressures.



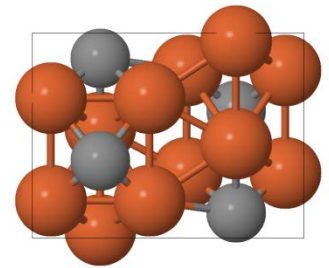
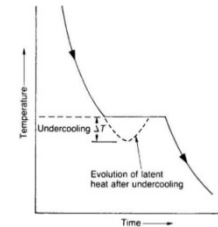
# Role of phase Transformation Kinetics

Nucleation effects (undercooling)

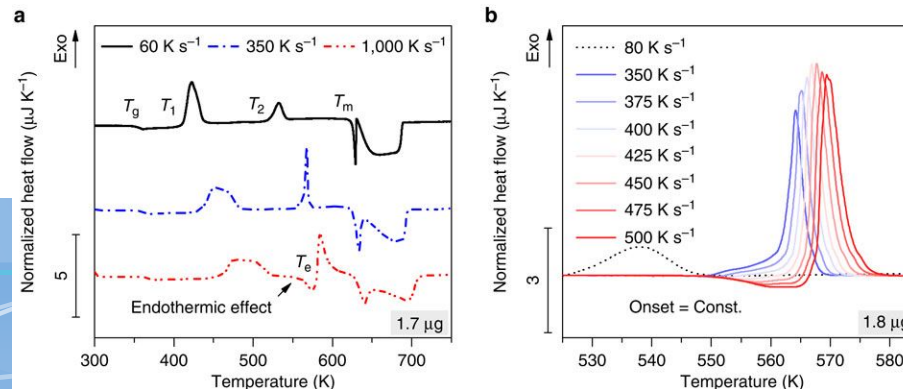
Formation of metastable phases

Shifting of Transformation-Start Temperature with Heating Rate

Cooling curve for a pure metal showing possible undercooling.



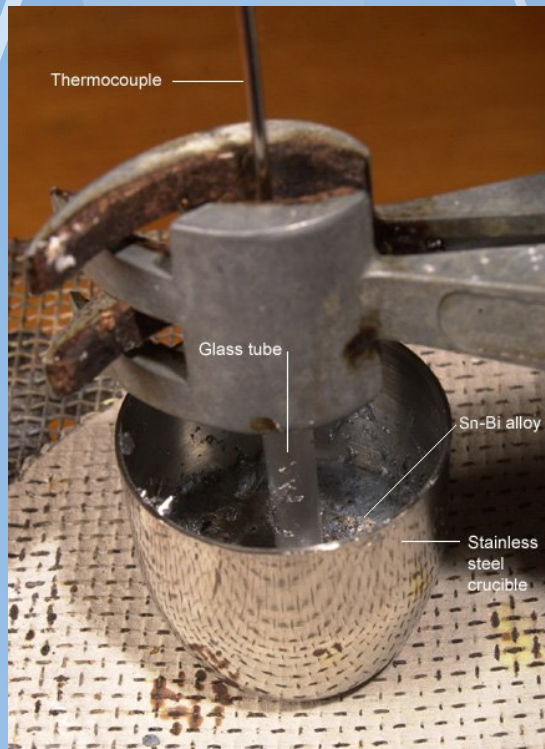
Cementite vs. graphite



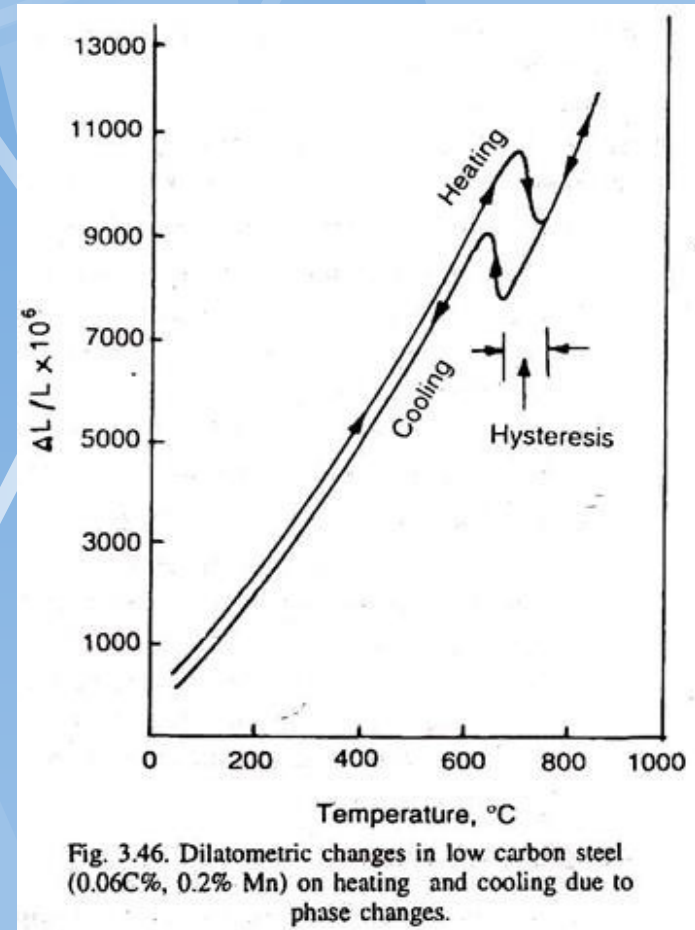
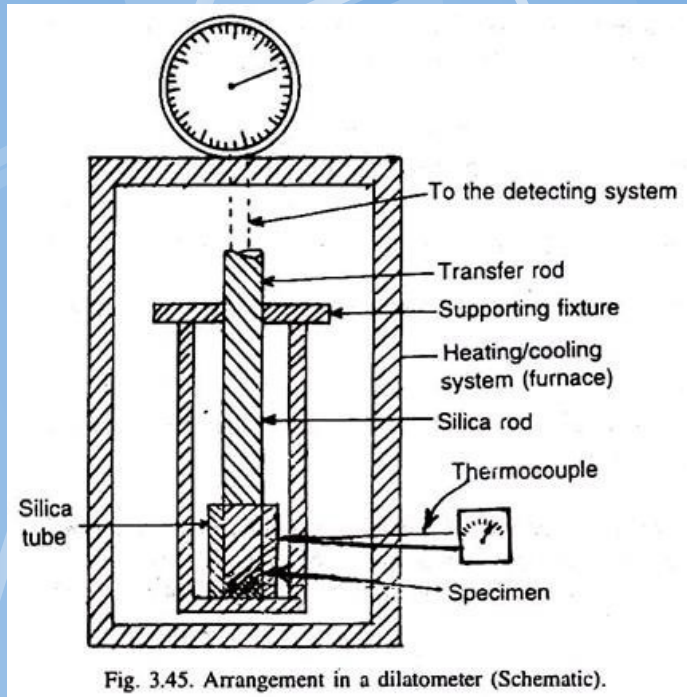
Heating of  $\text{Au}_{70}\text{Cu}_{5.5}\text{Ag}_{7.5}\text{Si}_{17}$ .



# Thermal analysis (viz samostatná lekce)



# Dilatometry

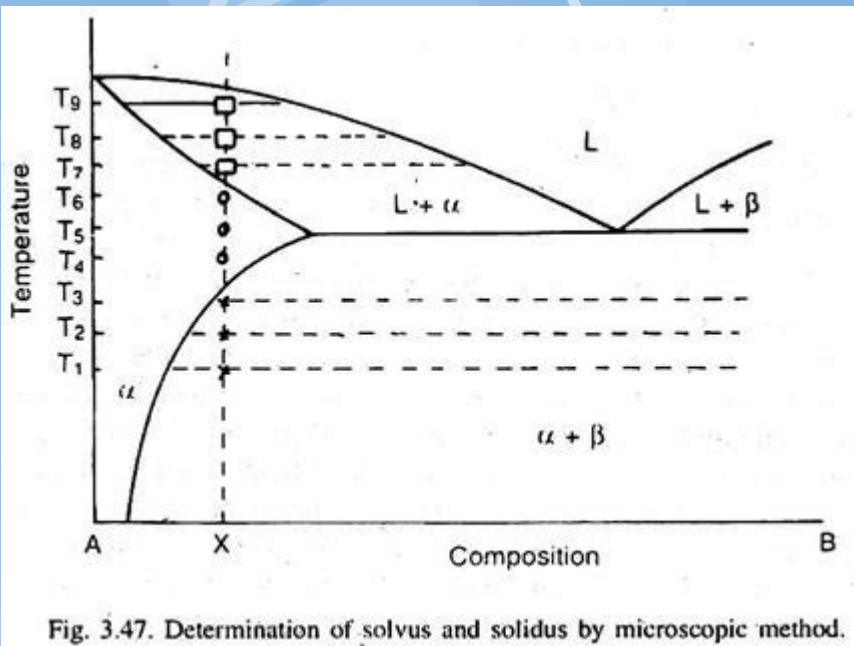


Dilatometry is based on the volume (length) change associated with most phase changes. Fig. 3.45 schematically shows the main features of a dilatometer. The temperature and dilation (change in length) of the sample are simultaneously monitored as a function of time. The simplest dilatometer usually consists of a silica tube with one end closed and provision for the sample to rest firmly upon the closed end inside the tube.

