EFDA
EUROPEAN FUSION DEVELOPMENT AGREEMENT

Structural Materials for Fusion Power Plants
Part II: Multi-scale Modelling Radiation Effects

Presented by J. L. Boutard [1]

[1] *EFDA CSU-Garching (Germany)*

Fusion Materials Topical group:
MAT-REMEV: Modelling Radiation Effects in EUROFER

- Co-Chairs: S. Dudarev (UKAEA), M. Rieth (FZK)
- Helsinki University: K. Nordlund, N. Juslin, C. Björkas
- VTT Finland: S. Tähtinen (VTT)
- Uppsala University: J. Wallenius, P. Olsson
- Riso National Lab: B. Singh
- UKAEA: S. Dudarev, D. Nguyen Manh, M. Lavrentiev
- SCK.CEN Mol: L. Malerba, D. Terentyev, M. Matijasevic,
- A. Almazouzi, P. Jaquet
- FZK: A. Moslang, M. Rieth, M. Klimenkov
- TU Bratislava : V. Slugen
- CRPP: R. Schaeublin, G. Lucas, A. Ramar
- CEA: F. Willaime, C. C. Fu, A. Barbu, L. Ventelon
- University Polytech. Madrid: M. Perlado
- University Alicante: M. J. Caturla, C. Ortiz
- TU Karlsruhe: D. Weygand, M. Mrovec

Fusion or Fission National Programmes:

- UK: P. Klaver (Uni Belfast), S. Roberts & M. Jenkins (Uni Oxford)
- France: D. Rodney, J. Chaussidon

Radiation Effects Modelling: The Initial Objectives of the EU Programme 2001(1)

- To study the radiation effects in the EUROFER RAFM steel
  - In the range of temperatures from RT to 550 ^{0}C
  - Up to high dose ~100dpa
  - In the presence of high concentrations of transmutation impurities (i.e. H, He)

- To Develop modelling tools and database capable of:
  - Correlation of results from:
    - The present fission reactors & spallation sources
    - The future intense fusion neutron source IFMIF
  - Extrapolation to high fluences and He & H contents of fusion reactors

- To experimentally validate the models on adequate sytems & at the relevant scale

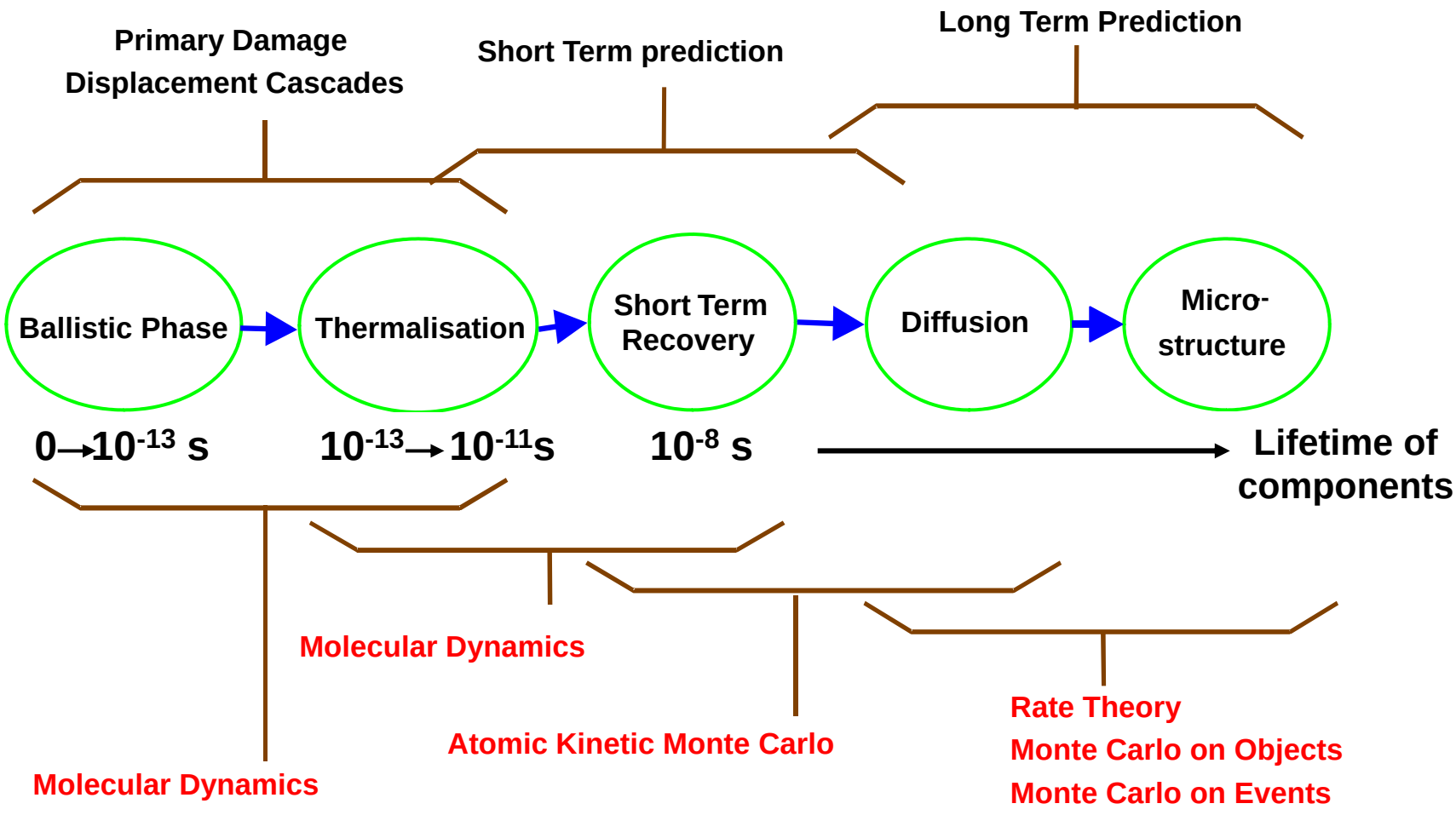
(1) M. Victoria, G. Martin and B. Singh, The Role of the Modelling Radiation Effects in metals in the EU Fusion Materials Long Term Program (2001)

Outline

- Radiation Induced Defects: Thermodynamics & Kinetics in α-Fe
- He diffusion mechanisms in Fe-C
- Phase Stability of Fe-Cr system, based on DFT
- Dynamical Properties of Dislocations in Fe and Fe-He
- Concluding remarks

Radiation Induced Defects: Thermodynamics & Kinetics in α-Fe

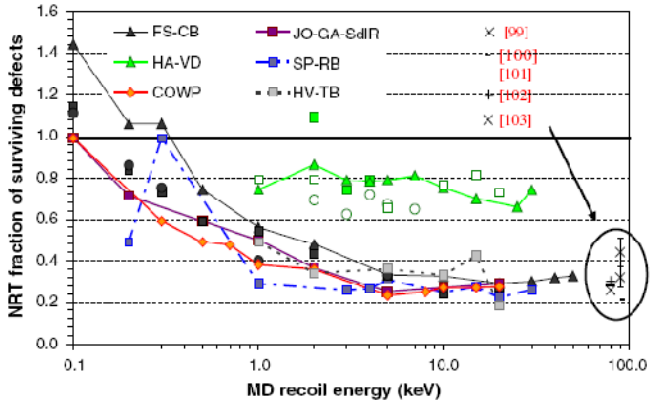
Radiation Modified Microstructure
Scale and tools for Multi-scale Modelling

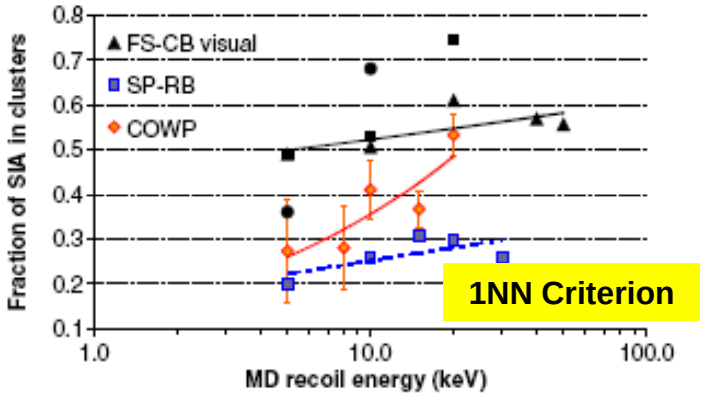


No long range strain

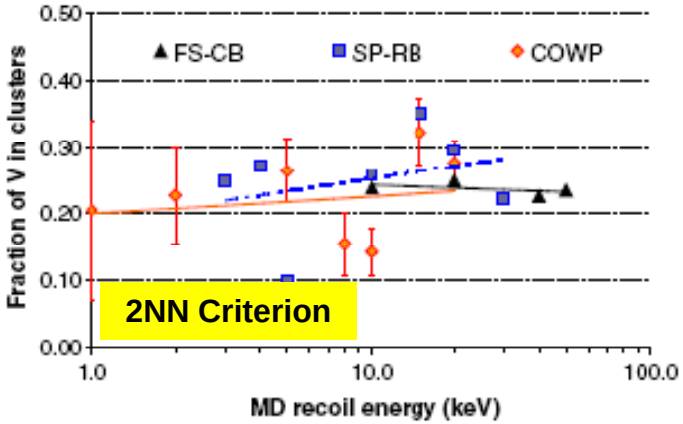
Only effect of dislocations is their bias and action as sink.

