Mike McKubre

+

Mike Staker

NAE = SAV = SPD + D

On the role of Super Abundant Vacancies (SAV) in hydrogen loading and production of the Fleischmann Pons Heat Effect (FPHE).

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Presented at
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Questions to be answered

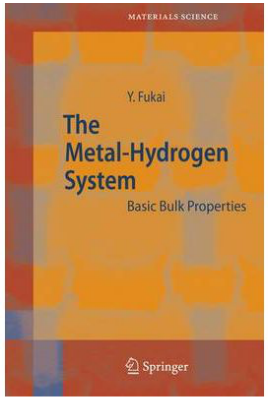
- What are “Super Abundant Vacancies, SAV”?
- What is the evidence for their existence?
- In what systems and situations have they been seen?
- What are their properties? Why should we care?
- What relevance do they have to the FPHE?
- What experiments are already incorporating SAV?
  - Knowingly? or
  - Unknowingly?
- How do we make them reliably and on large scale?

Fukai on SAV

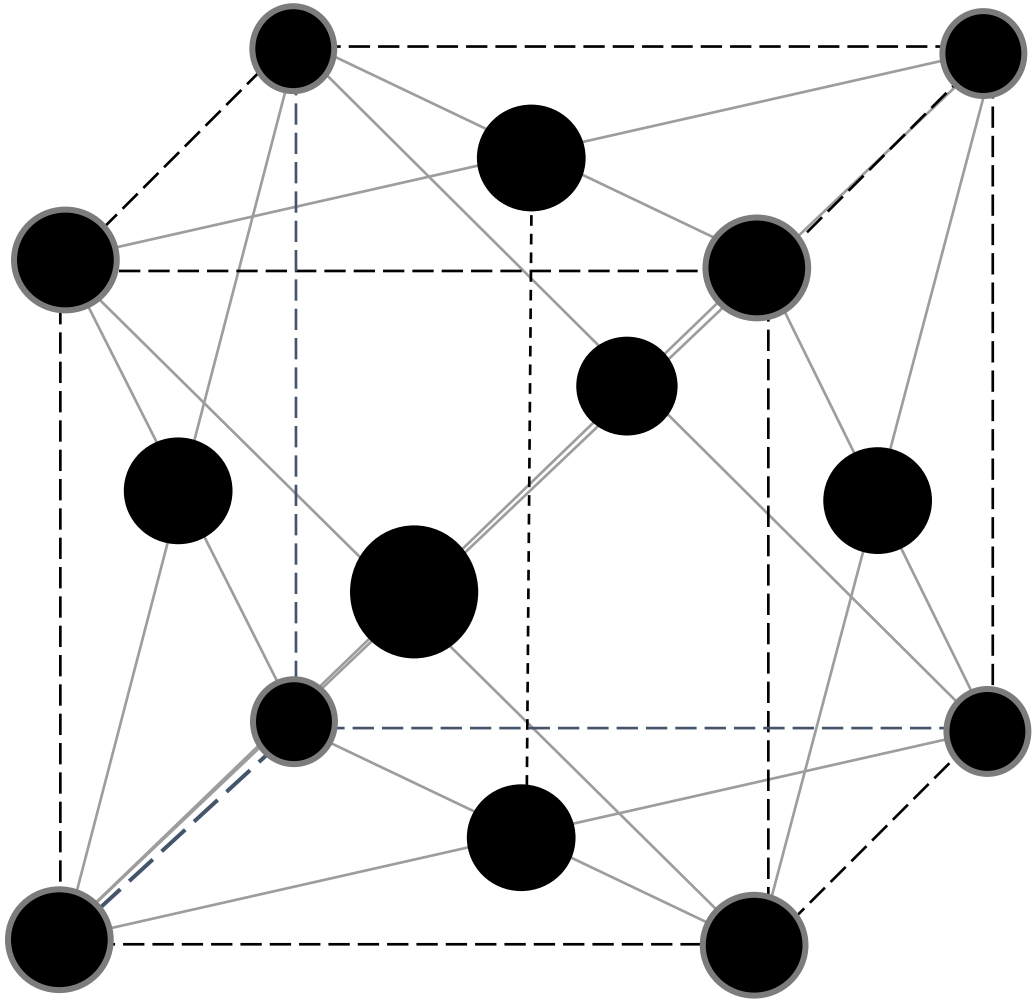
- *"…Most important implication in the physics of SAV is that the **most stable structure** of all M-H alloys is in fact the defect structure containing a large number of M-atom **vacancies.***
- *All M-H alloys should tend to assume such defect structures, ordered or disordered depending on the temperature, as long as the kinetics allows.*
- *In practice, however, M-H alloys are in most cases prepared under conditions where M-atom vacancies cannot be introduced.*
- *Thus it can be said that most (all) phase diagrams of M-H systems reported to date are metastable ones. These metastable diagrams are certainly useful as such, but the recognition that they are metastable ones is of basic importance.*
- *The **real equilibrium phase diagrams including M-atom[s] vacancies have not been obtained so far**."*

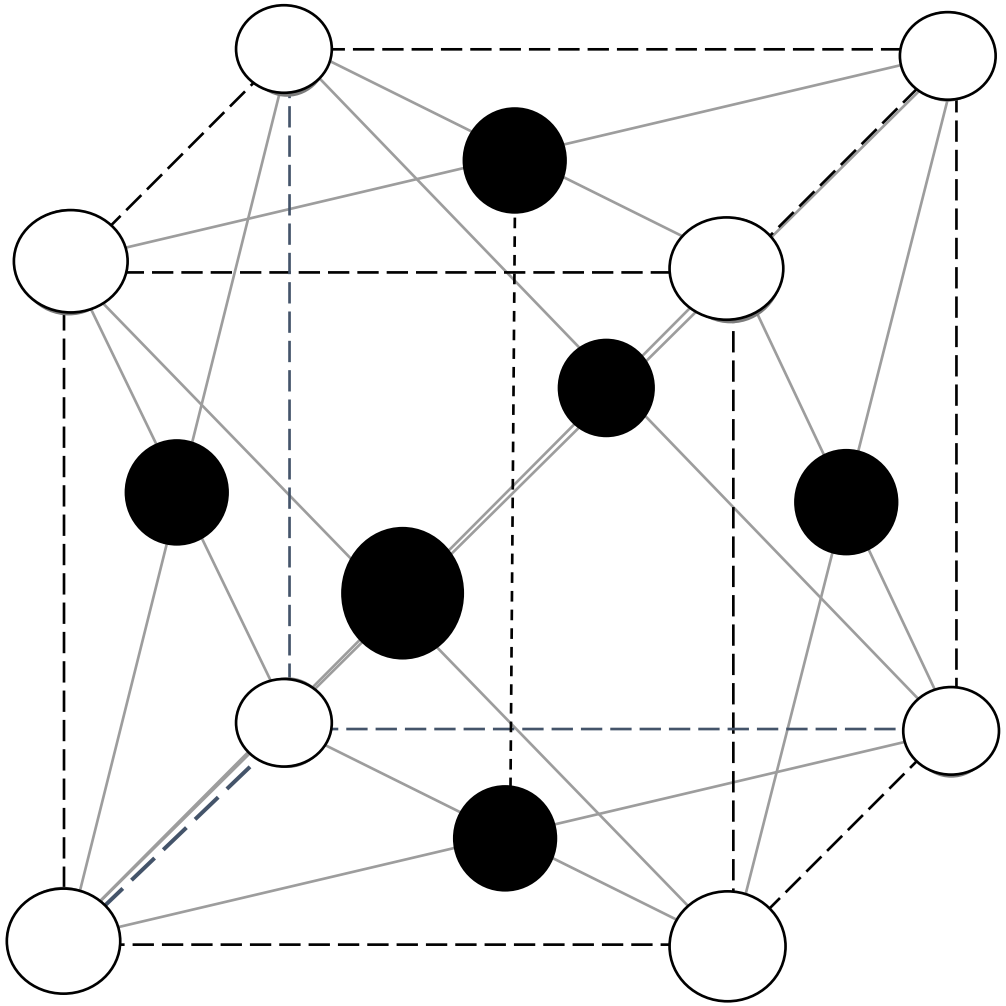
[emphasis added]

from: Y. Fukai, "*The Metal Hydrogen System – Basic Bulk Properties*", 2nd Ed.
Springer Berlin Heidelberg, New York, 2005, p225.



