



**The Abdus Salam
International Centre for Theoretical Physics**



2137-24

**Joint ICTP-IAEA Advanced Workshop on Multi-Scale Modelling for
Characterization and Basic Understanding of Radiation Damage
Mechanisms in Materials**

12 - 23 April 2010

Radiation damage in FeCr alloys

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Radiation damage in FeCr alloys

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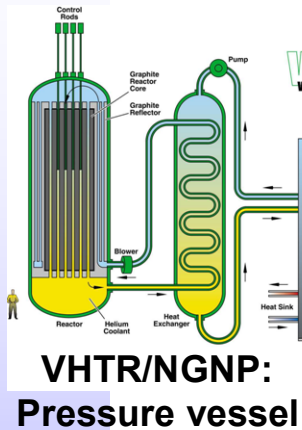
Structural Materials Group

Nuclear Materials Science Institute

SCK•CEN, Mol – Belgium

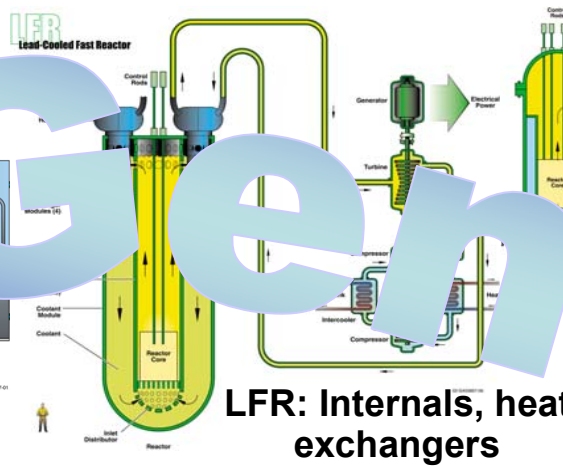
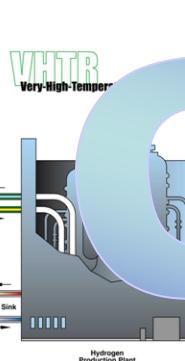
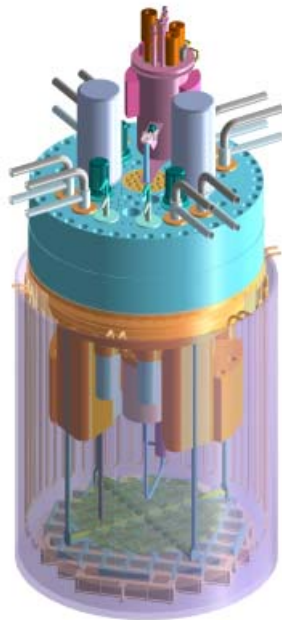
lmalerba@sckcen.be

High-Cr steels are key for future nuclear options



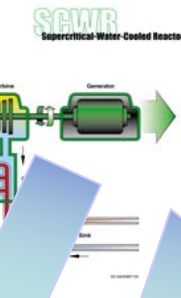
VHTR/NGNP:
Pressure vessel

X-ADS: clad tubes

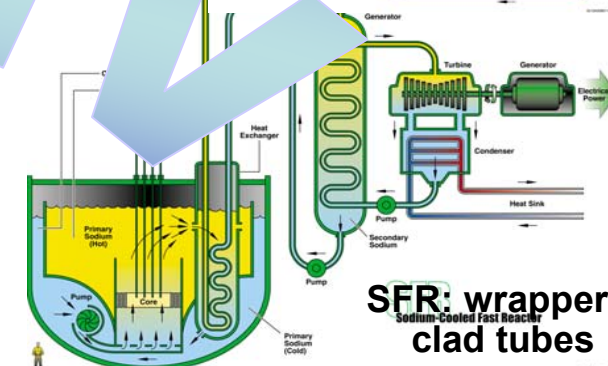
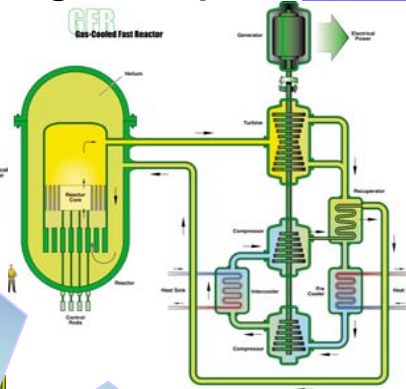


LFR: Internals, heat exchangers

SCWR: vessel, steam lines



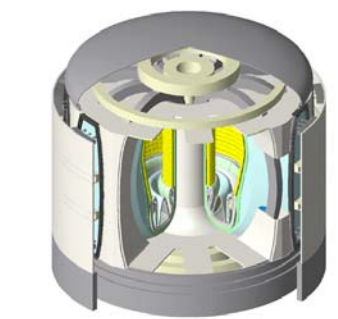
GFR: vessel, hot-gas components



SFR: wrappers, clad tubes

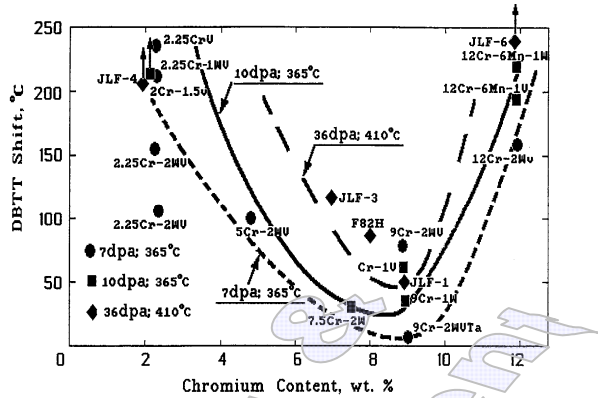
High-Cr ferritic/martensitic steels are candidate structural materials for key components in most future nuclear options:

- ❑ Several Gen IV concepts
- ❑ Accelerator-driven systems
- ❑ Fusion reactors

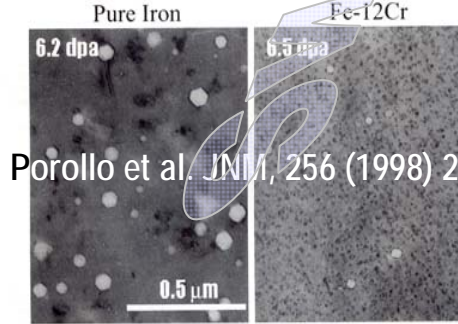
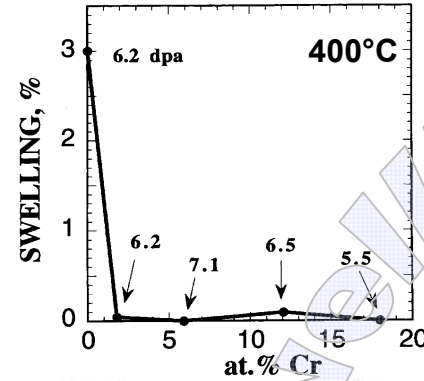
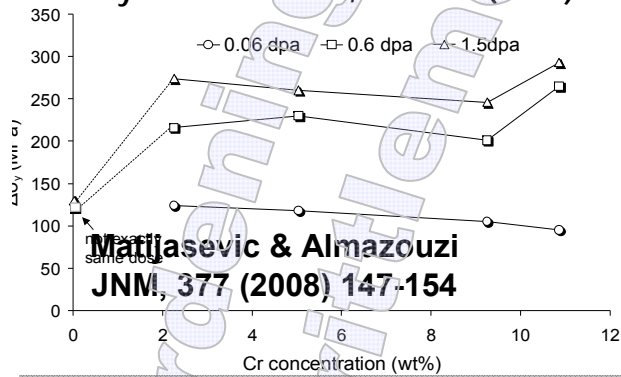


Fusion DEMO:
blanket

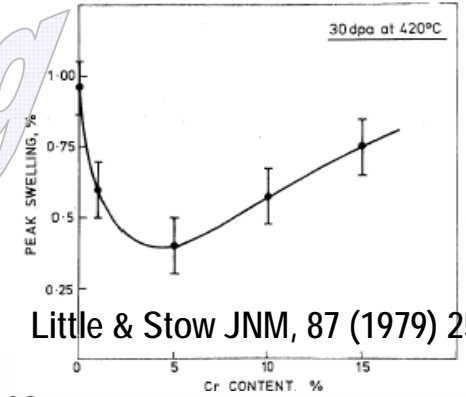
Crin Fe makes a difference



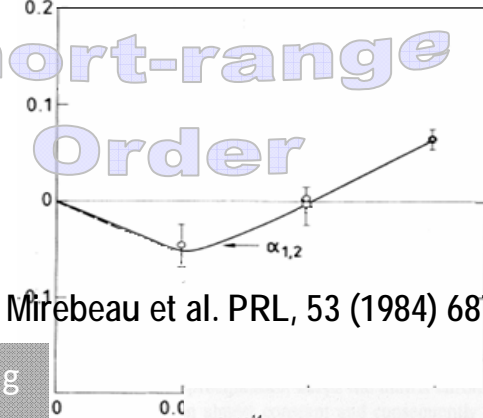
Kohyama et al. JNM, 233-237 (1988) 138



Porollo et al. JNM, 256 (1998) 247

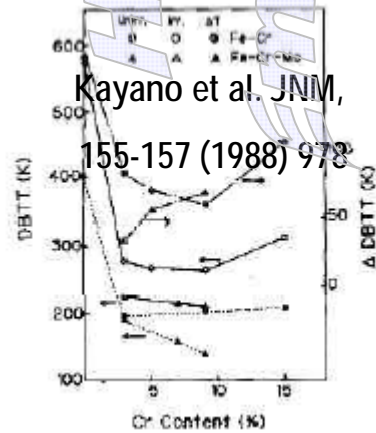


Little & Stow JNM, 87 (1979) 25

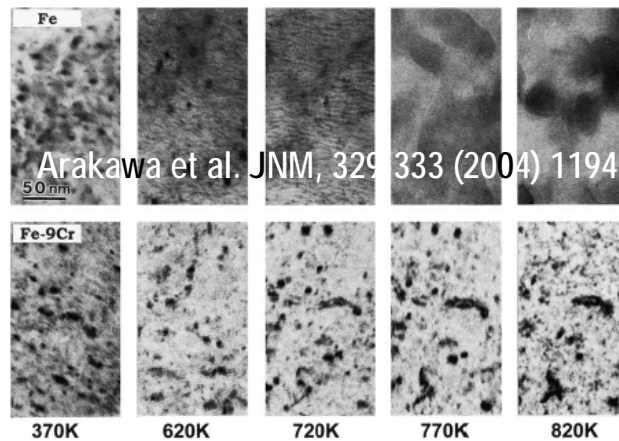


Mirebeau et al. PRL, 53 (1984) 687

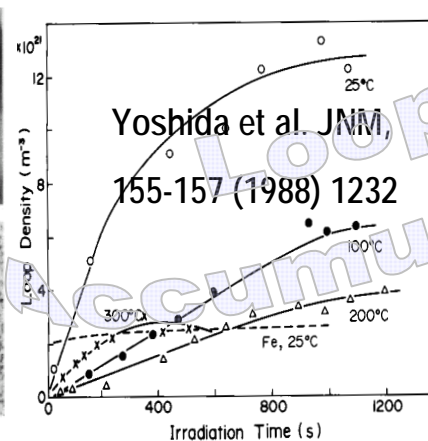
FeCr alloys are thus a suitable model material to understand the mechanisms causing the clear dependence on Cr content of high Cr steels' properties



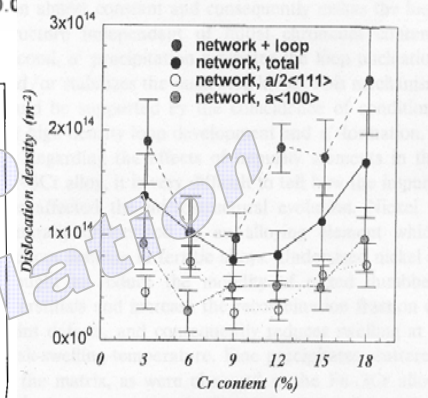
Kayano et al. JNM, 155-157 (1988) 978



Arakawa et al. JNM, 329-333 (2004) 1194

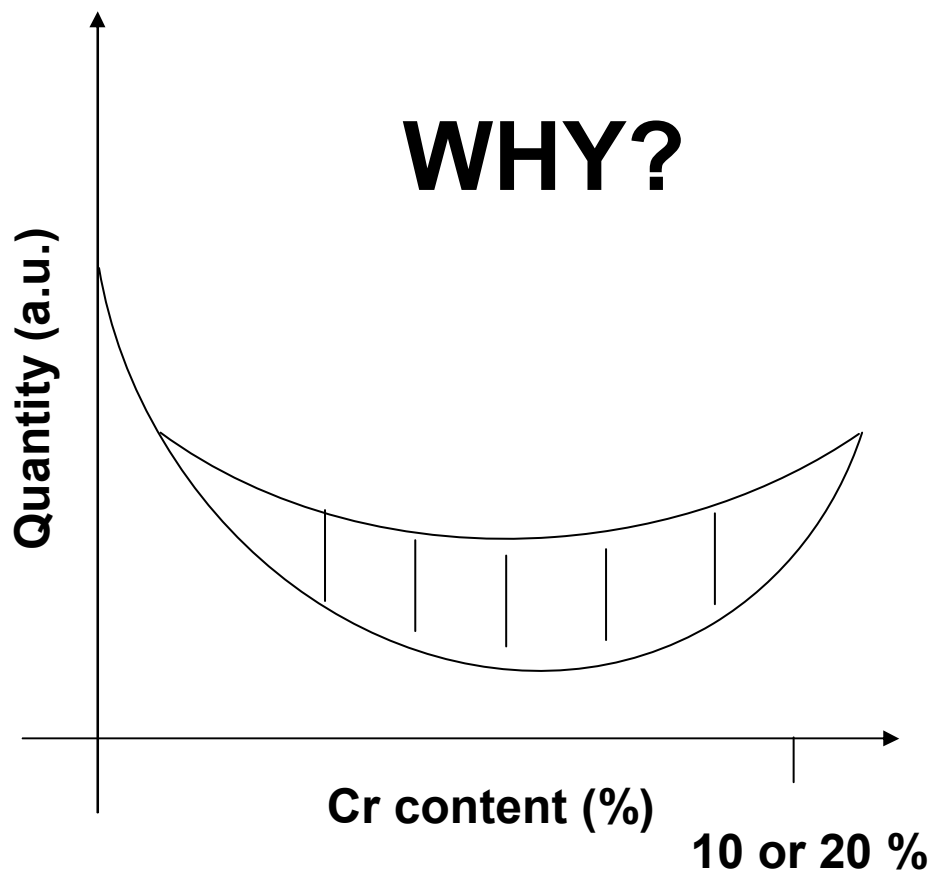


Yoshida et al. JNM, 155-157 (1988) 1232



Katoh, JNM 1995, dose 140dpa

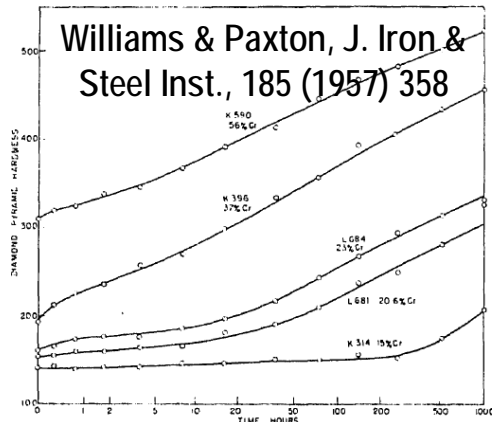
Main effect of Cr



smiles!

The story of how ab initio calculations changed the FeCr phase diagram

How hardness suggested the phase diagram

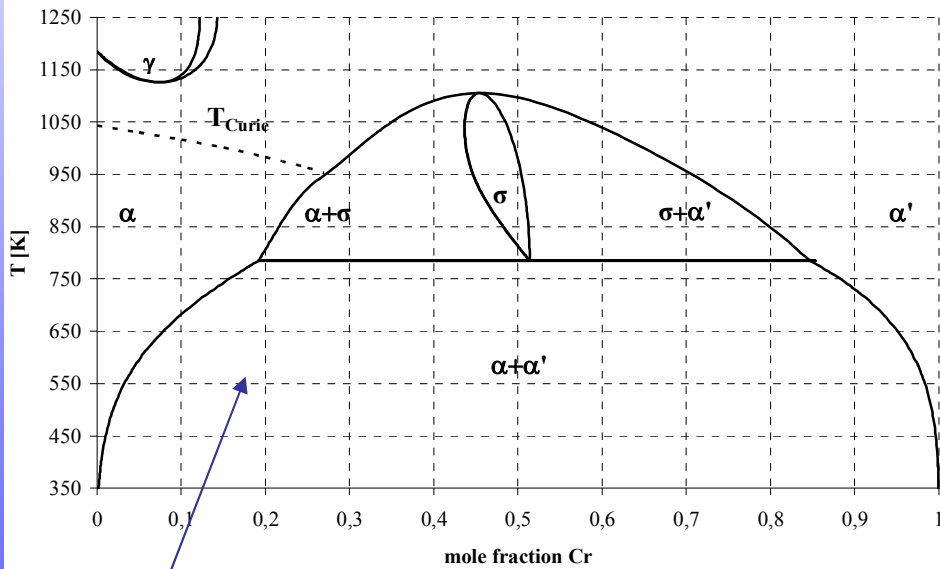


Hardening vs. time in FeCr aged at 475°C: the material becomes increasingly harder

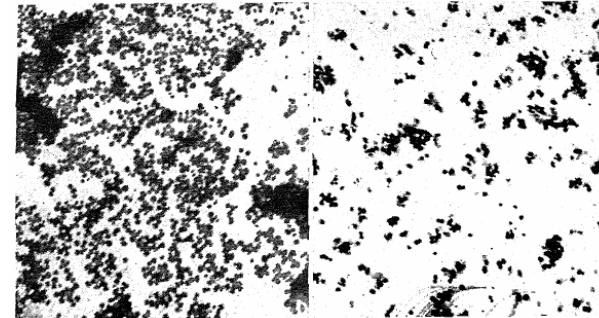
For a long time nobody knew why

The search for the reason for “475°C embrittlement” led to the discovery of the coherent, Cr-rich α' phase

Fig. 2--Hardening characteristics of high-purity Fe-Cr alloys during ageing at 475° C



