The Abdus Salam
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Primary damage in bcc and fcc metals

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Joint Advanced Workshop on Multiscale Modelling for Characterization and Basic Understanding of Radiation Damage Mechanisms in Materials
International Centre for Theoretical Physics and International Atomic Energy Agency
Trieste, Italy, 12-23 April, 2010

Primary damage in bcc and fcc metals

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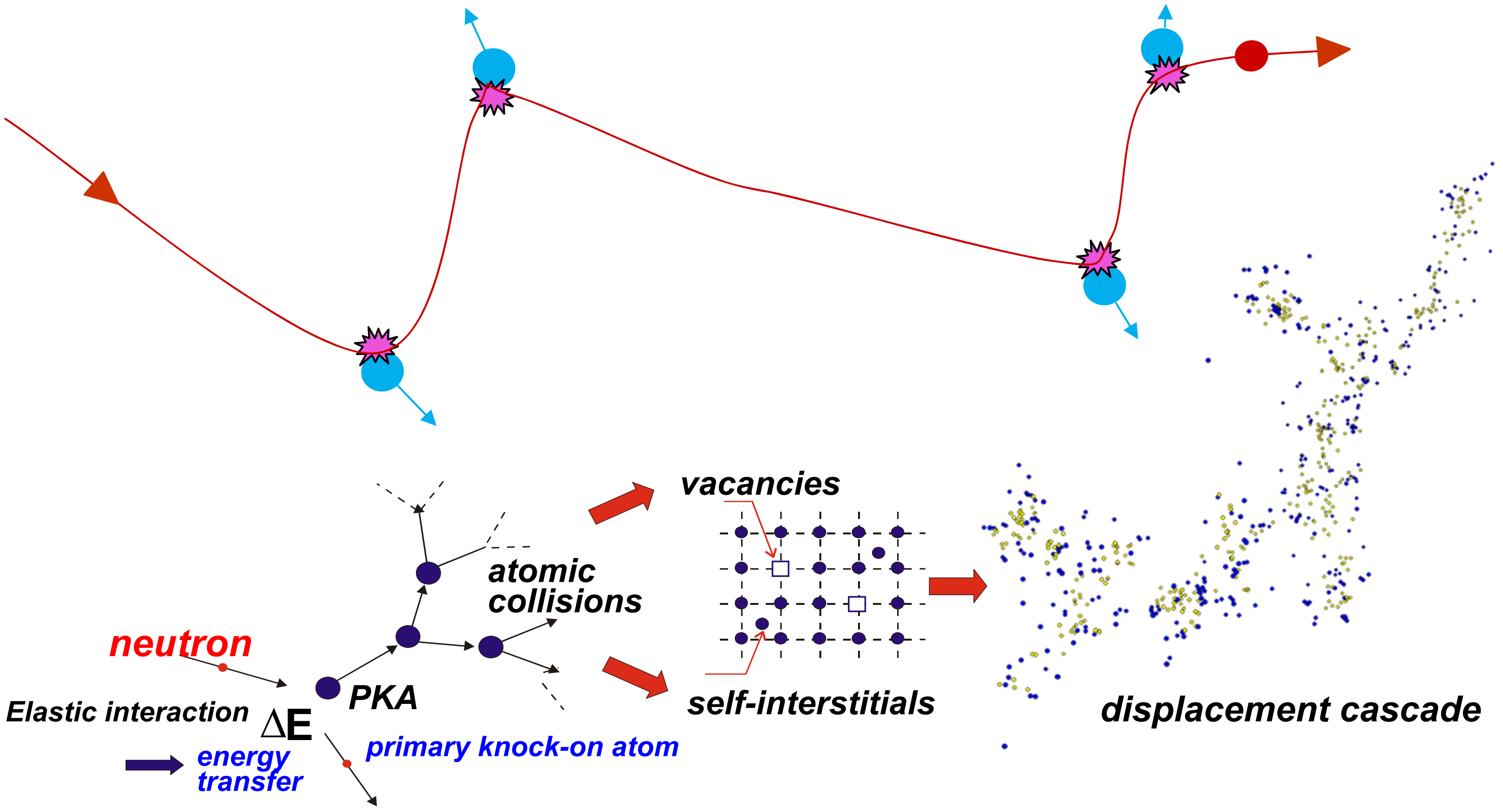
… It all starts with a neutron hitting an atom …

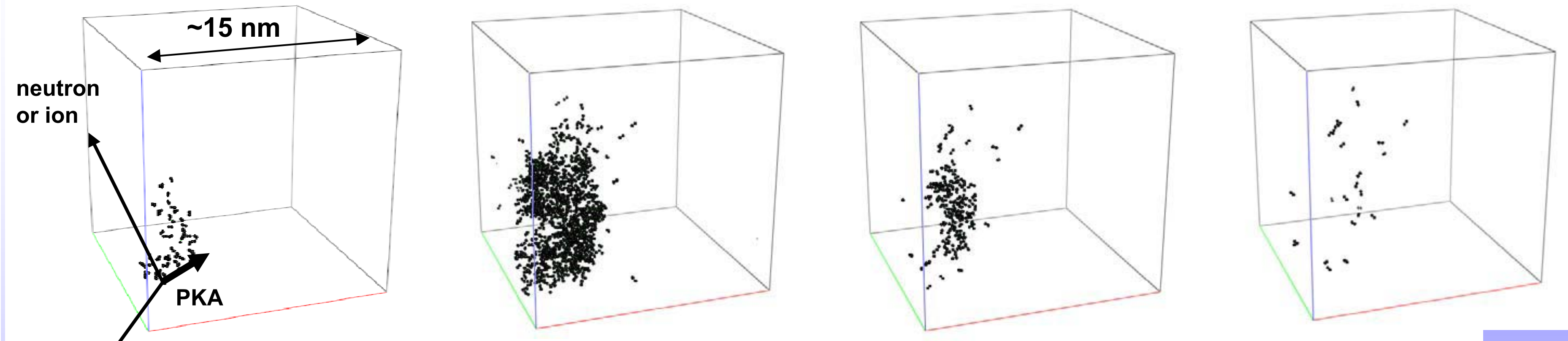
Neutrons = uncharged particles ⇒ can travel long distances in matter

When reacting with nuclei of atoms they can produce

- Activation
- Transmutation
- Displacement damage (elastic collisions)



A closer look at the cascade phases

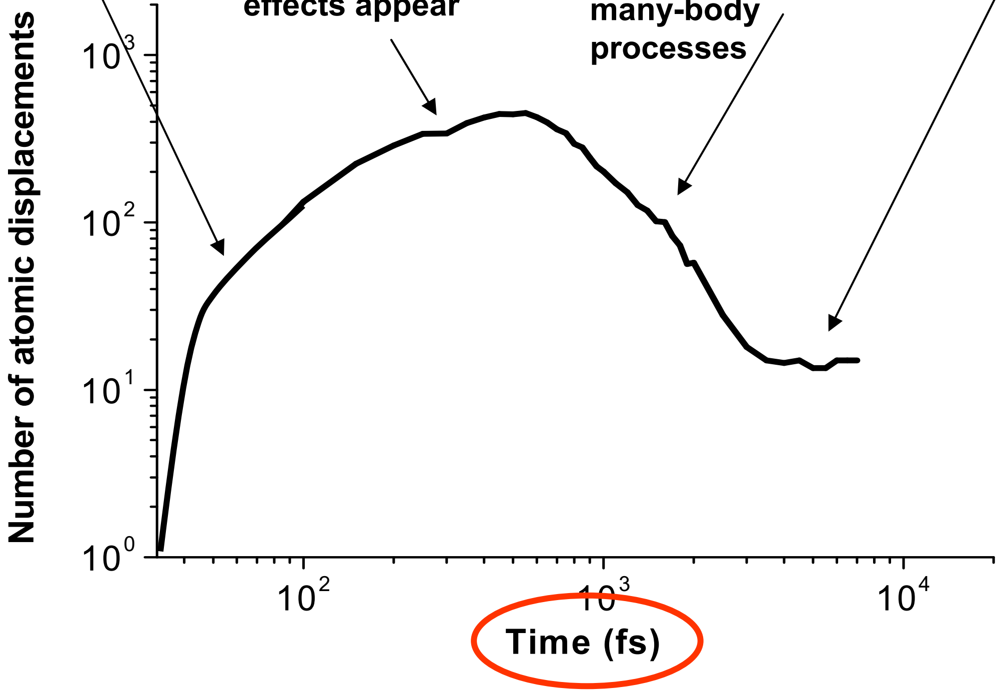


Ballistic phase: atoms behave like colliding hard spheres

Thermal spike: local temperature rises, collective effects appear

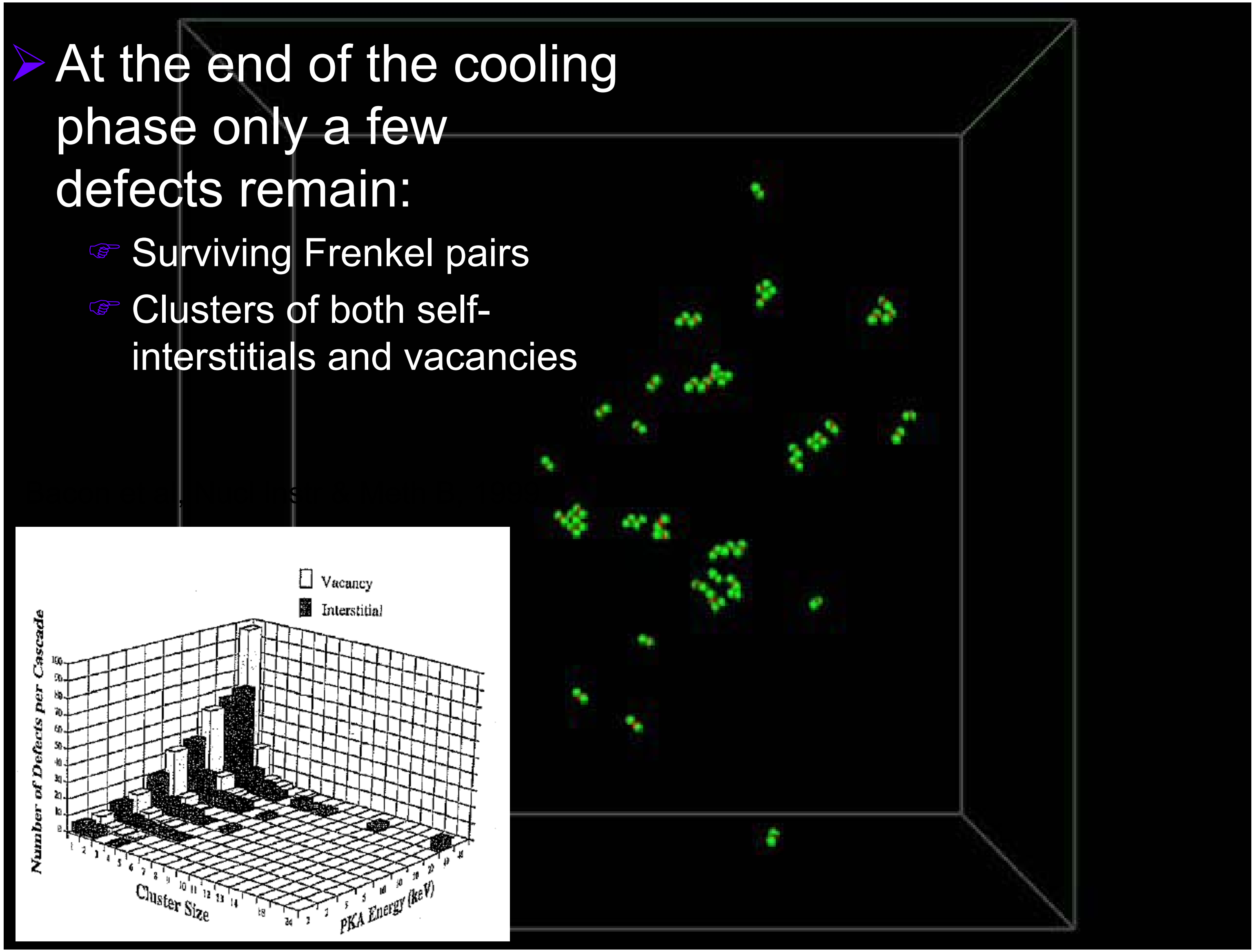
Cooling phase: most defects recombine, following complex many-body processes

Primary damage state: only a few point defects and clusters survive (cascade debris)



Primary state of damage (cascade debris)