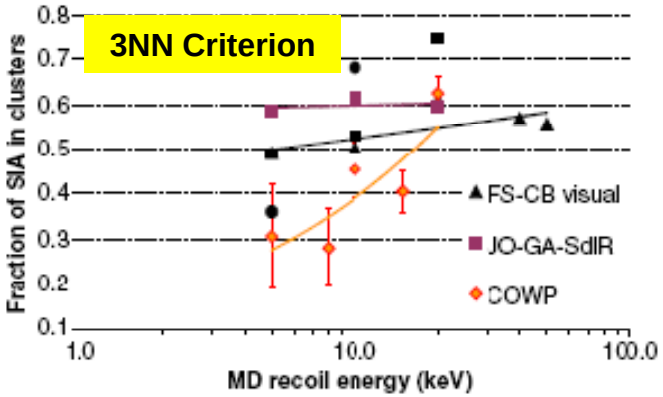
Molecular Dynamics Simulation
Production Efficiency & Fraction of Clustered Defects





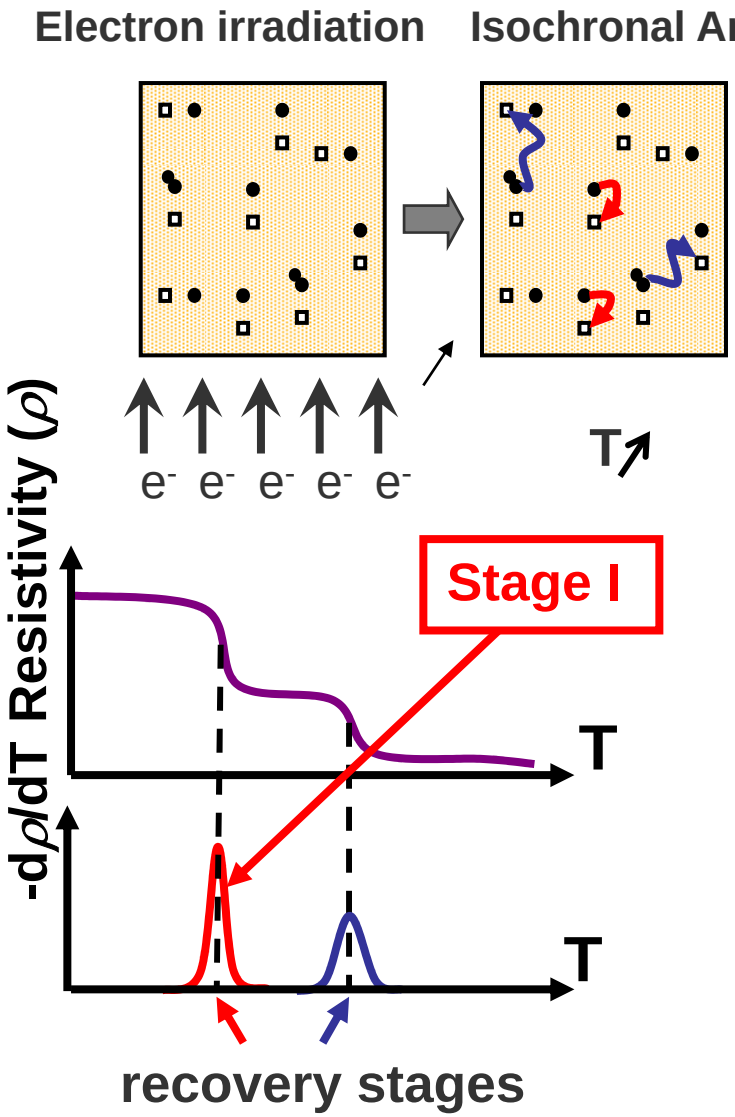
L. Malerba. J. Nucl. Mater. 351 (2006) 28-38





- **Important scattered in clustered defect fraction makes these MD simulation useless as the first block of radiation effects modelling**
  - **No convincing argument except**
  - **The inter-atomic potentials were predicting the <111> SIA as stable configuration in α-Fe**

Indirect Experimental Knowledge of Point Defect Energetics: Damage Resistivity Recovery in Pure Metals



Damage Recovery: Stage I

V: T<6K
Nb: T<6K
Ta: T<6K
Cr: T=40K
Mo: T=35K
W: T=27K

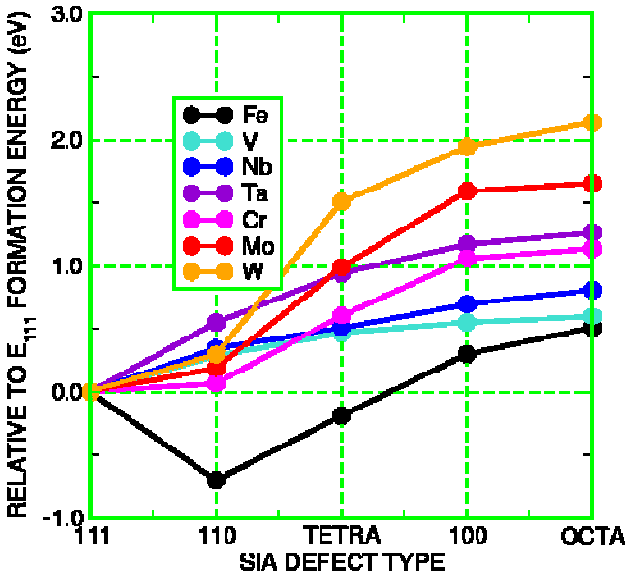
<111>
E^m ~a few 0.01eV

Fe: T=140K

<110>
E^m ~0.3-0.4 eV

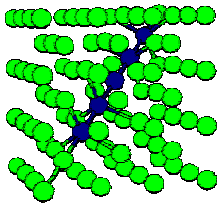
H. Schultz, Atomic Defects in Metals, Landolt-Börnstein New Series, Group III, vol. 25, Springer-Verlag Berlin, 1991, p. 115.

Self Interstitial Atoms in bcc Transition Metals: DFT Calculations



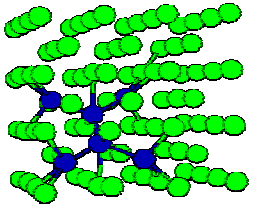
Non Magnetic

<111>

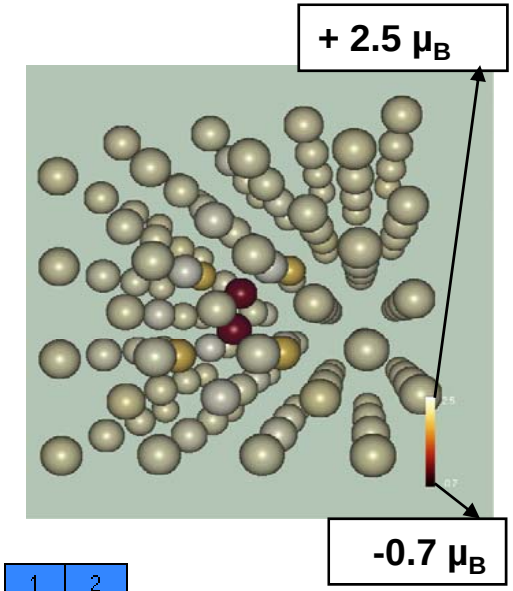


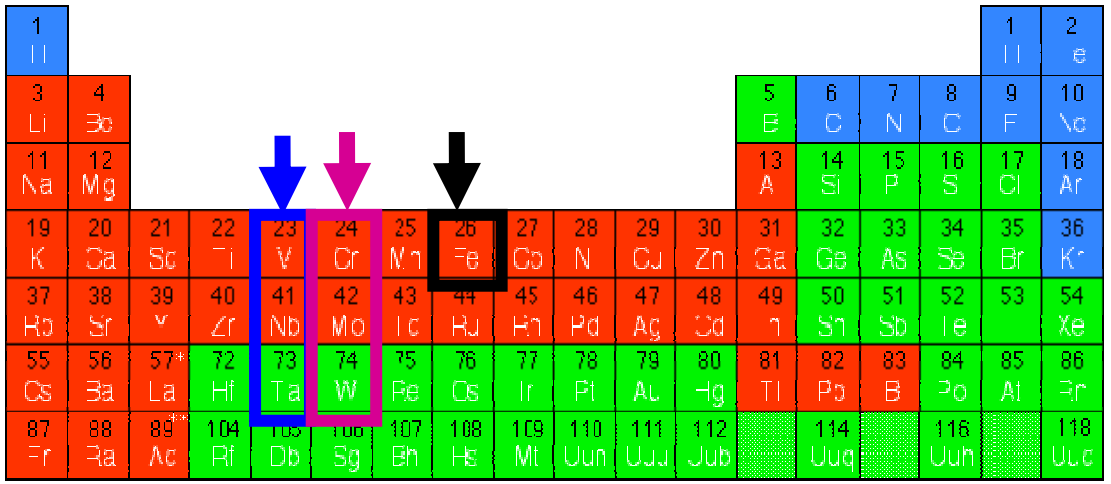
Magnetic Fe

<110>



Magnetisation Fe: <110>





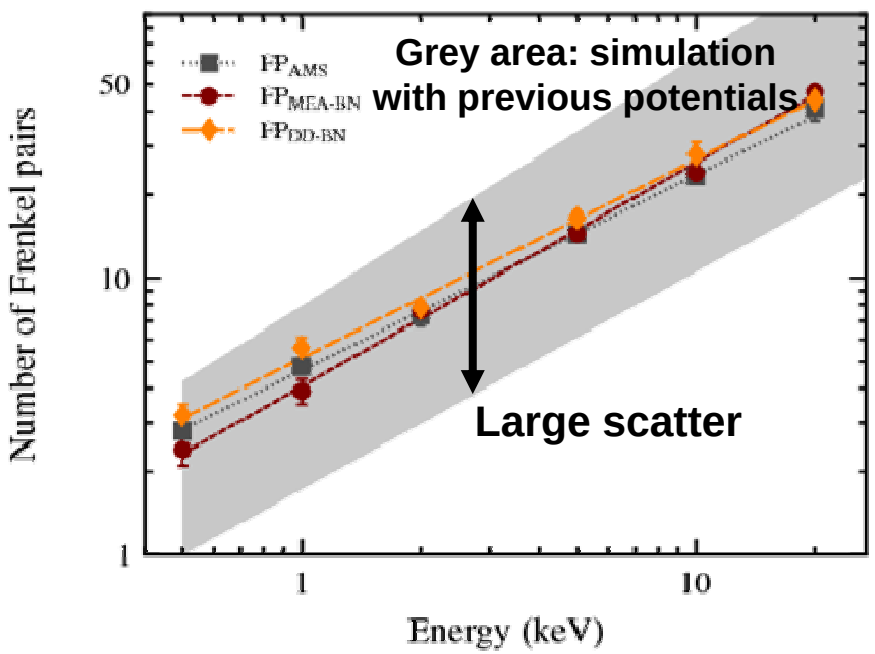
D. Nguyen-Manh, A. P.Horsfield and S. L. Dudarev Phys. Rev. B73 (2006) 20101.

