

An X-Ray Diffraction Study of Lattice Expansion and Phase Transformation  
in Electrochemically Loaded Palladium Hydrides

D.L. Knies<sup>i</sup>, V. Violante<sup>ii</sup>, K.S. Grabowski<sup>i</sup>, J. Hu<sup>iii</sup>, D.D. Dominquez<sup>i</sup>, J.  
He<sup>iv</sup>, S.B. Qadri<sup>i</sup> and G.K. Hubler<sup>i</sup>

Time resolved, in-situ, high-energy x-ray diffraction was performed on modified Fleischman-Pons electrolytic cells during electrochemical loading of palladium foil cathodes with hydrogen and deuterium. Concentrations of H and D up to 1:1 in 0.1 M LiOH/LiOD in H<sub>2</sub>O/D<sub>2</sub>O electrolytes were obtained with lattice constant data monitored throughout the range of concentrations. In addition to data on lattice constant versus H or D concentration and palladium hydride resistivity, some indication of the rapidity of loading and deloading of hydrogen from the Pd surface was obtained. The alpha-beta phase transformations were clearly delineated but no new phases at high concentration were definitively determined.

<sup>i</sup>U.S. Naval Research Laboratory, Washington, DC

<sup>ii</sup>ENEA, Frascati, Italy

<sup>iii</sup>NSLS, Brookhaven National Laboratory, Brookhaven, NY

<sup>iv</sup>Nova Associates, Alexandria, VA

# In Situ Energy-Dispersive X-ray Diffraction Study of Thin Pd Foil at D/Pd and H/Pd ~1

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D.L. Knies<sup>i</sup>, V. Violante<sup>ii</sup>, K.S. Grabowski<sup>i</sup>, D.D. Dominquez<sup>i</sup>, J. H.  
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<sup>i</sup>Naval Research Laboratory, USA

<sup>ii</sup>ENEA, Italy

<sup>iii</sup>Nova Research, USA

<sup>iv</sup>Brookhaven National Laboratory, USA

# Motivation

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- In situ XRD not performed for  $H/Pd > 0.76$  in Fleischmann-Pons electrolytic cells

## Possibility of learning

- Does a new  $\gamma$  phase was suggested by Tripodi et. al. for the electrochemically loaded palladium when the composition  $H/Pd$  approaching 1 exist?
  - Does temperature coefficient of resistivity of PdH versus the concentration of H anomaly show up in Pd crystalline structure (Tripodi et. al.)?
  - In the Pd-D system, new phases were found through deuterium thermal desorption spectra. Does anything show up on FPE system (Rybalko et. al.)?
  - Report showing oscillating resistivity for palladium hydrides at some concentration range of  $H/Pd > 0.9$  (Miley et. al.).
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- These proposed phase transitions are only based on indirect experimental data and have not been structurally determined.

# Temperature Coefficient of Resistance

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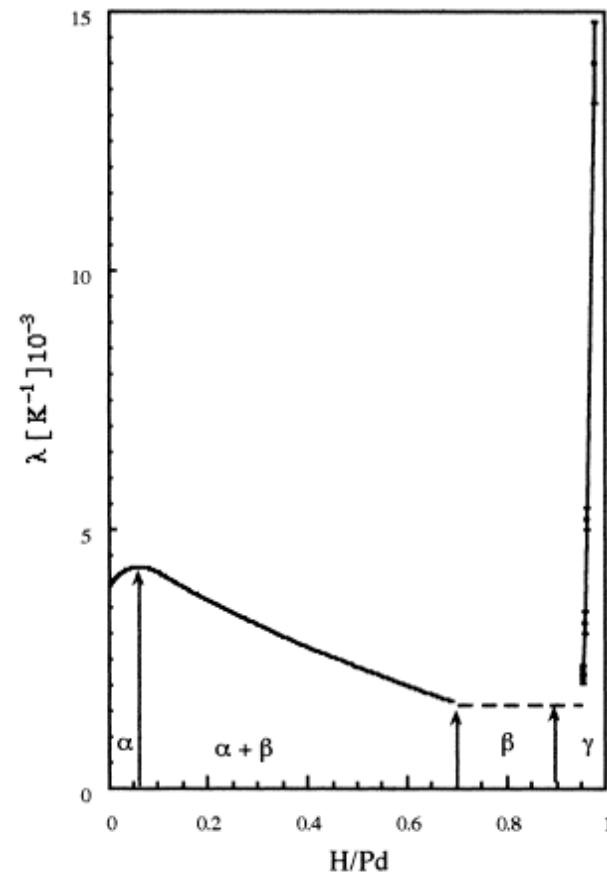


Figure 3: Temperature coefficient of resistivity  $\lambda$  for all phases. The dashed is the plateau value for  $\lambda$ .

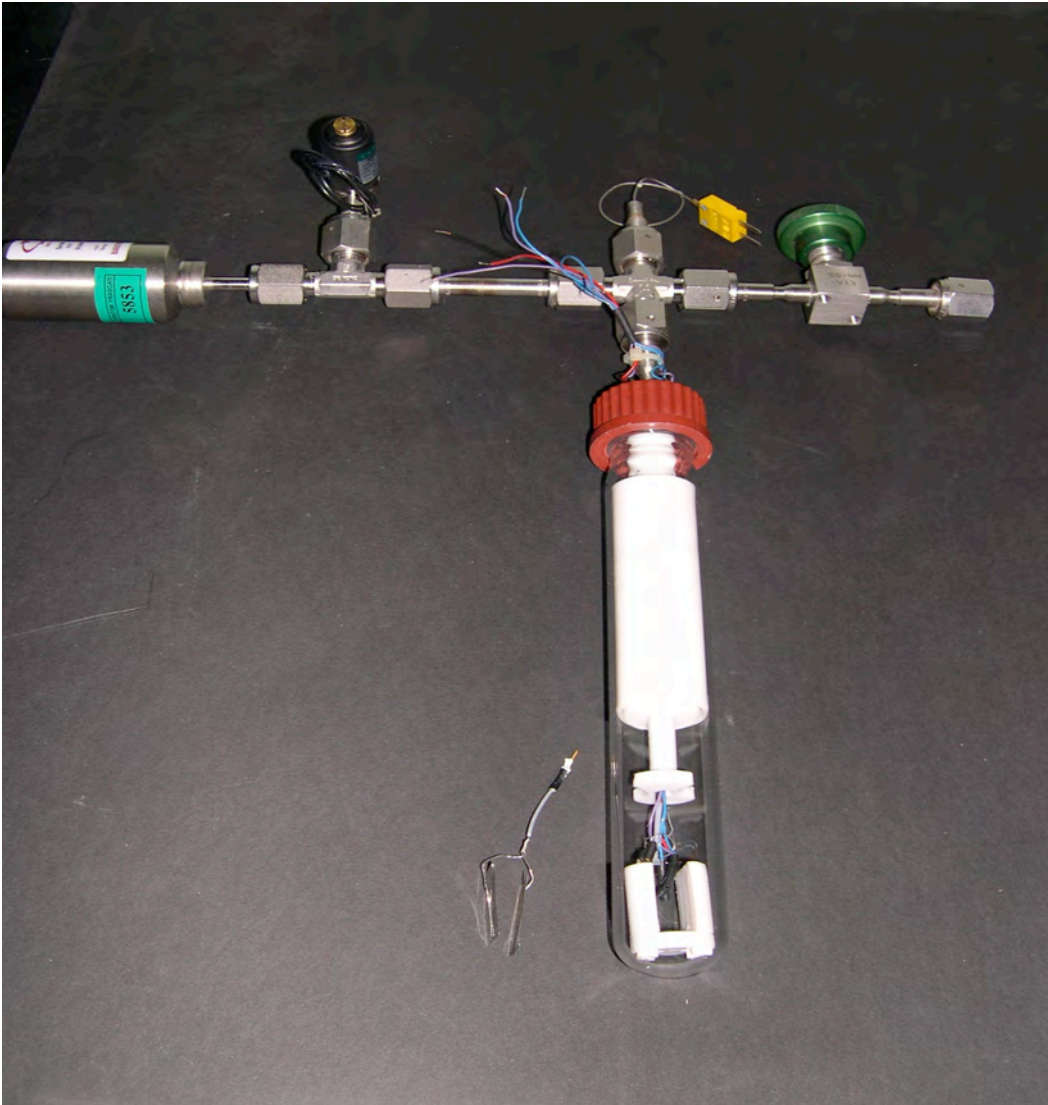
# Pd Foil Cathodes

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- Pd 0.9995 purity fabricated at ENEA by V. Violante
- Rolled from 1 mm thick bar to 50  $\mu\text{m}$  thickness, annealed 850 C for 8 hours, etched in aqua regia for 2 minutes, cleaned in water and alcohol
- 20 mm x 40 mm dimension
- $\sim 100$   $\mu\text{m}$  grain size

