UNIVERSITY OF LIVERPOOL

Radiation 'Damage'

Maulik Patel

Dept. Mechanical Materials & Aerospace
University of Liverpool

maulik.patel@liverpool.ac.uk

Joint ICTP-IAEA International School on Nuclear Waste Vitrification
Sept. 2019

Will the radiation interact with solid atoms?

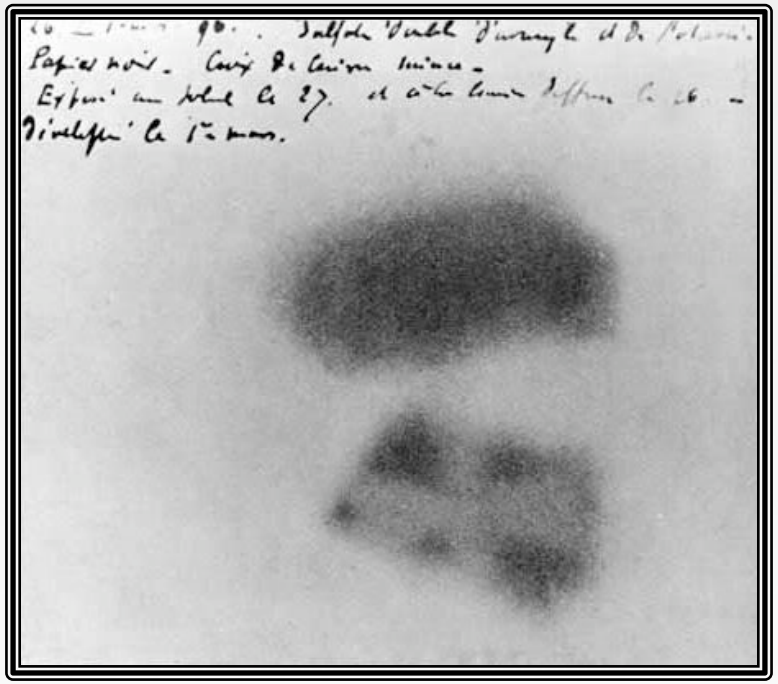
How will it interact?

Consequences of this interaction?

Are these consequences 'damaging' i.e. degrade the performance?

Early examples of radiation 'damage'

First example of ion-matter interaction



Fluorescence from uranium bearing salt in photographic paper by, Henri Becquerel (1896)

Journal
of
Applied Physics

Volume 17, Number 11 November, 1946

Theoretical Physics in the Metallurgical Laboratory of Chicago*

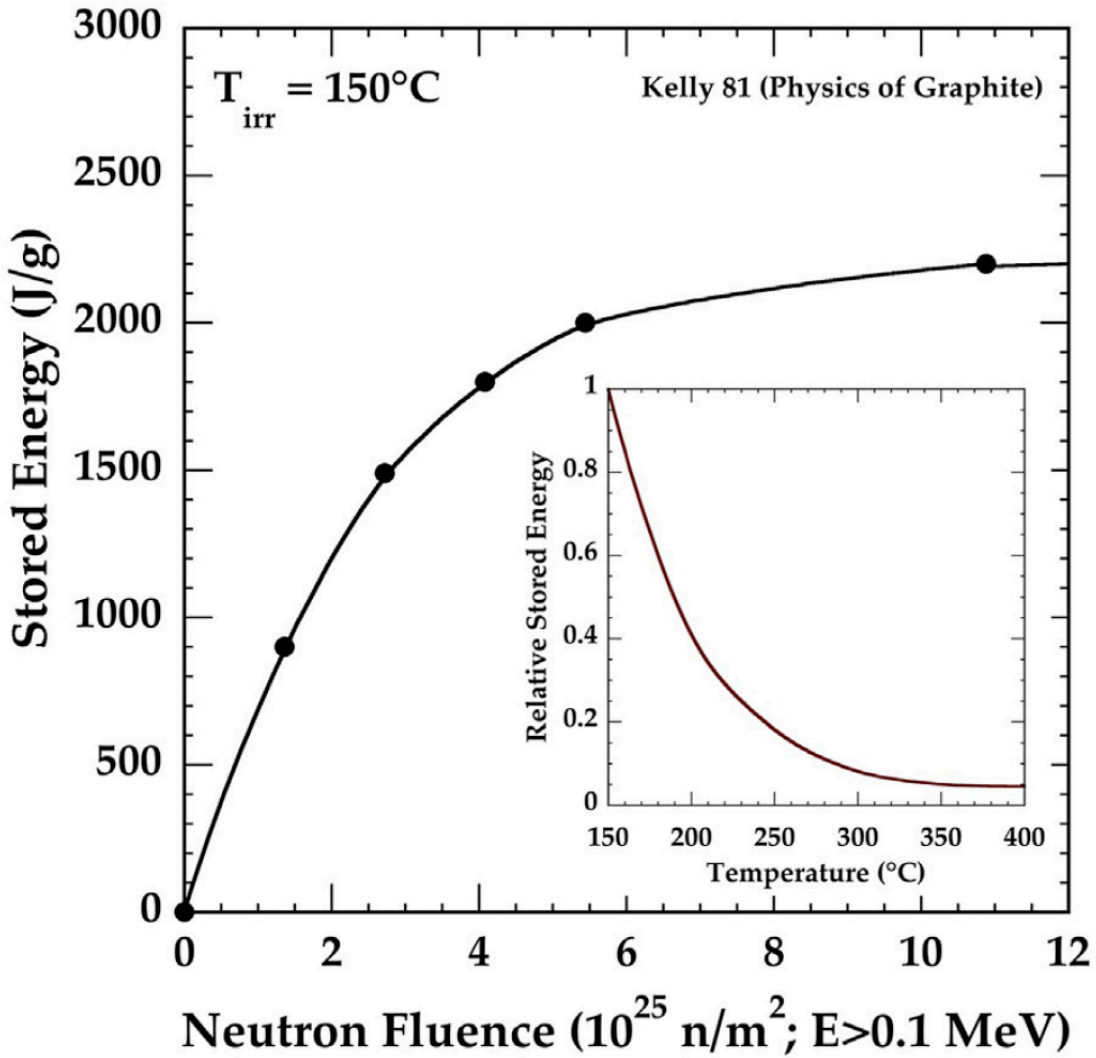
BY E. P. WIGNER
Clinton Laboratories, Oak Ridge, Tennessee

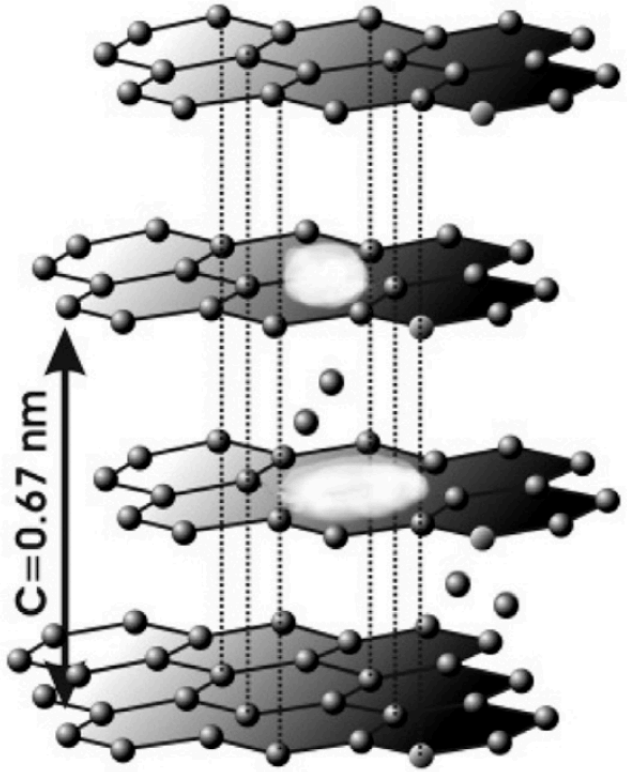
Clearly, the collision of neutrons with the atoms of any substance placed into the pile will cause displacements of these atoms. If the substance is a chemical compound, the displacement will result in chemical changes which were, of course, investigated already before chain reacting units came into being and are summarized, e.g., in the booklet of Lind.[7] All these changes are much more intense in the pile owing to the more intense radiation. But substantial effects can be expected in elementary substances also. The matter has great scientific interest because pile irradiation should permit the artificial formation of displacements in definite numbers and a study of the effect of these on thermal and electrical conductivity, tensile strength, ductility, etc. as demanded by theory. One may expect that

[7] Cf. e.g. S. C. Lind, *Chemical Effects of α Particles and Electrons* (Chemical Catalogue Company, New York, 1928).

Stored energy in graphite

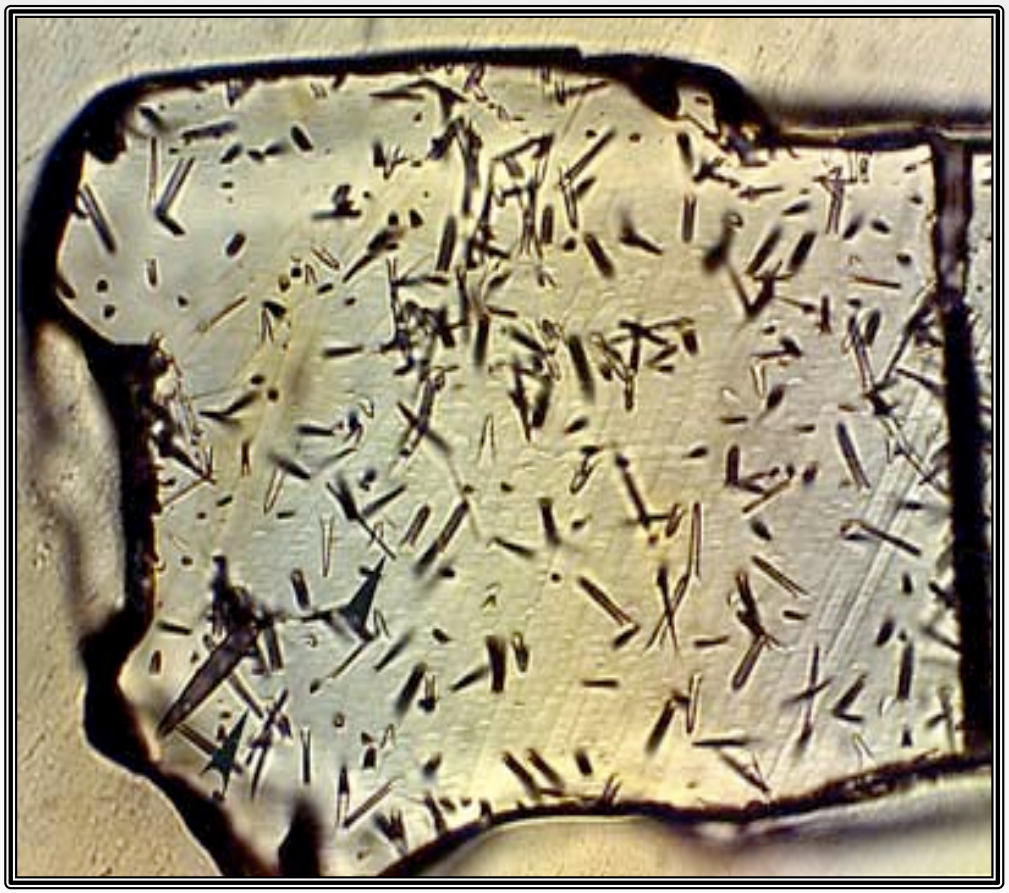
L.L. Snead et al. / Journal of Nuclear Materials 514 (2019) 181–188





UNIVERSITY OF LIVERPOOL

Natural Fission: Uranium 235, 238



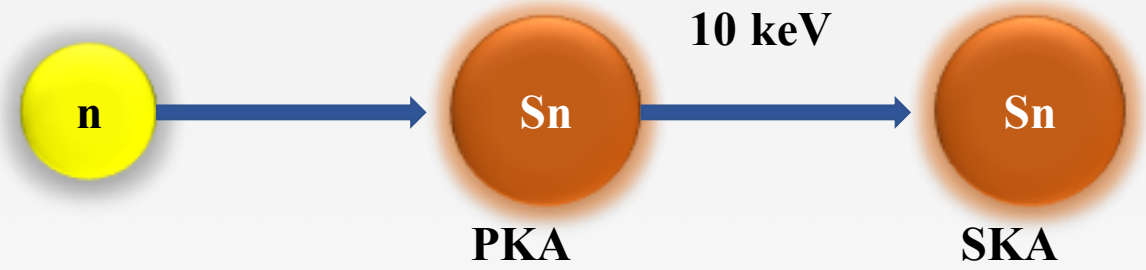
Apatite crystal : $Ca_5F(PO_4)_3$

Mean "virgin" track length 14.8-15.9 microns

Types of radiations

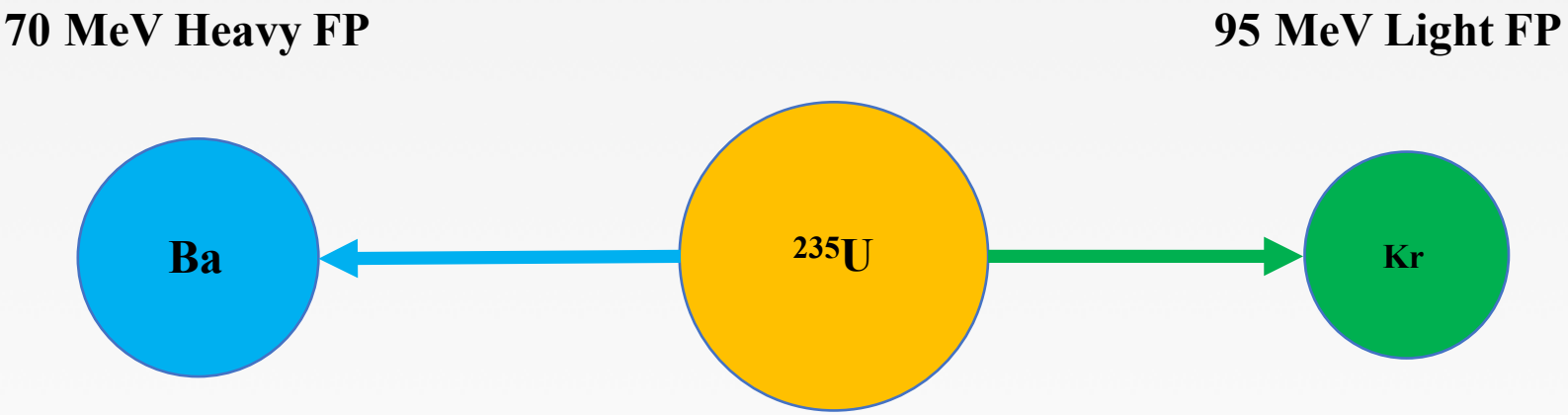
Audience (students) participation?

