Statistical physics for the modeling of non-equilibrium metallic alloys driven by irradiation

DE LA RECHERCHE À L'INDUSTRIE

cea den

Part of this work was supported by

- *the joint program "CPR ODISSEE" funded by AREVA, CEA, CNRS, EDF and Mécachrome under contract n° 070551.*
- *EERA-JPNM Matisse/Mefisto*
- *IREMEV, Eurofusion*

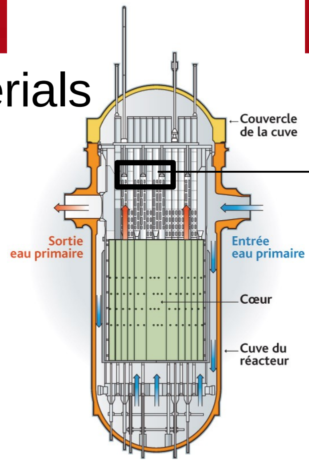
Thomas Schuler1,2, Luca Messina1,3, Frédéric Soisson1, Pär Olsson3, Maylise Nastar1

1CEA/SRMP, France
2Ecole Mines St Etienne, France
3KTH, Stockholm, Sweden

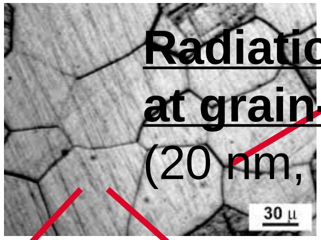
European Comission funded Enlargement workshop, KYIV, June 2017,

Irradiation damage in steels

Structural materials
Of nuclear
reactors



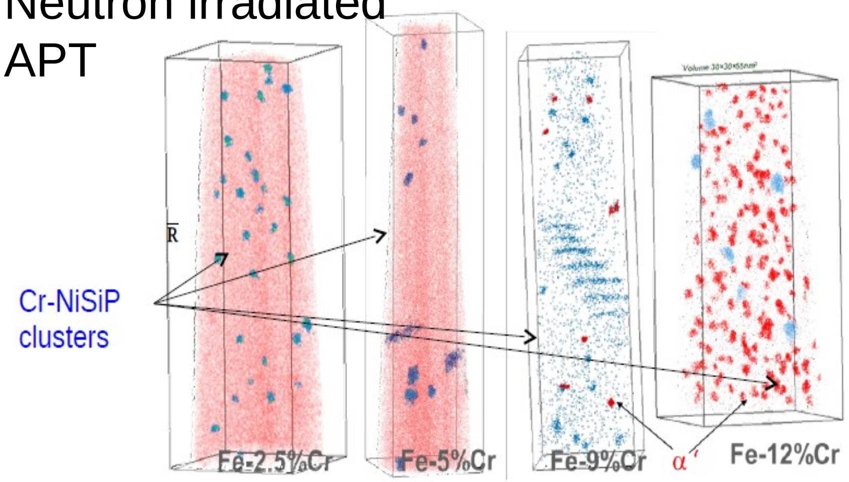
irradiation



<u>Radiation induced Segregation at grain-boundaries</u>
(20 nm, 1dpa)→IASCC

<u>Solute clustering in ferritic steels</u>

Neutron irradiated
APT

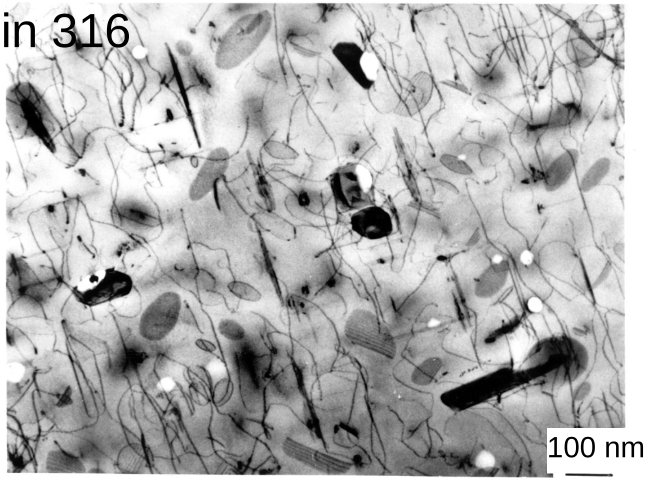


V. Kuksenko, PhD (2011); V. Kuksenko, C. Pareige, P. Pareige, J. Nucl. Mater. 432 (2013) 160

→ hardenning, embrittlement

<u>Radiation damage</u>
cavities, dislocation loops, etc.

TEM in 316

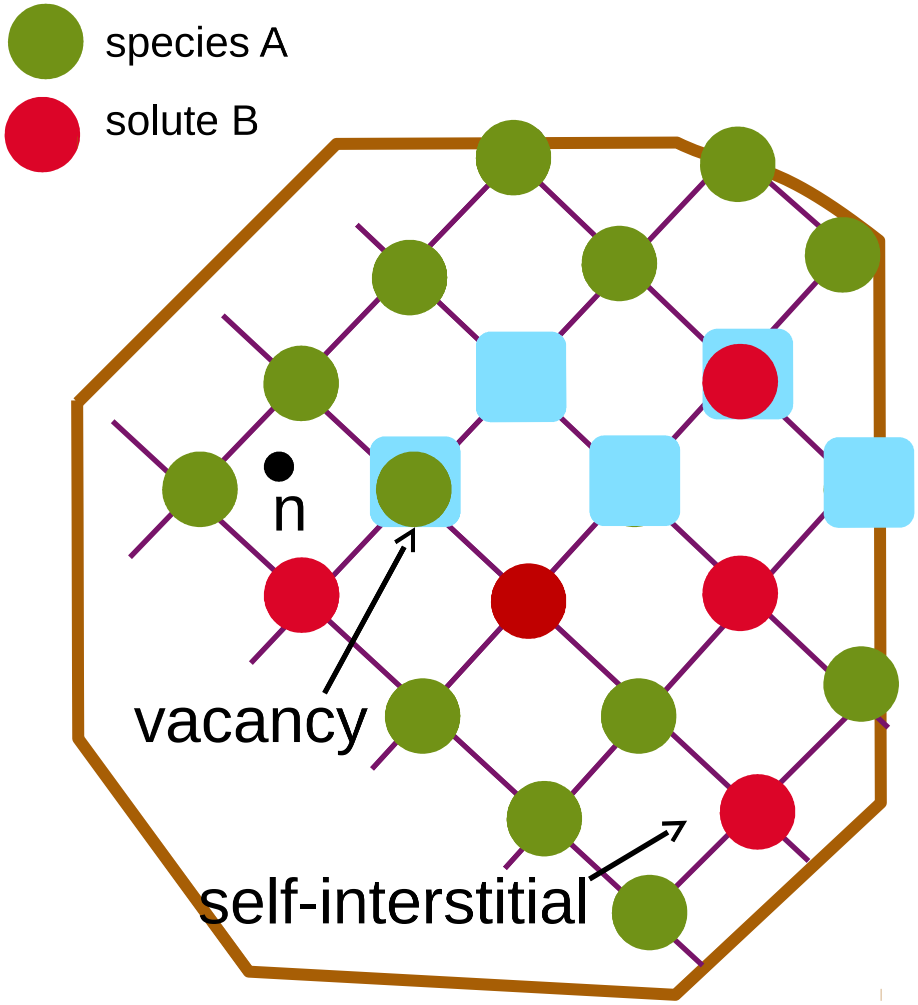


SA 316 irradiated in EBR-II to 1.9×10^{26} n/m^2 at 580 °C

→ embrittlement, swelling, etc.

