Multiscale Microstructural - Microchemical Processes

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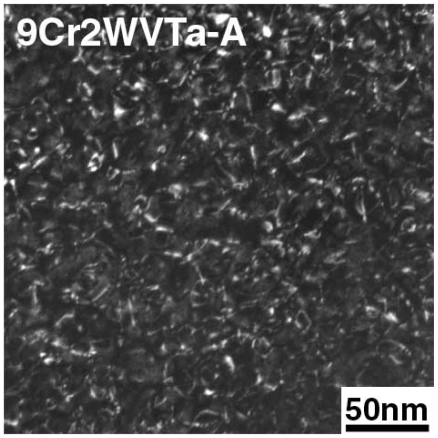
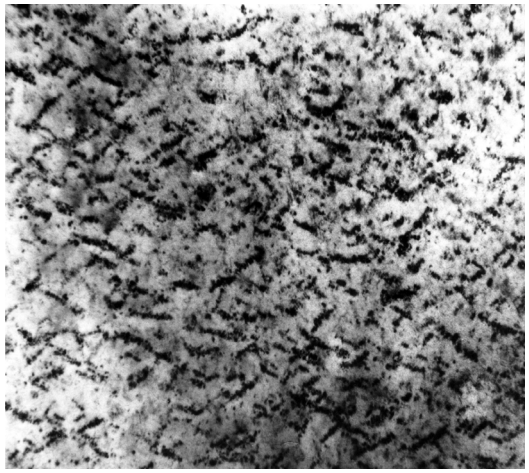
Introduction and objectives

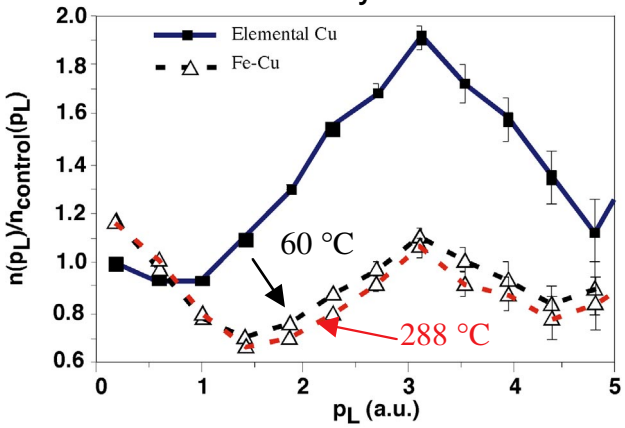
High density of <100> & <111> dislocation loops



Dislocation loop rafting



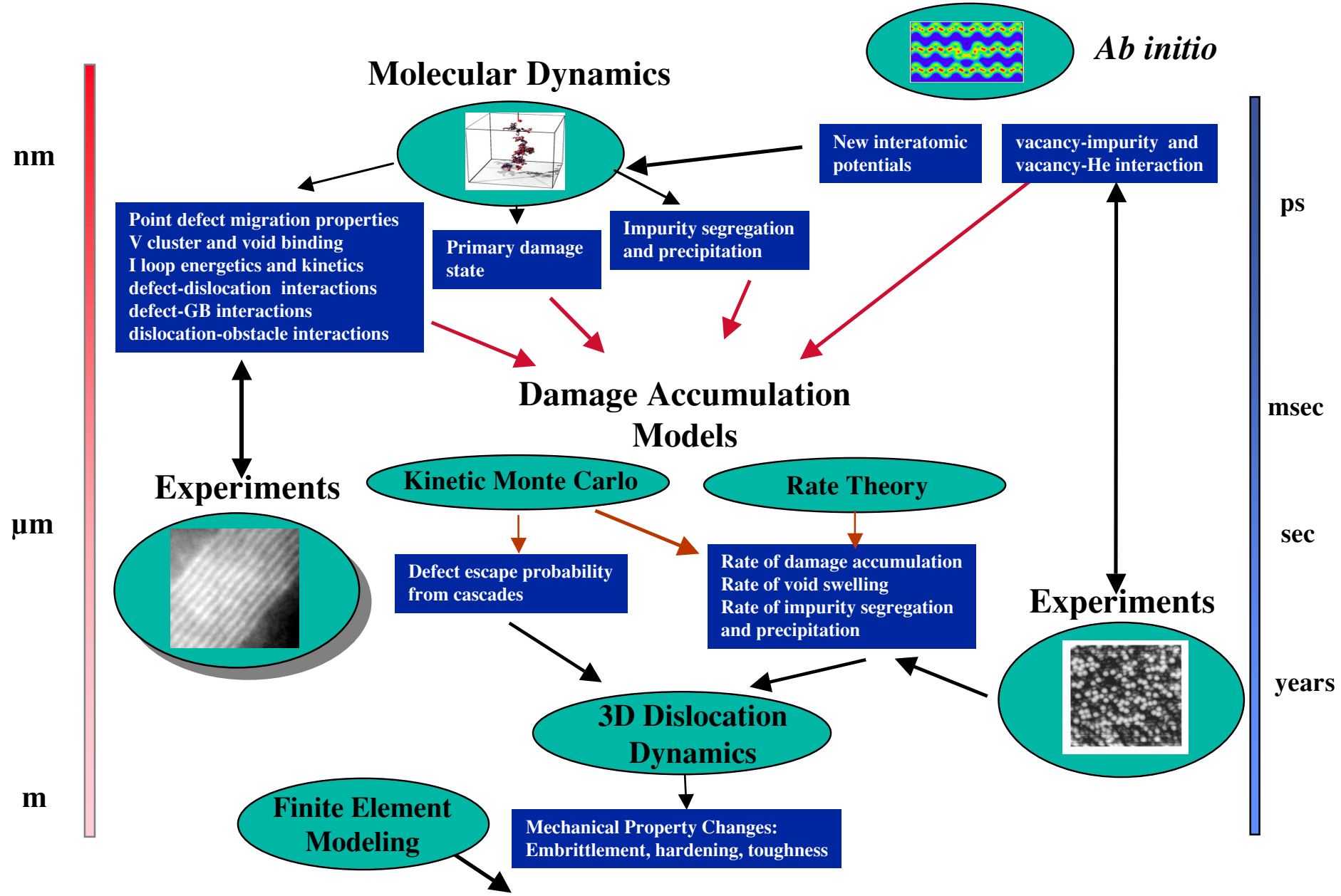
Positron OEMS
nano-vacancy clusters



	<d> (nm)	N (m^{-3})
<100>	20	$1x10^{22}$
<111>	30	$5x10^{21}$

- Review current state of understanding and look forward
  - Multiscale simulation and the computational microscope
  - Interatomic potentials (alloy) and point defect properties
  - Loops, loop interactions and impact of solutes & impurities
  - Radiation enhanced diffusion and segregation
  - Cascade defects and aging

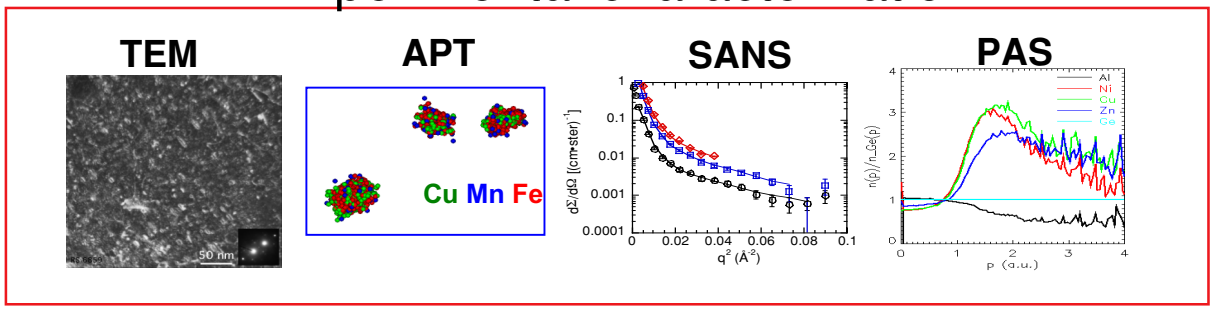
Multiscale modeling approach



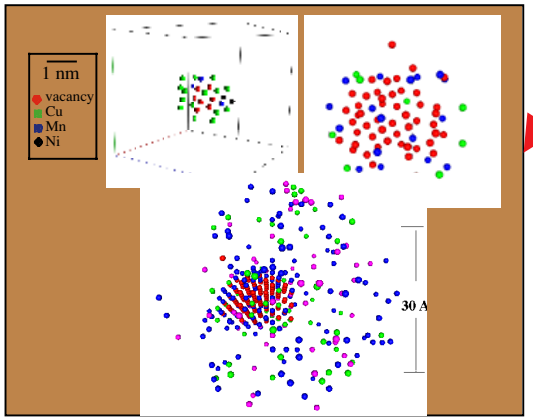
Computational microscope

Experimental characterization

feature 'signals'