What are SAV structures?





FCC Pd Lattice, Pd atom ●

Pd/Vac Ordered Lattice $Pd_3Vac_1D_4$ Vacancy ○

What do we know that's new?

- "*High hydrogen chemical potential lowers the formation energy of a vacancy-hydrogen cluster. This is a key to understanding vacancy formation under high hydrogen chemical potentials.**"
- Three such phases exist:
  1. The γ phase structure has the octahedral site filled with D (H) with half of the lattice cell corners atoms vacant; $Pd_7VacD_{6\text{-}8}$
  2. The δ phase has all corner atoms vacant; Pd_3VacD_4 with D (H) at the Octahedral sites
  3. The δ' phase has all corner atoms vacant; Pd_3VacD_4 with D (H) at the Tetrahedral sites**.

* R. Nazarov, T. Hickel, J. Neugebauer, "*Ab Initio Study Of H-vacancy Interactions in Fcc Metals: Implications for the Formation of Superabundant Vacancies*", Phys. Rev. B 89 (2014).

** L. E. Isaeva, D. I. Bazhanov, Eyvas Isaev, S. V. Eremeev, S. E. Kulkova and Igor Abrikosov, "*Dynamic Stability of Palladium Hydride: An ab initio Study*", International J. of Hydrogen Energy, (36), 1, (2011) 1254-1258.

What evidence do we have for SAV or a γ Phase?

- X-ray Diffraction (new lines)
- Thermal desorption spectra
- Physical density (volume change)
- DFT calculation
  - Hydrogen trapping is the main reason for forming Pd_3VacH_4
  - SAV are always present at high H fractions
- Temperature coefficient of Resistance, λ

Temperature coefficient of Resistance, λ

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30 October 2000

PHYSICS LETTERS A

Physics Letters A 276 (2000) 122–126

www.elsevier.nl/locate/pla

Temperature coefficient of resistivity at compositions approaching PdH

P. Tripodi [a,b,*], M.C.H. McKubre [a], F.L. Tanzella [a], P.A. Honnor [a,c], D. Di Gioacchino [b], F. Celani [b], V. Violante [d]

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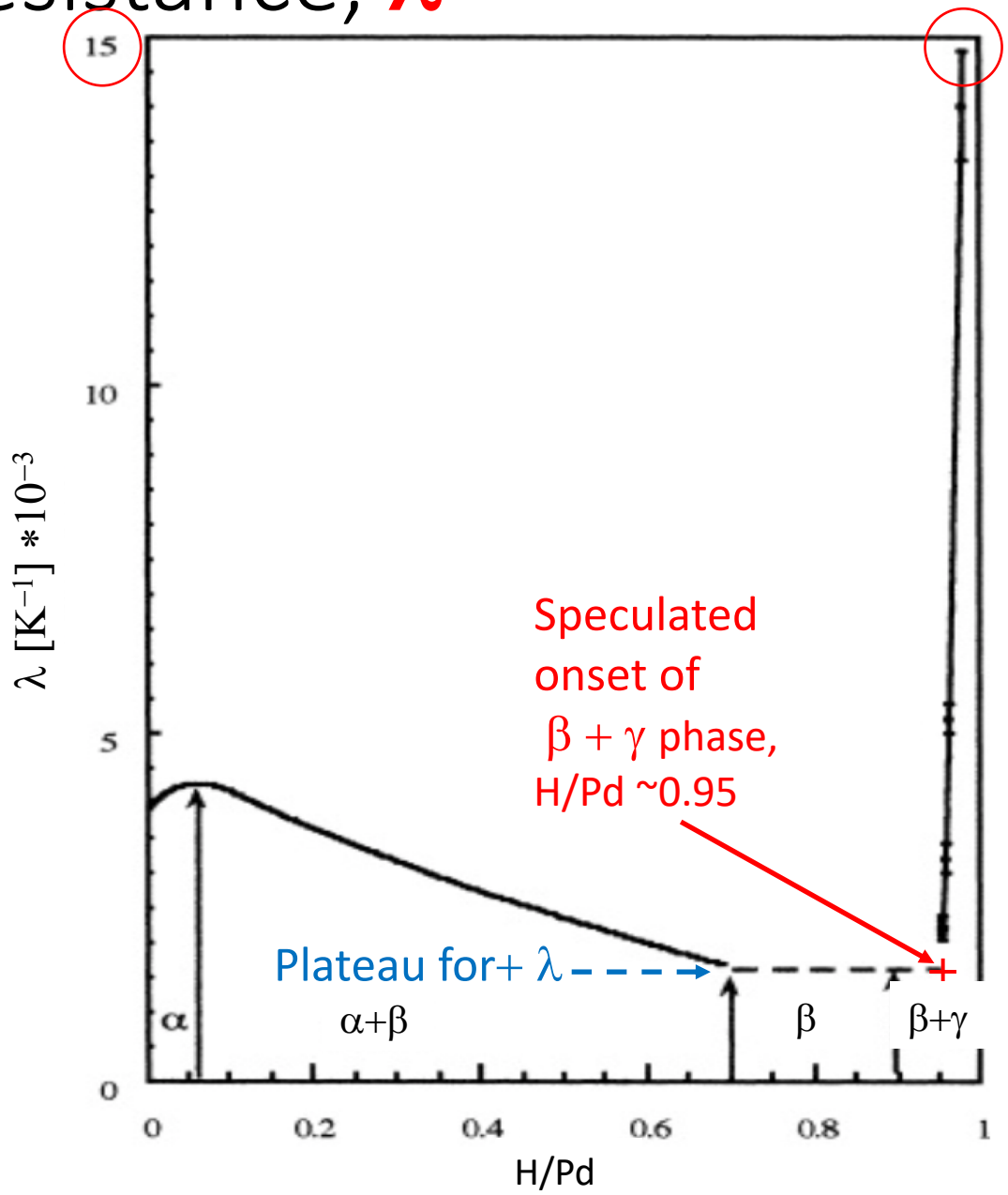


Tripodi Conjecture
2007, Catania*

*"To obtain excess heat in Cold Fusion we suggest to consider a **stoichiometry window** and not a **stoichiometry threshold**"* Paolo Tripodi (my emphasis)