Primary Knock-on Atom (PKA)



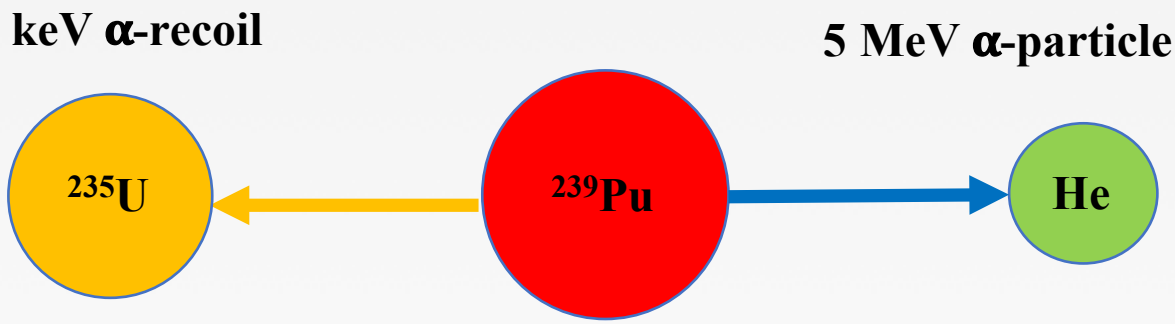
Fission Fragments

Fission Fragments:
Mass between Ga – Dy
Energies between 70 to 120 MeV



α-decay (α-particle & recoil)

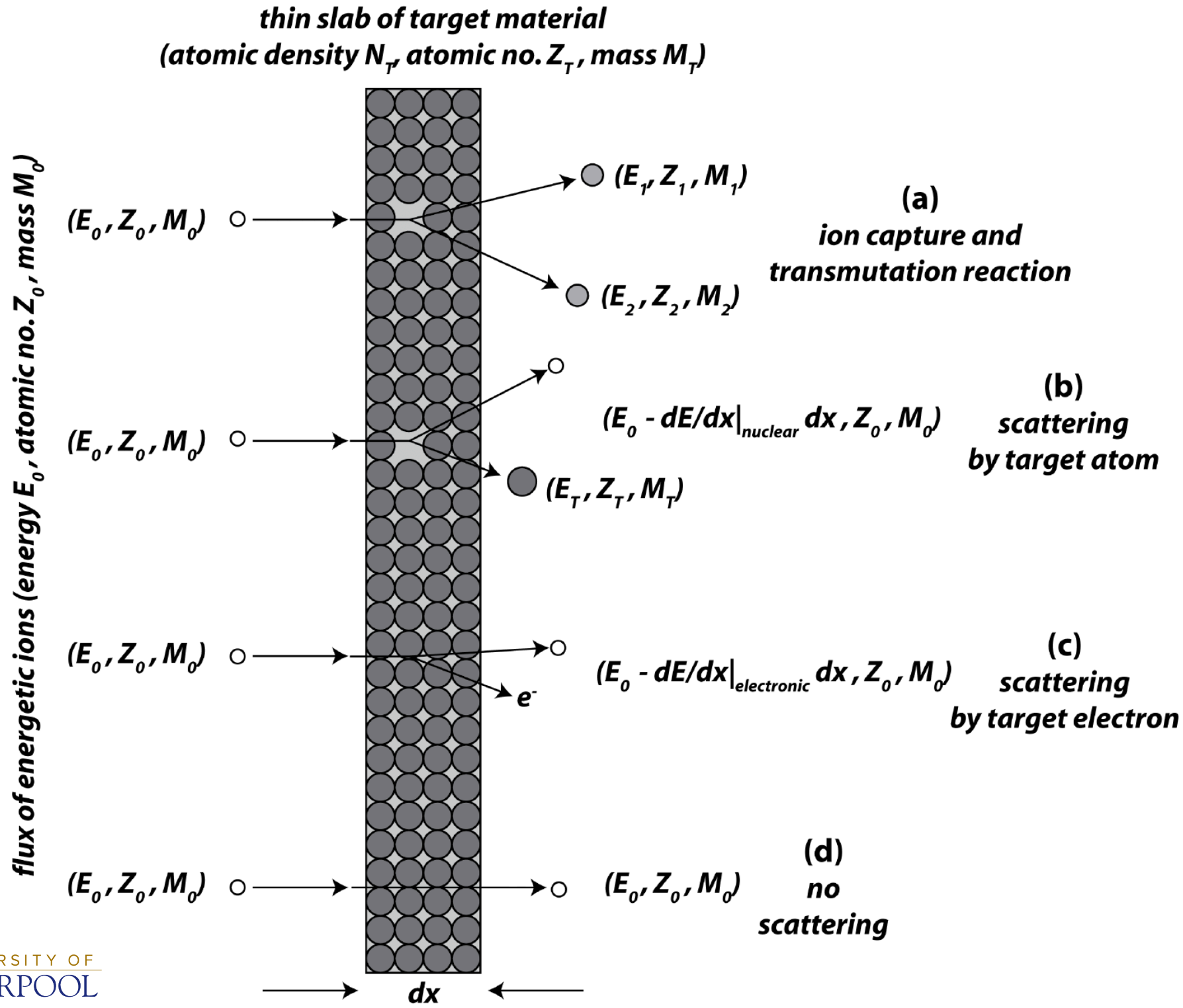
$$^{239}_{94}\mathrm{Pu} \xrightarrow[5.245\ \mathrm{MeV}\ \alpha]{t_{1/2}\ 2.4\times10^{4}\ \mathrm{years}} {}^{235}_{92}\mathrm{U} \xrightarrow[4.4572\ \mathrm{MeV}\ \alpha]{t_{1/2}\ 7.038\times10^{8}\ \mathrm{years}} {}^{231}_{90}\mathrm{Th} \xrightarrow{\beta} {}^{231}_{91}\mathrm{Pa} \xrightarrow[5.149\ \mathrm{MeV}\ \alpha]{t_{1/2}\ 32760\ \mathrm{years}}$$



β-Decay (high energy electron)

Lecture will be limited to effects of particle interactions with solids (ceramics and glasses)

Types of radiation interactions


thin slab of target material
(atomic density N_T, atomic no. Z_T, mass M_T)
flux of energetic ions (energy E_0, atomic no. Z_0, mass M_0)
(E_0, Z_0, M_0)
(E_1, Z_1, M_1)
(E_2, Z_2, M_2)
(a)
ion capture and
transmutation reaction
(E_0, Z_0, M_0)
$(E_0 - dE/dx|_{nuclear}\, dx, Z_0, M_0)$
(E_T, Z_T, M_T)
(b)
scattering
by target atom
(E_0, Z_0, M_0)
$(E_0 - dE/dx|_{electronic}\, dx, Z_0, M_0)$
e^-
(c)
scattering
by target electron
(E_0, Z_0, M_0)
(E_0, Z_0, M_0)
(d)
no
scattering
dx

What is the probability of these events occurring ?

Ion-solid interaction parameters that influence the probability for occurrence of an event ?

Interaction Cross-Sections (σ)

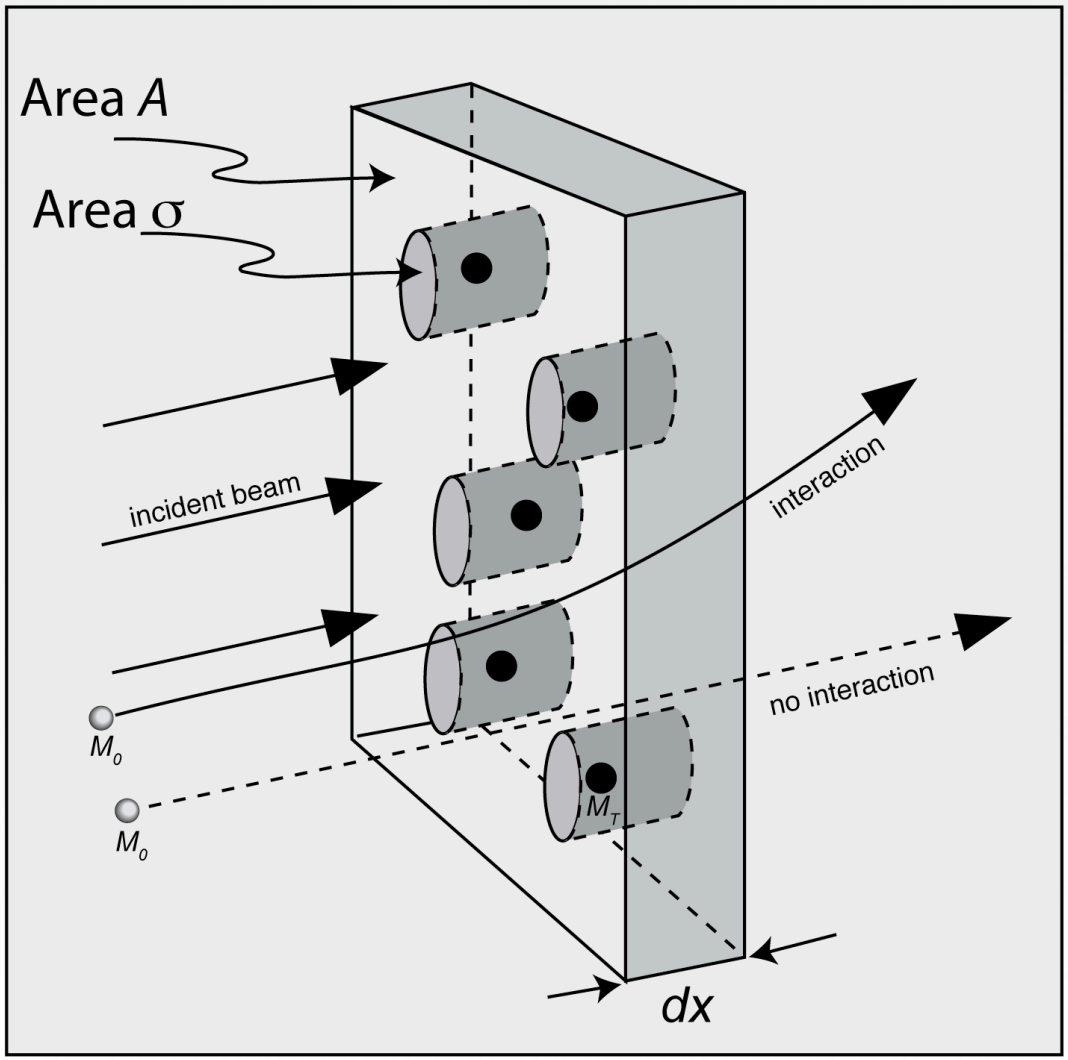
Probability for an interaction "event" (event to be specified)

$$P = \sigma N_T \, dx$$

Aerial density

Probability per ion

$$P = \frac{N_T \, (A \, dx) \, \sigma}{A} = \sigma \, (N_T \, dx)$$



Interaction Cross-Sections (σ)

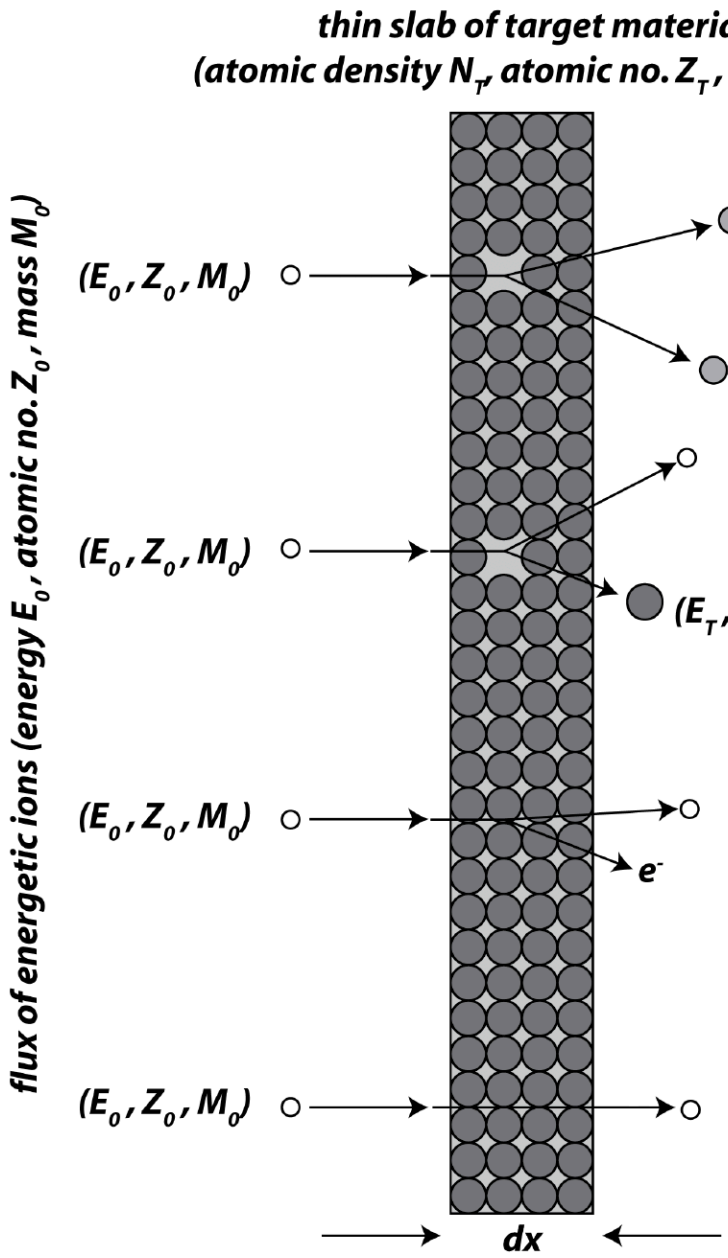
Probability per ion

$$P = \frac{N_T\,(A\,dx)\,\sigma}{A} = \sigma\,(N_T\,dx)$$

$$P\ \left[\frac{\text{number of events}}{\text{ion}}\right] = \frac{n\ \left[\frac{\text{number of events}}{\text{cm}^3}\right] A\ [\text{cm}^2]\ dx\ [\text{cm}]}{\Phi\ \left[\frac{\text{number of ions}}{\text{cm}^2}\right] A\ [\text{cm}^2]} = \sigma\ [\text{cm}^2]\ \ N_T\ \left[\frac{\text{number of target atoms}}{\text{cm}^3}\right] dx\ [\text{cm}]$$

$$\Rightarrow\ \frac{n\ \left[\frac{\text{number of events}}{\text{cm}^3}\right] dx\ [\text{cm}]}{\Phi\ \left[\frac{\text{number of ions}}{\text{cm}^2}\right]} = \sigma\ [\text{cm}^2]\ \ N_T\ \left[\frac{\text{number of target atoms}}{\text{cm}^3}\right] dx\ [\text{cm}]$$

$$\therefore\ \frac{n\ \left[\frac{\text{number of events}}{\text{cm}^3}\right] dx\ [\text{cm}]}{N_T\ \left[\frac{\text{number of target atoms}}{\text{cm}^3}\right] dx\ [\text{cm}]} = \sigma\ [\text{cm}^2]\ \ \Phi\ \left[\frac{\text{number of ions}}{\text{cm}^2}\right] = P_T\ \left[\frac{\text{number of events}}{\text{target atom}}\right]$$



(a) *ion capture and transmutation reaction*

$$P = \sigma_t \, N_T \, dx$$

$$P_T = \sigma_t \, \Phi$$

(b) *scattering by target atom*

$$P = \sigma_n \, N_T \, dx$$

$$P_T = \sigma_n \, \Phi$$

(c) *scattering by target electron*

$$P = \sigma_e \, (Z_T \, N_T) \, dx$$

$$P_{Te} = \sigma_e \, \Phi$$

(d) *no scattering*

$$P = 1 - ((\sigma_t + \sigma_n + Z_T \sigma_e) \, N_T \, dx)$$

Energy partitioning

How Does the Particle Slow Down?

Three interactions which stop particles

$$\left(-\frac{dE}{dx}\right)_{total} = \left(-\frac{dE}{dx}\right)_{n} + \left(-\frac{dE}{dx}\right)_{e}$$

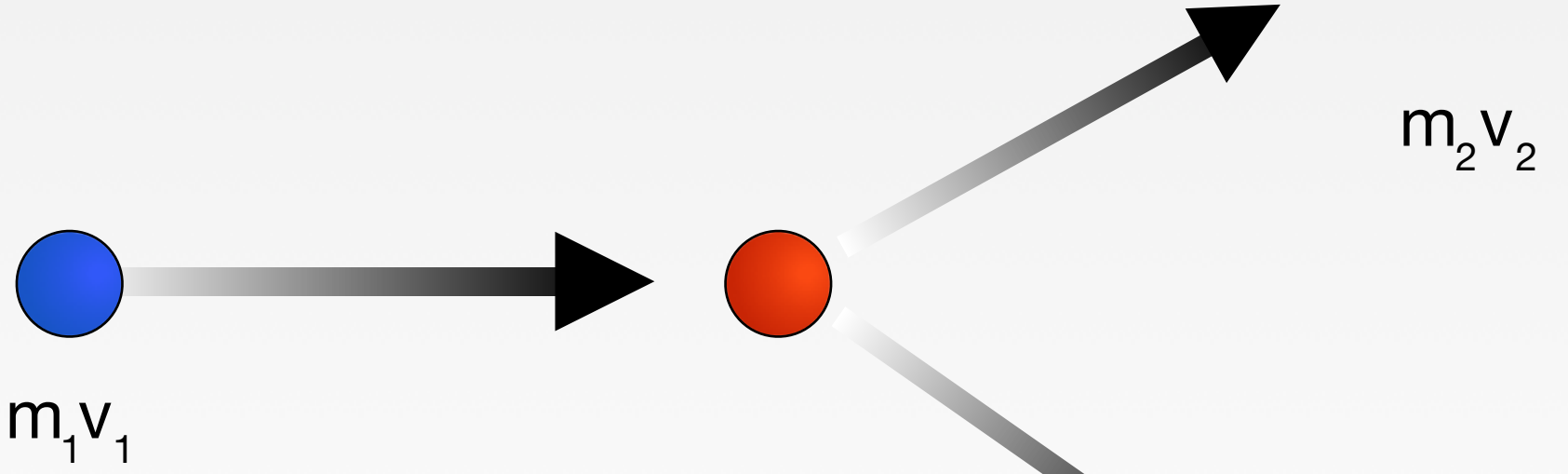
elastic (nuclear)

inelastic (electronic)

How do they behave?