Swelling, deformation, degradation of corrosion resistance and mechanical properties

Flux coupling

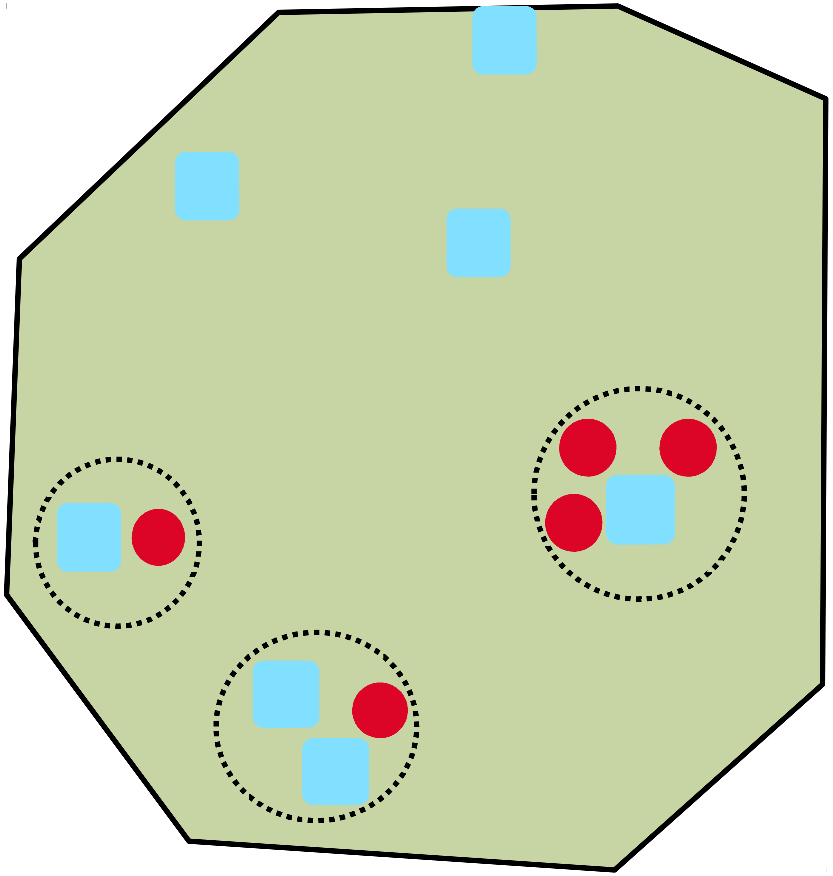


Mechanism of radiation induced segregation:

- ✓ Point defect (PD) driving force: elimination of PD at sinks
- ✓ Flux coupling between PD and atoms

Other phenomena involving a net flow of vacancies and potential flux couplings: Quenching, diffusion creep, sintering, carburization, oxidation, nitruration, etc.

Solute clustering/dissociation



<u>Mechanisms of solute clustering</u>

- ✓ Point defect driving force:
clustering of PD (cavity, dislocation loop, C15, etc.) + Solute segregation due to flux coupling

- ✓ Solute driving force:
Phase transformation and formation of a new phase

<u>Mechanisms of precipitate dissolution</u>

- ✓ Dynamic phase diagram

- ✓ Ballistic mixing

Outline

1. **Dynamic Phase Diagram of Fe(C,N,O)**

a) Vacancy-solute cluster binding energies

b) Solubility limits with respect to vacancy supersaturation

c) Vacancy induced dissolution versus ballistic mixing

2. **Radiation Induced Segregation in Fe(X) (X=C,N,O,metal)**

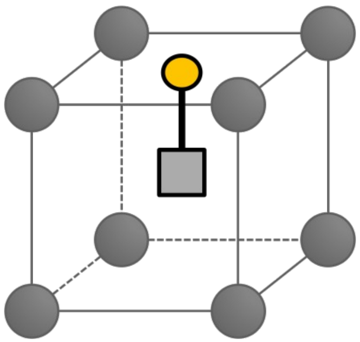
a) Vacancy-solute cluster transport coefficients

b) A multi-scale computation of the phenomenological coefficients Lijs

c) RIS in Fe(X=C,N,O or a transition metal) alloys

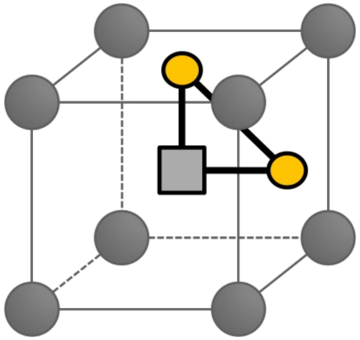
Vacancy-solute clusters: Insights from DFT

DFT calculations suggest strong binding energies between X and V

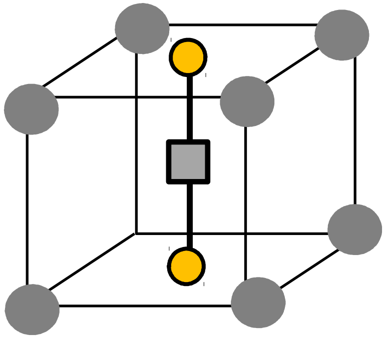


Ebt(V-X) (eV)	
X = C	0,41 - 0,65
X = N	0,71 - 0,92
X = O	1,41 – 1,69

[Domain04;Fu08;Paxton13; Förs t06;Jourdan11; Ohnuma09;Fu07;Jiang09]



Ebt(VC2)=1.18 eV



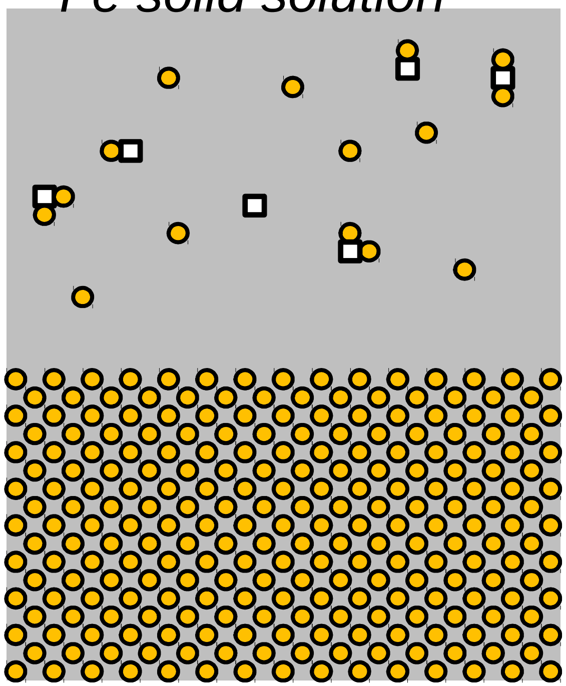
Ebt(VO2)=3 eV

Concentration of mixed point defect-interstitial clusters might be large

Dynamic solubility limit from a constrained chemical potential

Two phase system

Fe solid solution



Ordered compound FepXq

(infinite reservoir of X)

*T. Schuler, M. Nastar & F. Soisson, PRB 95 (2017) 014113

Solute chemical potential µX

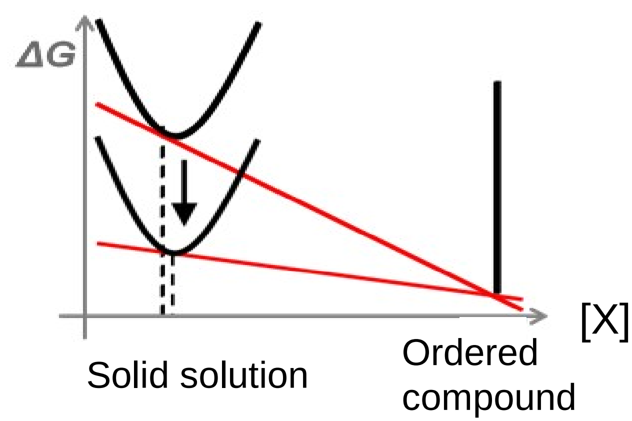
Average solute energy in a given phase

$$\mu_X \sim E\left[X \epsilon \mathrm{Fe}\right] - E\left[X \epsilon \mathrm{Fe_p X_q}\right]$$

Function of the supersaturation [V] and Cluster binding free energies

The ordered compound is assumed perfect. E=constant, deduced from thermodynamic database.

