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"Neutron Diffraction of ErD_2 powders"

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Structural Analysis of T-site occupancy in ErT_2 films is very challenging

- Difficult determination of (H,D,T) in host lattice via XRD (i.e. only $1e^-$).
- (D,T) scatter well for neutron diffraction experiments.
- Strong texture of ErT_2 films complicates structural analysis.
- Loose powders are more random, providing straightforward analysis.
- Loose powder of ErT_2 is major contamination issue.

- Loose powders of ErD_2 chosen as surrogate powders for structural analysis of the fluorite lattice.
  - Gain insight into site occupancy without hazards of tritium

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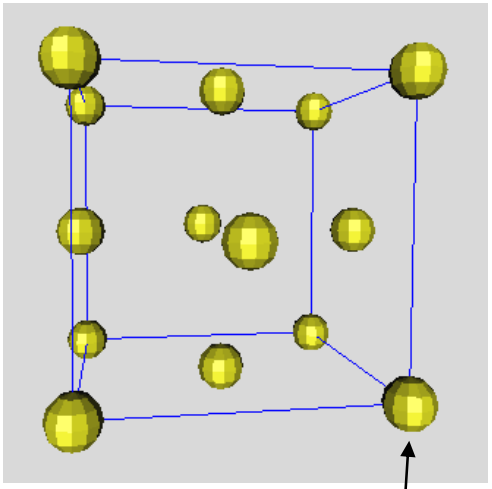
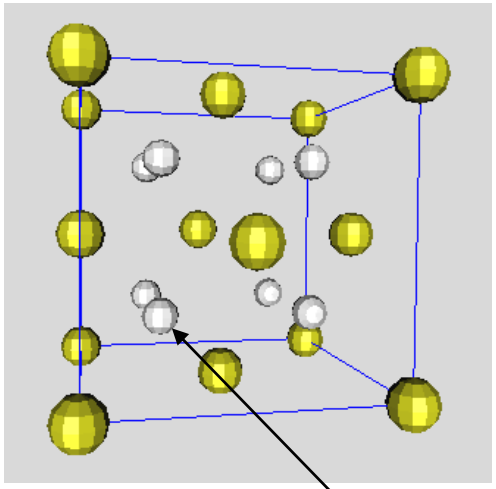
Fluorite structure of ErD_2

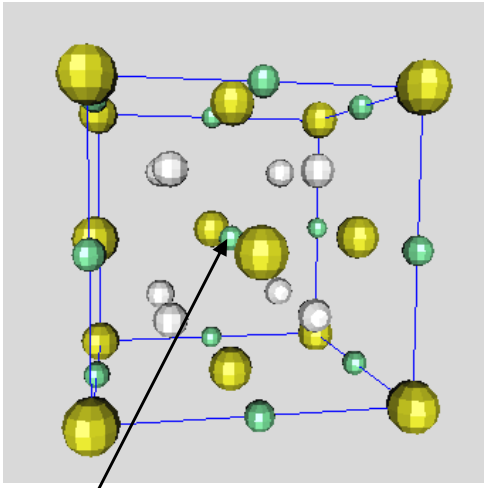
Where is the D going?



FCC lattice of Er



D occupies tetrahedral (¼, ¼, ¼) sites



Octahedral (½, ½, ½) sites could also contain D*

* T. J. Udovic, J.J. Rush, and I. S. Anderson, *Phys. Rev. B,* **50,** pp.7144 (1994)

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ErD_2 powder analysis

- Er metal D-loaded at various temperatures/pressures.
- ErD_2 powder specimens mixed with silicon powder standard.
- Powders placed in Vanadium canisters.
- Neutron diffraction data collected using HIPD at LANSCE/LANL.
- Structure refinements performed using GSAS software.
- Two run cycles (FY04 and FY05).

