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A Molecular Dynamics investigation of radiation-induced disorder in Pu-doped ceramics.

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Sheffield S1 3JD, UK

MD workshop, Warwick, June 1-5 2009

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Talk plan

- **Background**
- **Modelling Radiation Damage**
- **Zirconolite Potential**
- **Defect Analysis**
- **Topological Analysis**
- **Conclusions + Challenges**

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Background

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- The UK has around 105 tonnes of Pu mainly in the form of PuO_2.
- Its status is in limbo – neither a waste nor an asset.
- Nuclear industry is looking at immobilising it in a mineral/ceramic wasteform - SYNROC.

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- *SYN*thetic *ROC*k
- Developed in the 70's by Prof. Ted Ringwood and co-workers
- Essentially a multiphase ceramic for incorporation of actinides, rare earths
- Inspiration taken from the ability of natural minerals to encapsulate actinides over geological timescales

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SYNROC-C

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- Zirconolite ($CaZrTi_2O_7$) is a major phase of SYNROC-C
- It is essentially an anion deficient superstructure, based on the fluorite structure
- Actinides are substituted for Ca, Zr/Hf on the A-site; $Ca(Zr_{1-x}Pu_x)Ti_2O_7$

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Self-irradiation

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- Actinides such as Pu are α-emitters.
- Release of an α-particle leaves behind a heavy recoil nucleus
- Recoil nucleus has a kinetic energy of *ca*. 70 keV, sufficient to create a damage cascade.
- Over the course of time, repeated damage can lead to an amorphous material with associated volume increase (=> micro cracking)

TEM Images (Zirconolite)

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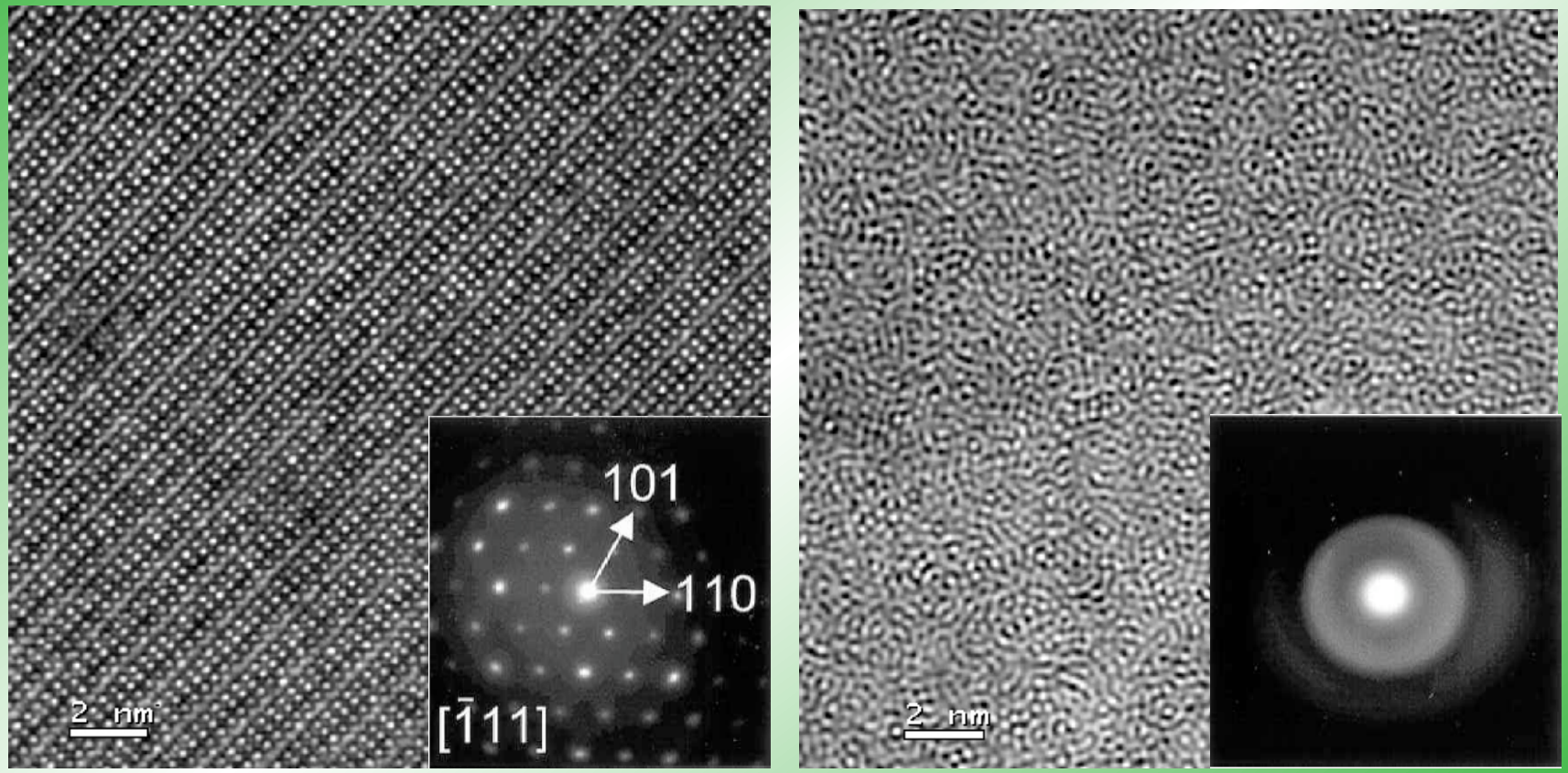

S. X. Wang, L. M. Wang, R. C. Ewing, G. S. Was and G. R. Lumpkin, "Ion irradiation-induced phase transformation of pyrochlore and zirconolite", Nuclear Instruments and Methods Physics Research B (1999) 704.

A. Meldrum, L.A. Boatner, R.C. Ewing, "A comparison of radiation effects in crystalline ABO4 -type phosphates and silicates", Mineralogical Magazine, 64(2000) 185

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Open questions

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- Why is radiation damaged zirconolite stable as an amorphous phase?
    - Synthesising amorphous zirconolite is extremely difficult.
- How can we better understand the behaviour of zirconolite as it undergoes amorphisation due to self irradiation damage?

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Aims of this work

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- To use Molecular Dynamics to simulate alpha recoil cascades in pure zirconolite ($CaZrTi_2O_7$) and also Pu doped zirconolite. $(Ca_{1-x}Pu_x)(Zr_{1-y}Pu_y)(Ti_{2-2x}Fe_{2x})O_7$
- To study in detail the cascade structure, using a defect based method, to provide a platform for further studies of completely amorphised zirconolite
- To analyse, topologically, the structural changes in radiation damaged zirconolite and assess the differences between defect based and topological based analysis methods

Model details

- **Born model of a solid**
- **Buckingham potential plus Coulombic term –**

$$A\exp(-r/\rho) - \frac{C}{r^6} + \frac{Q_1 Q_2 e^2}{4\pi\varepsilon_0 r}$$

- **Diverges to -∞ for some pairs e.g. O-O - problematic for radiation damage simulations.**

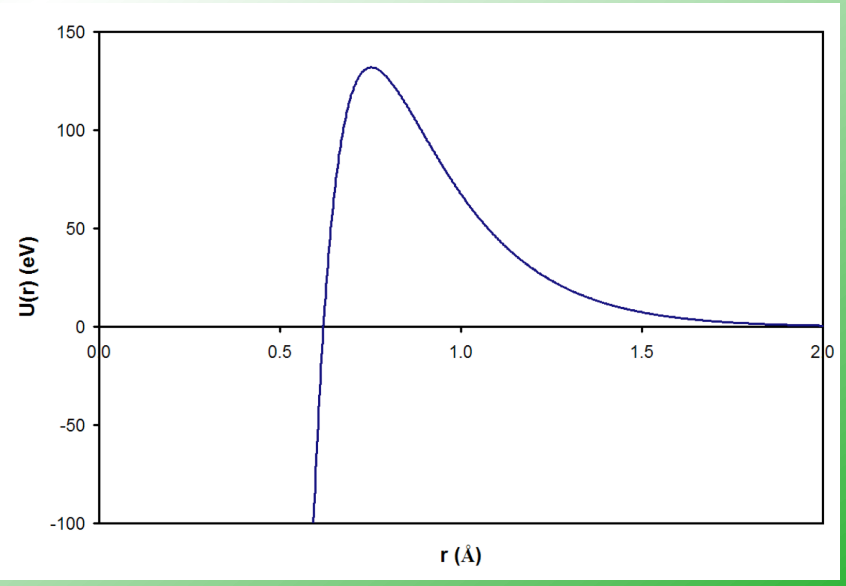

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Table 4.3: Zirconolite interaction parameters for the Buckingham potential.

Interaction Pair	A /eV	ρ /Å	C /eV Å^{-6}	Reference
O – O	9547.96	0.21916	32	Grimes, 1995
Ca – O	784.38	0.36356	0	Grimes, 1995
Zr – O	1502.11	0.3477	5.1	McCoy, 1997
Pu – O	1762.84	0.3542	11.48	Cleave, 2005
U – O	1761.76	0.3564	0	McCoy, 1997
Ti –O	2131.04	0.3038	0	McCoy, 1997
Fe – O	1414.60	0.3128	0.0	Minervini, 1998
Cat – Cat	0	1	0	

Ion	Charge
Ca	2+
Zr	4+
Ti	4+
O	2-
Pu	4+
U	4+
Fe	3+

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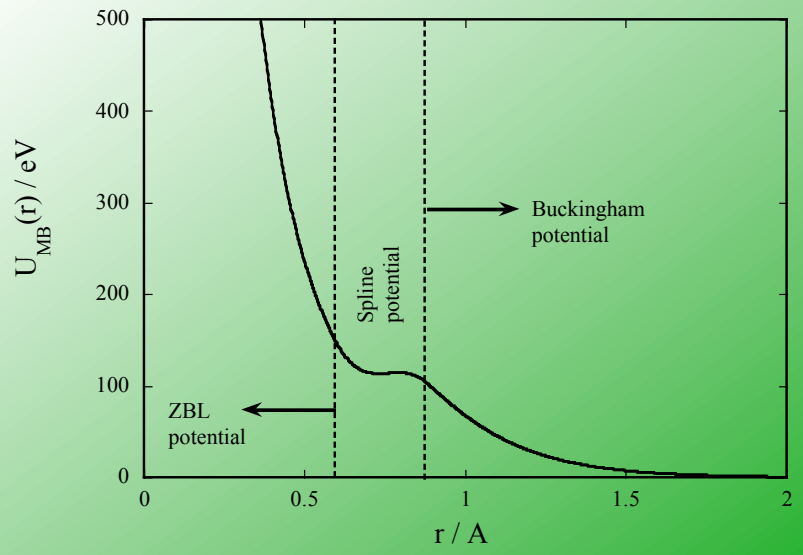
Solution: use ZBL potential for short range interaction, joined by a cubic spline to the Buckingham potential cut at its point of inflexion.

$$U(r) = \begin{cases} \dfrac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 r} \sum_{k=1}^{4} c_k \exp(-b_k r/a) & r < r_0 \\ p(r) & r_0 \le r \le r_1 \\ A\exp(-r/\rho) - \dfrac{C}{r^6} + \dfrac{Q_1 Q_2 e^2}{4\pi\varepsilon_0 r} & r > r_1 \end{cases}$$



Building Zirconolite

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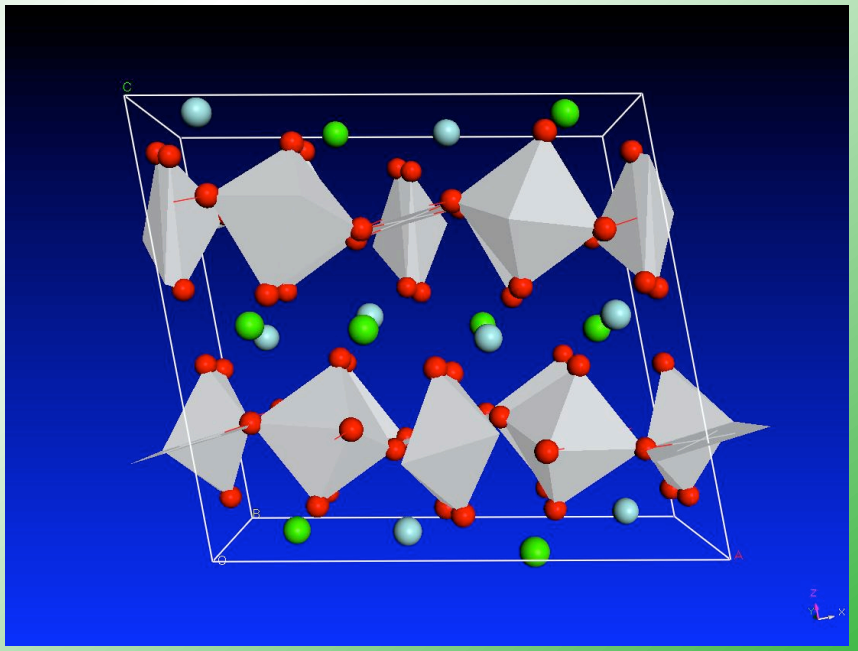
Structure by Rossell *et al*. Space group C2/c, monoclinic

Site	Point Set	*X*	*y*	*z*	Occupancy
Ca (M1)	*8f*	0.3718	0.1245	0.4952	1.0
Zr (M2)	*8f*	0.1225	0.1222	-0.0258	0.93
Ti (M2)	*8f*	0.1225	0.1222	-0.0258	0.07
Ti (M3)	*8f*	0.2498	0.1223	0.7465	1.0
Ti (M4)	*4e*	0.5	0.055	0.25	0.86
Zr (M4)	*4e*	0.5	0.055	0.25	0.14
Ti (M5)	*4e*	0.0	0.127	0.25	1.0
O (O1)	*8f*	0.310	0.133	0.275	1.0
O (O2)	*8f*	0.470	0.146	0.102	1.0
O (O3)	*8f*	0.197	0.083	0.573	1.0
O (O4)	*8f*	0.403	0.174	0.719	1.0
O (O5)	*8f*	0.702	0.169	0.590	1.0
O (O6)	*8f*	-0.001	0.111	0.414	1.0
O (O7)	*8f*	0.119	0.055	0.788	1.0
($\square_O$)	*8f*	(0.156)	(0.125)	(0.188)	(1.0)



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Validation

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Unit cell Structure is energy minimized using GULP code.