Standard FeCr phase diagram

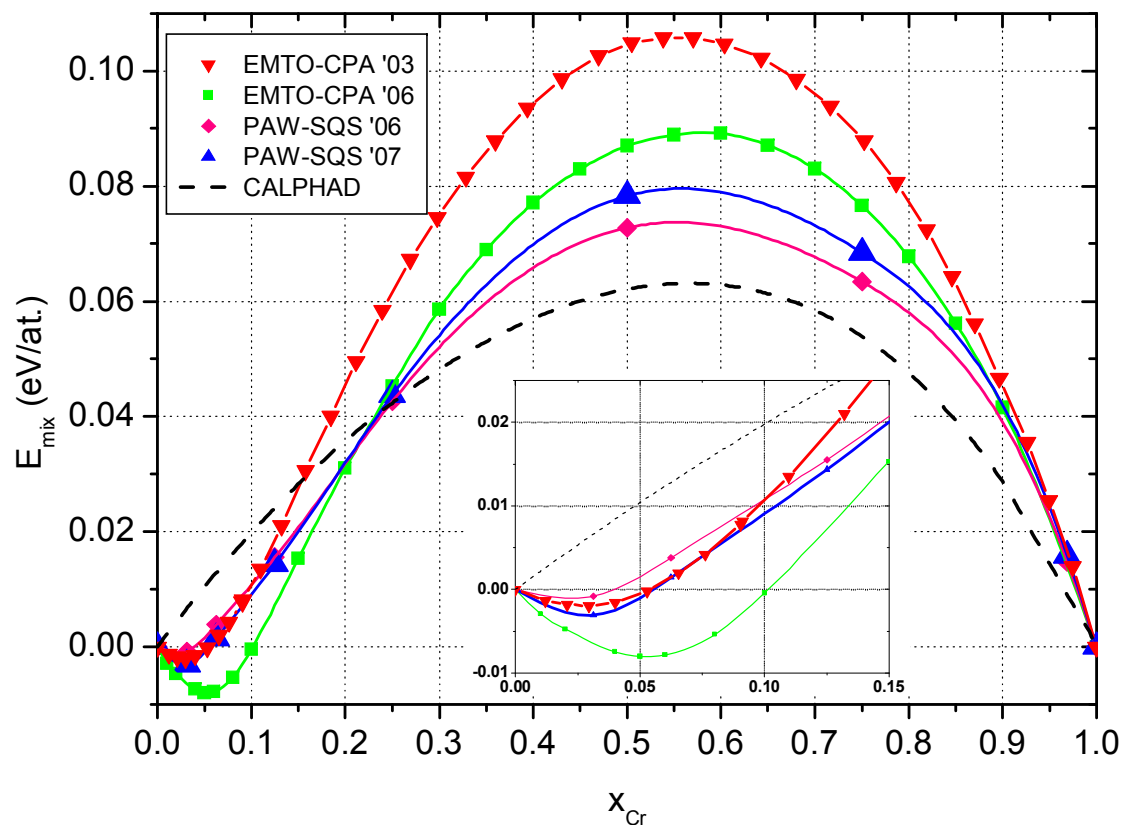


Fisher, Dulis & Carroll, Trans. AIME, 197 (1953) 690

First TEM observation of α' precipitation

How DFT changed the phase diagram

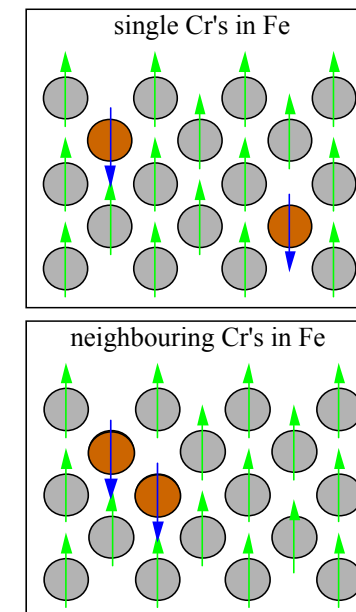
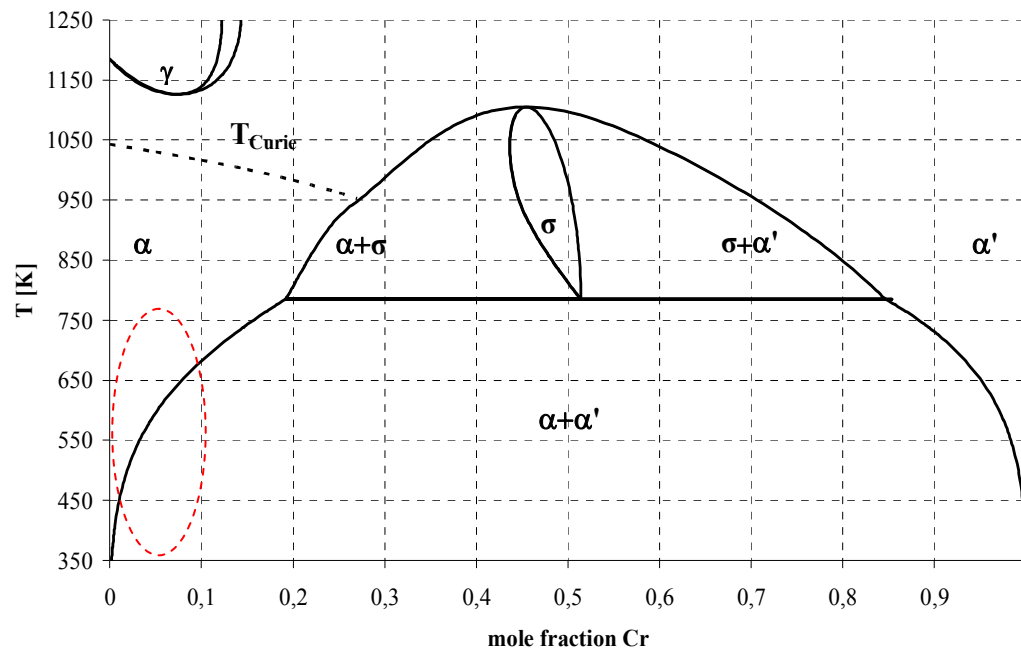
$$\text{Mixing enthalpy calculations: } H_{\text{mix}} = H_{\text{AB}} - x_{\text{A}}H_{\text{A}} - (1-x_{\text{A}})H_{\text{B}}$$



- DFT data published between 2003-07 agree, within scattering, on the fact that H_{mix} is negative for low Cr content and changes sign at $\sim 6\text{-}10\%$
- Standard mixing enthalpy (CALPHAD) does not include this feature !

How DFT changed the phase diagram

- Change of sign of mixing enthalpy in low-Cr alloys stems from **mutual repulsion between Cr atoms due to (antiferro)magnetism**
 - ☞ Effect of magnetic frustration, explained by *Klaver et al., 2006*
- **Long range ordering or even formation of Cr superlattice may occur**
 - ☞ *Lavrentiev et al., 2007* propose Fe-6.25%Cr
 - ☞ *Erhart et al., 2008* propose Fe-3.7%Cr
- **Both effects imply very high solubility of Cr in Fe**
 - ☞ **Standard Fe-Cr phase diagram seems to be wrong!**



Looking back at existing evidence

Experimental data from literature

Green points – observation of Cr ordering

Black points – observation of Cr precipitation

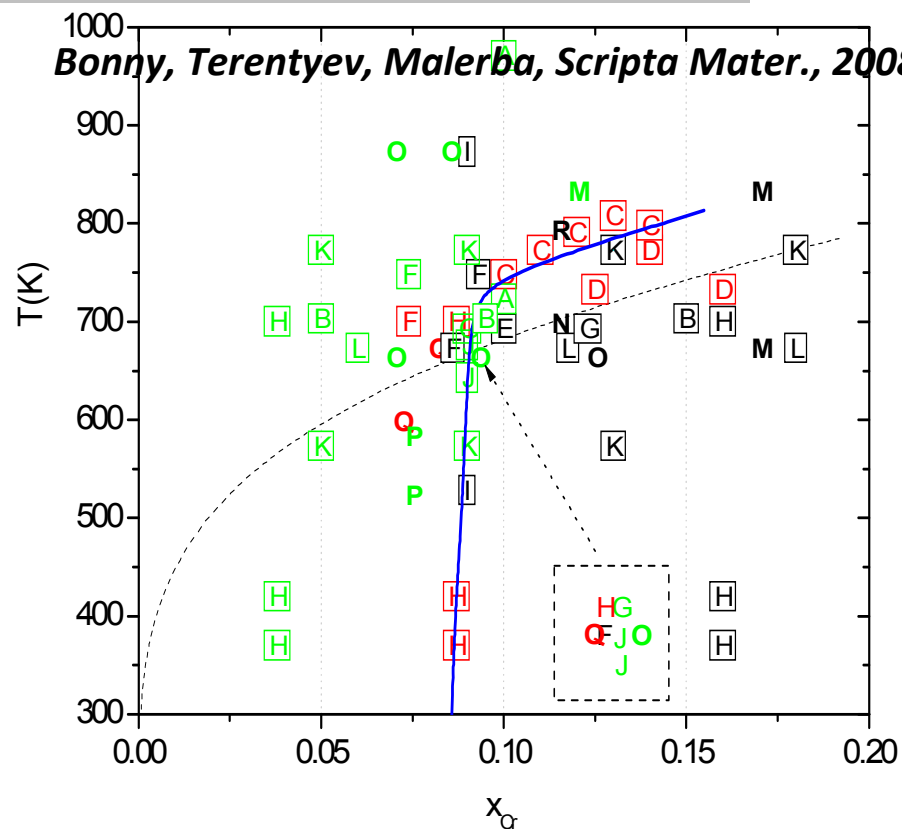
Red points – miscibility gap as suggested by investigators

1983, Hennion *et al.*: Effective pair potential changes its sign in Fe-Cr at 25%

1984, Mirebeau *et al.*: Diffuse neutron scattering shows change of the sign of SRO parameter from negative to positive at 10%Cr

2000, Filippova *et al.*: Mössbauer characterization of irradiated alloys shows change of SRO sign at ~9%

Bonny, Terentyev, Malerba, *Scripta Mater.*, 2008



Effort to build new FeCr phase diagram was then faced via development of adequate interatomic potentials

Interatomic potentials for Fe-Cr

- Standard EAM is not suitable to reproduce a mixing enthalpy whose shape deviates significantly from a skewed parabola

- Two-band model:

$$E_i = \frac{1}{2} \sum_j V(r_{ij}) + F_d(\rho_d) + F_s(\rho_s) \quad \text{Olsson et al. PRB 72 (2005) 214119}$$

- ☞ *Second embedding function introduces role of s-band*
- ☞ *Degree of freedom to fit sign-changing mixing enthalpy (concentration dependence is contained in the mixed s-density)*

- **Concentration dependent model**

$$E = \sum_i^N [F_{\alpha i}(\sum_{j \neq i} \rho_{\alpha i, \beta j}(r_{ij})) + 1/2 \sum_{j \neq i} V_{\alpha i, \beta j}(x, r_{ij})]$$

Caro et al. PRL 95 (2005) 075702

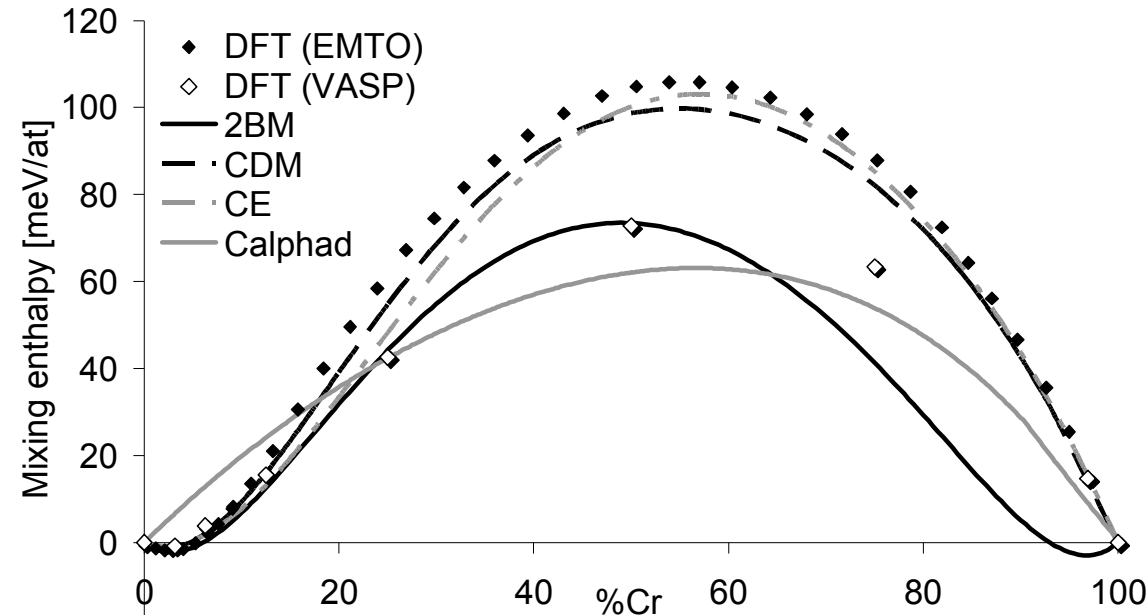
$$V_{\alpha i, \beta j}(x, r) = h(x) v_{AB}(r)$$

- ☞ *h(x) is obtained using a Redlich-Kister expansion of the heat of solution (CALPHAD methodology)*

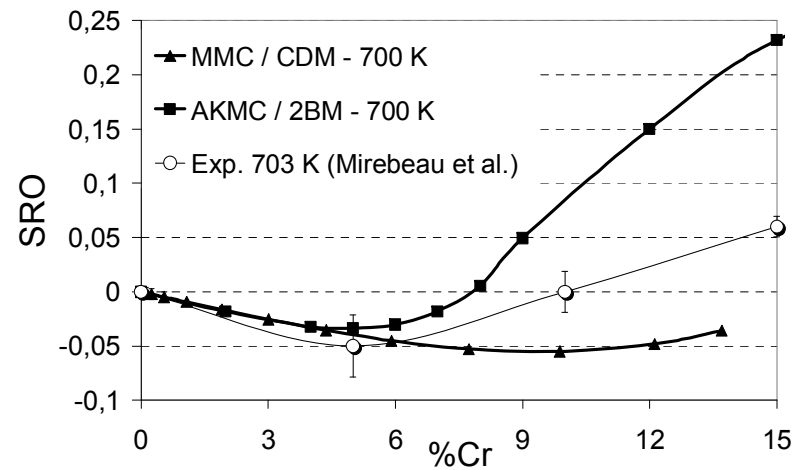
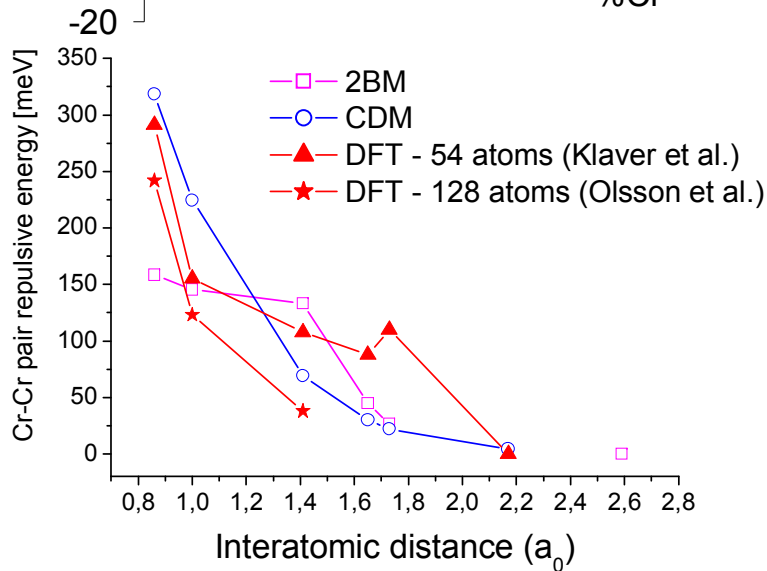
$$x_{i,j} = \frac{1}{2}(x_i + x_j) = \frac{1}{2} \left(\frac{\rho_i^B}{\rho_i} + \frac{\rho_j^B}{\rho_j} \right)$$

Local concentration postulated to be given by the ratio between electronic densities at the two-atoms

Interatomic potentials for Fe-Cr



The potentials provide predictions in fair agreement with ab initio and experiments!

