Defects in Metallic Materials

M. J. Demkowicz
MIT Department of Materials Science and Engineering, Cambridge MA, 02139

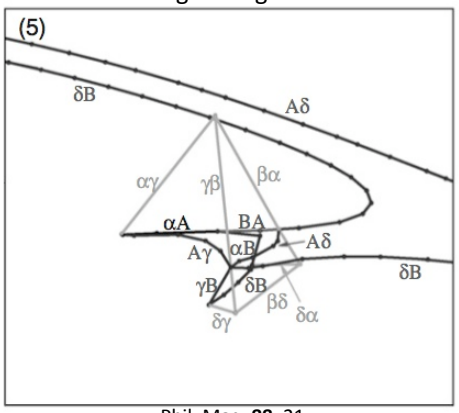
Center for Materials Science and Nuclear Fuels (CMSNF) Summer School: Microstructural Development in Systems Exposed to Extreme Environments Found Within a Nuclear Reactor Core

ATR National Scientific User Facility
June 6-10, 2011, Idaho Falls, ID

Updated files: http://web.mit.edu/~mikejd/Public/

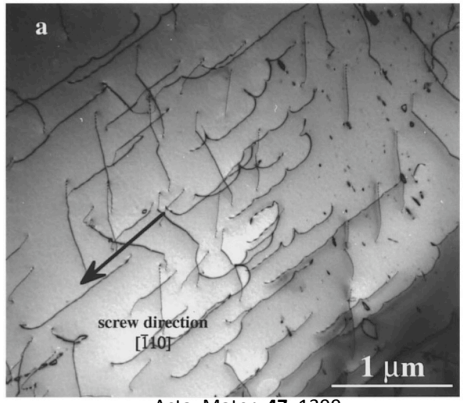
Defects in modern materials theories

Cutting through an SFT



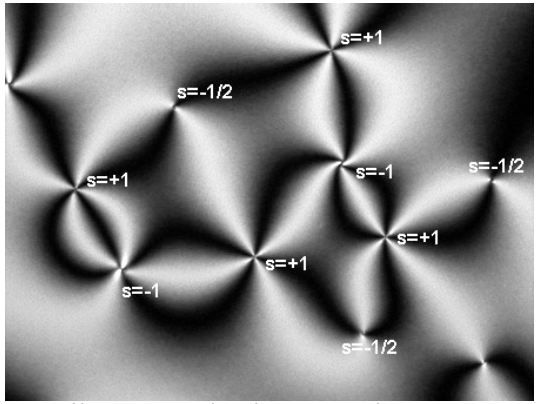
Phil. Mag. **88**, 21

Dislocations in γ-TiAl



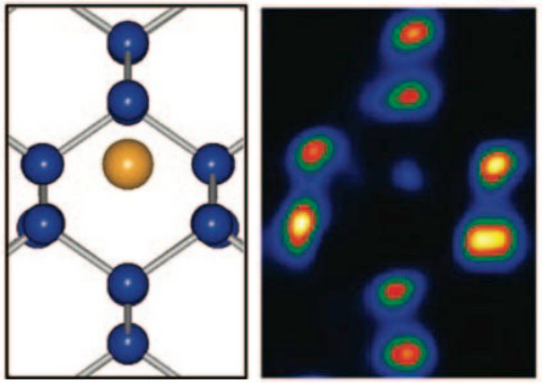
Acta. Mater. **47**, 1399

Disclinations in nematic liquid crystals



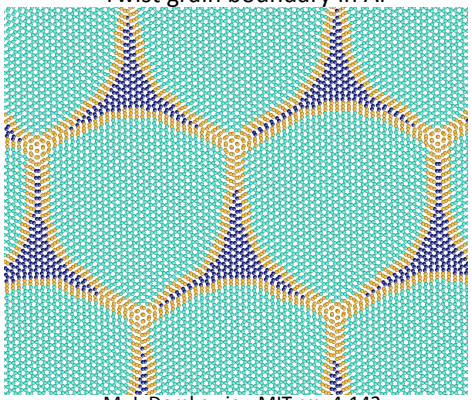
http://dept.kent.edu/spie/liquidcrystals/textures1.html

Au impurity in Si



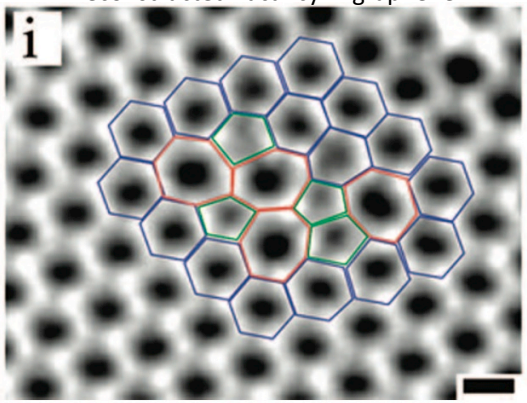
Nano. Lett. **8**, 1016

Twist grain boundary in Al



M. J. Demkowicz, MIT rm. 4-142

Reconstructed vacancy in graphene



Nano. Lett. **8**, 3582

Defects are central to modern materials theories. They are agents of "multiscaling" that connect atomic and macroscopic scales. Atomic-level physics determines defect structures and properties. Defect physics determines macroscale behaviors such as diffusion, plastic deformation, radiation response, phase transformations, microstructure evolution, and corrosion.

Lecture outline

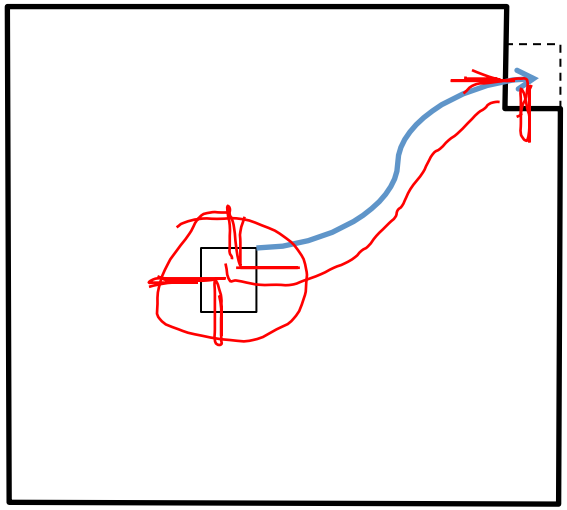
- Point defects
  - Vacancies and interstitials
  - Point defect reactions
- Dislocations
  - Review of definitions
  - Interaction with point defects
  - Climb, prismatic loops
- Grain boundaries and heterophase interfaces
  - Macroscopic and microscopic degrees of freedom
  - Interaction with point defects

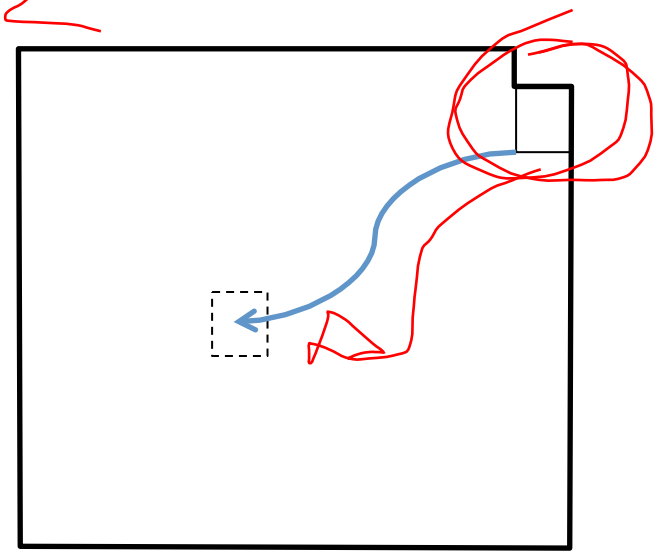
Point defect formation

Vacancy

$\Delta V \approx \Omega$

Self-interstitial

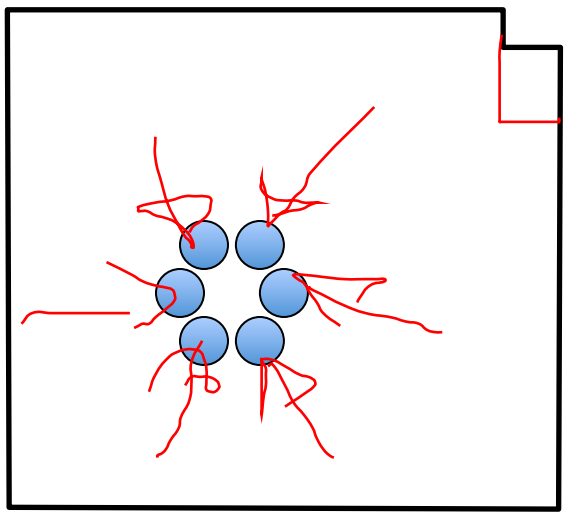




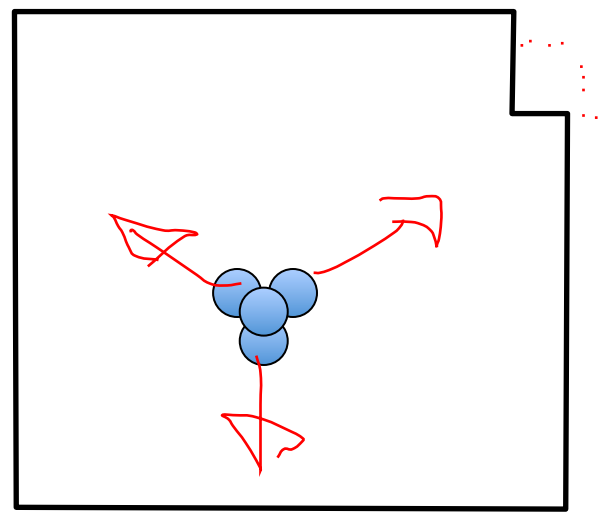
$\Delta E_v^f = N\epsilon/2$, ΔE_i^f

Relaxation volume

Vacancy



Self-interstitial



$\Delta V_v^r < 0$

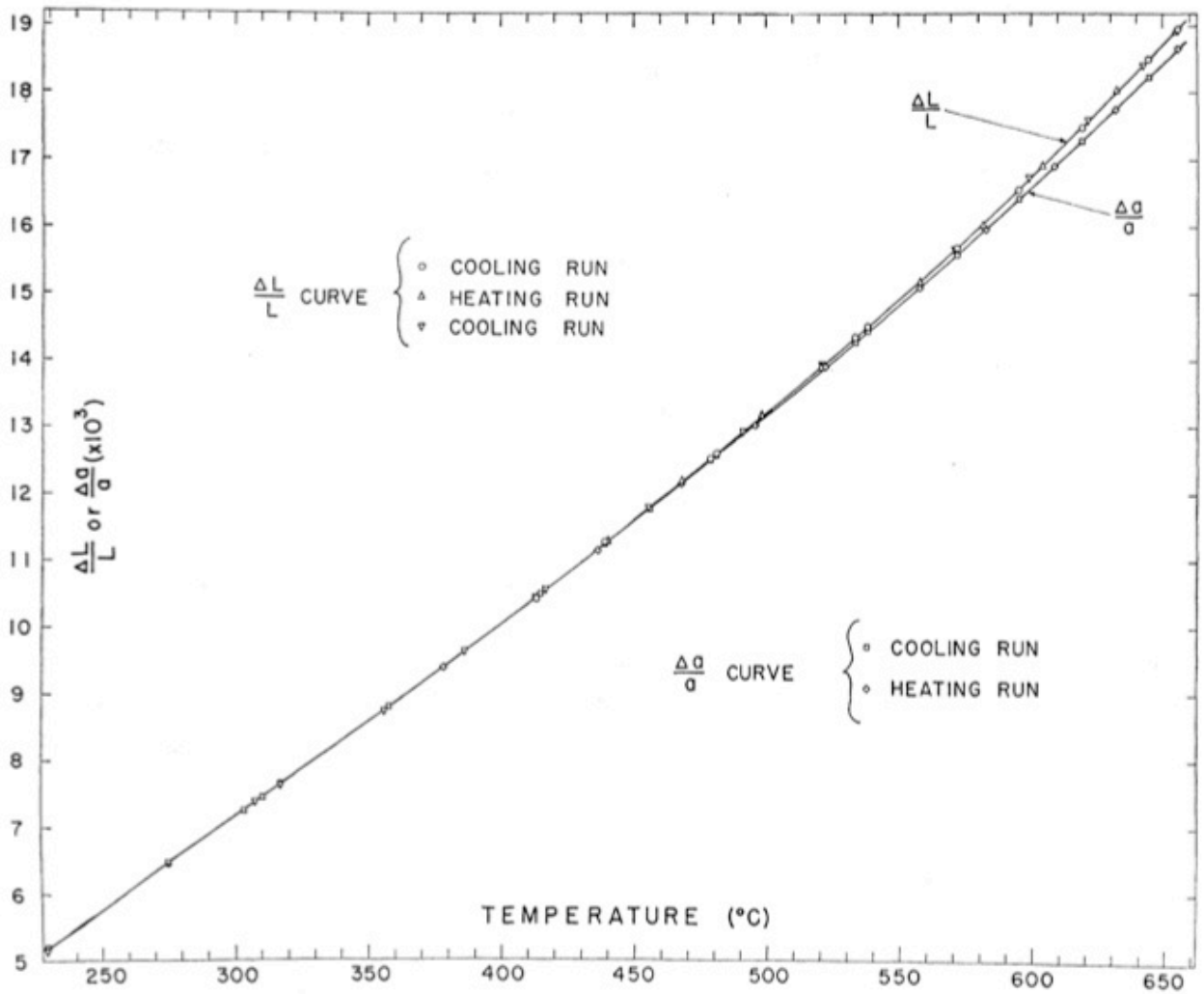
$\approx 0.1\,\Omega$

$\Delta V_i^r > 0$

$\approx \Omega$

$c = e^{-\Delta E_f / k_B T}$

Differential dilatometry



R. O. Simmons, R. W. Balluffi, Phys. Rev. **117**, 52 (1960)

Resistivity annealing

T_1

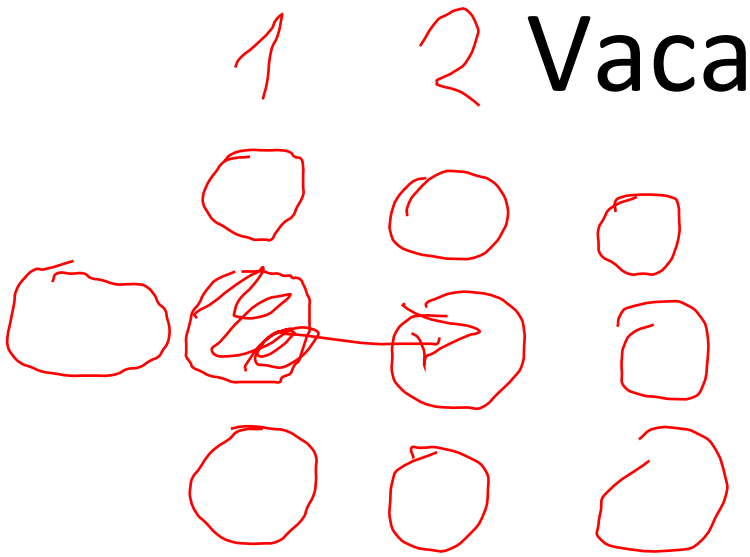
$$C_v = e^{-\Delta E_v^f \beta}$$

$$\rho \sim C_v$$

$T_2 << T_1$

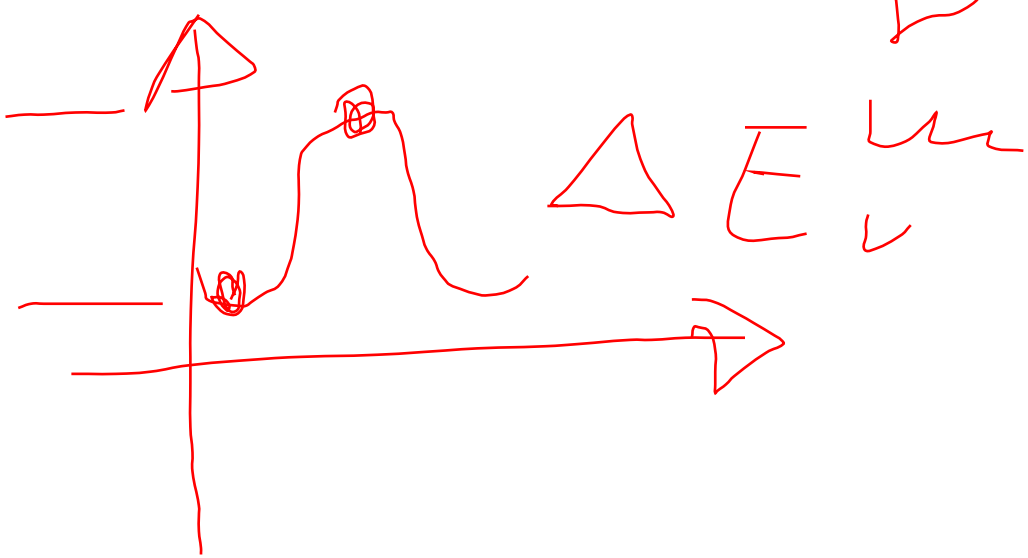
$$\rho(T_1) \sim e^{-\Delta E_v^f \beta}$$

Vacancy migration



$$\nu = \nu_0 e^{-\Delta E_v^m \beta}$$

$$\nu = \nu_{TST} \quad \text{— // —}$$



Vacancy data

Element	E_{coh} (eV)	ΔE_v^f (eV)	ΔS_v^f (k_B)	Δv_v (Ω)	ΔE_v^m (eV)
Ag	2.85	1.11	1.5	N/A	0.66
Al	3.36	0.67	0.7	-0.05	0.61
Cu	3.54	1.28	2.8	-0.25	0.70
α-Fe	4.29	1.59-1.73	N/A	-0.05	0.55
Mg	1.6	0.79	~0	0.5-0.6 (?)	N/A
Mo	6.81	3.0	1.6	-0.1	1.35
Pb	N/A	0.58	2.6	N/A	0.43
W	8.66	3.6	3.2	N/A	1.70
Zr	N/A	>1.5	N/A	-0.05	0.6-0.7

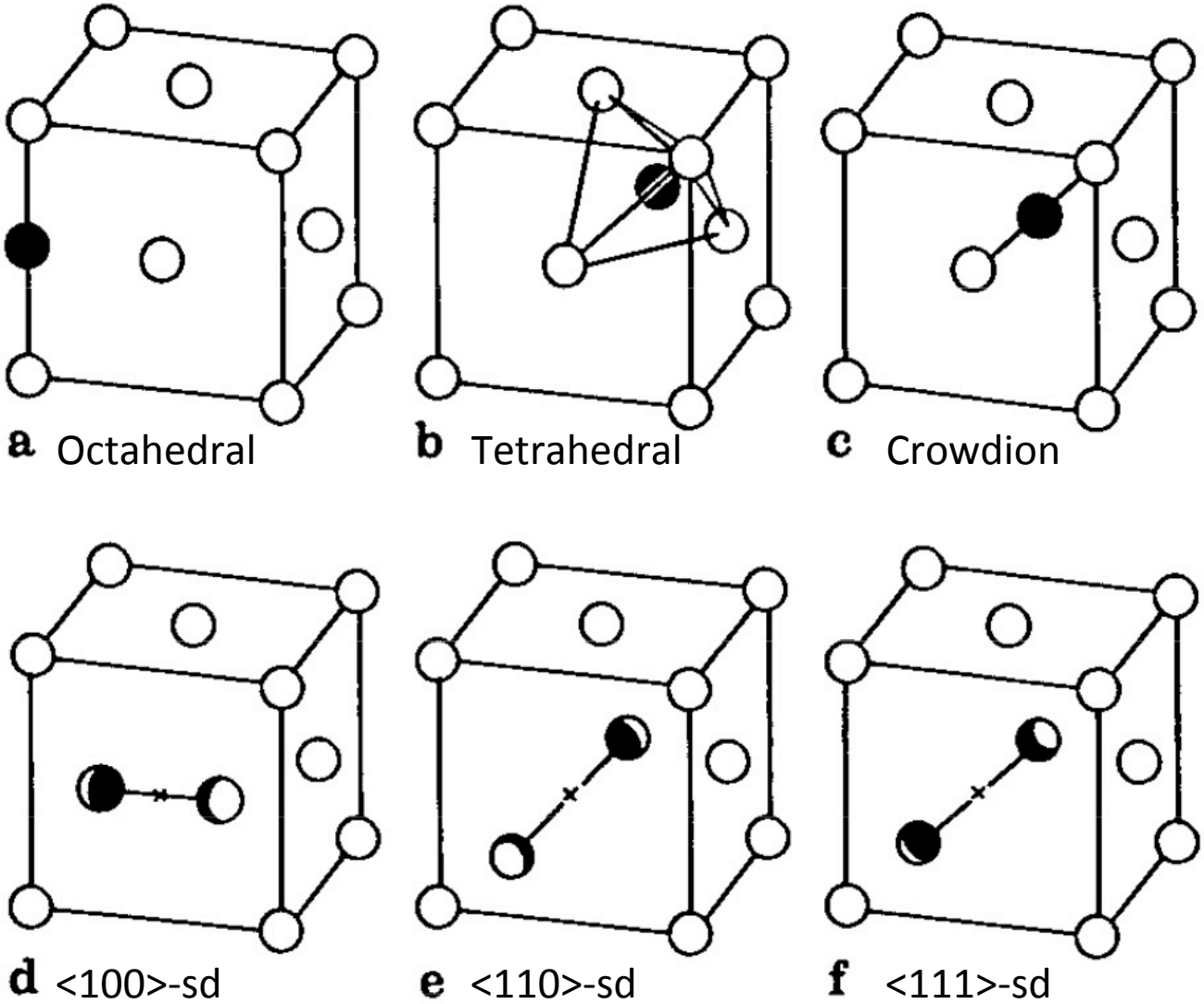
H. J. Wollenberger, "Point Defects" in Physical Metallurgy, R. W. Cahn and P. Haasen, eds. (North Holland, 1996)

