THERMAL STABILITY AND THE STRUCTURE OF IRRADIATION INDUCED SOLUTE-VACANCY-CARBON COMPLEXES IN RPV MATERIALS

M. J. Konstantinović
Studiecentrum voor Kernenergie/Centre d'Etude de l'Energie Nucleaire (SCK.CEN), Boeretang 200, B-2400 Mol, Belgium

STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

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Collaboration

Boris Minov, SKF
Marlies Lambrecht, SCK•CEN
Giovanni Bonny, SCK•CEN
Dmitry Terentyev, SCK•CEN
Lorenzo Malerba, SCK•CEN, CIEMAT
Christophe Domain, EDF

Frank Bergner, HZDR
Bertrand Radiguet, URouan
M. Mayoral, CIEMAT

Outline

- Introduction
  - Rector safety
  - Open scientific questions
  - RPV steel: Chemical composition and the role of alloying elements
- Solute-vacancy clusters; experimental characterization based on:
  - Positron annihilation, PAS
  - Atom probe tomography, APT
  - Small angle neutron scattering, SANS
  - Mechanical / magnetic relaxation (IF, MAE)
- Solute-vacancy clusters; formation, structure and stability
  - Post neutron irradiation annealing experiments
  - FeCu, FeMnNi, FeCuMnNi, RPV steels
  - Modelling results
  - The role of Cu, Ni and Mn
- Conclusion

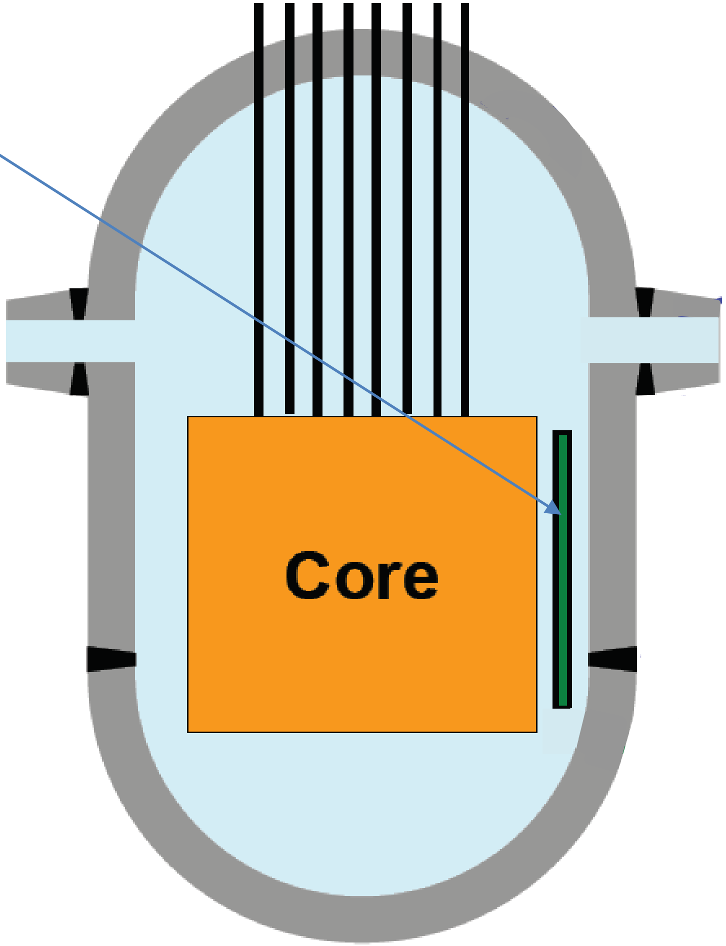
RPV safety

- ❑ Surveillance specimen characterization
- ❑ Mechanical properties
  - Charpy impact test
  - Tensile test
  - Fracture toughness

\+

- ❑ **Micro(nano)structural characterization**
  - **Atom probe tomography**
  - **Transmission electron microscopy**
  - **Small angle neutron scattering**
  - **Positron spectroscopy**
  - **------**
- ❑ **Modelling**

❑ Reactor pressure vessel



Scientific questions

- ❑ What type of defects are produced under neutron irradiation in RPV steels ?
- ❑ How they contribute to macroscopic changes of mechanical properties ?

Challenge

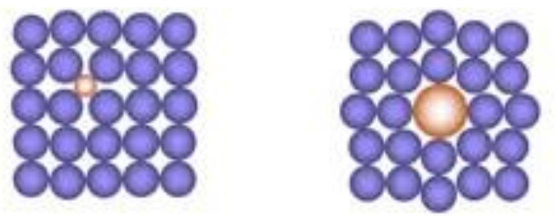
- Defects are very small … few nm and less
- Defects are complex and their role might be different…

Solute clusters - main contribution to hardening and embrittlement
Synergy with vacancies and carbon

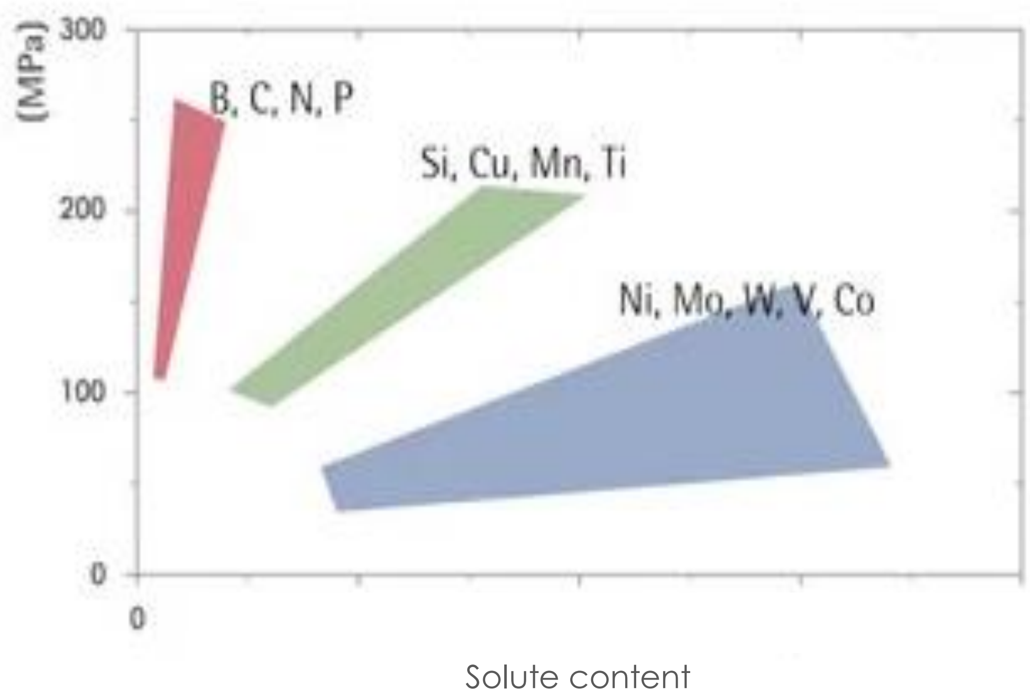
General role of alloying elements

1. Strengthening
2. Control of phase transformation and microstructure
3. Adding function: corrosion resistance, magnetic properties

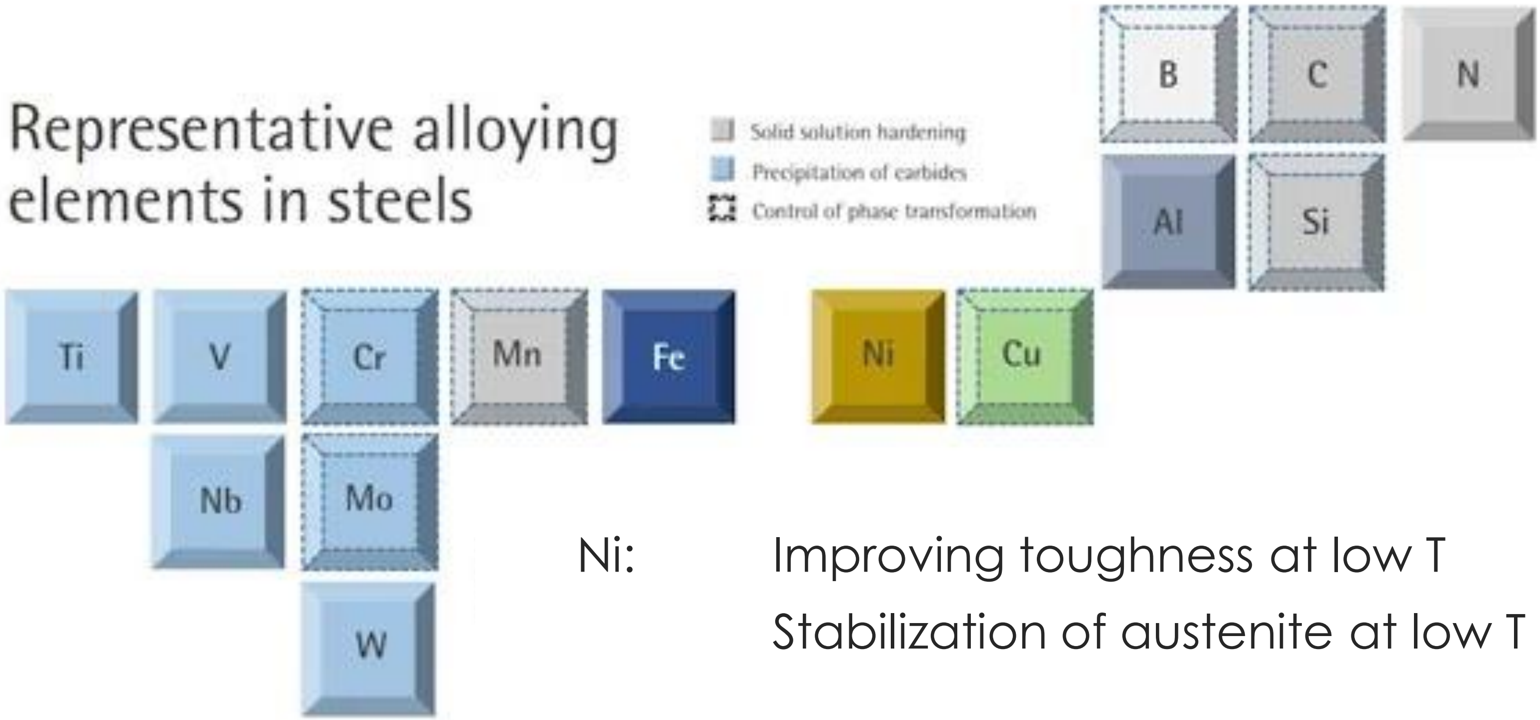
- ❑ Solid solution hardening



- ❑ Precipitation hardening (carbides formers)



General role of alloying elements



Ni: Improving toughness at low T
Stabilization of austenite at low T

Cu: Improving welding
Control of phase transformation

RPV steel - chemical composition

- Reactor pressure vessel steel

  - Base metal

chemical composition (wt%)

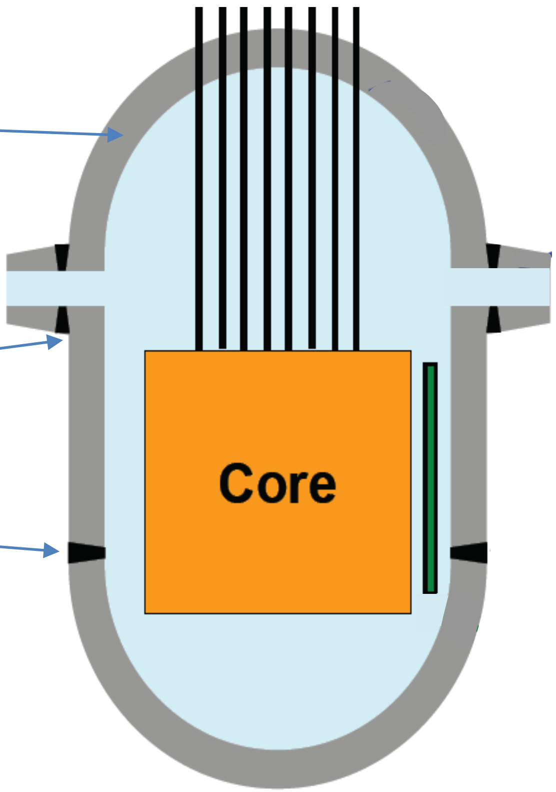
C	S	P	Mn	Si	**Ni**
0.159	0.008	0.005	1.37	0.24	**0.7-1.6**
Cu	Al	N	Mo	Cr	
0.06	0.023	0.07	0.5	0.17	

  - Weld

chemical composition (wt%)

C	S	P	Mn	Si	**Ni**
0.159	0.008	0.005	1.37	0.24	**0.7-1.6**
Cu	Al	N	Mo	Cr	
0.1-0.3	0.023	0.07	0.5	0.17	

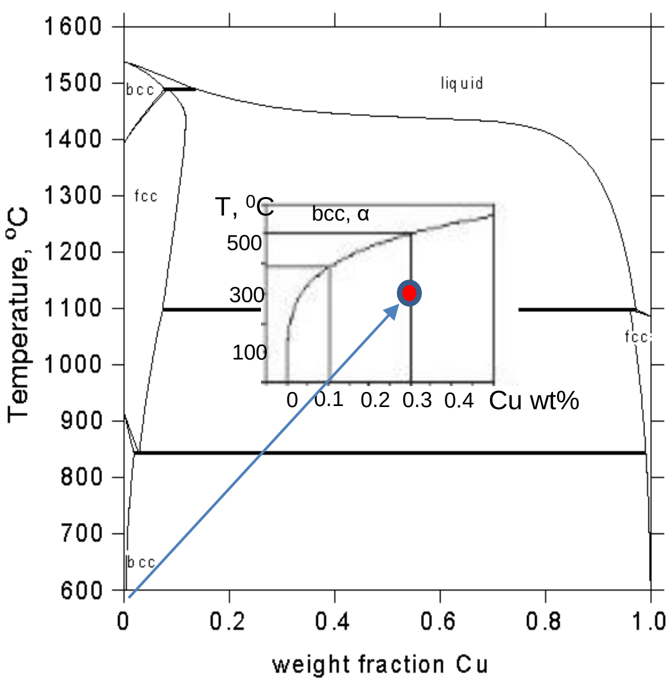
Reactor pressure vessel



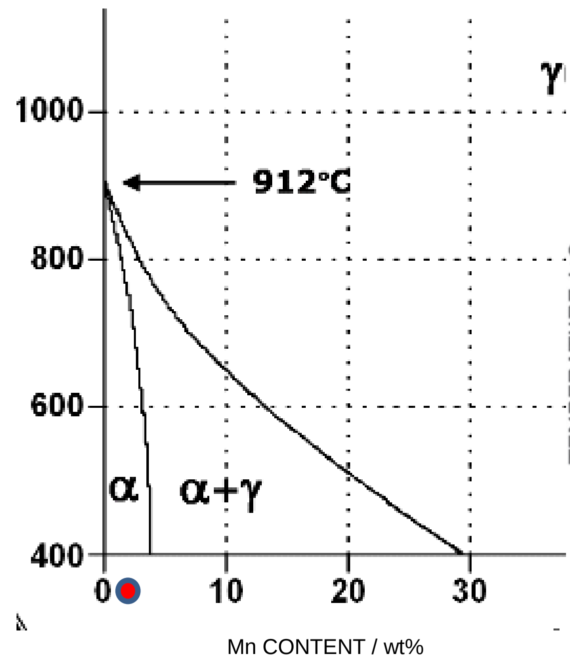
Fe-Cu (Ni, Mn) thermodynamics

❑ Binary phase diagrams

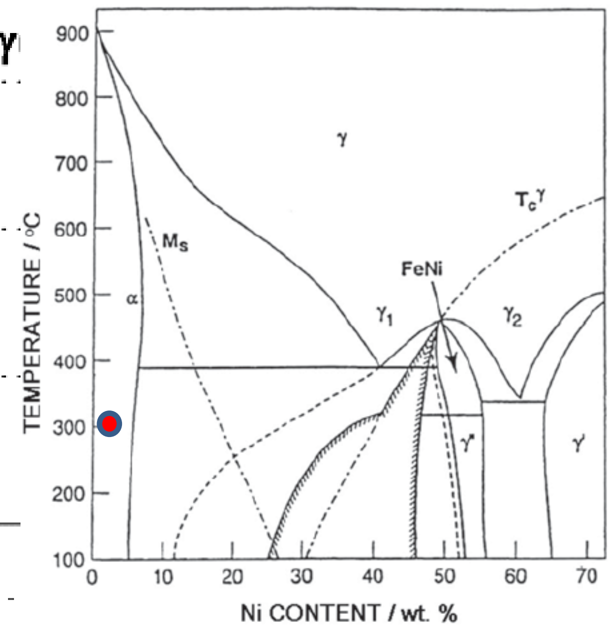
Fe-Cu (0.3 wt%)



