Parallel Trajectory Splicing Simulations of Cation Dynamics in Pyrochlore

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NNSA
National Nuclear Security Administration

Pyrochlores, disorder, performance

$Er_2Ti_2O_7$: hard to disorder, easy to amorphize

$Er_2Zr_2O_7$: easy to disorder, hard to amorphize
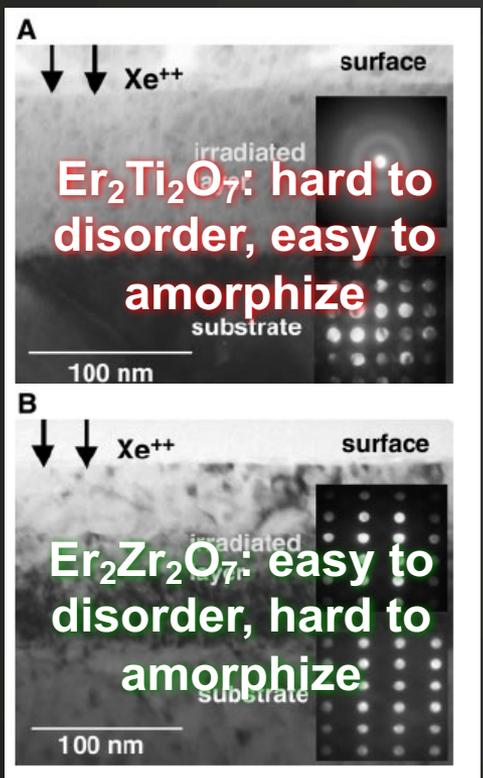
Sickafus et al., Science 289, 748 (2000)

Nuclear Waste Forms

Pyrochlore

Fast Ion Conductors

Cation Disorder

Defect Kinetics

$Gd_2(Zr_xTi_{1-x})_2O_7$
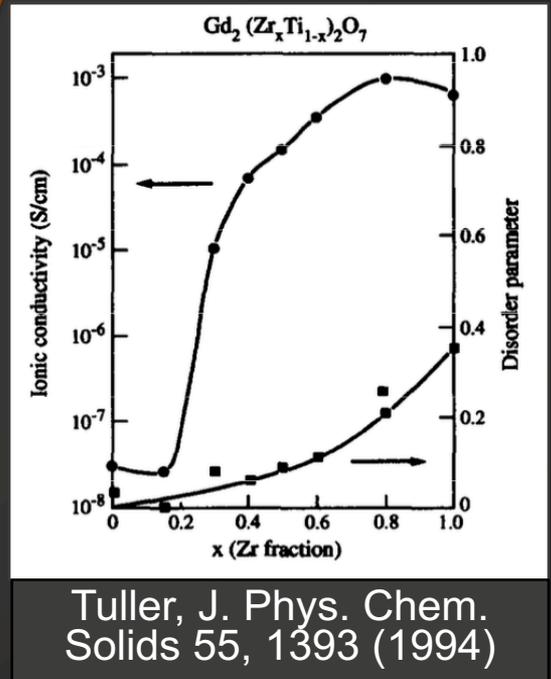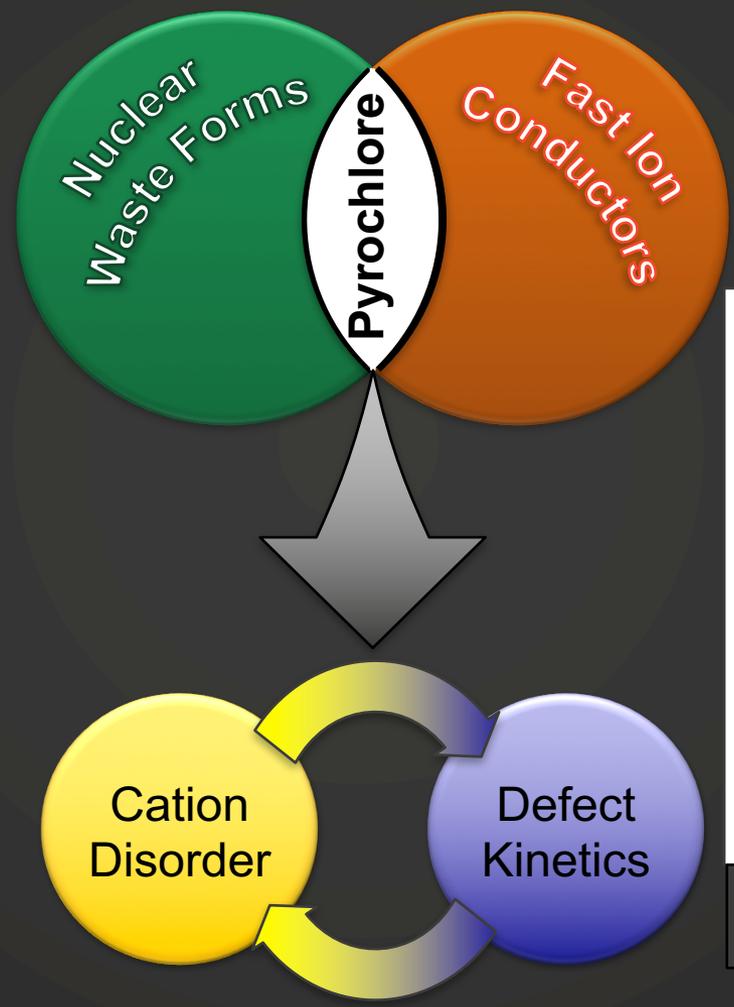
Tuller, J. Phys. Chem. Solids 55, 1393 (1994)

Disordering key for both rad tolerance and ionic conductivity

- **Chemistry of pyrochlore dictates propensity for cation disorder**

  - Chemistry critical to properties/ performance

    - Radiation tolerance

    - Ionic conductivity

- **Our goal: Connect chemistry/disordering with kinetics in pyrochlore**
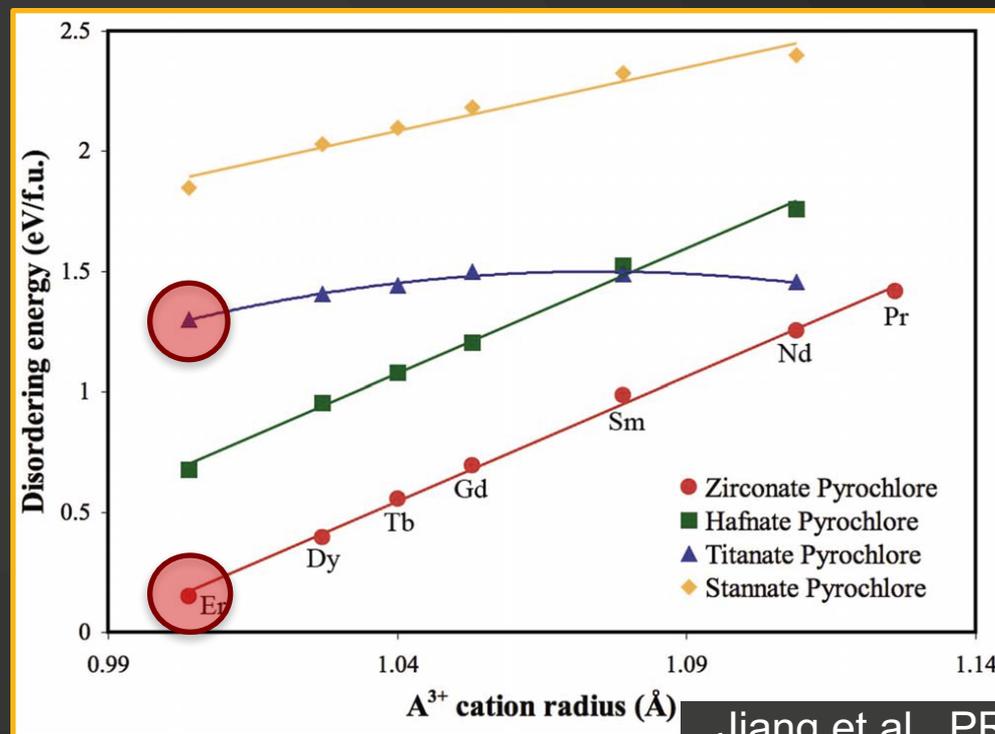
Jiang et al., PRB 79, 104203 (2009)

Structure of Pyrochlore
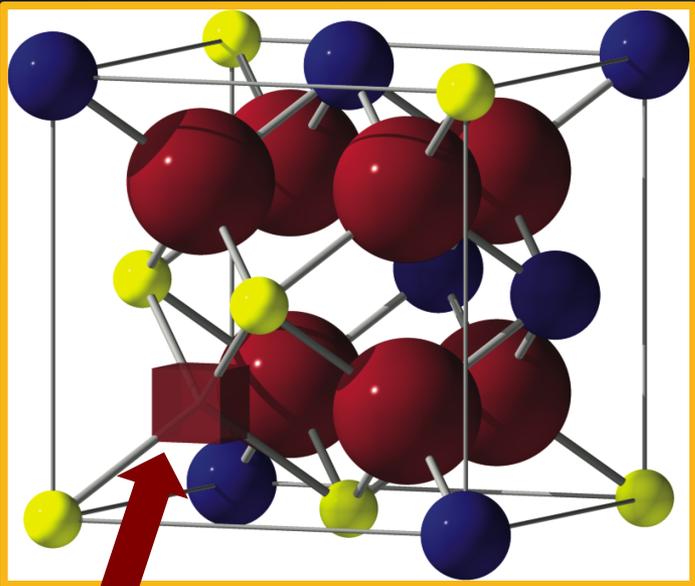
Pyrochlore is an oxygen-deficient fluorite derivative

Structural oxygen vacancies to charge compensate A^{3+} cations
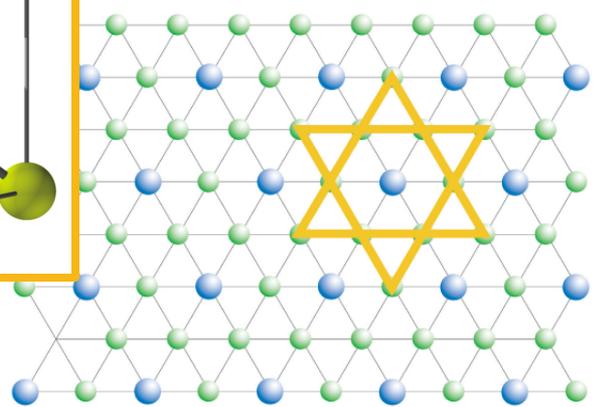
triangular atom net (*B kagome*)
Cation layer (M′)
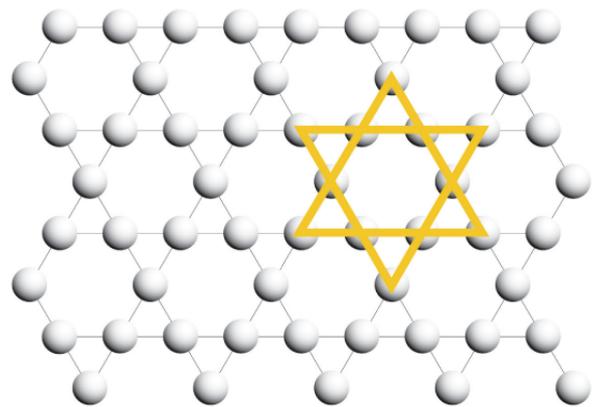
kagome pattern
Anion layer (o)

Layer Stacking Sequence: ....OMO oM′o OMO oM′o....