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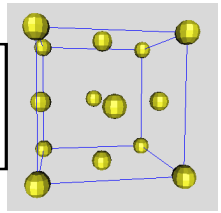
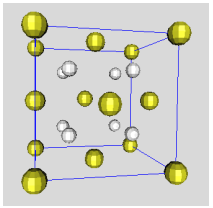
How D changes relative intensities (I_{rel}) for the ErD_2 fluorite-type structure

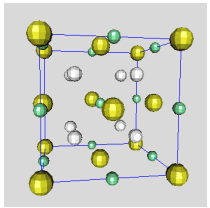
Model 1
Er only



Model 2
Er + D_{tet}



Model 3
Er + D_{tet}
+ 10% D_{oct}



XRD calculated patterns

hkℓ	d (Å)	I_{rel} (%) Model 1	I_{rel} (%) Model 2	I_{rel} (%) Model 3	Diff % 3-1
111	2.954	100	100	100	
200	2.558	51	49	49	-2
220	1.808	35	36	36	+1
311	1.543	40	40	40	
222	1.477	11	11	11	
400	1.279	5	5	5	
331	1.174	15	15	15	
420	1.144	13	13	13	
422	1.044	10	10	10	

Neutron calculated patterns

hkℓ	d (Å)	I_{rel} (%) Model 1	I_{rel} (%) Model 2	I_{rel} (%) Model 3	Diff. % 3-1
111	2.954	100	26	21	-79
200	2.558	56	6	5	-51
220	1.808	55	100	100	+45
311	1.543	78	20	16	-62
222	1.477	24	3	2	-22
400	1.279	13	24	24	+11
331	1.174	45	12	9	-36
420	1.144	43	5	4	-39
422	1.044	36	67	67	+31

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Neutron Powder Diffraction results - FY04

ErD_2 powder (450 °C) loading

Crystal structure data

atom	x,y,z	occ.	B(Å²)
Er	0,0,0	1.0	0.15(2)
D_{tet}	¼,¼,¼	1.00(1)	1.01(2)
D_{oct}	½,½,½	0.02(1)	1.01

a = 5.1187(2) Å

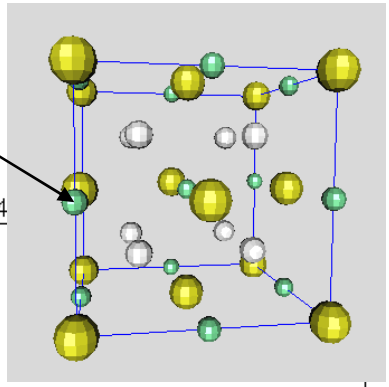
Formula: $ErD_{tet(2.02)}D_{oct(0.02)}$

Vol = 134.11 Å³

D_x = 8.48 g/cm³

Silicon 640c used as internal standard

D_{oct} ~2%



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Neutron Powder Diffraction results - FY04

ErD_2 powder (350 °C) loading

Crystal structure data

atom	x,y,z	occ.	B(Å²)
Er	0,0,0	1.0	0.28(2)
D_{tet}	¼,¼,¼	1.01(1)	1.25(3)
D_{oct}	½,½,½	0.10(1)	1.25

a = 5.1166(2) Å

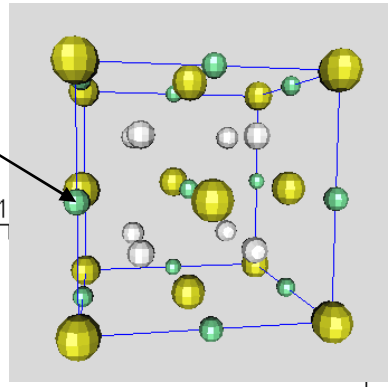
Formula: $ErD_{tet(2.02)}D_{oct(0.10)}$

Vol = 133.95 Å³

D_x = 8.51 g/cm³

Silicon 640c used as internal standard

D_{oct} ~10%



XRD shows a = 5.116(1)

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Results on ErD_2 powders – FY04

- At same pressure, lowering temperature (450 → 350 °C) encourages octahedral site occupancy.
- A corresponding shrinkage of the unit cell is observed with increased octahedral site occupancy.
- Tetrahedral site occupancy is essentially full for both structures.

