Primary damage in ceramics : complexity and inapplicability of the NRTdpa

Jean-Paul Crocombette

CEA Saclay, DEN-SRMP, France

Molecular Dynamics simulations of cascades

Talk centered on the diversity of **materials** response to ballistic cascades
No neutrons
Nothing on cross sections etc…

$$K = \int \phi(E)\sigma_d(E)dE \qquad \chi(E,T) = \sigma(E)\int \frac{1}{\partial T/\partial \mu} f(\mu,E,E')dE'$$

What is the nature of the primary damage in various ceramics ?
Tool molecular dynamics (MD) :

- A "large box" (~10-50nm) with atoms in it
- Complex interatomic interactions ➔ structure, elastic Cst., thermal properties,etc.
- Newtonian mechanics, for *all* atoms
- Thermalization (regular atomic vibrations)
- initial impulsion of a given energy for *one* atom (PKA) in the box
- movie of the subsequent atomic movements of all atoms

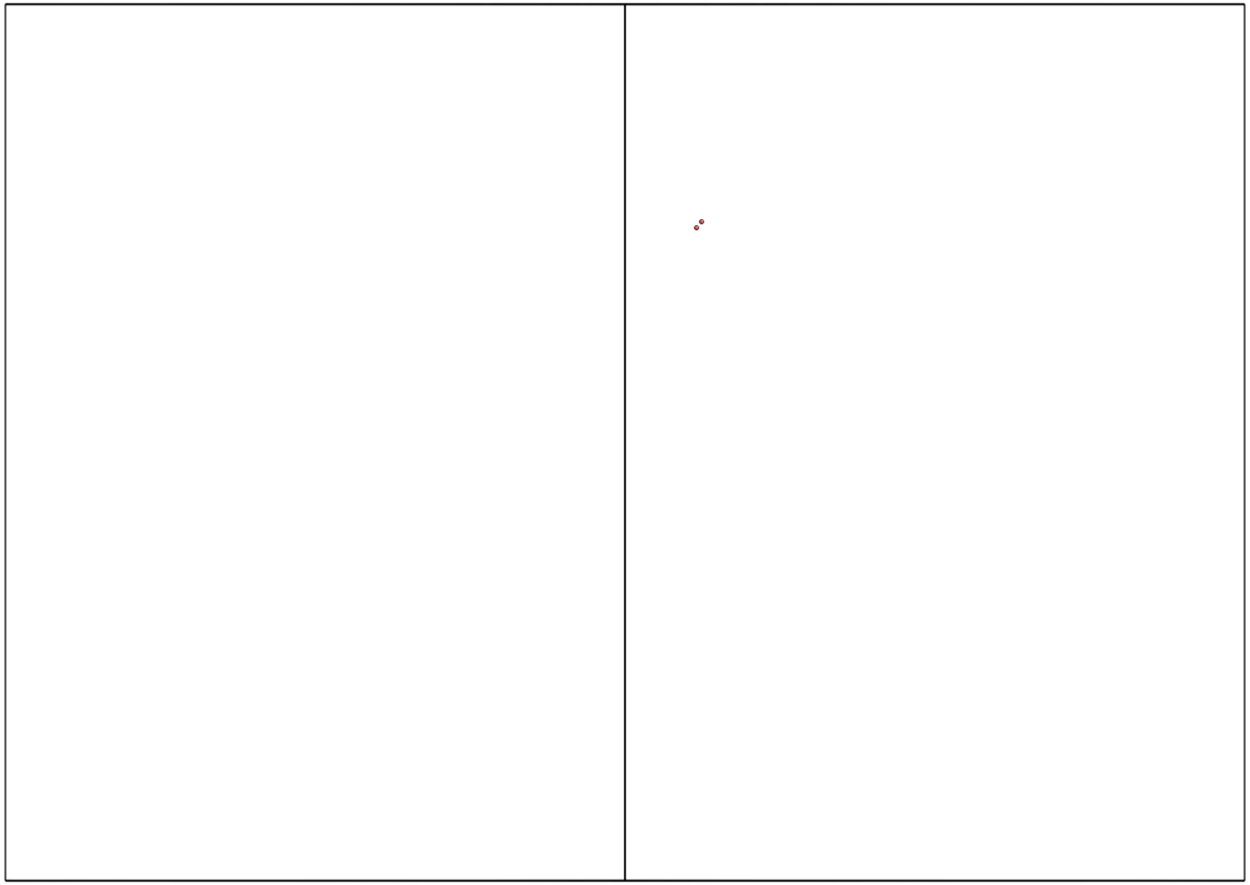
Purely ballistic losses, no electronic effects (very questionable in insulators, but …)

More information than BCA : ballistic and thermal phases, detailled atomic structure
Much heavier than BCA, limitation on energies (usual 20-80keV ; world record 400keV),
much less statistics (~100 cascades at most)

