Ultrasmall Angle X-ray Scattering (USAXS) and Wide-Angle X-ray Scattering (WAXS) Studies on the Complex Metal Hydride $NaAlH_4$:

New Possibilities for Understanding Complex Metal Hydrides via Synchrotron Studies

Tabbetha A. Dobbins[1] and Jan Ilavsky[2]

dobbins@rowan.edu

1. **Dept. of Physics & Astronomy, Rowan University, Glassboro, NJ**
2. **X-ray Operations Research, Advanced Photon Source, Argonne National Laboratory, Argonne, IL**

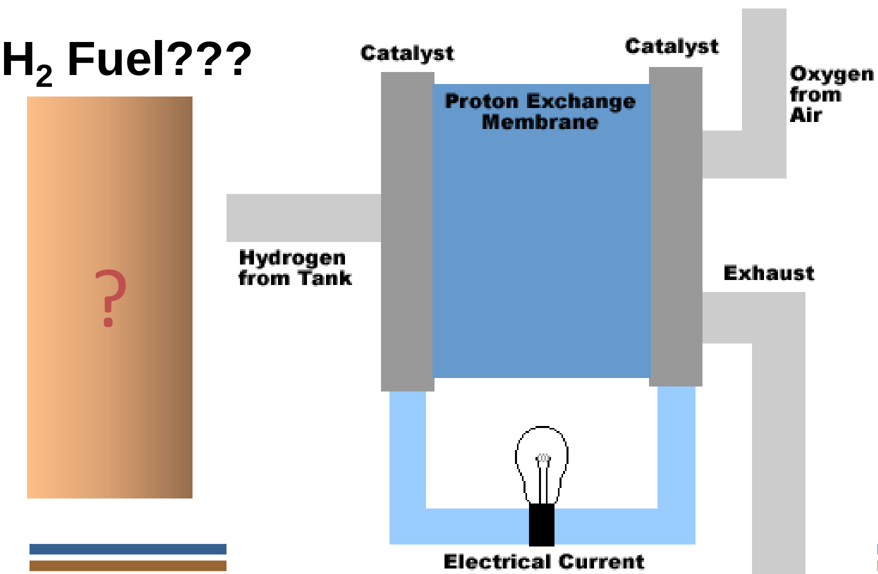
First Biennial African Conference on Fundamental Physics and Applications (ACP2018)
Material Physics Session
Chairs: Dr. Esmeralda Yitamben (ASP) and Dr. Dipti Ranjan Sahu (NUST)
June 28-July 4, 2018

“A (n) Inconvenient Truth”

(about Energy Production)

- The Fossil Fuel-based economy has limitations;
- An alternative fuel cell energy infrastructure (PEM Fuel Cells and Solid Oxide Fuel Cells) will penetrate energy markets;
- Technical challenges facing the fuel cell and the hydrogen economy are *nevertheless* substantial;
- Creative solutions are needed to tackle our societal need for *“cleaner and greener”* energy.

H_2 Fuel???