HYDROGEN ENERGY RESEARCH AGENCY

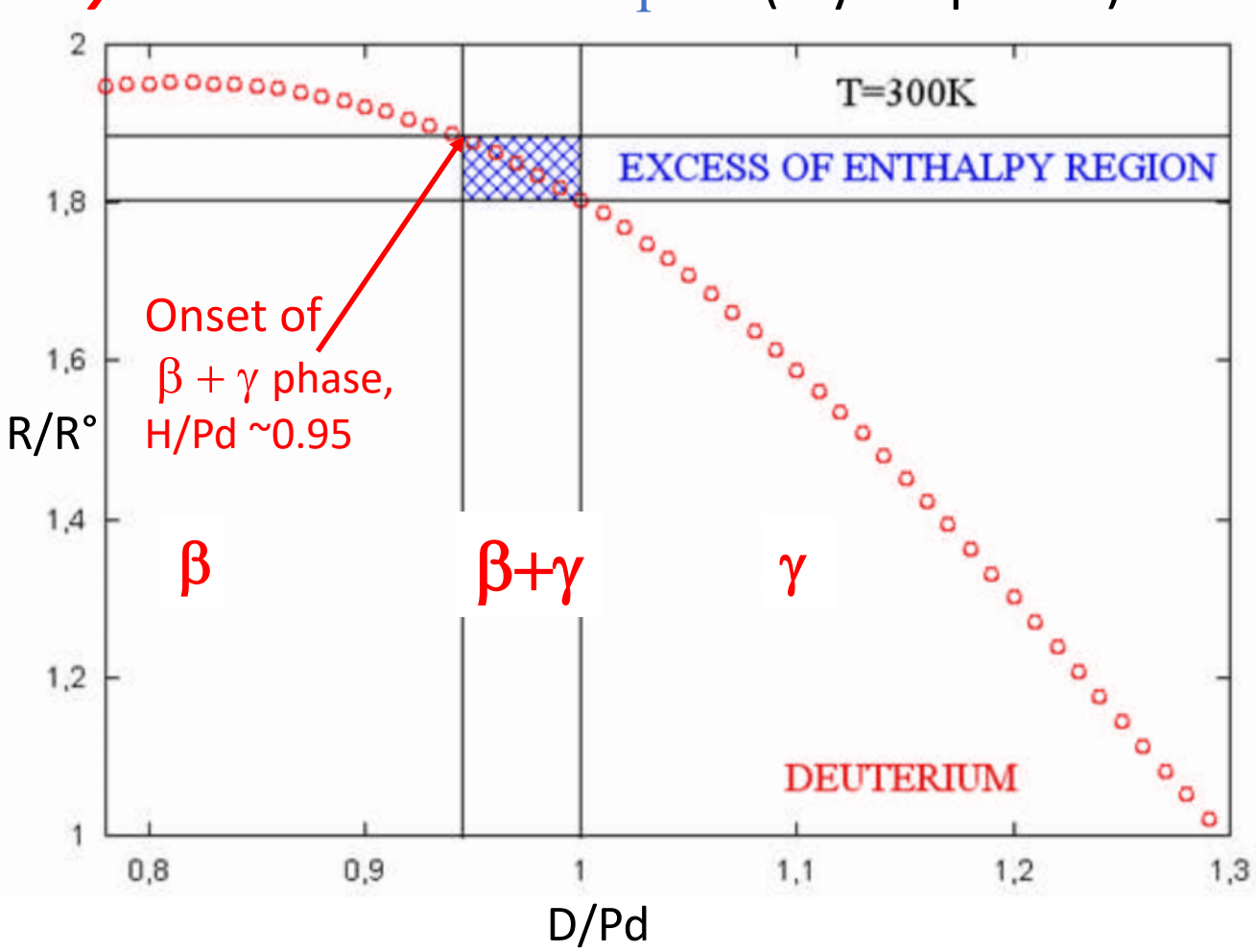
8th International Workshop on Anomalies in Hydrogen / Deuterium Loaded Metals
13-18 October 2007 - Catania - Sicily - Italy

PdH(D,T)x system:
are excess of enthalpy and superconductivity two concurrent phenomena affected by stoichiometry x ?

Paolo Tripodi
Daniele Di Gioacchino
Jenny Darja Vinko

Work Supported by Italian Ministry of Defense

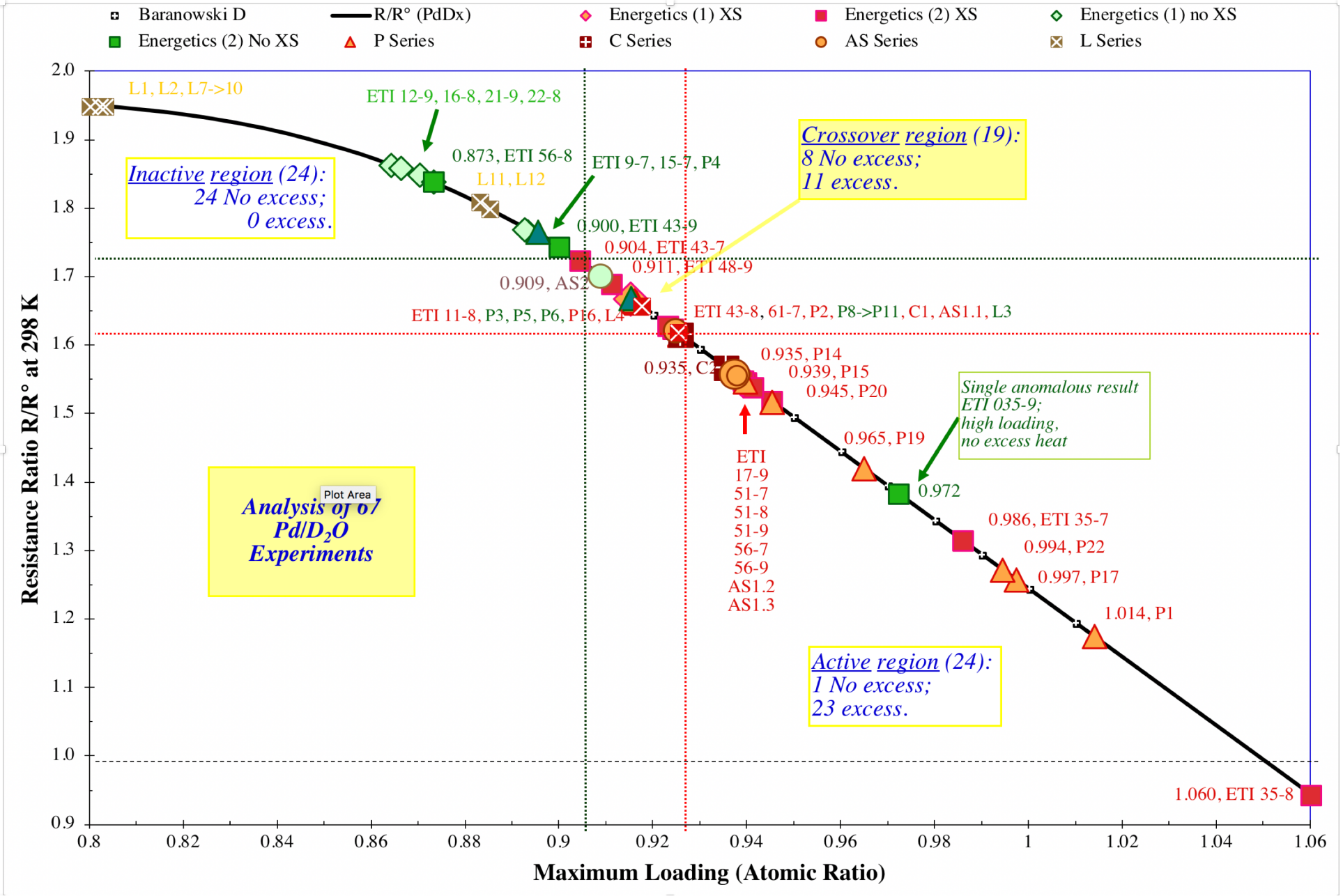
Dr. Paolo Tripodi



α phase in the stoichiometry range $0 < x < 0.05$
α + β phases in the stoichiometry range $0.05 < x < 0.70$
β phase in the stoichiometry range $0.70 < x < 0.95$
β + γ phases in the stoichiometry range $\mathbf{x > 0.95}$

* 8th International Workshop on Anomalies in Hydrogen / Deuterium Loaded Metals, October 2007 in Catania, Sicily.