A_2O_3 $A_2B_2O_7$ BO_2

Figures courtesy of Chris Stanek

What is an order-disorder transformation?

- **Complex ceramics (with multiple cation sublattices) can exhibit antisite disorder**

- **Pyrochlores ($A_2B_2O_7$) are fluorite (BO_2) derivatives and can be thought of as defective fluorites with**

  - Two ordered cation sublattices (A and B)

  - Ordered structural oxygen vacancies (relative to fluorite)

- **Upon irradiation (or heating)**

  - The cations mix

  - The structural vacancies randomly distribute

$$A_A + B_B \rightarrow A_B + B_A$$
$$O_O \rightarrow V_O + O_i$$
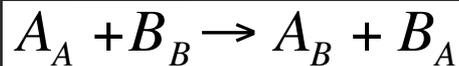
▶ Structurally indistinguishable from fluorite

A cation
oxygen
B cation

irradiation

$A_2B_2O_7$ pyrochlore

BO_2 fluorite
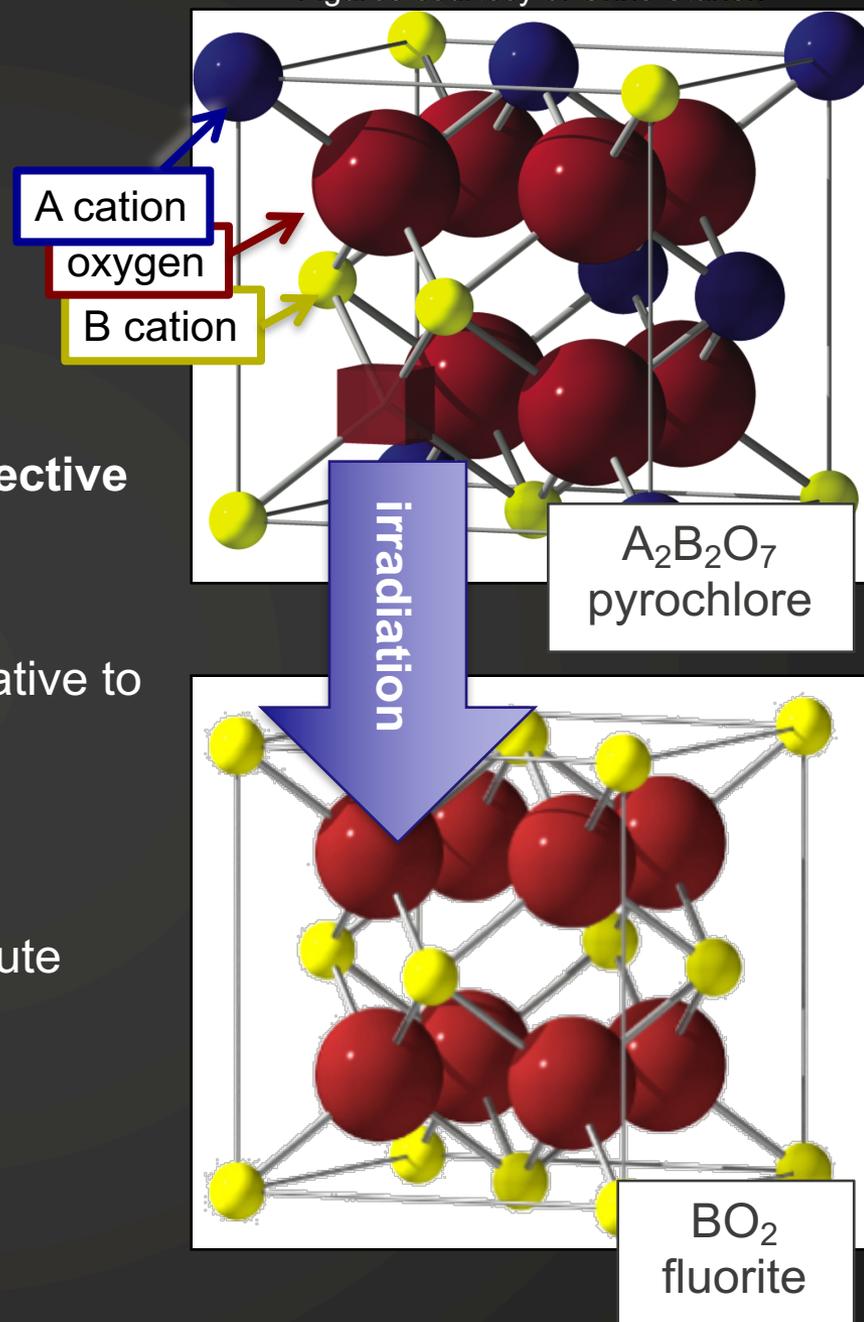
Kinetics in pyrochlore

- **Different regimes of defect mobility are responsible for different functionalities**

  - **Anion Kinetics**
    - Ionic conductivity

  - **Cation Kinetics**
    - Sintering
    - Radiation damage evolution

- **Both regimes depend on cation disorder**

Los Alamos National Laboratory

Kinetics in pyrochlore

cations

anions

TAD

Slow cation diffusion [2]

ParSplice

Slow cation/fast anion diffusion [3]

Rich dynamics, nice model system for accelerated methods

MD

F=ma

No diffusion

ion diffusion [1]

cation defects

cation disorder

ordered pyrochlore

disordered fluorite
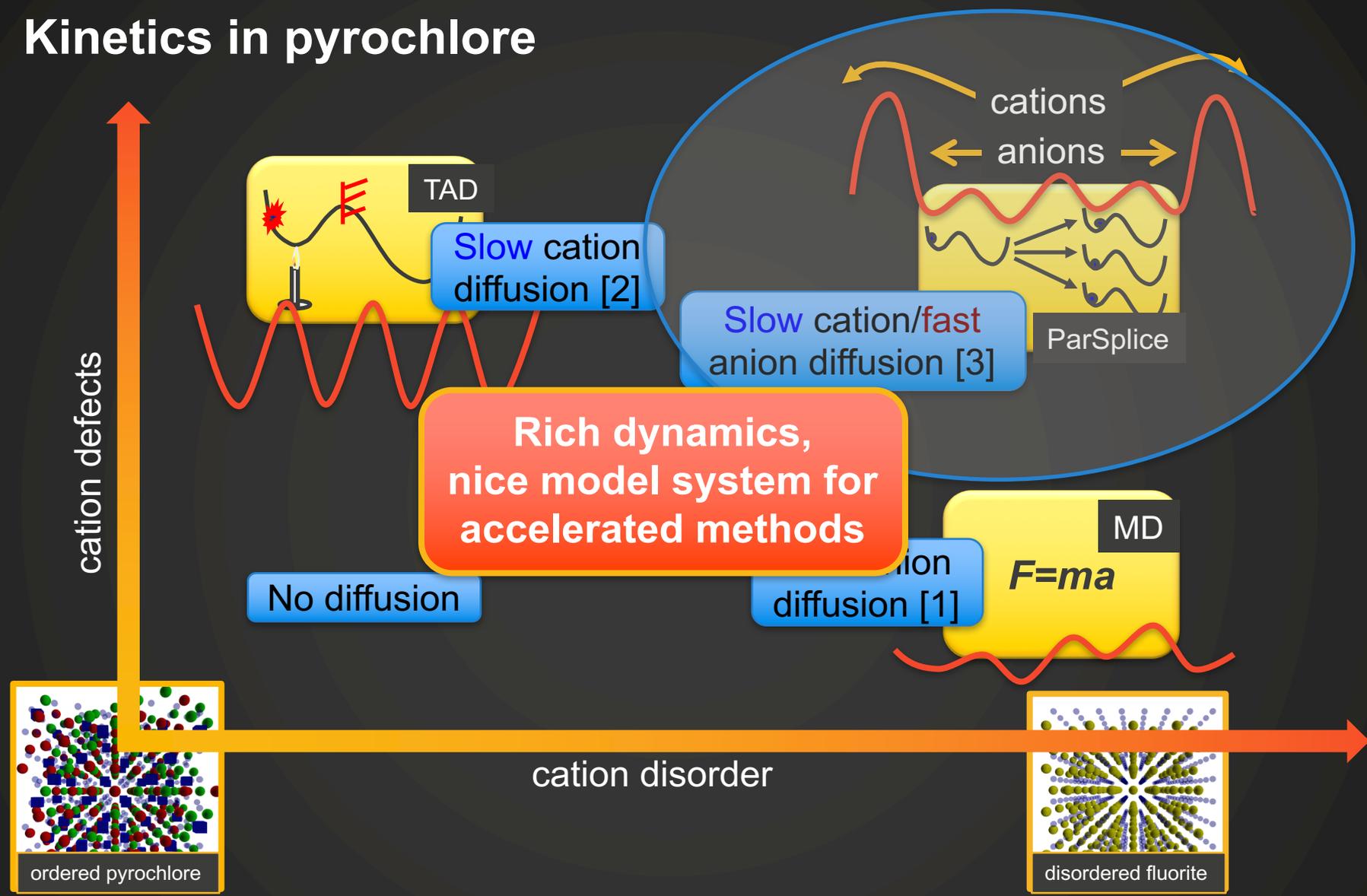
[1] Perriot & Uberuaga, J Mat Chem A 3, 11554 (2015)
[2] Uberuaga & Perriot, PCCP 17, 24215 (2015)
[3] Perriot, Uberuaga, Zamora, Perez, Voter, submitted.