Interstitial data

Element	Structure	ΔE_i^f (eV)	Δv_i (Ω)	ΔE_i^m (eV)
Cu[1]	<100>-sd	3.23	1.0	0.038
α-Fe[2]	<110>-sd	3.64	N/A	0.34
Cr[3]	Crowdion	5.66	N/A	<0.01
Mo[3]	<111>-sd	7.42	N/A	<0.01
W[3]	<111>-sd	9.55	N/A	<0.01
Zr[4]	Octahedral	2.84	1.16	N/A

[1]Y. Mishin, M. J. Mehl, D. A. Papaconstantopoulos, A. F. Voter, J. D. Kress, Phys. Rev. B 63, 224106 (2001)
[2]C.-C. Fu, F. Willaime, P. Ordejon, Phys. Rev. Lett. 92, 175503 (2004)
[3]D. Nguyen-Manh, A. P. Horsfield, S. L. Dudarev, Phys. Rev. B. 73, 20101 (2006)
[4]C. Domain, A. Legris, Phil. Mag. 85, 569 (2005)

Self-interstitial structures: fcc metals

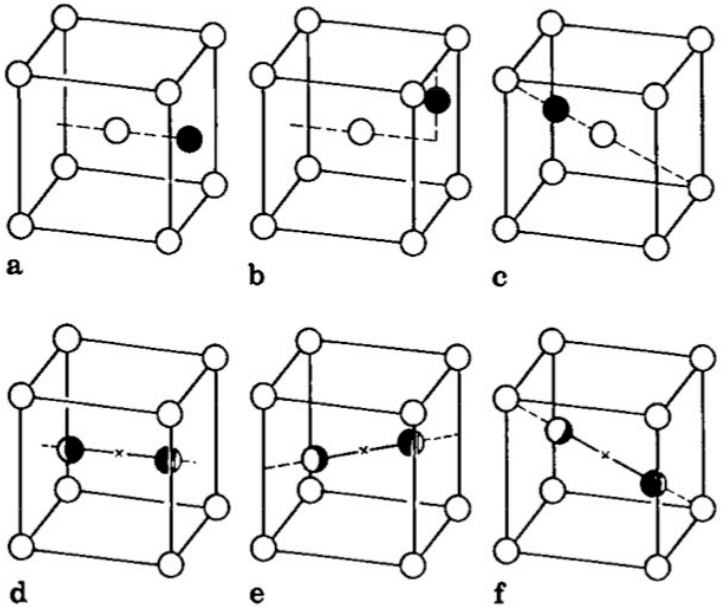


H. Landolt, P. Ehrhart, H. Ullmaier, Atomic Defects in Metals (Springer, 1991)

Self-interstitial structures: bcc and hcp

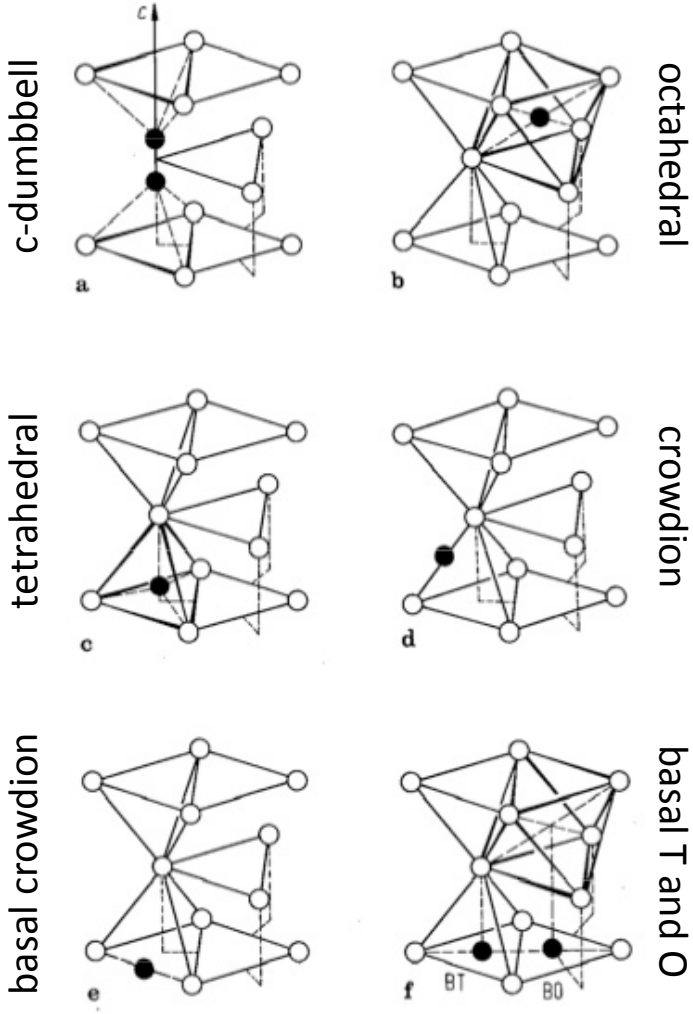
BCC

Octahedral Tetrahedral Crowdion



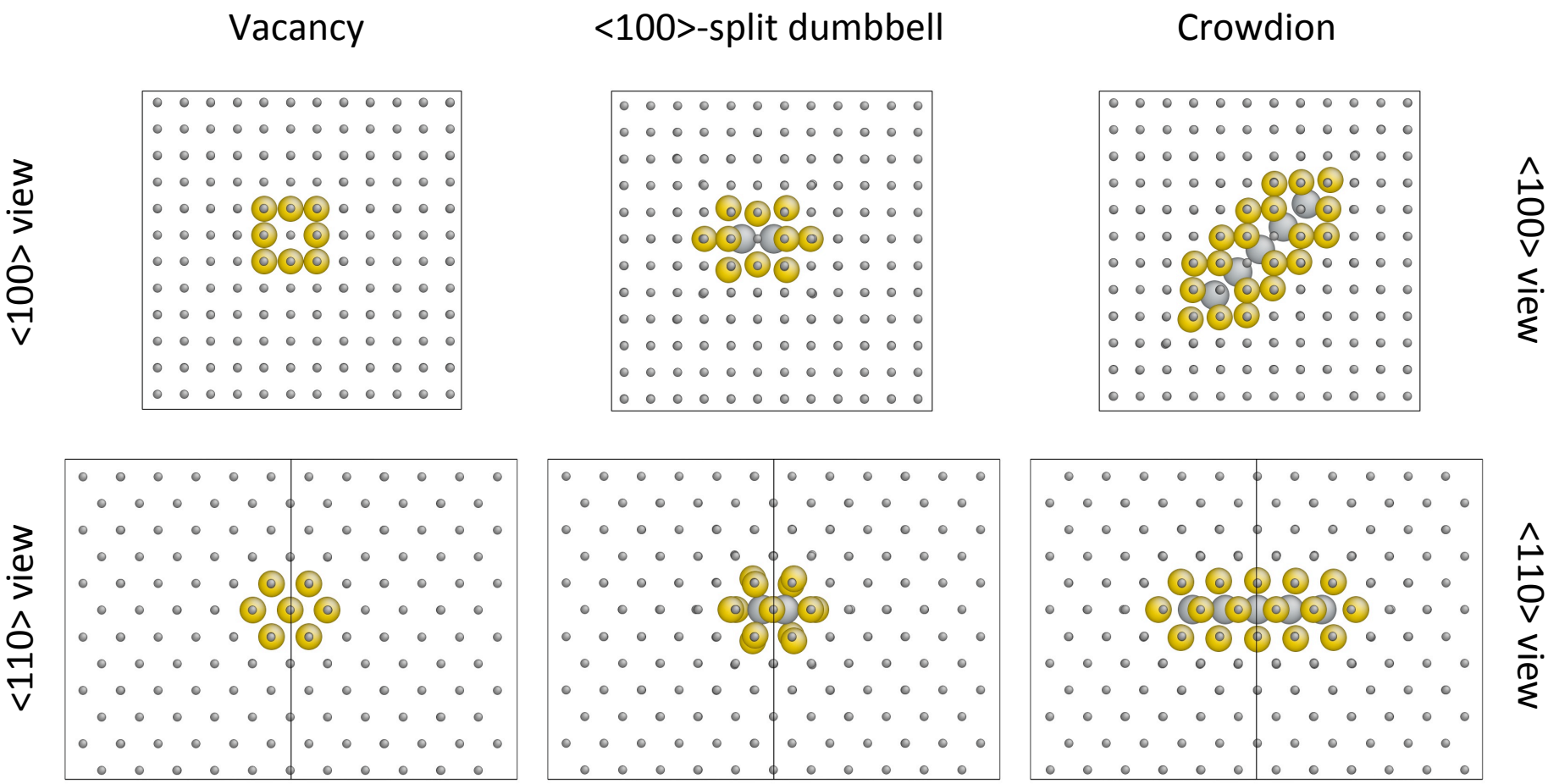
<100>-sd <110>-sd <111>-sd

HCP



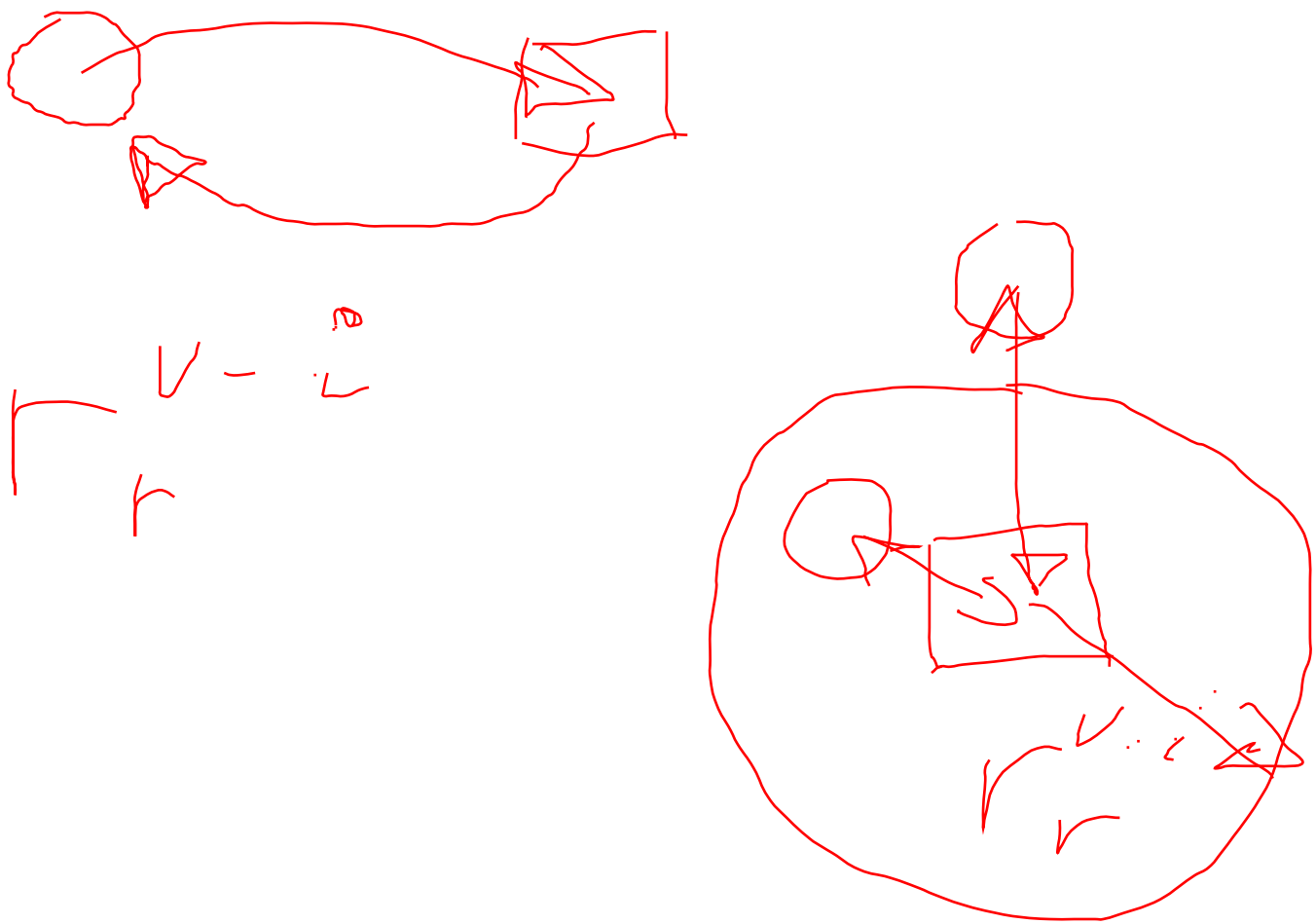
H. Landolt, P. Ehrhart, H. Ullmaier, Atomic Defects in Metals (Springer, 1991)

Vacancy and self-interstitials in Cu



Large gray: defect core; yellow: nearest neighbors to core atoms; small gray: all others

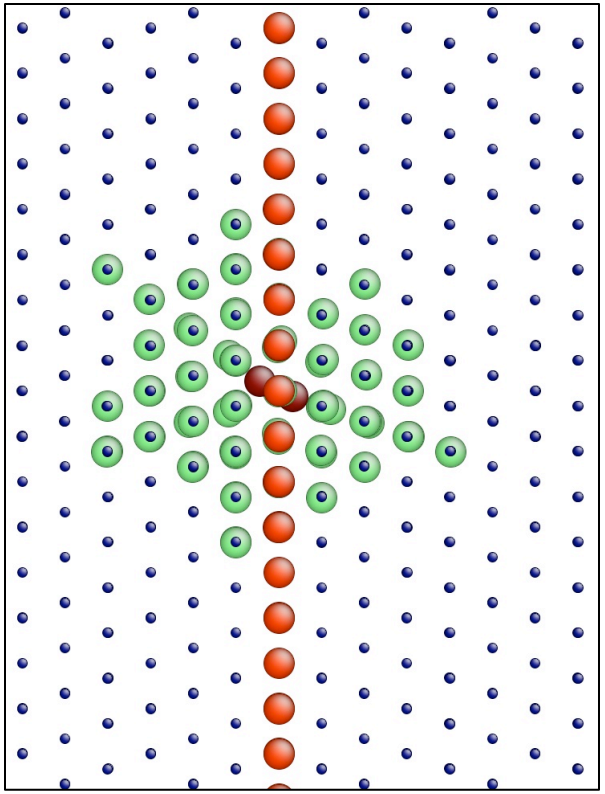
Frenkel pair formation and recombination



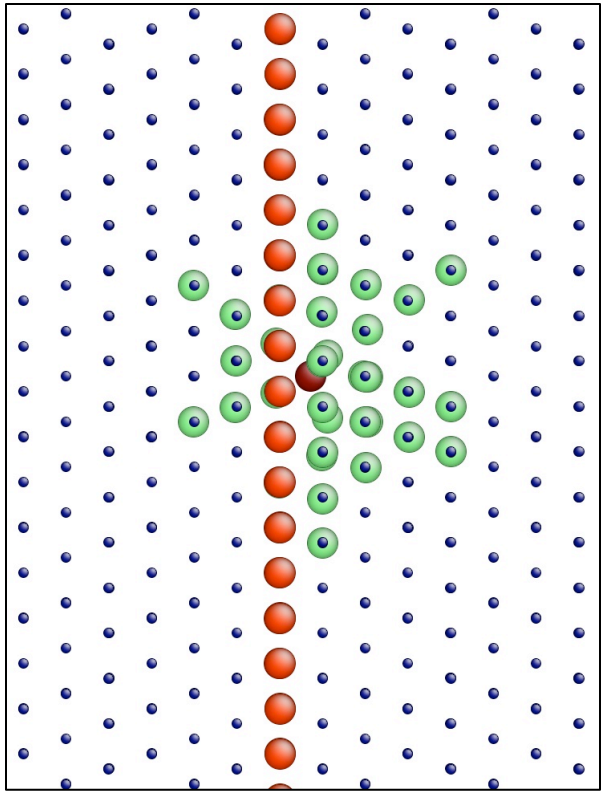
Vacancy-interstitial recombination

Near a Σ3 GB in Cu

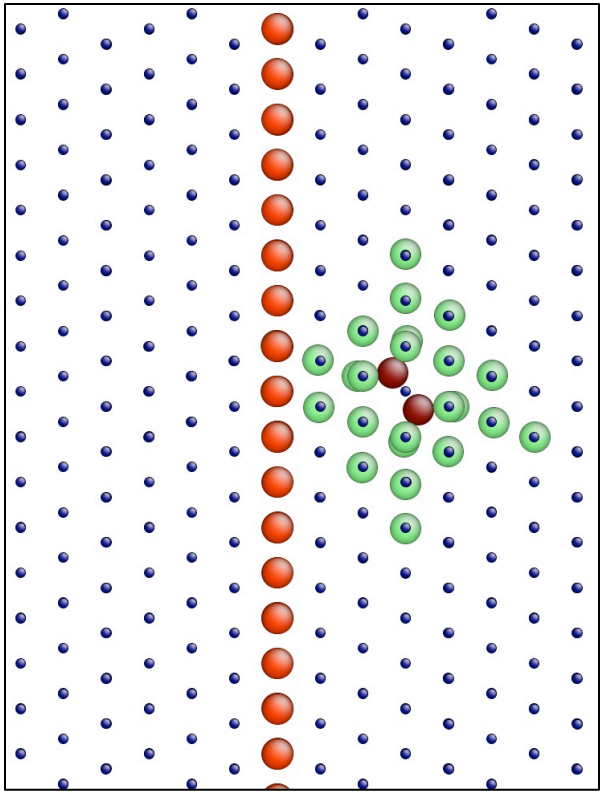
Dumbbell at twin GB



Octahedral near twin GB



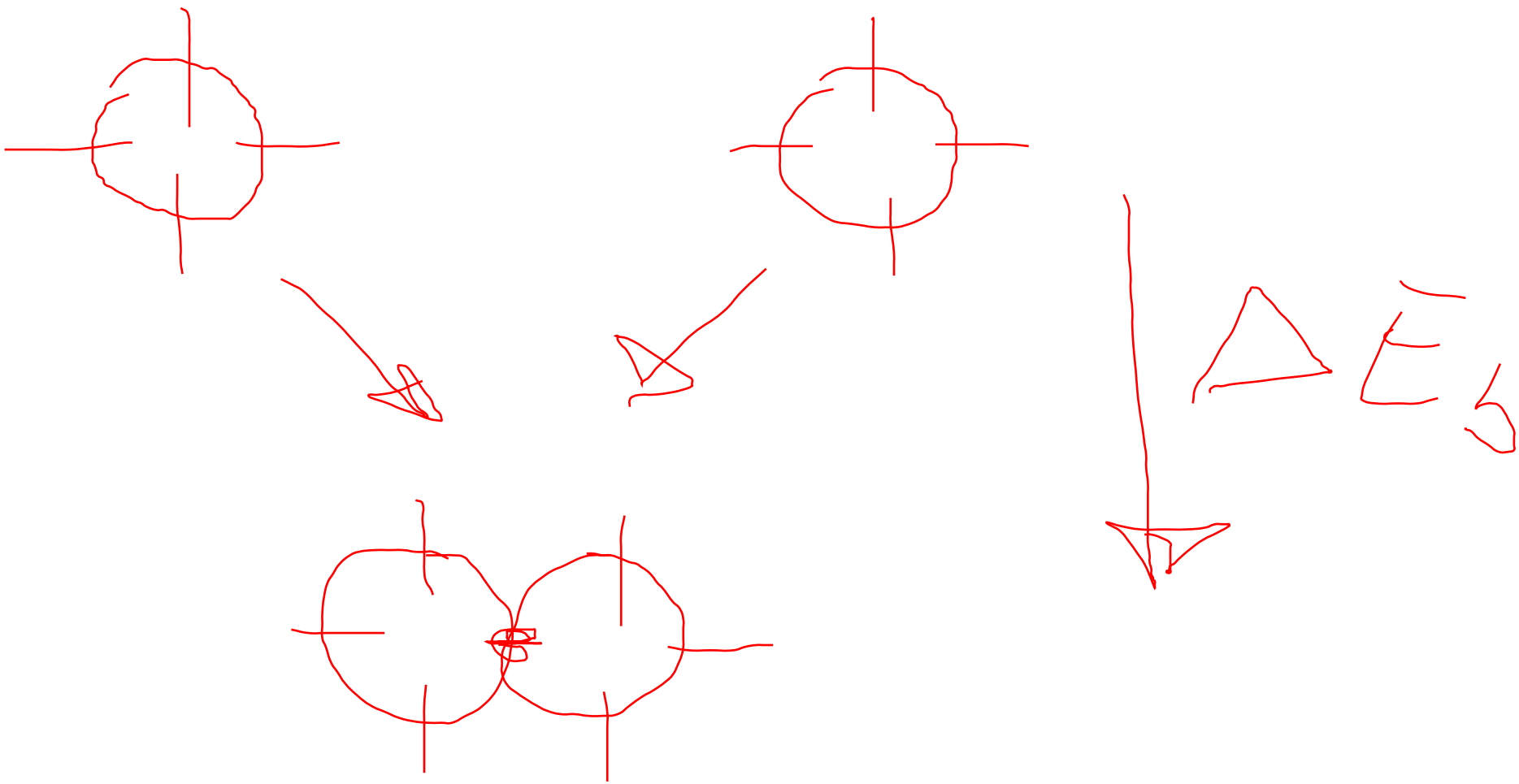
Bulk <100>-split dumbbell



Dark red: interstitial, light red: twin GB; green: recombination sites; small: all others

