Research issues associated with excess heat in the Fleischmann-Pons experiment

Peter L. Hagelstein
MIT
Cambridge, MA

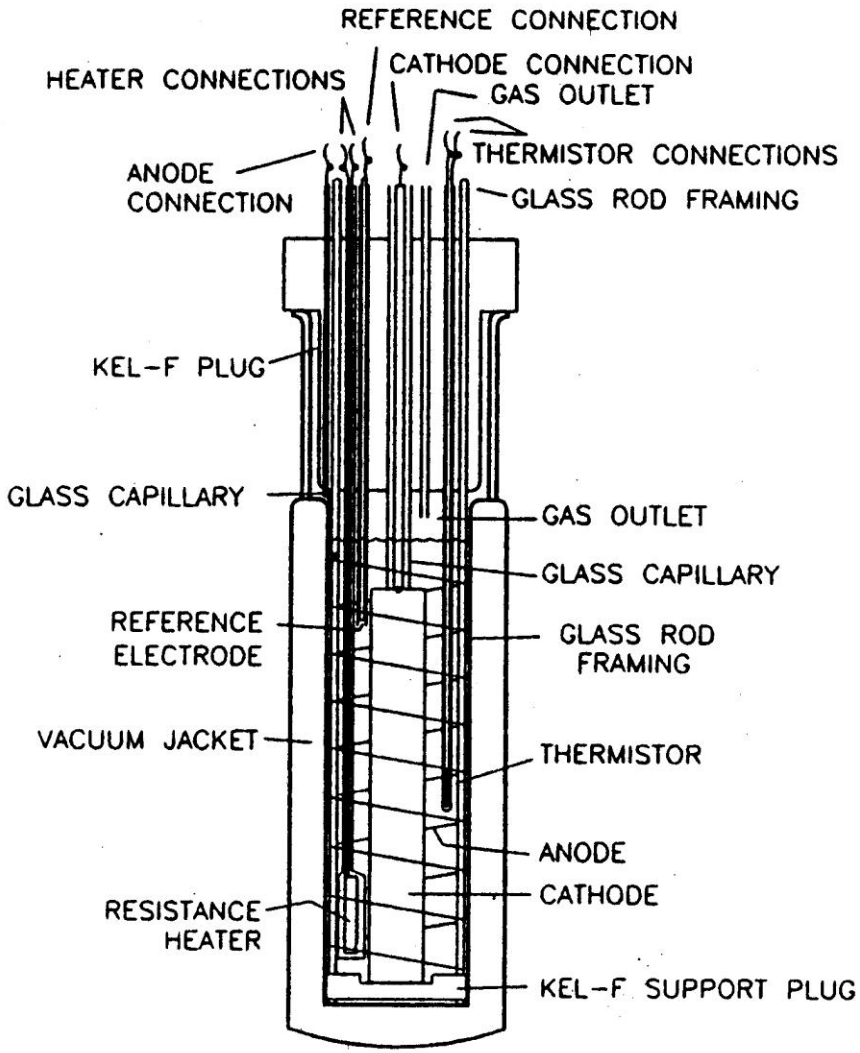
Warning!

- Cold fusion, LENR, excess heat and related topics are controversial
- Working in the field at present is dangerous to one's career
- Very powerful and energetic opposition
- Little or no governmental support in US
- Publishing is problematic, even now
- Research problems are very hard
- One's professional and personal life can both be impacted

Outline

- Introductory discussion of excess in in the F&P exp’t
- Correlation of excess heat and ^4He
- ^4He born essentially stationary
- Mechanisms and rates
- Conjecture about the reaction sites
- Loading requirements
- Early negative experimental results

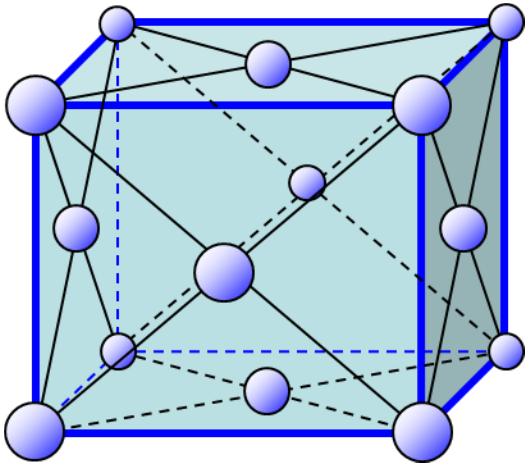
Fleischmann-Pons experiment

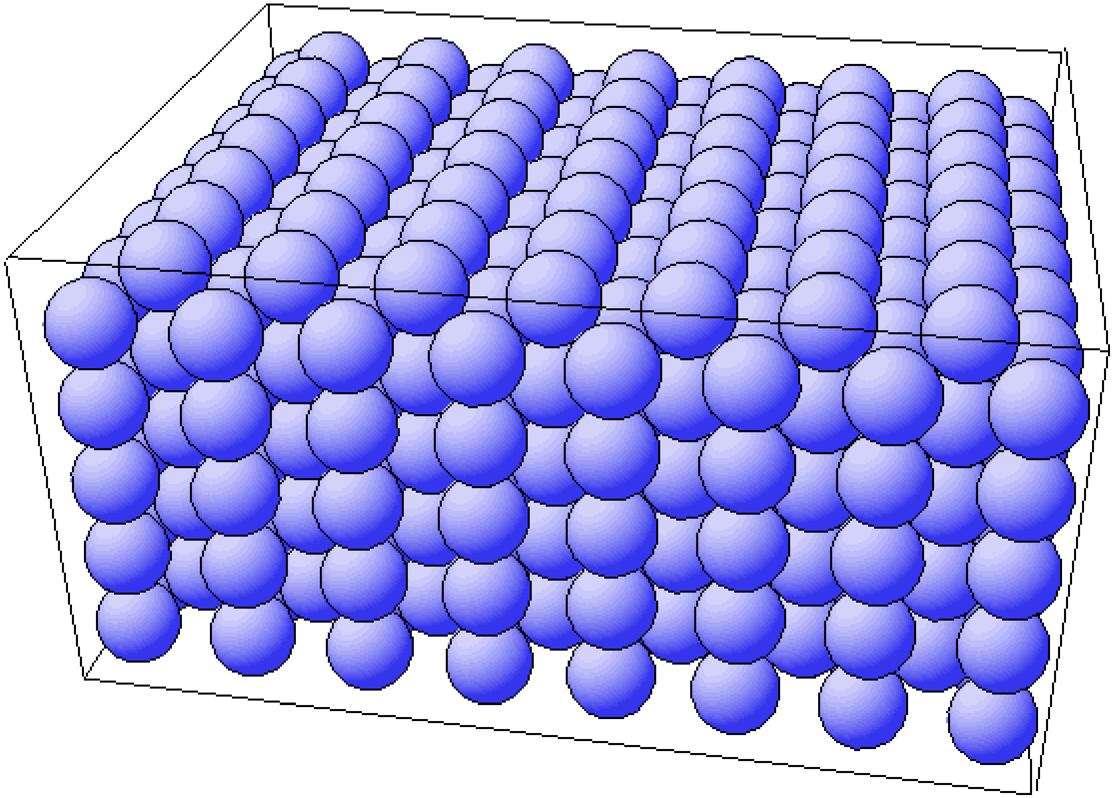


Thinking about electrolysis

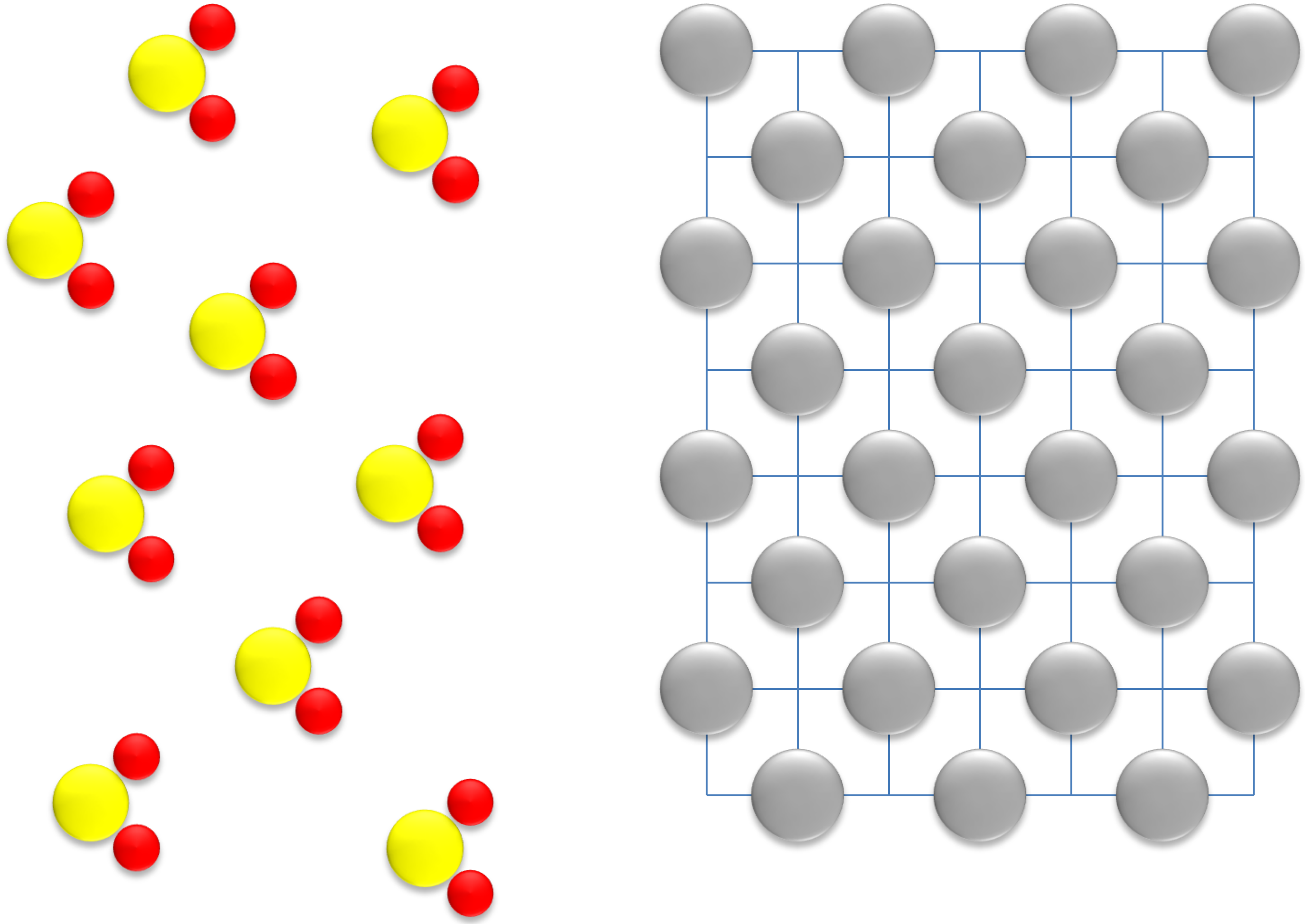
- Fleischmann-Pons experiment is an electrolysis experiment
- Current flows between anode and cathode
- Water molecules are split
- O_2 gas produced at anode
- Pd can be loaded with D by electrolysis
- D initially goes into Pd metal
- After Pd loaded then D_2 gas generated