# Microscopic Methods

**Rapid quenching:**  
method for conservation  
of chemical composition

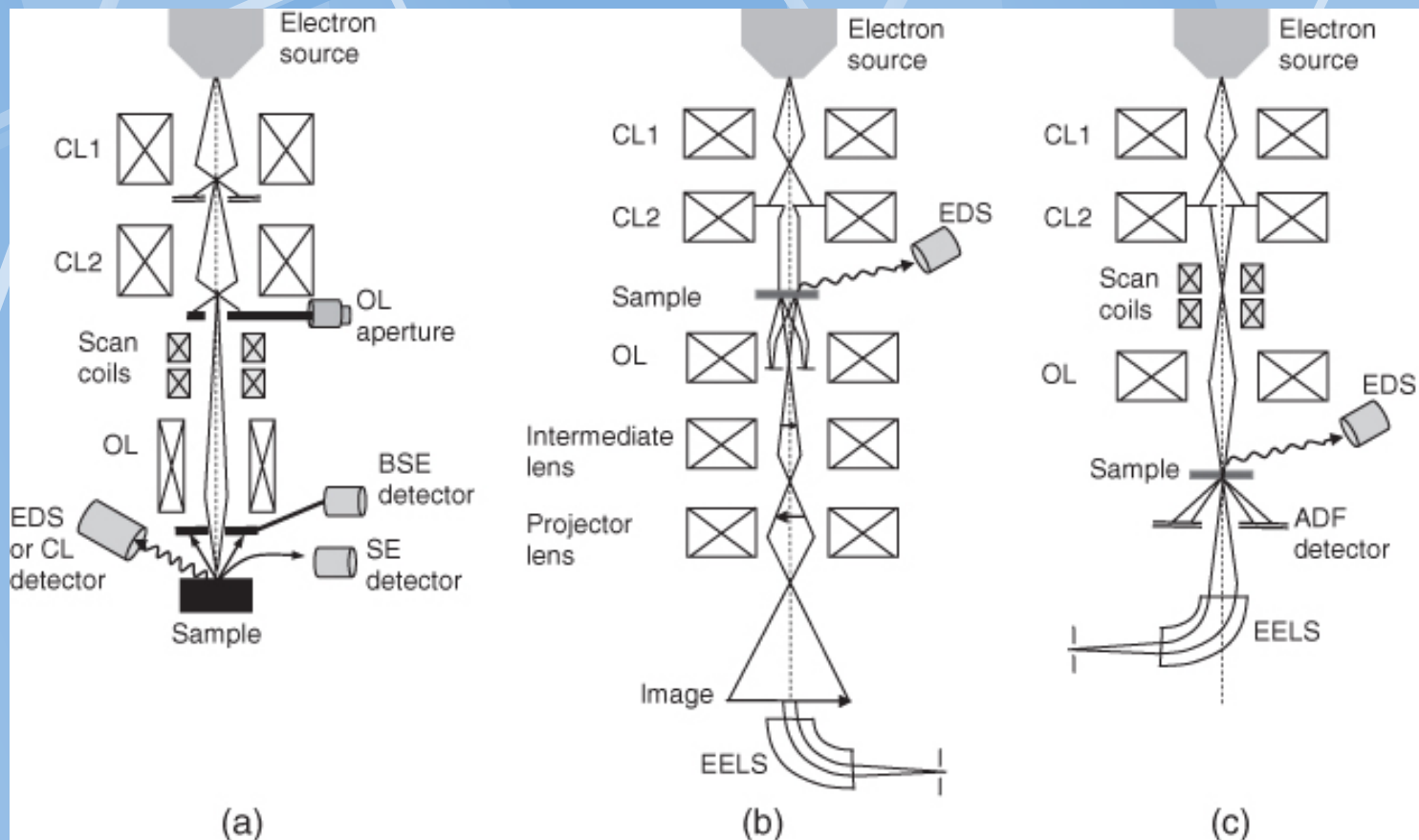
Light microscopy = history



There are various methods using microscopic techniques in determining the phase diagrams. Moreover, microscopic techniques are also used to verify the phase diagrams determined by other methods, where microscopic examination of cast and heat-treated alloys at small composition intervals across the system is done. It is a worth-while but laborious work.

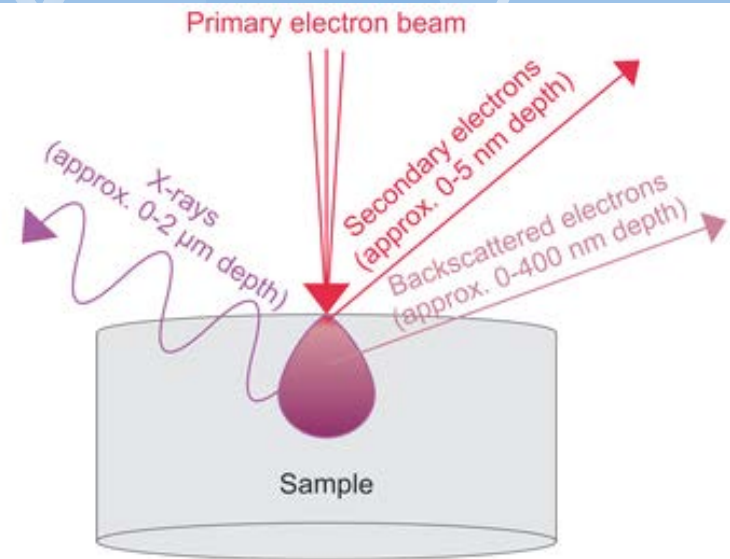
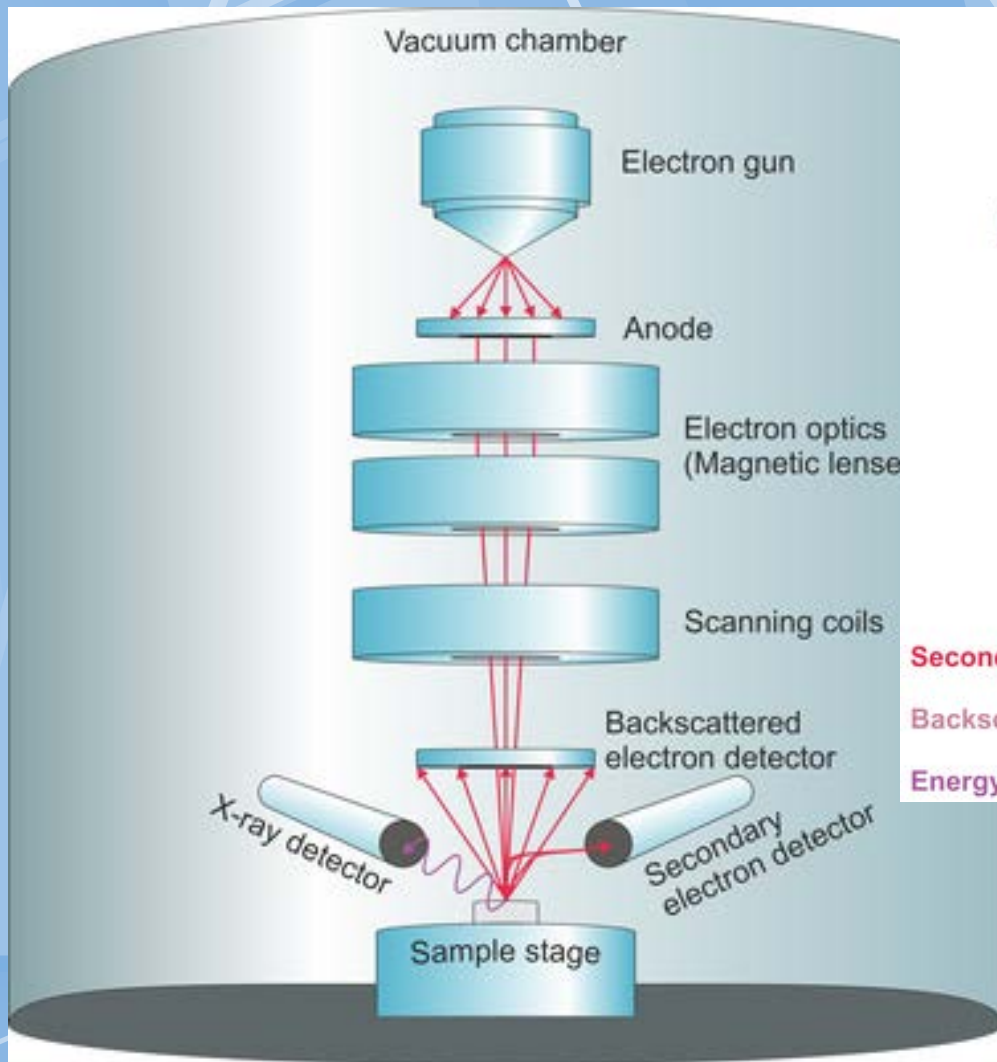


# Metody elektronová mikroskopie



Simplified schematic cross-sections of an (a) SEM, (b) TEM and (c) STEM instrument.

# Detectors



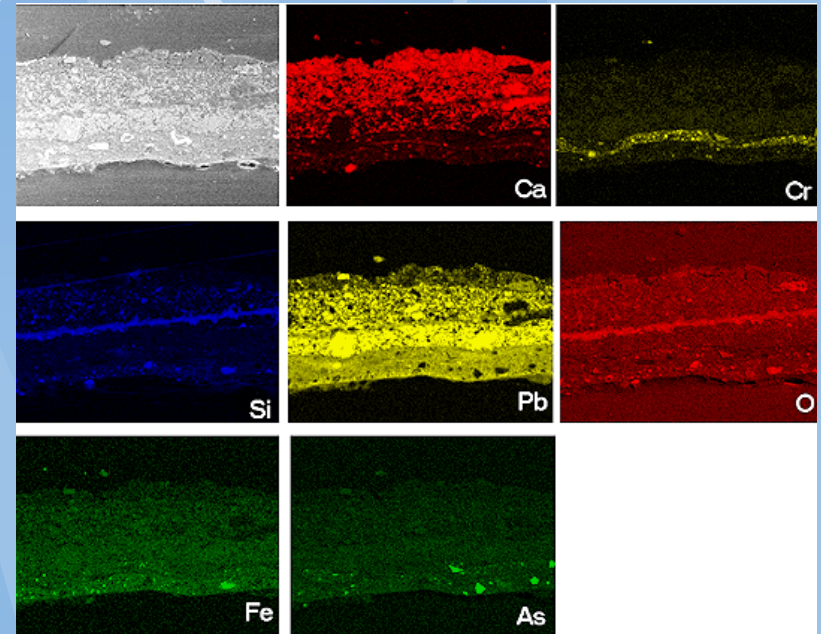
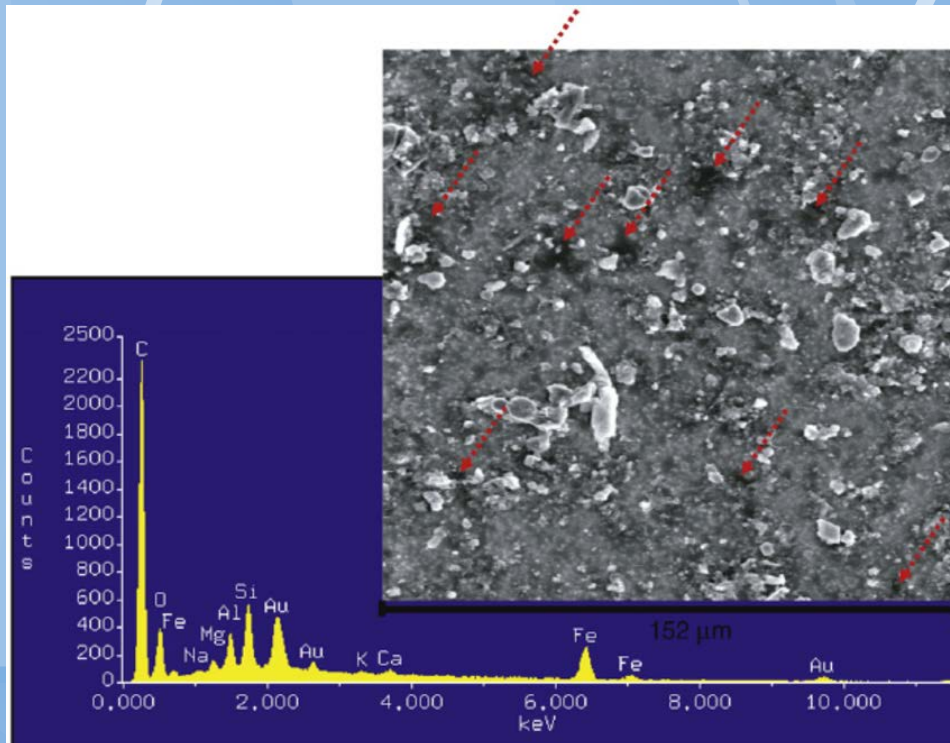
**Secondary electron imaging (SEI): mainly topography contrast**