Shift of the solubility limit



From binding energies to cluster concentrations

Statistical physics to average over various clusters and cluster configurations:

[Domb60]

[Ducastelle91]

Low-temperature expansions (LTE)

Geometrical multiplicity

Cluster binding energy (from DFT+cluster expansion)

Grand potential

$$\mathcal{A} = \mathcal{A}_0 - k_B T \sum_i g_i \exp\left(\frac{-\Delta E_i + \sum_\alpha \Delta n_\alpha (i)\, \mu_\alpha}{k_B T} \right)$$

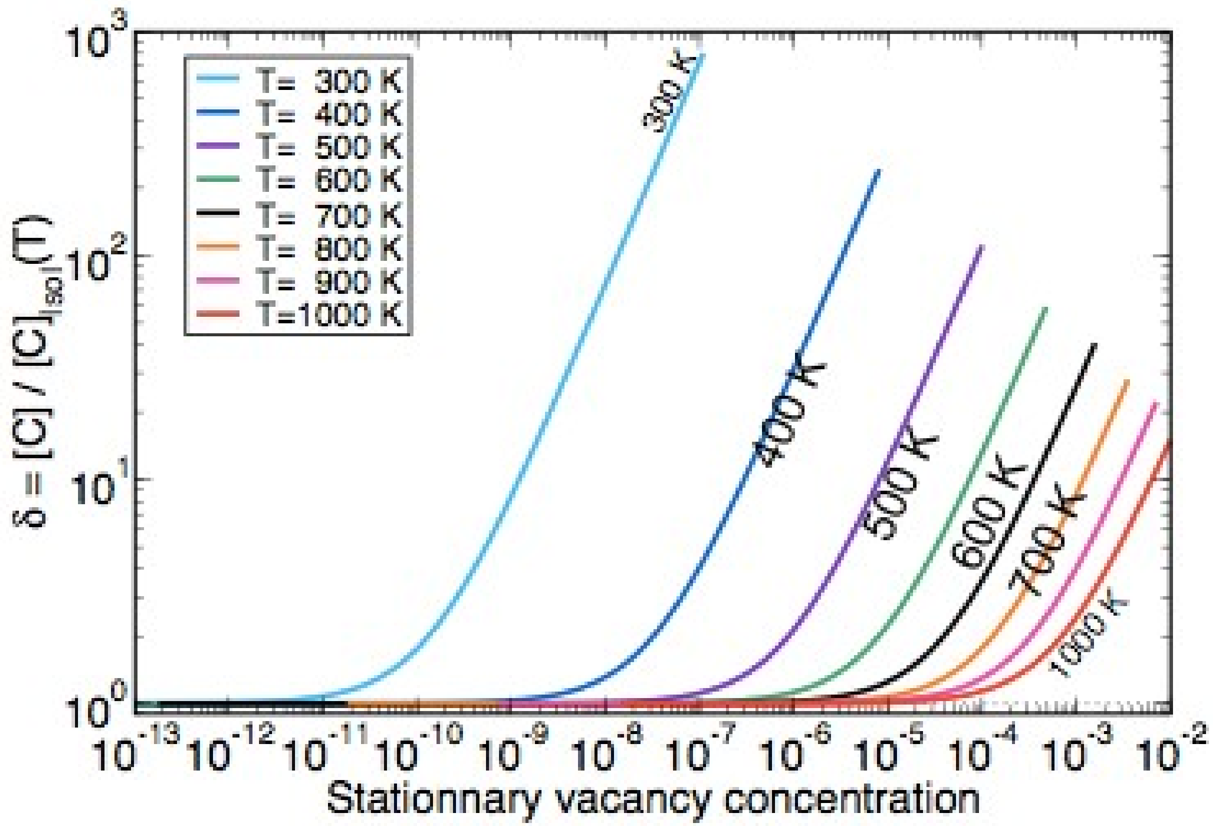
Reference: pure Fe

Excitation state = cluster

Dynamic solute solubility limit of C under irradiation

Irradiation modeled by a constant vacancy supersaturation

(steady-state and local equilibrium asumption)

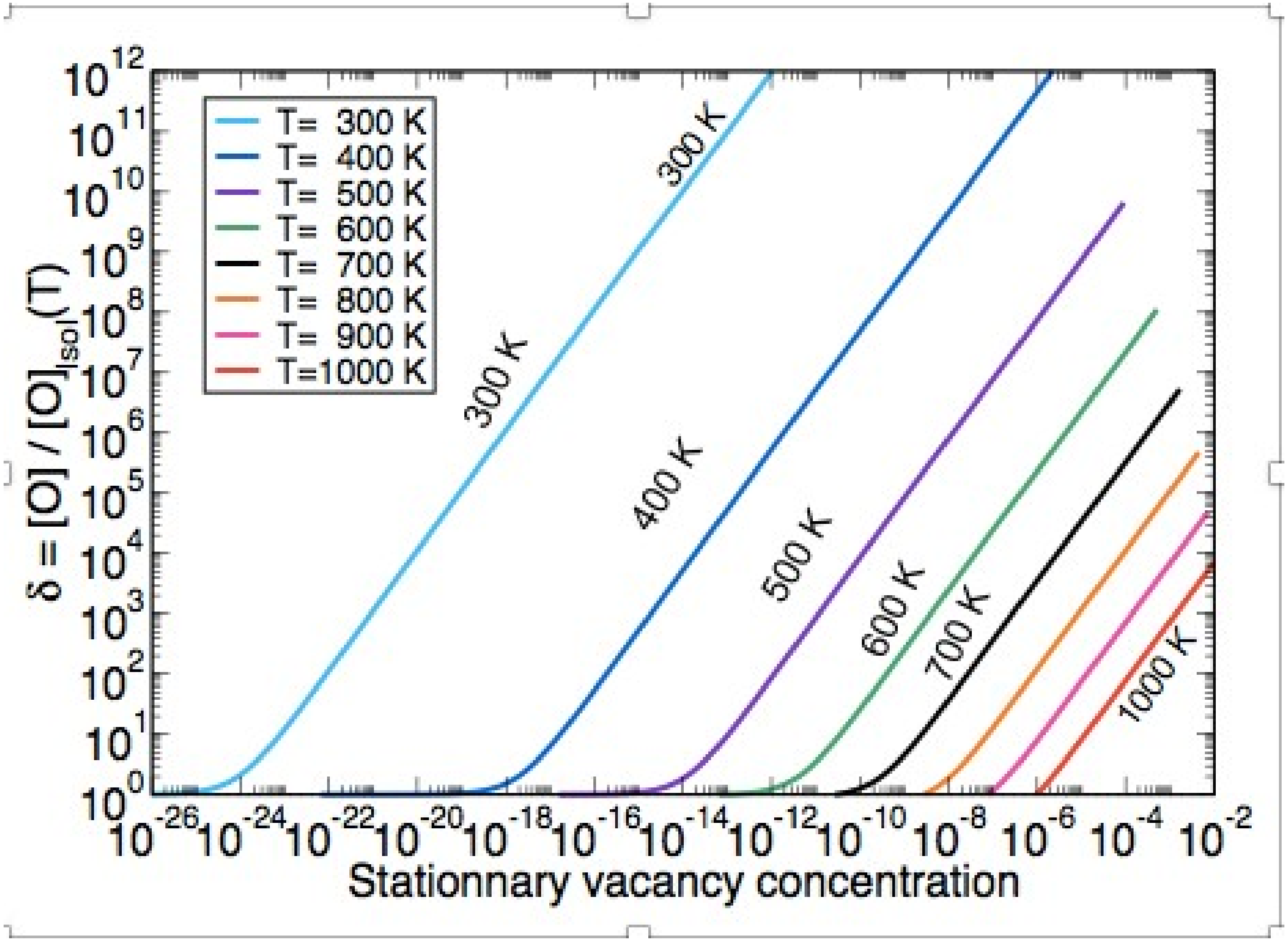


- ✓ Good agreement with AKMC simulations
- ✓ At low [V], the solubility limit is the equil. one
- ✓ linear trend of d because a single cluster dominates

*T. Schuler et al., PRB 95 (2017) 014113

Dynamic solute solubility limit of N & O under irradiation

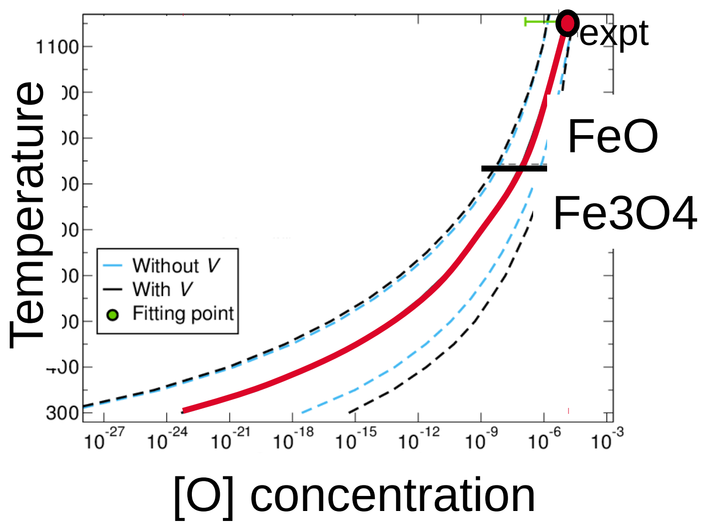
- ✓ Small amount of PD is required to increase the solubility limit by several orders of magnitude.