The appearance of Excess Heat *vs.* R/R° and D/Pd



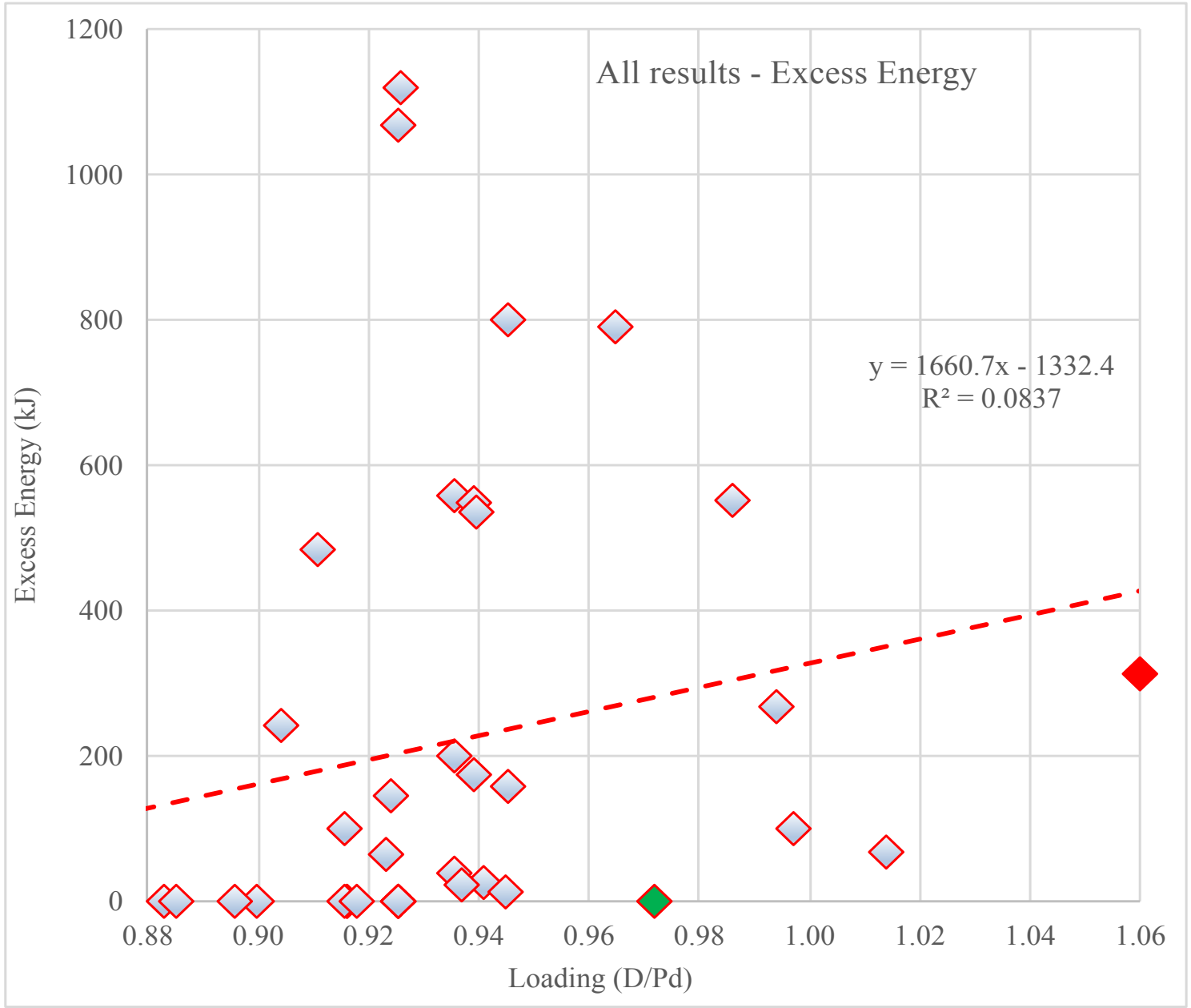
No Excess Heat:
Green, Yellow (33)

Excess Heat:
Red, Orange (34)

Points are plotted on the calibration curve at the Minimum values of R/R° on the right side of the resistance maximum.

These values therefore reflect the Maximum values of D/Pd obtained at any time in the experiment.