Empirical Potential based on ab initio Molecular Dynamics simulation of cascades in α-Fe

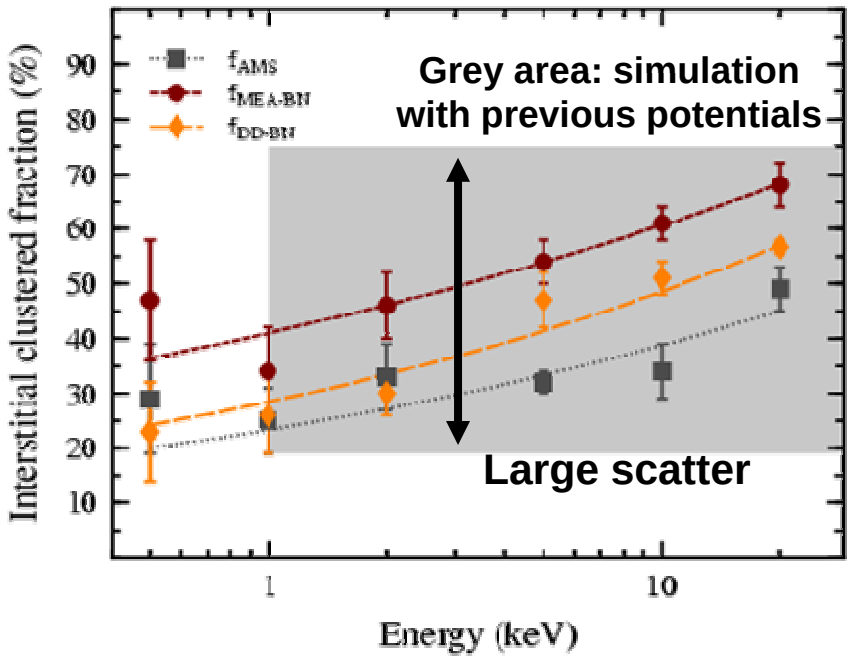
Three α-Fe Semi-Empirical potentials developed in 2006

- Based on different functional forms and physical assumptions

- Reproducing ab-initio SIA energetics: <110> SIA is the stable configuration in α-Fe



Number of Frenkel pairs
Strong reduction in the scatter



Interstitial clustered fraction
Still some scatter to understand

K. Nordlund (TEKES) to presented at ICFRM-13 Nice December 2007

Isochronal Thermal Recovery of Radiation damage in α-Fe
Ab initio based Event Kinetic Monte-Carlo

H. Schultz, Atomic Defects in Metals, Landolt-Börnstein New Series, Group III, vol. 25, Springer-Verlag Berlin, 1991, p. 115.

Takaki et al. Rad. Effects 79 (1983) 87

Damage Recovery: Stage I

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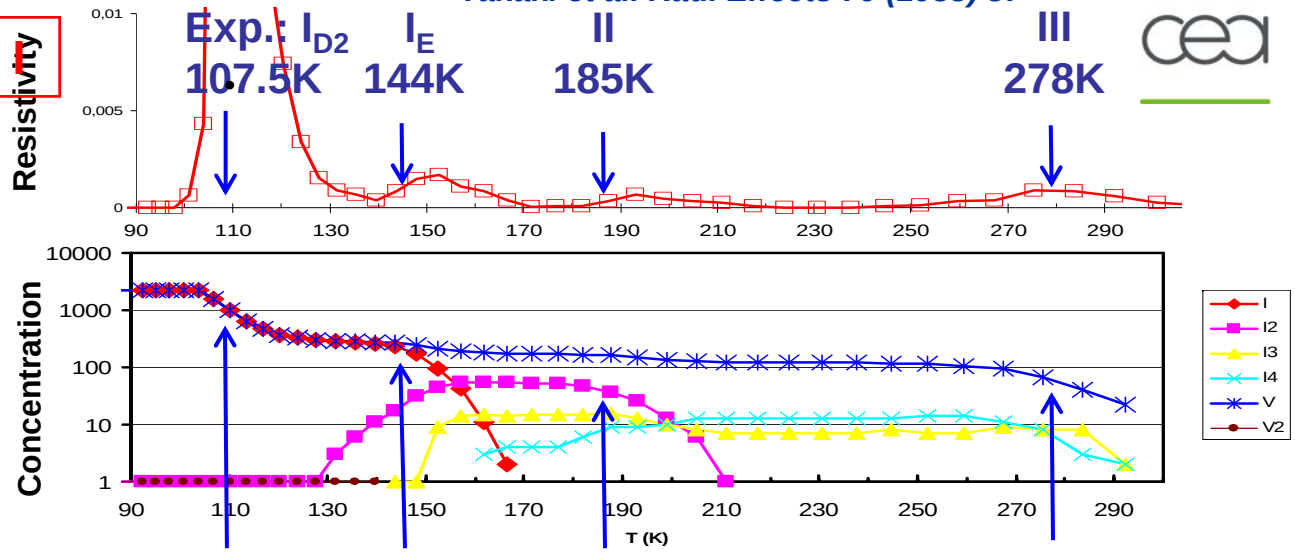
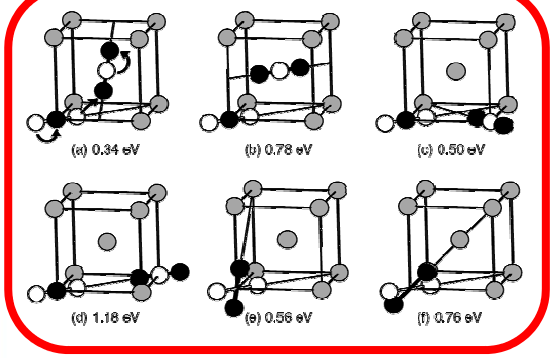


DFT: 3D Migration of SIA in α-Fe



Correlated Pairs

Interstitial Migration

Di-Interstitial Migration

Vacancy Migration

Ab initio

E^m (I) = 0.34 eV

E^m (I_2) = 0.42 eV

E^m (V) = 0.67 eV

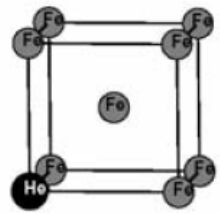
New Insights:
- I_2 and I_3 contribute to stage II
- V_2, V_3, V_4 contribute to stage (III)

Dose Effects:
- Peak shifts with dose are well reproduced
- Effect of C reasonably understood and reproduced (unpublished work)

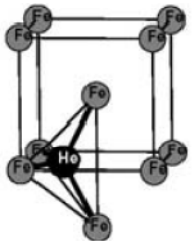
C.C. Fu, J. Dalla Torre, F. Willaime, J.L. Bocquet, A. Barbu, Nature Materials 4, 68 (2005)

He Diffusion Mechanisms in α-Fe-C

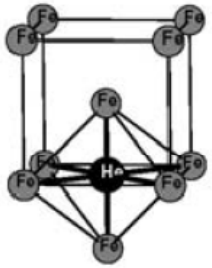
He & point defects energetics based on DFT: Solution Energy



Substitution: HeV



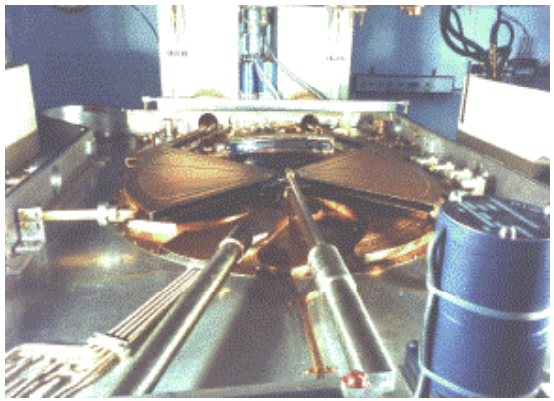
Tetrahedral: He



Octahedral: He

	HeV	He tetra	He octa
Esol(eV)	4.22	4.39	4.57

C. C. Fu and F. Willaime Phys. Rev B72 (2005) 064117.



23 MeV $^4He^{2+}$: Jülich Compact Cyclotron

Microstructure after Implantation:

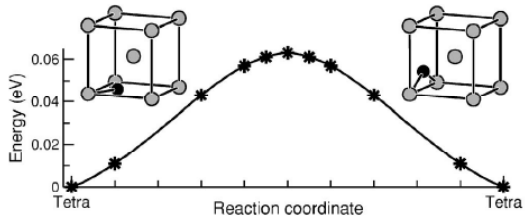
- **Frenkel Pairs**
- **He in substitution:**

He is Created as interstitial but E^m=0.06 eV so that migration is fast even at room temperature and reaction with vacancies easy

He and point defect energetics based on DFT: (2) Diffusion and Clustering with vacancies

- **Interstitial He Diffusion**

$$E^m = 0.06 \quad eV$$



- **Dissociative Diffusion Mechanism**

$$HeV \rightarrow He + V$$

$$\Delta E = E^b(He - V) = 2.20 \quad eV$$

- **Kick-out mechanism**

$$HeV + I \rightarrow He$$

$$\Delta E = E^b(He - V) - (E^f(I) + E^f(V))$$

$$\Delta E = -3.60 \quad eV$$

- **Vacancy mechanism by migration of HeV_2 Complex**

$$E^m(HeV_2) = 1.1 \quad eV$$

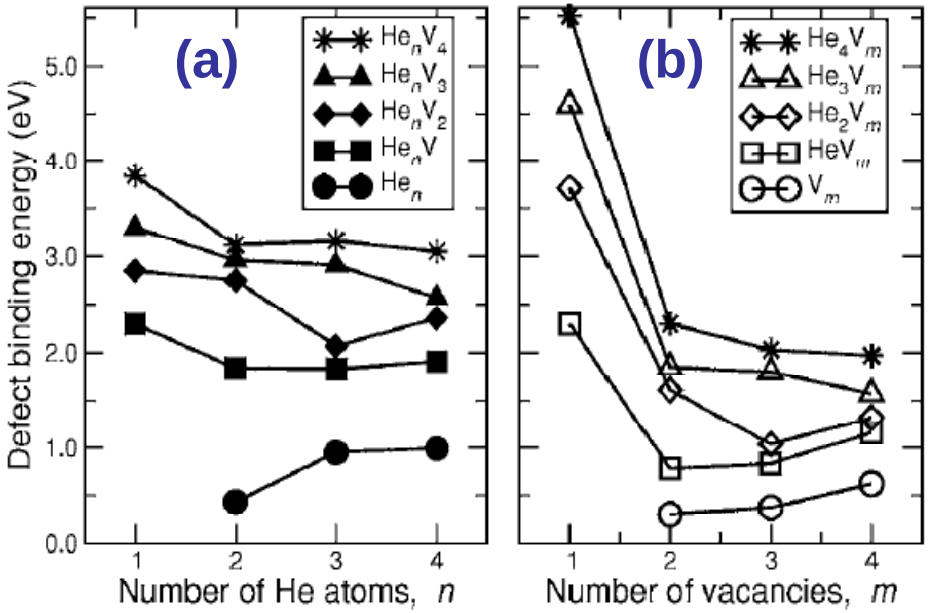
$$E^b(V - HeV) = 0.78 \quad eV$$

C.C. Fu and F. Willaime, Phys. Rev. B72, (2005) 064117.