example of MD simulations of cascades

Example ZrC PKA =Zr E=80keV

Movie of the displaced atoms



Ballistic phase

Thermal phase

Massive recristallization
Dynamics of cooling

final structure very different
from end of ballistic phase

Focus on the final structure

MD results in various ceramics

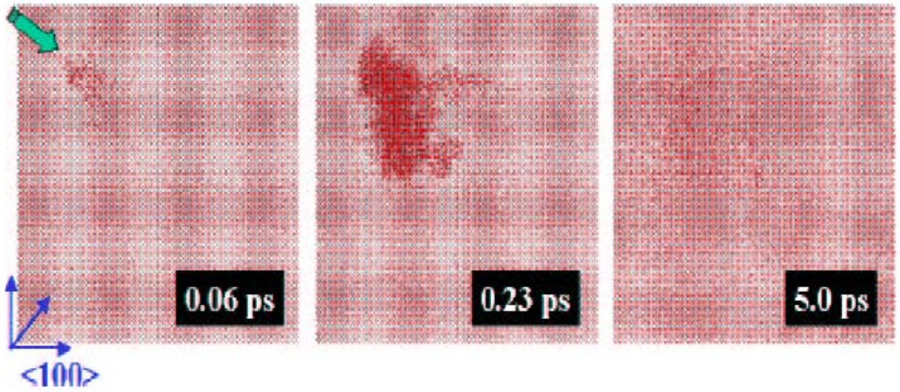
UO_2
Zircon
zirconolite
SiC

} problems with NRT norm
problems with dpa concept

Suggestions

Cascades in UO_2 : point defects

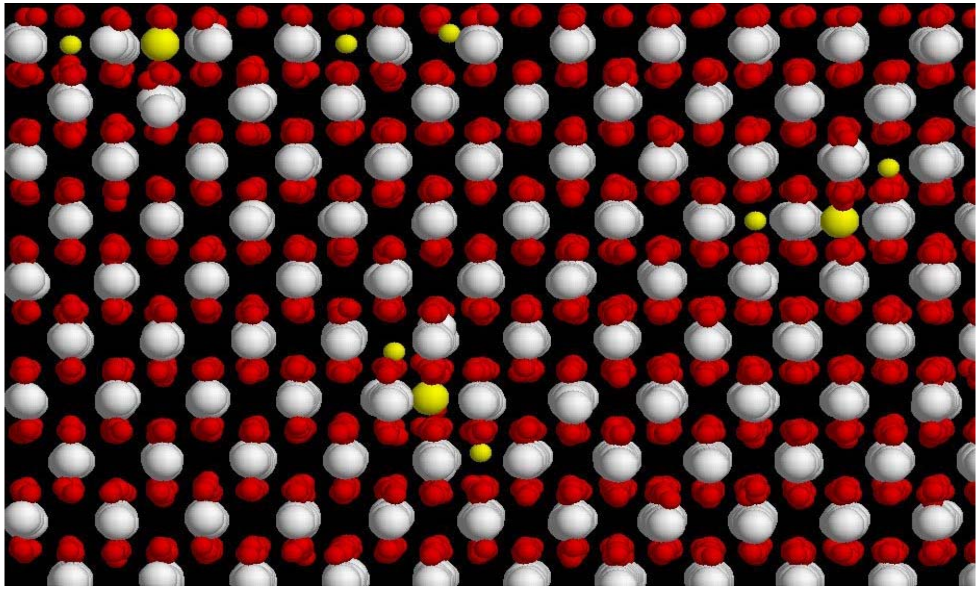
Snapshots of a 20keV U-PKA



Point defects : interstitials, vacancies

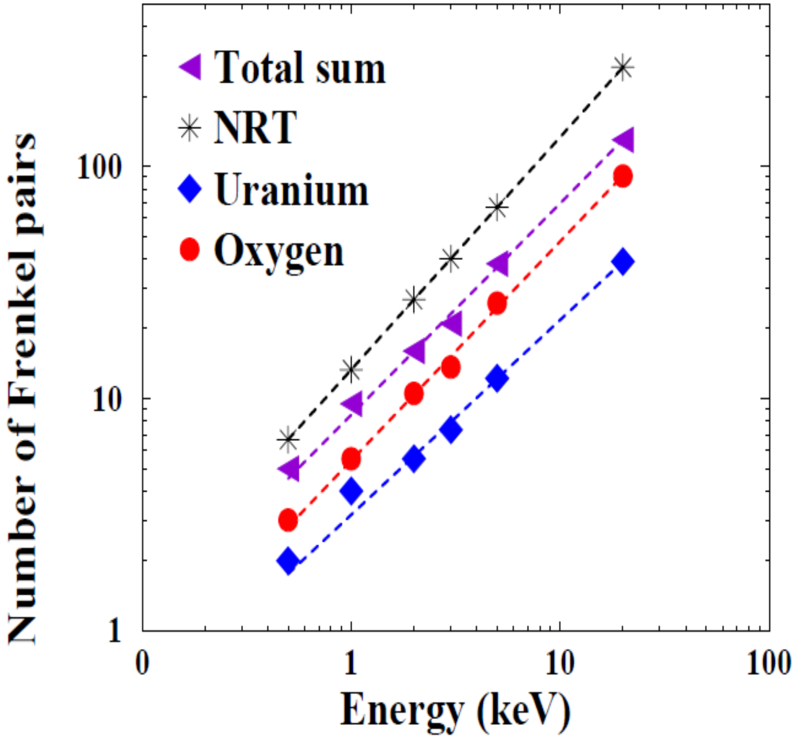
L. Van Brutzel, *et al.*, Philos. Mag. **83**, 4083 (2003)

Final structure after a 5keV U-PKA



U O int.

Cascades in UO_2 : applicability of the NRT law



$$N_{Uranium}\ \text{Frenkel pair} = 5.39\ E^{0.94}$$
$$N_{Oxygen}\ \text{Frenkel pair} = 3.15\ E^{0.84}$$
$$N_{Total}\ \text{Frenkel pair} = 8.51\ E^{0.91}$$

Usual problems of NRT law
Defect production efficiency

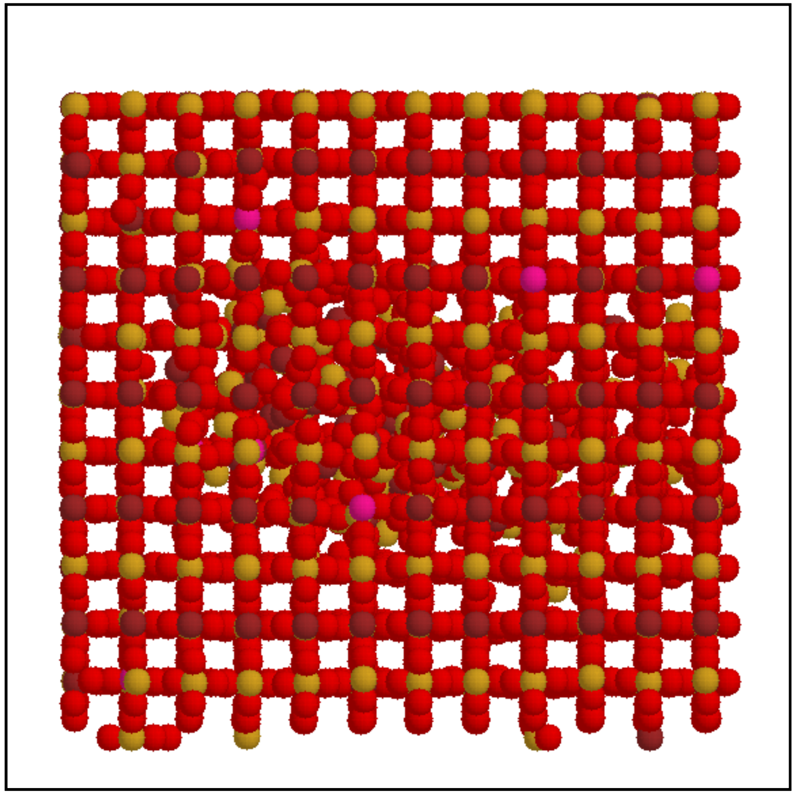
Log-log plots of the number of Frenkel pairs versus the initial PKA energy.