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More recent ErD_2 powders – FY05

- Sample powders were prepared using same temperature and pressure (350 ^oC, 32 torr).
- One powder was analyzed "as-prepared", while the other powder was annealed prior to neutron diffraction analysis.
- Powders were run as a function of temperature from 20 to 300 K.

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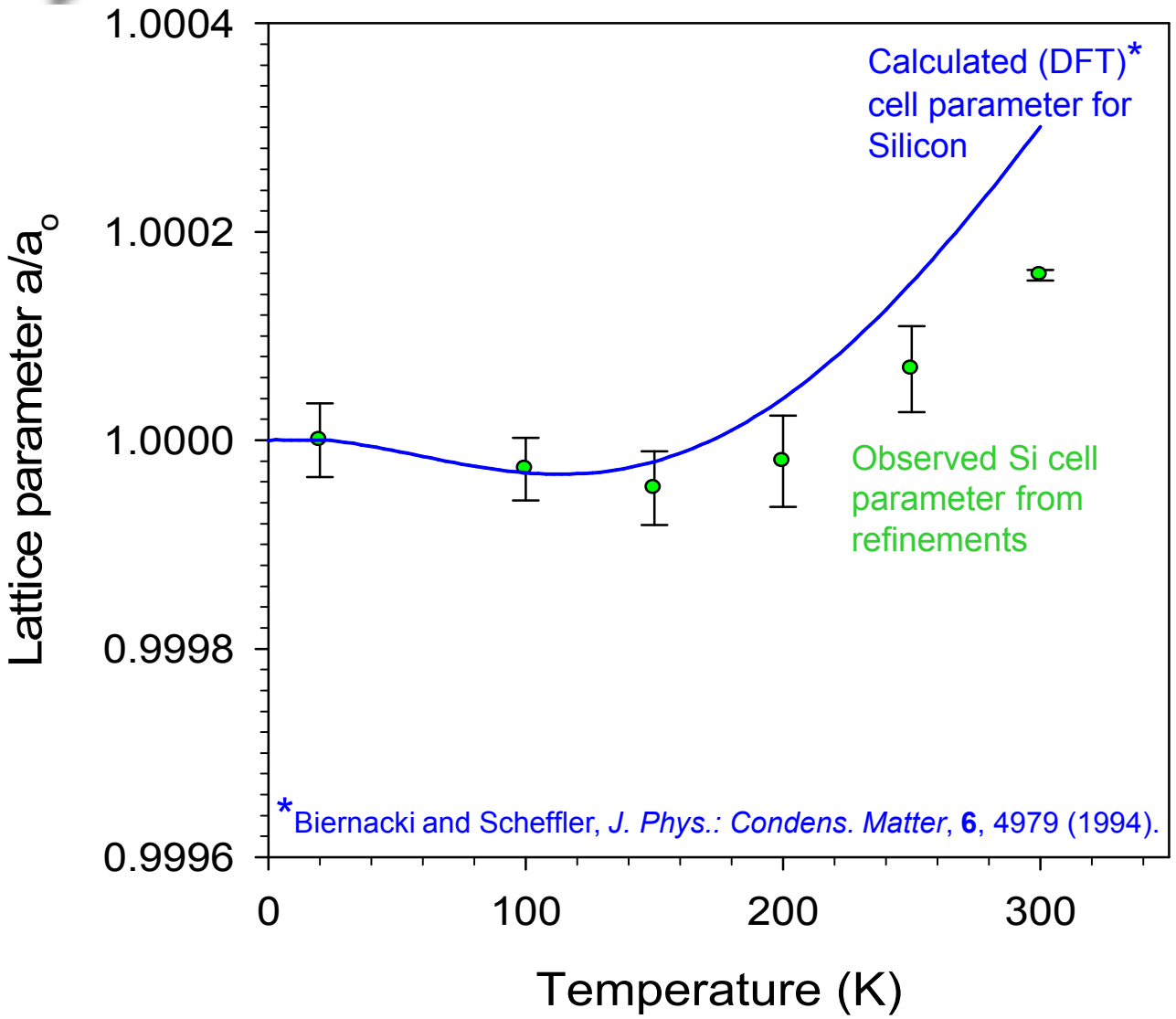
Silicon lattice parameters were modeled as 2nd phase and confirm accuracy of observed ErD_2 lattice parameters