Animation courtesy of:
http://www.humboldt.edu

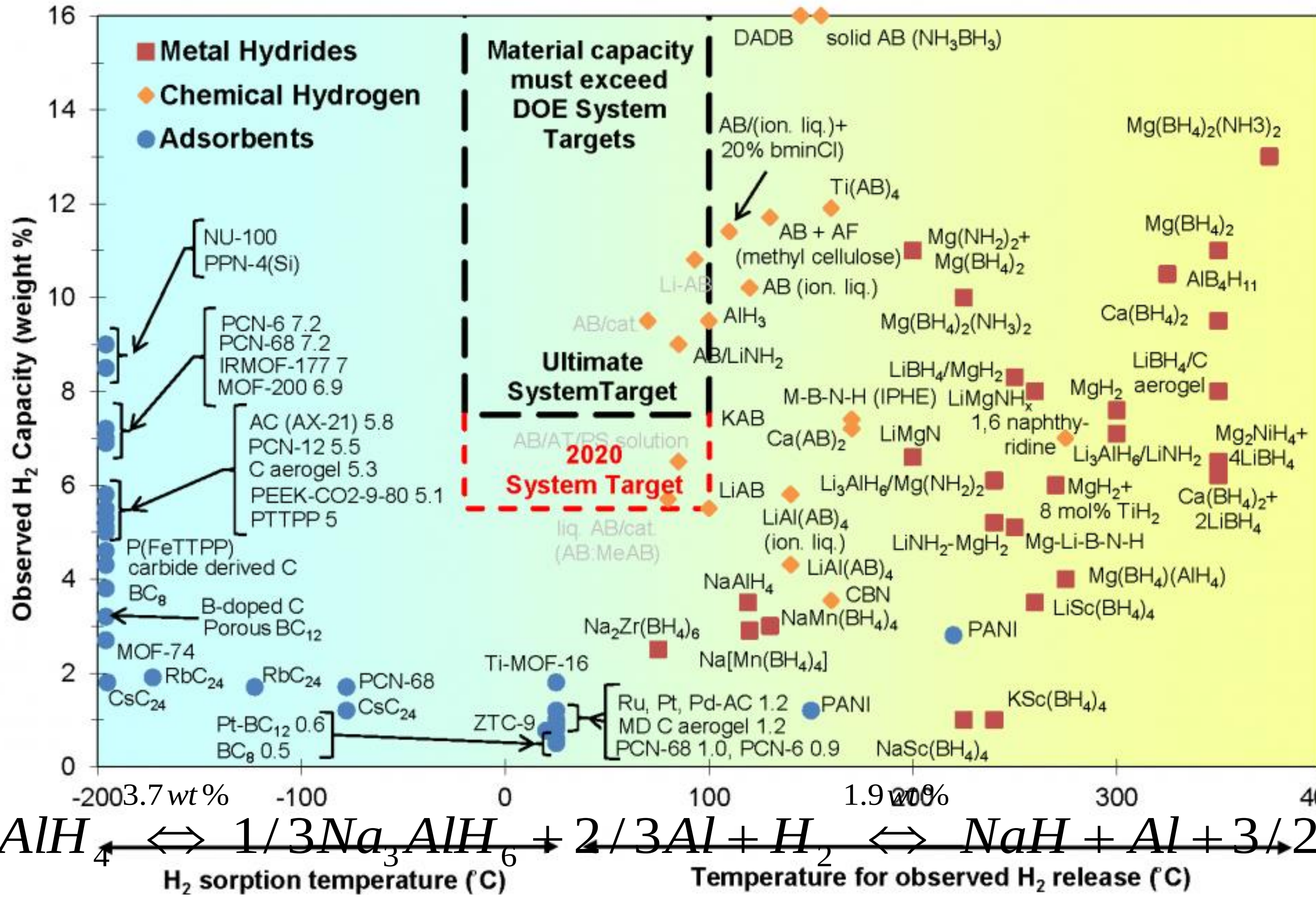
Hydrogen Storage

Image from Satyapal, Petrovic, Thomas (*Scientific American*, April 2007)

	Target	Chemi-
Storage Weight % (System)	6	3.4
Energy Efficiency %	97	88
Energy Density (W-h/L)	1100	1300
Specific Energy (W-h/kg)	2000	1080
Cost ($/Kw-h)	5	18
Operating Temperature (^{o}C)	Up to 50^{o}C	Up to 50^{o}C
Start-up Time (sec)	15	<15
Hydrogen Loss (scc/hr/L)	1.0	1.0
Cycle Life (#)	500	20-50
Refueling Time (min)	<5	undetermined
Recoverable Usable Amt	90%	>90%

Targets Table Reproduction from Millikan and Rossmeissl Aug. 14, 2002 Workshop

DoE EERE Targets for Hydrogen Storage Materials



$3.7\,wt\%$ $\qquad$ $1.9\,wt\%$

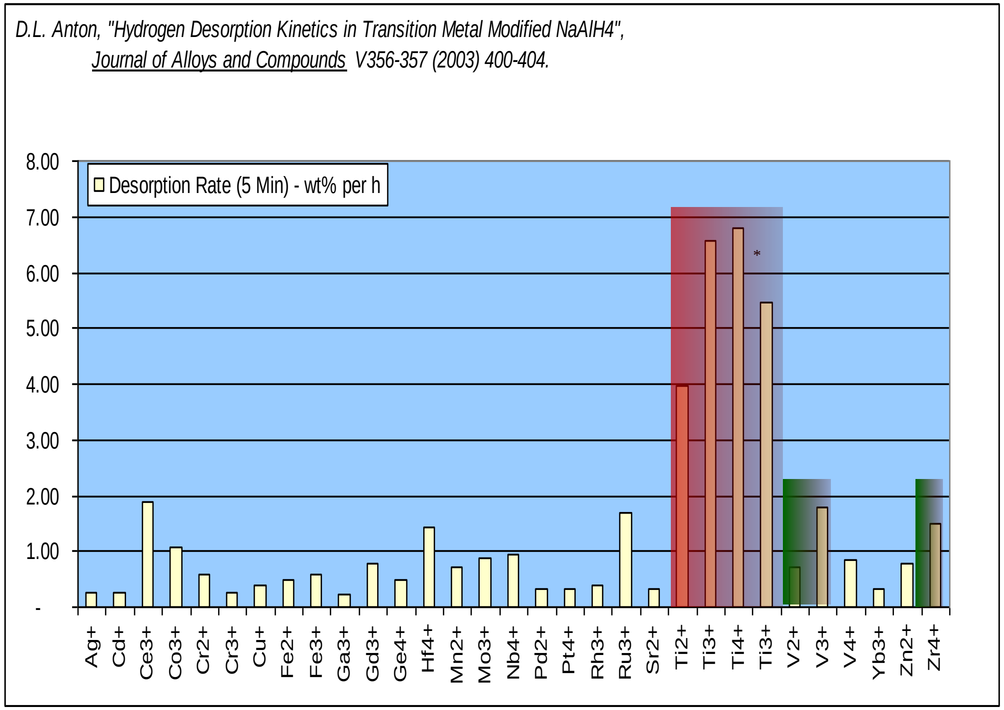
$$NaAlH_4 \Leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2 \Leftrightarrow NaH + Al + 3/2H_2$$

Image from: https://energy.gov/eere/fuelcells/materials-based-hydrogen-storage

Original Source: G. Thomas et al., Dept. of Energy (April 2007)

Fundamental Problems *still* not understood

$$NaAlH_4 \overset{3.7wt\%}{\Leftrightarrow} 1/3Na_3AlH_6 + 2/3Al + H_2 \overset{1.9wt\%}{\Leftrightarrow} NaH + Al + 3/2H_2$$