Fe-Mn (1.3 wt%)



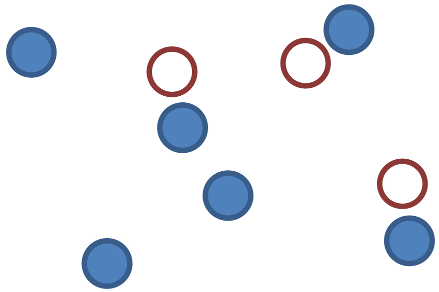
Fe-Ni (1.6 wt%)



- ❑ At 300 °C only Cu precipitation is thermodynamically expected
- ❑ Neutron irradiation: non-equilibrium vacancy concentration

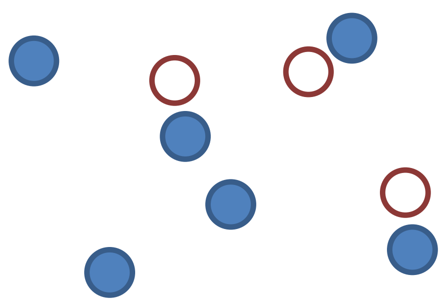
Solute clustering and precipitation

- Precipitation = formation of aggregates of solutes



Solute clustering

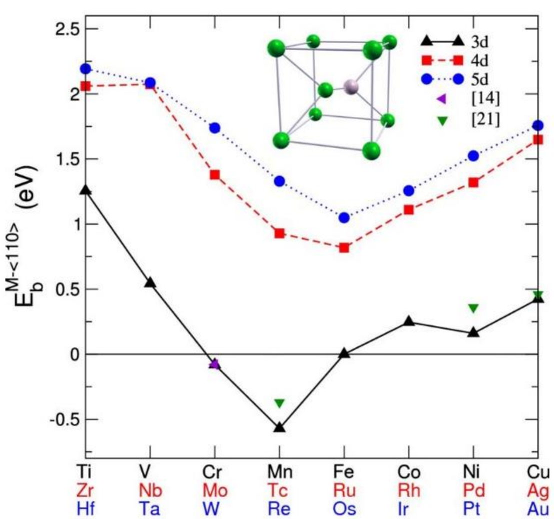
- Precipitation = formation of aggregates of solutes



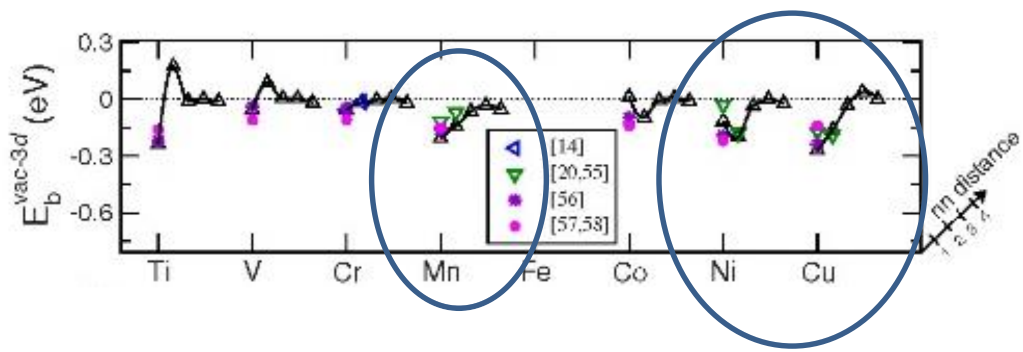
Under irradiation the presence of "extra" vacancies enhances and induce precipitation

If solutes bind with vacancies, the cluster will be a mixture

BE solute-SIA



BE vacancy-solute

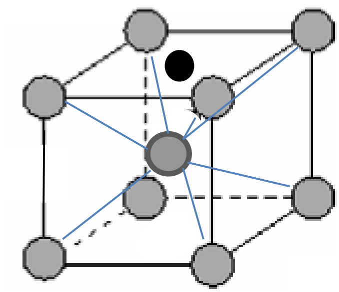


2nn vacancy-solute strongly binding for late 3D TM

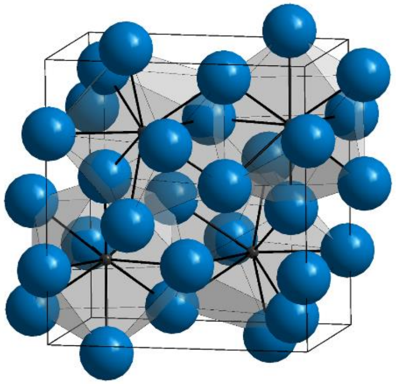
Olsson et al., PRB **81**, 054102 (2010)

Role of carbon

- Atomic carbon (low C)

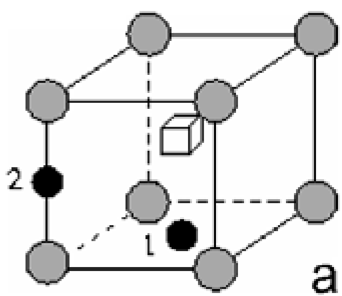


- Carbides $Fe3C$ (high C)

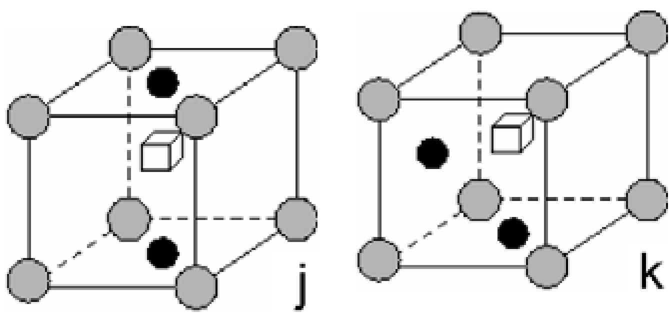


- Vacancy – carbon binding energy

C-V



C_2-V



Binding energy (eV) 0.65 1.1

C. Domain, et al., PRB**69**, 144112 (2004).

Synergy effects

solute transport by vacancy mechanism

+ carbon – vacancy binding

=

Solute-vacancy-carbon complex !

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Atom probe tomography-working principles

Solute clusters: How do we see them?

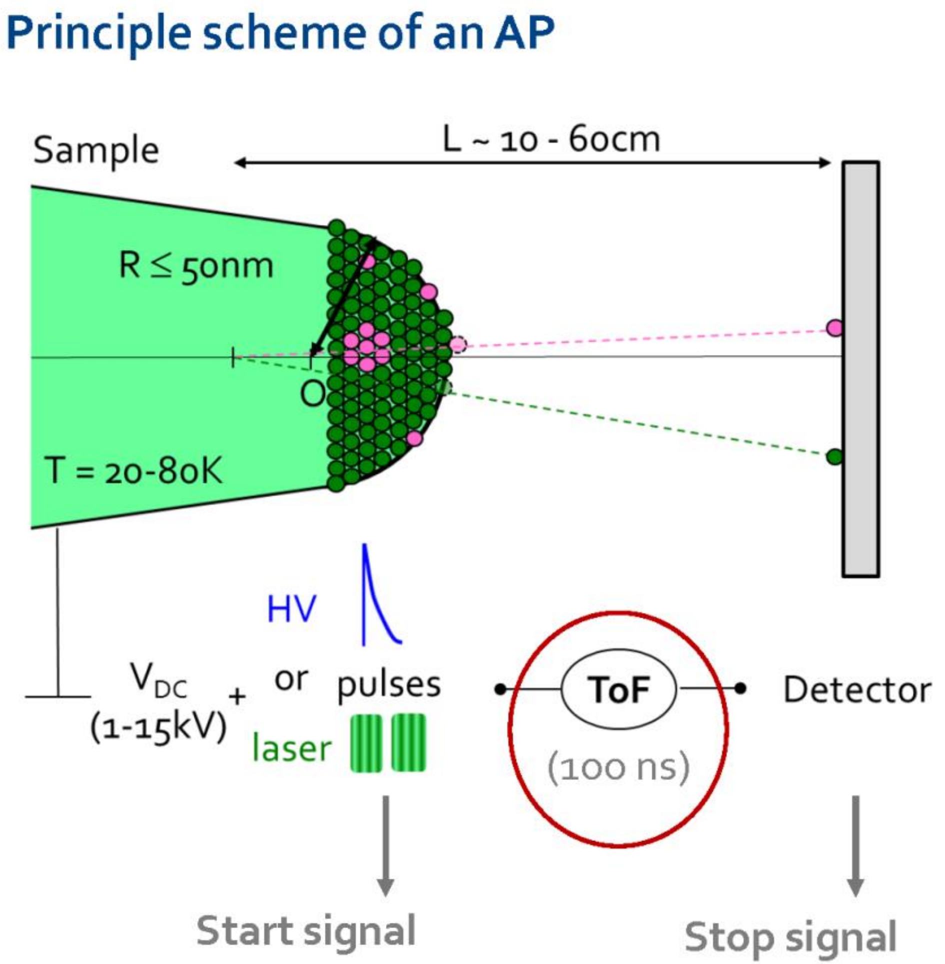
FEM + time of flight mass spectroscopy

$$E_p = qU$$

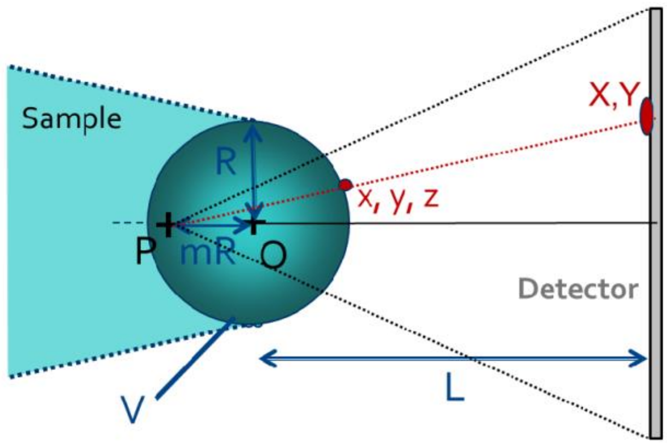
$$E_k = \frac{1}{2}mv^2$$

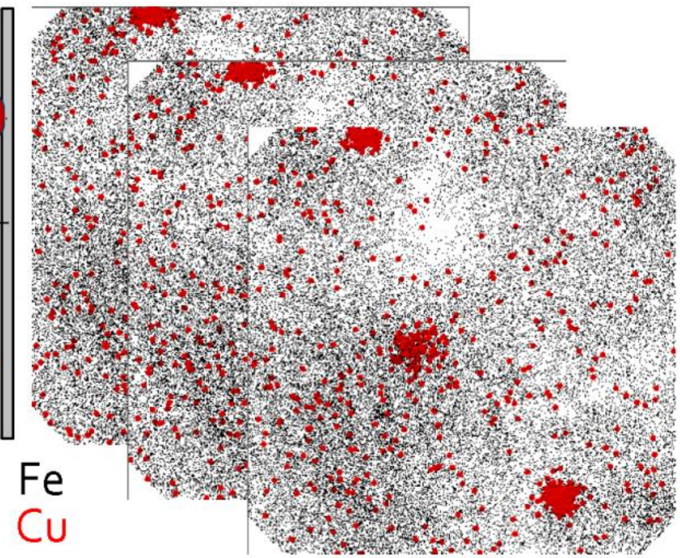
$$E_p = E_k \text{ and } v = \frac{d}{t}$$

$$\Rightarrow t = \frac{d}{\sqrt{2U}}\sqrt{\frac{m}{q}}$$



Atom probe tomography - 3D reconstruction



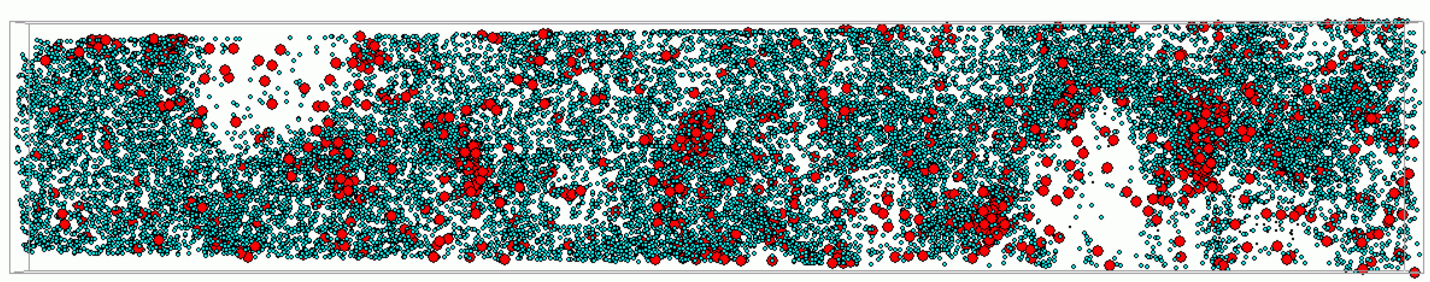


Magnification

$$G = \frac{L}{(m+1)R}$$

$G \sim 10^6 - 10^7$

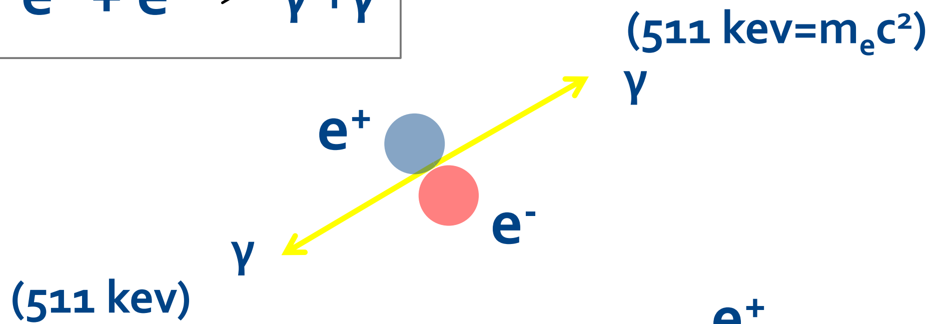
Reconstruction of the depth



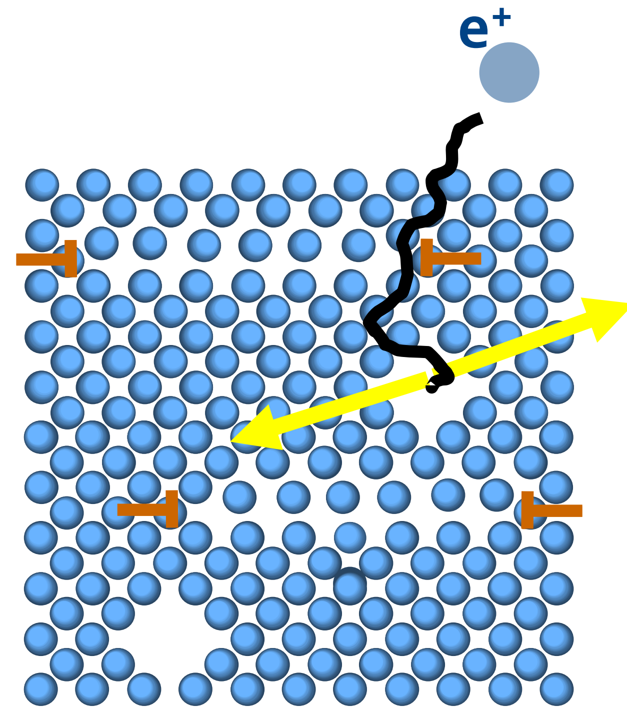
Positron annihilation

Vacancy clusters: How do we see them?