Crystalline Pd lattice

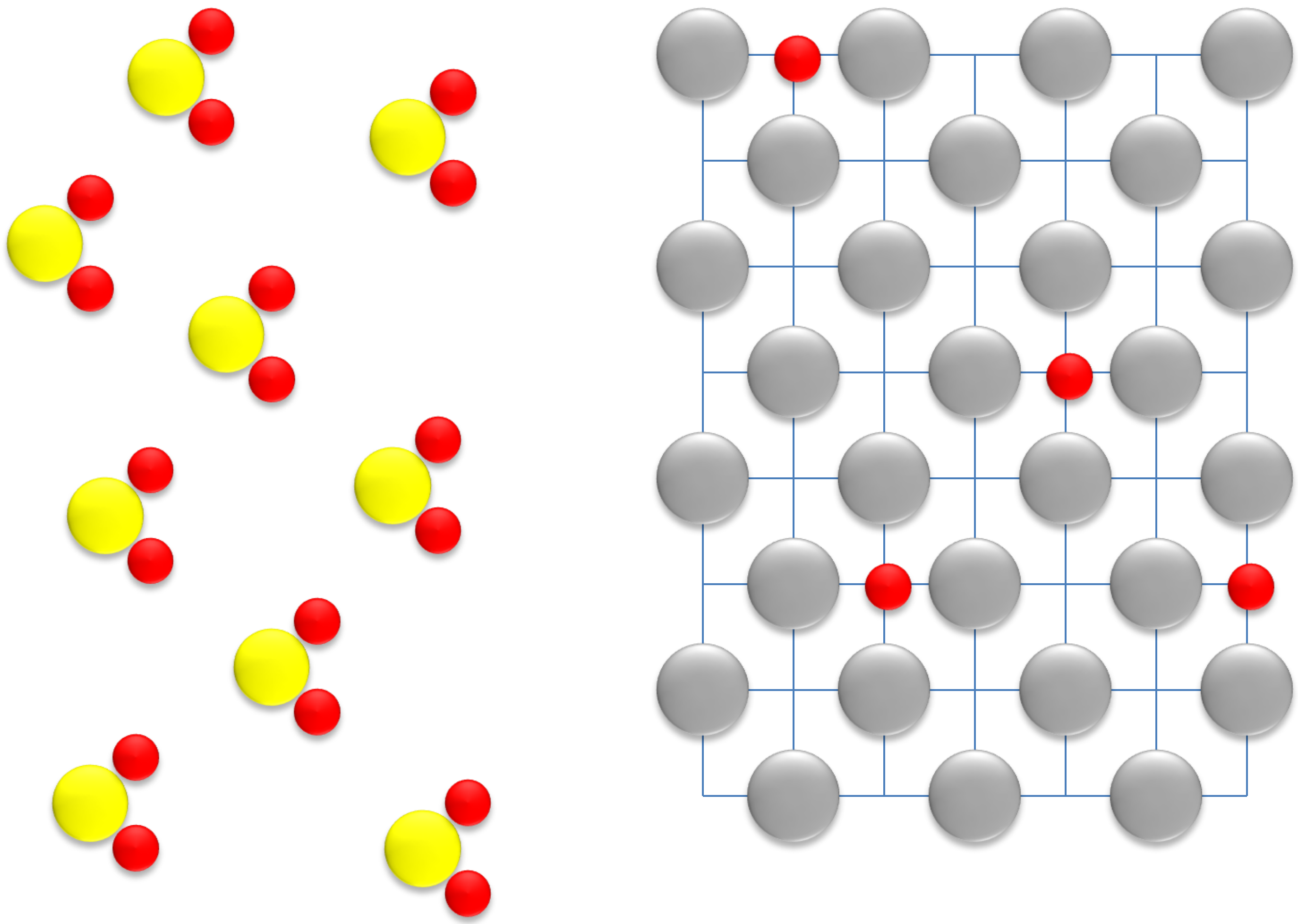




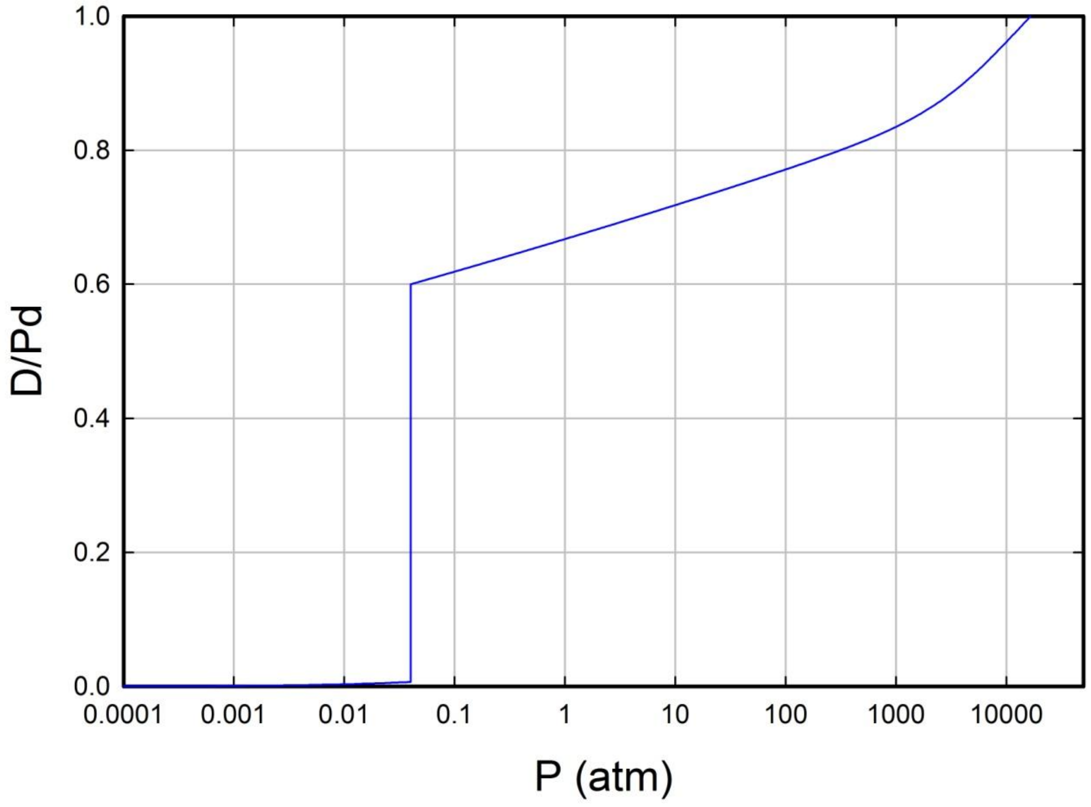
D_2O and Pd



Cathode loading



Loading of Pd in D_2 gas at 300 K

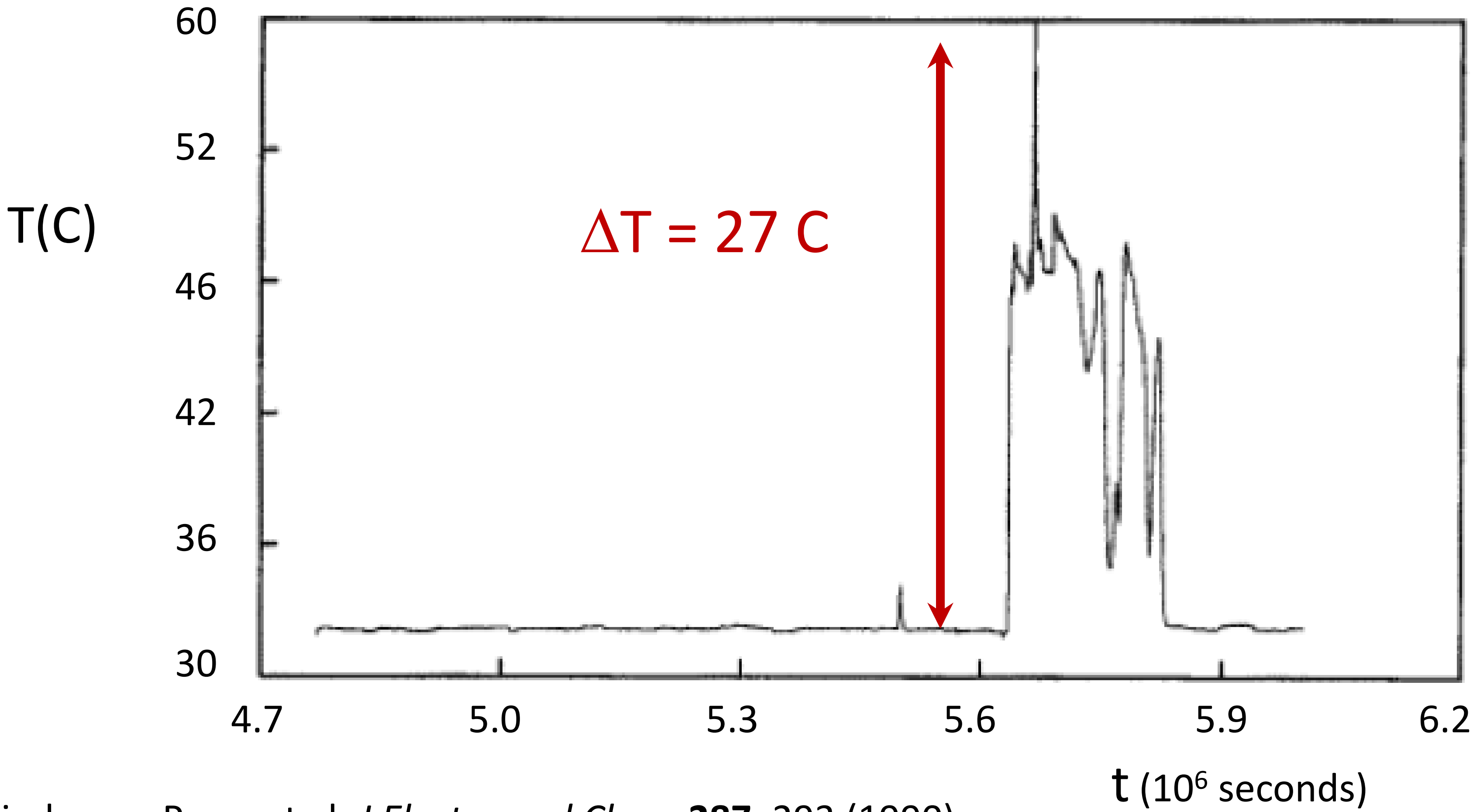


Hard to achieve very high loading

Take away message

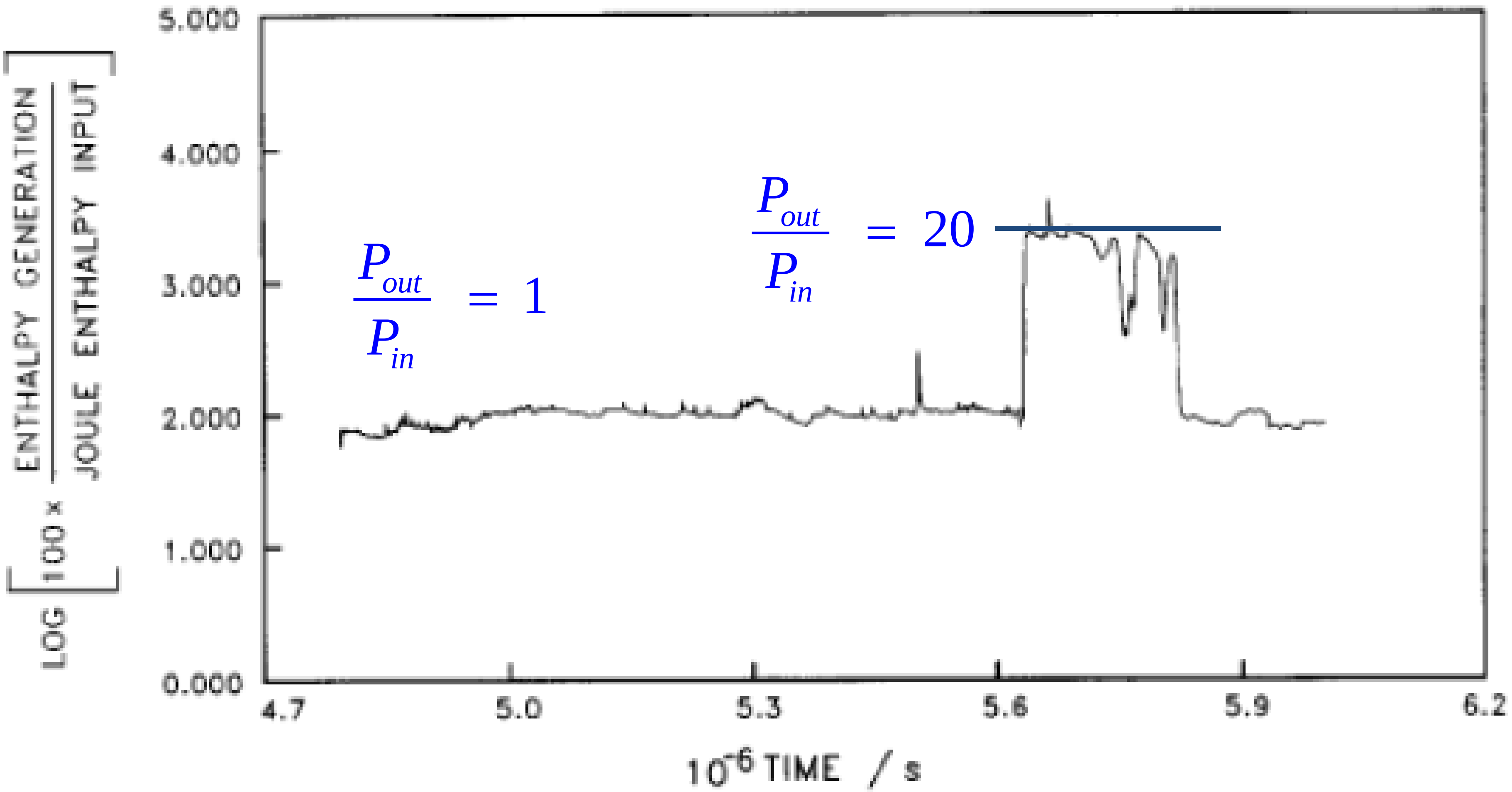
- Fleischmann-Pons experiment loads deuterium into Pd
- High D/Pd loading is needed to see excess heat
- Increasingly more difficult to load deuterium into Pd at high loading
- Wondering why high loading might be needed…

Observation of a heat burst

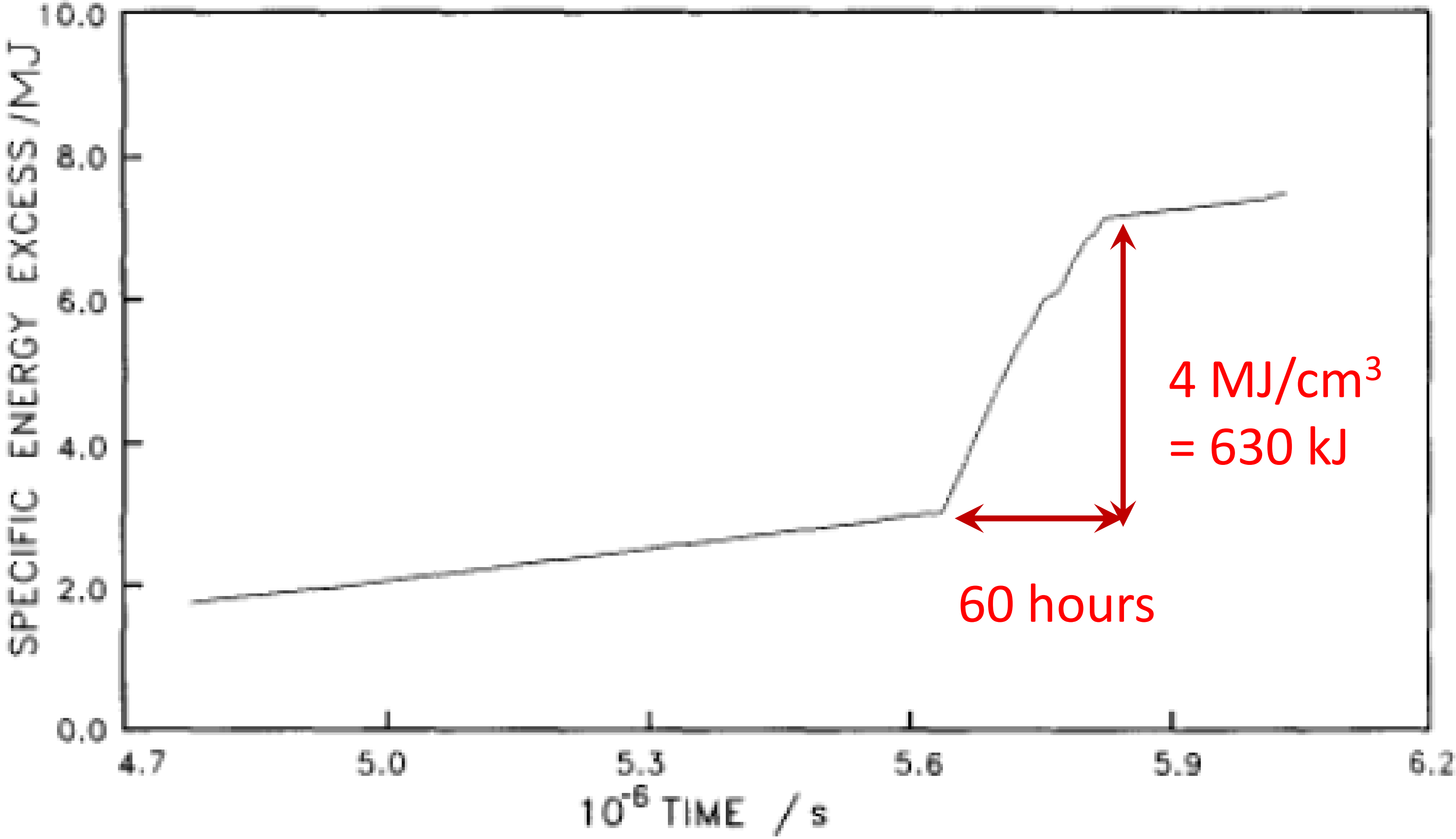


Fleischman, Pons, et al, *J Electroanal Chem* **287**, 293 (1990)

Excess power



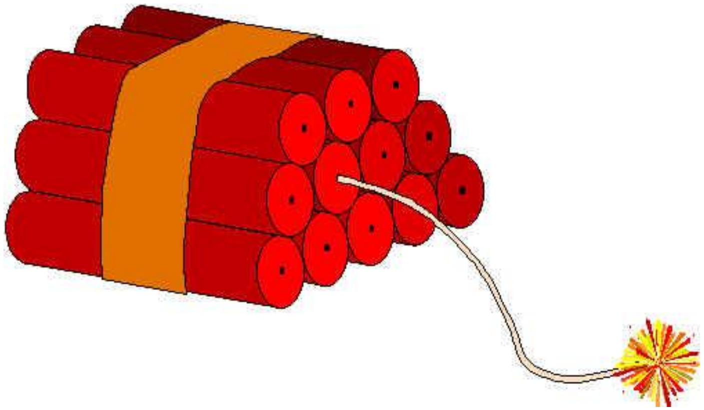
Integrated energy



Thinking about the energy

$$\frac{630\ \text{kJ}}{60\ \text{hr}} = 2.9\ \text{Watts}$$

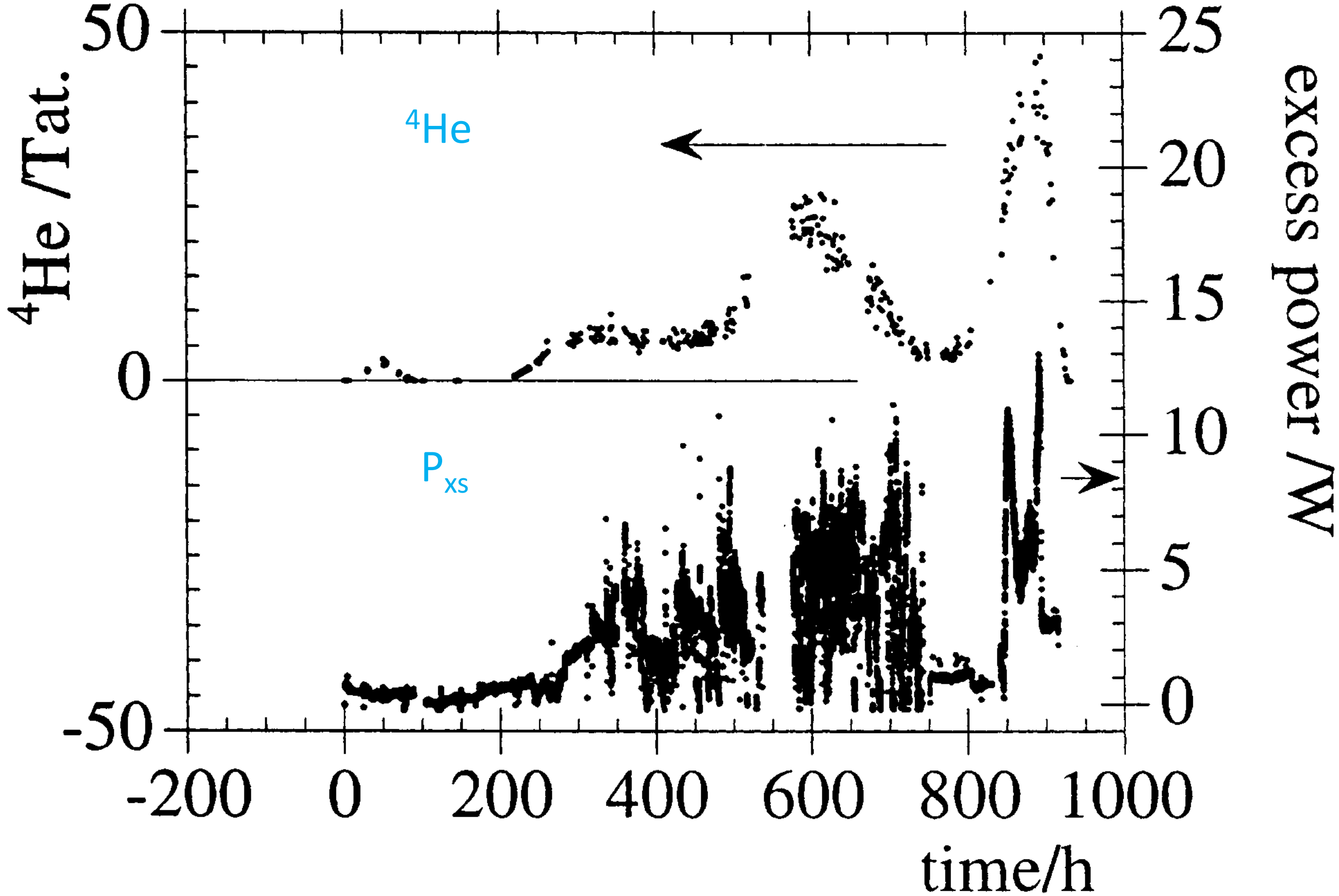
We would only get 1.2 kJ from detonating an equivalent volume (0.157 cc) as the Pd cathode of TNT



Excess heat effect

- Excess heat reported by Fleischmann and Pons
- Excess heat only after about a month of loading
- Effect was big, 20x power gain in 1990 paper
- Large total amount of energy, 630 kJ in 1990 paper
- No commensurate chemical products seen
- Fleischmann conjectured nuclear origin for the energy produced
- Subsequently many (mostly unsuccessful) searches for product nuclei
- Correlation between energy produced and ^{4}He in gas phase first reported by Miles, Bush, Lagowski et al (1993)

Time-correlation of P_{xs} and ^4He



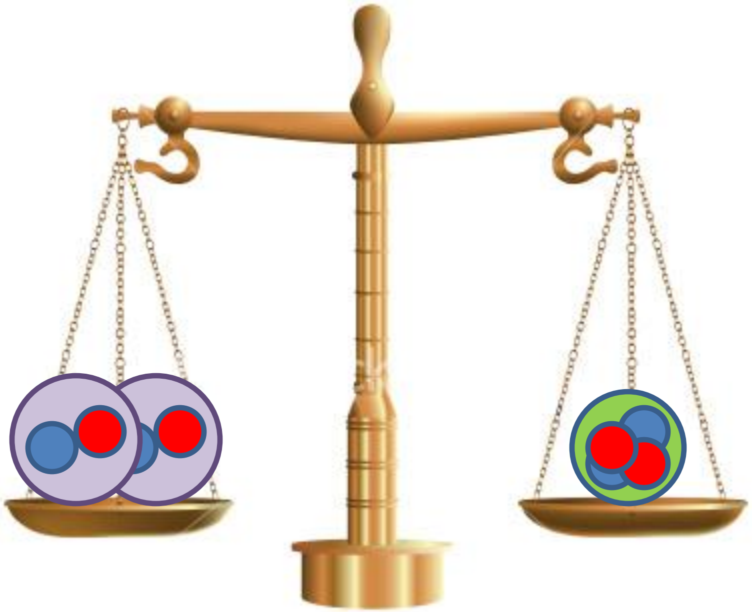
D. Gozzi, F. Cellucci, P.L. Cignini, G. Gigli, M. Tomellini, E. Cisbani, S. Frullani, G.M. Urciuoli, *J. Electroanalyt. Chem.* **452** 254 (1998).

Excess energy per ^{4}He

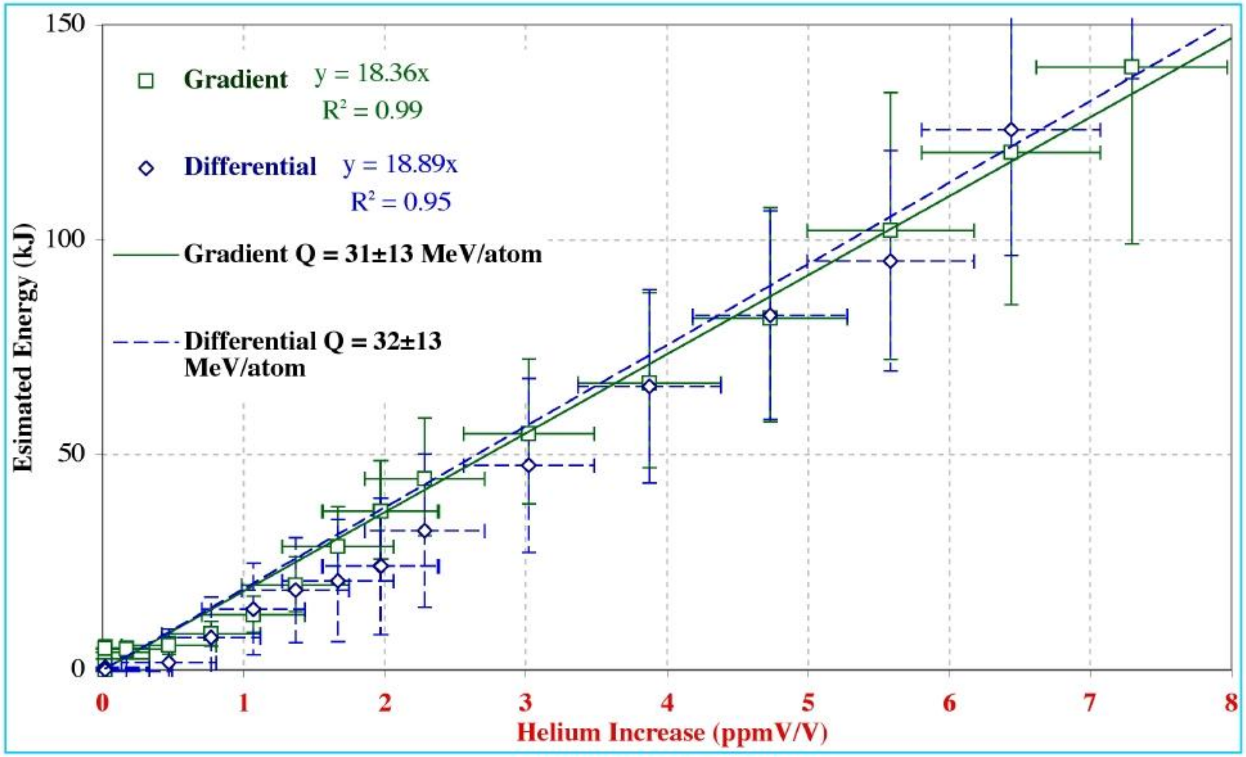
The mass difference between d+d and ^{4}He is

$$2M_d c^2 - M_{4He} c^2 \;=\; 23.85 \text{ MeV}$$

Is this consistent with experiment?