# Electrochemical Cell

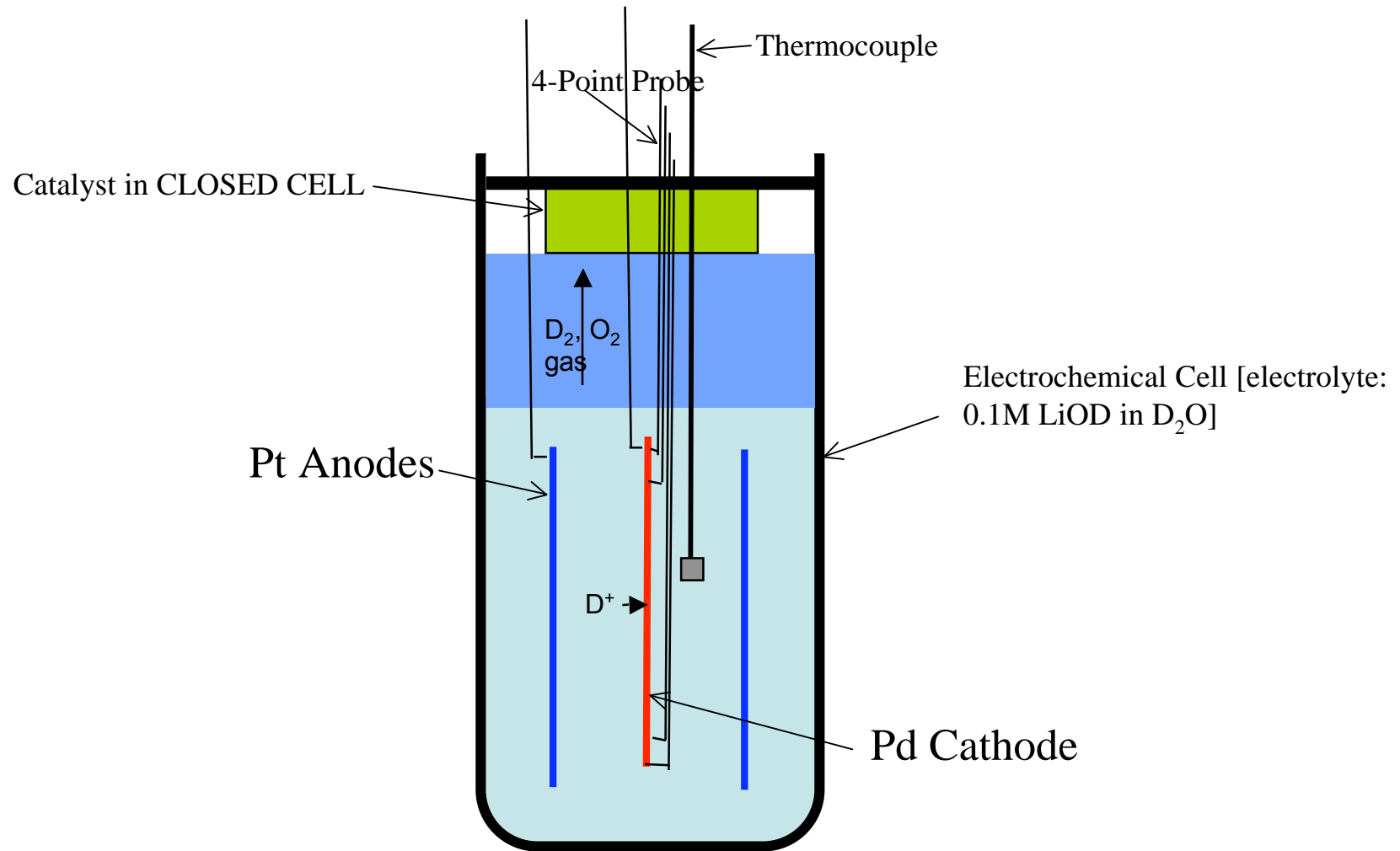
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- Designed and built by ENEA
- Dual Pt anodes

# Electrochemical Cell

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# Experimental Measurements

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## Cell Measurements

- Temperature
  - 1 thermocouple in electrolyte
  - 5 RTD's external to cell
- Electrolysis
  - Current
  - Voltage
- Cell Pressure
  - Baratron
  - Safety valve
- $R/R_0$ 
  - 4-point probe @ 1 kHz
- Time
- Data rate
  - 1/4 Hz

## X-Ray Measurements

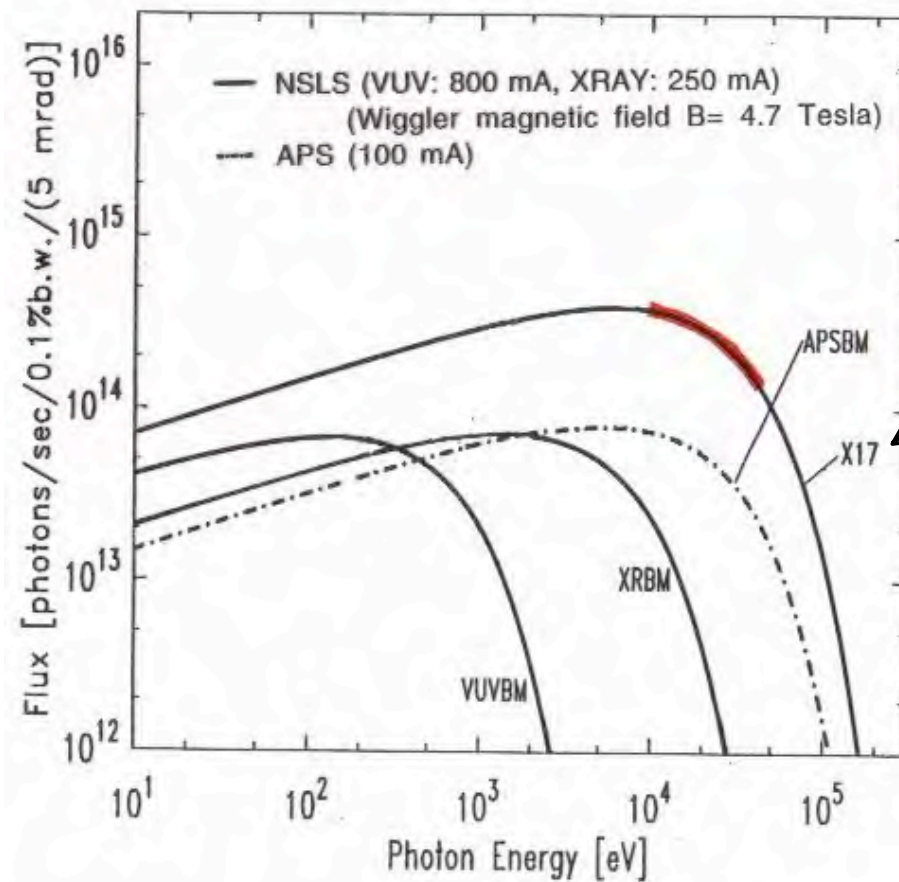
- 14  $\mu\text{m}$  tall, 23- $\mu\text{m}$  wide x-ray beam
- Diffraction spectra collection time ~5 minutes
- Ge high resolution detector

No Calorimetry!



# Brightness of NSLS Beam Lines

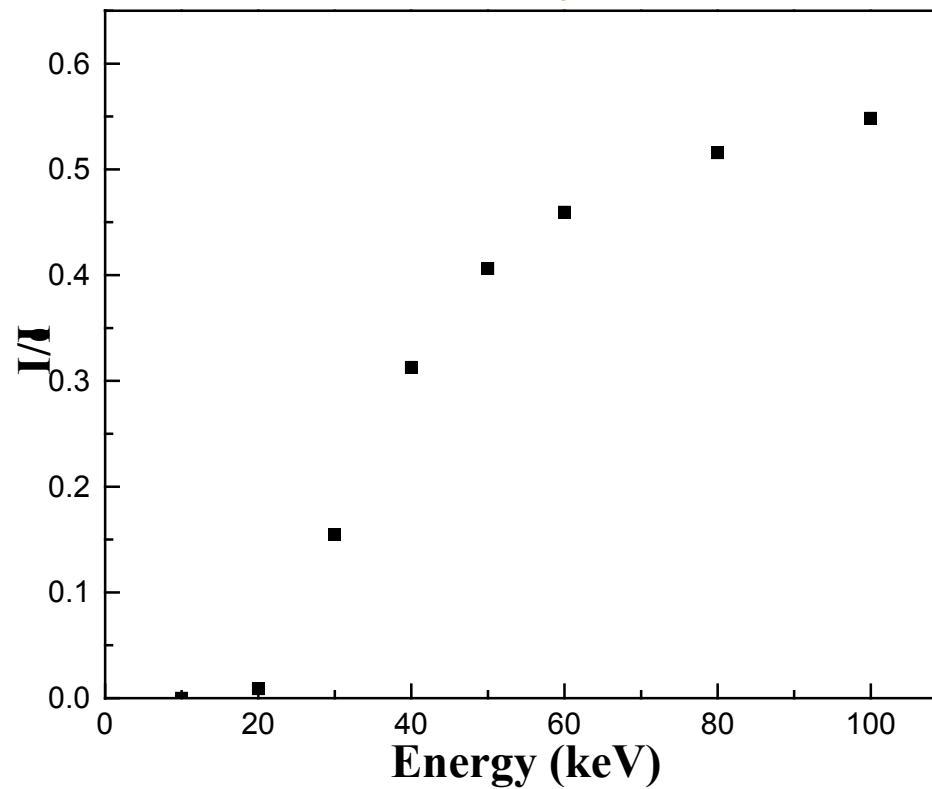
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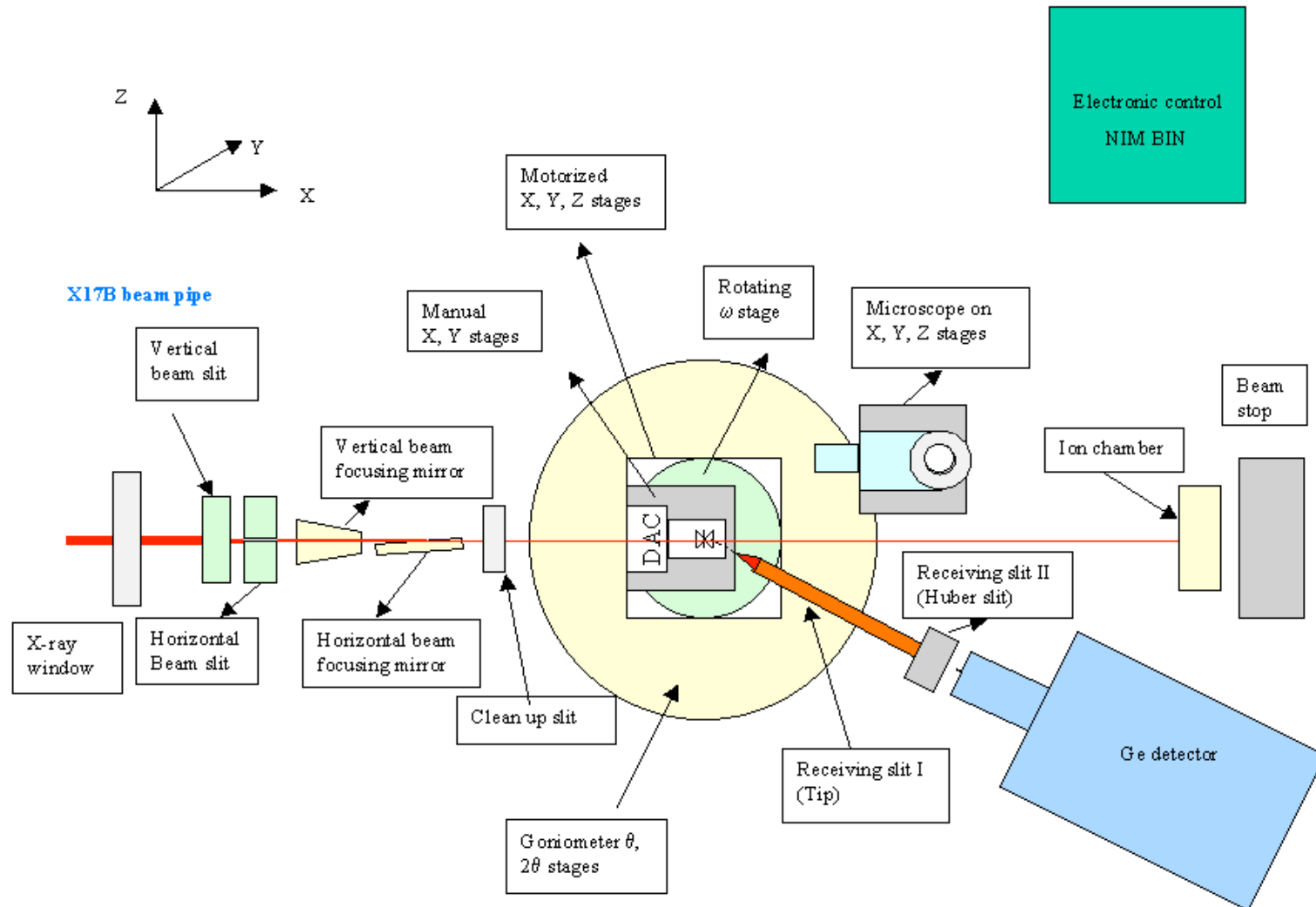
# X-Ray Transmission through Electrochemical Cell