Nuclear Stopping $\left(\frac{dE}{dx}\right)_n$

'The energy removed from the PKA through head-on collisions'



$$V(r) = \frac{K}{r} e^{-\frac{r}{\hat{a}}}$$

Electronic Stopping $\left(\frac{dE}{dx}\right)_e$

'The energy removed from the PKA and transfer to the electronic structure

At high energies - electron cloud cannot keep up with particle, hence particle is unshielded

Energy loss under these conditions predominantly interacts with electrons

Quantification of nuclear and electronic stopping and ion range in solids

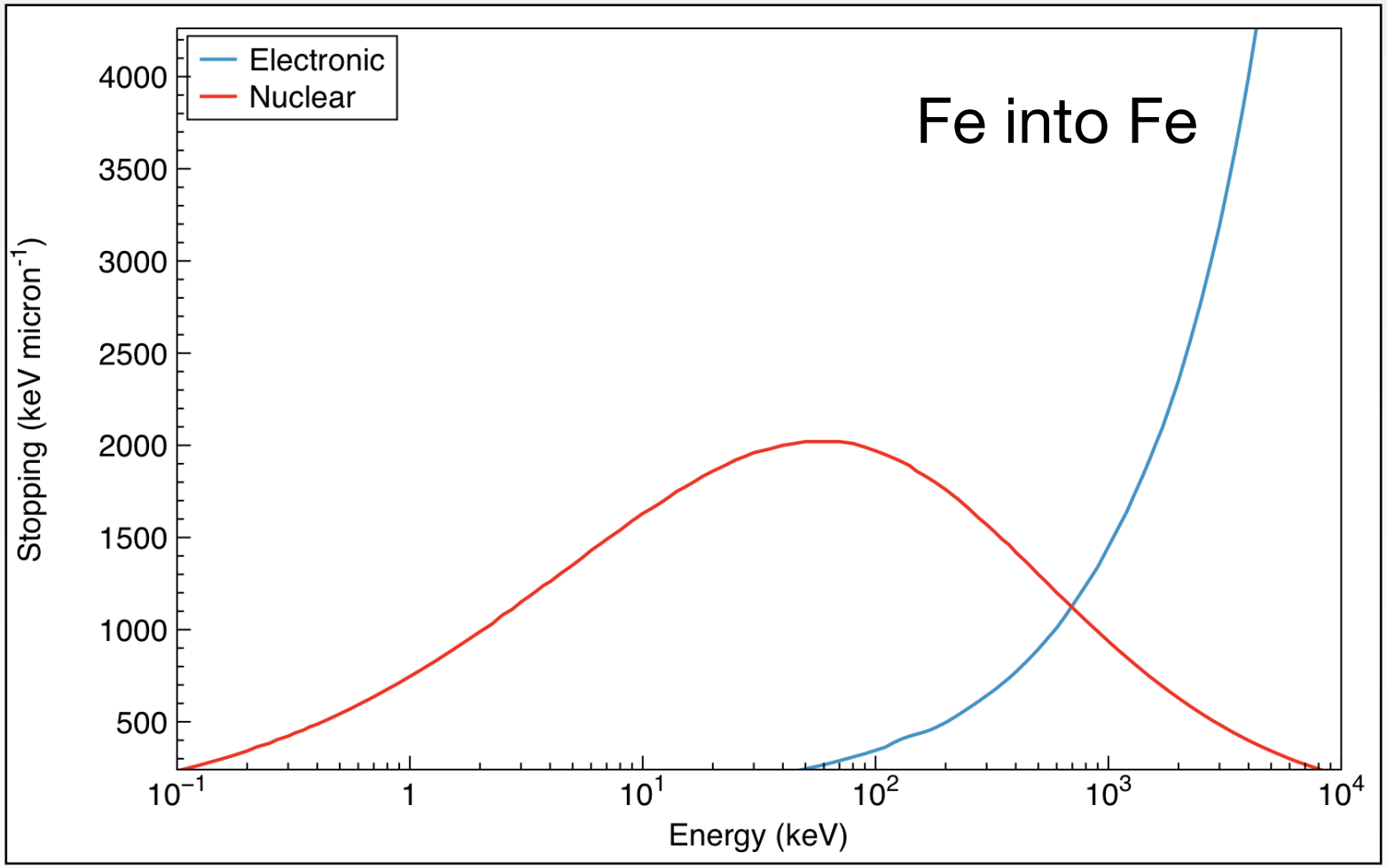
1960s by the Danish physicist, J. Lindhard and colleagues
LSS-theory
Lindhard, Scharff, and SchiØtt

Numerical algorithms for calculating energy loss and ion range
SRIM (Monte-Carlo)

How do they compare?

High mass / low energy - nuclear dominates

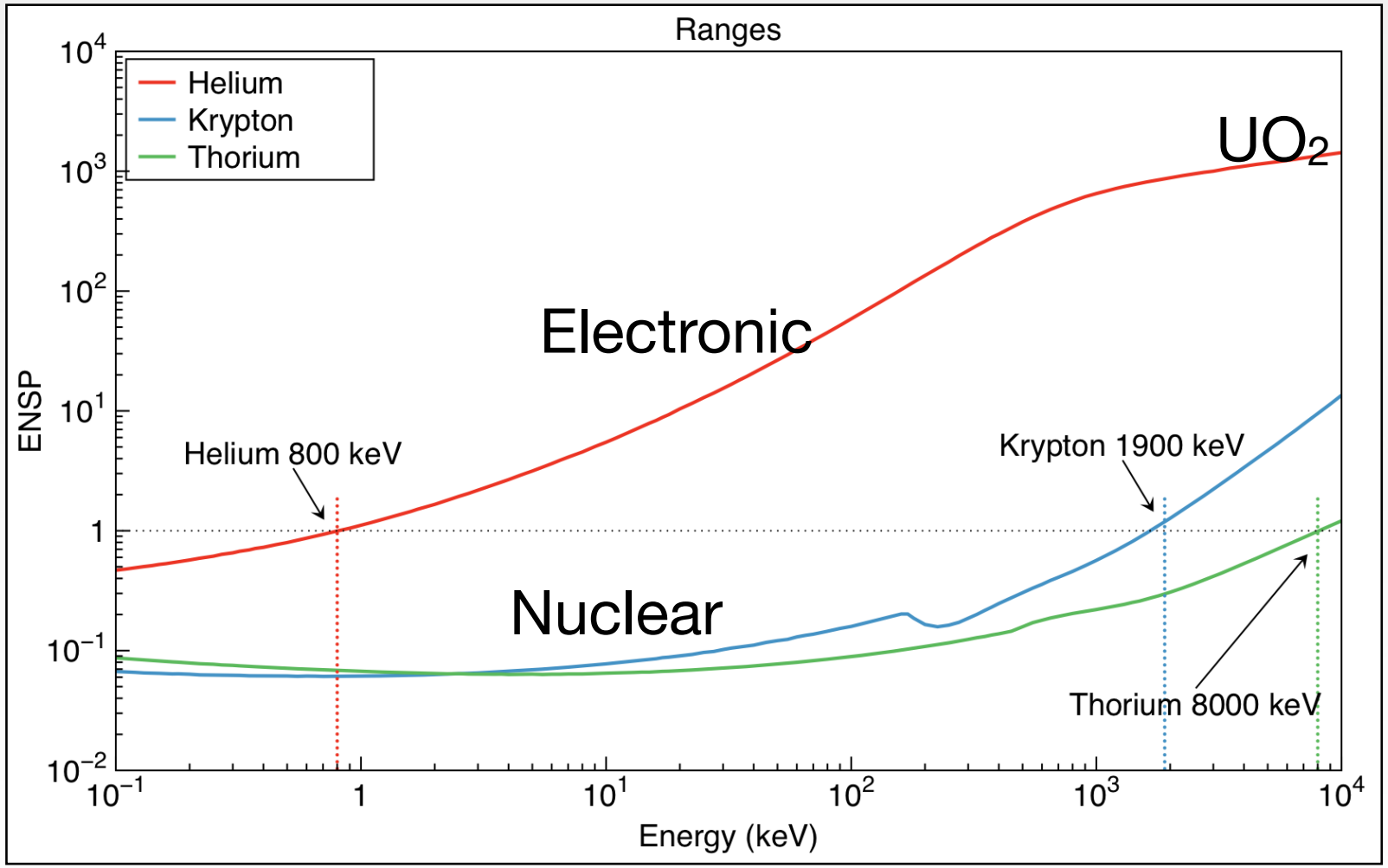
Low mass / high energy - electronic dominates



Electronic to Nuclear Stopping Power (ENSP)

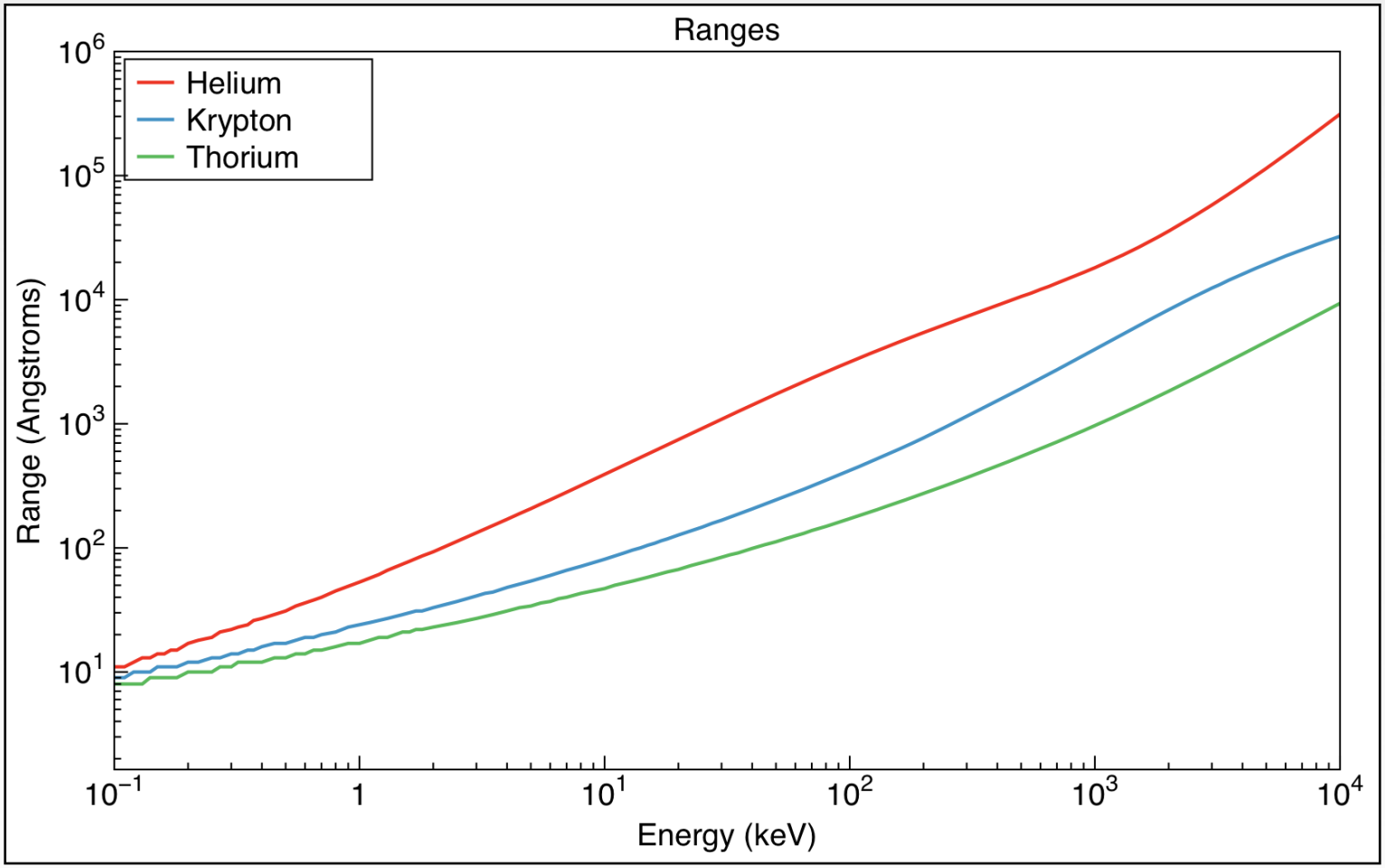
Ratio of electronic to nuclear stopping factors

$$ENSP = \left(-\frac{dE}{dx}\right)_e \Big/ \left(-\frac{dE}{dx}\right)_n$$



Ion Range (R)

$$R = \int_{E=E_0}^{E=0} \frac{dE}{\left(dE/dx\right)_{total}} = \int_{E=E_0}^{E=0} \frac{dE}{\left(dE/dx\right)_{nuclear} + \left(dE/dx\right)_{electronic}}$$



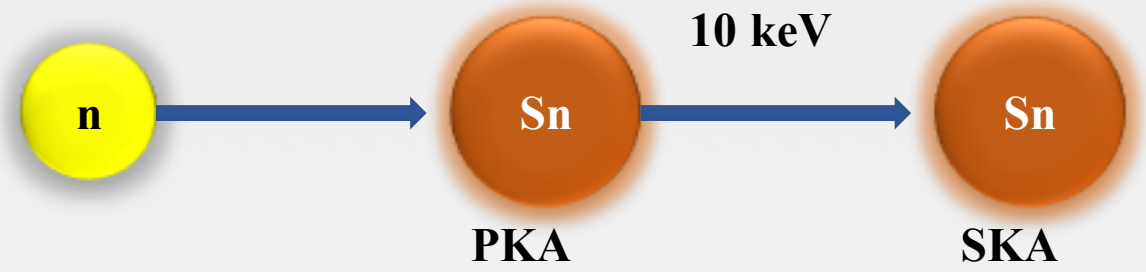
High energy low mass - far

Low energy high mass - not so far

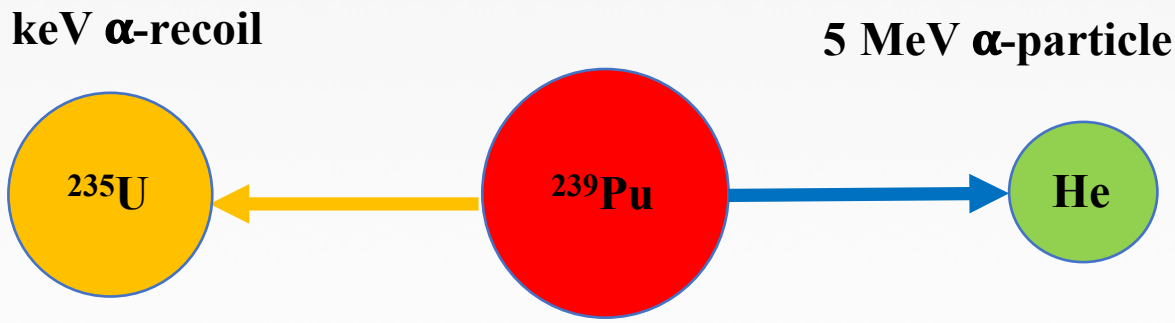
Then damage starts

Rest of the lecture will be limited to effects of low energy particle interactions with solids (ceramics and glasses)

PKA and α-Recoils



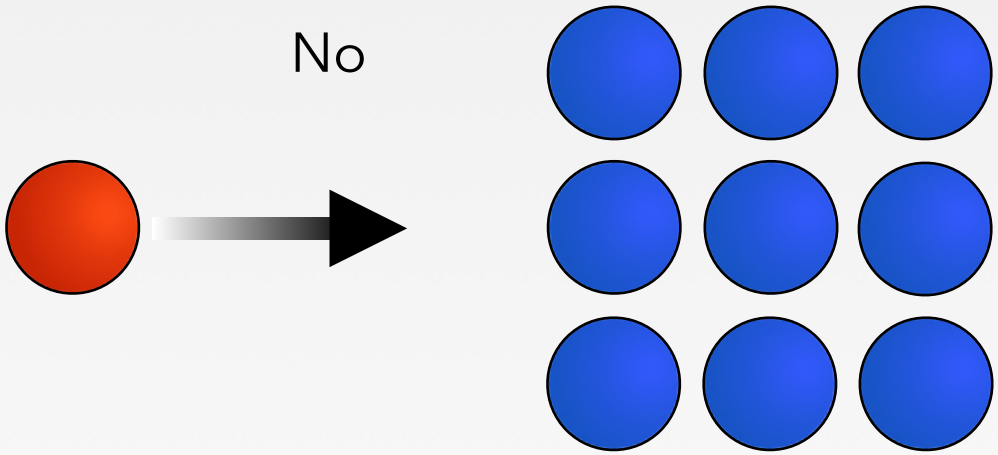
$$^{239}_{94}\mathrm{Pu} \xrightarrow[5.245\ \mathrm{MeV}\ \alpha]{t_{1/2}\ 2.4\times10^{4}\ \mathrm{years}} {}^{235}_{92}\mathrm{U} \xrightarrow[4.4572\ \mathrm{MeV}\ \alpha]{t_{1/2}\ 7.038\times10^{8}\ \mathrm{years}} {}^{231}_{90}\mathrm{Th} \xrightarrow{\beta} {}^{231}_{91}\mathrm{Pa} \xrightarrow[5.149\ \mathrm{MeV}\ \alpha]{t_{1/2}\ 32760\ \mathrm{years}}$$

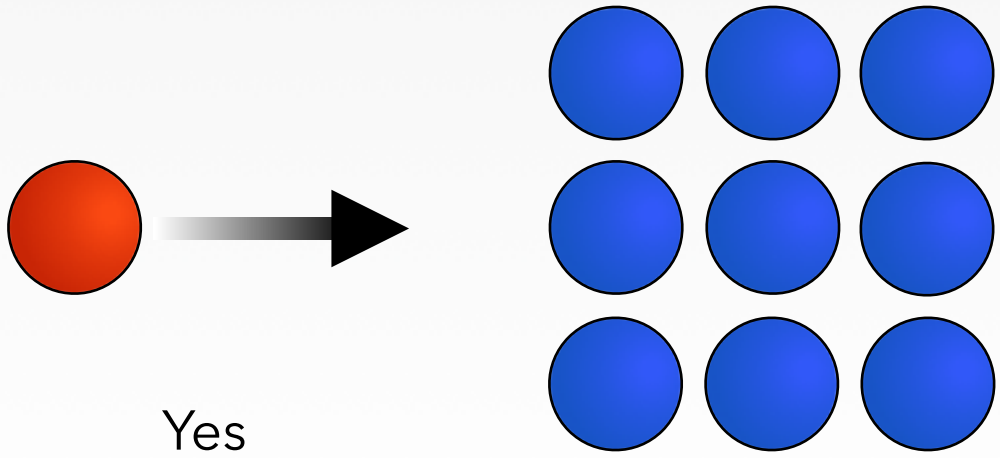


Primary defects ?