$$e^+ + e^- \rightarrow \gamma + \gamma$$



Conservation of:
1. energy
2. momentum
3. charge

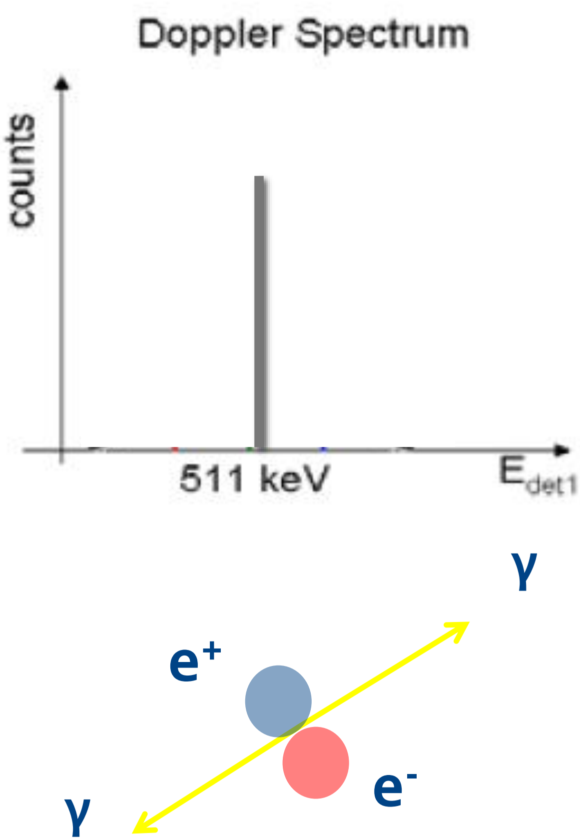


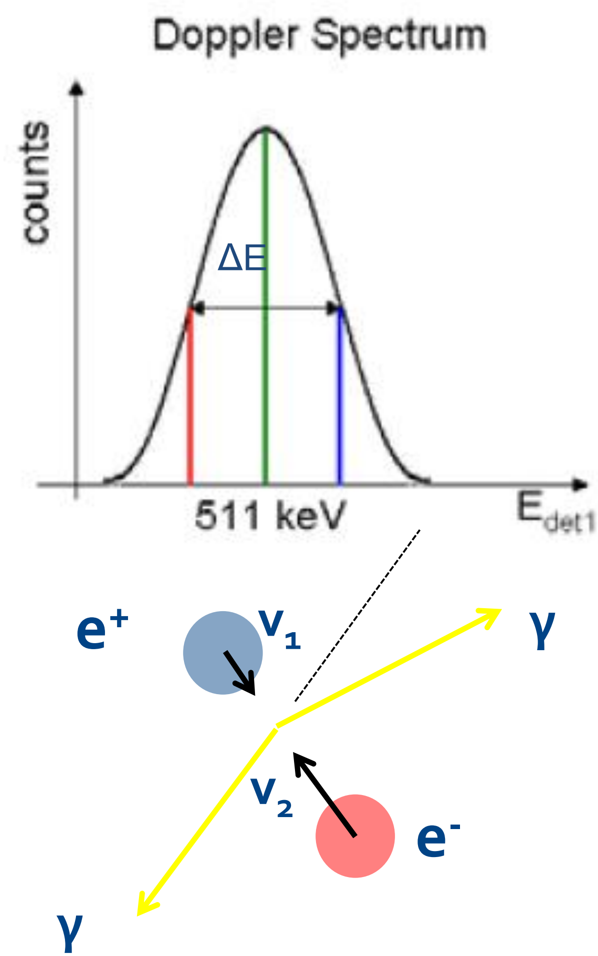
Annihilation probability

$$P = \pi r_0^2 c n_e$$

Site-selective probe: positron trapping and annihilating at positron affinitive site

Doppler broadening



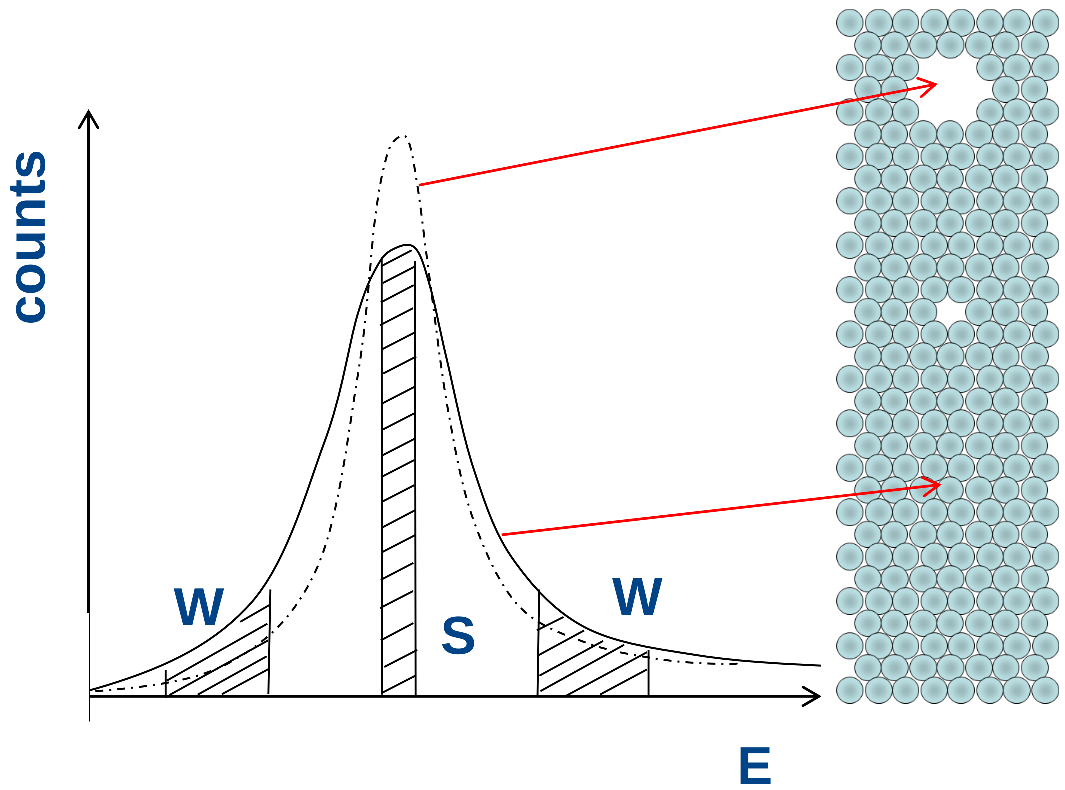


$$\Delta E = m_0 c(v_2 - v_1) \sim 10^{-2} - 10^{-3} m_0 c \sim 20\,keV$$

Doppler broadening: Momentum density curve

Positron trapping is manifested by a narrowing of the momentum density curve

- Conduction electron contribution - S
- Core electron contribution -W
- Large momentum events arise from deep-lying electron states (solute clustering contribution)
- **S probes el. density**
- **W probes solute clustering**

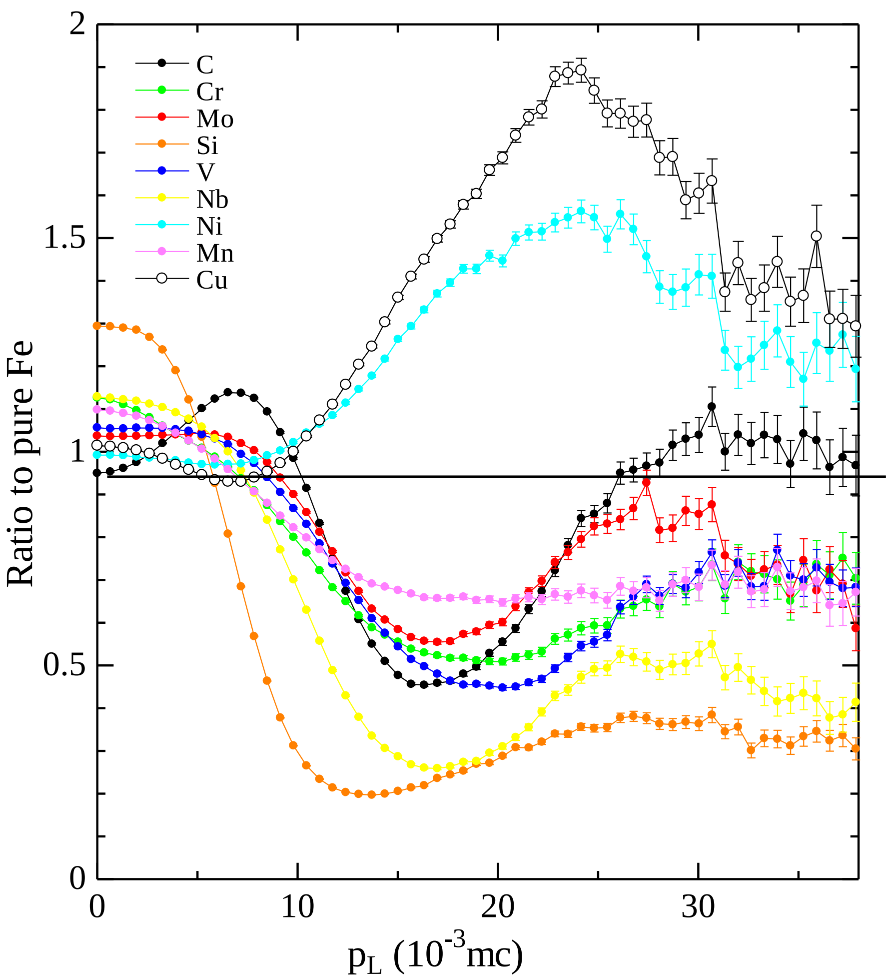


Positron chemical affinity

- The positron affinity reflects the preference of the positron for different components in heterostructures made of different atoms

- The positron affinity is the sum of the internal electron and positron chemical potentials