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Absorption thru the Cell with 2.7 cms of H<sub>2</sub>O and 0.3 cms of Glass with a density of 2.7 g/cm<sub>3</sub>)



# BNL X17C Hutch Equipment



# Bragg Condition

$$2d \sin\theta = n\lambda$$

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$$E = h\nu, \quad \lambda\nu = c$$

$$2d \sin\theta = nch/E$$

or

$$Ed \sin\theta = 6.1992n$$

Continuous energy picks out  $d$  for properly oriented planes

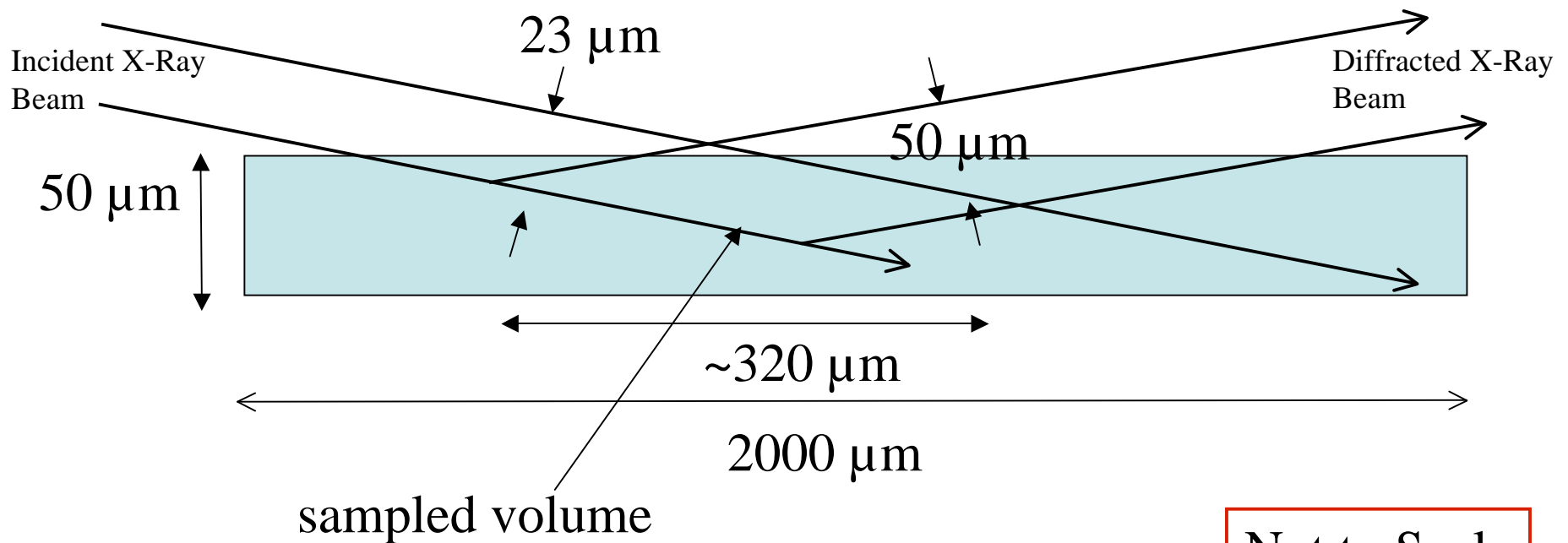
# Detection Volume - $1.6 \times 10^{-12} \text{ m}^3$

collimated X-ray beam is  $23 \mu\text{m}$  wide x  $14 \mu\text{m}$  tall

collimated diffracted beam is  $50 \mu\text{m}$  wide x  $500 \mu\text{m}$  tall

$2\theta = 13$  degrees

view from  
top

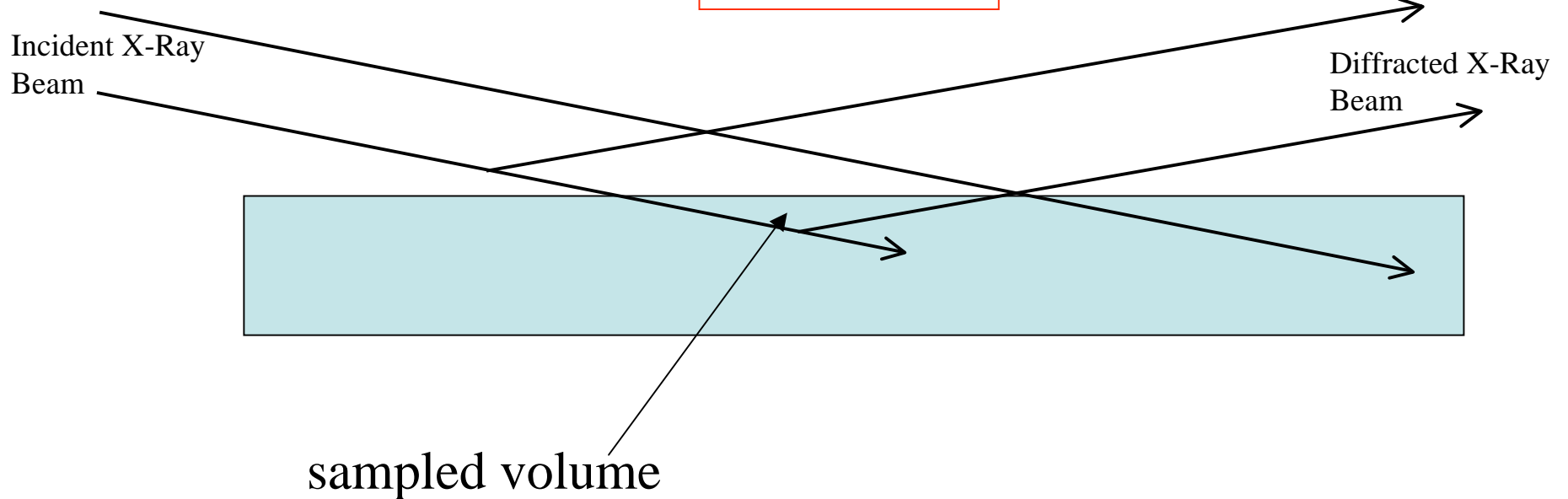


Not to Scale

# Detection Volume

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view from  
top



Near surface sampling (Pd x-ray fluorescence observed)

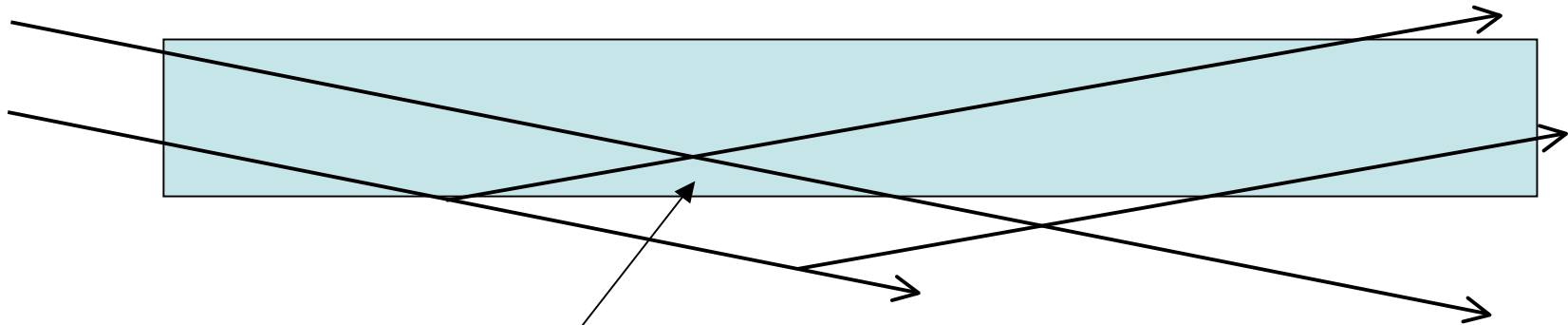
# Detection Volume

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view from  
top

Incident X-Ray  
Beam

Diffracted X-Ray  
Beam



sampled volume

Bulk sampling (No Pd x-ray fluorescence observed)

# Unexpected Challenges & Observations

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- Control of geometry difficult due to movement of foil from stresses caused by 13% volume change as cathode was loaded with hydrogen.
- Since beam covered only a few grains, diffraction condition often had to be found by x-y-z position scanning.
- When cell abruptly turned off at high loading fraction, electrolyte turned black and then clarified in ~ 60 seconds. Presumably this was caused by rapid removal of impurities plated on the cathode surface that then dissolved into the electrolyte.
- Observation of spontaneous deloading under current control.
- Observation of highest loading fractions early in loading cycle.