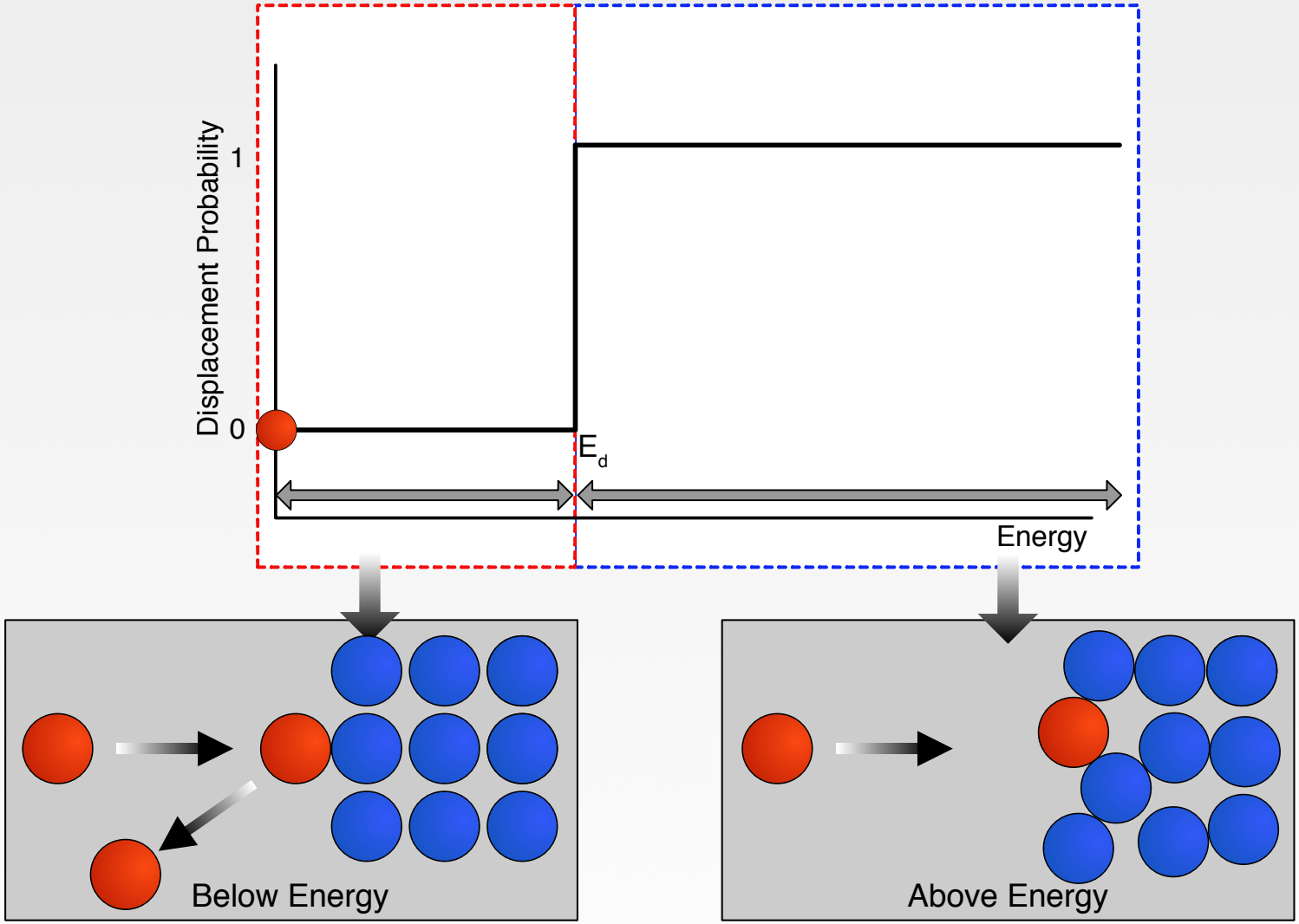
Mechanism of Damage

Does incoming particle have enough to displace an atom from it's position?

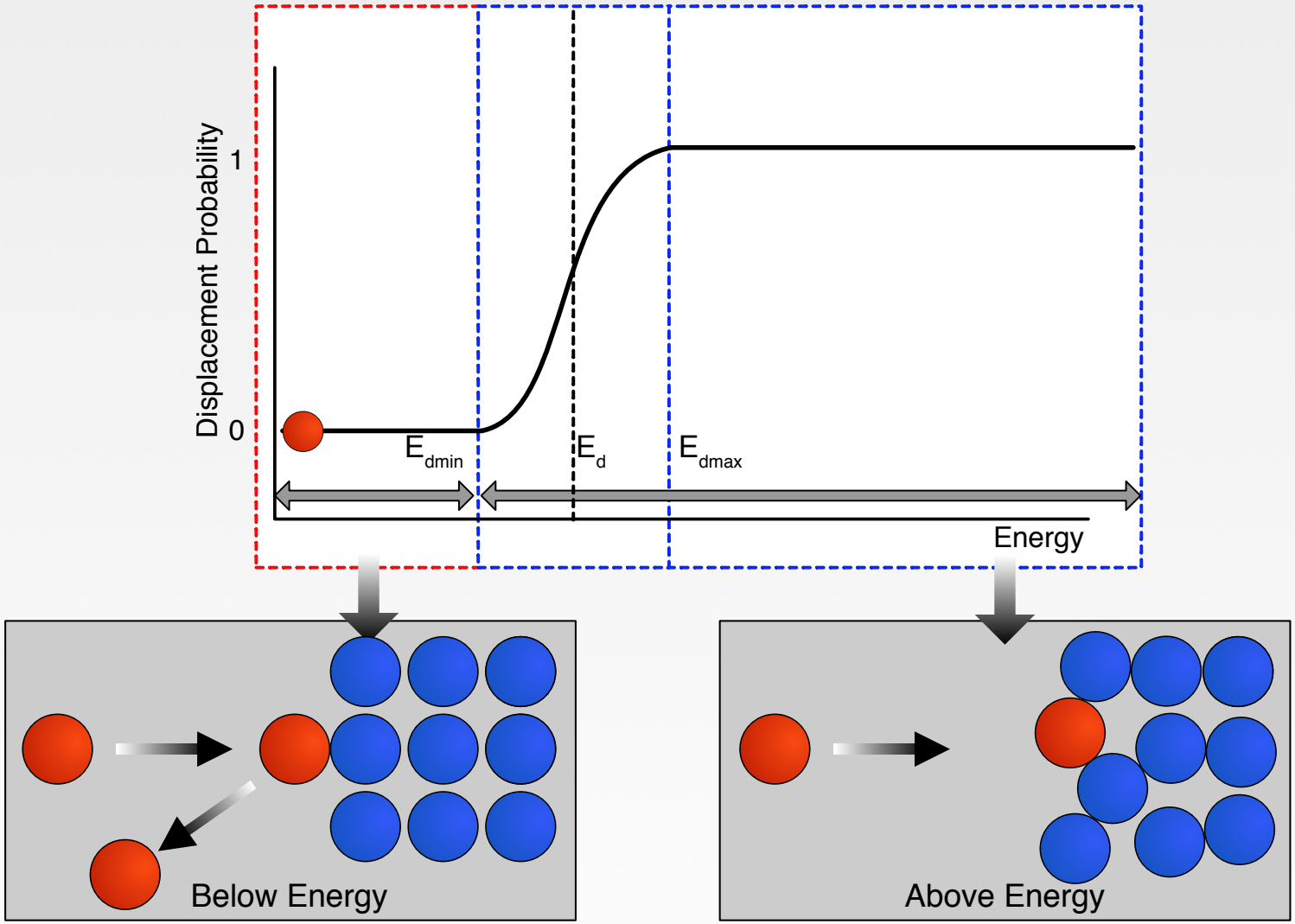




Probability of Displacement - 1



Probability of Displacement - 2



Displacement can occur at energies below Ed - why?

Displacement and Energy

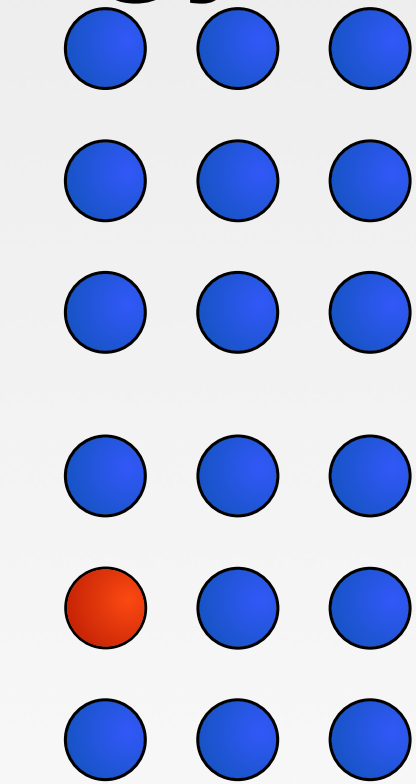
Lattice atoms are not fixed - they vibrate

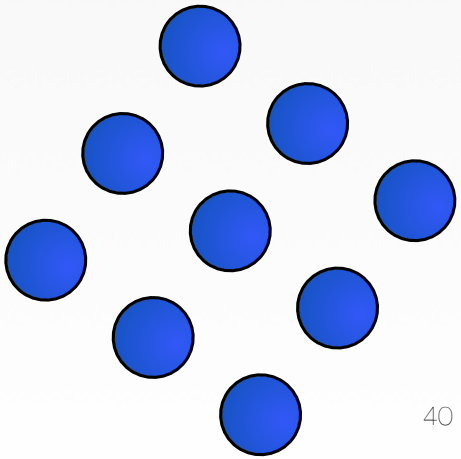
Temperature of sample

Intrinsic / Extrinsic defects

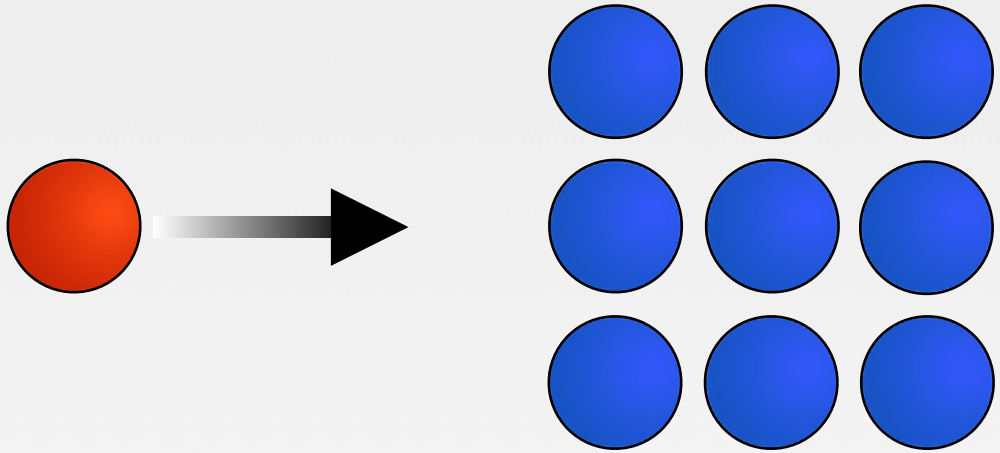
Orientation of crystal

Other…





Typical Time Scales in a Damage Process



Time(s)	Event
10^{-18}	Creation
10^{-13}	Displacement Cascades
10^{-11}	Defect Formation Pairs/Clusters
10^{-8}	Recombination

Predicting damage

Determining the numbers of displacements (i-v pairs) Kinchin - Pease

Key assumptions

1. Monoatomic solid
2. Damage cascades are **two-body** and **elastic**, i.e. (Hard Sphere)
3. There is no spread in probability, i.e. $P = 1$ for $E > E_d$
4. Ignores electronic stopping effects
5. Energy loss through electronic transfer/loss at high energies described by a simple cut off in energy, E_c, above which only electronic stopping occurs
6. $E_c \cong M_T$ (target atomic mass in amu)
7. Atomic arrangement is random (crystal structure is ignored)

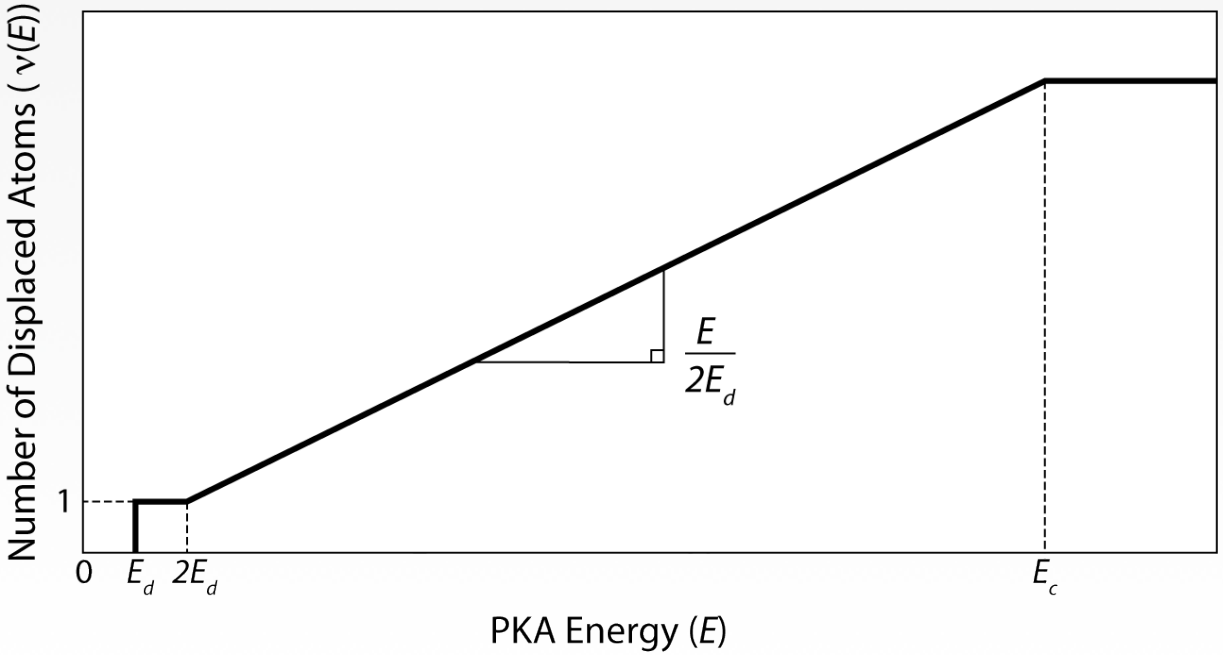
No. of Frenkel pairs (i-v) as a function of energy

$$N_d = \begin{cases} 0 & ; \quad 0 < E \leq E_d \\ 1 & ; \quad E_d < E \leq 2E_d \\ \dfrac{E}{2E_d} & ; \quad E > 2E_d \end{cases}$$

replacement collision

net number of displacements can exceed one

Eg. for a target atom with a displacement threshold of 50 eV (2Ed = 100 eV), a 1 keV incident ion produces 10 displacements, a 10 keV ion produces 100 displacements, a 100 keV ion produces 1000 displacements, and so on