Energy as a function of ^{4}He from SRI replication of Case's experiment



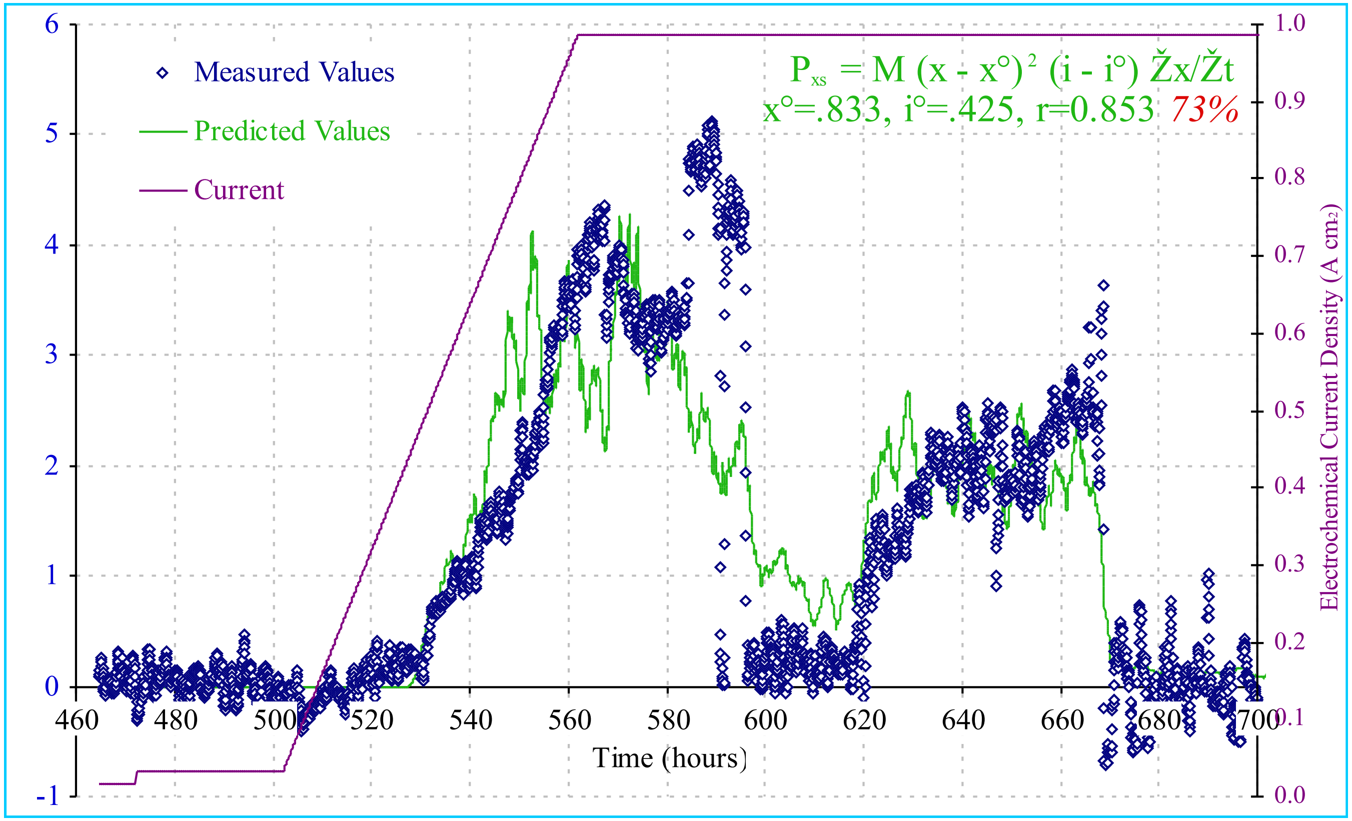
M C H McKubre, "review of experimental measurements involving dd reactions," Short course presented at ICCF10 (2003)

Not quite 24 MeV/^{4}He atom

- A moderate number of experiments with excess heat and ^{4}He
- Hoping for 24 MeV/^{4}He
- Instead, less ^{4}He seen in most experiments
- Conjecture that some of the ^{4}He stays in the cathode
- Need to scrub it out to get it all

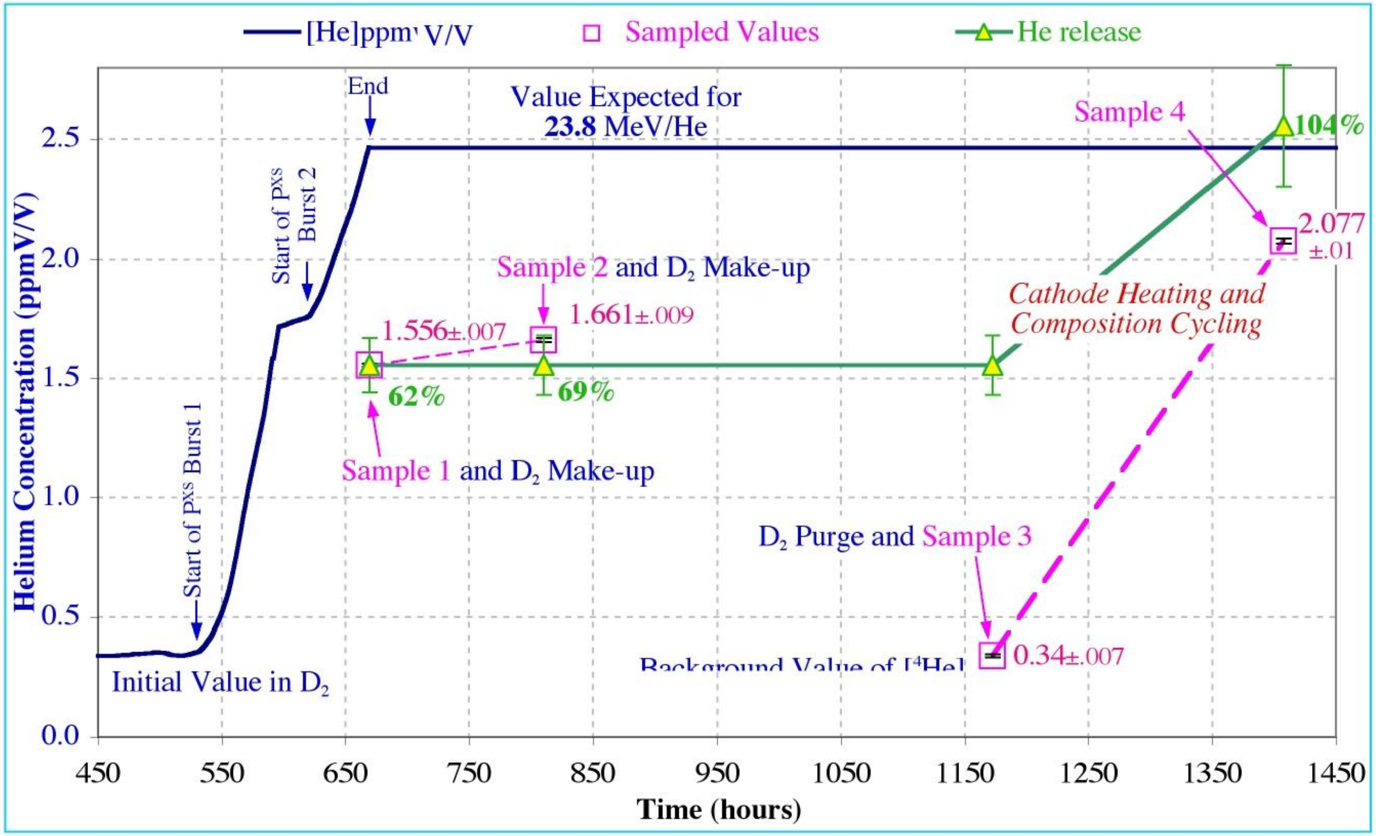
M4: Excess Power Correlation at SRI

[Closed, He-leak tight, Mass-Flow Calorimeter, Accuracy ±0.35%]



M C H McKubre, “review of experimental measurements involving dd reactions,” Short course presented at ICCF10 (2003)

^{4}He measurements



M C H McKubre, "review of experimental measurements involving dd reactions," Short course presented at ICCF10 (2003)

Consistent with 24 MeV/^{4}He atom

- Excess energy and ^{4}He measured in SRI M4 experiment
- About 2/3 of ^{4}He seen in off-gas
- Consistent with other results
- Effort made to scrub out residual ^{4}He
- Total ^{4}He measured consistent with 24 MeV/^{4}He
- One experiment carried out at ENEA Frascati with similar result
- (Absence of resources has not allowed further experiments so far)

Take away message

- Excess energy measured as heat in F&P exp’t
- No commensurate chemical products
- ^{4}He observed in amounts commensurate with energy produced
- Consistent with mass energy different between d+d and ^{4}He
- In nuclear physics d+d usually gives p+t or n+^{3}He
- ^{4}He + γ pathway is down by 10^{-7}
- Excess heat effect inconsistent with (incoherent) d+d fusion

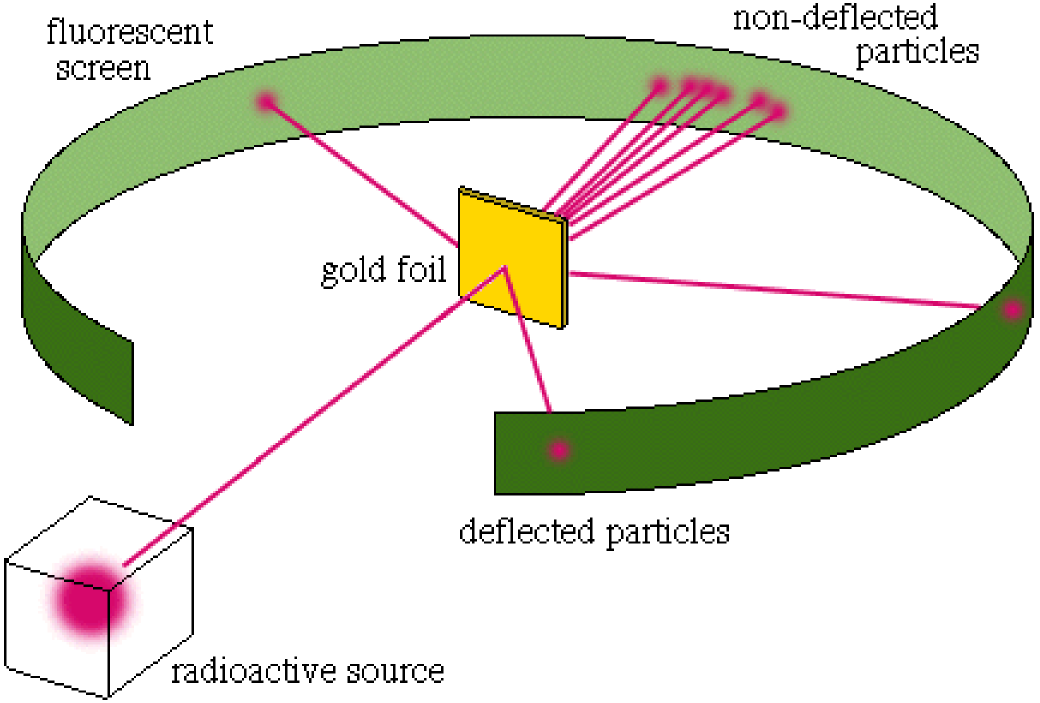
Begin to think about reaction…

- Experimental results consistent with some kind of mechanism that involves two deuterons and gives ^{4}He and energy
- But inconsistent with nuclear physics, since in accelerator exp'ts we see

$$\mathrm{d+d} \rightarrow {}^4\mathrm{He} + \gamma\left(24\ \mathrm{MeV}\right)$$

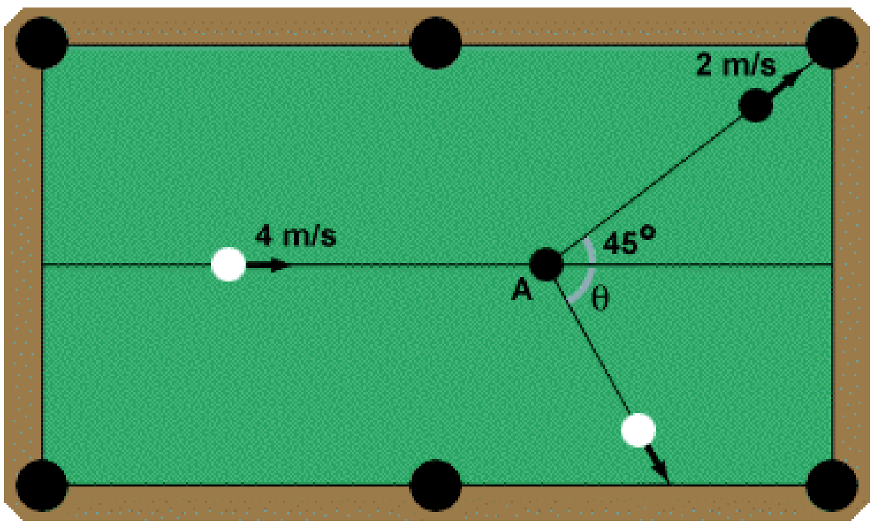
- 24 MeV gammas not present in amounts commensurate with energy (and so far not seen at all)
- Must be some new kind of mechanism?
- Where does the energy go?

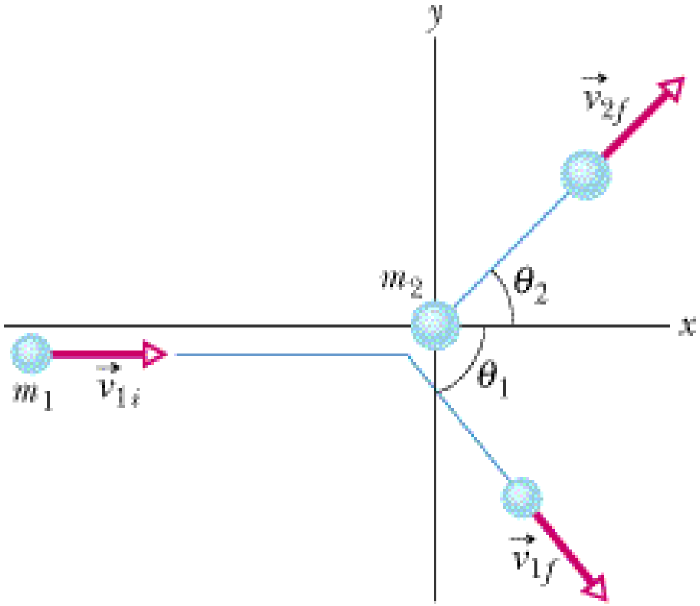
Dawn of nuclear physics



E. Rutherford

Nuclear scattering like billiard balls on a pool table





Energy and momentum conservation

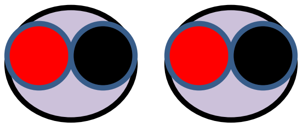
In nonrelativistic limit, can determine final state energies and momenta from conservation

$$\left(\mathbf{p}_1 + \mathbf{p}_2\right)_f = \left(\mathbf{p}_1 + \mathbf{p}_2\right)_i$$

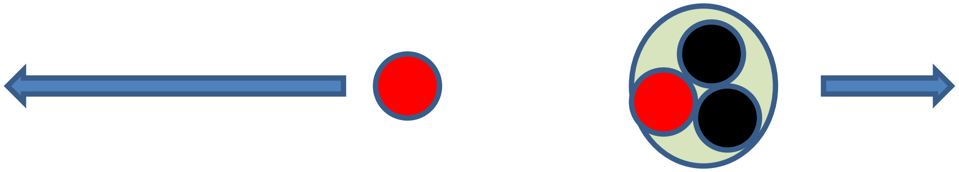
$$\left(\frac{1}{2}m_1\left|\mathbf{v}_1\right|^2 + \frac{1}{2}m_1\left|\mathbf{v}_2\right|^2\right)_f = \left(\frac{1}{2}m_1\left|\mathbf{v}_1\right|^2 + \frac{1}{2}m_1\left|\mathbf{v}_2\right|^2\right)_i + Q$$

Energy and momentum conservation

Initial state:



Final state:



$$\frac{1}{2}M_1|\mathbf{v}_1|^2 = \left(\frac{M_2}{M_1+M_2}\right)Q = \frac{3}{4}Q$$

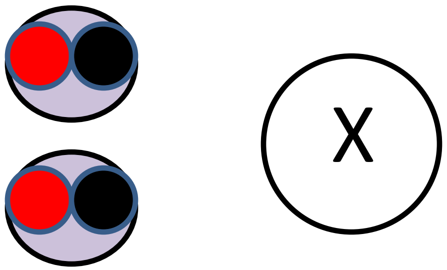
$$\frac{1}{2}M_2|\mathbf{v}_2|^2 = \left(\frac{M_1}{M_1+M_2}\right)Q = \frac{1}{4}Q$$

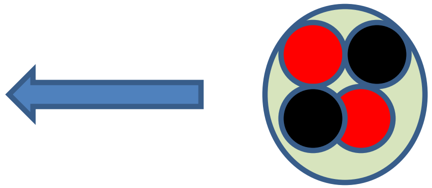
Can learn about the reaction if we knew ^{4}He energy

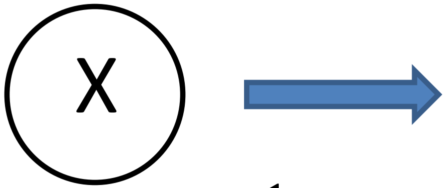
A proposed reaction scheme:

$$d + d + X \rightarrow$$

$$^4\mathrm{He} + X + 24\ \mathrm{MeV}$$







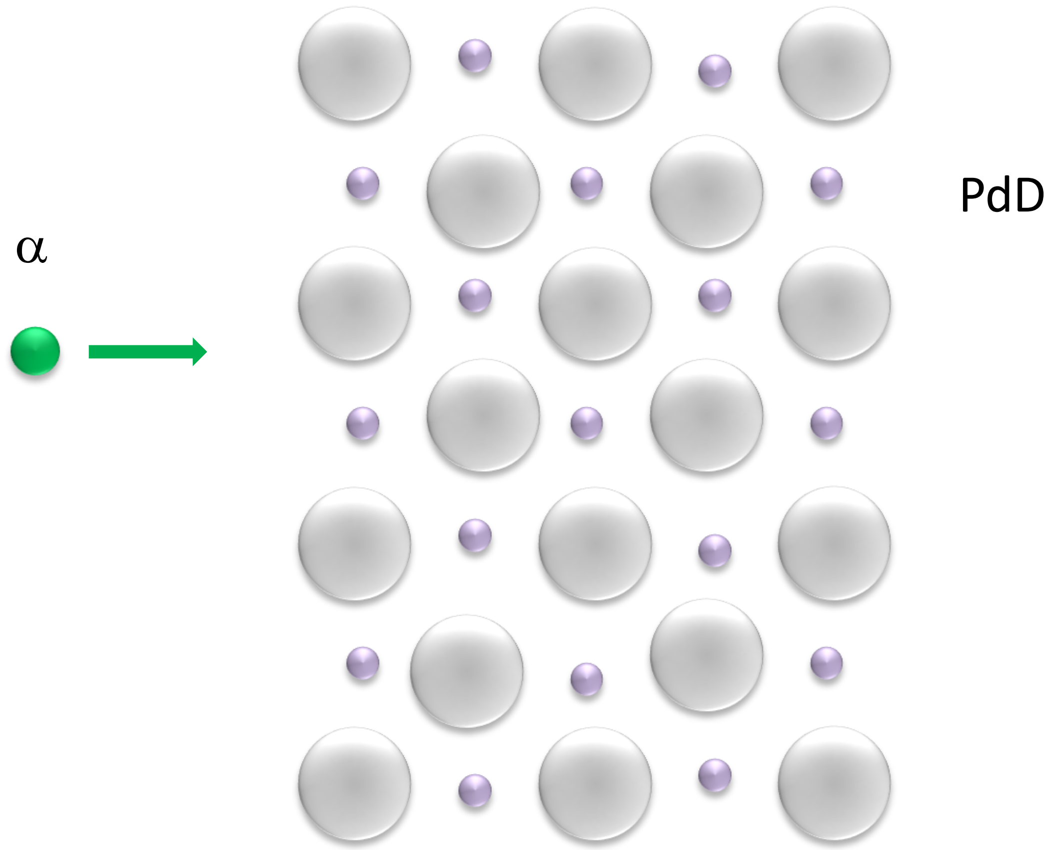
$$\frac{1}{2} M_{4He} \left|\mathbf{v}_{4He}\right|^2 = \left(\frac{M_X}{M_{4He} + M_X}\right) 24\ \mathrm{MeV}$$

$$\frac{1}{2} M_X \left|\mathbf{v}_X\right|^2 = \left(\frac{M_{4He}}{M_{4He} + M_X}\right) 24\ \mathrm{MeV}$$

Want to measure ^4He energy

- Silicon surface barrier detectors normally used for α spectroscopy
- Not so compatible with electrochemical cell
- Could use CR-39 emulsion detector
- But would get α only if it left the cathode
- Not an easy task to get at α