Temperature (K)	Si lattice parameter (Angstroms)
20	5.43033(19)
100	5.43018(16)
150	5.43008(19)
200	5.43022(24)
250	5.43070(22)
300	5.43119(05)

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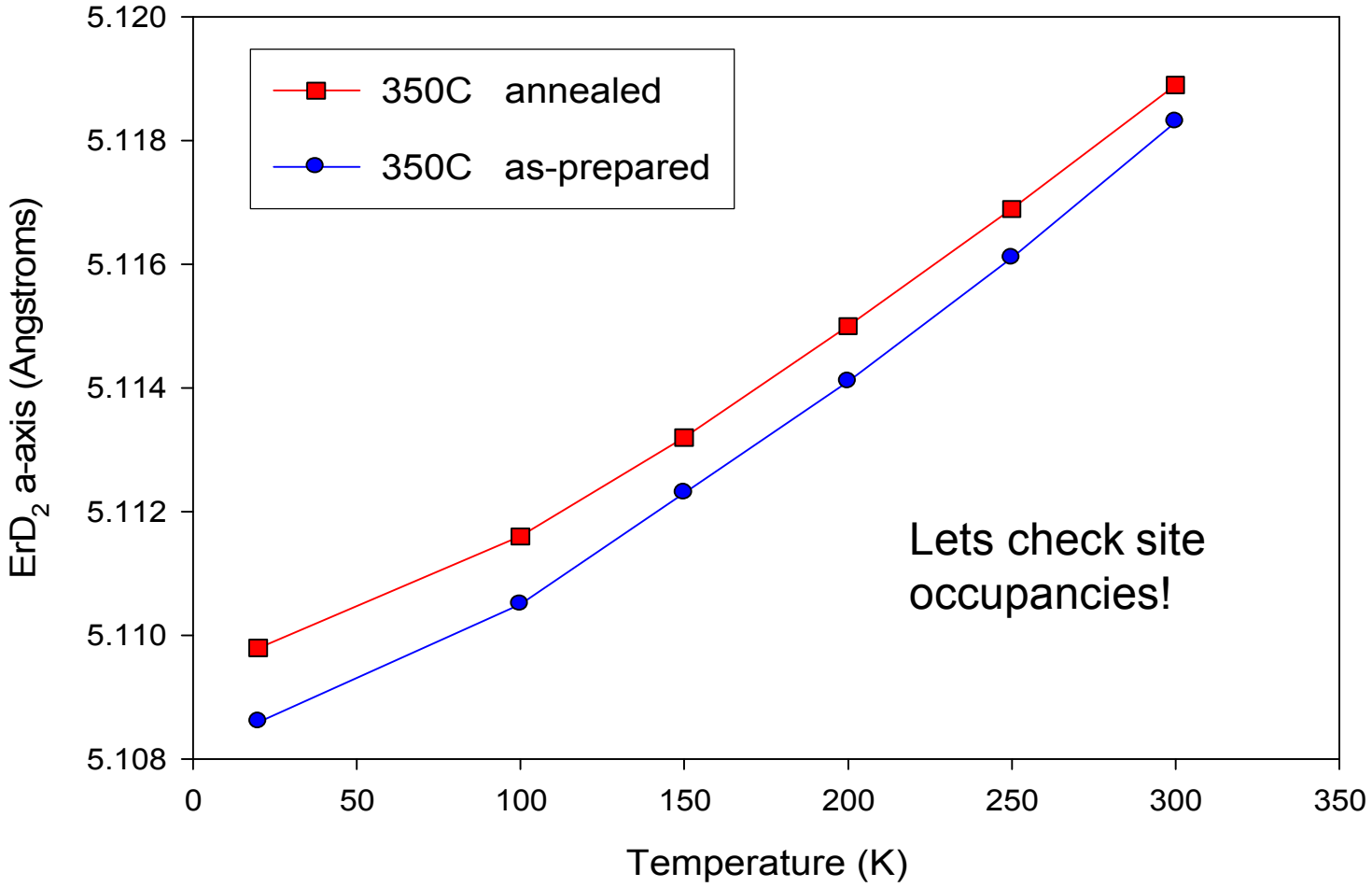
ErD_2 lattice parameter for annealed powder showed consistently larger unit cell as compared to as-prepared.