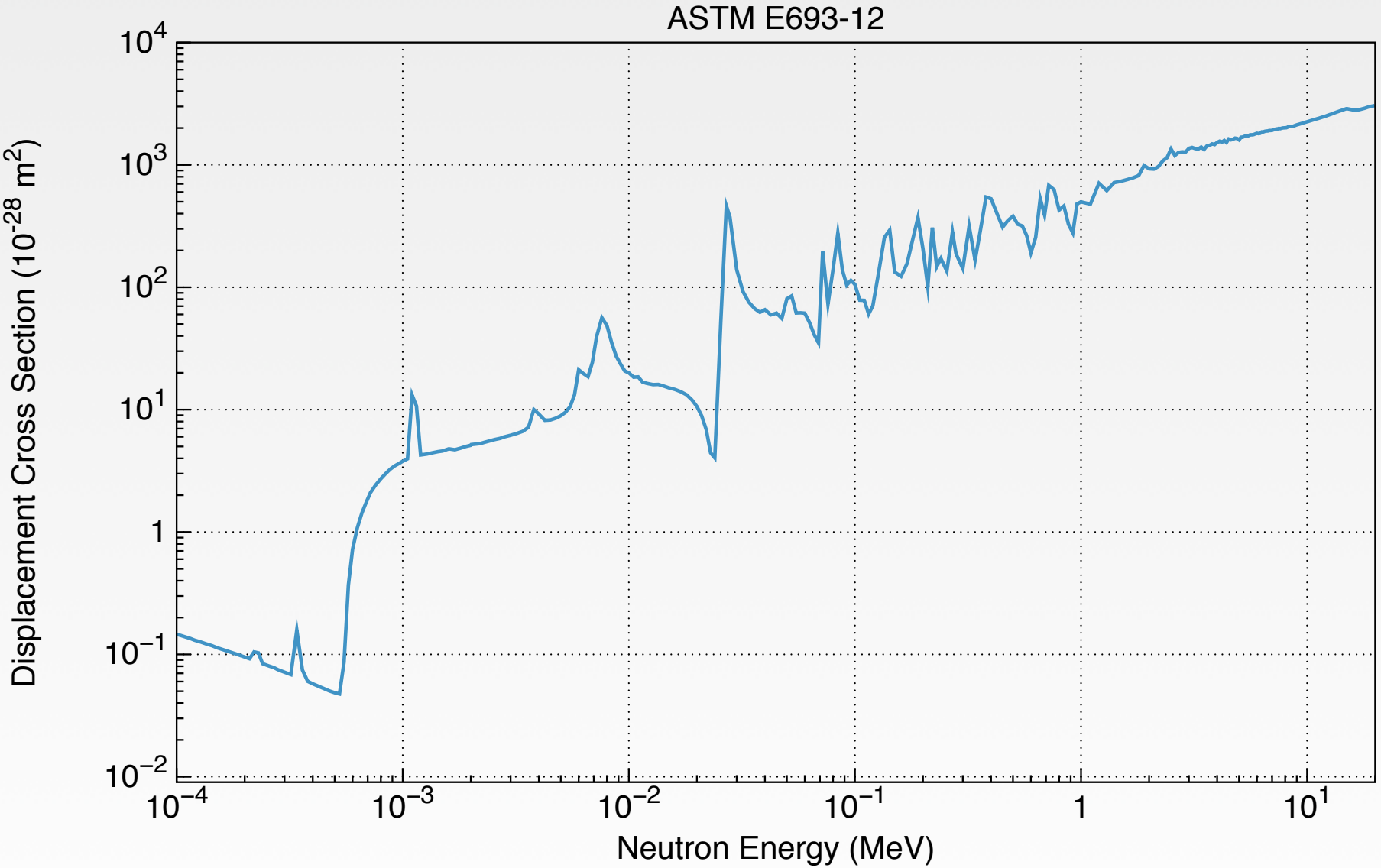
Norgett, Robinson and Torrens (NRT)
Modified KP

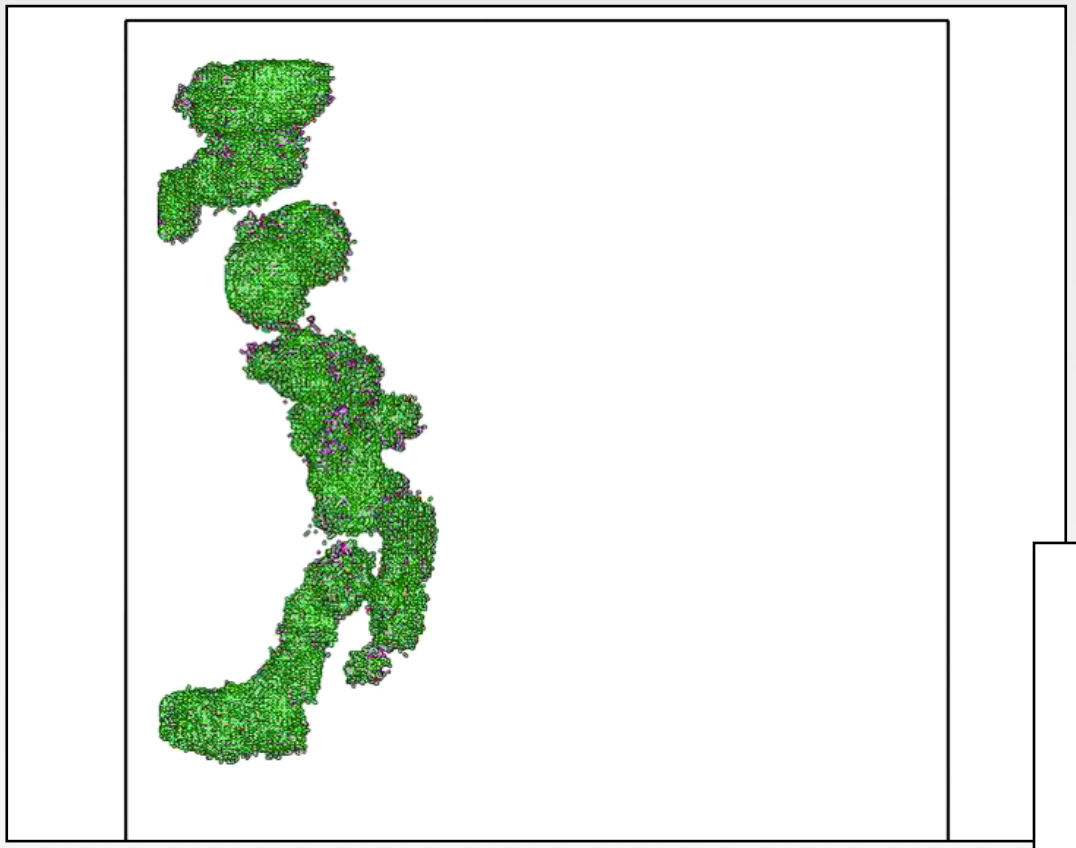
$$N_d = \begin{cases} 0 & ; \quad 0 < E \leq E_d \\ 1 & ; \quad E_d < E \leq 2\,E_d \\ \dfrac{0.8\;\xi(E)}{2\,E_d} & ; \quad E > 2\,E_d \end{cases}$$

ζ(E) fraction of E partitioned to displacement damage events

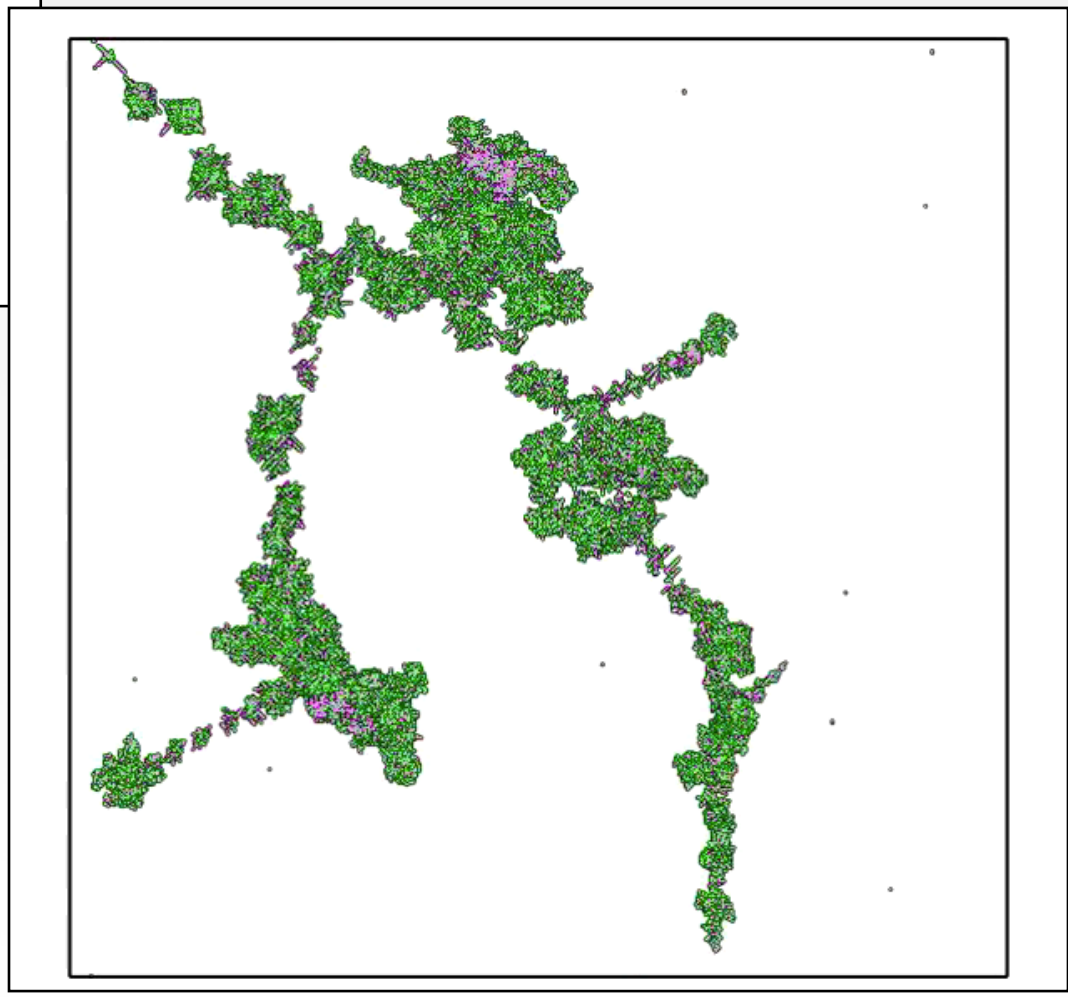
Method used in the ASTM standard for neutron irradiation of steels (ASTM - E693)

CAUTION: this model does not take into account recovery, structure or efficiency of neutron interaction


ASTM E693-12
Displacement Cross Section (10^{-28} m^2)
10^4
10^3
10^2
10^1
1
10^{-1}
10^{-2}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1
10^1
Neutron Energy (MeV)



Courtesy:
Kostya Trachenko Queen Marry University



UNIVERSITY OF LIVERPOOL

How Is Damage Defined?

Standard method is to use **‘displacements per atom’ - dpa**

‘number of times each atom has moved averaged per atom in the system’

1 dpa means that on average each atom in the system has moved once.

In some systems a value of 0.3 - 0.6 is enough for amorphisation in others 100 is not enough for amorphisation

Method for calculation different for neutron damage, recoil damage, and particle damage

Which type of solids can we apply this formalism ?

The above concepts does not take into consideration the translation and rotational symmetry in materials

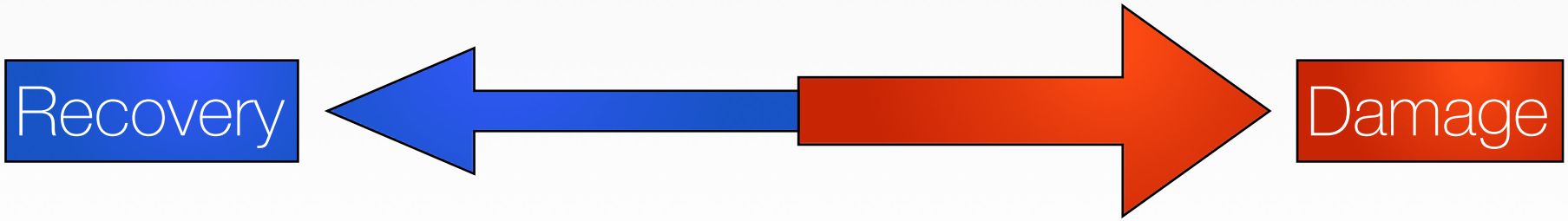
Damage vs Recovery

For **every** damage cascade - multiple recovery profiles

- Annihilation
- Migration
- Defect formation

Two types of recovery process

- **Thermally** activated
- **Displacement** enhanced



It is interesting that the process of making one point defect in a solid actually makes two point defects!

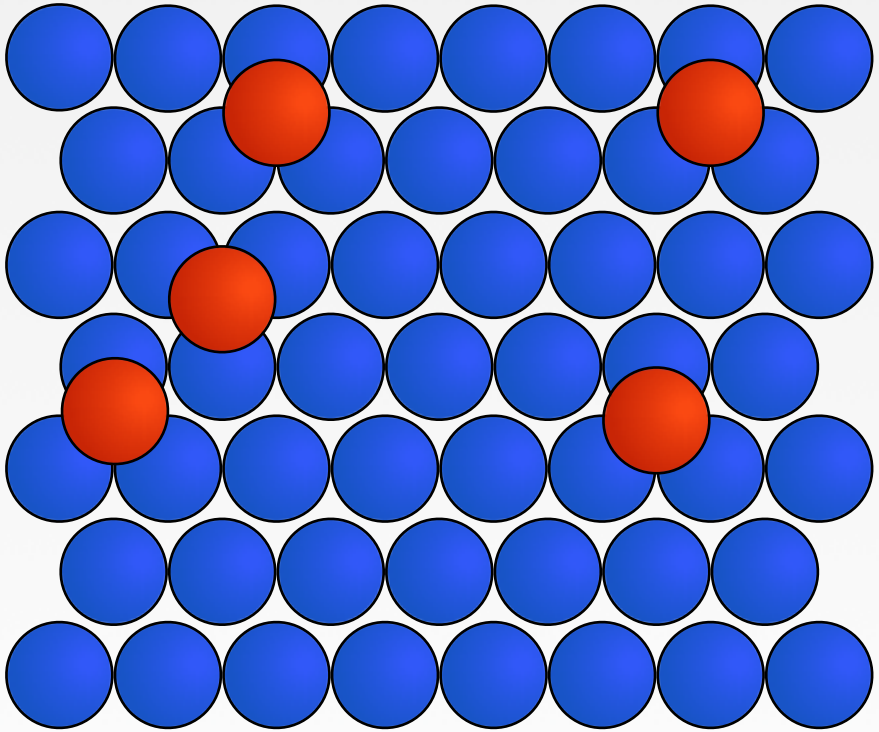
The process of producing a point defect begins with knocking one atom off of its lattice site into an interstice in the lattice. This produces an interstitial (i) atom.

However, at the same time, a vacancy (v) is produced, because the knock-on atom leaves behind an empty lattice site.

In some instances, the energy of the projectile ion that initiates the knock-on event is sufficiently low that it comes to rest following its knock-on collision. It then spontaneously fills the vacated site and only one net defect is produced (the interstitial). This is known as a replacement collision.

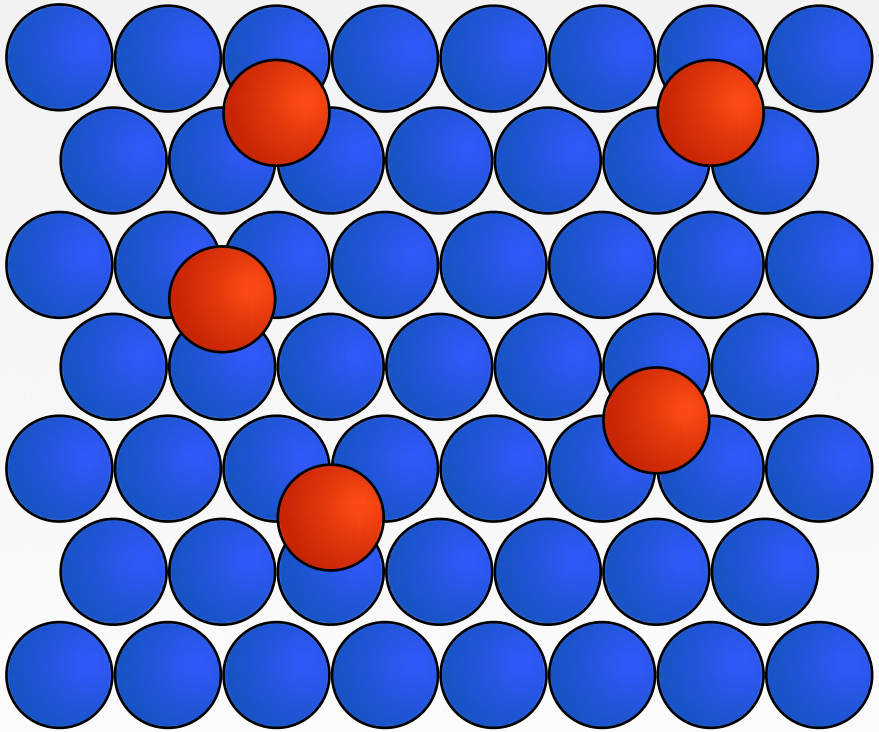
Annihilation

Interstitials migrate to vacancies - zero sum



Defect Loop - Interstitial

Interstitial atoms migrate to form stacking fault which can migrate



Fate of Irradiation-Induced Interstitials (Chemical Rate Theory)