Parameter	Experimental Value [ref]	Calculated Value	Difference (%)
Volume (Å^3)	1014.0604	999.3713	-1.45
a (Å)	12.4458	12.1417	-2.44
b (Å)	7.2734	7.1538	-1.64
c (Å)	11.3942	11.6781	2.49
α (deg)	90.000	90.000	0.00
β (deg)	100.533	99.857	-0.67
γ (deg)	90.000	90.000	0.00

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Simulation details

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- 228,096 atoms (12 x 18 x 12 unit cells)
- DL_POLY 3.06 used
- Simulation cell surrounded by pseudo layer (4Å)
- Recoil energies of 10 – 34.7 keV
  - Limited by computer power
- Variable time step used
  - Timestep increases as recoil atom loses energy
  - Maximises processing capability

Damage animation

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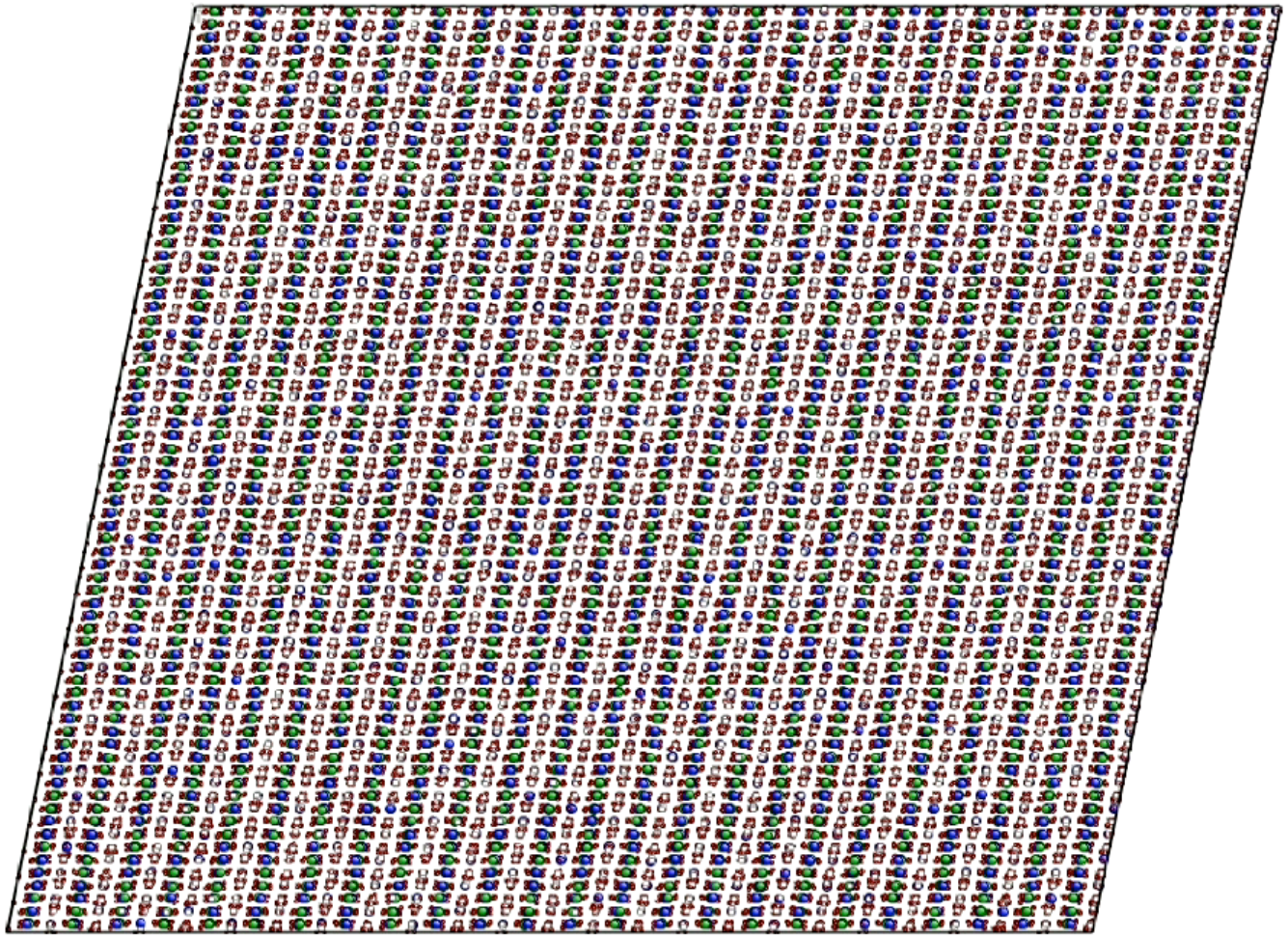

Cascade animation

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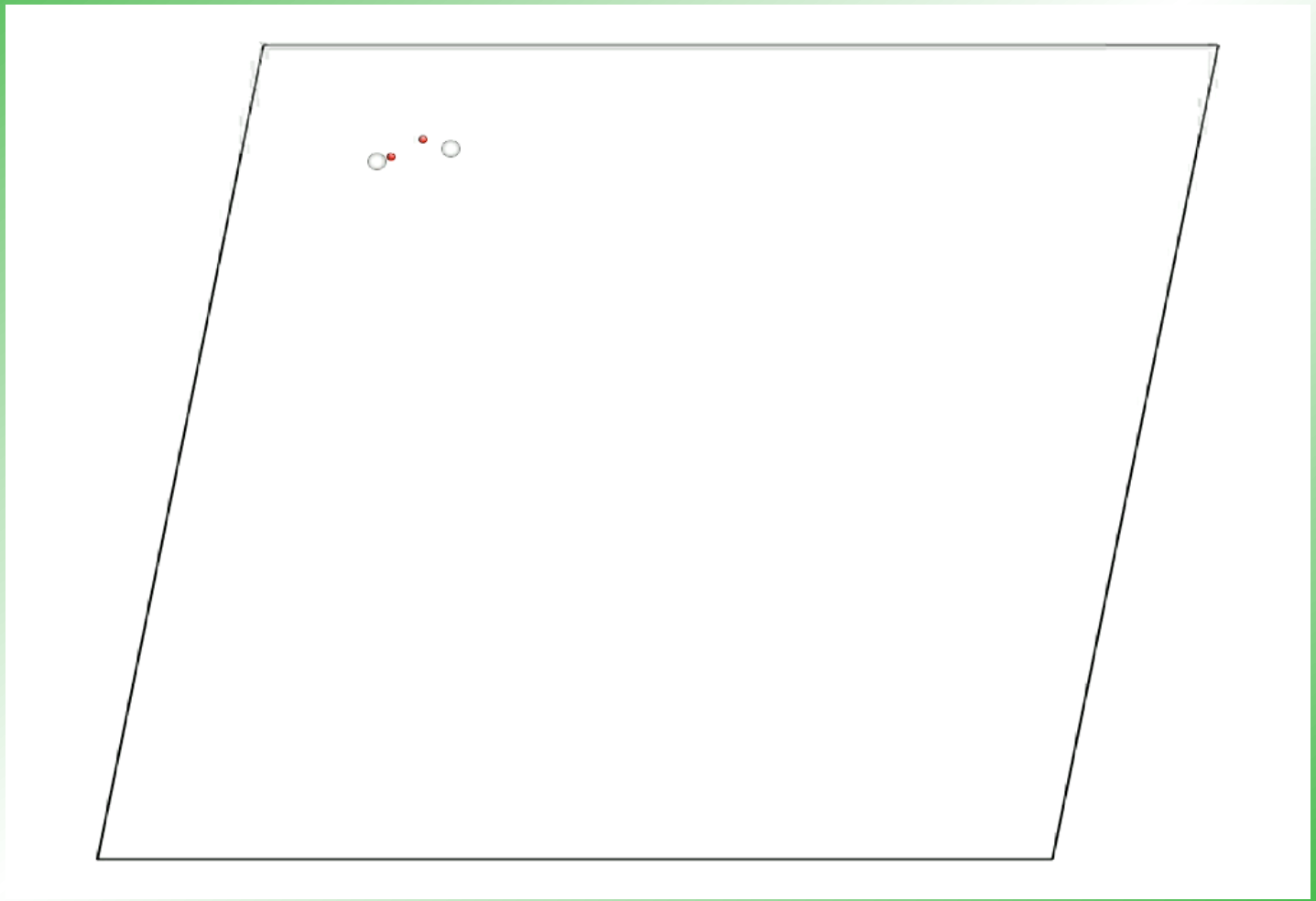
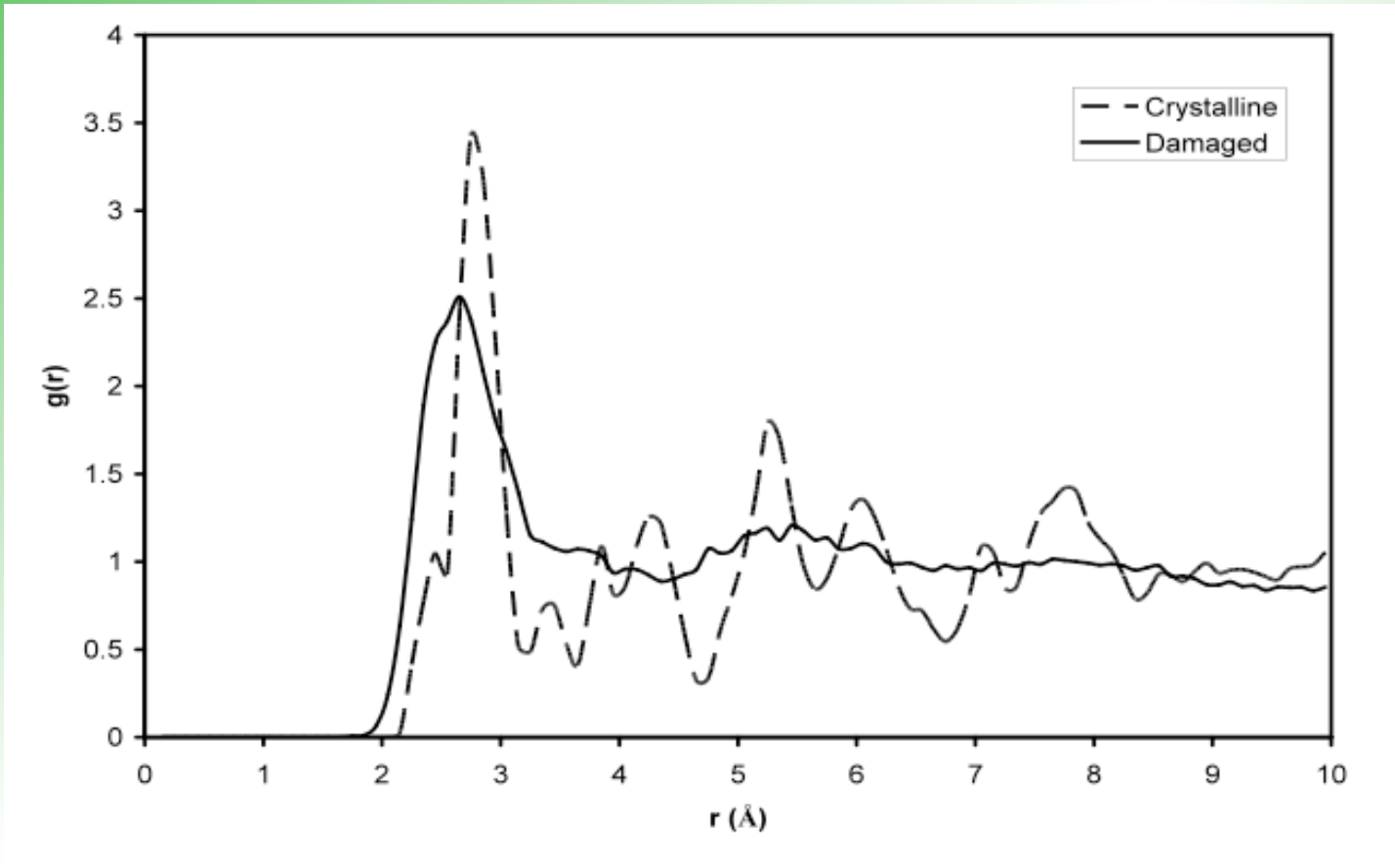