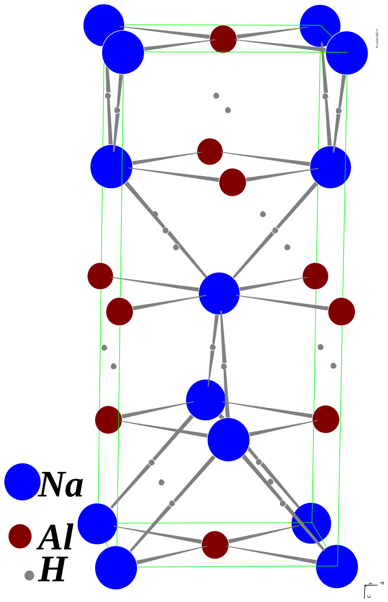
- **Work of Bogdanovic and Schwickardi (1997) demonstrates reversible hydrogen desorption after milling with Ti.**
- **Anton (2003) showed kinetic enhancements for various transition metals.**

<u>"Effect of Ti-catalyst content on the reversible hydrogen storage properties of the sodium alanates":</u> Sandrock, et al. {<u>J. Alloy Comp.</u> (2002)} *shows decrease in reversible capacities associated with increasing Ti-dopant content.*

LSU's Center for Advanced Microstructures and Devices (CAMD) (Baton Rouge, LA)

- **0.3 Mile, 1-2GeV ring of electrons in *storage ring*.**
- **Extended X-ray Absorption Fine Structure (EXAFS) at Ti K-edge.**
- **Collaborator: Amitava Roy**

SPECTROSCOPY



SCATTERING

Advanced Photon Source (APS) at Argonne National Laboratory

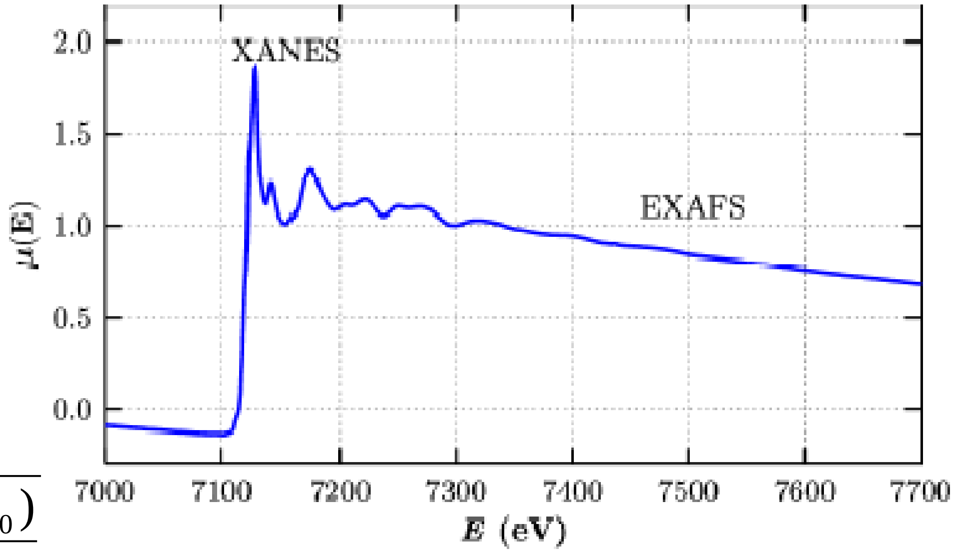
- **1.3Mile, 7GeV ring of electrons in *storage ring*.**
- **Ultrasmall-Angle X-ray Scattering (USAXS) for quantitative morphology (feature size and surface area).**
- **Collaborator: Jan Ilavsky**

X-ray Absorption Spectroscopy (XAS) performed at the DCM beamline at CAMD

X-ray Absorption Near Edge Structure (XANES) Analysis

- Comparison of spectral absorption edge position with *standard compounds* to give **oxidation state**.