*T. Schuler et al. RB 95 (2017) 014113

Radiation induced dissolution of oxide in Fe(O)

Equilibrium phase diagram



✓ Balistic mixing is dominant at low T and high flux

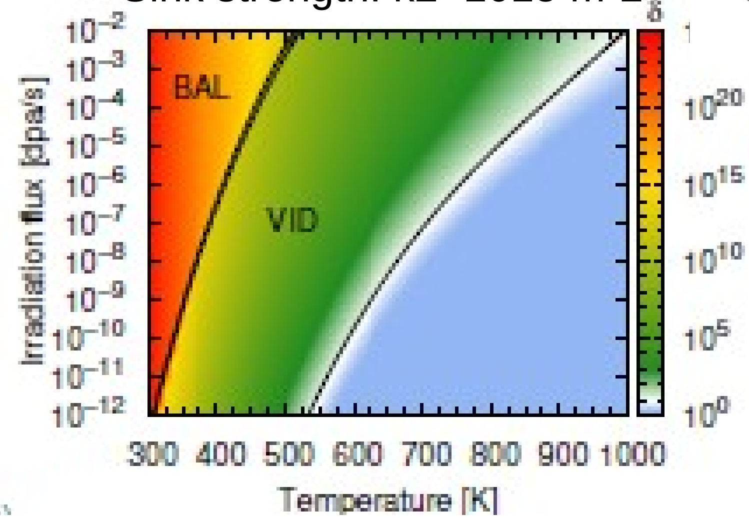
✓ Vacancy induced dissolution Is dominant at intermediate flux and T

✓ This mechanism should be considered in ODS steels

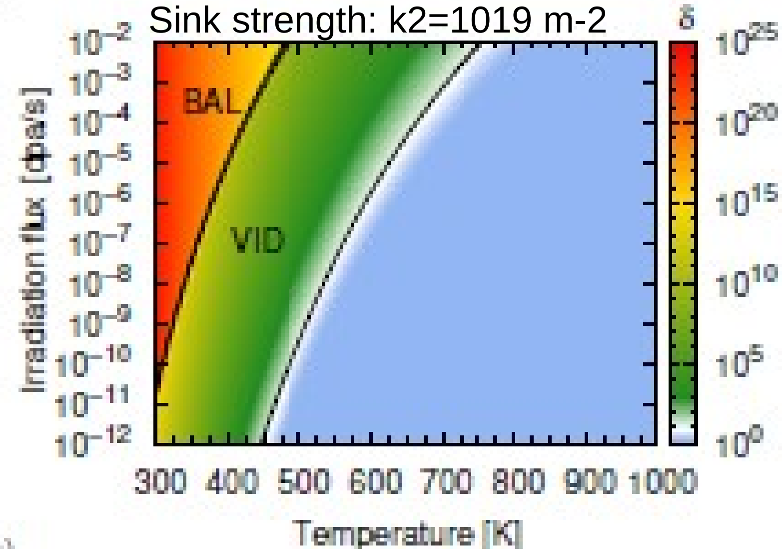
Solubility limit increase with flux and T

$$\delta = \frac{[O]_{sol}^{cons}}{[O]_{sol}^{eq}}$$

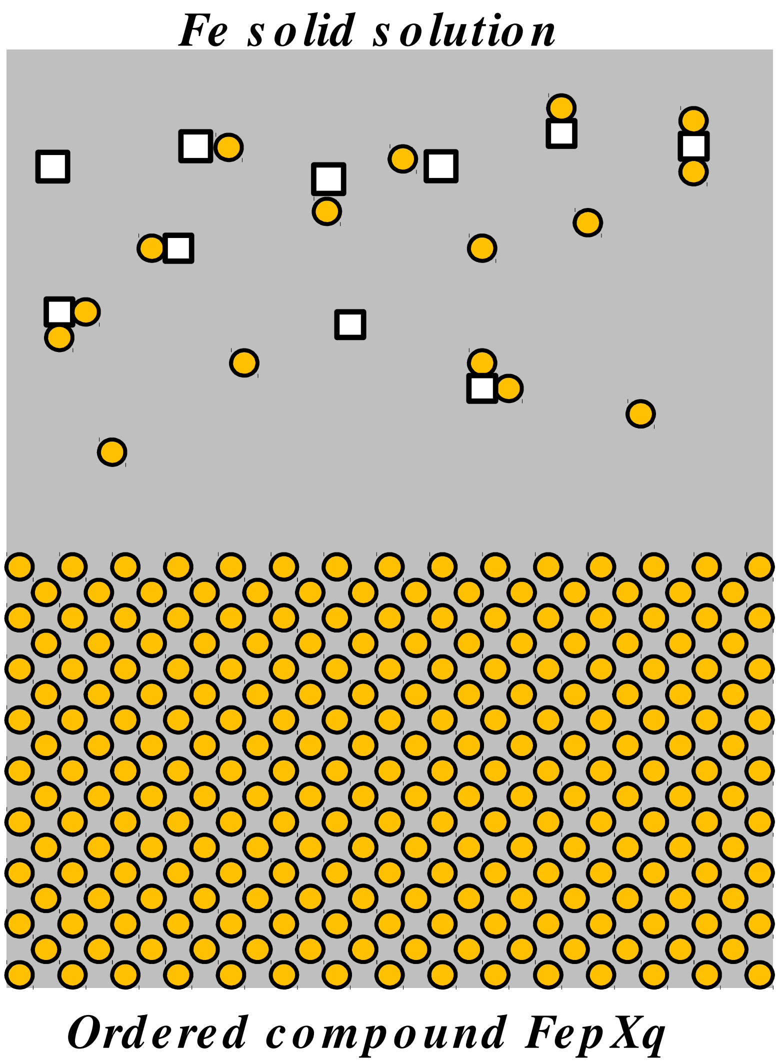
Sink strength: k2=1015 m-2



Sink strength: k2=1019 m-2



Flux coupling between interstitials and vacancy

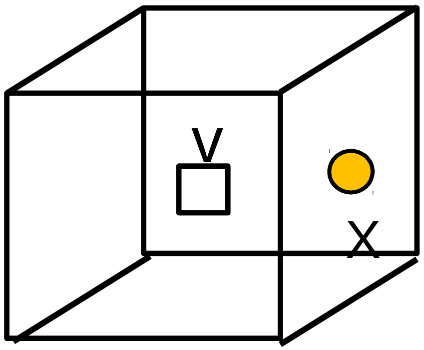


sign and amplitude of the flux coupling?

or

$$J_X = -L_{XV}\nabla\mu_V - L_{XX}\nabla\mu_X$$
$$J_V = -L_{VV}\nabla\mu_V - L_{XV}\nabla\mu_X$$