Multiscale modeling

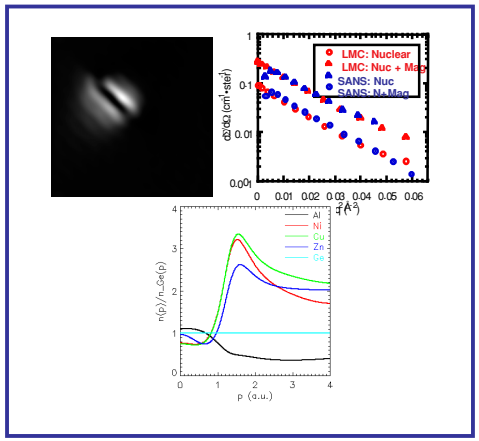


self-consistent 'understanding'

predict features

simulate observables

TEM, SANS, Positron theory



Apply complementary experimental measurements, closely coupled to modeling and positron theory

Ab-initio calculations lead to improved V potential

- Different EAM type potentials give very different predictions for Vanadium
- None of the EAM potentials correctly predict the stable form of the interstitial
- New interatomic Vanadium potential fit to experimental data and 1st principles calculations of: cohesive energy, bulk modulus, C_{11}, C_{12}, C_{44}, and vacancy formation energy

	vacancy	[100] split	[110] split	[111] split	[111] crowdion	Octa-hedral	Tetra-hedral
First Principles	2.60	3.57	3.48	3.14	3.15	3.62	3.69
Finnis-Sinclair	2.63	3.60	3.66	3.25	3.21	3.60	3.64

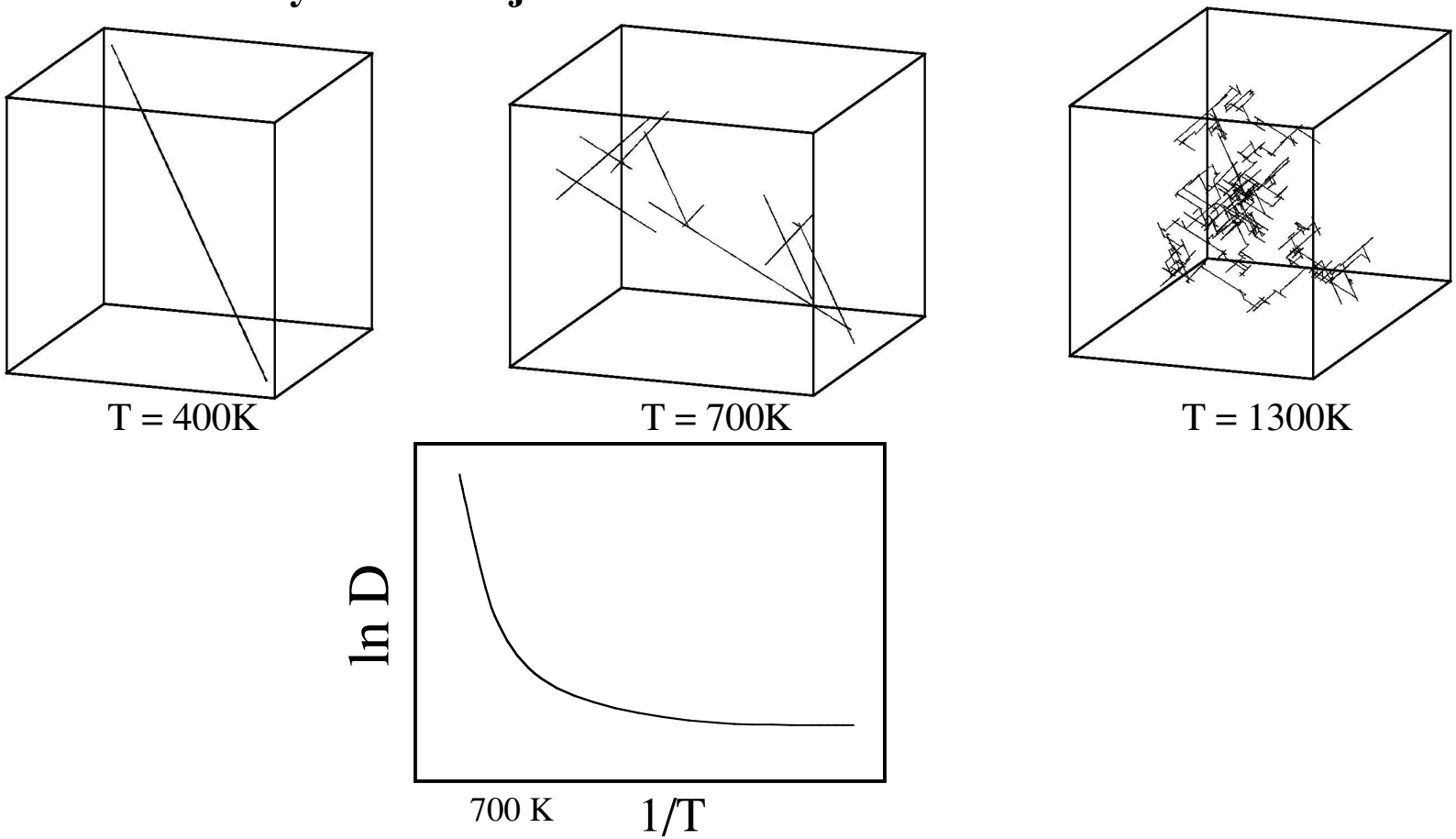
→ stable interstitial

Units: eV

- Very good agreement with 1st principles calculations
- Split [111] interstitial is most stable

Point defect migration in Vanadium

molecular dynamics trajectories of center of mass of <111> dumbbells



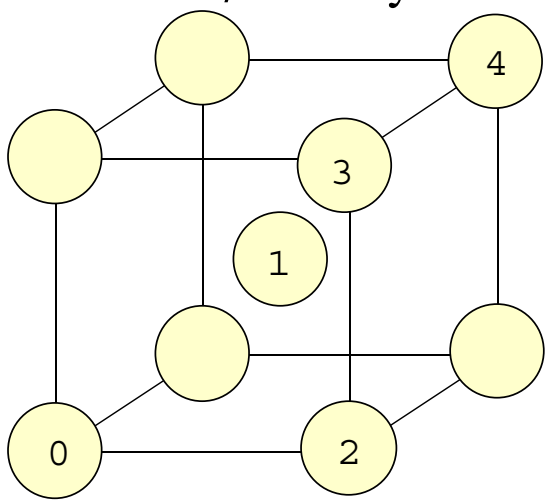
- <111> split dumbell migration is 1-d at low T (nearly athermal)
- Increasingly 3-d at high T
- Apparent activation energy for diffusion increases with increasing T
- Associated with temperature dependent “correlation factor”

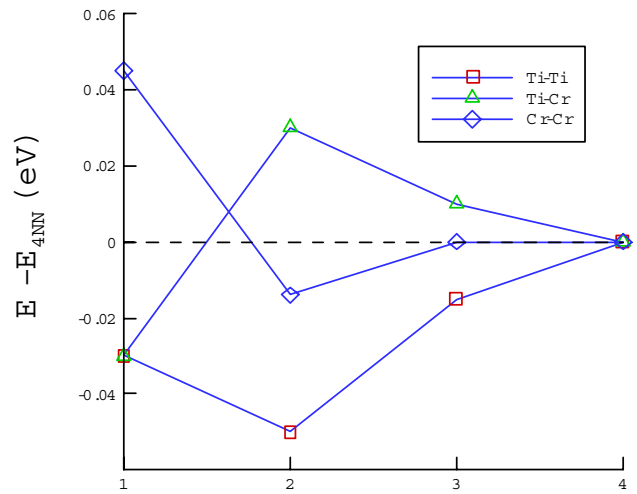
Alloy Interatomic Potentials Strategy

1. Generalized Finnis-Sinclair potential form
2. Fit to experimental single crystal data, intermetallics, $(da/dc)|_{c=0}$ for alloys
3. Fit to first principles data on interstitials, "random" alloy
4. Automate fitting to include whatever type of data is available

First Principles Alloy Input

- Full array of "bond" strengths
- Full array of interstitial/vacancy formation energies for all solvent-solute geometries