XAS = XANES + EXAFS

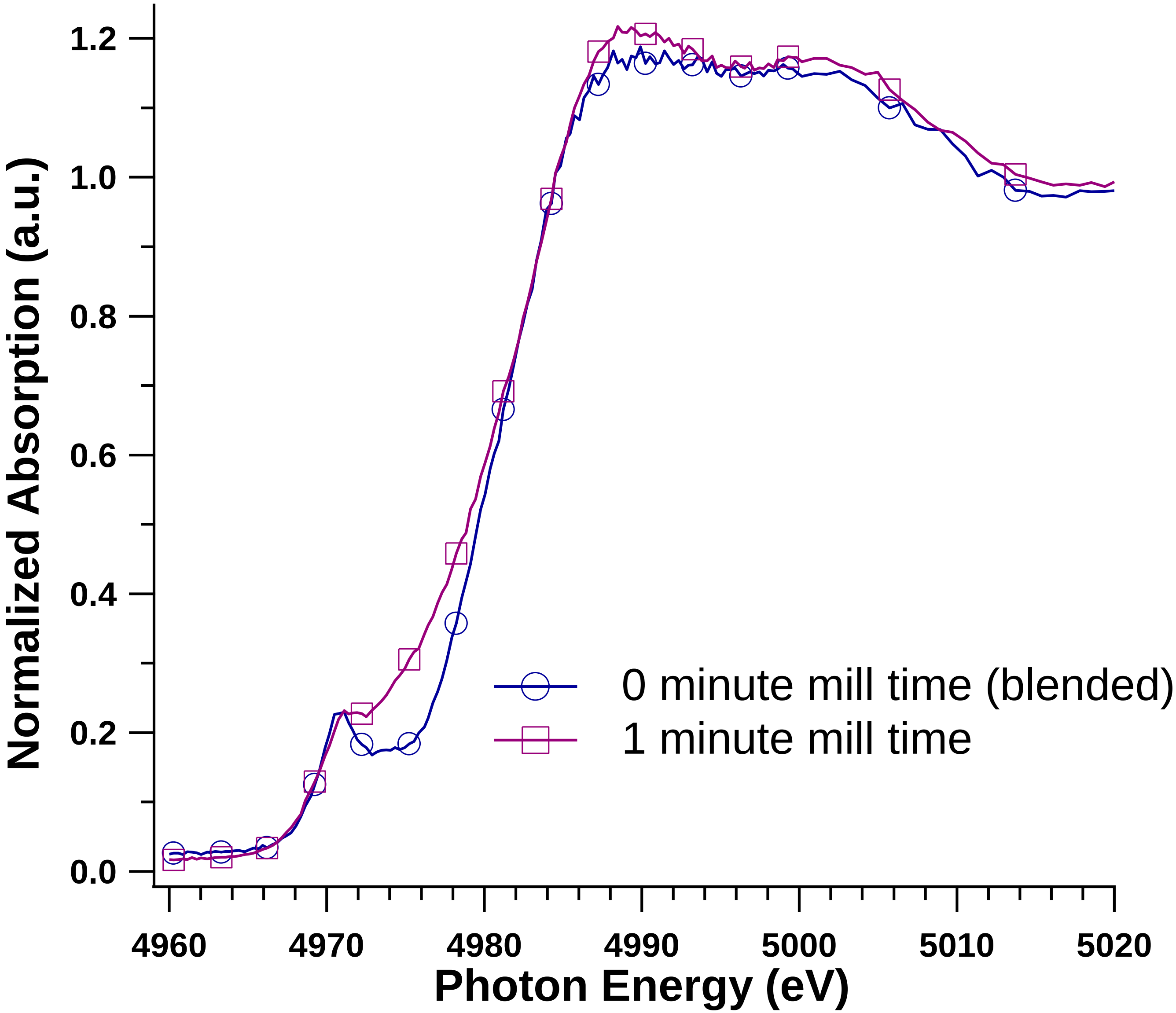


Extended X-ray Absorption Fine Structure (EXAFS) Analysis [Stern, Sayers, Lytle (1971)]

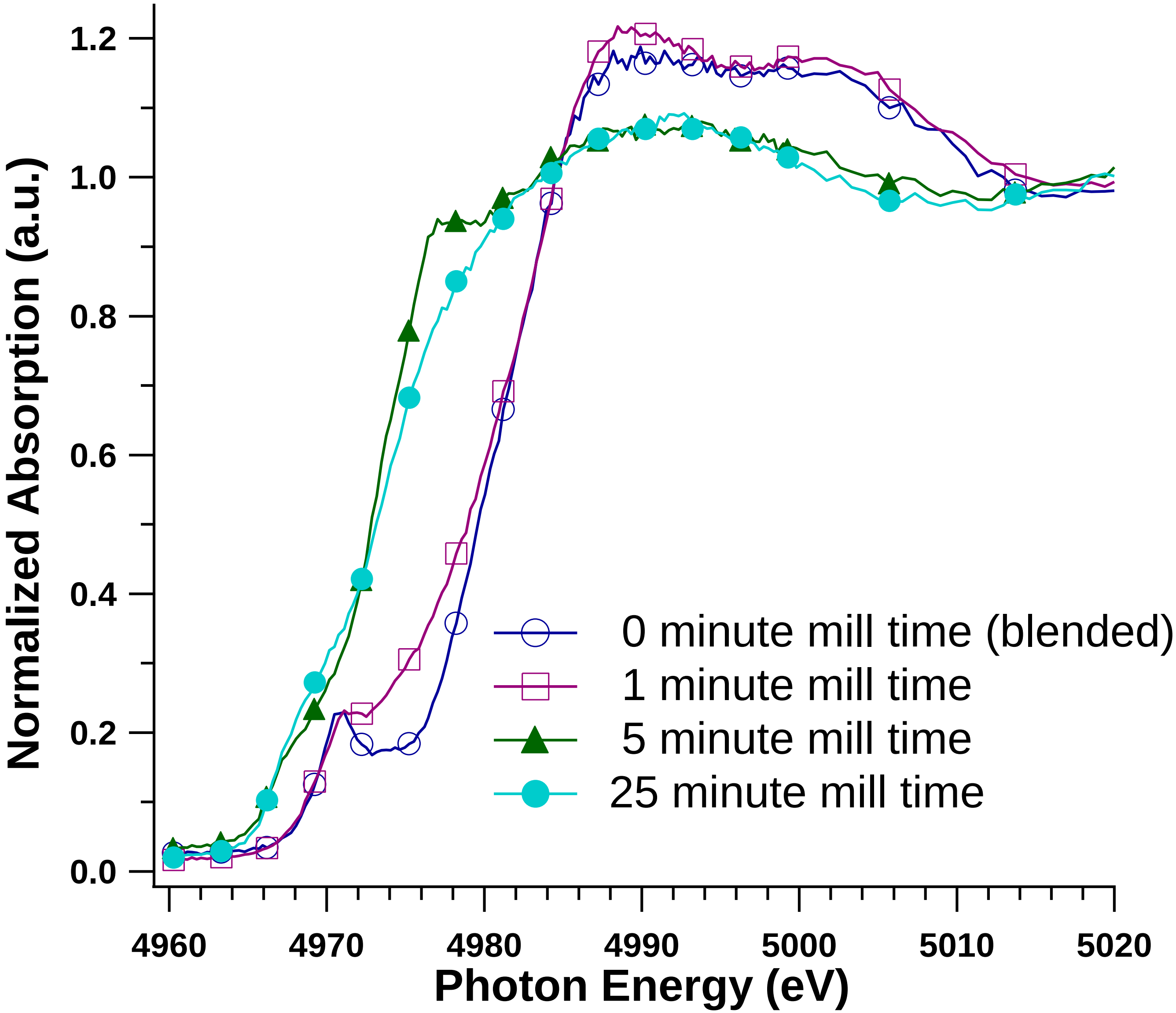
$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \qquad k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