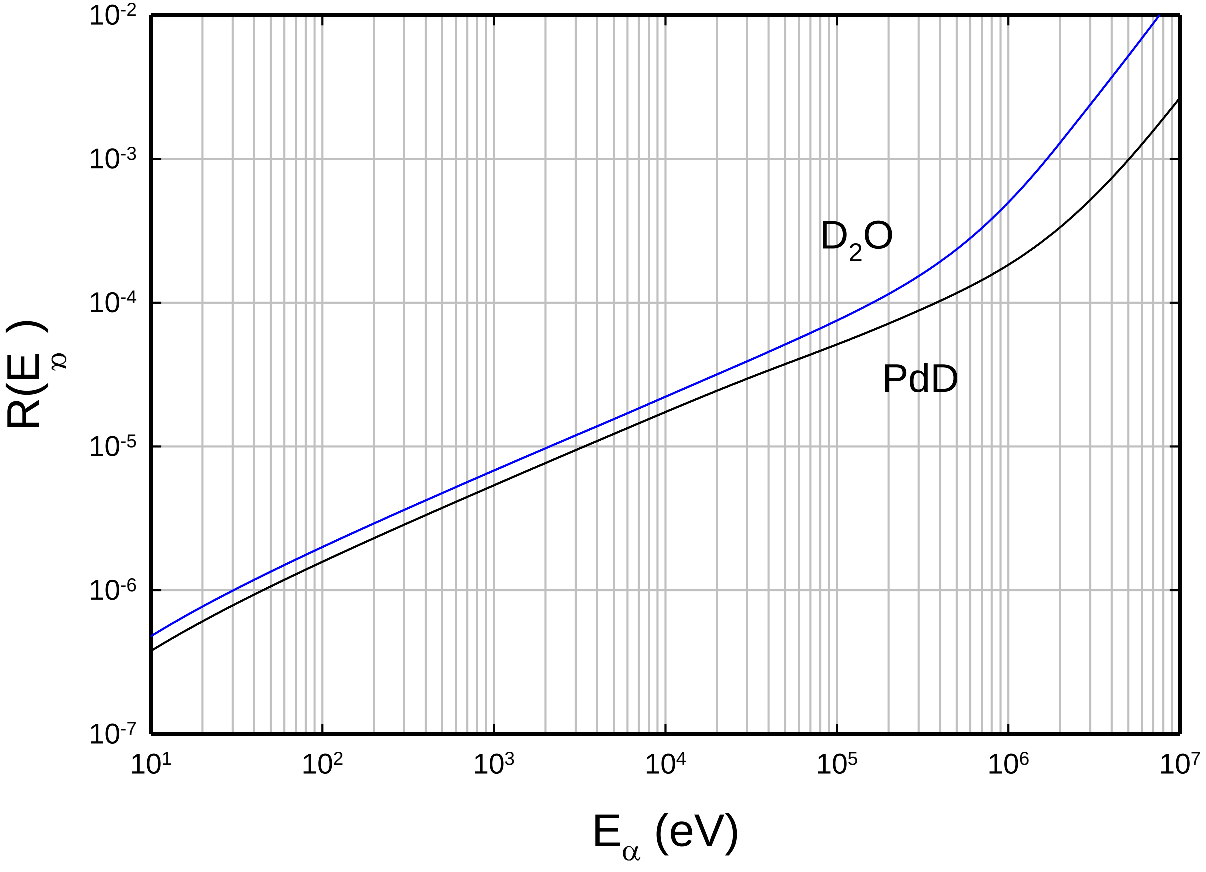
Propose using PdD as detector



Loaded cathode as detector

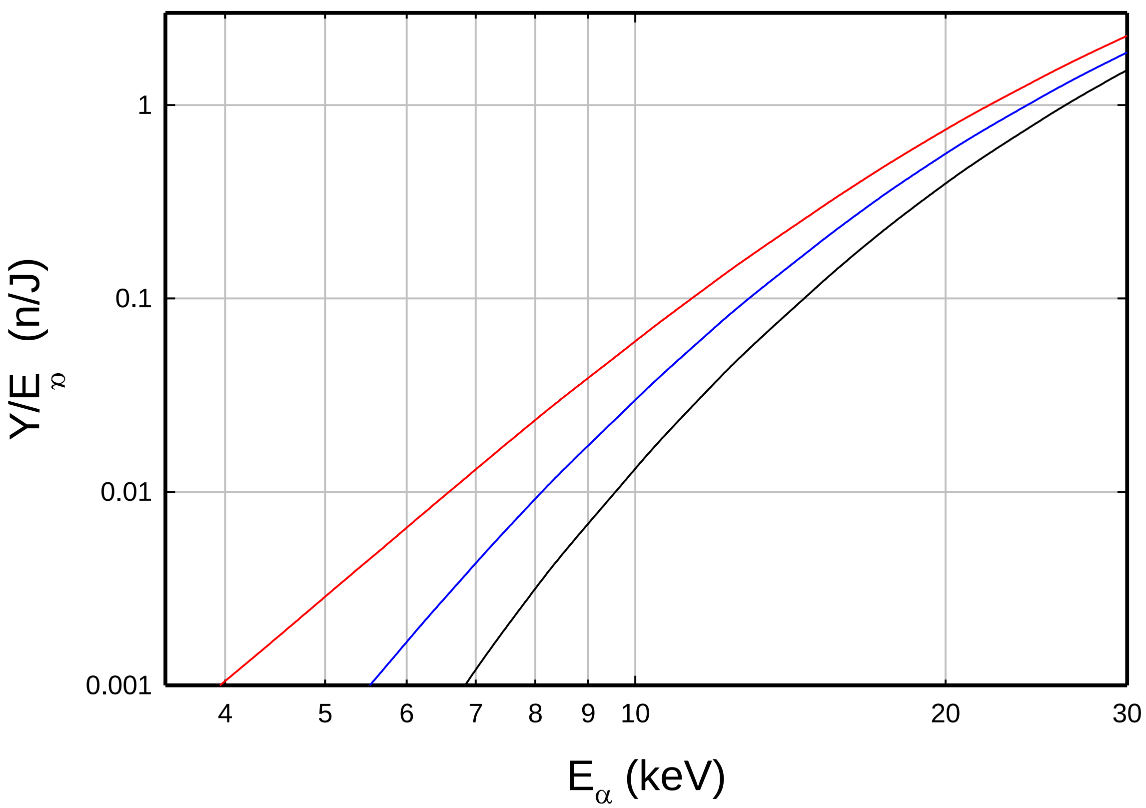
- Think of PdD (or D_2O) as the detector
- Fast alpha breaks up deuteron, makes neutrons
- Less fast alpha can hit deuteron, causes secondary d+d reaction (which makes a neutron)
- So, need to calculate neutron yields
- And then look at experiment to see how many neutrons come out!

Range



10-2
10-3
10-4
10-5
10-6
10-7
R(E_α)
D2O
PdD
10^1
10^2
10^3
10^4
10^5
10^6
10^7
E_α (eV)

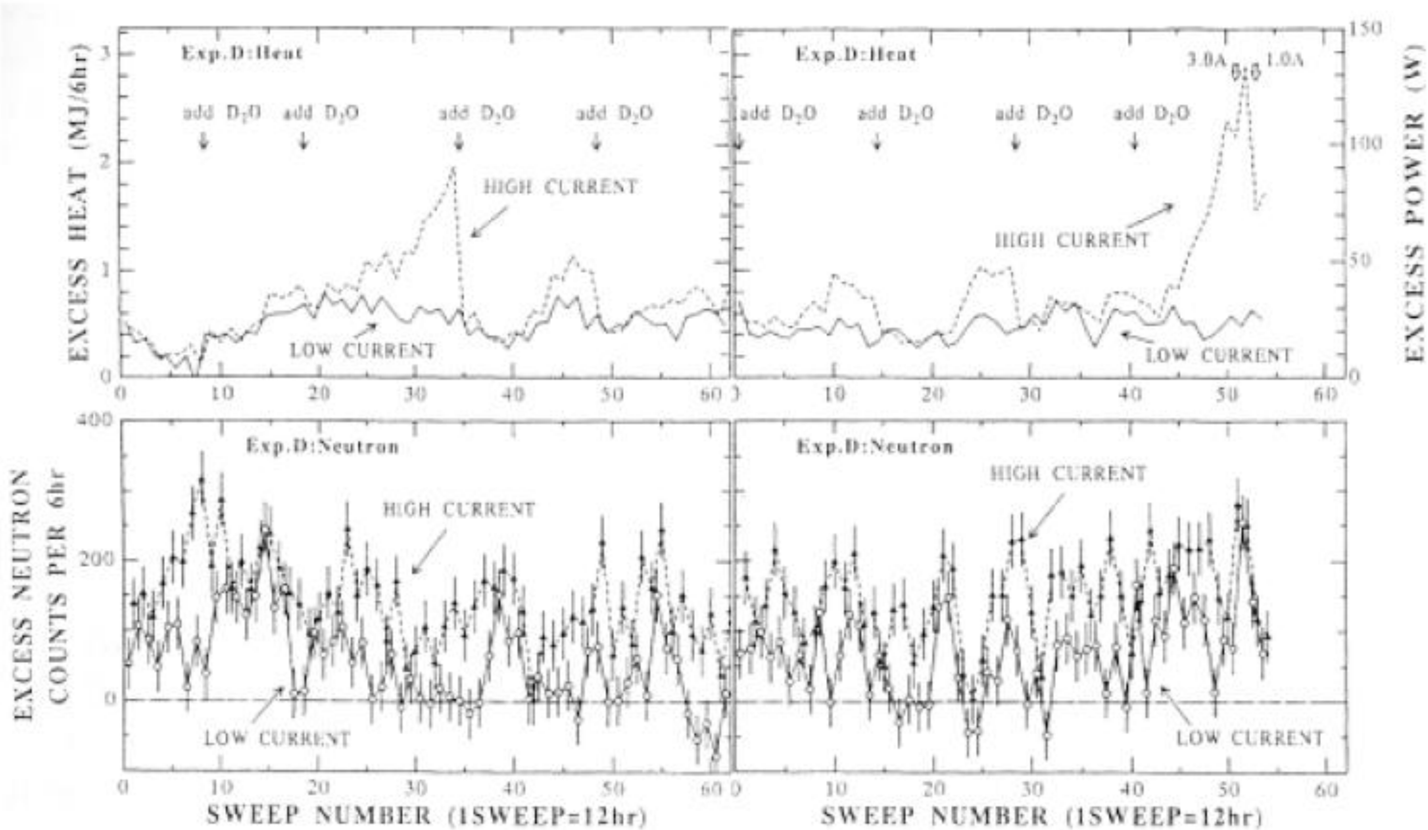
Biggest yield at low energy from secondary neutrons



Very sensitive detector!

- PdD turns out to be a very sensitive detector for fast alphas
- α range in the 10s of microns range and below
- Reactions that generate neutrons for α energy below 10 keV
- Can detect neutrons outside of cell
- Get similar numbers for D_2O

Turn to experiment

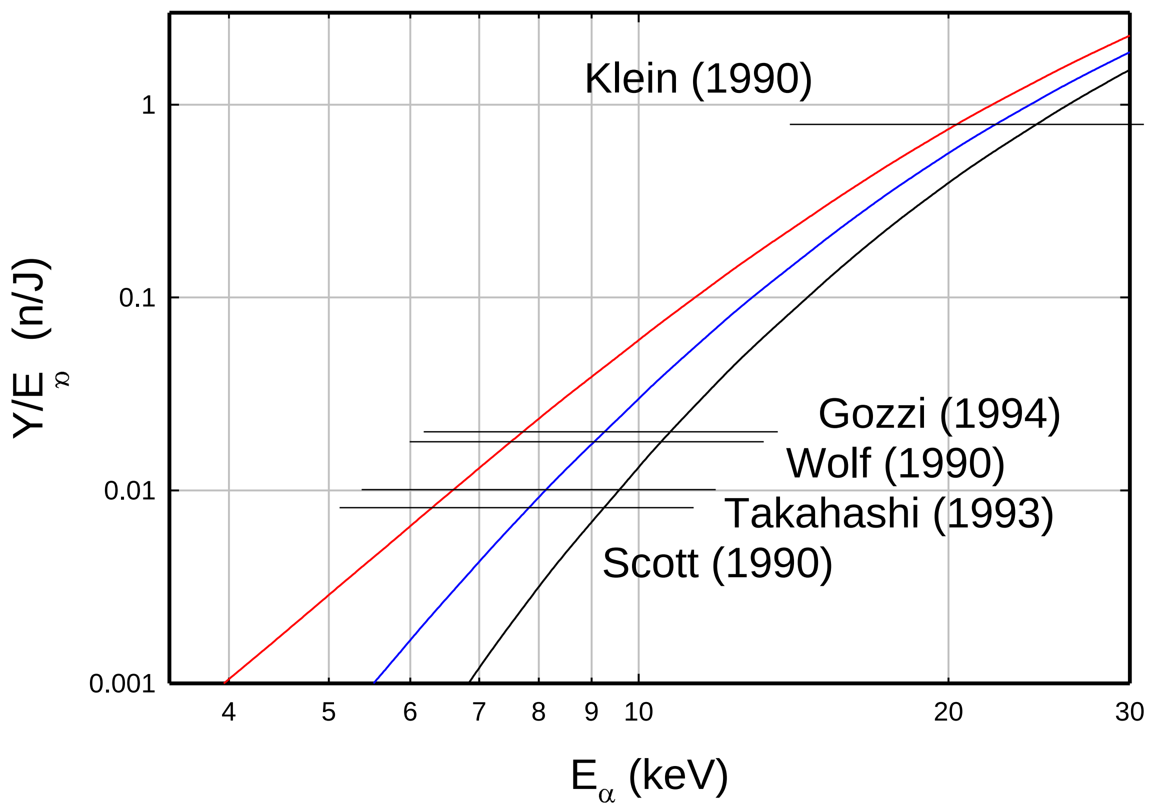


A. Takahashi, A. Mega, T. Takeuchi, H. Miyamaru, and T. Iida, *Proc. ICCF3* **79** (1993).

Result

- Roughly 10 experiments where neutron detection working when excess heat seen
- Neutron emission not correlated with P_{xs}
- Five of these documented in enough detail to estimate upper limit on the source neutrons per joule
- Get upper limit near 0.01 neutrons/Joule

Yield/energy for secondary neutrons



P. L. Hagelstein, *Naturwissenschaften* (2010)

Examine d+d+X candidates

$$d + d + \mathrm{Pd} \rightarrow {}^{4}\mathrm{He}\left(23.0\ \mathrm{MeV}\right) + \mathrm{Pd}\left(0.85\ \mathrm{MeV}\right)$$

$$d + d + d \rightarrow {}^{4}\mathrm{He}\left(7.95\ \mathrm{MeV}\right) + d\left(15.9\ \mathrm{MeV}\right)$$

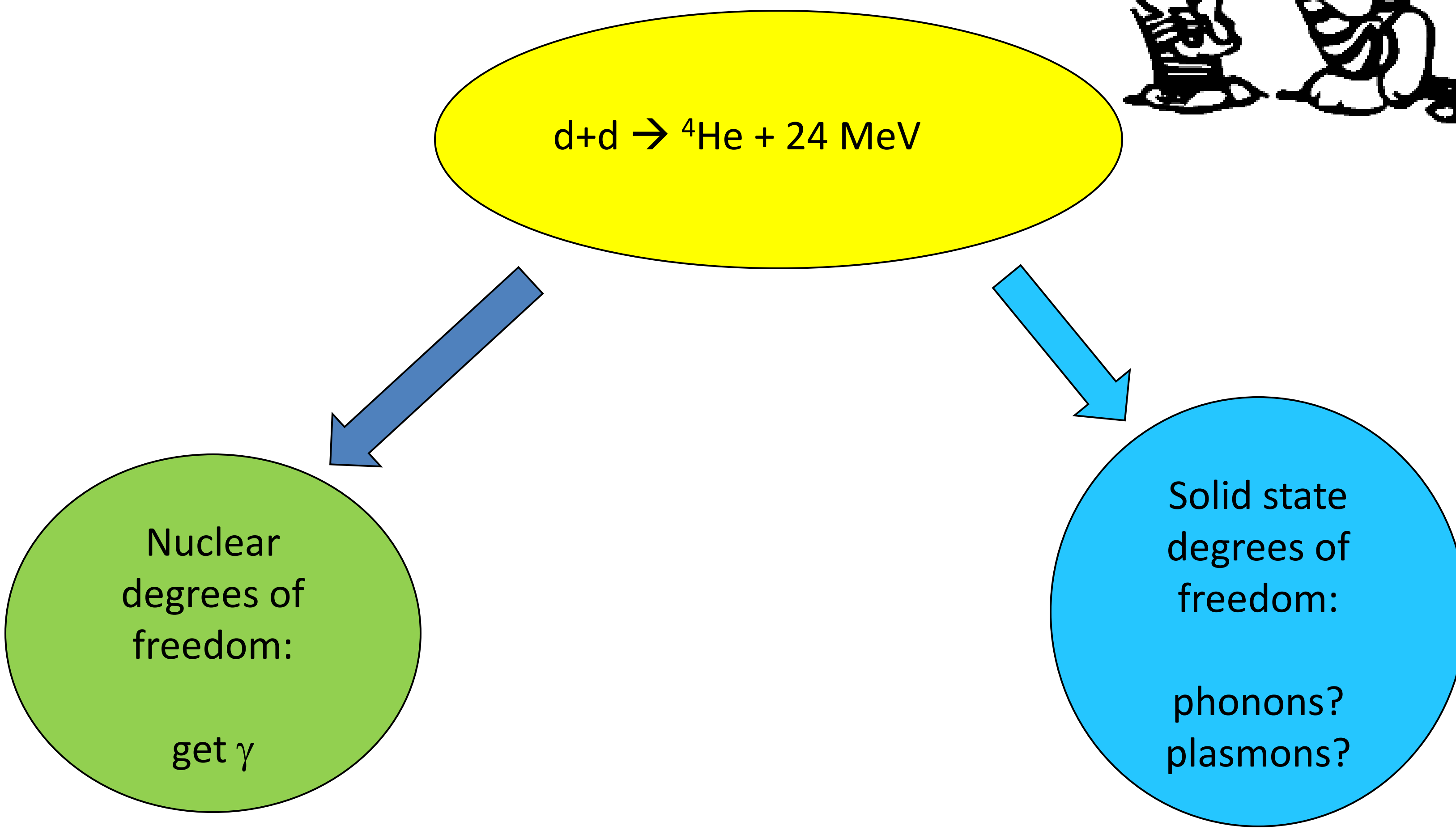
$$d + d + e^{-} \rightarrow \mathrm{He}\left(76\ \mathrm{keV}\right) + e^{-}\left(23.77\ \mathrm{MeV}\right)$$

We can rule out all Rutherford picture d+d+X reactions as inconsistent with experiment

Take away message

- Goal was to learn something about reaction mechanism by determining α energy
- Propose to use PdD and D_2O as detectors
- Less than 0.01 neutron/Joule in experiments
- Conclude ^4He born with less than 20 keV
- Consistent with no plausible Rutherford picture reaction
- ^4He is born essentially stationary…wonder where the energy goes

What is nature up to?



Letts 2-laser experiment

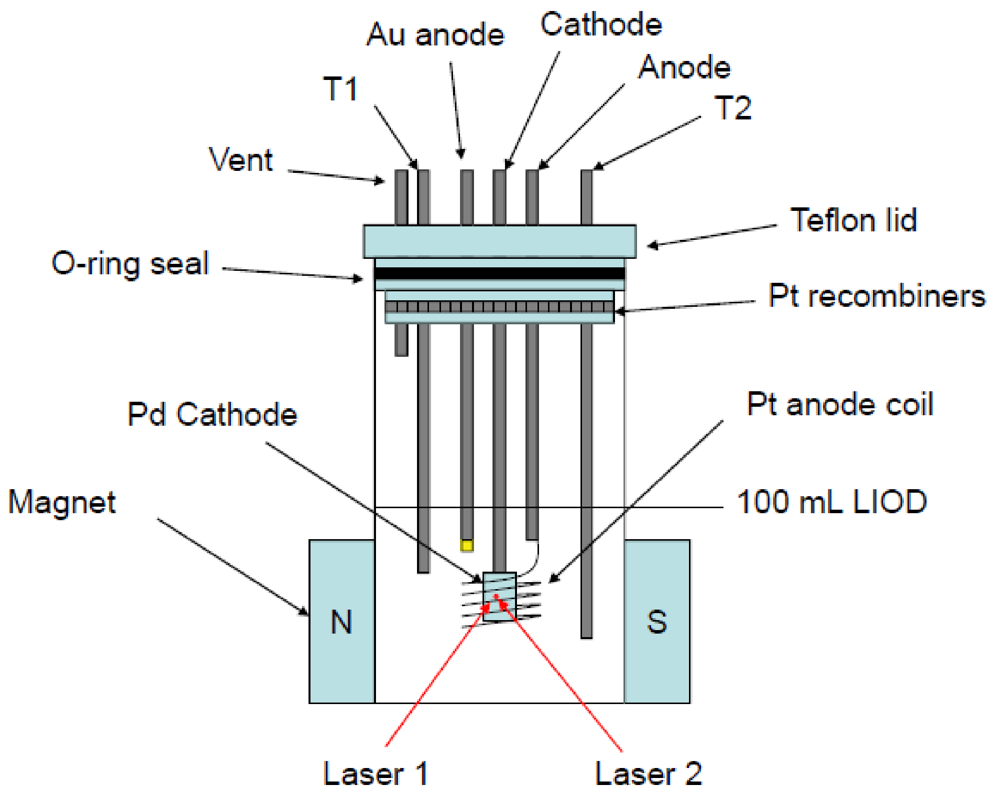
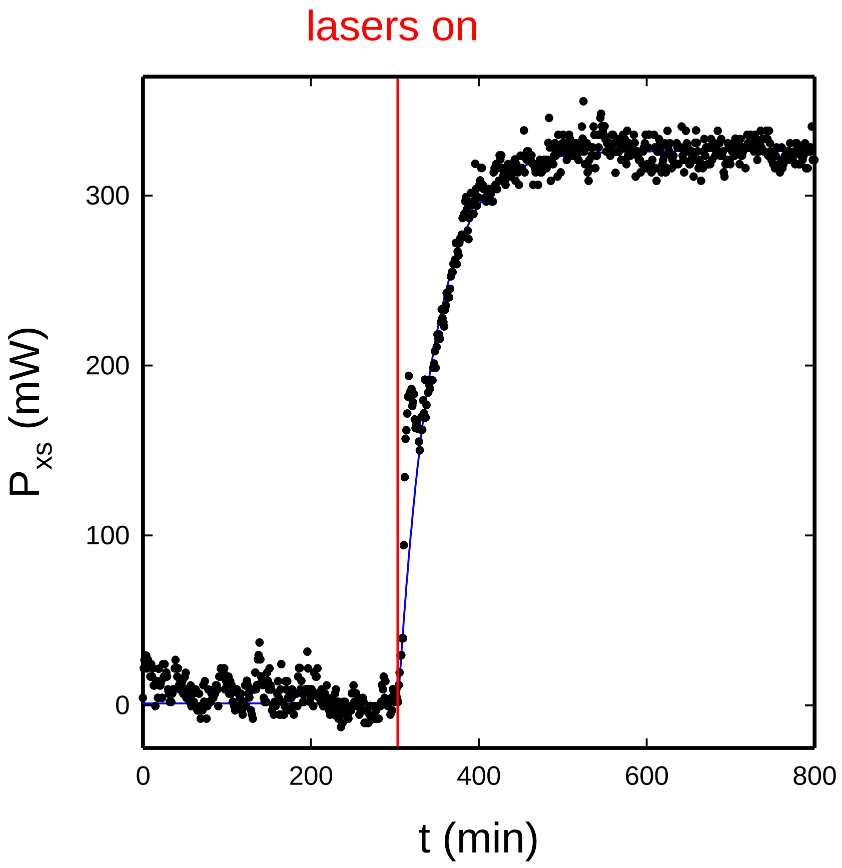


Figure 1. Schematic of the experimental set-up.