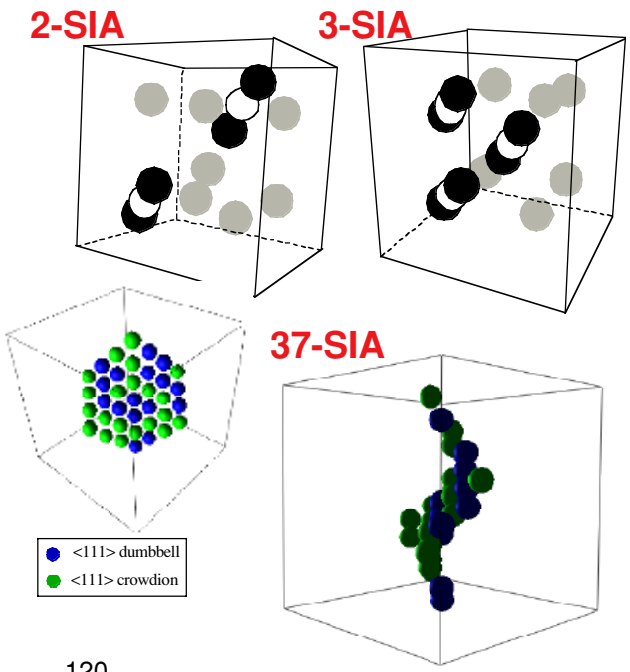




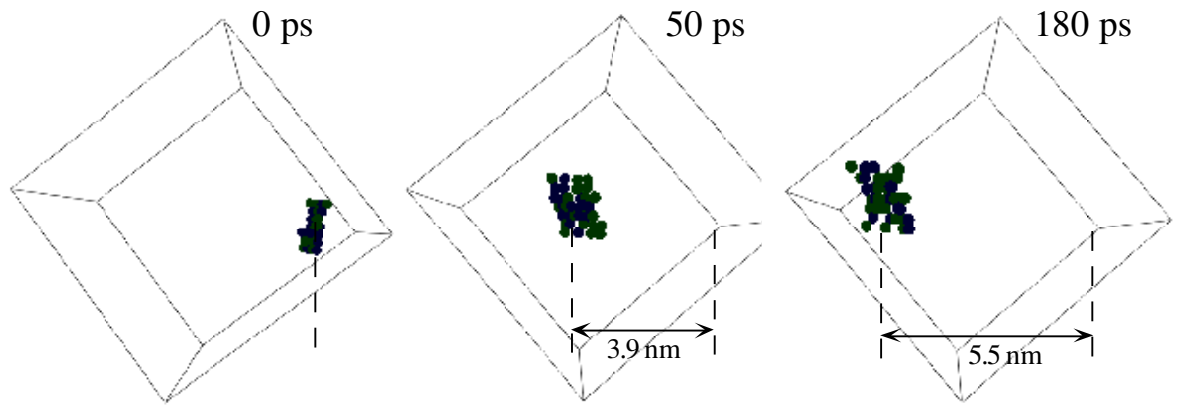
	Ti	V	Cr
Atomic radius (Å)	1.32	1.22	1.18
Covalent radius (Å)	2.00	1.92	1.85

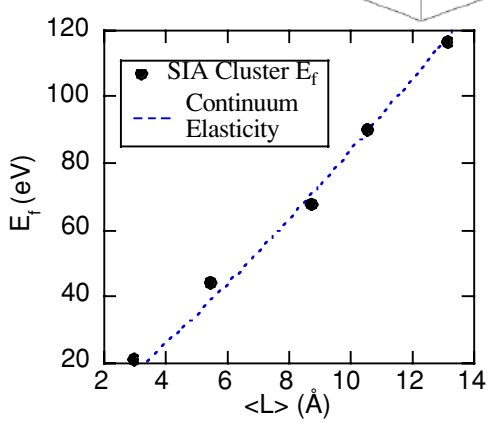
Ferritic alloys: self-interstitial clusters: <111> loops

- **Stability of <111> self-interstitial atom (SIA) clusters revealed by recent atomistic modeling (*Finnis-Sinclair and EAM-type interatomic potentials*)**
- **Stable single SIA is <110> split-dumbbell**



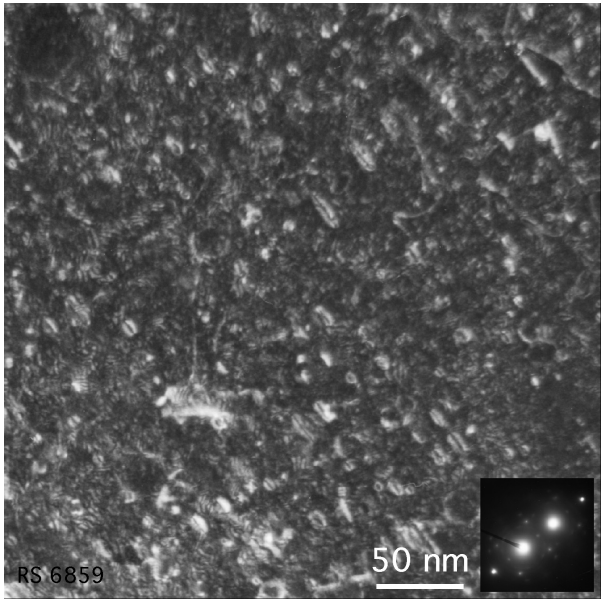
MD simulations at T=560 K reveal rapid (E^m < 0.1 eV) 1-D migration





- Form highly kinked, proto-<111> dislocation loops directly in cascades
- Migrate in 1-dimension with high mobility

Dislocation loop formation in ferritic steels

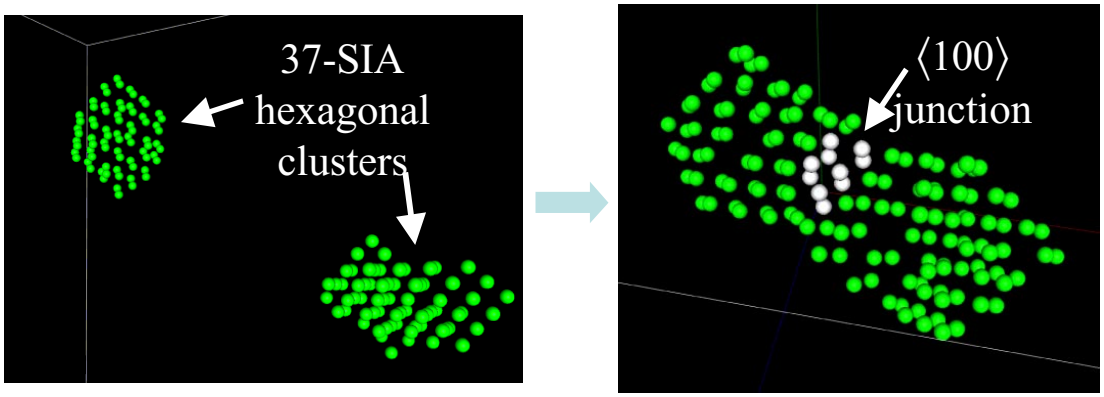


Irradiated ferritic steel (Fe-8Cr)

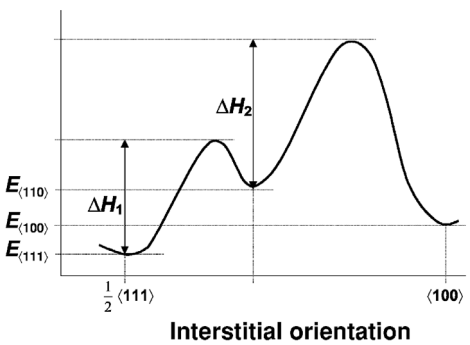
- **Large density of <100> loops observed (TEM) at high dose**

- New insight: <100> junctions form through interaction of highly mobile, <111> loops:

$$\frac{a_o}{2}[111] + \frac{a_o}{2}[1\bar{1}\bar{1}] \rightarrow a_o[100]$$



$\frac{1}{2}[111]$ $\frac{1}{2}[1\bar{1}\bar{1}]$ $\rightarrow$ $[100]$



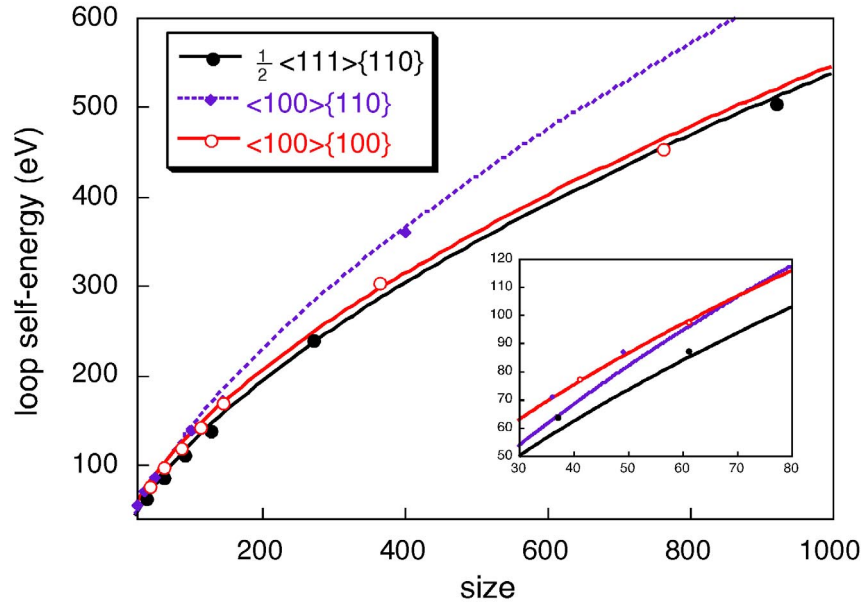
- Junction propagates or dissolves by 2-step mechanism