Structural changes



Defects 1: vacancies

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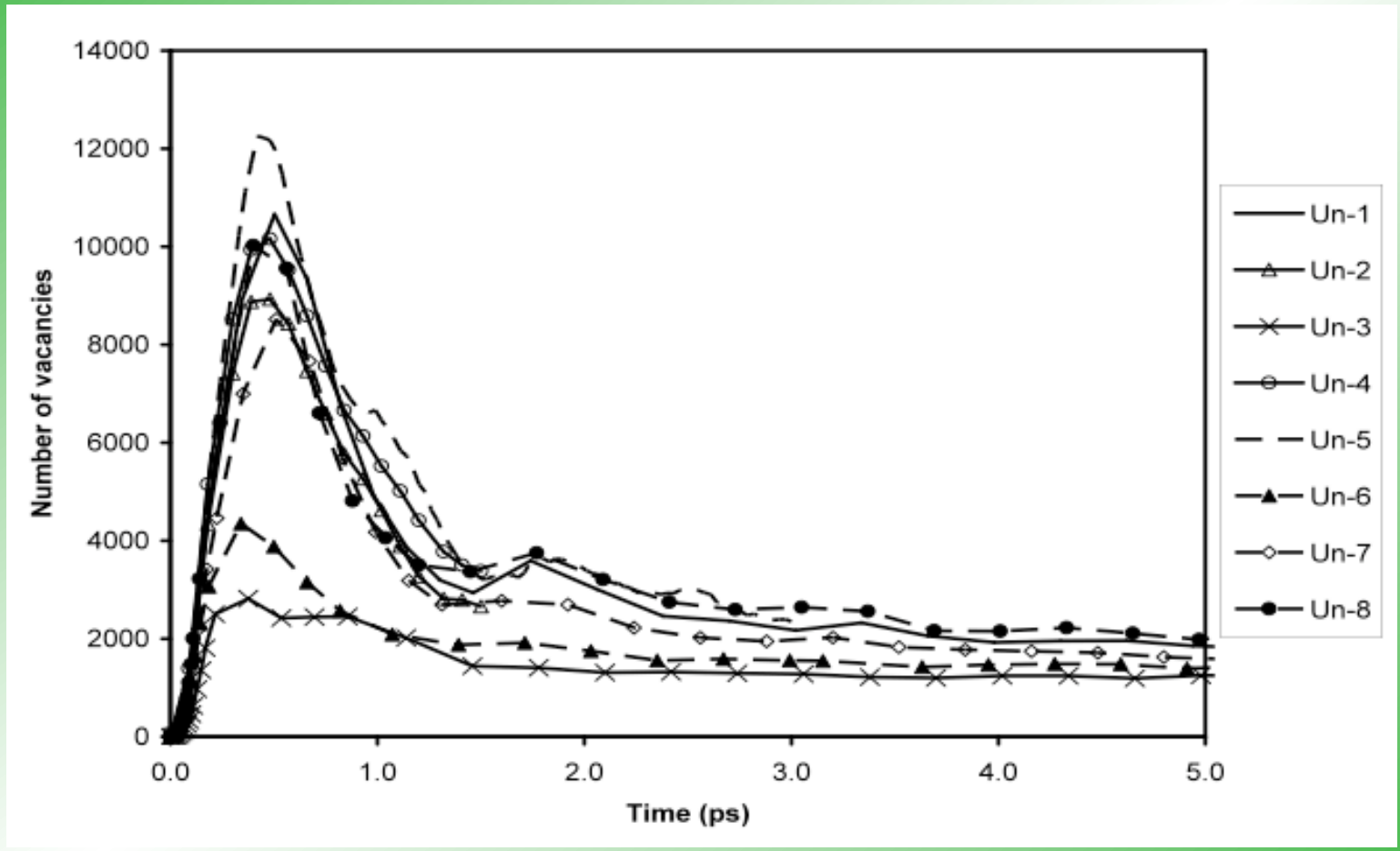

Defects 2: cation antisites

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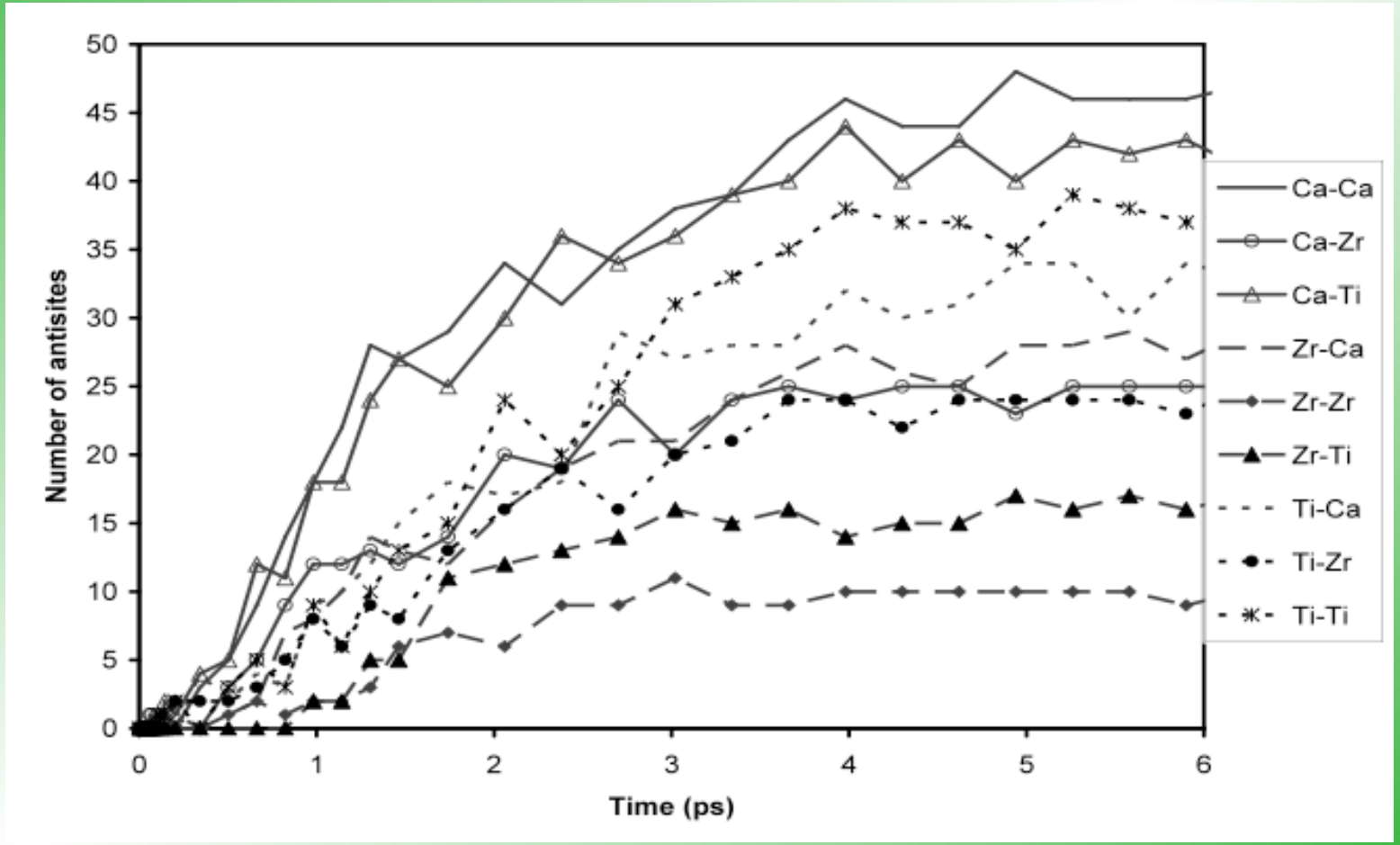