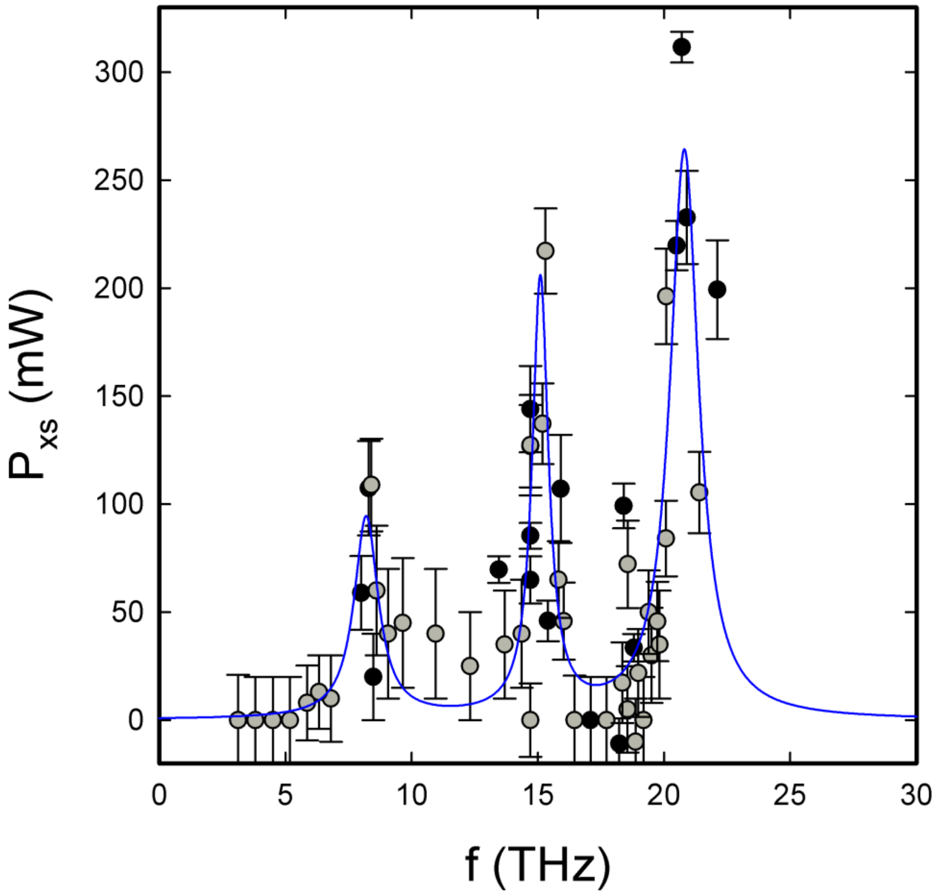
D. Letts, D. Cravens, and P.L. Hagelstein, *LENR Sourcebook* Volume 2, ACS: Washington DC. p. 81-93 (2009).

Excess power with 2 lasers

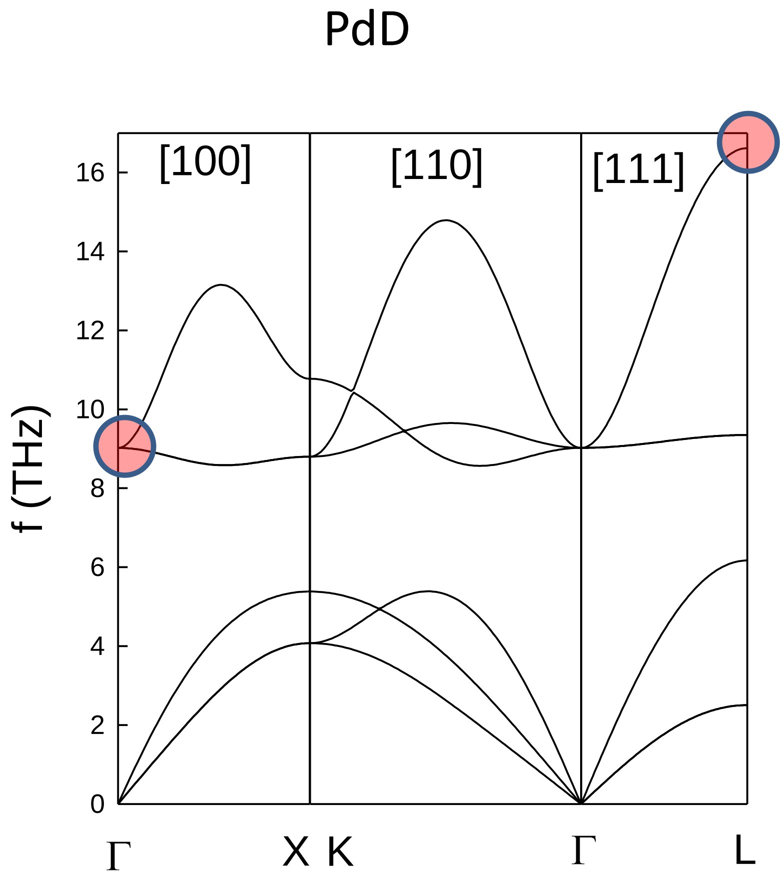


P. Hagelstein, D. Letts, and D. Cravens, *J Cond. Mat. Nucl. Sci.* **3** *59, 77 (2010)*

Sweet spots in the spectrum

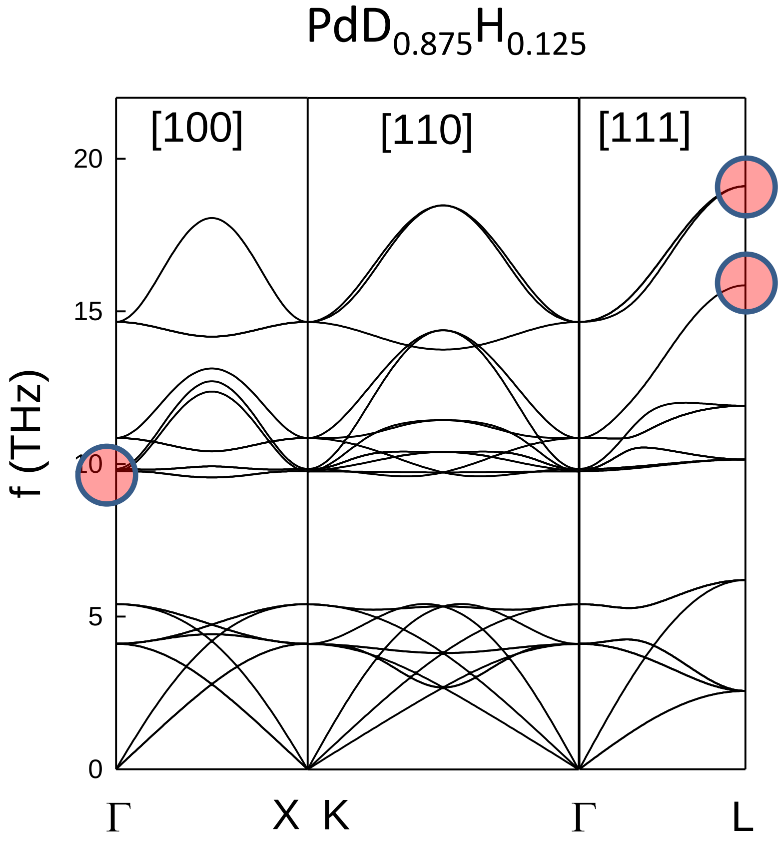


Dispersion curve for PdD



Operation was predicted on compressional modes with zero group velocity

Dispersion curve for PdD with some H



Importance of 2 laser exp'ts

- Interested in question of where the nuclear energy goes
- In Letts 2-laser experiment, P_{xs} responds to beat frequency
- …as if effect stimulated by optical phonons
- By analogy with laser, might expect nuclear energy to go into optical phonons
- Excess power unchanged after two lasers turned off
- Interpret experiment as providing indirect evidence that nuclear energy goes directly into optical phonon modes

Take away message

- Experiments show ^{4}He in amounts commensurate with energy
- ^{4}He born essentially stationary
- Indirect evidence from two laser experiment that nuclear energy goes into THz vibrations
- (Not like any normal nuclear process)

Moving toward a model

- Much effort working on theory… (too much to go into detail here)
- Basic idea is that there is a “simple” mechanism capable of splitting a large quantum into many small ones
- A theory has been worked out that describes this, using two-level systems, a highly-excited oscillator, and loss
- Coupling between nuclear motion and internal nuclear degrees of freedom in relativistic model

$$\hat{H} = \sum_j \mathbf{M}_j c^2 + \mathbf{a}_j \cdot c\hat{\mathbf{P}}_j + \sum_k \frac{|\hat{\mathbf{p}}_k|^2}{2m} + \sum_{j<j'} \frac{Z_j Z_{j'} e^2}{4\pi\varepsilon_0 |\mathbf{R}_j - \mathbf{R}_{j'}|}$$

$$+ \sum_{k<k'} \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_j - \mathbf{r}_{j'}|} + \sum_{j,k} \frac{Z_j e^2}{4\pi\varepsilon_0 |\mathbf{R}_j - \mathbf{r}_k|}$$

Current status…

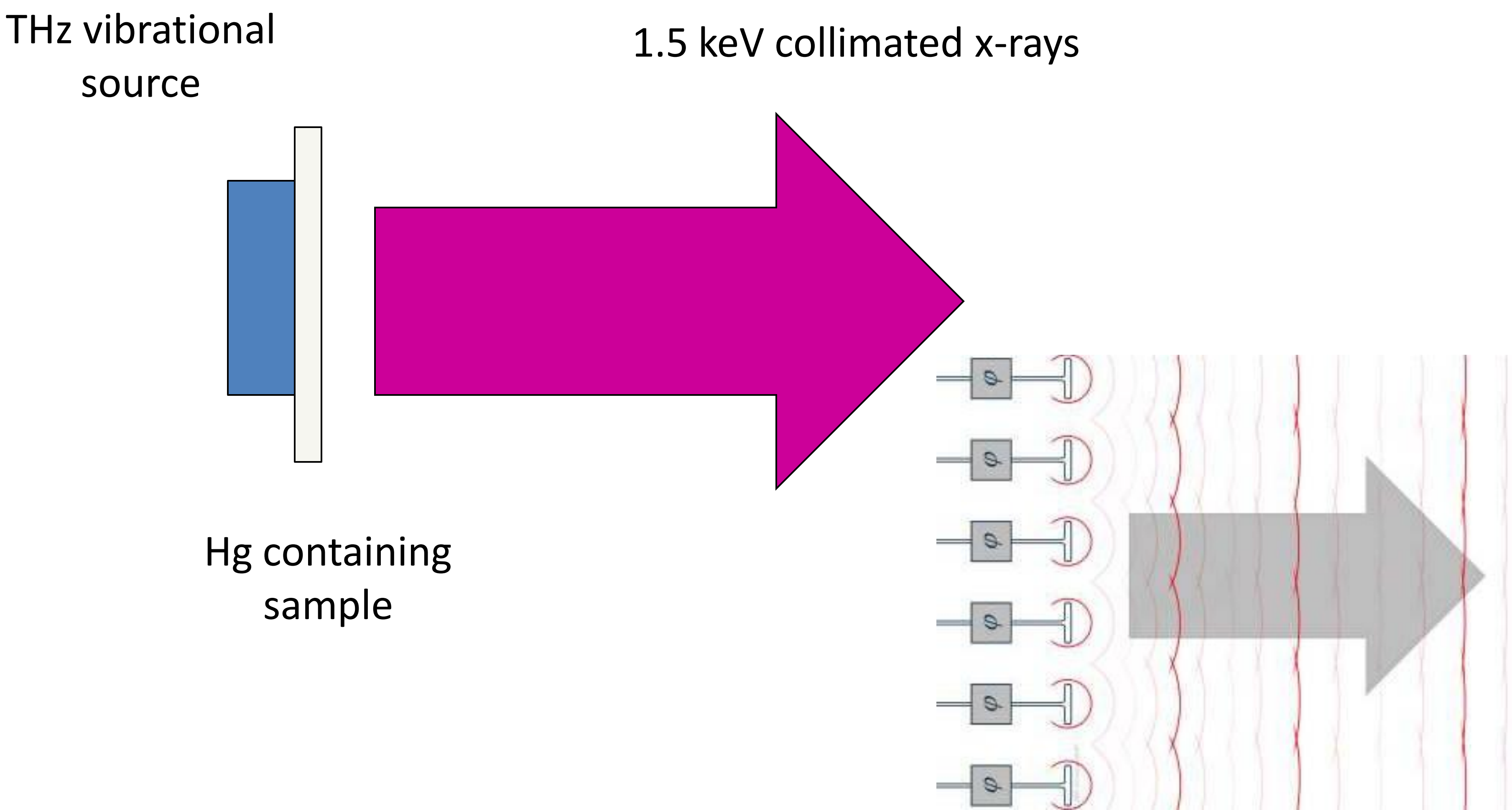
- Governing fundamental Hamiltonian specified
- Estimates for rates for fractionation of large quantum worked out
- Coulomb tunneling factor comes in only once (instead of twice as in incoherent reactions), so no heroics needed in model to overcome barrier
- Predicted rates for excess heat comparable to experiment right out of the box
- F&P exp't involves down-conversion, but maybe should be able to see up-conversion of vibrations to produce nuclear excitation

What are lowest energy nuclear transitions?

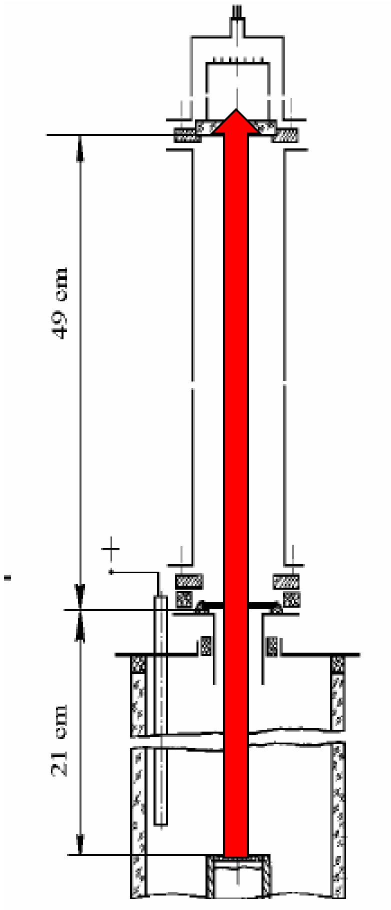
Nucleus	Excited state energy (keV)	half-life	multipolarity
^{201}Hg	1.5648	81 ns	M1+E2
^{181}Ta	6.240	6.05 μs	E1
^{169}Tm	8.41017	4.09 ns	M1+E2
^{83}Kr	9.4051	154.4 ns	M1+E2
^{187}Os	9.75	2.38 ns	M1(+E2)
^{73}Ge	13.2845	2.92 μs	E2
^{57}Fe	14.4129	98.3 ns	M1+E2

P. L. Hagelstein, "Bird's eye view of phonon models for excess heat in the Fleischmann-Pons experiment," *J. Cond. Mat. Nucl. Sci.* **6** 169 (2012)

Conceptual design



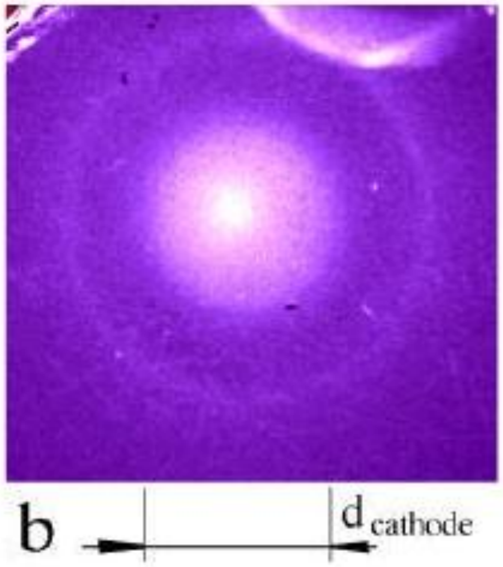
Karabut experiment (ICCF10)



Collimated x-rays near 1.5 keV seen with different metals (Al, V, Fe, Zn, Mo, Pd, W, others)

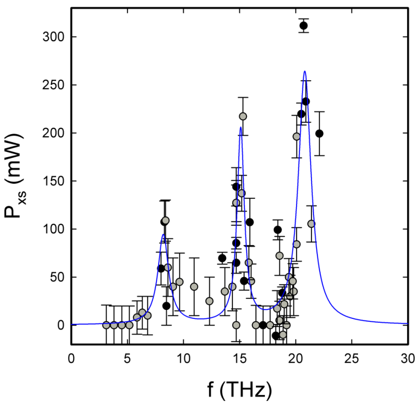
…and with different gasses (H_2, D_2, Kr, Xe)

Pinhole camera image

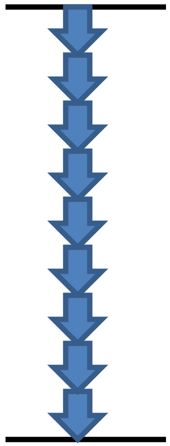


Down-conversion, up-conversion

Fleischmann-Pons

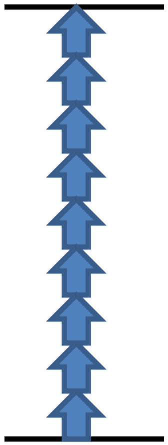


D_2



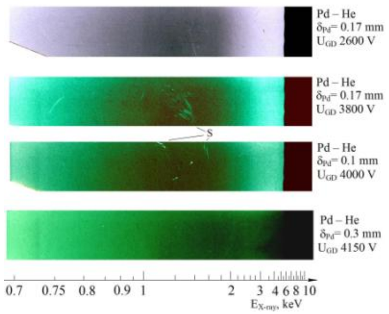
^4He

^{201}Hg (1565 eV)



^{201}Hg (0 eV)