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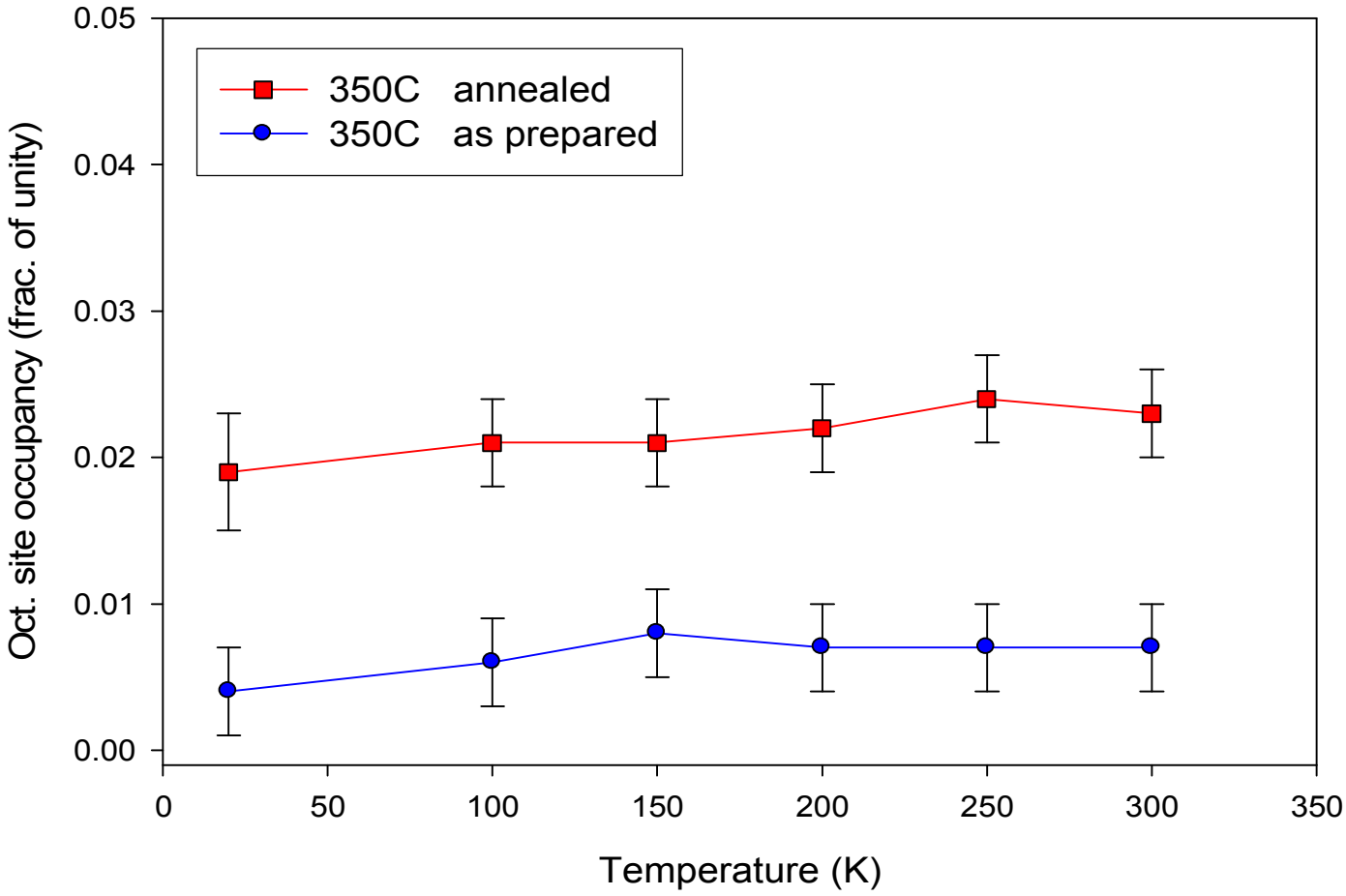
Annealed powder has higher occupancy (~2%) of octahedral site when compared with the as-prepared powder.