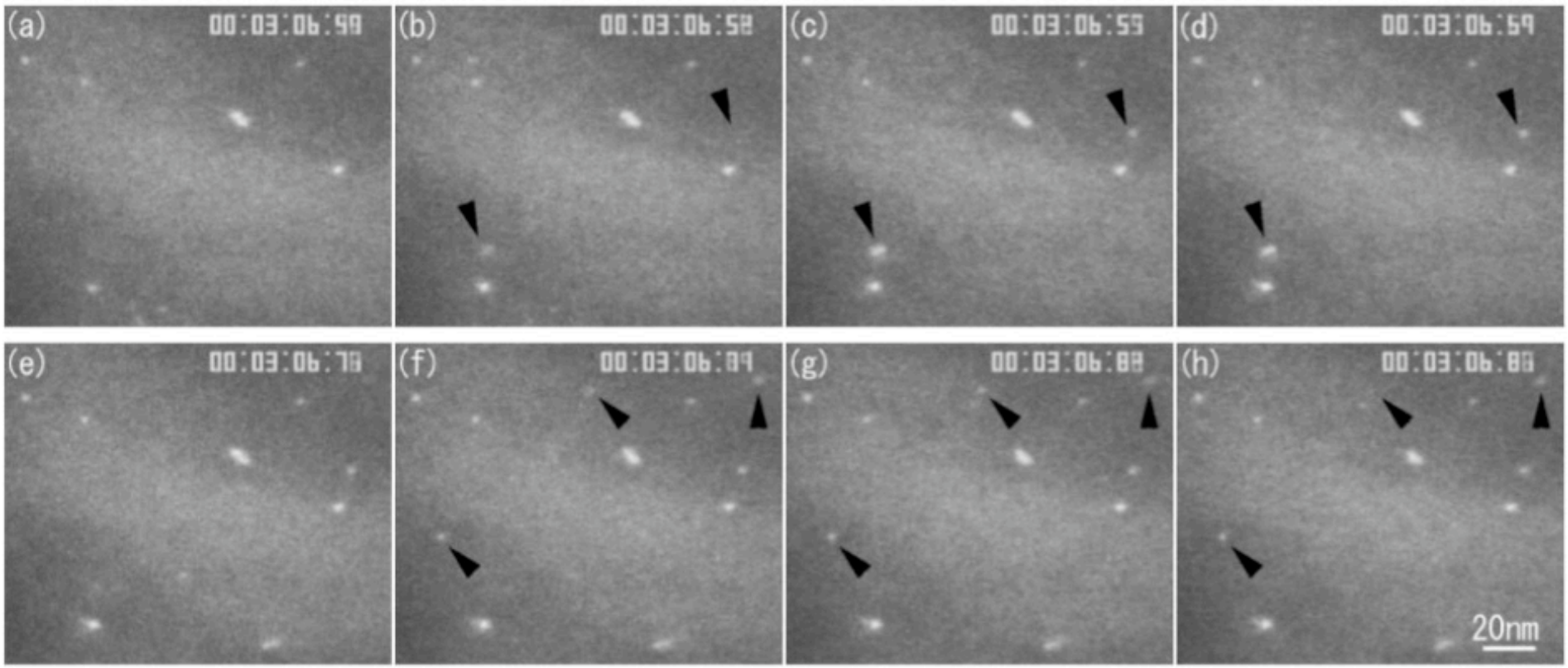
M. J. Demkowicz, O. Anderoglu, *et al.*, JMR **in press** (2011)

Defect clustering



TEM of Vacancy and interstitial clusters

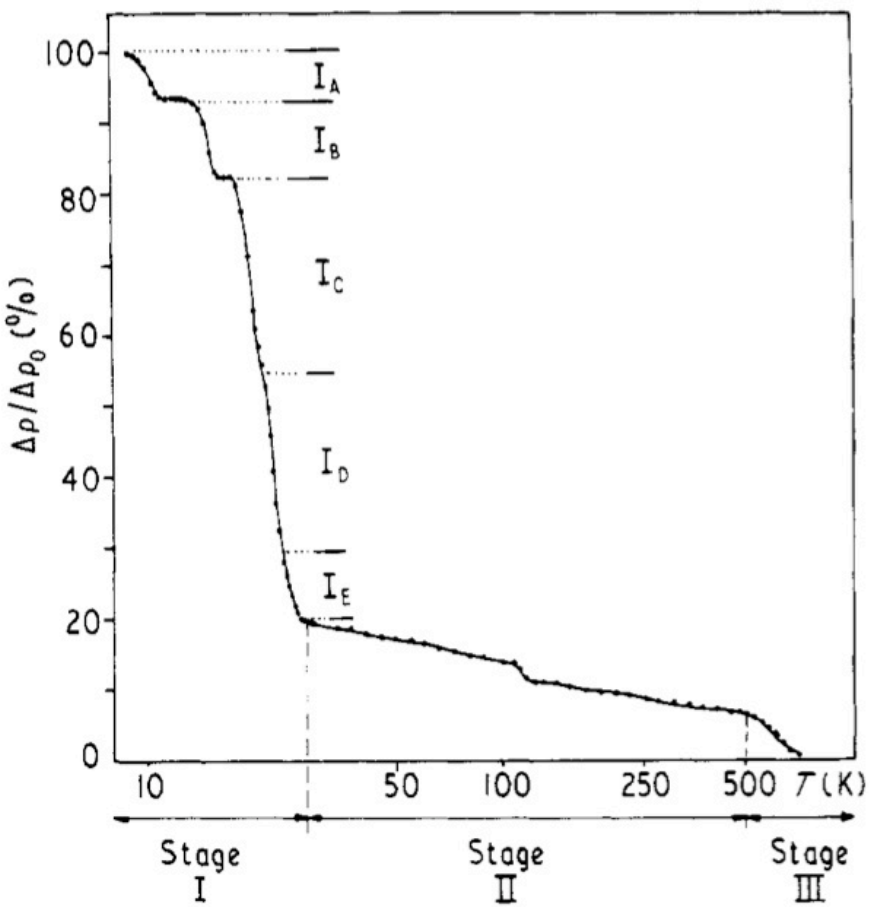
Mobile point defect clusters in Cu implanted with 240keV Cu^+ at 828K



H. Abe, N. Sekimura, T. Tadokoro, Mater. Trans. 46, 43 (2005)

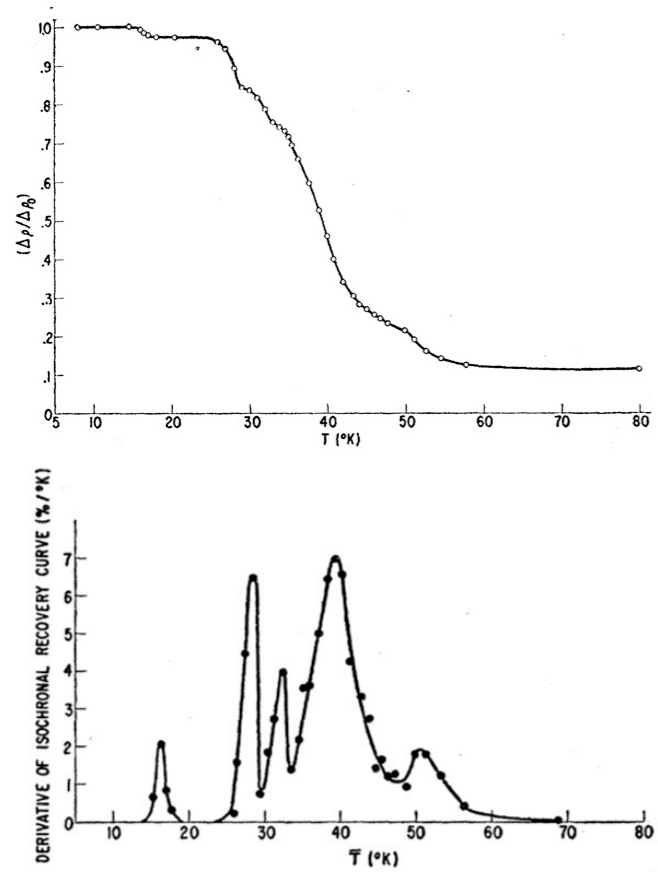
Point defect annealing stages

Isochronal annealing of Pt



W. Schilling, K. Sonnenberg, J Phys. F 3, 322 (1973)

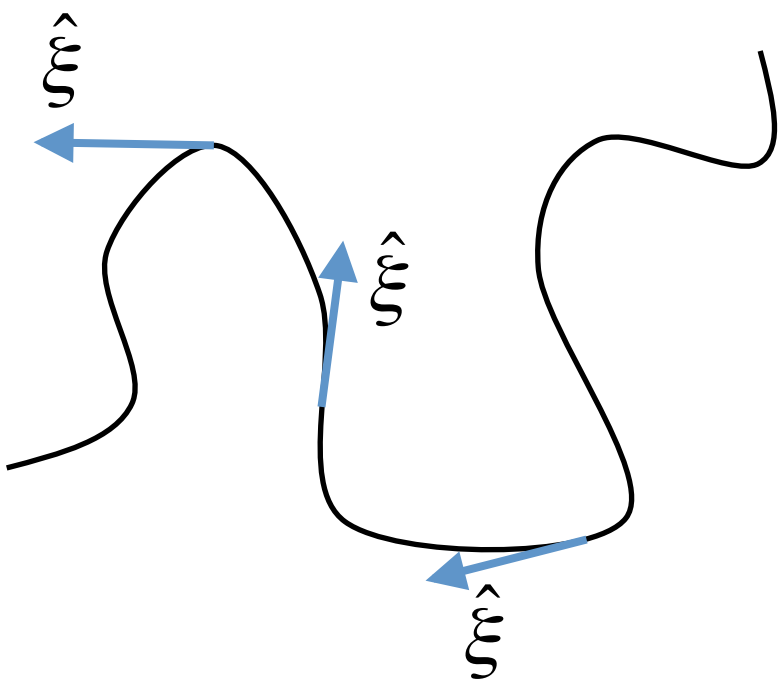
Isochronal annealing of Cu



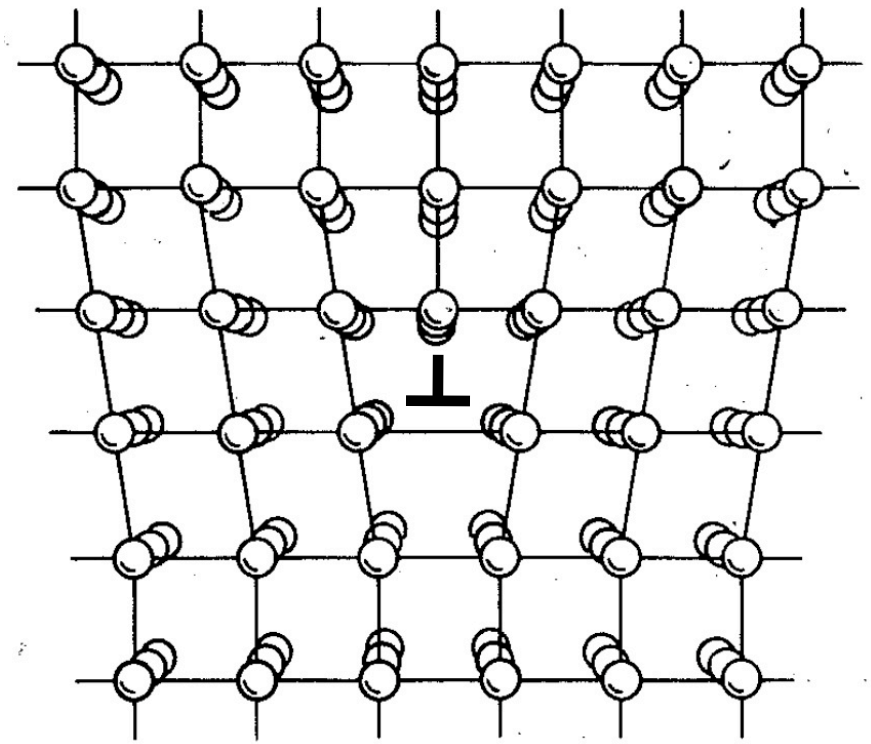
W. Schilling, K. Sonnenberg, J Phys. F 3, 322 (1973)

Dislocations

Line vector

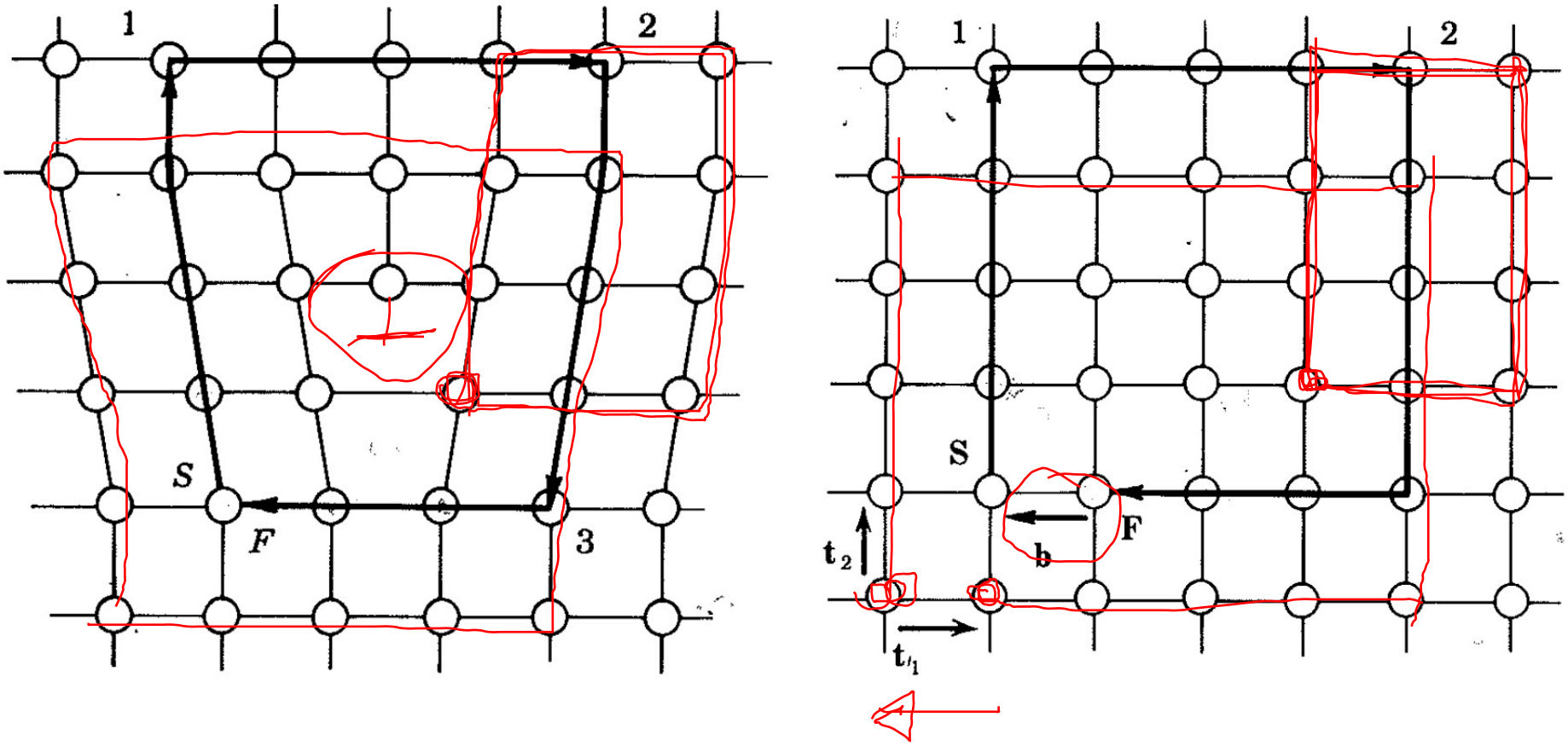


Extra half-plane



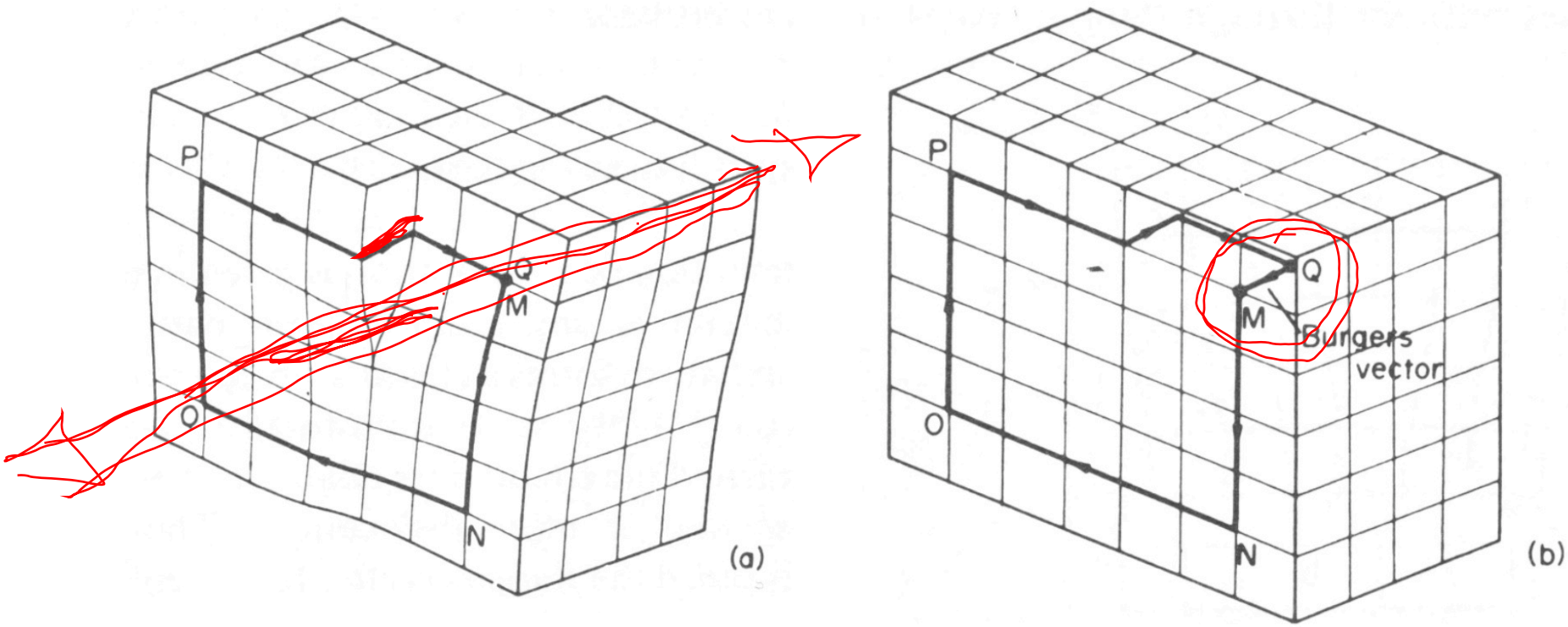
J. P. Hirth, J. Lothe, Theory of Dislocations (Krieger, 1992)

Burgers circuit: edge dislocation



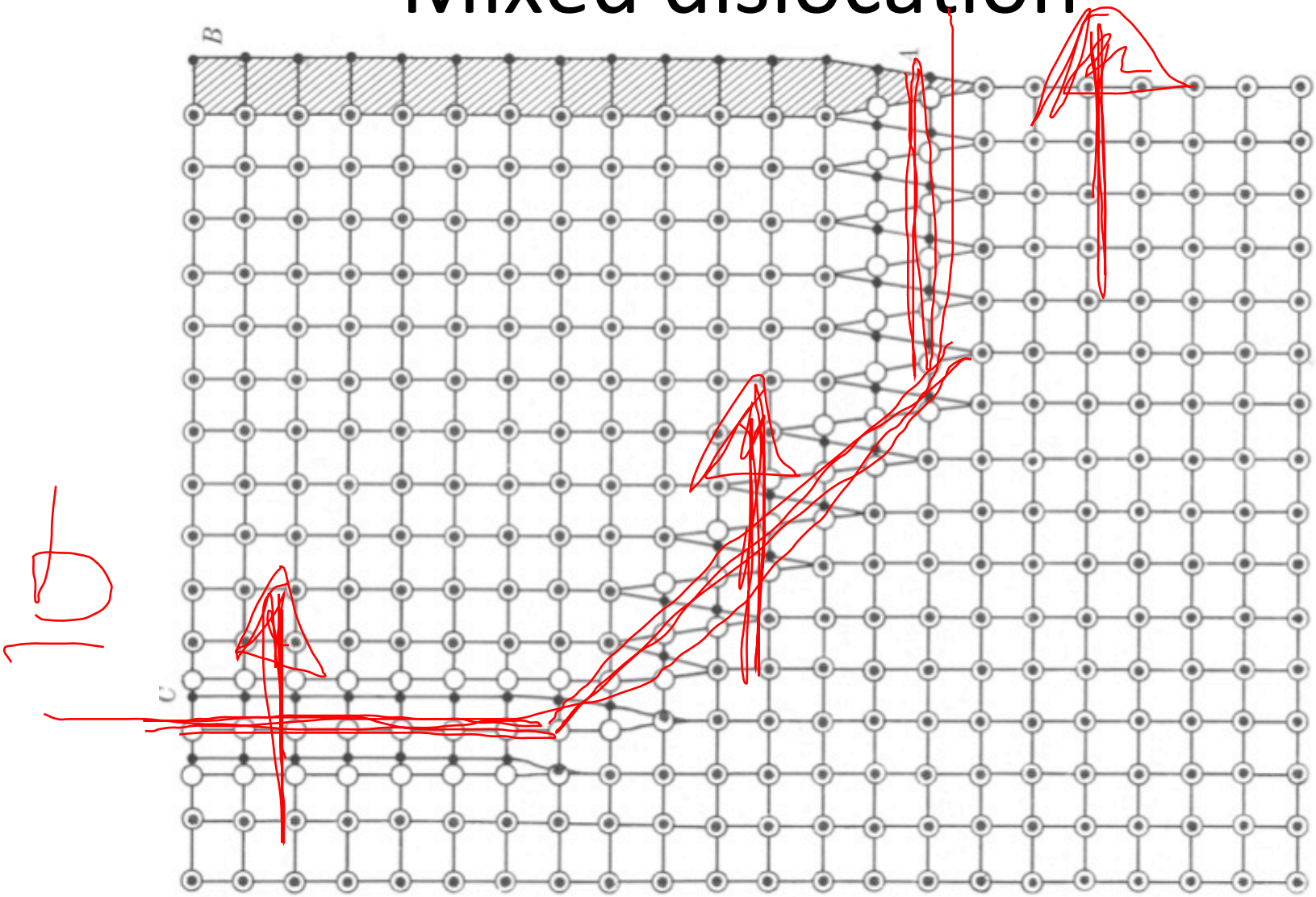
J. P. Hirth, J. Lothe, Theory of Dislocations (Krieger, 1992)

