Hard X-ray Studies of Thin Films and nanoclusters

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Birzeit University

Hard X-ray Studies of Thin Films and nanoclusters

- Overview
  - Hard X-ray Characteristics
  - In situ studies of superconductors
  - Studies of battery electrodes
- Hydrogen in Pd/Nb multilayers and bimetallic electrodes
- Hydrogenated metallic clusters

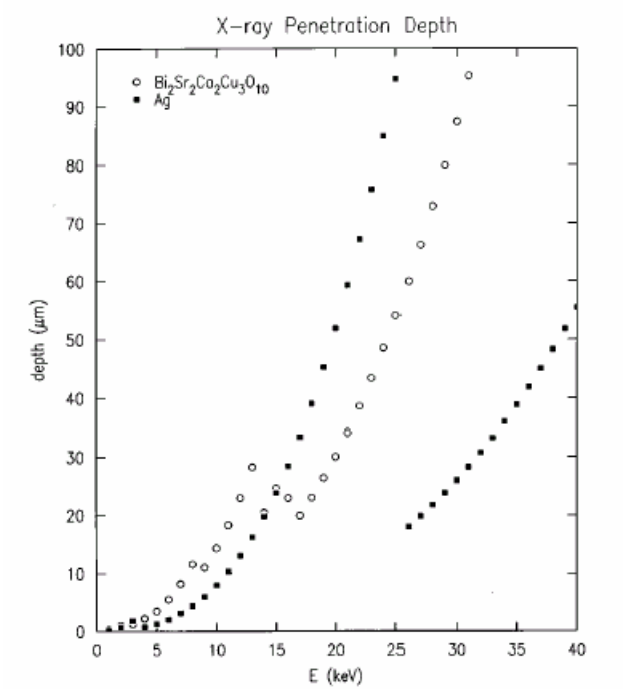
Hard X-ray Study of Superconductors

Collaborators:

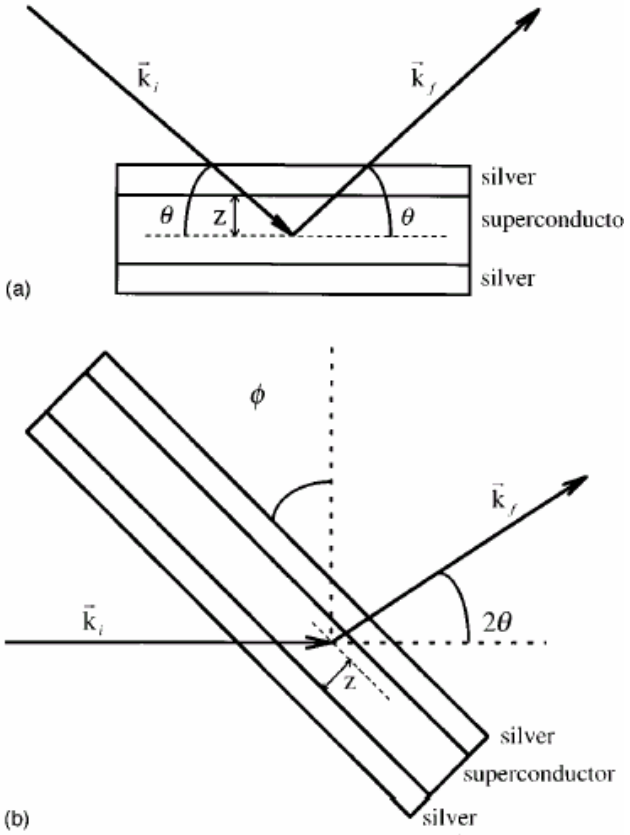
T. Thurston, J. McBreen

S. Mukerjee, M. Suenaga

Penetration and Scattering Geometry



IG. 1. Absorption penetration depth of Ag and 2223 as a function of x-ray hoton energy. The large change in the silver penetration depth at ~25.5 eV is a signature of the *K* edge for this material.



T.R.Thurston et.al. J. Aqppl. Phys. **79**, 3122(1996).

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Example

Note that up to 10,000 counts/sec are possible in transmission

Development of the High Tc 2223 Phase

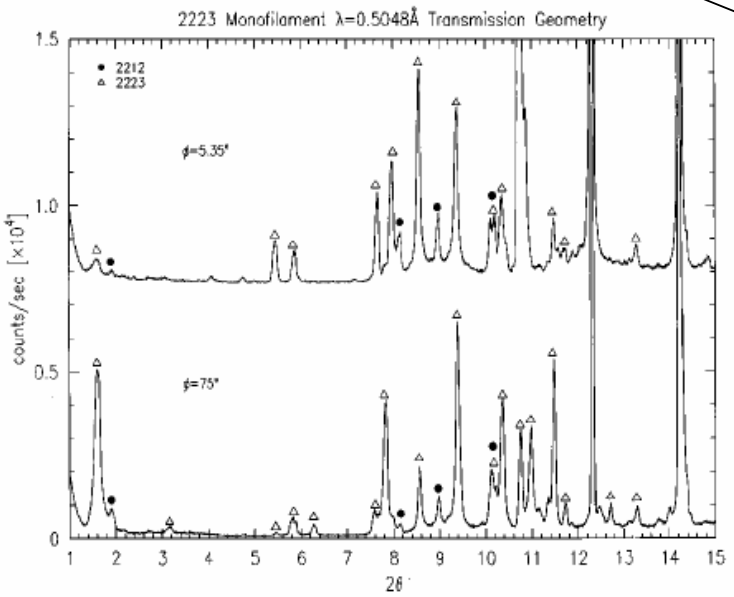
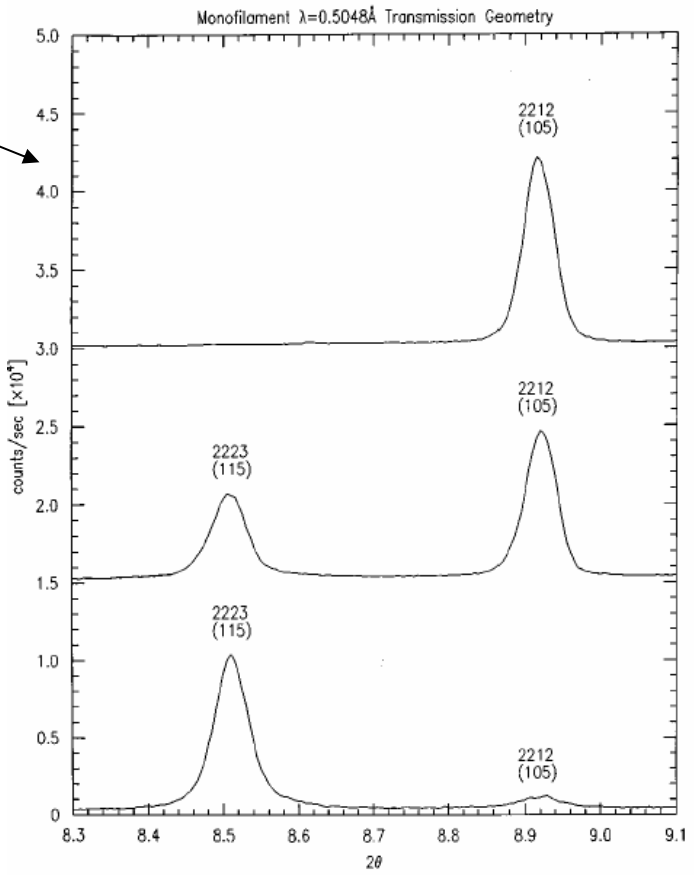


FIG. 4. Transmission geometry 2θ scans of a monofilament tape with the sample rotation angle ϕ fixed at two different values. These data were taken with 24.5 keV photons (λ=0.504 77 Å); to convert peak positions to those for Cu K_α use the formula $2\theta_{Cu}=2\sin^{-1}[1.54\sin(2\theta/2)/0.504\ 77]$.



$LiMn_2O_4$ Example

T.R. Thurston et.al. Appl.Phys. Le
69, 194(1996).

Industrial Prototype with X-rays going through casing and battery material

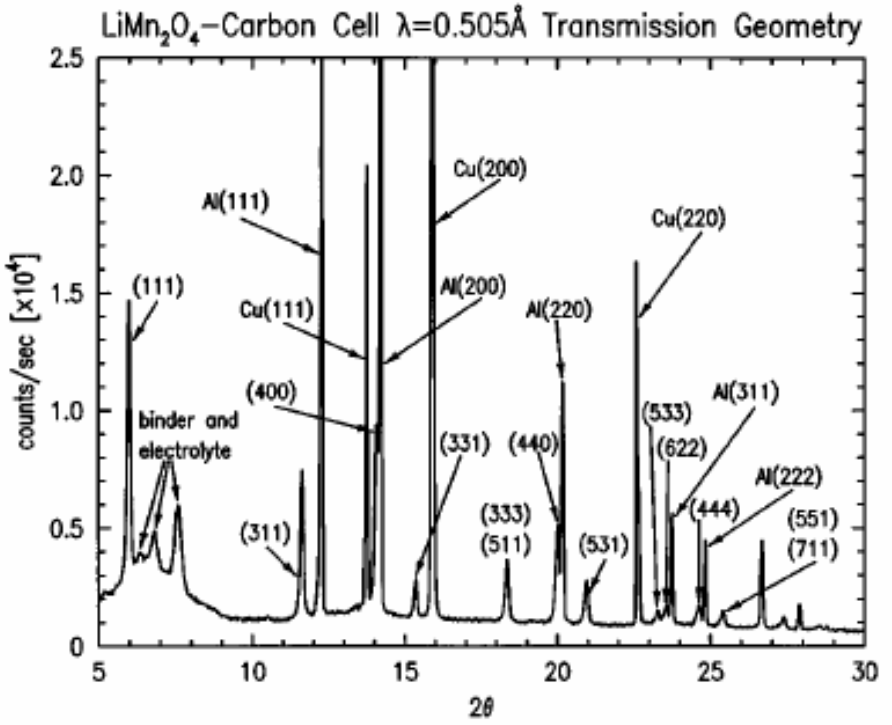


FIG. 1. 2θ scan taken on a $LiMn_2O_4$-carbon cell when it was charged to 2.25 V. Peaks arising from aluminum, copper, binding materials, and the electrolyte are labeled. The rest of the indexed peaks are from the $LiMn_2O_4$ cathode material.

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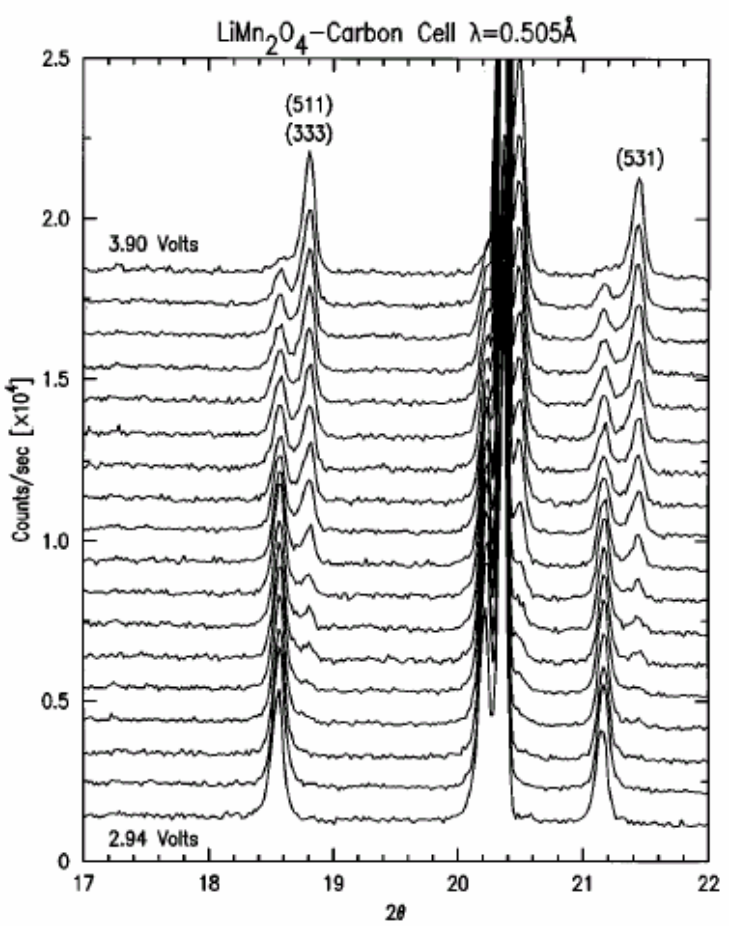
Details of Phase Transformation

"Rocking Chair" battery transformation probed during operation.



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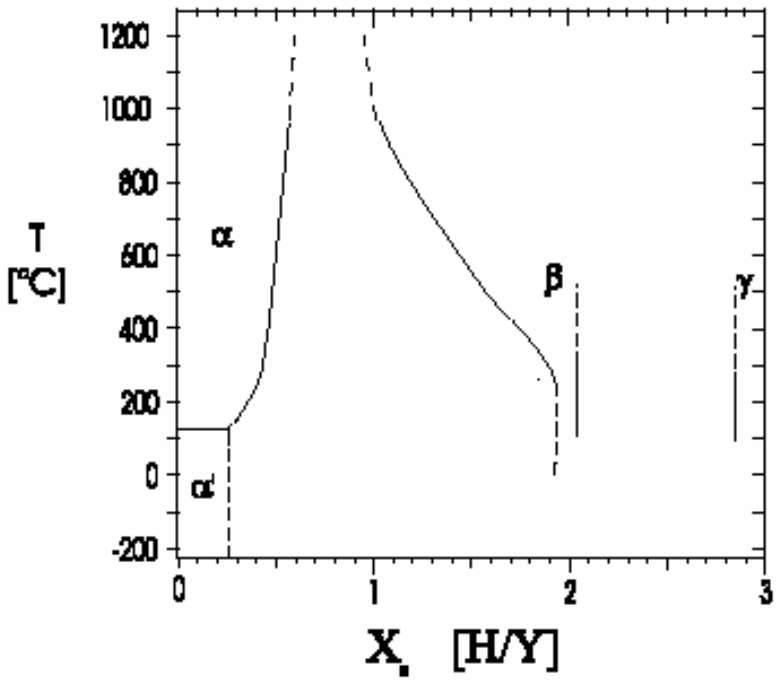
Nb thin films

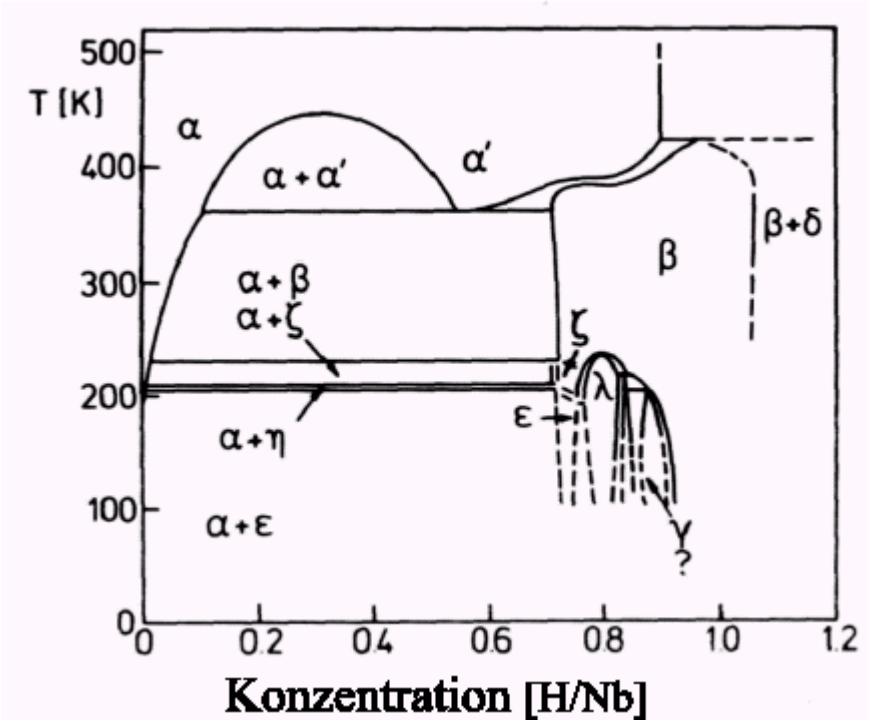
Collaborators:

M. Dornheim, A. Pundt, and R. Kirchheim

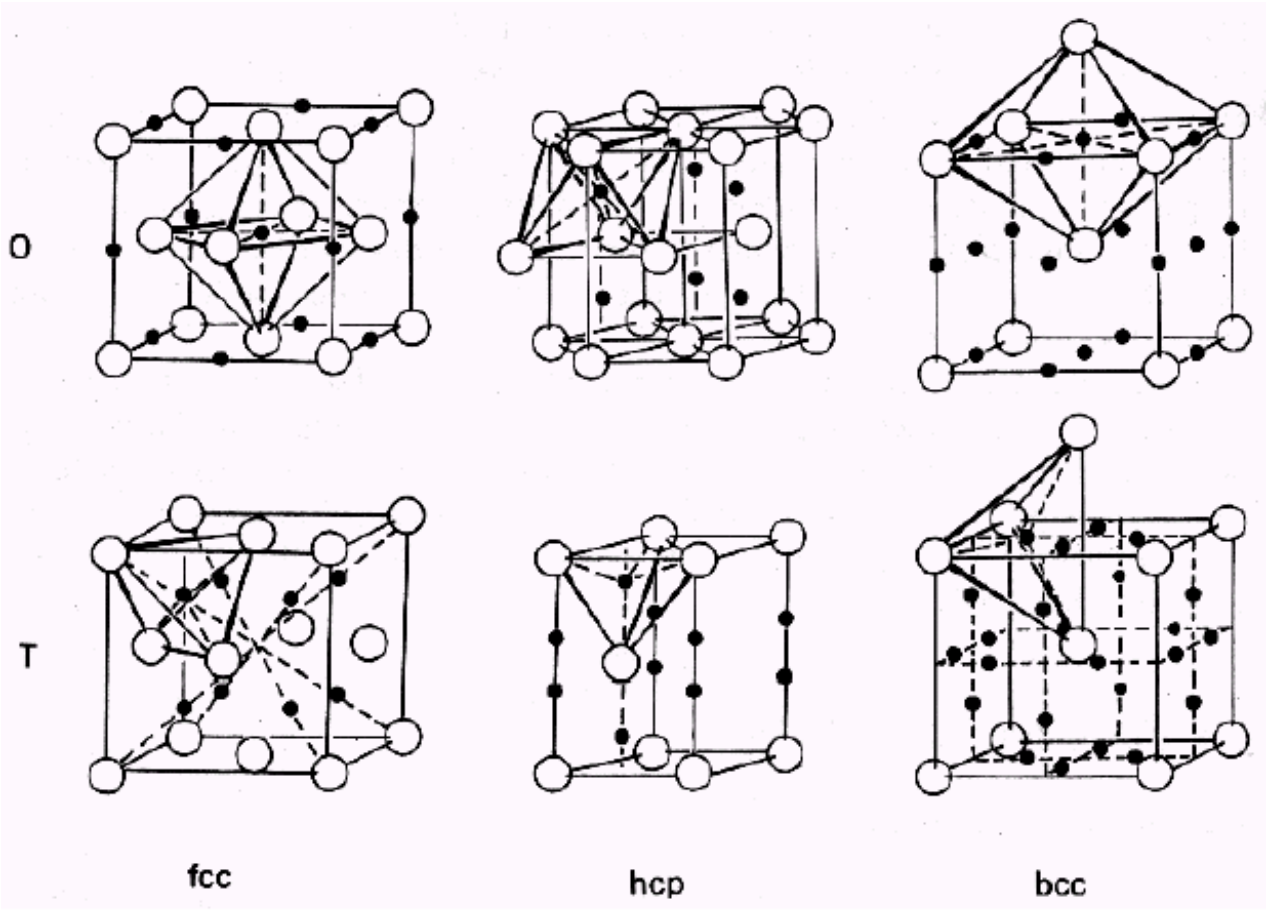
B. Ocko and M. Strongin

Hydrogen-metal phase diagram

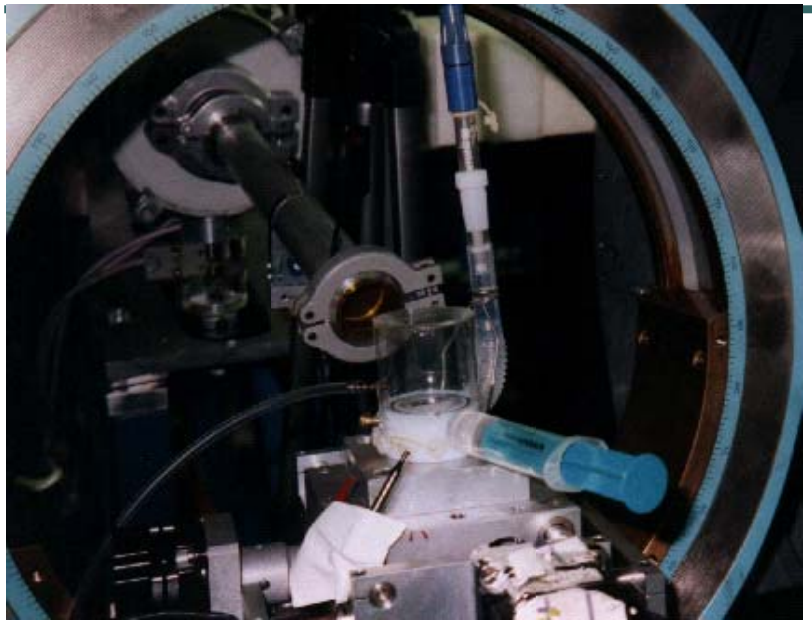




Hydrogen in Metal Films

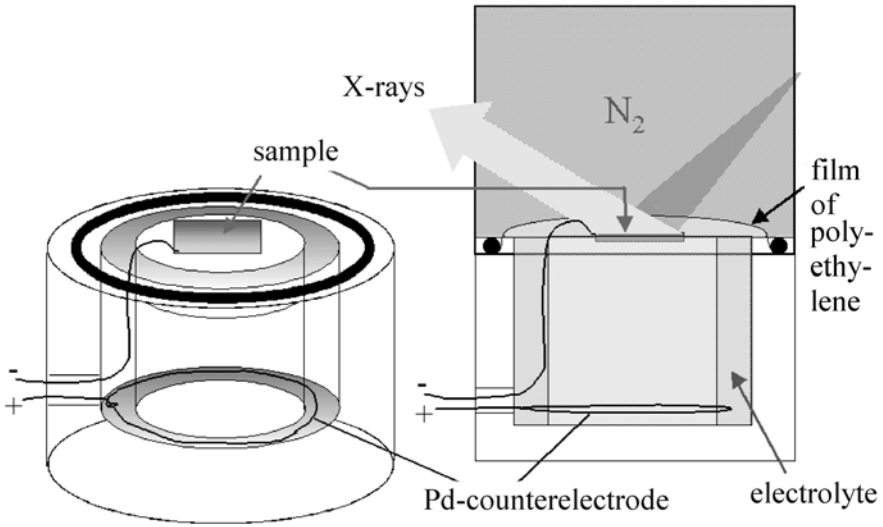


Thin Film In Situ Electrochemical Cell

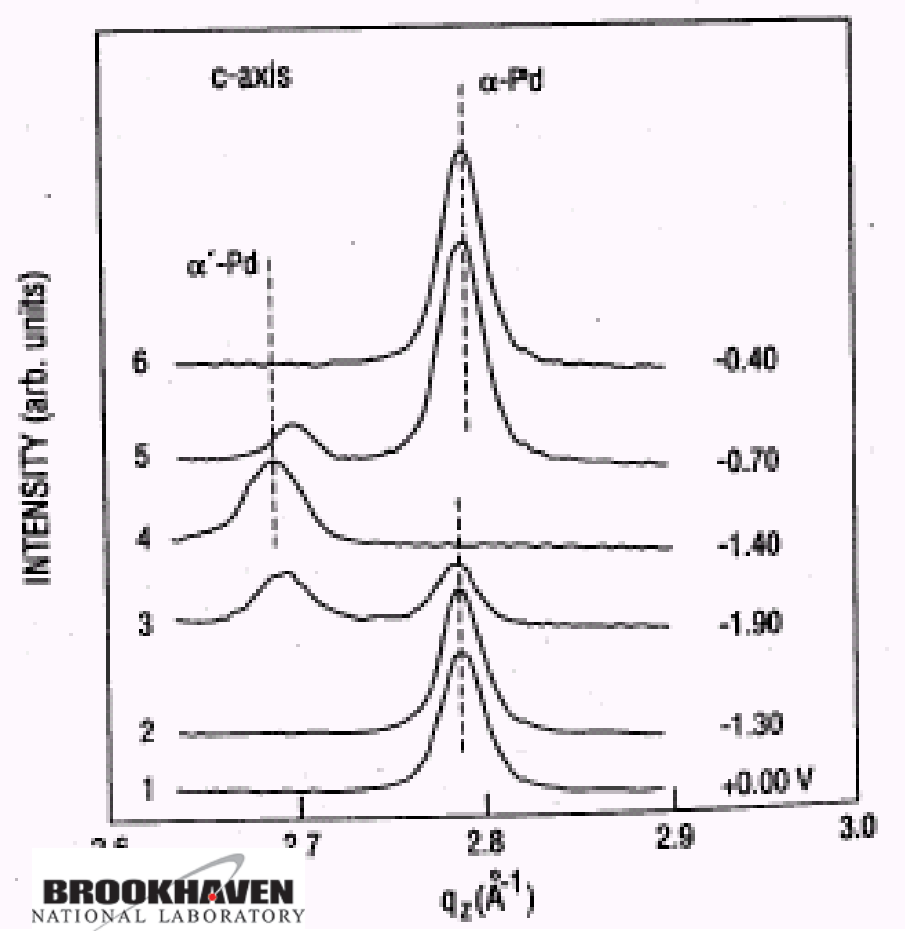


Euler cradle of B2 at Hasylab

ECC made from Teflon

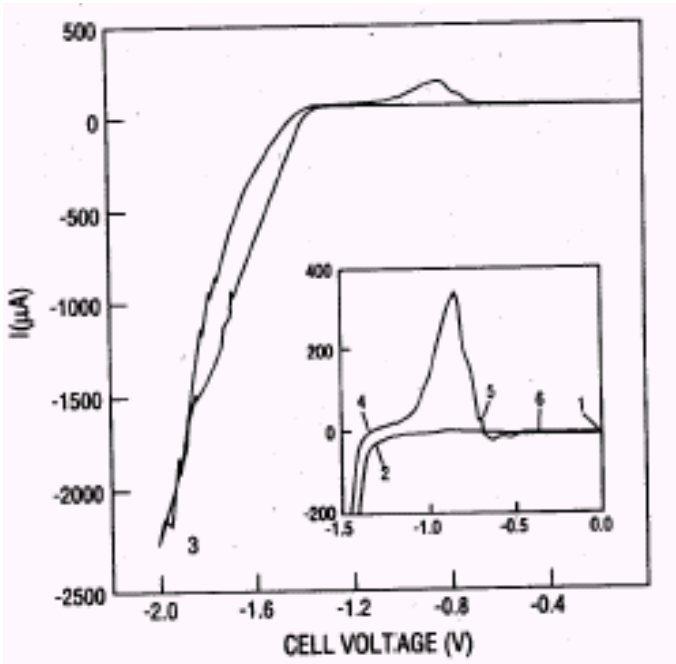


Hydrogen in Bimetallic Electrodes

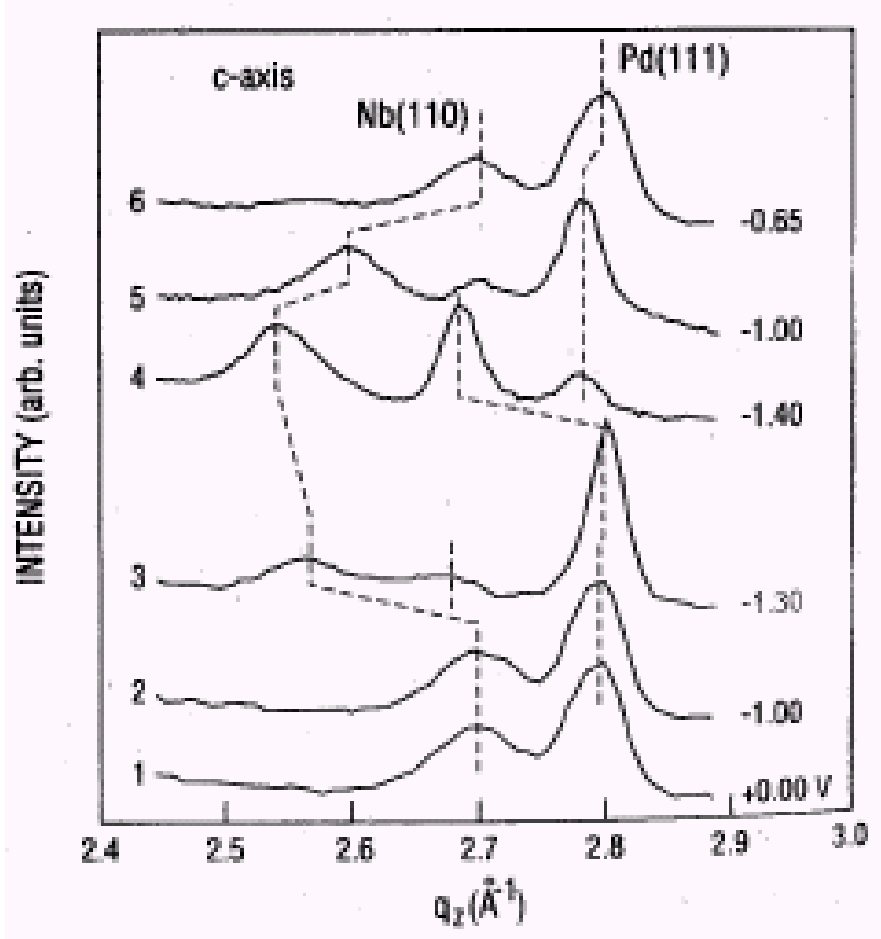


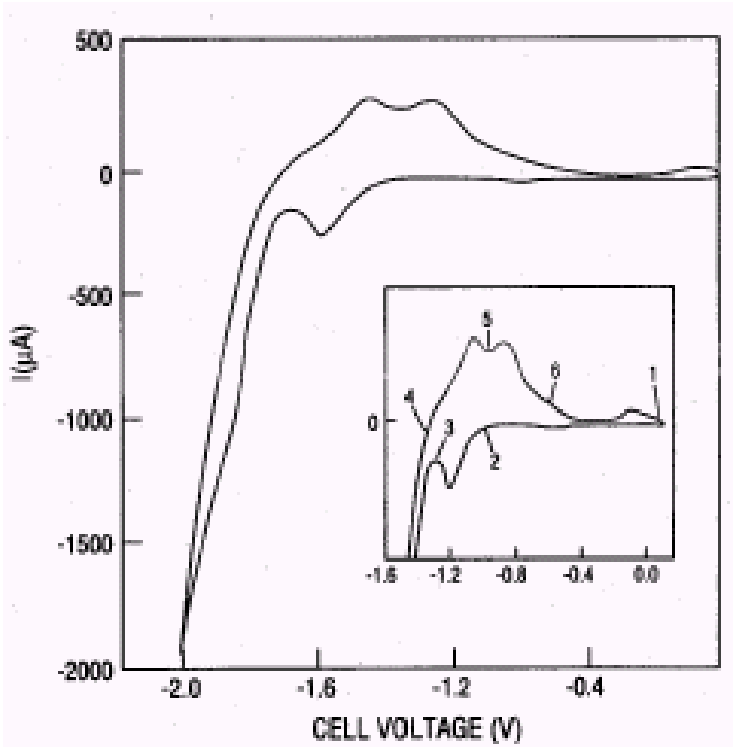
N.M. Jisrawi et.al. J. mater. Res. **12,** 2091(1997).