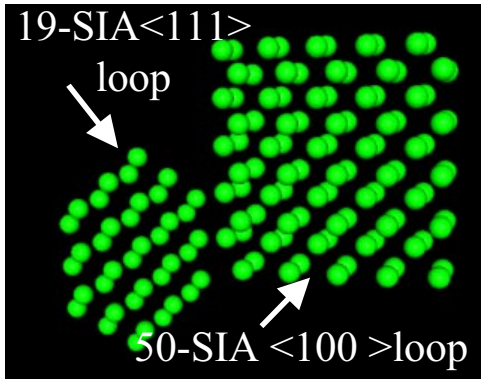
Energy landscape favors <100> growth

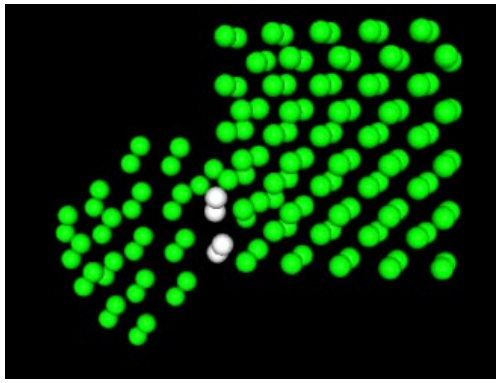
Growth mechanisms of <100> loops

- **Despite being metastable with respect to <111> loops, <100> loops grow by absorption of smaller <111> loops**

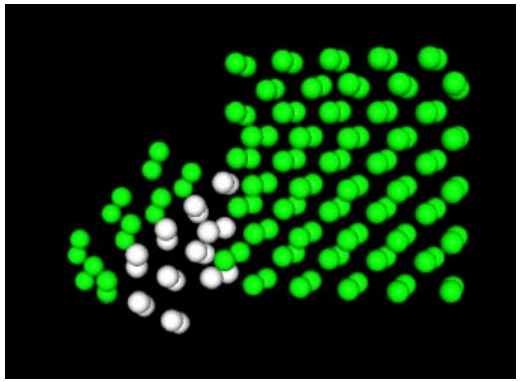
$$\int \langle 100\rangle + 2\,\frac{1}{2}\langle 111\rangle \rightarrow \langle 211\rangle \rightarrow \langle 100\rangle$$

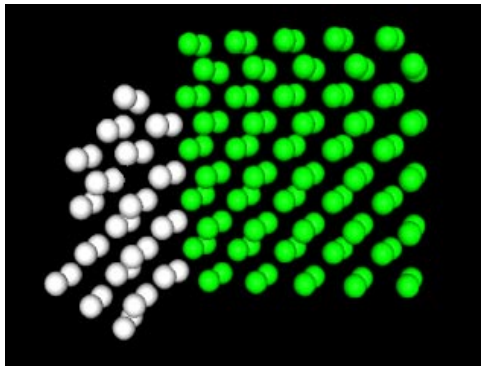


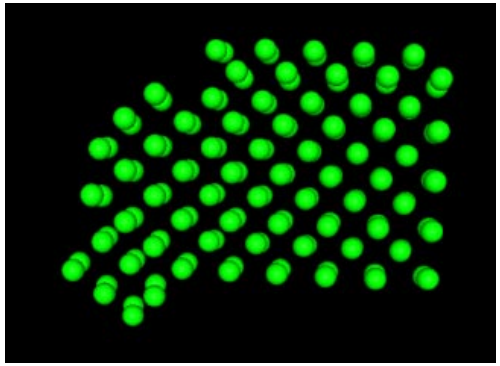




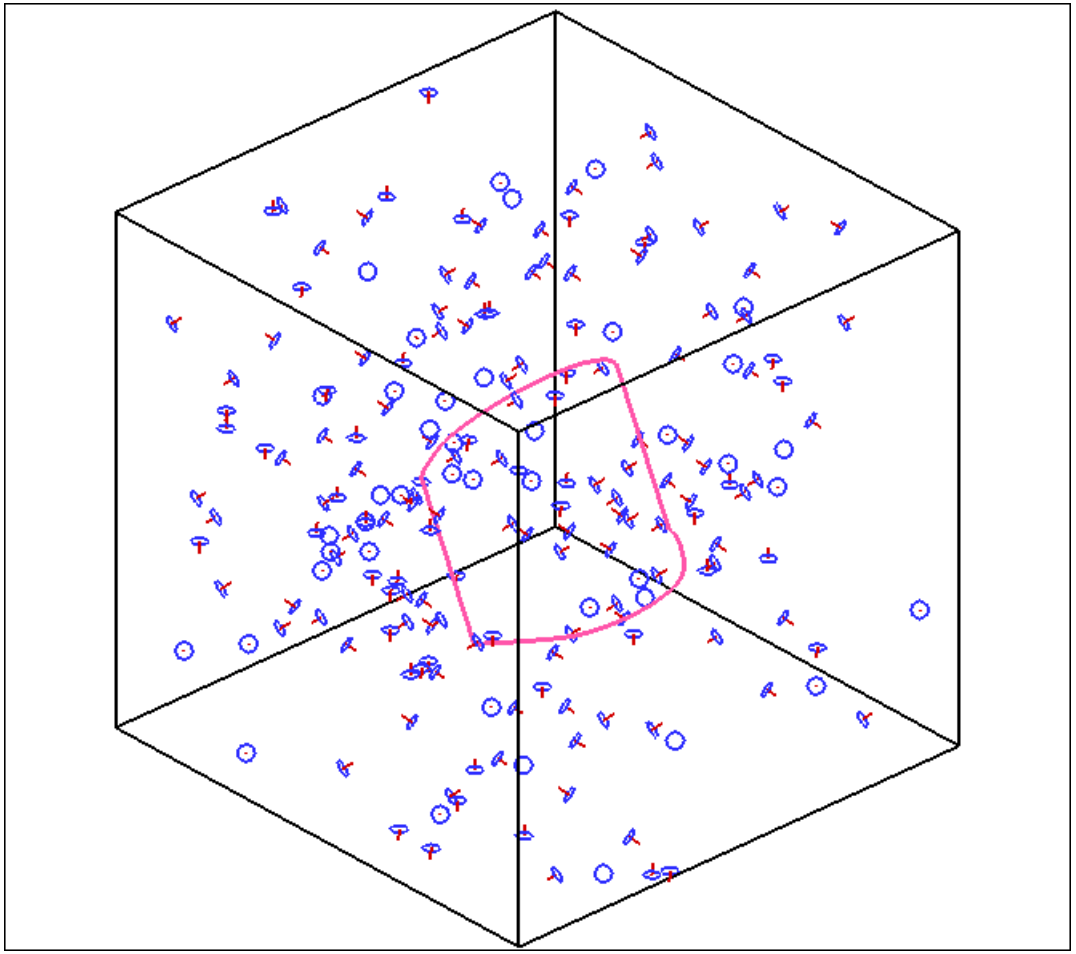
- Atoms shown in white, are rotating to join the <100> loop according to above reaction





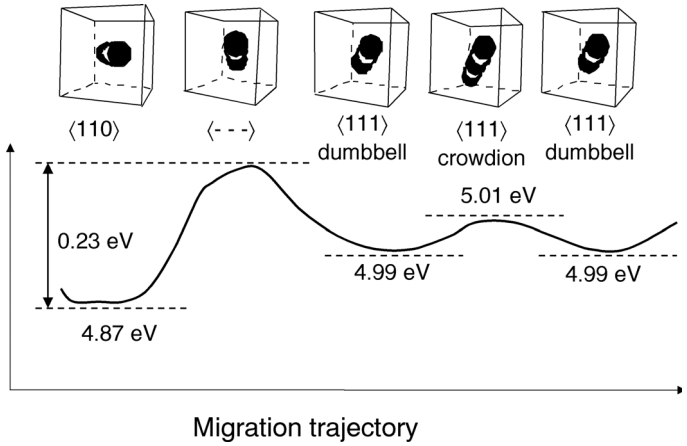


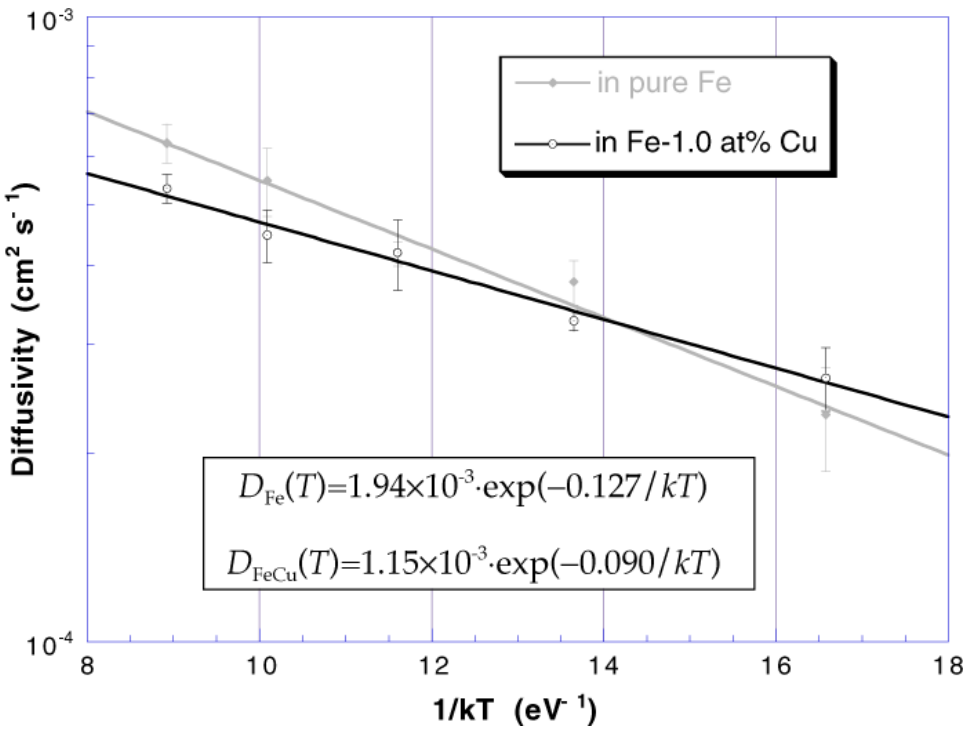
Loop - dislocation interactions: dislocation decoration & rafting