- **Binding Energy:**

(a) He **with** $He_{m-1}V_m$

(b) V **with** He_nV_{m-1}



C. C. Fu and F. Willaime Phys. Rev B72 (2005) 064117.

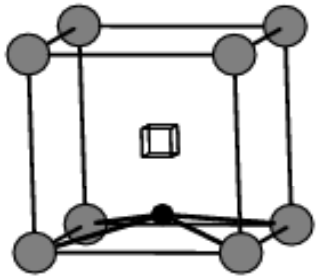
- **Mobile Defects: V, SIA & di-SIA**

$$E^m(SIA) = 0.34 \quad eV \quad E^m(di - SIA) = 0.42 \quad eV$$

$$E^m(V) = 0.97 \quad eV$$

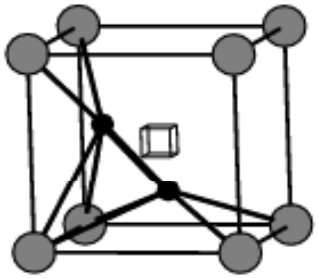
C.C. Fu et al. Nature Materials 4, 68 (2005)

Interaction of carbon with V & He-V clusters



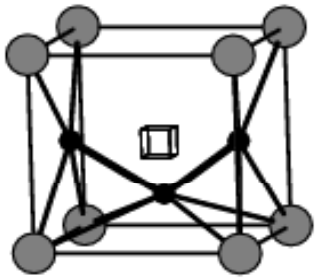
VC

$E_b^{V-C} = 0.52$ eV



VC_2

$E_b^{VC-C} = 0.89$ eV

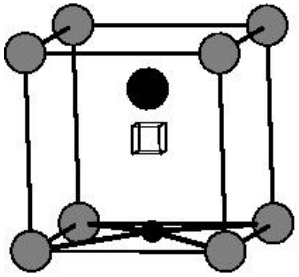


VC_3

$E_b^{VC_2-C} = 0.12$ eV

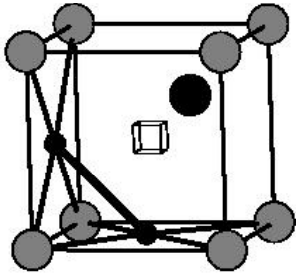
* C.C Fu et al. Sol. State Phen. **139**, 157 (2008)

Strong vacancy-carbon interaction
=> reduces the effective migration energy of vacancies



V + He → **HeV**

E_b = 2.3 eV



VC + He → **HeVC**

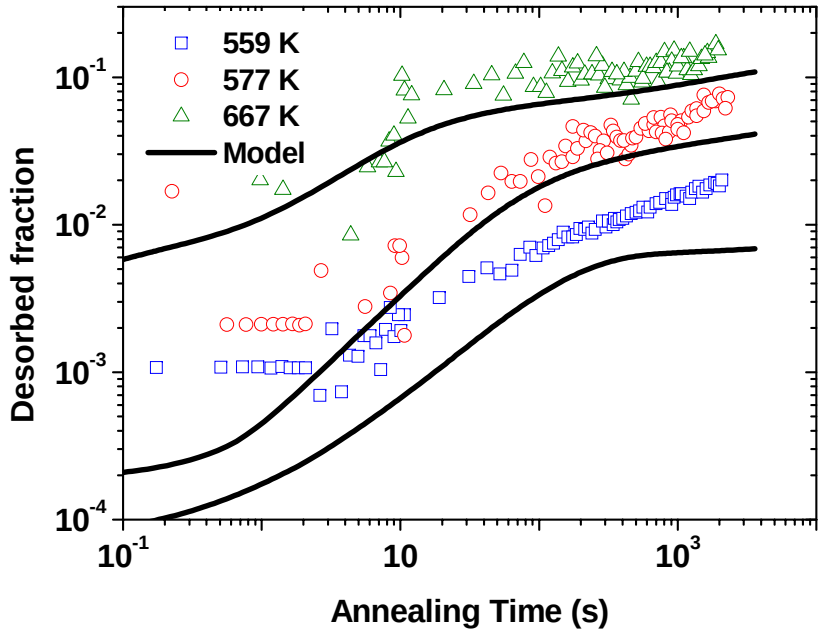
E_b = 2.09 eV

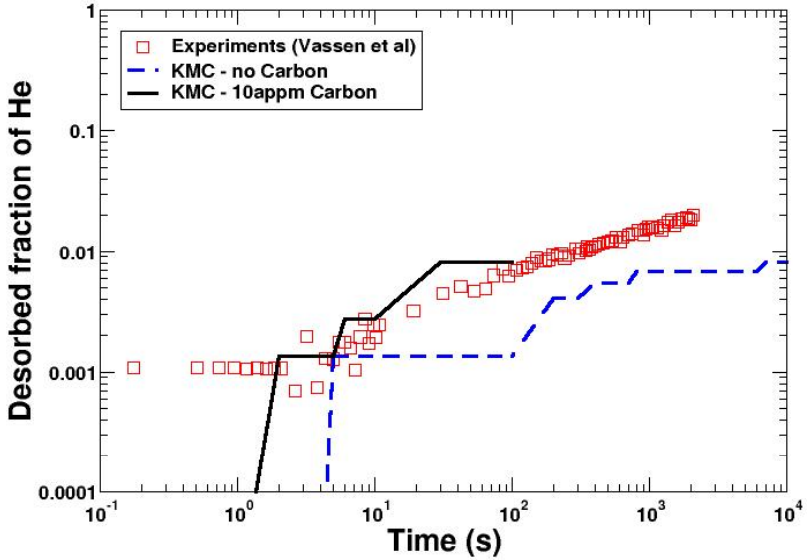
VC_2 + He → **$HeVC_2$**

E_b = 0.94 eV

Carbon reduces the He-V binding energy

Fe-C: Ab initio Kinetic Modelling of He-Desorption





- Vacancies are mainly trapped in CV and VC_2.
- Carbon traps a large amount of V, which inhibits the growth of stable He-V clusters

→ **He desorption favored.**

But there are other mechanisms also involving Helium…

1) $HeV + C_{int} \rightarrow HeVC$ and 2) $HeVC + C_{int} \rightarrow HeVC_2$ occur easily with 50 appm C

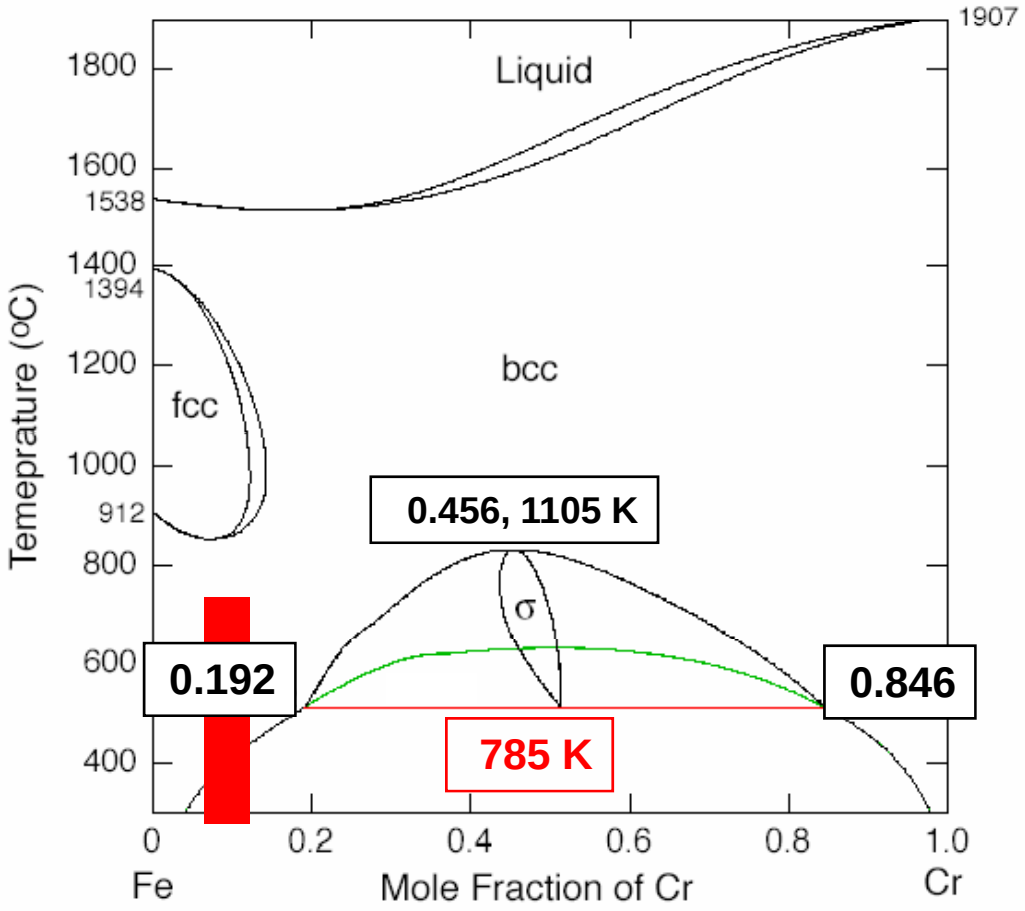
3) $HeVC_2 \rightarrow VC_2 + He_i$. $HeVC_2$ releases Helium with a low E_{diss}(1.0 eV) of $HeVC_2$ much lower than E_{diss} of HeV (2.30 eV).

→ **He desorption is enhanced.**

Universitat d'Alacant
Universidad de Alicante

Phase Stability based on DFT calculated Enthalpy of Atomic Configurations

CALPHAD Fe-Cr Phase Diagram



The important region for Fusion is the low temperature 9-14%Cr domain where

Experiments are difficult since low temperature means low time to reach equilibrium

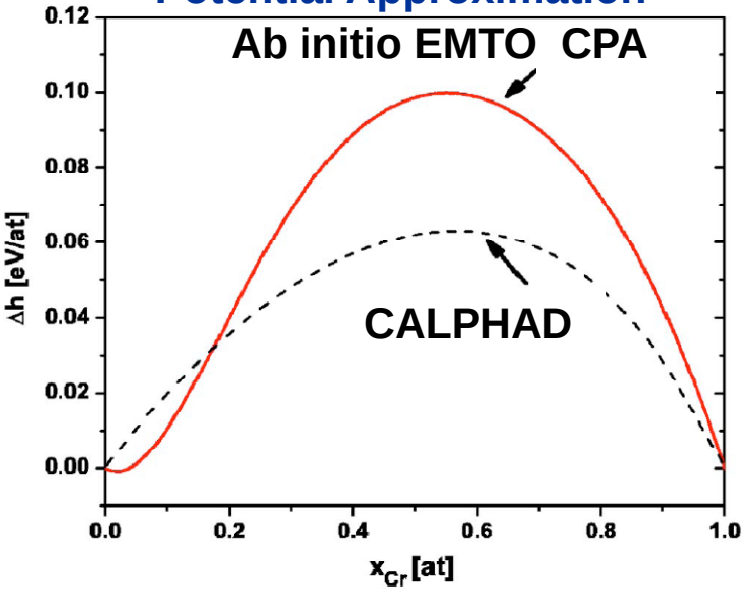
There is phase instability at lower temperature range