Burgers circuit: screw dislocation



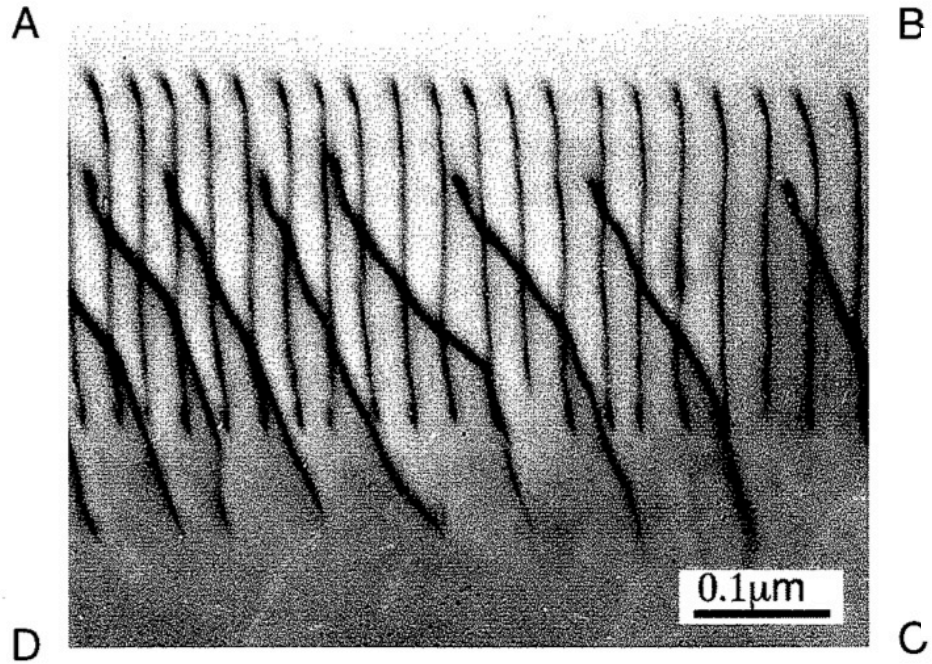
D. Hull, D. J. Bacon, Introduction to Dislocations (Butterworth-Heinemann, 1984)

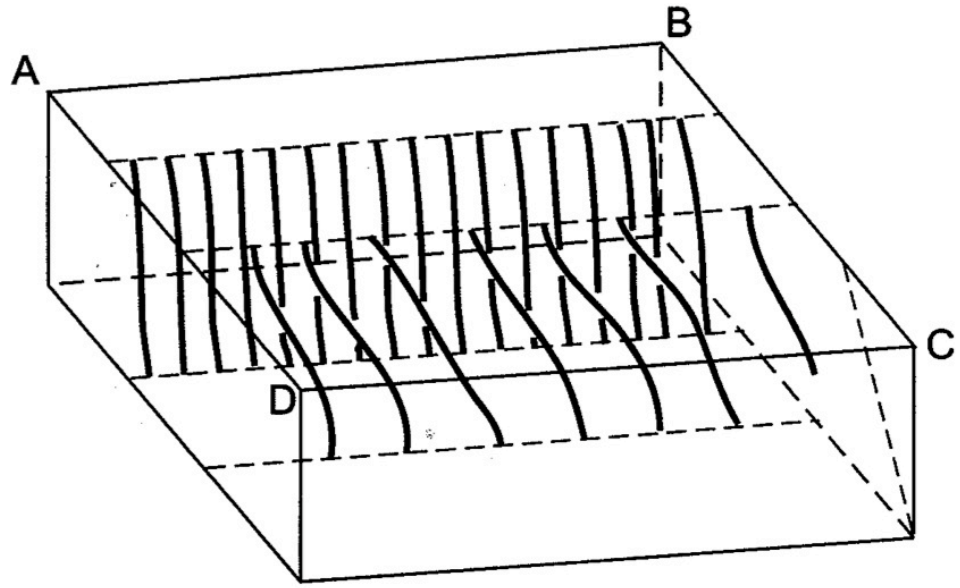
Mixed dislocation



F. A. McClintock, A. S. Argon, Mechanical Behavior of Materials (Addison-Wesley, 1966)

TEM observation of dislocations, 1

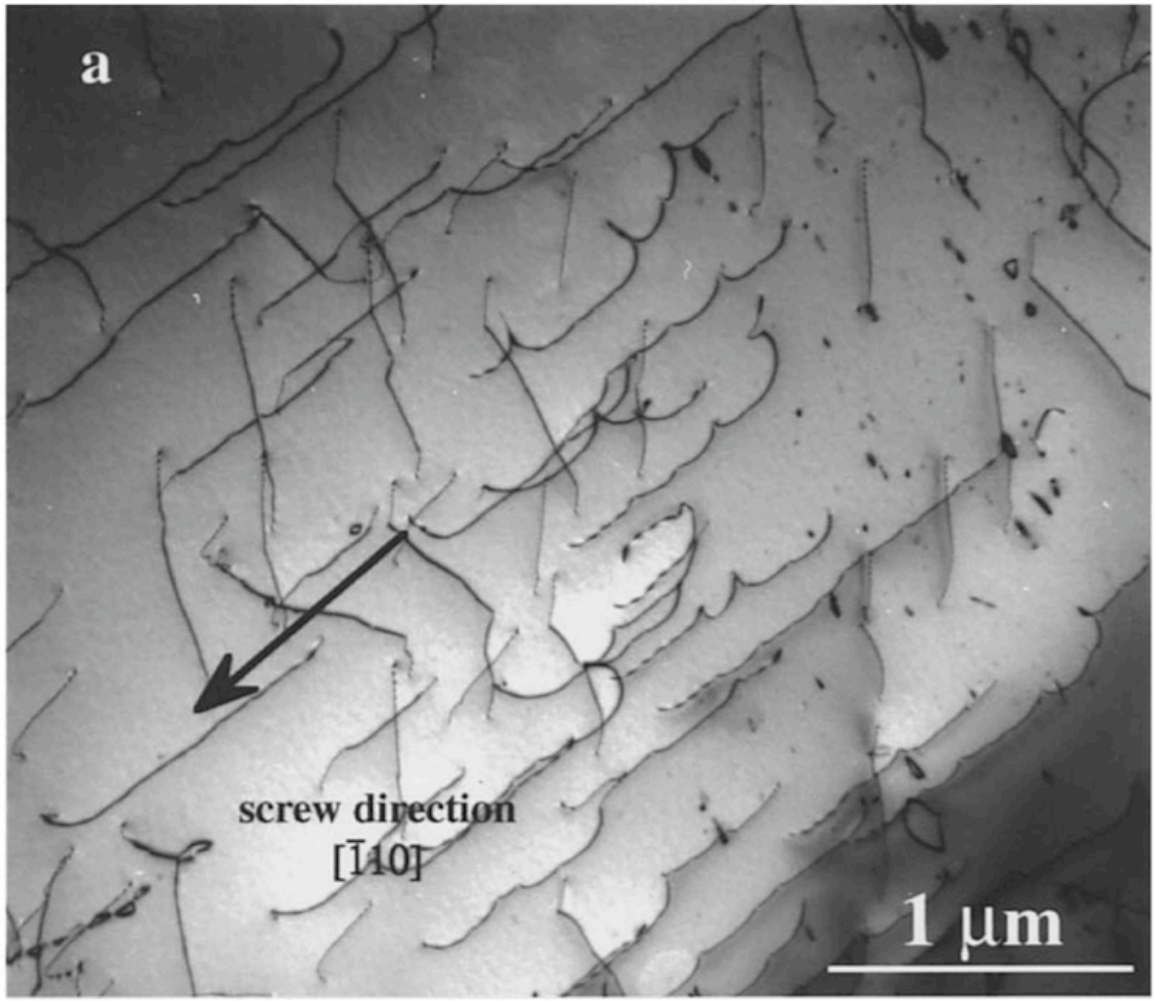




D. Hull, D. J. Bacon, Introduction to Dislocations (Butterworth-Heinemann, 2001)

TEM observation of dislocations, 2

in γ-TiAl



G. B. Viswanathan, V. K. Vasudevan, M. J. Mills, Acta Mater. **47**, 1399 (1999)

Dislocation core and surrounding "good material"

Dislocation stress fields

Screw

$$\sigma_{xz} = -\frac{\mu b}{2\pi}\cdot\frac{y}{x^2+y^2},\ \sigma_{yz} = \frac{\mu b}{2\pi}\cdot\frac{x}{x^2+y^2}$$

Edge

$$p = -(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

$$\sigma_{xx} = -Dy\frac{3x^2+y^2}{\left(x^2+y^2\right)^2},\ \sigma_{yy} = Dy\frac{x^2-y^2}{\left(x^2+y^2\right)^2}$$

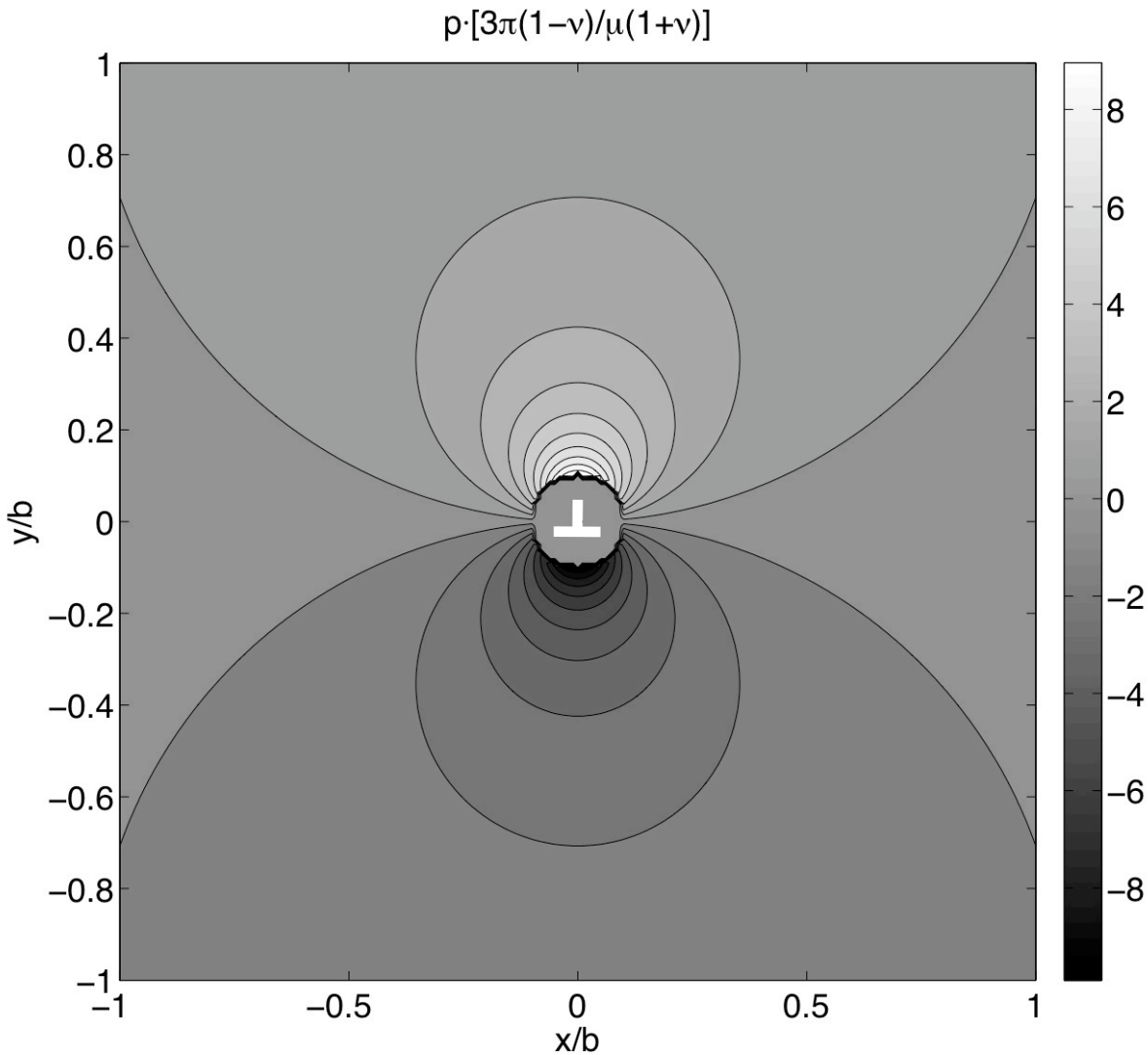
$$\sigma_{xy} = \sigma_{yx} = Dx\frac{x^2-y^2}{\left(x^2+y^2\right)^2},\ \underbrace{\sigma_{zz} = \nu\left(\sigma_{xx}+\sigma_{yy}\right)}_{\text{plane strain}}$$

$$D = \frac{\mu b}{2\pi(1-\nu)}$$

Pressure around an edge dislocation

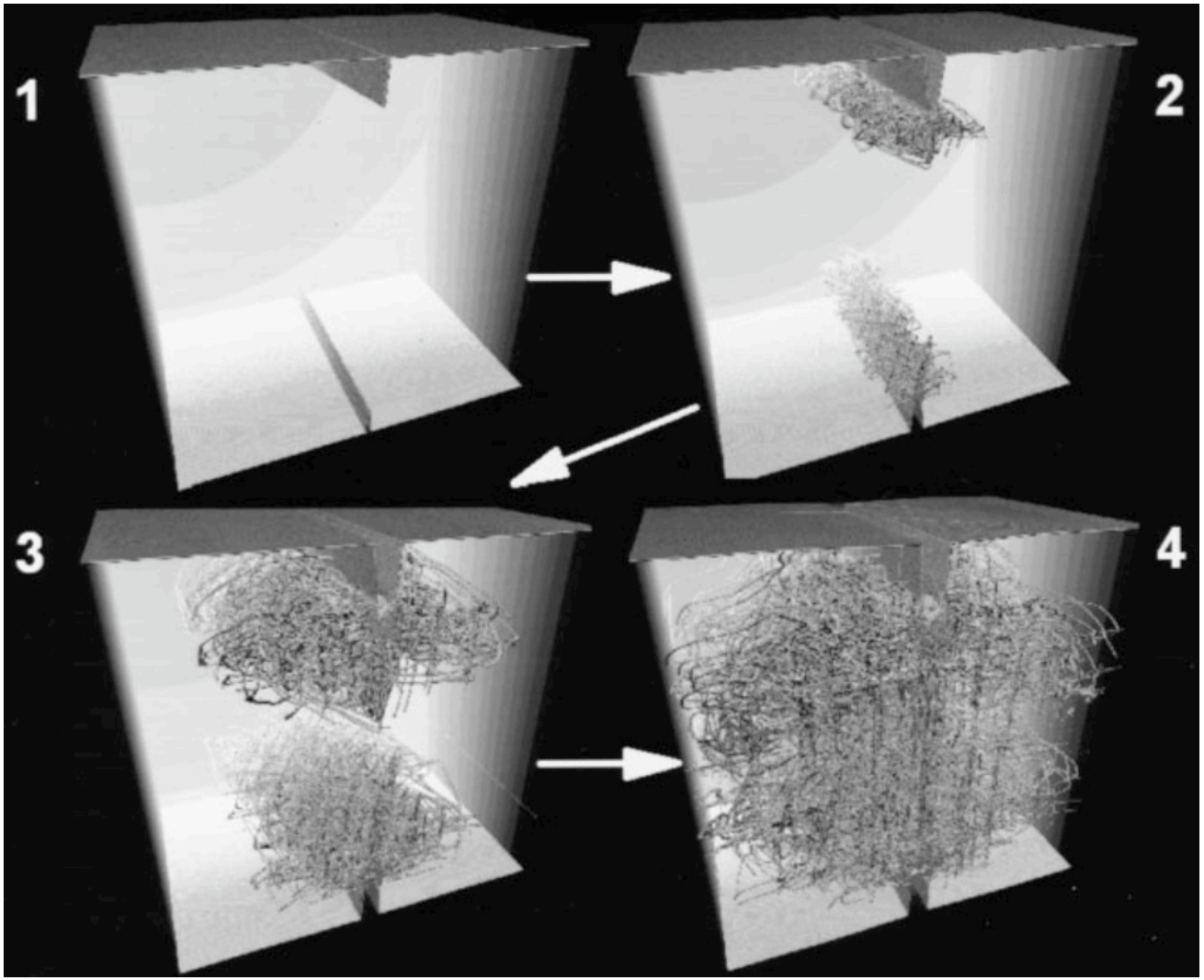
ΔV_v

ΔV_i



Atomistic modeling of dislocations, 1

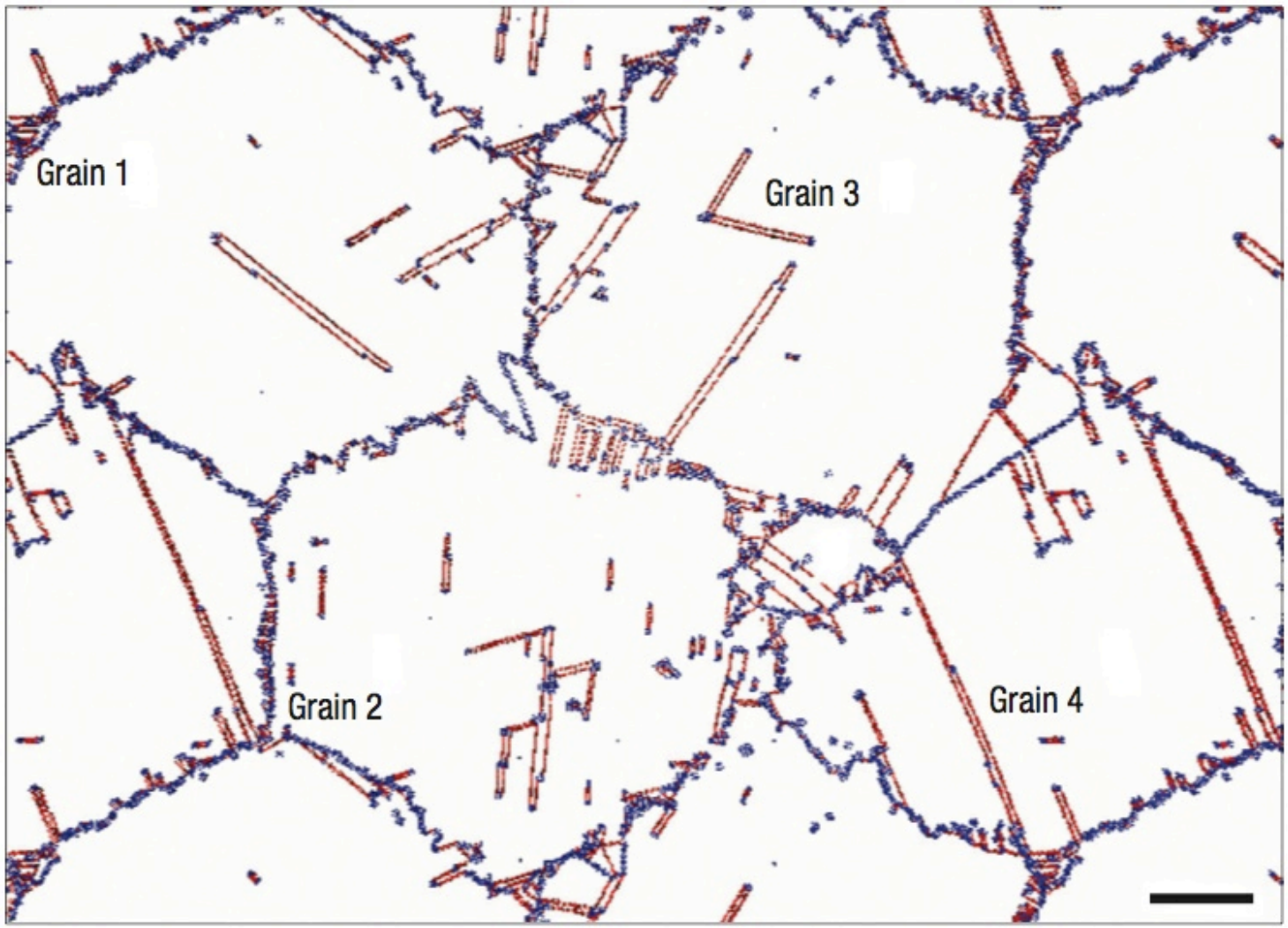
Dislocation emission from crack tip in Jennard-Jones fcc solid