Lij from the atomic jump frequencies

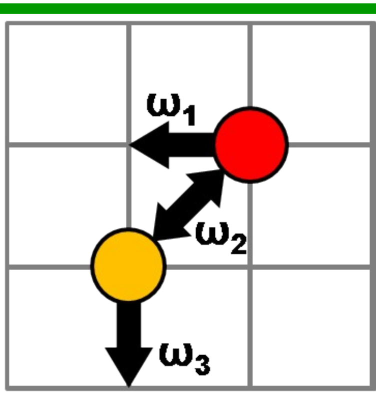


Computation based on the SCMF theory

Cluster transport coefficients
Computed using the automated code KineCluE

$$\{\omega_{p\to q}\}$$

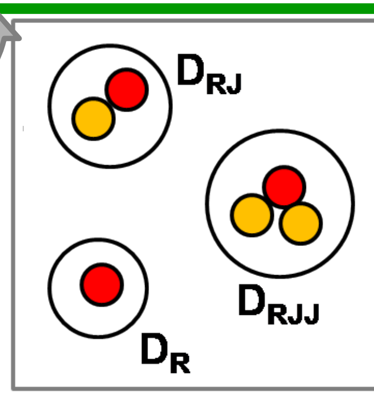
Atomic jump frequencies



DFT+SCMF

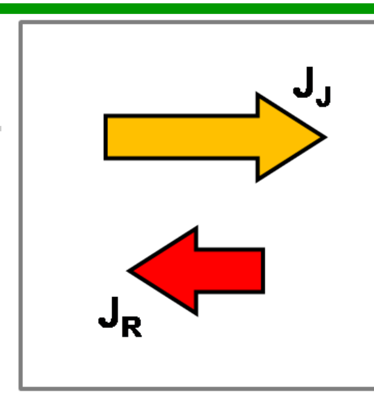
$$\begin{pmatrix} L^{eq}_{VV}(c_i) & L^{eq}_{VX}(c_i) \\ L^{eq}_{XV}(c_i) & L^{eq}_{XX}(c_i) \end{pmatrix}$$

Cluster transport coefficients



$$\begin{pmatrix} L_{VV} & L_{VX} \\ L_{XV} & L_{XX} \end{pmatrix}$$

Continuous description (TIP)



$$L_{\alpha\beta} = \sum_{c_i} [c_i]\, L^{eq}_{\alpha\beta}(c_i)$$

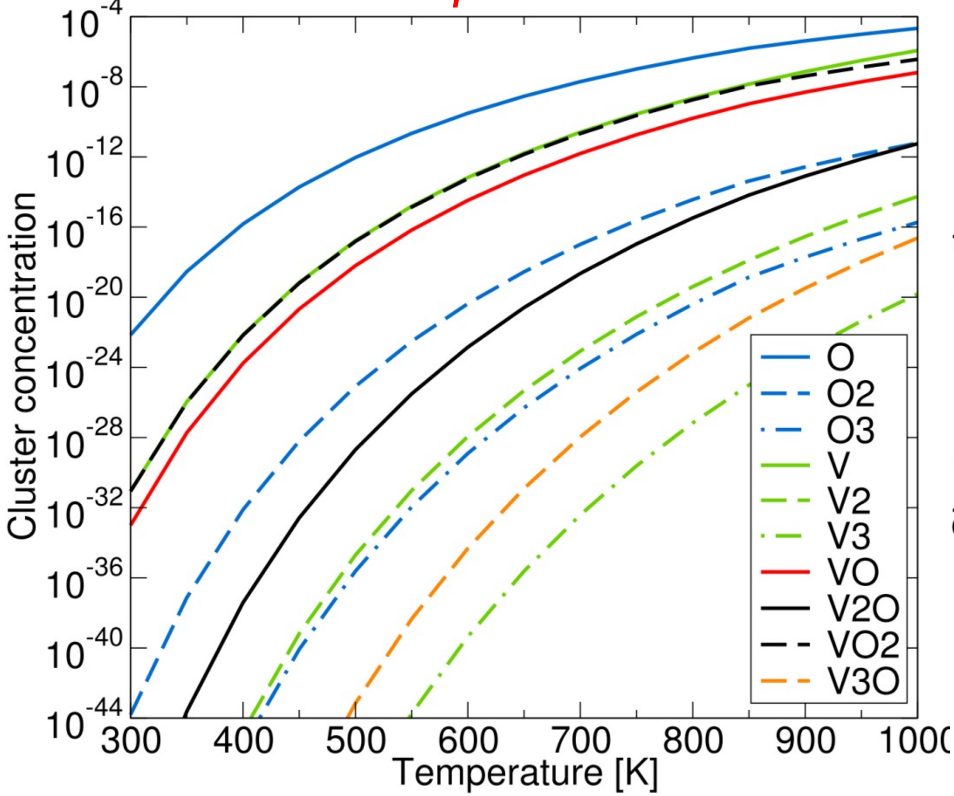
**T. Schuler at al., DIMAT 2017 - Haifa, Israel*

VnOm cluster distributions

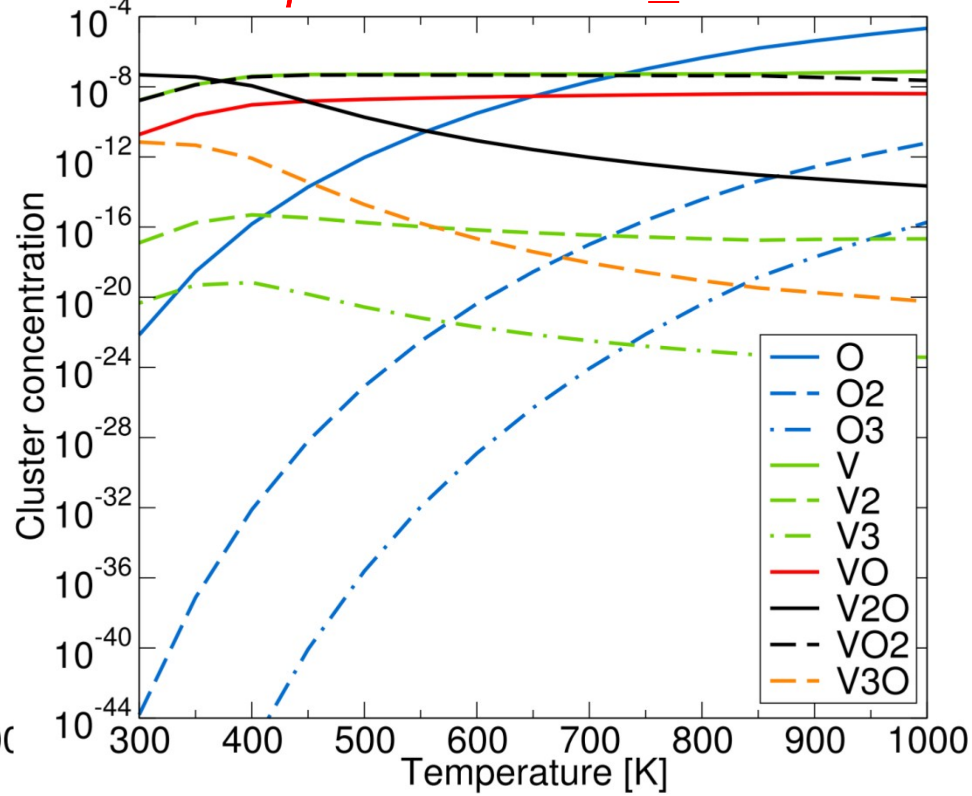
Lattice cluster expansion based on DFT calculations → Low temperature expansion

Barouh et al. Phys. Rev B 90, 054112 (2014)