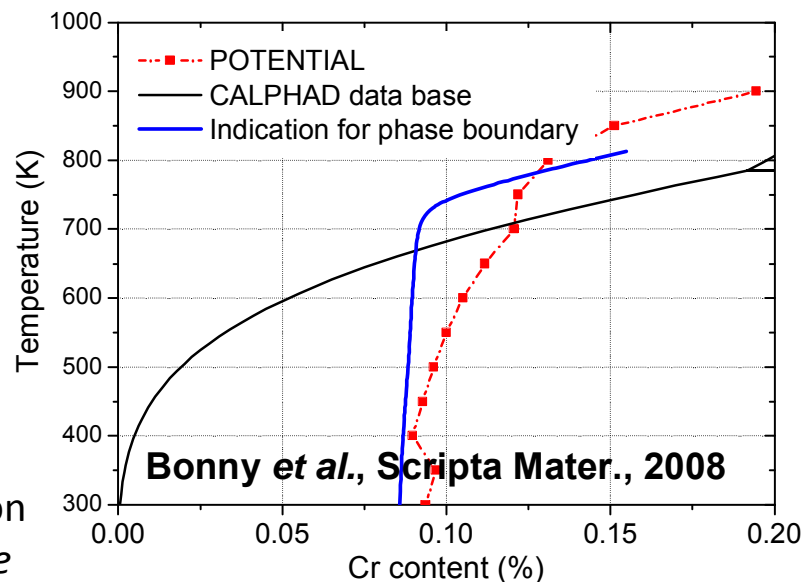


Malerba, Caro & Wallenius, JNM, 2008

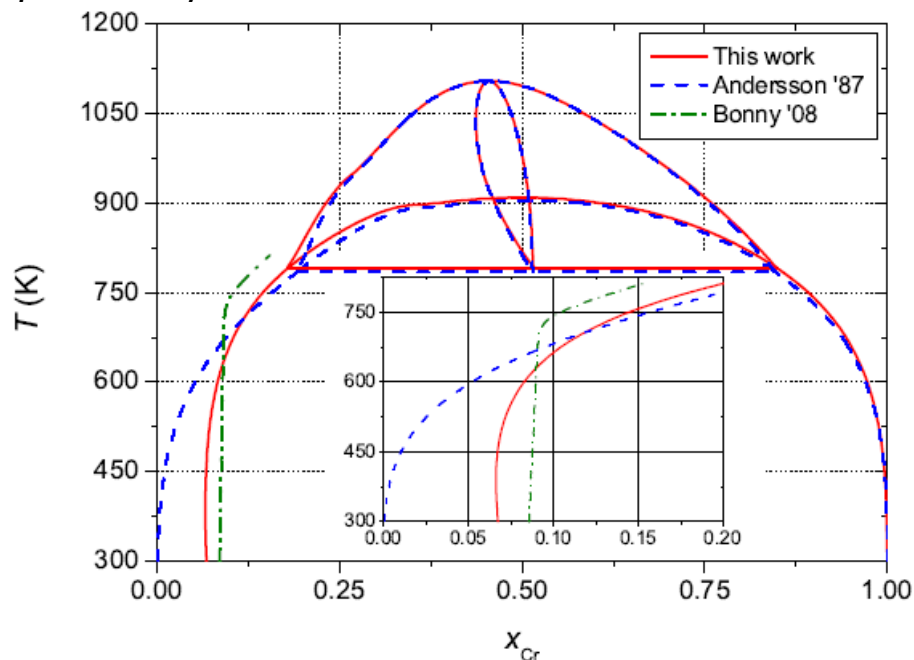
The revised phase diagram

➤ Metropolis Monte Carlo methods can be used to estimate phase boundaries given an interatomic potential

☞ *Results are good in region of interest*



Newly proposed Calphad parameterisation for FeCr phase diagram (*Bonny et al, to be published*)

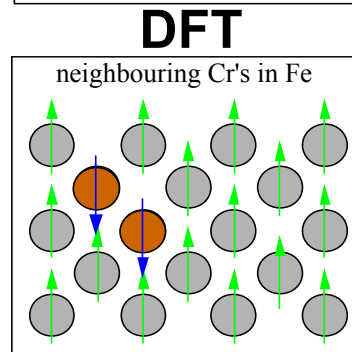
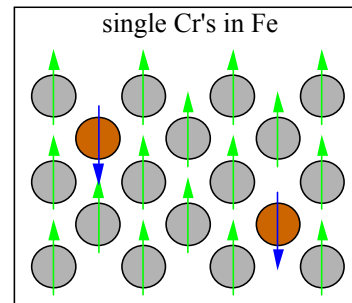
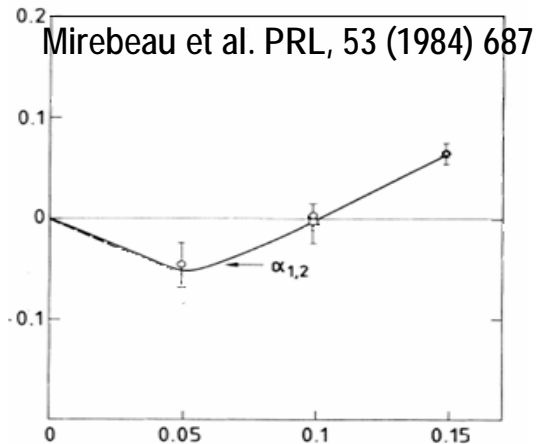


This large solubility of Cr in Fe has important consequences for radiation effects

E.g. α' precipitation not expected at any T below ~9%Cr

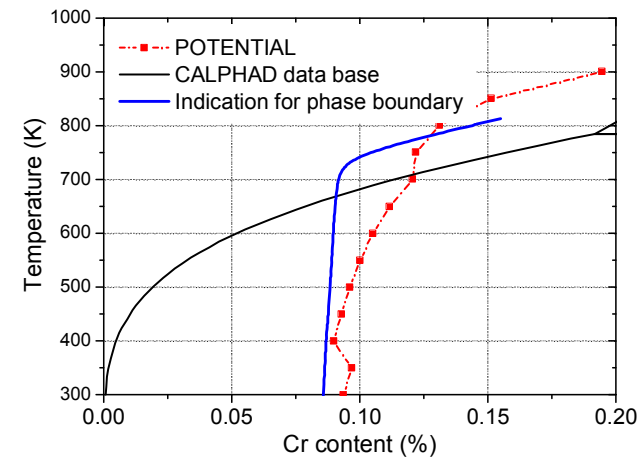
In summary, *first smile* explained: Ordering and clustering vs Cr content

Experiment



DFT

Potentials & Thermodynamic modelling

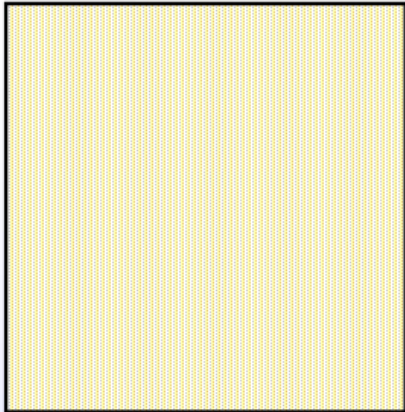


- Considerations based on FeCr magnetic properties supported by DFT explain inversion of order parameter
- The combination of revisited experimental data, development of DFT-based interatomic potentials, application of techniques to trace phase diagram given a cohesive model, show that
 - ☞ ***In the T region of interest for most nuclear applications the solubility limit of Cr in Fe is high: ~7-8%***

Radiation damage recovery stages in FeCr alloys

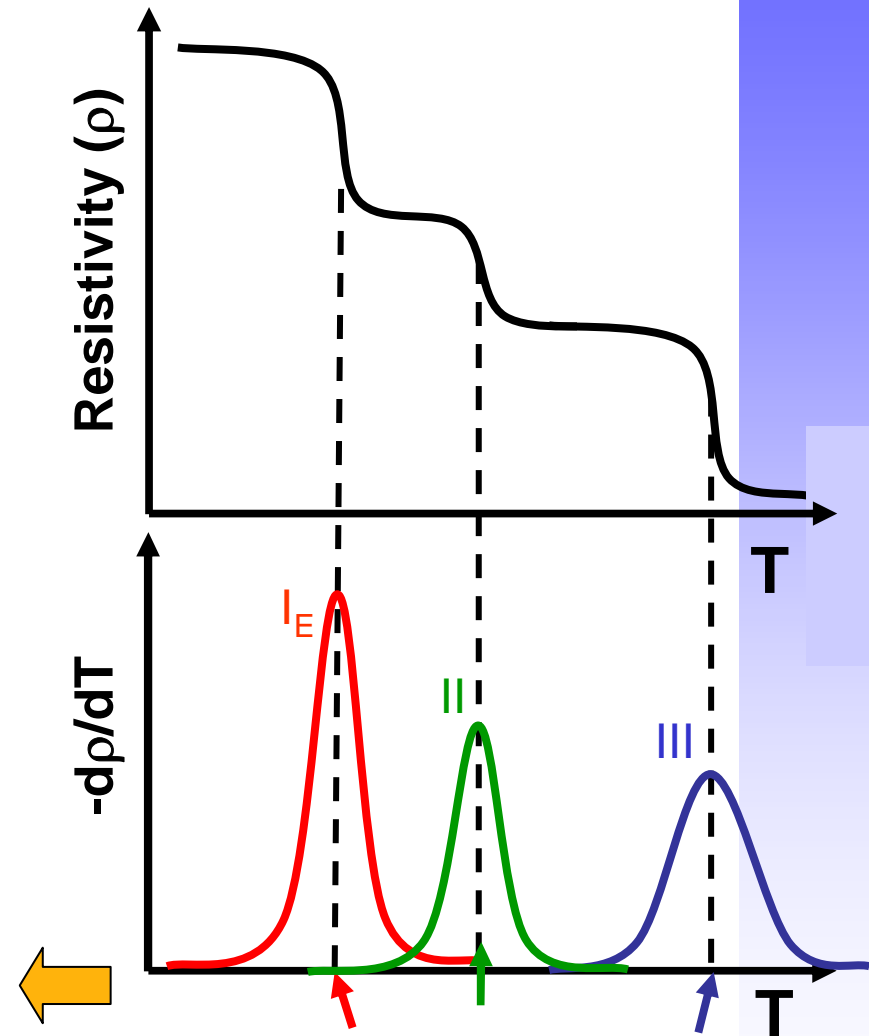
Stories of ordinary resistivity

movie



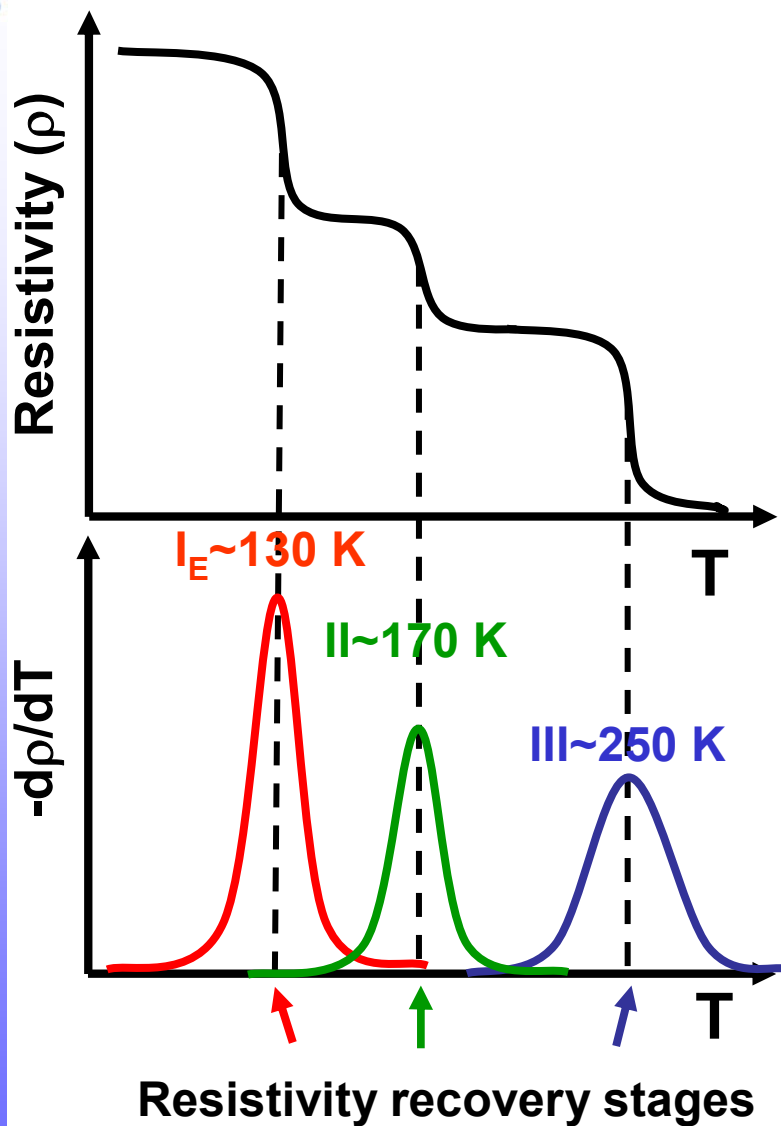
Analysis of these recovery stages allows characteristic migration (and dissociation) energies to be identified

The interpretation of the stages is however based on assumptions to be carefully verified (not always possible experimentally)



Resistivity recovery stages

Isochronal annealing recovery: Example of pure Fe



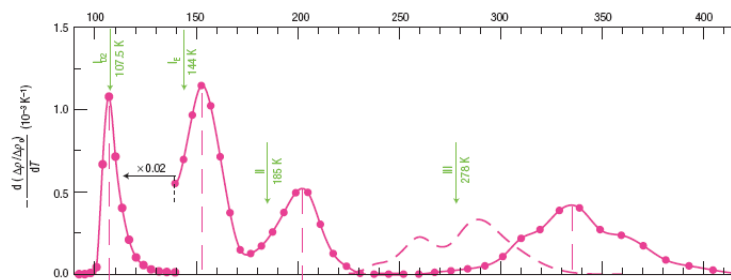
Interstitial mobility from *ab initio*:

- Single SIA: 0.34 eV (exp: ~ 0.3 eV)
- Di-SIA: 0.42 eV (exp: ~ 0.4 eV)
- Tri-SIA 0.43 eV, larger - immobile

Vacancy mobility from *ab initio*:

- Single Vacancy: 0.67 eV (exp: ~ 0.57 eV)
- Di-Vacancy: 0.62 eV
- Tri-Vacancy: 0.35 eV
- 4-Vacancy: 0.48, larger - immobile

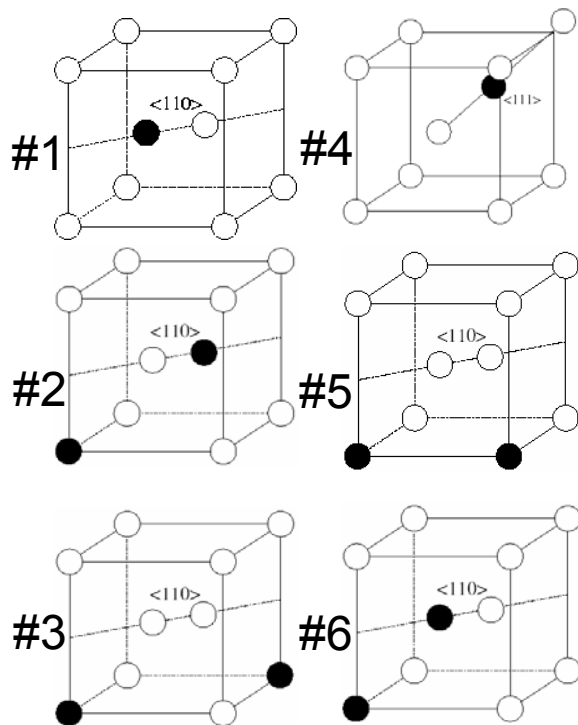
C.C Fu et al., Nature Materials 2004



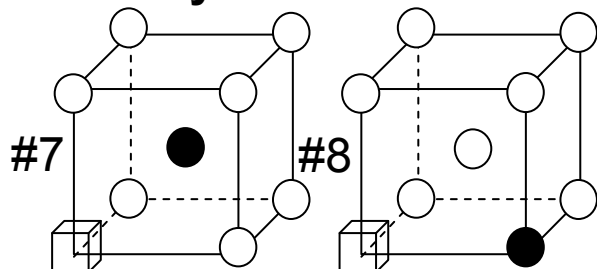
When the self-interstitial met the Cr atom

Binding energies

SIA-Cr Interaction



Vacancy-Cr Interaction

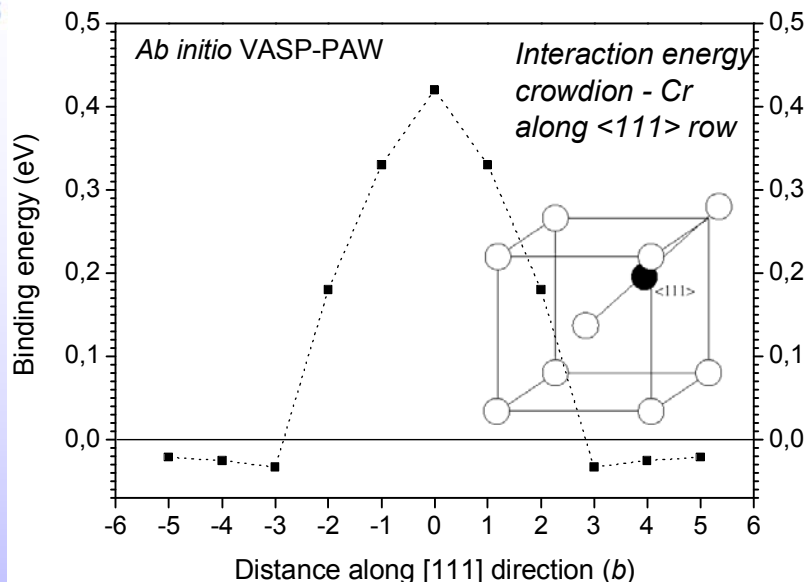


Configuration	DFT	Potential
SIA – Cr Interaction energy [eV]		
#1	-0.08	-0.14
#2	-0.15	-0.05
#3	-0.15	-0.19
#4	-0.37	-0.40
#5	0.04	0.05
#6	0.21	0.10
Vacancy – Cr interaction energy [eV]		
#7	0.057	0.007
#8	0.014	-0.0053

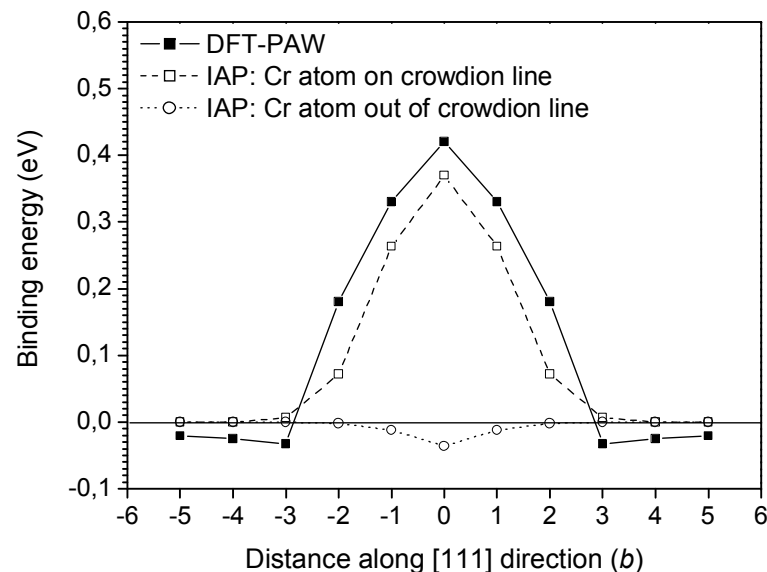
(negative sign denotes attraction)

Terentyev et al. Comp. Mater. Sci. 43 (2008) 1183

When the self-interstitial met the Cr atom



Olsson et al, PRB 75 (2007) 014110

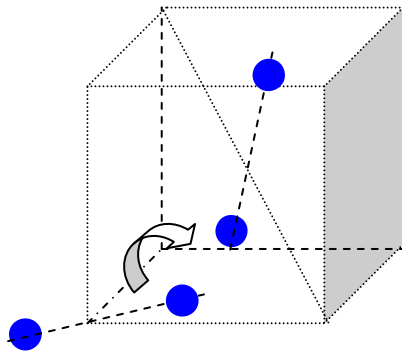


Terentyev et al, JNM 362 (2007) 167

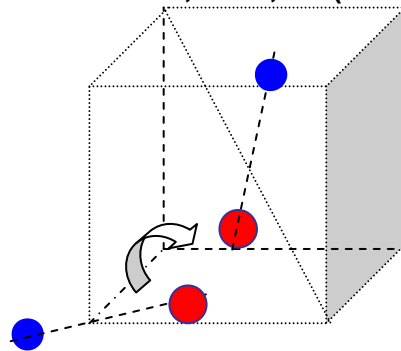
- ♣ Ab initio calculations reveal strong interaction between single self-interstitial and nearby Cr atoms
 - Stable mixed dumbbell
 - Trapping due to Cr atoms outside dumbbell
 - Strong crowdion-Cr attraction
- ♣ Some calculations even suggest strong effect of faraway, monatomically dispersed Cr atoms on self-interstitials! (*Klaver et al., PRB 76 (2007) 214110*)
- ♣ Vacancies, however, hardly interact with Cr ($E_b < 0.1$ eV)