F. F. Abraham, R. Walkup, H. J. Gao, M. Duchaineau, T. D. de la Rubia, M. Seager, PNAS 99, 5783 (2002)

Atomistic modeling of dislocations, 2

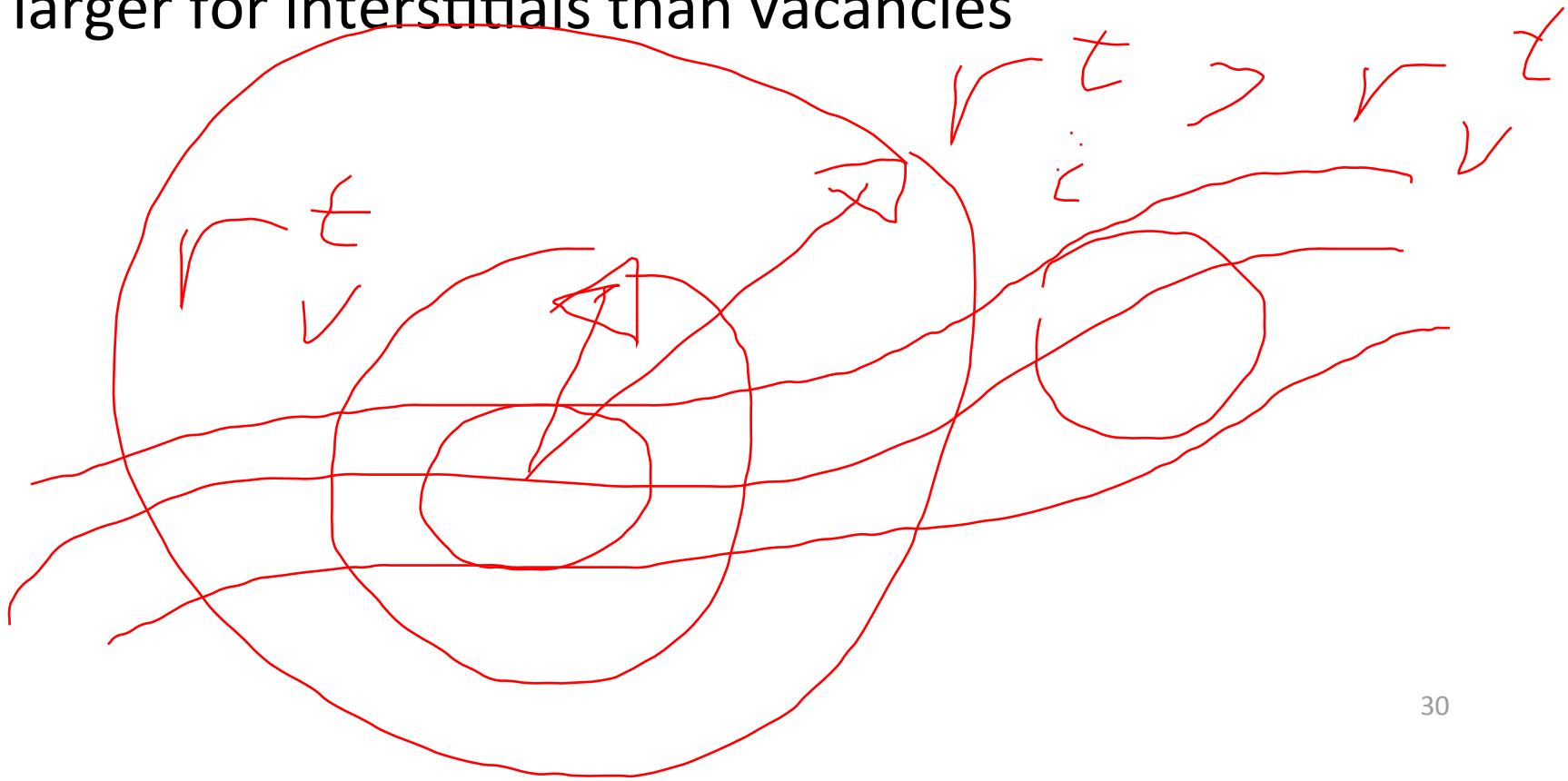
Dislocation emission from grain boundaries in nc-Al



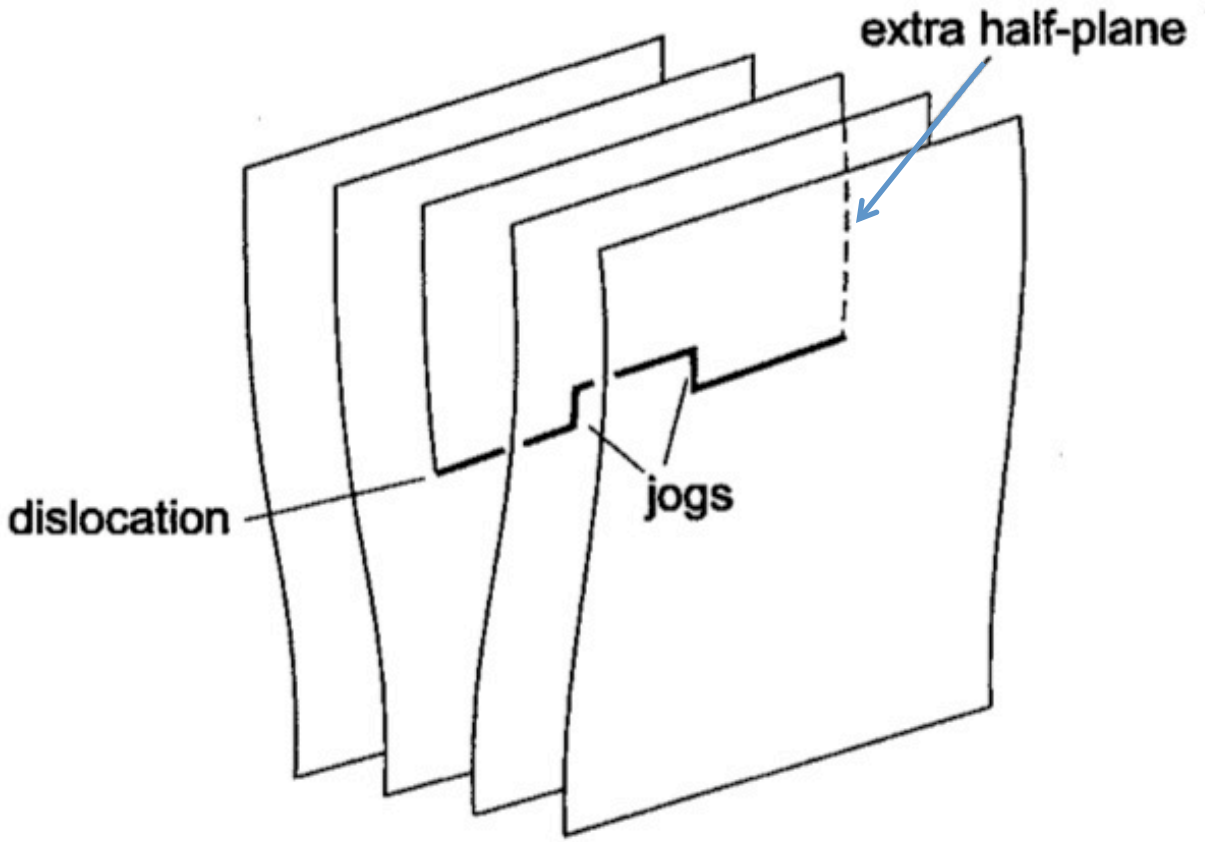
V. Yamakov, D. Wolf, S. R. Phillpot, A. K. Mukherjee, H. Gleiter, Nature Materials 1, 1 (2002)

Point defect trapping at dislocations

- Interactions often described by a trapping radius:
  - larger for edge dislocations than screw dislocations
  - larger for interstitials than vacancies



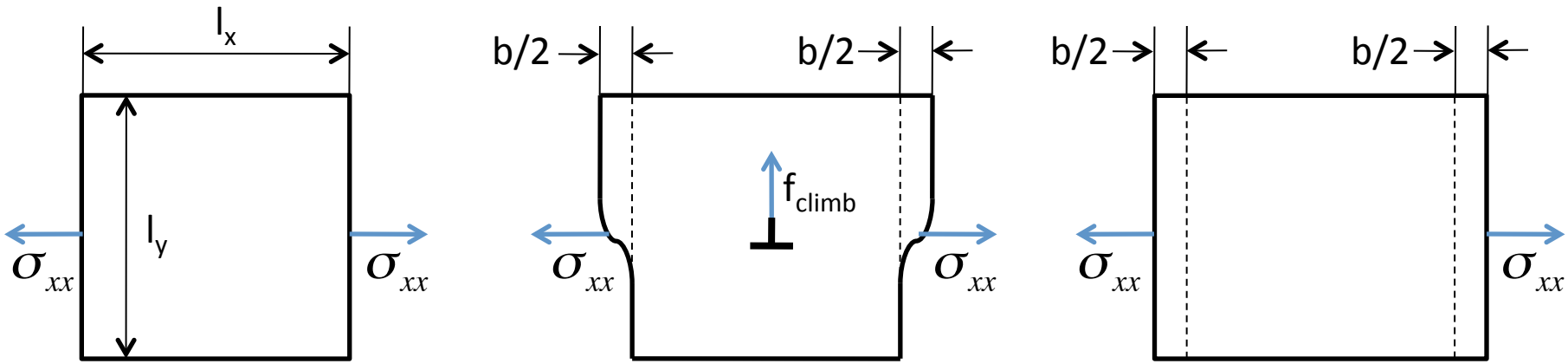
Jogs

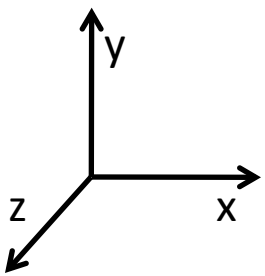


D. Hull, D. J. Bacon, Introduction to Dislocations (Butterworth-Heinemann, 2001)

Forces on dislocations

Peach-Koehler climb force

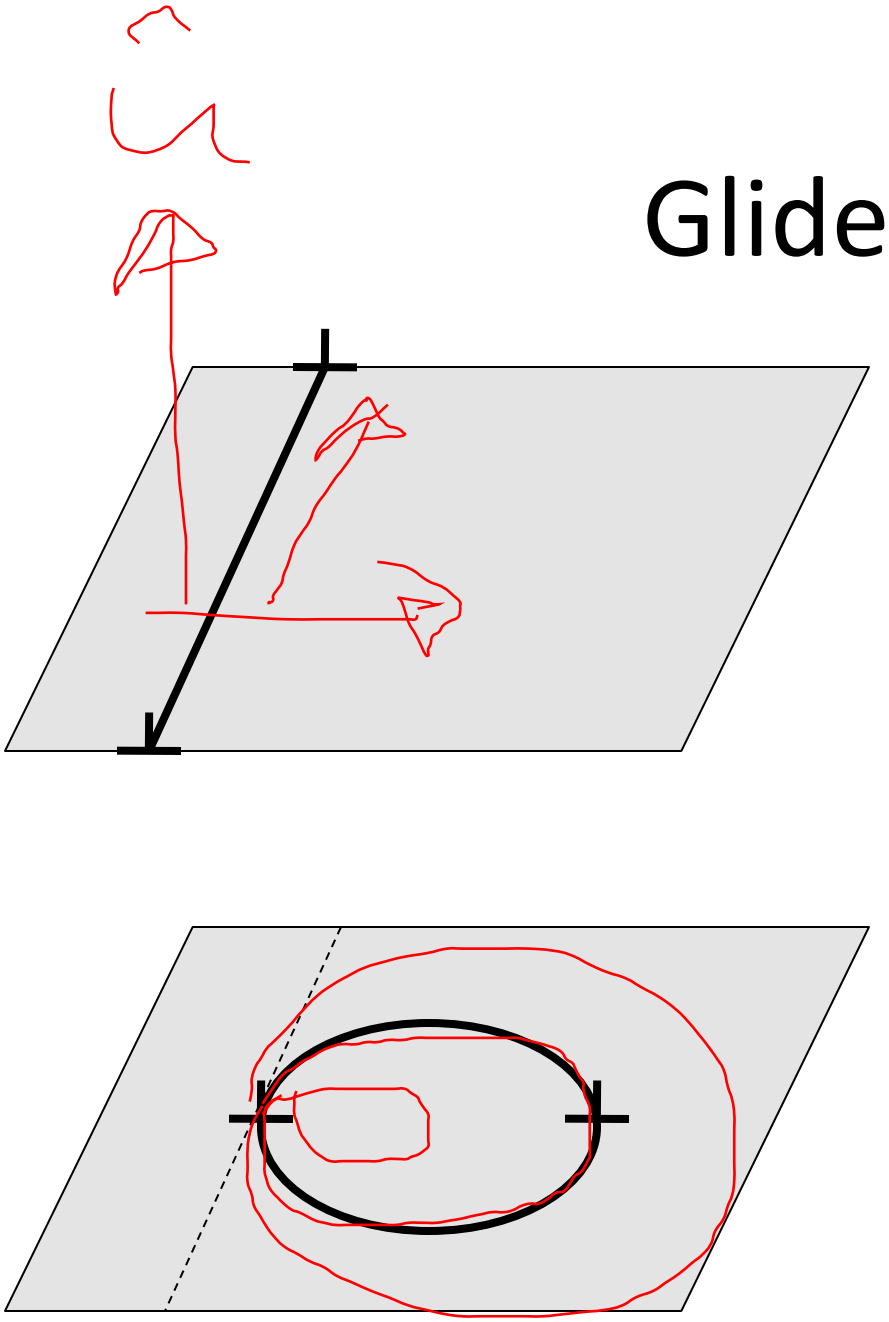




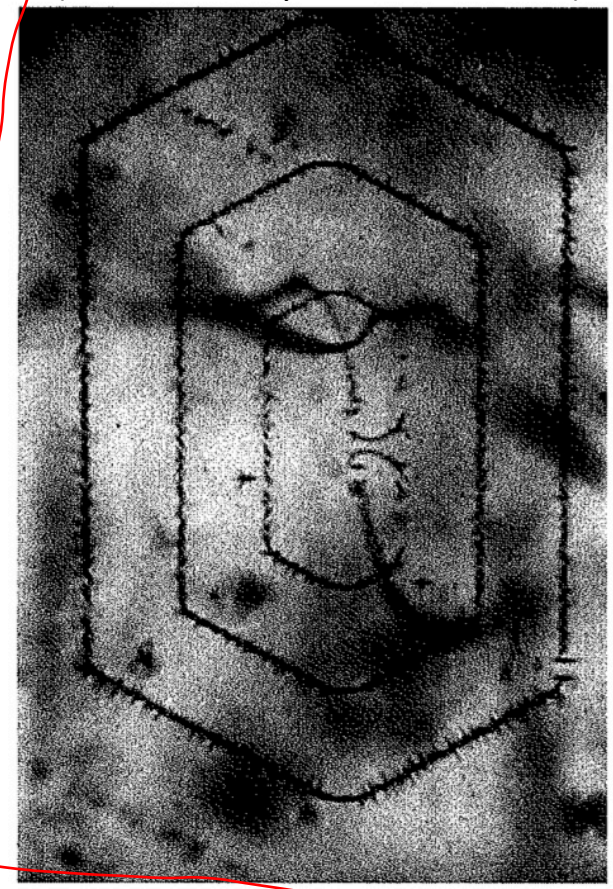
$$W = \underbrace{\left(\sigma_{xx} l_y l_z\right) b}_{\text{Work done by } \sigma_{xx}} = \underbrace{\left(f_{\text{climb}} l_z\right)\left(-l_y\right)}_{\text{Work done by } f_{\text{climb}}} \Rightarrow f_{\text{climb}} = -\sigma_{xx} b$$

Curvature and osmotic forces

Glide loop

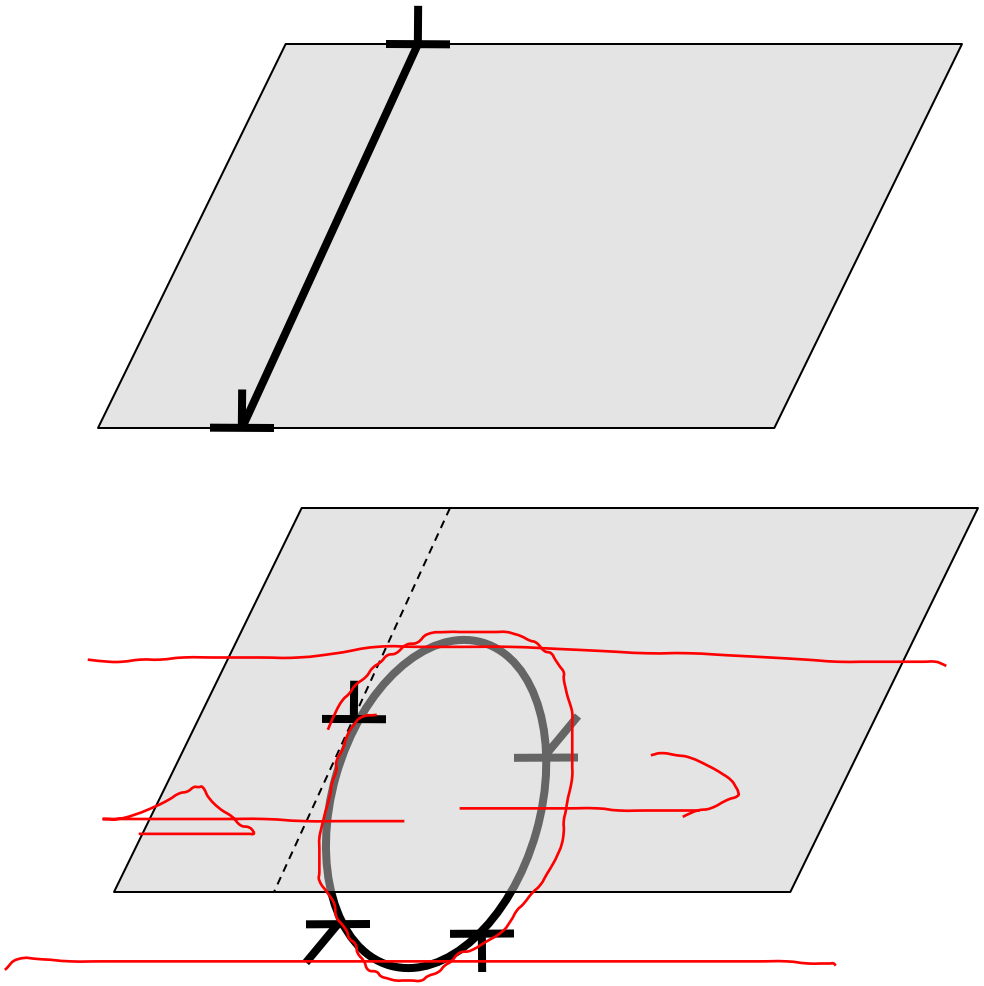


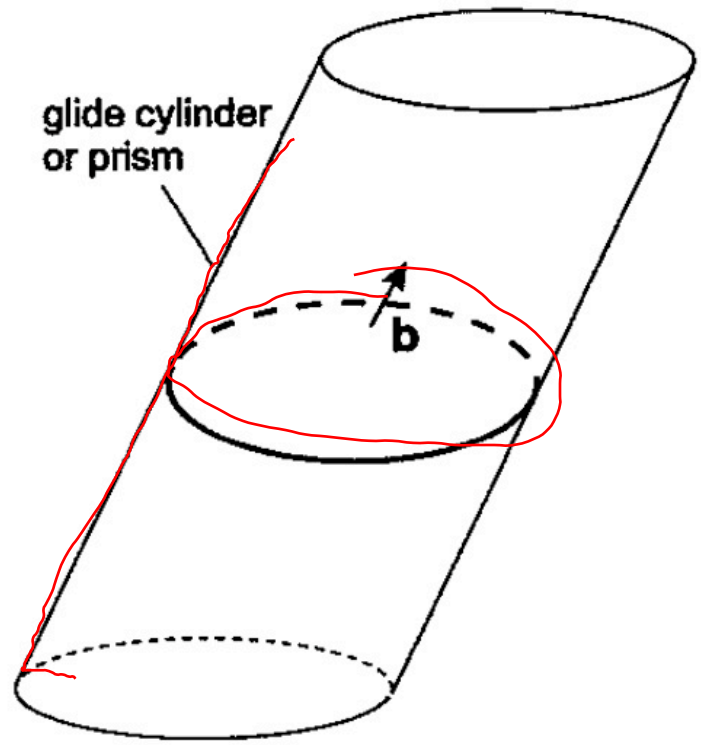
Glide loops created by a Frank-Read source in Si
(immobilized by solute decoration)