# Cathode Loading Descriptions

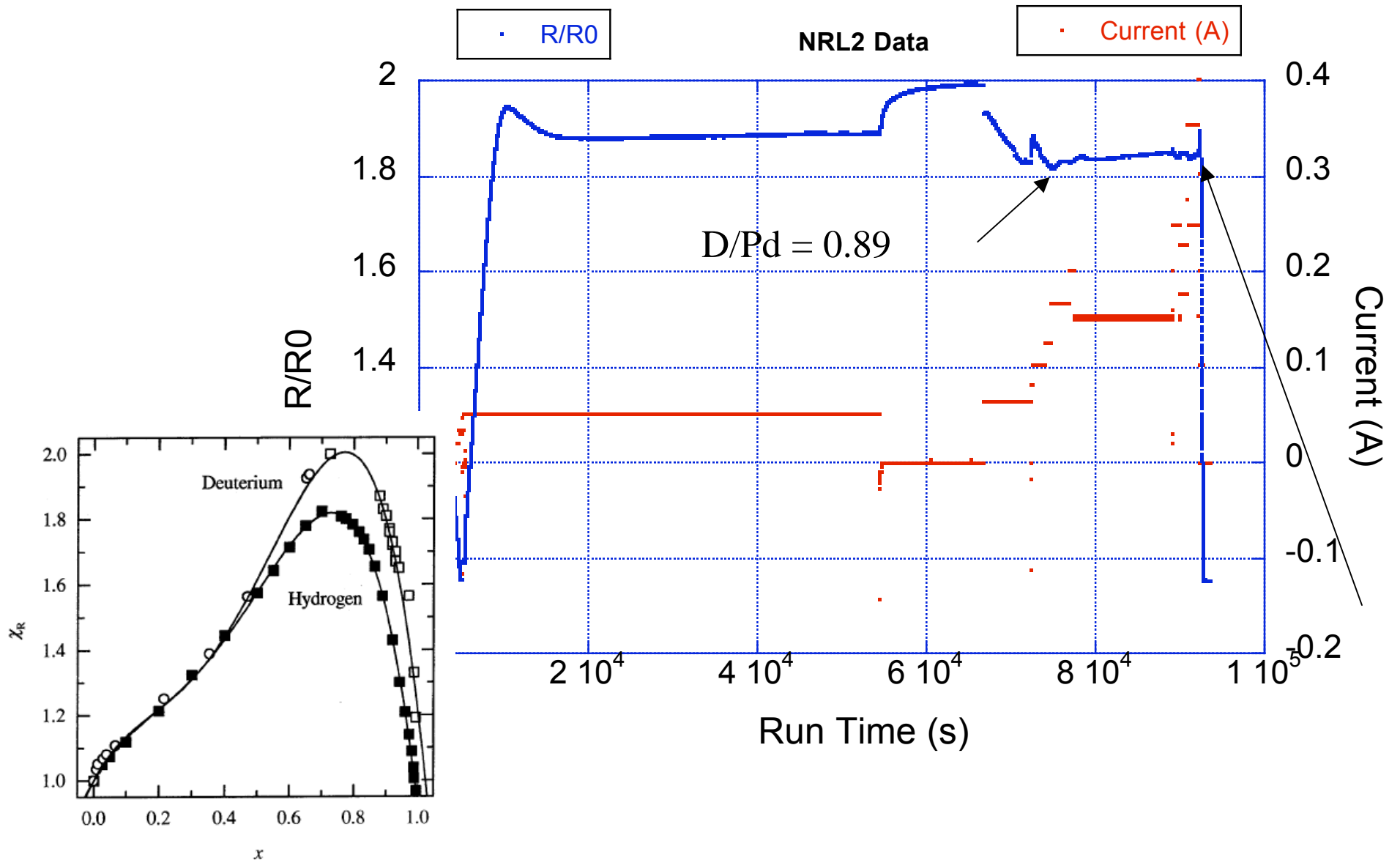
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Cathode	Electrolyte 0.1M LiOD in	R0 mOhm	Total Time	Total Charge (C)	Total Energy (kJ)	Maximum H/Pd Ratio fr resistivity	Maximum (H,D)/Pd Ratio fr lattice const.
NRL#2	D <sub>2</sub> O	3.69	46:15	6337	22.14	0.85	0.89
L23	D <sub>2</sub> O	3.82	30:15	5974	18.32	0.87	0.93
B2	D <sub>2</sub> O	10.08	48:22	110947	783.24	0.95	1.02
L5	H <sub>2</sub> O	5.24	09:56	4354	18.19	0.97	1.01

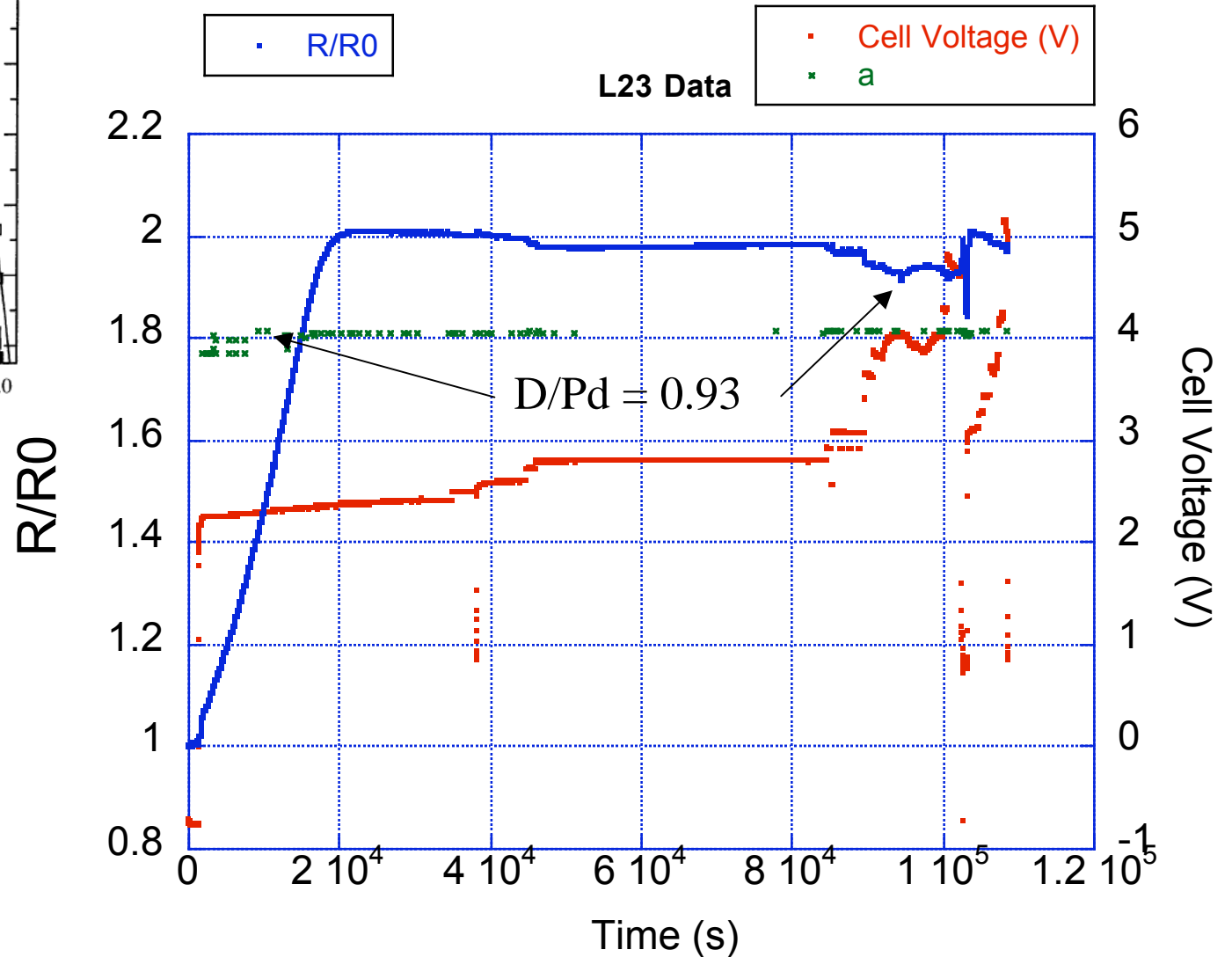
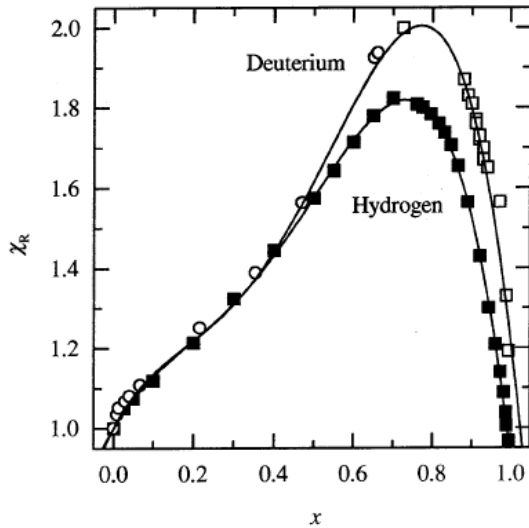
## Tentative observations:

- R/R0 four point probe underestimates loading ratio
- R/R0 is a good in situ qualitative guide for loading ratio
- Thinner foils loaded to higher ratio