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What is happening here?

- **These powders should be essentially the same. Annealing was only difference.**
- **Annealed sample shows larger unit cell *but also has a higher occupancy of the octahedral site.***
- **FY04 analysis showed that the cell contracted with D_{oct} occupancy.**

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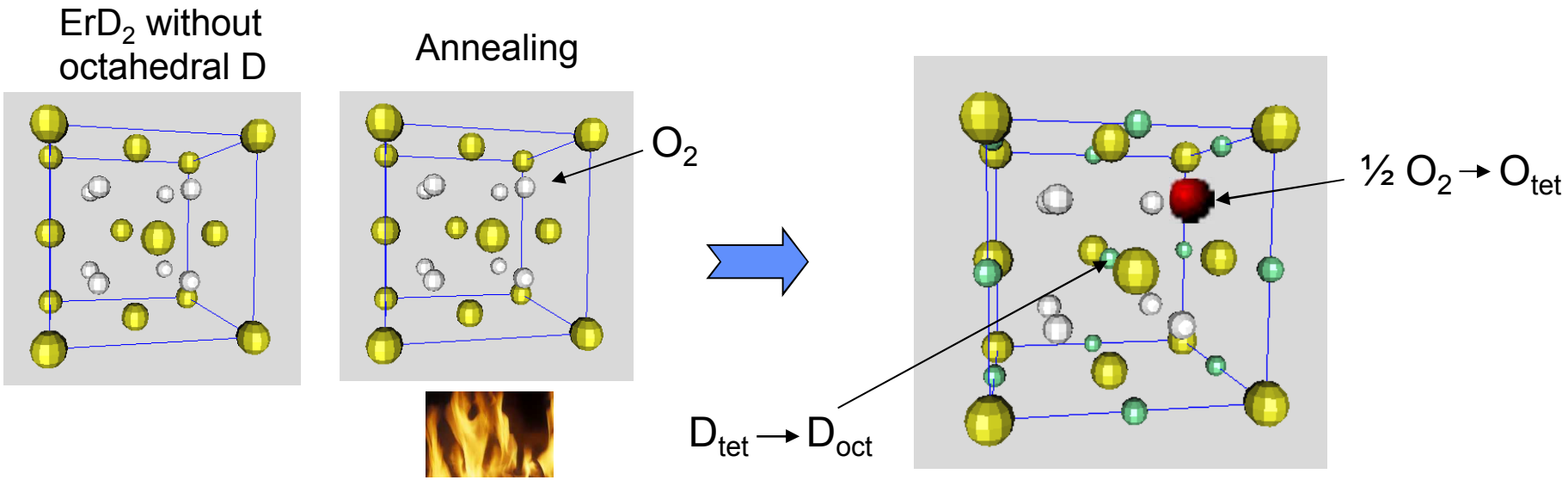
Working theory regarding effect of annealing

- Additional annealing step allowed for oxygen solubility within the ErD_2 lattice.



- Incorporation of oxygen defect at tetrahedral site <u>expands</u> lattice and drives tetrahedral deuterium to octahedral site.