$$\chi(k) = \sum_j \frac{N_j f_j(k) \exp\left(\frac{-2R_j}{\lambda(k)}\right) \exp\left(-2k^2\sigma_j^2\right)}{kR_j^2} \sin\left[2kR_j + \delta_j(k)\right]$$

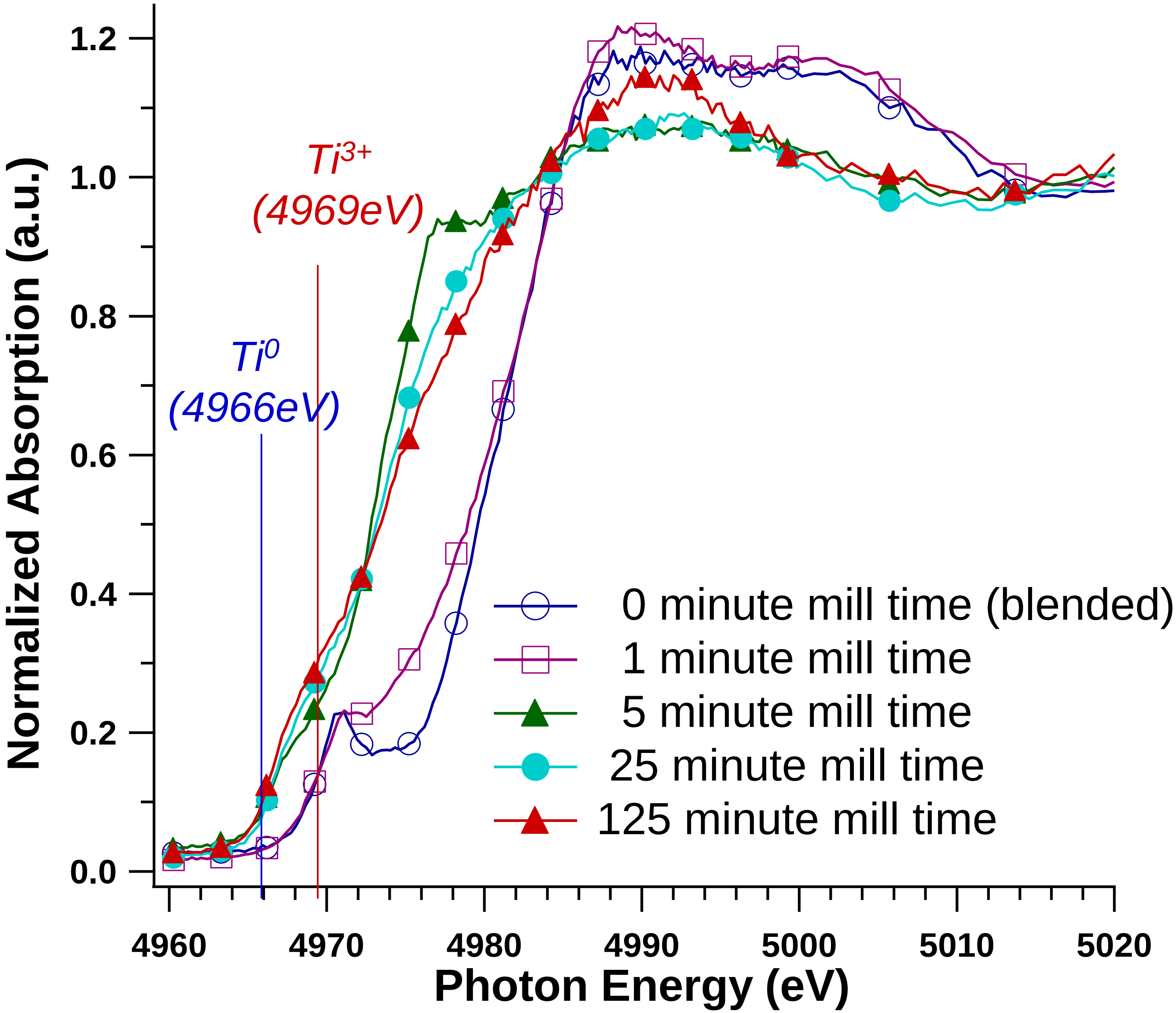
XANES: Changes in Ti^{3+} oxidation state during milling with $NaAlH_4$