Cascades in zircon : direct impact amorphization

Zircon : $ZrSiO_4$, contemplated oxyde material for actinide waste storage

Known to amorphize : loss of crystalline order under irradiation (DRX, HRTEM)

Final structure after U 5keV



Si Zr O U

Amorphous track

So-called Direct impact amorphization

what is a dpa in this context ?

What is a vacancy ?

How to measure the damage ?

J.P. Crocombette et D. Ghaleb, J. Nucl. Mater. 295, 167 (2001).

Cascades in zircon : displaced atoms ?

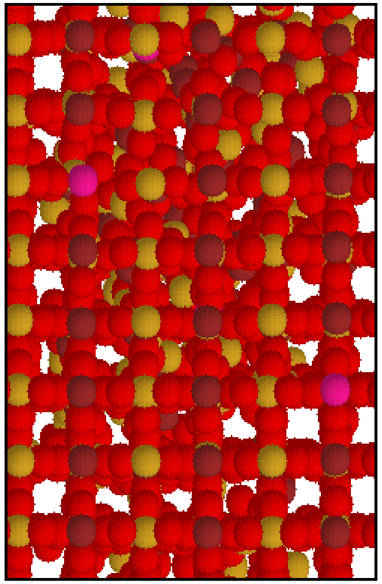
First draft of the paper : bare indication of the number of atoms displaced by more than 1Å

Referee : Too many displaced atoms in view of your Ed and NRT law

JPC : What is the NRT law ? A displacement is a displacement.

Referee : You idiot ! dpa means surviving Frenkel pairs

JPC : What do you call a Frenkel pair in this area ?

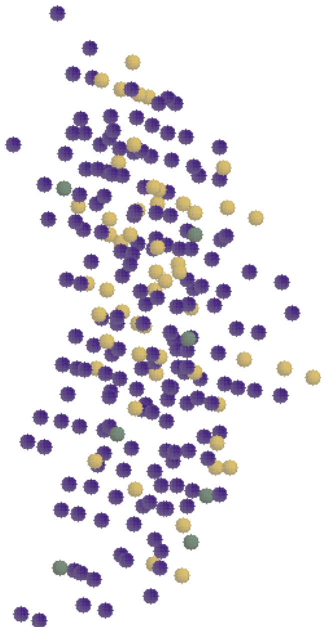


Amorphous pocket : impossible to define Frenkel pairs
~All atoms are in defective positions. As many defects as atoms…

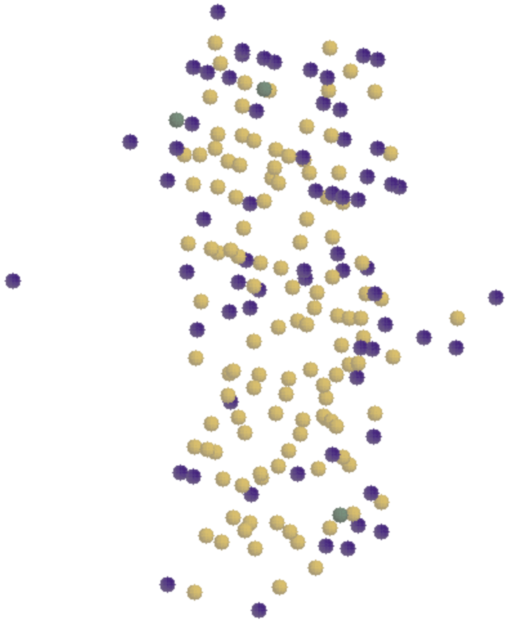
Defect production efficiency w.r. NRT is meaningless

rDisplaced atoms indicate the size of the cascade

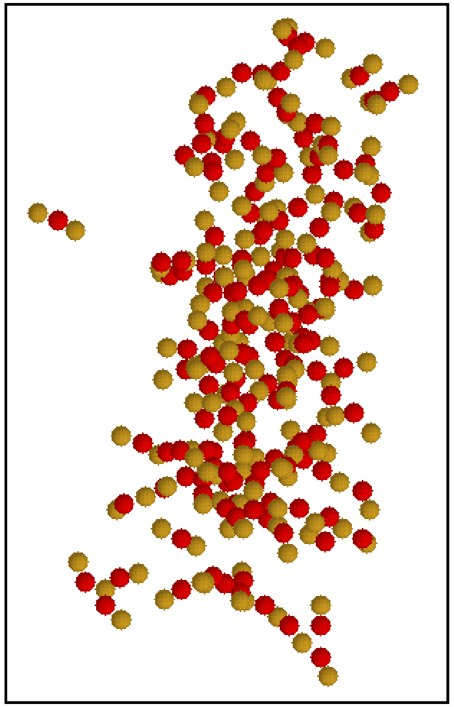
Cascades in zircon : nature of damage



Disordered cations



Distorted cations



connected SiO_4 tetrahedra

Damage is much more complex than just point defects
The existence of disordered cations and connected tetrahedra can be measured

Displaced atoms indicate the size of the cascade.
All the cascade track ends up amorphous, number of displaced atoms scales as the damage