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Interatomic Potential

- **Short-range Buckingham term**

$$Ae^{-r/\rho} - \frac{C}{r^6}$$

- **Long-range electrostatic term**
  - Coulombic interactions calculated with either Ewald or PPPM techniques
- **Shells not included**
- **Model does not account for charge transfer**
- **Parameters from Minervini *et al., J Am Ceram Soc* 83, 1873 (2000)**

> **We do not expect numbers to be quantitatively correct, but we do expect observed trends to be physically meaningful.**

Foundation of AMD methods: Infrequent Event System
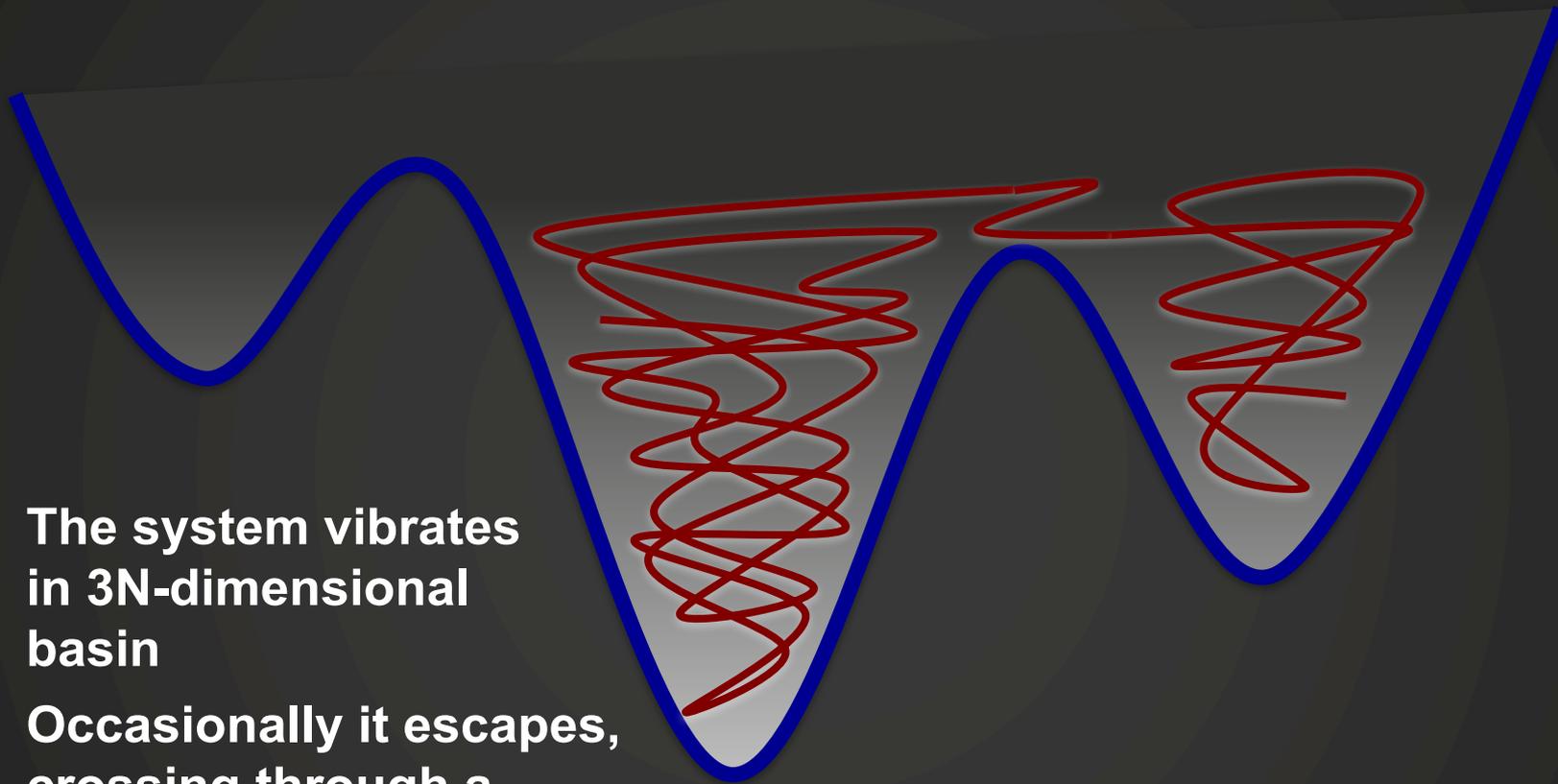
- **The system vibrates in 3N-dimensional basin**

- **Occasionally it escapes, crossing through a dividing surface to a new basin**

- **This behavior characterizes solid-state diffusion, as well as many other processes**

The Parallel-Replica Algorithm
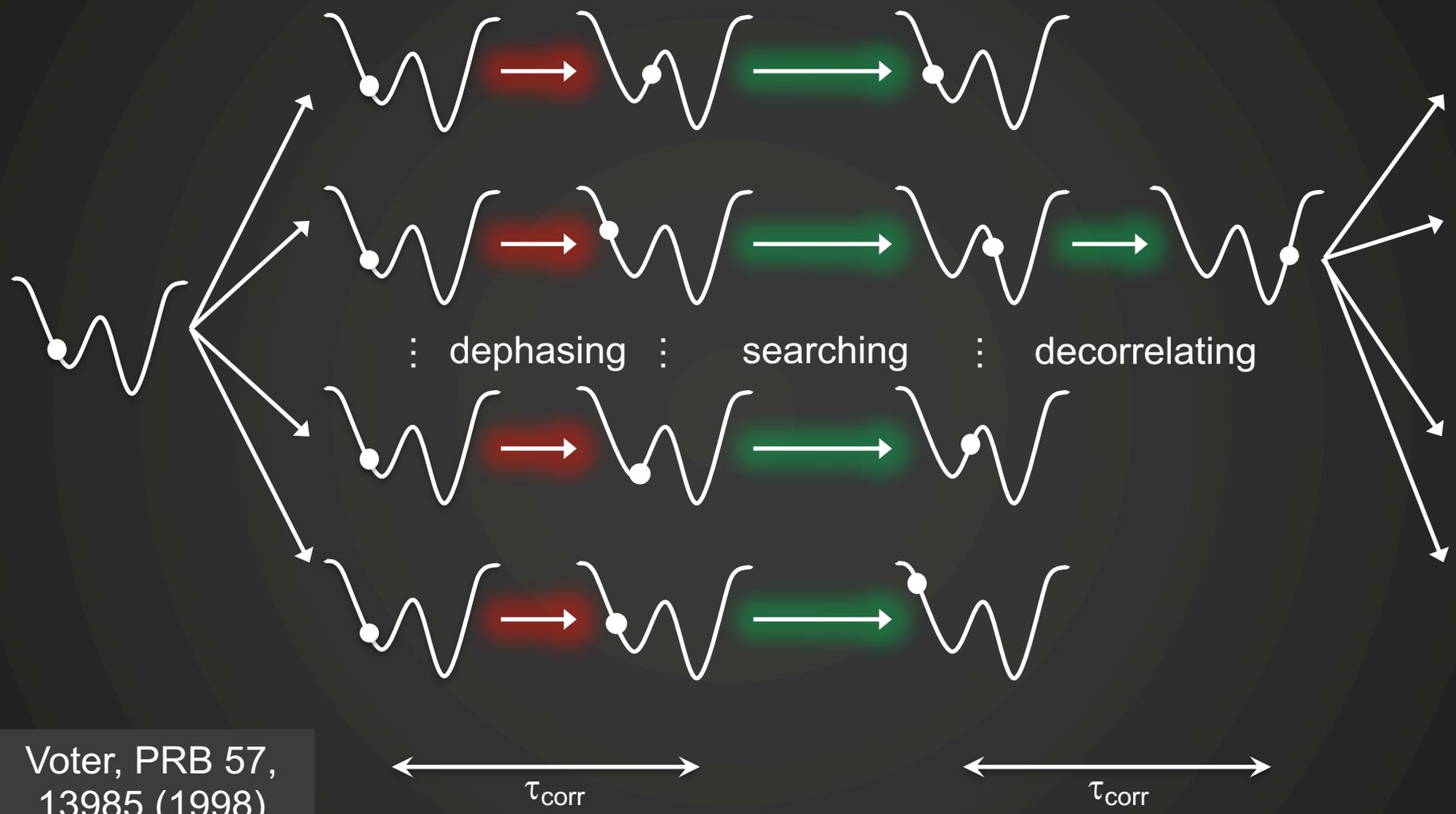
dephasing : searching : decorrelating

Voter, PRB 57, 13985 (1998)

τ_{corr}

τ_{corr}

The Parallel-Replica Algorithm

: dephasing : searching : decorrelating

Voter, PRB 57, 13985 (1998)

τ_{corr}

τ_{corr}
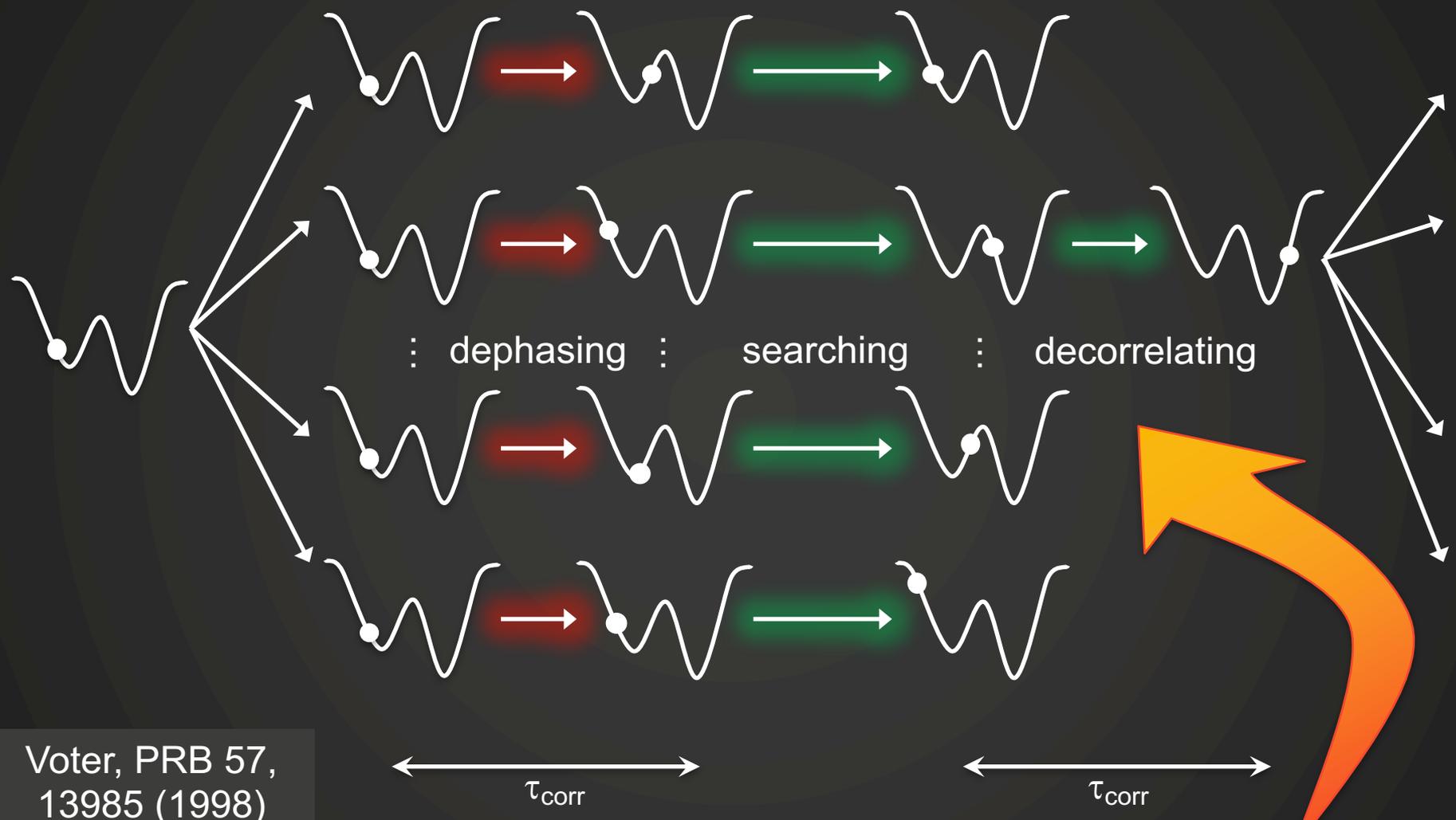
Defining/detecting transitions is a critical step