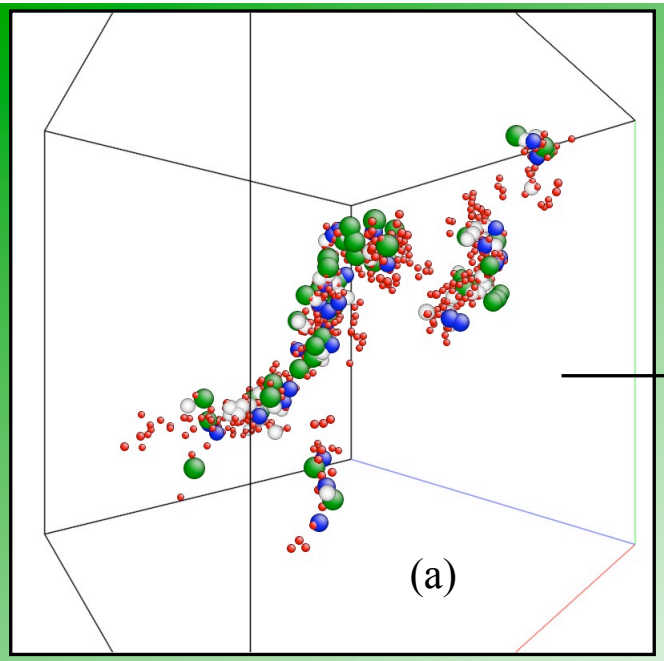

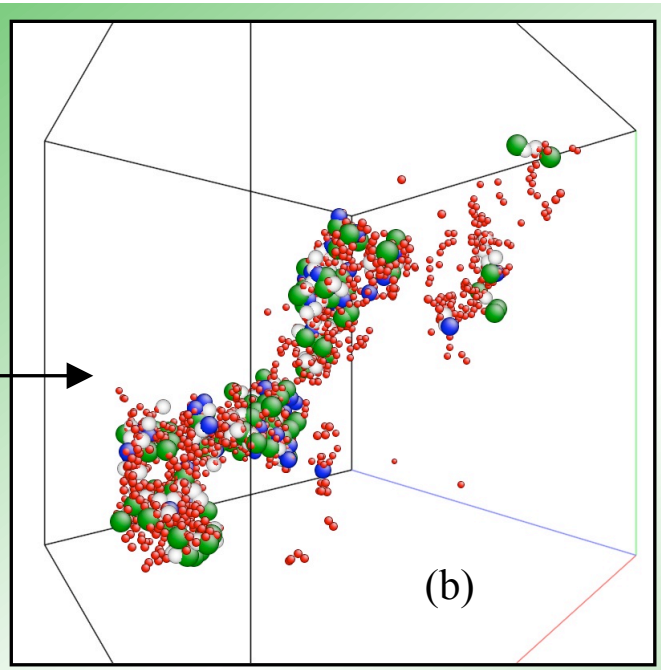

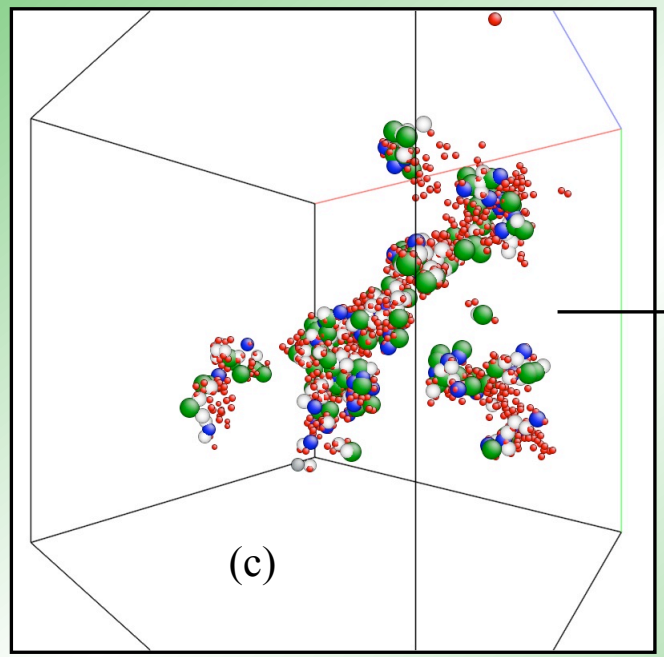

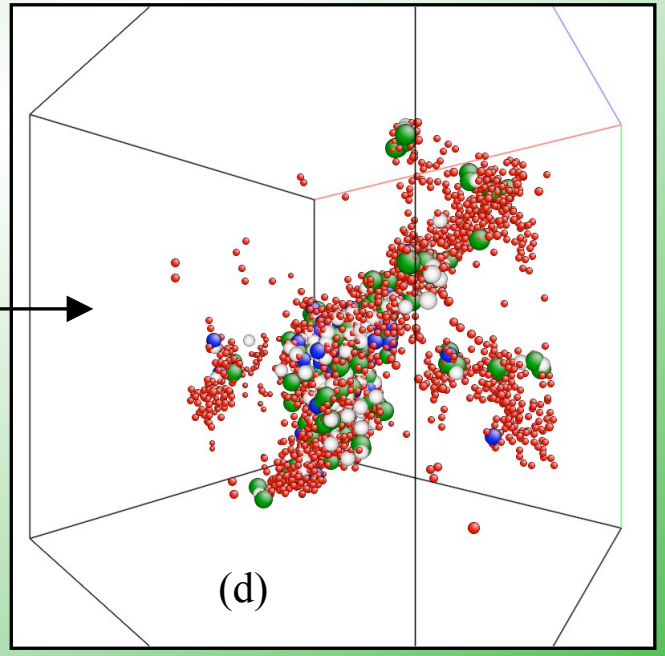

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(a) & (b): Un-3

Un-doped

(c) & (d): Un-6

Annealing behaviour

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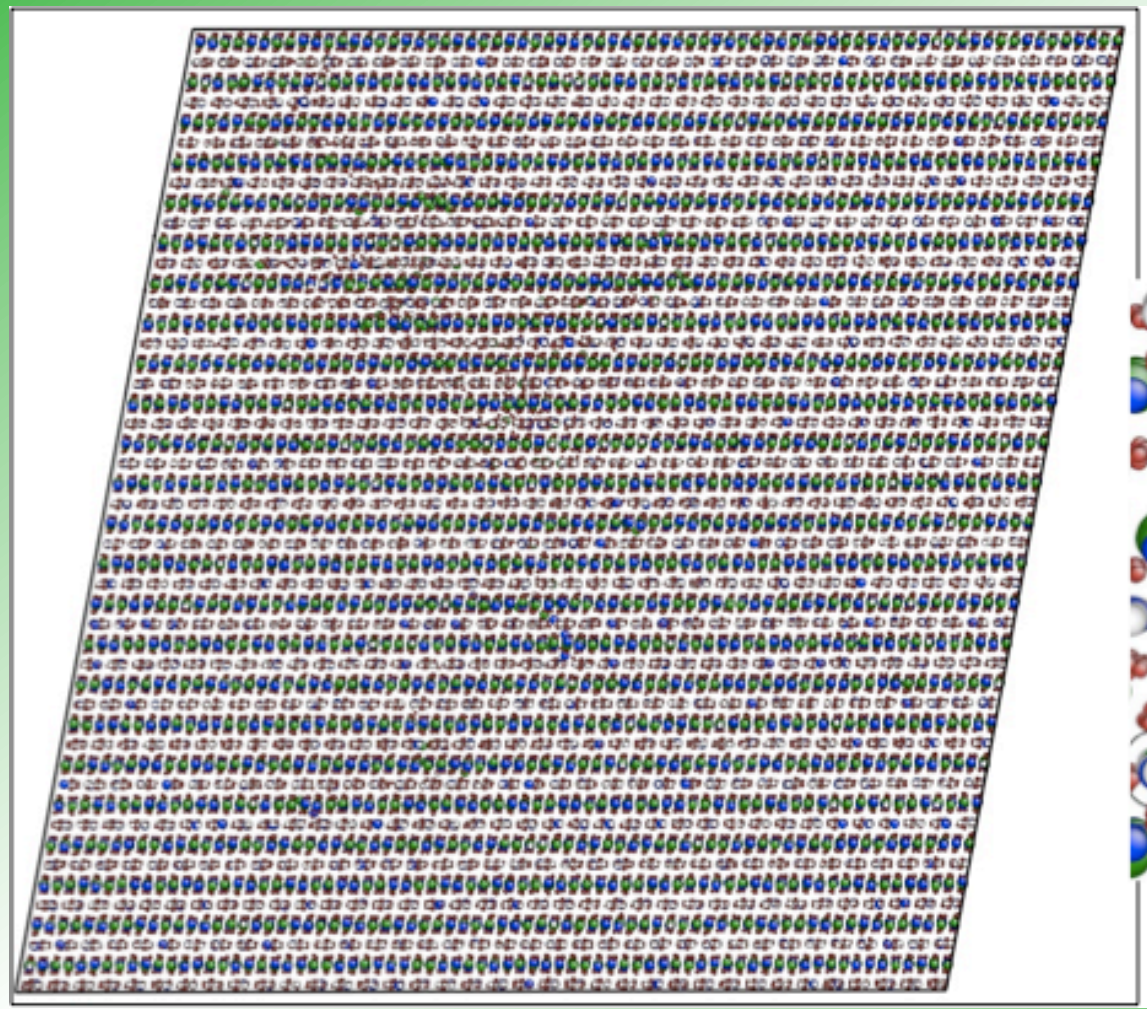

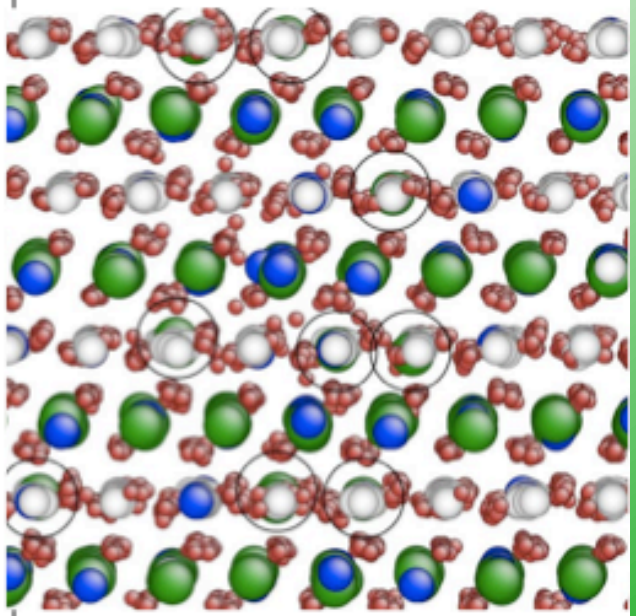

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Actinide Doping

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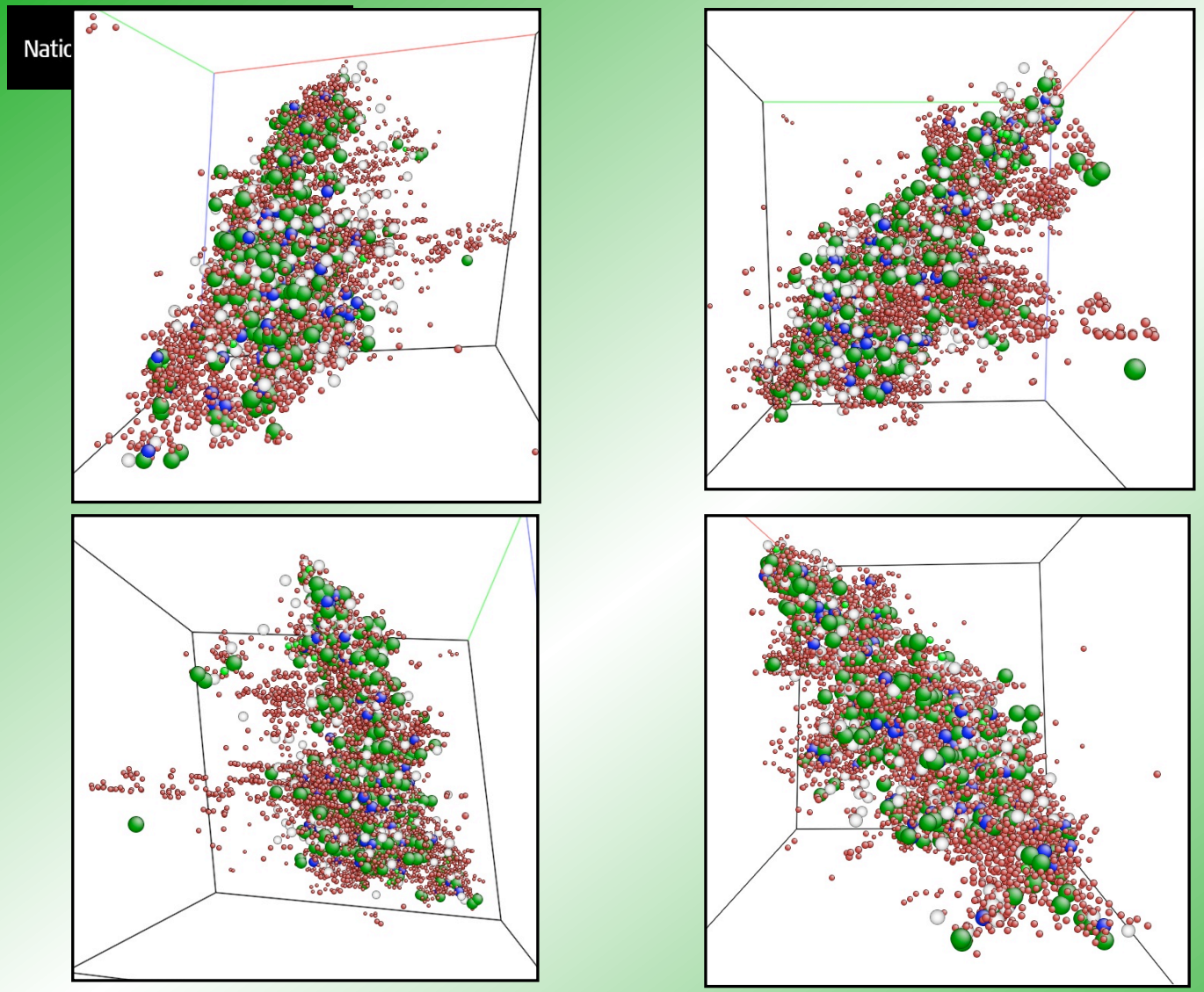
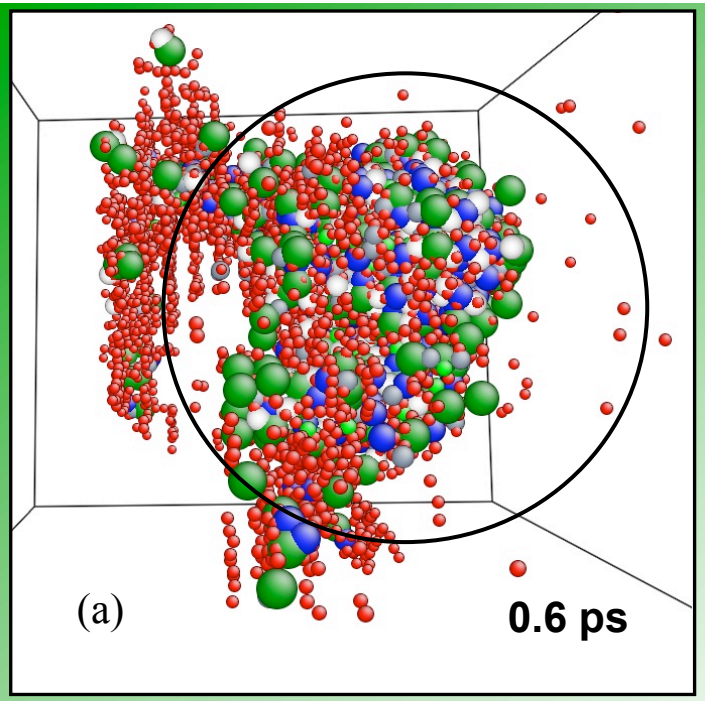
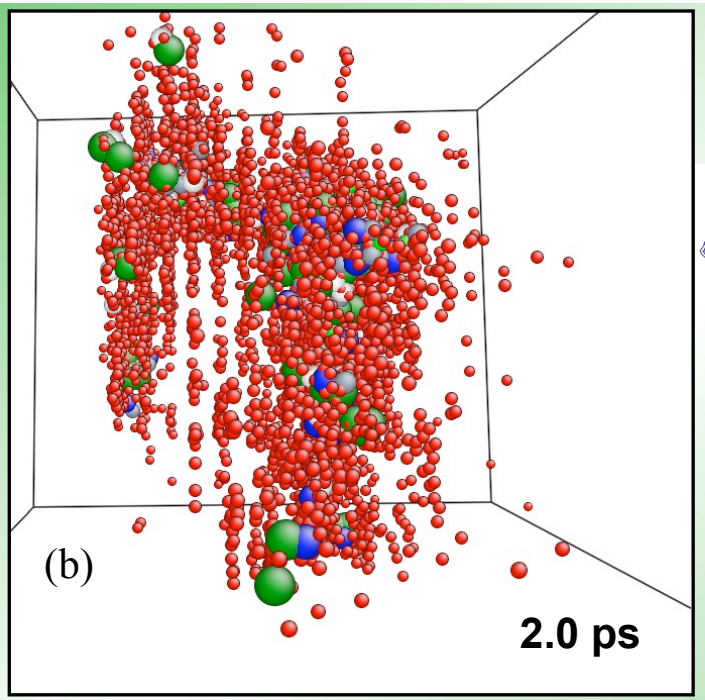
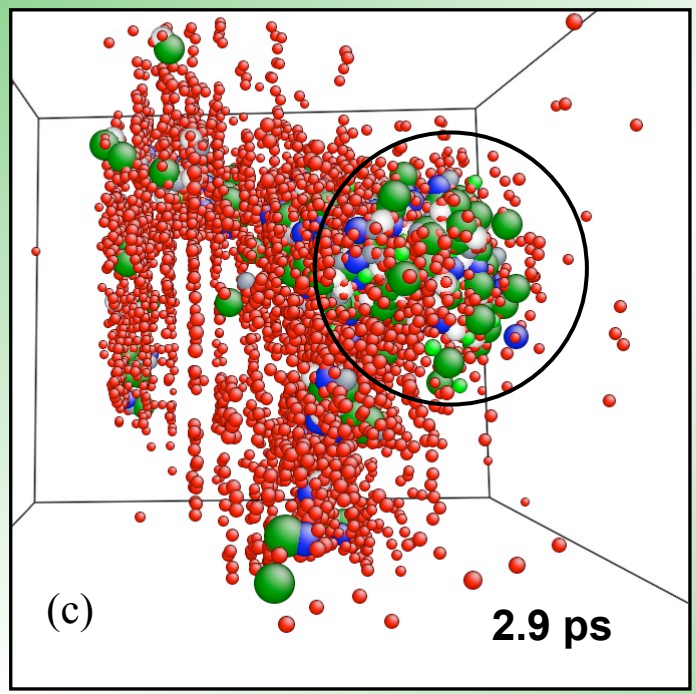
- 30% doping of Pu on Ca or Zr sites.
- Damage extends further.
- Less sub-cascades due to heavy actinides
  - More general ‘destruction’ of the crystalline structure
- More interesting cascade behaviour
  - Double Cascades
  - Damage channelling along 001 direction