Equilibrium



V supersaturation C_V=1e-7



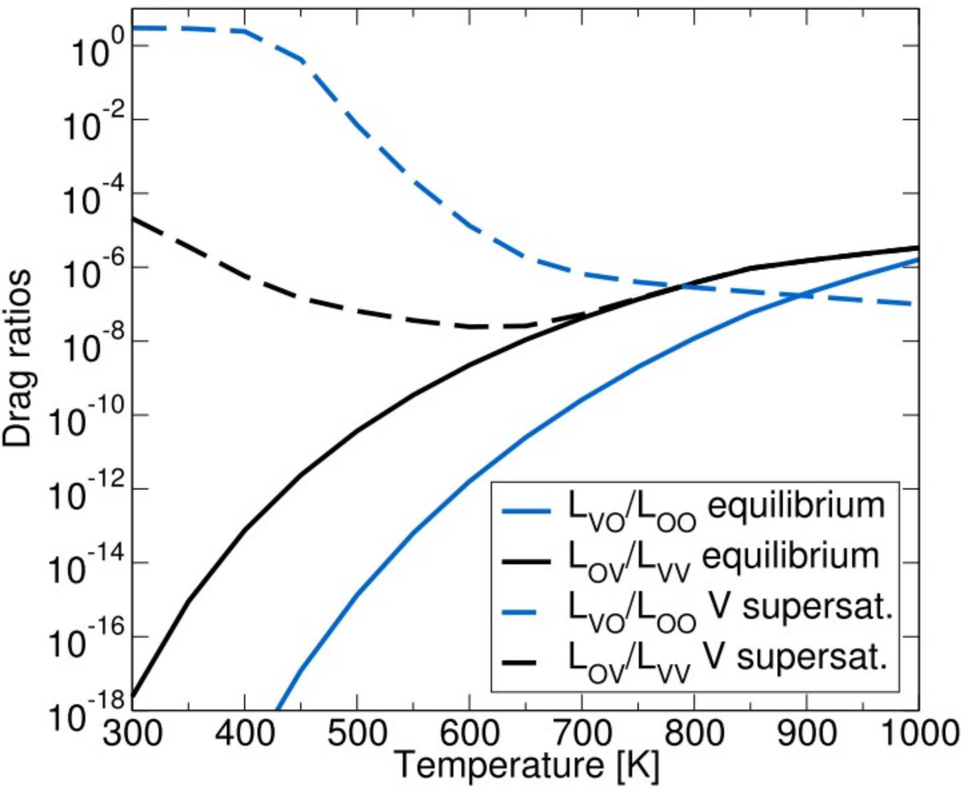
**T. Schuler at al., DIMAT 2017 - Haifa, Israel*

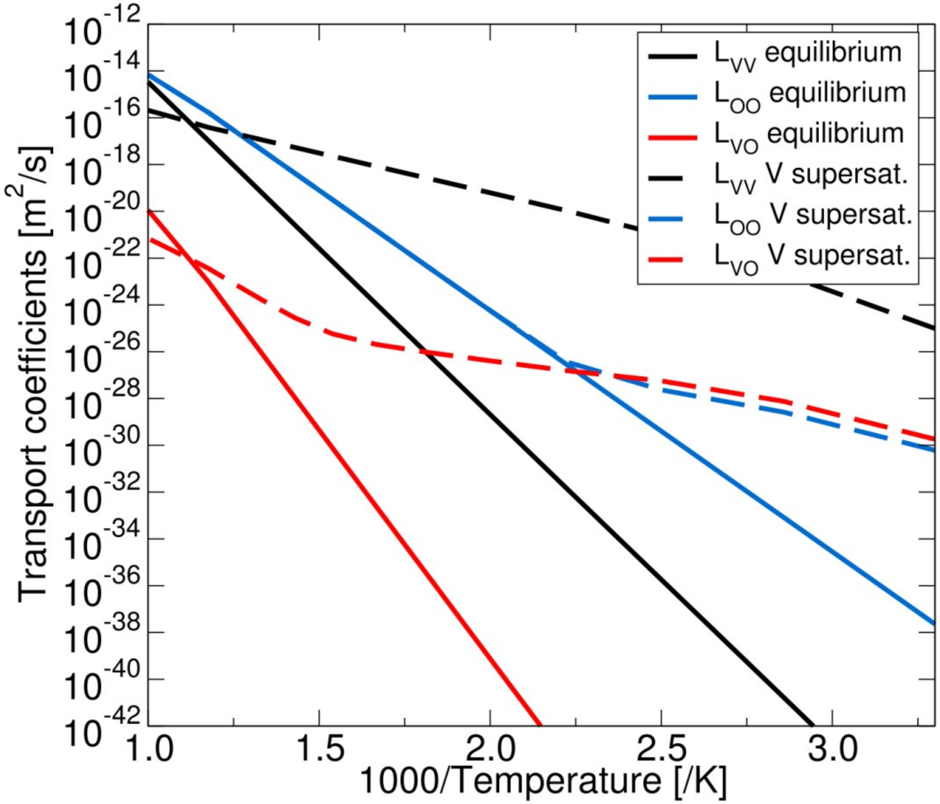
Total transport coefficients

Cluster distributions + cluster transport coefficients:

$$L_{\alpha\beta} = \sum_{c_i} [c_i]\, L^{eq}_{\alpha\beta}(c_i)$$

Ci : O, O2, O3, V, V2, V3, VO, V2O, VO2, V3O

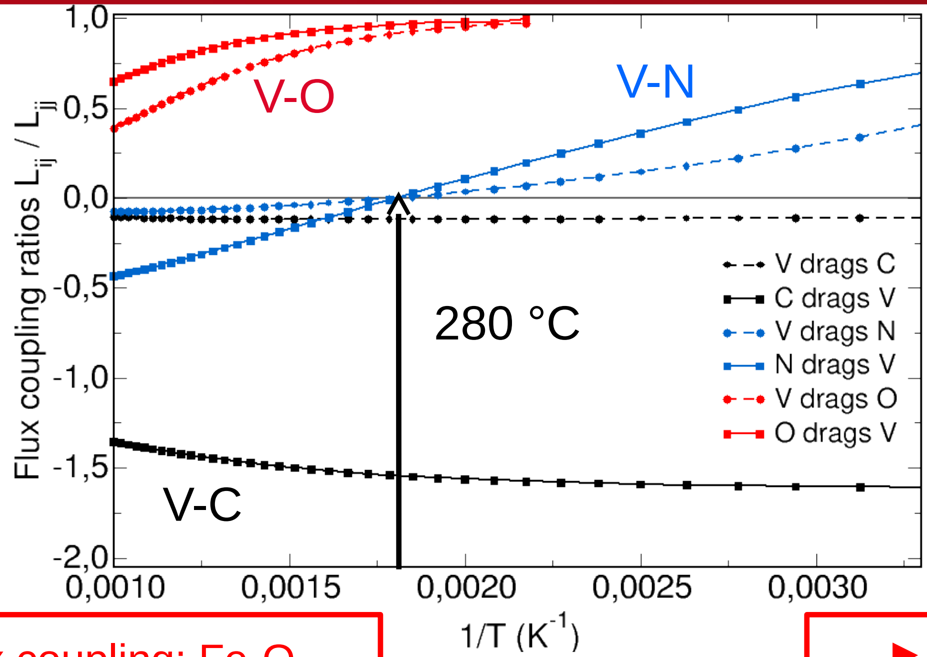




**T. Schuler at al., DIMAT 2017 - Haifa, Israel*

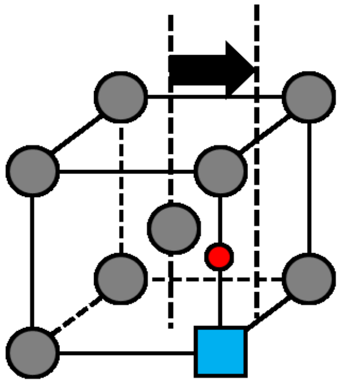
Flux coupling including paires VX

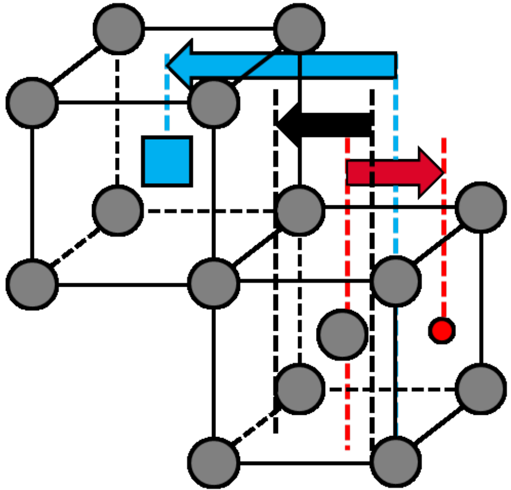
*T. Schuler & M. Nastar, PRB 93 (2016), 224101



