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First Principles (Density Functional Theory) Calculations on $PdT_{0.65}$ and ErT_2

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Outline

$PdT_{0.65}$:

- Are there substantial fluctuations in bulk T-density at 300K? (Yes)
- Does T surface segregate? (Yes) Are there substantial fluctuations in the surface T concentration at 300K? (Yes)
- Does He prefer to diffuse through low-T regions? (Yes) What is the activation barrier in the bulk? (0.22 eV)
- Can we compute the fluctuations at 300K? (Yes, using DFT-MD and a new ASCII code)

ErT_2:

- Are there basic principles for using dopants to trap He and reduce early release and postpone catastrophic release? (Yes)
- Do we have numerical results? (Yes, substitutional Cu traps six or more He, but Cu also forms inclusions which can also trap He)
- Can we find a mixture that will produce both point and inclusion defects? (Yes, Cu inclusion trapping and Ag substutional trapping are being studied now)

Method

Density Functional Theory (DFT) in the Generalized Gradient Approximation (GGA) of the PBE form.

The ASCII SeqQuest gaussian based code and pseudopotentials of Peter Schultz (9235). See www.cs.sandia.gov/~paschul/Quest/ .

Use supercells [i.e., $Pd_{32}T_{21}$ (65.6%) and $Er_{32}T_{64}$]

This gives the structural energies at 0 K. Compare these for stability at 300K (need 0.7 eV energy differences to be stable at RT).

Use the nudged elastic band (NEB) method to find diffusion barrier paths and heights.

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Palladium Tritide Bulk Results

LATTICE CONSTANTS, theory:

Pd bulk: 3.89 Å (fcc)

$PdT_{0.65}$: 4.05 Å (+ 4% is important for diffusion barrier)

T-DISTRIBUTION WITHIN BULK $PdT_{0.65}$:

Clustered-T: Relaxed cell energy = -1887.744 Ry

Random-T spread out): Relaxed cell energy = -1887.756 Ry

(diff = 0.2 eV, 1 Ry = 13.6 eV)

☞ **There exist RT fluctuations in T density (need DFT-MD simulations, now available with the parallel Quest code)!**

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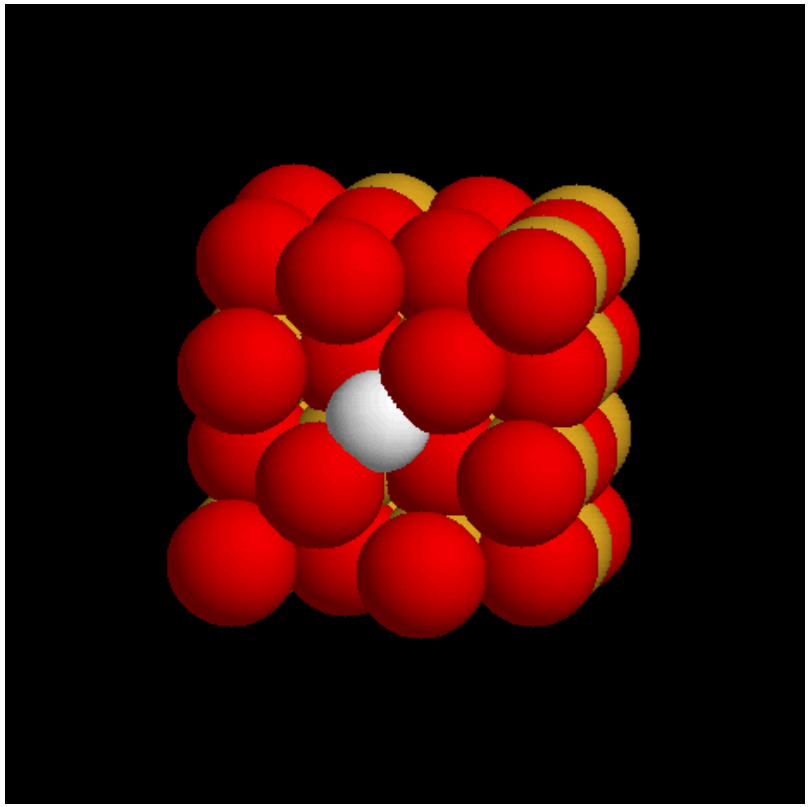
Palladium Tritide Diffusion Results