When the self-interstitial drags the Cr atom

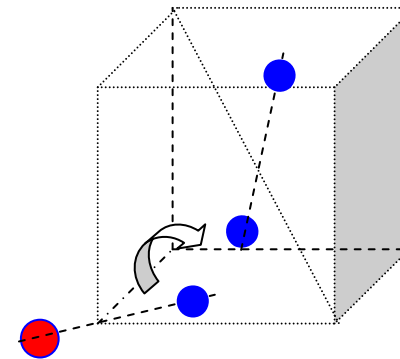
Olsson *et al.*, PRB, 75 (2007) 014110



Fe-Fe dumbbell
 $E_m(\text{DFT})=0.34 \text{ eV}$
 $E_m(\text{2BM})=0.31 \text{ eV}$

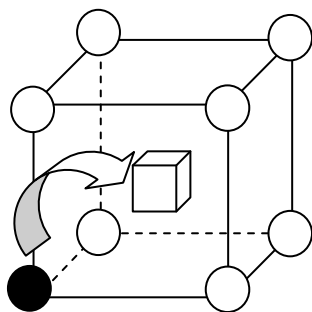


Fe-Cr dumbbell
 $E_m(\text{DFT})=0.23 \text{ eV}$
 $E_m(\text{2BM})=0.24 \text{ eV}$

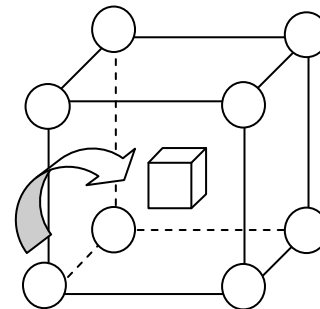


Cr-Fe dumbbell
 $E_m(\text{DFT})=0.33 \text{ eV}$
 $E_m(\text{2BM})=0.32 \text{ eV}$

⇒ Mixed dumbbell migrates with lower migration energy than FeFe dumbbell



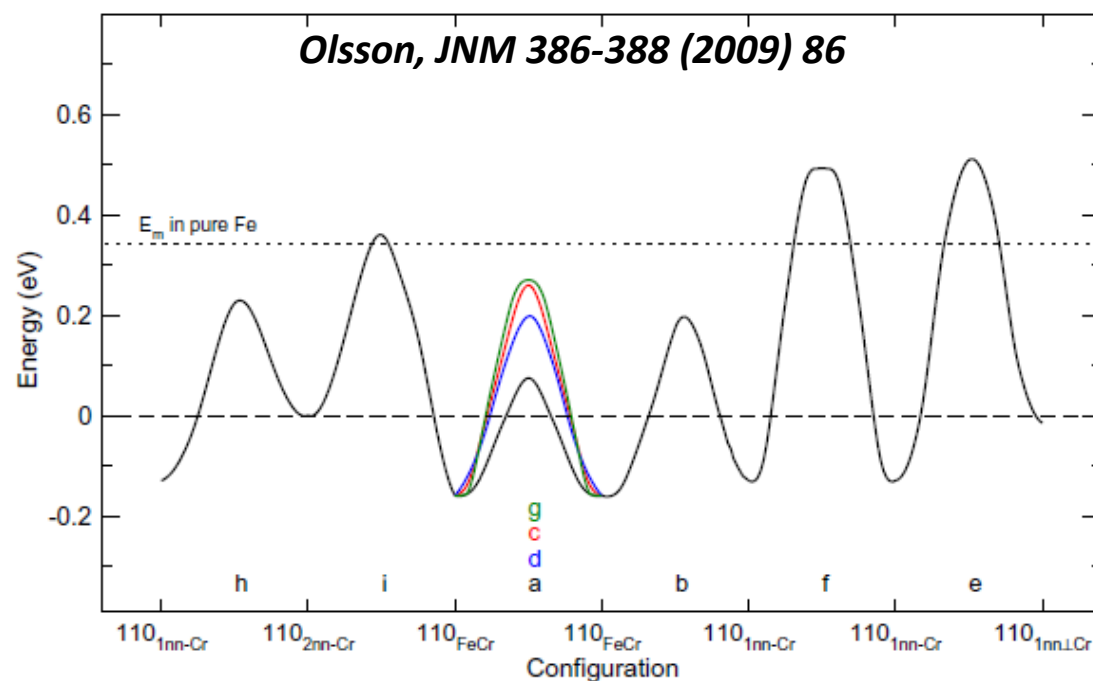
Cr-Vac exchange
 $E_m(\text{DFT})=0.55 \text{ eV}$
 $E_m(\text{2BM})=0.56 \text{ eV}$



Fe-Vac exchange
 $E_m(\text{DFT})=0.65 \text{ eV}$
 $E_m(\text{2BM})=0.65 \text{ eV}$

**⇒ Cr atoms diffuse faster by exchange with vacancies than Fe atoms
 (in agreement with experimental measurements of diffusion coefficients)**

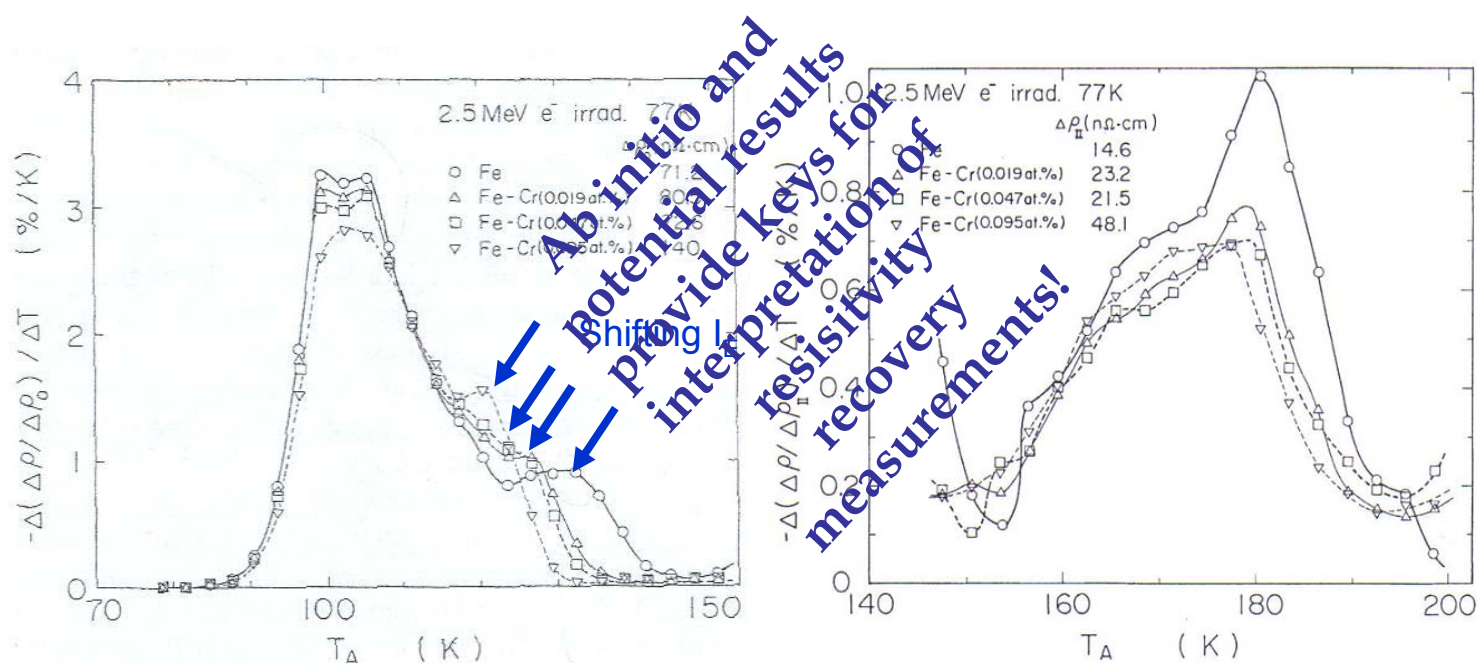
When the self-interstitial drags the Cr atom



- Not only the mixed dumbbell is stable according to DFT: it also migrates with lower migration energy than the Fe-Fe dumbbell (~0.2 eV vs. ~0.3 eV)
- ⇒ Cr atoms can be dragged by migrating dumbbells and diffuse in this way towards sinks (grain boundaries, dislocations, loops, ...)

Isochronal annealing recovery in dilute FeCr

- ♣ Resistivity recovery studies in diluted FeCr alloys show
 - Shift to lower T of stage I (self-interstitial migration): sign of mixed dumbbell stability, with migration energy lower than FeFe dumbbell
 - Slight decrease and shift of stage II with increasing Cr content

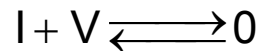


Maury et al, J. Phys. F: Met. Phys. 17 (1987) 1143;

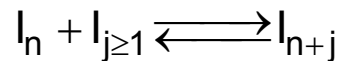
Abe & Kuramoto J. Nucl. Mater. (1999) 209

Pure Fe*

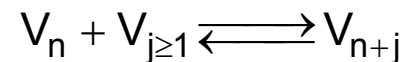
- Recombination of point defects



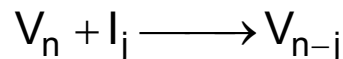
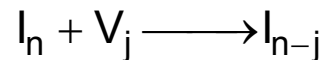
- Agglomeration interstitial defects



- Agglomeration vacancy defects



- Recombination defects/anti-defects



Mobile species: I, V, I_{2-4}, V_{2-4}
 ICr, I_2Cr

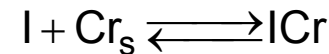
Model used with success to reproduce RR in Fe

C. J. Ortiz and M. J. Caturla, Phys. Rev. B 75, 184101 (2007)

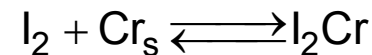
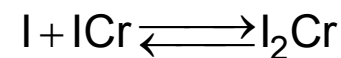
C. C. Fu et al, Nature Mater. 4, 68 (2005)

Cr containing species

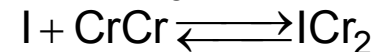
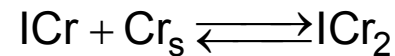
- Formation of mixed dumbbell ICr (mobile)



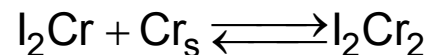
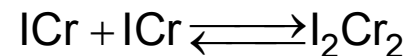
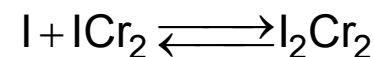
- Formation of I_2Cr (mobile)



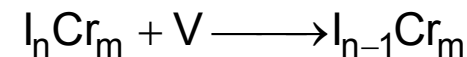
- Formation of ICr_2 (immobile)



- Formation of I_2Cr_2 (immobile)



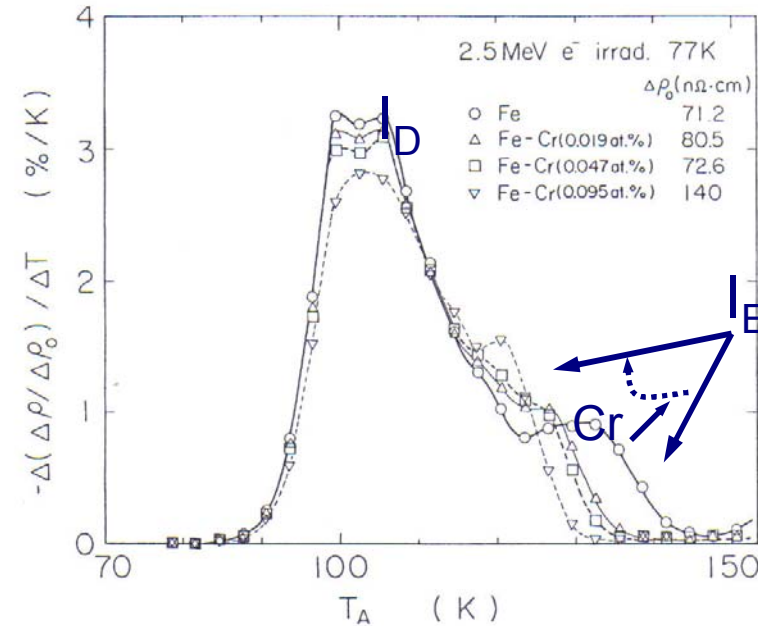
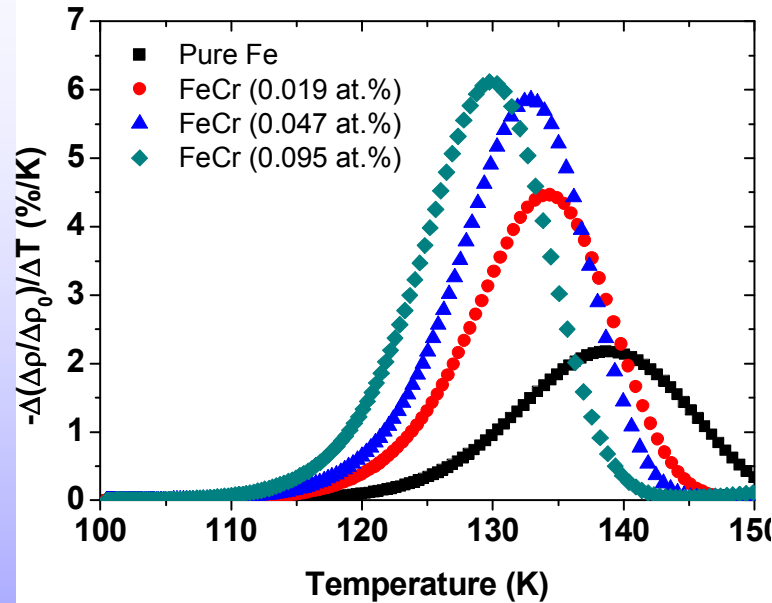
- Recombination with vacancy V



Dilute alloys: Stage I

Stage I_E: Abe results

Stage I_E: RT results



*Abe & Kuramoto, JNM 271&272, 209 (1999)

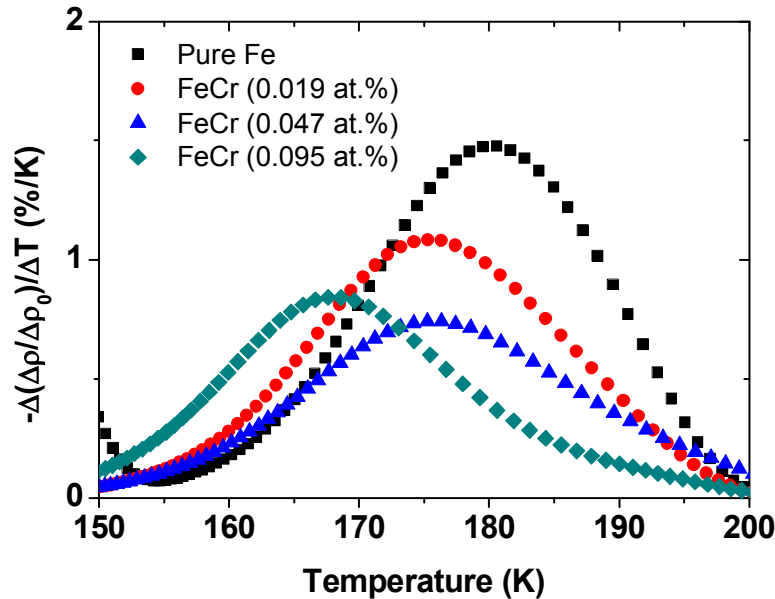
Results in qualitative agreement with experimental observations.

Model reproduces:

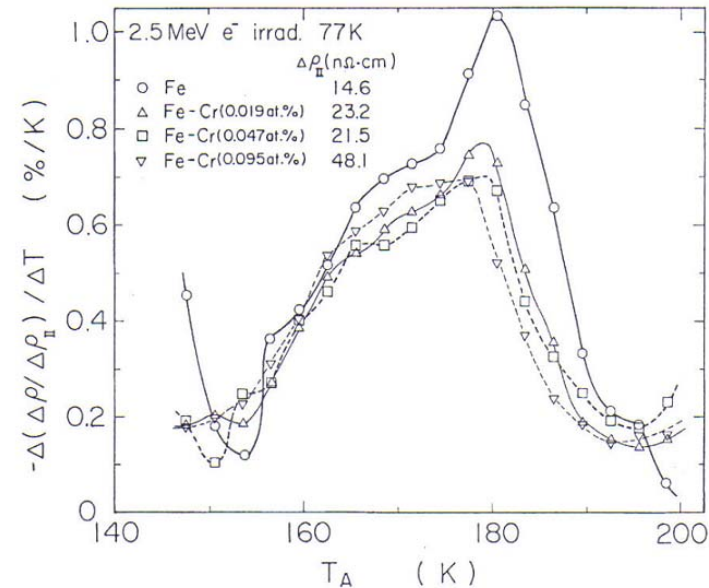
- shift of stage I_E towards lower temperatures with Cr content
- increase of amplitude stage I_E with Cr content.I.

Dilute alloys: Stage II

Stage II: RT results



Stage II: Abe results



*Abe & Kuramoto, JNM 271&272, 209 (1999)

Results in qualitative agreement with experimental observations.

Model reproduces

- **stage II slight decreases with Cr content**
- **slight shift towards lower temperatures**

Picture in (very) diluted alloys

- Preferential migration of Fe-Cr mixed dumbbell
 - ☞ *Cr atoms can diffuse via interstitial mechanism*
 - ✓ By definition this implies SIA & Cr fluxes in same direction
 - ☞ *In agreement with resistivity recovery studies (Maury et al., 1987; Abe & Kuramoto, 1999)*

- Preferential Cr-vacancy exchange
 - ☞ *Cr atom is fast diffuser (in agreement with common knowledge)*
 - ☞ *Absence of binding energy with vacancy excludes drag*
 - ✓ Fluxes of Cr atoms and vacs will be opposite

What about concentrated alloys?