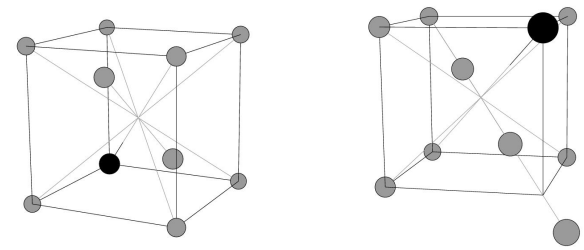
SIA Cluster Interaction with Dislocation Demonstrating the Importance of Cluster Rotation on Dislocation Decoration

Effect of substitutional solutes on self-interstitial migration

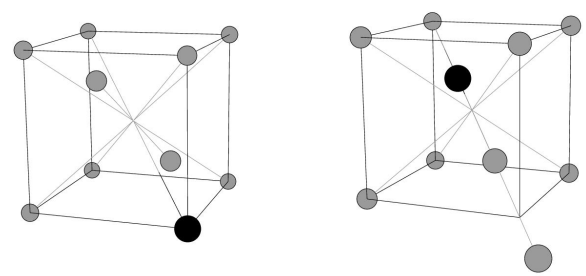




e_b= 0.02 eV e_b= 0.01 eV

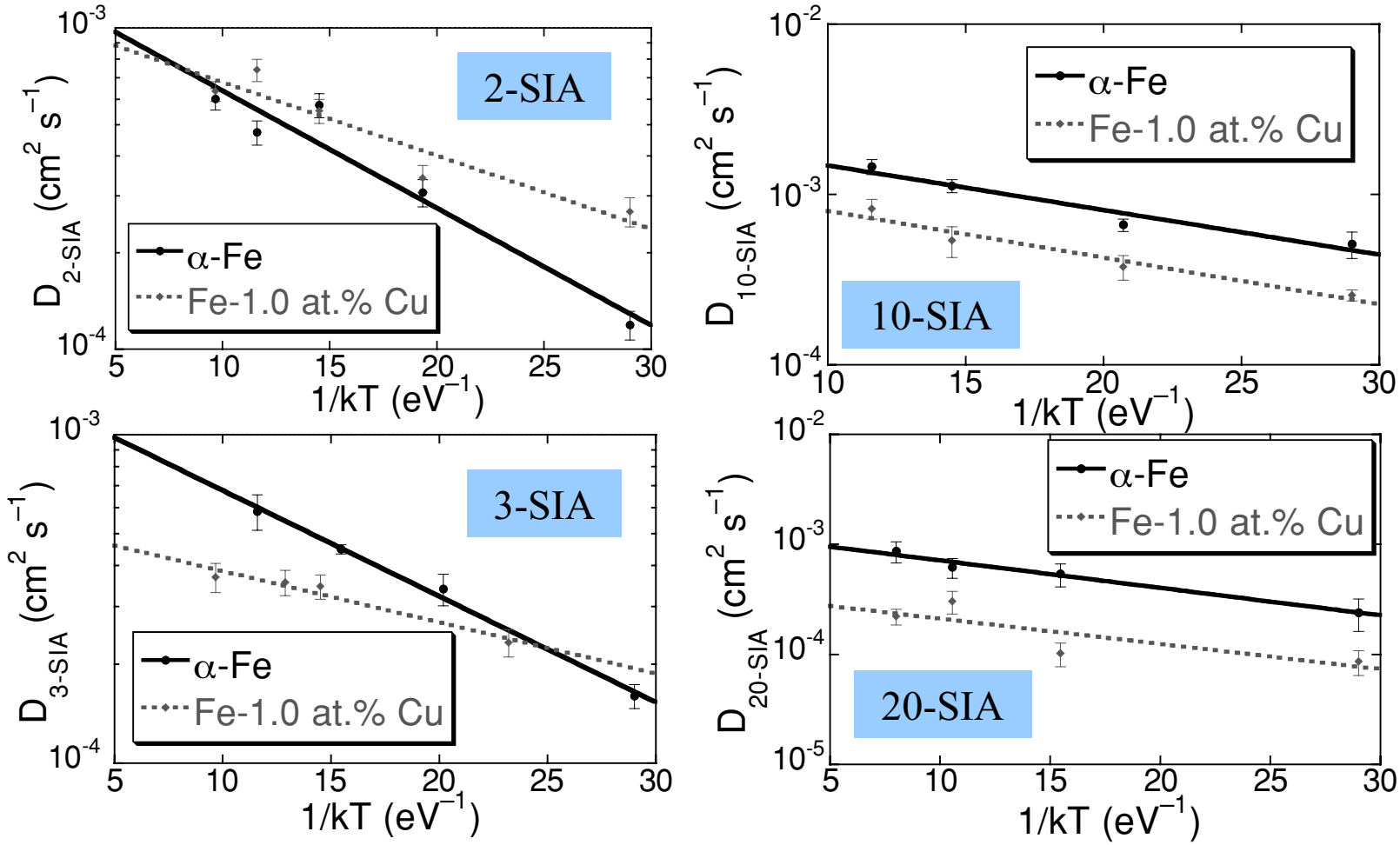


e_b= –0.04 eV e_b= –0.08 eV



Slight, but noticeable impact of 1% Cu on SIA migration - governed by displacement field interactions

Effect of substitutional solutes on self-interstitial cluster migration

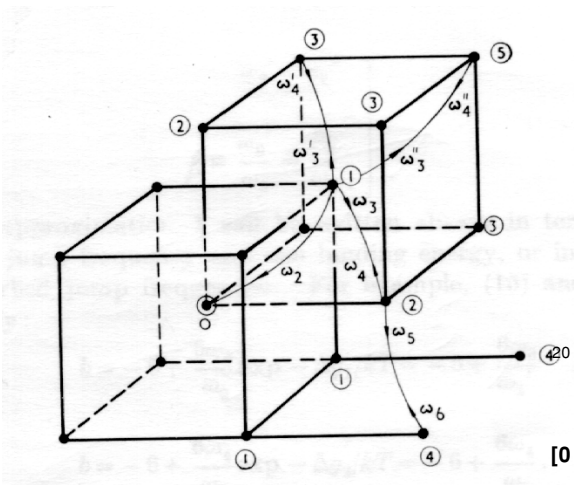


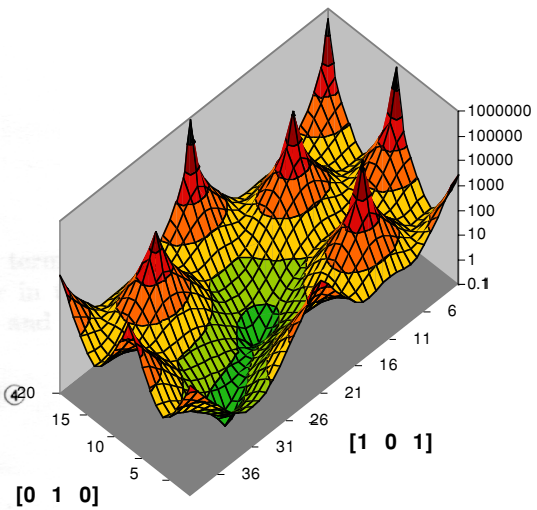
Small clusters (3-D migration)
Decrease E^m and D_o