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Behavior of cations in disordered pyrochlore

- As cations are swapped, the local environment of each cation carrier becomes unique
  → *local trapping*

- Oxygen "sea" in the background
  → *cation states not so cleanly defined, rough landscape*

- Identifying all transitions would be horribly inefficient

- Parallel-replica ideal method for this situation
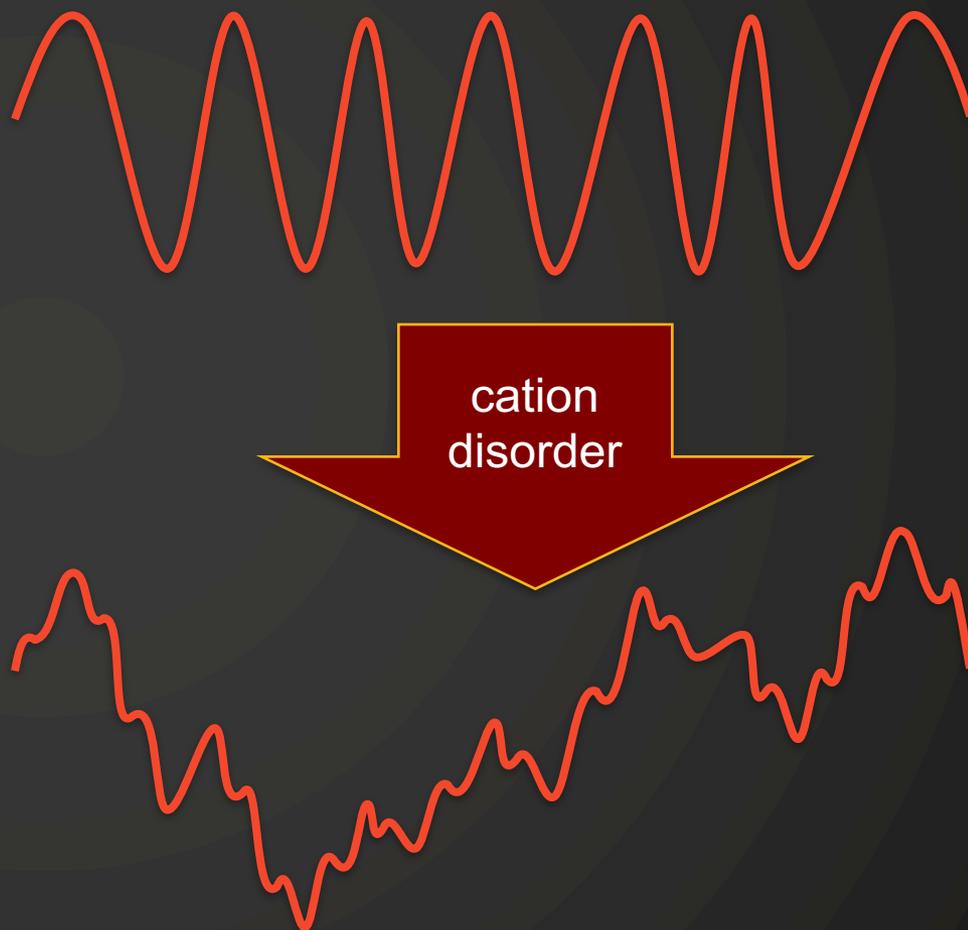
cation disorder

Events in disordered pyrochlore

- **In disordered pyrochlore, oxygen mobility is extremely high**
  → *many oxygen events per cation event*
- **Ignore oxygen dynamics, detect only cation events**
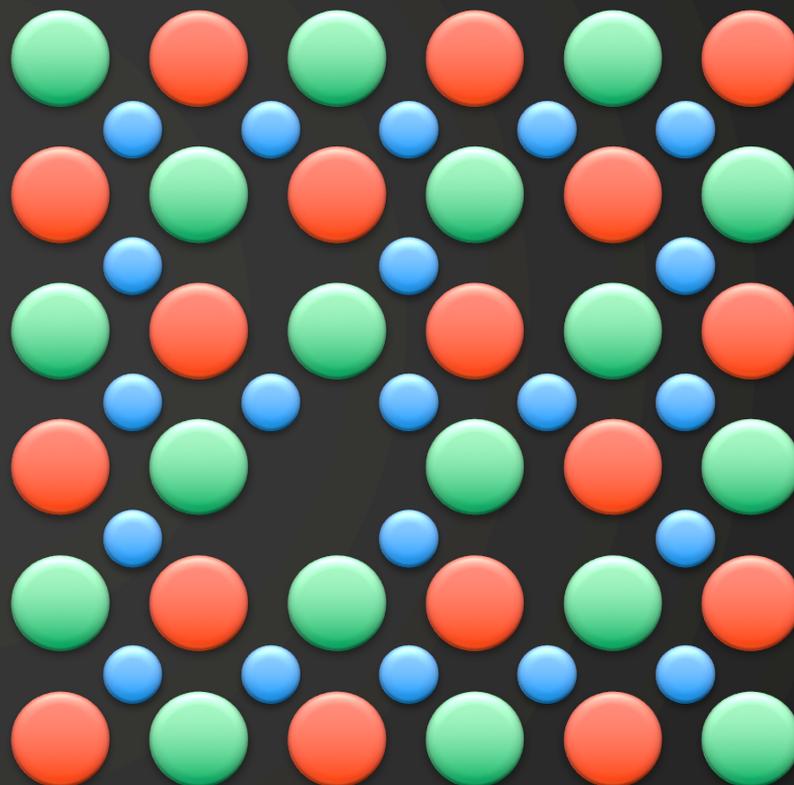
Defining cation arrangements

- **Defining cation arrangements is non-trivial**
  - Connectivity-based scheme isn't fool-proof
  - RDF never goes to zero
  - Small fluctuations in cation position change connectivity

- **Solution: map cation structure onto Voronoi volumes of reference structure**
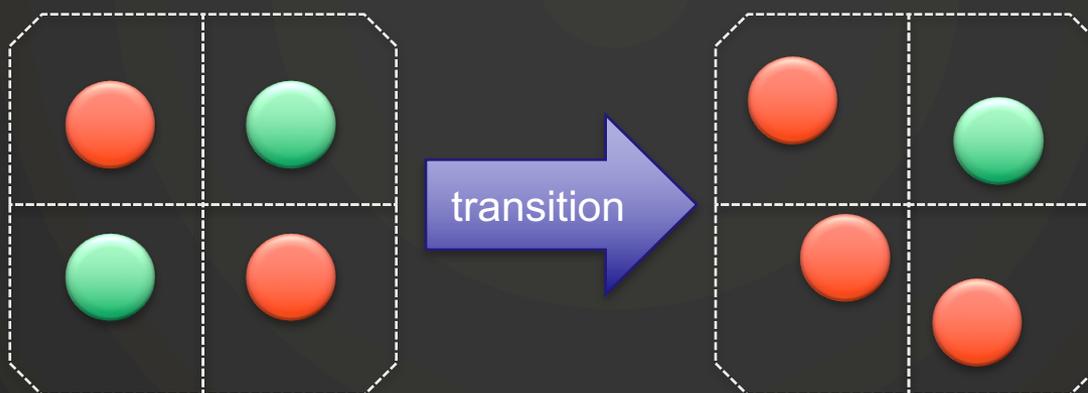
transition

- Transitions defined by change in cation identity within a volume
- Automatically accounts for permutations in atom number

Is ignoring oxygen appropriate?

- **For efficiency, preferable to ignore fast oxygen dynamics**
- **Used MD to measure "escape time" or rate of cation hops (ignoring oxygen dynamics)**
  - Gd$_2$Ti$_2$O$_7$ at 3000 K
- **Cation kinetics exhibits first order kinetics**
- ➢ **Can define events based on cations only**
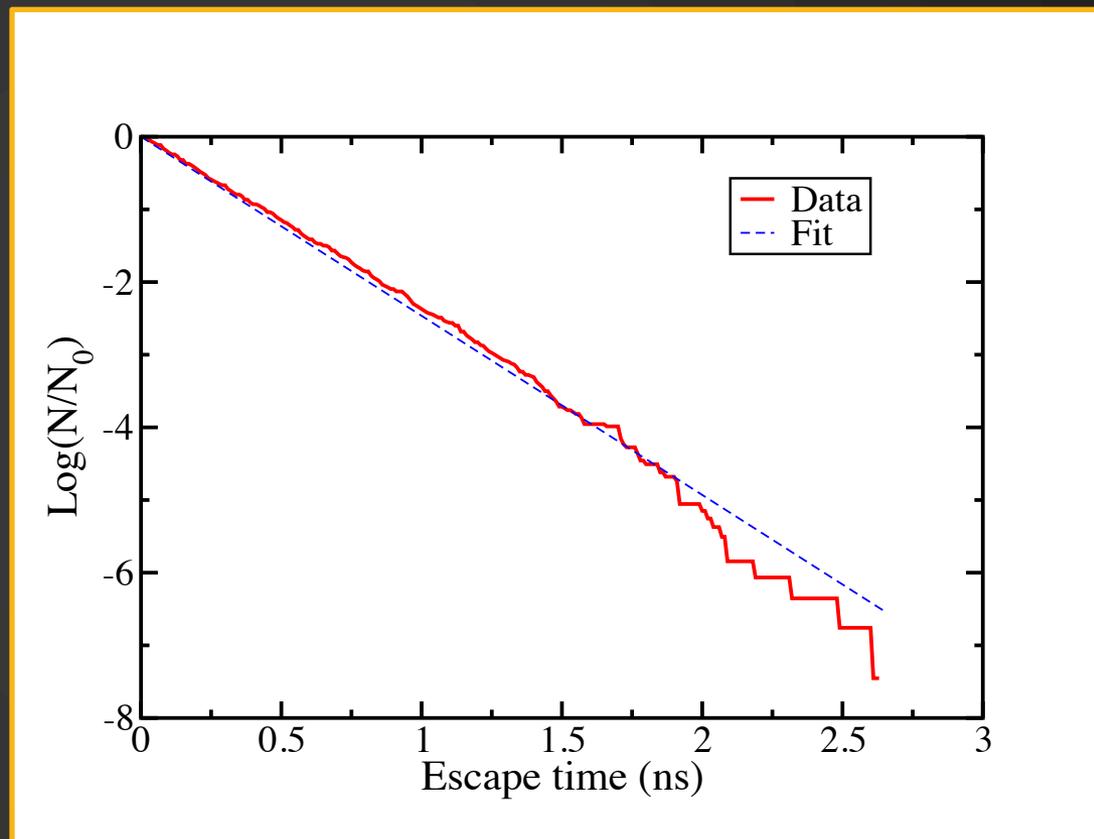
ParSplice