D. Hull, D. J. Bacon, Introduction to Dislocations (Butterworth-Heinemann, 2001)

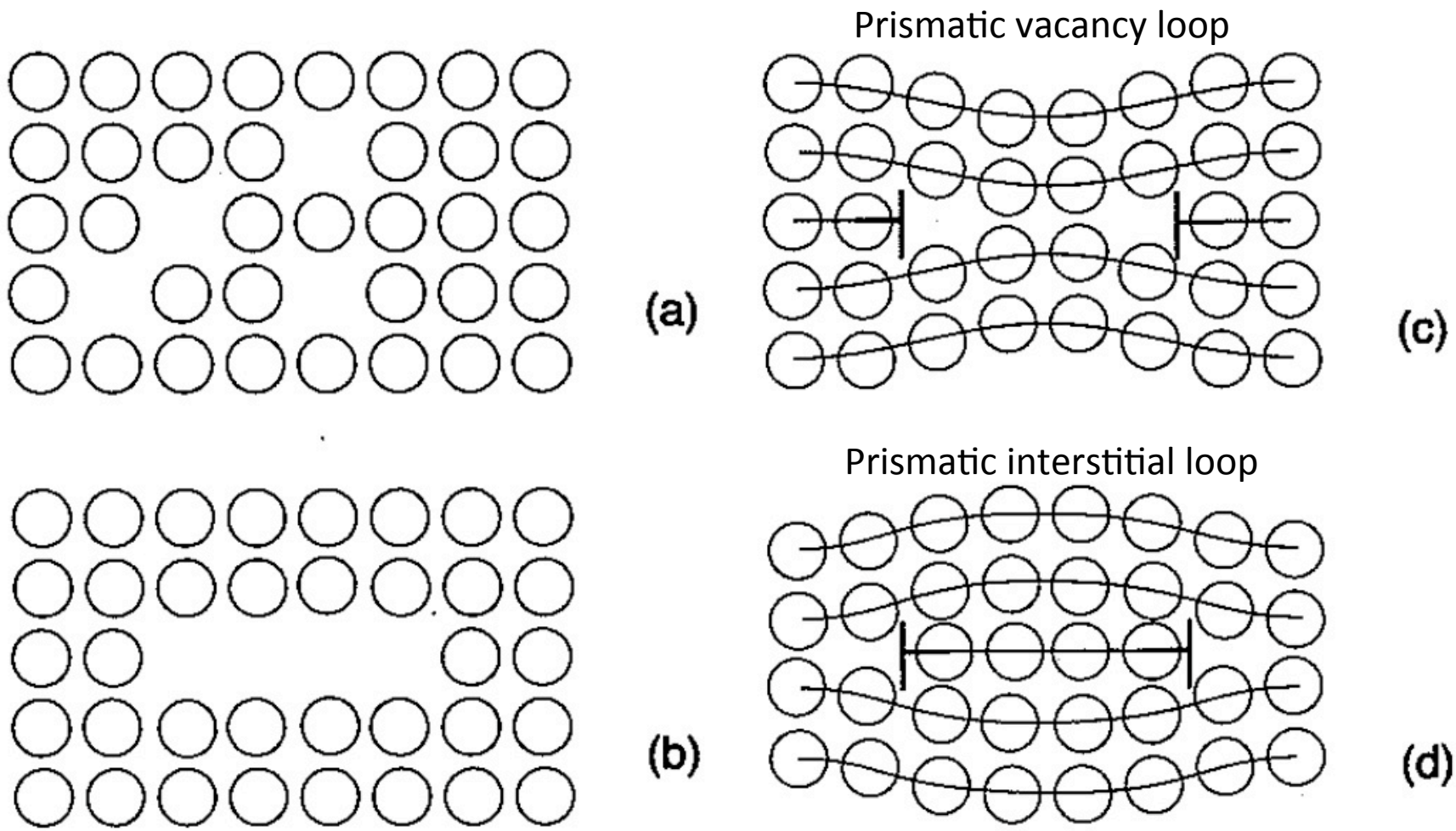
Prismatic loop





D. Hull, D. J. Bacon, Introduction to Dislocations
(Butterworth-Heinemann, 2001)

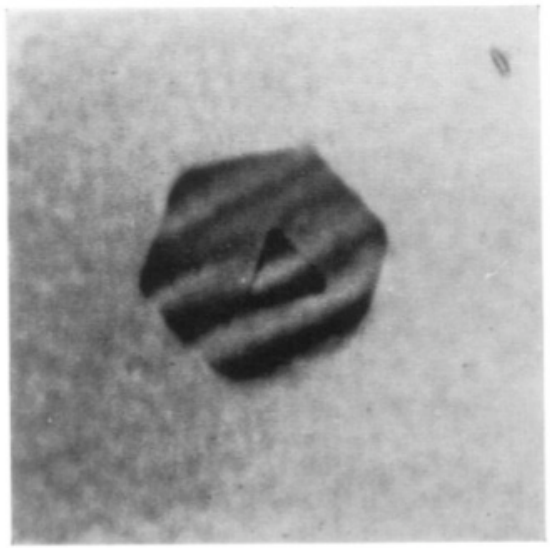
Formation of prismatic loops by vacancy or interstitial clustering



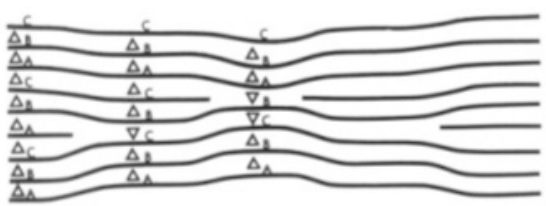
D. Hull, D. J. Bacon, Introduction to Dislocations (Butterworth-Heinemann, 2001)

TEM observation of prismatic loops

Vacancy loop in quenched Al

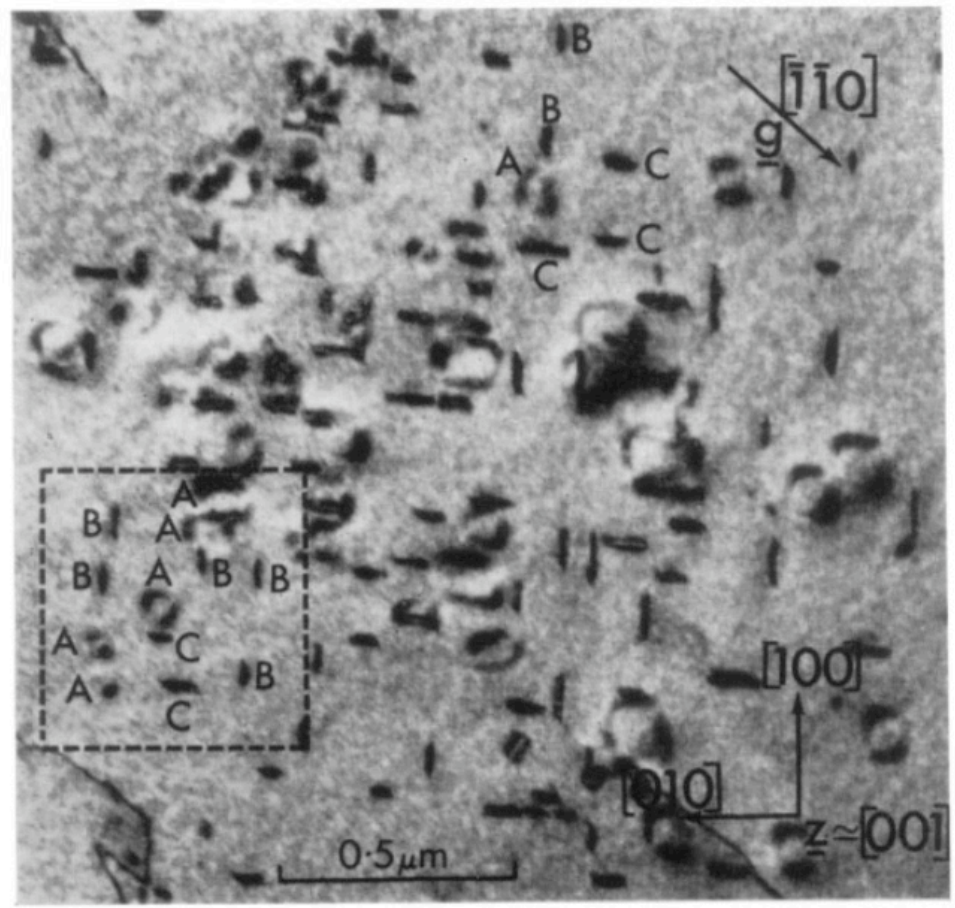


(a)



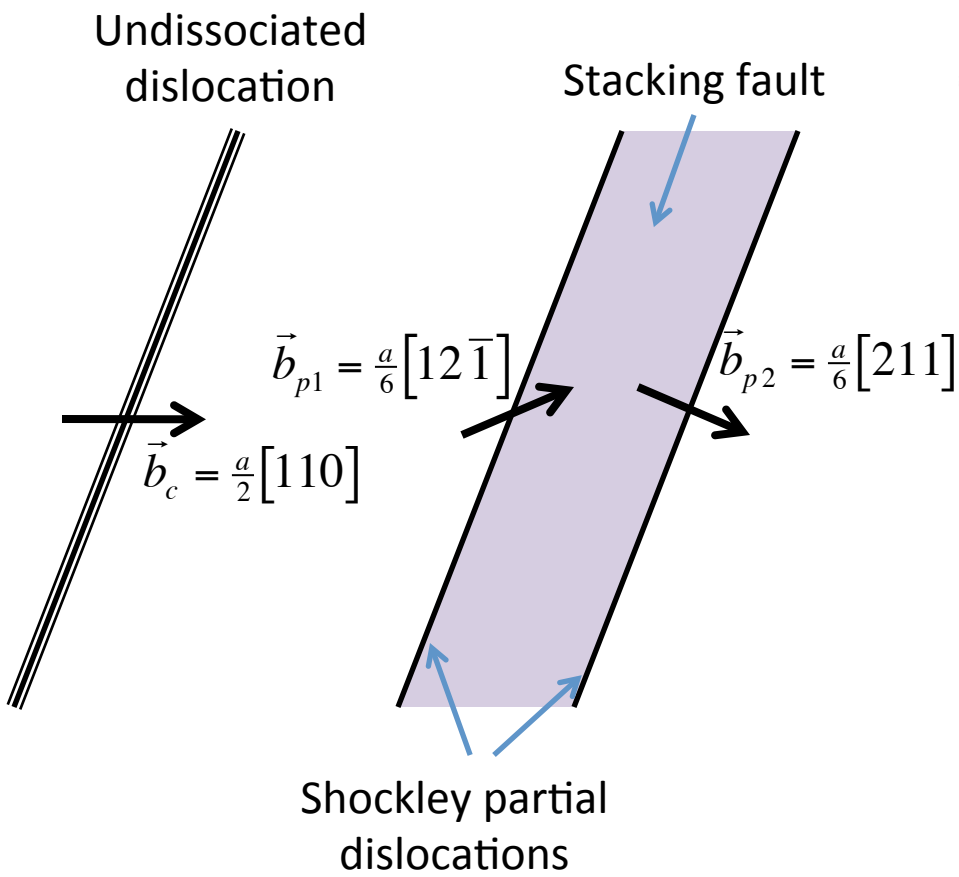
(b)

<100> interstitial loops in α-Fe

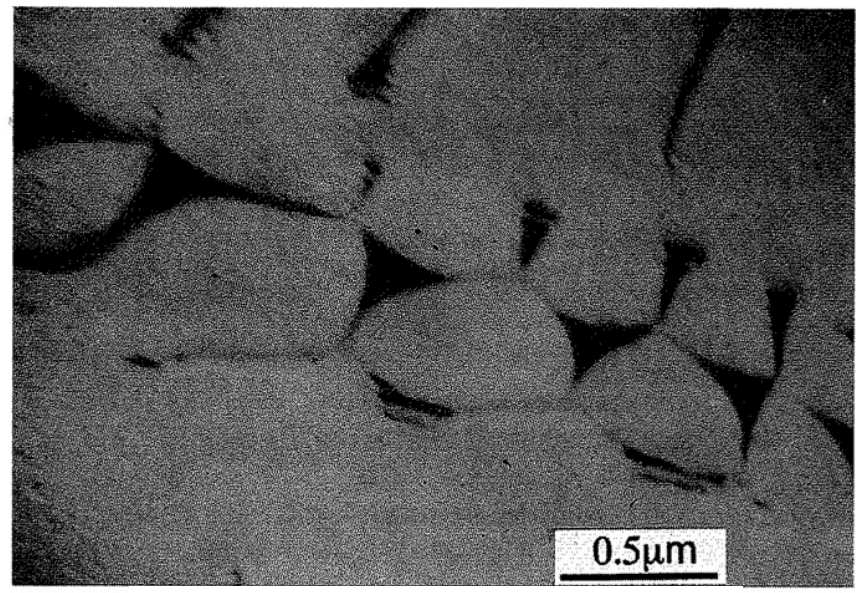


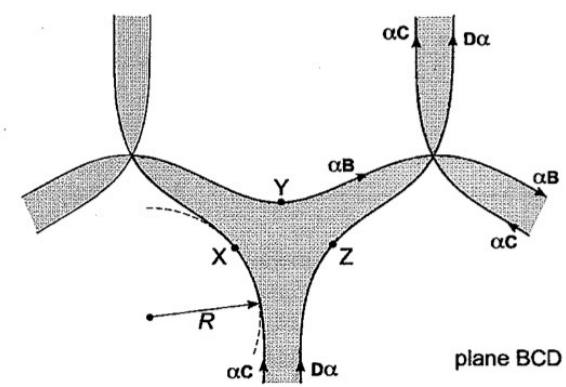
B. L. Eyre, J. Phys. F 3, 422 (1973)

Dissociated dislocations in FCC metals



$$\vec{b}_c = \vec{b}_{p1} + \vec{b}_{p2}$$

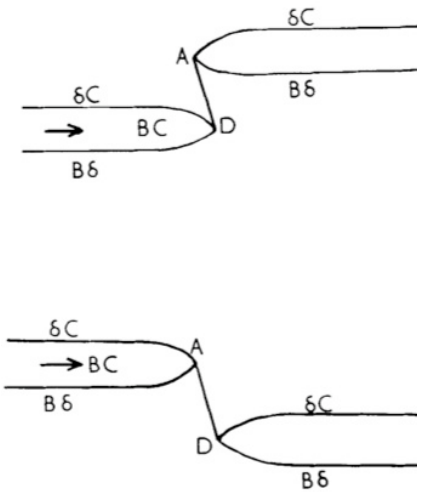




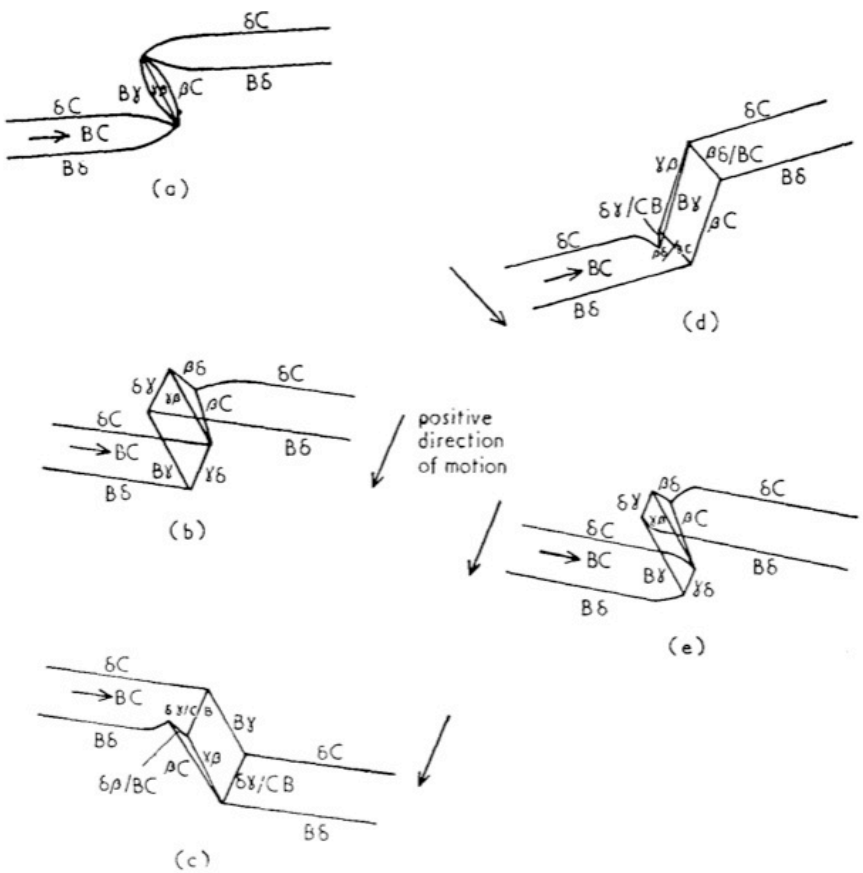
D. Hull, D. J. Bacon, Introduction to Dislocations (Butterworth-Heinemann, 2001)