Non-symmetric Fe-Cr Formation Enthalpy

- **Fe-Cr System: DFT Calculation of the Formation Enthalpy**

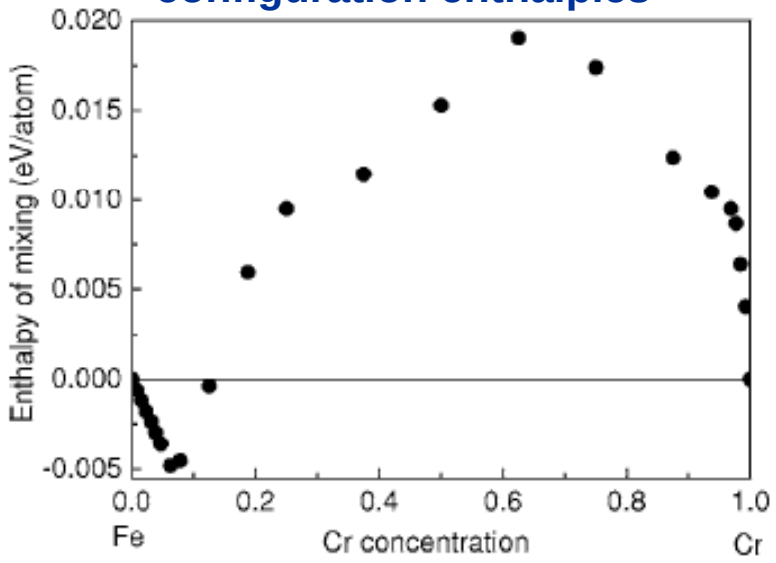
$$\Delta H_{mix} = H[(1-x)Fe + xCr] - (1-x)H_{Fe} - xH_{Cr}$$

Random Solid Solution described by Coherent Potential Approximation



P. Olsson et al. J. Nucl. Mater. 321(2003) 84-90

Minimum value obtained by Exchange Monte Carlo on a ab initio set of configuration enthalpies

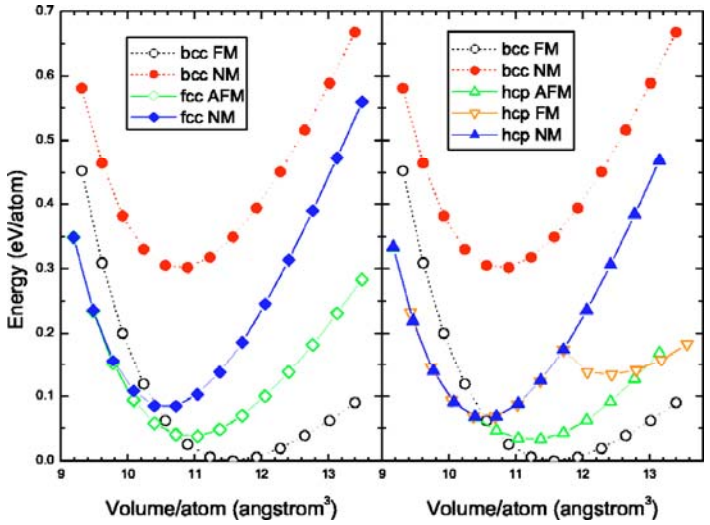


M. Yu. Lavrentyev Phys. Rev. B 75, (2007) 014208

- **Consequences of the sign change in the Fe rich domain at 0K: Cr is soluble in Fe &above ~6%Cr the system unmix into Cr and Fe- ~6%Cr alloy**
- **Present CALPHAD Fe-Cr phase diagram does not reproduce this behaviour as the Formation Enthalpy does not change Sign (see Part III)**

Phase Stability of Fe-Cr: Essential Role of Magnetism

- **Fe: Large Ferromagnetic Ordering Energy ~0.3 eV/atom. Stabilisation of the ferromagnetic bcc crystalline structure versus:**
  - **NM fcc structure: high temperature crystalline structure of Fe**
  - **NM hcp structure: structure of the isovalent 4d (Ru) and 5d (Os)**



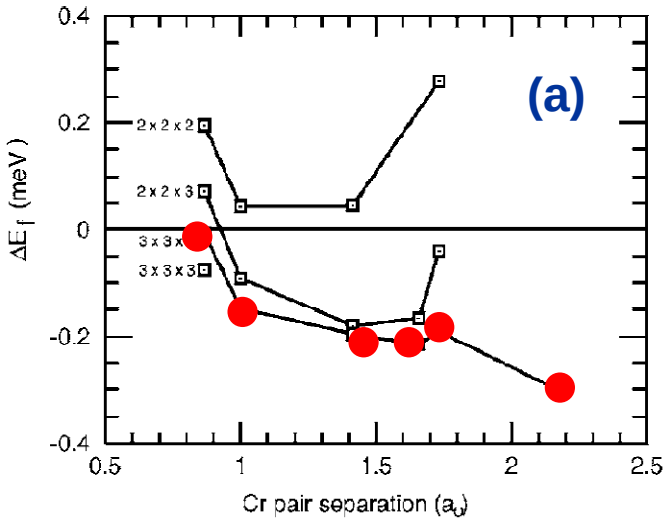
G. Liu, D. Nguyen-Manh, B.G. Liu and D. G. Pettifor Phys. Rev. B71, (2005)174115

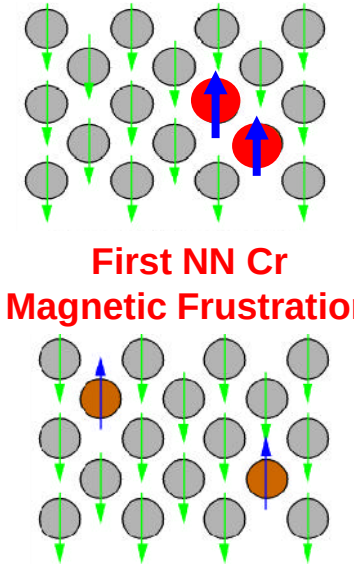
- **Cr: spin density wave or anti-ferromagnetic ground state are matter of debate, with very small energy difference. Metallic impurities (Mn) are reported to stabilize the Anti-Ferromagnetic Magnetic (AFM) order:**
  - **The AFM-ordering energy is weak ~ 0.014 eV/atom.**

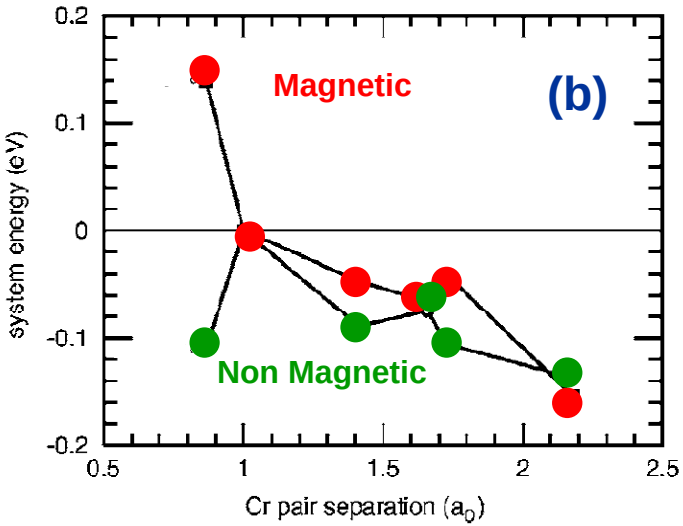
T. P. C. Klave, R. Drautz and M. W. Finnis Phys. Rev. B74 (2006) 094435.
R. Hafner, D. Spisák, R. lorentz and J,. Hafner J. Phys.: Condens. Matter 13 (2001) L239-L247.

Cr-Solution & Cr-Cr interaction in the Fe-Cr System

- **Solution energy of Cr in α-Fe is slightly negative: $\Delta E^{sol} \sim -3$ meV/atom**







(a) For a system with two Cr the highest energy is when both Cr are Nearest Neighbours (NN) and the system energy decreases monotonically with Cr separation by at least 0.3 eV:

Such an energetics maximize Cr-Cr separations favours ordering and the existence of solid solution and ordering

(b) The nearest neighbour Cr-Cr repulsion is due to magnetism as it has completely changed in the Non Magnetic (NM) case.

Magnetic frustration is governing the solubility of Cr in Fe in the Fe-rich domain

T. P. C. Klaver, R. Drautz and M. W. Finnis Phys. Rev. B74 (2006) 094435.

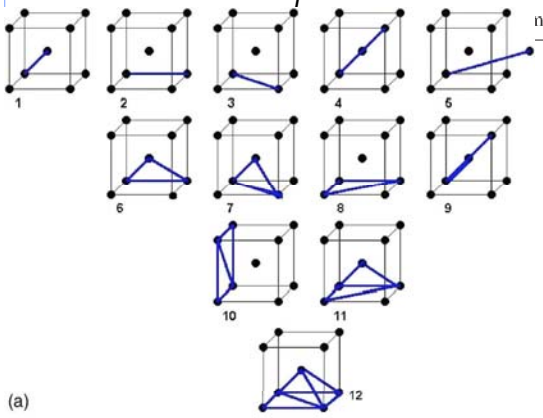
Phase Stability in the Fe-Cr systm (MCX &CE)
(1) Cluster Expansion (CE) based on DFT calculation

- **The Mixing enthalpy calculated ab initio can be mapped exactly onto Ising-like Hamiltonian:**
- **Where :**

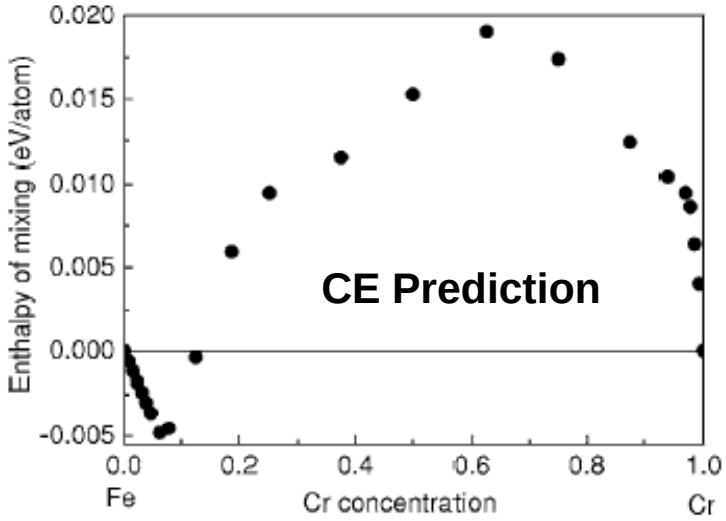
$$E^{CE} = J_0 + \sum_{sites} J_i \sigma_i + \sum_{pairs} J_{ij} \sigma_i \sigma_j + \sum_{triplets} J_{ijk} \sigma_i \sigma_j \sigma_k + \ldots$$

  - $J_i \quad J_{ij} \quad J_{ijk}$ are an infinite set of effective interaction independent of the atom occupying the site I, j or k
  - is equal to 1 if the site i is occupied by a Fe atom
  - σ_i is equal to -1 if the site I is occupied by a Cr atom