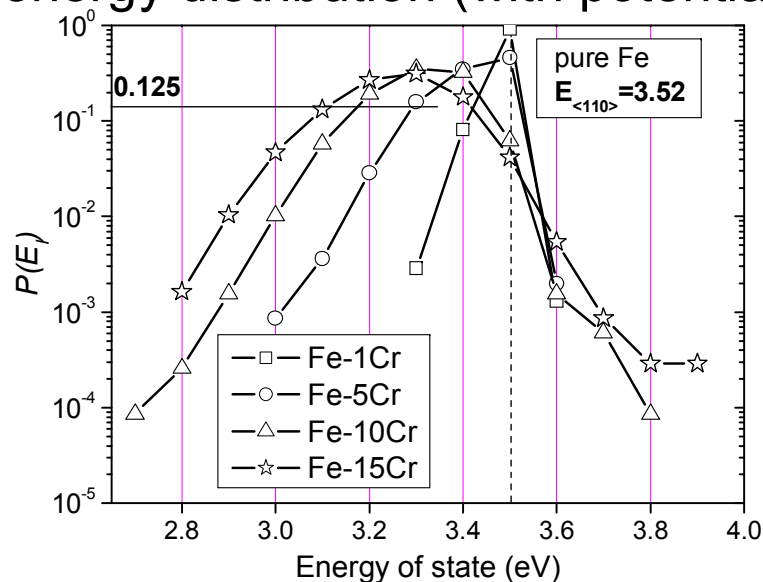
Problem: all characteristic energies in concentrated alloys are functions of the local atomic configuration:
There is no ‘migration’ or ‘binding’ energy’ but a distribution of such energies!

DFT study of SIA/Cr interaction in “less dilute” FeCr alloys in Klaver & Olsson, PRB, 76 (2008) 214110

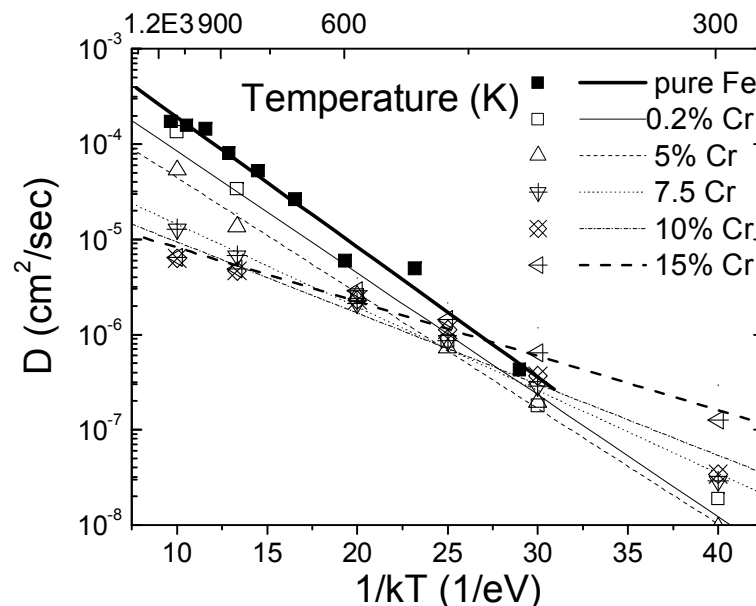
Joint ICTP-IAEA Workshop on Multiscale Modelling, 12-23 April, 2010 – L. Malerba – Fundamentals of Radiation Damage

Single SIA in concentrated FeCr alloys

Static calculations of formation energy distribution (with potential)



Dynamic calculations of migration energies



1. SIA can be trapped in Cr configurations with $E_{trap} \sim 0.2-0.4$ eV
2. **Effective migration energies lower than in Fe because of “percolation”:** jumps through “connected traps” – traps are so only if not connected
3. Trap concentration $\sim 1-100$ ppm
4. Escape from these traps requires time $\sim \exp(-(E_{TR} + E_{MIG})/k_B T) > 100$ ns

Alloy	E_{mig} (eV)	D_0 (cm^2/sec)
Fe	0.31	$4.43 \cdot 10^{-3}$
Fe-0.2%Cr	0.29	$1.60 \cdot 10^{-3}$
Fe-5%Cr	0.28	$7.26 \cdot 10^{-4}$
Fe-7.5%Cr	0.26	$4.02 \cdot 10^{-4}$
Fe-10%Cr	0.25	$1.34 \cdot 10^{-4}$
Fe-15%Cr	0.23	$9.33 \cdot 10^{-5}$

Terentyev *et al.*, *Comp. Mat. Sci.*, 2008

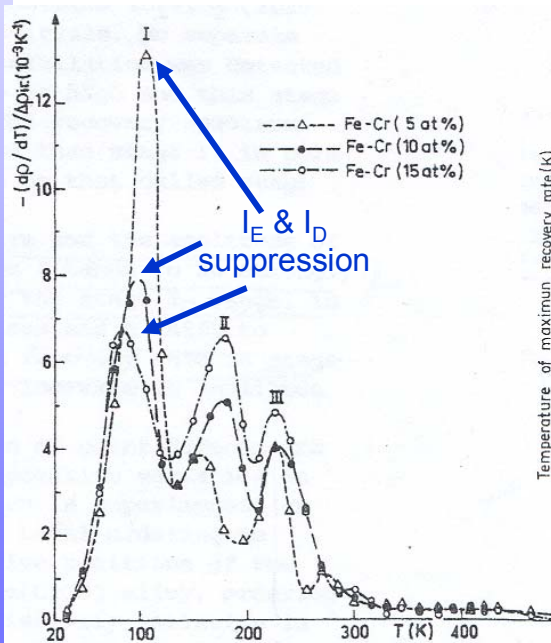
Picture in concentrated alloys

- Single SIA migration is slowed down in FeCr vs Fe, due to time spent at traps
 - ☞ *However, diffusion is faster between traps*
- Vacancy diffusion not strongly affected by Cr in Fe
 - ☞ *Experiments indicate so, except unclear effects at high T*
 - ☞ *Recent studies (Sampedro, 2009, master thesis) with CDM improved potential seem to confirm absence of significant effects*
- In isochronal annealing terminology, we expect:
 - ☞ *Shift of stage I_E to lower energies at low Cr concentration*
 - ☞ *Suppression of stage I_E at sufficiently high Cr content*
 - ☞ *Appearance of SIA de-trapping peaks at higher temperatures (stage II)*
 - ☞ *No significant effect on stage III*

And indeed ...

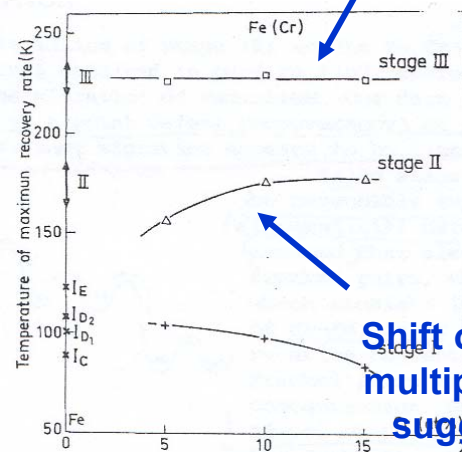
Isochronal annealing recovery in concentrated FeCr

- ♣ Resistivity recovery studies in concentrated FeCr alloys show
 - Suppression of stage I
 - Appearance of stage(s) attributable to self-interstitial de-trapping (or vacancy correlated recombination)
 - No influence on stage III (vacancies unaffected) / SIA may start to diffuse only at higher temperature than vacancies

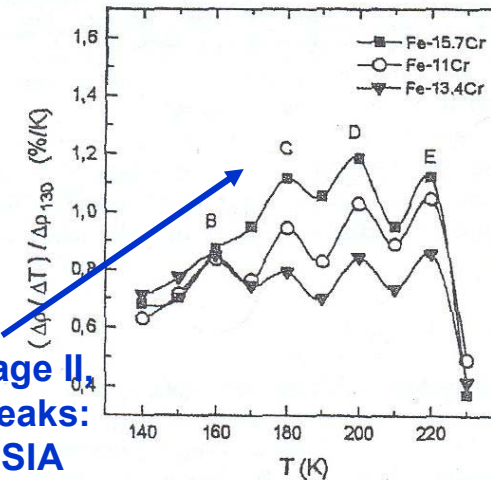


Benkaddour et al, Mat. Sci. Forum 15-18 (1987) 1263; Dimitrov et al, Ann. Chim. Fr. 16 (1991) 319

Stage III unaffected



Shift of stage II, multiple peaks: suggest SIA detrapping



Nikolaev et al, J. Phys. Condens. Matter 9 (1997) 4385; Nikolaev, *ibid.* 11 (1999) 8633

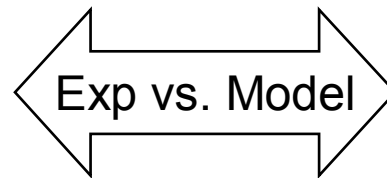
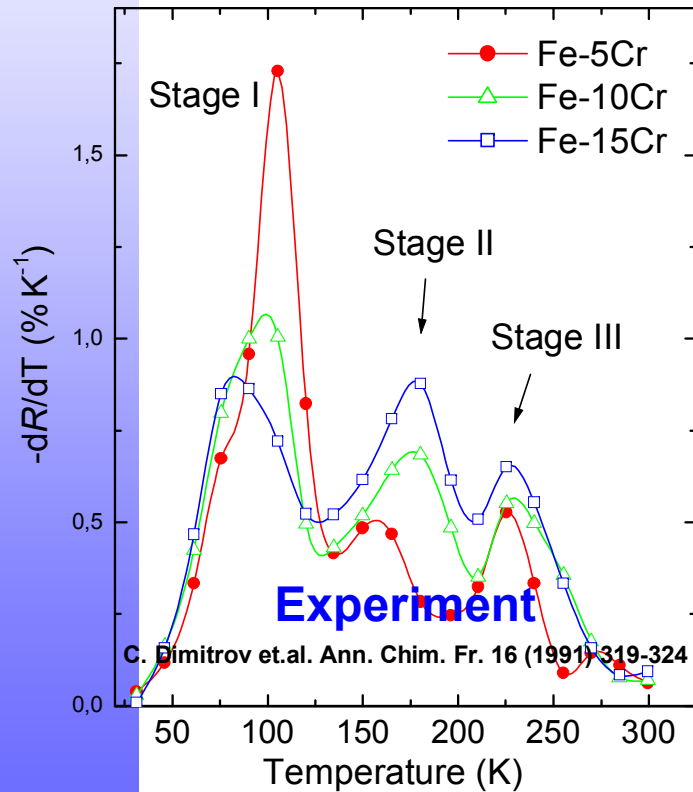
Rate theory model for isochronal annealing in concentrated FeCr

Terentyev, PhD thesis

Very simple model, used as screening of hypotheses

Traps for SIA defects are introduced explicitly (pinning SIAs for a time $\sim \exp(-E_{TR}/kT)$)

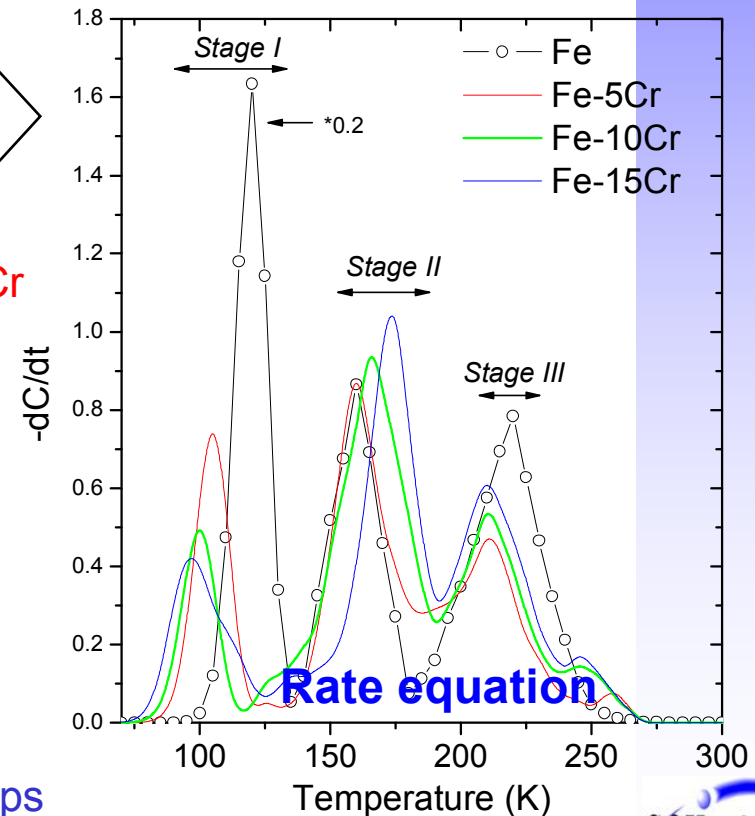
Concentrations & energies are fitted to experiments



With increase of Cr content:

1. $T_{stage I} \downarrow$
2. $T_{stage II} \uparrow$
3. $T_{Stage III} \leftrightarrow$

But we can't reproduce the full complexity of configurational traps



Isochronal annealing: defect properties in Fe & FeCr

- In pure Fe
 - ☞ *Good agreement with experiment can be obtained if:*
 - ✓ $E_m(\text{SIA})=0.33$ eV, $E_m(\text{di-SIA})=0.42$ eV
 - ✓ *Ab initio* calculations predict $E_m(\text{VAC})=0.65$ eV, whereas agreement with experiment is achieved only if $E_m(\text{VAC})=0.55$ eV

- In Fe-Cr alloys, with 5-15%Cr:
 - ☞ *Trends as seen in experiments can be obtained if:*
 - ✓ $E_m(\text{SIA})\sim 0.25$ eV, and two classes of traps are introduced:
 - *Shallow:* $E_{TR}\sim 0.2$ eV
 - *Deep:* $E_{TR}\sim 0.4$ eV
 - ✓ Concentration of deep traps increases with Cr content
 - ✓ $E_{\text{MIG}}(\text{VAC})\sim 0.55$ – i.e. unaffected in the presence of Cr

- Comparison of RT study and experimental recovery spectra, obtained in concentrated alloys, suggest:
 - ☞ *Mobility of single vacancy is not affected by Cr*
 - ☞ *Mobility of single SIAs is enhanced in diluted FeCr alloys but reduced progressively by increasing Cr content*
 - ☞ *Stage II has different origin in Fe and dilute FeCr alloys (di-SIA migration) from concentrated Fe-Cr alloys (SIA release from shallow traps)*
 - ☞ *Onset of long-range SIA migration in concentrated FeCr alloys may occur above stage III (after vacancy migration !)*
 - ☞ *Stage III is vacancy migration and release of SIAs from deep traps*

Radiation damage accumulation in FeCr alloys

Mobility of SIA clusters in pure Fe

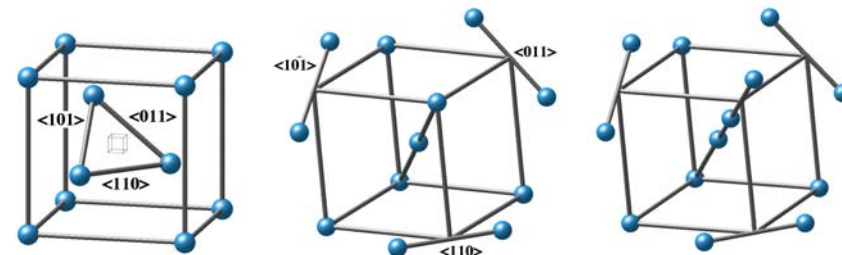
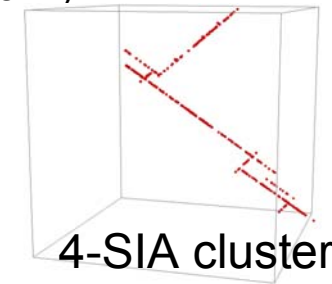
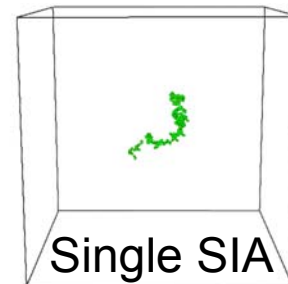
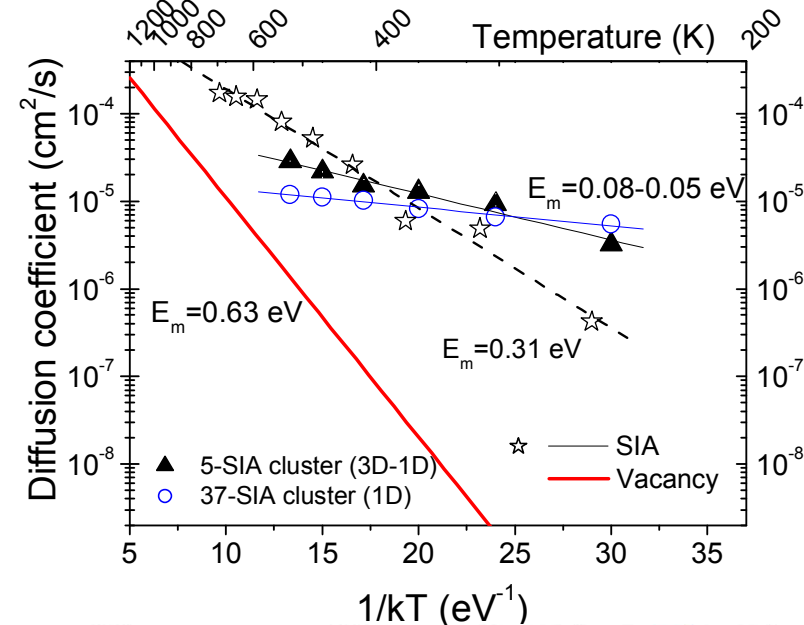
Two classes of SIA clusters exist in pure Fe:

Parallel configurations

- 3D or 3D-1D migrating clusters of $\langle 110 \rangle$ dumbbells (up to ~ 5 SIAs)
- Fast 1D migrating clusters (loops) formed by platelets of $\langle 111 \rangle$ crowdions ($E_m \sim 0.05$ eV)
- Slowly 1D migrating $\langle 100 \rangle$ loops