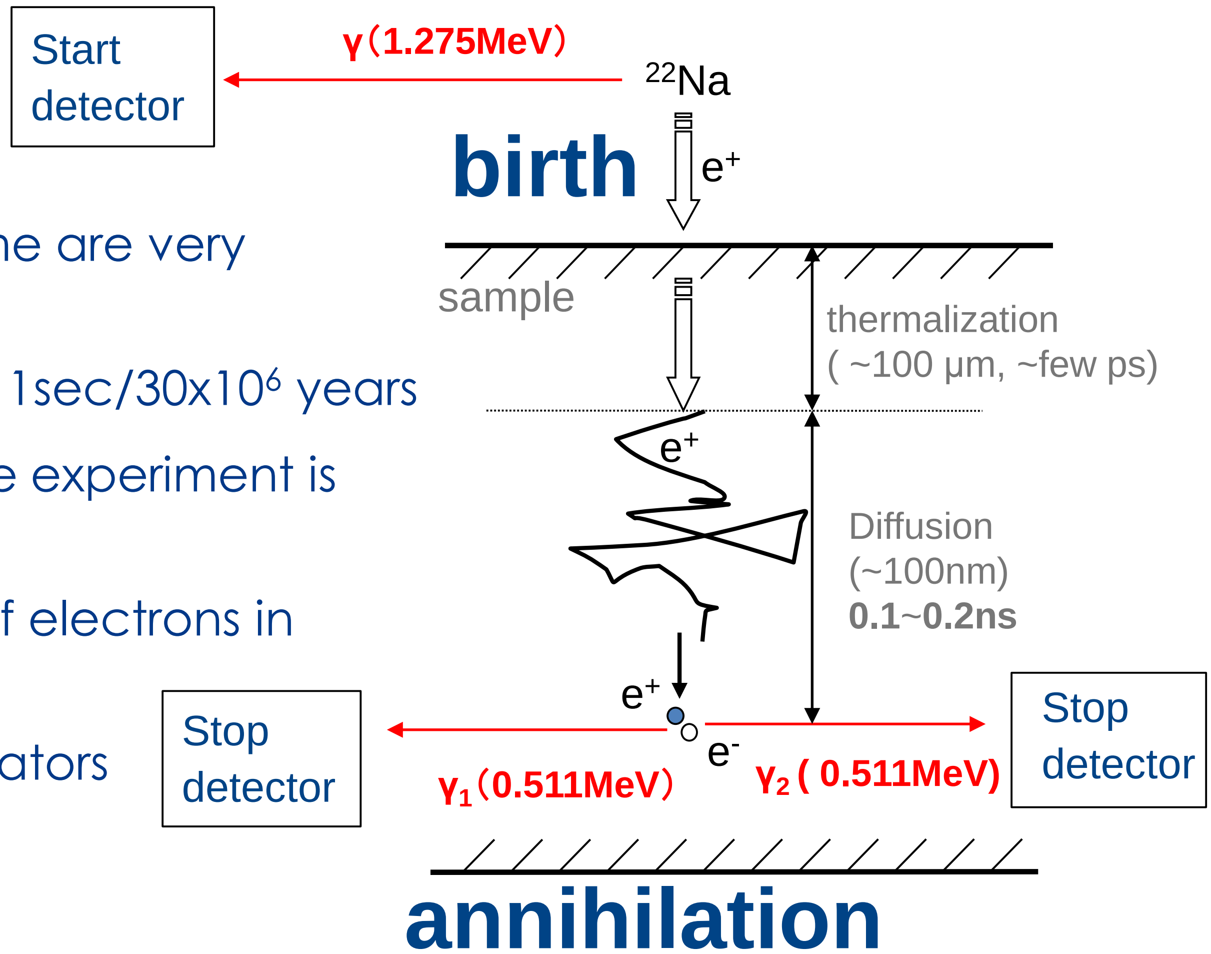
Mn < Fe < Ni < Cu



T. Takeshi private comm.

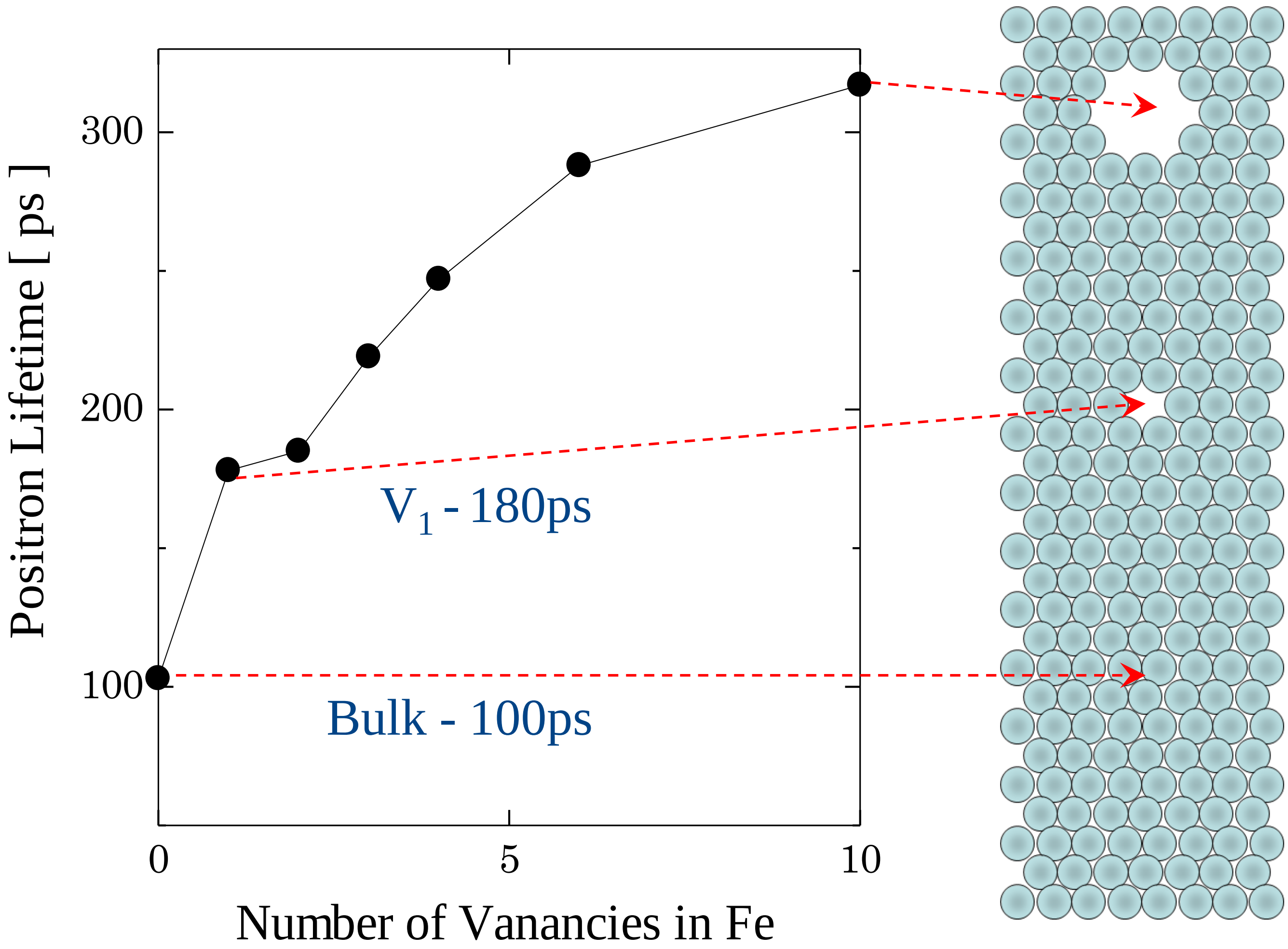
Positron lifetime

β⁺-decay of radioactive isotopes $^{22}Na \longrightarrow {}^{22}Ne + \beta^+ + \nu_e + \gamma.$



- The measurements of time are very accurate
- Atomic clock accuracy 1sec/30x10⁶ years
- Time resolution in lifetime experiment is determined by
  - ✓ transit time spread of electrons in photomultipliers
  - ✓ decay time in scintillators

Positron lifetime in vacancy clusters

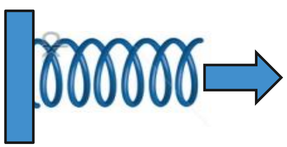


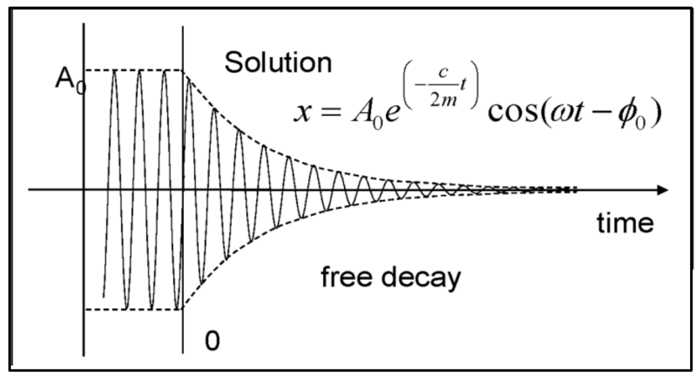
Relaxation experiments: Observation of light interstitials / carbon

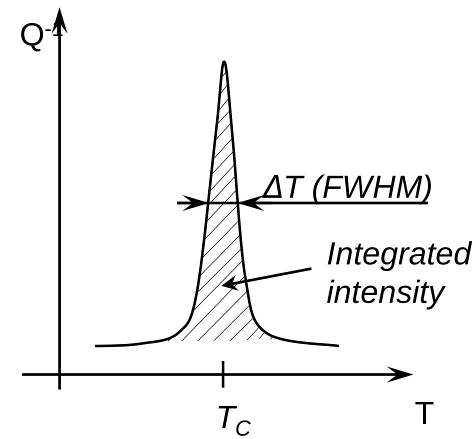
- Mechanical and magnetic relaxation experiments. Internal friction & magnetic after effect.

IF

Damping ≡ energy loss

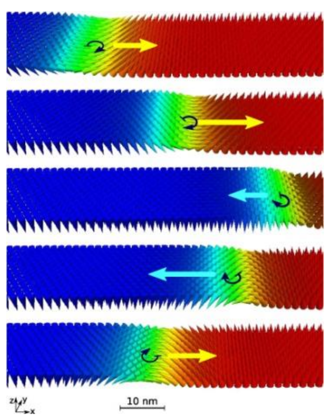


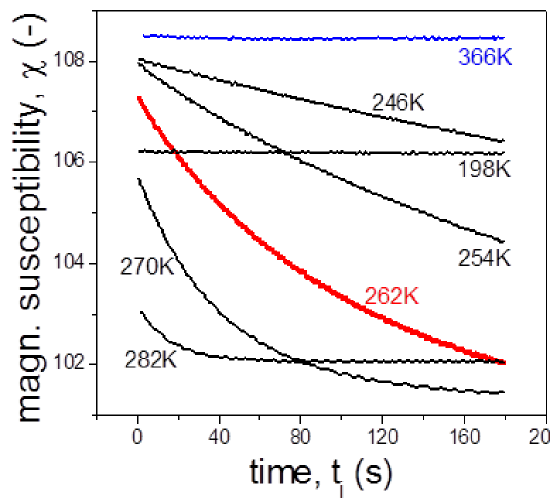


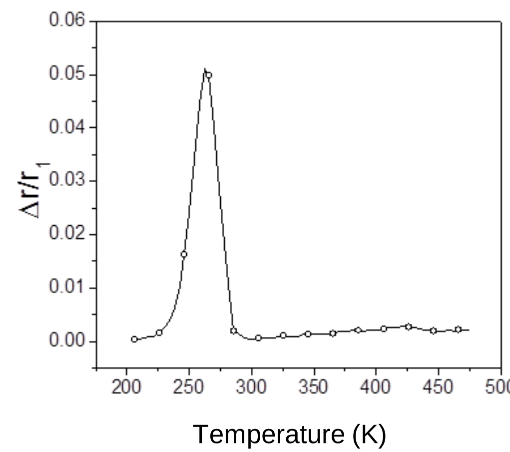


MAE

Domain wall relaxation







Small angle neutron scattering

Solute-vacancy synergy: How do we see this?

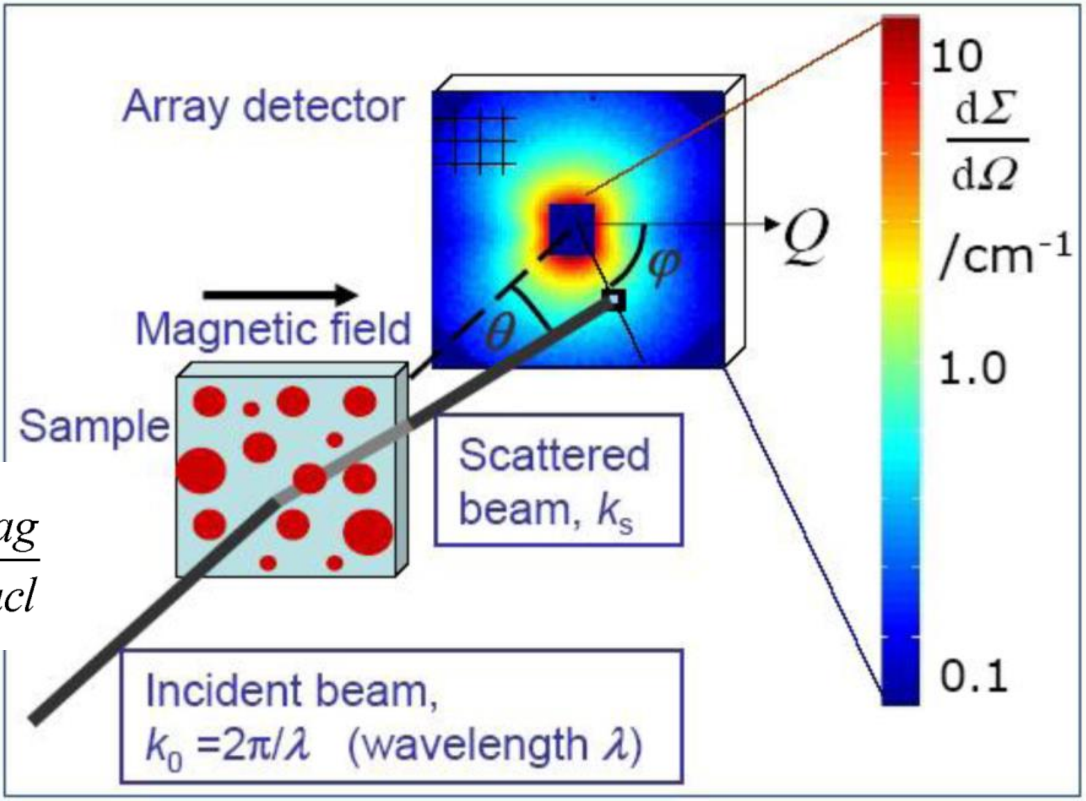
Two mechanisms of neutron scattering:
- ❑ Short range / nuclear
- ❑ Long range dipolar / magnetic

$$\frac{d\Sigma}{d\Omega} = \frac{d\Sigma}{d\Omega}_{nuc} + \frac{d\Sigma}{d\Omega}_{mag} \sin^2 \varphi$$

$$A = \frac{d\Sigma_{\perp}}{d\Sigma_{\parallel}} = \frac{d\Sigma nucl + d\Sigma mag}{d\Sigma nucl} = 1 + \frac{d\Sigma mag}{d\Sigma nucl}$$

$$\boxed{A = 1 + \frac{\rho_{mag}^2}{\rho_{nucl}^2}}$$

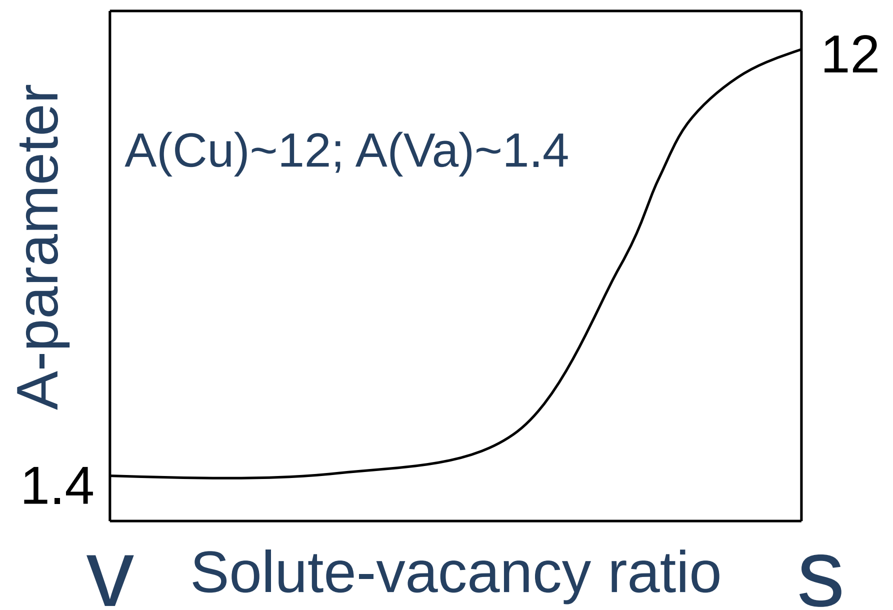
Application of magnetic field



Small angle neutron scattering

The structure of solute-vacancy clusters

- Provides information on cluster composition
- Very useful for neutron irradiated samples
- Possible link with positron annihilation



Take a home massage

Vacancy clusters	Positron annihilation
Carbon	Relaxation methods: Mechanical and magnetic
Solute clustering and precipitation	Atom probe tomography
Synergy effects: Solute – vacancy – carbon complexes	PAS, SANS

SANS

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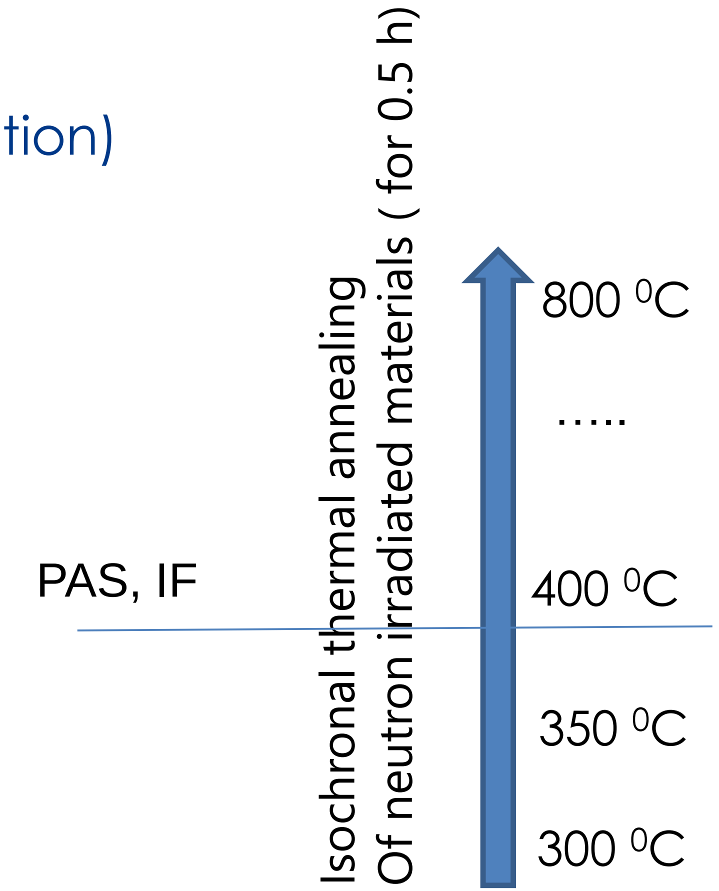
Materials, conditions, and PIE