σ_i



nber of atoms in cluster	CE coefficients (meV)
2	(1) −46.18 (NN)
	(2) 0.00039 (NNN)
	(3) 0.001 (3rd NN)
	(4) 2.35 (4th NN)
	(5) 2.85 (5th NN)
3	(6) −0.46
	(7) 1.52
	(8) −2.62
	(9) 6.66
4	(10) −4.95
	(11) 2.49
5	(12) 5.53



With 12 clusters and CE J coefficients independent of the occupancy of the crystalline site:

DFT formation enthalpies (4x4x4 supercell) of 74 atomic configurations are reproduced with a predictive error ~7 meV

M. Yu. Lavrentiev, R. Drautz, D. Nguyen-Manh, T.P.C. Klaverand S.L. Dudarev Phys. Rev.B75 (2007) 014208

Phase Stability in the Fe-Cr system (MCX & CE)
(2) Exchange Monte Carlo (MCX) based on Cluster Expansion (CE)

- **Exchange Monte Carlo (MCX) allows:**
  - sampling the various configurations in system where configuration disorder is important like in Fe-Cr and
  - calculating easily enthalpies and variation of Gibbs free energy at thermal equilibrium
- **A random exchange between the different atoms of a pair is proposed. The decision whether to accept or to reject the move is made according the Metropolis scheme:**
  - If the induced energy change ΔU is negative the change is accepted,
  - if ΔU is positive the exchange is accepted with if the probability

$$P = \exp(-\Delta U / kT) > r$$

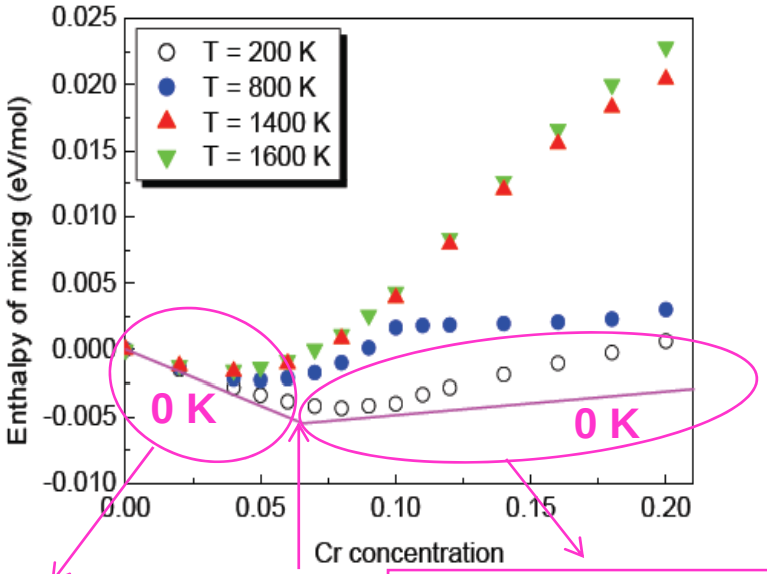
r is a random figure between 0 and 1

- **System handled can have a few hundreds of thousands of atoms:**
  - 40x40x40 bcc units cells (128,000 atoms), 60x60x60 unit cells 432,000 atoms or 80x80x80 unit cells (1,024,000 atoms)
  - with for each run a total of ~10^8 exchanges
- **Mixing enthalpy versus T and Cr content**
- **Chemical potentials in the semi-grand canonical ensemble**
- **Clustering and Ordering behaviour**

Phase stability in the Fe-Cr system (MCX & CE)
(3) Enthalpy of mixing and clustering

One large cluster

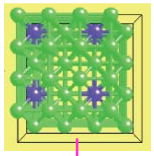
10 %Cr, 0K



No clustering

10 %Cr, 800K

Solid Solution Fe-Cr



Unmixing into Fe-6.25%Cr and Cr phase

Clustering

10 %Cr, 200 K

Ordered Compound Fe-6.25%Cr
8 Cr atoms in the 4x4x4 super-cell (128 atoms)
Cr are not closer than 6th NN

M. Yu. Lavrentiev et al.Phys. Rev.B75 (2007) 014208

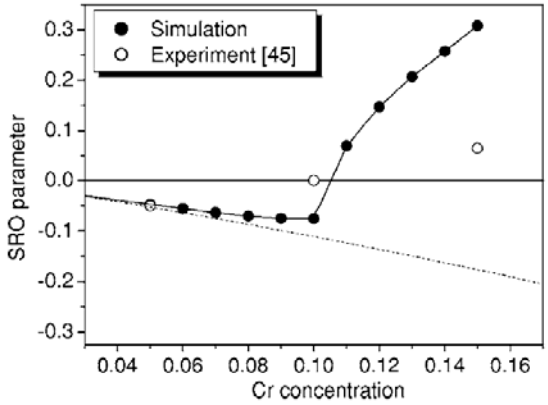
Clustering

11 %Cr, 800K

Comparison with experimental data: Short Range Order inversion in Fe-Cr

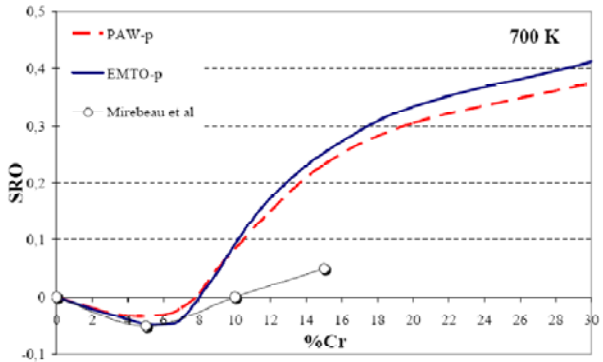
- **Short Range Order**
  - Described by the Warren-Cowley parameter $\alpha_n(x) = 1 - \frac{P_n^{Cr-Fe}}{1-x}$
  - P_n^{Cr-Fe} Is the conditional probability of finding Fe atom in the Nth coordination sphere of a Cr atom
  - If no Short Range Ordering: $P_n^{Cr-Fe} = 1-x$ therefore $\alpha_n(x) = 0$
  - If Cr clustering: $P_n^{Cr-Fe} < 1-x$ therefore $\alpha_n(x) > 0$
  - If Cr ordering: $P_n^{Cr-Fe} > 1-x$ therefore $\alpha_n(x) < 0$
- **Diffuse neutron scattering & electrical resistivity measurements showed that the SRO parameter change sign at 705 K around 10% Cr (*)**

Simulation CE+MCX



M. Yu. Lavrentiev et al.Phys. Rev.B75 (2007) 014208

Simulation 2b-EP+kMC

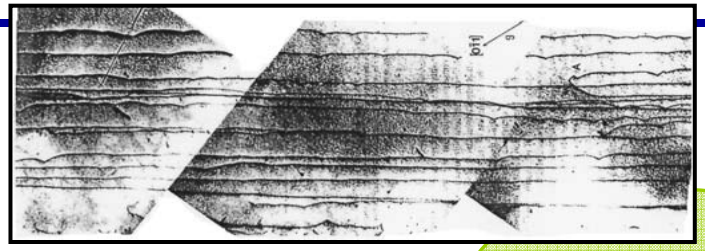


P.Olsson, K. Nordlund and al.

(*) I. Mirebeau, M. Hennion and G. Parette Phys. Rev. Lett. 53 (1983) 2351.

Modelling Dynamical Properties of Dislocations

Multiscale modeling of Dislocation Coupling with experiments



Time

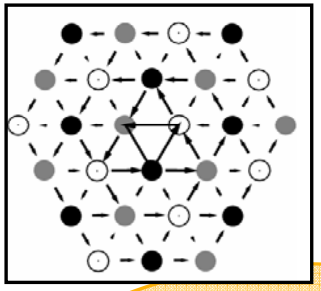
100 ps

1 ps

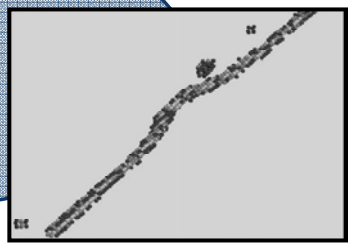
Experiments

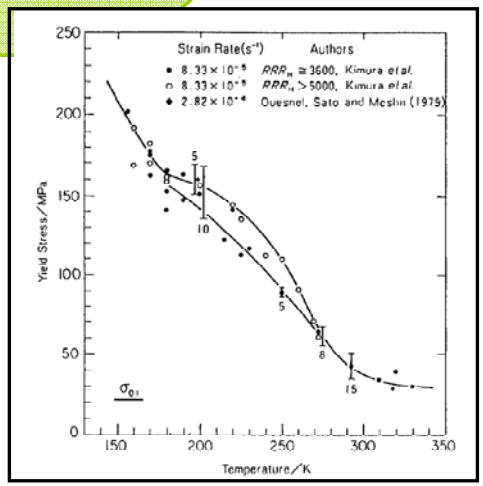
Dislocation Dynamics

- Perfect dislocations
- T = 0 K
- σ = 0



Molecular dynamics
Empirical potentials





Ab initio
Electronic structure calculations

- Dislocations with kinks
- T ≠ 0 K
- σ ≠ 0

10^2 atoms

10^6 atoms

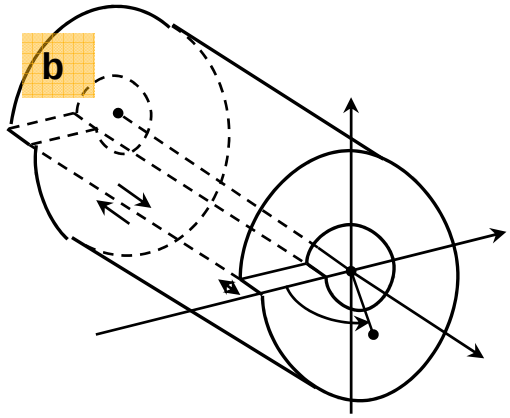
System size

After F. Willaime SRMP CEA/Saclay

Dislocations in bcc metals Elasticity Theory (1)