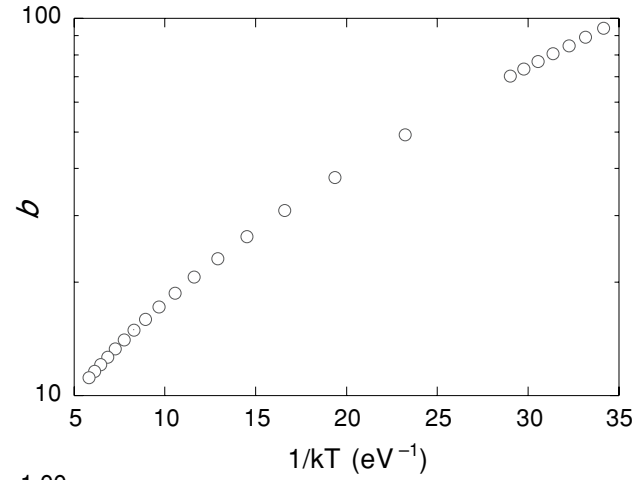
Larger clusters (1-D migration)
Decrease D_o, no change E^m

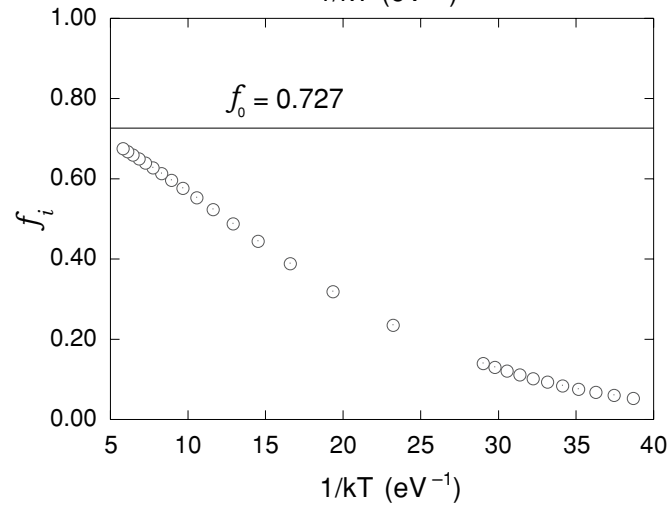
Radiation enhanced diffusion - atomistic modeling

- Le Claire five frequency model to calculate D_{cu} - including solute enhancement (b) and correlation factors (f_i) -- attempt frequencies and E_m^s from harmonic approximation theory using molecular statics (0 K) and EAM potential

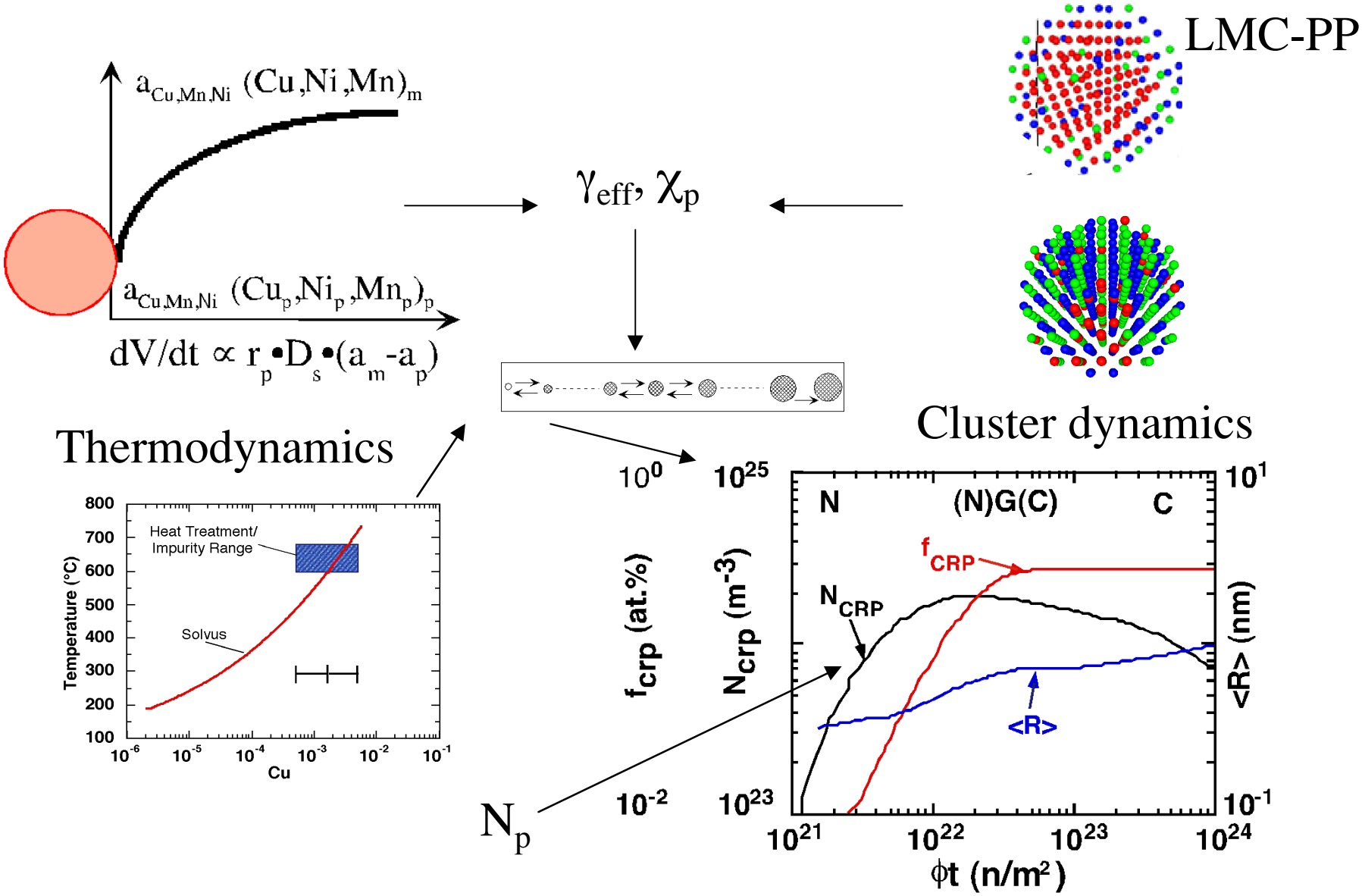




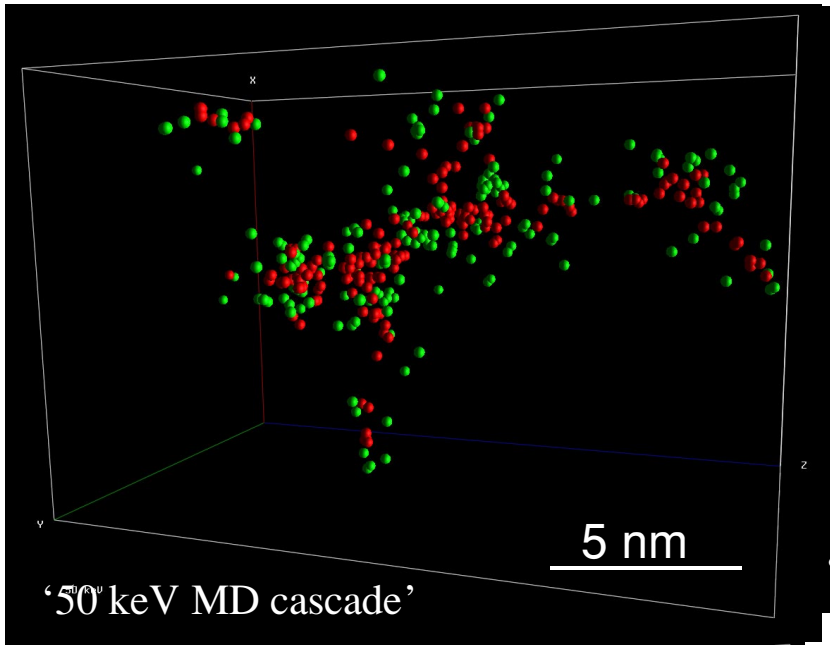


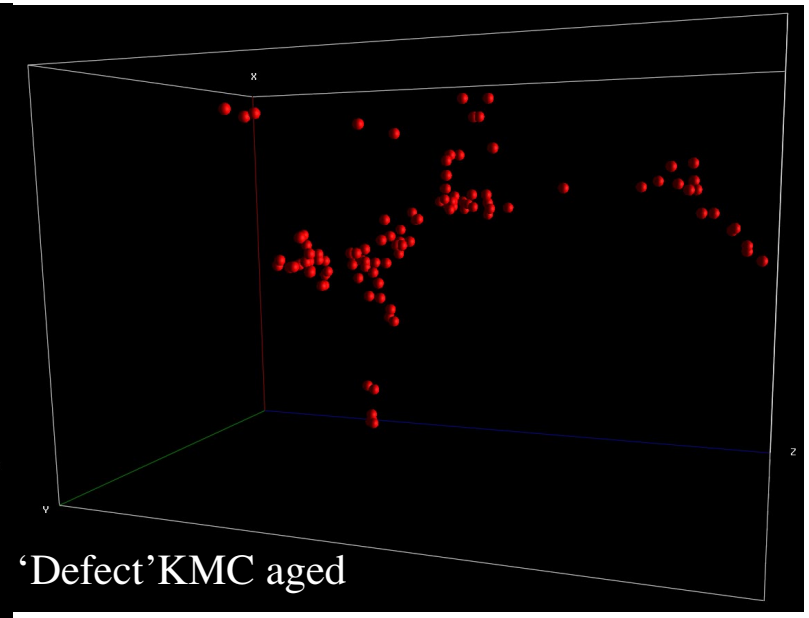


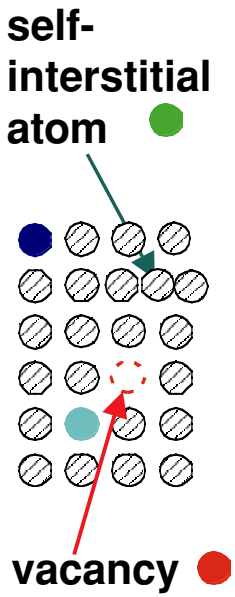
Modeling thermodynamics and phase stability