Cascades in zirconolite : mixed damage

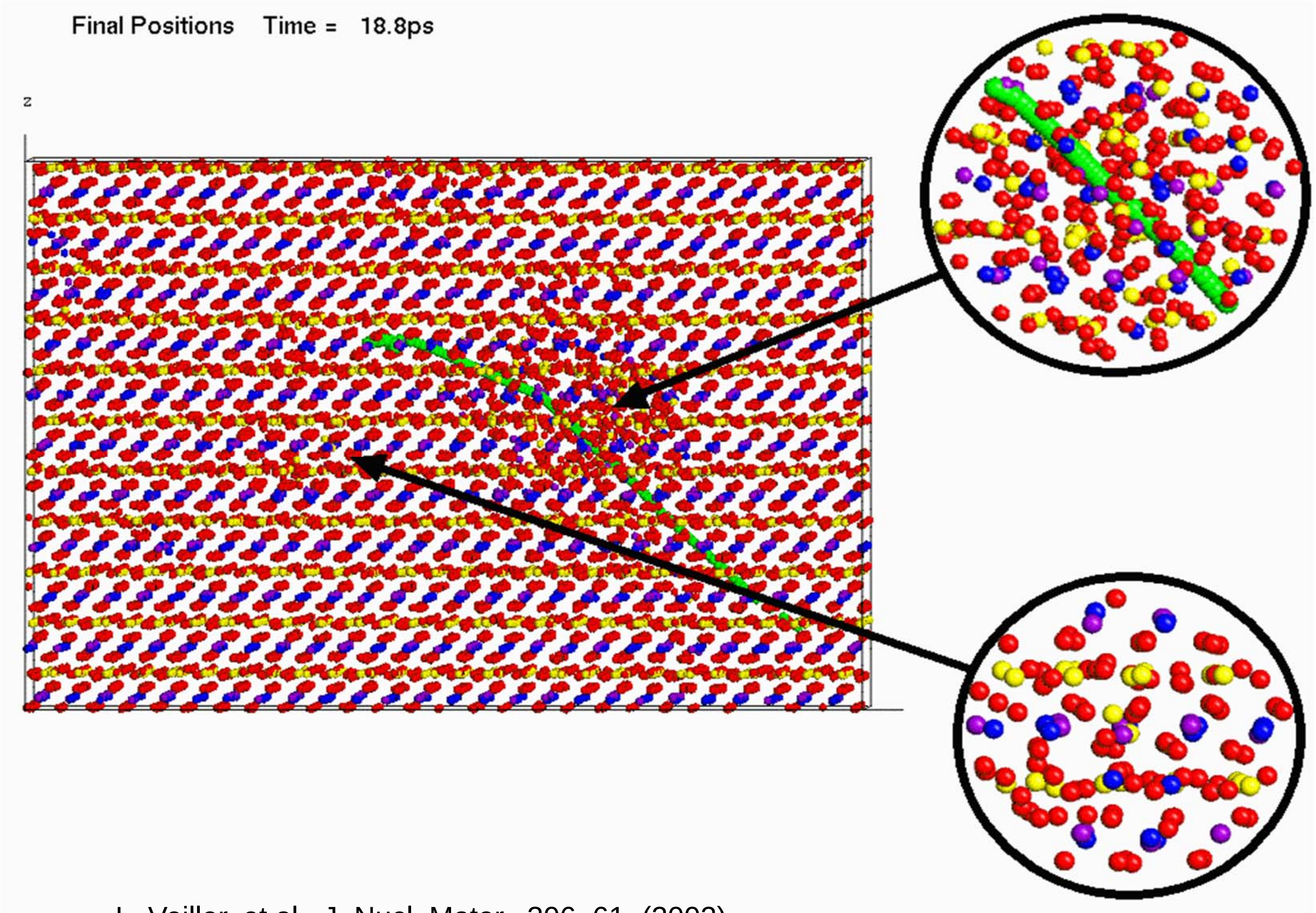
Zirconolite $CaZrTi_2O_7$; another possible waste material

Final structure after 12 keV U PKA

amorphous core

+ point defects

in periphery

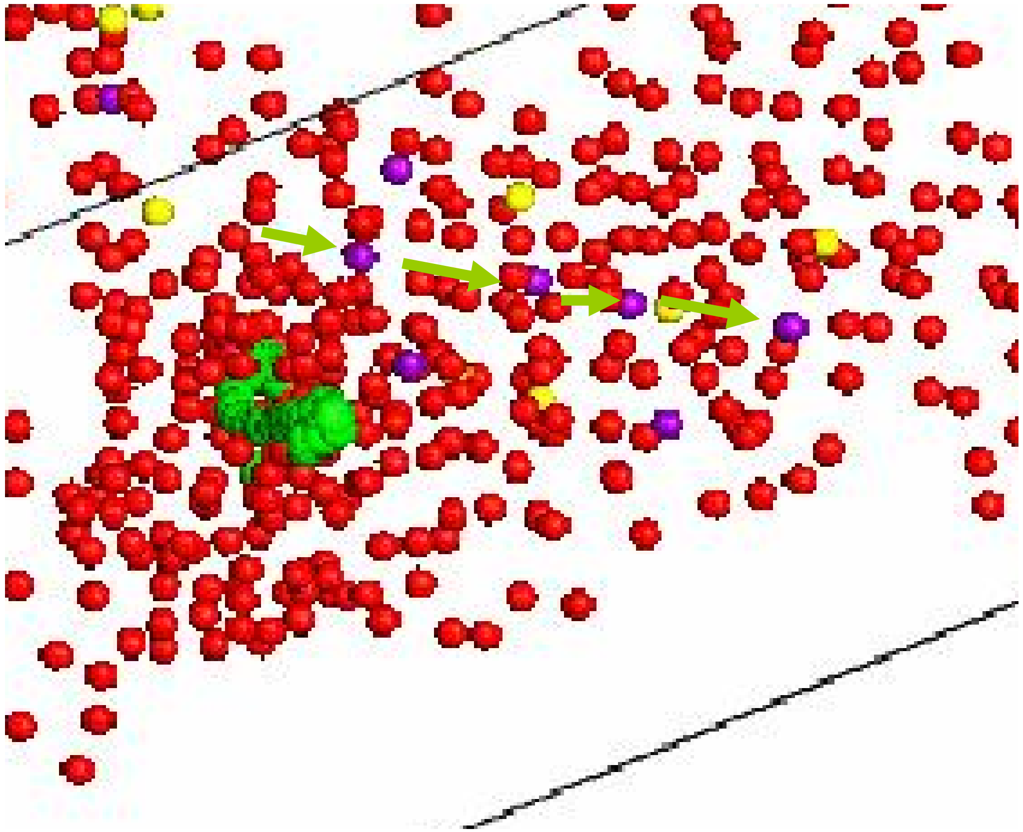


L. Veiller, et al., J. Nucl. Mater. 306, 61 (2002).

Cascades in zirconolite : mixed damage

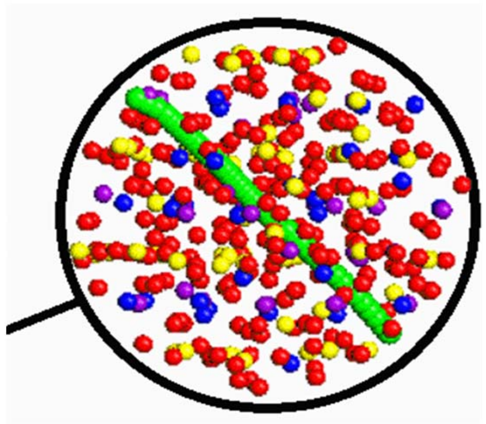
Zirconolite $CaZrTi_2O_7$ 8 keV U PKA

amorphous core
+ point defects in periphery
+ Replacement
Collision Sequences
in Ti planes
purple atoms green arrows



Cascades in zirconolite : amount of damage ?