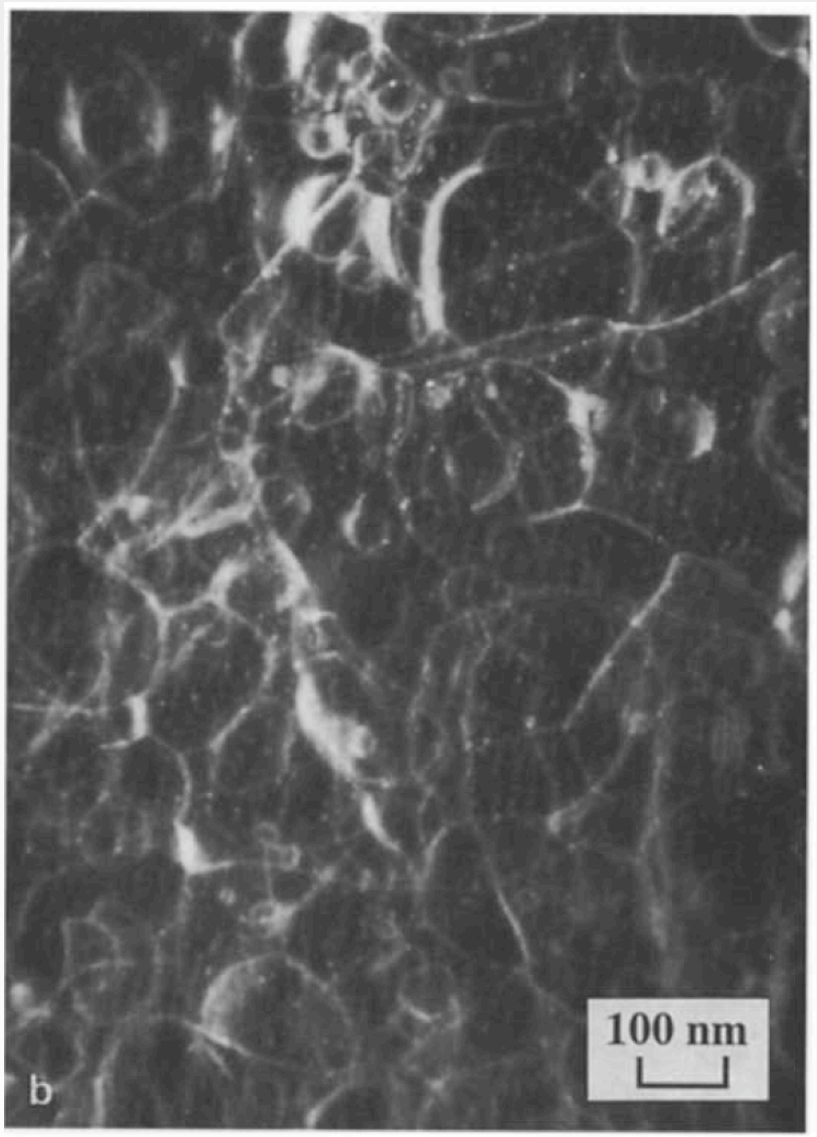
$$\frac{dC_i}{dt} = P_i \quad \left(A_A \longrightarrow A_i + V_A\right)$$ *Frenkel pair* production rate

$$- R_{i-v} \quad \left(A_i + V_A \longrightarrow A_A\right)$$ } *i-v* recombination rate — Harmless

$$- N \quad (\text{nucleation rate for interstitial loops})$$
$$- G \quad (\text{growth rate for interstitial loops})$$
} BAD!

Intersecting unfaulted dislocation loops and dislocation network arising in single-crystal Al_2O_3 irradiated to $3x10^{25}$ n/m^2 (3 dpa) at 1015 K

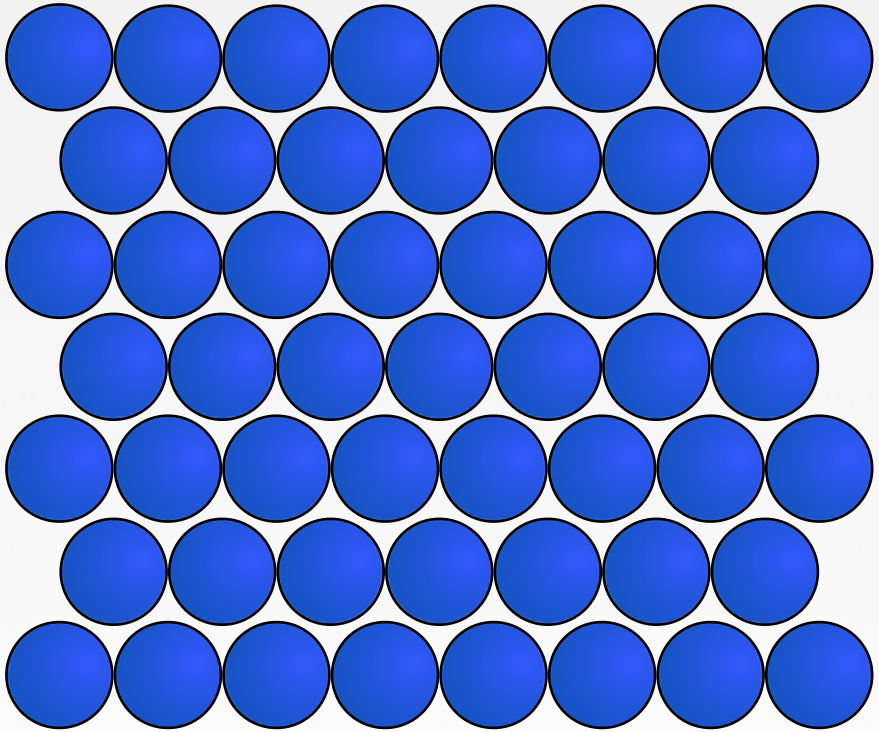
Alumina (α-Al_2O_3)



Micrograph courtesy of Frank Clinard, Los Alamos National Laboratory

Defect Loop - Vacancy

Vacancies migrate to form stacking fault which can migrate



Fate of Irradiation-Induced Vacancies (Chemical Rate Theory)

$$\frac{dC_v}{dt} = P_v \qquad \left(A_A \longrightarrow A_i + V_A\right)$$ *Frenkel pair* production rate

$$-R_{i-v} \qquad \left(A_i + V_A \longrightarrow A_A\right)$$ } *i-v* recombination rate

Harmless

The concentration of vacancies is not diminished by the nucleation (*N*) and growth (*G*) of interstitial loops

The Net Result ??
An irradiation-induced *Vacancy Bias*

The concentration of vacancies begins to exceed (eventually greatly) the concentration of freely-migrating interstitials:

$$C_v \text{ (very low dose)} \simeq C_i \text{ (very low dose)}$$

$$C_v \text{ (low dose)} > C_i \text{ (low dose)}$$

$$C_v \text{ (high dose)} >> C_i \text{ (high dose)}$$

As irradiation proceeds, interstitials are gobbled up by the nucleation & growth of extended defects (i-loops), leaving behind un-paired vacancies (v) in the lattice.

The concentration of these v point defects increases until eventually, the concentration is so large, that these v defects condense to form voids.

Fate of Irradiation-Induced Vacancies at high dose (or moderate dose at high temperature)

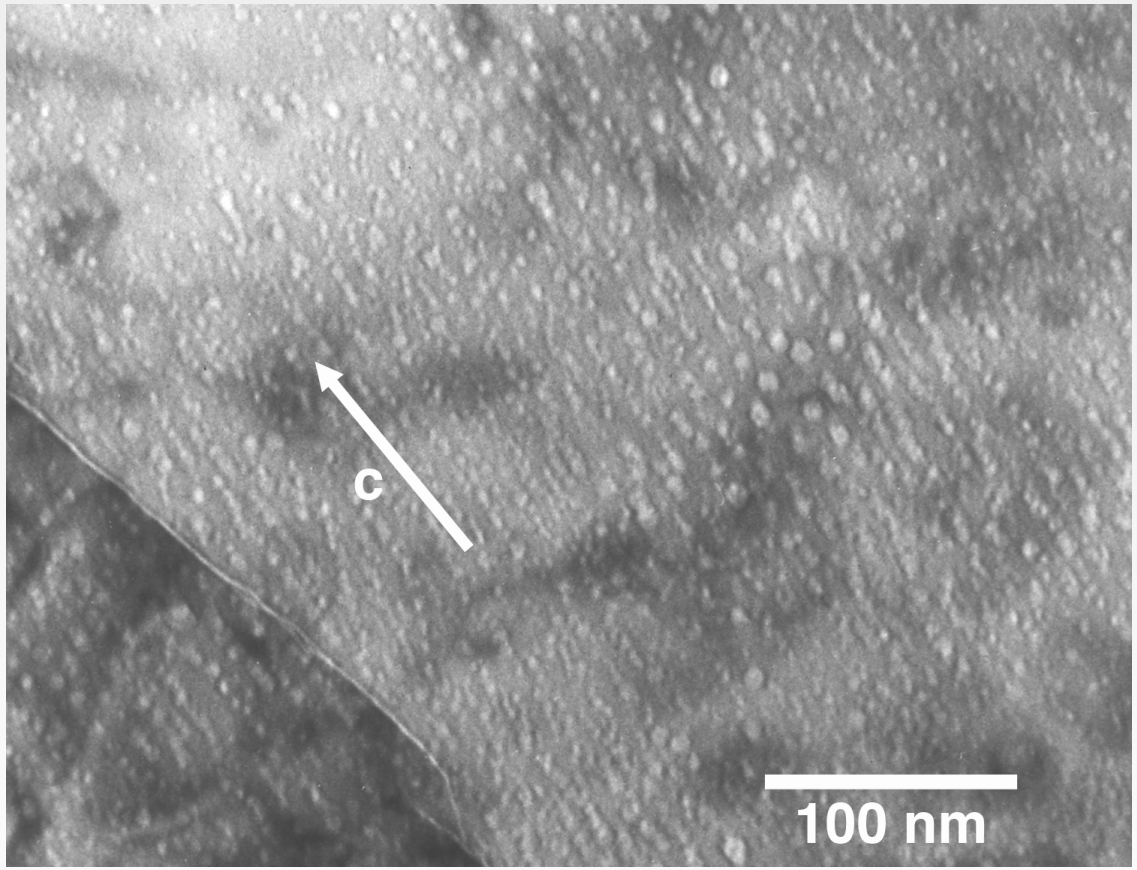
$$\frac{dC_v}{dt} = P_v \quad \left(A_A \longrightarrow A_i + V_A\right)$$ *Frenkel pair* production rate

$$- R_{i-v} \quad \left(A_i + V_A \longrightarrow A_A\right)$$ } *i-v* recombination rate — Harmless

$$- N^* \quad (\text{nucleation rate for voids (or vacancy loops)})$$
$$- G^* \quad (\text{growth rate for voids (or vacancy loops)})$$
} BAD!

Void nucleation and growth causes swelling, micro-cracking and ultimately, catastrophic mechanical failure of the material

High density of small voids (2-10 nm diameter), arranged in rows along the c-axis of the hexagonal unit cell for the α-Al_2O_3 in single-crystal Al_2O_3 irradiated to $3x10^{25}$ n/m^2 (3 dpa) at 1015 K



Micrograph courtesy of Frank Clinard, Los Alamos National Laboratory

Key to Enhancing Radiation Tolerance

$$\frac{dC_i}{dt} = P_i \quad \left(A_A \longrightarrow A_i + V_A\right)$$ *Frenkel pair* production rate

$$- R_{i-v} \quad \left(A_i + V_A \longrightarrow A_A\right)$$ } *i-v* recombination rate — Harmless

$$- N \quad (\text{nucleation rate for interstitial loops})$$
$$- G \quad (\text{growth rate for interstitial loops})$$
} BAD!

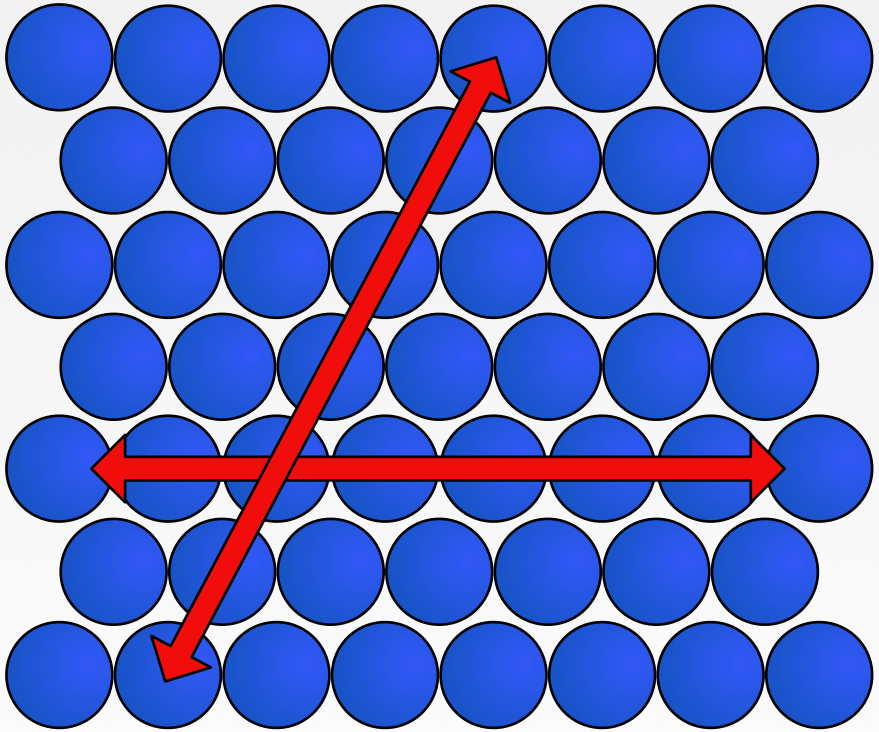
1. **Enhance harmless *i-v* recombination.**
2. **Suppress harmful nucleation and growth of interstitial loops.**

In other words, avoid the *vacancy bias*

How Do Defects Migrate?

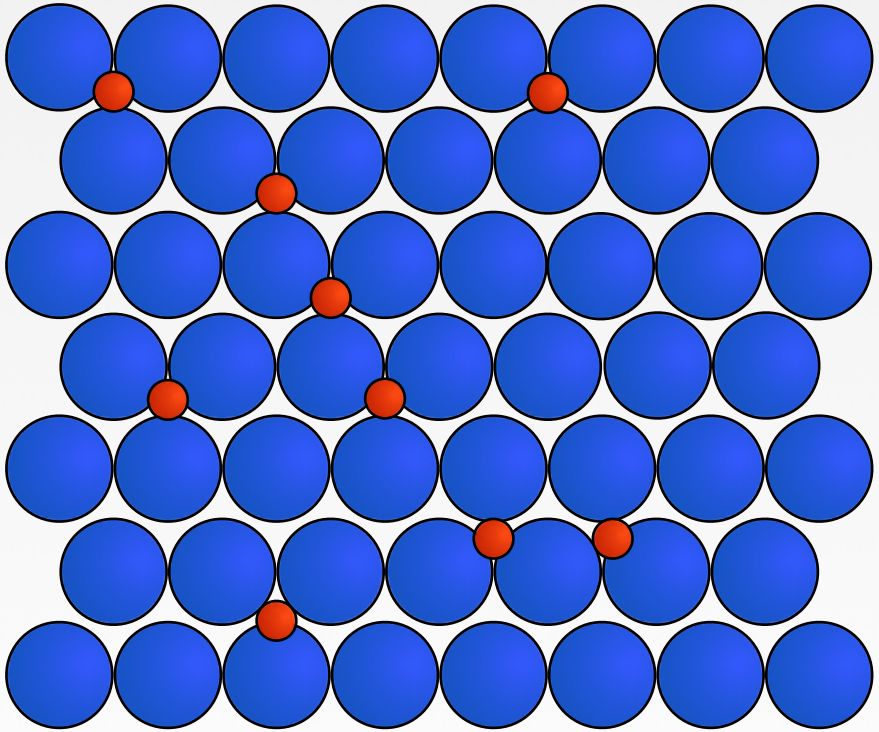
Loops generally migrate along Buerger's vectors within lattice

Lower energy requirement for migration



Gas Bubble Formation

Interstitial gas atoms (arising from fission/fusion) migrate/ nucleate forming bubbles



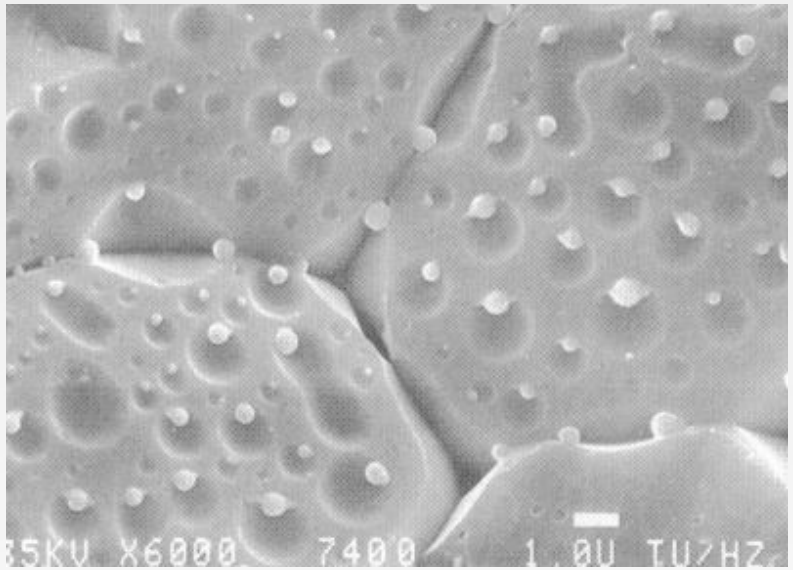
Where Do Gas Bubbles Form?