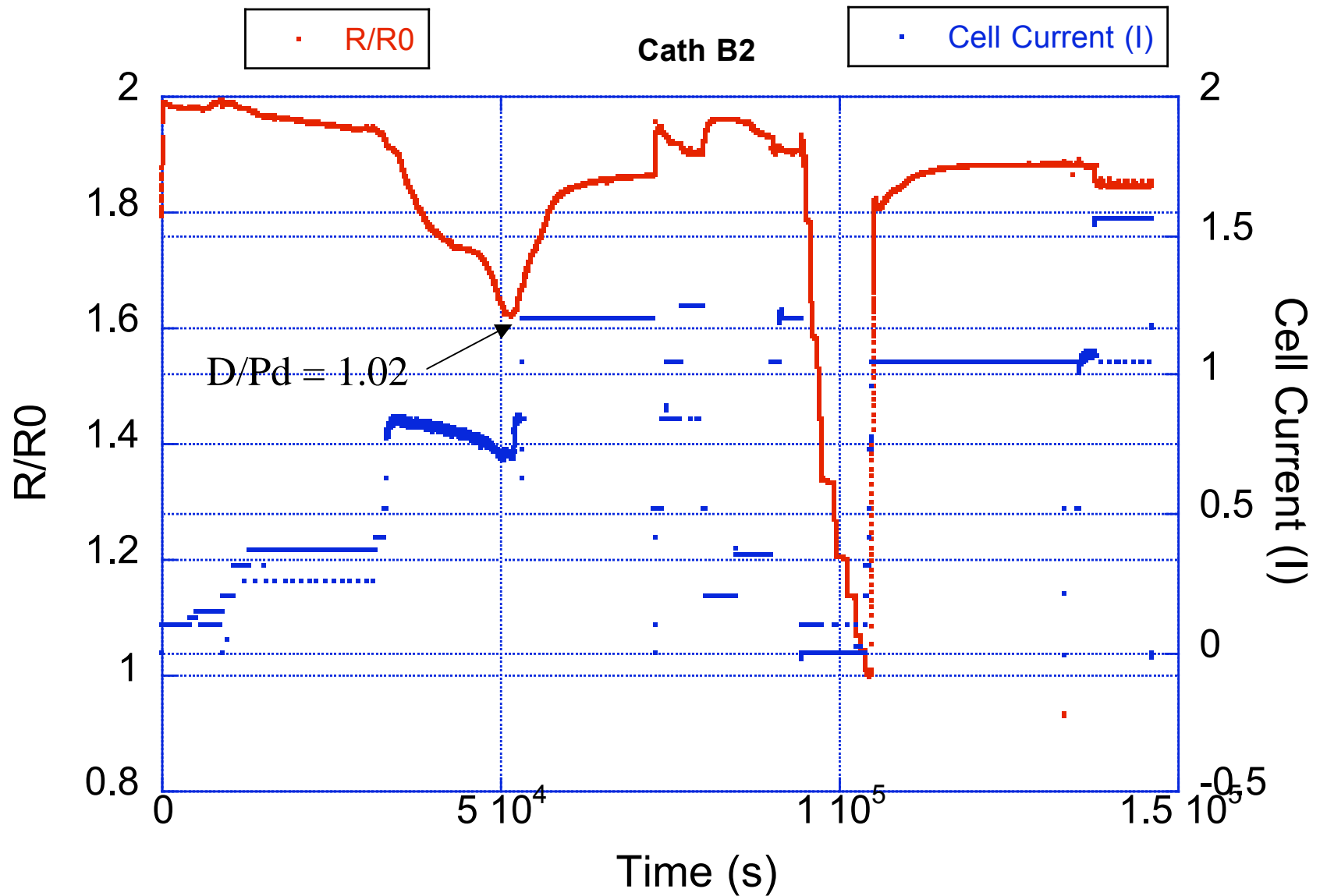
# Observation of Spontaneous Deloading



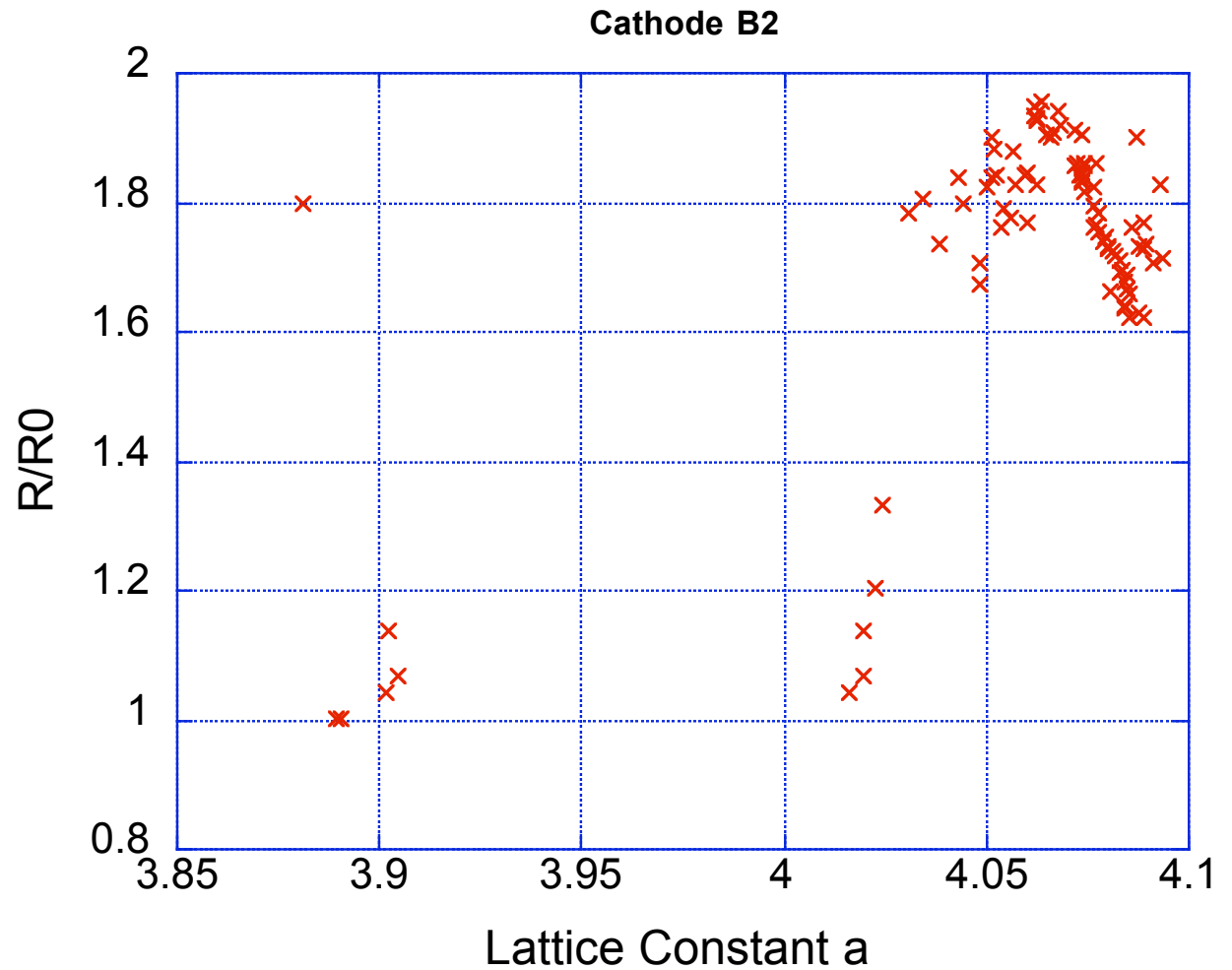
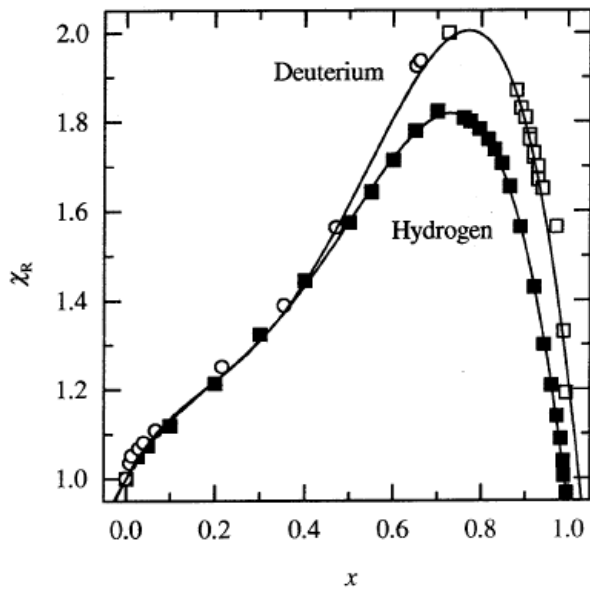
# Electrochemical History



# Electrochemical History

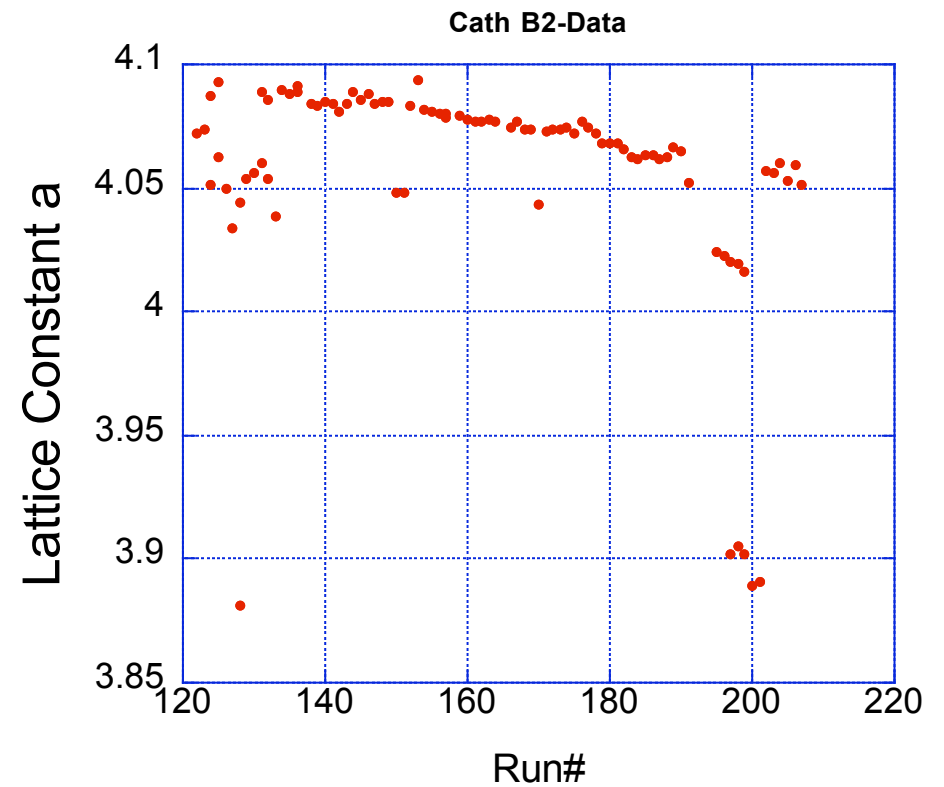
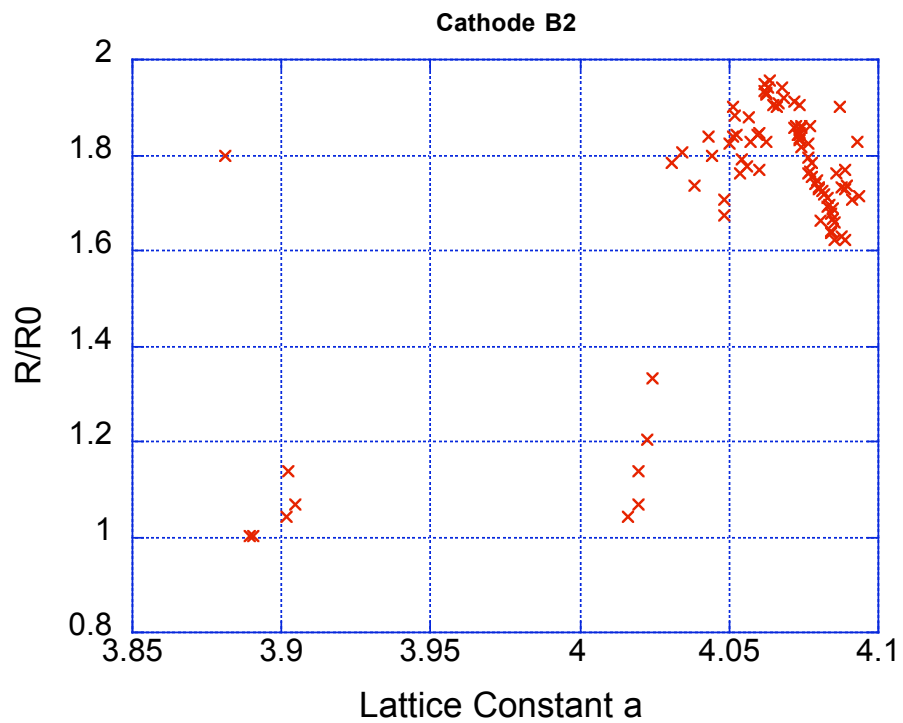