- 800 A Pd film.

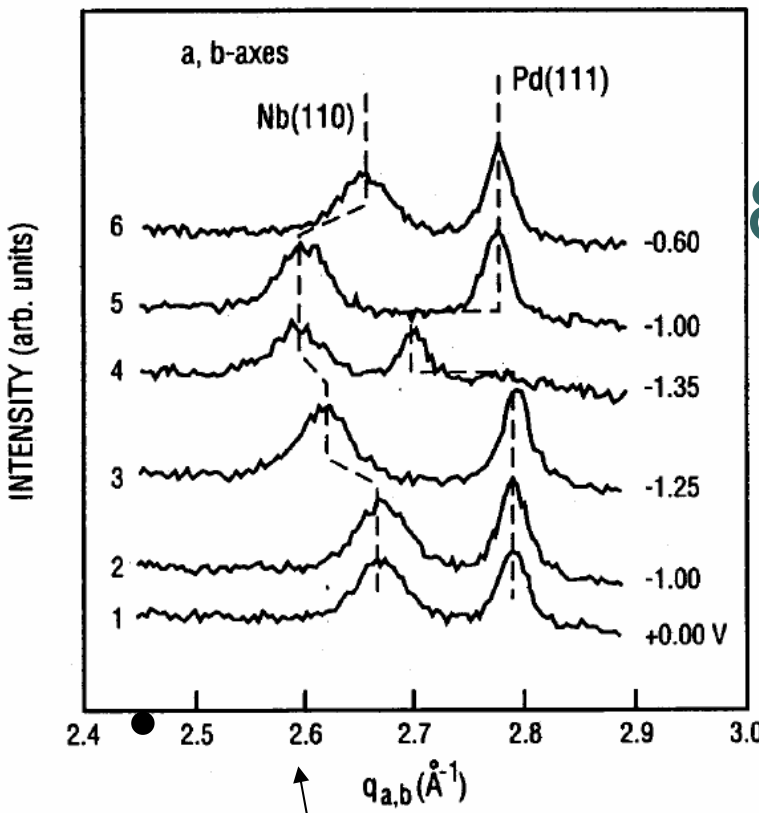


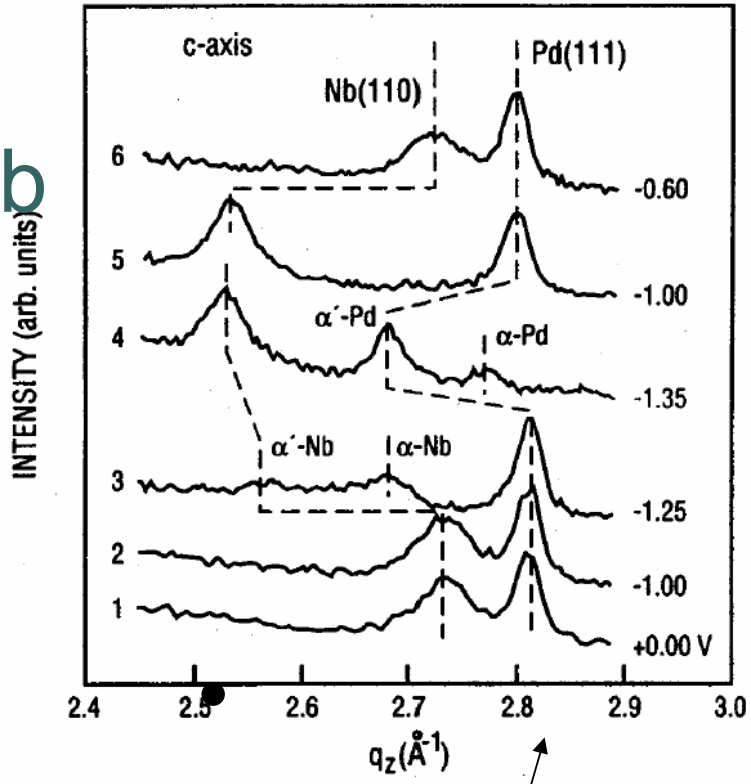
Nb/Pd/Nb (800/200/800)





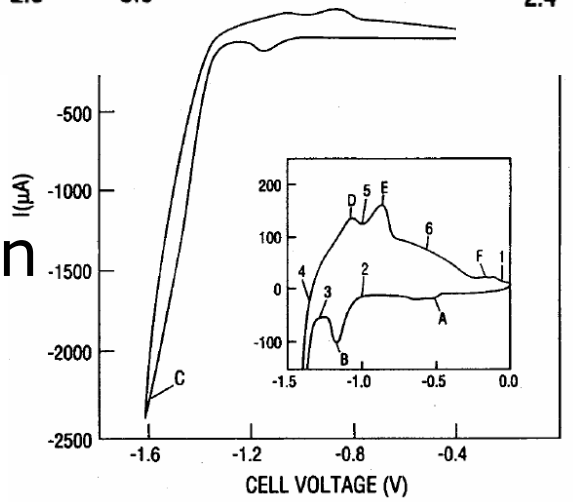
800 A Nb





In-plane expansion

C-axis expansion



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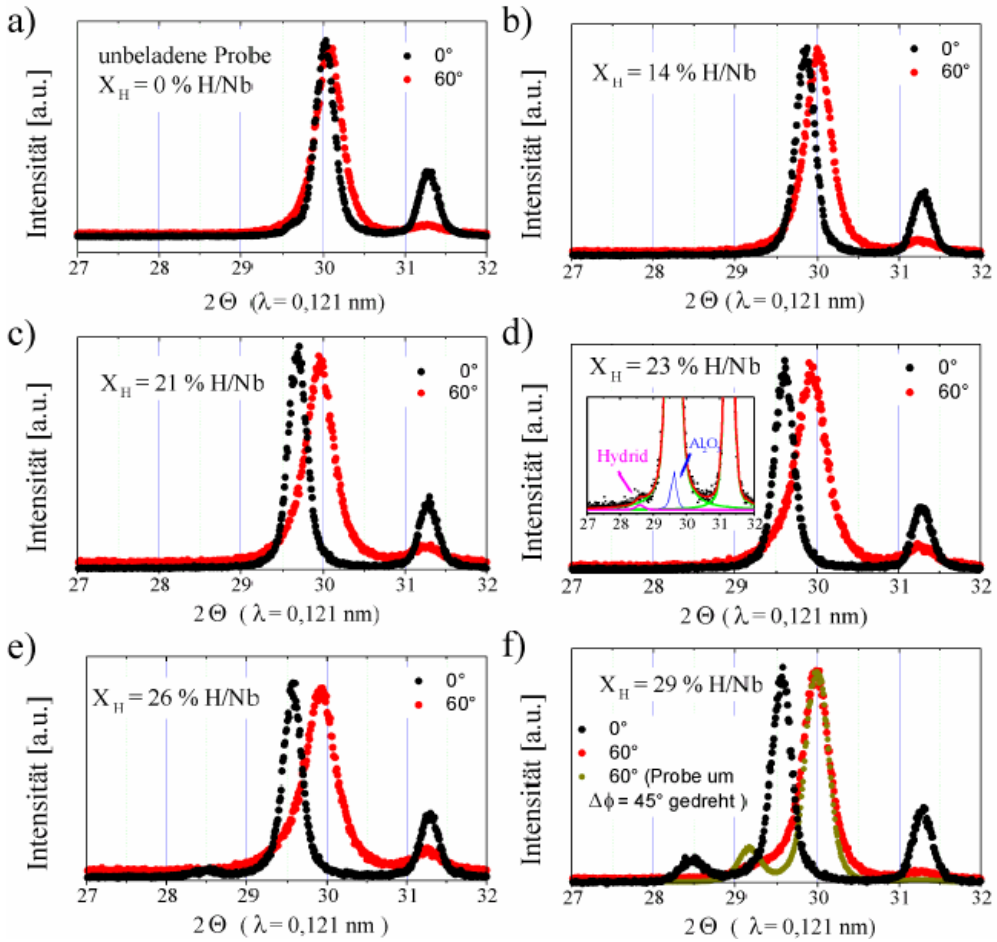
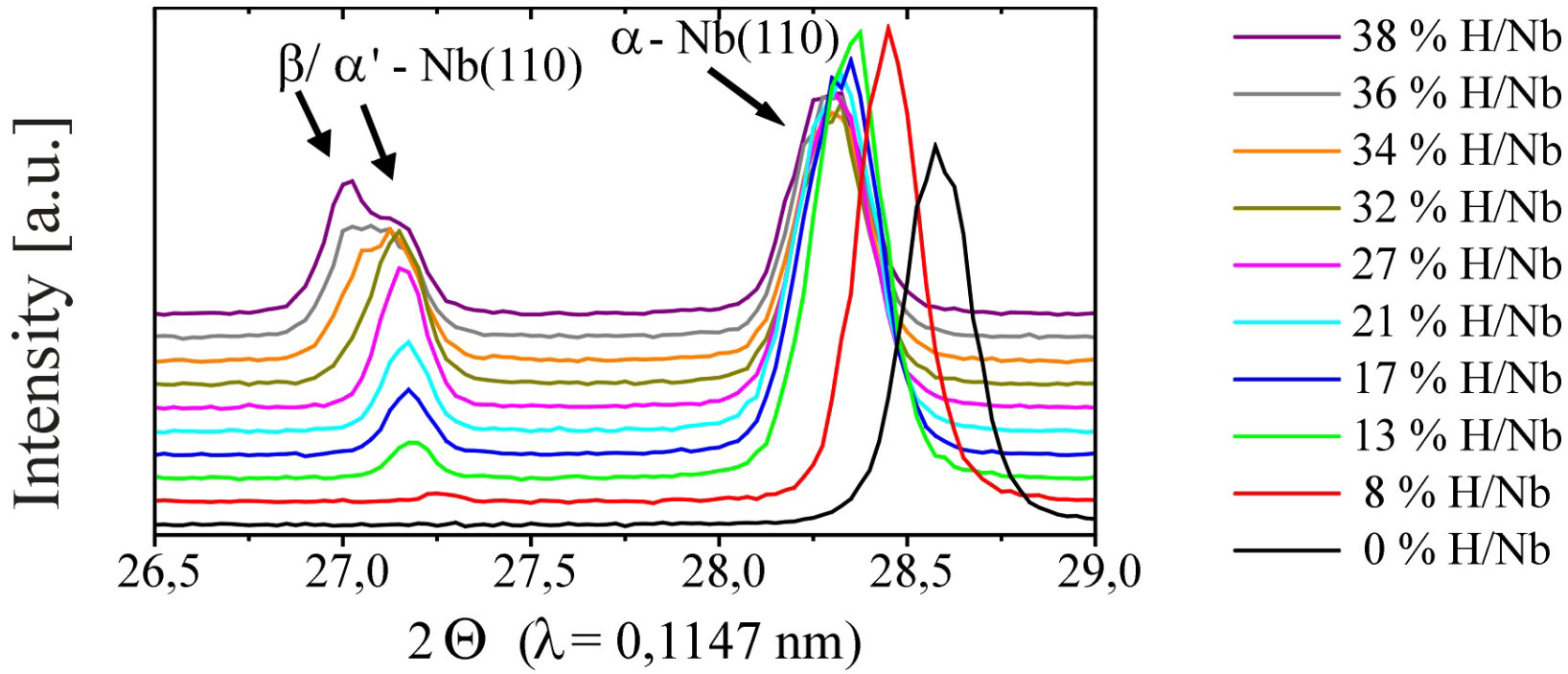
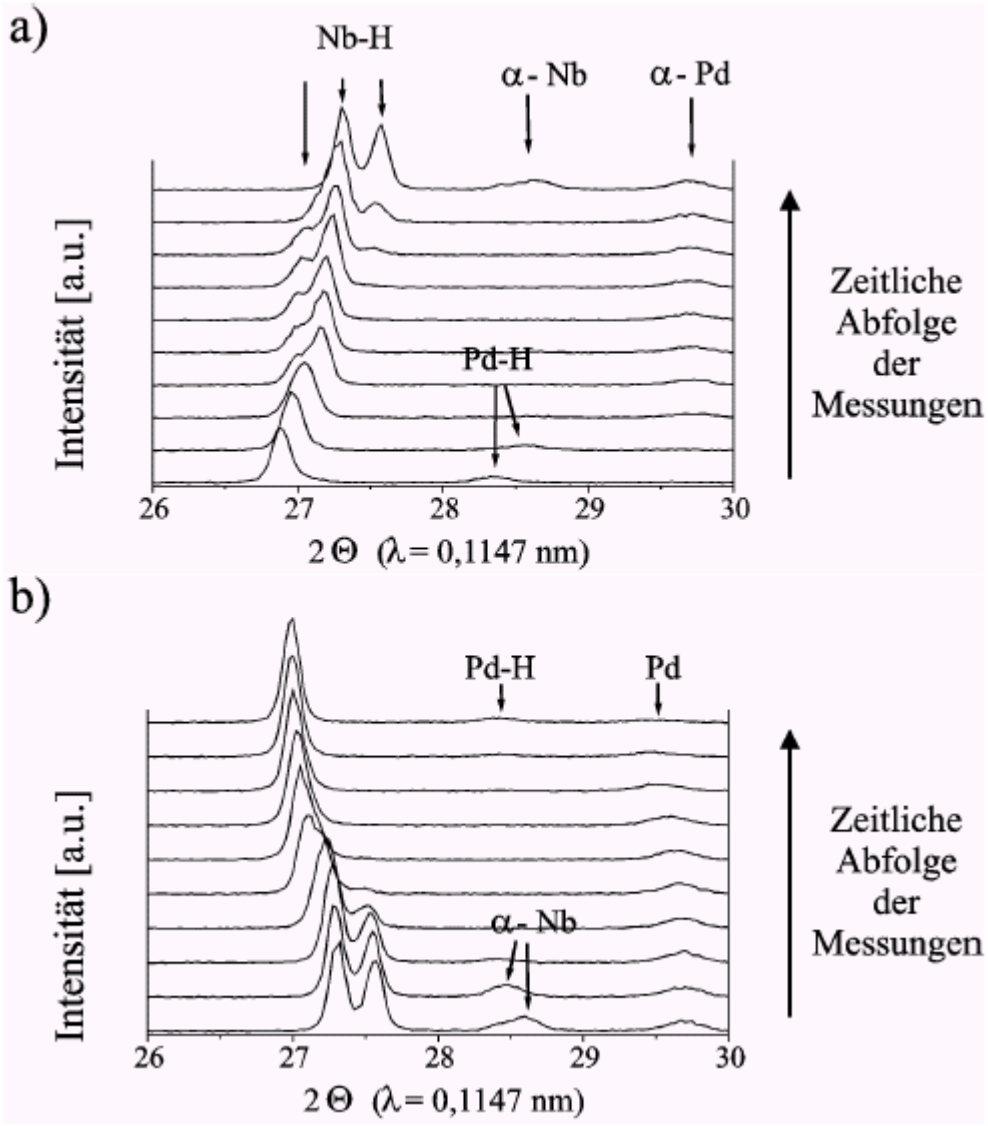
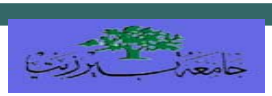
Phase Changes in Nb



Development of the β-phase




a)
Nb-H
α - Nb
α - Pd
Pd-H
Intensität [a.u.]
Zeitliche Abfolge der Messungen
26
27
28
29
30
2 Θ (λ = 0,1147 nm)
b)
Pd-H
Pd
α - Nb
Intensität [a.u.]
Zeitliche Abfolge der Messungen
26
27
28
29
30
2 Θ (λ = 0,1147 nm)



Y-Films

Collaborators:

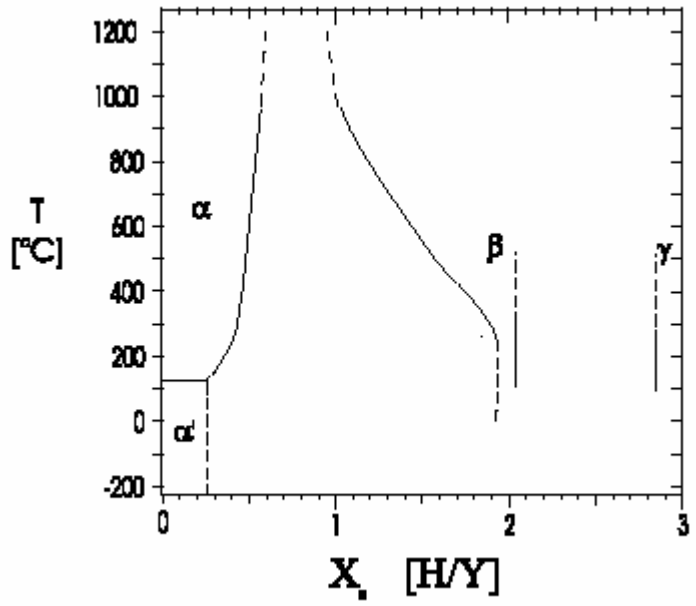
M. Dornheim

S. Kooij

B. Ocko

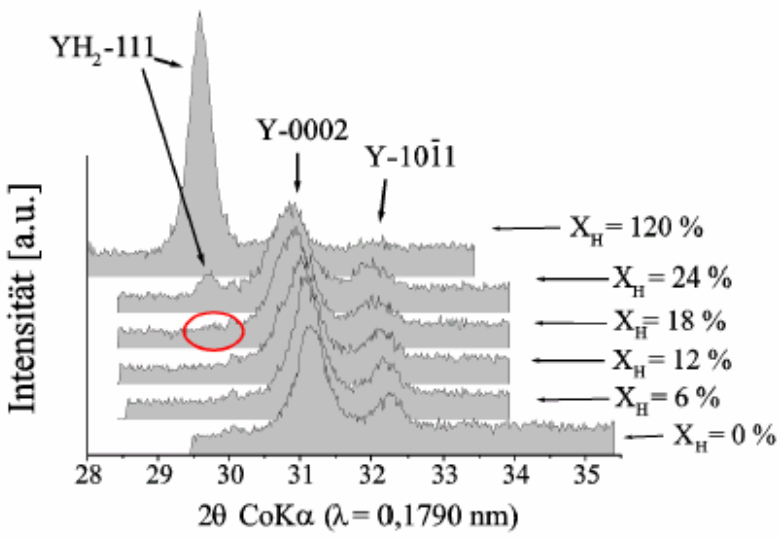
M. Strongin

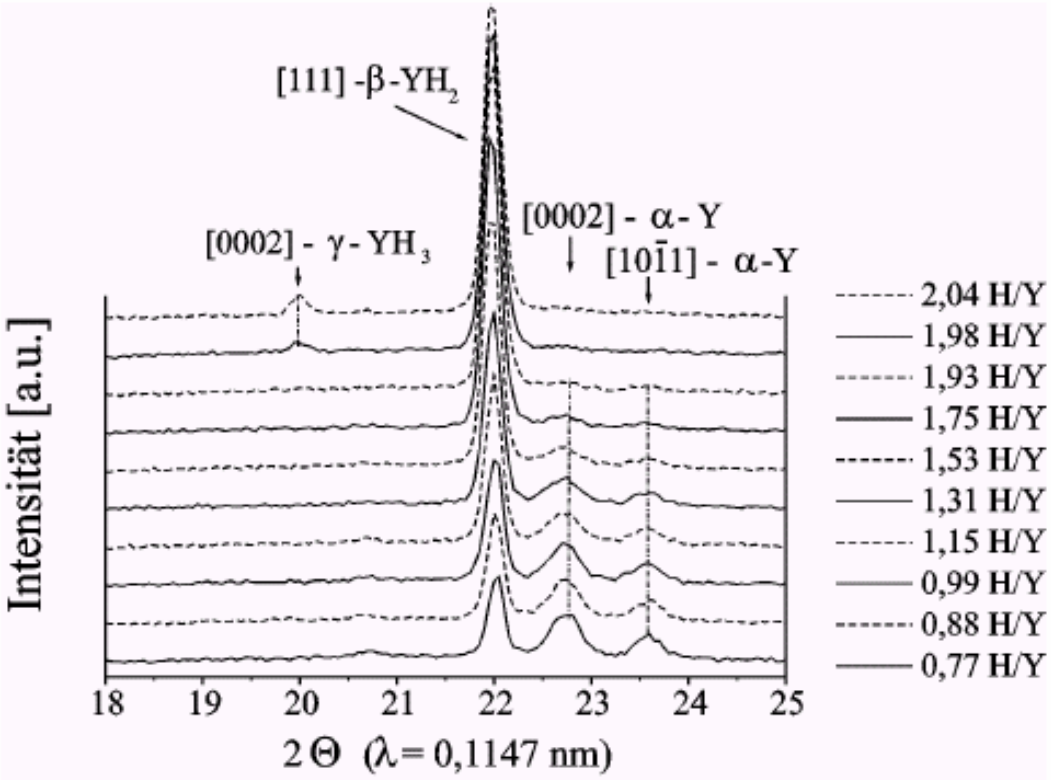
Y-H Phases

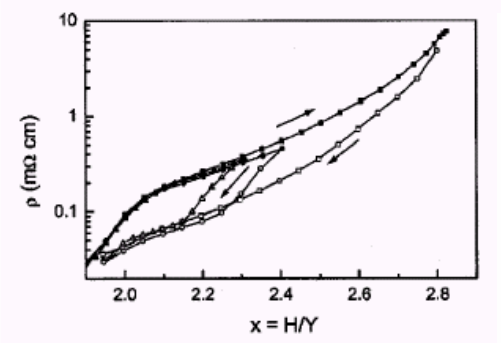


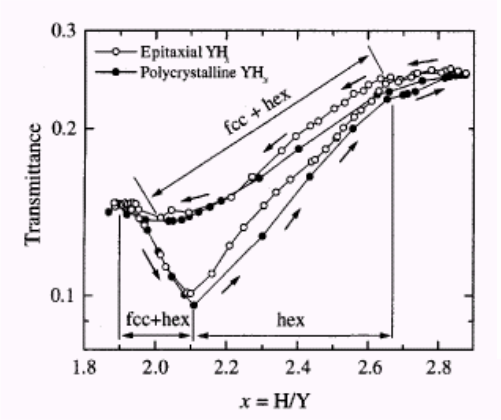
H-Y phase diagram

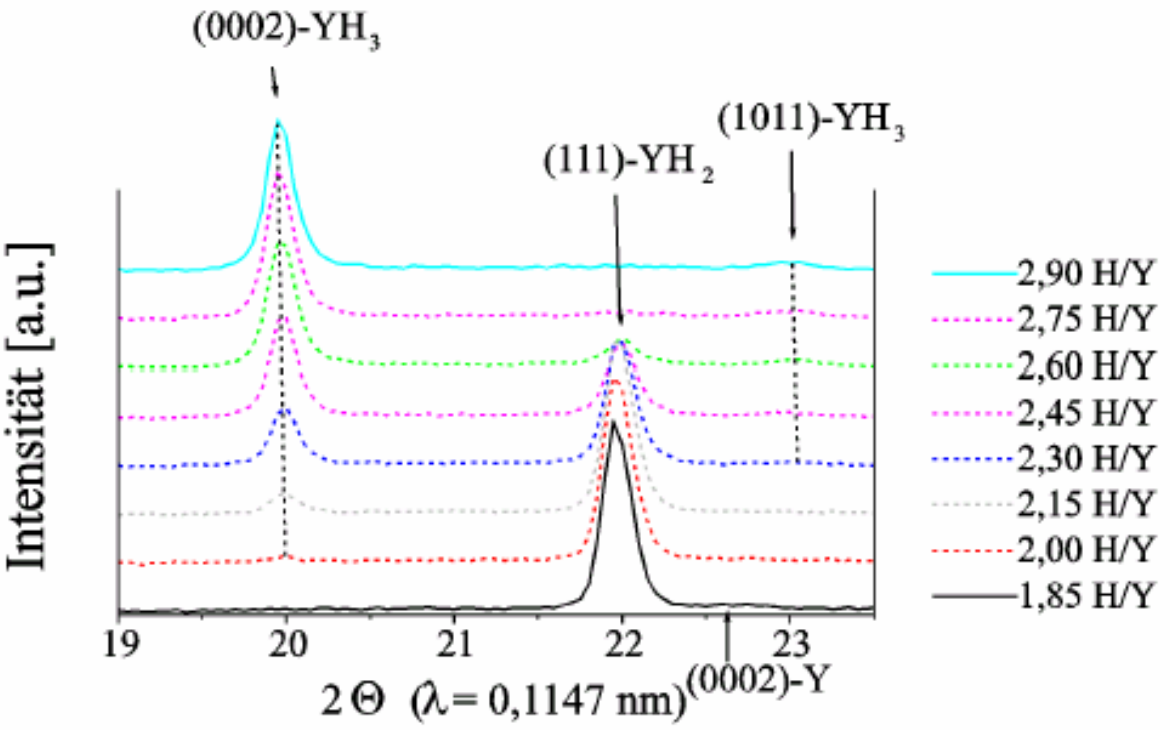
Measurement X'pert machine: 6 h /scan

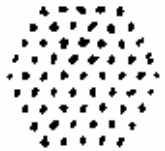



[111] -β-YH2
[0002] - γ - YH3
[0002] - α - Y
[10$\bar{1}$1] - α-Y
Intensität [a.u.]
18
19
20
21
22
23
24
25
2Θ (λ= 0,1147 nm)
2,04 H/Y
1,98 H/Y
1,93 H/Y
1,75 H/Y
1,53 H/Y
1,31 H/Y
1,15 H/Y
0,99 H/Y
0,88 H/Y
0,77 H/Y

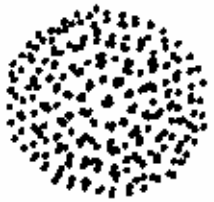

10
1
0.1
ρ (mΩ cm)
2.0
2.2
2.4
2.6
2.8
x = H/Y


0.3
0.2
0.1
Transmittance
Epitaxial YH
Polycrystalline YH
fcc + hex
fcc+hex
hex
1.8
2.0
2.2
2.4
2.6
2.8
x = H/Y


Intensität [a.u.]
(0002)-YH3
(111)-YH2
(1011)-YH3
(0002)-Y
19
20
21
22
23
2Θ (λ= 0,1147 nm)
2,90 H/Y
2,75 H/Y
2,60 H/Y
2,45 H/Y
2,30 H/Y
2,15 H/Y
2,00 H/Y
1,85 H/Y



CLUSTERS

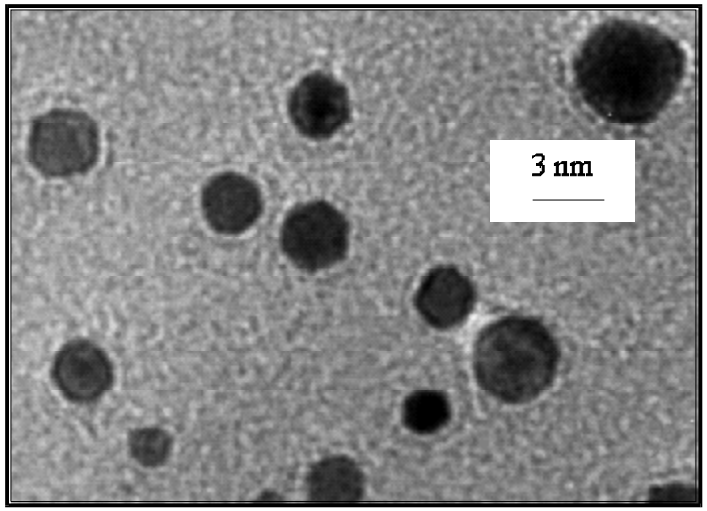


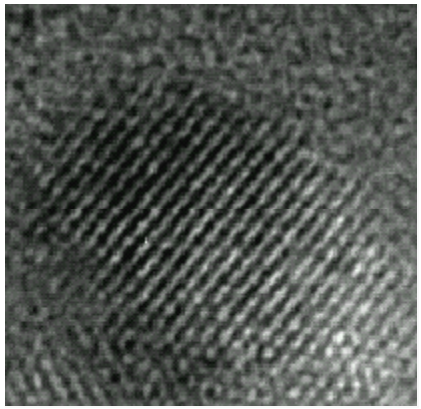
Collaborators:

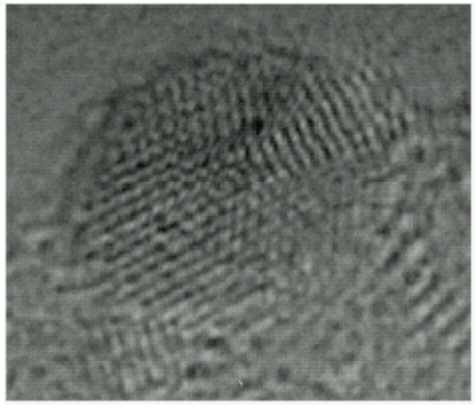
M. Suleiman, A. Pundt, R. Kirchheim, H. Teichler

S. AbdulHadi and I. Ladadwa

TEM





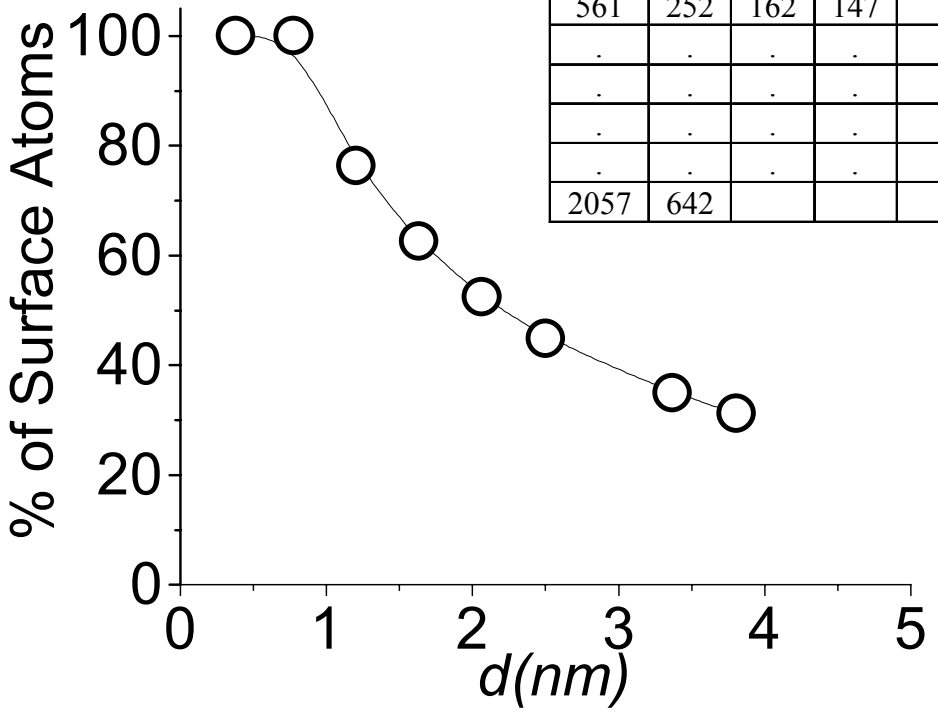


Low resolution: Faceting

High Resolution: Crystal Symmetery

Magic Numbers

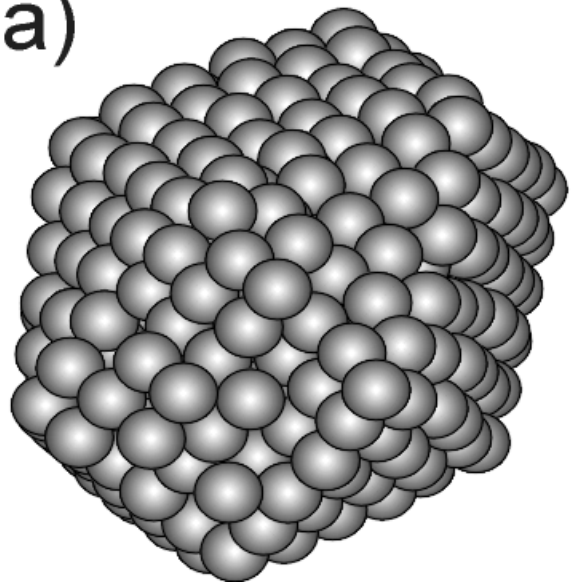
Number of shells	Number of atoms	Cluster Diameter (nm)
2	13	0.70
3	55	1.13
4	147	1.56
5	309	2.00
6	561	2.44
7	923	2.88
8	1415	3.33
9	2057	3.77
10	2869	4.21
11	3871	4.65
12	5083	5.09
13	6525	5.53
14	8217	5.98
15	10179	6.42
16	12431	6.86
17	14993	7.30
18	17885	7.75
19	21127	8.19
20	24739	8.63