Jogs on extended dislocations

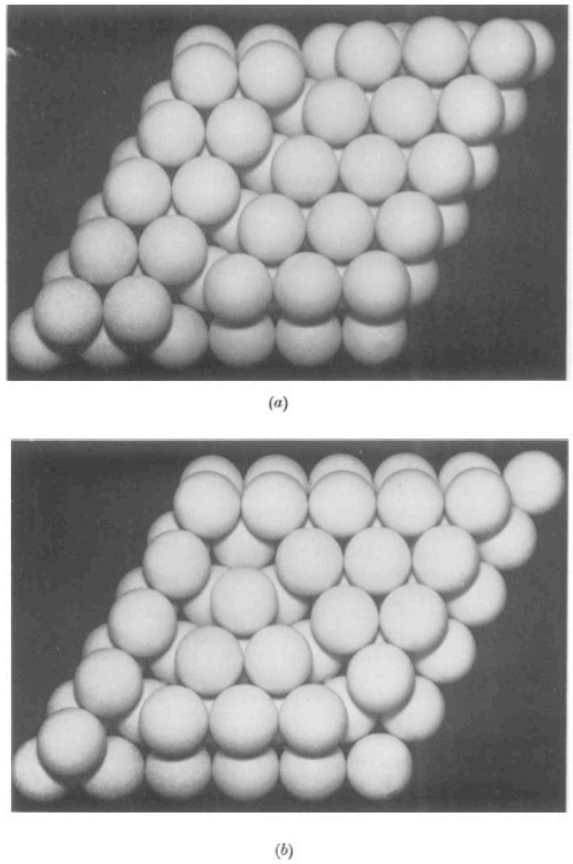
Compact jogs



Extended jogs

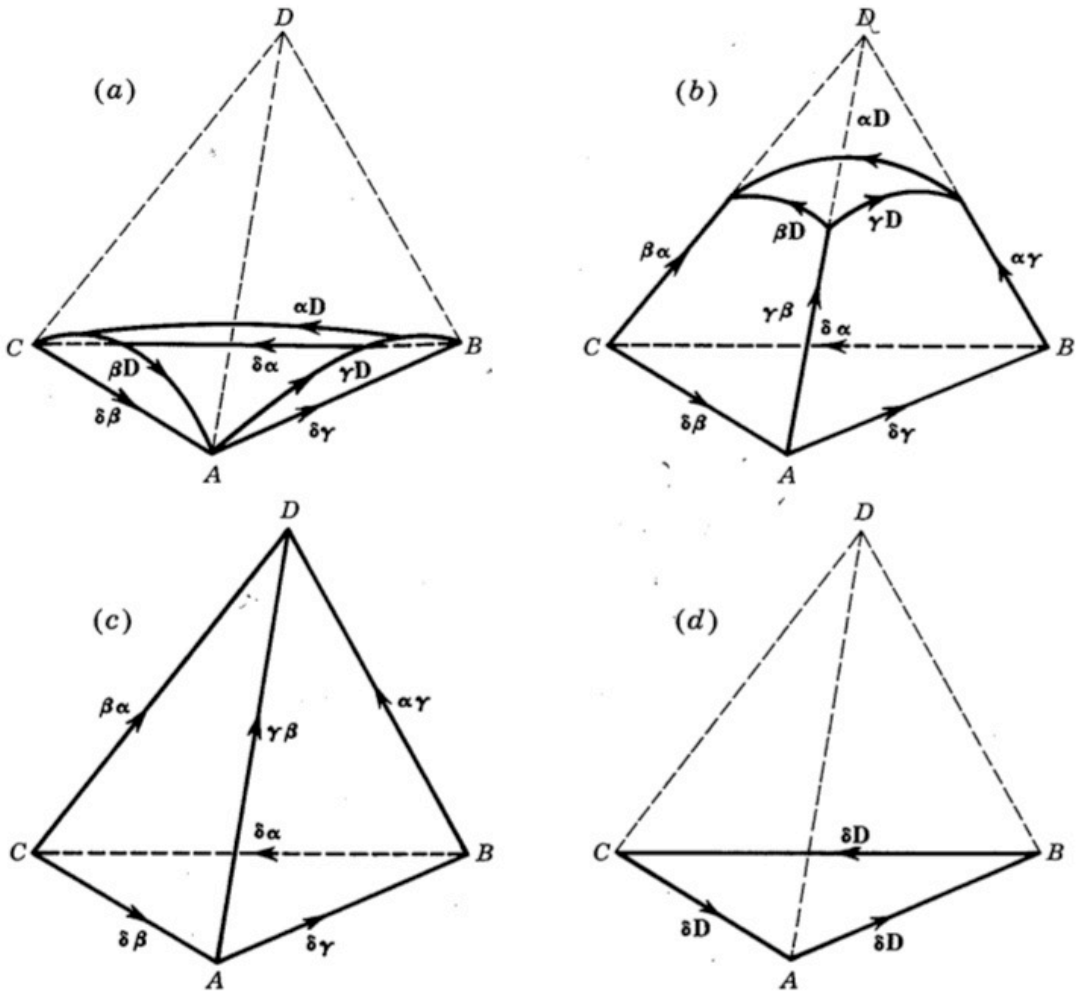


Manual molecular dynamics

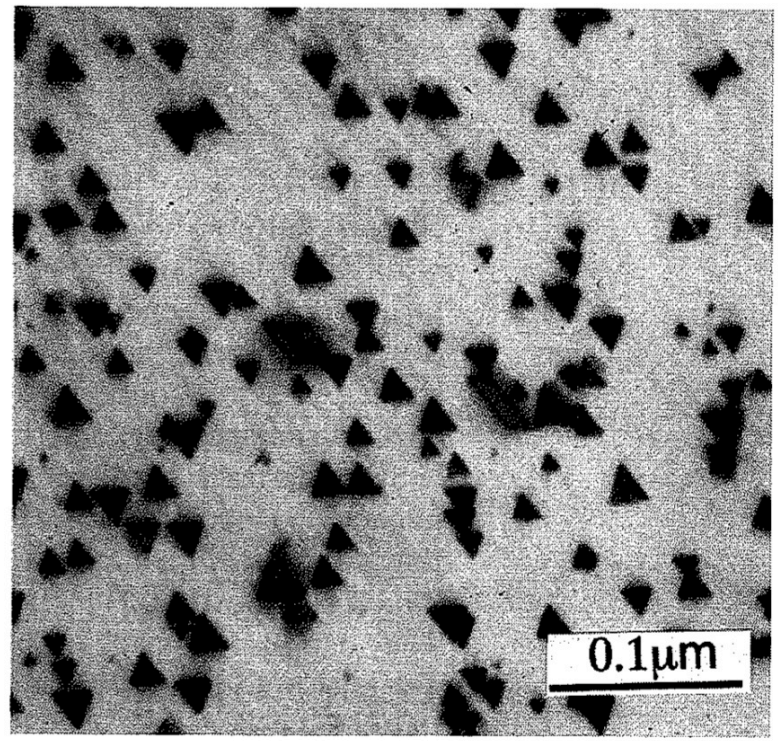


P. B. Hirsch, Philos. Mag. 7, 67 (1962)

Stacking fault tetrahedra

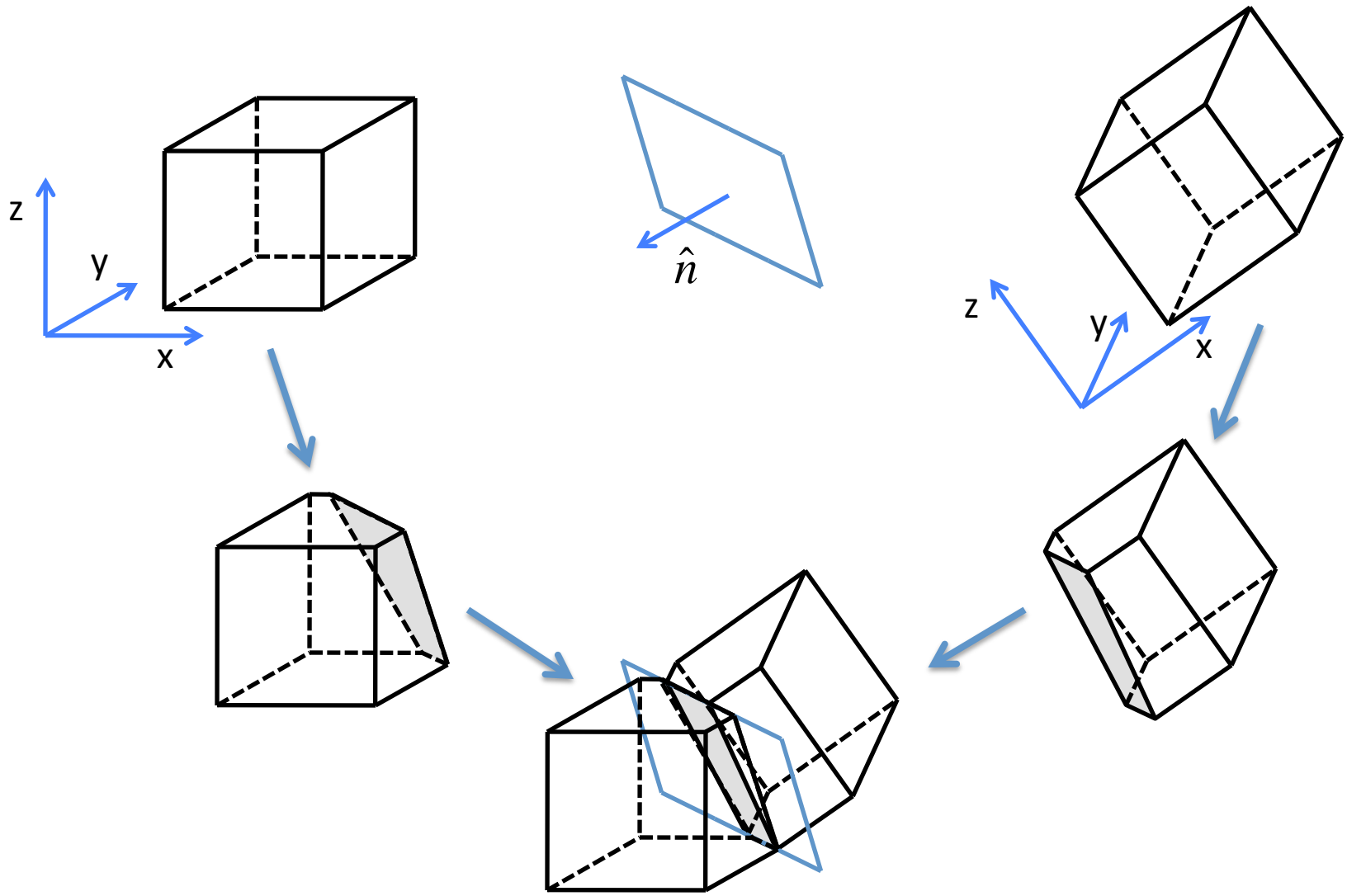


J. P. Hirth, J. Lothe, Theory of Dislocations (Krieger, 1992)

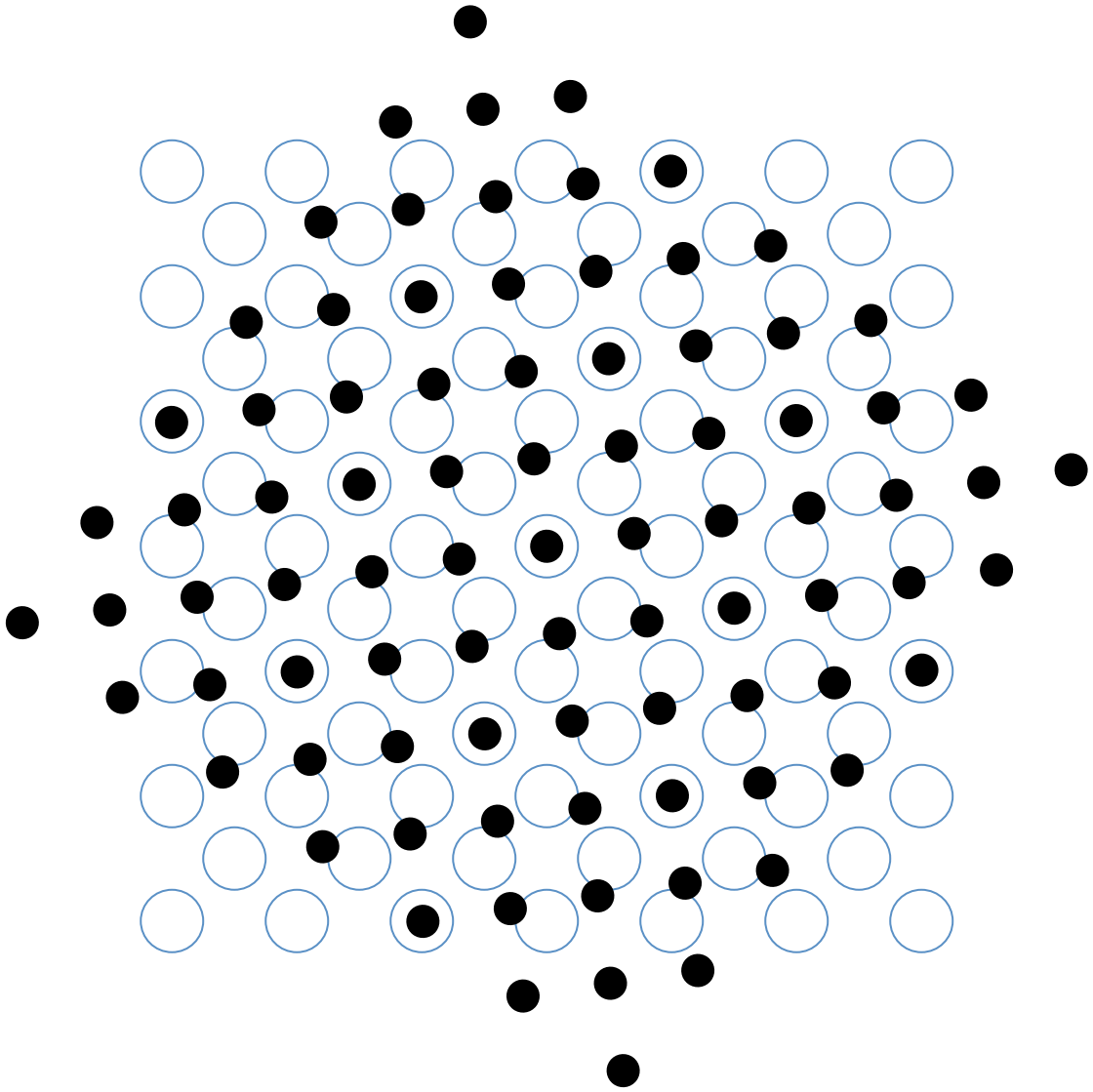


D. Hull, D. J. Bacon, Introduction to Dislocations (Butterworth-Heinemann, 2001)

Grain boundary macroscopic degrees of freedom



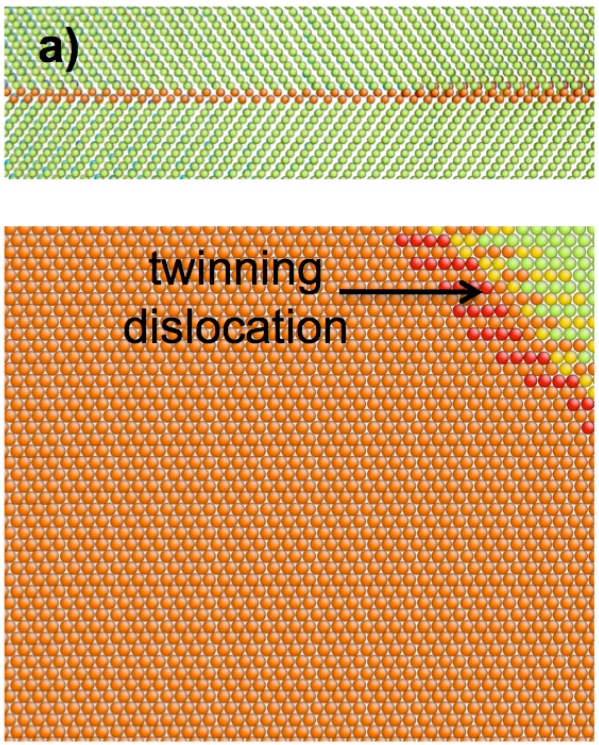
Coincidence-site lattice (CSL)



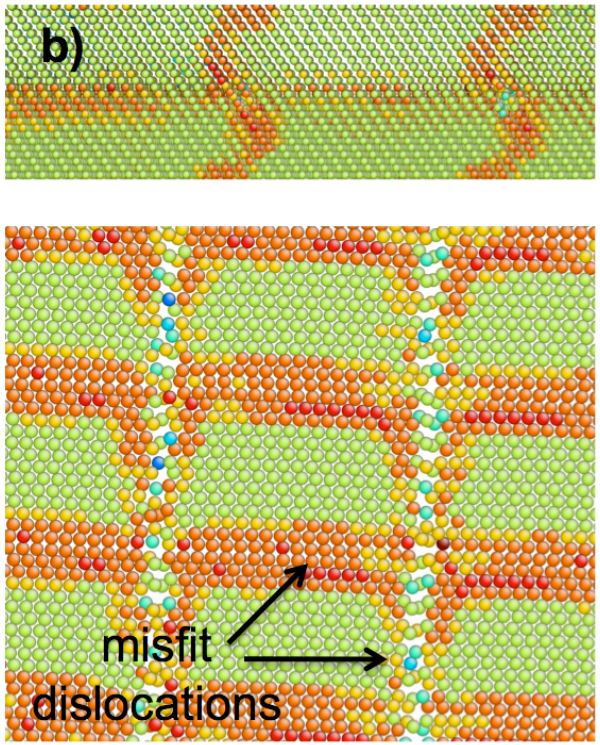
Coherent/semicoherent/incoherent

GBs on {112} planes in α-Fe

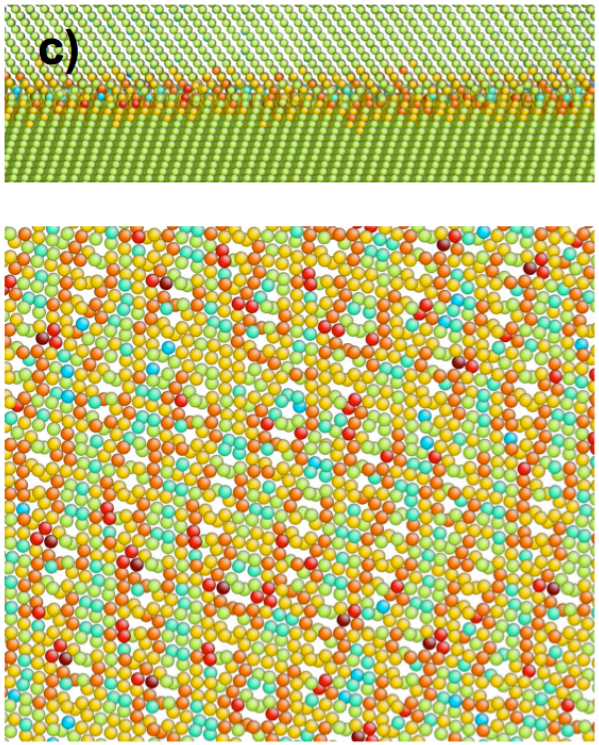
Coherent (Σ3 {112} twin)



Semicoherent (5° twist)

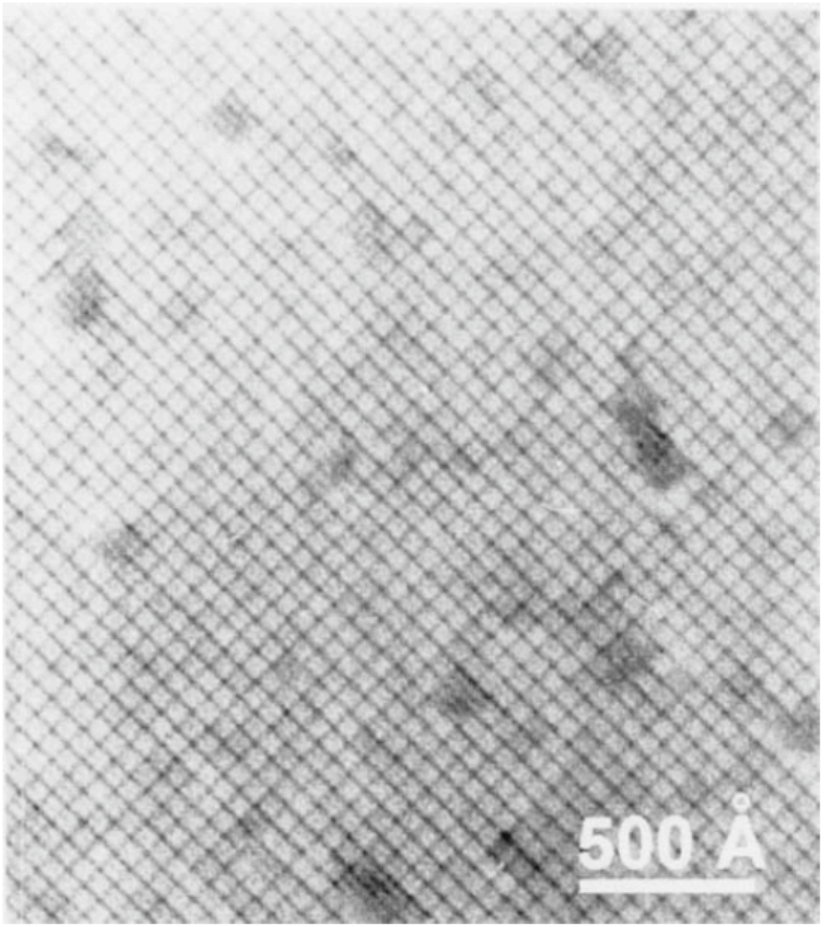


Incoherent (30° twist)



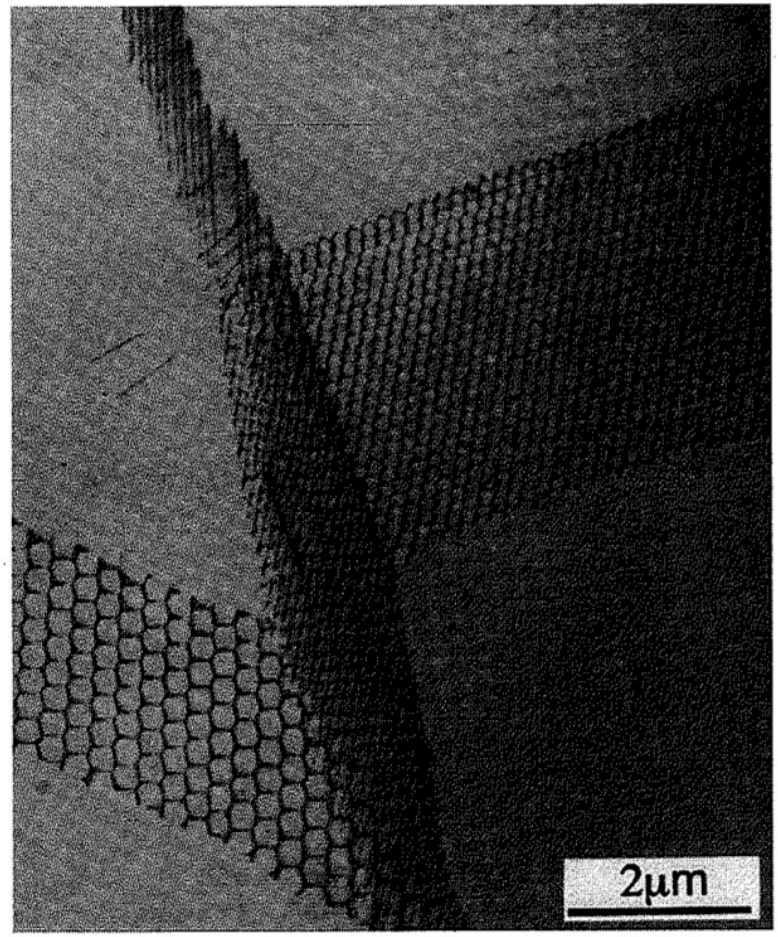
TEM observation of semicoherent GBs

Si twist GB



C. Chen *et al.*, Philos. Mag. A 80, 881 (2000)

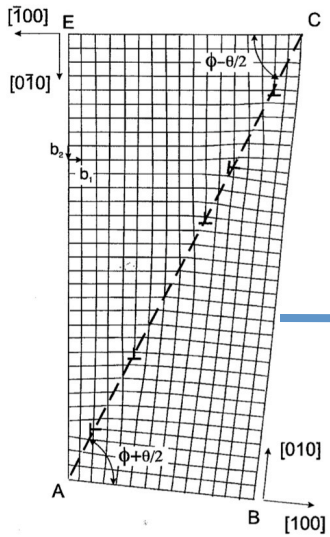
α-Fe



D. Hull, D. J. Bacon, Introduction to Dislocations (Butterworth-Heinemann, 2001)

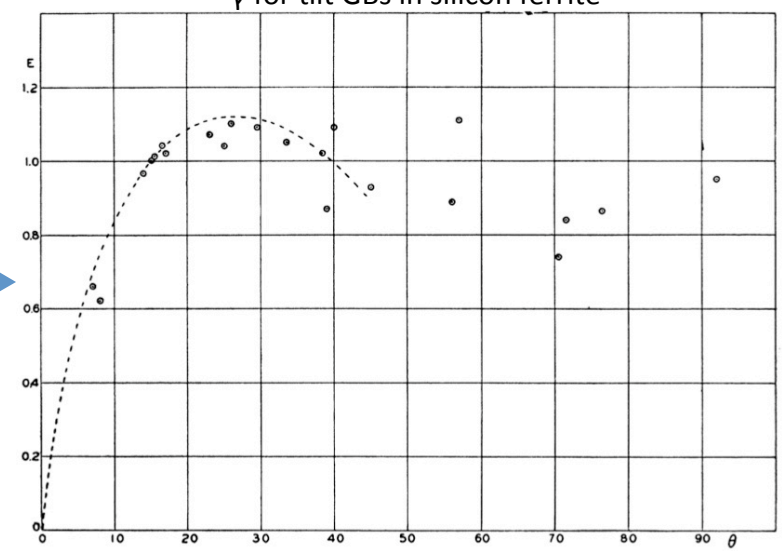
Read-Shockley model

Tilt GB



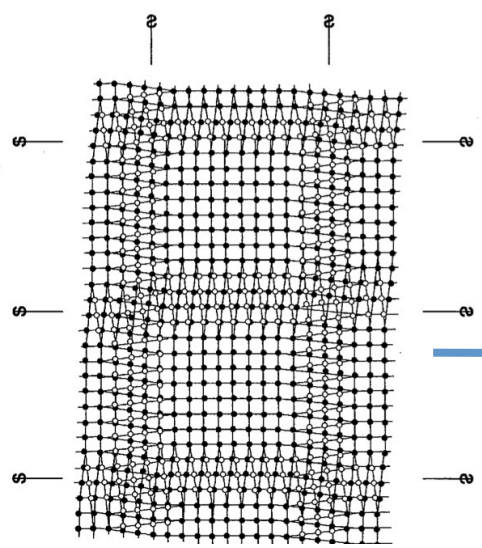
$$\gamma_{GB} = \frac{\mu b}{4\pi(1-\nu)}\theta(1-\ln\theta)$$