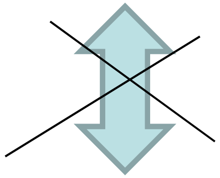
How to measure the amount of damage ?

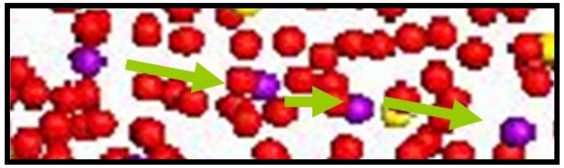


Amorphous core :

impossible to define point defects, NRT law innaplicable

Use displaced atoms (~ zircon) ?





Point defects and RCS at periphery:

Displaced atoms are irrelevant (~metals)

Surviving Frenkels pairs can be counted : NRT law can be used

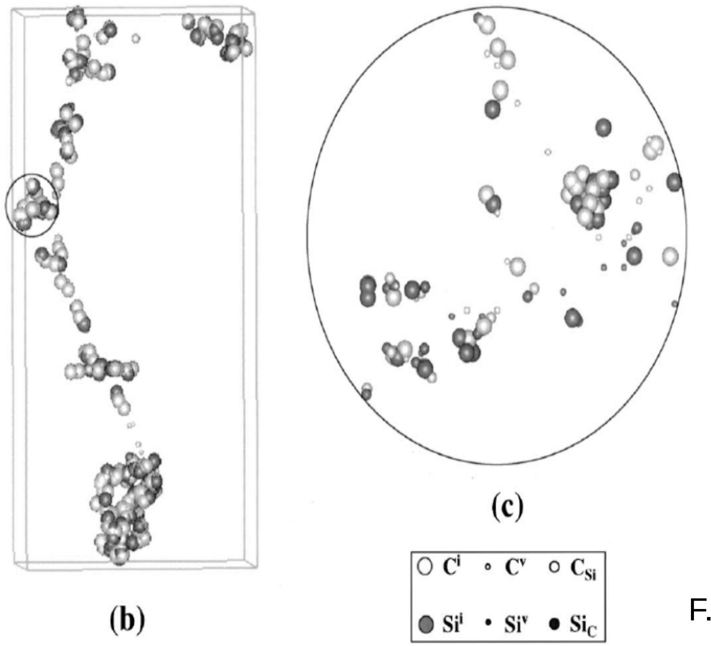
I could not find a single number to measure the amount of damage

Cascades in SiC : Nature of the PKA

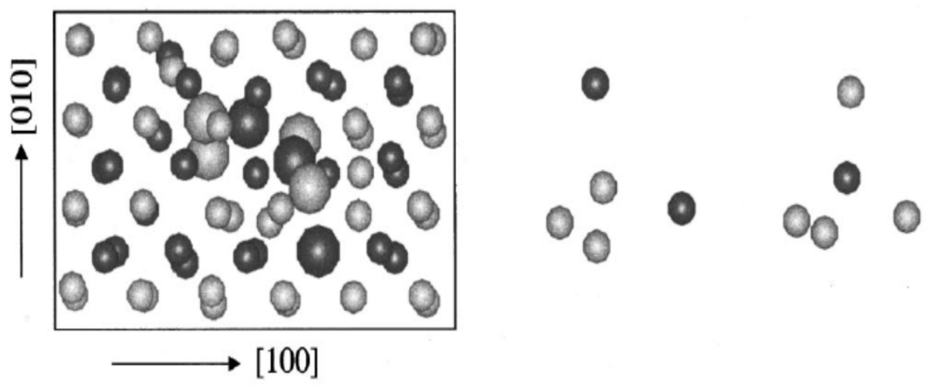
SiC coatings or structural material for GenIV or fusion freactors

Point defects and sub-nano clusters of defects

Displaced atoms after 50 keV **Si** PKA



structure of nano-clusters



F. Gao, *et al.*, Nucl. Instrum. Meth. Phys. Res. B 180, 176 (2001).

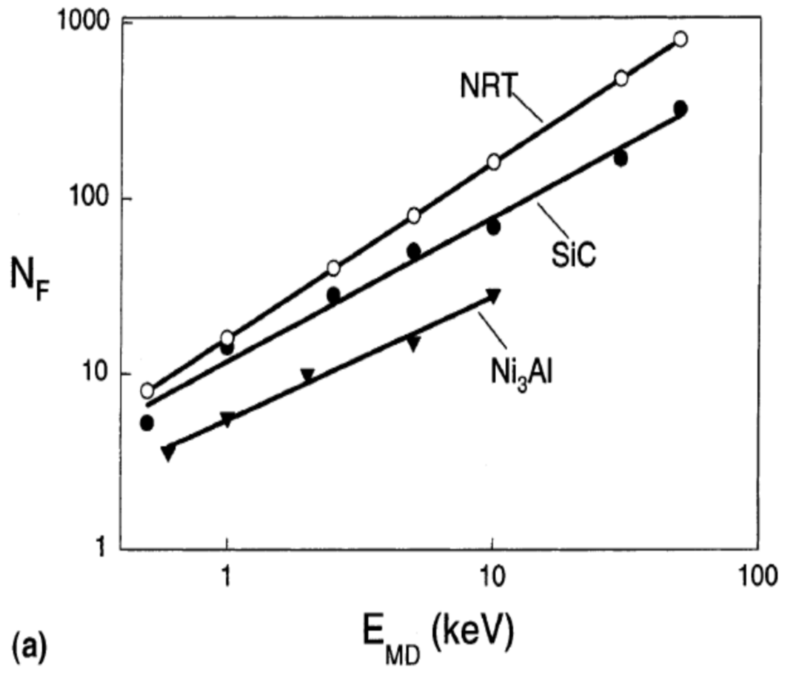
Cascades in SiC with Si PKA : NRT law ?