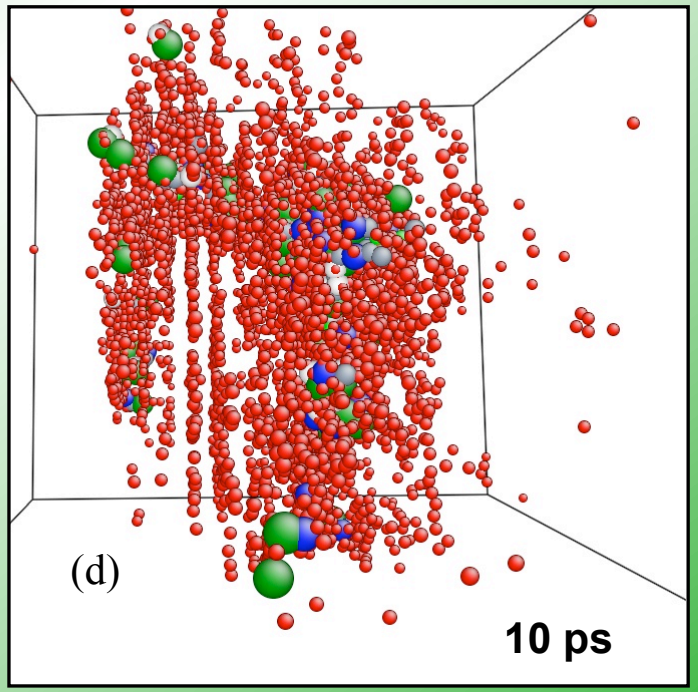


Zr-doped









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Ca-doped

An alternative analysis of damage using ring statistics

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• Standard crystallographic space group methods based on symmetry operations provide a good description of crystalline systems using a *unit cell*, but lack the ability to describe disordered or highly defective systems.

• Topological analysis uses atom connectivity and is therefore applicable to disordered, defective and amorphous systems as well as crystalline ones. It produces a *local cluster*, based on nearest neighbour and connectivity constraints specified to be representative of the system of interest.

Topological Analysis using Graphs

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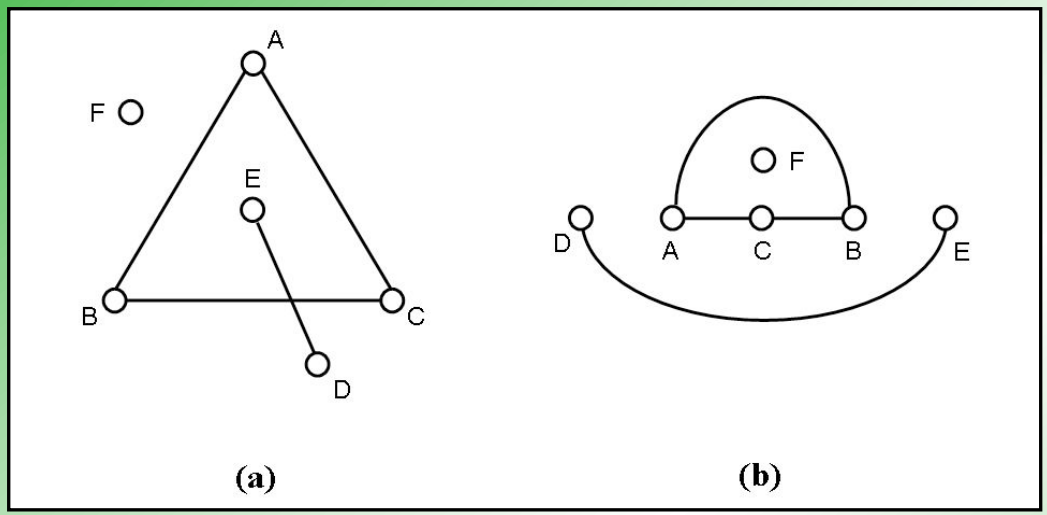

Both (a) and (b) are equivalent graphs and are defined by the sets

$$\{A, B, C, D, E, F\}$$

and

$$\{\{A, B\}, \{A, C\}, \{B, C\}, \{D, E\}\}$$

In atomistic simulation, complex 3-dimensional structures consisting of collections of atoms can be described quantitively by an analysis of the shortest number of connections (edges) joining sets of atoms (nodes) to form a *path.* A *ring* is defined as a closed path that does not intersect itself, and each has an *order* defined by the number of vertices in that ring.

Primitive Rings

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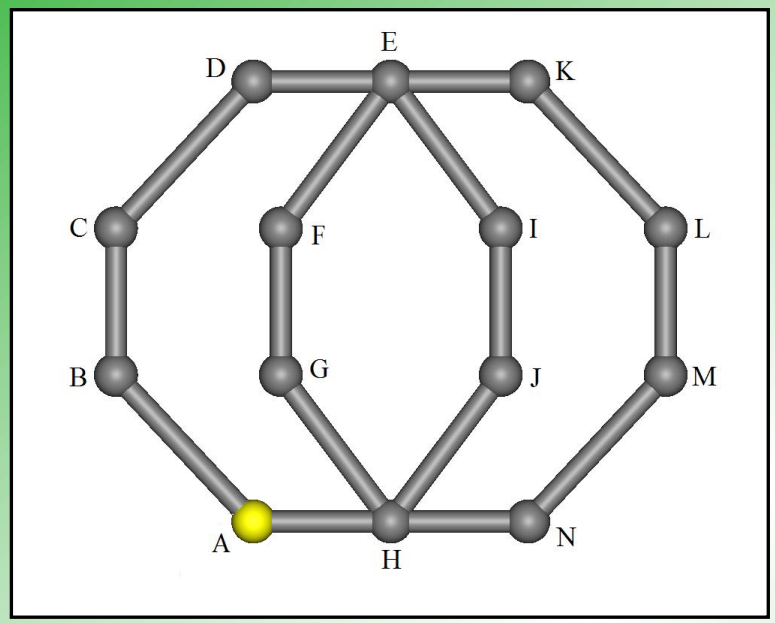

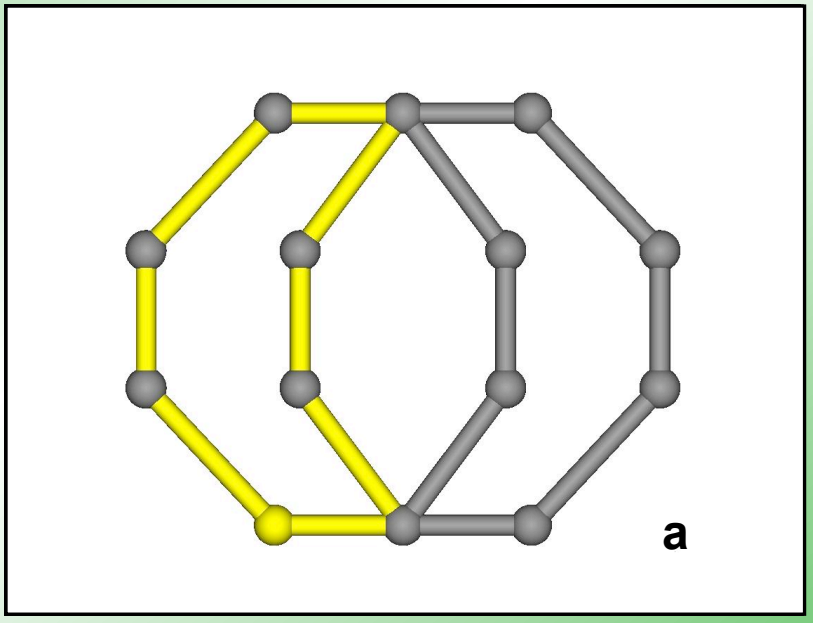

The 8-ring ABCDEFGH (denoted by yellow colouring in (a)) is primitive, while the 10-ring, ABCDEKLMNH (b) is not primitive because it encompasses three rings, the 8-ring ABCDEFGH, the 6-ring JIEFGH (c) and the 8-ring JIEKLMNH (d) – all of which have lower order. The 8-ring ABCDEIJH (e) is also primitive, because, although it is the sum of the 8-ring ABCDEFGH and the 6-ring JIEFGH, only the 6 ring is of lower order.

Primitive Rings

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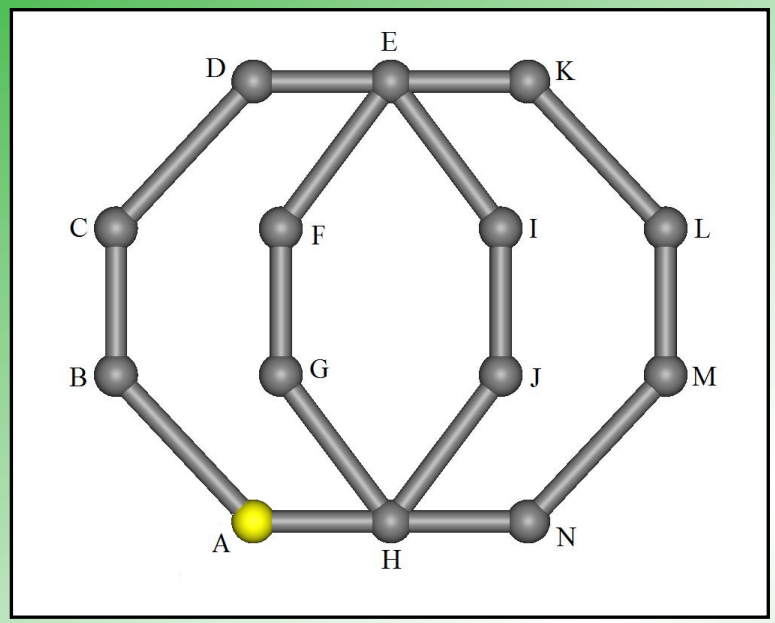