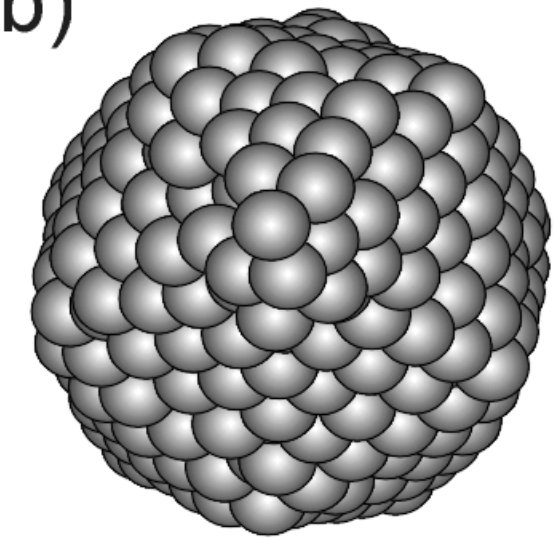
N	N_S	N_{SS}	N_B	D_N(nm)
55	42	12	1	1.2
147	92	42	13	.
309	162	92	55	.
561	252	162	147	2.5
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.
2057	642			3.5

Cuboctahedral vs Icosahedral

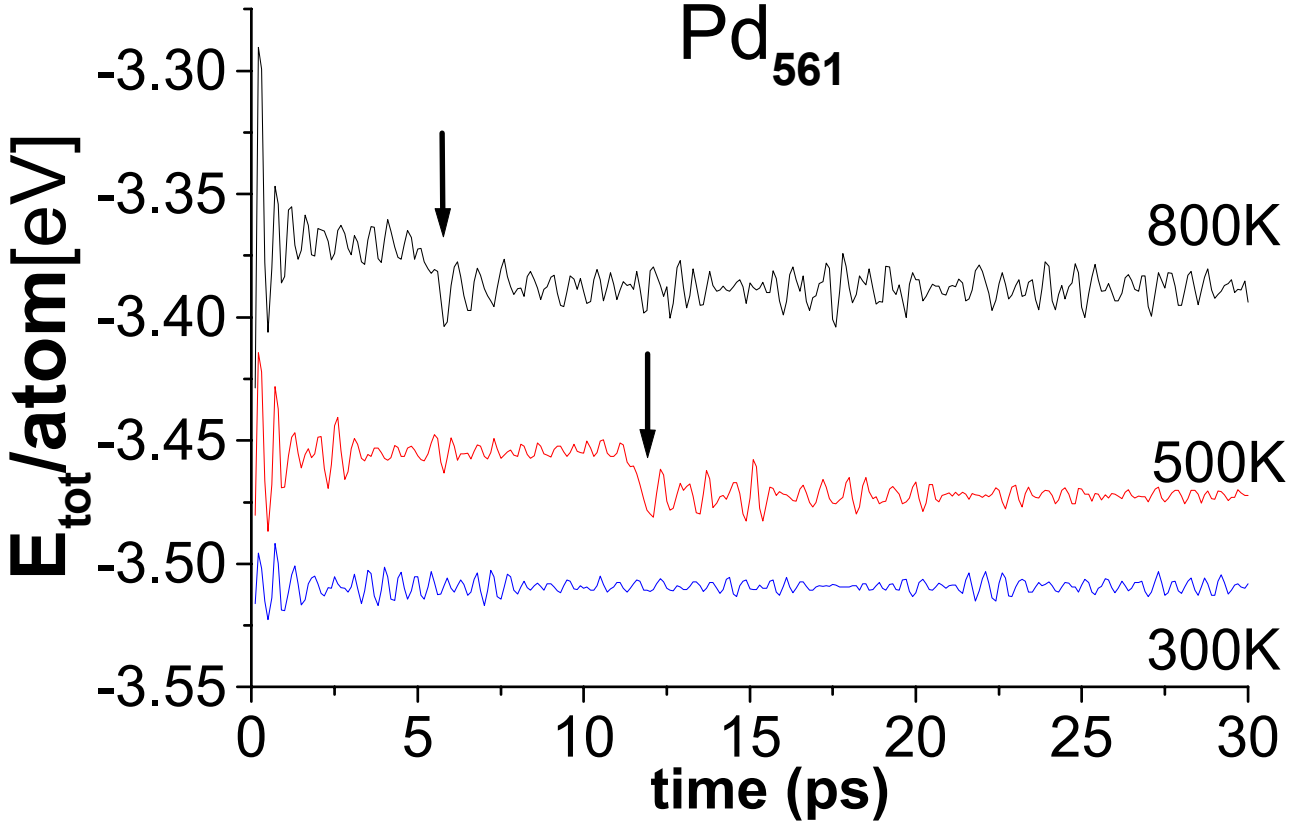
a)

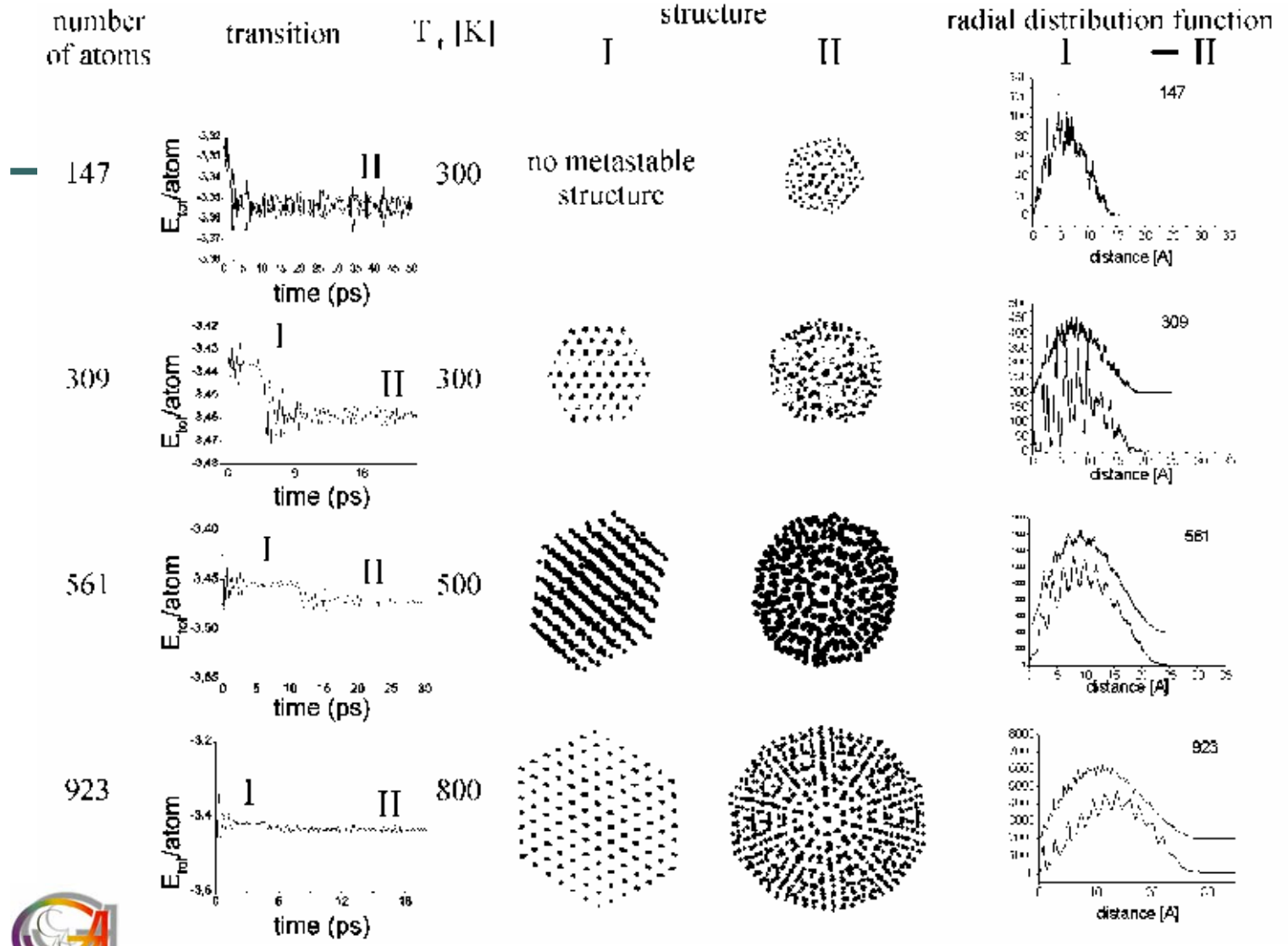


b)

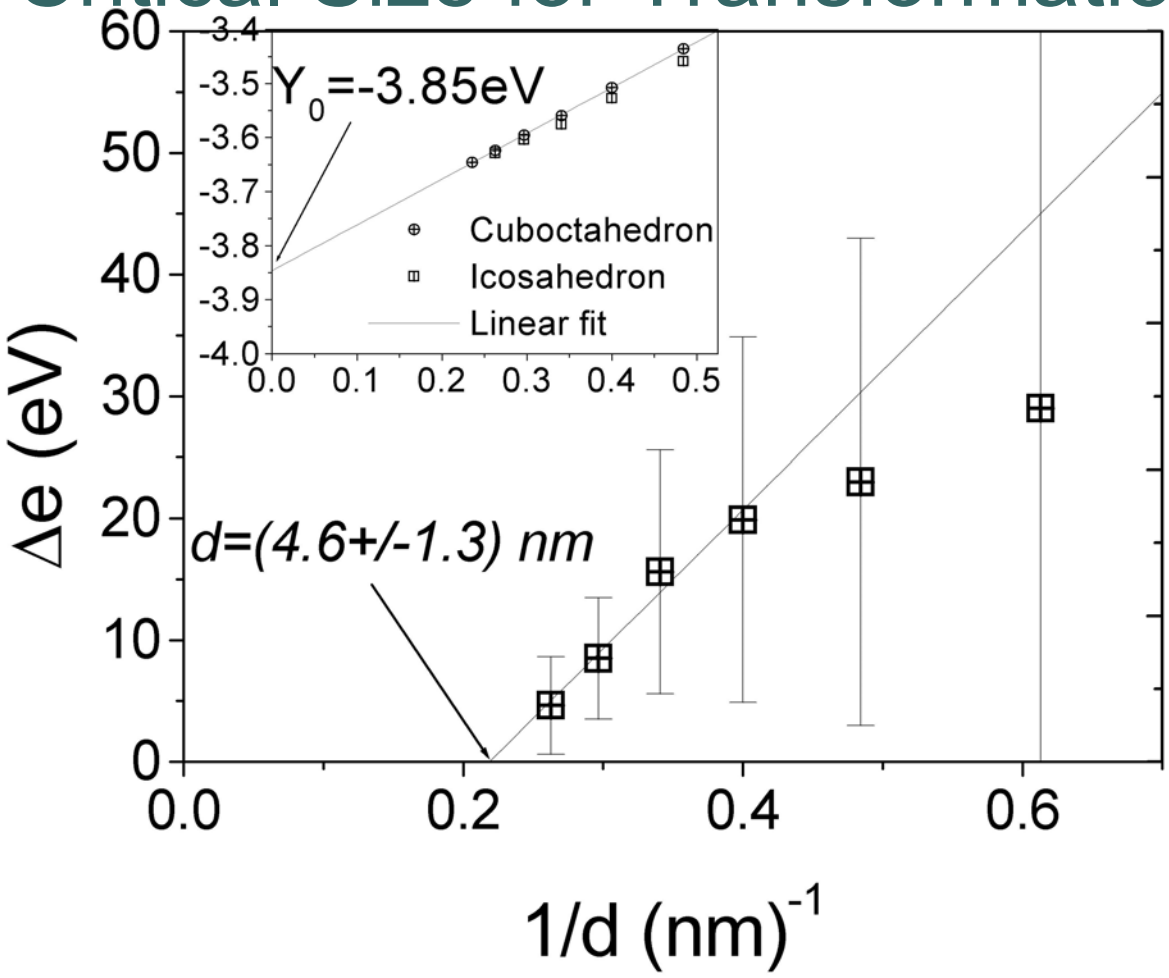


Cuboctahedral to Icosahedral Transition

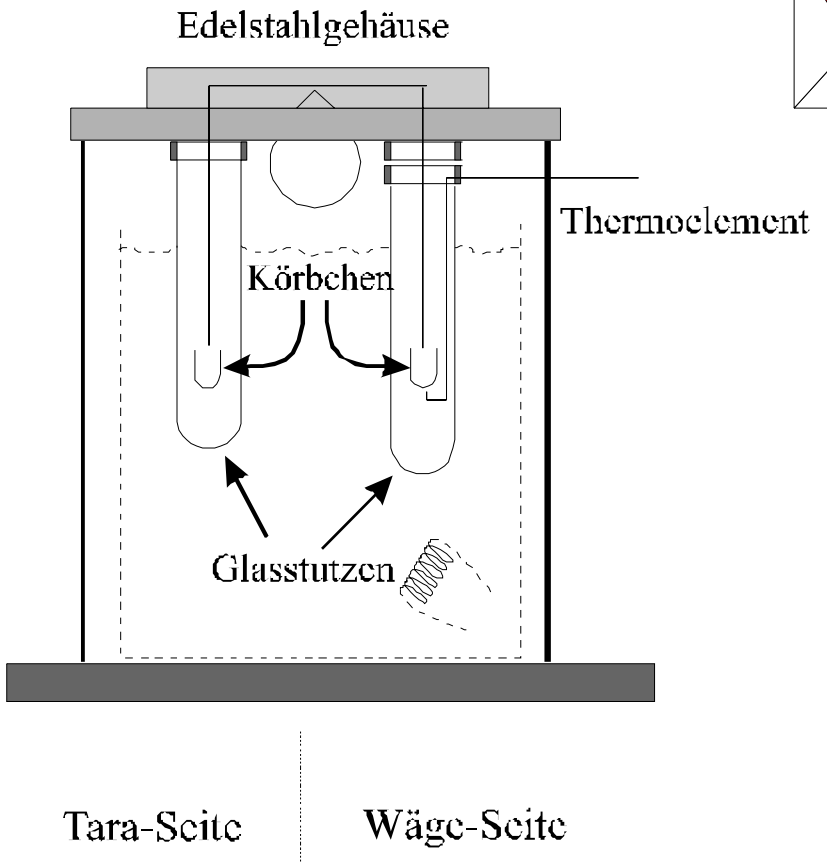



number of atoms
transition
T_t [K]
structure
I
II
radial distribution function
I — II
147
300
no metastable structure
309
300
561
500
923
800
E_tot/atom
time (ps)
distance [A]