Non-parallel configurations

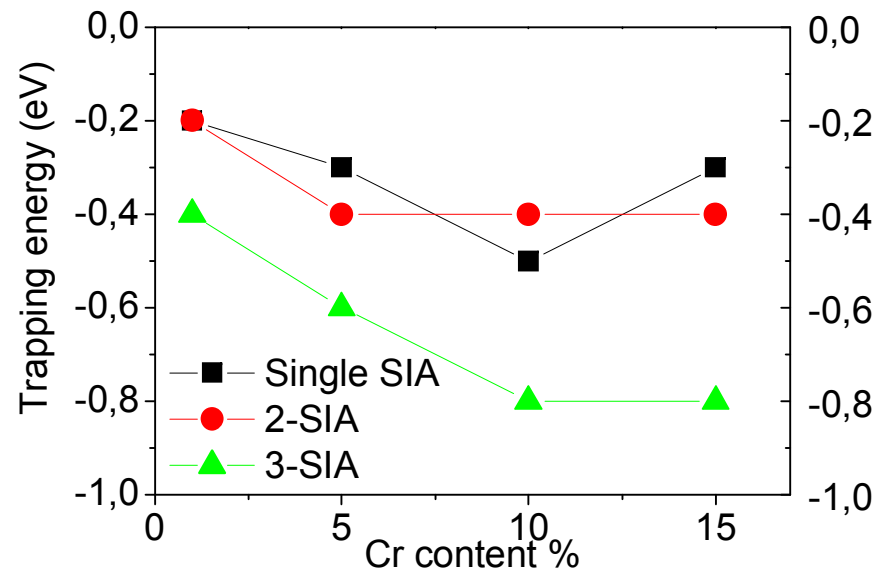
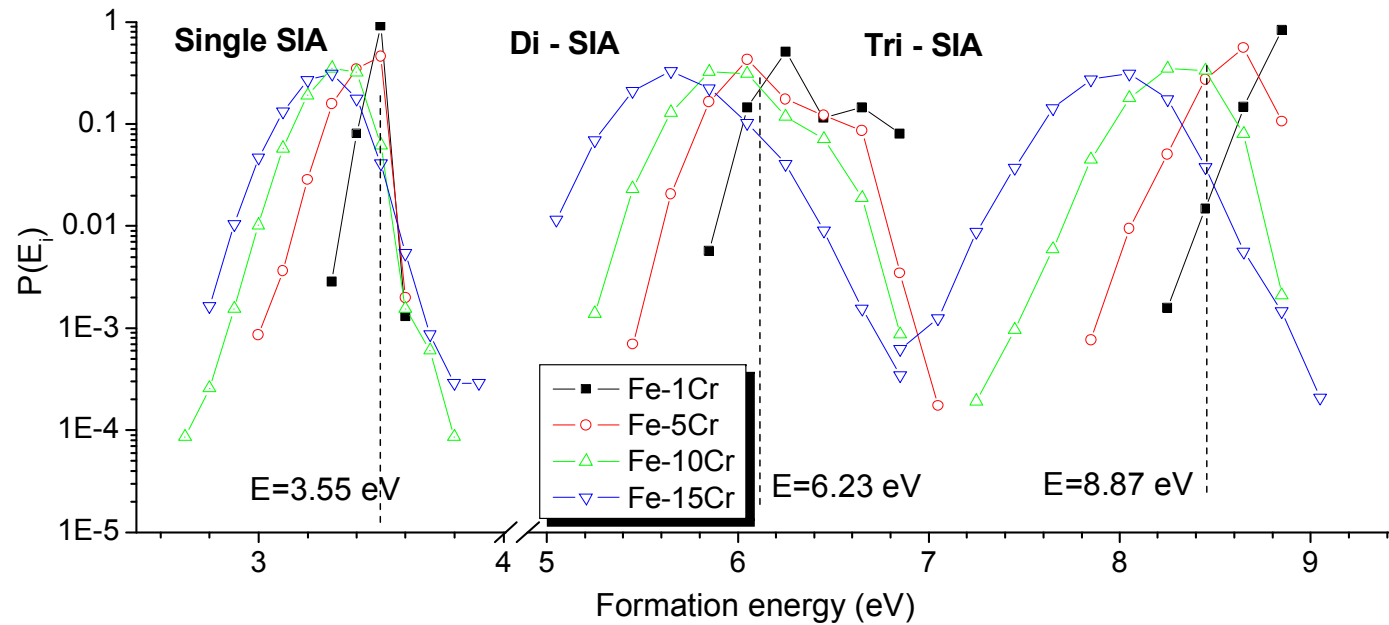
Clusters formed by non-parallel dumbbells which cannot migrate, unless they 'unfault' to parallel configurations



Pb of mobility of SIA clusters in FeCr

- Difficulty of studying non-parallel configurations and $\langle 100 \rangle$ loops by atomistic techniques makes pb of SIA cluster mobility a **still open issue even in pure Fe**
- Existence of many possible configurations and migration mechanisms obliges the problem in FeCr to be formulated as:
 - ☞ **Estimation of local-atomic-configuration-dependent E_m for given migration mechanism**
- So far, attention focused on 1D migrating SIA clusters, assuming invariant migration mechanism
- In case of small SIA clusters, only a study of configurational trap concentration and strength has been performed

Traps for small SIA clusters in FeCr alloys



Terentyev *et al.*, JNM, 2009

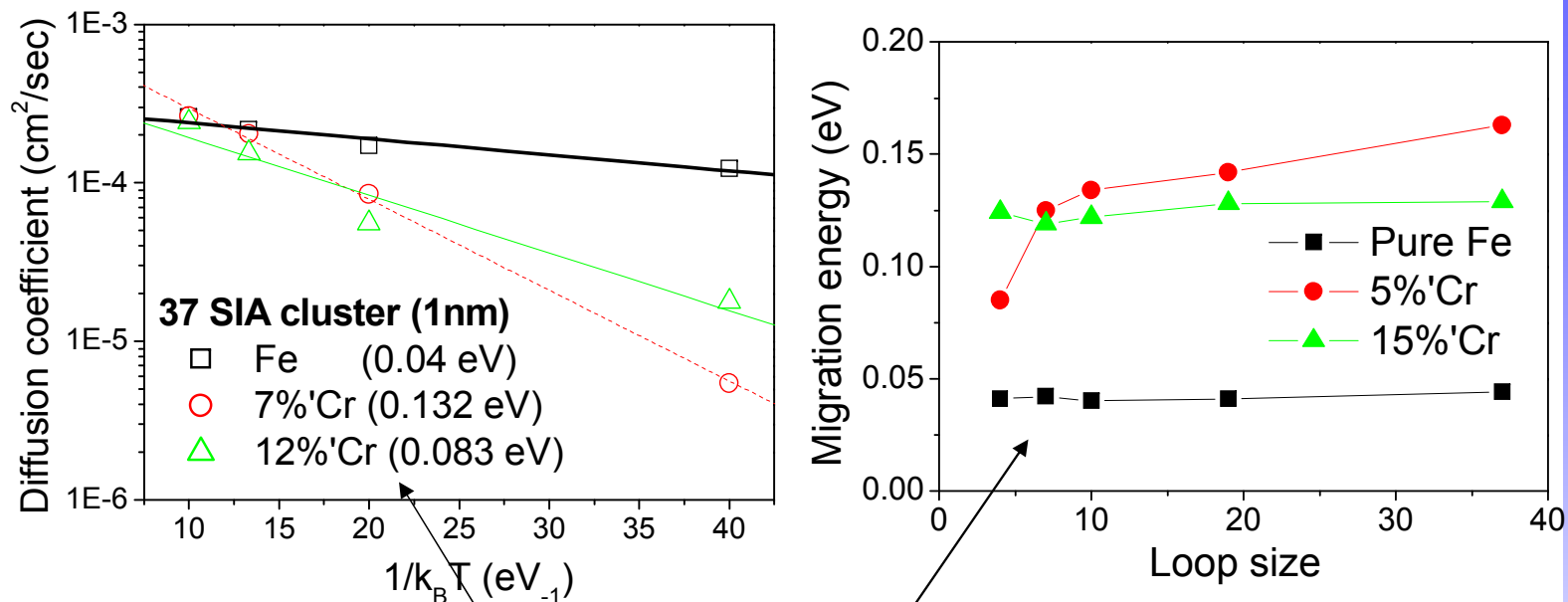
Summary for small, 3D-migrating SIA clusters

- Single SIAs ($\langle 110 \rangle$ dumbbells) migrate slightly faster in presence of Cr, but are expected to get trapped
- Di-SIAs migrate with the same energy as single SIA and appear not to be strongly trapped*
- Tri-SIA clusters are strongly trapped and may probably be considered immobile in concentrated FeCr alloys, without significant loss of generality*
- Approximate trapping energy (E_{TR}) and concentration (C_{TR}) for single and 3D-mobile SIA clusters are estimated as: $E_{TR} = 0.2-0.8$ eV $C_{TR} = 10^2 - 5 \times 10^3$ ppm, in alloys with 5-15%Cr
- The trapping effect grows monotonically or stabilises at a plateau, with Cr content up to the studied concentrations
- The reduction of the mobility (or total immobilization) of SIA clusters will enhance recombination with vacancies

A fully quantitative characterisation of mobility of 3D-migrating clusters is hindered by existence of non-parallel configurations and of combinatorially large number of possible local Cr configurations

See also Terentyev and Castin, *Comp Mat Sci*, 2009

1D migrating SIA clusters in FeCr vs Fe

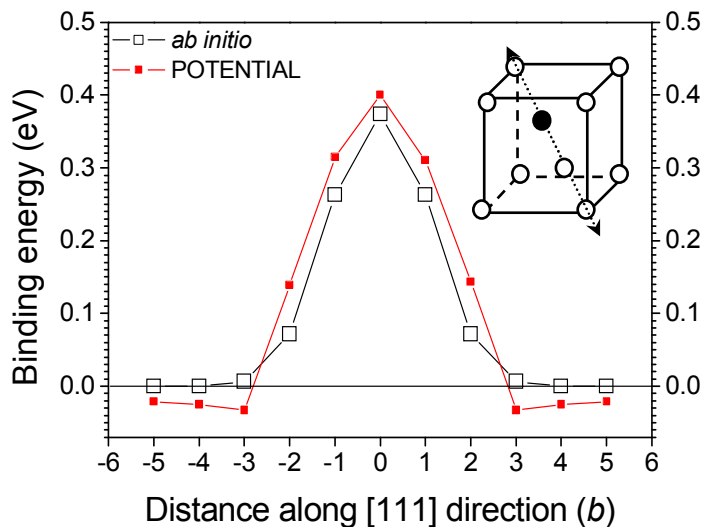


$$D = D_0 \exp(-E_m / k_B T)$$

- Presence of Cr reduces mobility of 1D-migrating SIA clusters
 - ☞ Increase of migration energy by a factor 2-3 → decrease of diffusion coefficient by 1-2 orders of magnitude
- Effect depends on both Cr content and cluster size

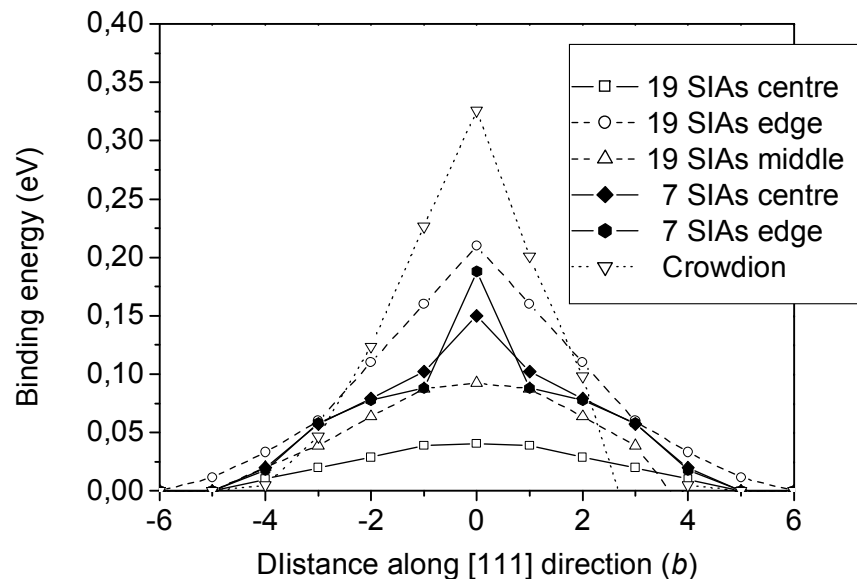
What's the origin of this effect?

Crowdion/Cr interaction



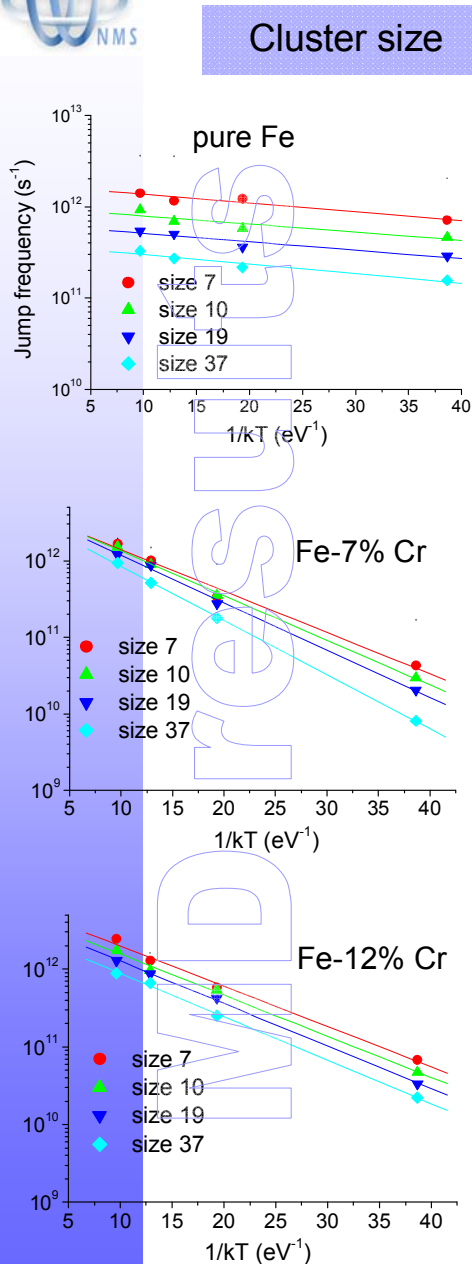
Single-crowdion/Cr- atom interaction is strong and long-range

Crowdion/Cr interaction loses strength in clusters, but remains significant and long-range



The origin of reduction in the diffusivity of SIA clusters stems from strong interaction of Cr with $\langle 111 \rangle$ crowdions

Cr as a red traffic light for SIA clusters



Cluster size

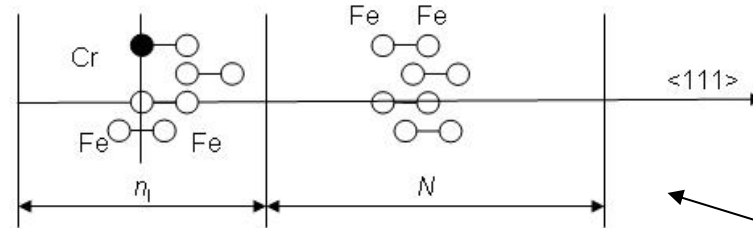
Interaction length

Nr. interacting Cr atoms

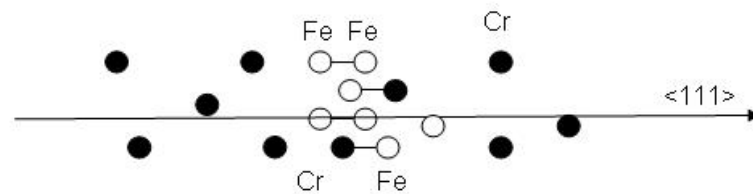
Cr content

$$K_n = n n_I C_{Cr}$$

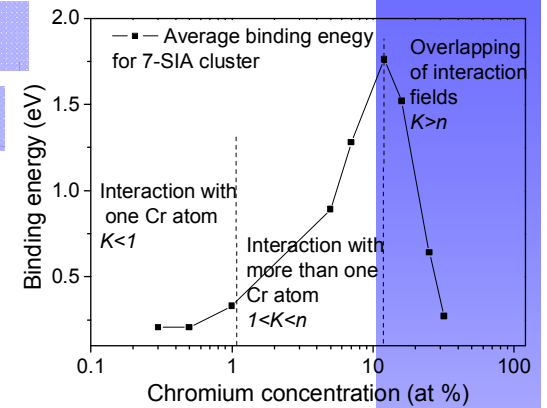
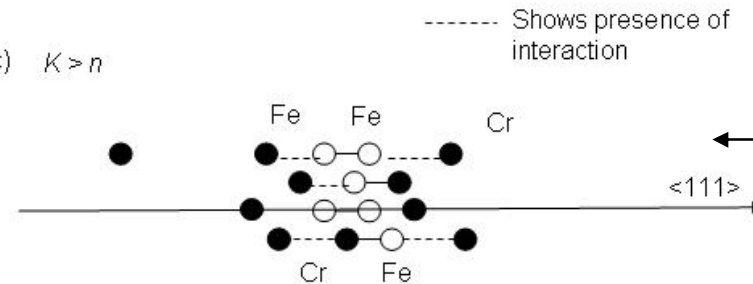
a) $K < 1$



b) $1 \leq K \leq n$



c) $K > n$



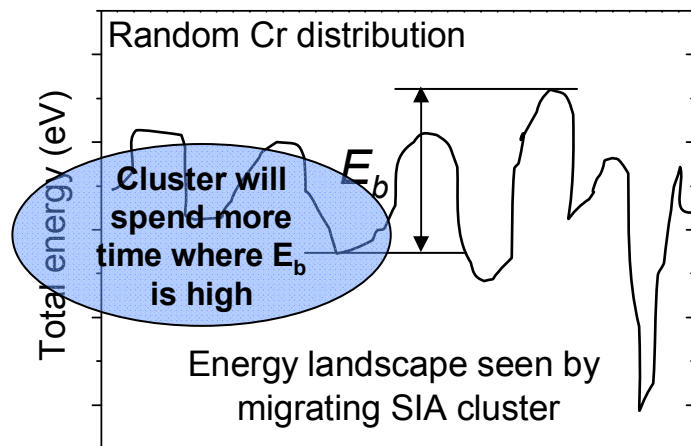
One red light at a time: trapping effect

The larger the size, the more red lights

Too many red lights! Size doesn't matter any more

Static & dynamic study of 1D-migrating SIA cluster diffusion coefficient reduction in Fe-Cr alloys

Assumption



SIA-cluster free energy variation can be estimated as

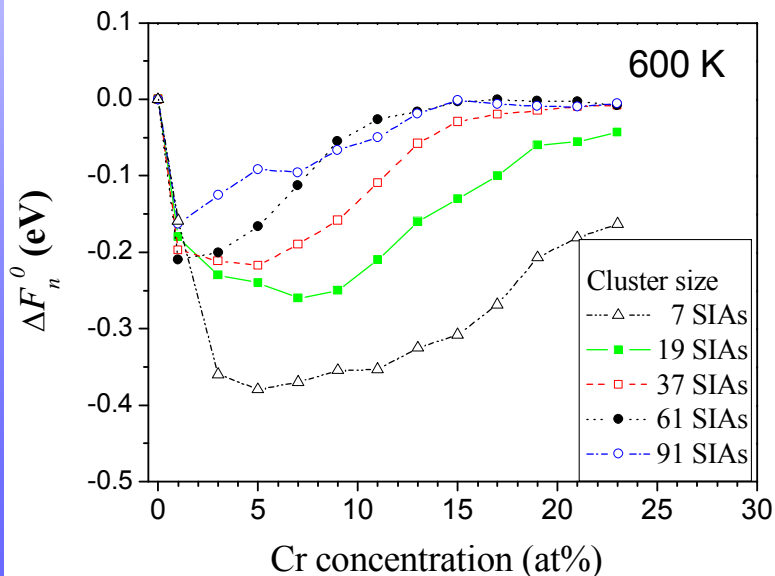
$$\Delta F \cong k_B T \ln \langle \exp(-E_b / k_B T) \rangle$$