# Systemmatics of Loading



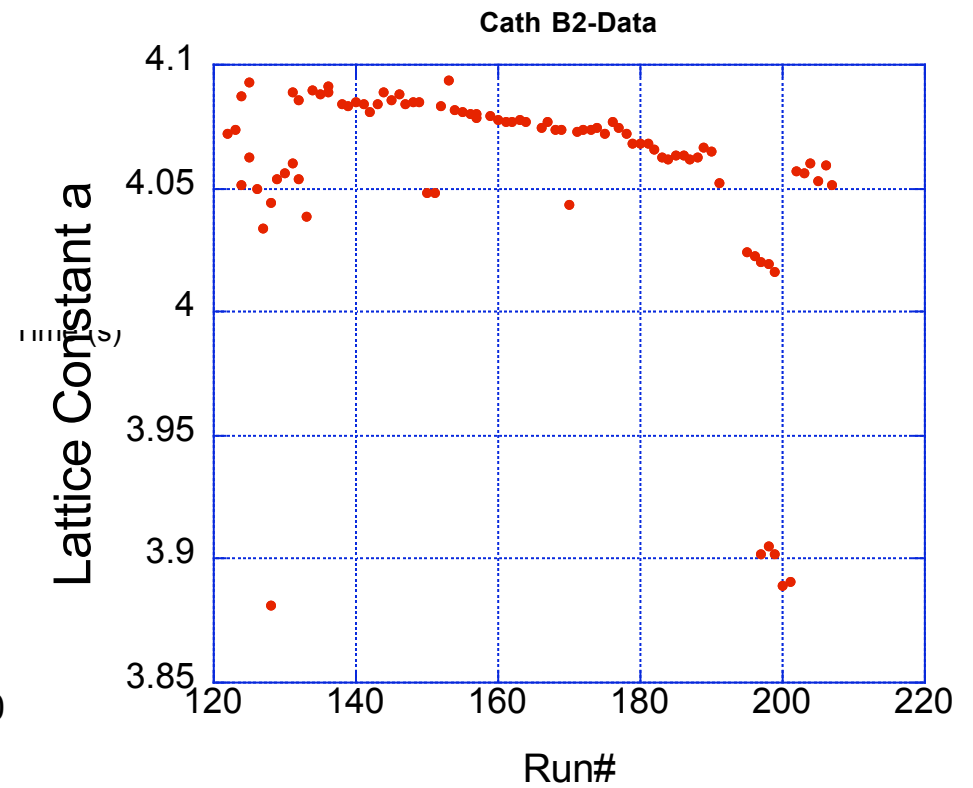
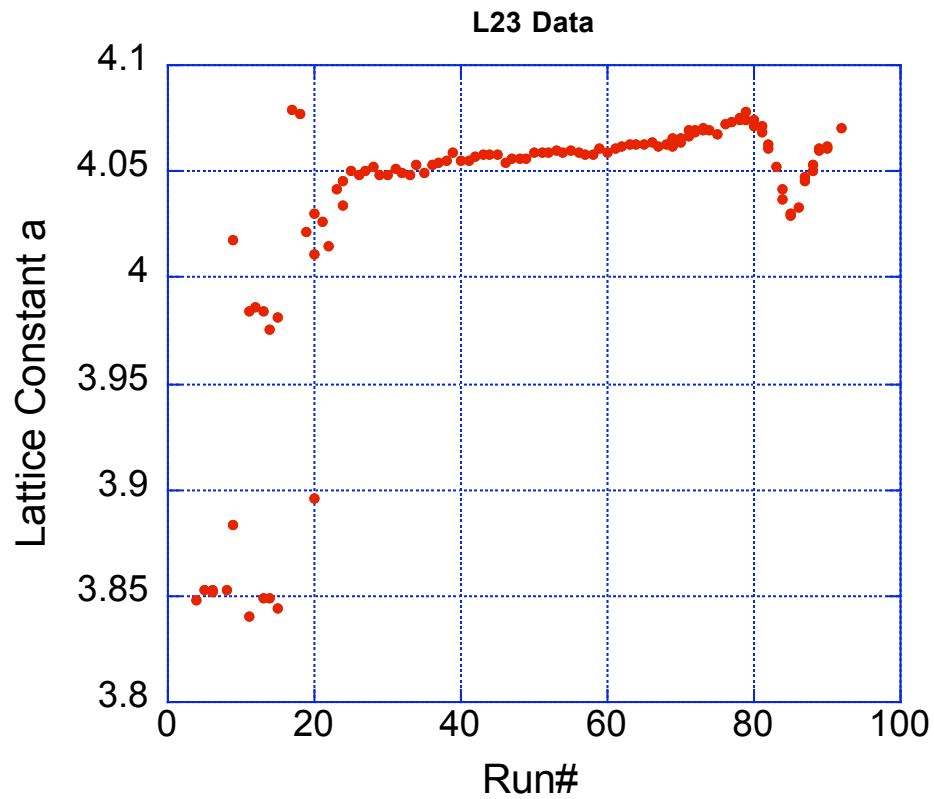
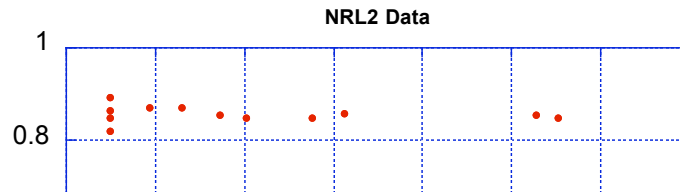
# Systematics of Loading

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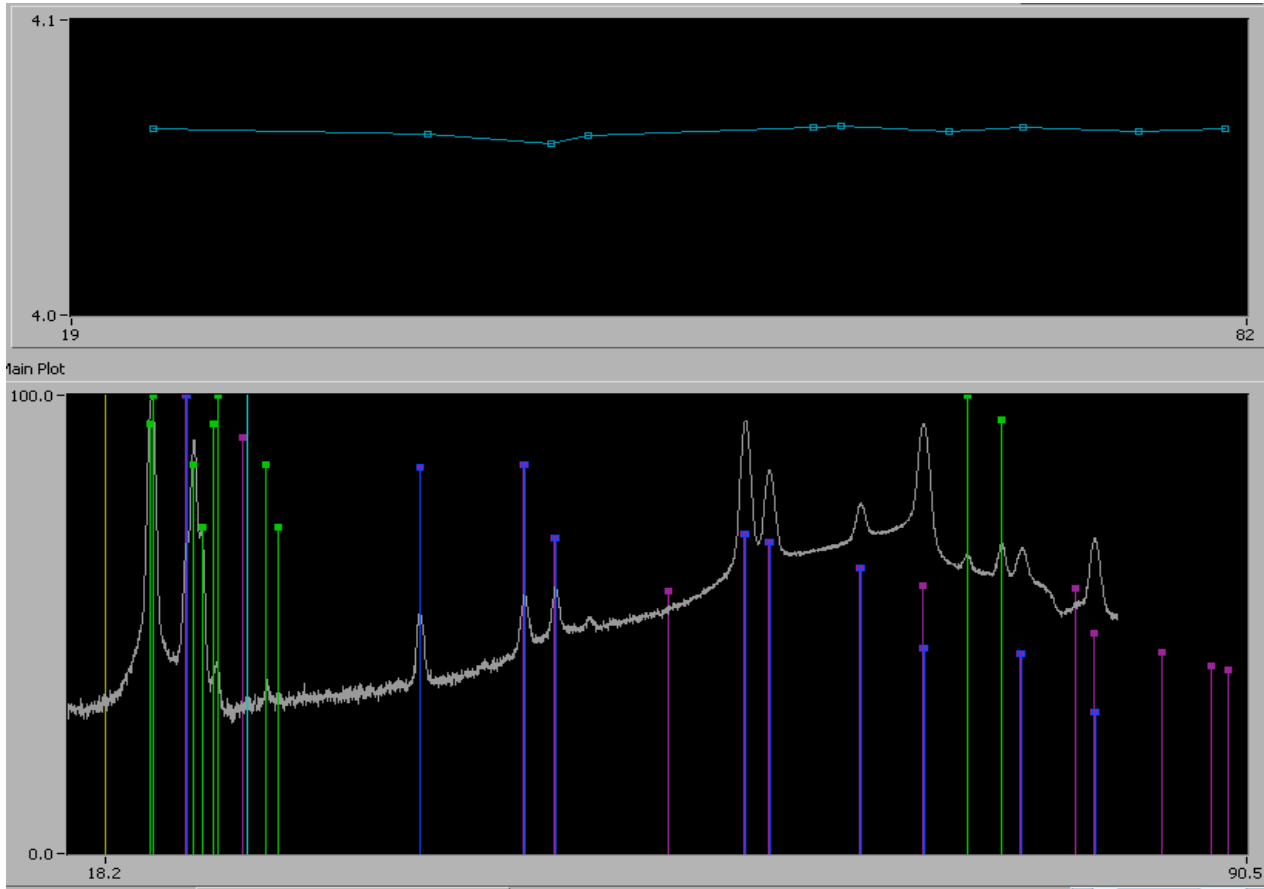
# High Loading Fractions at Early Time