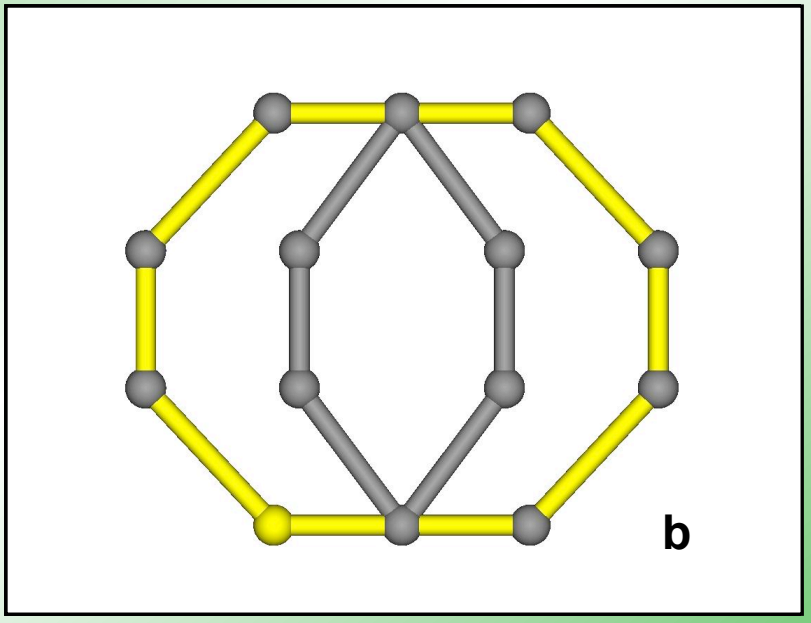

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Topological Analysis

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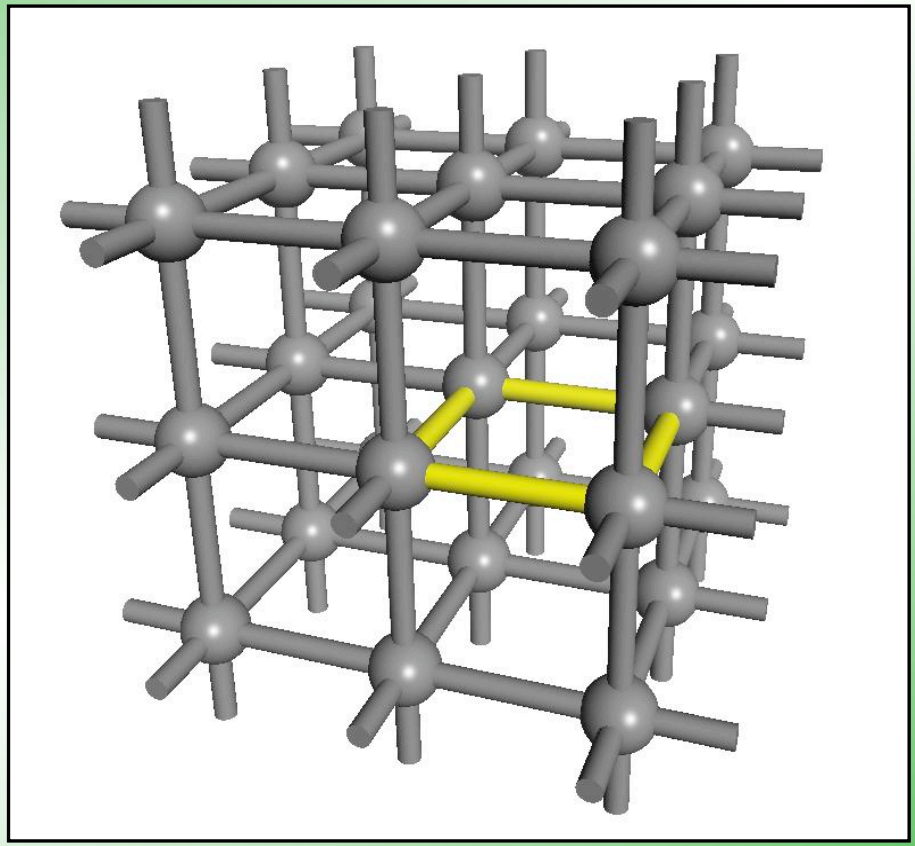

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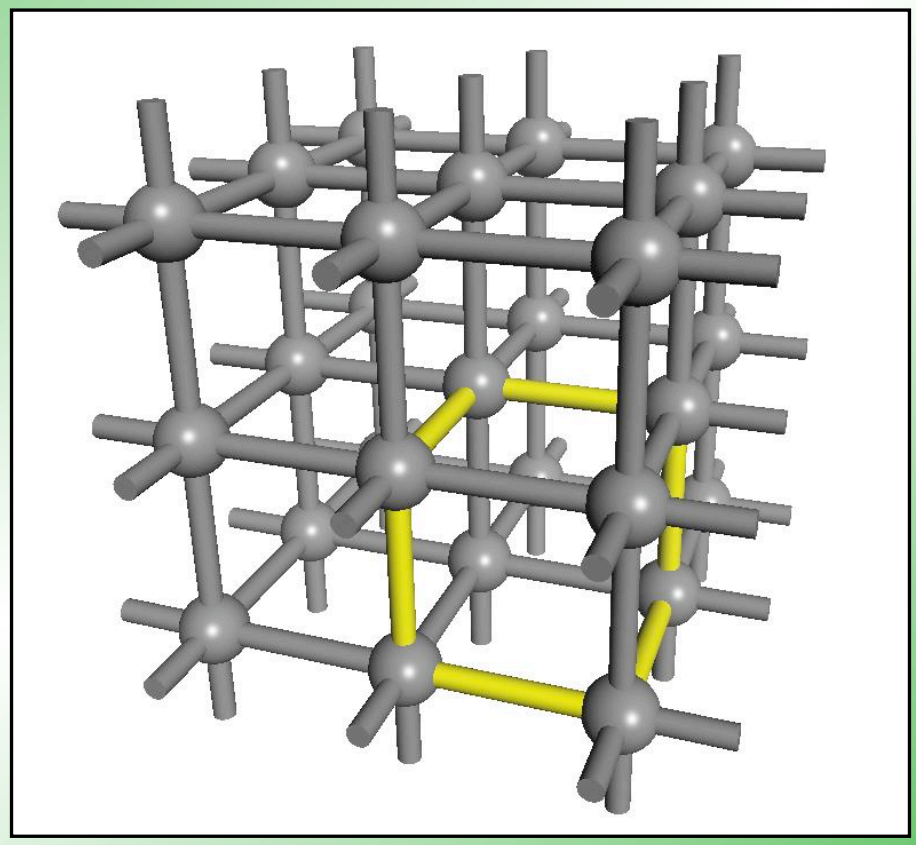

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Defining the nearest neighbour cut-off distance

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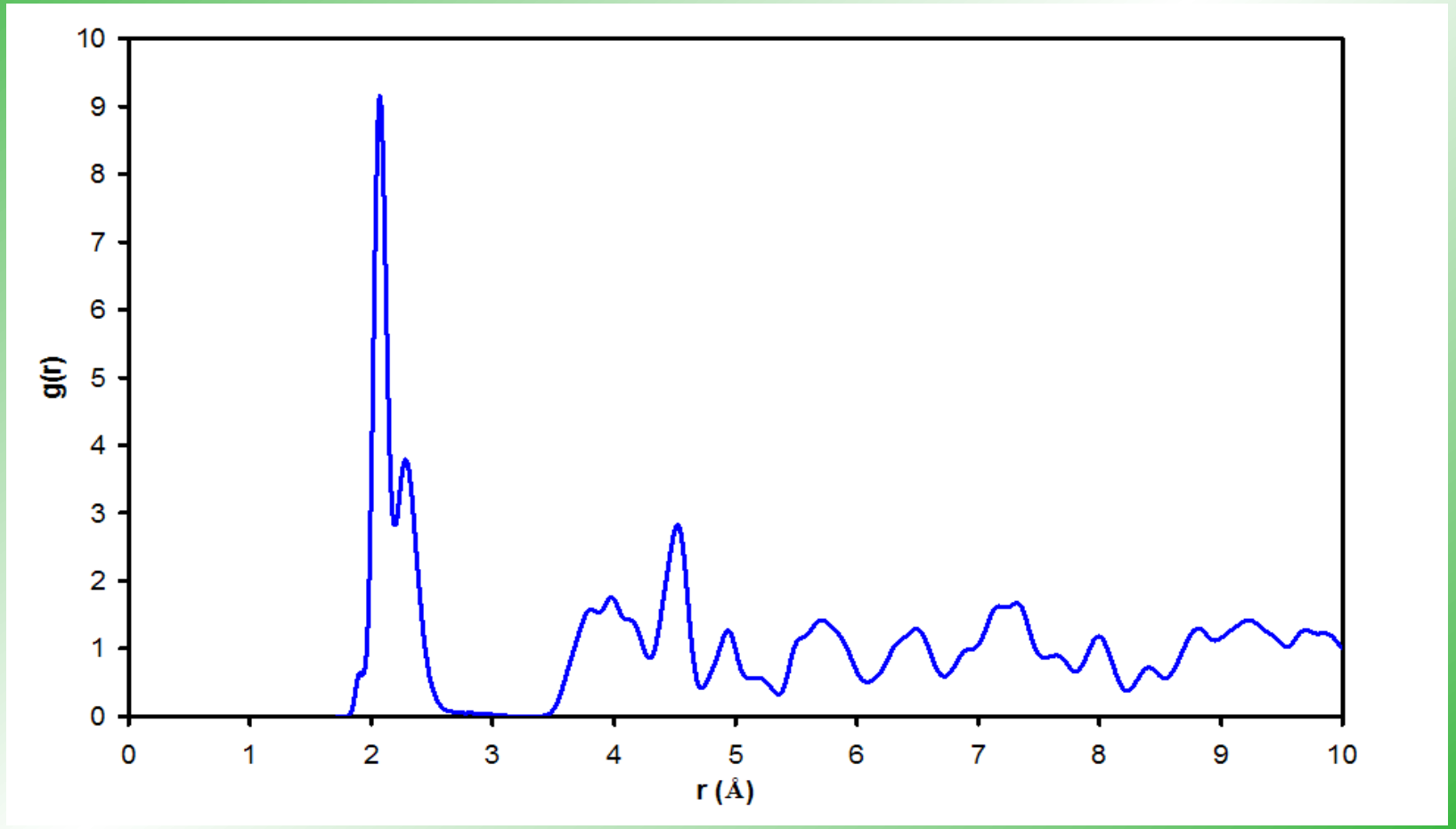

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Defining the nearest neighbour cut-off distance

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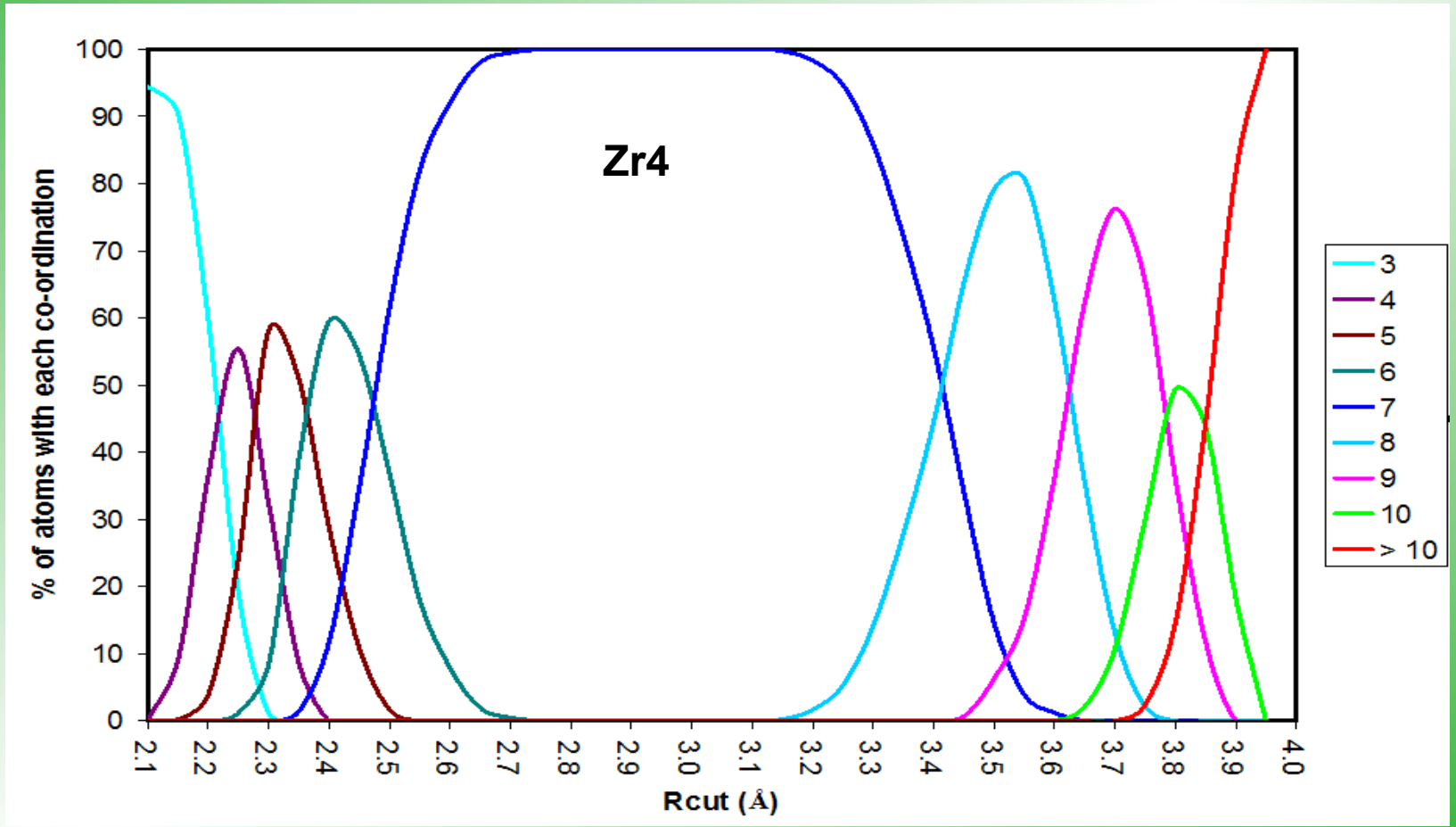

Chosen nearest neighbour distance cut-offs

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R_{cut} (Ca-O) = 3.0 Å

R_{cut} (Zr-O) = 3.0 Å

R_{cut} (Ti-O) = 2.9 Å

R_{cut} (O-O) = 0 Å

R_{cut} (Anion-Anion) = 0 Å

These cut-offs allowed for the maximum number of atoms to be in their documented co-ordination during equilibrium simulations.