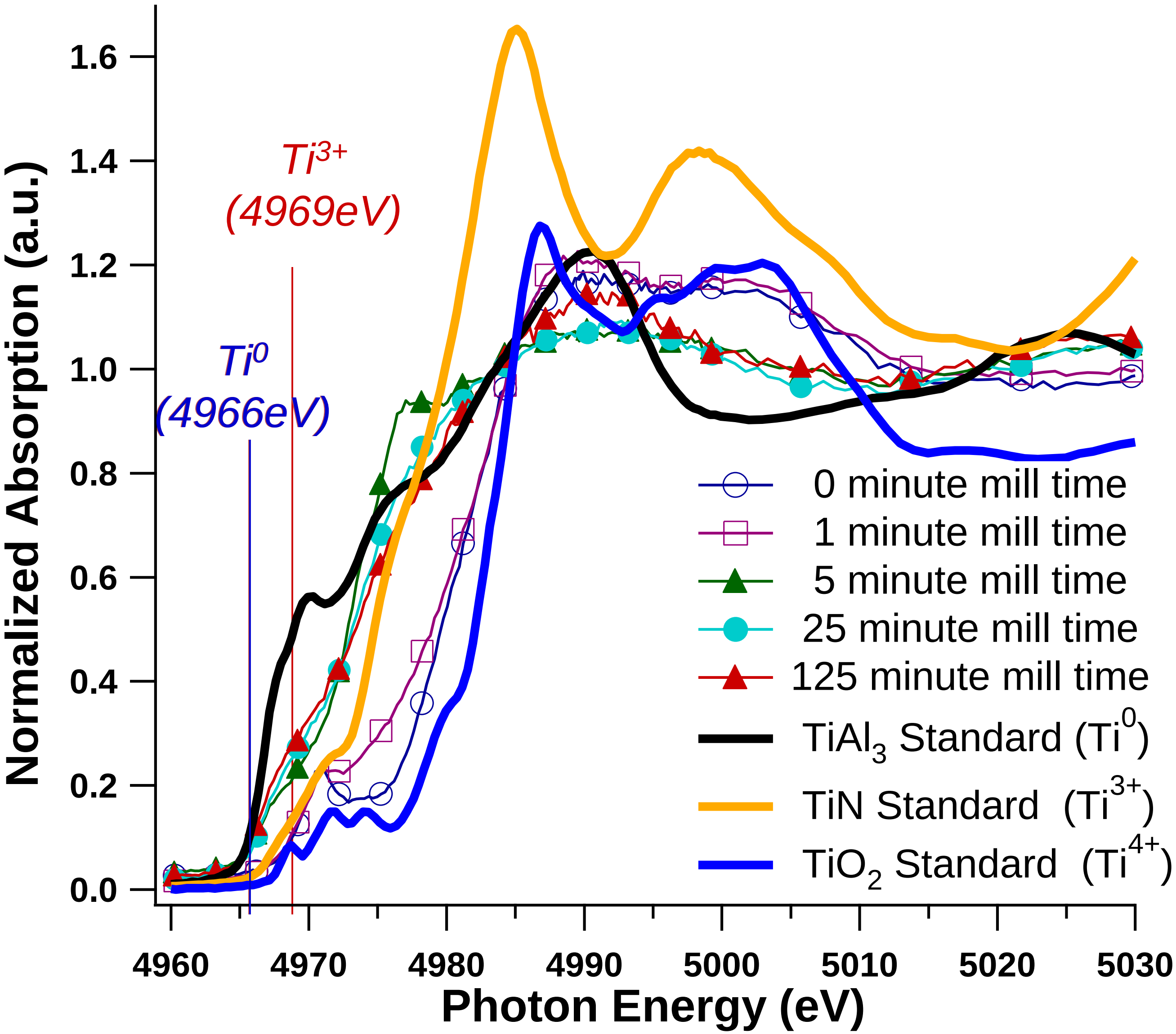
XANES: Changes in Ti^{3+} oxidation state during milling with $NaAlH_4$