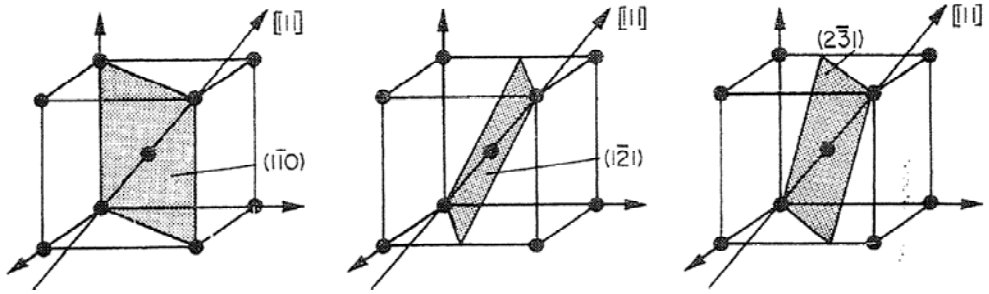
Screw dislocation:

b is parallel to the dislocation line



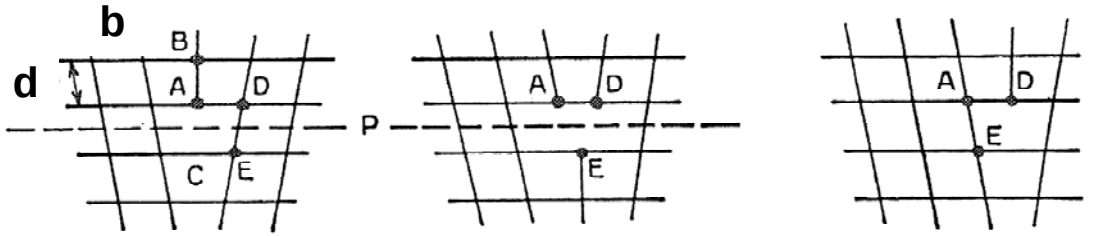
Geometry and Crystallography

- **The dislocation line separates two parts of the crystal (i) one has glided (ii) the other has not.**
- **The glide is defined in direction and value by the Bürgers vector b equal to a/2<111>**
- **b can belong two three planes (110), (120) and (231), which are a priori possible glide planes**



Peierls Barrier or Peierls Nabarro stress

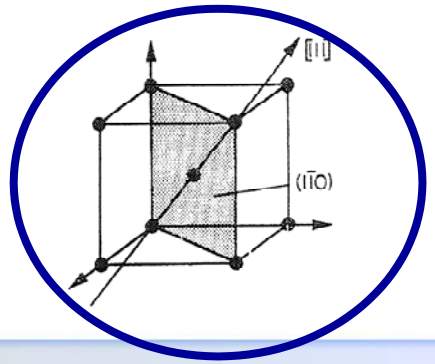
To move a dislocation as a whole from the equilibrium A to the next one C to overcome an enthalpy of activation per unit line ΔW or a critical stress σ_{PN} characteristic of the position B



A B C

$$\Delta W = \frac{\mu b^2}{2\pi K}\exp(-\frac{2\pi}{K}\frac{d}{b}) \qquad \sigma_{PN} = \frac{2\mu}{K}\exp(-\frac{2\pi}{K}\frac{d}{b})$$

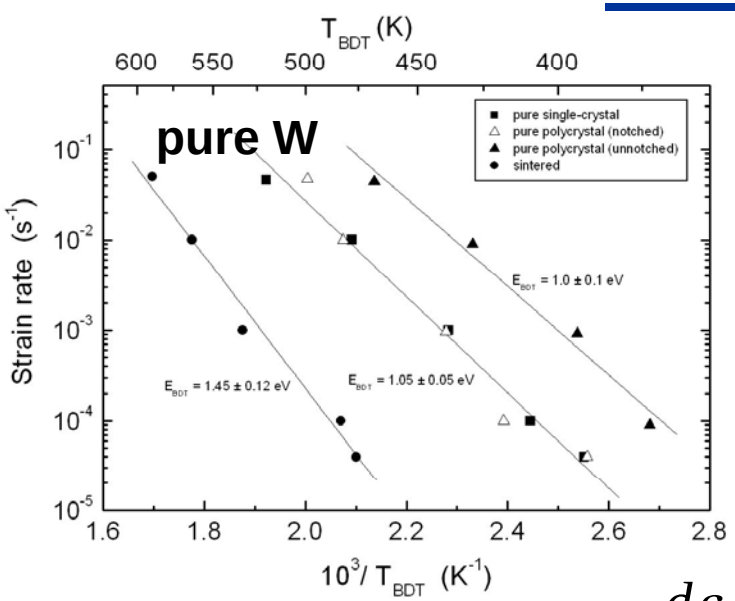
The a/2 {110} glide system is the most favourable in agreement with experimental observation in bcc Fe [a]



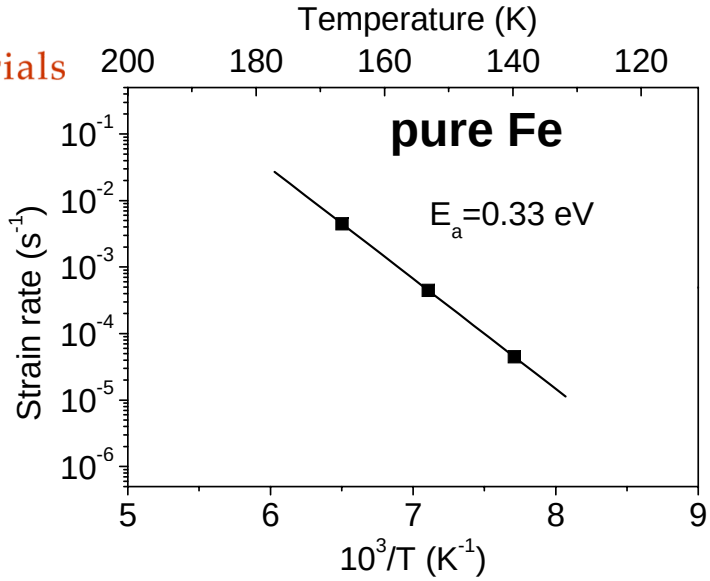
h k l	110	121	231
ΔW in meV per b	1.1	24	104
σ_{PN} in GPa	0.14	3.2	14

[a] W.A Spitzig and S. A. Keh, Acta Metall. 18 (1970)611

Dislocation Mobility and Ductile-Brittle Transition (DBT) Temperature



OxfordMaterials

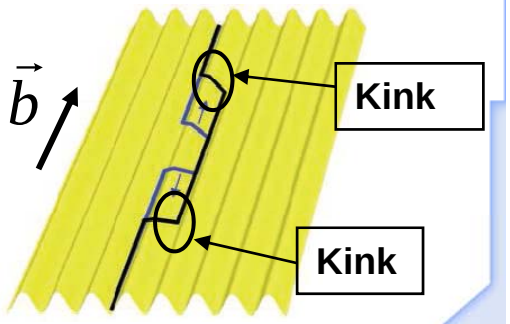


$$\frac{d\varepsilon}{dt} = A\exp(-\frac{\Delta H_{DBT}}{k.T_{DBT}})$$

ΔH_{DBT} is equal to the activation energy of the yield strength

$$\Delta H_{DBT} = \Delta H_d = H^{formation}_{double.kink} - \Omega.\sigma \approx 0.5 H^{formation}_{double.kink}$$

		Fe	W
H (kink-pair)	eV	0.8	2
ΔH_{DBT}	eV	0.2 to 0.3	1.05
$T_{DBT}(10^{-3}\ s^{-1})$	K	150	475-525

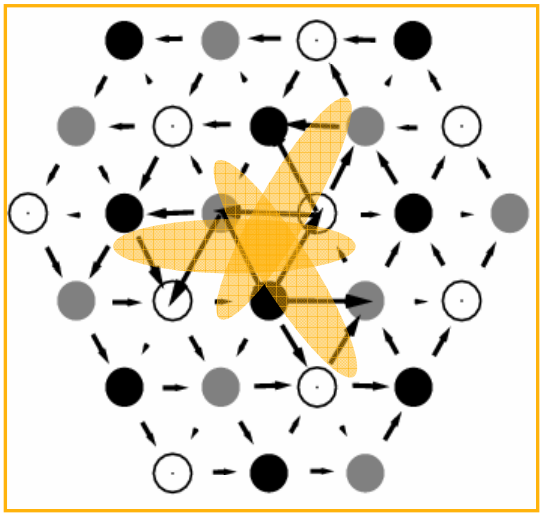


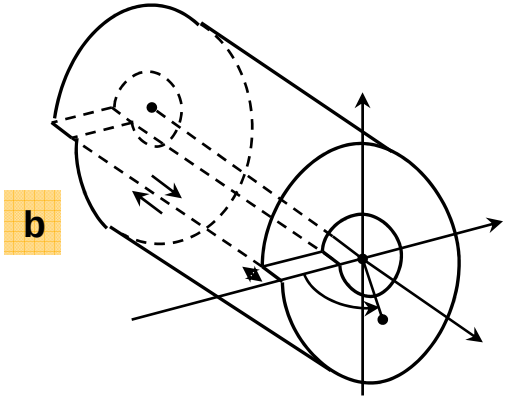
A. Giannattasio, M. Tanaka, T. D. Joseph and S. G. Roberts Phys. Scripta T128 (2007)87-90

Core structure of <111> screw dislocations in bcc metals

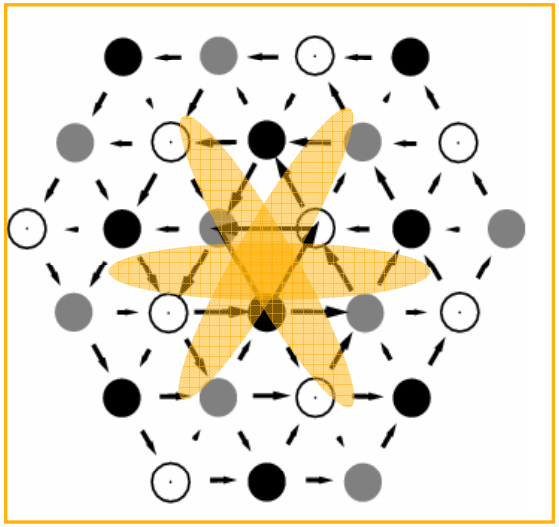
Lisa Ventelon & F. Willaime Invited talk ICFRM-13 Dec2007 Nice (F)

Degenerate core





Non-degenerate core



- Pair potentials (Vitek, '70)
- For bcc Fe:
  - Dudarev-Derlet (J. Phys. Cond. Mat. 2005)
  - Ackland (Phil. Mag.1997)

- DFT in V, Ta, Nb, Cr, Mo, W and Fe
- Mendelev potential in Fe (Phil. Mag. 2003)

Molecular Simulation of Fe screw dislocation with degenerate core : a/2 {112} is the glide system at odds with experimental results

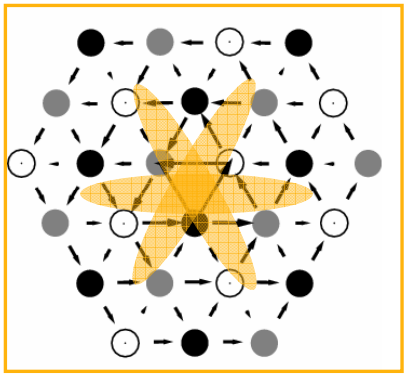
J. Marian, W. Cai and V. Bulatov Nature Materials, Vol 3, March 2004, 158-163