Three zirconolite systems

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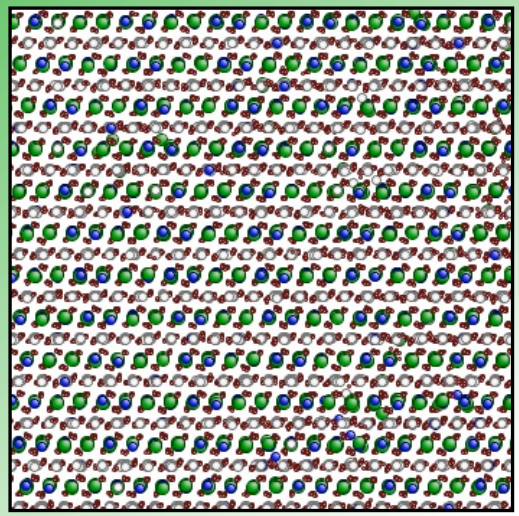
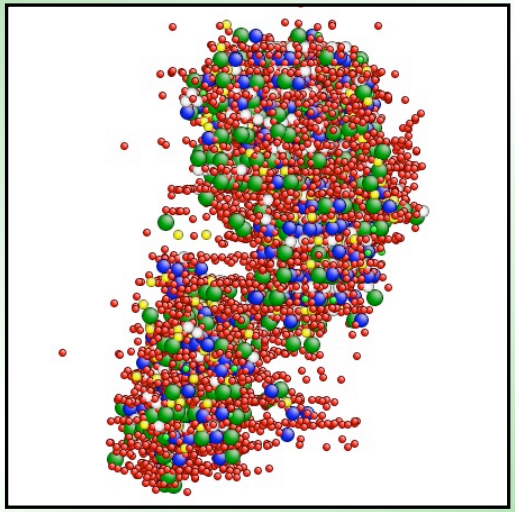
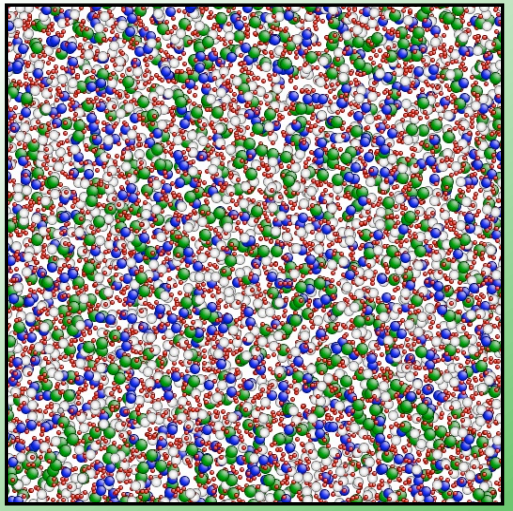


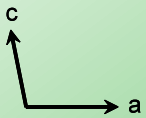
Crystalline



Radiation Damaged



Melted



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Local Clusters

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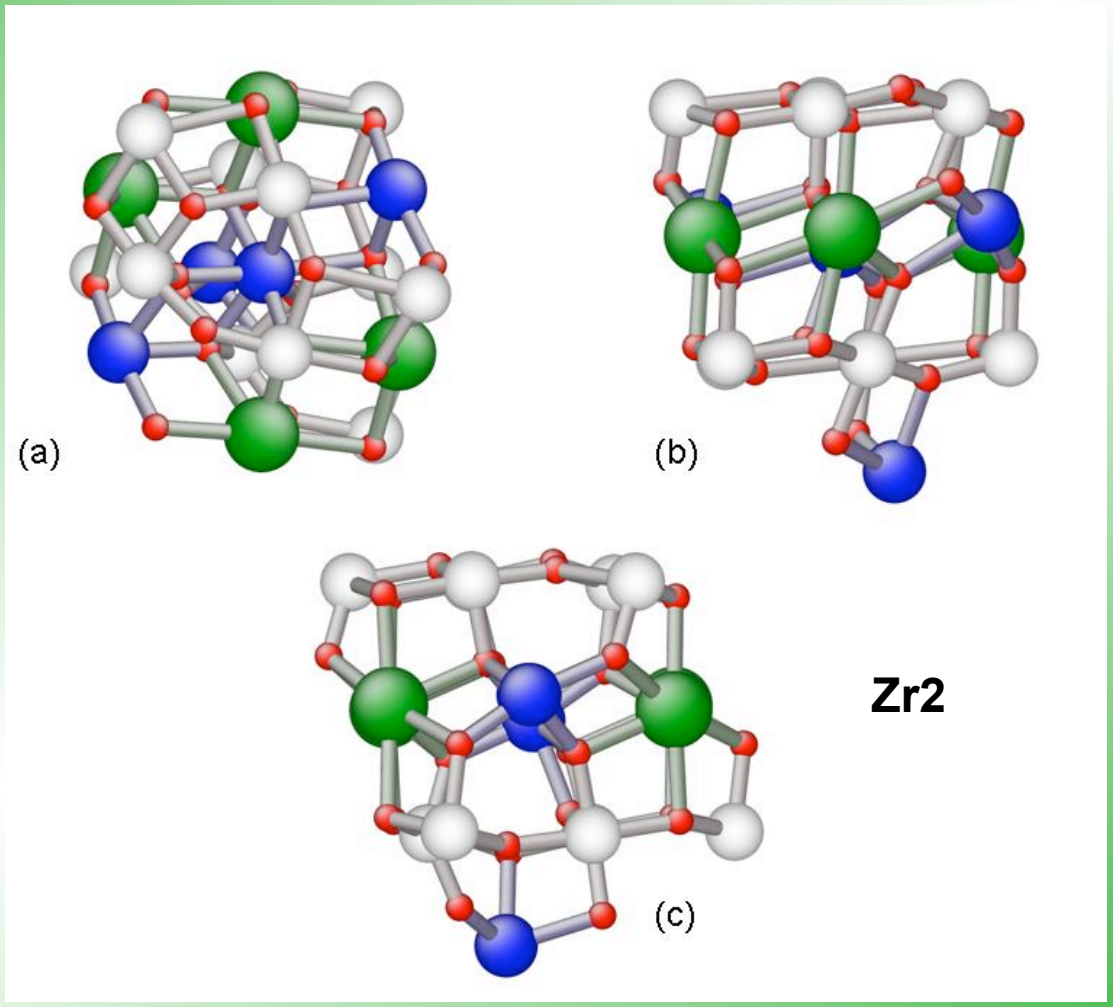

Melted vs. Radiation damaged

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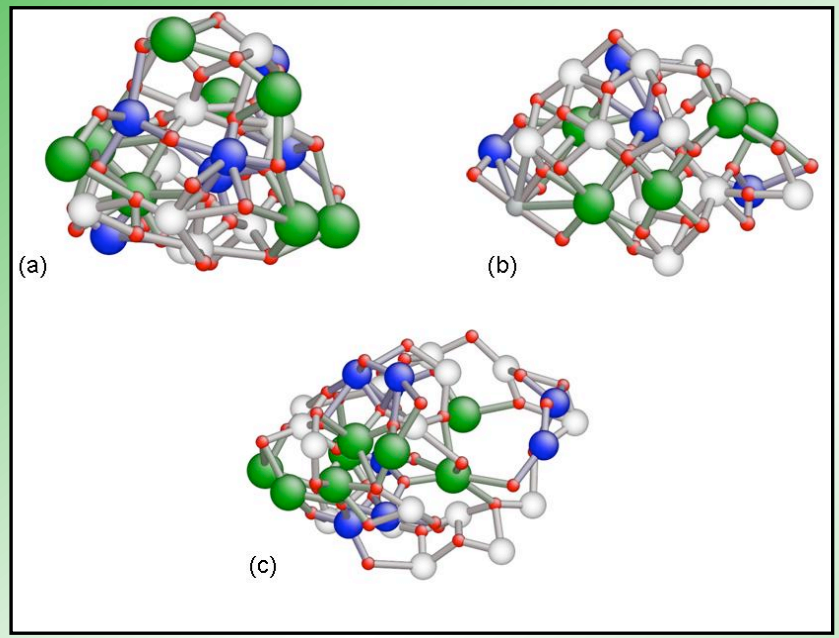
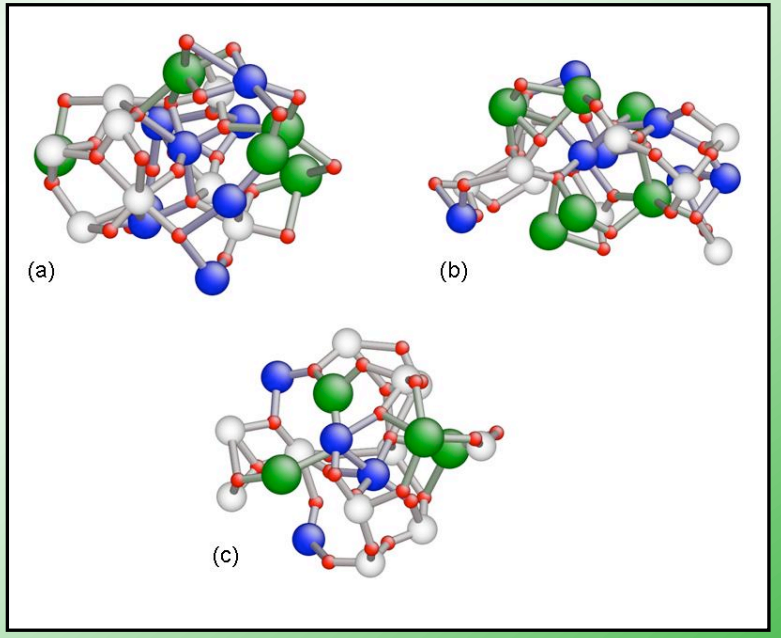


Radiation Damaged



Melted

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Closer inspection

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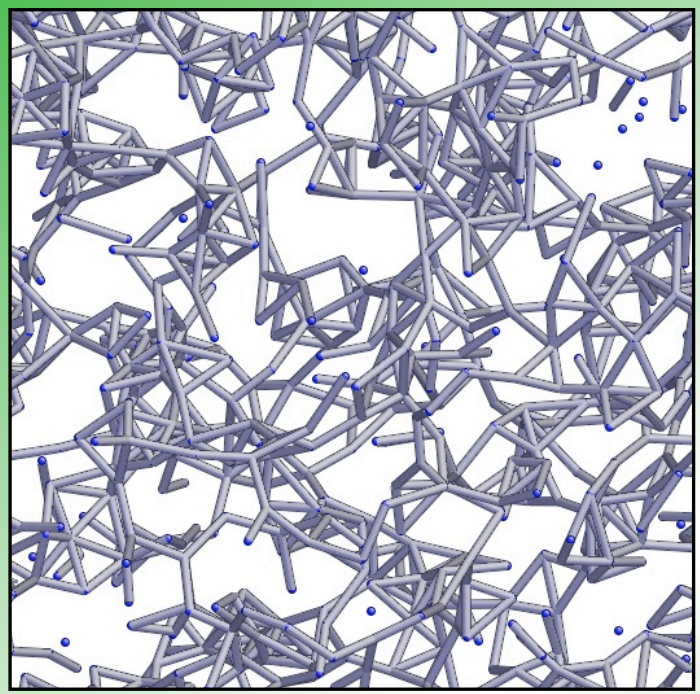

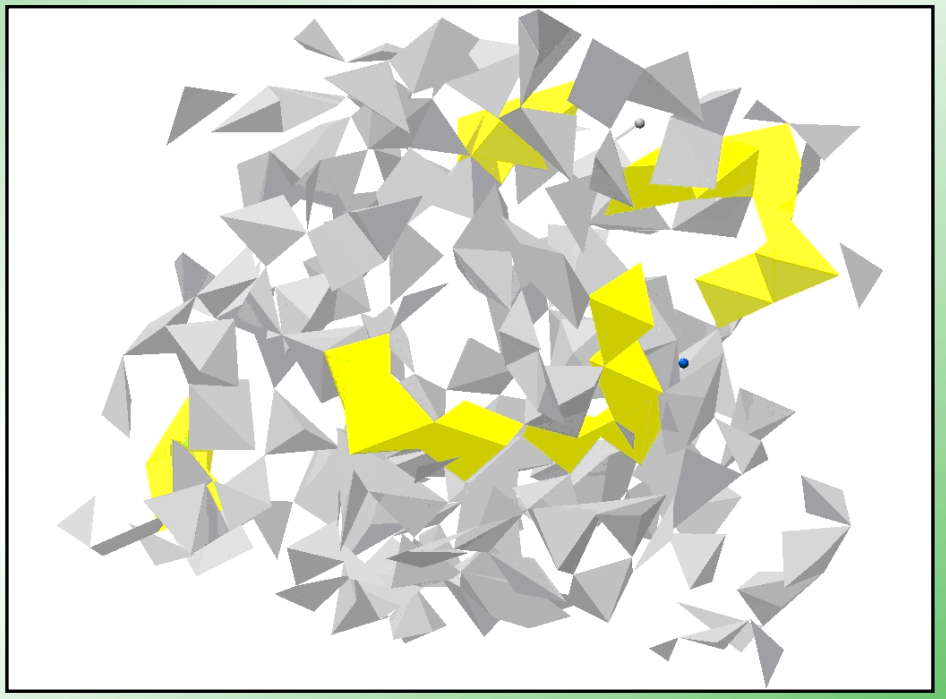

We find edge-sharing chains of TiO_x polyhedra throughout the radiation damaged structure