- Neutron irradiation
  - Material testing reactor
  - NPP surveillance specimens
  - Dose: 0.1 -0.2 dpa (~ 40 years of operation)

- Materials
  - Fe-Cu binary alloy
  - Fe-Mn-Ni ternary alloy
  - Fe-Mn-Ni-Cu quaternary alloy
  - Base NPP steel (low Cu content)
  - Weld NPP steel (high Cu content)
  - Base NPP steel (high Ni content)

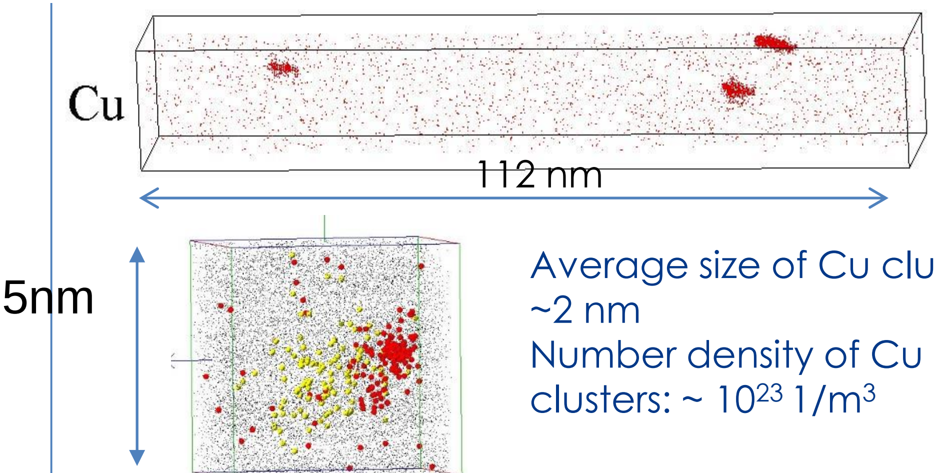
- PIE: PAS, SANS, APT, IF



Fe-0.1(0.3)Cu-C

- APT results

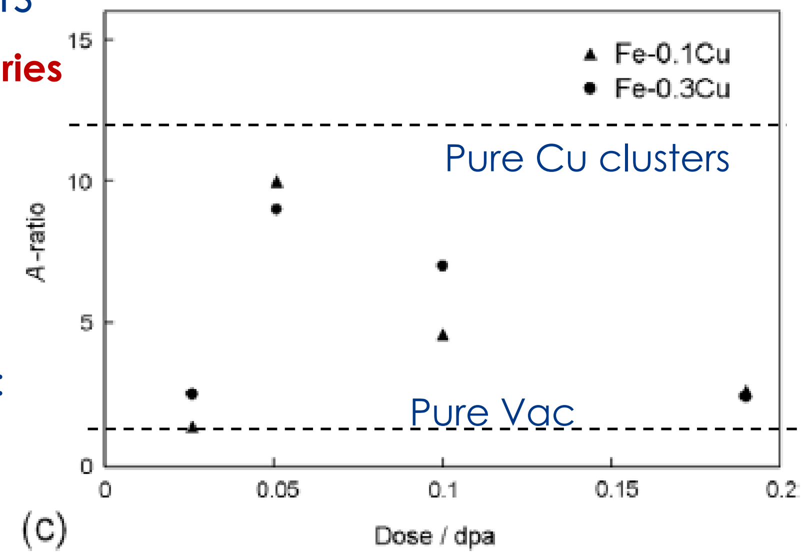
Neutron irradiation 0.1-0.2 dpa



- SANS results

Vac to Cu ratio varies

Meslin et al. JNM 406 (2010) 73–83



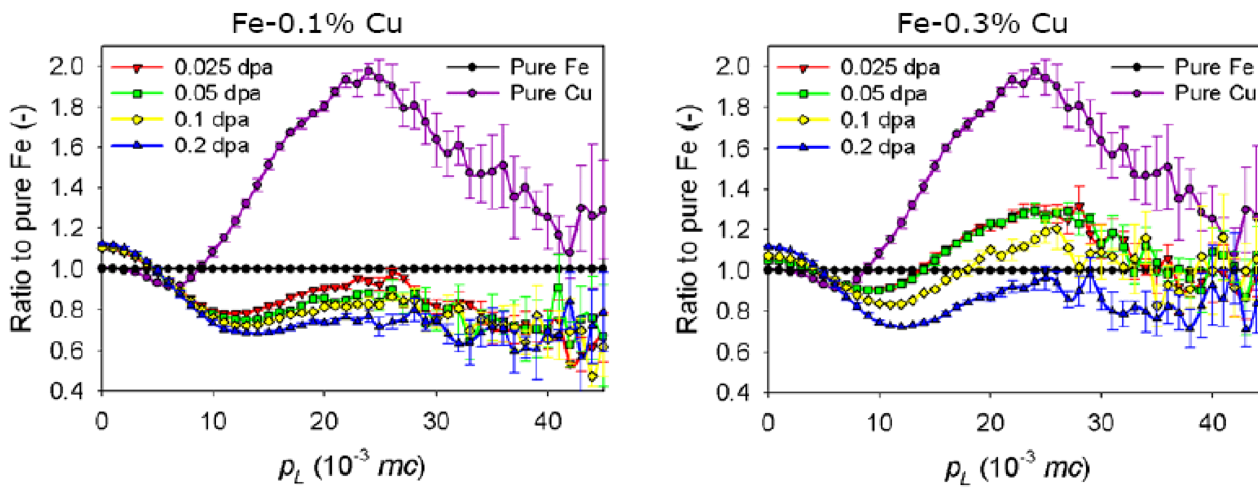
Average size of Cu clusters: ~2 nm

Number density of Cu clusters: ~ 10^{23} $1/m^3$

- PAS results

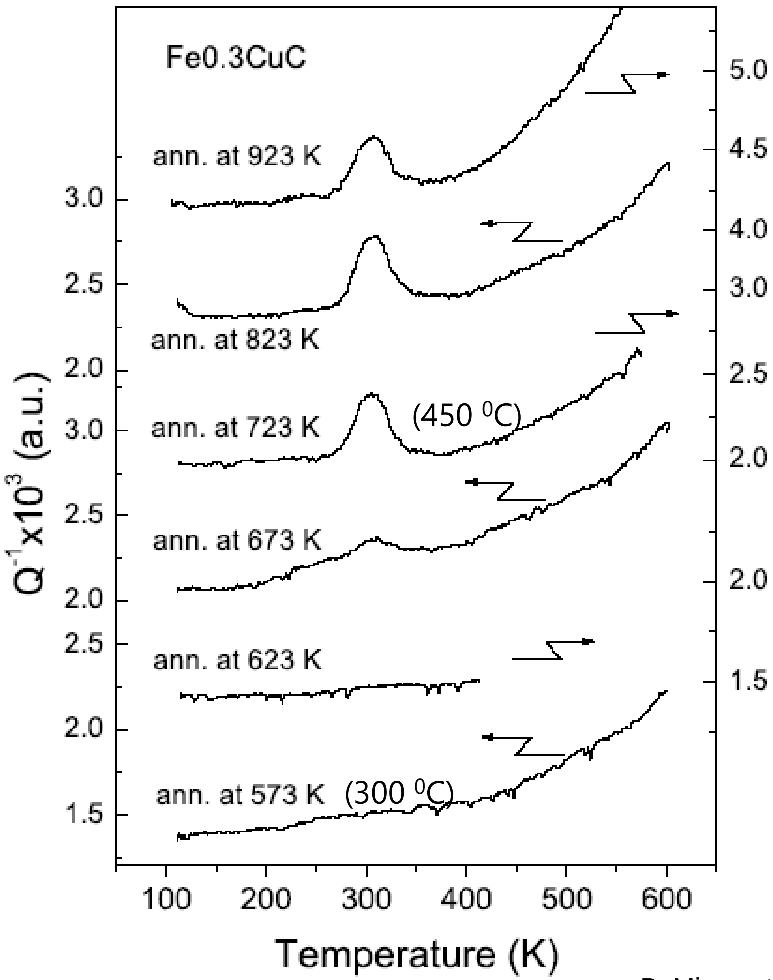
Increase of both S and W parameters

Average size 5-8 vac.

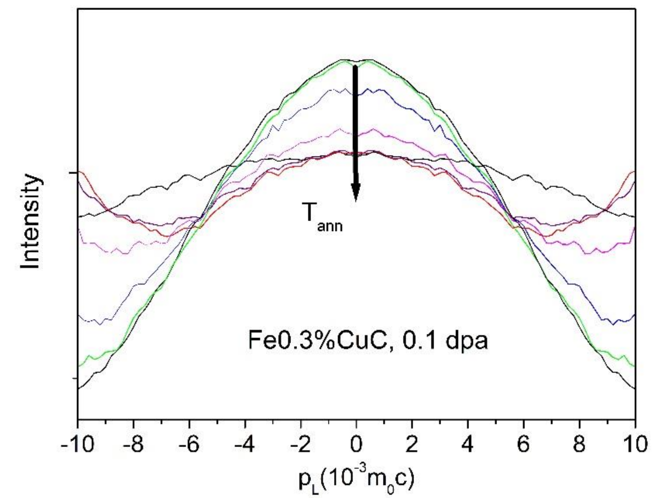


Fe-0.3Cu-C: post irradiation annealing

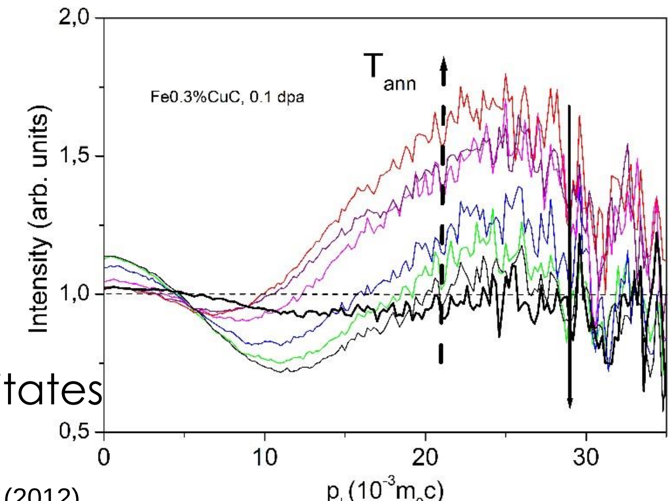
- Internal friction
- PAS - Doppler broadening



vacancy + carbon



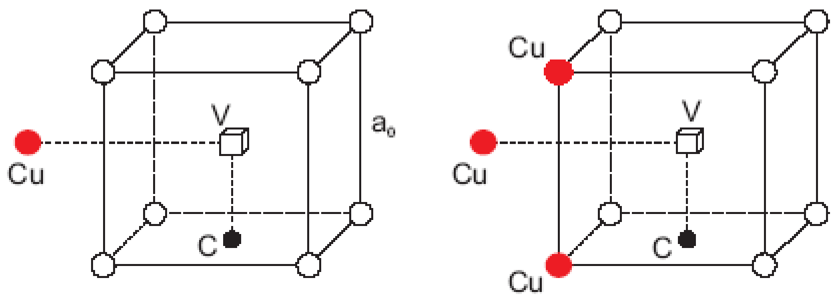
Cu precipitates



B. Minov et al., PRB **85**, 024202 (2012)

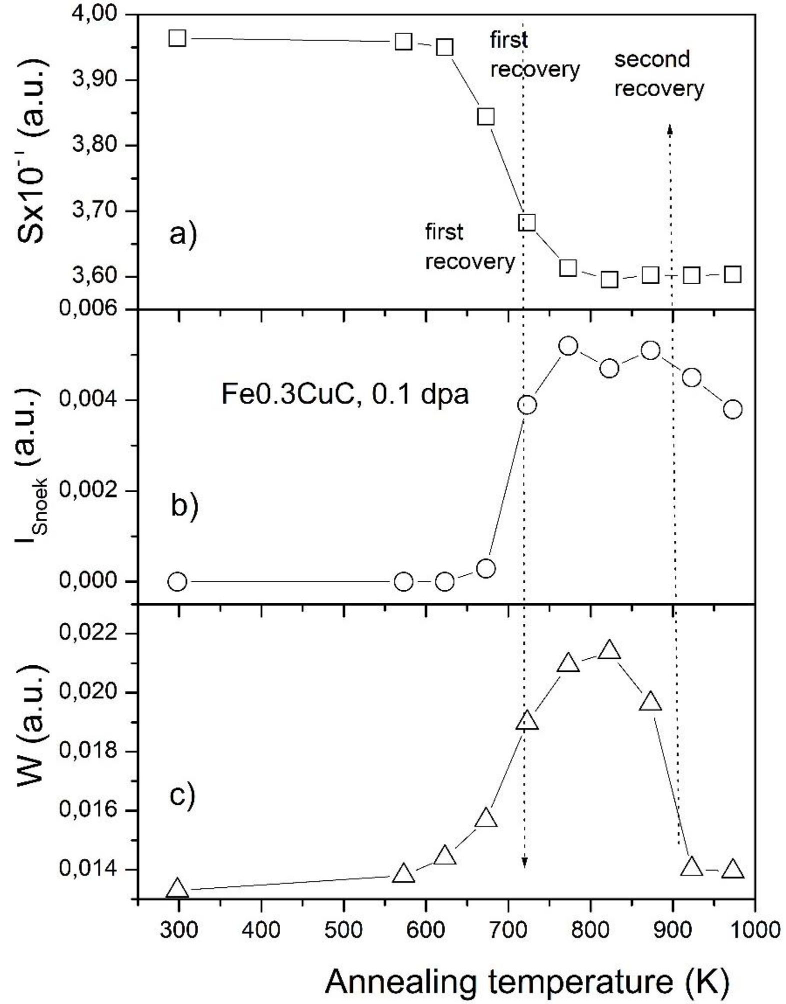
Fe-0.3Cu-C

- *ab-initio* calculation



- Binding energy V-Cu-C = 0.83 eV > binding energy Cu-V =0.65 eV
- Carbon atoms are bound to neutron irradiation-induced defects that dissolve at about 400 ^{0}C (V-Cu complexes).