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Summary

- Presence of deuterium at octahedral site (~10% site occupancy) contracted the overall cell volume of the ErD_2 fluorite lattice.
- The ErD_2 lattice contracts uniformly with decreased temperature from 300 to 20 K.
- Annealed ErD_2 powder showed significant fluorite unit-cell expansion and corresponding increase in octahedral site occupancy when compared against as-prepared sample.
- Annealing result may be explained by the addition of oxygen defects within the host lattice.

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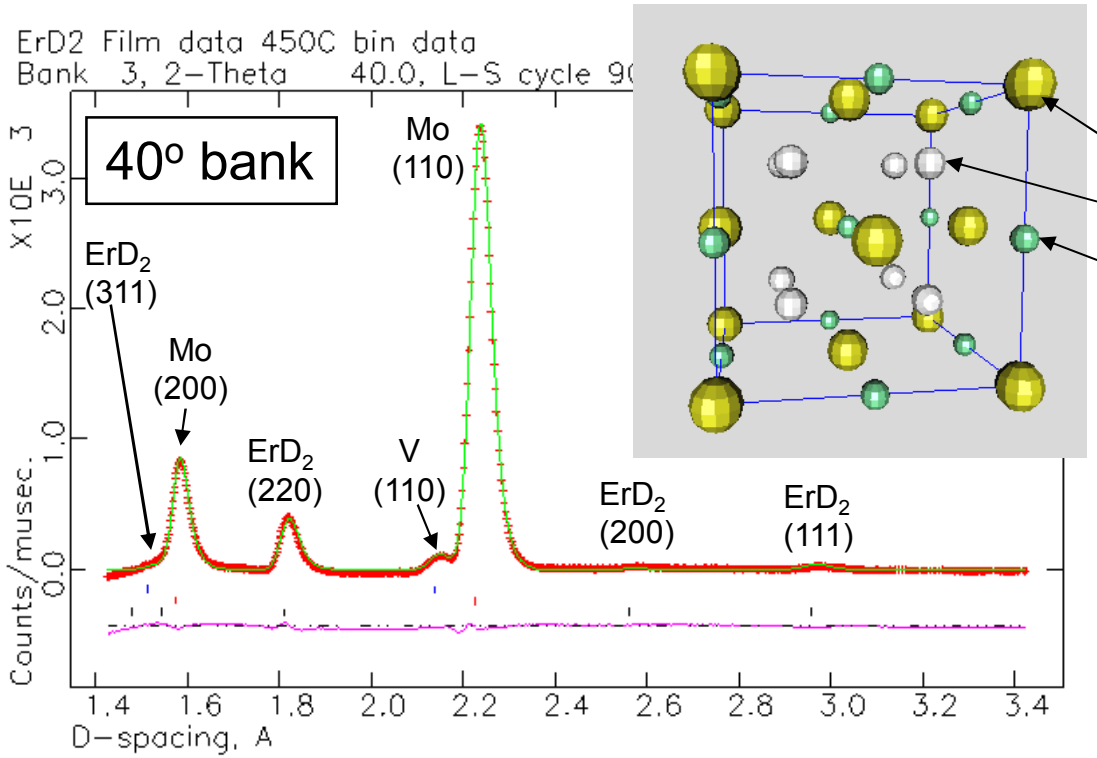
Neutron scattering analysis of ErD_2 thin films from FY05 run cycle (450C D-loading) shows similar result to that of annealed sample. Suggests oxygen defect presence in films.