- **An extension to parallel-replica**
- **In parallel-replica, the states are explored sequentially**
  - This limits the number of processors that can be used
- **In ParSplice, explore states in parallel**
  - More effective use of processors; ParRep in each state plus multiple states
  - Splice together segments of trajectories to build a complete trajectory
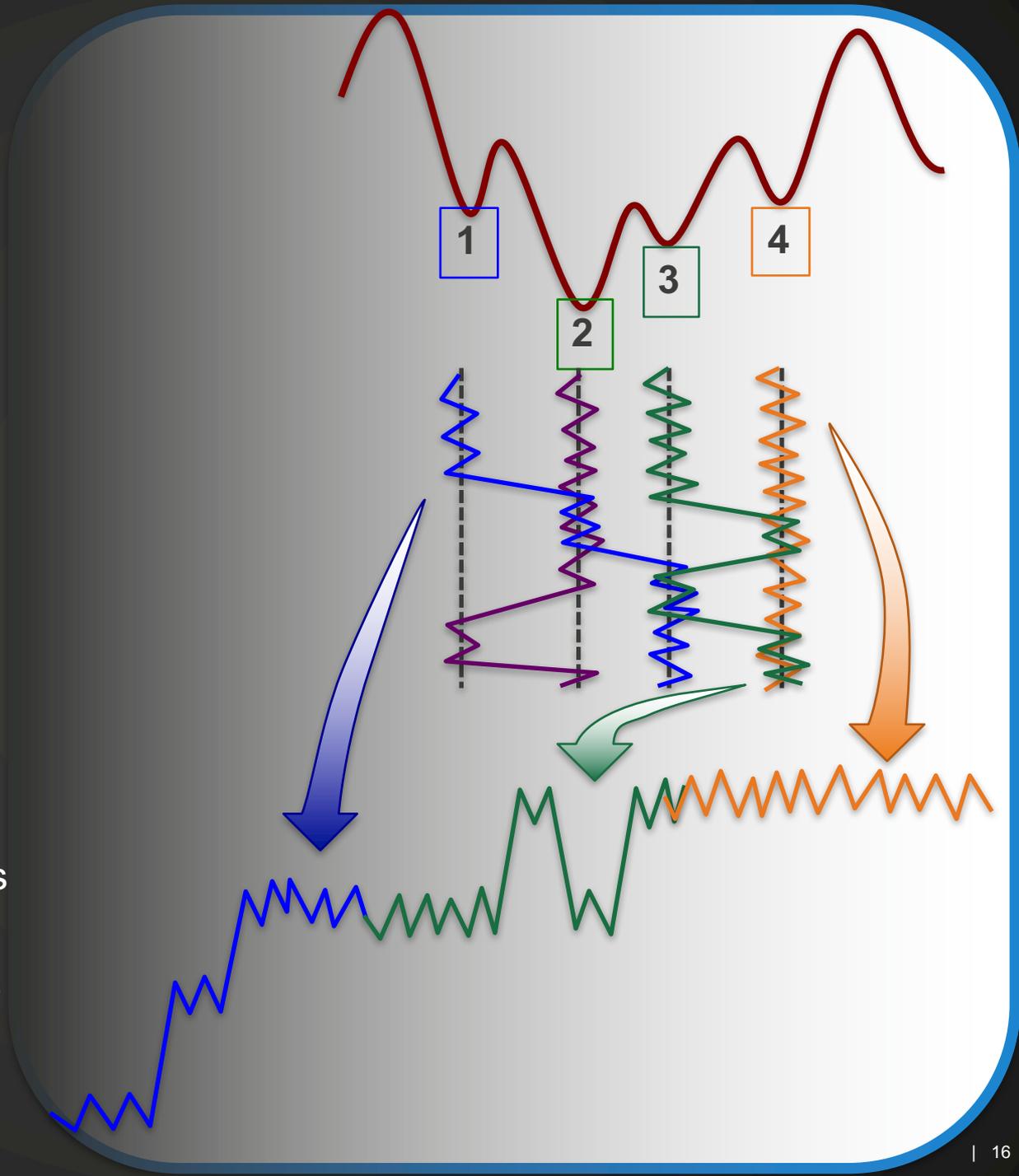
ParSplice algorithm
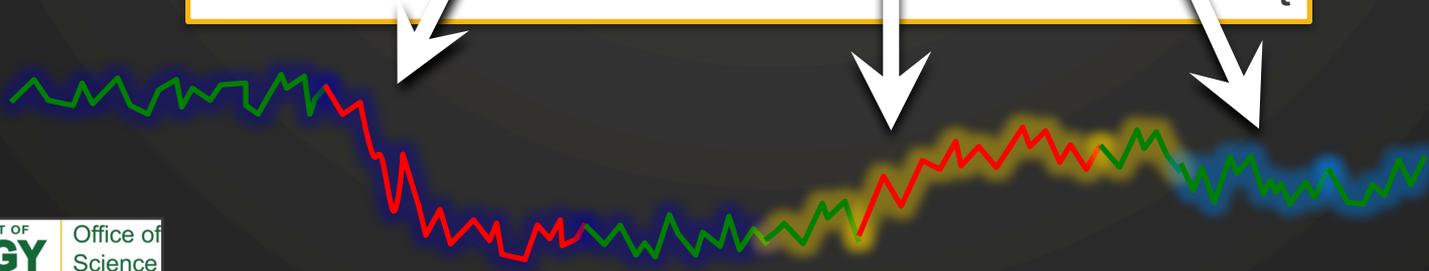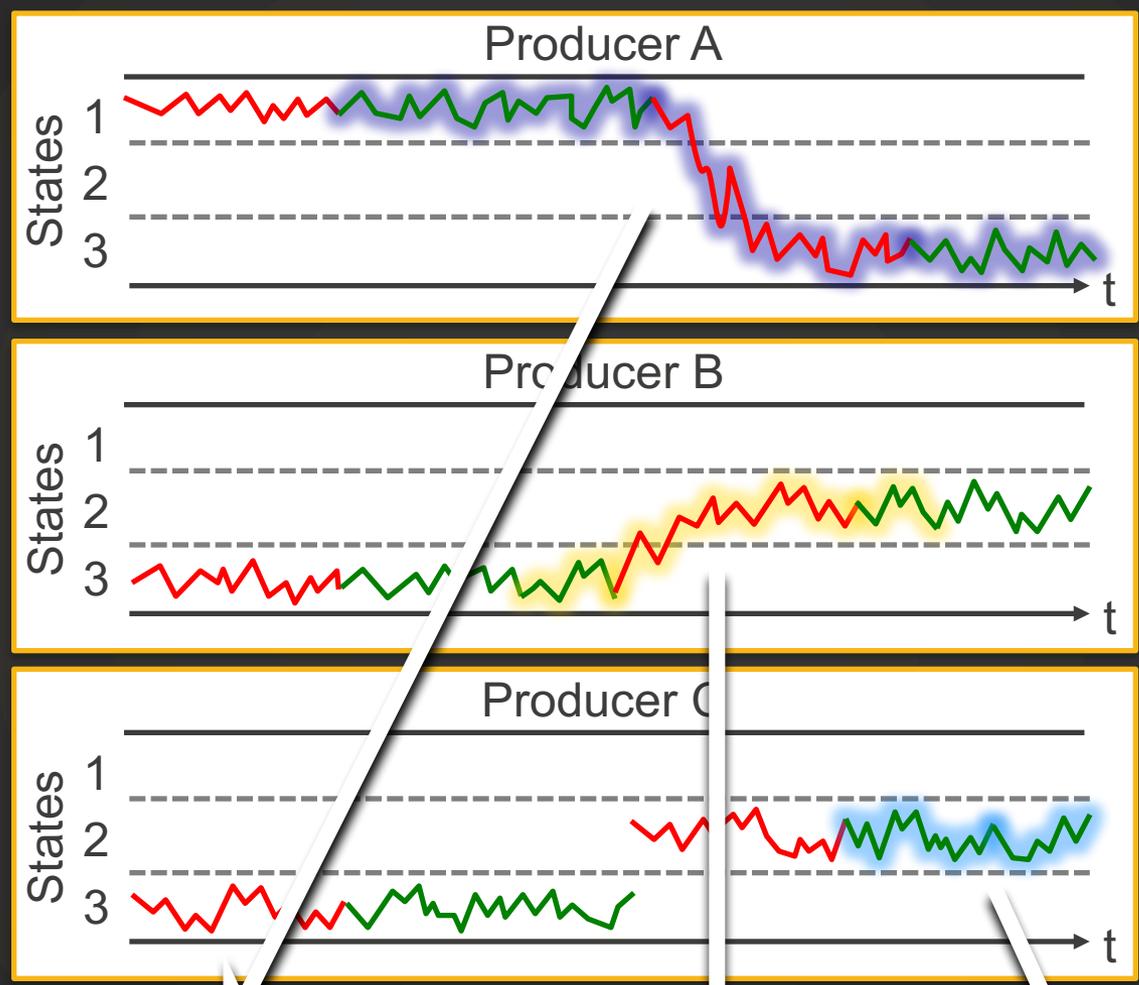
Defining disorder

- **Disorder can either be measured**
  - Globally: fraction of B cations on A sites and vice versa
  - Locally: number of neighboring cations of either A or B flavor
- **We opt for a global measure**
  - Disorder $y = 2*x*100$ %
  - $(Gd_{1-x}Ti_x)_2(Gd_xTi_{1-x})_2O_7$
  - Consistent with experimental estimates from diffraction studies
- **x determined by counting number of antisites**
- **Number of antisites measured via reference lattice method**
- **Note: results consistent with a local measure as well**

ParSplice simulation of cation interstitial in disordered $Gd_2Ti_2O_7$ pyrochlore

- **Partially disordered pyrochlore (12.5% disorder)**
  - Showing only the defects
- **Temperature: 3000 K**
- **Total simulation time: 11 microseconds**
- **Interstitial diffuses through system, annihilating antisites**
  - Level of disorder changes quickly during the course of the simulation
- **Interstitial is primarily Gd (A) in character, though changes to Ti (B) at times**