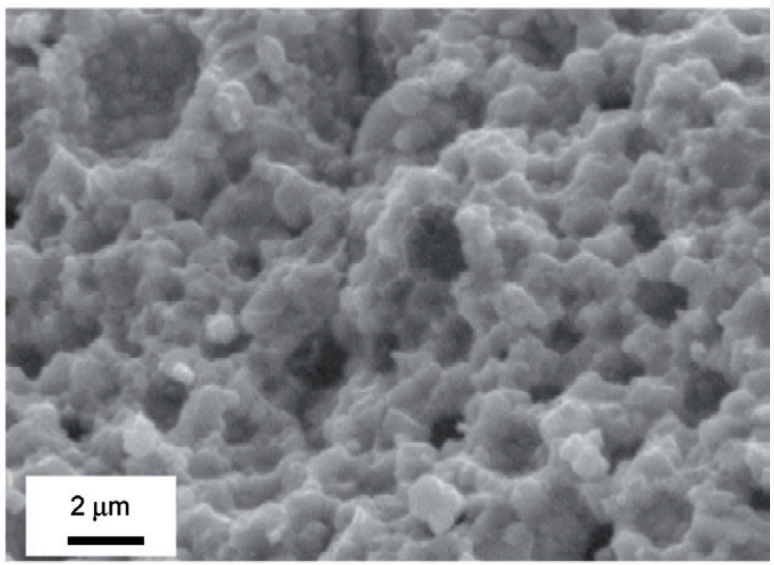
Grain boundaries

Around metallic particles

Regions in stress/strain

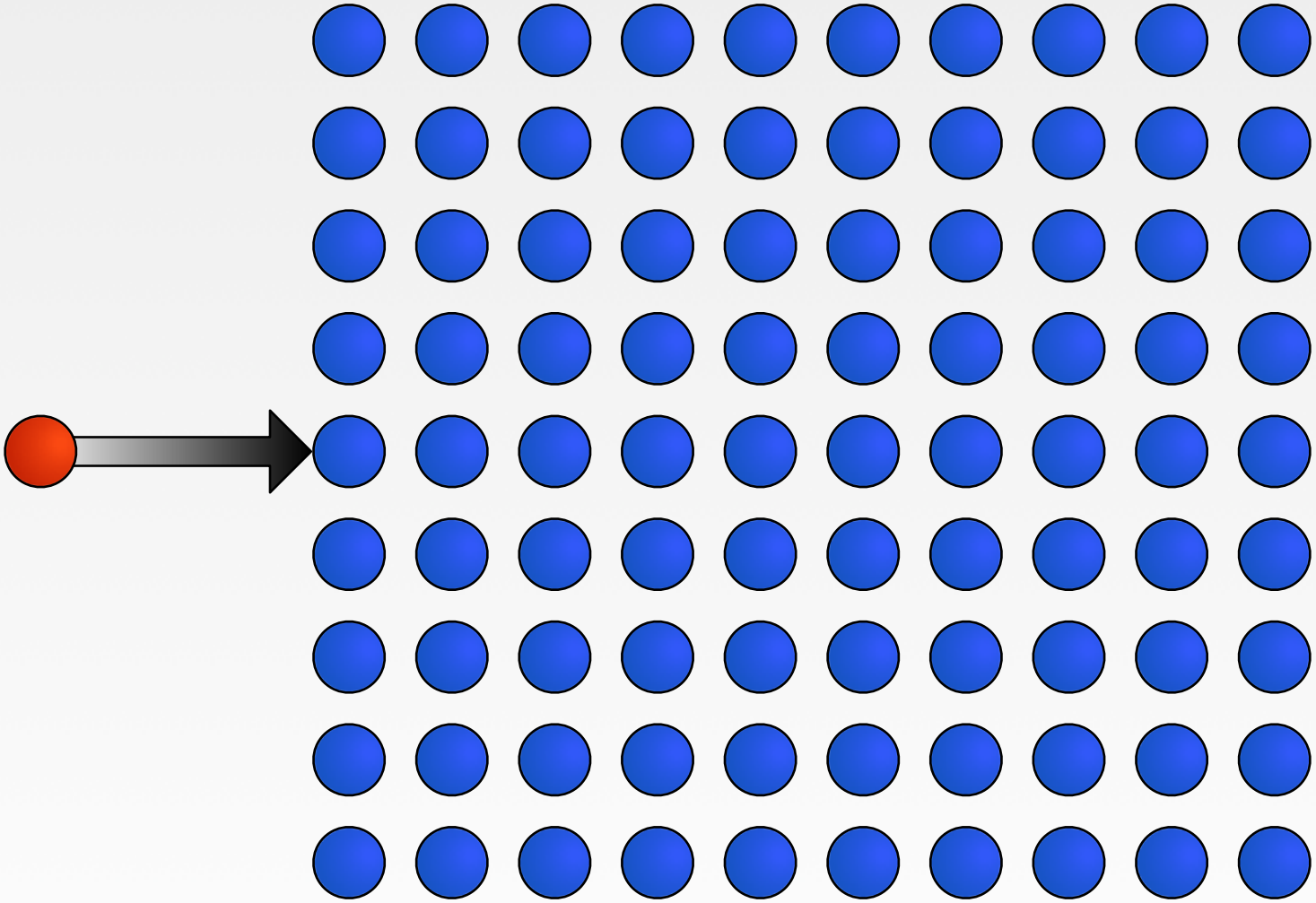
Nicoll JNM 1997



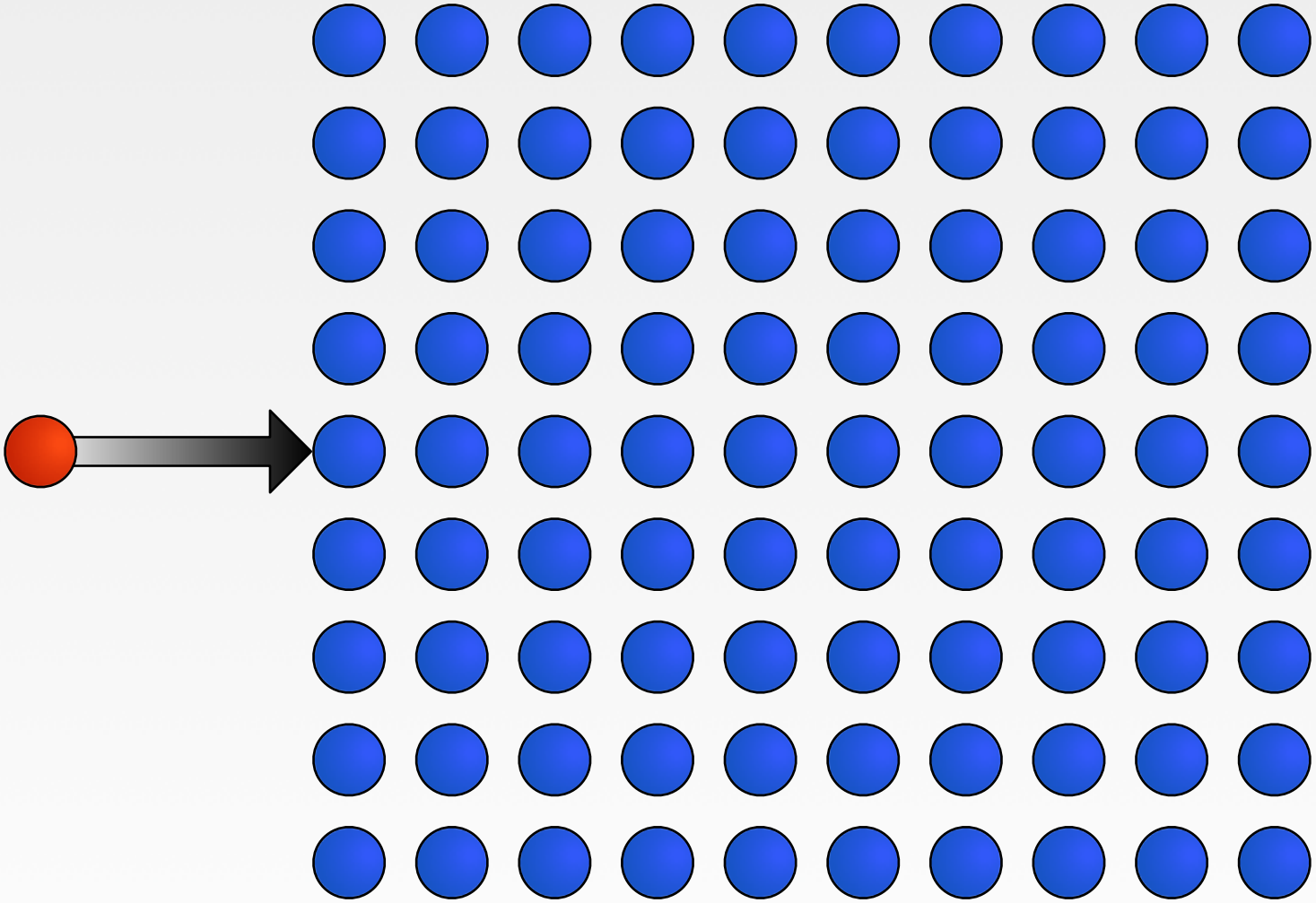


Materials Today 13(12) 24 (2010)

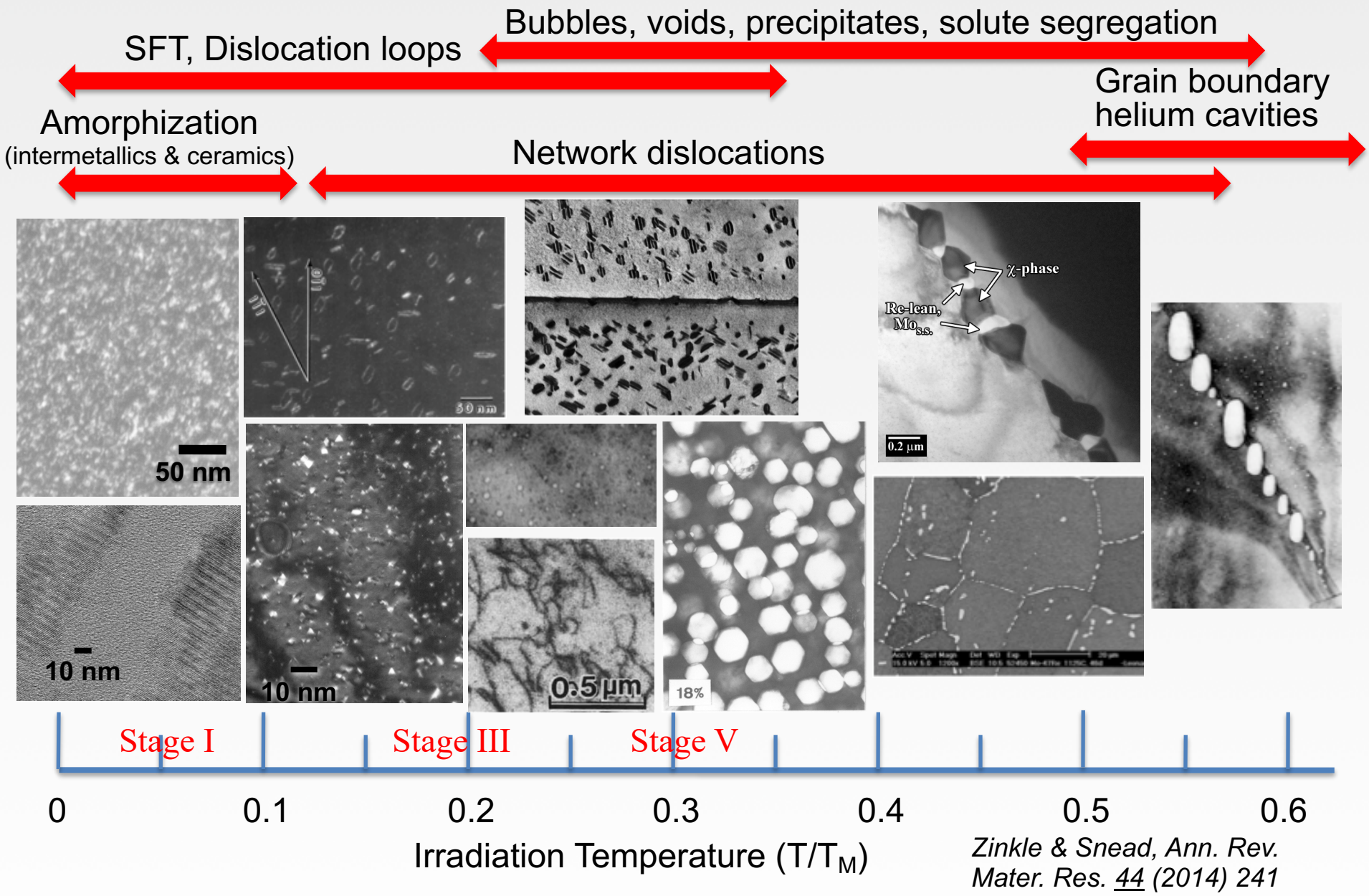
‘Pure’ Cascade



‘Real’ Cascade

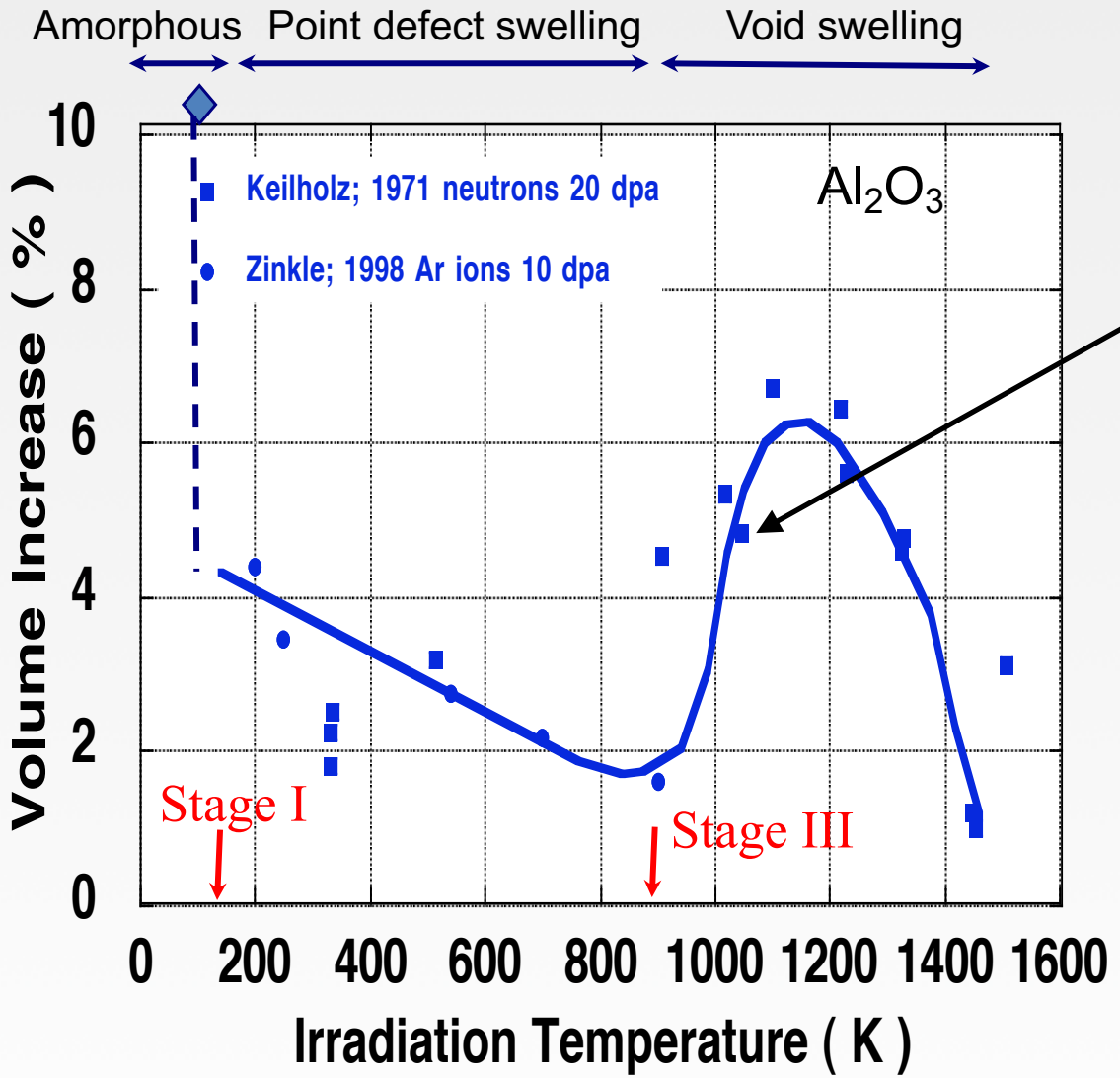


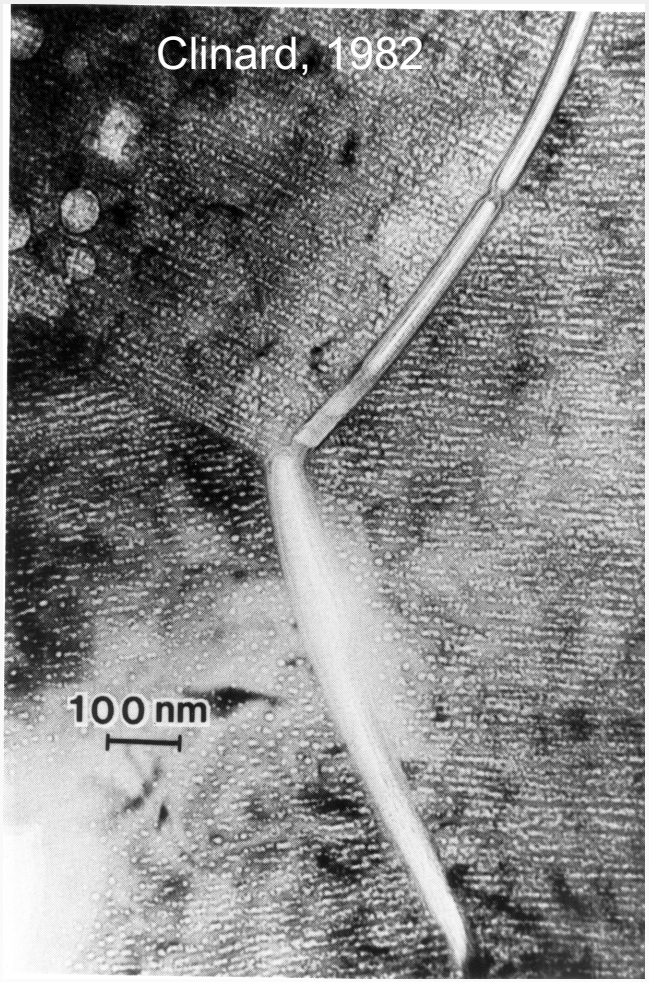
Nucleation and growth of extended defects in ceramics