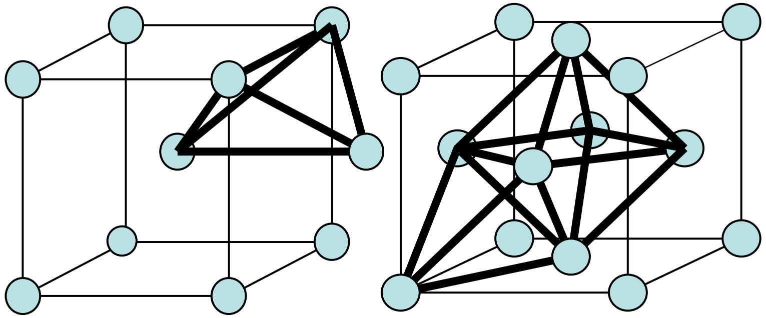
- At the end of the cooling phase only a few defects remain:
  - Surviving Frenkel pairs
  - Clusters of both self-interstitials and vacancies



Outline

- How is a cascade simulated by MD
- Which type of information is extracted from the simulation
- Primary damage in archetypal bcc metal for nuclear applications: Fe (and its alloys)
- Primary damage in archetypal fcc metal for nuclear applications: Cu
- Summary

Ferritic steels
BCC-structure

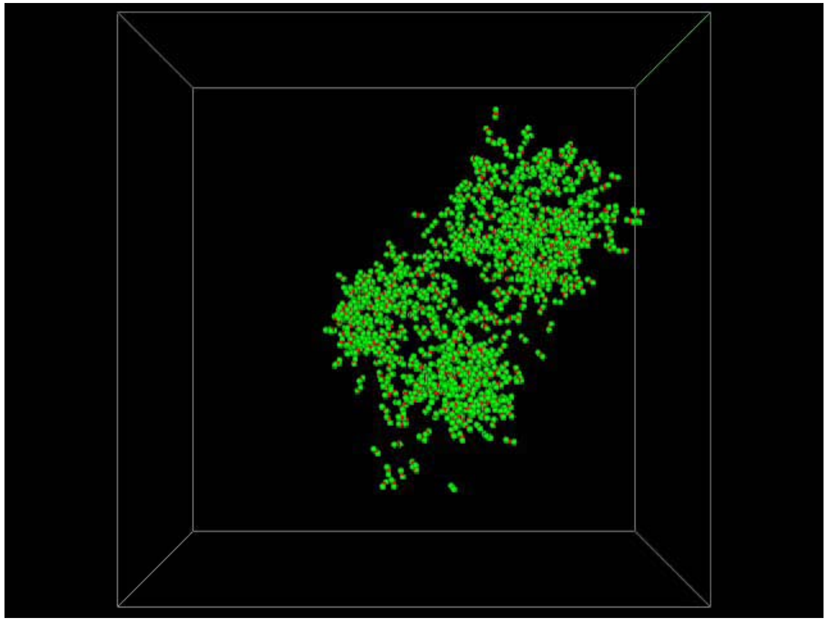


Austenitic steel
FCC-structure

Different crystallographic structures determine significant difference in type of primary damage

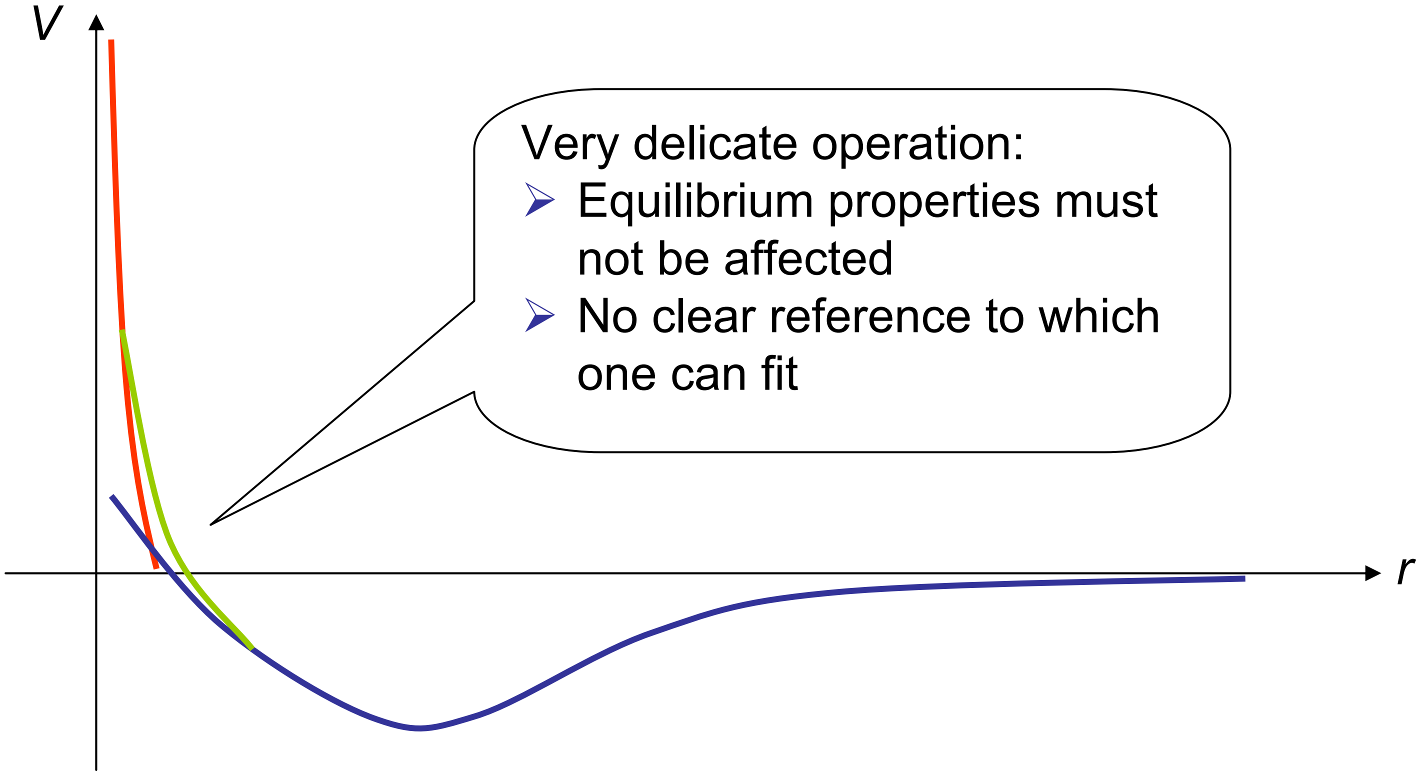
Molecular dynamics for cascades

- MD is the technique "par excellence" for displacement cascade simulations:
  - *one atom is given a kinetic energy of a few keV to tens of keV*
  - *the dynamic evolution of the system is followed*
  - *the ballistic phase is spontaneously reproduced*
  - *the equilibrium defect configurations are also correctly treated, compatibly with the validity of the potential*



MD cascade simulation tips

- Interatomic potential generally fitted to equilibrium properties
  - ☞ *To treat short interatomic distances necessary to switch smoothly to different, appropriate short-range potential**



Very delicate operation:

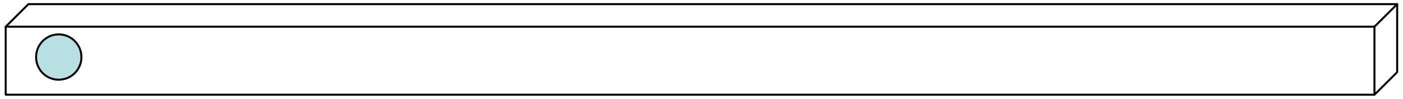
- Equilibrium properties must not be affected
- No clear reference to which one can fit

***Generally, "universal" potential by Ziegler, Biersack & Littmark (ZBL), 1985**

MD cascade simulation tips

- Initially, system must be equilibrated at temperature of interest for as long time as possible (tens of ps)
- PKA set into motion with pre-defined kinetic energy along random, high-index crystallographic direction (⟨123⟩, ⟨135 ⟩, …), to avoid channelling and limit RCS
  - ☞ *Channelling = motion of atom along "empty" directions with little or no interaction with other atoms*

    ⇒ long distances covered before producing cascade of displacements

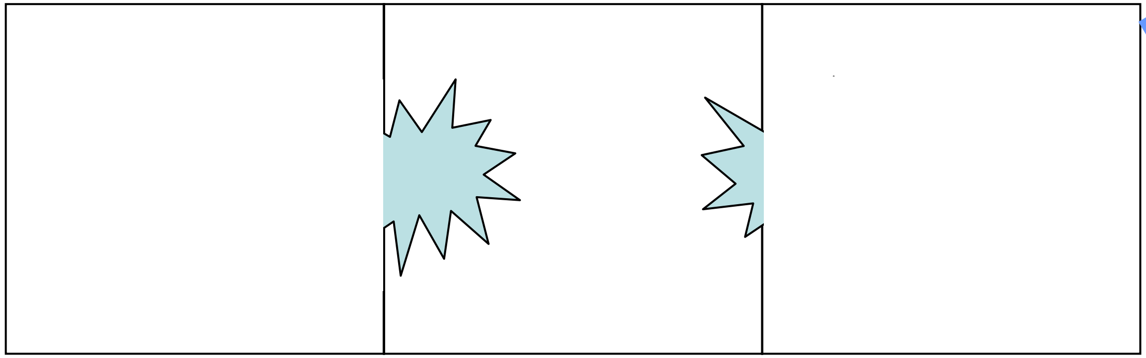


  - ☞ *RCS = replacement collision sequence = sequence of replacements along the same direction, leading to production of displacement far away from triggering displacement*

MD cascade simulation tips

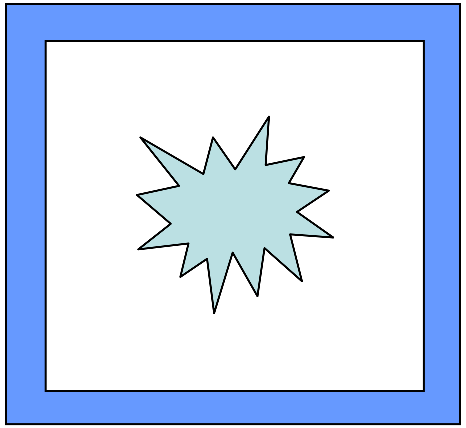
In all cases, simulation boxes must be as large as possible, the larger the energy, the larger the box

- Periodic boundary conditions



  - ☞ It does not matter in which direction cascades evolves, IF box is big enough to avoid interaction of cascade with itself
  - ☞ Heat introduced by transformation of PKA kinetic energy into thermal agitation is NOT extracted

- Heat extracting boundaries



  - ☞ Boundaries are special regions where atomic motion is damped:

    total energy not conserved any more!

  - ☞ Care must be taken to avoid cascade interaction with boundaries

Information extracted from MD simulation of cascade

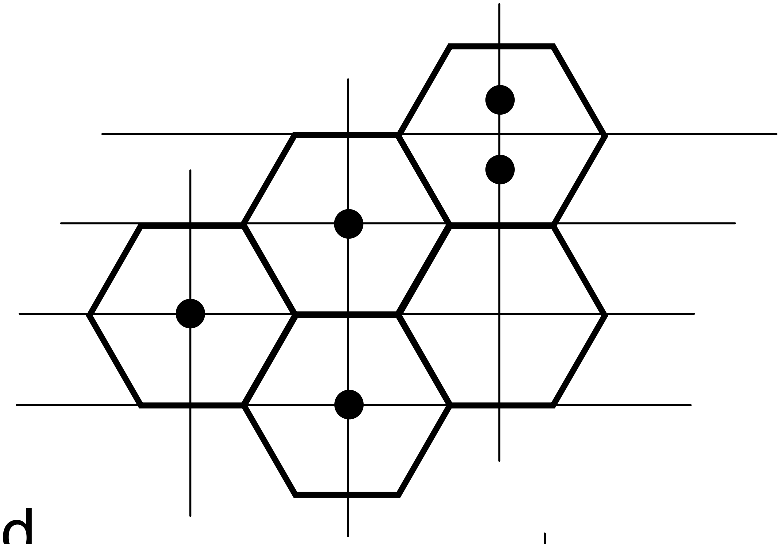
- Characteristic times:
  - ☞ *peak time, cooling time, …*
- Characteristic volumes/densities:
  - ☞ *volume occupied at peak time*
  - ☞ *volume occupied by cascade debris, vacancies and SIAs*
- **Number of atomic displacements/defects**:
  - ☞ *displacements at peak time*
  - ☞ ***displacements/defects at the end of cooling phase ("surviving" defects)***
    - ⇒ Comparison with NRT standard
- **Clusters**
  - ☞ ***Fraction of point-defects in cluster***
  - ☞ ***Number of clusters***
  - ☞ ***Clusters' size distribution***
  - ☞ …

How to identify defects & clusters?