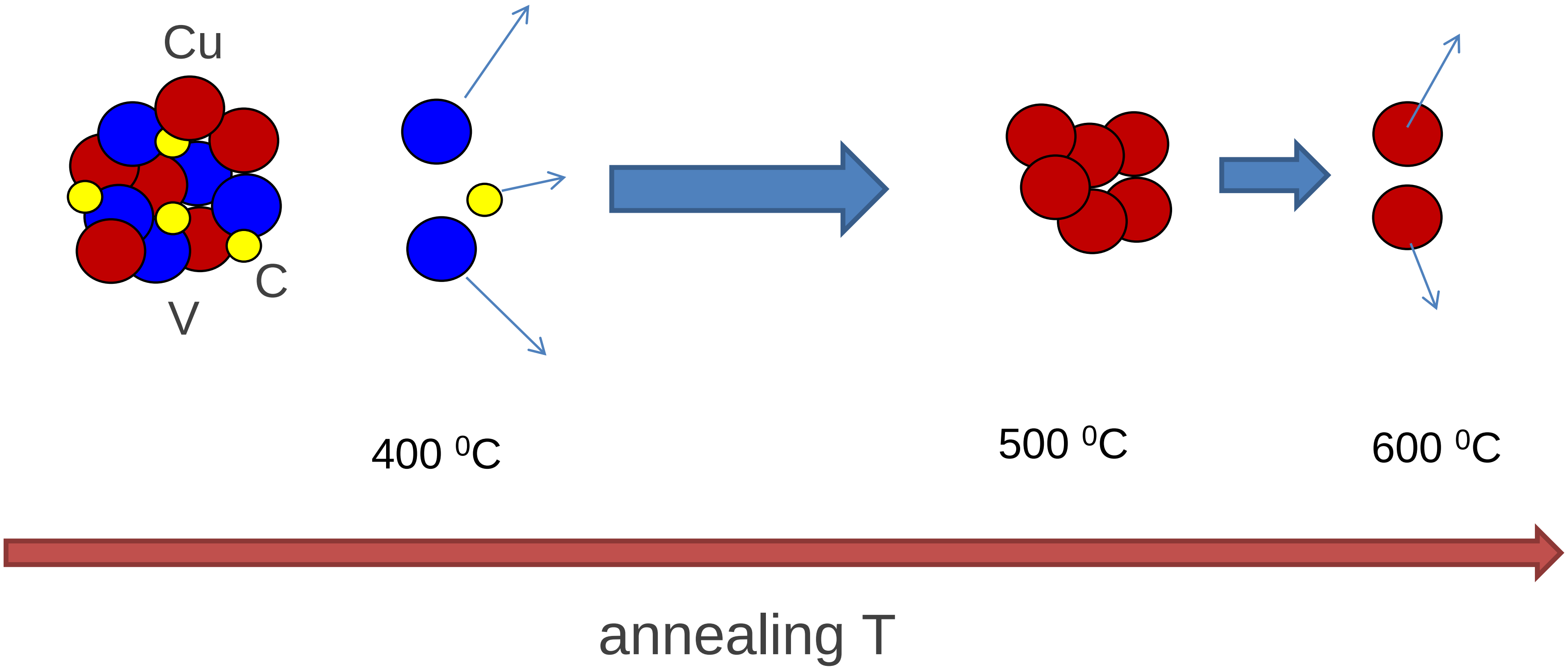
Synergy of Cu, V and C



B. Minov et al., PRB **85**, 024202 (2012)

Cu-V cluster dissolution

Cu-V-C and V-C cluster groups



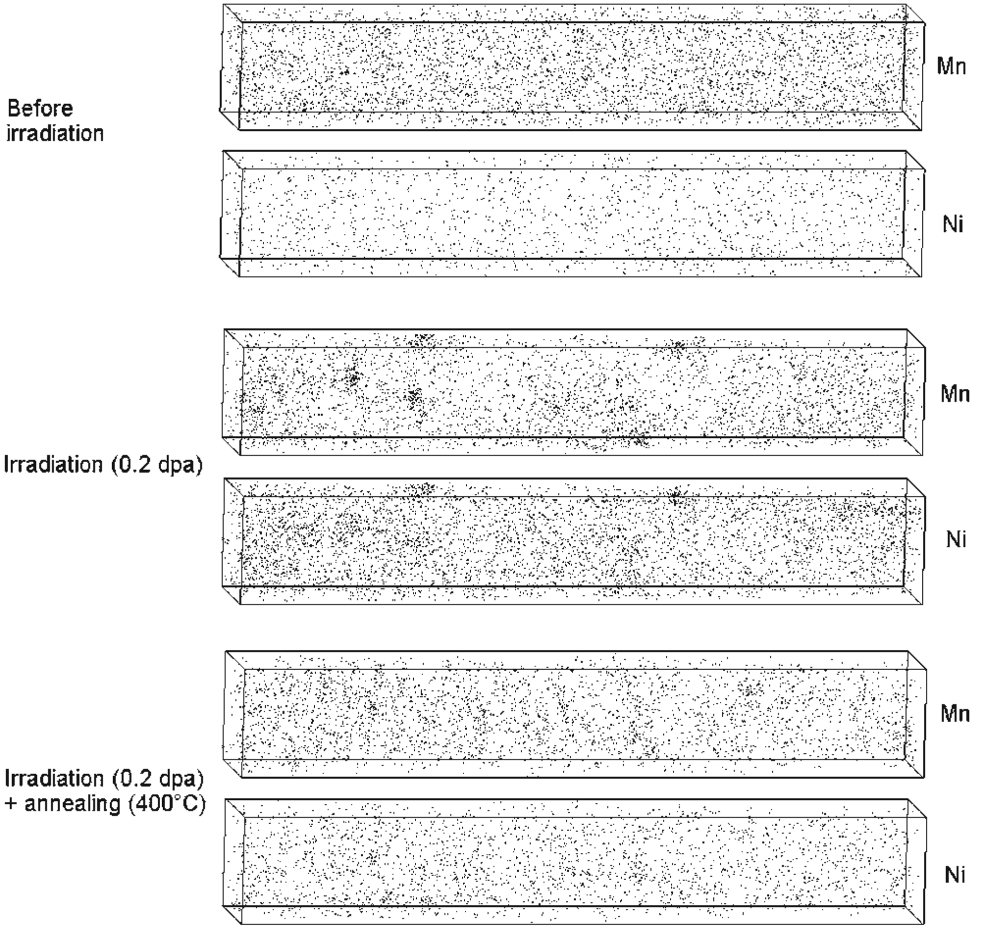
Fe1.1Mn0.7Ni - ATP

- Diameter ~ 0.8 nm

(much smaller than in FeCu for the same dose)

- Number density ~ 6.9 x 10^{23} $1/m^3$

- All cluster dissolve after annealing at 400 ^0C

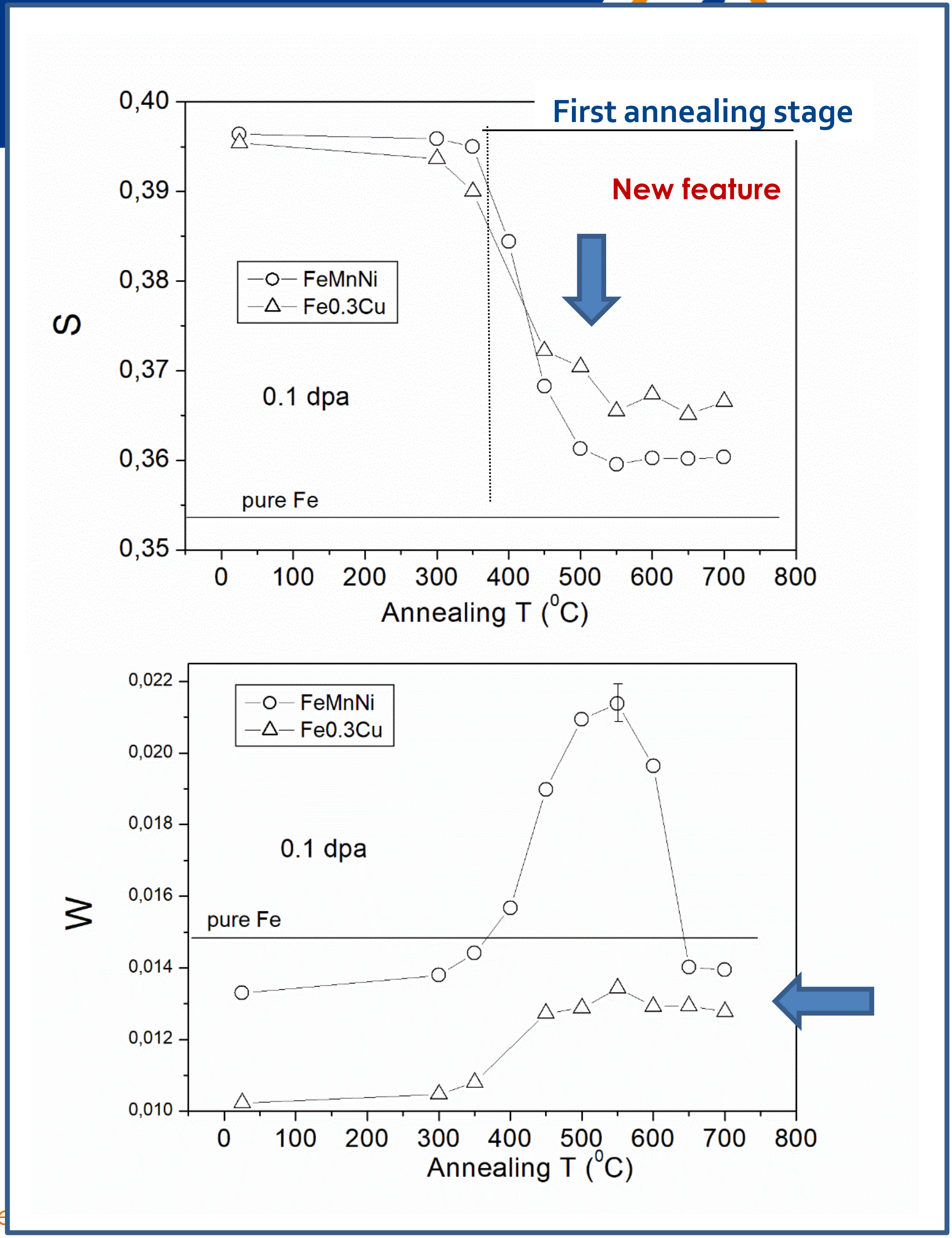


Meslin *et al.*, Experimental Mechanics (2011) 51:1453–1458

Fe1.1Mn0.7Ni - PAS

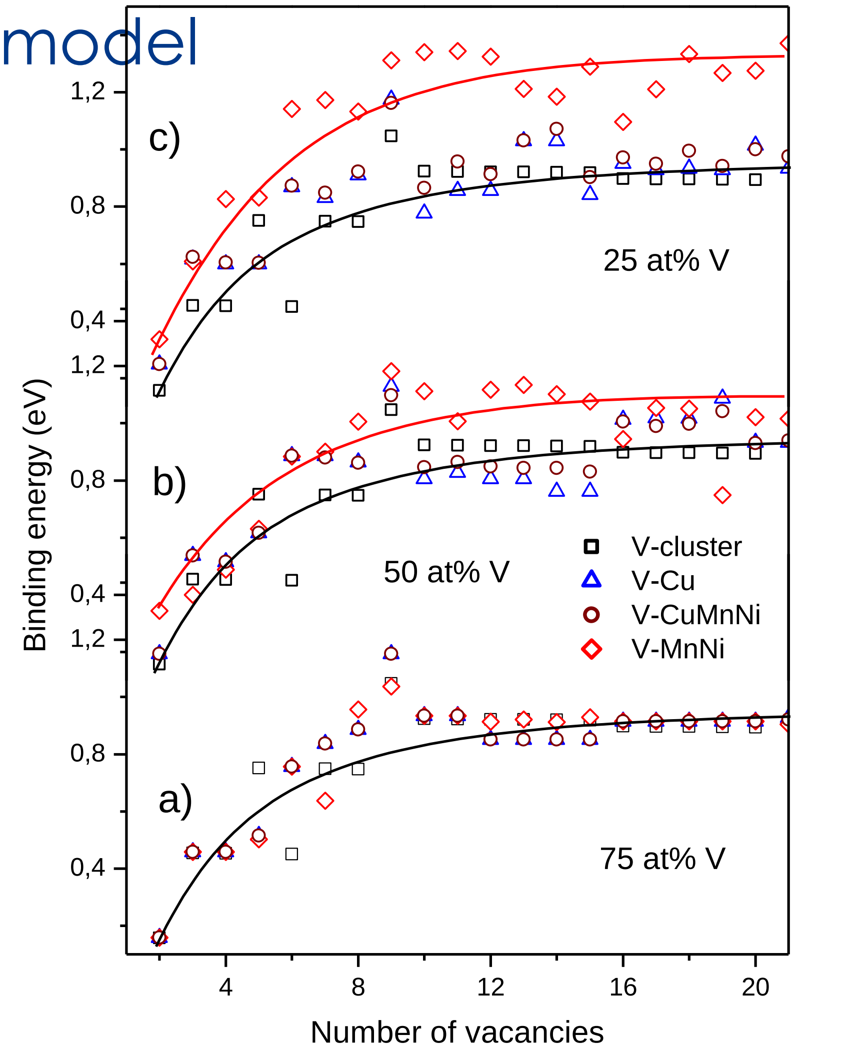
- New annealing stage at about 500-550 °C
- Additional stability of vacancy clusters due to presence of Mn and Ni?
- No indication of Ni solutes in W parameter after vacancy annealing

M. J. Konstantinovic, G. Bonny Acta Mat. **85**, 107 (2015)



Ni, Mn, cluster stability

- Vacancy dissociation energy as function of the cluster composition, rigid ion model