Karabut



$$\text{Direct: } \Delta n = \frac{\Delta E}{\hbar\omega_0} = \frac{24 \text{ MeV}}{33 \text{ meV}} = 10^9$$

$$\text{Direct: } \frac{\Delta E}{\hbar\omega_0} = \frac{1565 \text{ eV}}{500 \text{ neV}} = 3\times 10^9$$

$$\text{With subdivision: } \Delta n = \frac{\Delta E}{\hbar\omega_0} = 10^7$$

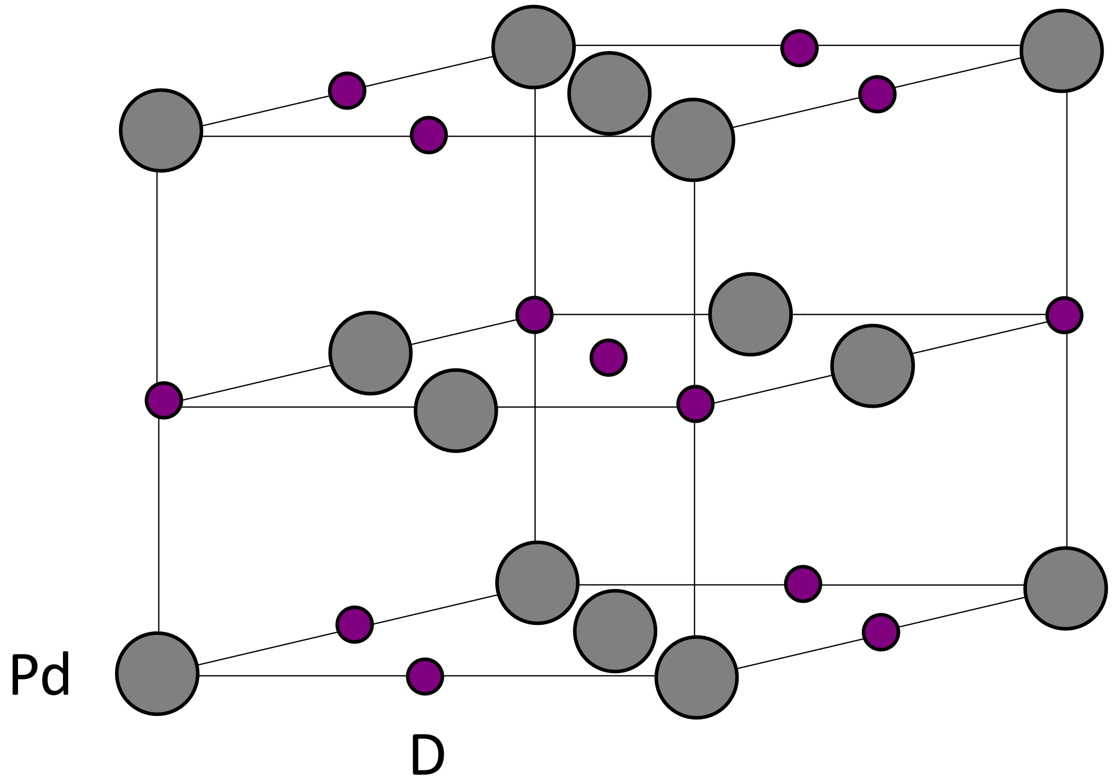
Take away message

- Many theories proposed
- Conjecture that coherent processes are involved
- Need to be able to down-convert large quantum for this to work
- Model discovered in 2002 capable of coherent down-conversion and up-conversion
- Relativistic interaction Hamiltonian proposed for coupling between vibrations and internal nuclear degrees of freedom
- Model able to describe excess heat effect and give reaction rates comparable to experiment
- Want to develop collimated x-ray emission experiment to confirm/study

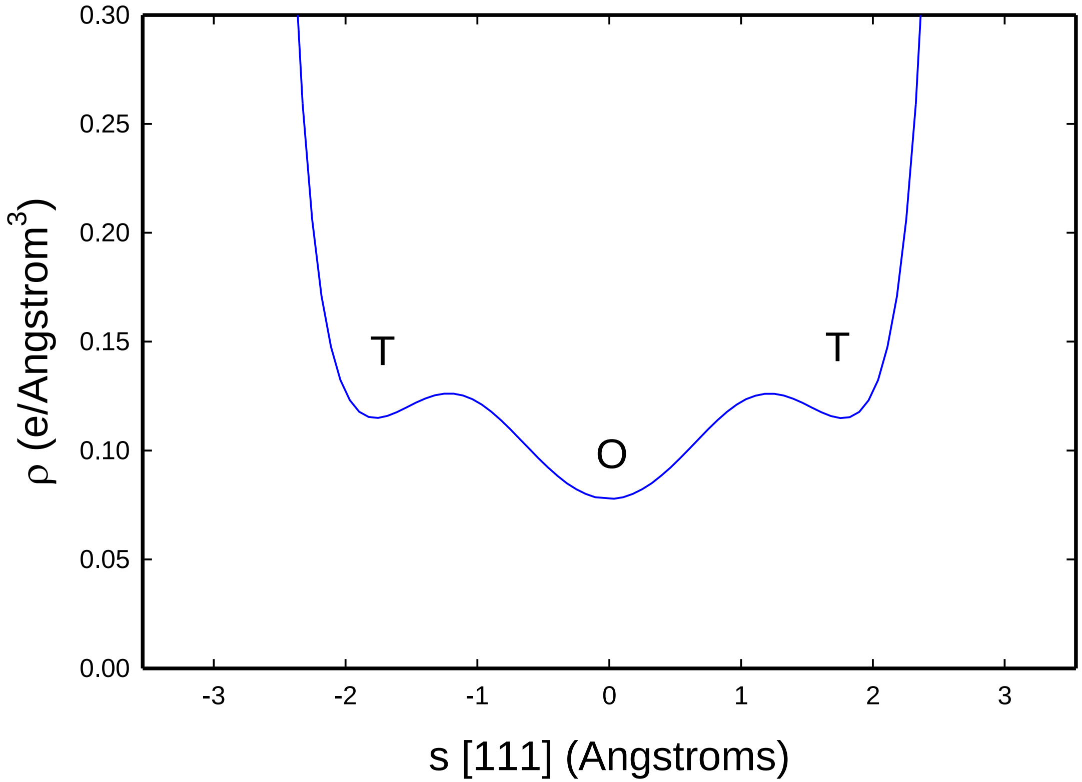
Looking for reaction sites

- Experiment suggests new kind of coherent d+d reaction in F&P exp't
- If so, still need sites for deuterons to react
- Want to have them be close
- But was argued in 1989 that deuterons don't get close in PdD

PdD lattice structure (fcc)

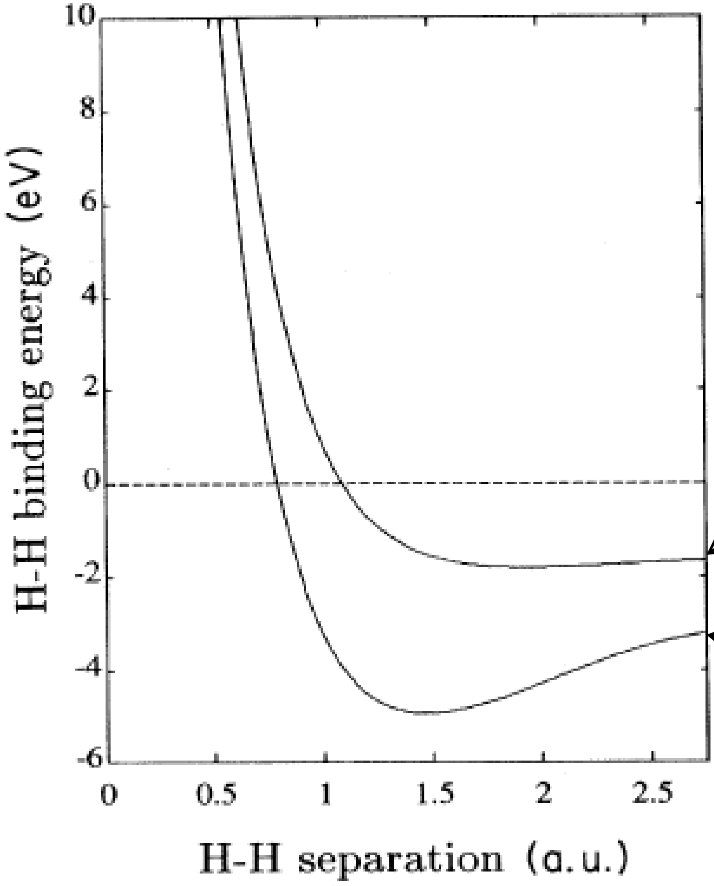


Background electron density due to Pd in PdD



P L Hagelstein, "Molecular D_2 near vacancies in PdD and related problems," *J. Cond. Mat. Nucl. Sci.* ***13*** *138 (2014)*

H_2 in jellium



O B Christensen et al, *Phys Rev B* **40** 1993 (1989)

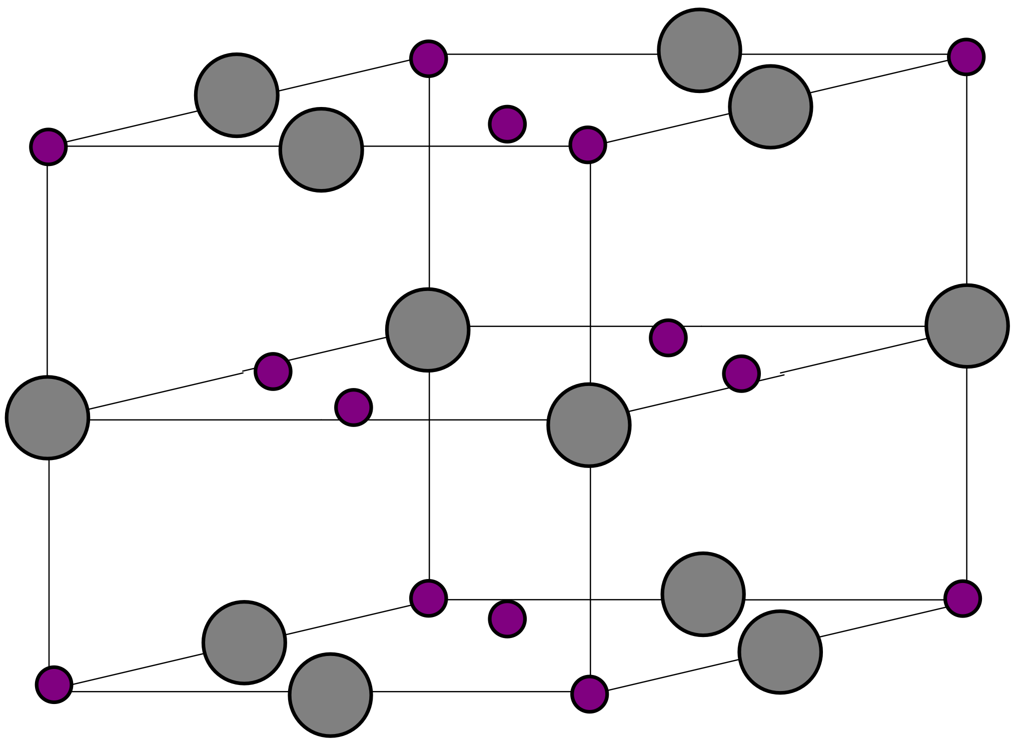
0.063 e/A^3

vacuum

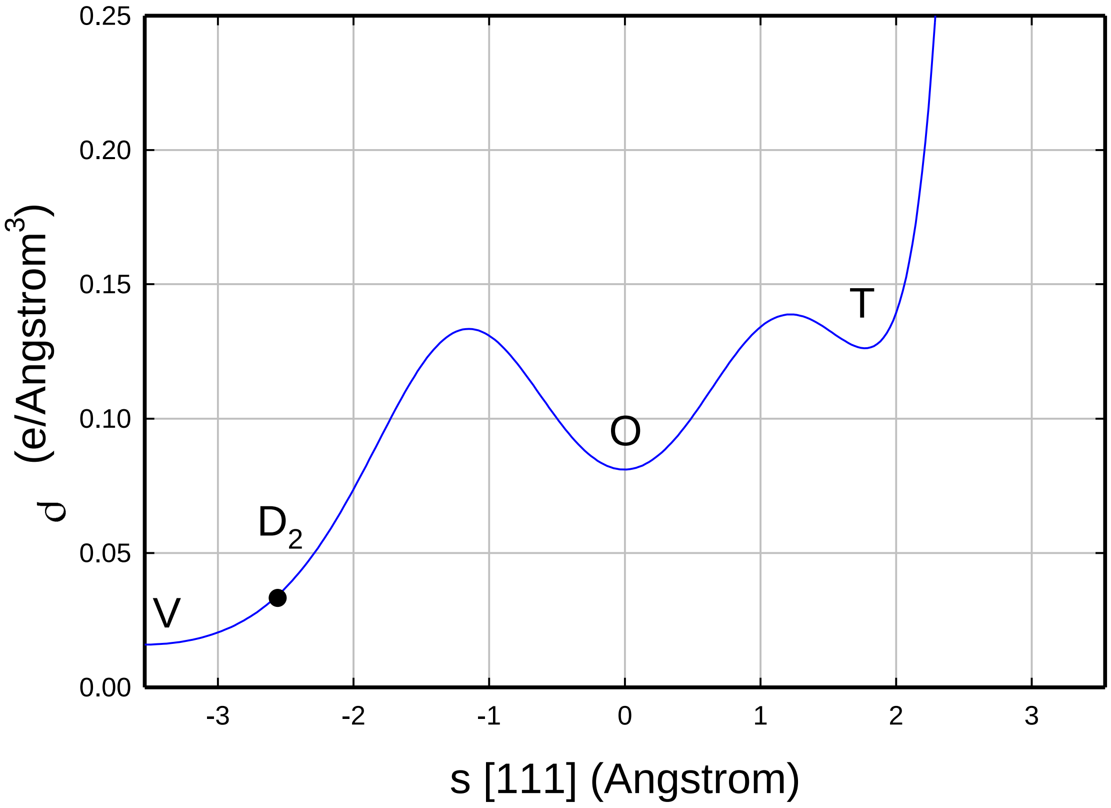
Electron density too high

- Background electron density around 0.08 e/A^3 at O-site
- Expect occupation of 1σ_u (antibonding) orbitals
- Expect deuterium atoms to push apart
- If so, then PdD would be expected to be inert for excess heat production
- Need environment with lower background electron density
- Focus on Pd monovacancy

PdD Host lattice vacancy



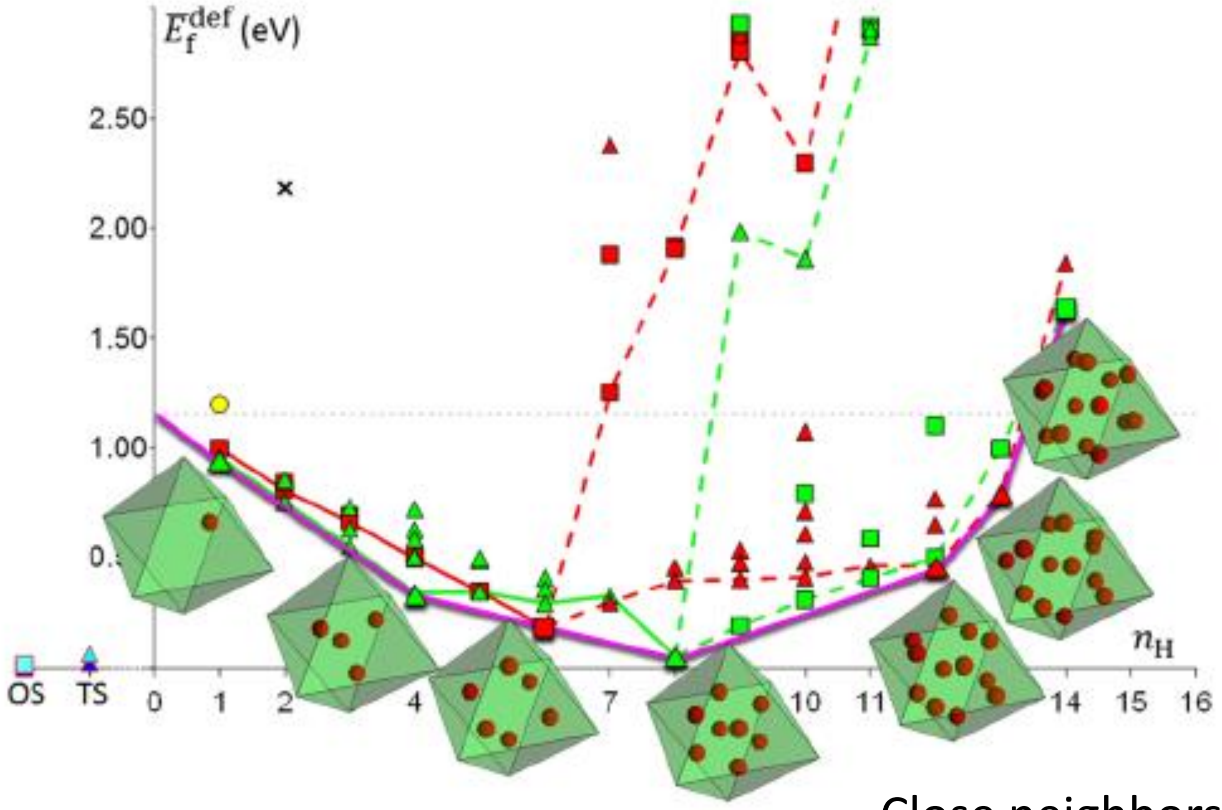
Background electron density



Low background electron density

- Low electron density around monovacancy
- Expect around 0.03 e/A^3
- Lower than background electron density for PdD_2 molecule
- For years thought we should look for molecular D_2 in monovacancies
- Recent calculations suggest more interesting situation
- O-site and T-site occupation of monovacancy possible
- At high enough loading, can get O-site and T-site neighbors occupied

O-site, T-site occupation around a monovacancy



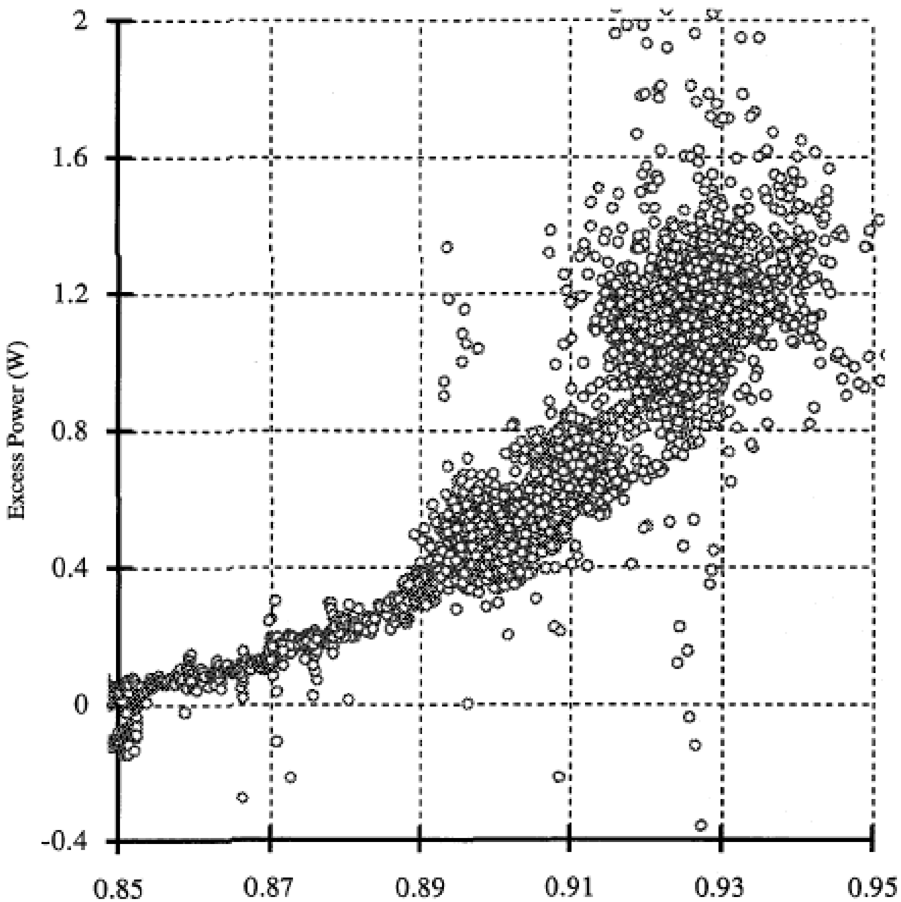
(c) Pd

Close neighbors with more than 8 H or D atoms in monovacancy

Nazarov et al, *Phys. Rev. B* **89** 144108 (2014)

P_{xs} versus D/Pd ratio

P_{xs}(W)



D/Pd

M C H McKubre et al, *EPRI Report* (1994)

Take away message

•Electron density too high in PdD, so bulk PdD is inert

•Conjecture that monovacancies in PdD are active sites

•Can load up to 14 deuterium atoms into a monovacany

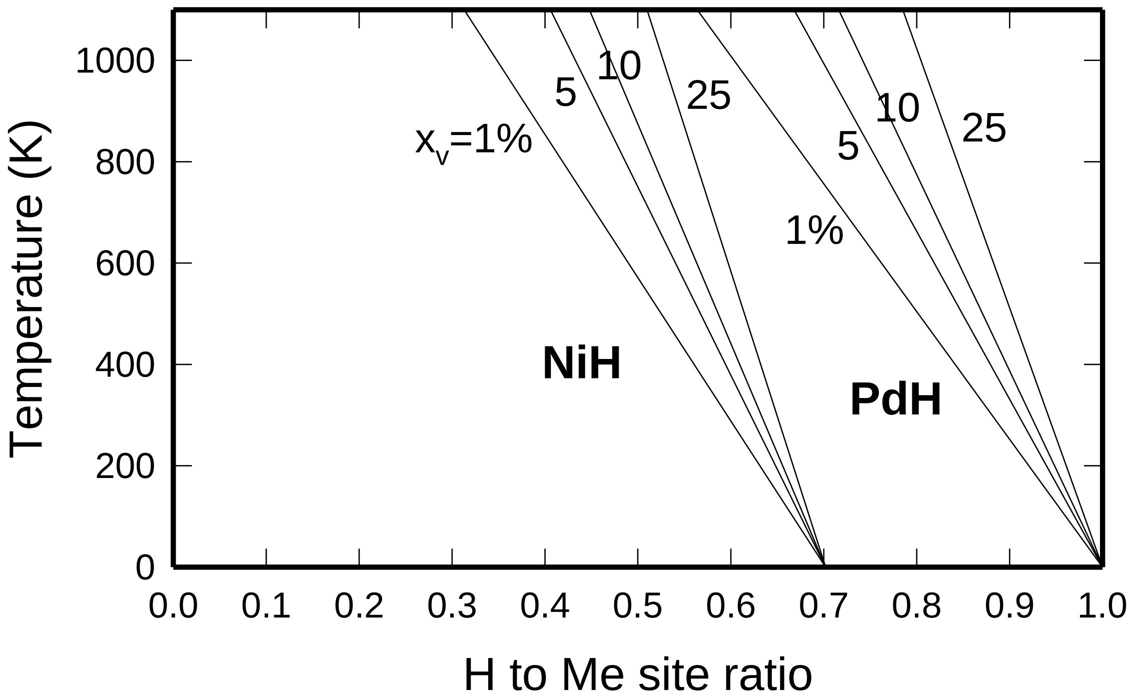
•Can hold up to 8 without being close together