- Wigner-Seitz cell method

  If no atom in cell → vacancy

  If two atoms in cell → SIA

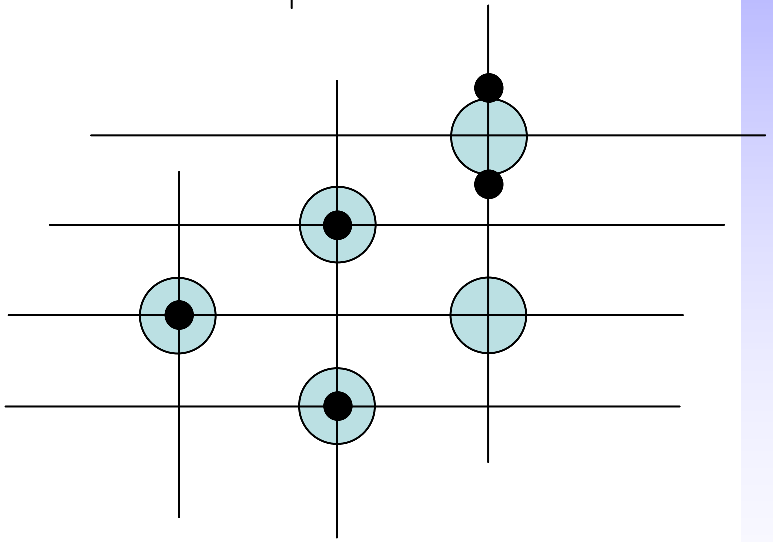


- Equivalent sphere method

  If no atom in site → site vacant

  If atom outside sphere → displaced atom

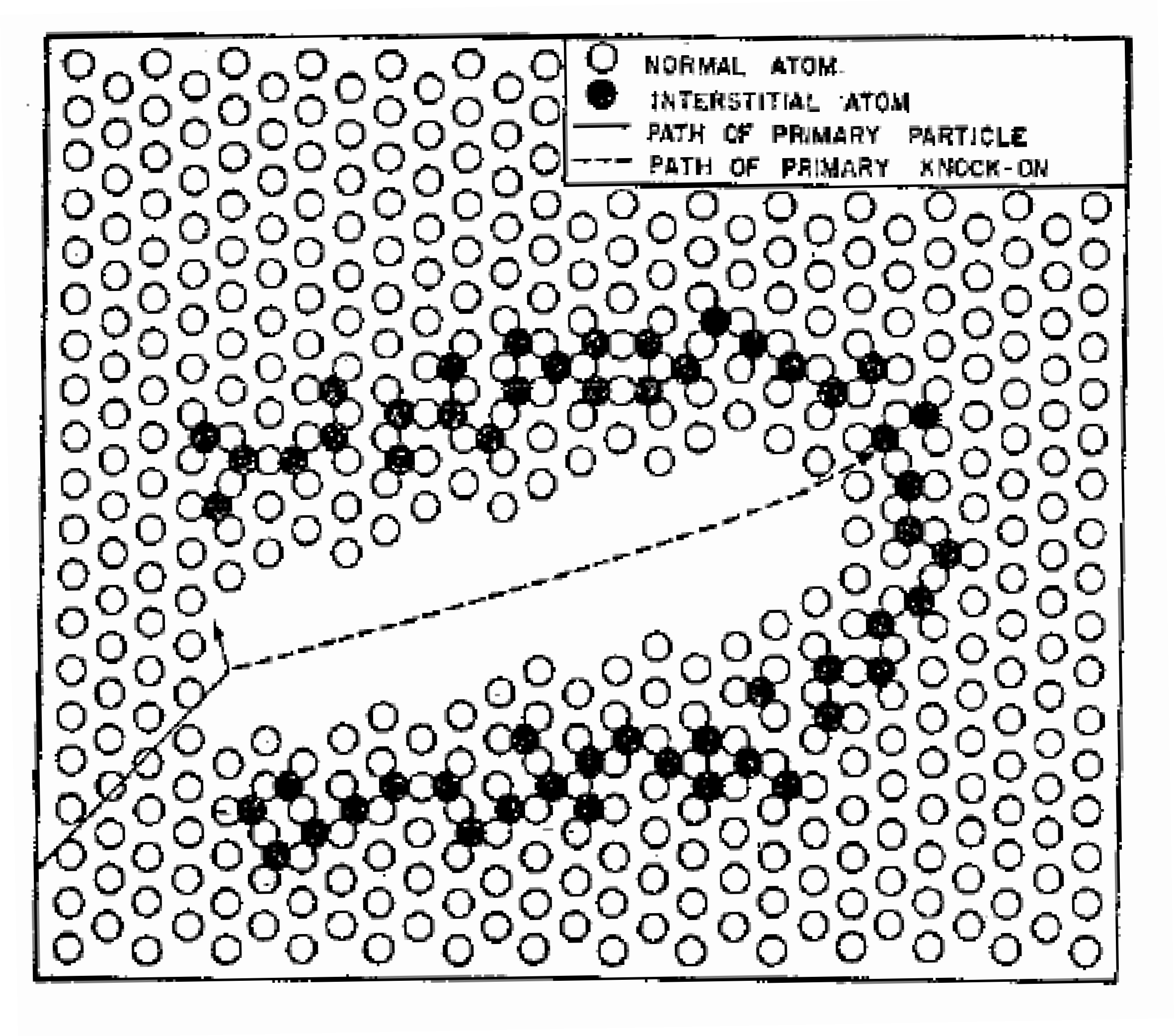
  Further treatment needed to count vacancies and SIAs by substractions on site



- Clusters

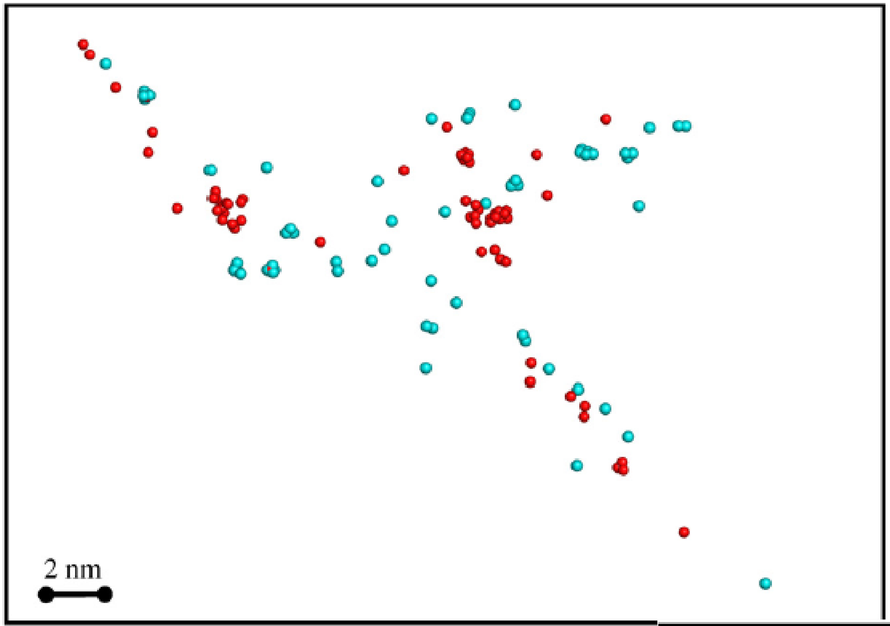
  Need to establish criterion of neighbourhood or visual inspection

The early cartoon for a displacement cascade



J.A. Brinkman, American Journal of Physics, 1956

The current cartoon for a displacement cascade



Primary damage in pure Cu:

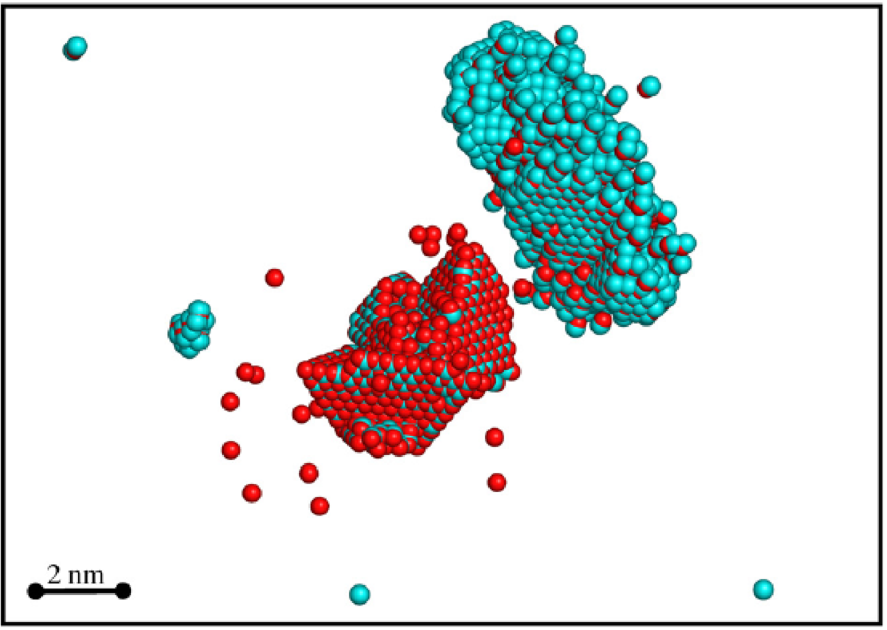
Two very different examples of the outcome of a 25 keV cascade

R. Voskoboinikov et al., J. Nucl. Mater., 2008

🔵 Displaced atoms

🔴 Vacancies

Hardly any resemblance with Brinkmann's model …



Recall of NRT standard (for dpa calculation)

Energy of the cascade =
damage energy

Number of
displacements
per cascade

$$n_{displ} = 0.8\frac{T_d}{2E_{displ}}$$

Threshold energy to
produce a single
displacement

$$n_{displ} \underset{E_d=40\,eV\,(Fe)}{=} 10T_d[keV]$$

- This *NRT* (Norgett-Robinson-Torrens)* *model* is based on the assumption that no more displacements are created after the energy of each atom is < $2E_d$, corrected by a 0.8 factor obtained based on BCA (binary collision approximation) simulations
- MD reveals that this is a very crude approximation
- However dpa are still conventionally calculated based on NRT standard

$$dpa = \int_0^{t_{irr}} dt \int_0^{\infty} dE_n \phi(E_n) \times \sigma_d(E_n \rightarrow T_d) \times n_{displ}(T_d)$$

***M.J. Norgett, M.T. Robinson, I.M. Torrens, Nucl. Eng. & Des. 33 (1975) 50**

Cascades in Fe with old potentials*

Potentials' features

E^f_{SIA} (eV)	COWP	FS-CB	HA-VD	HV-TB	JO-GA-SdlR	SP-RB	Ab initio	EXP
⟨110⟩ db	4.15	4.76	6.98/6.01	2.95	4.33	3.67	3.41-3.94	stable config is ⟨110⟩ db: 4.7
⟨111⟩ db	↓	4.87	↓ /5.45	↓	nr	↓		
⟨111⟩ cd	4.02	4.91	6.77/5.20	2.59	nr	3.54	4.11-4.66	
$E_{\langle 111\rangle-\langle 110\rangle}$	-0.13	0.15	-0.21/ -0.81	-0.36	nr	-0.13	0.72	

TDE (eV)	COWP	FS-CB	HA-VD	HV-TB	JO-GA-SdlR	SP-RB	EXP	EXP
⟨100⟩	22**(20)**	18	21**(20)**	19**(18)**	19	17**(16)**	17	17
⟨110⟩	37**(20)**	31	31**(20)**	51**(20)**	27	47**(40)**	>30(35)	>30(35)
⟨111⟩	29**(48)**	>70	18**(28)**	19**(38)**	nr	21**(20)**	20	20
Mean (Median)	*31**(54)***	nc *(40)*	*26**(32)***	*34**(48)***	nc	*32**(42)***	*26*	*26*