Diffusion coefficient then decreases as

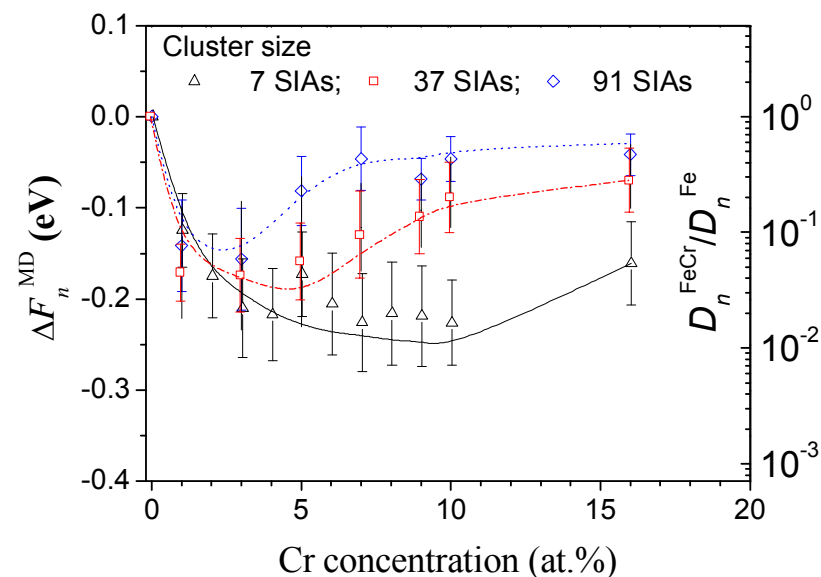
$$D_n^{\text{FeCr}} = D_n^{\text{Fe}} e^{\beta \Delta F_n}$$

Which accounts for probability of meeting low energy states

Results of static calculations

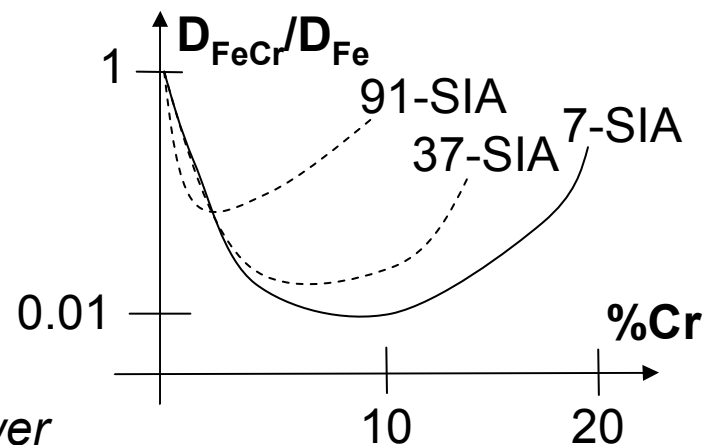


Verification using MD

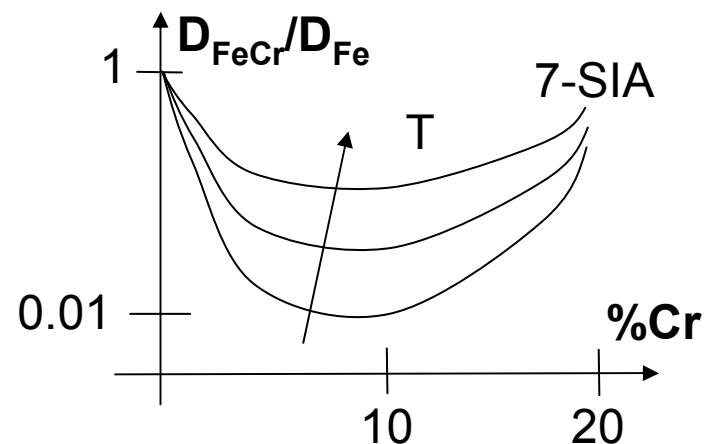


Summary for 1D-migrating SIA clusters

- 1D-migrating $\langle 111 \rangle$ -SIA clusters are slowed down in Fe-Cr alloys, following a non-monotonic dependence on Cr content
- D_{FeCr}/D_{Fe} also depends on:
 - ☞ Cluster size: less reduction for lower Cr content with increasing size
 - ☞ Temperature: less reduction with increasing temperature
 - ☞ Cr distribution:
 - ✓ Cr ordering (negative SRO parameter) makes ΔF less dependent on cluster size
 - ✓ α - α' separation makes D_{FeCr}/D_{Fe} independent on initial Cr content (for clusters moving in the depleted matrix)

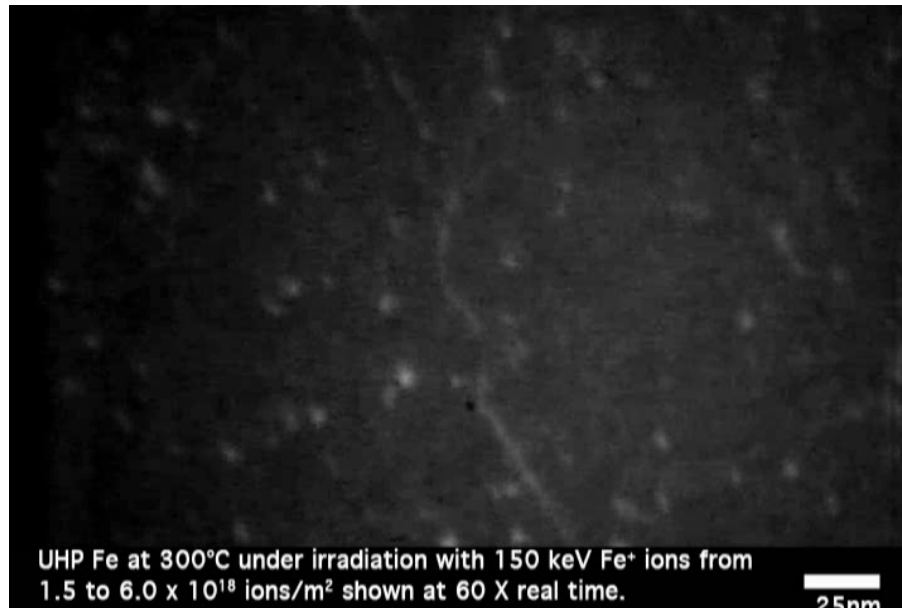


NB: MIN(D_{FeCr}/D_{Fe}) ~5-10% (below solubility limit) for small (in-cascade-created) 1D migrating SIA clusters



Terentyev *et al.*, Phil Mag Lett, 2005; JNM, 2007; Phil Mag, 2008

Slowing down of SIA clusters in FeCr: THE MOVIE

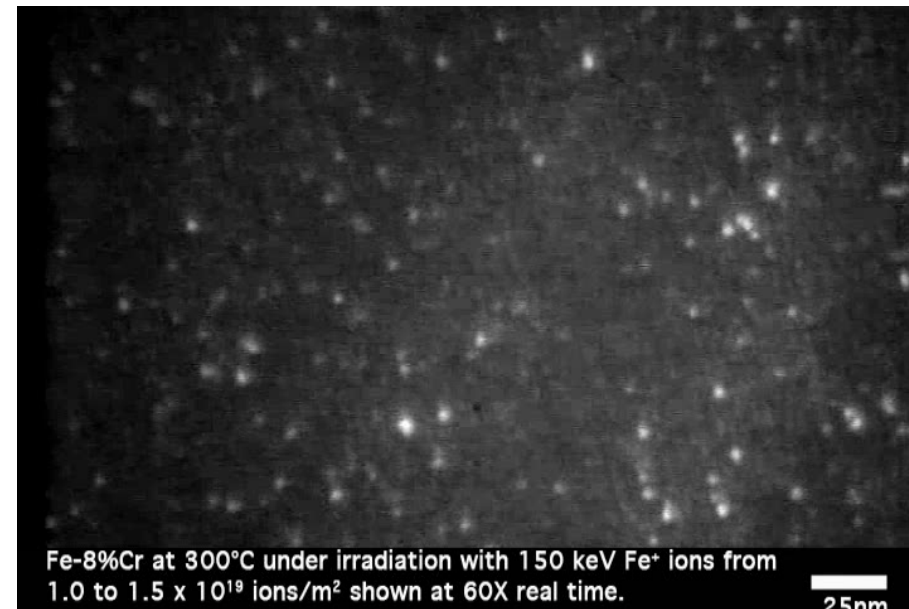


← Ion irradiation of pure Fe to high dpa at 300°C

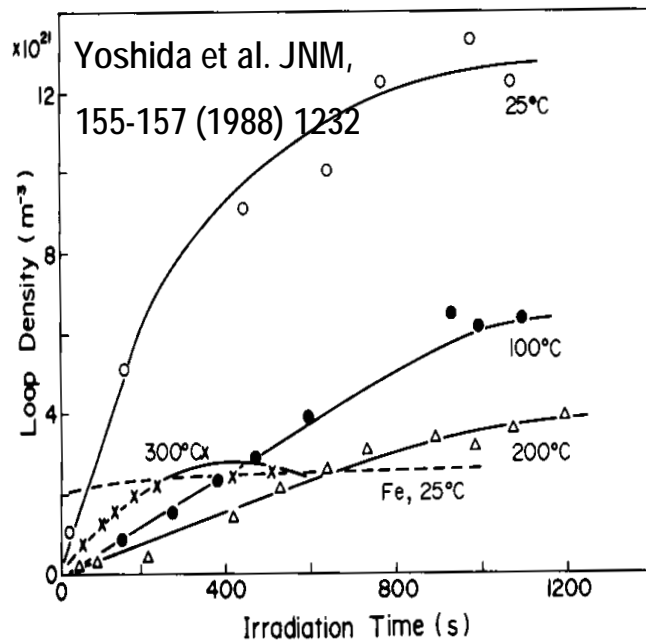
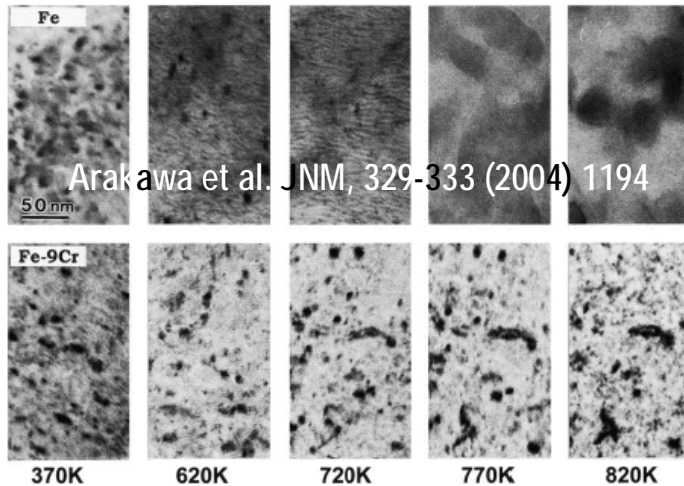
SIA clusters form but many of them move away and die at the surface

Ion irradiation of Fe8%Cr to high dpa at 300°C →

SIA clusters form and since they move less accumulation takes place



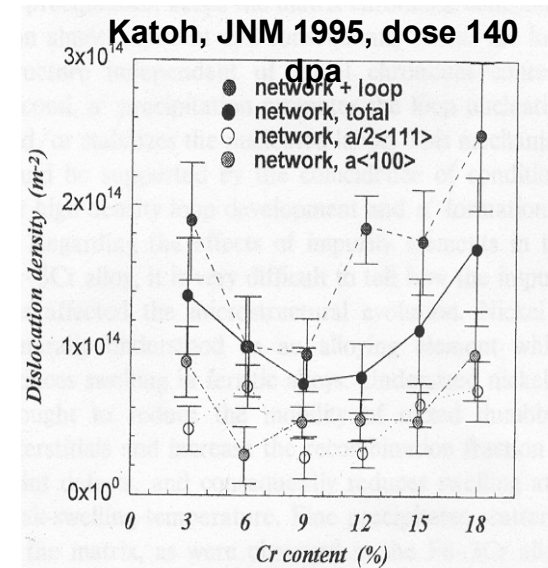
Higher loop stability, lower loop mobility → higher loop density in FeCr



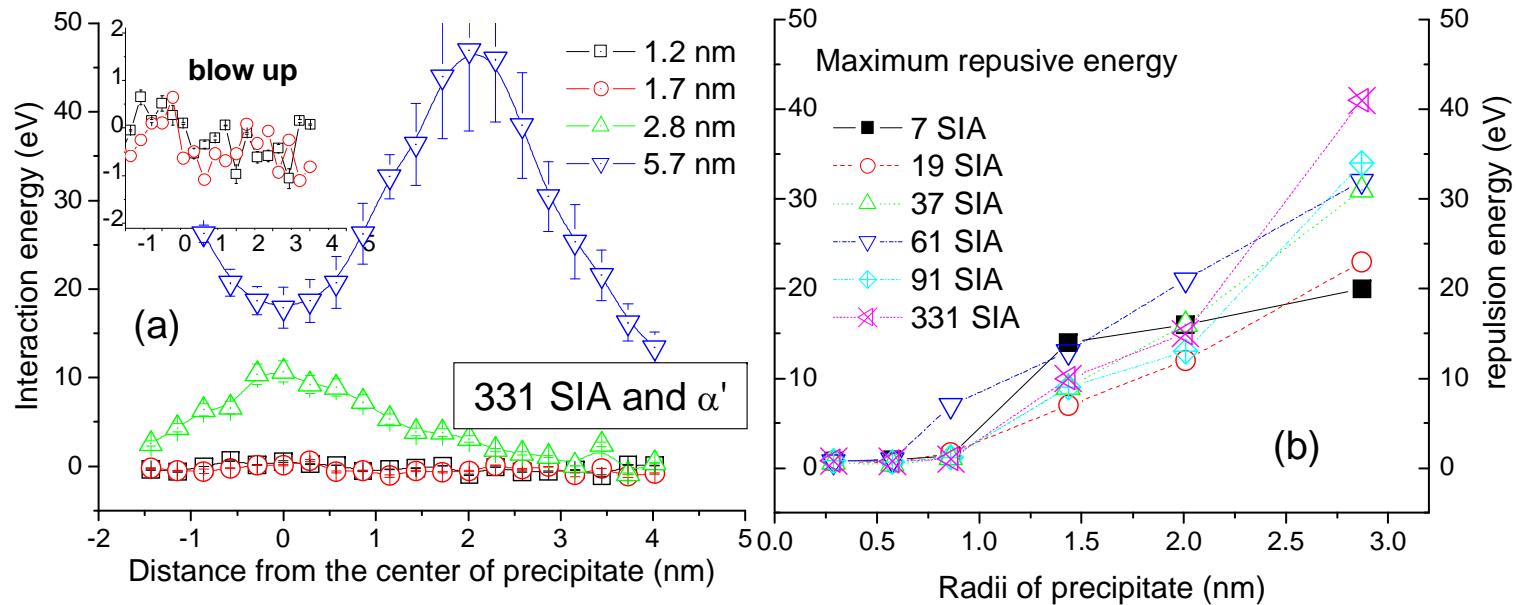
Crowdion-Cr affinity qualitatively explains higher stability (although strength of the interaction vanishes for large loops – see Terentyev, Klimenkov & Malerba, JNM, 2009)

Reduced mobility explains higher density (less clustering) / size should be accordingly smaller

Enhanced recombination when slowing down is strongest explains non monotonic dependence of density on Cr content

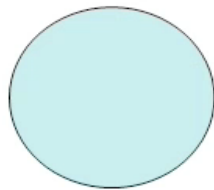


Cr-rich precipitates repuls 1D migrating SIA clusters

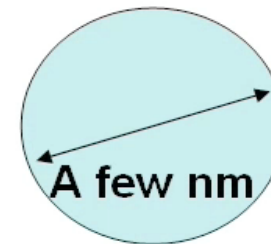


Terentyev *et al.*, JNM, 2007

Cr precipitate



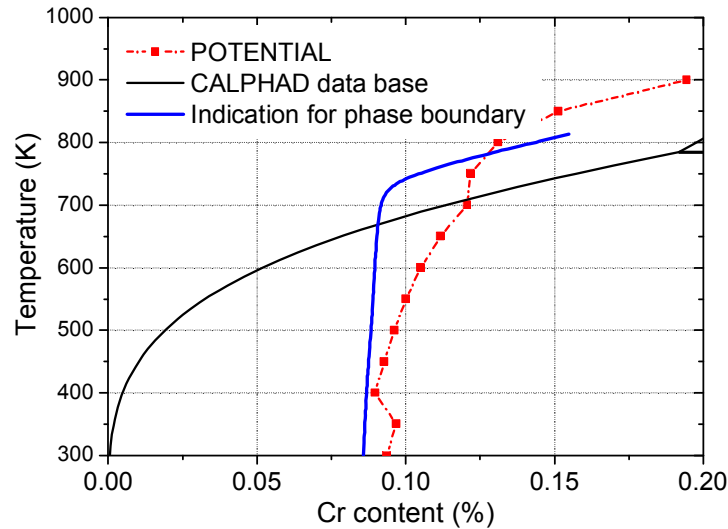
$N \sim 10^{24} \text{ m}^{-3}$



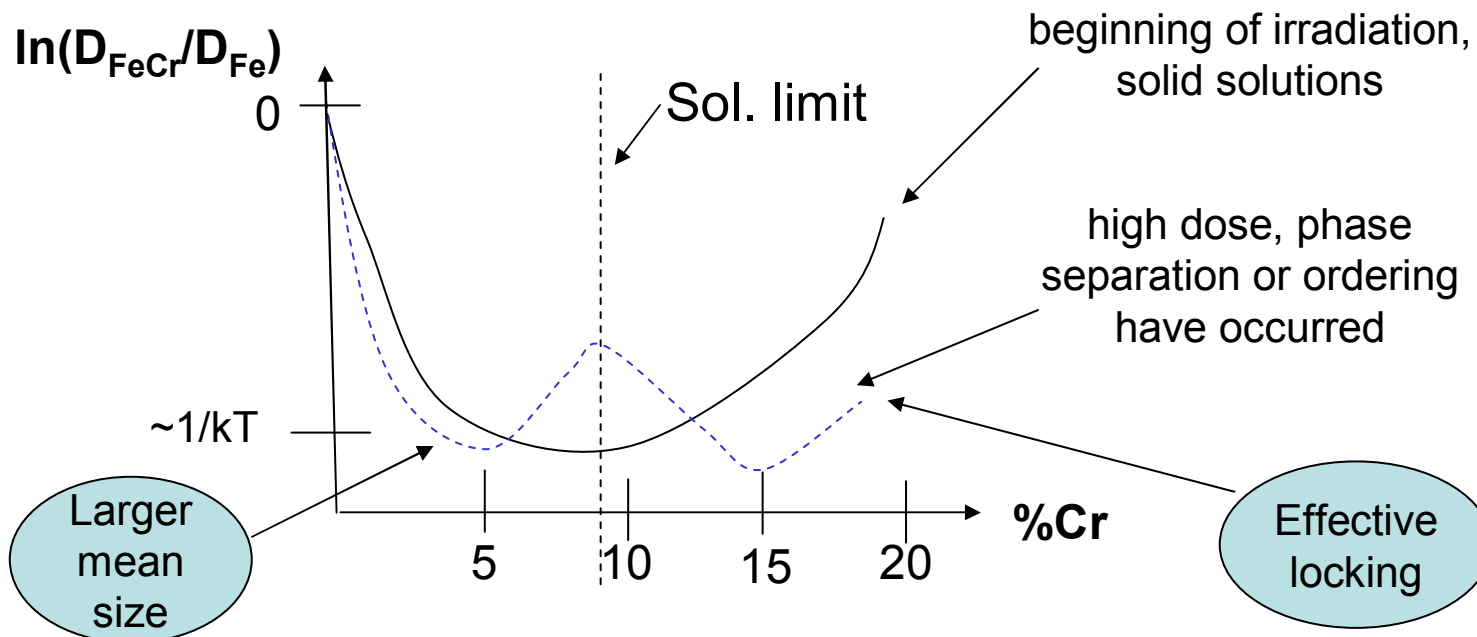
movie

- ✓ 1D migrating SIA clusters can remain locked between α' precipitates \rightarrow further mechanism to reduce diffusivity