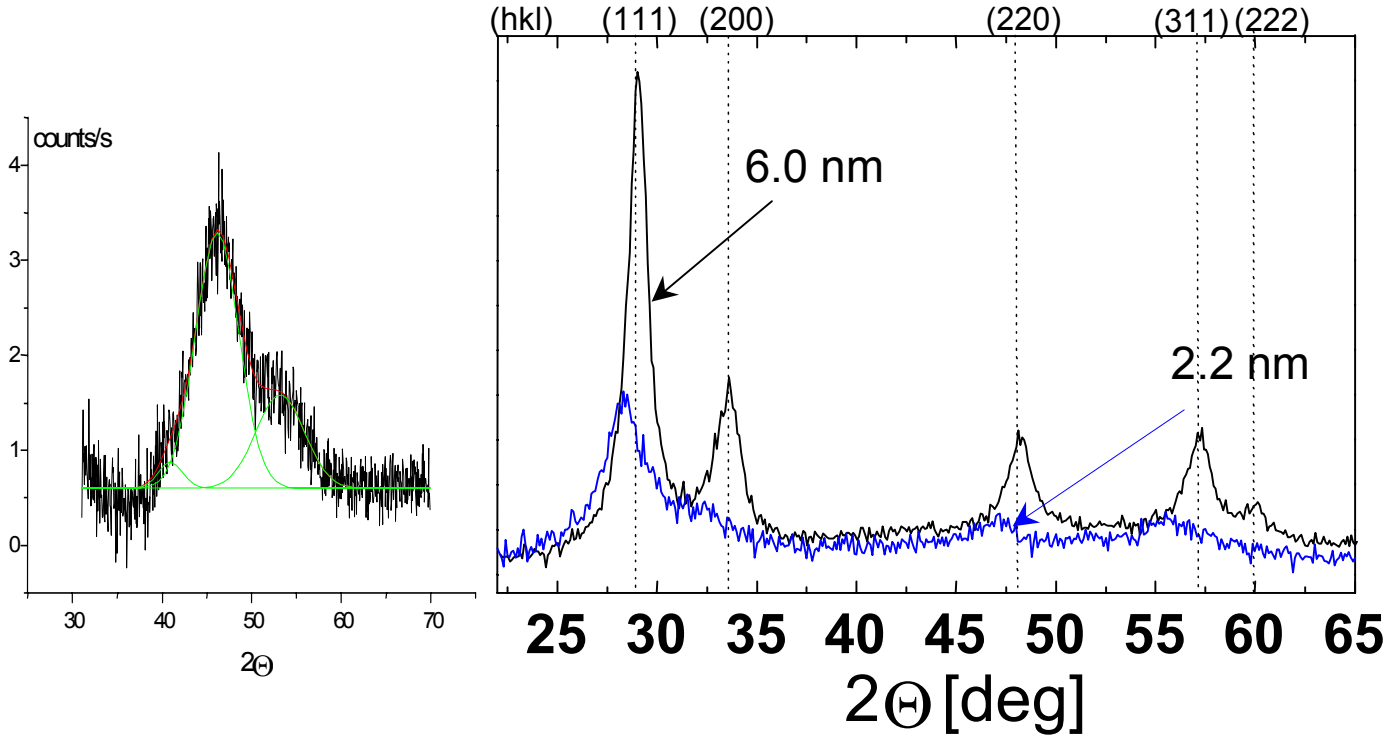
Critical Size for Transformation



Hydrogen Gravimetry

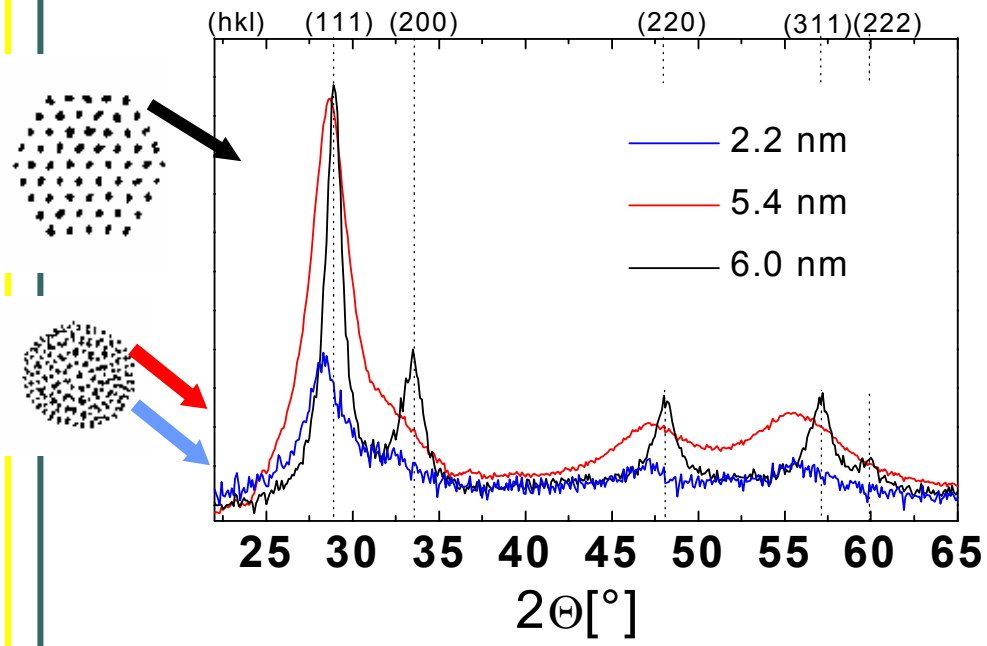


Synchrotron X-rays

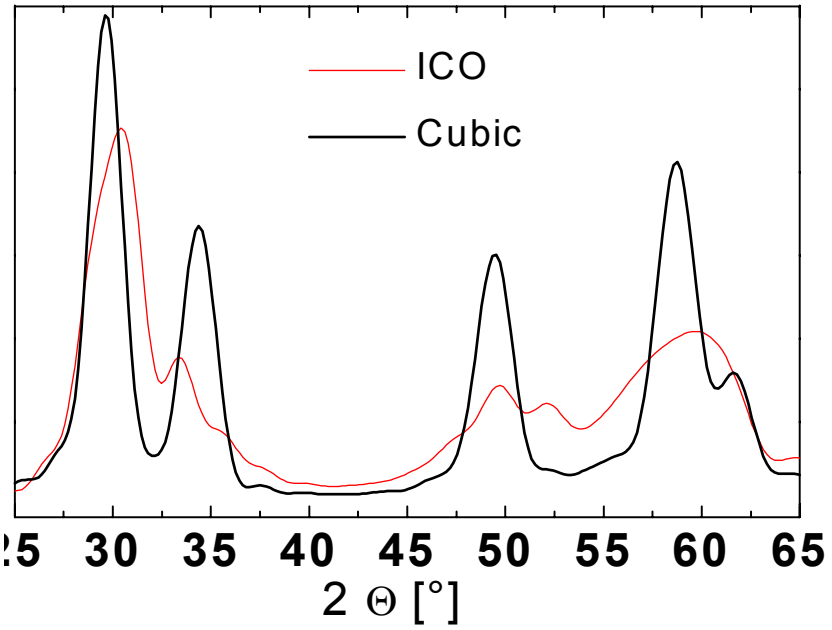


XRD: Structure of as-prepared clusters

Experiment: As-prepared samples



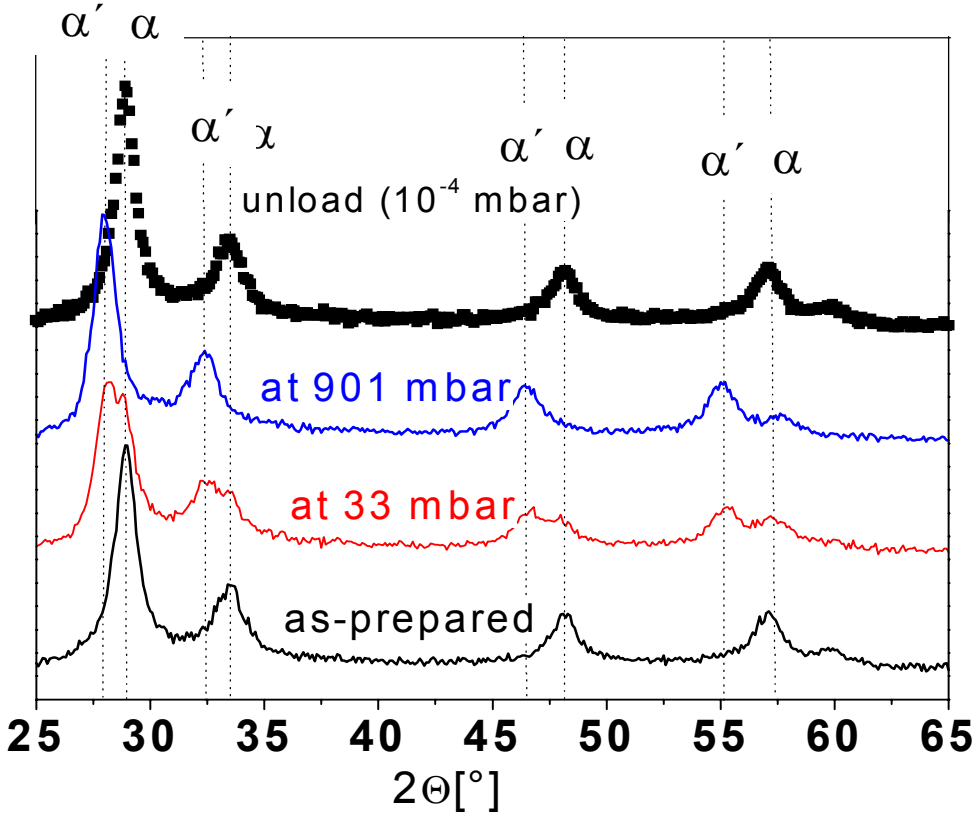
Theory: MD- Simulation



small clusters have icosahedral structure.The number of nearest neighbours is large & the surface energy is low.

large cluster has (ca. 6 nm) cubic structure. Interatomic spacing in not uniform in an ico. ➡ mechanical stresses.

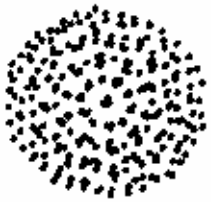
In-situ XRD HASYLAB: ∅ 6 nm Cluster "cubic"

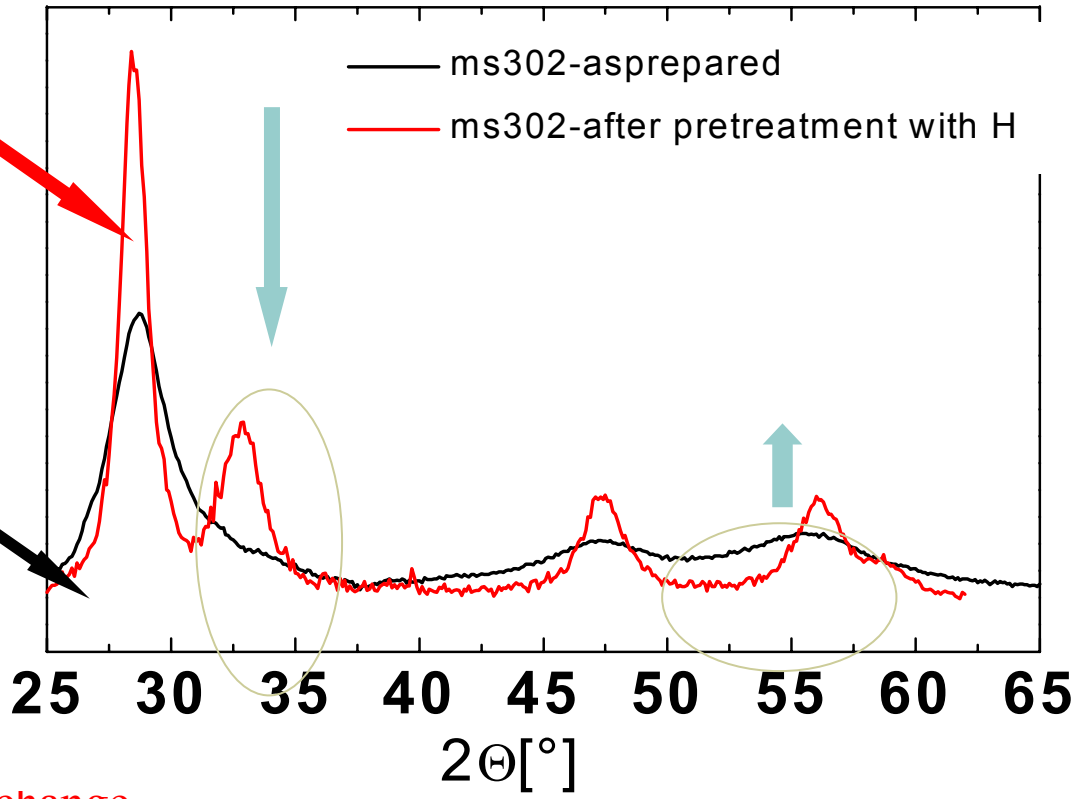


- as-prepared cubic structure
- lattice expansion
- phase transition (α- α´) (26 - 36 mbar)
- reversible