**Backscattered electron imaging (BEI): mainly material contrast**

**Energy-dispersive X-ray spectroscopy (EDX): elemental analysis**

# SEM

## Scanning electron microscopy

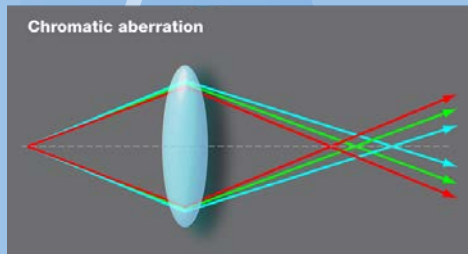
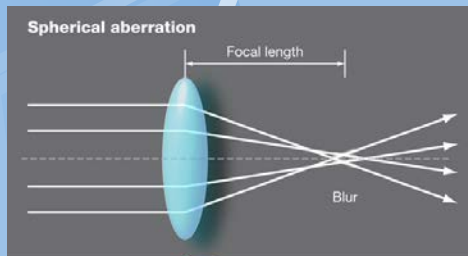


Mapping of elements

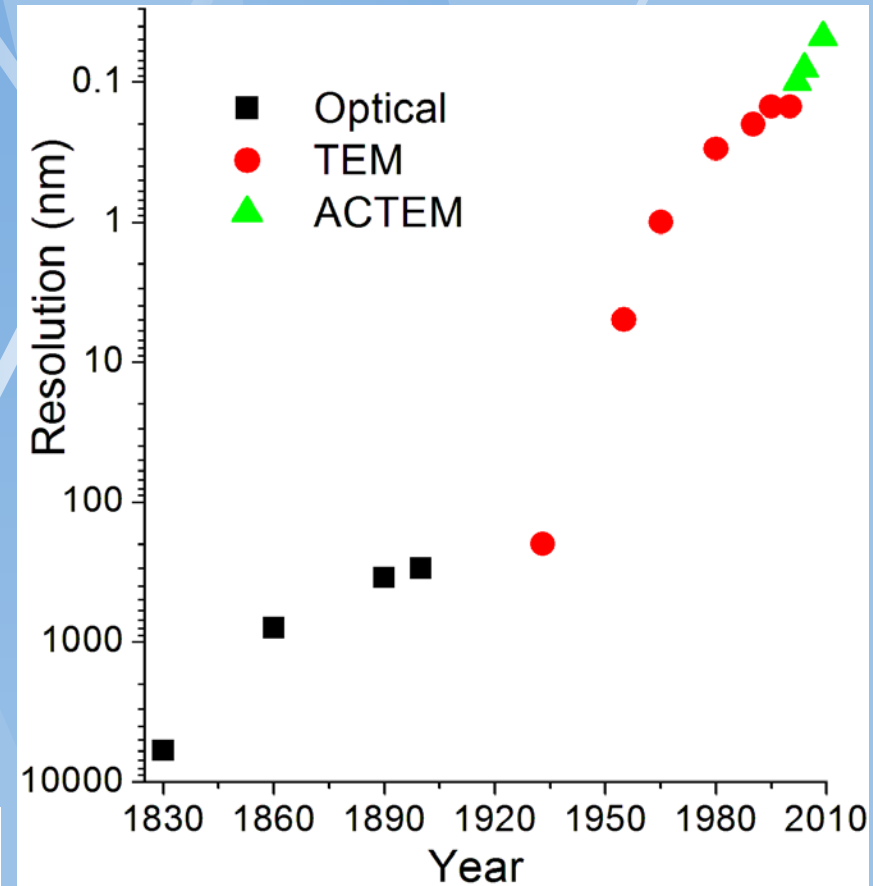
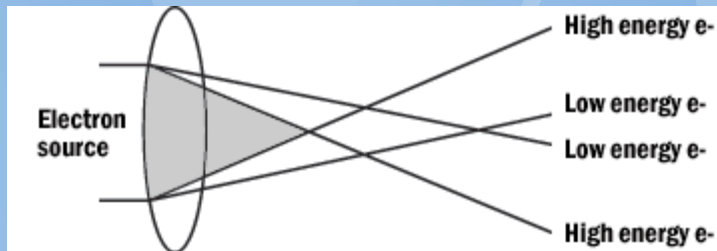
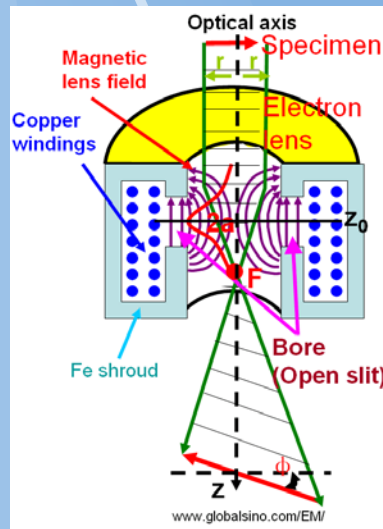
# HRTEM

## (aberration corrected TEM)

Light beam

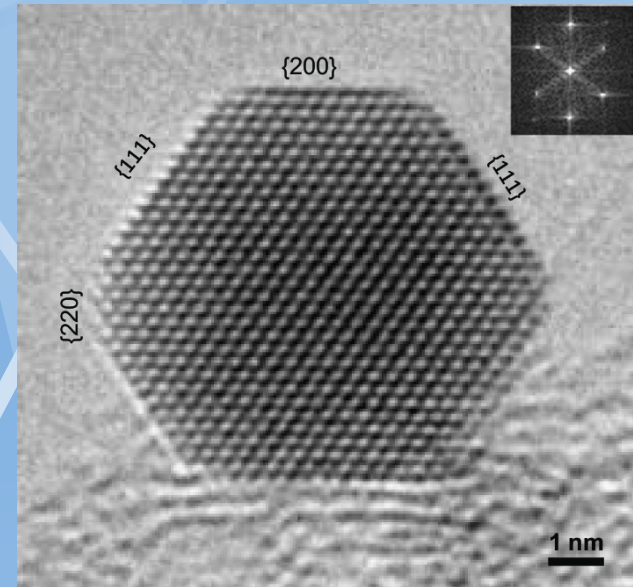
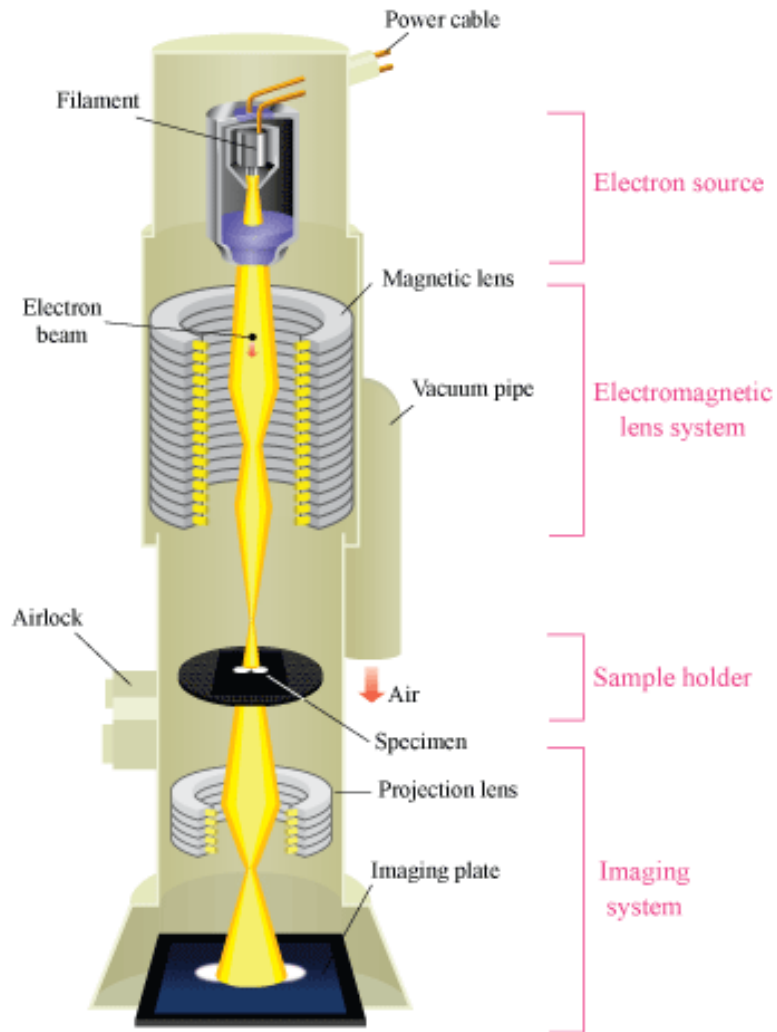