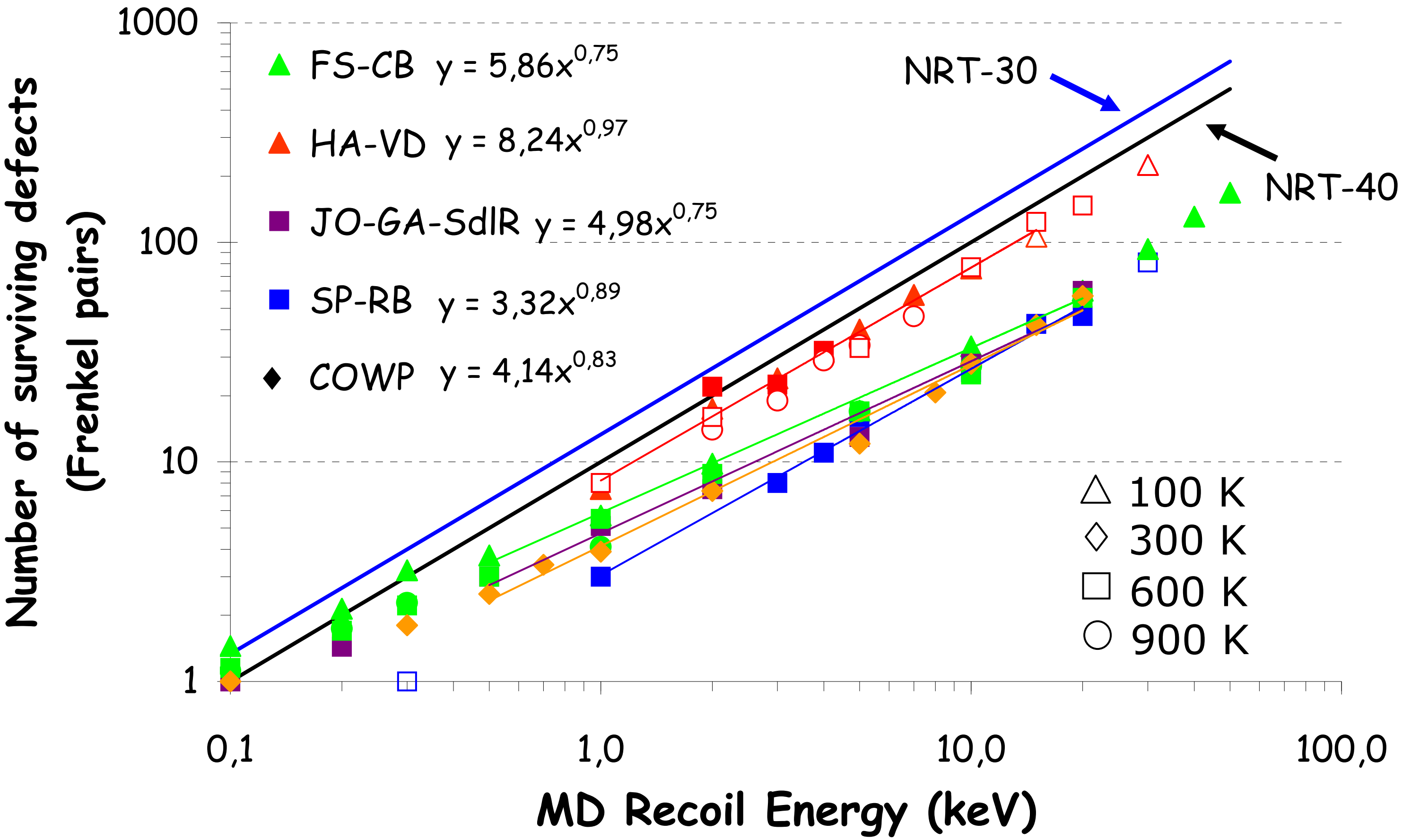
- **<u>OLD potentials</u>: Different description of SIA configuration and energy difference; <u>different threshold displacement energies</u>**

<u>COWP</u>: Malerba, Terentyev, Olsson, Chakarova & Wallenius, J. Nucl. Mater. 329-333 (2004) 1156; Chakarova, Pontikis & Wallenius, Delivery report WP6, SPIRE project, EC contract no. FIKW-CT-2000-00058, June 2002, available at http://www.neutron.kth.se/publications
<u>FS-CB</u>: Finnis & Sinclair, Phil. Mag. A 50 (1984) 45; *ibid.* 53 (1986) 161 (Erratum); Calder & Bacon, J. Nucl. Mater. 207 (1993) 25.
<u>HA-VD</u>: Haftel, Andreadis & Lill, Phys. Rev. B 42 (1990) 11540; Doan & Vascon, Annales de Physique C3, suppl. No. 3 20 (1995) 57
<u>HV-TB</u>: Harrison, Voter & Chen, in: "Atomistic Simulation of Materials – Beyond Pair Potentials", Eds. Vitek & Srolovitz, Plenum New York (1989) 219; Turbatte, Master Thesis, U. Marne la Vallée, 1995, unpublished
<u>JO-GA-SdlR</u>: Johnson & Oh, J. Mater. Res. 4(5) (1989) 1195; Guellil & Adams, J. Mater. Res. 7(3) (1992) 639; Soneda & de la Rubia, Phil. Mag. A 78(5) (1998) 995
<u>SP-RB</u>: Simonelli, Pasianot & Savino, MRS Symp. Proc. 291 (1993) 567; Becquart, Domain, Legris & Van Duysen, J. Nucl. Mater. 280 (2000) 73; J.M. <u>Raulot</u>, Master Thesis, U. Marne la Vallée, 1998, unpublished.

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

Cascades in Fe with old potentials*

Surviving Frenkel pairs



$\mathrm{NRT}=0.8/2\times E_D/E_d$

NRT-40/30 ⇔ E_d=40 eV (ASTM) / 30 eV (also used)

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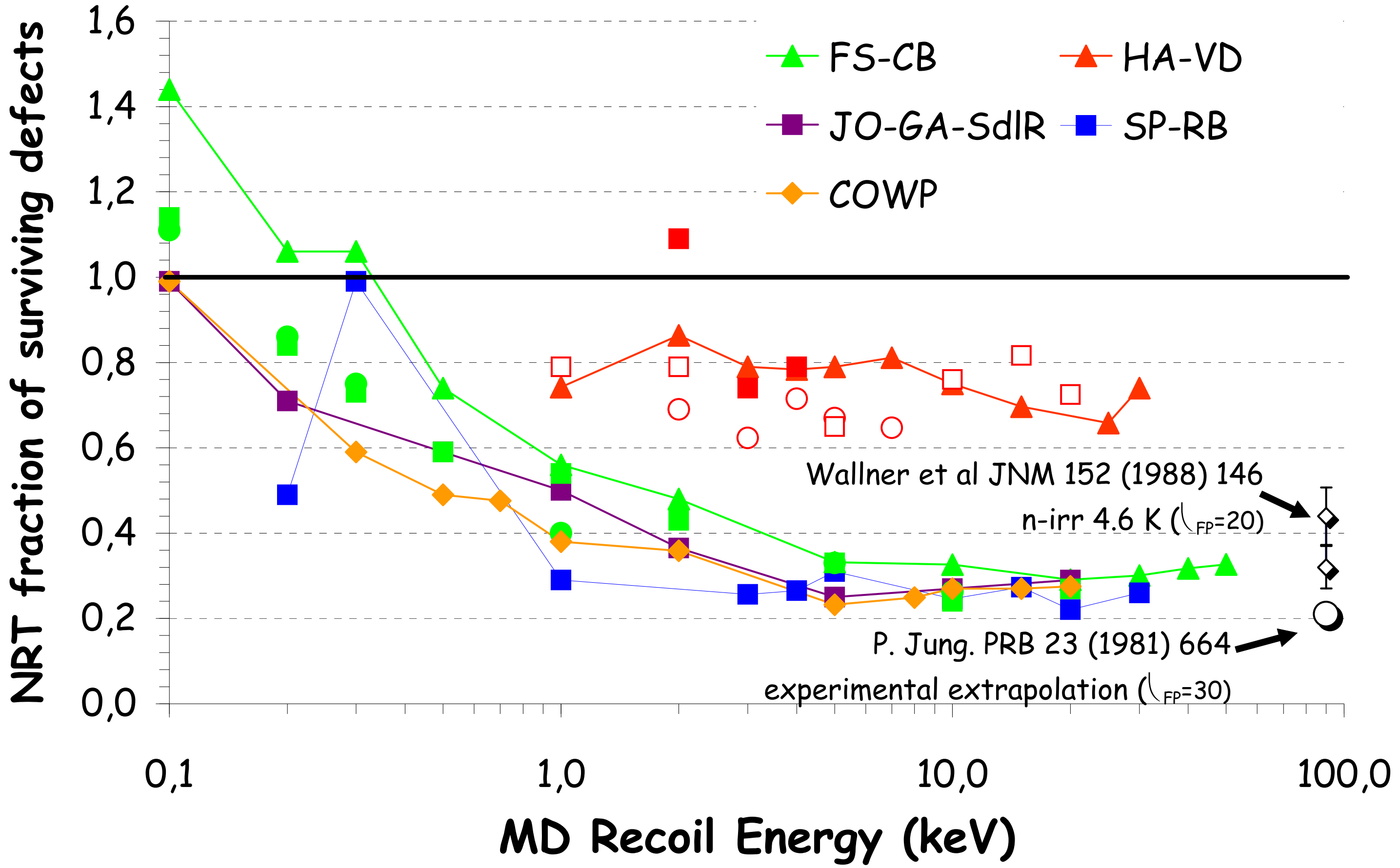
Cascades in Fe with old potentials*

Surviving Frenkel pairs



NRT=$0.8/2\times E_D/E_d$

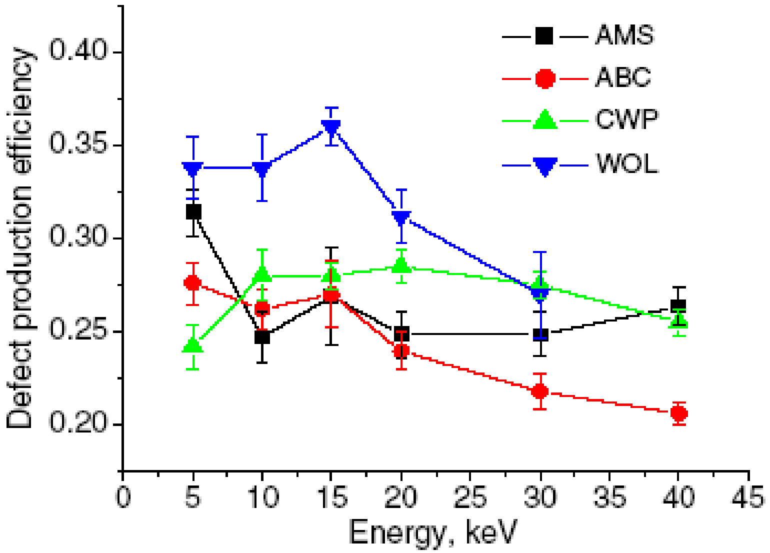
Fraction = FP(MD)/FP(NRT)

△ 100 K
◇ 300 K
☐ 600 K
○ 900 K

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

Cascades in Fe with recent potentials

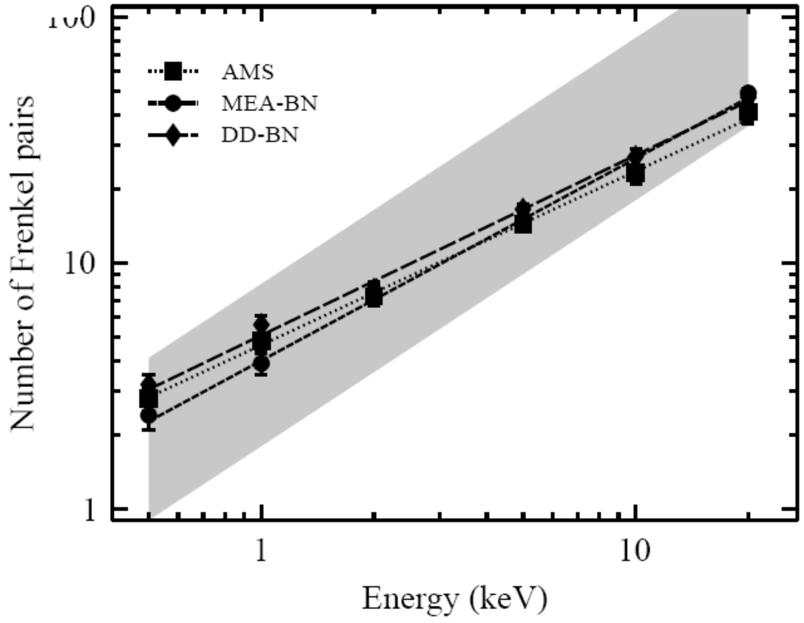
Terentyev et al, J. Nucl. Mater. 351 (2006) 65