Cascades with Si PKA: Possible to define surviving FPs, applicability of NRT law ?

$$N_F = A*(E_{PKA})^{0.82}$$

	C	Si
N_F	243	76
N_{AS}	110	123

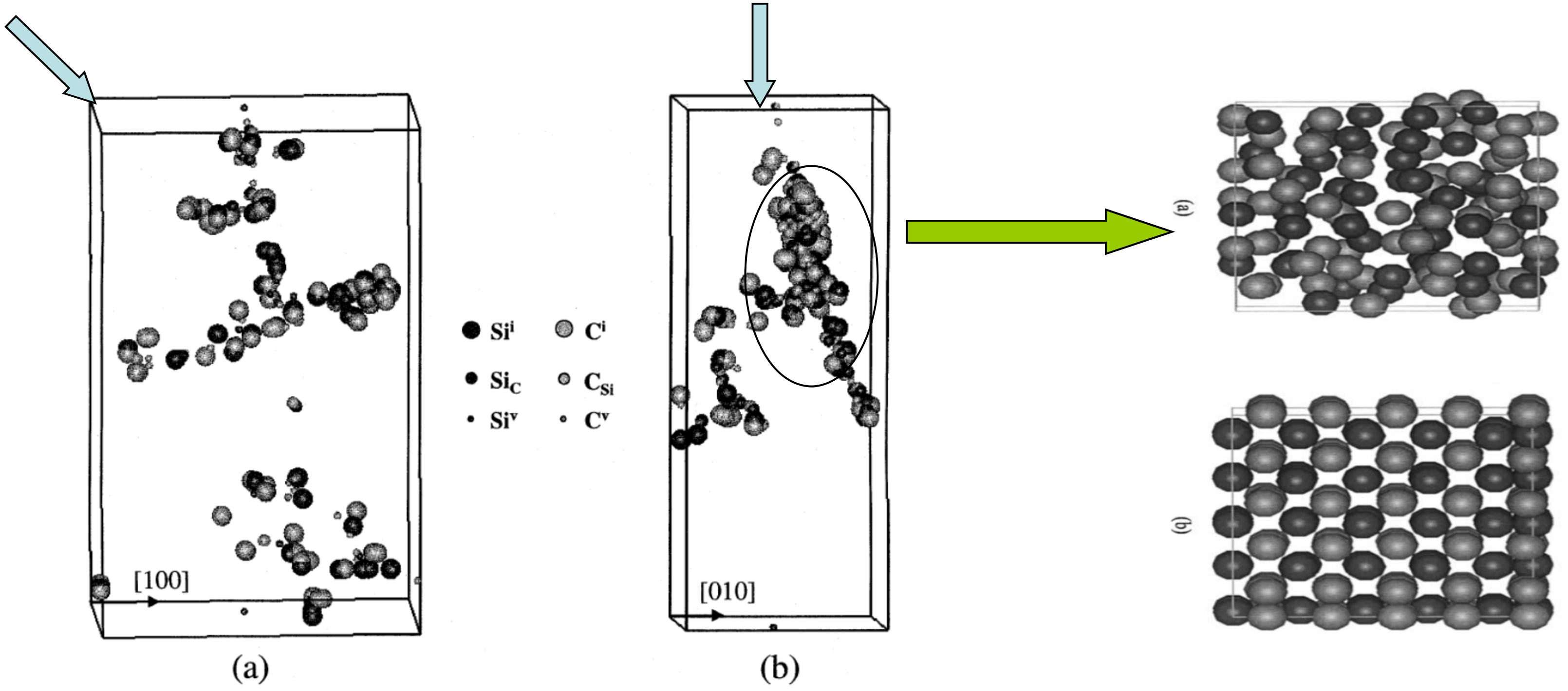
About as many antisites as FPs



Cascades in SiC : Si vs Au PKA

Cascades with **Si** or **Au** PKA : 10keV

Si: point defects and sub-nano clusters | **Au: mixed damage** some large amorphous clusters



Nature of damage depends not only on energy but on ion type

NRT law : Ndep =0.4* E_{bal}/Ed no reference to nature of PKA…

Lessons from cascades in ceramics

Some ceramics behave regularly: point defects, Frenkel pairs

➔Usual problems of NRT law

Some ceramics amorphize by direct impact

NRT dpa is irrelevant as Frenkel pairs cannot be defined

Number of displacements is relevant, measures the size of cascade/amount of damage

Some ceramics show mixed damage (amorphous AND point defects

No proper measure of the amount of damage

Nature of damage may depend on the PKA type,

It is impossible to define a measure of damage that will work for

all materials (metals, ceramics, amorphizable or not, etc..)

all irradiations (energy, mass)

What remains of the NRT dpa ?

Suggestions for the NRT dpa standard

General Suggestion

Stop trying to better describe the response of the material with ONE number.

If details are needed do a detailed study

Iconoclastic and paradoxical routes of evolution of the norm

1/**Change nothing** and move on.

We are used to use the NRT dpa, it makes some sense, weaknesses are known.

2/**Forget about the material, focus on the amount of ballistic energy**

Suggestions for the NRT dpa standard

2/Forget about the material, focus on the amount of ballistic energy

2.a Forget about $0.8/2*E_d$

Deal with "ballistic energy deposited per atom" (bEpa)

Close to the Gy but : amount of ballistic energy only ; per atom instead of per kg

Interest : does not pretend to do more than it does.

2.b Continue to speak in terms of "dpa".

Use NRT but with a fixed Ed common to all atomic types in all materials.

e.g. 20 eV➔ $N_{dep} \sim E_{ball}(eV)/50$ for al materials and atomic types

Interest : allows to keep the same orders of magnitude as before and prevents from transforming the old results

0.01dpa = not much of damage

100 dpa = a lot of damage

Should be stressed that this measure (like NRT-dpa) is just an indication of the amount of ballistic deposited energy transformed in per atom quantity by a rule of thumb

Modified dpa for metals ?