Legend
▲ antisite
■ vacancy
● interstitial
green=Gd
red=Ti

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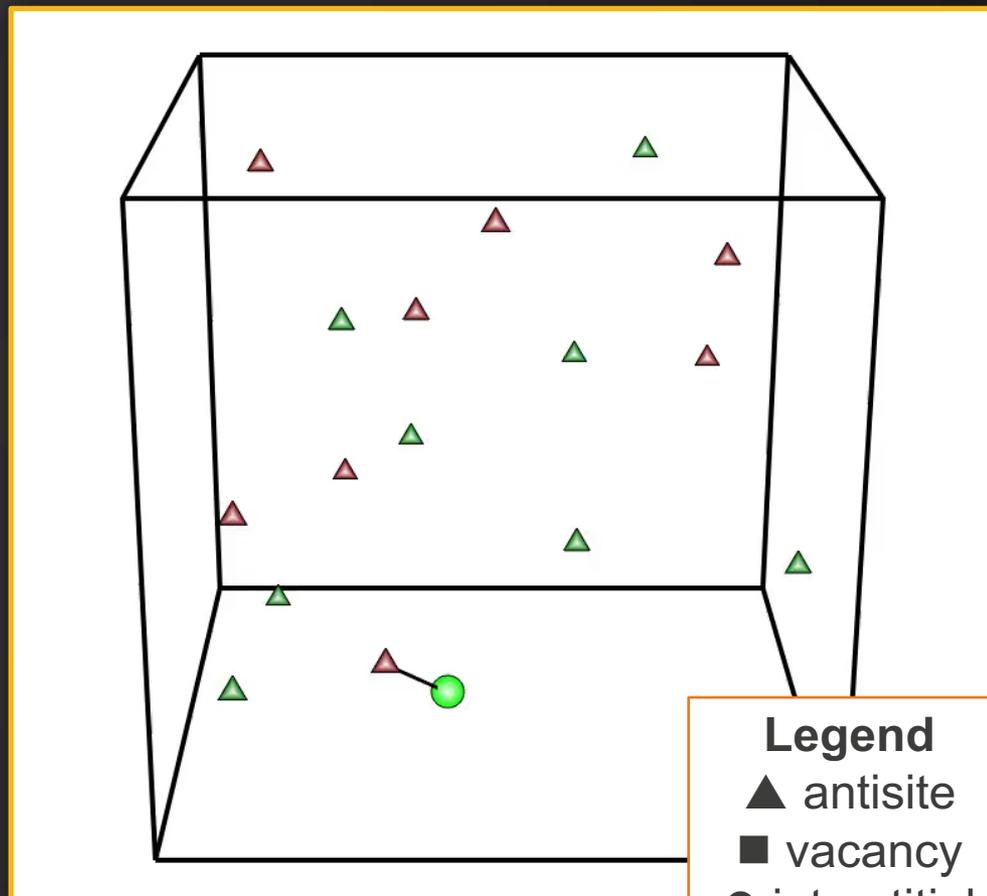
Vacancy-mediated cation diffusion in disordered pyrochlore

- **T=3500 K**
- **Combination of both ParSplice and MD**
  - MD simulations ~ 120 ns
- **Multiple regimes of cation diffusion**
  - Constant diffusivity at low disorder
  - Diffusivity begins to increase for disorder greater than 25%
  - Possibly saturates at 75% disorder
- **As vacancy diffuses, it reorders the material, and thus slows down**
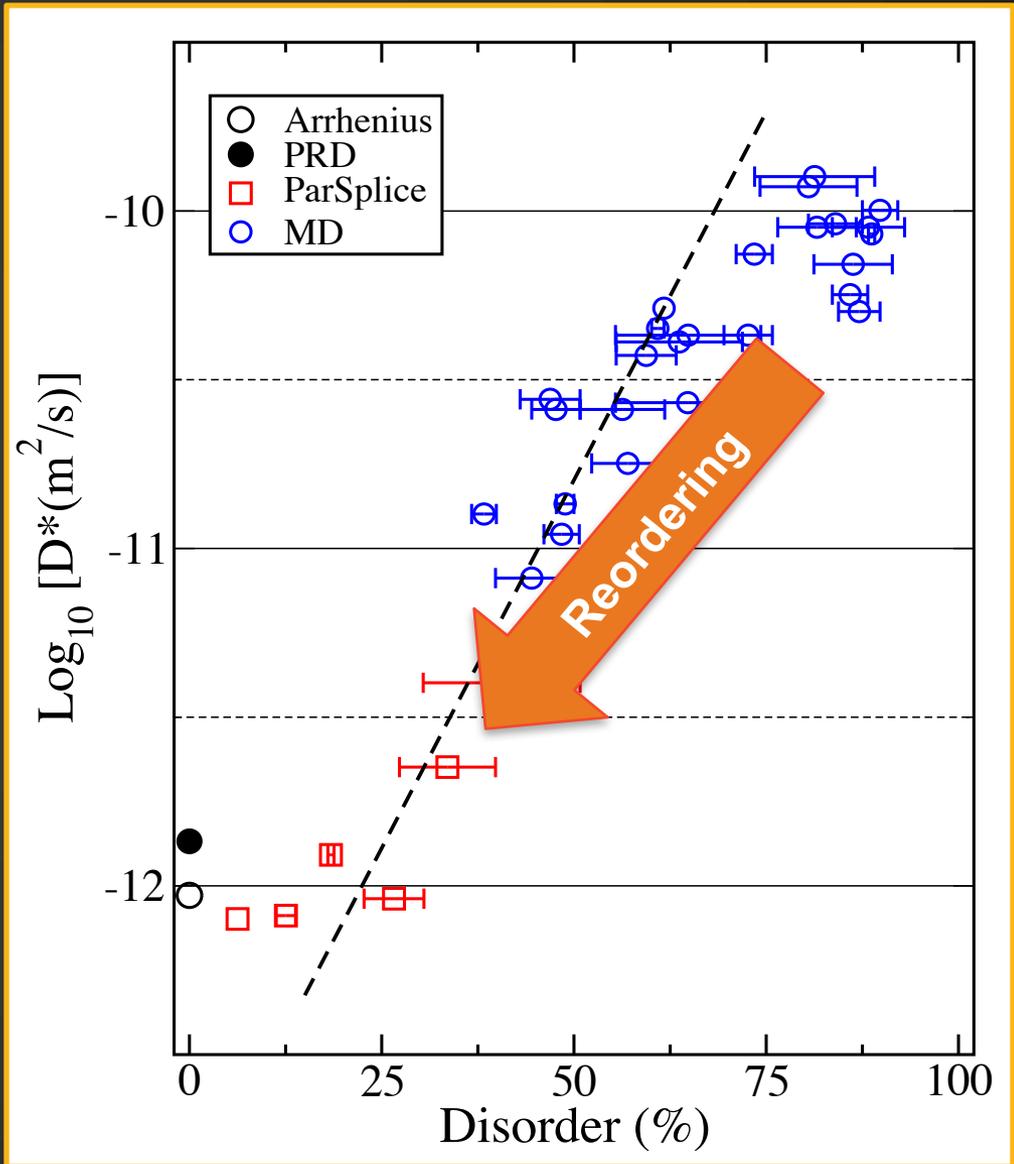
Antisite annihilation rate

- **The vacancy annihilates antisites at a higher rate when the level of disorder is higher**

- **At lower disorders (below 50%), annihilation rate decreases exponentially (annihilation time increases)**

  - Consequence of both slower vacancy migration and fewer antisites to annihilate
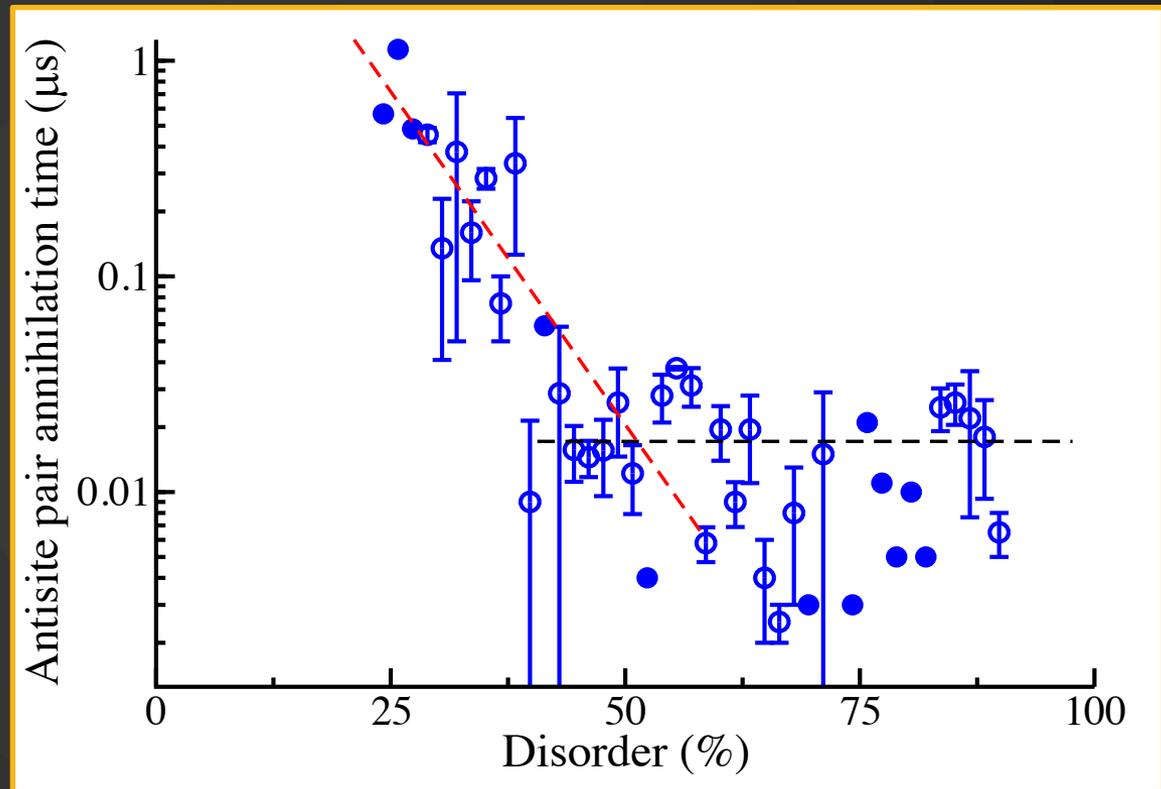
Balance between mobility and disorder