← NRT-40 fraction remains well within 0.2-0.4 range for all potentials

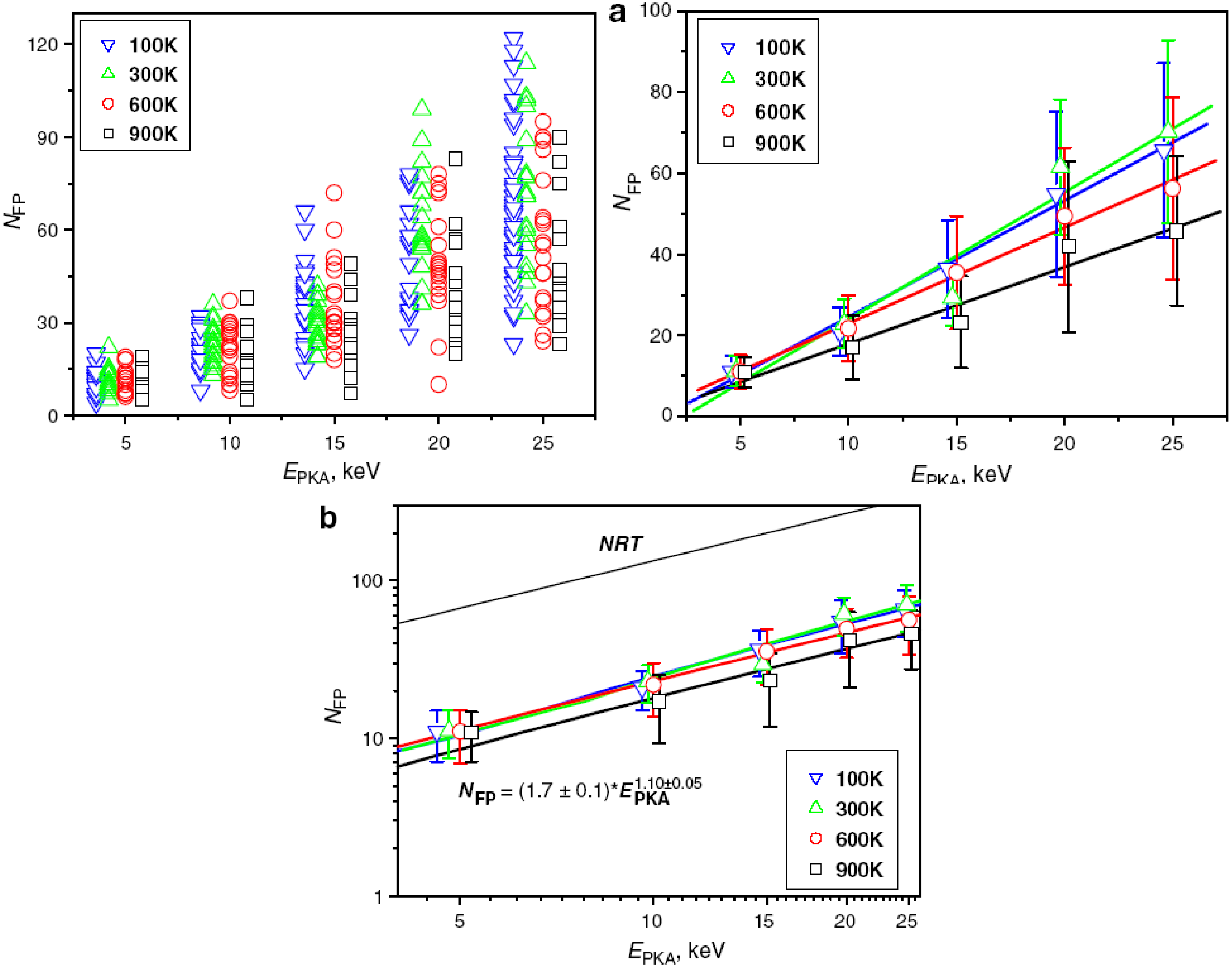
Total number of surviving FPs essentially coincident for all potentials ↓

AMS: Ackland, Mendelev, Srlolovitz, et al. J. Phys.: Condens. Matter 16 (2004) 1.
ABC: Ackland, Bacon, Calder, Harry, Philos. Mag. A 75 (1997) 713
CWP: Malerba, Terentyev, Olsson, Chakarova & Wallenius, J. Nucl. Mater. 329-333 (2004) 1156; Chakarova, Pontikis & Wallenius, Delivery report WP6, SPIRE project, EC contract no. FIKW-CT-2000-00058, June 2002, available at http://www.neutron.kth.se/publications
WOL: Wallenius, Olsson, Lagerstedt, Nucl. Instr. & Meth. B 228 (2005) 122.
MEA-BN: Müller, Erhart& K. Albe, J. Phys.: Condens. Matter 19 (2007) 326220
DD-BN: Dudarev & Derlet, J. Phys.: Condens. Matter 17 (2005) 7097



Björkas & Nordlund, Nucl. Instr. & Meth. B, 259 (2007) 853

Cascades in Cu with large statistics*



*Voskoboinikov, Osetsky & Bacon, J. Nucl. Mater. 377 (2008) 385

Conclusions *(consistent with about 2 decades of cascade simulations)*:

Number of surviving point defects after a cascade of given energy is about the same *independently of the potential* used *(with only one pathological case)*

NRT standard *overestimates* by about a factor 3-5 (depending also on material and temperature) the number of surviving point defects

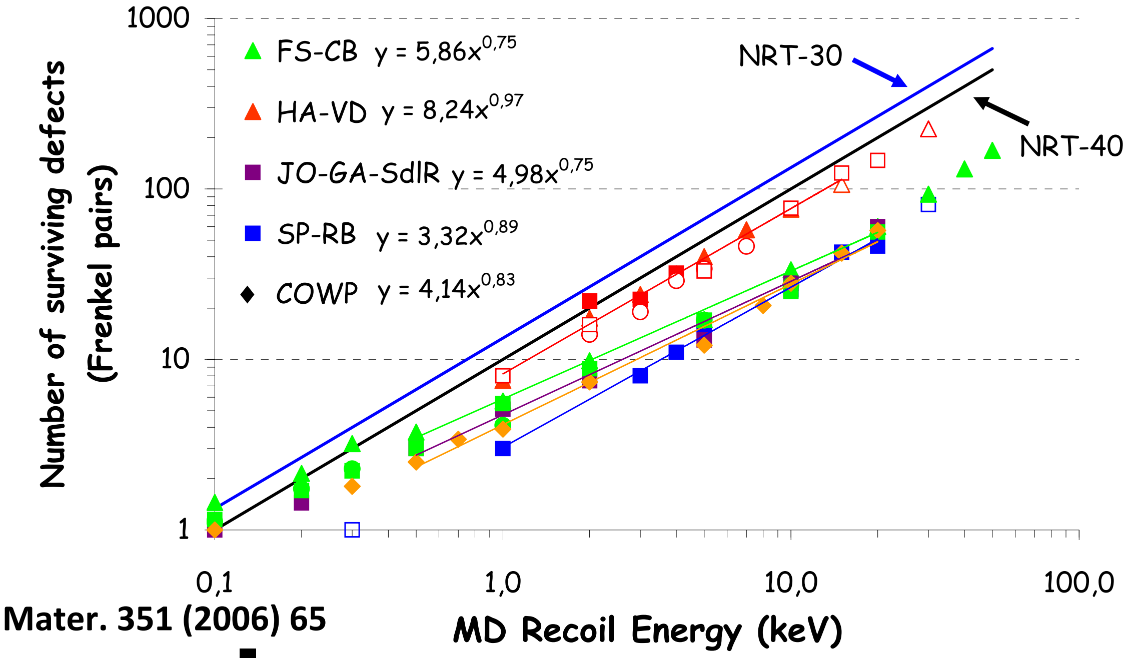
Generalised expression for number of displacements that *should* be used for dpa calculations *(but it is not)*

$$n_{displ} = \xi(T_d, T)\frac{0.8T_d}{2E_{displ}}$$

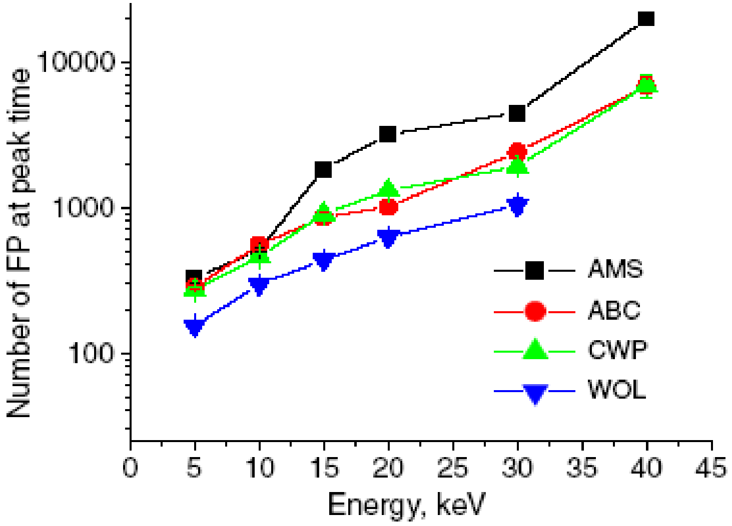
Another unexpected failure of NRT

Threshold energies

ABC	41
WOL	37
COWP	53
MHS[a]	35
AMS[a]	35
SP-RB	43
HA-VD	31
HV-TB	45
JO-GA-SdlR	33
FS-CB	35



Terentyev et al, J. Nucl. Mater. 351 (2006) 65



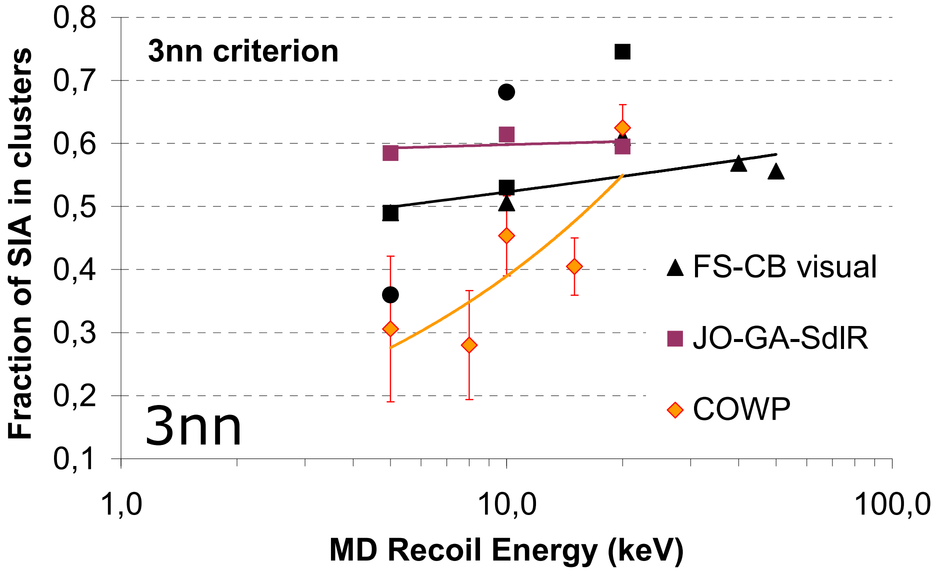
No clear correlation between number of peak or surviving defects and threshold energy!

Other factors play more important role: local temperature, cascade density, …

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

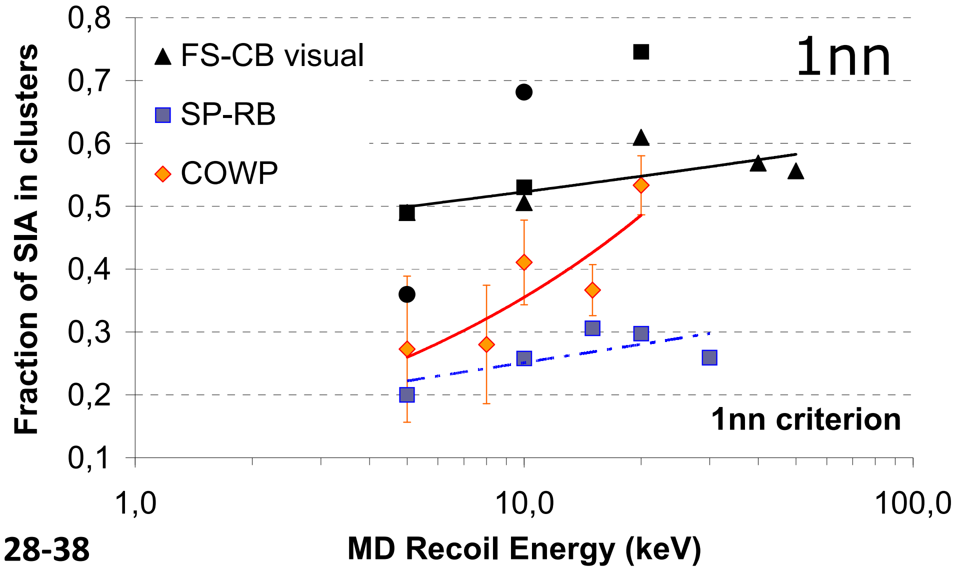
SIAs in clusters in Fe: old potentials

Fraction of SIA in clusters (≥ 2)