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# Typical X-Ray Spectrum

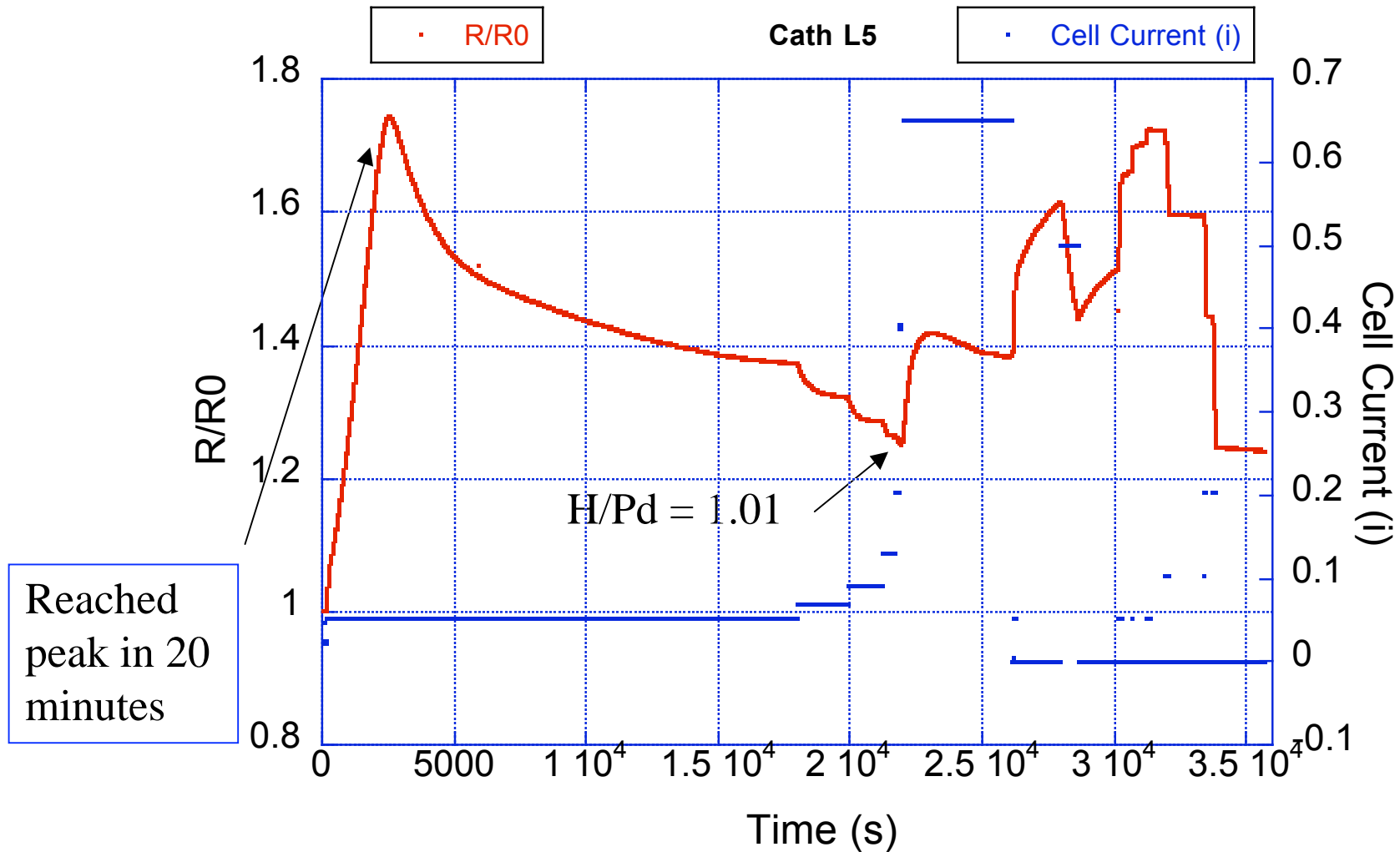
## Semi-Log Plot



- Intensity falls off at low E due to absorption in electrolyte
  - Pd K-edge absorption below 23 keV
  - Intensity falls off at high E due to x-ray beam intensity fall-off
  - In this spectrum, 10 x-ray diffraction peaks fit well
- 
- Fluorescence peaks for Pb and Sn appear during all cell runs
  - Pd fluorescence used to monitor surface
- 
- Only a few instances where Alpha and Beta diffraction seen simultaneously. Therefore, within ~ 3-5 min intervals, the phase change is complete
  - Only several grains interrogated



# Cathode Loaded with Hydrogen



# Summary - Electrolysis of 4 Cathodes

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## Observations consistent with literature

More difficult to load D than H

Spontaneous deloading under current control

Evidence of large amount of deposited impurities on surface

R/R0 in situ resistivity measurement is a good *qualitative* guide to loading ratio

Once a cathode has been loaded to high a ratio, it can not be loaded a second time

## Tentative new observations

Higher starting resistivity foils (thinner foils) loaded to higher D/Pd ratio

Highest loading ratios occur at early time in loading cycle

All four ENEA-prepared cathodes loaded to high D/Pd ratios

# Summary - X-Ray Diffraction

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## Observations consistent with literature

alpha-beta phase change

## Tentative new observations

Rapid surface deloading and reloading

Very few x-ray spectra with both Alpha and Beta phases present suggests that within multiple grains, the transformation from Alpha to Beta is very rapid (within the 3-5 minute time resolution of the data)

Highest D/Pd ratio early in loading cycle

## New observations

High D content by x-ray diffraction ( $D/Pd = 1.02$ )

R/R0 measurement consistently underestimates the loading ratio

No obvious new phase at high loading fractions (for Pd sublattice only)

First time x-ray diffraction performed in FPE cell at concentrations greater than  $D/Pd > 0.76$

# Conclusions

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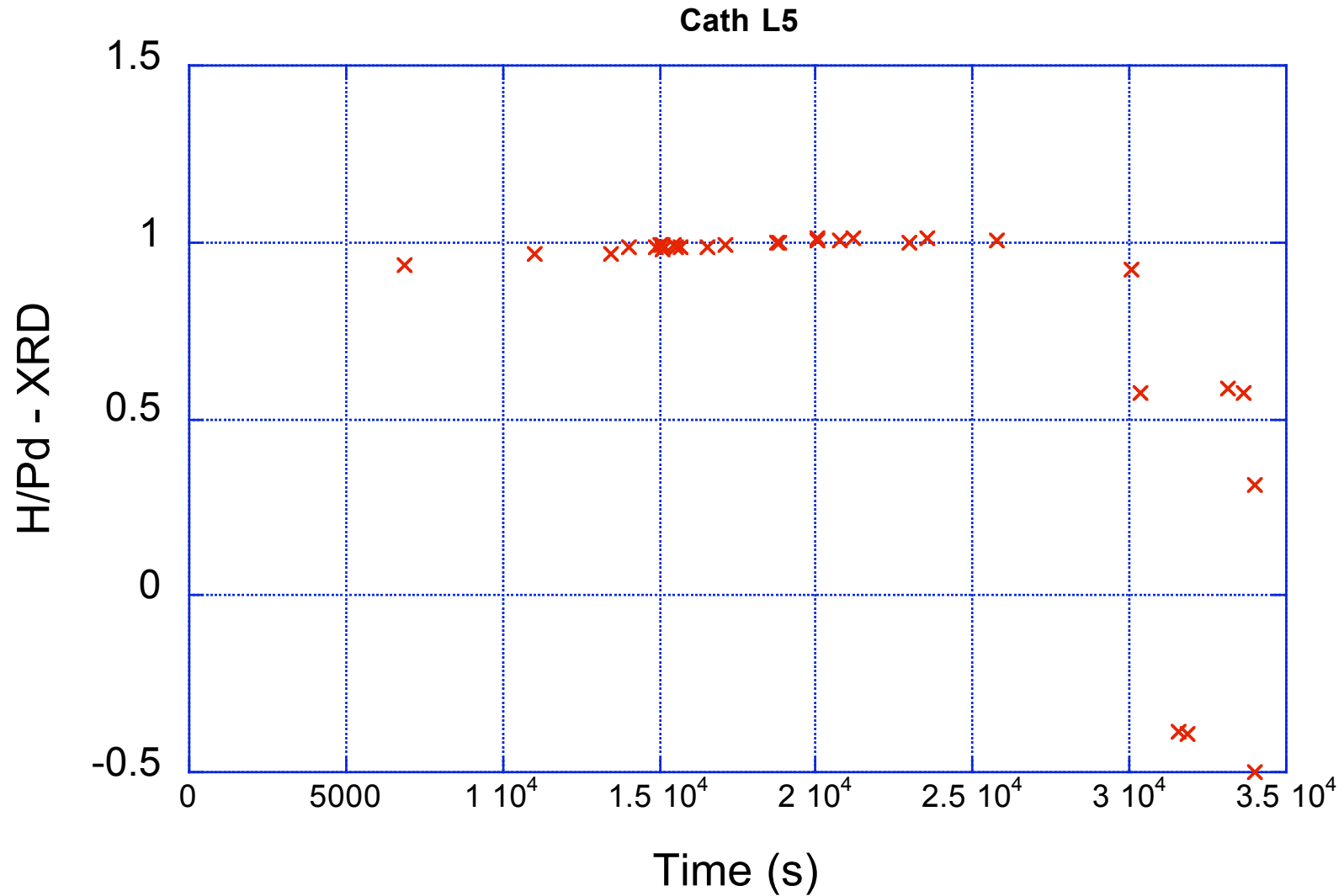
- Time resolved, in-situ, high-energy x-ray diffraction was performed on modified Fleishman-Pons electrolytic cells during electrochemical loading of palladium foil cathodes with hydrogen and deuterium.
- Concentrations of H and D up to 1:1 in 0.1 M LiOH/LiOD in H<sub>2</sub>O/D<sub>2</sub>O electrolytes were obtained.
- While very interesting data in its own right, no new anomalous behavior was observed that identifies a mechanism of FPE.

Table I: Maximum Electrolytic Loading Ratios Achieved in the Pd-H and Pd-D systems.