- **Example from ParSplice simulation of 50% disorder**
- **Vacancy diffuses faster in disordered pyrochlore**
- **As vacancy diffuses through system, it annihilates antisites, reordering material**
- **Vacancy diffuses slower in ordered pyrochlore**
- **Antisite annihilation rate drops**
  - Also because fewer antisites
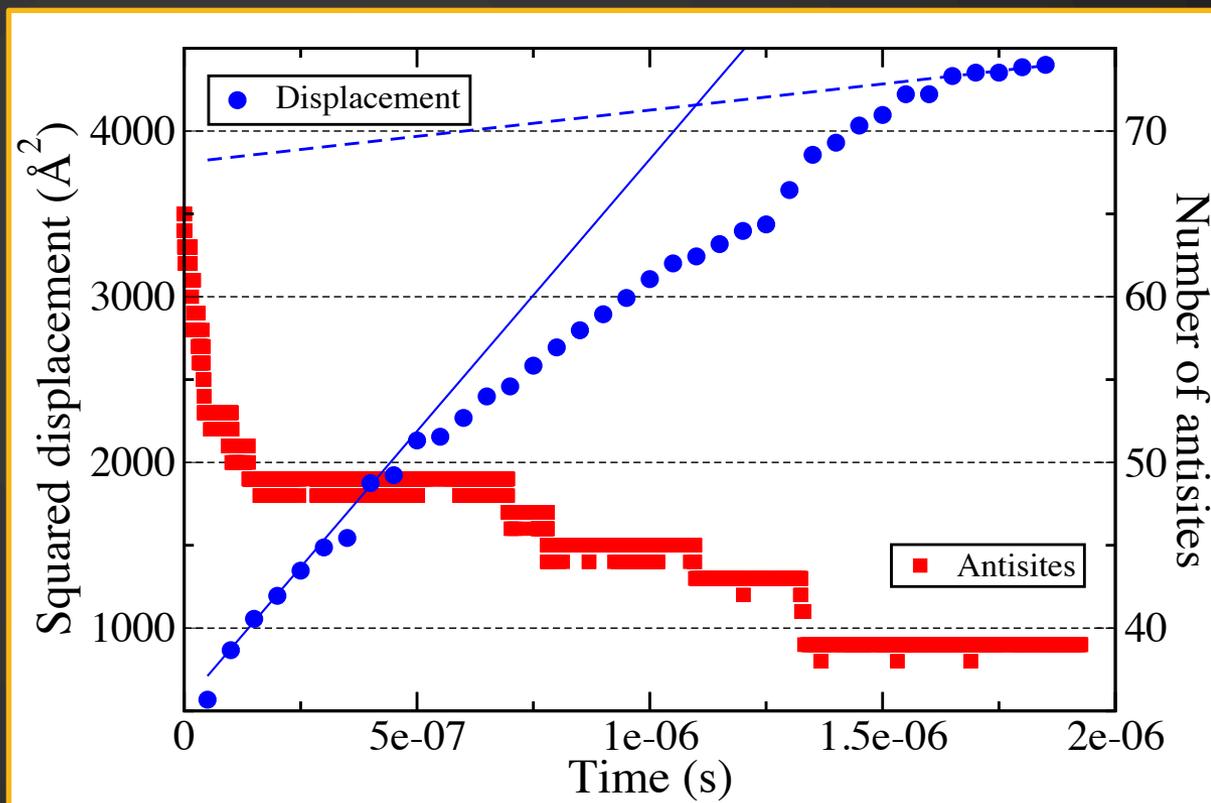
Diffusion of A vs B cations

- **Cation diffusivity dominated by A cations**
  - Always 1-2 orders of magnitude faster than B cations
- **A cation mobility requires a critical level of disorder before it increases**
- **B cation mobility increases continuously for all levels of disorder**
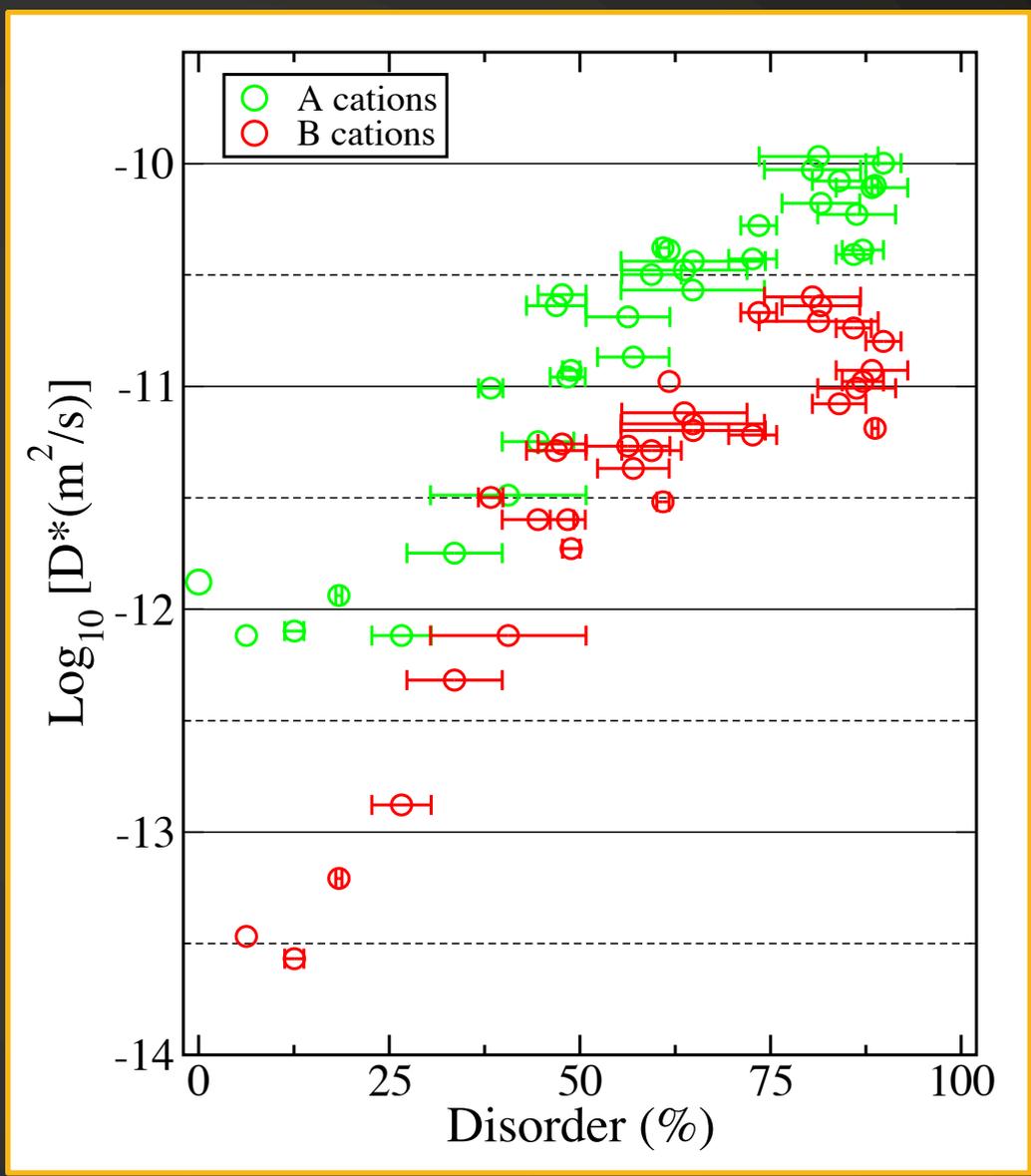
Effective cation diffusivity in defect fluorite versus pyrochlore

- **Measure diffusion constant at multiple temperatures, extract effective activation energy for vacancy-mediated diffusion**
- **Activation energy for vacancy-mediated cation diffusion much higher in defect fluorite than in ordered pyrochlore**
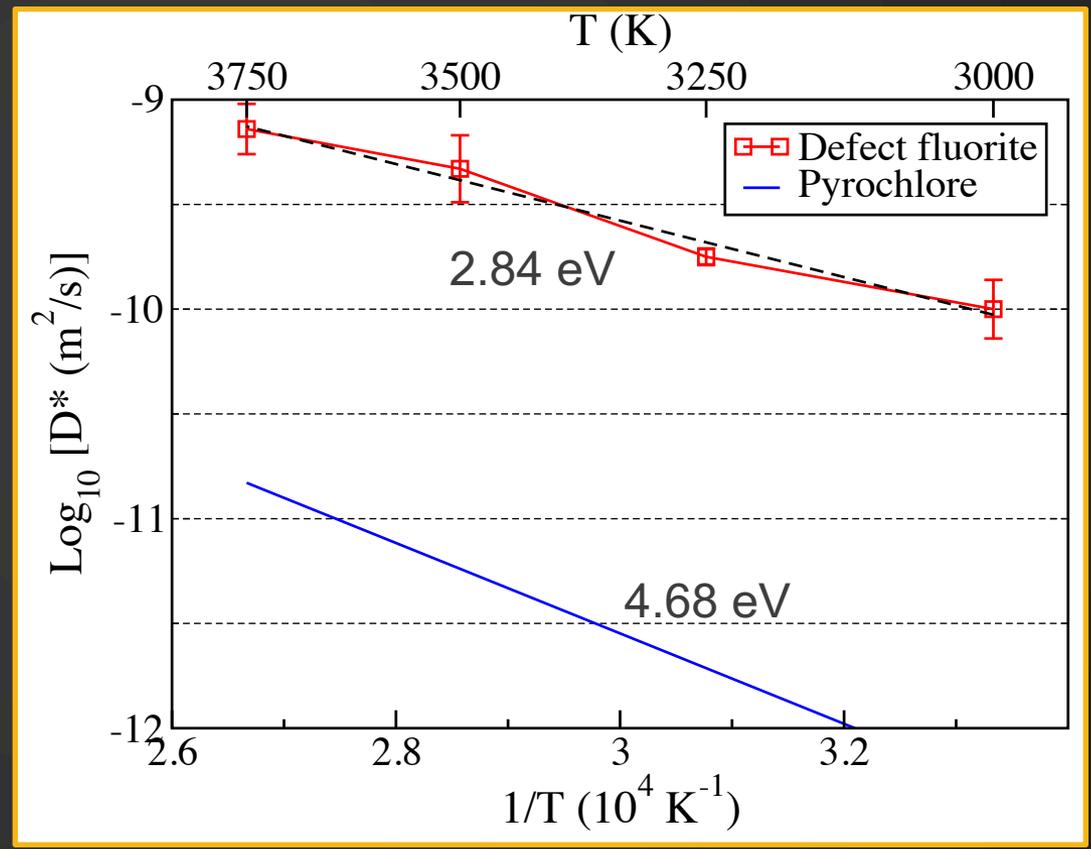
Percolation behavior

- **Dynamics revealed critical level of disorder for increasing diffusion → percolation behavior?**
- **Evidence for percolation behavior**

(a) The vacancy strongly prefers disordered cation environments

V$_{Gd}$ environment

6
5

0.24

(b) That preference is not simply a function of possible environments

Distribution of environments

6
5

0.16

Slow diffusion

Pyrochlore

Fluorite

Fast diffusion

Pyrochlore

Fluorite

(c) hopping rate the vacancy is high between disordered sites

N[Gd$_{Ti}$]
4
3
2
1
0
0 1 2 3 4 5 6
N[Ti$_{Gd}$]

10^{10}
10^{9}
rate (Hz)
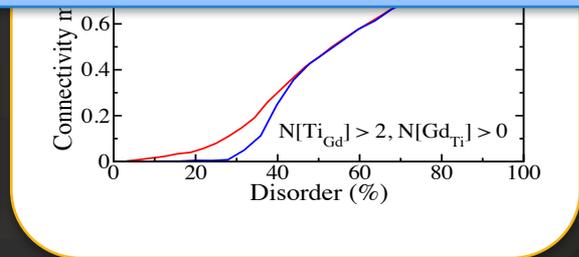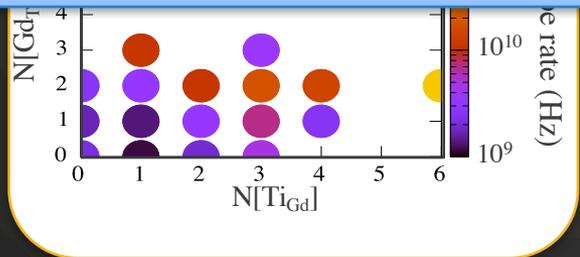
The connectivity of disordered sites increases above disorder levels of 25%