Same data: Excess Energy (kJ) *vs*. $D/Pd_{Max.}$



E_{XS} = 1661 $D/Pd_{Max.}$ - 1332 kJ

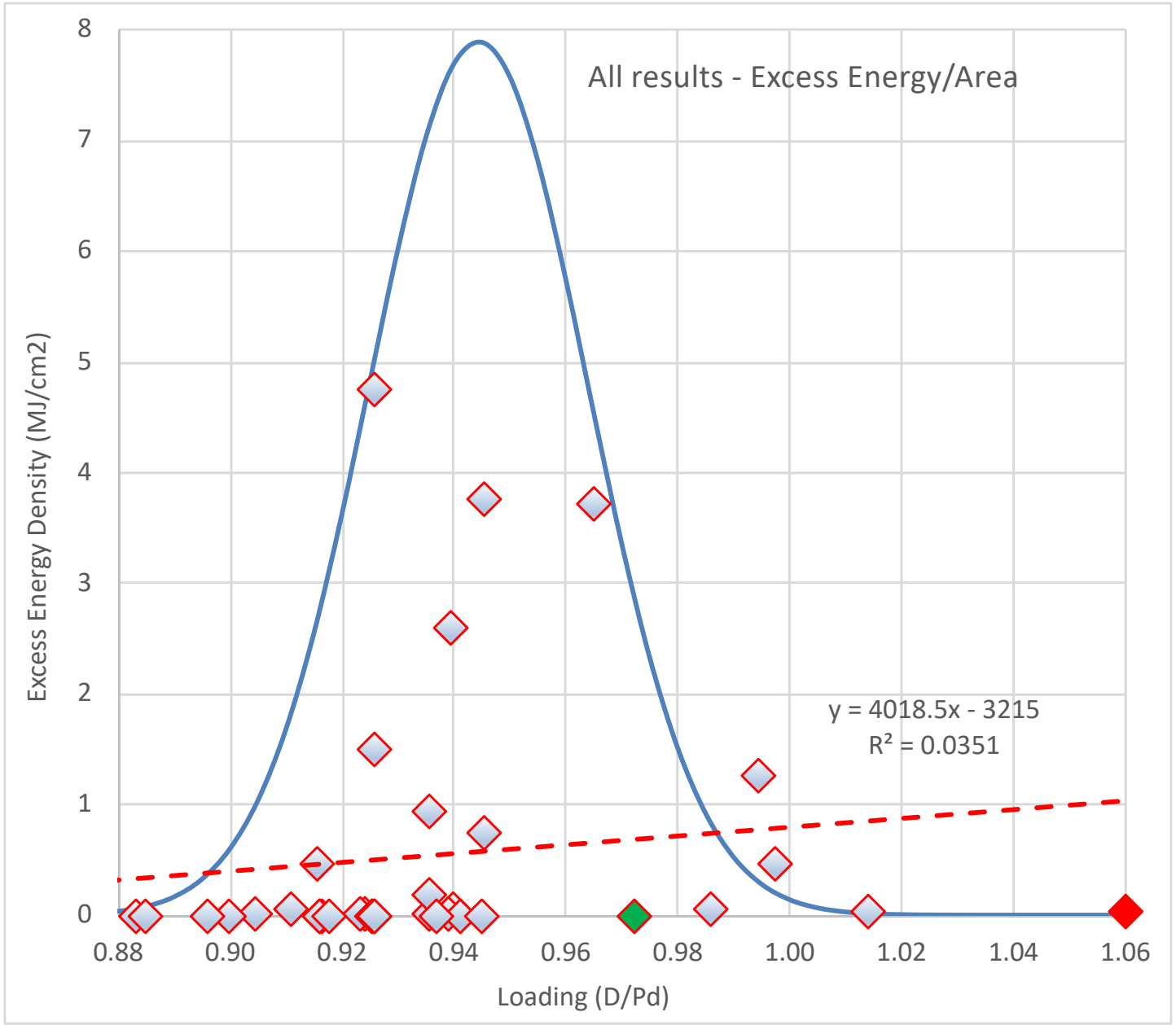
R^2 = 0.0837 🤔

Green point is ETI 35-9 ◆
for which increased Tritium was measured but not Excess Energy

Red point is ETI 35-8 ◆
which showed large loading but modest Excess Energy

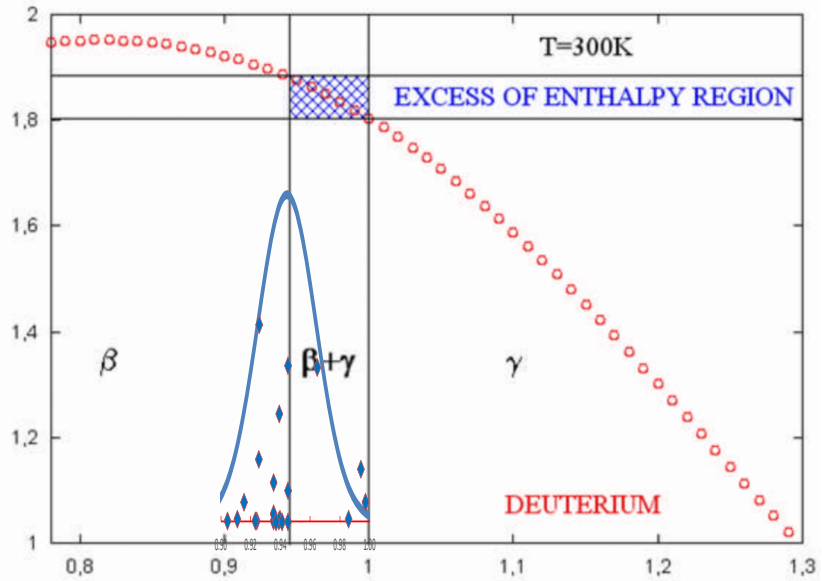
ETI 35-9 and ETI 35-8 ran simultaneously in identical calorimeters with Violante foil cathodes.

Same data: Excess Energy (MJ/cm^2) *vs*. $D/Pd_{Max.}$

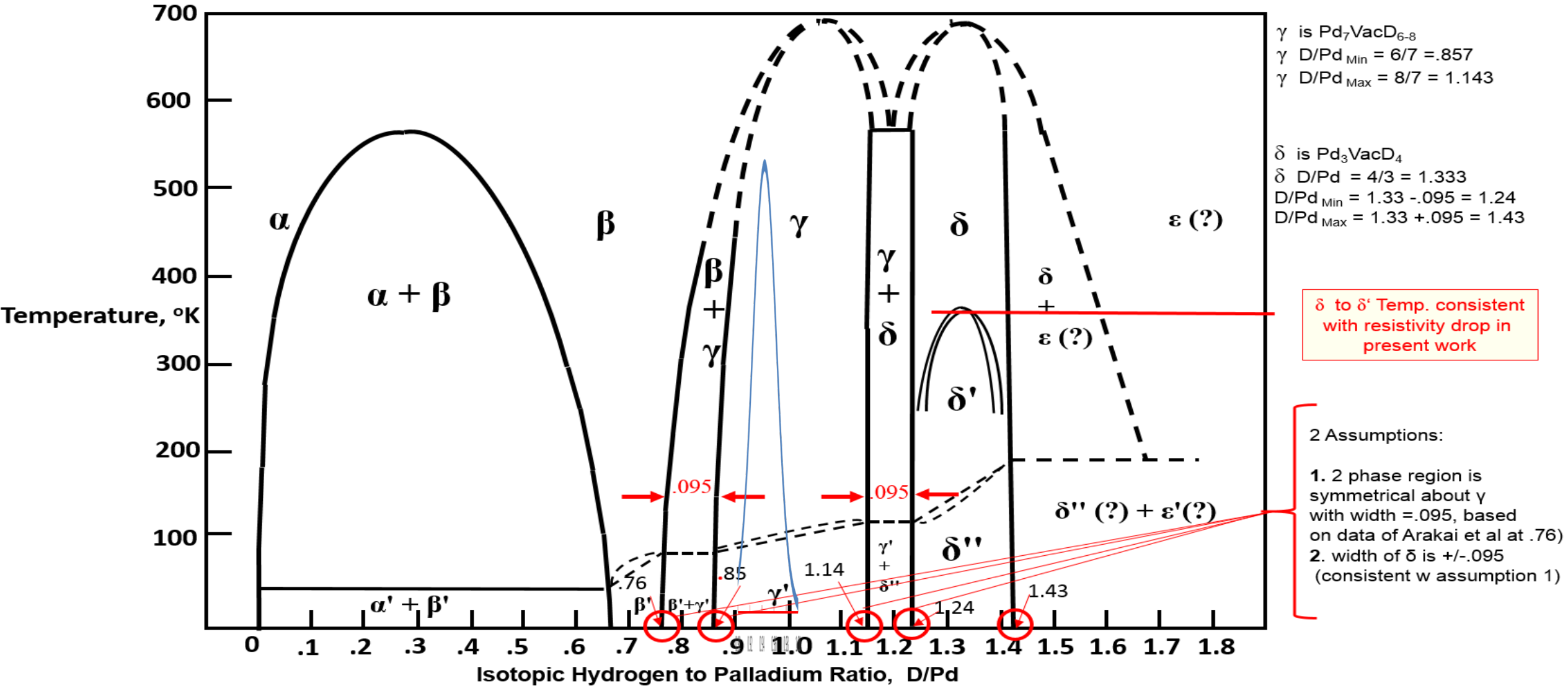


Energy Data normalized by Electrode Surface Area

Blue Gausian drawn using the Statistical Mean (**D/Pd** = 0.944) and Standard Deviation (σ = 0.020) of all results exhibiting positive energy excess.



Equilibrium Phase Diagram for Deuterium – Palladium



Phase Diagram: Staker [ICCF21 Proceedings – *available on request*].