System	Loading Ratios	Loading Conditions and/or Sample Preparation	In Situ X-Ray or Neutron Diffraction	Year	Ref
Pd-D	0.72	0.1 M LiOD	x-ray diffraction	1998	27
Pd-D	0.92-0.96	1M LiOD, stepwise changed current density; 0.96 if etched with aqua regia, 0.92 if polished with diamond grit	none	1997	12
Pd-H; Pd-D	0.78-0.82	0.1 M/1M LiOH or LiOD, 50 mA/cm <sup>2</sup>	none	1996	13
<b>Pd-H; Pd-D</b>	<b>0.76</b>	0.1 M LiOD	x-ray diffraction	1995	14
Pd-H;Pd-D	0.85-0.90	1 M LiOH and LiOD	none	1995	15
Pd-D	0.91-0.93	Pd was vacuum annealed and acid etched.	none	1994	16
Pd-D	0.55	0.1 M Li <sub>2</sub> O in D <sub>2</sub> O	neutron diffraction	1990	66

# High H Content

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# Pd-H Phase Diagram

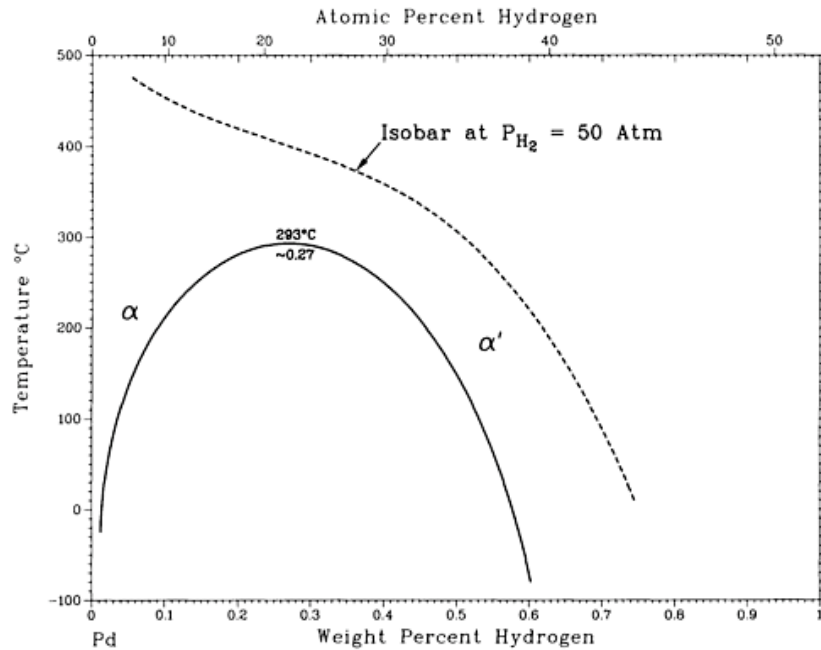


Figure 1: The phase diagram of Pd-H system.

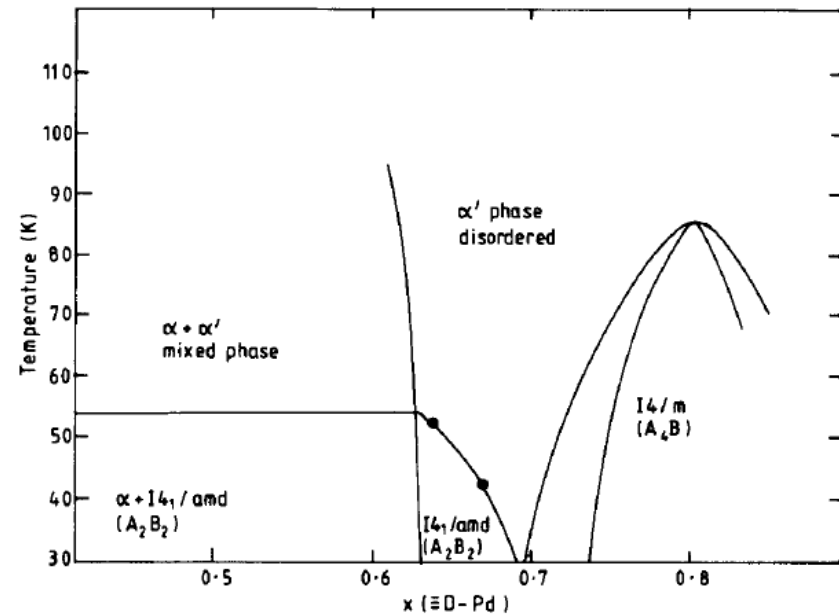


Figure 2: The phase diagram of Pd-D system (Here,  $\alpha'$  phase means  $\beta$ ) at low temperatures.

# Shifts in XRD peaks with time

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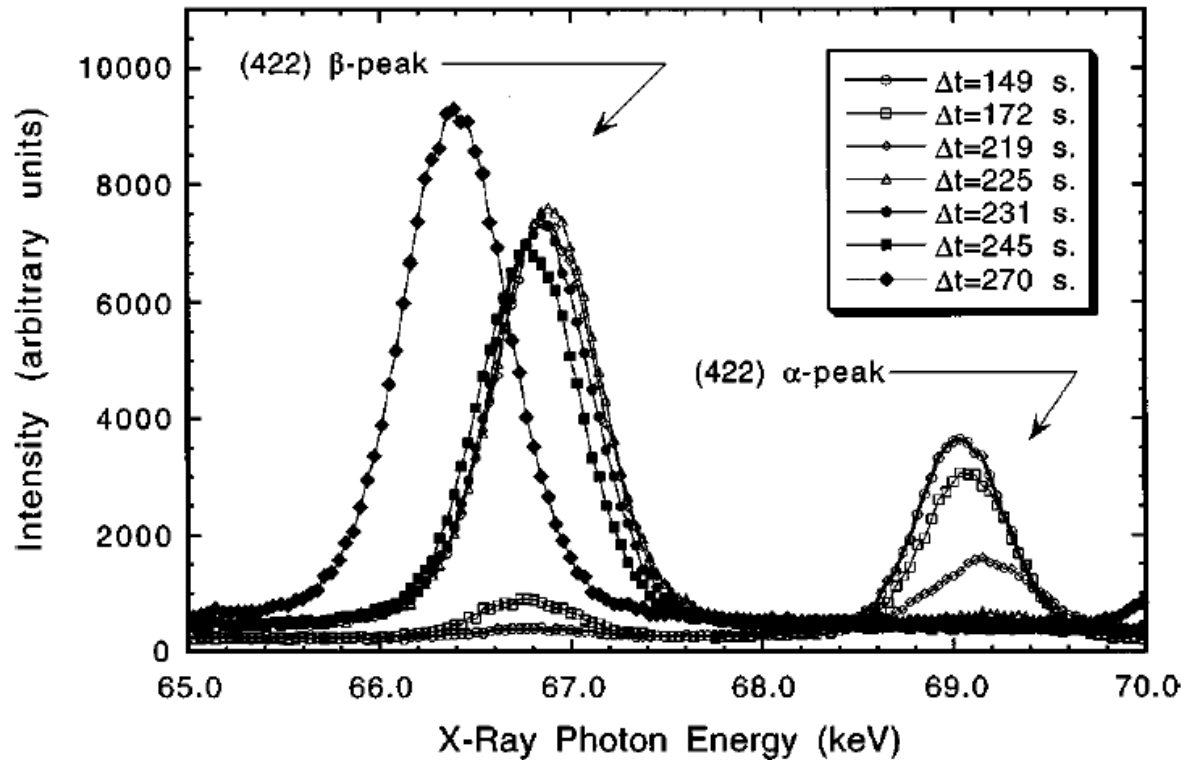
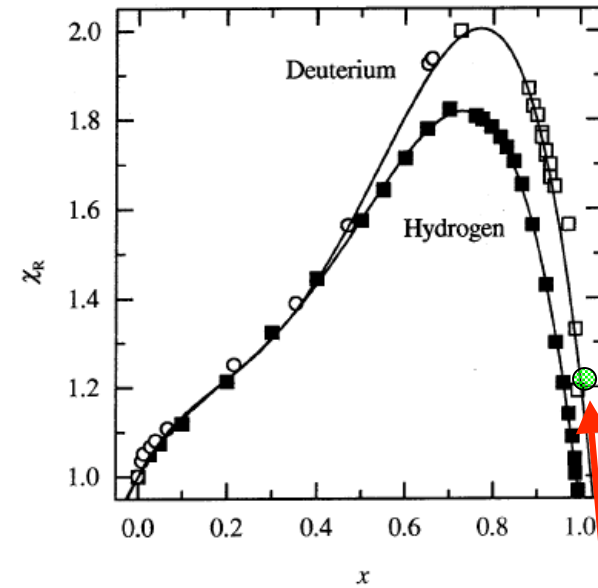
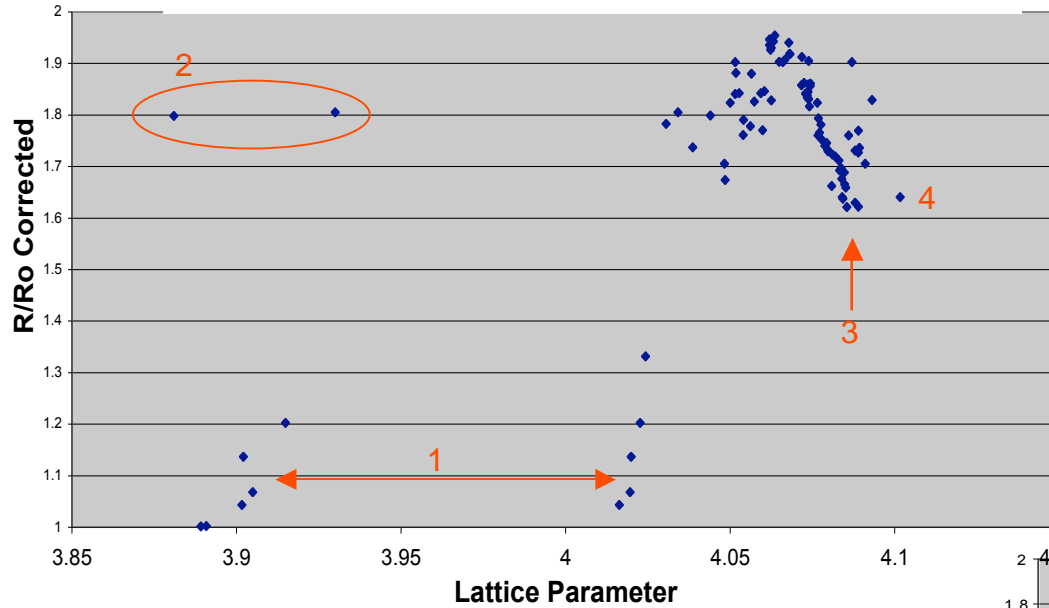


Figure 5: Temporal dependence of the intensity of (422) diffraction peaks of  $\alpha$  and  $\beta$  phases.



# D/Pd > 1

In-situ measurement of D/Pd



- 1 alpha-beta phase change
- 2 rapid surface deloading
- 3 high D content
- 4 suggestion of phase change