Electron beam

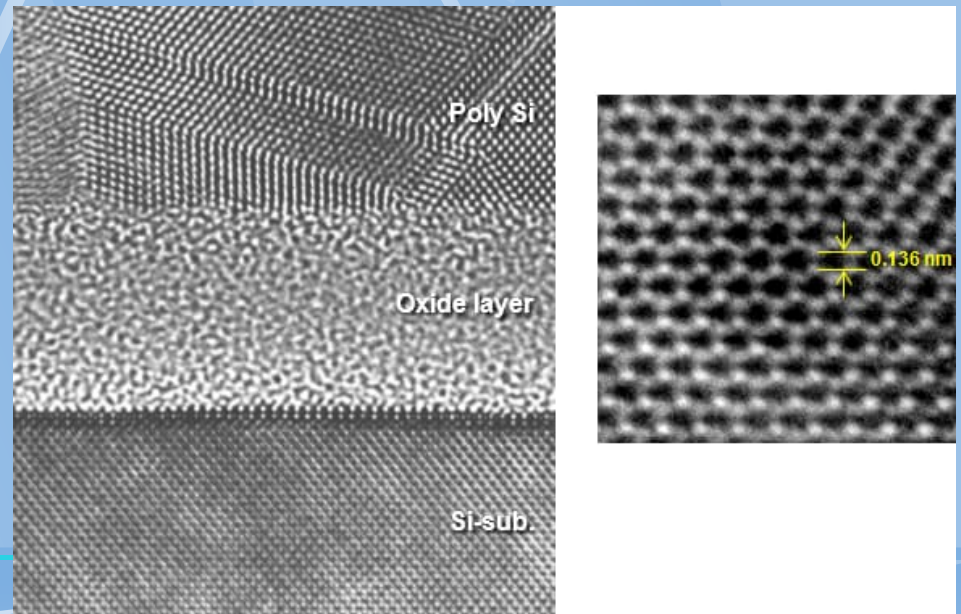




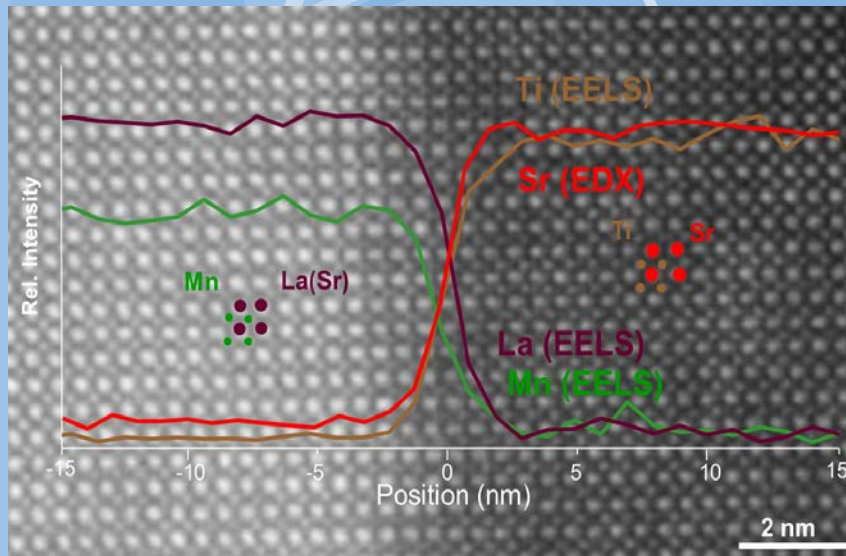
# HRTEM



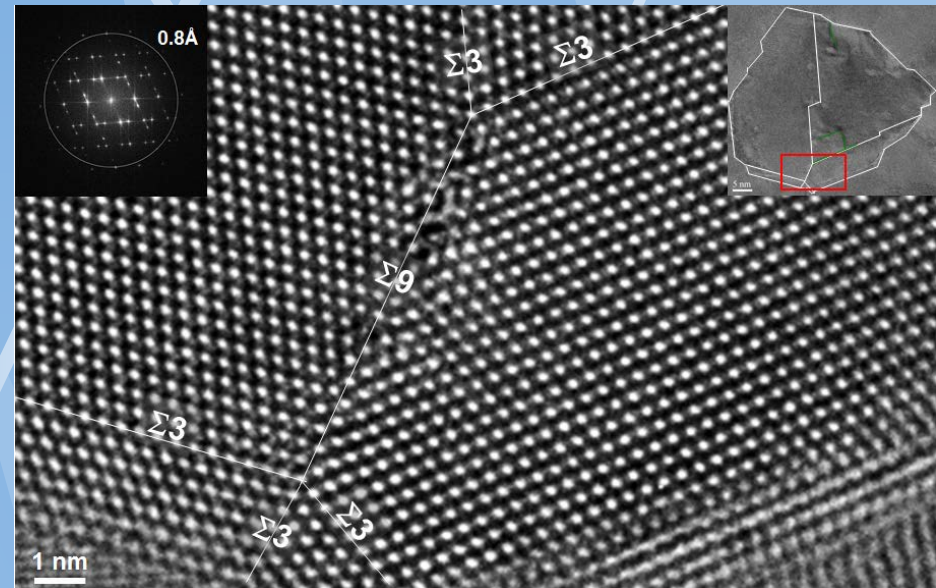
[https://www.researchgate.net/figure/High-resolution-TEM-image-of-an-AgI-nanoparticle-recorded-parallel-to-the-01104-zone\\_fig21\\_278072402](https://www.researchgate.net/figure/High-resolution-TEM-image-of-an-AgI-nanoparticle-recorded-parallel-to-the-01104-zone_fig21_278072402)



# Examples (FEI Titan 80–300)



*HAADF-STEM image (filtered by NAD) of a  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3/\text{SrTiO}_3$  interface with the individual atomic columns well resolved across the interface. Overlaid is an EELS/EDX intensity profile across this interface. P.M. Leufke and D. Wang et al., *Thin solid films*, 2012, 520, 5521-5527.*



*Fig. 2: Atomic resolution TEM image of a triple and a quadruple line at the interface between  $\Sigma 3$  boundaries and a  $\Sigma 9$  boundary in nanocrystalline palladium. H. Rösner and C. Kübel et al., *Acta Mat.*, 2011, 59, 7380-7387.*

# X-Ray Diffraction Methods

**X-rays are used while alloys are in solid-state to:**

- (i) Identify composition of a phase
- (ii) Crystal structure of the phase
- (iii) Lattice parameter of the crystal structure.

And, thus, are used to locate the solvus lines in phase diagrams.

The method of lattice parameter measurement depends on the fact that crystal dimensions, i.e., lattice parameter increases with the increase of the solute content in the solid solutions, till it gets saturated.

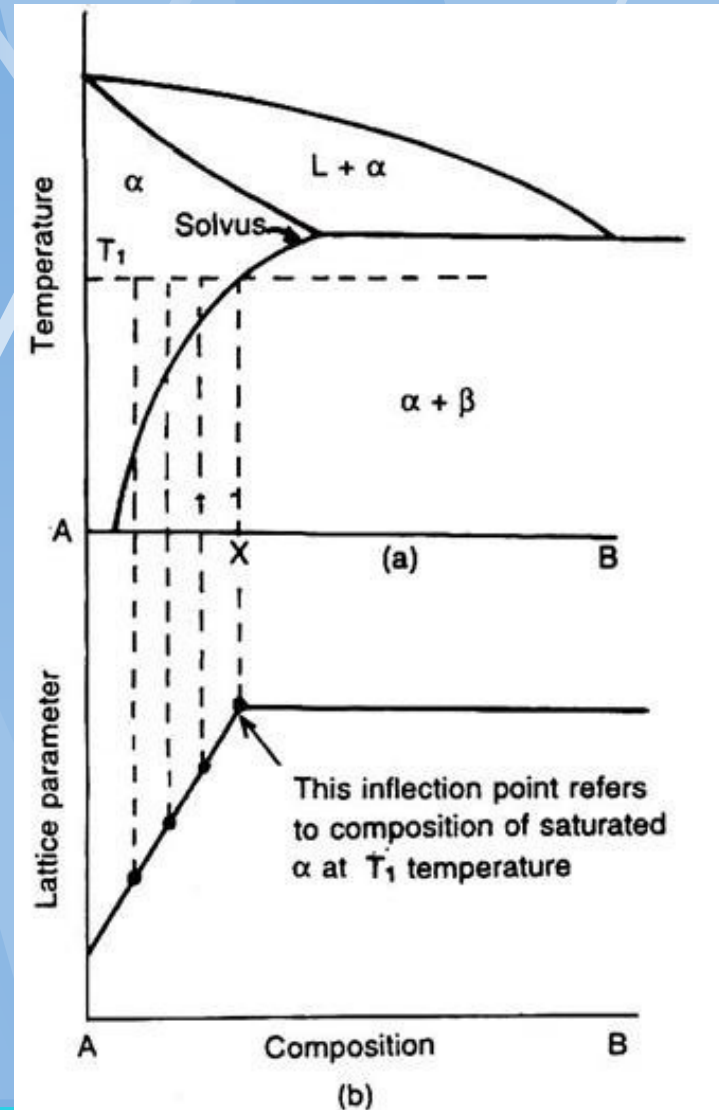
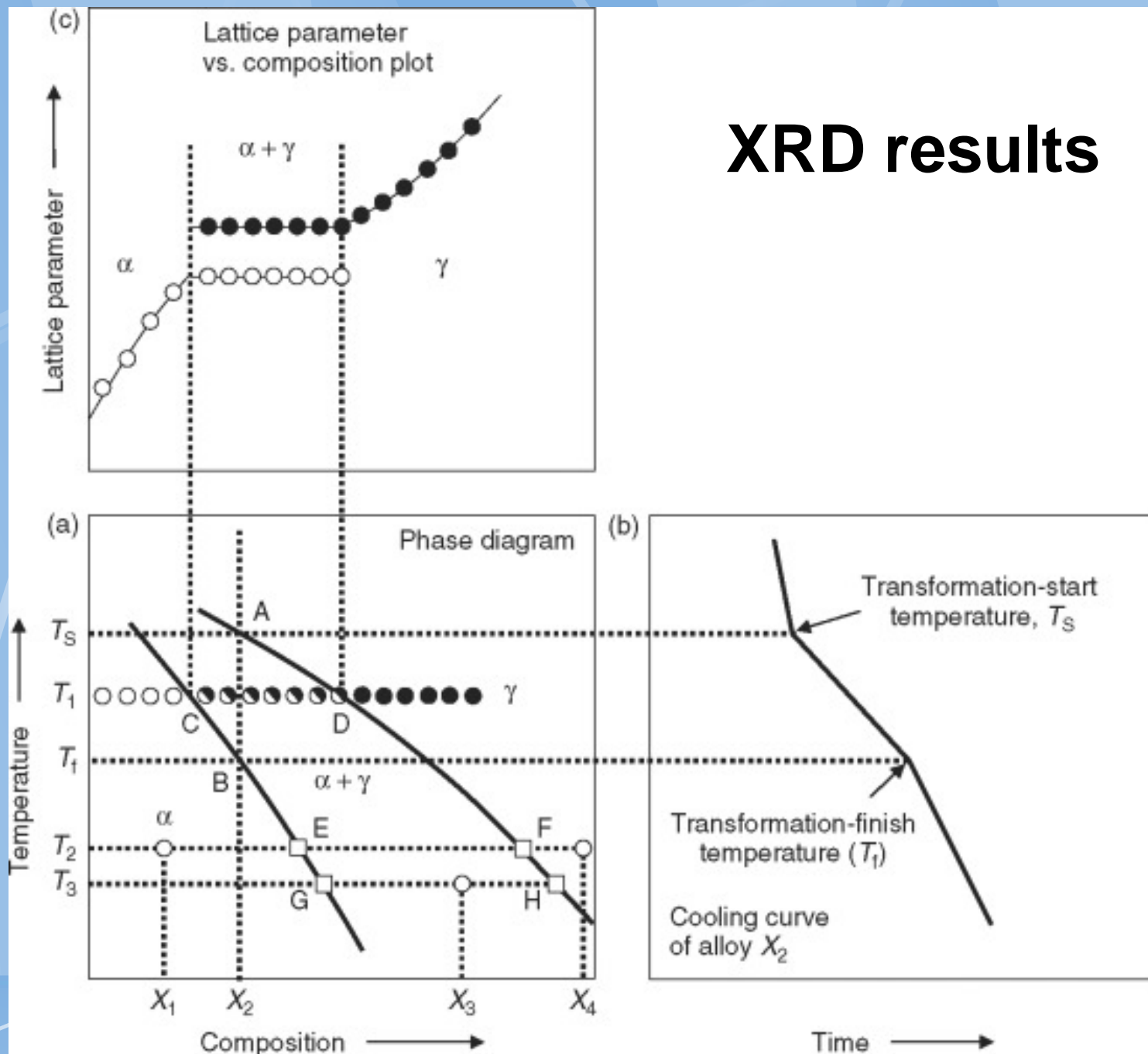