γ for tilt GBs in silicon ferrite

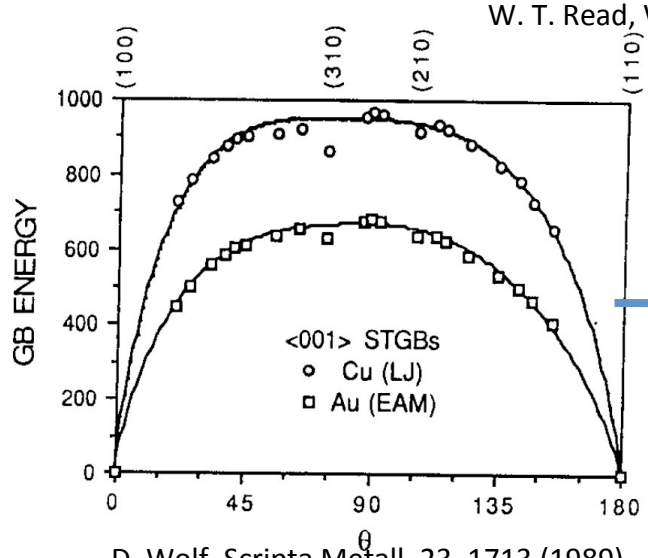


W. T. Read, W. Shockley, Phys. Rev. 78, 275 (1950)

Twist GB



D. Hull, D. J. Bacon, Introduction to Dislocations (Butterworth-Heinemann, 2001)

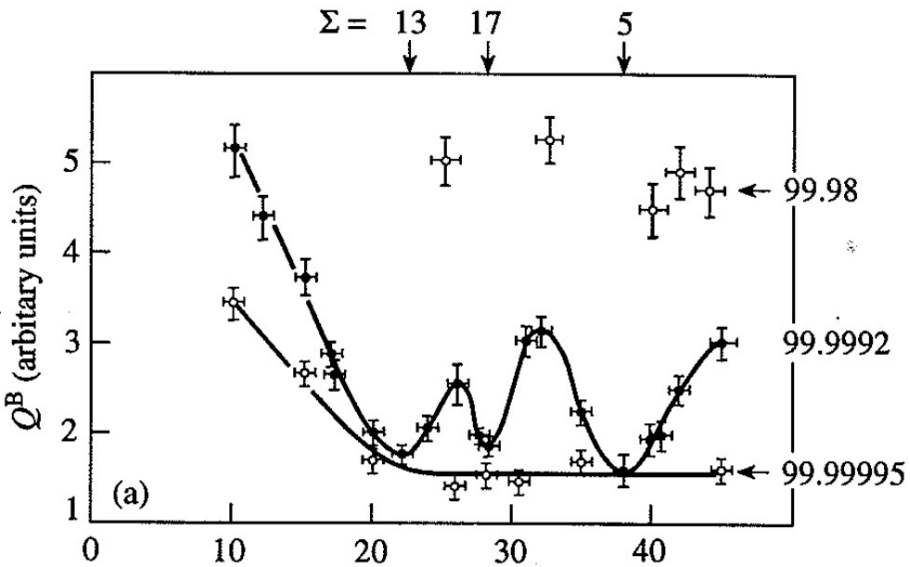


D. Wolf, Scripta Metall. 23, 1713 (1989)

$$\gamma_{GB} = \gamma_{GB}^{0}\theta\left[A - \ln(\sin\theta)\right]$$

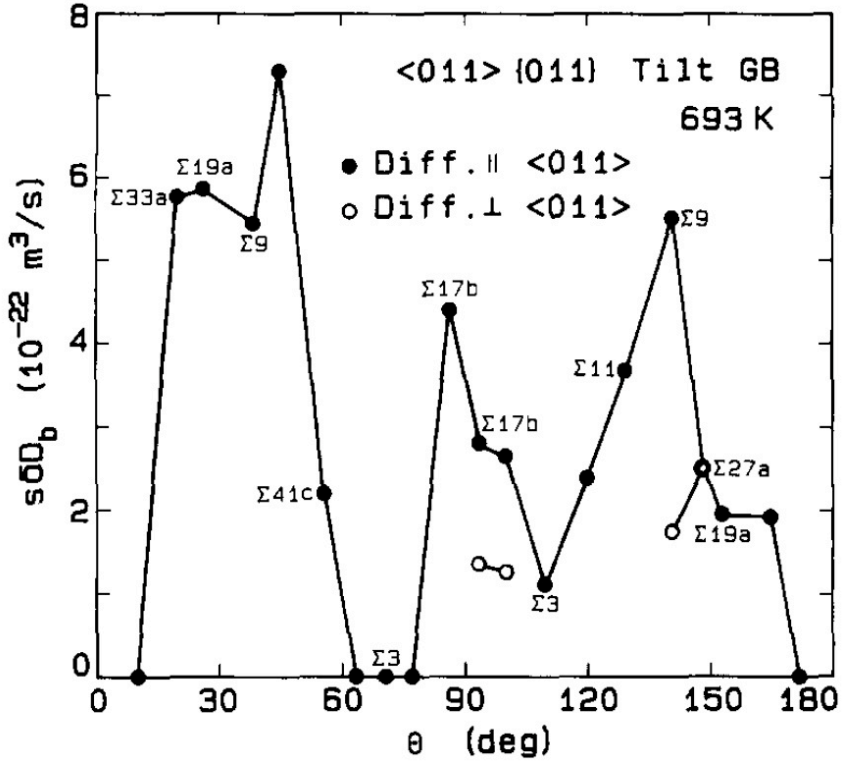
GB mobility and diffusivity

GB migration in Al



E. M. Fridman *et al.*, Z. Metall. 66, 533 (1975)

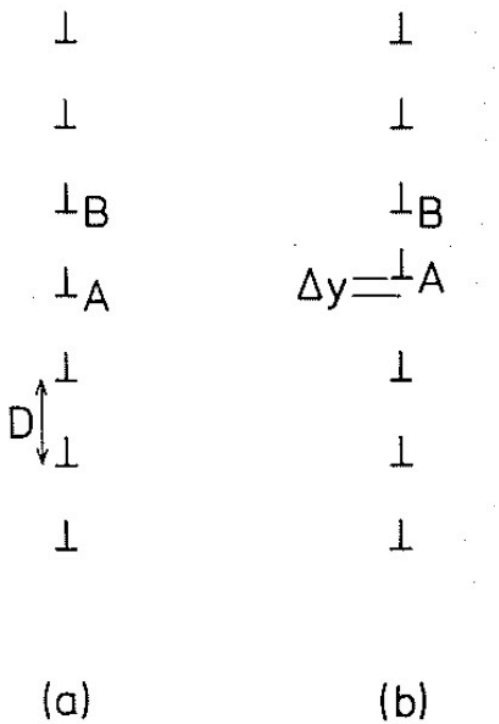
Zn diffusivity in Cu GBs



R. Schmelzle *et al.*, Acta Metall. Mater. 40, 997 (1992)

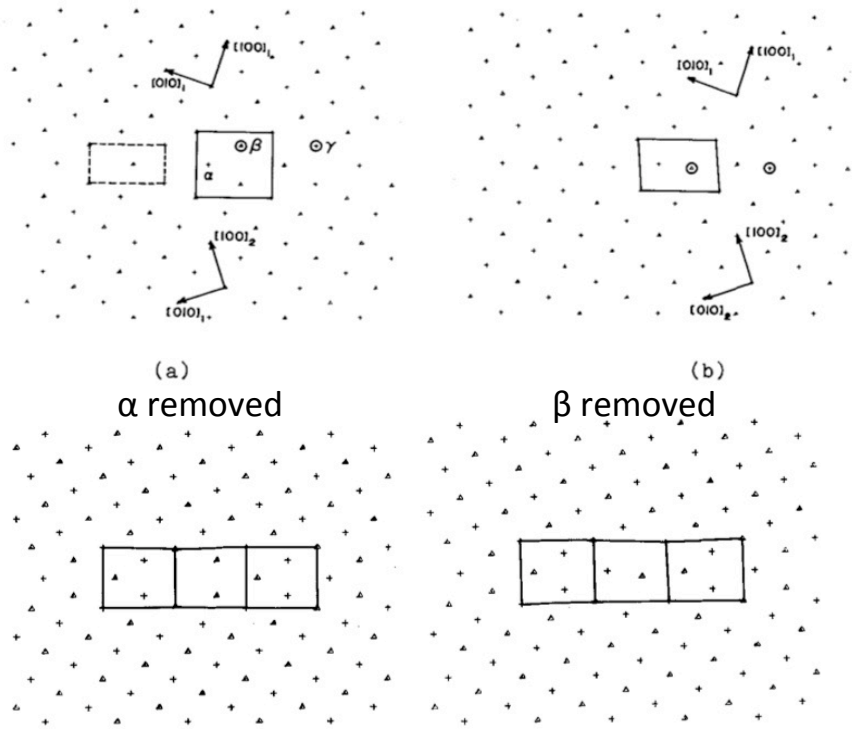
GB-point defect interactions

Dislocation model of tilt GB sink



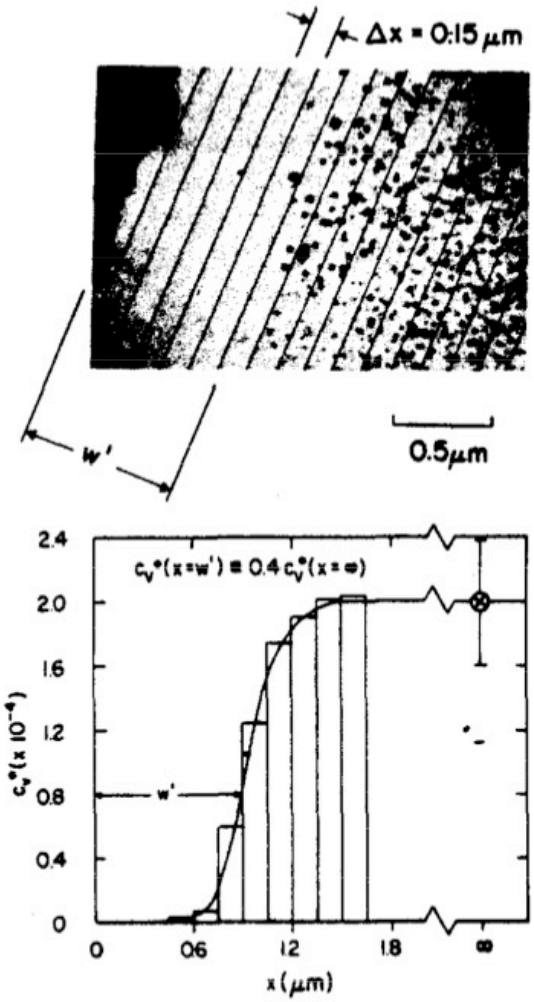
A. H. King, D. A. Smith, Metal Science 14, 57 (1980)

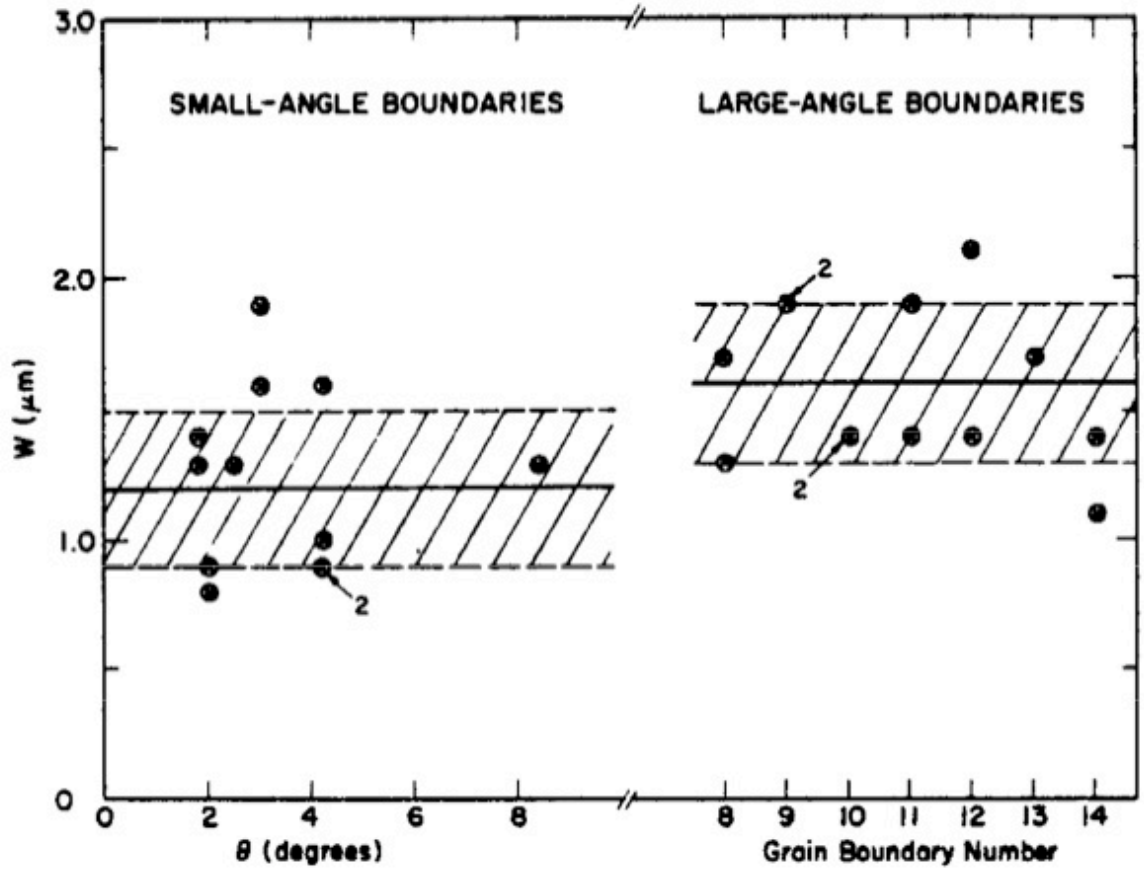
Structural unit model of vacancy trapping



V. Vitek, Y. Minonishi, G. J. Wang, J. Phys. 46, 171 (1985)

GB sink strength

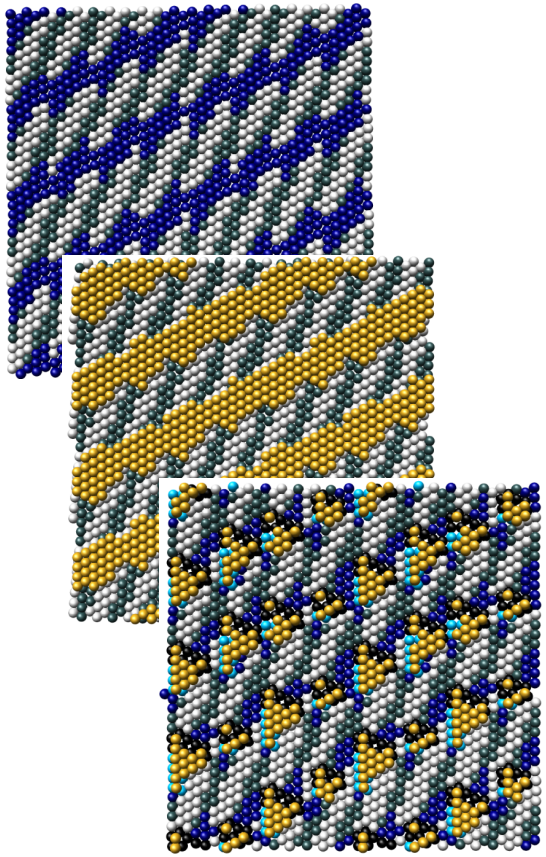




R. W. Siegel, S. M. Chang, R. W. Balluffi, Acta Metall. 28, 249 (1980)

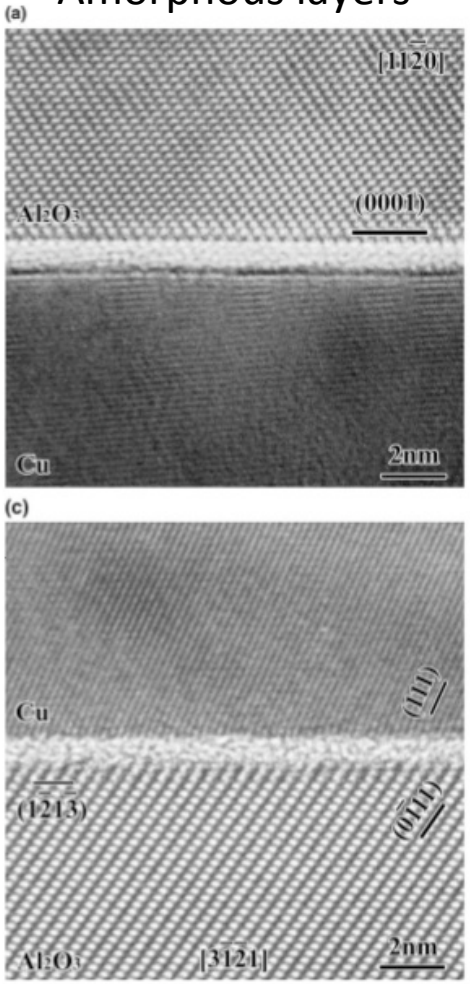
Heterointerfaces

Multiple atomic configurations at Cu-Nb interfaces



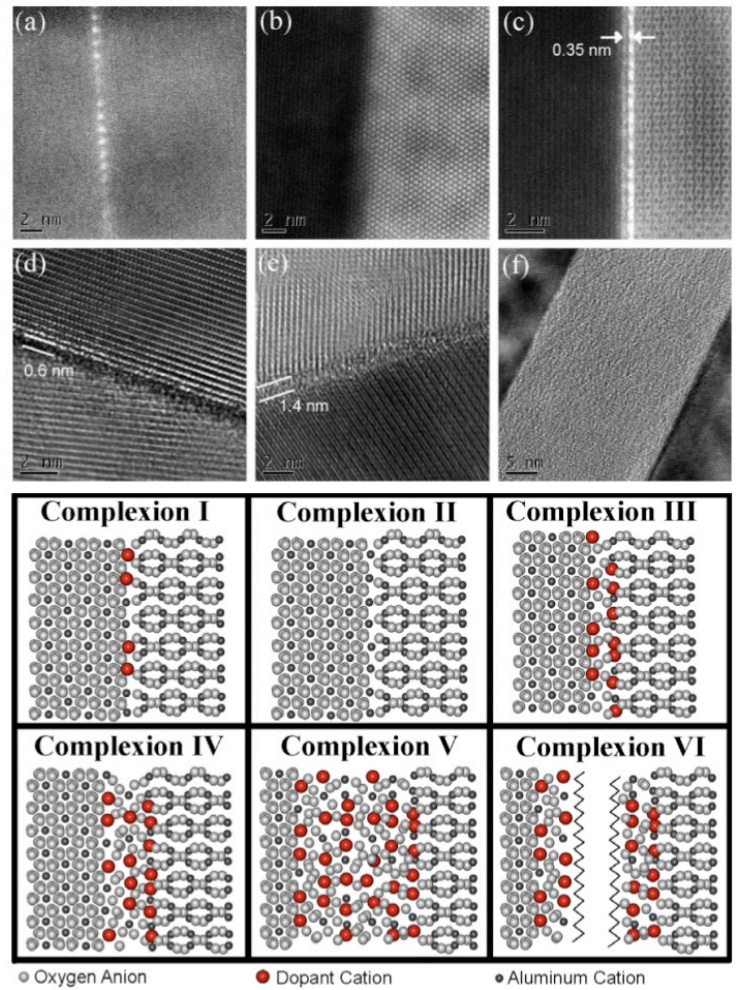
M. J. Demkowicz, R. G. Hoagland, J. P. Hirth, PRL 100, 136102 (2008)

Amorphous layers



A. Avishai, C. Scheu, W. D. Kaplan, Acta Mater. 53, 1559 (2005)

Complexions in variously doped Al_2O_3



S. J. Dillon, M. Tang, W. C. Carter, M. P. Harmer, Acta Mater. 55, 6208 (2007)

Summing up…

Important things to keep in mind:

- Vacancies and interstitials undergo reactions:
  - Recombination, clustering
- Point defects interact with dislocations
  - More strongly with edge than with screw
  - Interstitials more strongly than vacancies
  - Cause climb, prismatic loop formation
- A variety of grain boundary and heterophase interface structures are possible, resulting in a variety of interactions with point defects