Shape of average SIA cluster slowing-down curve vs Cr content and dose



In the region of interest for nuclear applications, the solubility limit of Cr in Fe is ~8-9%: above this concentration Cr-rich ppts will (rapidly) form



“Production bias”: the key to understand swelling

Main concepts:

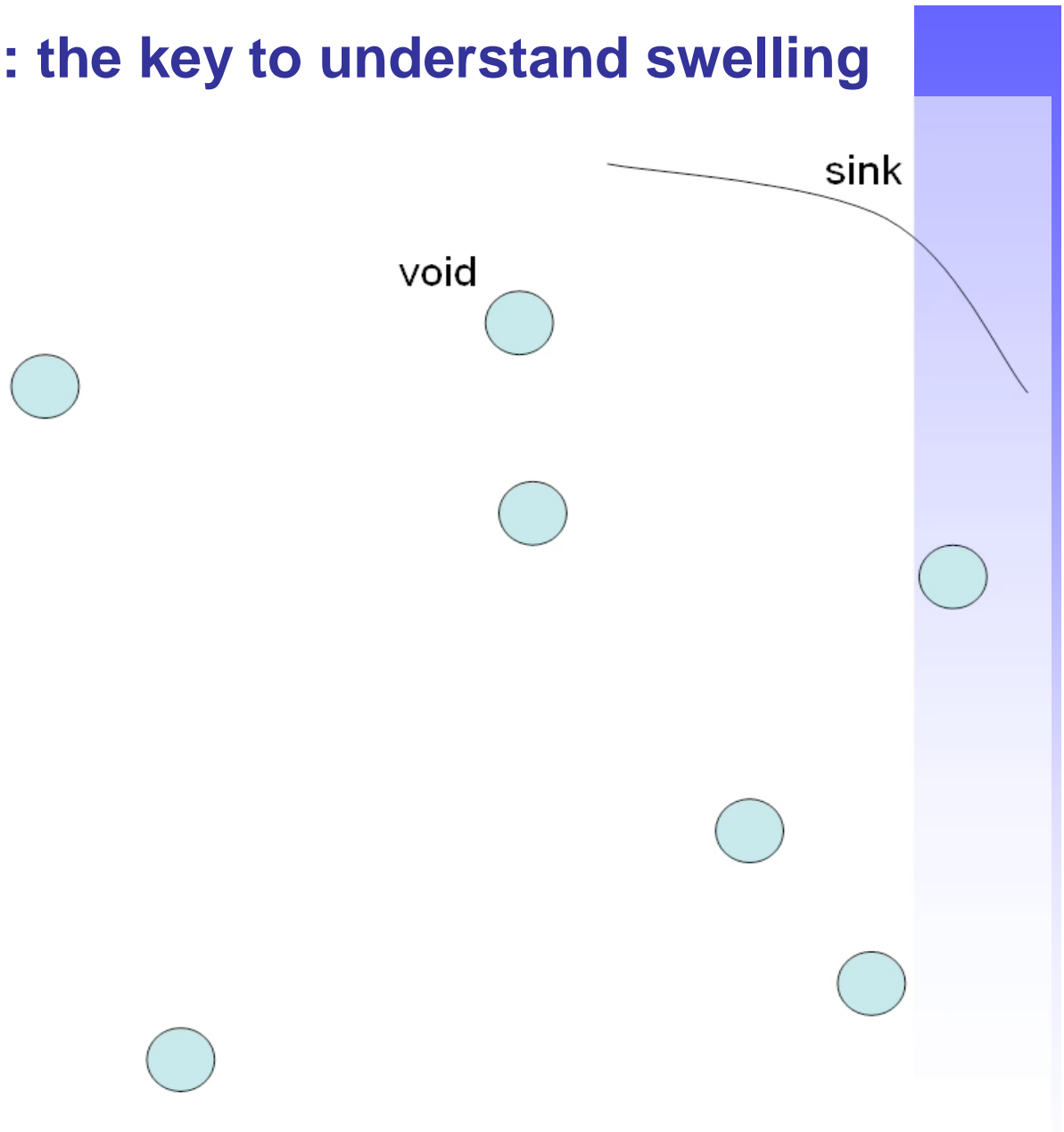
SIA clusters, as well as vacancy clusters, are produced directly in cascades

SIA clusters migrate one-dimensionally and (fairly) fast

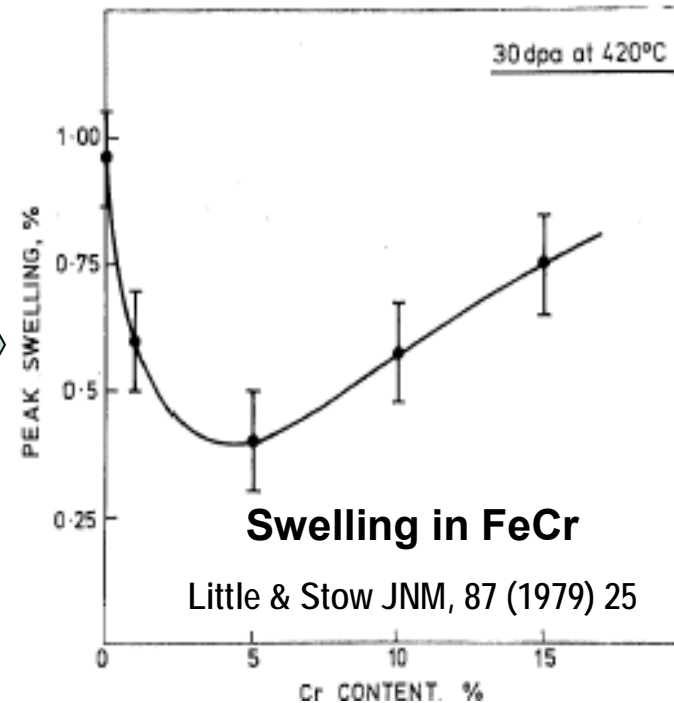
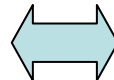
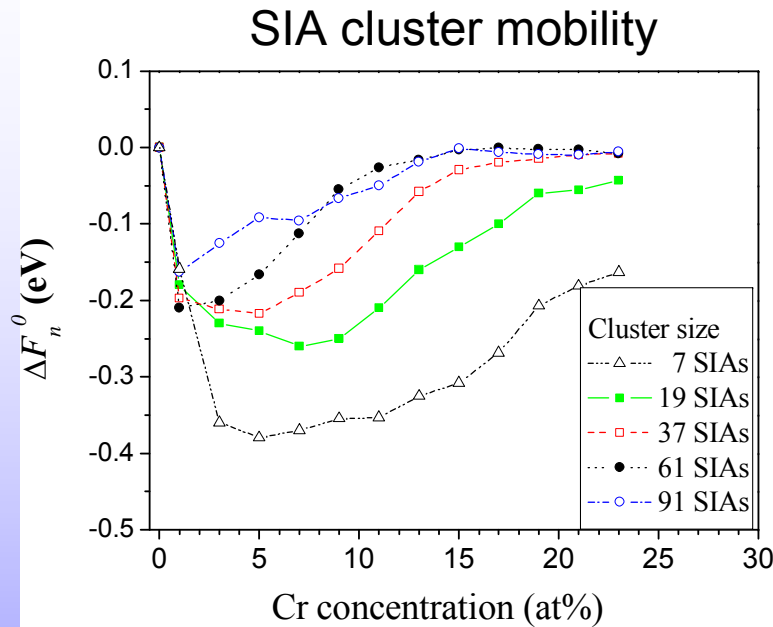
Vac. clusters can be considered immobile in comparison

SIA clusters will reach very efficiently sinks (surfaces, dislocations and grain boundaries)

Vacancies will tend to remain in the bulk and form (almost) immobile voids



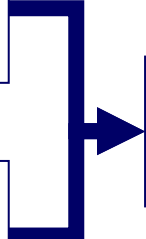
Second smile explained: Swelling vs Cr content



**Reduced SIA cluster mobility,
especially 1D migrating**

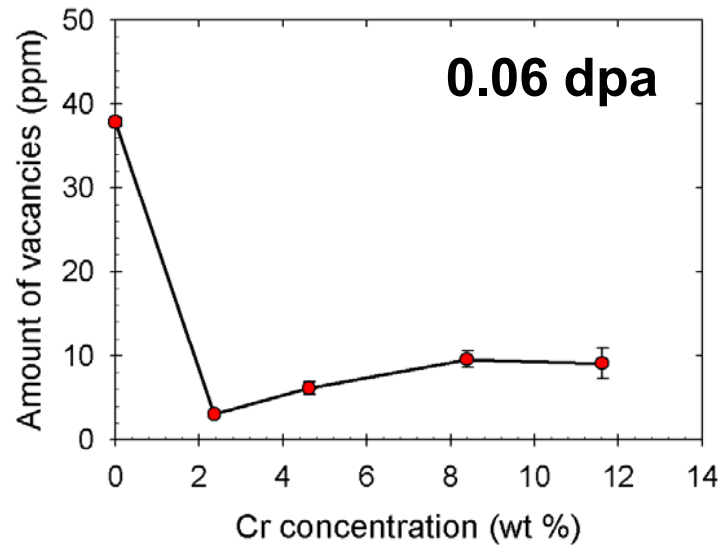


**Enhanced recombination with
Cr-unaffected vacancies**



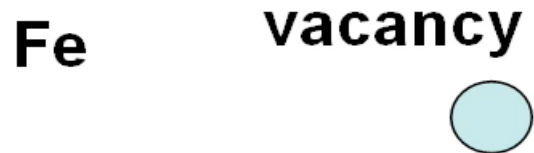
**Reduction of
swelling**

Enhanced recombination

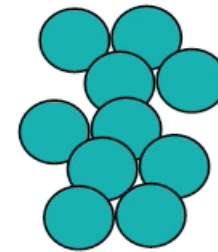


Lambrecht, PhD thesis, 2009

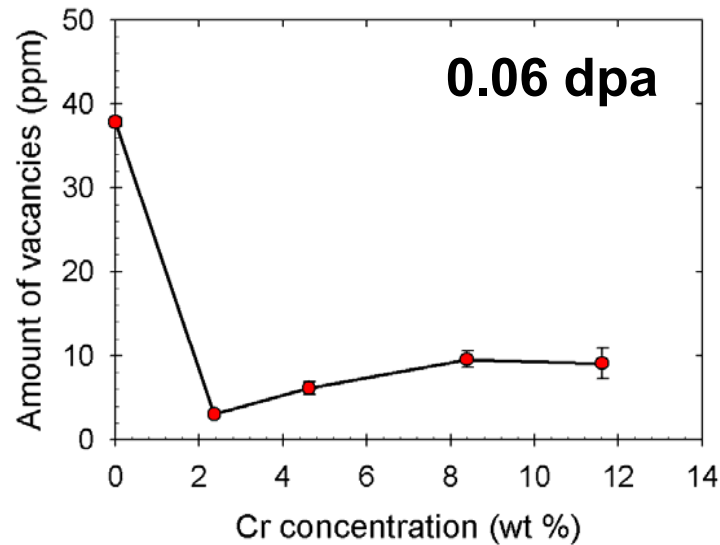
Positron annihilation studies show that total amount of vacancies in n-irradiated FeCr alloys decreases with Cr content



SIA cluster



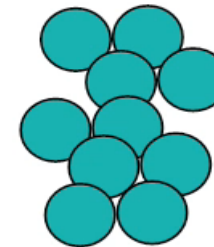
Enhanced recombination



Lambrecht, PhD thesis, 2009

Positron annihilation studies show that total amount of vacancies in n-irradiated FeCr alloys decreases with Cr content

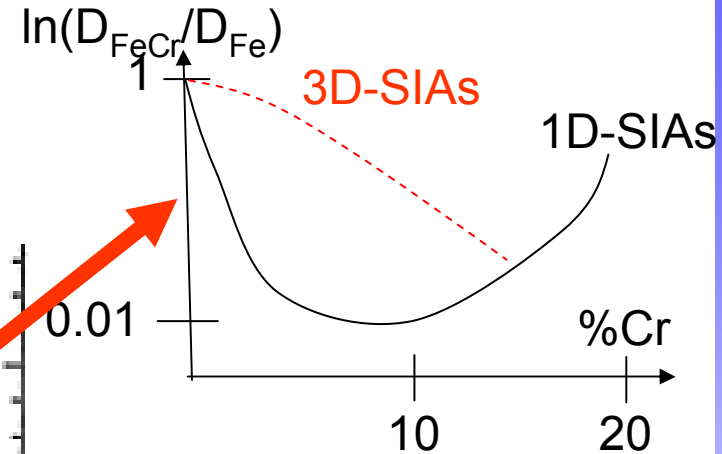
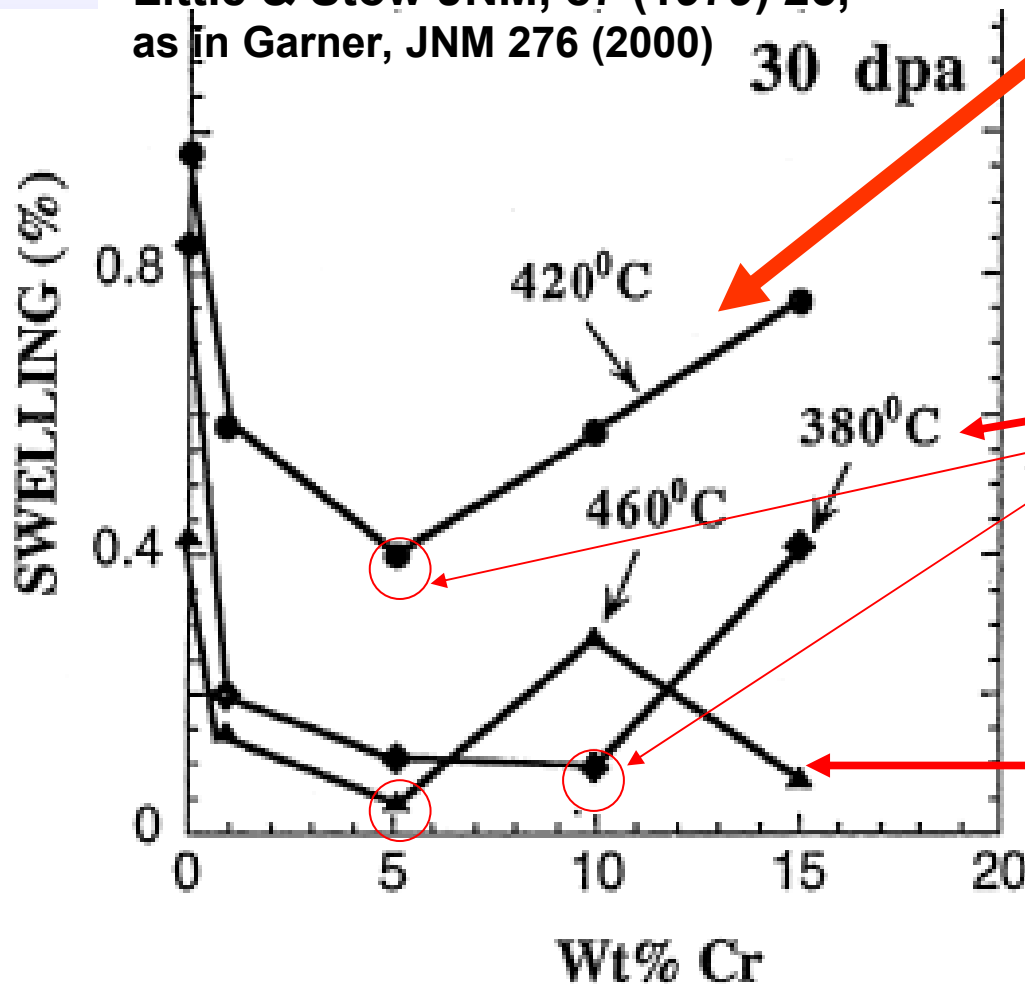
FeCr



Some like it swollen

Little & Stow JNM, 87 (1979) 25,
as in Garner, JNM 276 (2000)

30 dpa



Lower temperature:
Minimum shifts from
5 to 10%Cr - average
smaller size clusters?

Higher temperature:
Further reduction of
swelling at 15%Cr -
accelerated α'
formation with locking
of SIA clusters?

What have we learnt: the basic principles

- Progress in science is measured by the capability of understanding a number of different and apparently uncorrelated phenomena based on a reduced number of basic principles
- In the case of the behaviour of FeCr alloys, particularly under irradiation, our research has shown that three magnetism-driven basic properties of Cr in Fe seem to explain a large amount of phenomena, namely:
 - ☞ *Repulsion between Cr-Cr pairs in Fe (until screened by large concentration)*
 - ☞ *Attraction between dispersed Cr atoms and self-interstitial atoms in Fe*
 - ☞ *Repulsion between Cr precipitates and defects in Fe*
- As it often happens in science, in this case, too, the gap between stating the basic principles and applying them in a quantitative and predictive way to any complex situation remains large
- However, based on the understanding of the basic principles it is possible to provide an interpretation of experimental results and to formulate sensible hypotheses about trends to be expected

Radiation damage in FeCr alloys

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The End