•At high D/Pd loading above 0.83 conjecture begin to achieve more than 8 deuterium atoms/vacancy, and get close O-site and T-site D

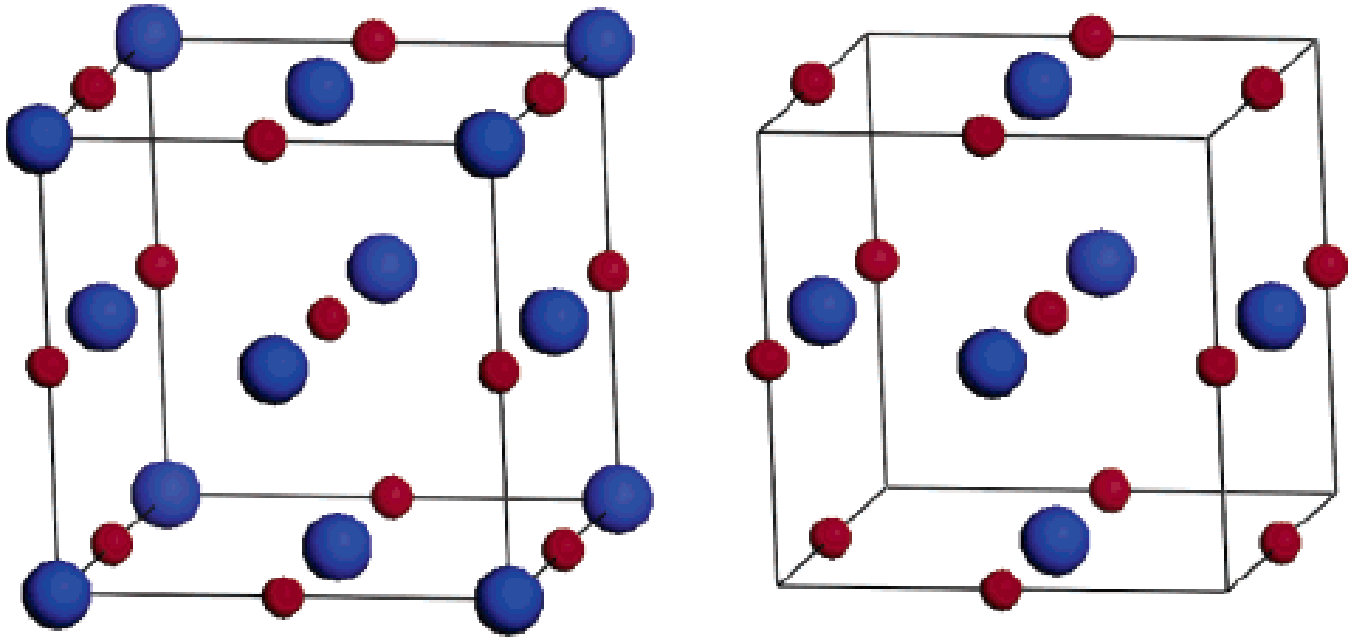
How do we get monovacancies?

- Cannot get deuterons close in PdD, electron density too high
- Need monovacancies to get lower electron density
- But not many monovacancies present in Pd under normal conditions
- Vacancy creation energy in Pd near 1.6 eV
- Vacancy creation energy reduced as loading increased, by more than 220 meV per neighboring D
- Monovacancies are favored thermodynamically at high loading

Vacancies in host lattice



Superabundant vacancy phase structure



Fukai and Okuma used this effect to make $Pd_{0.75}H$ with large numbers of Pd vacancies, by heating PdH under high pressure

Y. Fukai and N. Okuma, *Phys. Rev. Lett.* **73** 1640 (1994).
C. Zhang and A. Alavi, *J. Am. Chem. Soc.* **127** 9808 (2005).

Diffusion of vacancy cluster

Fukai et al, J. Alloys and Compounds **313** 121 (2000)

$$D = D_0 \, e^{-\Delta E / k_B T}$$

$$D_0 = 3.8 \times 10^{-4} \text{ cm}^2/\text{sec}$$

$$\Delta E = 1.2 \text{ eV}$$

Characteristic distance diffused in 10^6 seconds at room temperature:

$$L = \sqrt{D\tau} = 0.15 \text{ Angstrom}$$

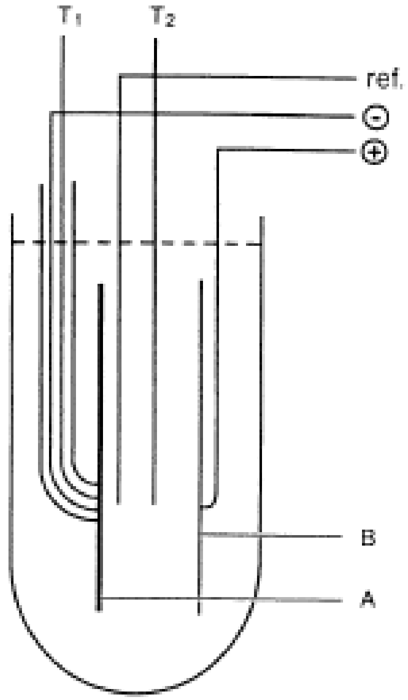
Conclude that vacancy diffusion does not occur through this mechanism

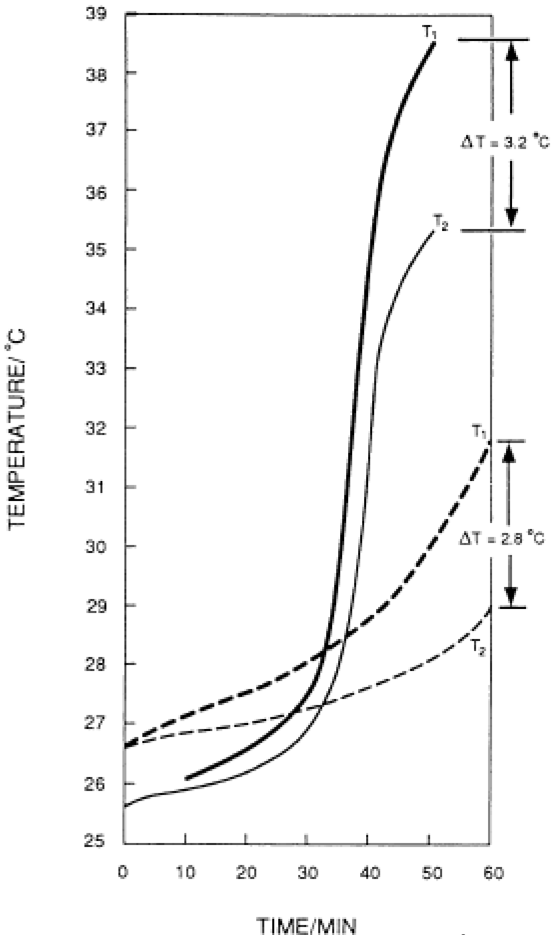
What about near room temperature?

- Monovacancies thermodynamically favored near room temperature above about D/Pd = 0.95
- Vacancy diffusion astronomically slow near room temperature
- PdD_x at high loading wants to turn into vacancy phase lattice, but need millions of years to do so
- But new Pd codeposited on surface at high surface loading can form vacancy phase structure
- Motivates an interest in Letts variant of Szpak co-deposition experiment

Szpak codeposition exp't

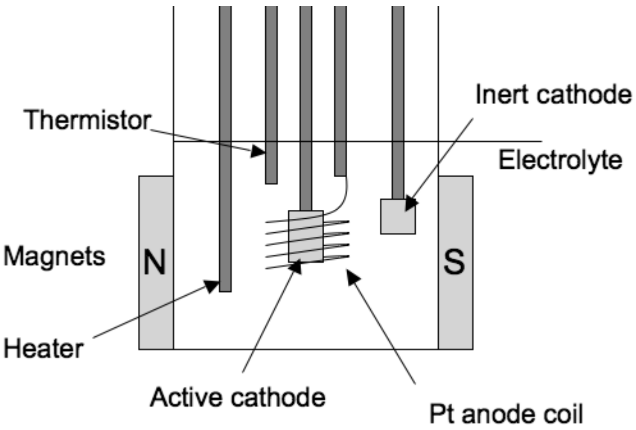
$PdCl_2$ in electrolyte

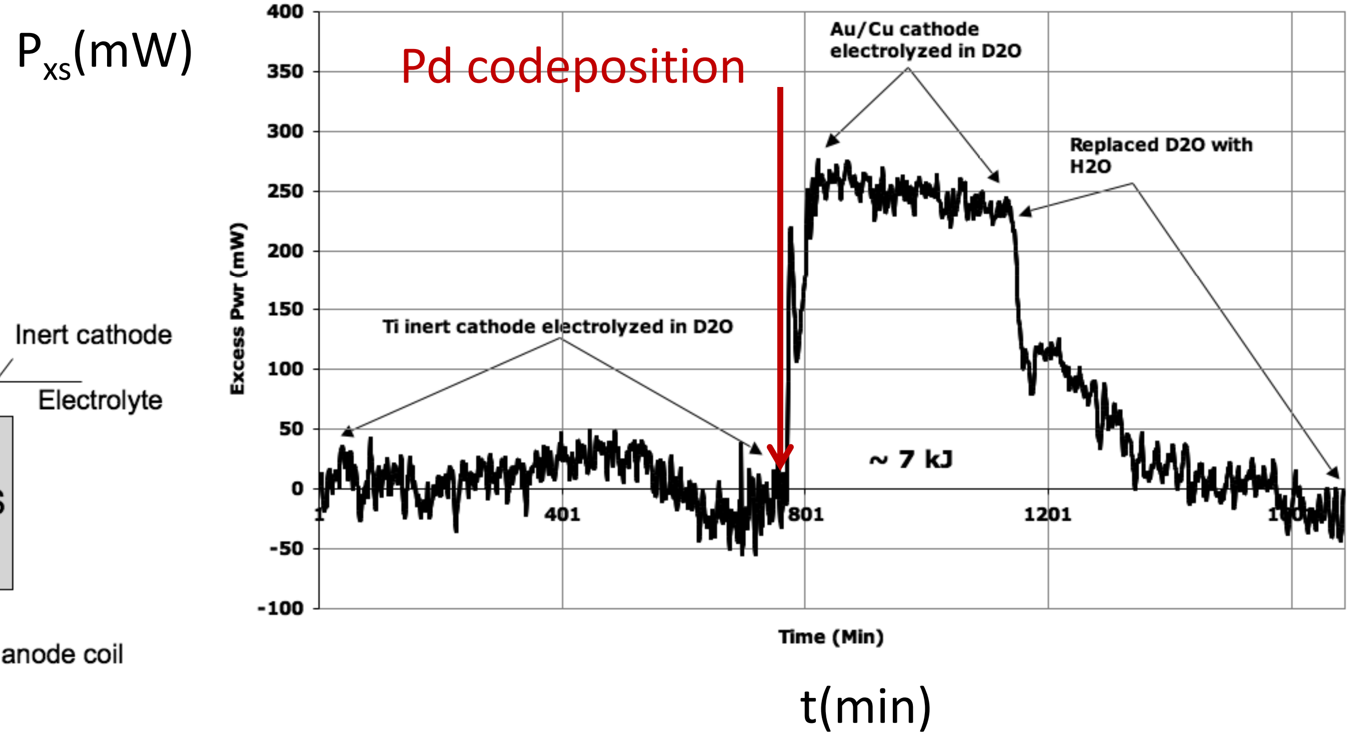




S. Szpak, P. A. Mosier-Boss and J. J. Smith, *J. Electroanalytical Chem.* **309** 273 (1991)

Excess power in Letts codep experiment



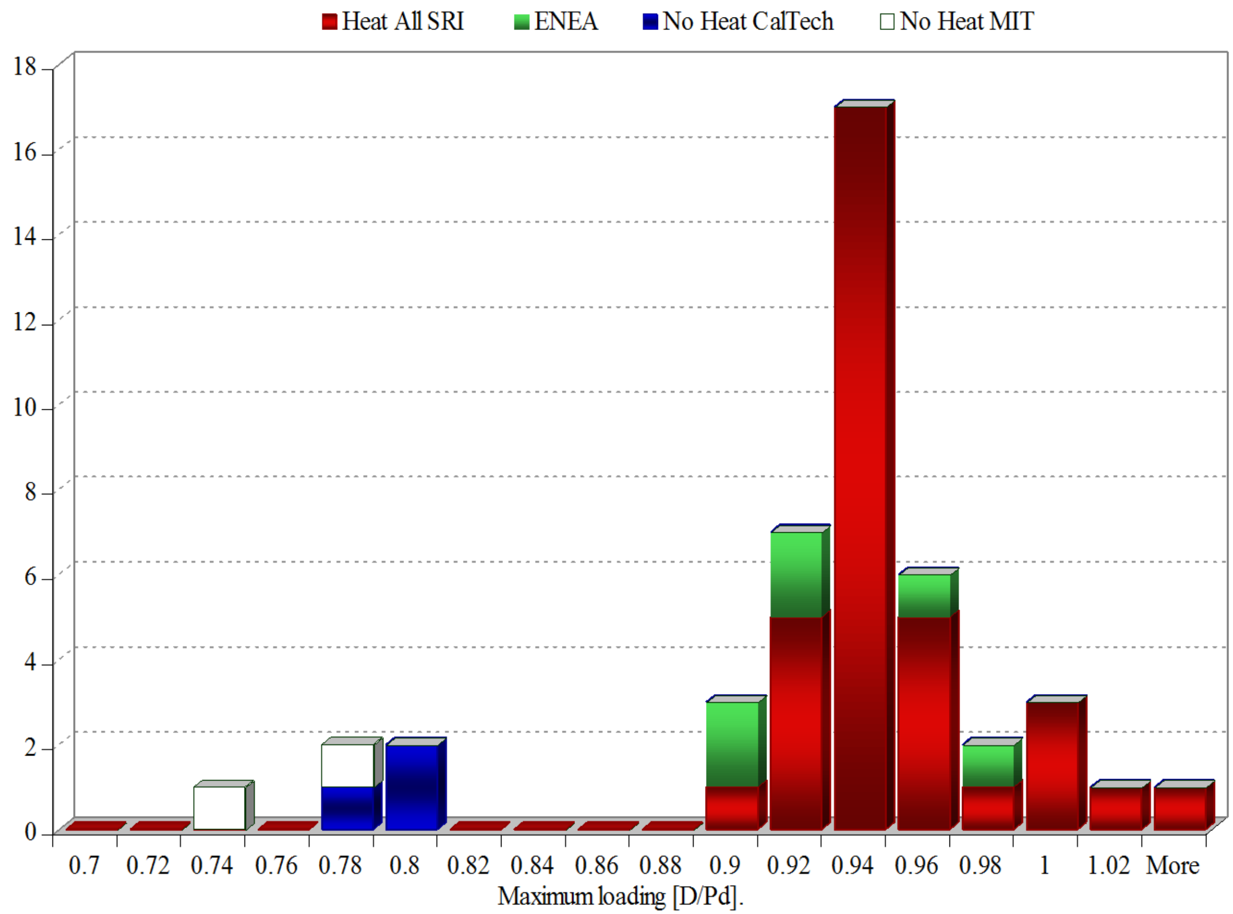


D. Letts and P. L. Hagelstein, *J. Cond. Mat. Nucl. Sci.* **6** 44-55 (2012)

Take away message

- Conjecture that monovacancies are active sites, since electron density is low
- Monovacancies are thermodynamically favored at high D/Pd loading above D/Pd=0.95 near room temperature
- Szpak observed excess heat shortly after co-deposition
- Letts co-deposition protocol co-deposits Pd at high surface loading, with prompt excess heat production
- Supports picture proposed for active sites

Maximum D/Pd ratio as predictor of success



M. C. H. McKubre *Proc. ICCF15* (2009).

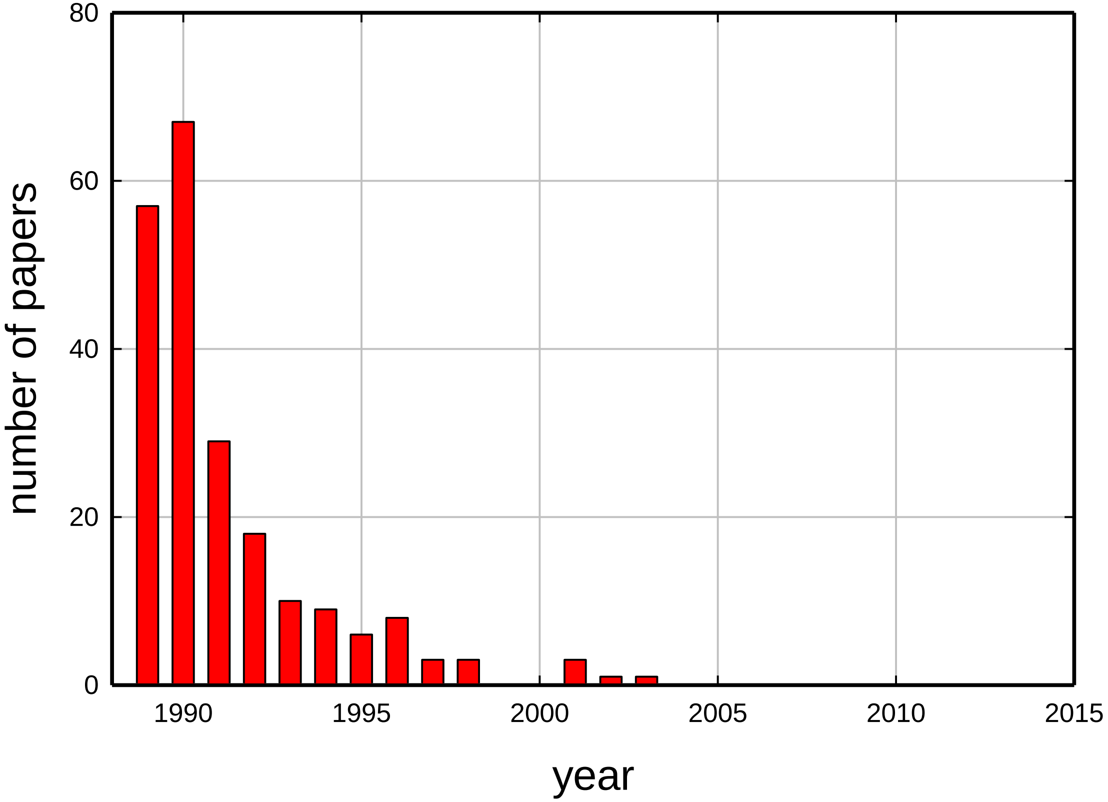
Interpretation

- Cathodes that loaded above D/Pd=0.95 showed excess heat at SRI, and at ENEA Frascati
- Interpretation is that at high loading, inadvertent co-deposition of Pd occurs
- Get thin layer of PdD with superabundant vacancies
- Monovacancies then serve as active sites
- If high loading not achieved, or Pd not co-deposited, then not enough active sites