Blue curve drawn using the Statistical Mean (**D/Pd** = 0.944) and Standard Deviation (σ = 0.020) of all results exhibiting positive energy excess.

In what systems do SAV occur?

- Hydrogen-induced vacancy formation has been observed in the following list of metals:
  - **M = Ni, Pd, Ag, Rh, Pt, Au, Al, Cu, Ir, Mo, Fe, Nb, Cr, Co, Mn, Ti, and Zr,**
  - and alloys: **M-N = Pd-Rh, Pd-Ag, Cu-Ni.**
- These elements and alloys overlap closely with those of greatest interest in CMNS heat effects.

How do we make SAV on a useful timescale?

- The SAV phases are the thermodynamically stable state of highly loaded FCC metals and some alloys.
- What prevents them from simply forming?
- **Time!**
- How do we defeat or cheat Time?
- **Strain!**
- Move Pd (or other selected) atoms to within a short distance of their preferred final equilibrium position before loading:
  - Stabilize structure by loading which also facilitates vacancy movement
  - Electromigration also causes vacancy movement

How do we create SAV?

Vacancy structures can be formed using the following methods:

1. High Temperature, High Pressure Gas *via* Anvil Compression …. Fukai.
2. Alloying …. Sendai?
3. Conventional aqueous Electrolysis.
4. Co-deposited Electrolysis …. Szpak/Spawar+++?
5. Solid State Electrolysis (dry electrolyte).
6. Ion Beam Implantation …. SRI/Swartz?
7. Plasma-Injection …. Energetics?
8. Surface cavitation …. Stringham?
9. Ball milling …. Ahern +++?
10. Small dimension materials … $t = x^2/2D$ …. Many.
11. Severe Plastic Deformation, SPD … talk about later

What role do SAV already play in the FPHE? [1-6 of 10]

1. Loading-deloading cycles. In his original work in the early `90's Mike Staker used axial electric current densities to promote electro-diffusion and excess heat production (quite successfully). He prepared his cathodes by repetitively loading and unloading them precisely to create dislocations, hence vacancies, hence SAV.

2. Piantelli's heat and H treatment. Piantelli conditions his successful "electrodes" by manipulating H_2 pressure and temperature to load/unload and create his desired surface (and bulk).

3. Electron beam irradiation. Electron and neutron beam irradiation at ~MeV levels are very capable of creating sizable populations of vacancies in bulk matter. At SRI we worked on this concept with Peter Hagelstein and Mitch Swartz using e^--beam irradiation in the early-mid `90's.

4. Helium implantation. Without intending to produce SAV many of the most successful, early SRI FPHE Pd experiments implanted ^4He or ^3He to depths of 3μm that undoubtedly introduces strain and vacancies – and (potentially) moves Pd atoms to SAV-favored positions?

5. Stressed thin films. Following (ultimately posthumously) Preparata's guidance Del Giudice *et al* prepared palladium thin film structures that were patterned "bustraphedically". Patterns were formed 54 μm wide, 1 or 2 μm thick and 100 cm long by sputter deposition of Pd on a non-conducting surface. These structures were used as cathodes in D_2O electrolysis and subjected to repeated cycles of loading and unloading in the presence of an axial current flow.

6. Ball milling. Pursuing his own hypothesis but following Arata's experiments, and working under EPRI contract, Brian Ahern intensively ball-milled partially oxidized $Zr_{0.65}Ni_{0.3}Pd_{0.05}$ to obtain nanoparticles in the 3-12nm range. He successfully reproduce Arata's original work (currently being pursued in Sendai).

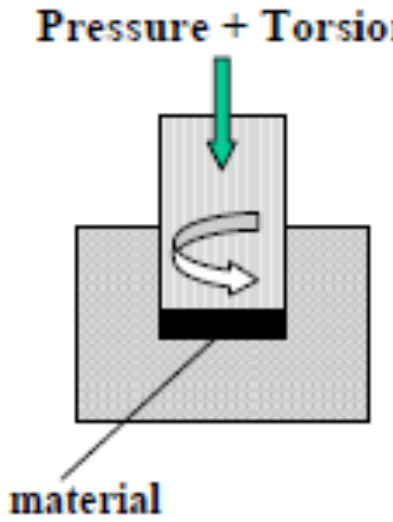
What role do SAV already play in the FPHE? [7-10 of 10]

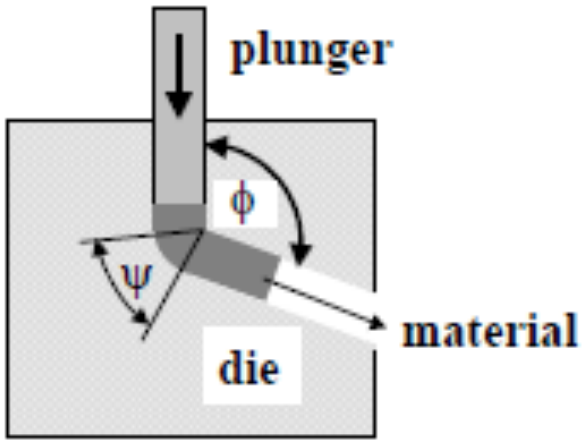
7. The Nanor family. Mitch Swartz has been reporting excess heat production from various generations of objects. He has been quite secretive but uses axial current flow. My guesses are:
   - The heat excess is real and may scale to useful dimensions
   - A key element of this heat excess are SAV achieved mechanically
   - Mitch has a ½ mile Ni cathode that he calls MOAC (the mother of all cathodes) the winding strain leads to SAV.
8. Torsion. This is speculative and I have seen one callout in the literature on this point , but it would seem that the necessary amount of strain (defect density) could be introduced in a manner that favors the near-surface where we want it. This could easily be done by drawing a wire through a series of two (or more) dies, at least one of which rotates to introduce calculated amounts of torsional strain.
9. Knots. Since ICCF17 in Korea, Celani has been reporting excess heat production from successive generations of wires exercised by axial current flow at elevated temperatures in H_2 and D_2 gases. Recently Celani has introduced knots in his wires. He recently reports that the presence of knots in the constantan wire has created or exacerbated excess heat production. Is this due to strain?
10. Compression or rolling against a rough rigid surface. In order to create points (or lines) of stress intensification to nucleate small cracks to support his hypothesis, Ed Storms embosses one surface of a Pd plate (typically 1 mm thick) by pressing (rolling) against a metal file. This creates enormous stress. One side of the plate is fixed in place while the other elongates resulting in a trapezoidal strain pattern. While this is not Ed's intent, his technique results in "severe plastic deformation" precisely of the type needed to produce SAV…

Severe Plastic Deformation: SPD to create SAV

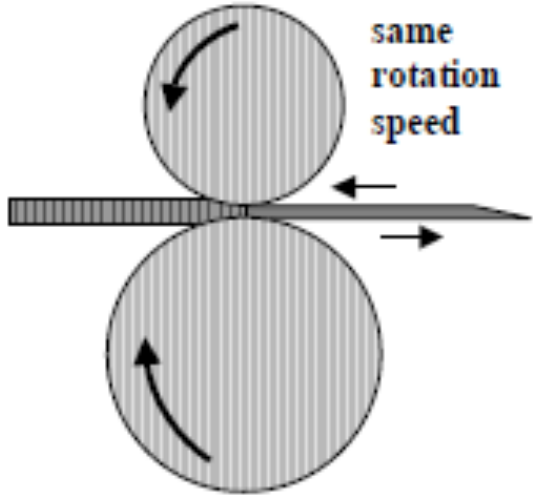
- At the “Toulouse” Airbus meeting in 2015 Daniel Fruchart (CNRS in Grenoble), working with Nataliya Skryabina (Perm State University, Perm, Russia) presented an astonishing paper titled: *“Is Super Abundant Vacancy a singular state in the Hydrogen-in-Metal paradigm?”*
- Fruchart uses SPD successfully to facilitate SAV creation and stabilization in experiments employing:
  - Gas pressure,
  - Electrochemical loading
  - Plasma loading experiments
- Fruchart (and several others in the literature) have created the Fukai phases (SAV) simply by ”torturing” metals and then treating them with H_2 …. or D_2?