Fig. 3.48. Solvus point determination by use of x-ray diffraction measurement of lattice parameter.



# XRD results





# Electrical Resistivity Method

The technique of measurement of electrical resistivity is often used to locate the solvus and horizontal isotherms in the solid state of the alloys.

The electrical resistivity of a solid solution changes nonlinearly with the increase in concentration of the solute. But the electrical resistivity of a phase-mixture is not characteristic of any one of the conjugate phases, but changes linearly with the volume fraction of the phases, Fig. 3.49 (b). The sudden change in the slope of the graph indicates the location of the phase boundary (solvus).

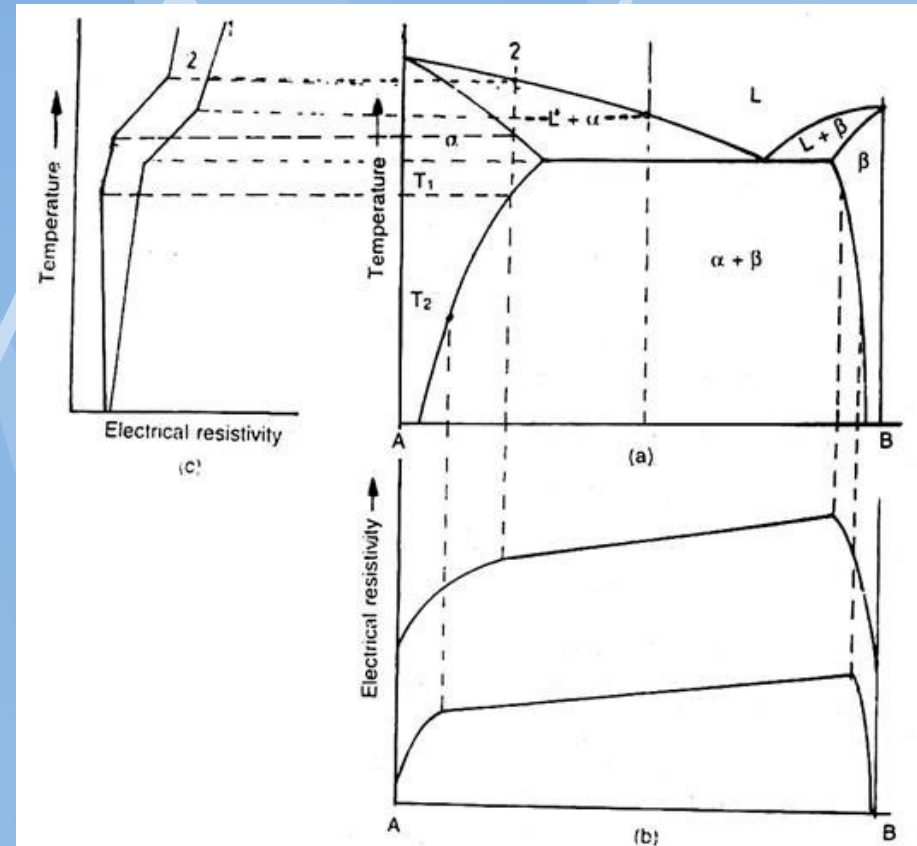
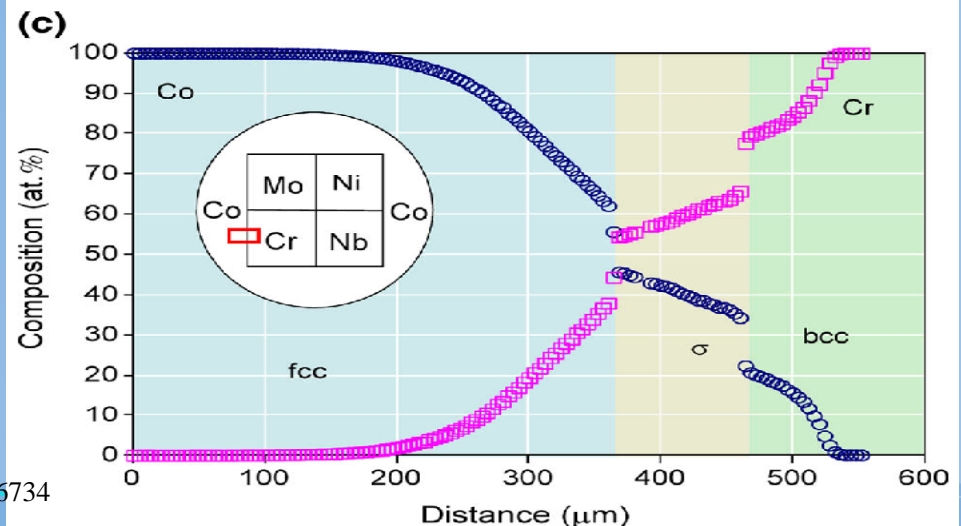
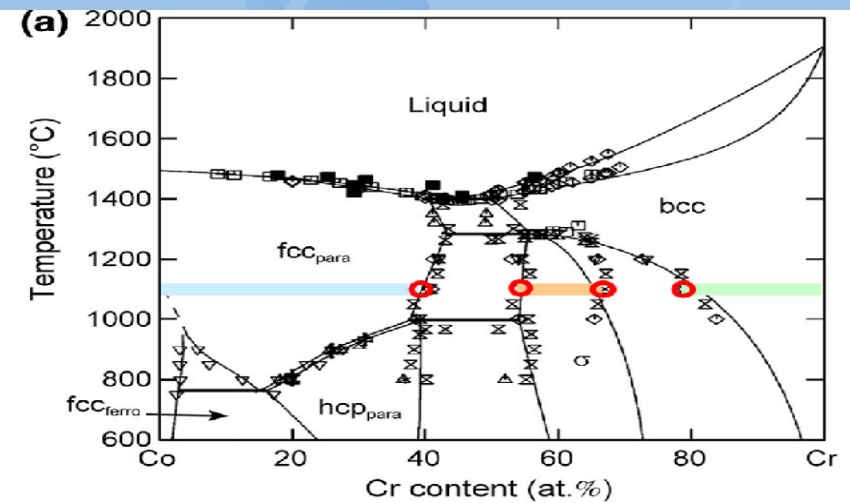


Fig. 3.49 Electrical resistivity as a means to locate the points of solvus.