Early negative exp’t results

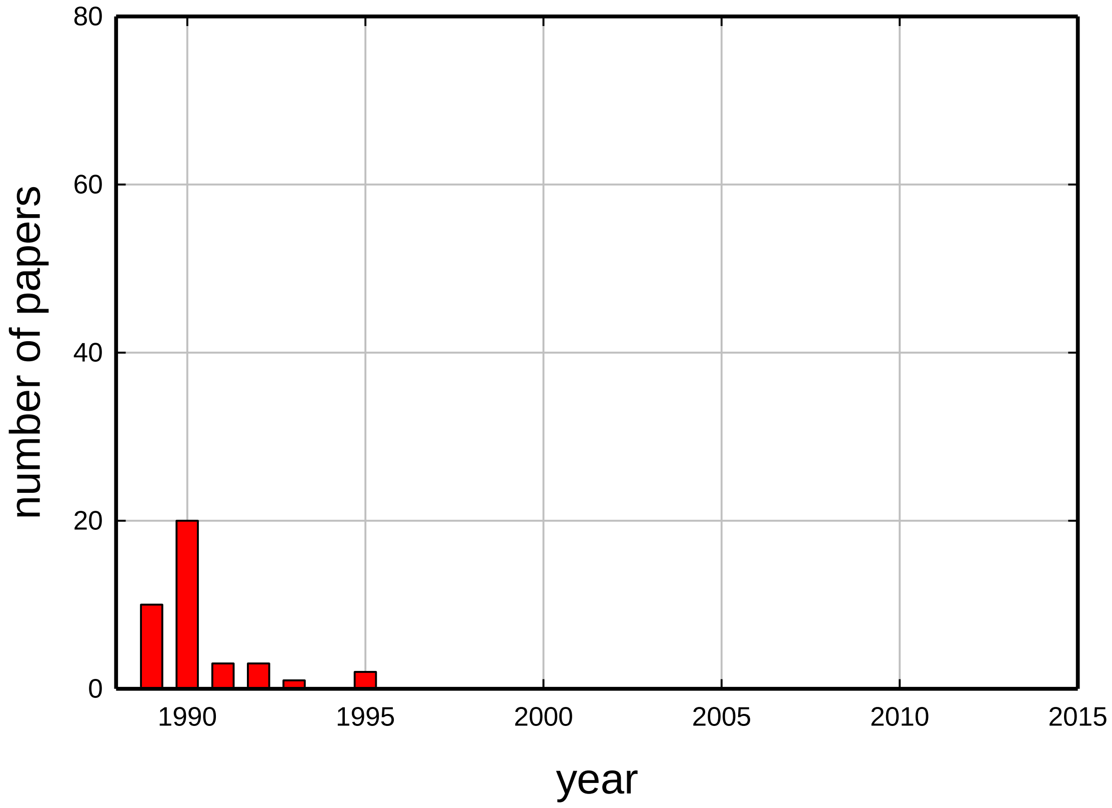
- Hundreds of exp’ts with negative results reported in 1989, 1990
- Argument made that excess heat effect not reproducible
- Perhaps some of these experiments done when little was known about the experiment
- Go back and look over the papers
- Try to understand what happened
- Aided by bibliography of Dieter Britz

Number of papers with negative experimental results



217 in all

Number with calorimetry, Pd and electrochemistry



39 in all

Thinking…

•Many different effects claimed by Fleischmann and Pons

•Lots of experiments looking for neutrons

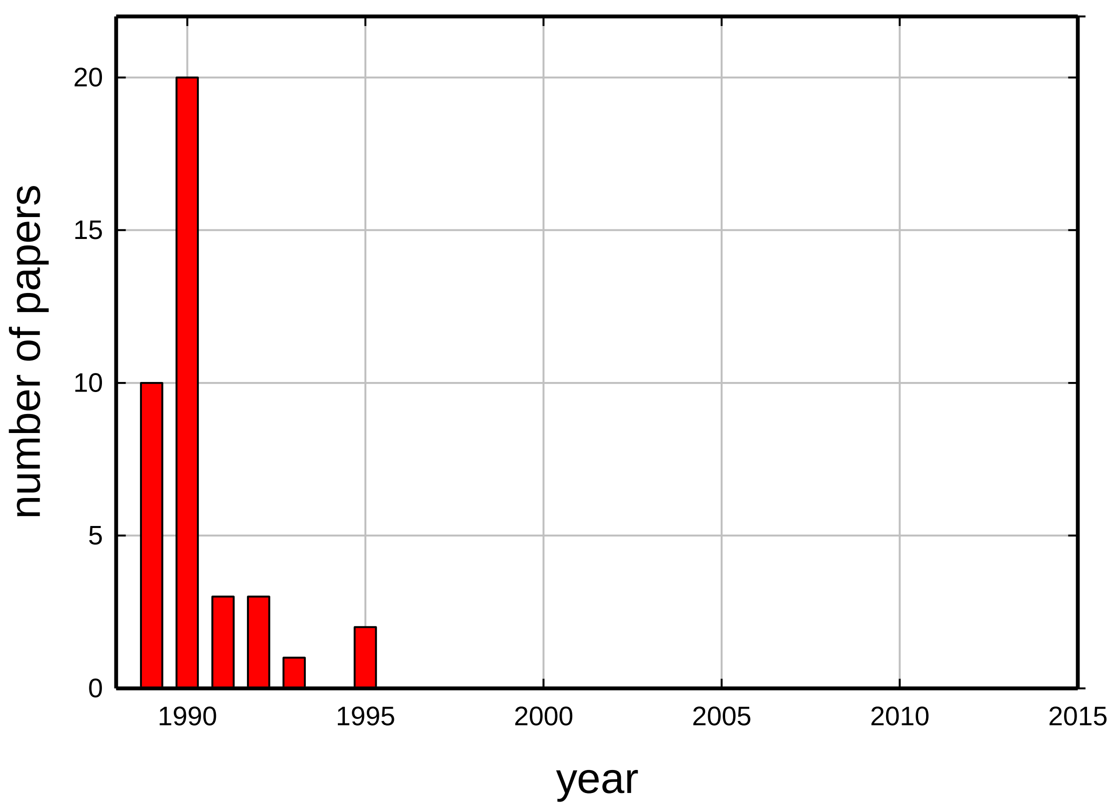
•In some cases argument was made that can determine energy produced by measuring neutrons

•Remember that neutrons uncorrelated with energy, with an upper limit near 0.01 neutron/Joule

•But 39 experiments with negative results still a big number

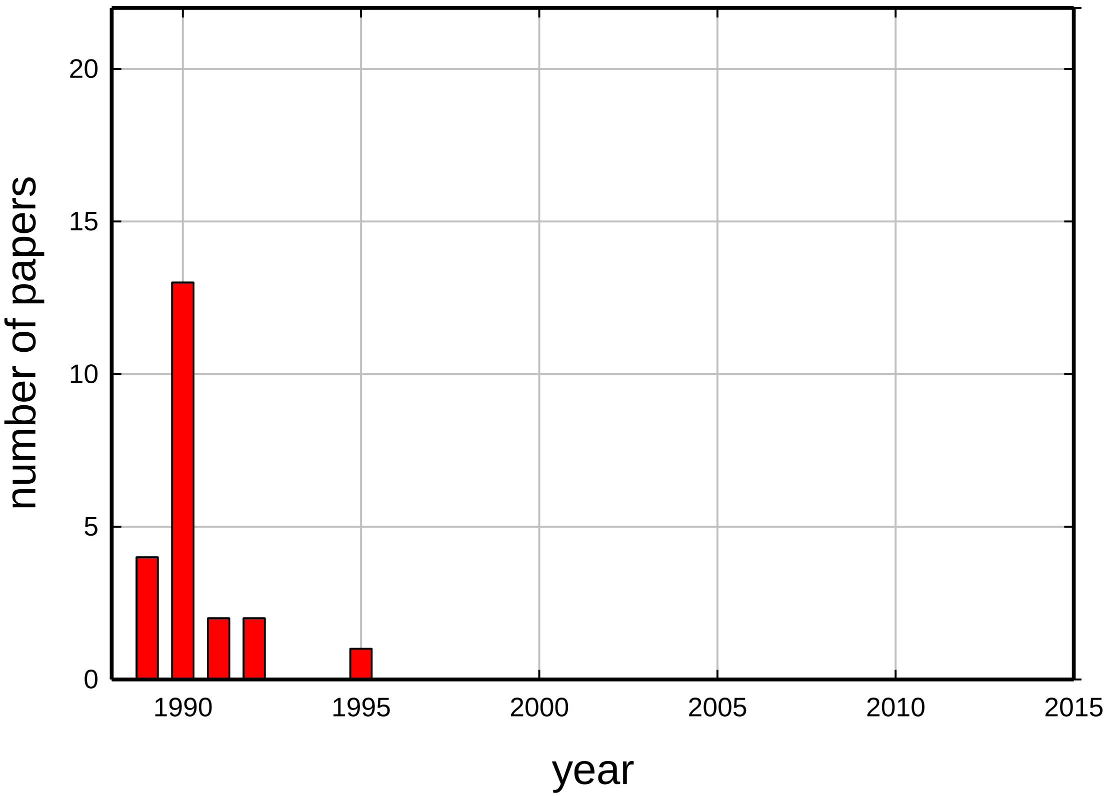
•Wonder if the researchers knew they needed high loading…

Look at negative publications again…



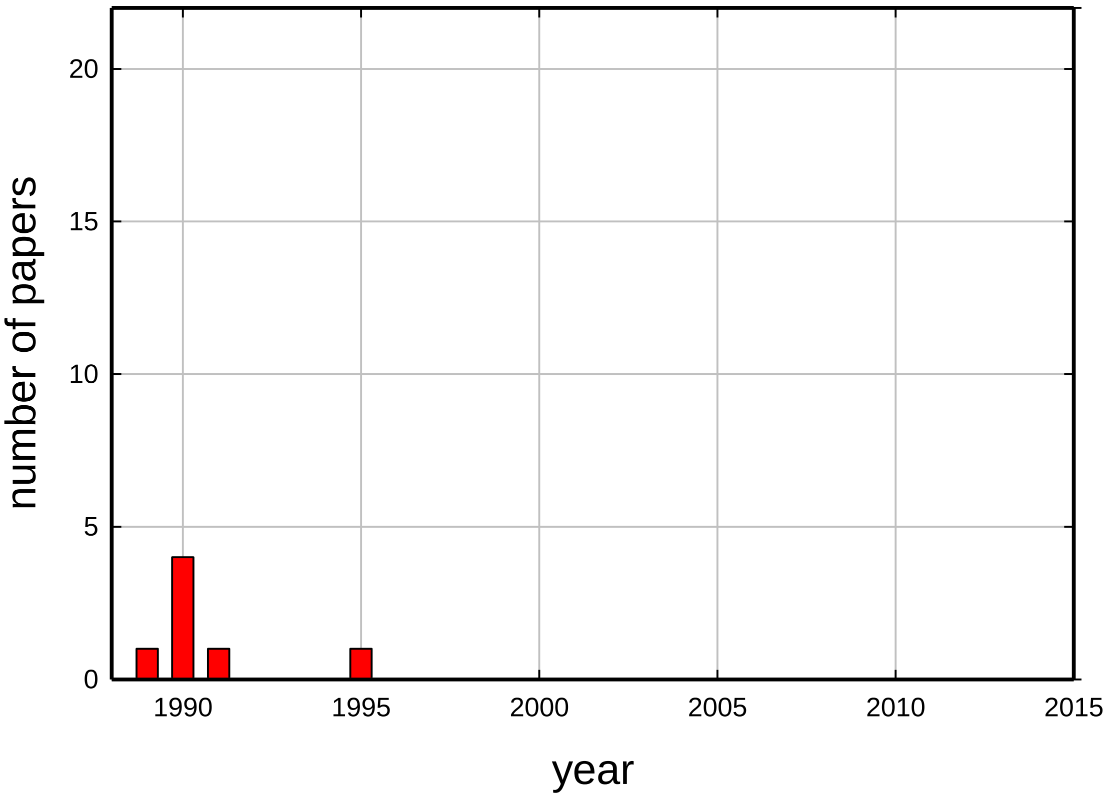
39 negative

Require some mention of D/Pd loading



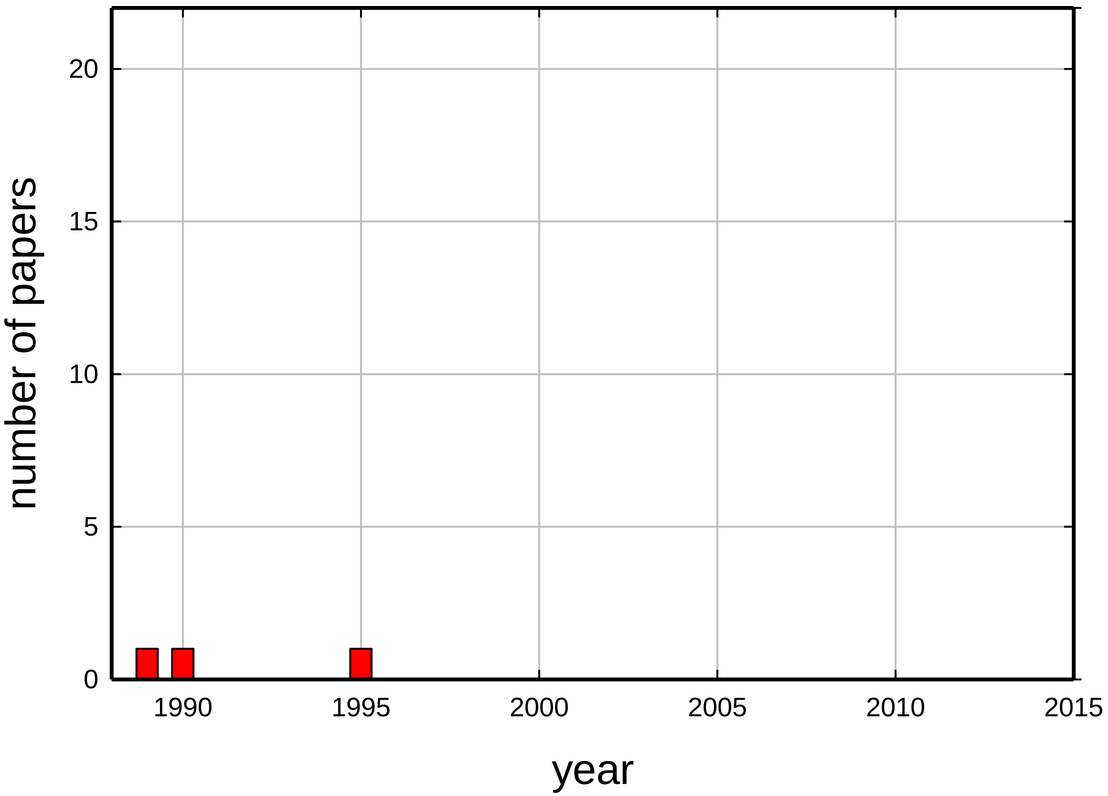
22 left

…with a D/Pd ratio of at least 0.83



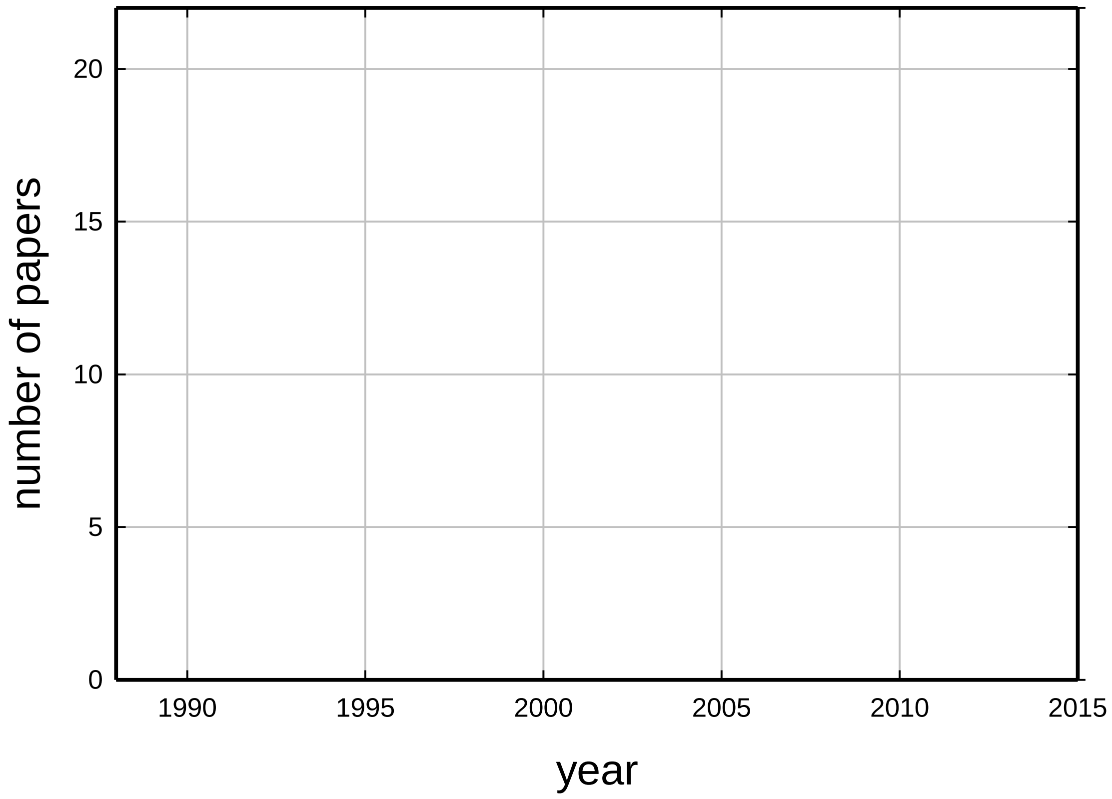
7 left

…with a D/Pd ratio of at least 0.90



3 left

…would have been expected to work

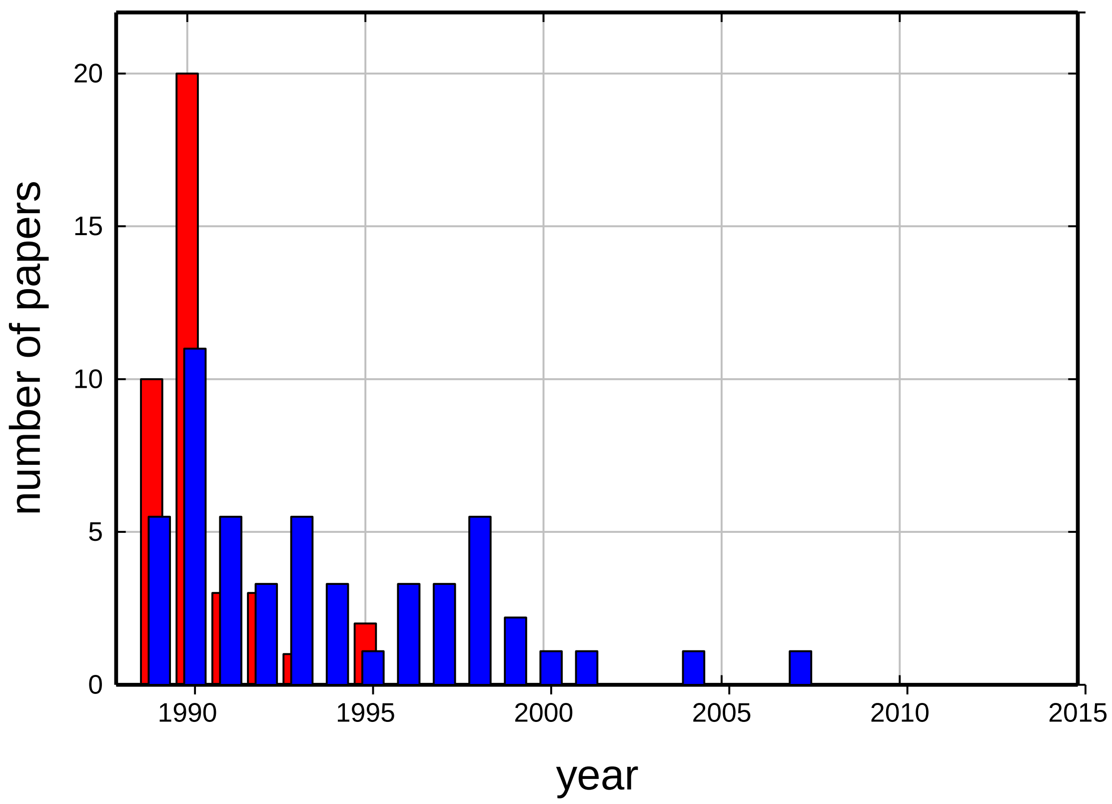


0 left

Take away message

- Need to carry out something like F&P experiment to count…
- Need high loading to get excess heat
- Not all groups understood need for high loading
- Recall that it is hard to get high D/Pd ratio
- Only 1 of the early negative experiments is close to what was needed
- (There are other requirements not discussed here)
- The case for excess heat in the F&P experiment not being reproducible is overstated

Now compare with small number of positive excess heat results listed by Britz



39 negative

49 positive

Take away message

- High D/Pd loading needed to see excess heat in F&P exp’t
- Conjecture requirement connection with development of monovacancy active sites from (inadvertent) Pd co-deposition at high surface loading
- Requirement not understood (or believed) by all in 1989, 1990
- Only small number of early negative experiments in relevant regime
- Case for experiment not being reproducible is overstated

Conclusions

- Excess heat effect in Fleischmann-Pons experiment looks real
- …and reproducible
- ^{4}He seen in amounts commensurate with energy produced
- Impossible to account for through incoherent nuclear reactions
- Only plausible explanation involves coherent processes
- Model developed based on down-conversion, relativistic interaction
- Active sites conjectured to be monovacancies
- Created through co-deposition with high surface loading
- Argument for lack of reproducibility was over-stated

Warning!

- Cold fusion, LENR, excess heat and related topics are controversial
- Working in the field at present is dangerous to one's career
- Very powerful and energetic opposition
- Little or no governmental support in US
- Publishing is problematic, even now
- Research problems are very hard
- One's professional and personal life can both be impacted