Screw Dislocation in bcc Fe
(3) DFT calculation of Peierls Barrier

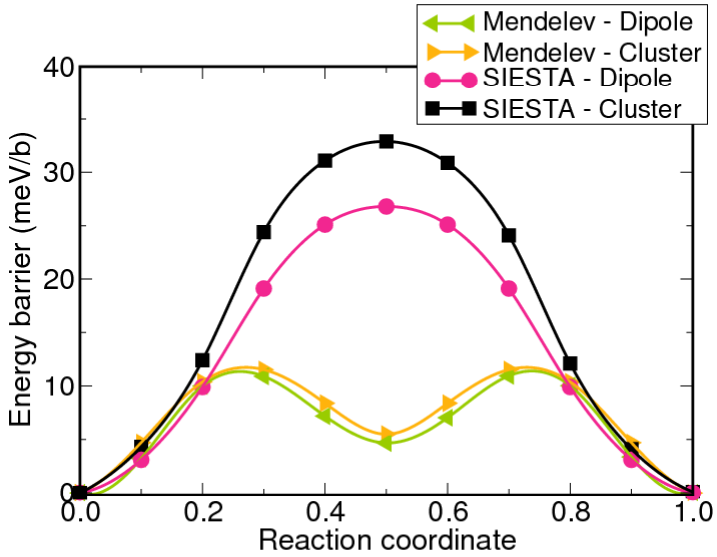
Lisa Ventelon & F. Willaime Invited talk ICFRM-13 Dec2007 Nice (F)

- **Energy Barrier of a Screw Dislocation calculated ab initio with SIESTA and via MD with the Mendelev Empirical Potential [*M. I. Mendelev et al. Phil. Mag.83 (2003) 3977*]**

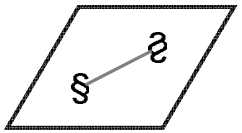
Non-degenerate core: MD & SIESTA



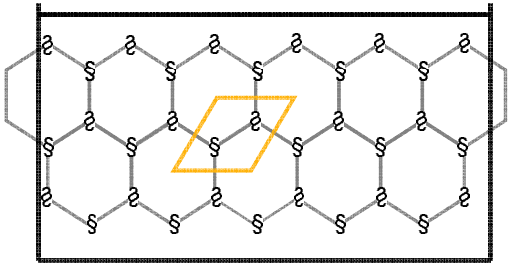
In agreement with other DFT calculations on bcc Fe by:
S. L. Frederiksen and K.W. Jacobsen Phil. Mag. 83 (2003)365.



- **Dipole Method as rationalized by Cai & Bulatov**

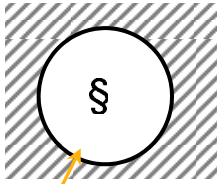


Unit cell

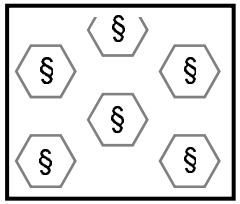


with Periodic Boundary Conditions

- **Cluster Method similar to Woodward et al.**



Unit Cell
Outer layer fixed to elastic displacement field



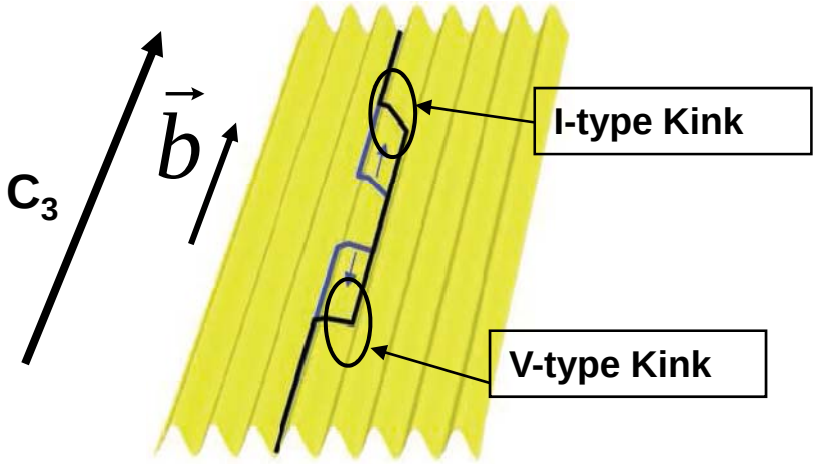
with Periodic Boundary Conditions

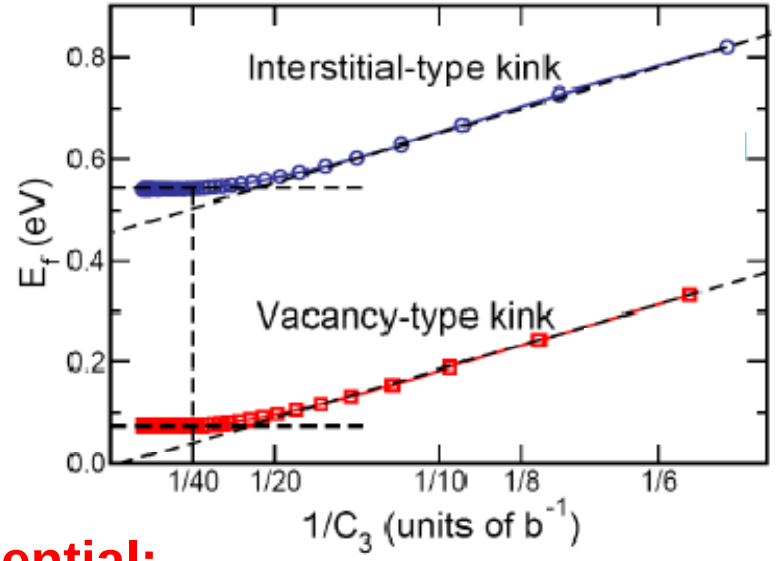
Activity 4: Screw Dislocation at Low Temperature in α-Fe: (2) Kink Formation Energy

Development of a New Procedure for:

Dislocation Line Arrangement & Boundary Conditions to handle one type of kink V-or- I

Feasibility with Empirical Potential





Empirical Potential:

Feasibility & Convergence demonstrated for long enough dislocation line.

Preliminary DFT results:

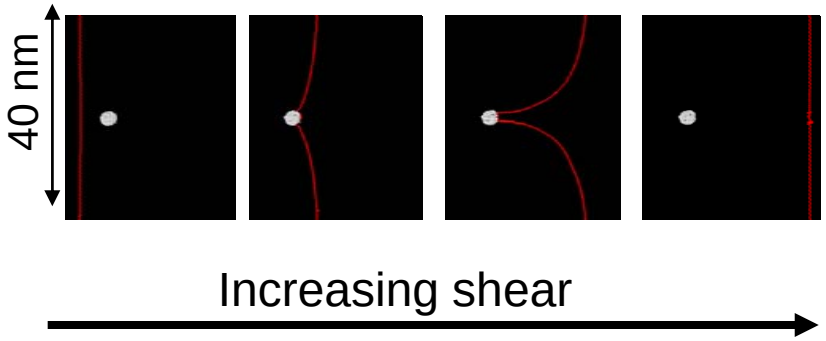
Calculation achieved with 63 atoms along the dislocation line,

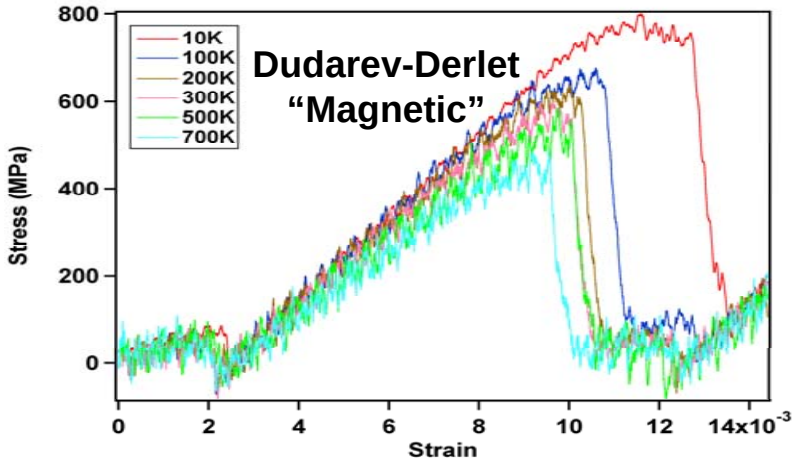
Convergence obtained with 135 atoms.

Unpublished Work by L. Ventelon & F.Willaime

Dynamical Properties of Dislocation: MD simulation of Hardening induced by He, and He-V-Clusters

- **Obstacle forces: 2nm void**





- **Molecular Dynamic Simulation**
  - **Strain Controlled : 3.10^7 s^{-1} (60 m/s)**
  - **T: 10, 100, 200, 300, 500, 700 K**
  - **Simulation cell: 14 nm x 20nm x 20 nm**

- **Obstacle strength ranking**
  - **He atom: negligible**
  - **Void : strong obstacle**
  - **He-V cluster:**
    - **Similar to voids: He/V<5**
    - **Stronger than void: He/V>5**

Robin Schaeublin et al. CRRP-EPFL (CH)

Conclusion

Thank you for your Attention

Comptes Rendus Physique

"Materials Subjected

to Fast Neutron Irradiation"

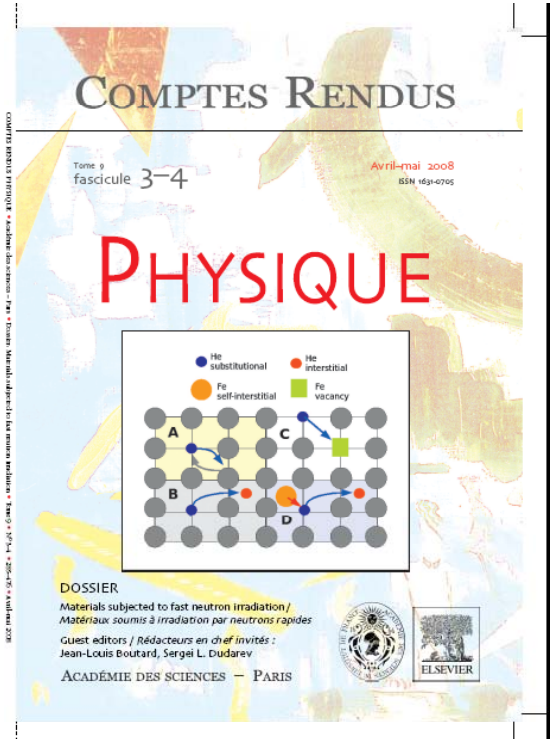
Volume 9, nº 3-4, April-May 2008

Elsevier Publishers

(online on ScienceDirect)

Guest Editors:

J. L. Boutard, S. L. Dudarev



Thank you for your Attention