# Diffusion couples

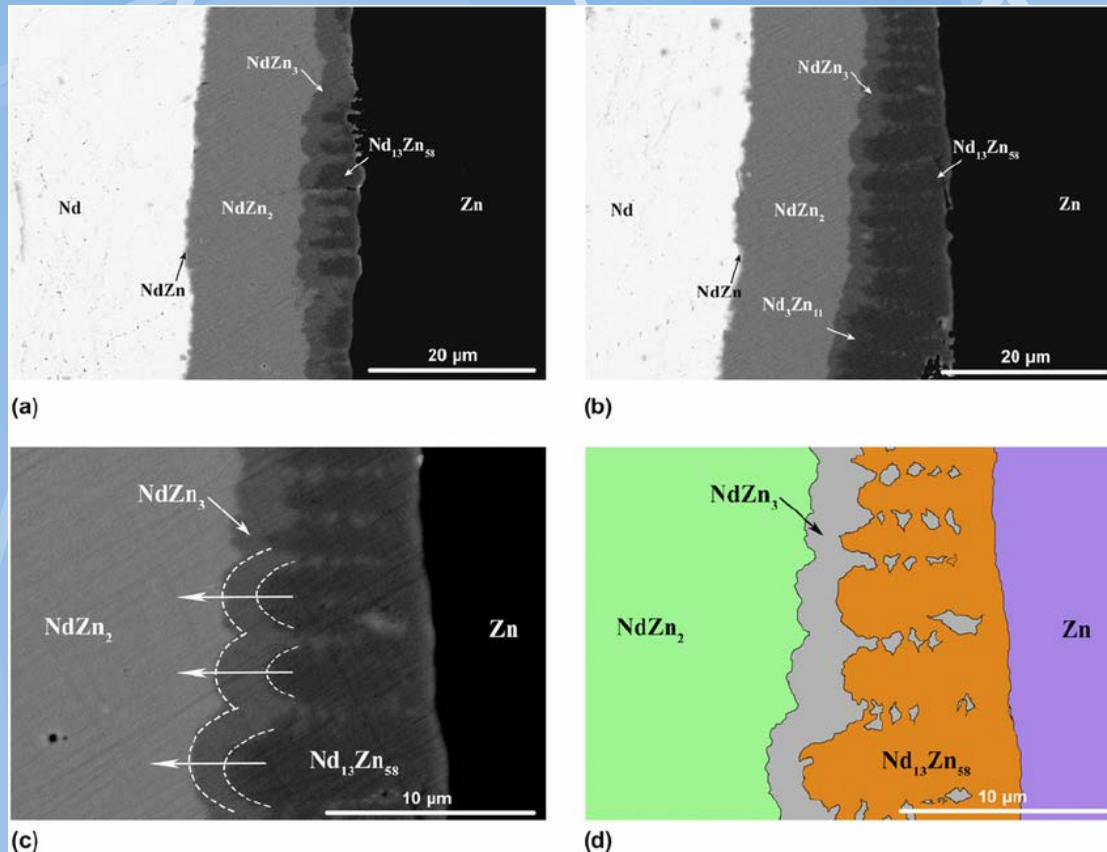
The use of **diffusion couples** in **phase diagram** studies is based on the assumption of local equilibria in the **diffusion** zone. The latter implies that each infinitely thin layer of such a **diffusion** zone is in thermodynamic **equilibrium** with the neighbouring layers.



# Studium difúzních párů

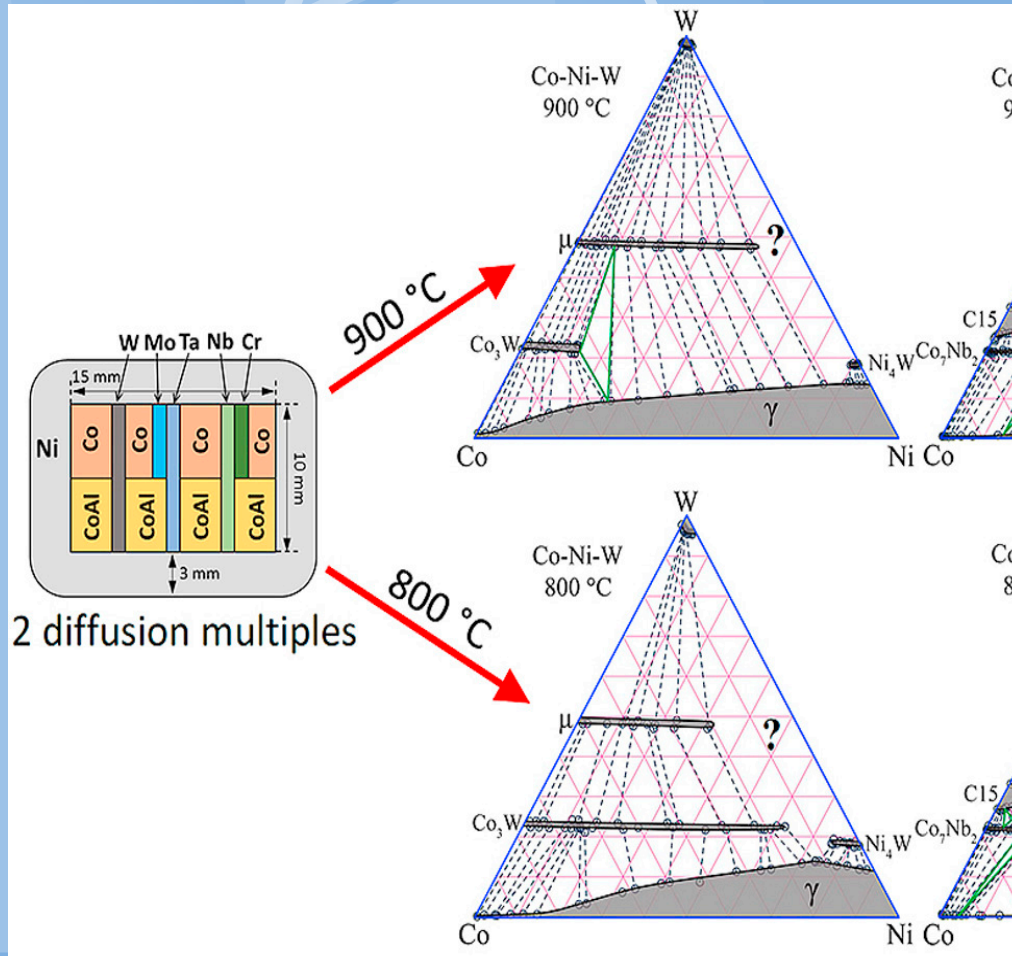
## Problems:

- nucleation
- diffusion
- local stress
- Kirkendal effect

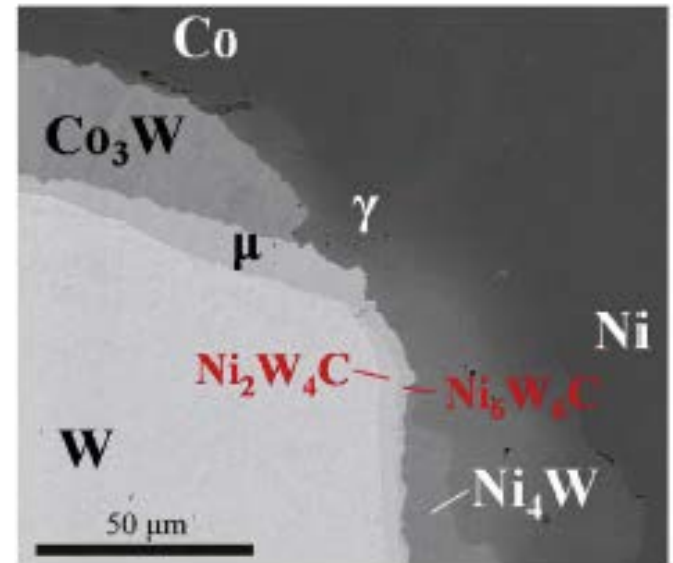


[https://www.researchgate.net/figure/267028713\\_fig7\\_FIG-14-Evolution-of-phase-growth-in-the-Nd-Zn-diffusion-couple-annealed-at-300-C-for](https://www.researchgate.net/figure/267028713_fig7_FIG-14-Evolution-of-phase-growth-in-the-Nd-Zn-diffusion-couple-annealed-at-300-C-for)

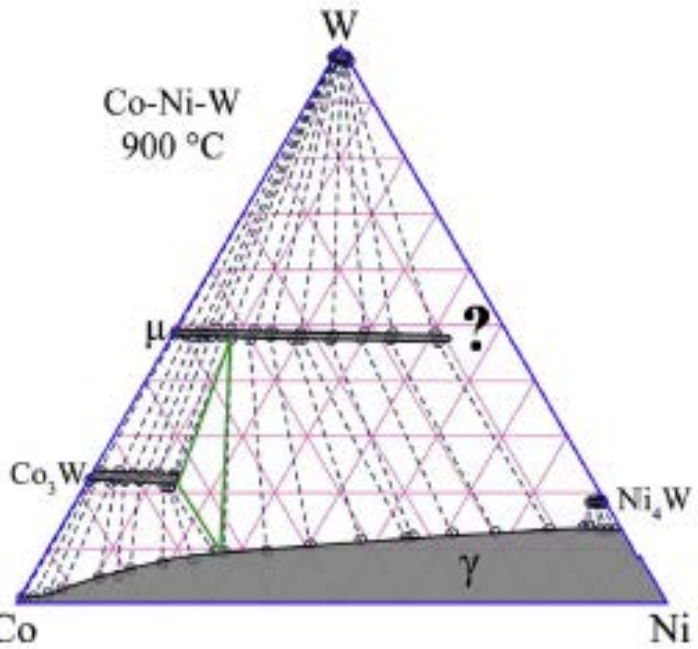
# Diffusion multiples



(a)



(b)