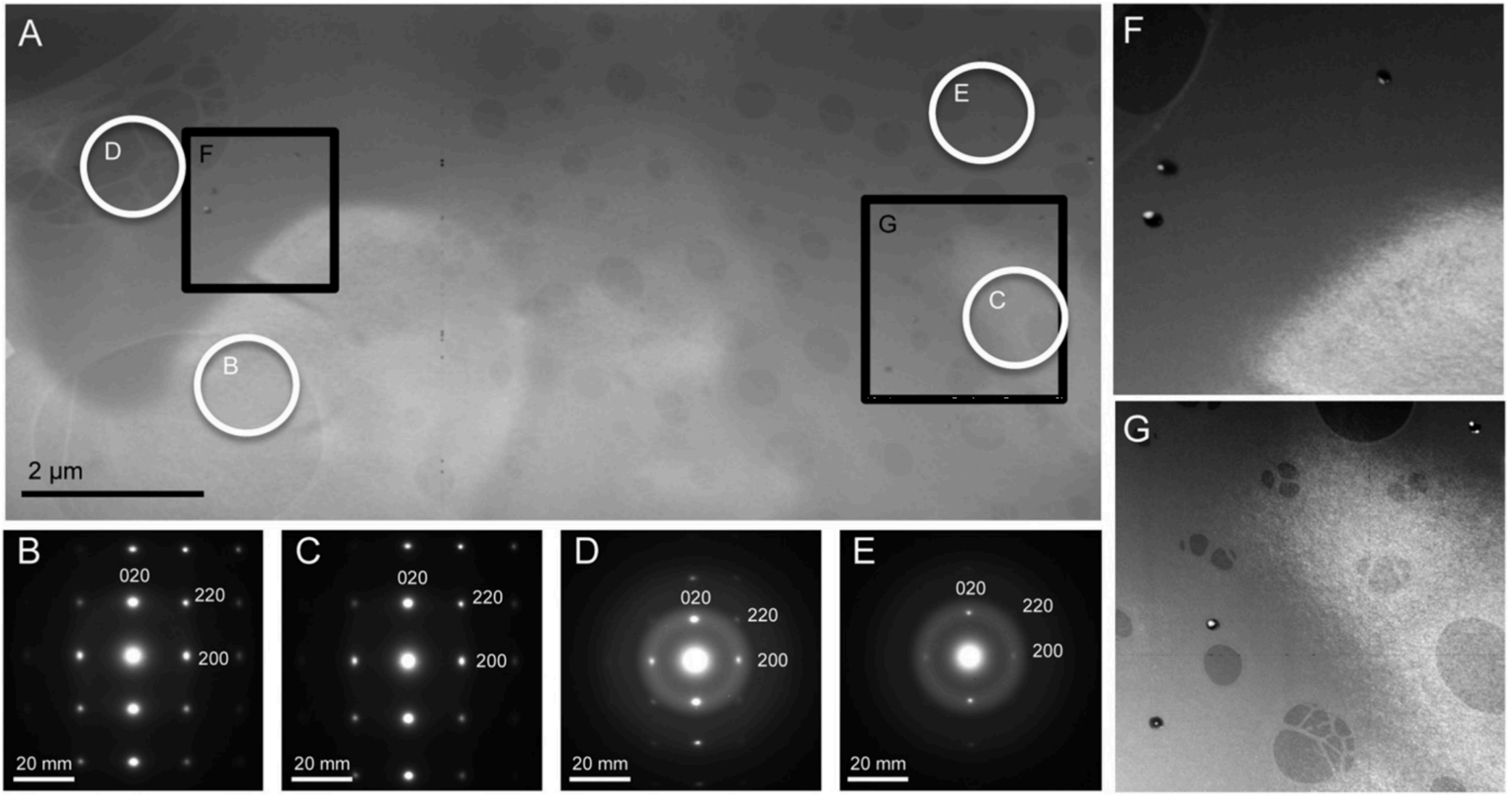
Zinkle & Snead, Ann. Rev. Mater. Res. 44 (2014) 241

Three distinct swelling regimes are observed in irradiated Al_2O_3





Radiation Induced Amorphization in Ceramics



Defining disorder from a periodic arrangement of atoms to an aperiodic arrangement of atoms

Topology: Distance & angles have no importance but shapes, relative positions & arrangements do

Network topology in translating radiation effects from ordered to disordered systems

Linn W. Hobbs

Journal of Non-Crystalline Solids 192 & 193 (1995) 79
Journal of Non-Crystalline Solids 182 (1995) 27
Nuclear Instruments and Methods in Physics Research B 91 (1994) 30

Topological connectivity approaches are usefully applied in making assessments of glass-forming ability and in providing a local description of network structure

The structural freedom required to form aperiodic networks is directly related to connectivity, and the range of allowable structural possibilities can be enumerated using combinatorial geometry

A.R. Cooper, Phys. Chem. Glasses 19 (1978) 60; J. Non-Cryst. Solids 49 (1982) 1

J.C. Phillips, J. Non-Cryst. Solids 34 (1979) 153; 43 (1981) 37; 44 (1981) 17; Phys. Today 35 (1982) 27; Solid State
Phys. 37 (1982) 93; in: The Structure of Non-Crystalline Materials, ed. P.H. Gaskell, J.M. Parker and E.A. Davis (Society of Glass Technology, New York, 1982) p. 123.

P.K. Gupta and A.R. Cooper, J. Non-Cryst. Solids 123 (1990) 14.

Radiation Induced Amorphization in Crystalline Silica

α-Quartz

Cristobalite

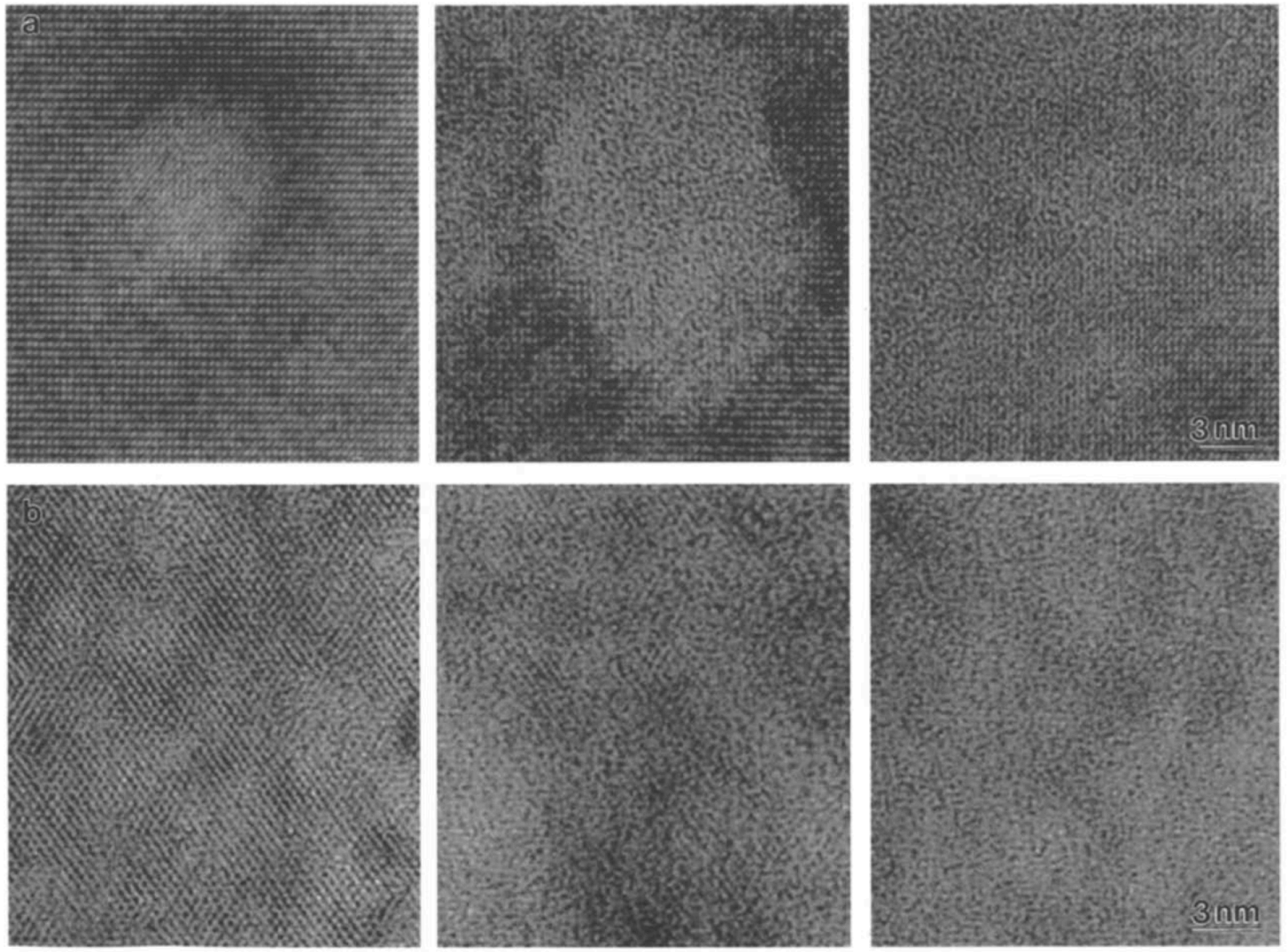


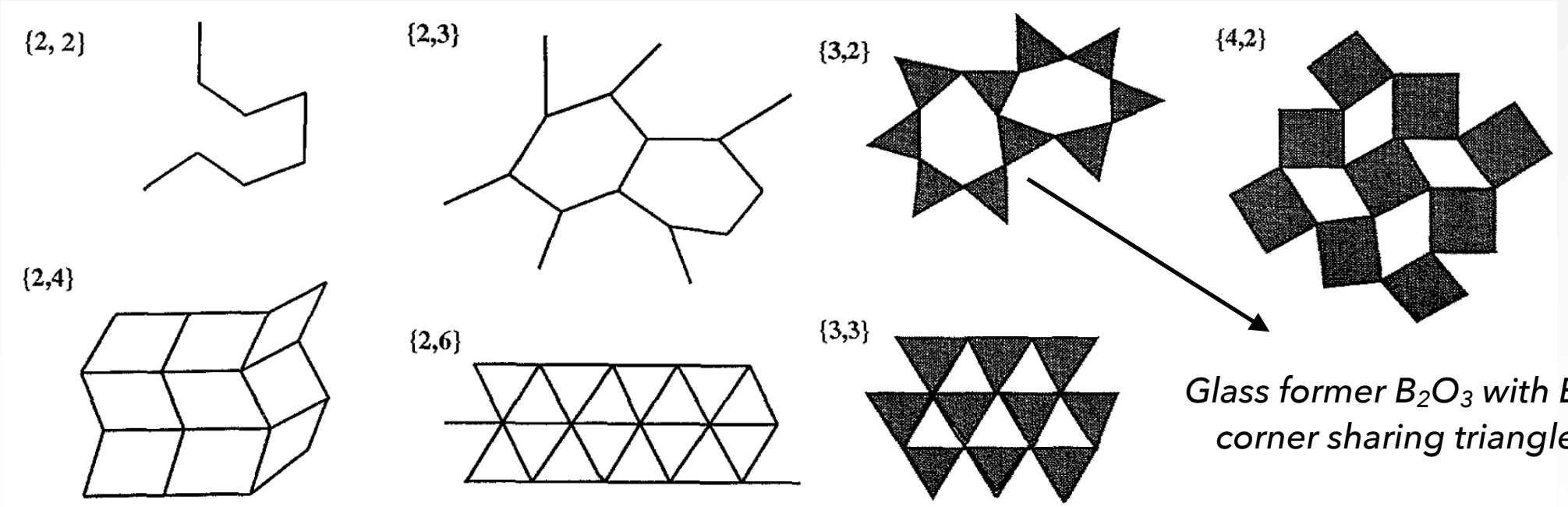
Fig. 8. Sequences of high-resolution transmission electron microscope images of (a) α-quartz and (b) α-cristobalite undergoing progressive amorphization in a 200-kV electron beam. Quartz nucleates strained inclusions which expand; cristobalite (like tridymite, which behaves similarly) proceeds more uniformly to the metamict state. Cristobalite is the most easily amorphized of the three polymorphs.

Definitions in network topology

Rigid identical structural units, called polytopes, share their V vertices with each other

Their connectivity C is defined by the average number polytopes common to a vertex

The structural connectivity is represented by {V,C}



Two- & three-dimensional networks constructed using identical one-dimensional rod polytopes

Definitions in network topology

$$f = d - h = d - C\left[\delta - \{\delta(\delta + 1)/2V\}\right]$$

d = degree of structural freedom at each vertex
(equal to the number of degrees of freedom)

h = number of constraints
(imposed by neighbouring structures)

δ = dimensionality of the structuring polytope itself number of constraints

Example: an arrangement of identical rods (δ = 1) in two dimensions (d = 2) sharing each vertex with one other rod is represented {2, 2} itself number of constraints. This results in one remaining degree of freedom (f = 1) per vertex

Zachariasen's *Random Network* Hypothesis for Glasses

The atoms in a glass must (as in crystals) form extended three-dimensional networks.

For example, in SiO_2 the only difference between glass and crystalline forms is that in vitreous silica, the relative orientations of the adjacent $(SiO_4)^{4-}$ tetrahedra is variable, whereas in each of the crystalline polymorphs of SiO_2, these orientations are constant throughout the structure.

Relation between f & amorphisation

Coordination, connectivity, structural freedom and amorphizability for some common structures

Structure	Polyhedra : sharing	{V,C}	f	Amorphization dose (eV/atom) [a]
MgO	Octahedra : edges	{6, 6}	−10	> 5000 [43]
α-Al_2O_3	Octahedra : faces, edges	{6, 4}	−6.25	> 3400 [43]
TiO_2	Octahedra : edges, corners	{6, 3}	−4	[b]
c.p. metal	Rods : ends	{2, 12}	< −3	[b]
SiC	Tetrahedra : corners	{4, 4}	−3	44 [50]
Si_3N_4	Tetrahedra : corners	{4, 3}	−1.5	> 700 [48]
$CaTiO_3$	~ Octahedra : corners	{6, 2}	< −1	66 [39]
ReO_3	Octahedra : corners	{6, 2}	−1	[b]
SiC	*Tetrahedra : corners*	*{4, 2}*	*< 0*	*44* [50]
$ZrSiO_4$	Dodecahedra : edges; tetrahedra : edges		$-3 < f < -1$	36 [34]
$CaSiO_3$	Octahedra : edges; tetrahedra : corners		$-1.33 < f < 0$	11 [34]
Si	*Tetrahedra : corners*	*{4, 2}*	*0*	*11* [49]
$AlPO_4$	Tetrahedra : corners	{4, 2}	0	10 [38]
SiO_2	Tetrahedra : corners	{4, 2}	0	7 [34]
$Pb_2P_2O_7$	~ Tetrahedra : corners	{4, 1.75}	< +0.4	< 0.5 [37]
P_2O_5	Tetrahedra : corners	{4, 1.75}	+0.38	[b]
Si	Rods : ends	{2, 4}	< +1	11 [49]
B_2O_3	Triangles : corners	{3, 2}	+1	[b]