Large potential dependence

Not so large criterion dependence



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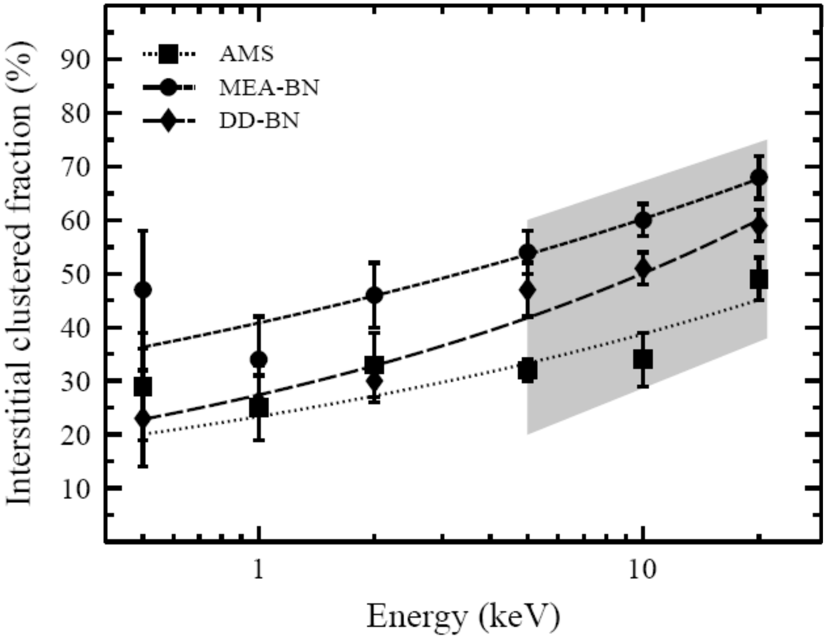
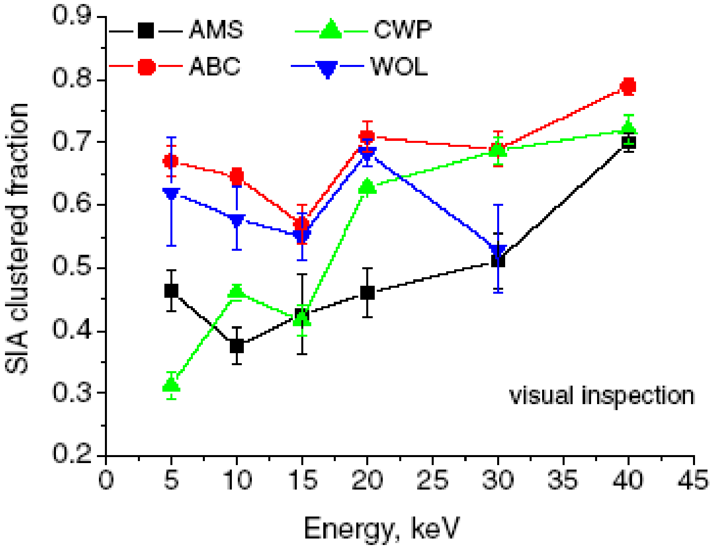
SIAs in clusters in Fe: recent potentials

Fraction of SIA in clusters (≥ 2)

Björkas & Nordlund, Nucl. Instr. & Meth. B, 259 (2007) 853





Terentyev et al, J. Nucl. Mater. 351 (2006) 65

Trend to increase of SIA clustered fraction with energy

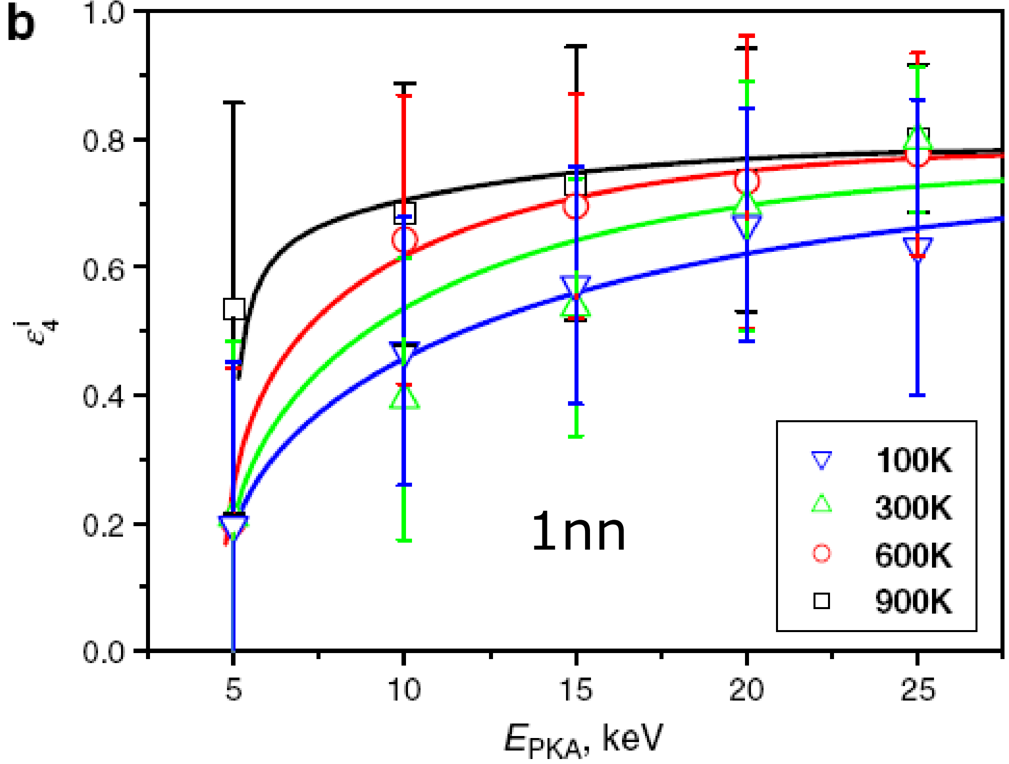
Scatter somewhat reduced, but not so much

Larger statistics needed

SIAs in clusters in Cu: large statistics

Fraction of SIA in clusters (≥ 4)

Voskoboinikov, Osetsky & Bacon, J. Nucl. Mater. 377 (2008) 385

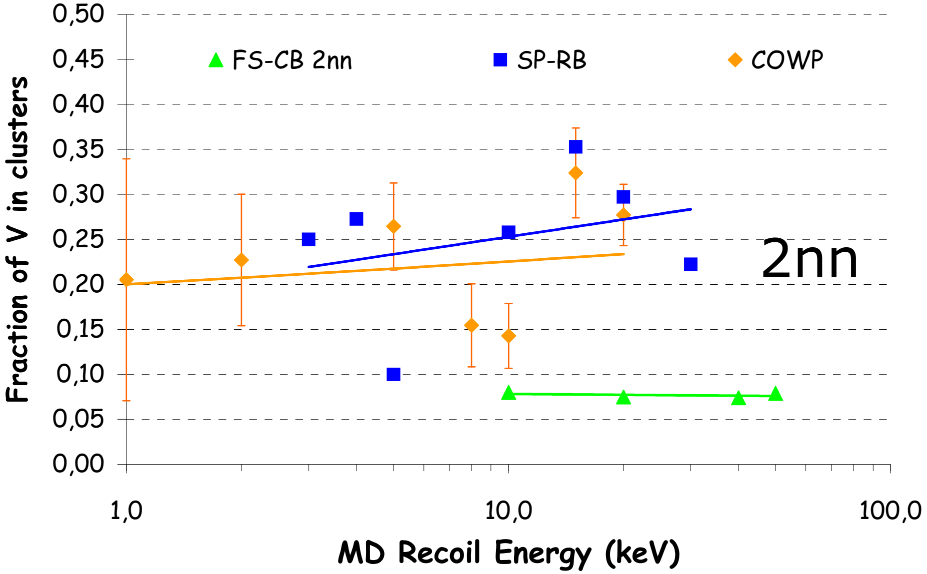


Trend to increase SIA clustered fraction with energy is confirmed, but scatter remains large

Effect of temperature exists, too

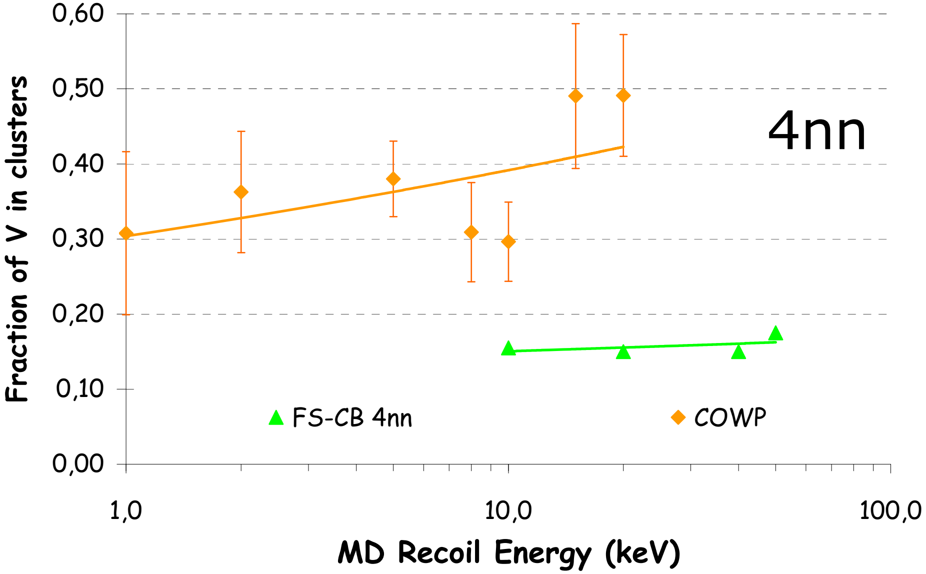
Vacancies in clusters in Fe: old potentials

Fraction of V in clusters (≥ 2)



Large potential dependence

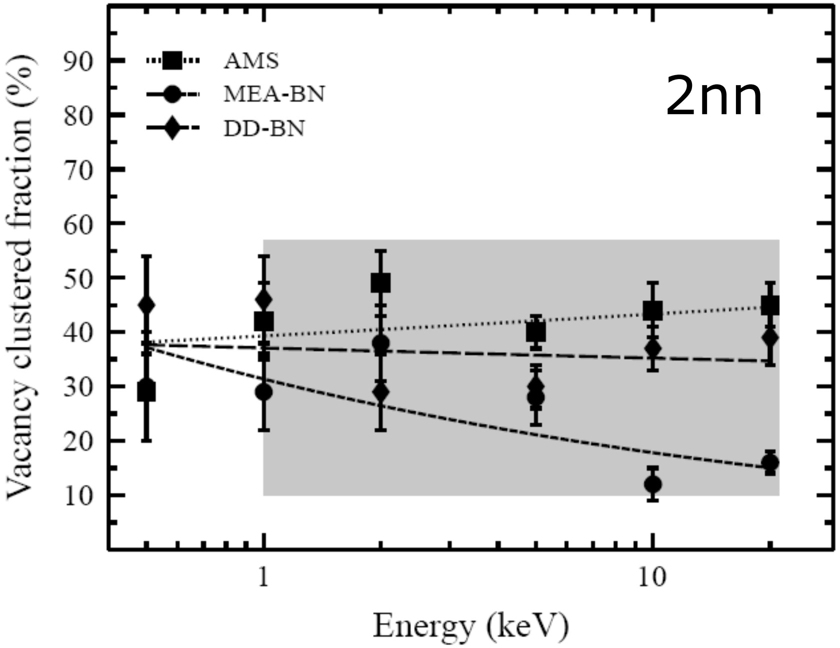
And also clear criterion dependence

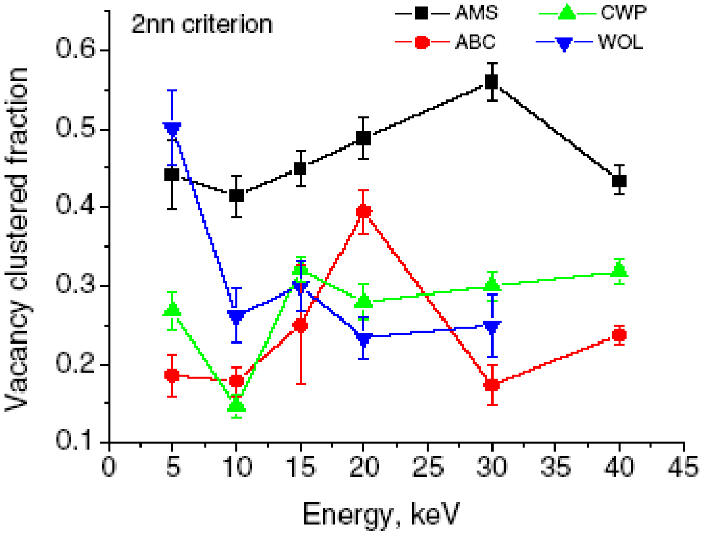


Vacancies in clusters in Fe: recent potentials

Fraction of V in clusters (≥ 2)