Ball Milling





ECAP = Equal Channel Angular Pressing



Differential Rolling

Some SPD machines

and we can all think of ways to torture wires...

Pulling around a corner or a small roller (with or without coating)

Tight winding on a mandrel

Celani's "capuchin knots"

Etc.

Summary: who says what:

- Fukai *and many others*: SAV phases are the thermodynamically stable state of highly loaded FCC metals and alloys. Three phase exist; γ, δ and δ'. All they need is time …. (or temperature) at high hydrogen chemical potential…
- Tripodi + SRI: the huge increase in λ at H(D)/Pd > 0.95 signifies the onset of the γ phase.
- Tripodi conjecture: *"To obtain excess heat in Cold Fusion we suggest to consider a stoichiometry window and not a stoichiometry threshold".*
- McKubre: the FPHE is observed in a narrow range of Maximum loading.
- McKubre + Staker: NAE = SAV = SPD + D We can facilitate the formation of NAE (or NAZ) by moving Pd (or other selected) atoms to within a short distance of their preferred equilibrium position before loading.
- Staker (1989/90): this can be done using the cold work of loading/deloading + electro-diffusion..
- There are many other ways to do this and some of you already have…
- Piantelli, Swartz, SRI, Preparata, Arata/Ahern/Sendai, Celani, Storms: have done this in their experiments, adventitiously, by various means, with successful results.
- Fruchart (*and others*): SPD is used **routinely** to create materials containing Fukai phases.

Conclusions: 4 step process

1. Strain FCC materials – the more strain the better but <u>avoid brittle fracture</u>:

pre-SAV

   a. numerous means possible
   b. some already in use by some of you…

2. Load with D:

SAV + D

   a. good electrochemistry (F&P, SRI/ENEA, Storms, Cravens, Celani, *etc*.),
   b. plasma / glow discharge (Energetics, Fruchard, *others*?)
   c. extreme pressure (Fukai *et al*)

3. Stimulate:

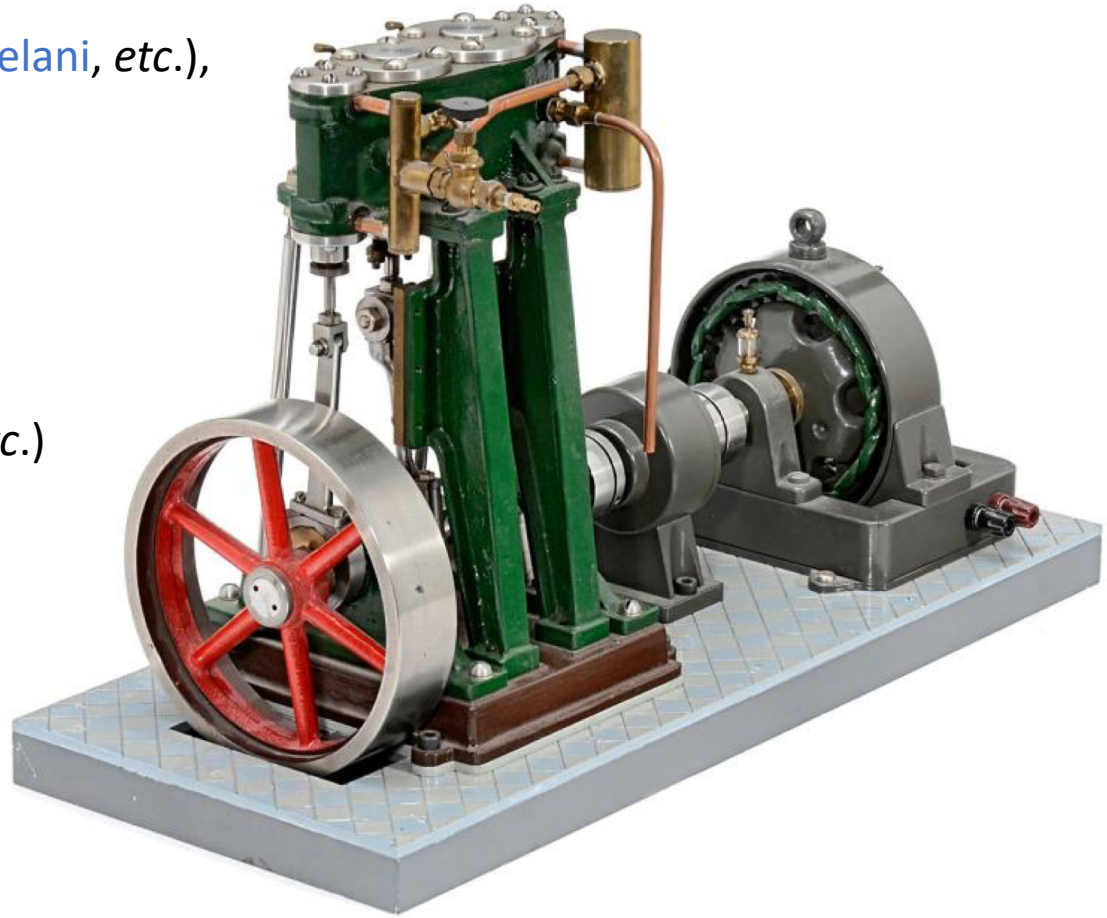
NAE

   a. current (dc OK, pulse better? Dardik, Godes, *etc*.),
   b. magnetic (dc OK, pulse better? Boss, La Gatta, *etc*.)
   c. laser (single OK, dual better? Letts, Cravens, Hagelstein, *etc*.)

4. Large heat effects … the 5 -tions:

Excess Heat

   a. Verification
   b. Correlation
   c. replication
   d. demonstration
   e. utilization