► Positive flux coupling: Fe-O
V drags O

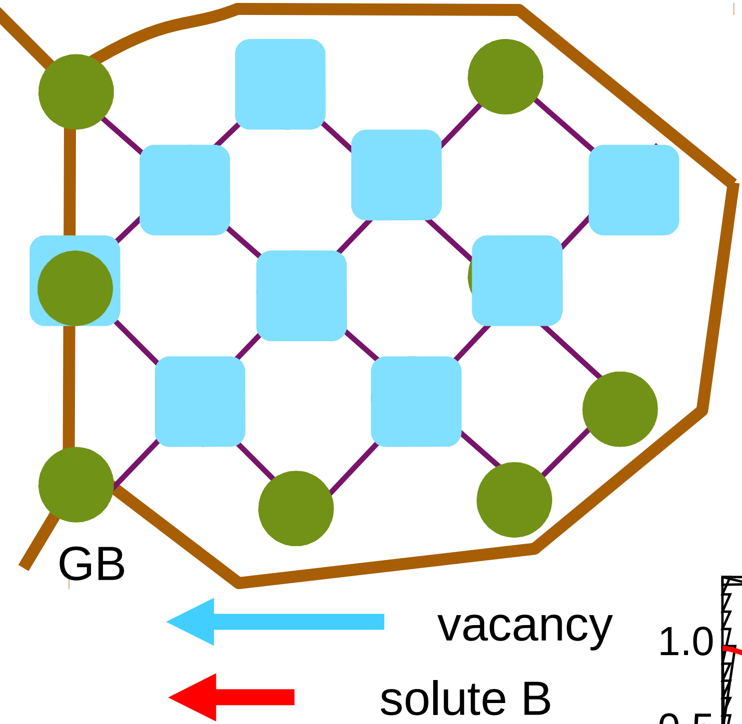
► Negative flux coupling: Fe-C
V « repels » C

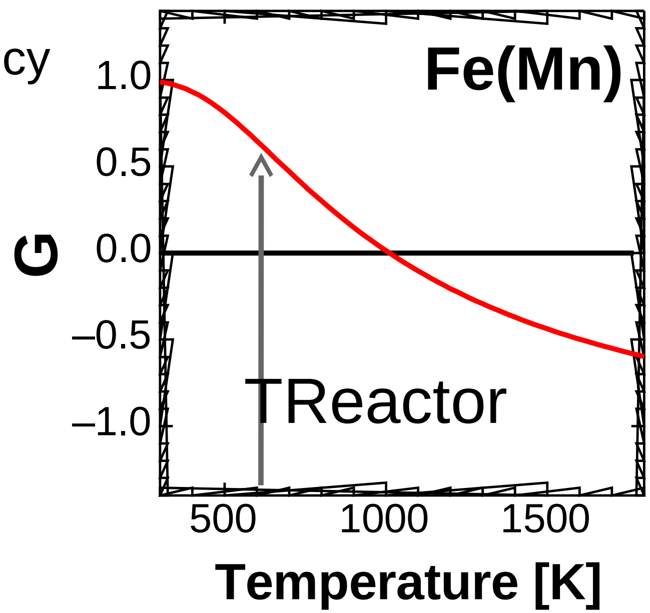




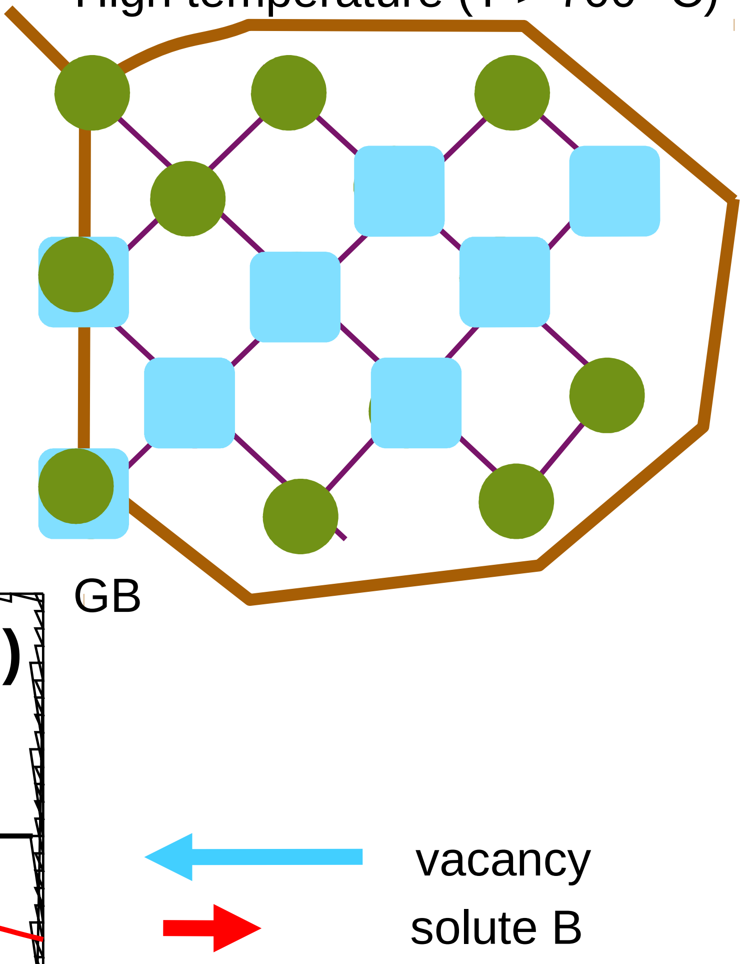
Vacancy flux coupling in Fe(X)

Low temperature (T < 700 °C)



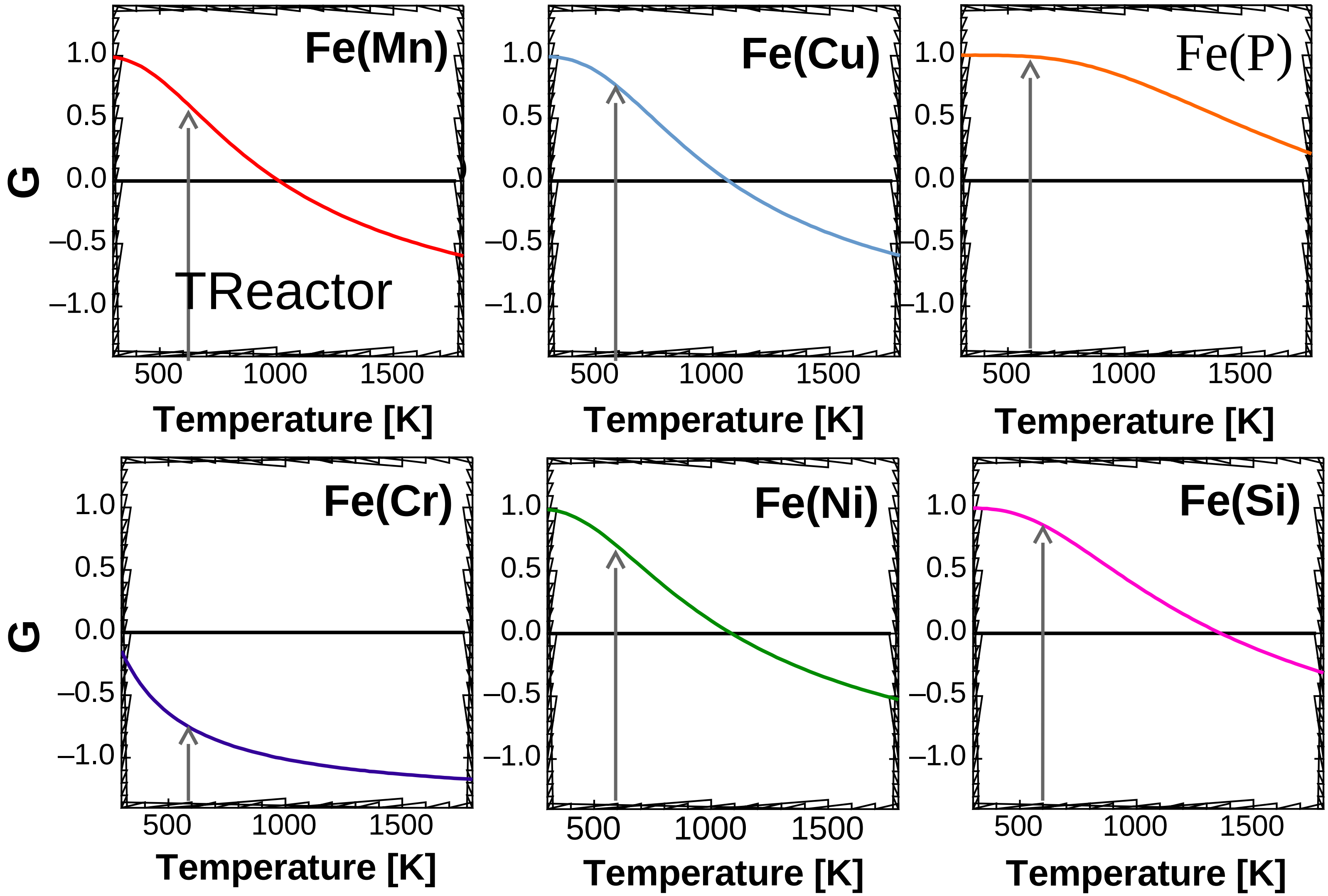


High temperature (T > 700 °C)



*L. Messina et al., PRB **90** (2014).