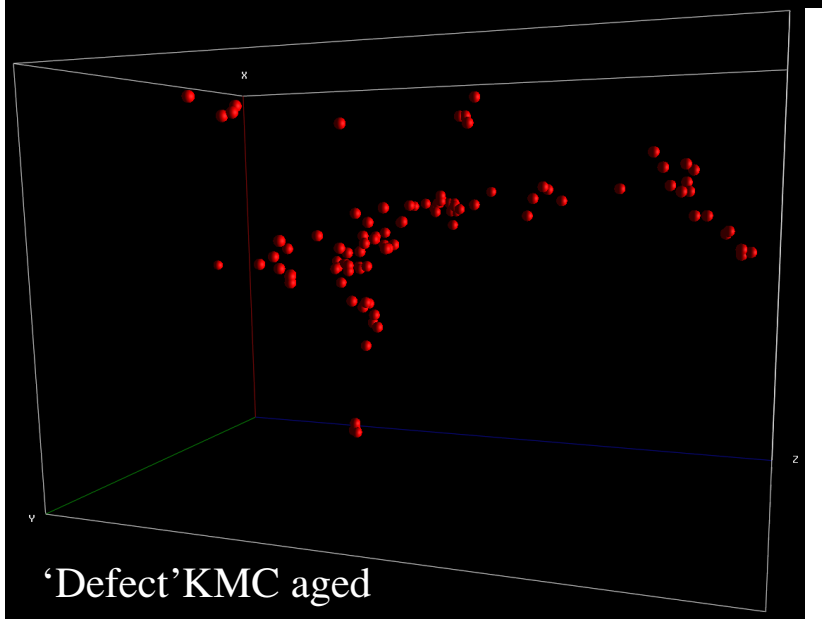


Initial cascade aging in Fe - 1st 100 ns, 290°C



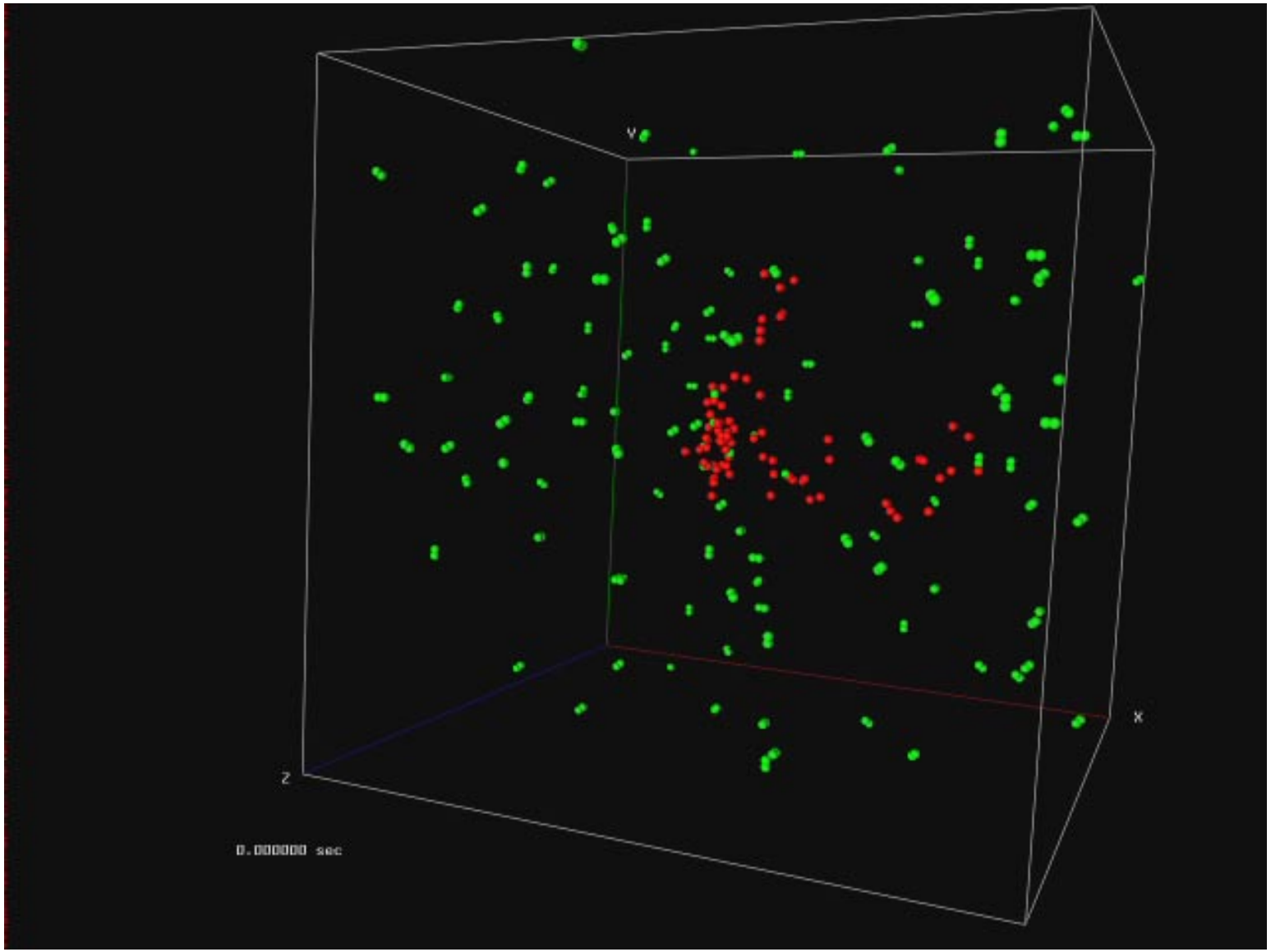






Cascade energy (keV)	MD defects (~ 100 ps)	Surviving vacancies (~ 100 ns)
20	54	47 (87%)
40	111	80 (72%)
50	176	111 (63%)

Long-term cascade aging in Fe-0.3 Cu, 290 °C, ~ 10^{-8} dpa/s



Vacancy-Cu cluster evolution movie at 5×10^{-8} dpa/s

- 20, 40 or 50 keV cascades introduced randomly at 5×10^{-8} dpa/s
- Initial evolution to ~0.6 mdpa

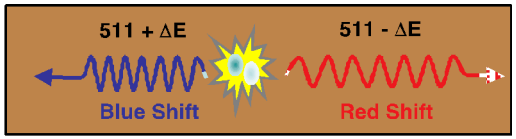
vacancy

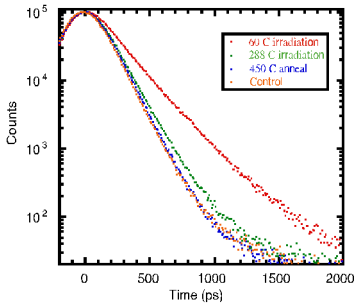
Cu

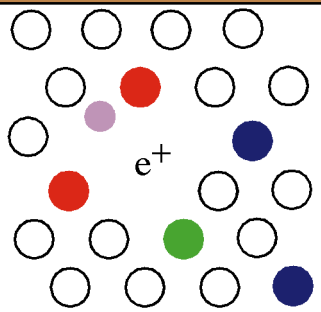
- Only 'clustered' Cu atoms are shown

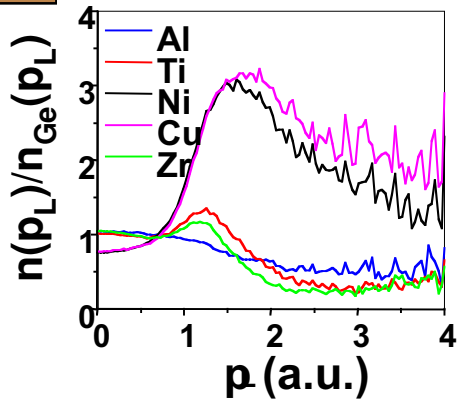
Validation of sub-nm vacancy-solute clusters