He diffusion, theory:

- **The He diffusion barrier through LOW-T regions is 0.22 eV, in “fair agreement with experiment” (?) (see Don Cowgill)**
- **The path is NOT octahedral-tetrahedral-octahedral, but is direct, w/He passing between two Pd atoms**



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Palladium Tritide Surface Results

SURFACE SEGREGATION FOR $PdT_{0.65}(111)$:

surface T/Pd ratio		E(Ry)	ΔE(eV)	
0.625	Relaxed Energy =	-1886.828	0.00	(~bulk)
0.75	Relaxed Energy =	-1886.842	-0.20	
0.875	Relaxed Energy =	-1886.861	-0.46	
1.00	Relaxed Energy =	-1886.885	-0.80	

(room T fluctuating!)

☞ **Should do DFT-MD at 300K to determine AVERAGE surface T density!**

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Erbium Tritide Bulk Results

LATTICE CONSTANTS, theory(experiment):

Er bulk: a = 4.00(3.56) Å (hexagonal)

ErT_2: 5.11(5.11) Å (CaF_2 structure)

(expansion = 28%)

BASIC PRINCIPLE OF He TRAPPING:

Use an element with:

1) **a smaller metallic radius than Er and,**
2) **which does not bind strongly to it (e.g., trivalent Er, radius = 1.78 Å, vs. *monovalent* Cu, radius = 1.28 Å)**

This way you form a NN region with a *lower* valence electron density

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Erbium Tritide He Trapping Results

Energetics of He NN's to substitutional Cu vs. He's (i.e., in bulk)

Number of He in Cell (NN to Cu or not)		Delta E
1: 0NN, RELAXED CELL ENERGY =	-1778.51 Ry	0.0 eV
1NN: RELAXED CELL ENERGY =	-1778.58	-0.9 (RT stable)
2: 0NN, RELAXED CELL ENERGY =	-1784.13	0.0
2NN, RELAXED CELL ENERGY =	-1784.19	-0.7 (RT stable)
3: 0NN, RELAXED CELL ENERGY =	-1789.73	0.0
3NN, RELAXED CELL ENERGY =	-1789.91	-2.4
4: 0NN, RELAXED CELL ENERGY =	-1795.35	0.0
4NN, RELAXED CELL ENERGY =	-1795.49	-1.8
6: 4NN, RELAXED CELL ENERGY =	-1806.5	0.0
6NN, RELAXED CELL ENERGY =	-1806.6 Ry	-1.4 eV

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Erbium Tritide Cu Inclusion Results

TENDENCY TO FORM A Cu INCLUSION?

AS Er SUBSTITUTIONAL DEFECTS:

- **Four Separate Cu: CONVERGED ENERGY (Rydberg) = -1880.96**
- **Four Clustered Cu: CONVERGED ENERGY (Rydberg) = -1880.94 (NO)**

AS ONE Er SUBSTITUTIONAL + 3 T SUBSTITUTIONAL *(have NEAR IDEAL Cu-Cu spacings):*

- **Four Separate Cu: CONVERGED ENERGY (Rydberg) = -2032.78**
- **Four Clustered Cu: CONVERGED ENERGY (Rydberg) = -2033.39 (ΔE ~ 7eV)**

  *****DEFINITELY YES*****

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Future Plans

For Pd-T:

Perform DFT-MD calculations, using the new parallel Quest code, to study bulk and surface fluctuations in T-concentration; determine and average surface T-density.

For Er-T:

Study He trapping at the Cu inclusion interface.

Study substitutional He traps which do not make inclusions, e.g. maybe Ag (radius = 1.44 Å).

Study He bubble energetics [“coins” between (111) planes which make (111) bubble surfaces].

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