Mike McKubre

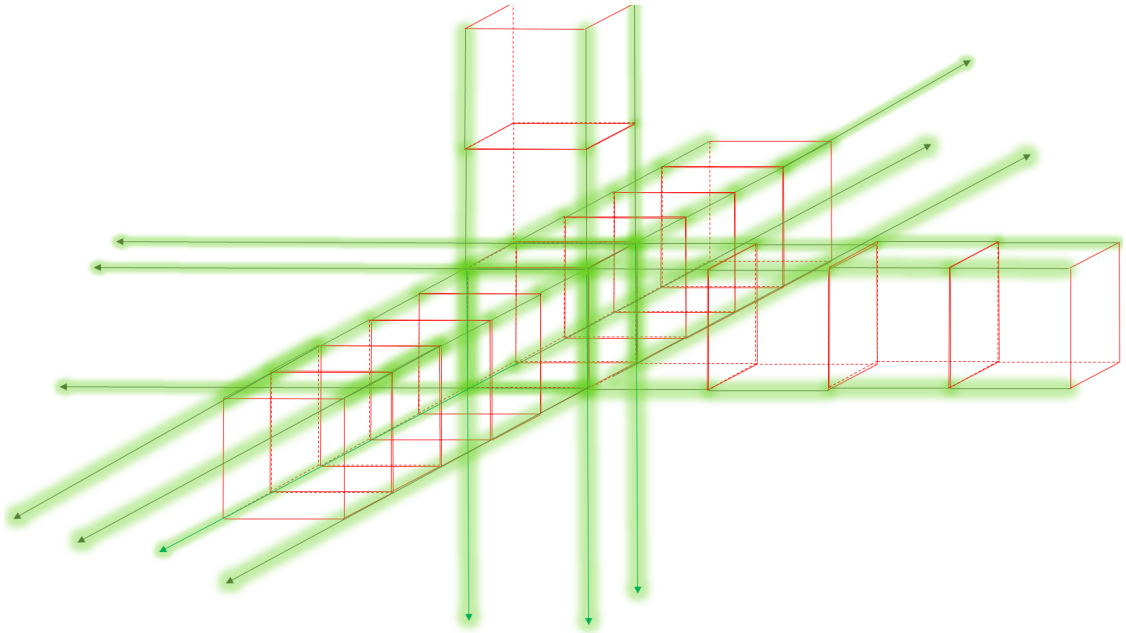
+

Mike Staker

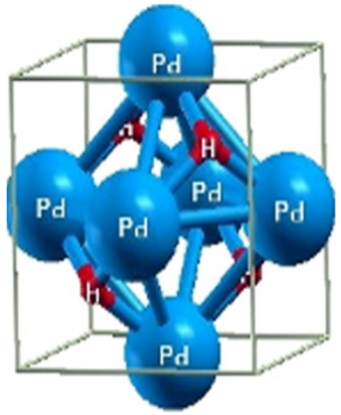
NAE = SAV = SPD + D

Let’s do it!

Storms Model: Staker conjecture.

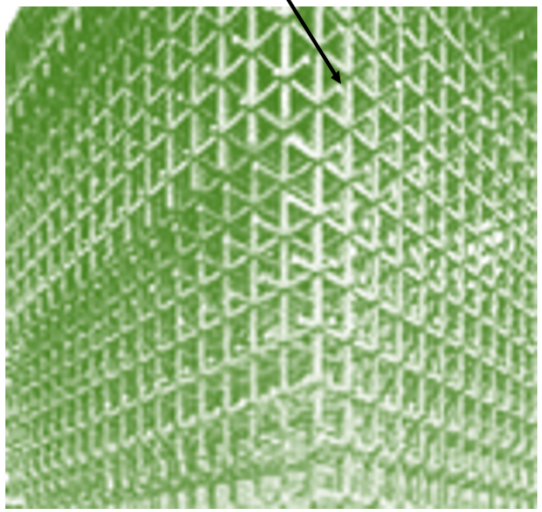


H (D) in T^h

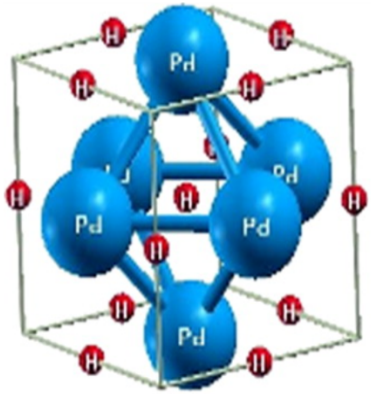


δ‘ phase

Each tube is empty
(void of Pd atoms, or
void of Pd but suffused with D(H))



H (D) in O^h

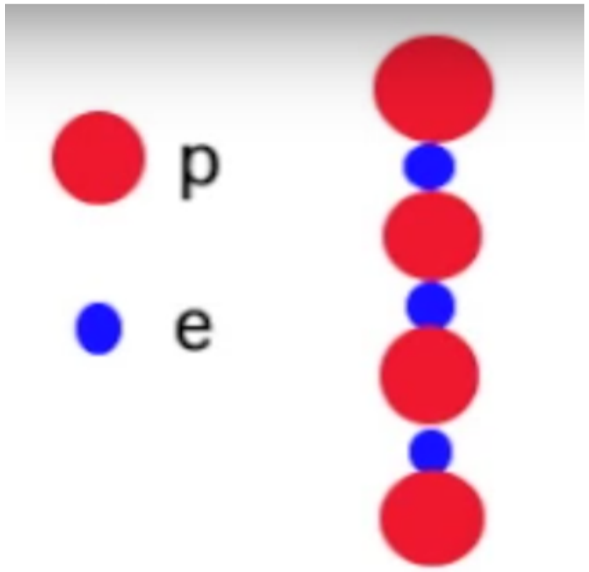


δ phase

Tubes for each unit cells of either **δ** or **δ’** phases. These phases form a 3-D vacancy tube lattice or network of intersecting tunnels. The tube lattice (green) has Pd and H (D) in the space between tubes in **δ‘** (left image = Pd_3VacD_4 - T), or has only Pd atoms (right image = Pd_3VacD_4 - O) in the space with D+ *inside* the tubes in **δ**. Unit cell images (blue and red) after Isaeva *et al**.

* L. E. Isaeva, D. I. Bazhanov, Eyvas Isaev, S. V. Eremeev, S. E. Kulkova and Igor Abrikosov, “Dynamic stability of Palladium hydride: An *ab initio* study”, International J. of Hydrogen Energy, (36), 1, (2011) 1254-1258.

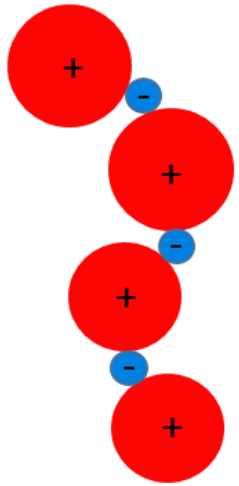
Storms Model: Staker conjecture.



A string of hydrogen nuclei and electrons between them – shielding the charge – are situated in the crack *tube*

Storms' Model

- Storms has modeled electron shielding in a two-dimensional crack.



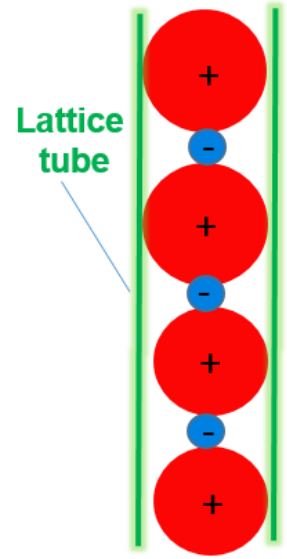
A 1-D string buckles In a 2-D environment

Euler

Buckling Problem

- A string of alternating electrons and deuterons will buckle when left in a two-dimension channel with a third dimension of width of 1 atom

δ' Phase H (D) in T^h



Avoids a 1-D string buckling In a 2-D environment

A 1-D string in a 1-D *tube* remains aligned

Present Model

- The present SAV view corrects the buckling problem since the lattice tube is 1 atom in diameter and maintains alignment when compressed axially.

M. R. Staker, *"Coupled Calorimetry and Resistivity Measurements, in Conjunction with an Emended and More Complete Phase Diagram of the Palladium - Isotopic Hydrogen System",* Proceedings ICCF21, 2018 *(*submitted).

Grateful acknowledgment to my esteemed colleagues...

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