Connectivity
0.6
0.4
0.2
0
0 20 40 60 80 100
Disorder (%)

N[Ti$_{Gd}$] > 2, N[Gd$_{Ti}$] > 0

Performance of ParSplice: Visited states vs time

- 'state id' is unique identifier for visited states

- Evolution of state id versus time shows clear regimes of relatively constant id and others in which the id changes quickly

- Signature of super basins
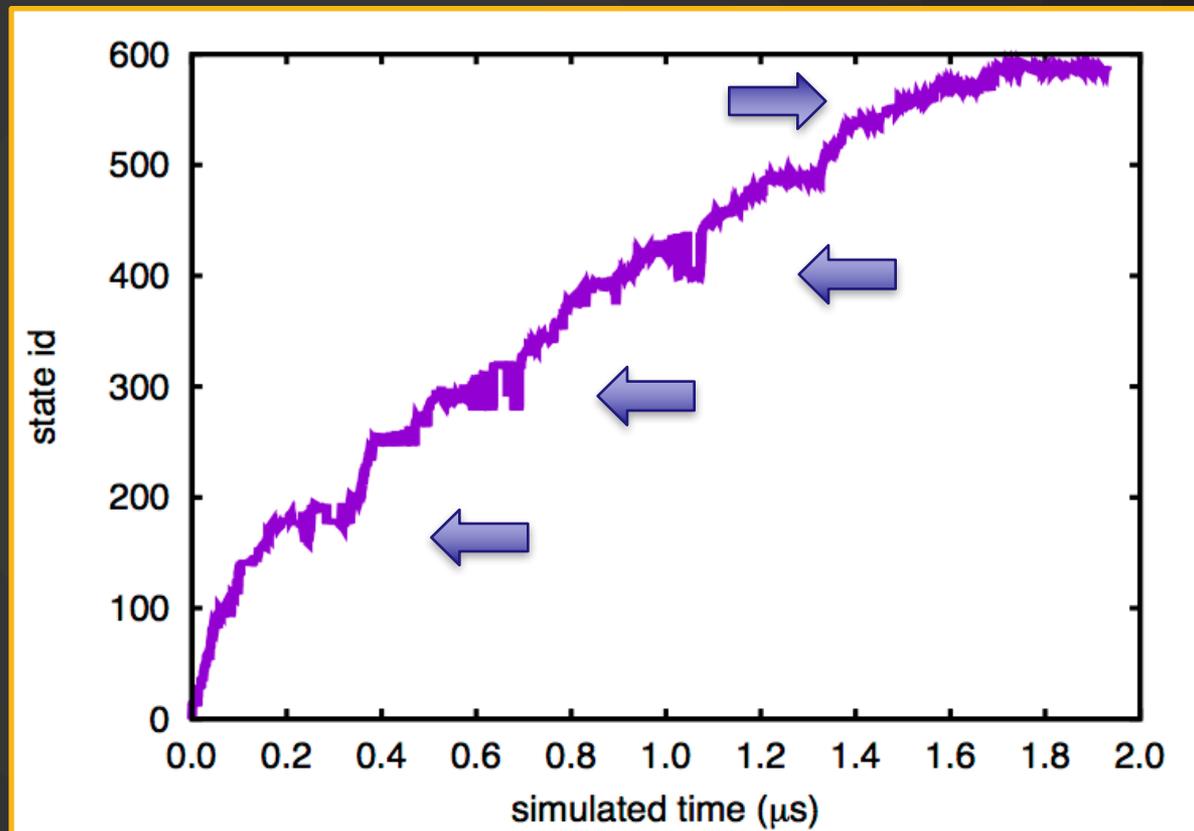
Performance of ParSplice: Segment generation/use

- **At the beginning, only about half of the segments generated are used**
  - A consequence of both the development of the database and the transient nature of the dynamics
- **As the system finds super-basins, more and more segments are generated**
  - ParSplice becomes more efficient
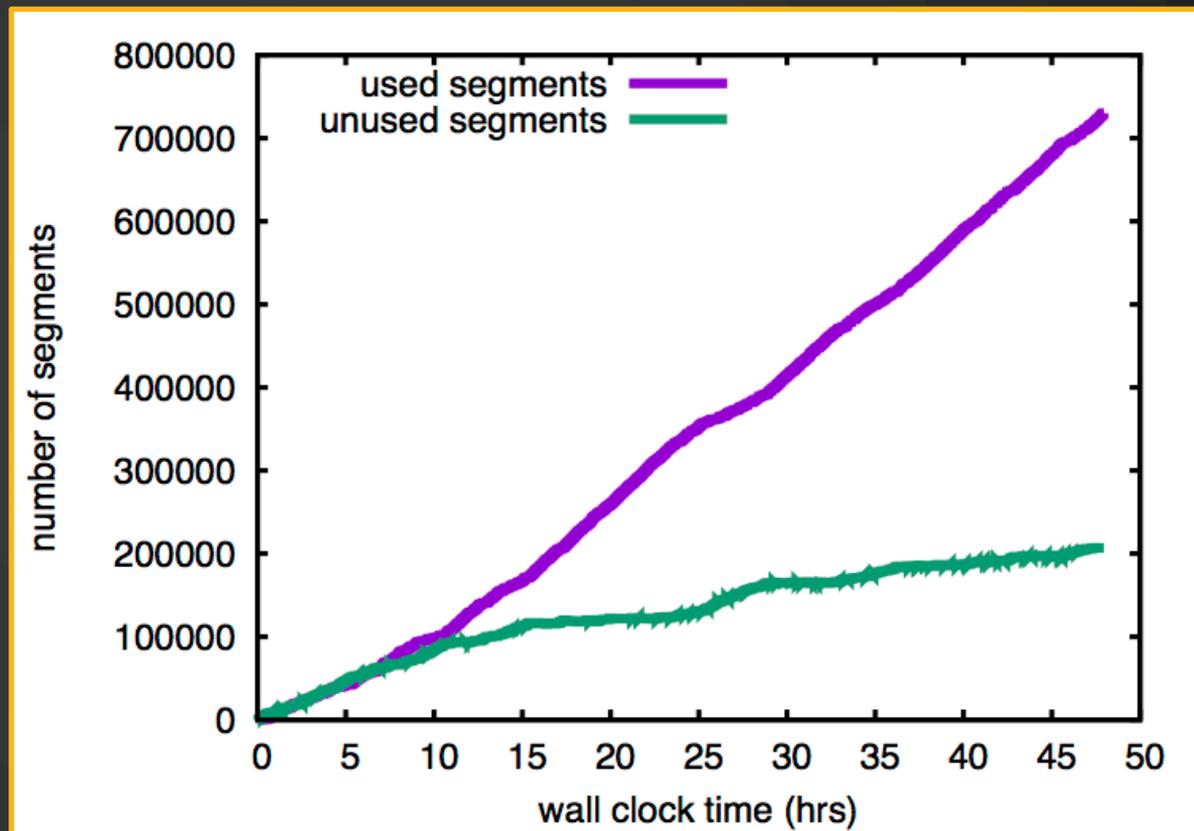
Speculation: critical point in disorder during irradiation?

- **Starting with some level of disorder, cation mobility will lead to reordering of material**
  - Annihilation rate depends on level of disorder
- **Under irradiation, disorder created via external driving force**
- **Does this competition lead to a closed loop and a critical point?**
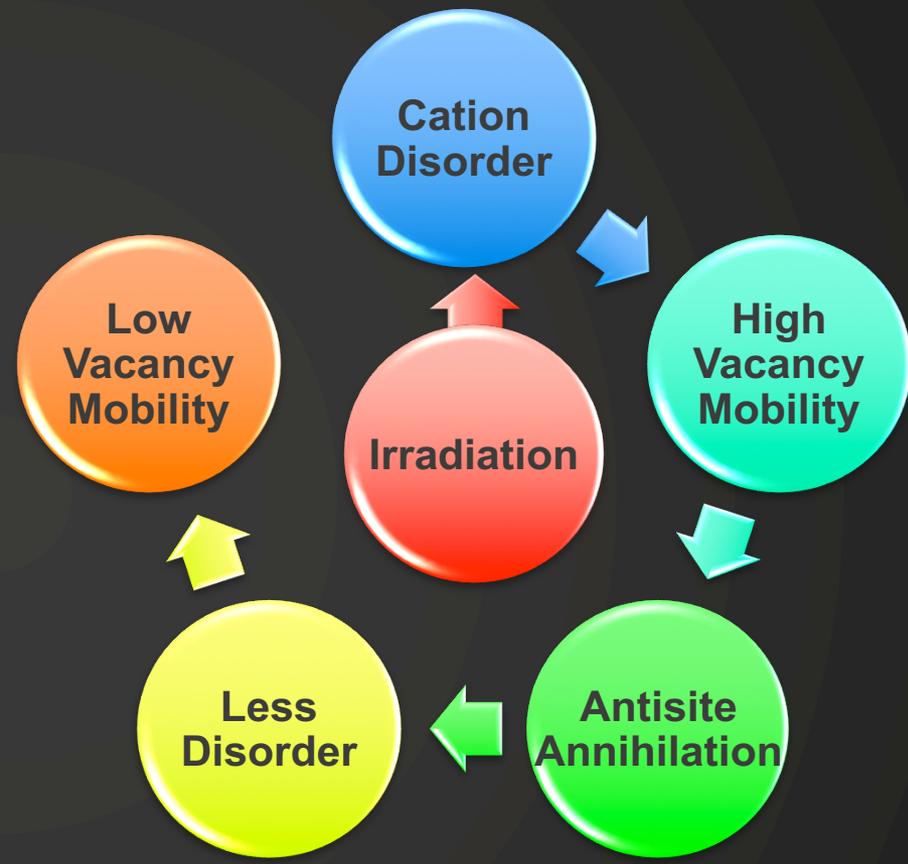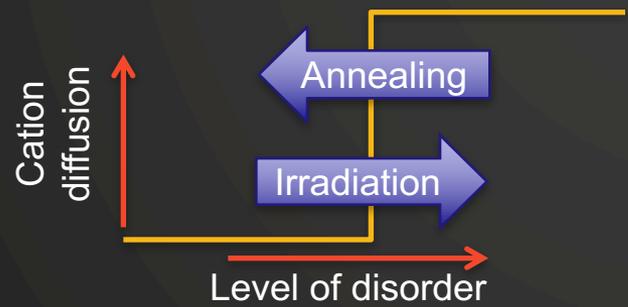
- **Future work: develop model of this loop**

Conclusions

- **Cation diffusion in pyrochlore is a strong function of the level of disorder**
- **As cations migrate, they reorder the crystal**
- ➢ **Cation migration slows down as the material reorders**

- **There is a critical level of disorder for cation diffusion to activate**
- **Evidence for a percolation transition:**
  - Cation vacancies spend more time in disordered regions
  - Cation vacancies move faster in disordered regions
  - Connected regions of disorder occur for higher levels of disorder
- ➢ **Cation diffusion driven by a percolation threshold of disordered fluorite within pyrochlore**

- ➢ **ParSplice can accelerate dynamics even in such complex landscapes**