# Reactive or volatile elements

**High vapour tensions:** alkali metals, Zn, Cd, Mg, Ga,..., Se, Te, ...Hg, In, As, Sb, Bi , ....

**Reactive elements:** S, P,

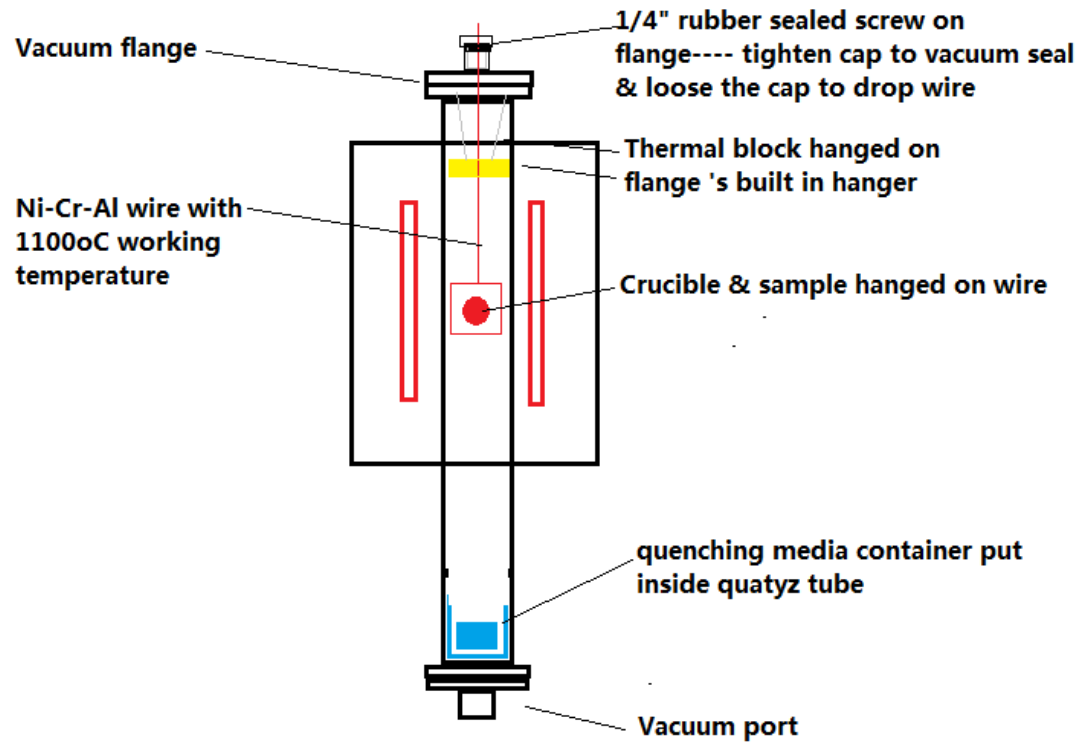
**Special container materials:** stable oxides,  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , ..., SiC, graphite, quartz, Teflon, ....., Mo, W

**Special atmospheres or vacuum**

**Advantages:** activity measurements, galvanic cells, weight loss measurements, MS apply, Analysis of gases above samples,.....

# Ceramic Systems

## Quenching sample in Vacuum

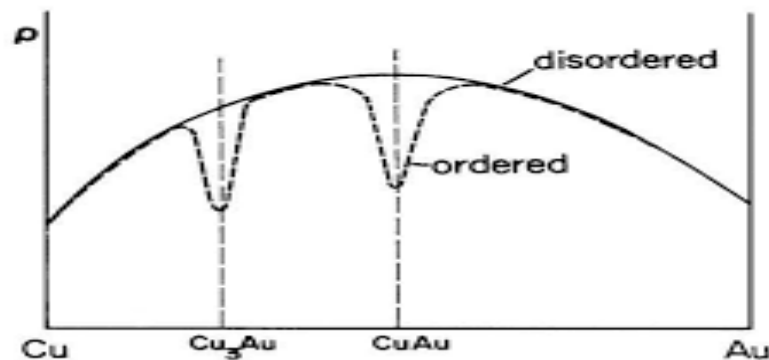
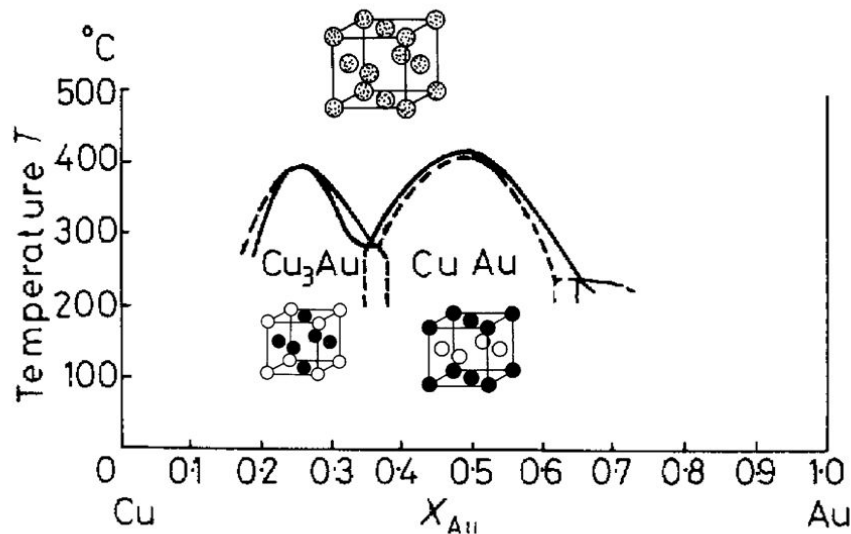


## Problems:

- No suitable container material
- high temperature experiment

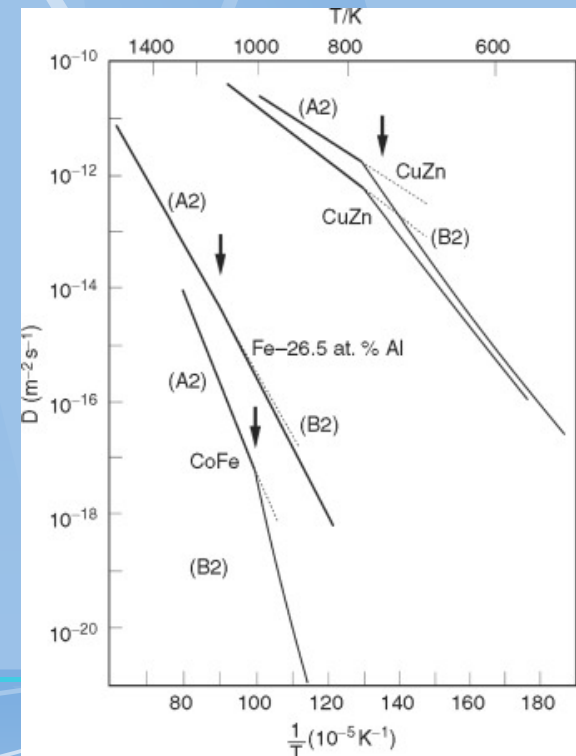
# Order – disorder systems

**A Phase Diagram Which Includes a Typical Disorder to Order Transformation**



## Methods:

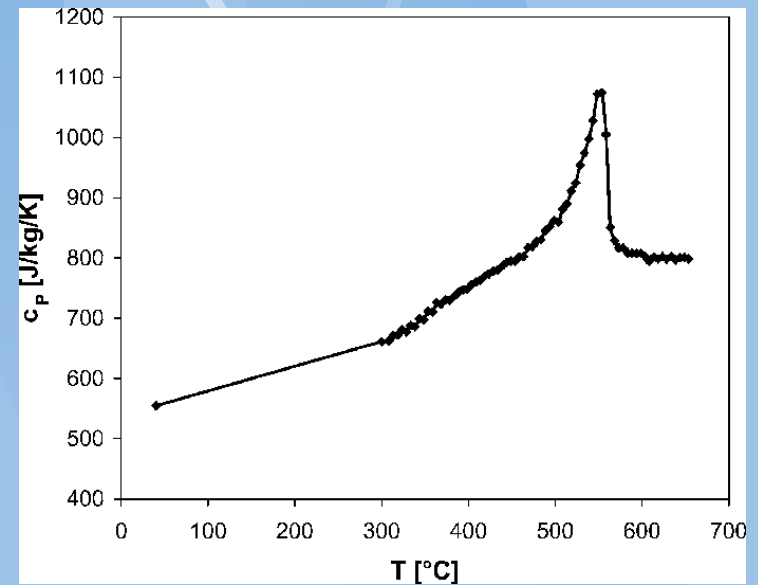
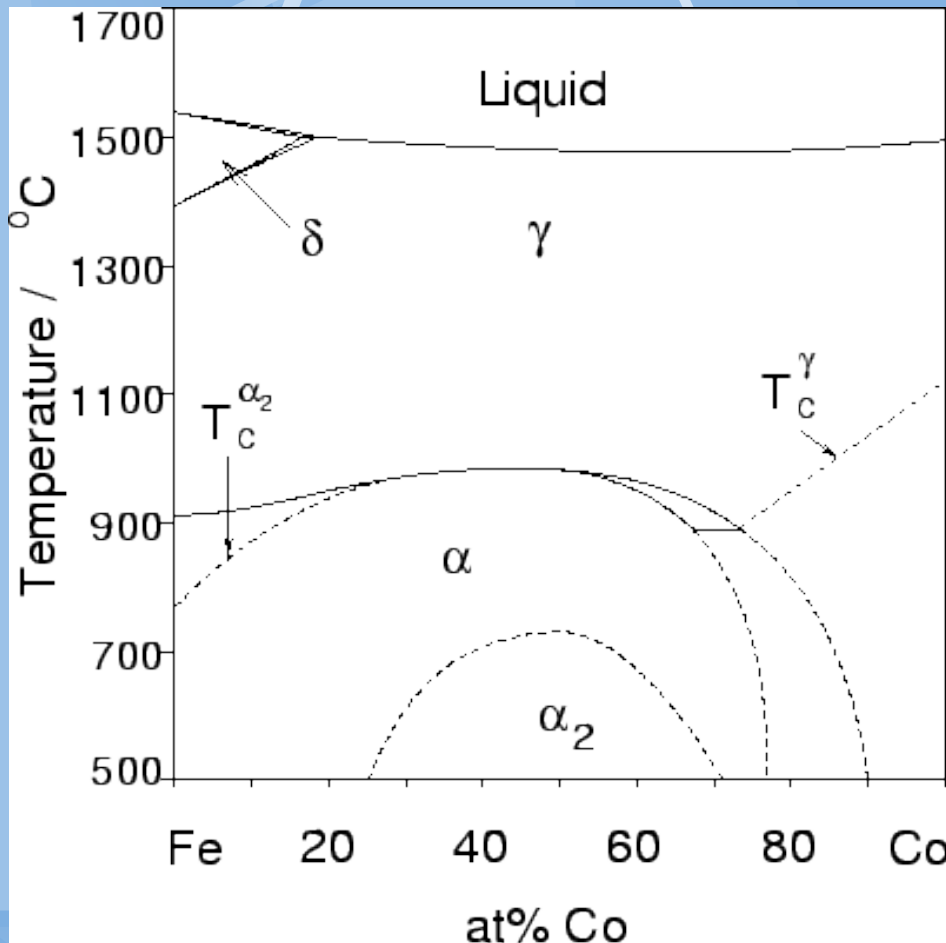
- Electric resistivity
- Thermal analysis
- Singular point methods:



# Magnetic transformation

## Methods:

- Measurement of magnetism
- Thermal analysis - TGA



The temperature dependence of the heat capacity of the Fe 3 Al-5 at.% Cr



# Pressure Dependent Phase Diagrams

Pumps, detonators, ...