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Topology of all Ca atoms

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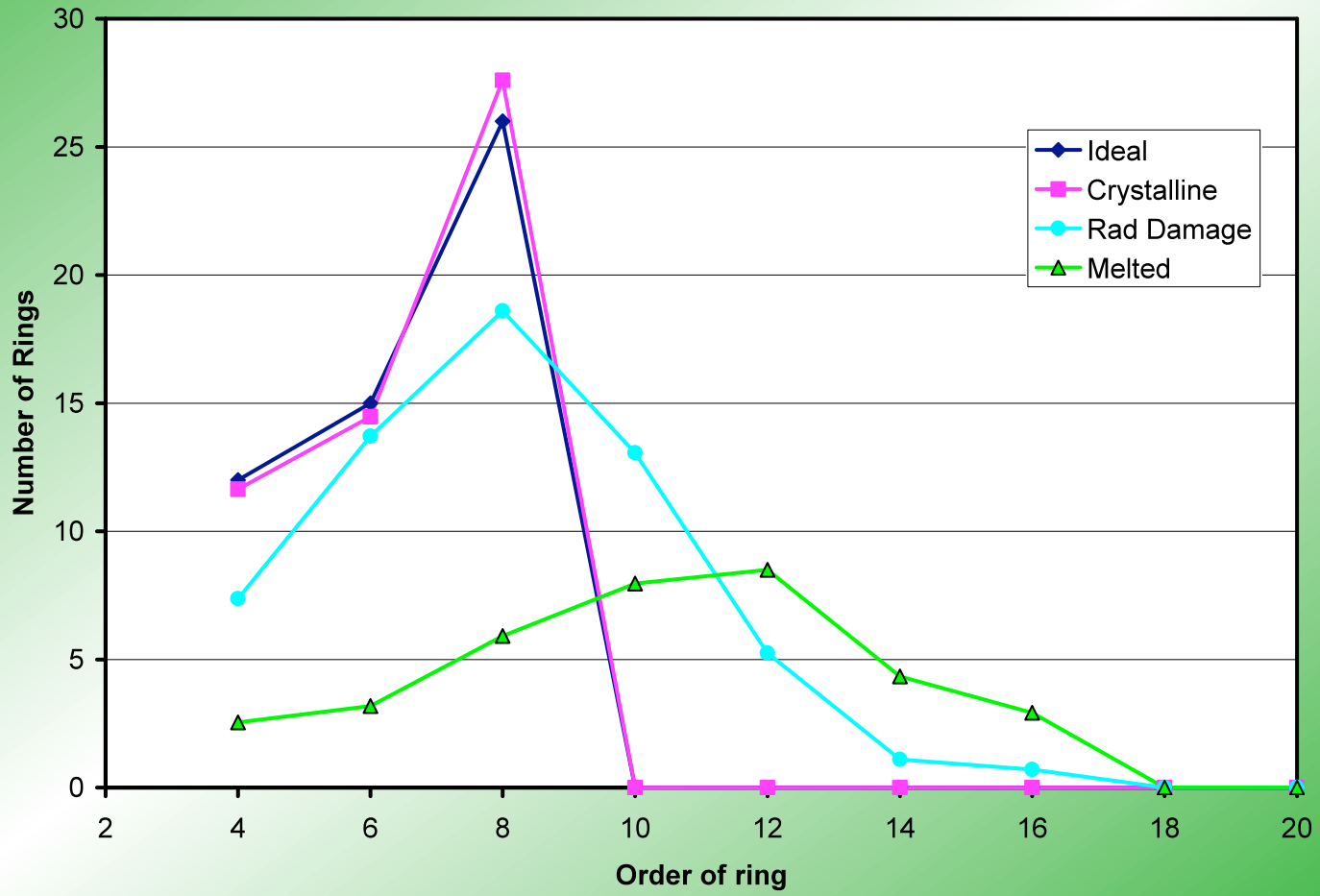

Conclusions

- Initially, radiation damaged structures look very different.
- Defect-based analysis methods would suggest different structures
- However, topology shows that a radiation structure is in-fact still closely linked to its crystalline cousin
- Topological analysis shows stable configurations of TiO_x polyhedra, with a first order phase transition needed for recovery of crystalline order
    - i.e. melting.

Challenges for Simulation

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- MD is limited to < 10^{-6} s and distances on the nanometre length scale.
- How to scale up these results?
  - Microcracking?
  - Leaching?

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Table 4.3: Zirconolite interaction parameters for the Buckingham potential.

Interaction Pair	A /eV	ρ /Å	C /eV Å^{-6}	Reference
O – O	9547.96	0.21916	32	Grimes, 1995
Ca – O	784.38	0.36356	0	Grimes, 1995
Zr – O	1502.11	0.3477	5.1	McCoy, 1997
Pu – O	1762.84	0.3542	11.48	Cleave, 2005
U – O	1761.76	0.3564	0	McCoy, 1997
Ti –O	2131.04	0.3038	0	McCoy, 1997
Fe – O	1414.60	0.3128	0.0	Minervini, 1998
Cat – Cat	0	1	0	

Ion	Charge
Ca	2+
Zr	4+
Ti	4+
O	2-
Pu	4+
U	4+
Fe	3+

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Topology of all Zr atoms

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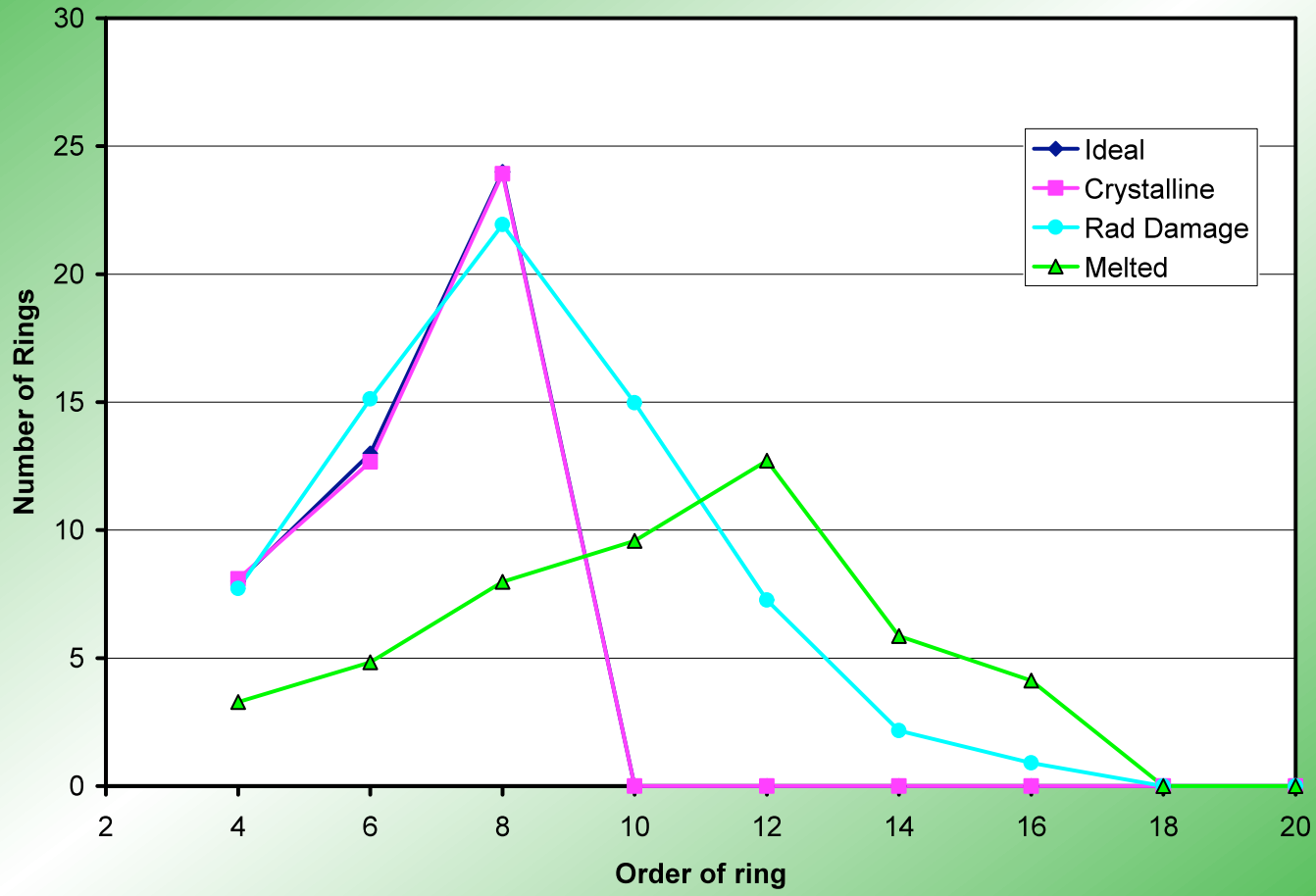

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Topology of all Ti atoms

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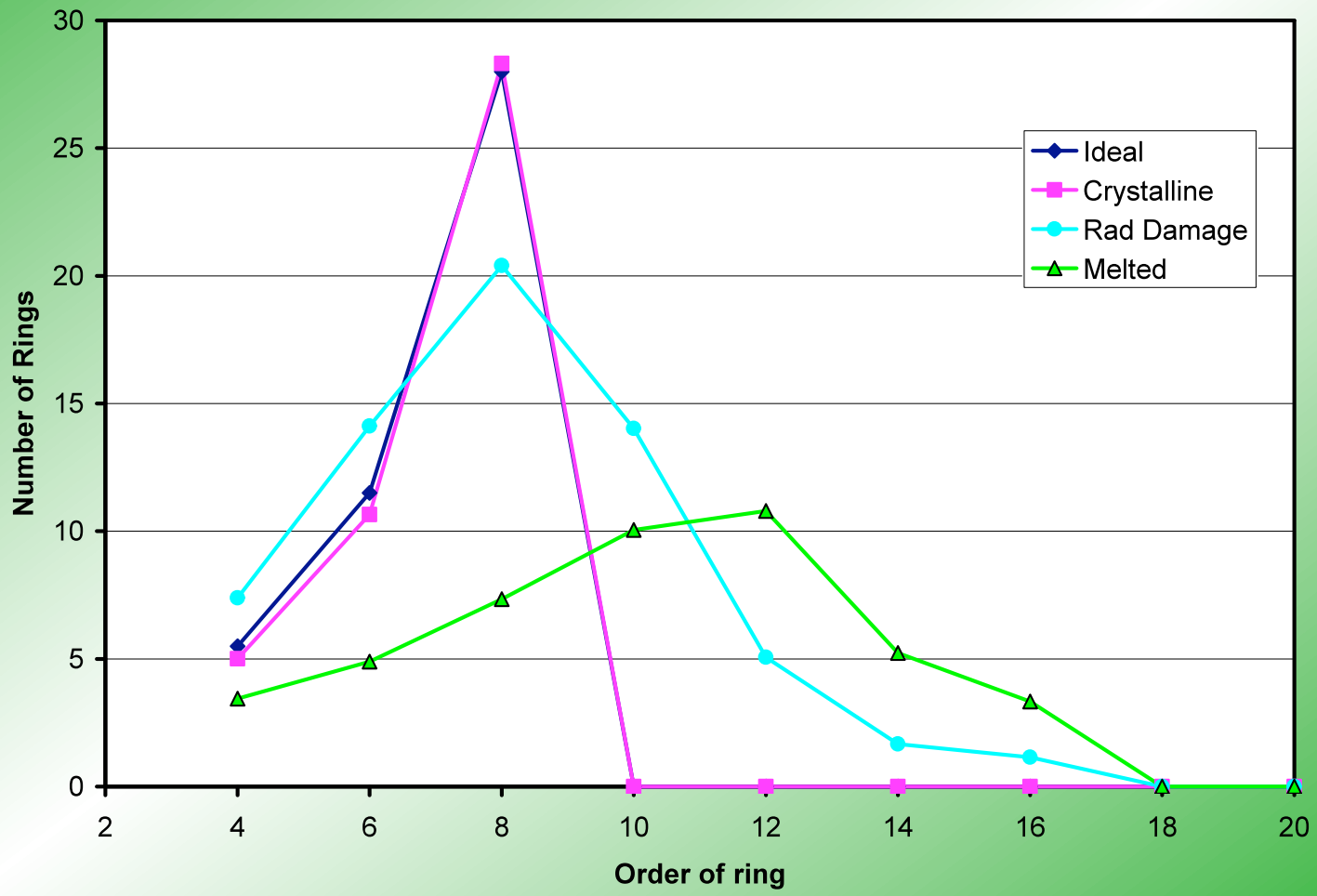

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Thermal spike

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