✓

In-situ XRD HASYLAB : ∅ 5.4 nm Cluster in H-Atmosphere

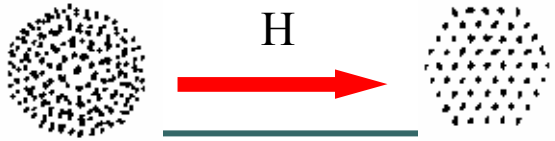




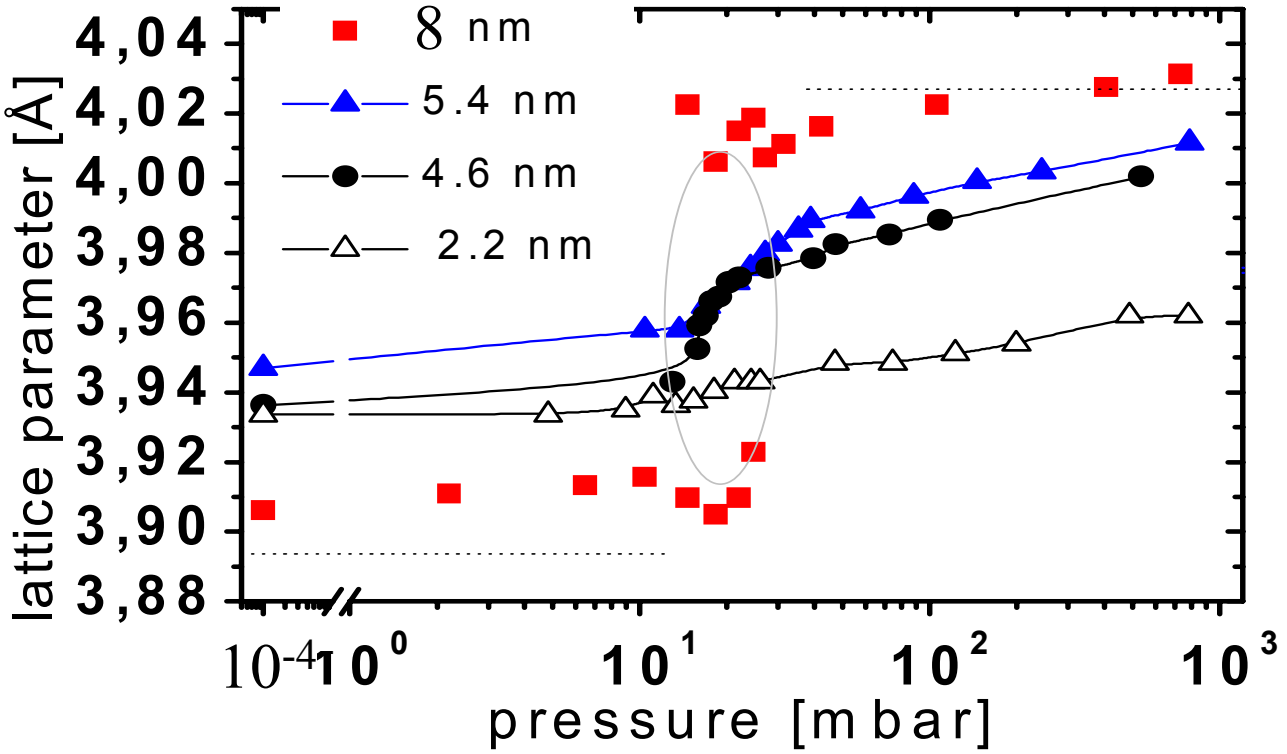
* Intensity change

•Change in the diffractogramm

• Structural change

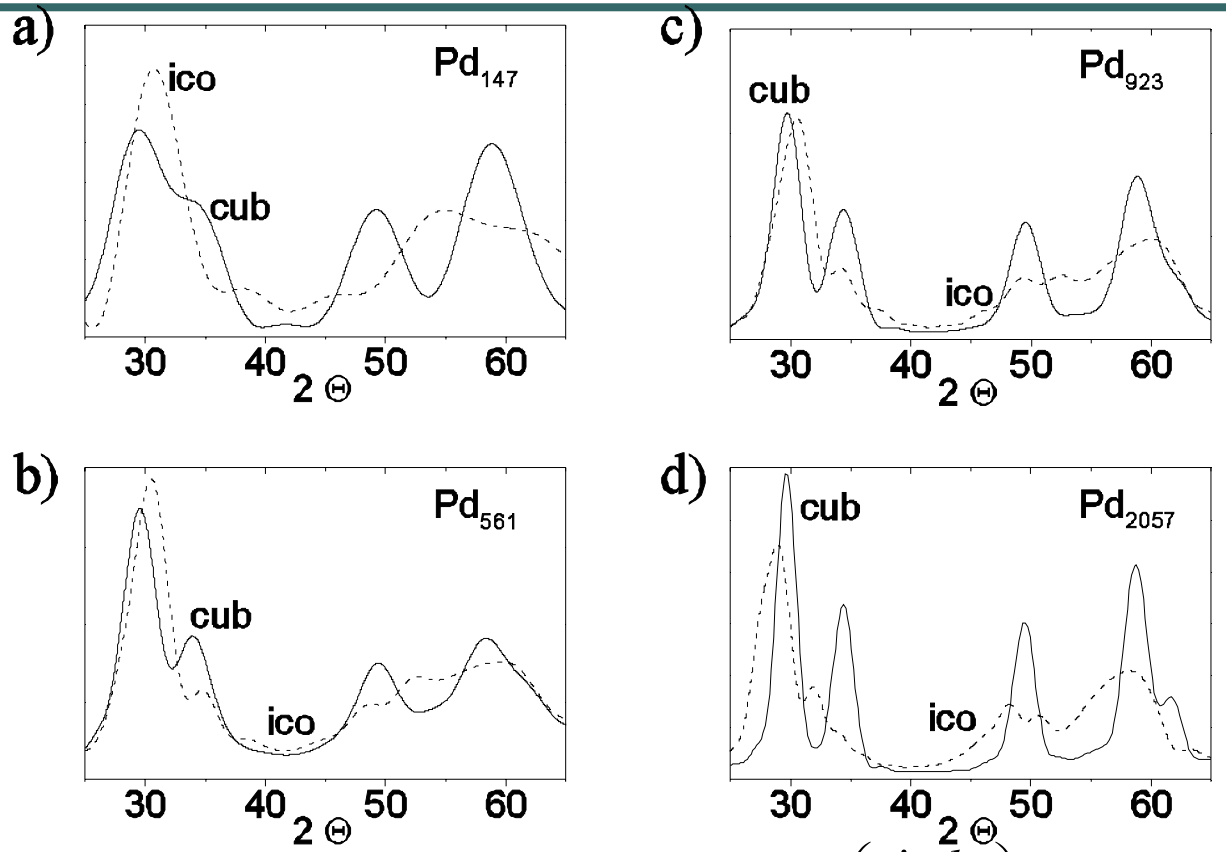


In-situ XRD HAYSLAB: lattice parameter change for different cluster sizes



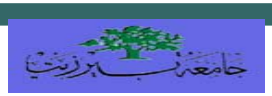
• the lattice parameter change is less than that in the bulk Pd- H system

Computed Patterns



$$S(k) = 1 + \int 4\pi r^2 [\rho(r) - \rho_0] \left(\frac{\sin kr}{kr} \right) .dr$$

$$S(k) = \left[I^{coh}(k) / N - f^2 \right] / f^2$$



Clusters Simulation

Collaborators:

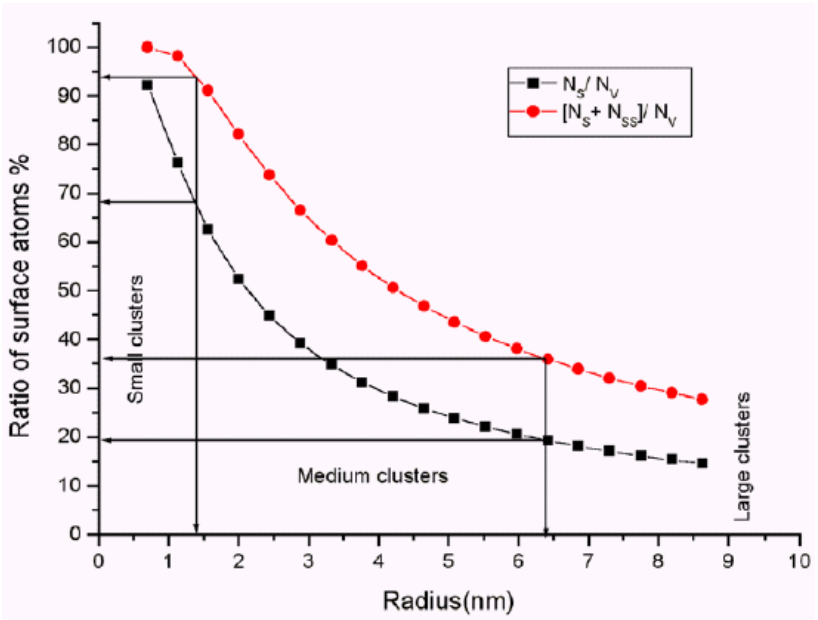
Saja Abdul Hadi

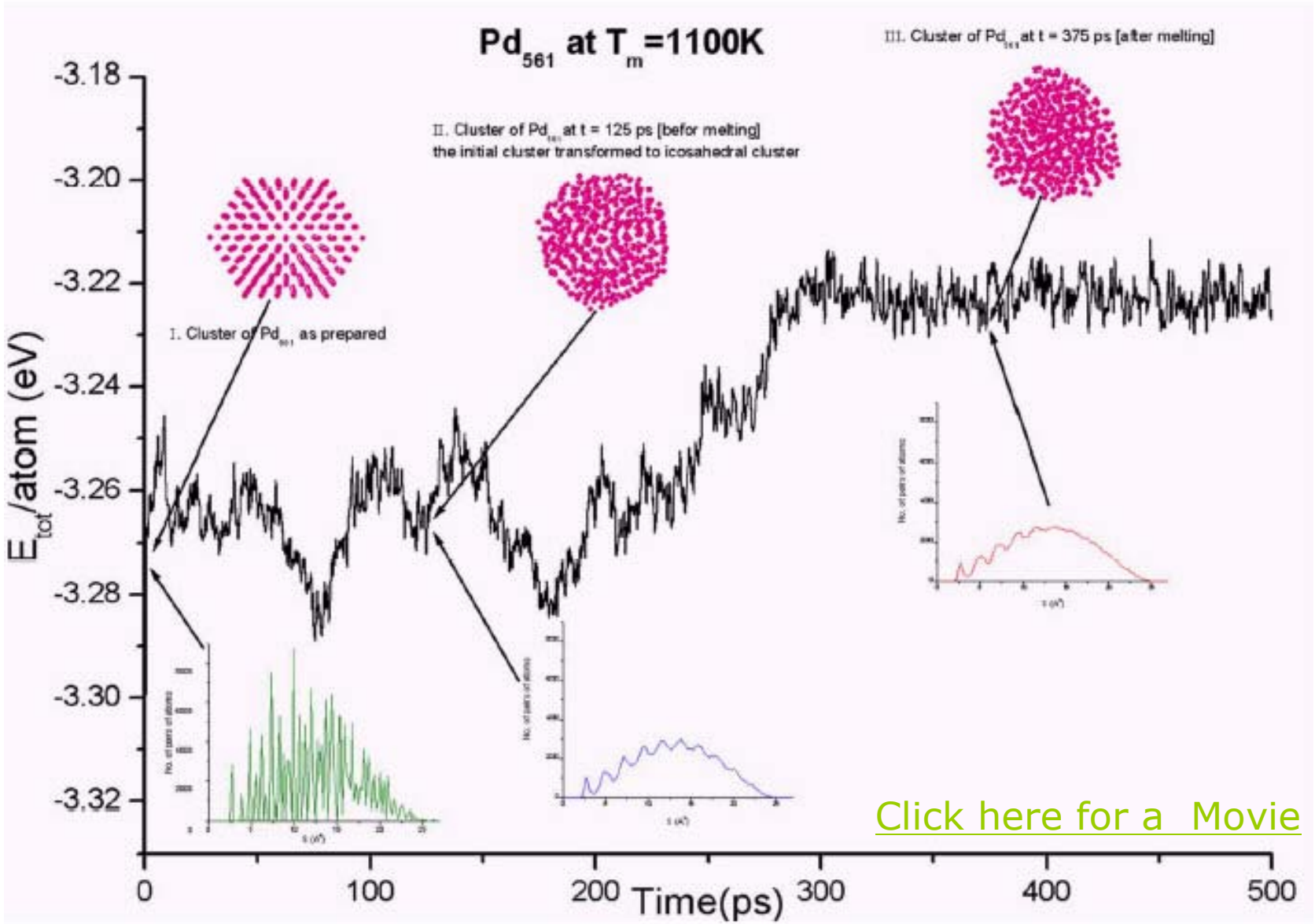
Surface and Subsurface!

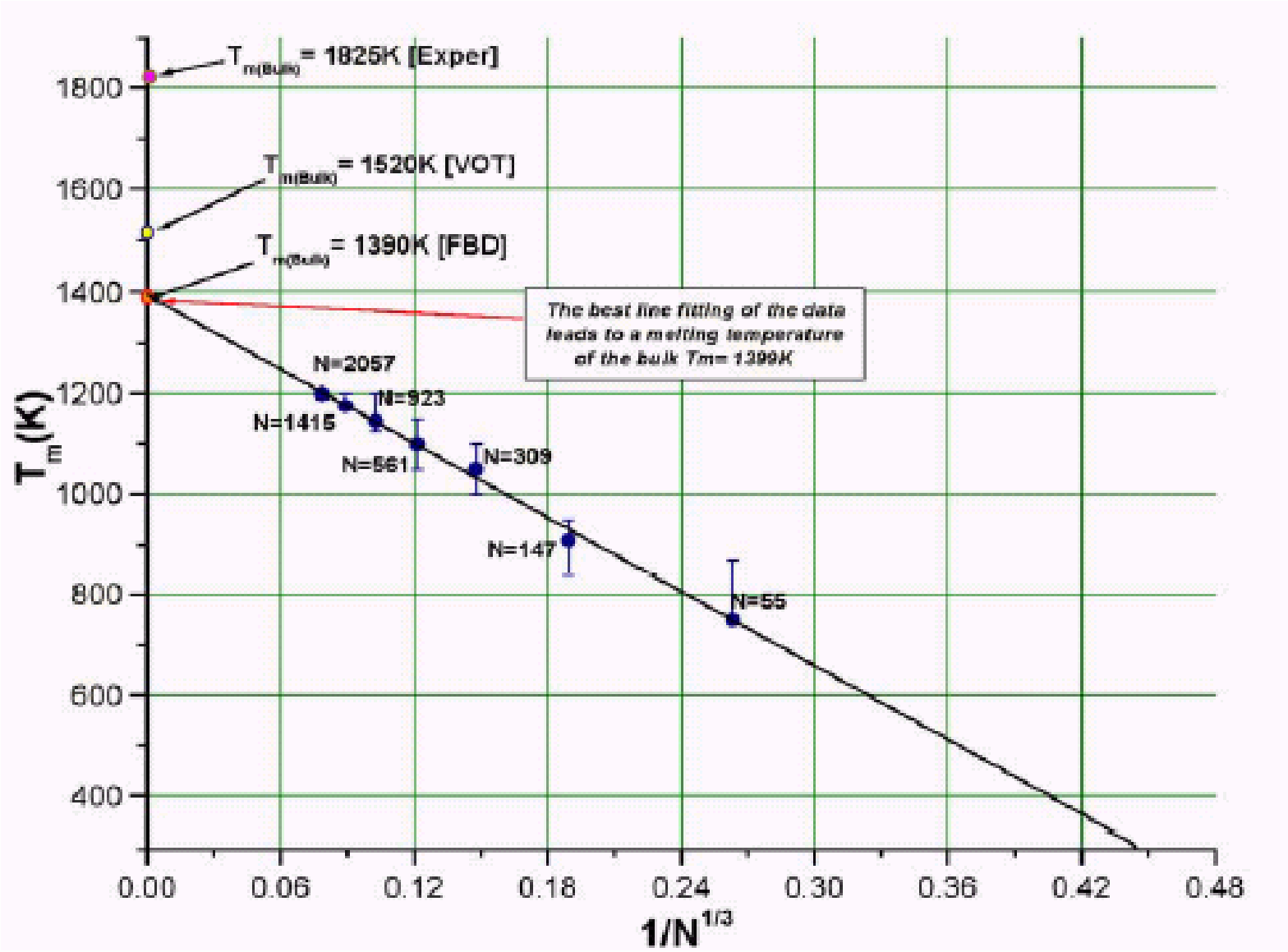
Table 1 The total number of atoms contained in *k* closed shells, with the added atoms according to the increase of *k*, and the ratio of the number of surface to volume atoms .

Shell Index *k*	1	2	3	4	5	6	7	8	9	10	11	12
New added atoms N_S^*	1	12	42	92	162	252	362	492	642	812	1002	1212
N_{SS}^*		1	12	42	92	162	252	362	492	642	812	1002
N_C^*			1	13	55	147	309	561	923	1415	2057	2869
Total No. of atoms N_v	1	13	55	147	309	561	923	1415	2057	2869	3871	5083
Ratio $\frac{N_S}{N_V}$ %	100	92.3	76.4	62.6	52.4	44.9	39.2	34.8	31.2	28.3	25.9	23.8
Ratio $\frac{N_S + N_{SS}}{N_V}$ %	100	100	98.2	91.2	82.2	73.8	66.5	60.3	55.1	50.7	46.9	43.6

**Ns* :number of surface atoms, *Nss* : number of subsurface atoms, *Nc* : number of "core" atoms and *Nv* :total number of atoms in the cluster.




Pd561 at Tm=1100K
III. Cluster of Pd561 at t = 375 ps [after melting]
II. Cluster of Pd561 at t = 125 ps [befor melting]
the initial cluster transformed to icosahedral cluster
I. Cluster of Pd561 as prepared
Etot/atom (eV)
-3.18
-3.20
-3.22
-3.24
-3.26
-3.28
-3.30
-3.32
0
100
200
300
400
500
Time(ps)
Click here for a Movie


$T_{m(Bulk)}$ = 1825K [Exper]
$T_{m(Bulk)}$ = 1520K [VOT]
$T_{m(Bulk)}$ = 1390K [FBD]
The best line fitting of the data leads to a melting temperature of the bulk Tm= 1399K
N=2057
N=1415
N=923
N=561
N=309
N=147
N=55
T_m (K)
1800
1600
1400
1200
1000
800
600
400
0.00
0.06
0.12
0.18
0.24
0.30
0.36
0.42
0.48
$1/N^{1/3}$

Melting Properties

Table 4 The melting temperature of the bulk for palladium using different types of EAM potentials, the first column is of this work, the other three are of previous work. The experimental value of the melting of palladium is 1825K.