Positron annihilation spectroscopy

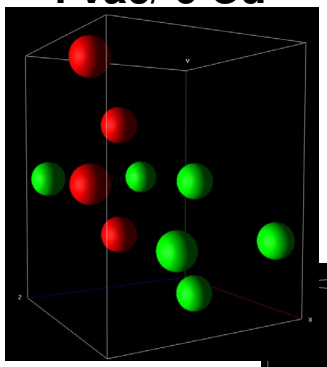






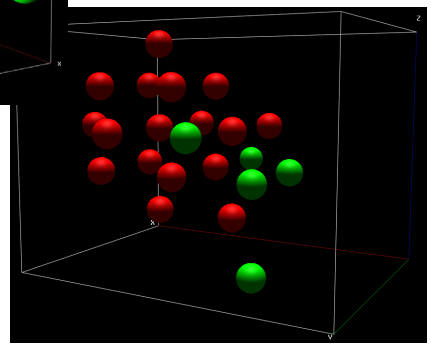


4 vac/ 6 Cu



KMC predicts vacancy-Cu clusters

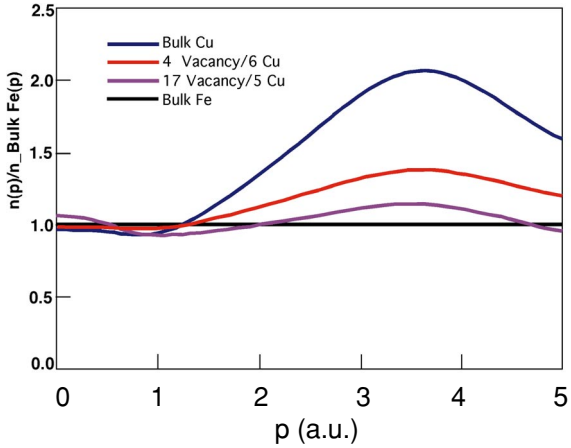
17 vac/ 5 Cu



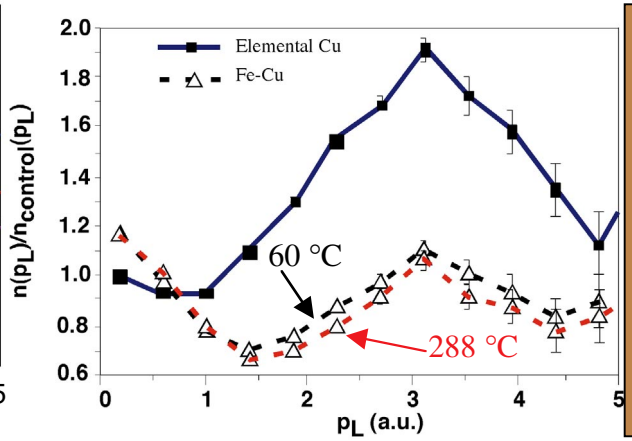
Predicted positron lifetimes

Vac/Cu	τ (ps)
3/6	173
4/6	216
17/5	350
>50/x	520

Predicted OEMS



Measured OEMS

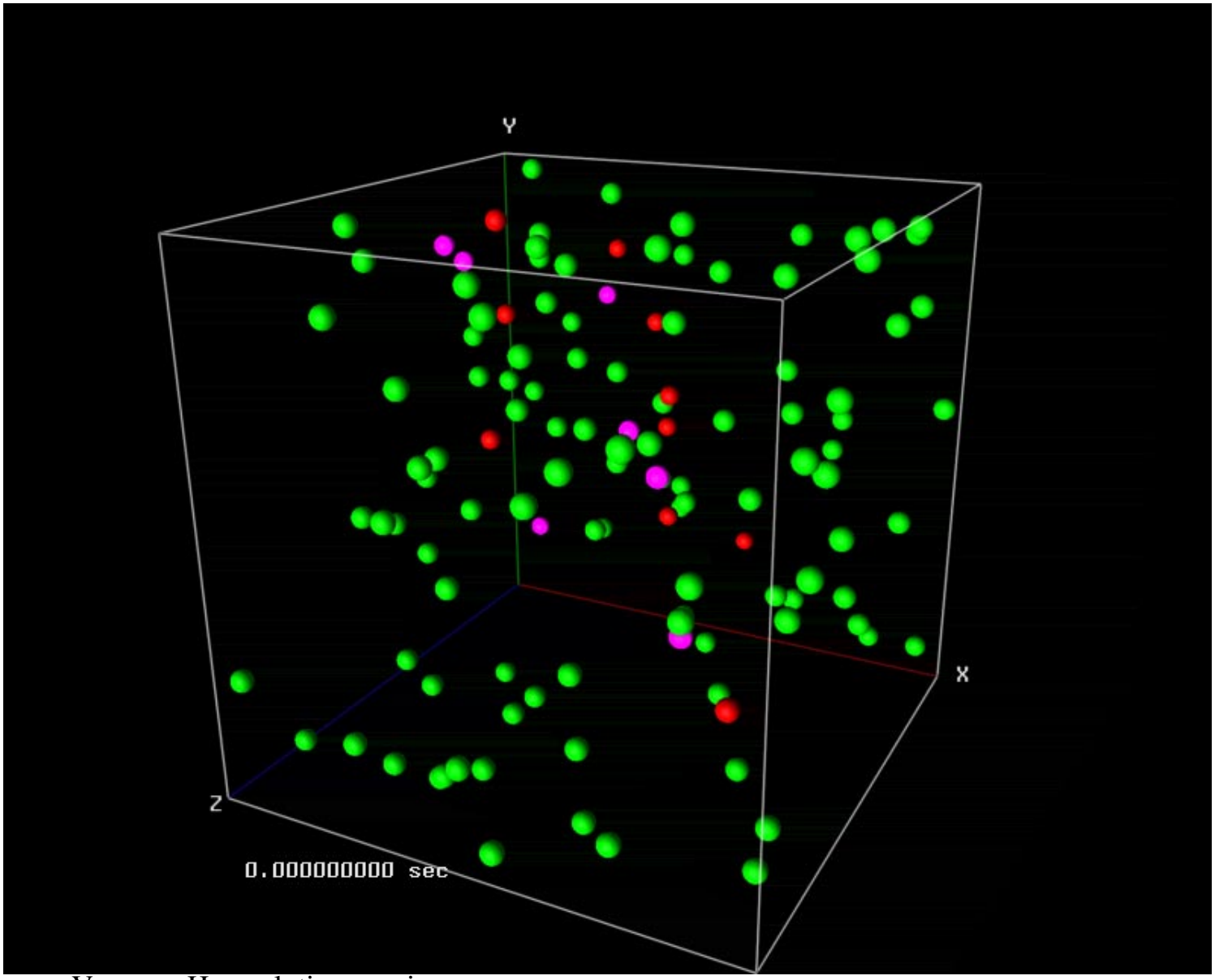


Measured positron lifetimes

τ (ps) - 60°C
178
355

τ (ps) - 288°C
222
520

Lattice KMC simulations of vacancy-He diffusion and clustering



Vacancy-He evolution movie

- 650 K, random vacancy distribution + HeS & HeI
- Rapid motion & trapping of HeI - dissolution of di-He, HeS+HeI
- Vacancy sink at cell boundary

Interstitial He

He substitutional

vacancy

Summary

- Importance of modeling - experimental interface; computational microscope
- Ab-initio simulations provide information on defect structure, alloy interactions important to understanding radiation damage and developing semi-empirical interatomic potentials
- Atomistic MD simulations provide information on defect cluster properties and defect - solute interactions
  - Self-interstitials in Vanadium: <111> crowdion, 1-D/3-D mobility
  - Self-interstitial clusters in Fe: <111> with high 1-D mobility, interactions and energetics explain <100> loop formation
  - Impact of solute impurities on SIA cluster mobility in Fe-Cu alloys
  - Solute transport by vacancy-mediated radiation enhanced diffusion
- Kinetic lattice Monte Carlo simulations provide information on long-time aging of displacement cascades
  - Formation of small, 3-dimensional vacancy-solute clusters
  - Implementation for investigating He-vacancy clustering and bubble nucleation

Outstanding Issues in Vanadium Alloys

- Why does the addition of Fe, Cr to V greatly increase swelling rates?
- How does the addition of Ti decrease swelling rates in V-4Cr?
- What are the thermodynamics/kinetics of Ti-interstitial precipitate formation?
- Characterize point defect clusters, why do <100> dislocation loops form in Ferritic alloys, but not Vanadium alloys?
- What other alloying additions should be considered for swelling reduction, interstitial gettering, and strengthening?
- What oxygen containing coatings are compatible with vanadium?
- Extract reduced order models for alloy design
- He effects on defect cluster properties and evolution?

A look ahead for ferritic alloys

- He effects on defect cluster properties and cascade aging evolution
- He trapping efficiencies and management strategies
- Effect of interstitial and solute impurities on defect cluster properties, in particular, radiation enhanced diffusion and radiation induced segregation
- Self-interstitial cluster/dislocation loop interactions with impurities, system sinks
- Interface structure and thermal/radiation stability of nano-oxide dispersoids, defect/He trapping efficiency