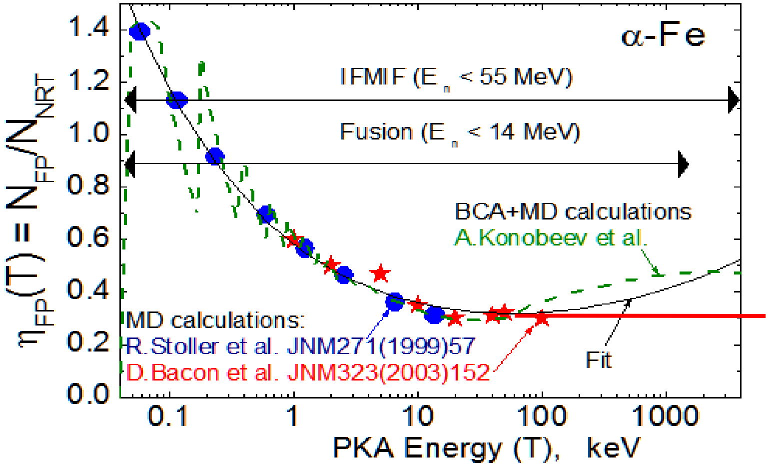
The new formula is the result of a « detailled study » $N_{dep} = a'(E)^{b+1} + c'E$

1/Is the new formula correct for all energies ?

A. Konobeev showed BCA-DM calc. In which the defect production efficiency decreases with energy then rises again. This effect is not in the new formula.

Suppose we had this meeting 20 years ago. What would have been the new formula ?

$N_{dep} = A(E)^m$?

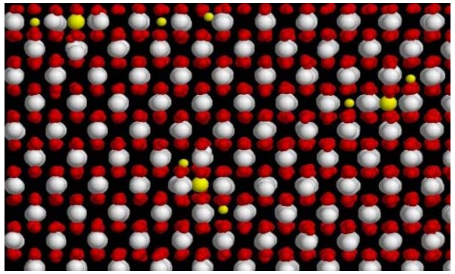


Modified dpa for metals ?

2/Will this new formula work for metalic *alloys* ?

Ordered alloys : will the mixing be as large as predicted ?

UO_2 : No antistes !



3/If a modification of NRT standard is to be put in place for metals, I suggest changing names of the quantities

Otherwise everyone will be lost. There will be three different dpa :

NRT-dpa, arc-dpa, amc-dpa.

Suggestions:

NRTdpa,

Surviving Frenkel pairs : fppa,

Mixing, replacements : rpa

Thank you for your attention !

Beyond initial state of damage

Focus of the primary state of damage

Materials response depend on much more than that !

Structural and micro-structural evolution

Temperature effects, Flux effects

Detailled informations on materials response requires devoted studies

Simulations tools must describe the **time evolution** of defects, microstructure etc..

Kinetic Monte-Carlo (atomic, object, Event)

Rate theory

DDD

.

.

Importance of temperature :example of SiC

Y. Katoh et al. / Journal of Nuclear Materials 351 (2006) 228–240

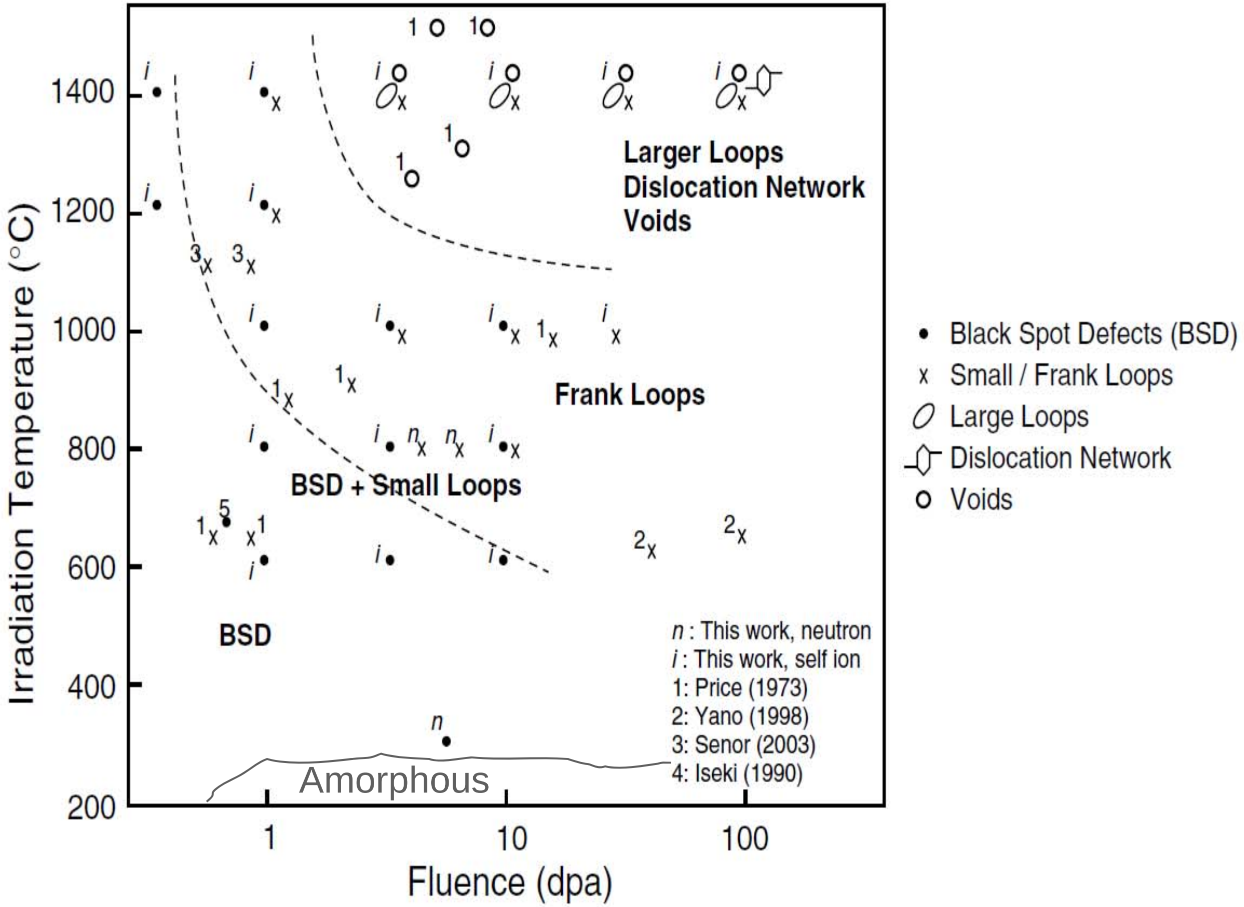
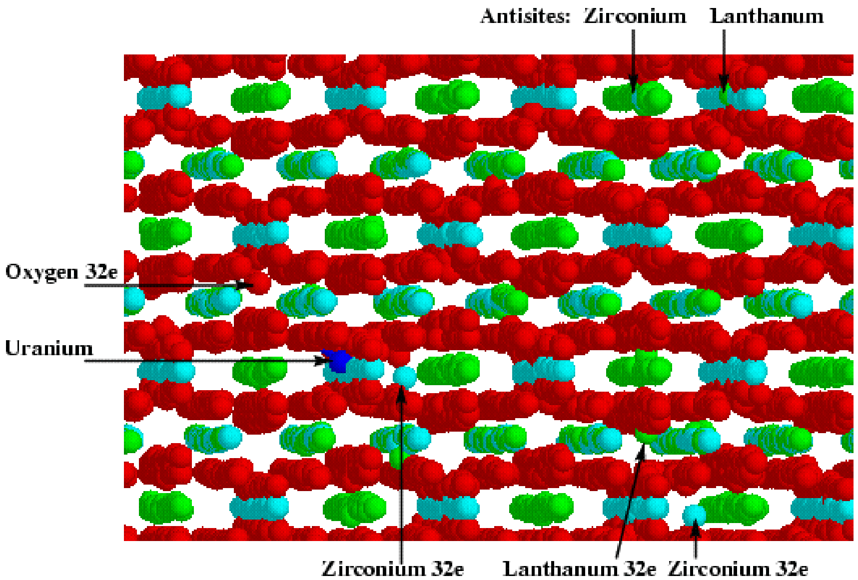