Björkas & Nordlund, Nucl. Instr. & Meth. B, 259 (2007) 853





Terentyev et al, J. Nucl. Mater. 351 (2006) 65

Vacancy clustered fraction roughly independent of energy

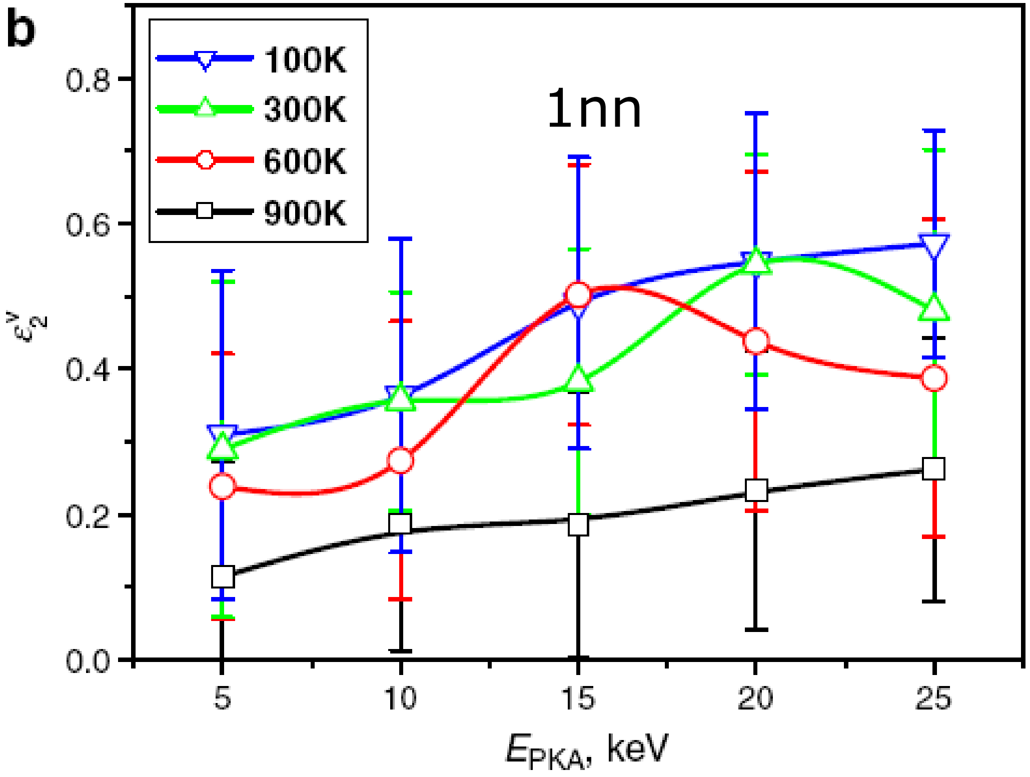
Scatter hardly reduced

Larger statistics needed

Vacancies in clusters in Cu: large statistics

Fraction of V in clusters (≥ 4)

Voskoboinikov, Osetsky & Bacon, J. Nucl. Mater. 377 (2008) 385



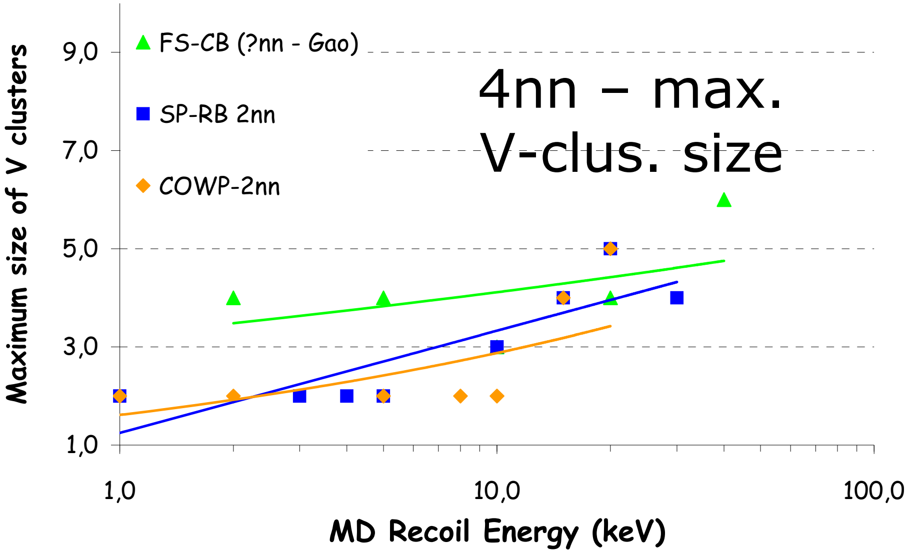
Trend to slight increase of V clustered fraction with energy

Scatter remains large

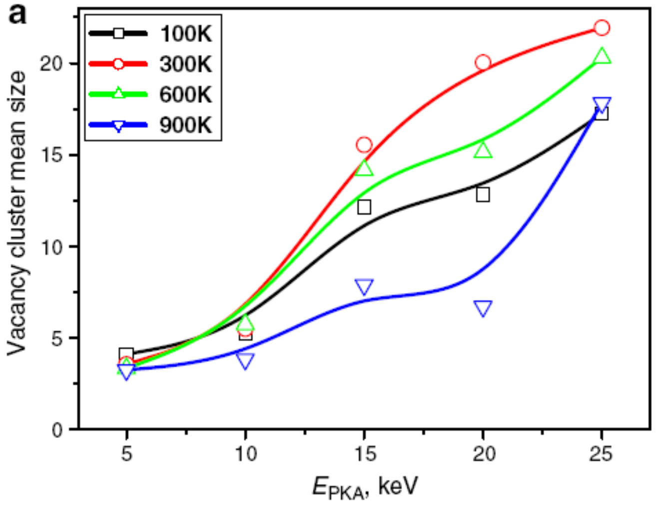
Effect of temperature is significant

Main difference between bcc (Fe) and fcc (Cu)

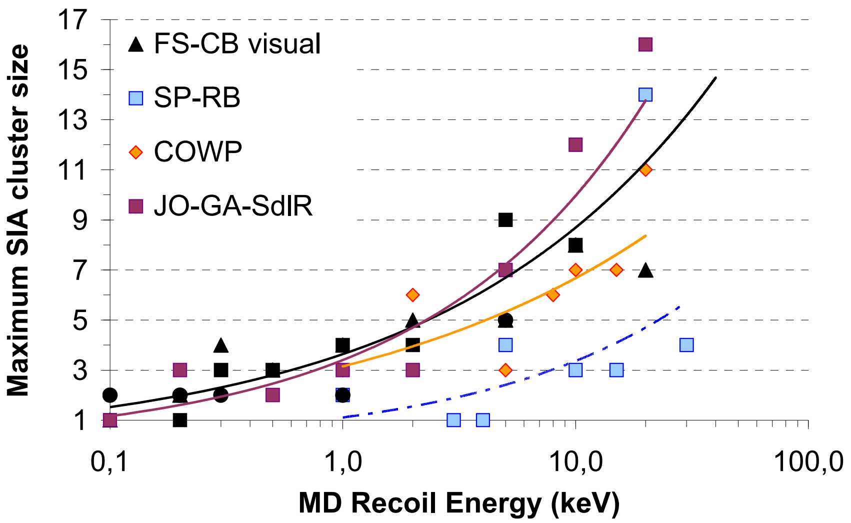
Size of defect clusters

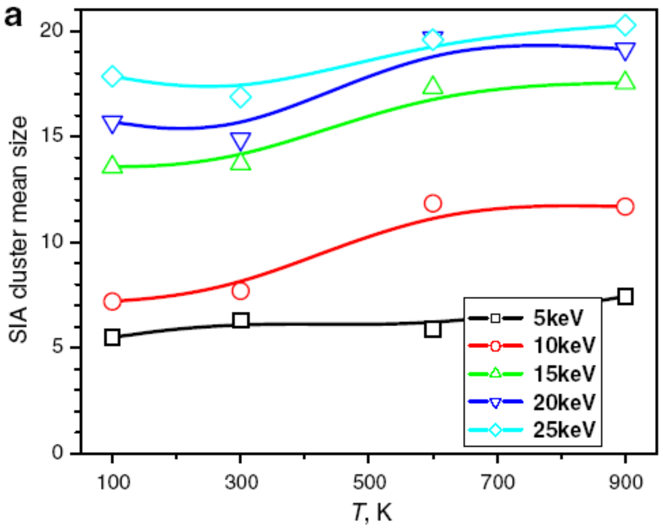


4nn – max. V-clus. size



Size of SIA clusters is comparable ↓ but V clusters are smaller in Fe ↑



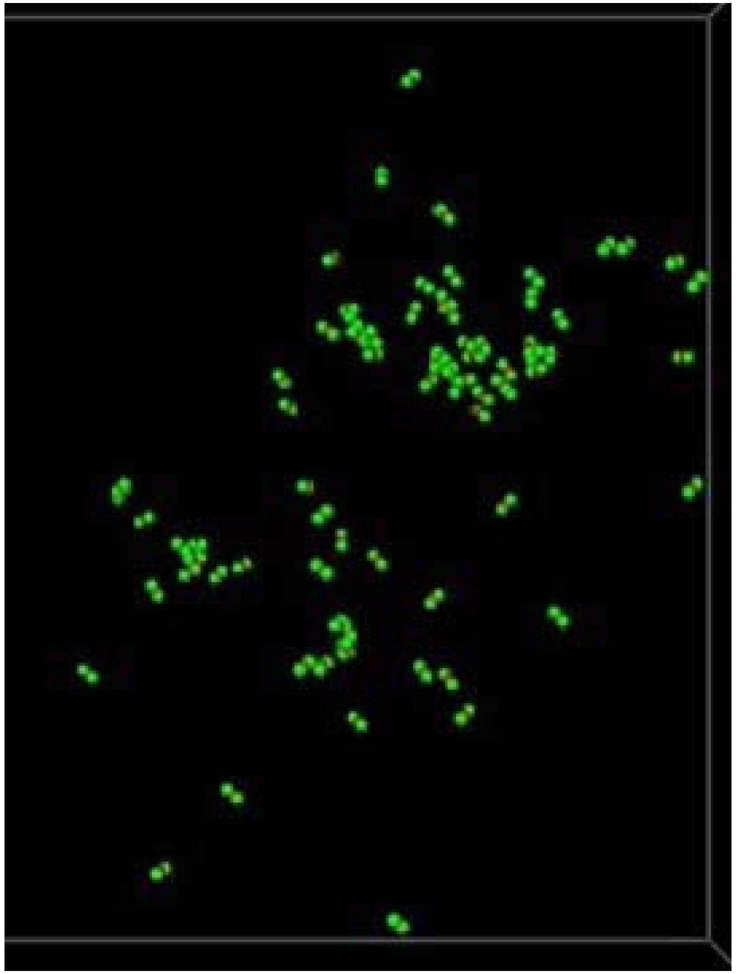


Main difference between bcc (Fe) and fcc (Cu)