Potential	Melting temperature of the bulk [38](K)[a]	Latent heat (KJ/mol)	Latent heat (mev/atom)
EAM (Foils, Daw and Baskes)	1480[a] 1390[b]	7.79[a]	80.7
EAM (Voter)	1588[a] 1520±150[c]	9.96[a]	103.2
EAM (PDW3)[a]	1728[a]	10.2[a]	105.7
EAM (PDW5)[a]	1828[a]	9.84[a]	102.0
Results of this work [figures (3.2-4) and (3.2-7)]	1399	~7.12 8.99	~74 93.2
Experimental	1825	16.7[d]	173.1

a Wolf, Mansour, Lee, and Ray work using many types of embedded atom potentials (PDW3), (PDW5) are two methods developed by this group.
b Foiles and Adams, from the pervious reference.
c Ercolessi and Voter, from the pervious reference.
d Iida and Guthrie, from the previous reference.

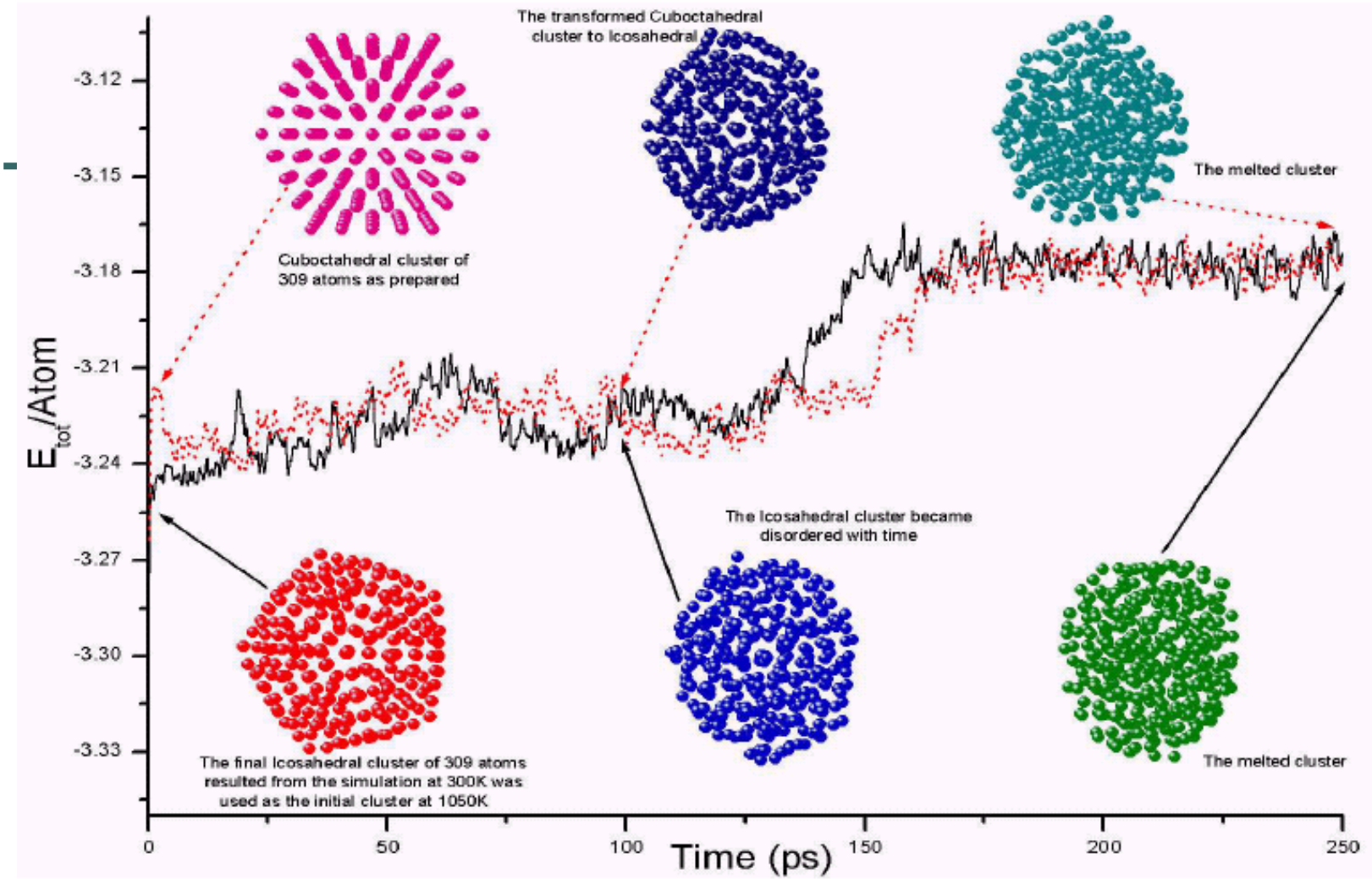


Figure 3.2-14 Total energy per atom as a function of time for two palladium clusters of 309 atoms at T_m($icosPd_{309}$)= 1050K. The initial structures are Cuboctahedral for the first (dotted line), and Icosahedral for the second (solid line) with the shapes of the clusters plotted with time.

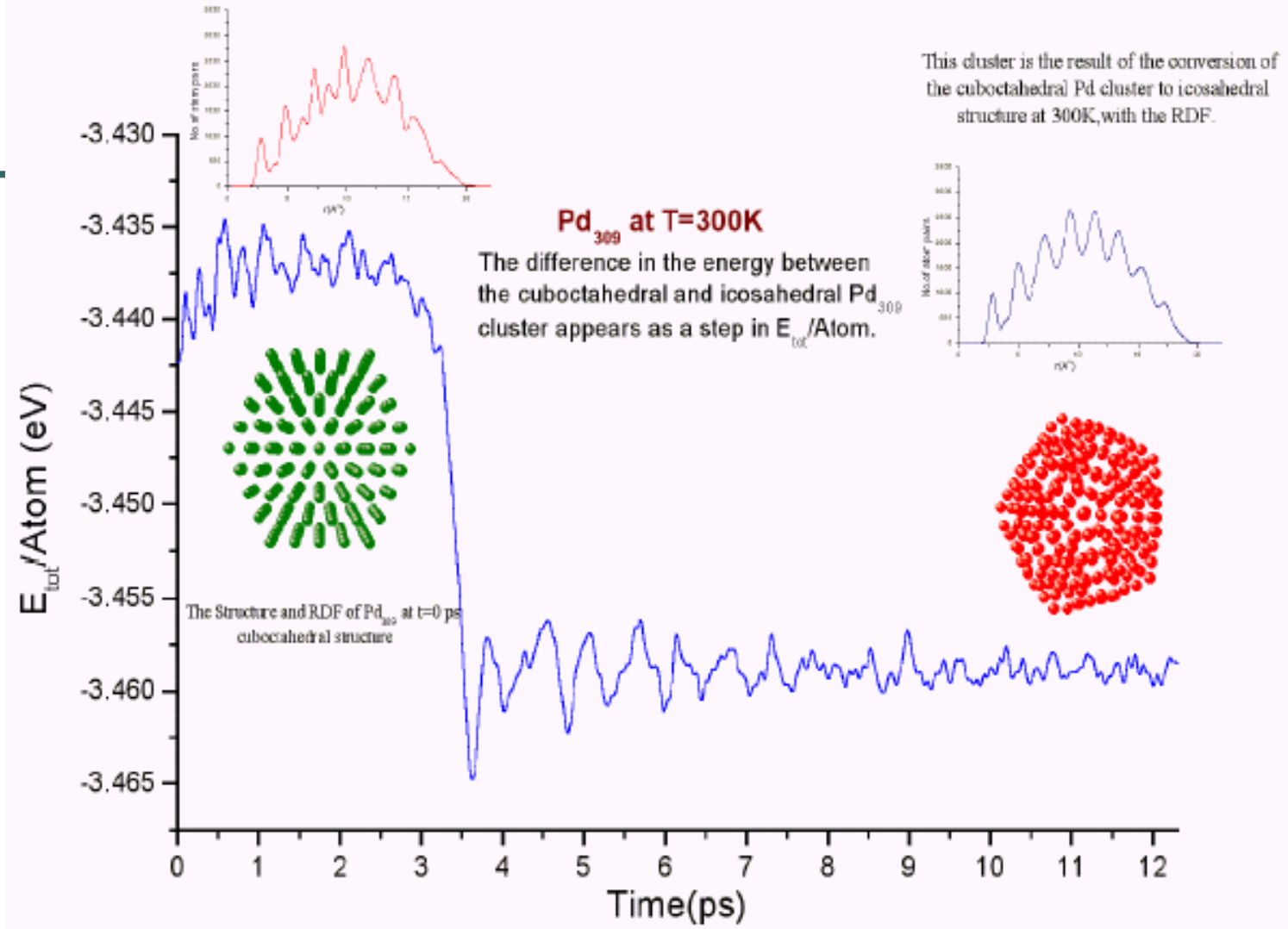


Figure 3.3-1 Etot/atom with time shows the change in the energy caused by the transformation of the Cuboctahedral cluster to icosahedral cluster

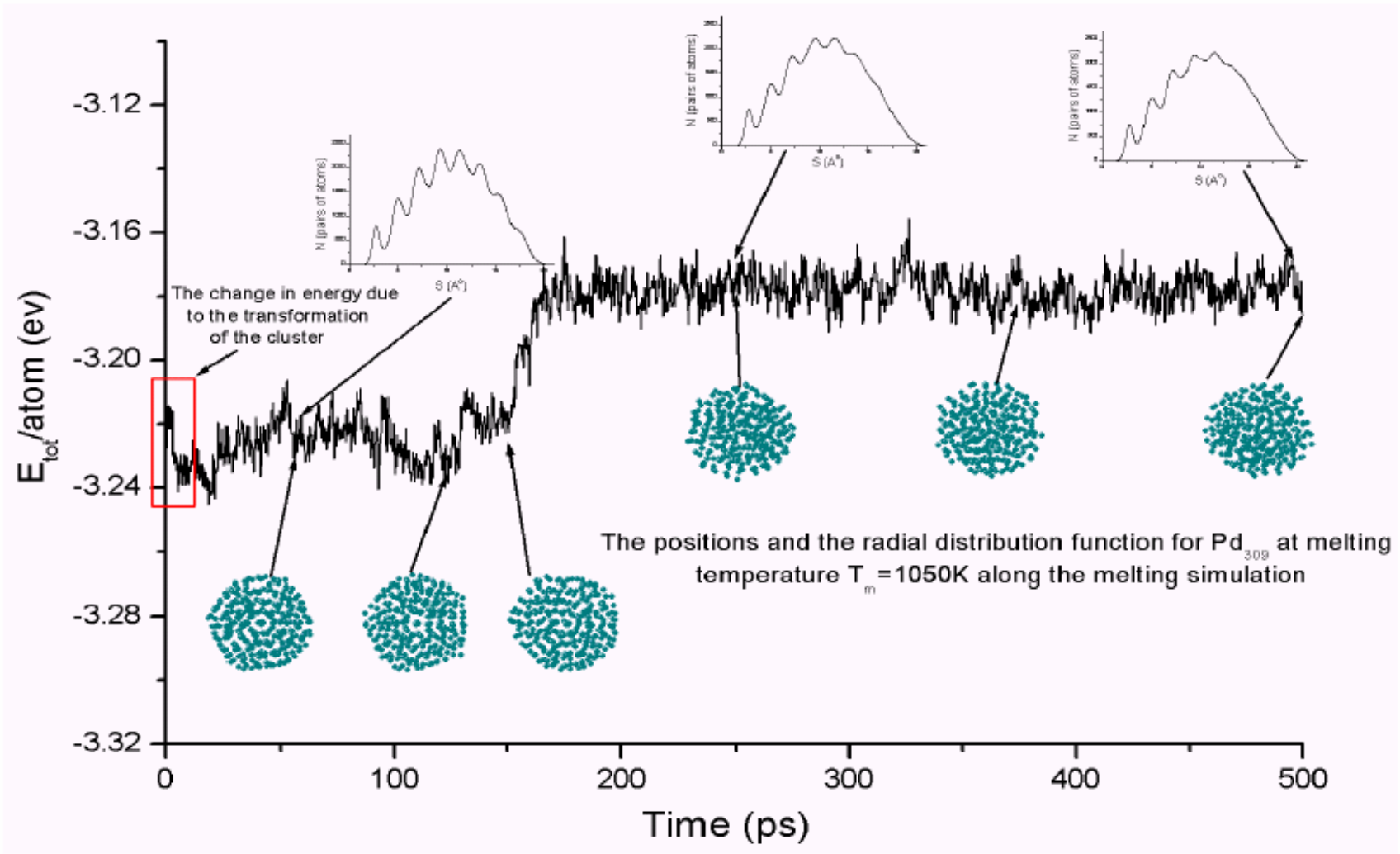


Figure 3.3-5 A detailed figure of Pd_{309} at melting temperature shows clearly the transformation of the Cuboctahedral cluster to icosahedral cluster in about 6 ps then the melting process starts after about 150ps, with the shape and the RDF of the clusters.

Melting Movie

46 106.40

Pd

Palladium

Electron Binding Energies in electron volts

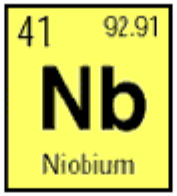
$K\ 1s$	$L_1 2s$	$L_2 2p_{1/2}$	$L_3 2p_{3/2}$	$M_1 3s$	$M_2 3p_{1/2}$	$M_3 3p_{3/2}$	$M_4 3d_{3/2}$	$M_5 3d_{5/2}$
24,350.	3,604.	3,330.	3,173.	671.6	559.9	532.3	340.5	335.2

$N_1 4s$	$N_2 4p_{1/2}$	$N_3 4p_{3/2}$
87.1	55.7	50.9

K and L shell emission lines in electron volts

$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\gamma_1$
21,177.1	21,020.1	23,818.7	2,838.61	2,833.29	2,990.22	3,171.79	3,328.7

Source: X-ray data booklet:
http://xdb.lbl.gov/Section1/Periodic_Table/Pd_Web_data.htm



Electron Binding Energies in electron volts

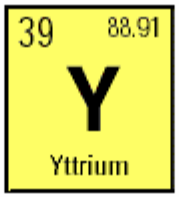
K 1s	$L_1$2s	$L_2$2$p_{1/2}$	$L_3$2$p_{3/2}$	$M_1$3s	$M_2$3$p_{1/2}$	$M_3$3$p_{3/2}$	$M_4$3$d_{3/2}$	$M_5$3$d_{5/2}$
18,986.	2,698.	2,465.	2,371.	466.6	376.1	360.6	205.0	202.3

$N_1$4s	$N_2$4$p_{1/2}$	$N_3$4$p_{3/2}$
56.4	32.6	30.8

K and L shell emission lines in electron volts

$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\gamma_1$
16,615.1	16,521.0	18,622.5	2,165.89	2,163.0	2,257.4	2,367.0	2,461.8

http://xdb.lbl.gov/Section1/Periodic_Table/Nb_Web_data.htm



Electron Binding Energies in electron volts

K 1s	$L_1$2s	$L_2$2$p_{1/2}$	$L_3$2$p_{3/2}$	$M_1$3s	$M_2$3$p_{1/2}$	$M_3$3$p_{3/2}$	$M_4$3$d_{3/2}$	$M_5$3$d_{5/2}$
17,038.	2,373.	2,156.	2,080.	392.0	310.6	298.8	157.7	155.8

$N_1$4s	$N_2$4$p_{1/2}$	$N_3$4$p_{3/2}$
43.8	24.4	23.1

K and L shell emission lines in electron volts

$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$
14,958.4	14,882.9	16,737.8	1,922.56	1,920.47	1,995.84

http://xdb.lbl.gov/Section1/Periodic_Table/Y_Web_data.htm