Vacancy flux coupling in Fe(X)

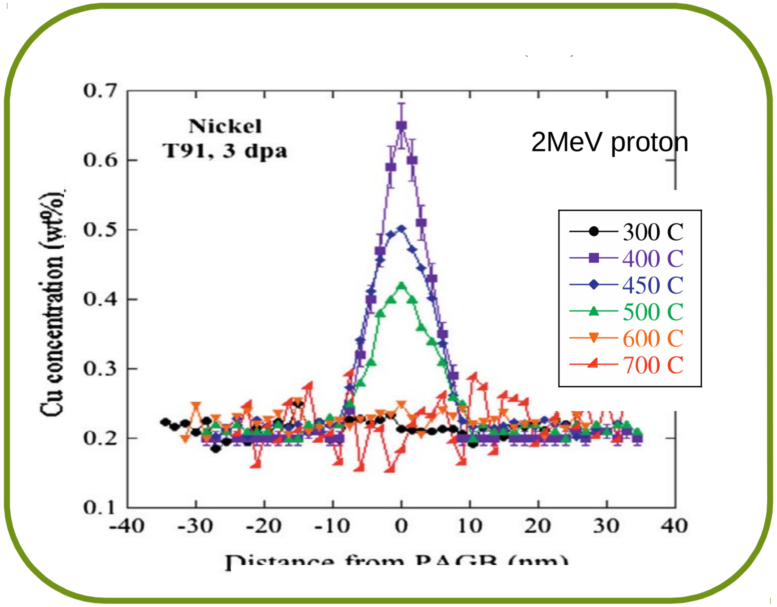


*L. Messina et al., Phys. Rev. B **90**, 104203 (2014).

Assessment of the predicted solute drag in ferritic steels

Minor element segregation in T91

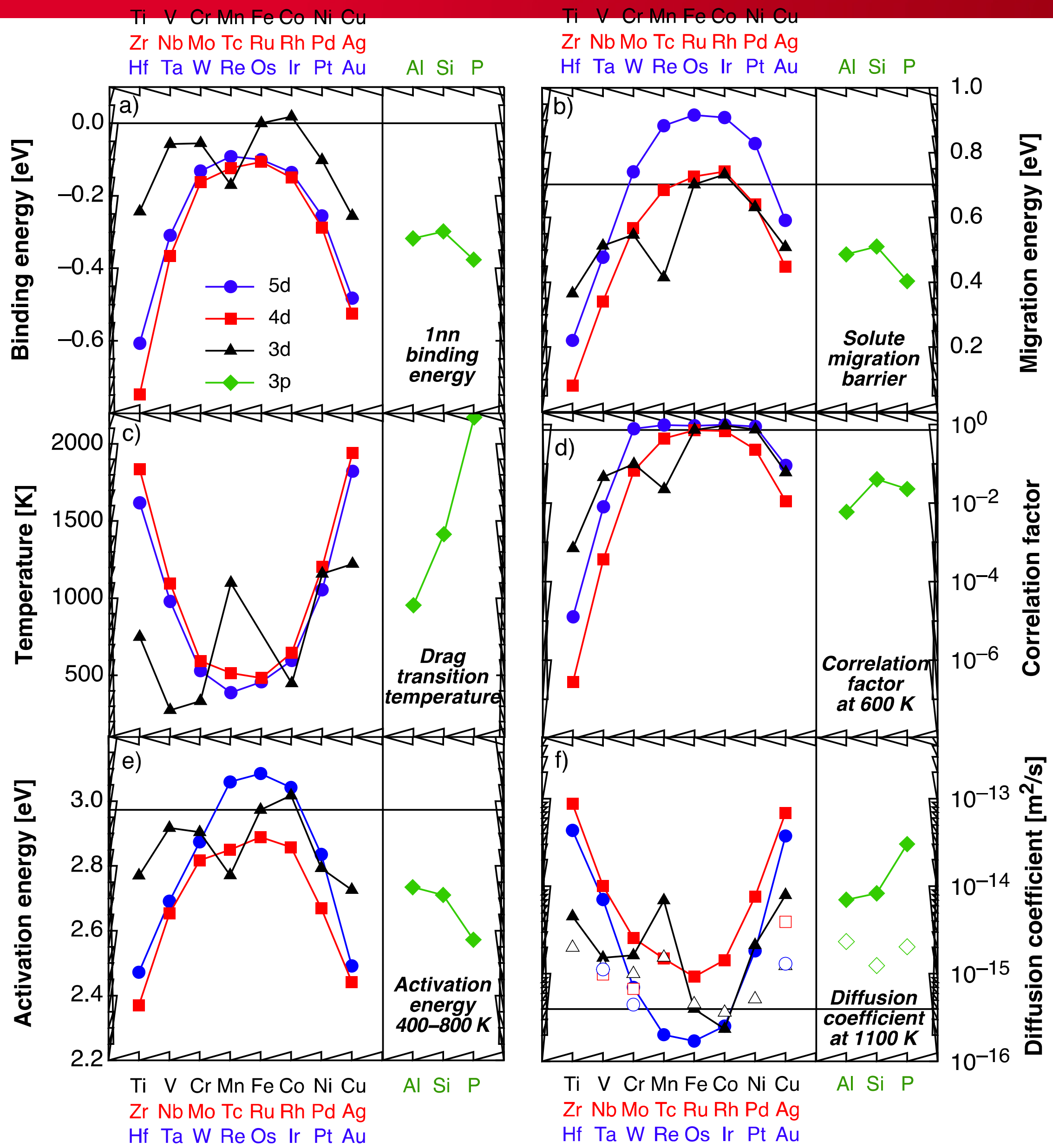
*J.P. Wharry, G.S. Was, JNM 442 (2013) 7-16



- ✓ Enrichment of Ni, Si, Cu at grain-boundaries observed in T91 steels conforts the predicted solute drag by vacancy in the binary model alloys Fe (X = Ni,Si,Cu).

- ✓ Solute drag by vacancy might contribute to the formation of blooming phases (Cr,Ni,Si,P).

Systematic analysis of vacancy drag



- Extension to all transition-metal impurities.
- Identified common trends for wide range of properties.
- Impurity diffusion and flux coupling linked to electronic interactions between iron, impurities, and vacancies.
- Drag for all impurities! Even with repulsive solute-vacancy interactions.
- Electronic origin might suggest similar trends in other metals.

*L. Messina et al. PRB (2016)

Conclusions & Perspectives

✓ **Dynamic Phase Diagrams of Fe-C, Fe-N and Fe-O**

- Large increase of the solubility limit induced by stationnary vacancy supersaturation
- VID is the dominant dissolution mechanism at intermediate irradiation flux and temperature against the ballistic mixing

✓ **RIS in Fe-based alloys**

- Fe(C,O,N)**:**

Positive flux coupling solute interstitials and vacancy except N at high T and C.

Non monotenous variation with T and vacancy supersaturation

- Fe(substitutional X)

Vacancy: solute drag at T<700 °C except Cr and solute depletion at high T

Thank you for your attention

This work was supported by

- the joint program "CPR ODISSEE" funded by AREVA, CEA, CNRS, EDF and Mécachrome under contract n° 070551.
- the Joint Programme on Nuclear Materials (JPNM) of the European Energy Research Alliance (EERA)
- The program IREMEV of the Euro-Fusion consortium