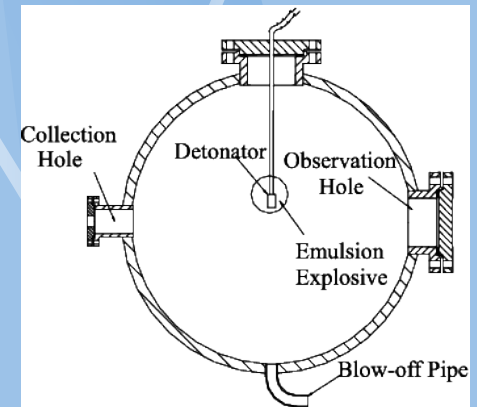
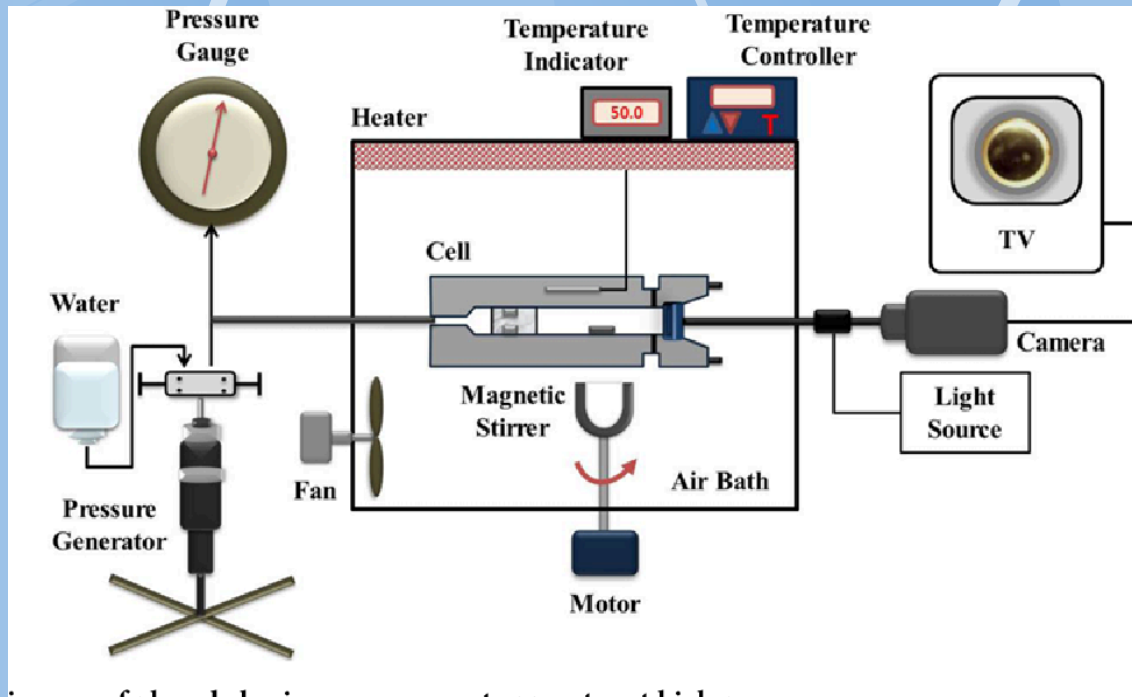


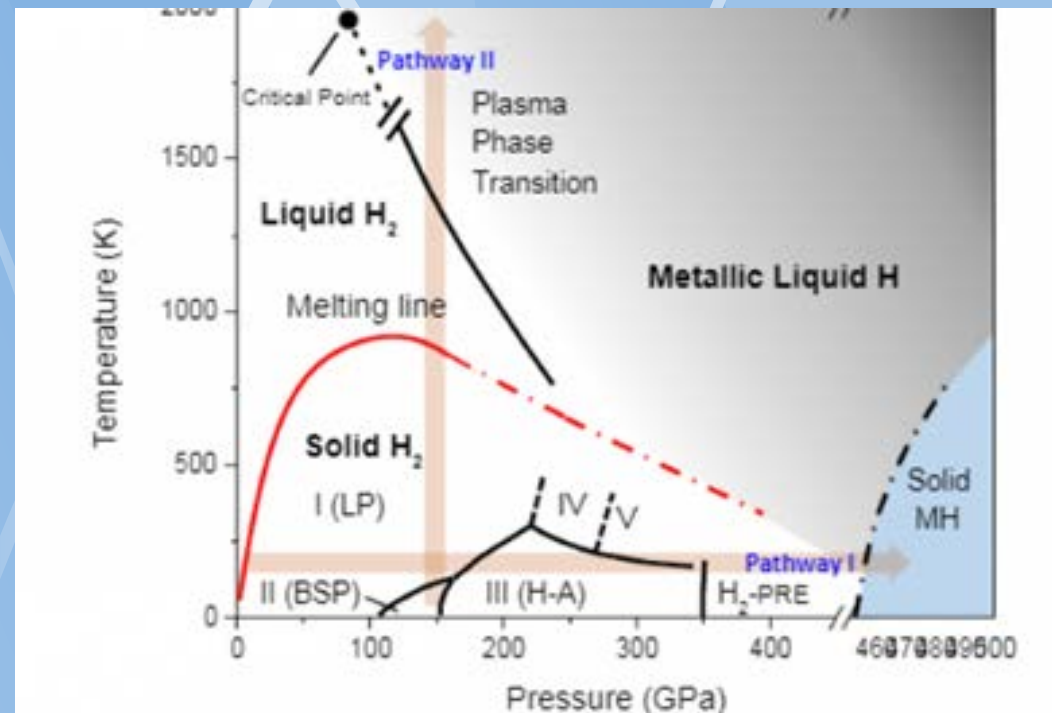
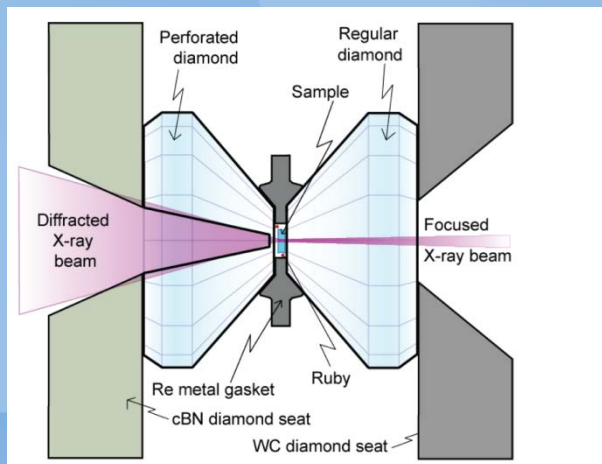
Diagram of phase behavior measurement apparatus at high pressure

[https://www.semanticscholar.org/paper/Phase-behavior-for-the-poly\(2-methoxyethyl-mixture-Jang-Choi/0807df69cc920c2c6c8315e83f321fbdd9b8302b/figure/6](https://www.semanticscholar.org/paper/Phase-behavior-for-the-poly(2-methoxyethyl-mixture-Jang-Choi/0807df69cc920c2c6c8315e83f321fbdd9b8302b/figure/6)

# Diamond – anvil –Cell

## Techniques:

Diamond – anvil –Cells  
is transparent for VIS,  
UV, gama X-rays, IR,



<https://www.nextbigfuture.com/2016/11/preparation-of-diamonds-for-diamond.html>

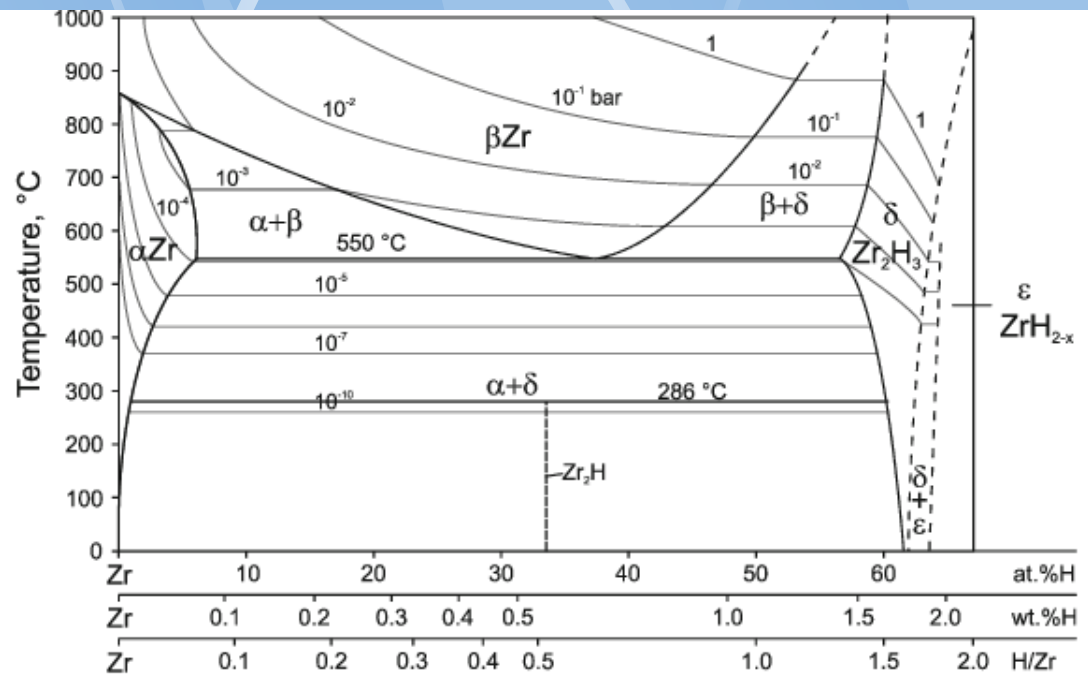
Podobně i pro Fe a další

# Hydrogen Containing Systems

## Techniques:

- General H pressure measurements

**Nuclear power industry:**  
material design



# Diskuse