Crystal data

Atom	occ.	B_{iso}(Å^2)
Er	1.0	0.15
D_t	1.04(2)	1.01
D_o	0.15(3)	1.01

a = 5.119(1) Å

Vol = 134.2 Å^3

R_{wp} = 0.0087

R_p = 0.0073

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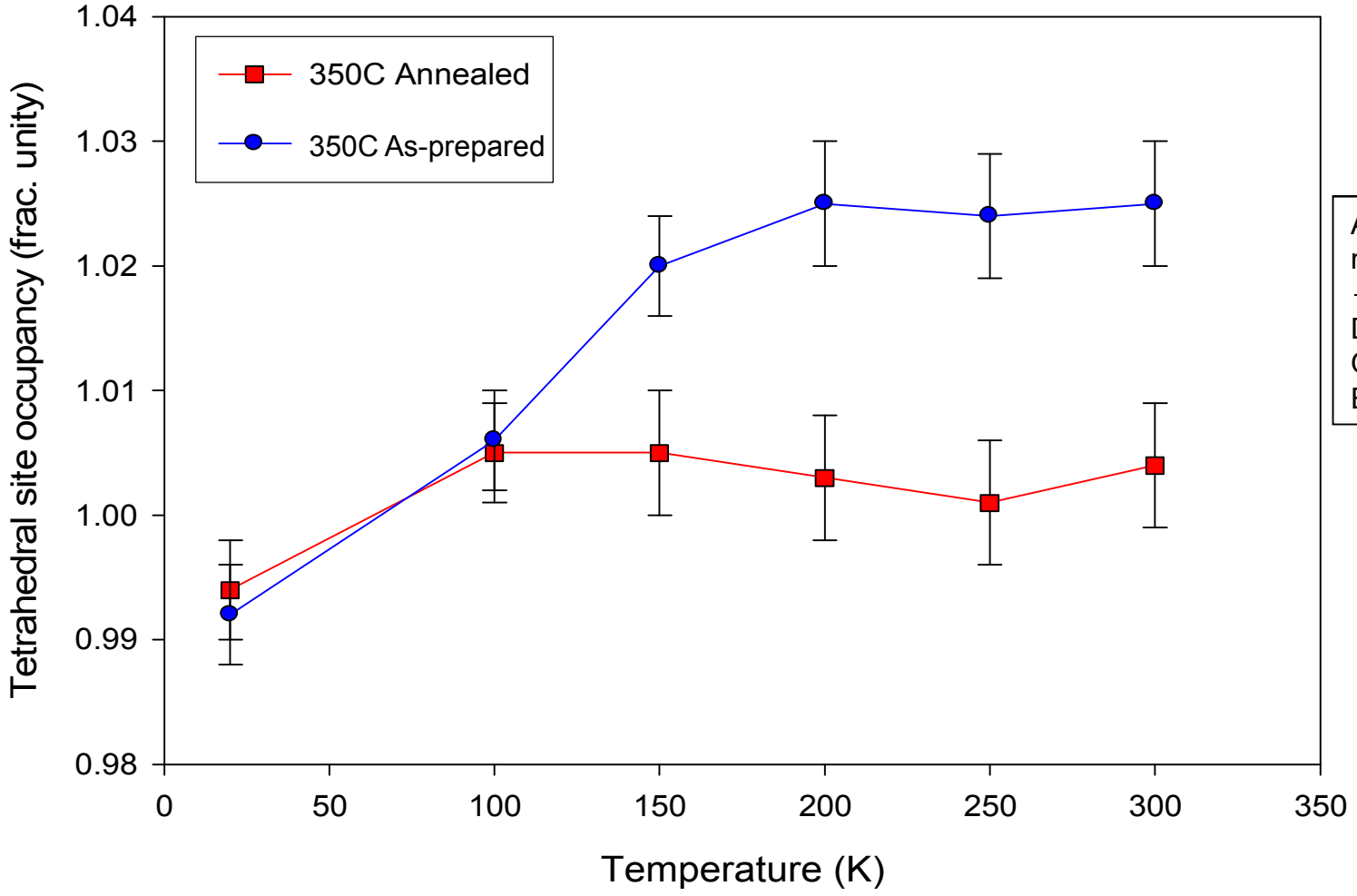
Decrease in D_{tet} site occupancy is consistent with doping of oxygen for deuterium in annealed ErD_2



Atom name	n-Scattering length (fm)
Deuterium	6.67
Oxygen	5.80
Erbium	7.79

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