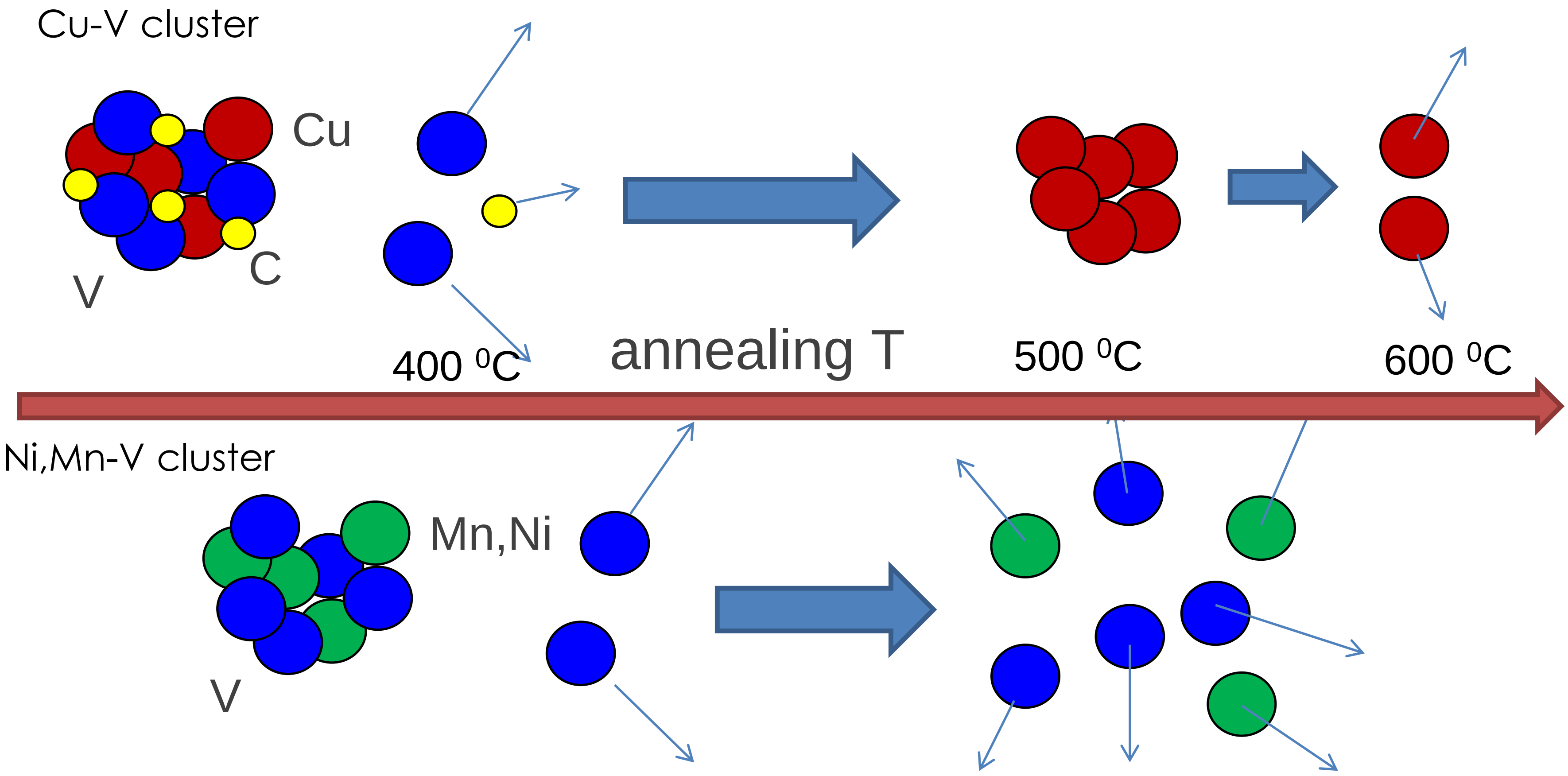


- The variation of vacancy concentration with respect to the solute cluster concentration mainly affects V-MnNi clusters
- The dissociation energy of vacancy solute clusters fall into two distinct groups
- Dissolution stage at about 500– 550 °C is assigned to the **dissolution of V-MnNi clusters**

M. J. Konstantinovic, G. Bonny Acta Mat. **85**, 107 (2015)

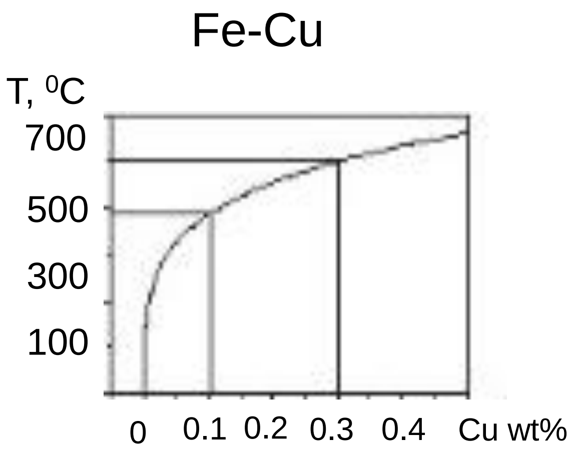
Solute cluster dissolution

- Take a home message

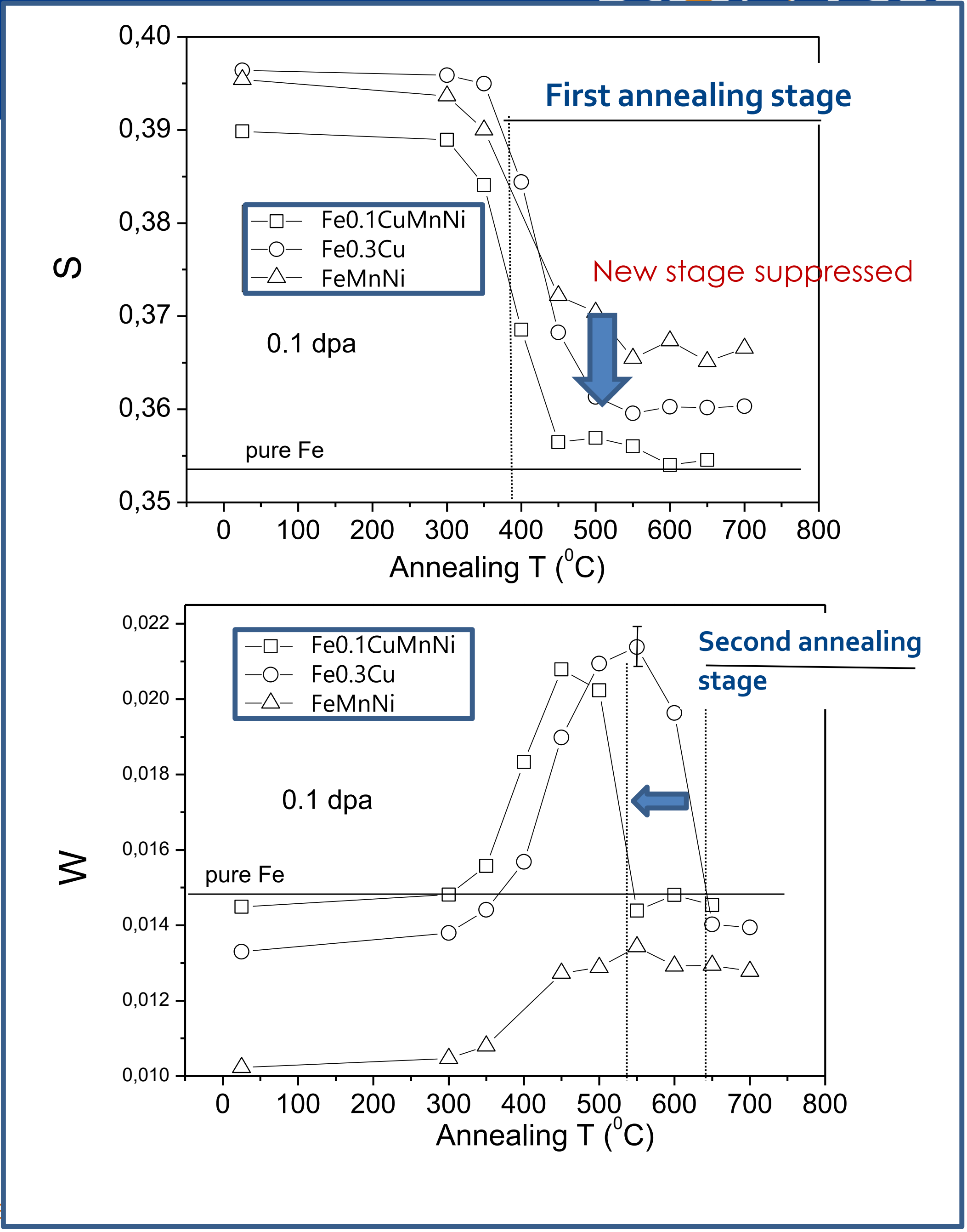


FeCu+MnNi

M. J. Konstantinovic, G. Bonny Acta Mat. **85**, 107 (2015)



- First annealing stage – vacancy release
- Second stage – dissolution of Cu cluster – Cu dependent
- Stability of mixed cluster governed by Cu content



Take a home message

- Cu –Va-C synergy / once vacancies are dissolved, Cu clusters remains thermally stable / irradiation enhanced precipitation

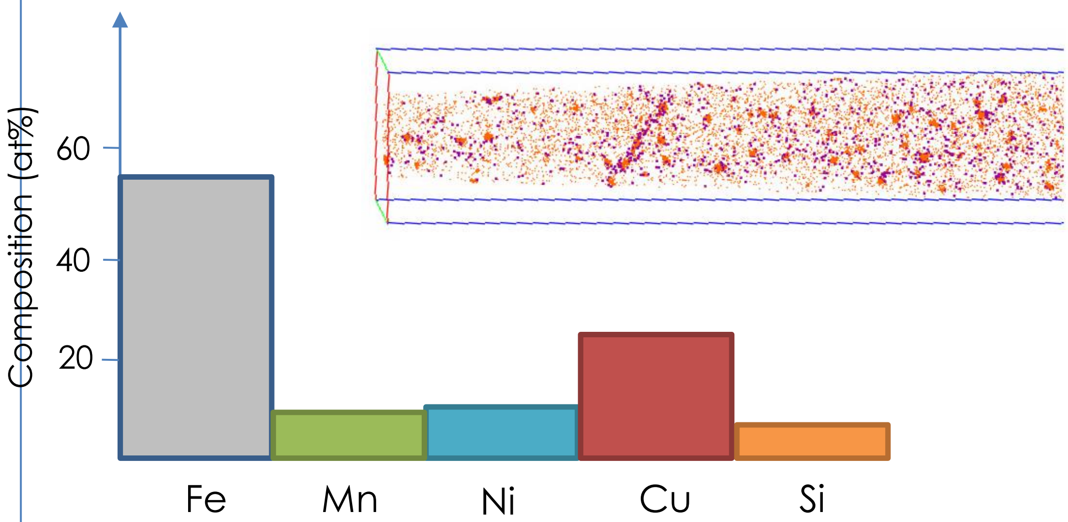
- Ni, Mn precipitation is irradiation induced - dissolution of vacancies dissolves solute cluster.

- In ternary alloys, the clusters is a mixture of all solute elements
  - Thermal stability mainly depend on Cu concentration (if Cu content is larger than solubility limit)

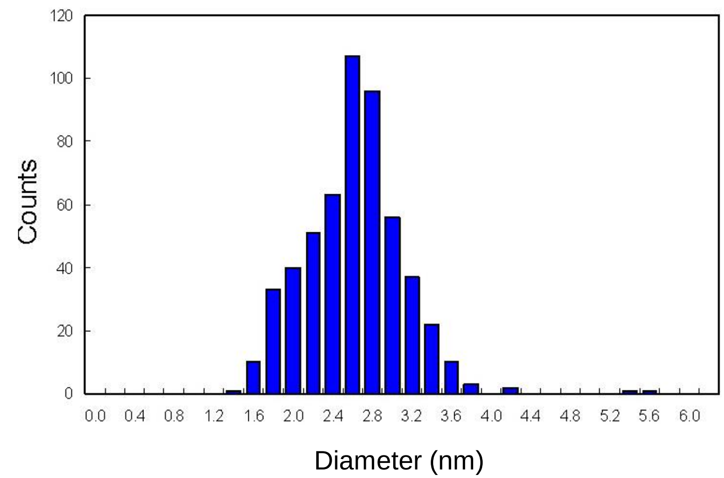
- Ni, Mn – Vac cluster dissolution is driven by vacancies (however at slightly higher T – vacancy cluster is more stable by adding Ni and Mn)

High Cu RPV steels (welds)

- RPV steels, surveillance specimens - weld, Cu~0.25 wt%



Nd ~ 4.1 x 10^{23} m^{-3}



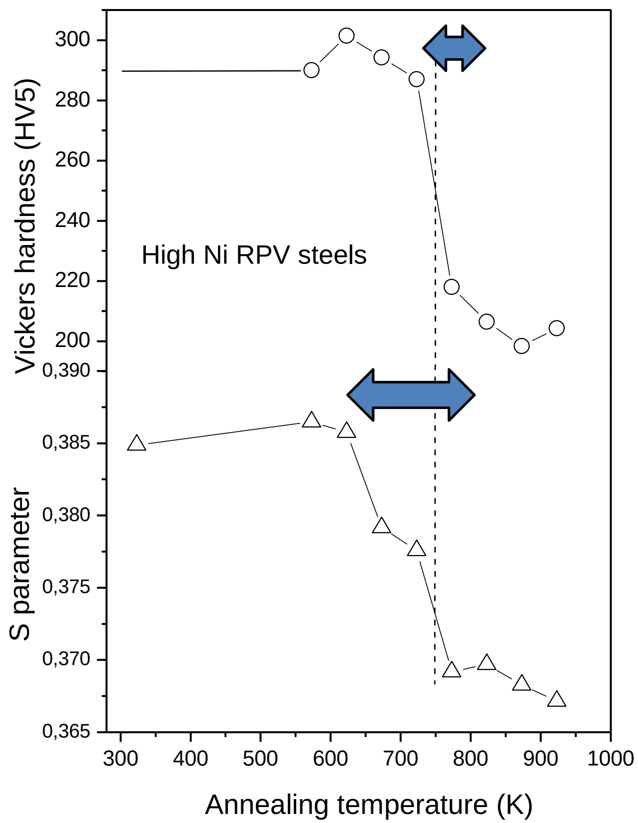
- Cu rich clusters are well developed in high Cu RPV steels (welds)
- High number density of Cu rich clusters
- Not much difference between high and low neutron flux

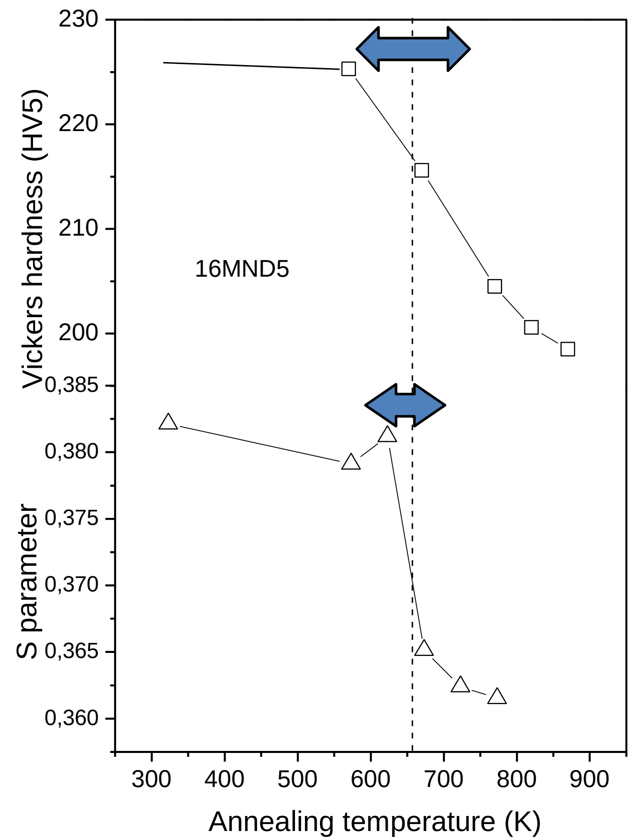
Soneda, et al., IGRDM 2015

High Ni RPV steels

- ❑ Base steel - gradual loss of hardening starting already from 623 K (350 ^{0}C)
- ❑ High Ni RPV steel – abrupt loss of hardening from 723 K (450 ^{0}C)
- ❑ Opposite effect for S parameter