Fig. 8. Summary of the microstructural development in cubic SiC during neutron and self-ion irradiation.

- Primary state of damage : cascade simulations

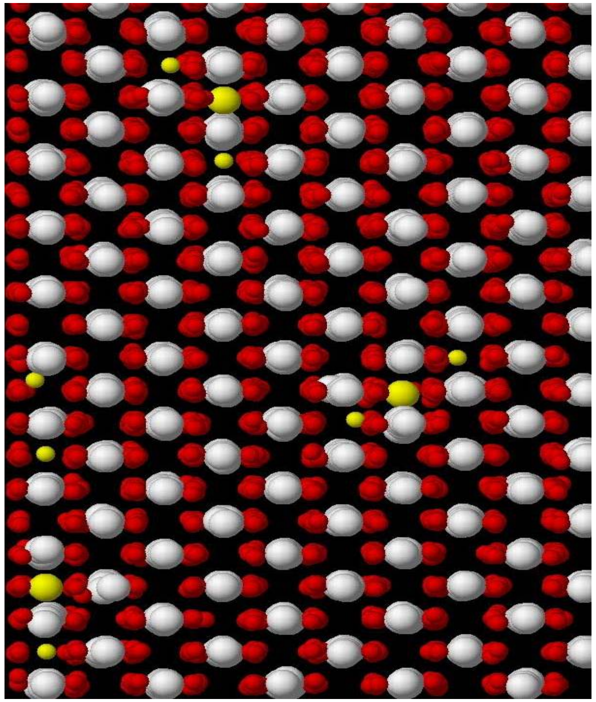
Point defects only

lanthanum zirconate pyrochlore ($La_2Zr_2O_7$)



Chartier et al, J.Nucl. Mat (2003)

Urania (UO_2)



Van Brutzel et al, J.Nucl. Mat (2006)

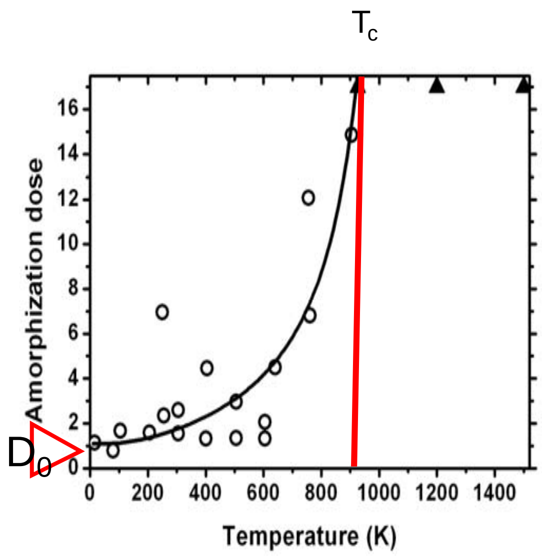
Different kinds of cascade debris : direct impact, mixt, point defects

Lanthanum zirconate does amorphize ; urania does not...
The source term is not enough to understand the behaviour under irradiation

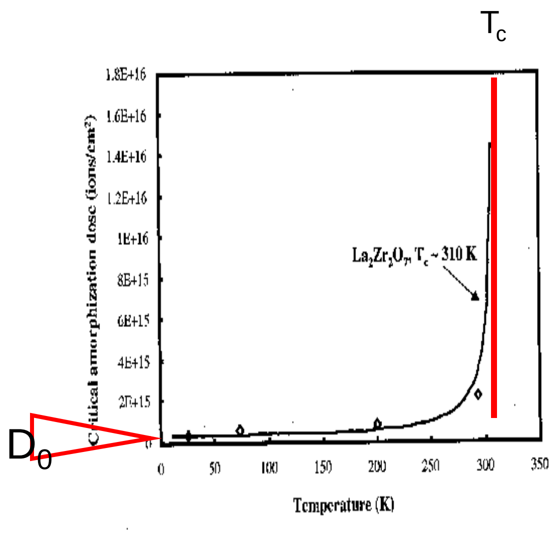
Importance of annealing : amorphization thermokinetics

Cascade produce only point defects : Frenkel pairs accumulation in $La_2Zr_2O_7$ and UO_2

in $La_2Zr_2O_7$ pyrochlore:
➔Reproduction of the increase of the amorphization dose with temperature/critical temperature



MD calc. J-P Crocombette, APL(06)



exp. Lian-Ewing (02)

in UO_2
➔ no amorphization irrespective of temperature

Difference comes from the different dynamics of the FPs recombinations

Quantitative agreement with experiments after correction for the flux effect