Type of defect clusters

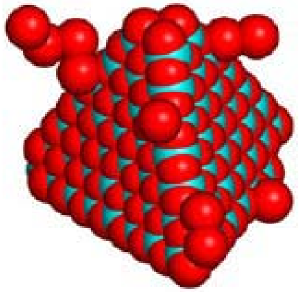
Cascade in Fe

SIA clusters, small cavities

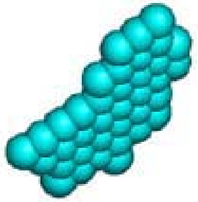


Cascade in Cu

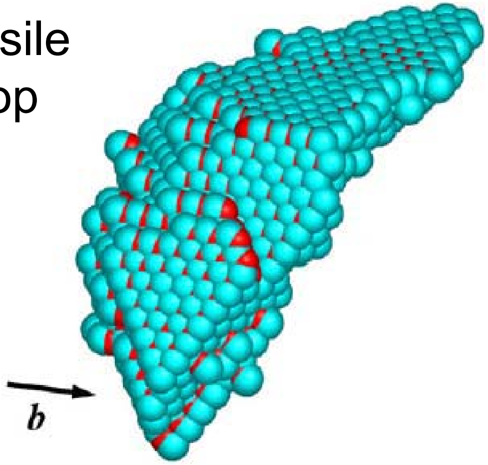
Stacking fault tetrahedron



Faulted loop

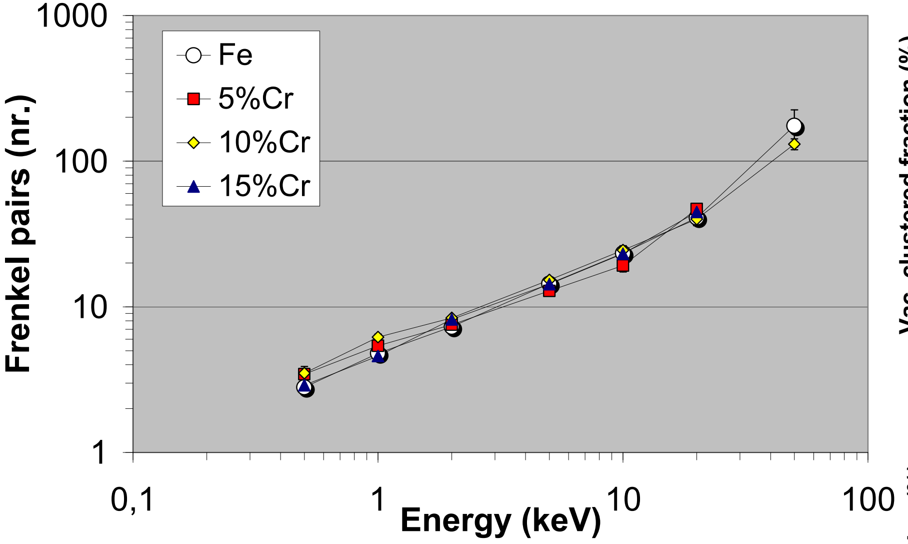


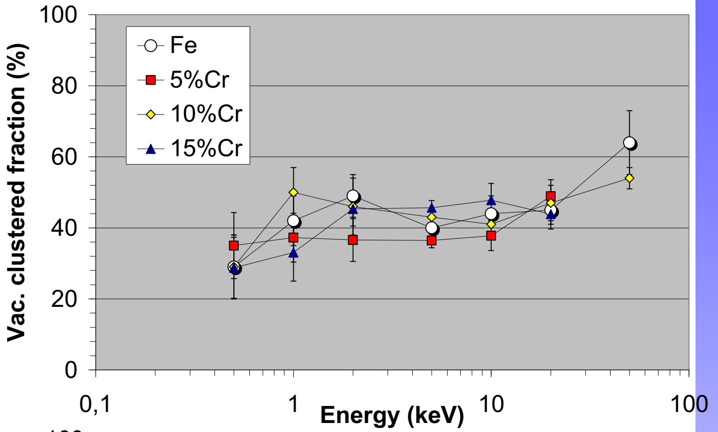
Glissile loop

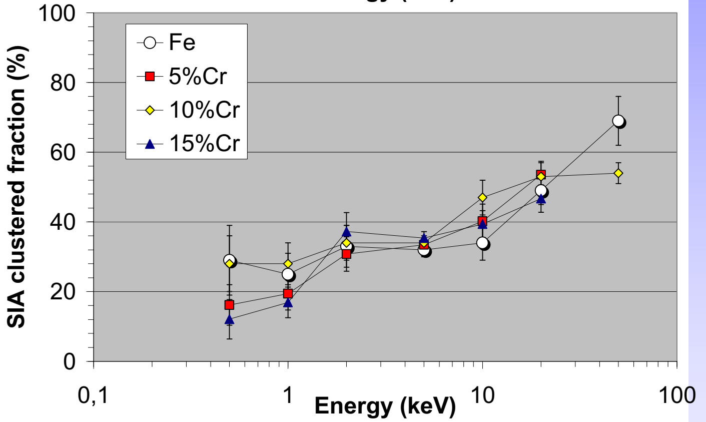


What about alloying elements?
Ex: cascades in concentrated FeCr alloys

(No) effect of Cr on defect production







- Negligible effect of Cr on damage production

- Defects produced are:
  - ***Self-interstitials**: single <110> dumbbells 70-40%, <110> clusters with size: 2÷5; <111> with size 5÷20;*
  - ***Vacancies**: single 50%, spherical clusters with size 2÷10, very rare <100> platelets with size ~20*

Vörtler et al., JNM, 2008; Terentyev et al., JNM, in press

Cascades and microchemistry

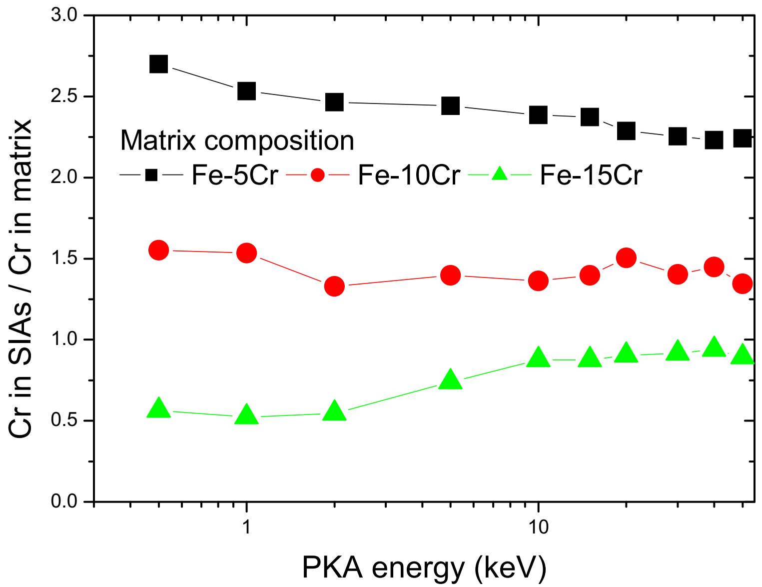
Observed effects :

- SIA defects are enriched in Cr
- Cascades induce SRO in Fe-5 and Fe-15Cr

Origin :

- Binding energy SIA-Cr
- Negative ΔSRO (5%Cr) : breakup of Cr-Cr 1st pairs
- Positive ΔSRO (15%Cr) formation of Cr clusters during solidification

Chemical composition of SIA defects

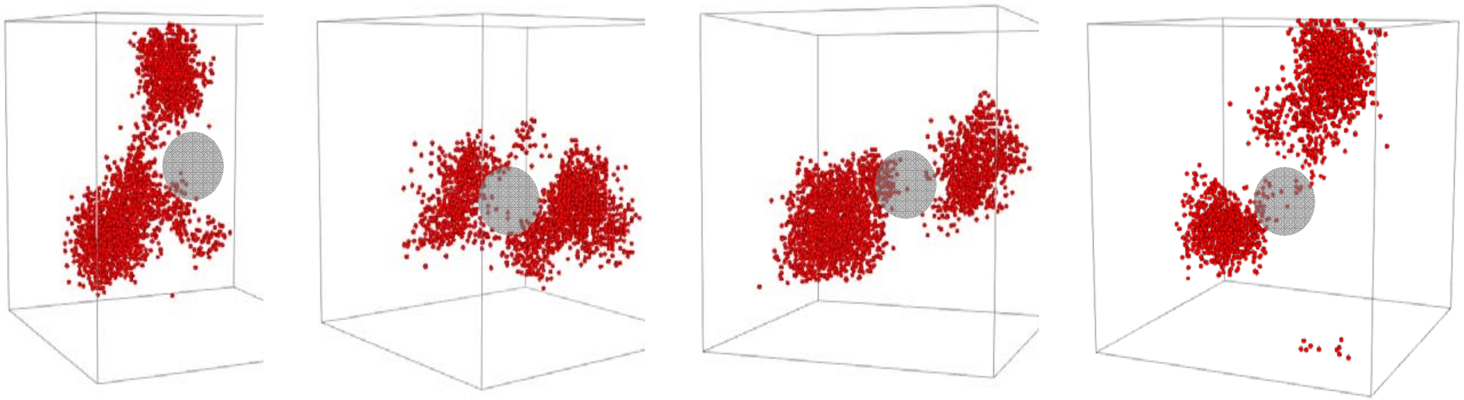


ΔSRO parameter in random Fe-Cr alloys

5 KeV cascade	Fe-5Cr	Fe-10Cr	Fe-15Cr
ΔSRO/dpa×10^{-3}	-7 ± 2	-2 ± 4	12 ± 2

Vörtler et al., JNM, 2008; Terentyev et al., JNM, in press

Cr precipitates and cascades



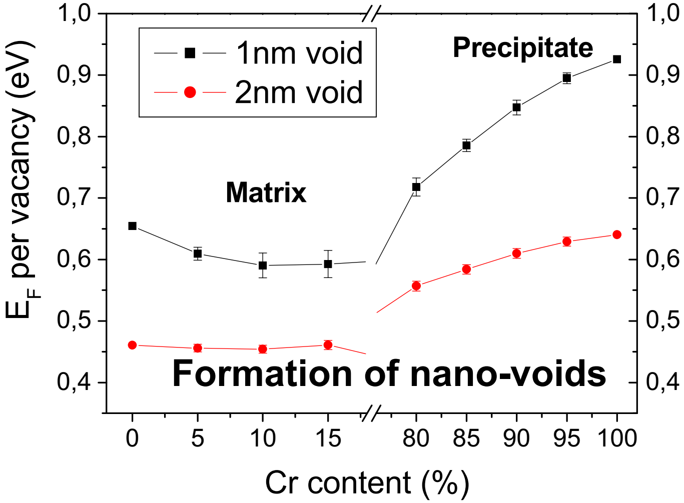
- Precipitates act as scatterers for displacement cascades and are not affected by them!
  - *Enhanced subcascade formation*
  - *Slight effect on FP number because of less recombinations*

This happens because defect formation energy is higher in Cr than in Fe

$\Delta E(\text{Vacancy}) = 2.64 - 2.15 = +0.5$ eV

$\Delta E(\text{<110> - dumbbell}) = 5.68 - 3.75 = +1.93$ eV

$\Delta E(\text{<111> - crowdion}) = 5.76 - 4.45 = +1.31$ eV



Primary damage Fe vs. Fe-Cr: Summary

Common features of primary damage in both Fe & Fe-Cr

1) Defect production efficiency saturates at 0.3

2) Fraction of clustered vacancies ~0.5, weakly depends on E_{PKA}

3) Fraction of clustered SIAs grows monotonically with E_{PKA} from 0.3 to 0.5

4) SIAs in clusters are:
    - relatively large <111>, containing up to 50 defects
    - small <110>, containing up to 5 defects

5) Vacancies in clusters are:
    - 95% of vacancy clusters are nano-voids
    - <100> vacancy loops are produced only in dense cascades

Specific features of primary damage in Fe-Cr alloys:

1) Formed SIA and SIA clusters are Cr-enriched in Fe-5,10%Cr, but not in Fe-15%Cr!

2) Rearrangement of Cr atoms within cascade timeframe occurs. In Fe-5Cr, Cr atoms have tendency to order, in Fe-15Cr to precipitate

3) Pre-existing Cr precipitates are not affected by cascades but act as scatterers, inducing more subcascade production and slightly hindering in-cascade recombination

Variation of Cr ‘enrichment’ at SIA defects is the main effect detected

In general, limited effect of presence of other elements

- Dilute solutions, including carbon
  - ☞ *No effects*
- Concentrated solutions
  - ☞ *Limited effect, visible if significant difference in atomic size exists*
  - ☞ *Association between point-defects and elements with affinity for them is observed*
  - ☞ *He, by occupying vacancies, may reduce recombination*

Other cases studied

- Cascade overlap *(unlikely under neutron irradiation)*
  - *Accumulation of damage is not linear: recombination is enhanced, though SIA clusters may grow*
- Cascades on pre-existing large defect (loops, voids)
  - *No spectacular effect*
  - *Defects are not dissolved, except when small*
  - *SIA clusters may split and/or shrink*
- Cascades from high mass recoil
  - *High mass → Denser cascades, enhanced recombination & less surviving defects*
  - *When large loops created, also large voids created and viceversa*
- Effect of electron-phonon coupling
  - *Less recombination & more surviving defects if coupling is significant*

Summary

- Displacement cascades are complex stochastic processes governed mainly by collective effects, rather than by binary collisions
- Large scale molecular dynamics simulations have been and still are instrumental to gain insight into cascade physics
- Each cascade is different from any other and large scatter characterises any measured quantity
- Trends are however fairly robust, especially concerning the number of surviving defects
- A significant part of the surviving defects will be in clusters, although each cascade is different in this respect
- Large SIA cluster production seems to correlate with large vacancy cluster production
- Effect of alloying elements or impurities is generally negligible
- Main difference between bcc and fcc metals is production of larger (visible) defects in fcc, especially stacking-fault tetrahedra