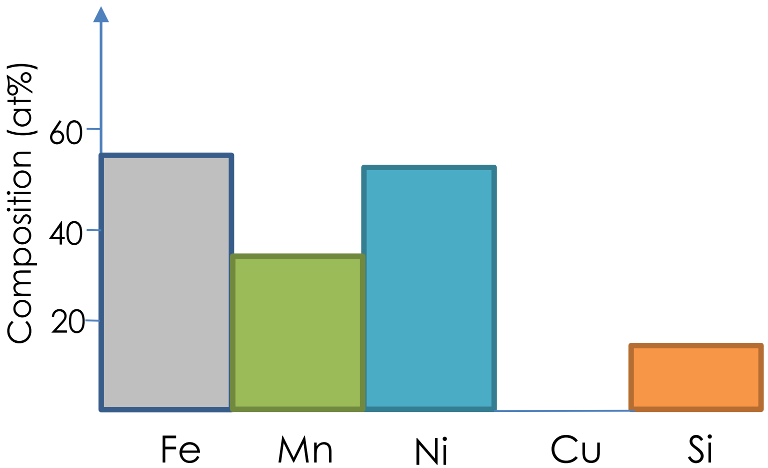
M.J. Konstantinovic et al. IGRDM 18

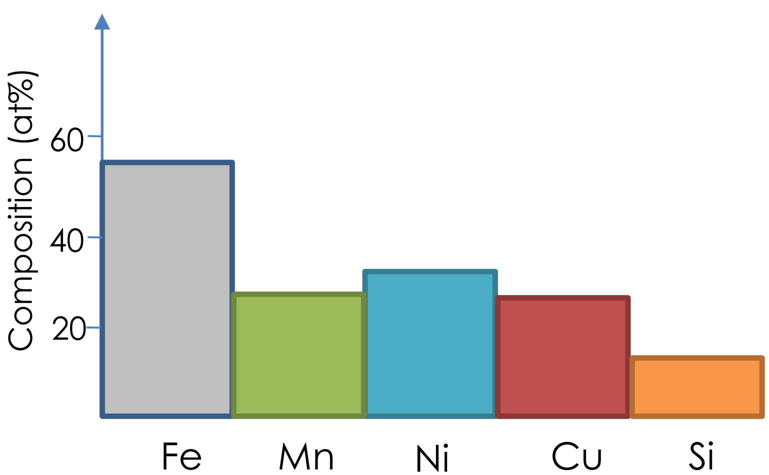


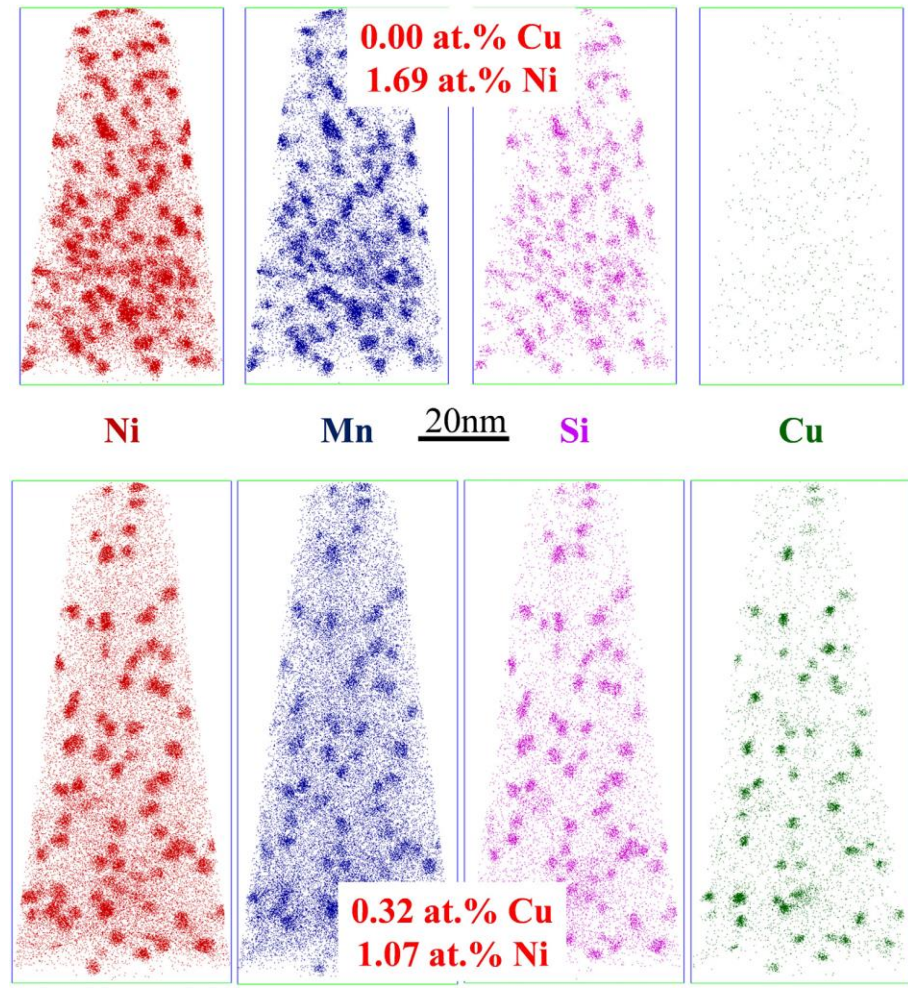


High Ni RPV steels

At high Ni and high fluence Cu does not play key role





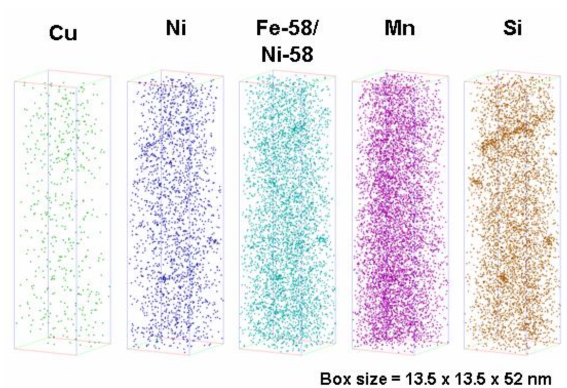


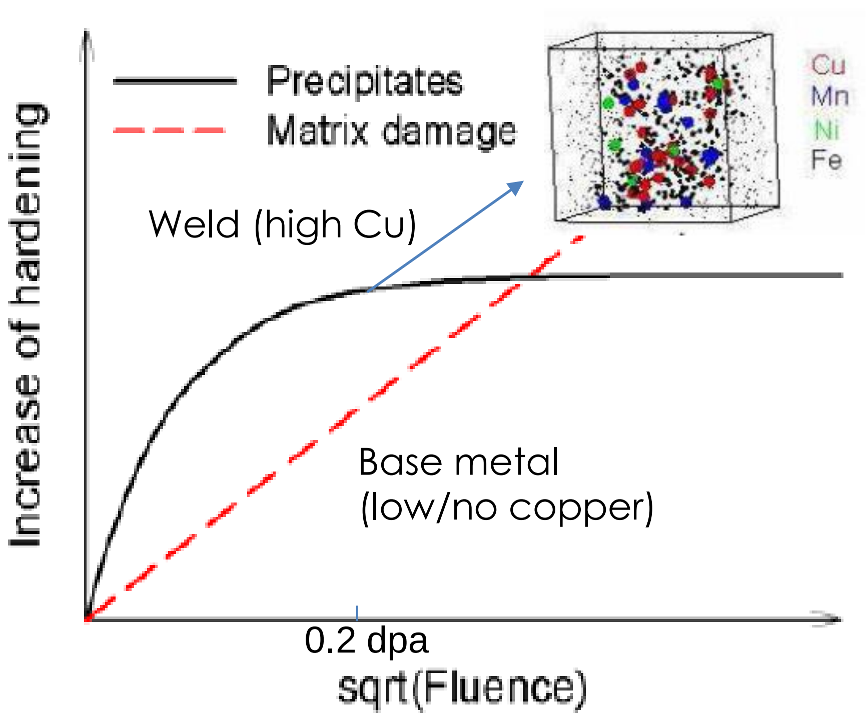
Wells *et al.*, Acta Materialia 80 (2014) 205–219

Low Cu RPV steels

- Usually no solute clustering is observed in low Cu (Cu<0.06 wt%) surveillance specimens (low neutron flux)

- Low Cu steels irradiated in MTR (high flux) do develop MnNi clusters





Conclusions

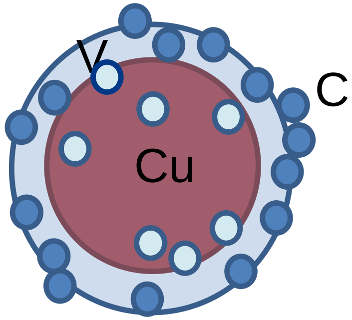
- Synergy of solute atoms vacancies and carbon or phosphorus
- Cu precipitation is irradiation enhanced; may also occur as a result of thermal ageing;
- Ni, Mn precipitation is irradiation induced; cluster is uniform mixture of solute atoms and vacancies
- In concentrated alloys and steels alloys, the clusters is a mixture of all solute elements
- Thermal stability mainly depend on Cu concentration (if Cu content is larger than solubility limit)
- At high Ni and high fluence the role of Cu is strongly reduced
- Flux effect is expected to be observed for solute clusters which are irradiation induced / low Cu alloys and steels

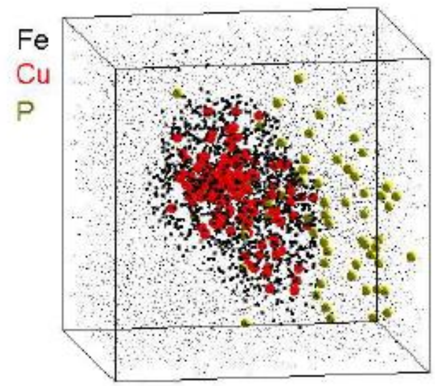
Additional slides

Solute cluster composition

- Cu-Vac-C

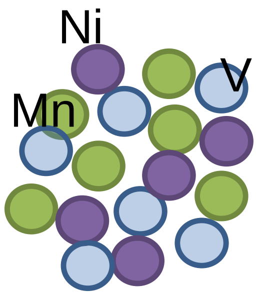
Irradiation enhanced

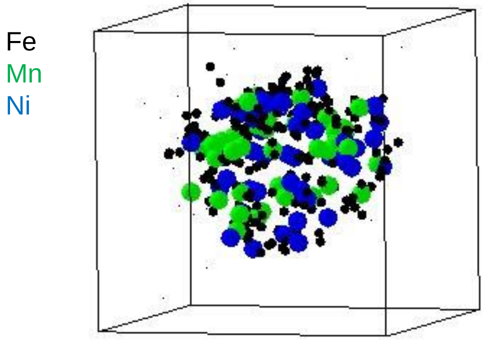




- Mn,Ni-Vac

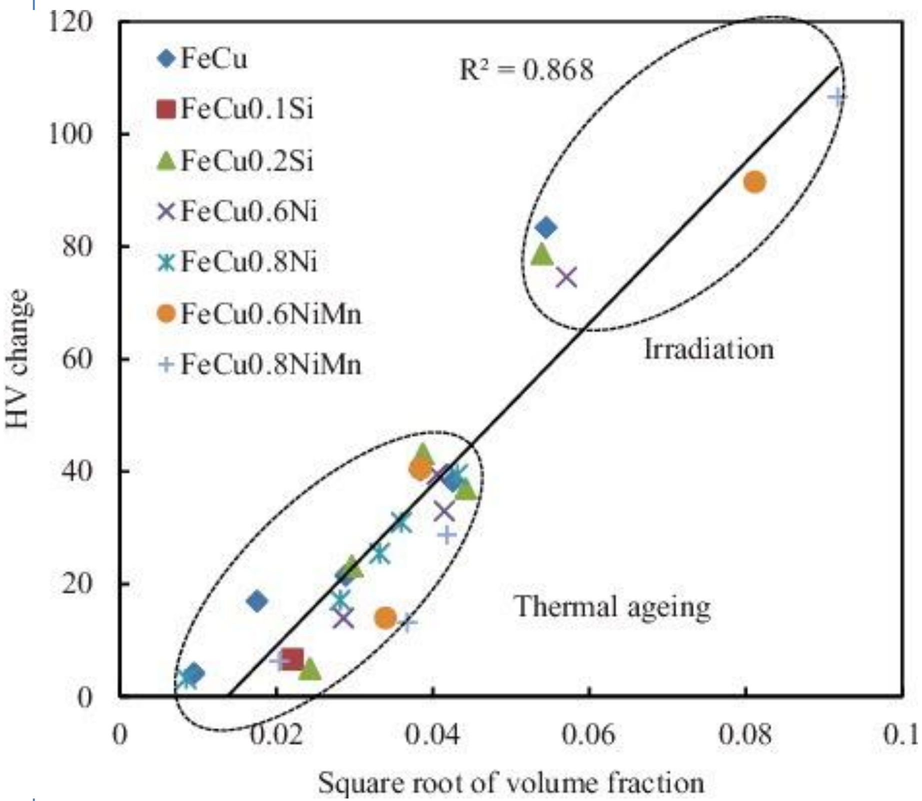
Irradiation induced



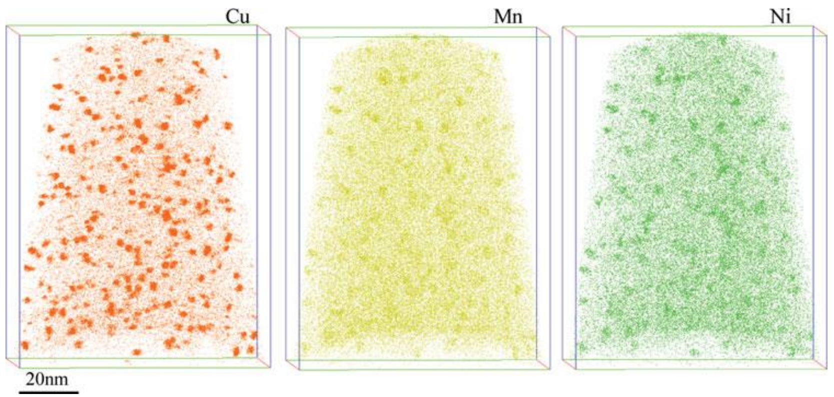


Cu effect - general

Model alloys with Cu



All solutes cluster together

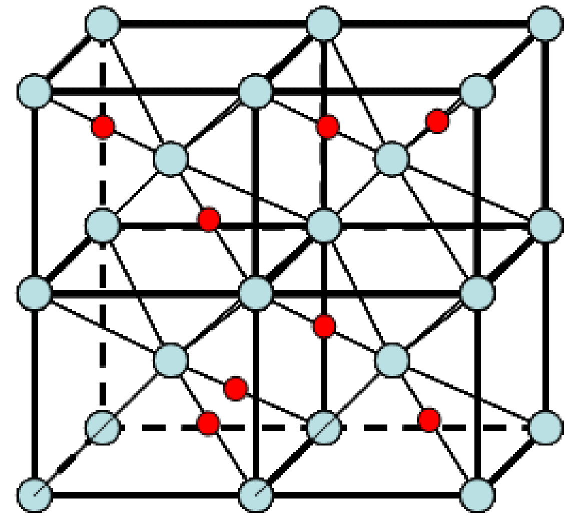


More Mn and Ni atoms in clusters after neutron irradiation then in clusters formed after thermal ageing

Liu et al., JOURNAL OF NUCLEAR SCIENCE AND TECHNOLOGY 2016, VOL. 53, 1546.

Take a home massage

- Debye relaxation



$$Q^{-1} \approx \Delta \frac{\omega \tau}{1+(\omega \tau)^2}$$

$$\tau = \tau_0 e^{\frac{E}{k_B T}}$$

$T_C = activation\ \ energy$

$I \sim defect\ concentration.$

$\Delta T \sim distribution\ of\ E_A$