XANES: Changes in Ti^{3+} oxidation state during milling with $NaAlH_4$

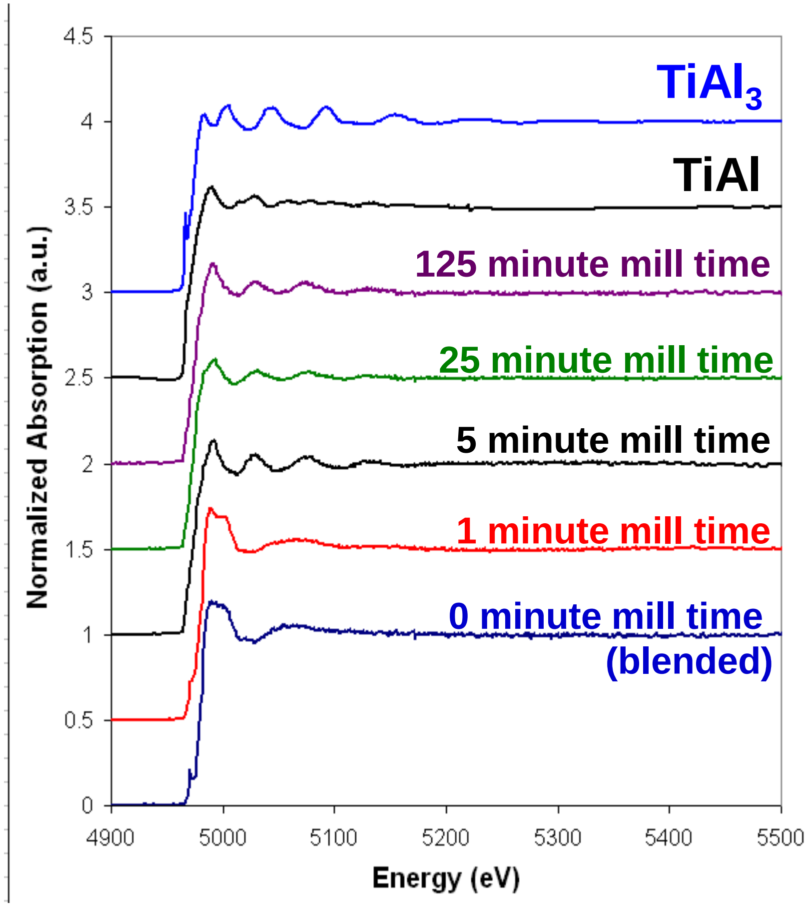


XANES: Changes in Ti^{3+} oxidation state during milling with $NaAlH_4$

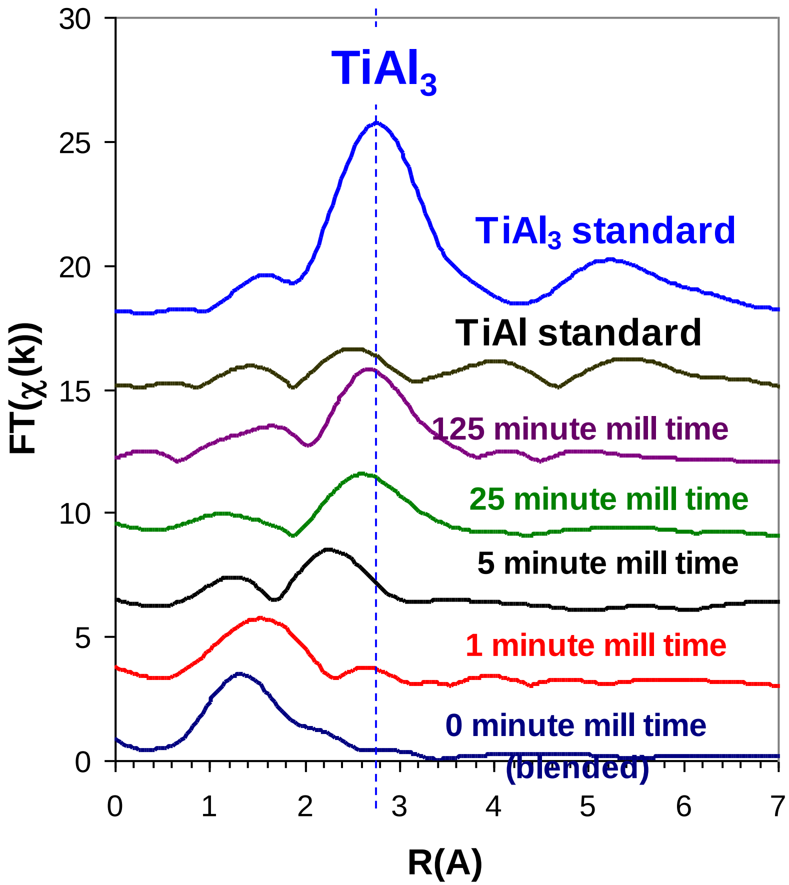


EXAFS: TiAl precedes $TiAl_3$ formation during milling

Normalized Absorption



Radial Distribution Function



Summary : SPECTROSCOPY

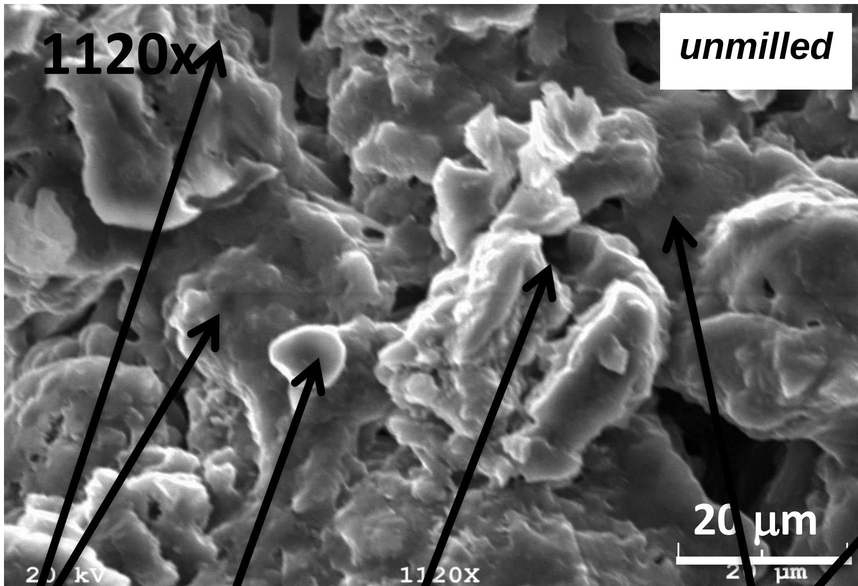
New understandings of changes in titanium during introduction to (and use in) $NaAlH_4$:

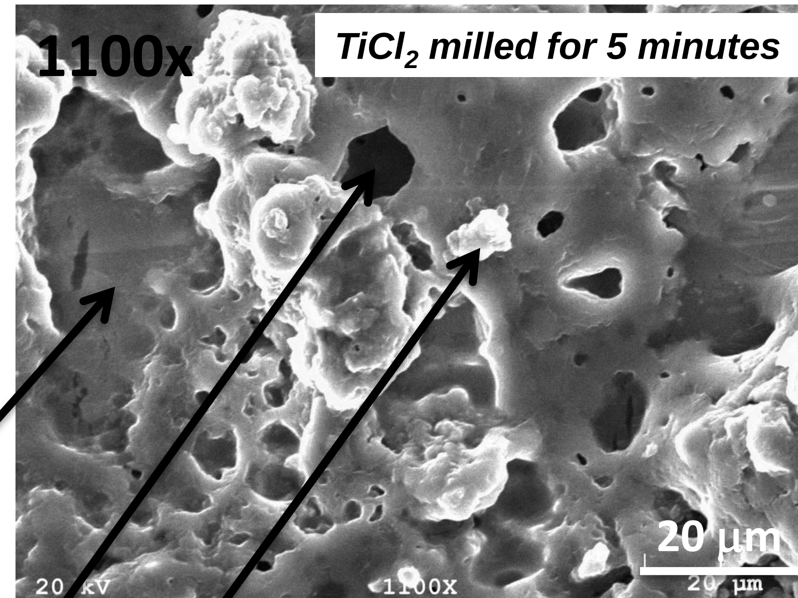
- $TiCl_3$ eventually forms metallic titanium (either nm-Ti, TiAl or $TiAl_3$).

New questions about the role of Ti:

- TiAl and $TiAl_3$ are irreversible, stable products. Can they be the catalysts? Or are they a by-product?
- Could Ti serve another role– such as facilitating atomic motion through lattice substitution?

Morphology of $NaAlH_4$





Rough surfaces

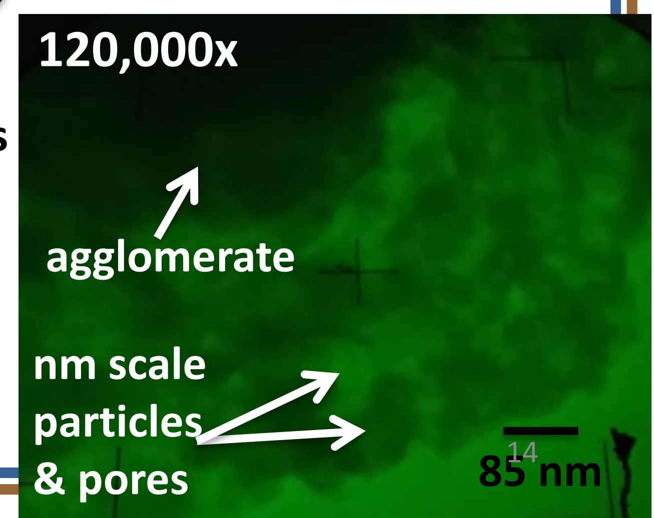
µm particles

µm pores

Smooth surfaces

µm pores

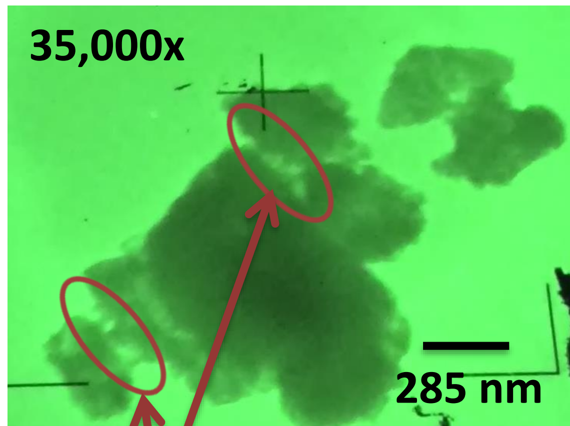
µm particles



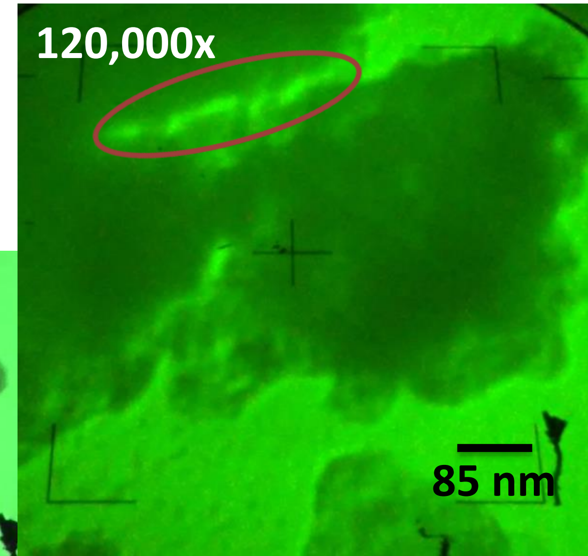
"Microstructure damage—including amorphization of the lattice—occur upon (de)/rehydrogenation excursions."
---Howard K. Birnbaum in presentation at the Fall 2004 MRS Meeting – Symp. N: Hydrogen Storage Materials.

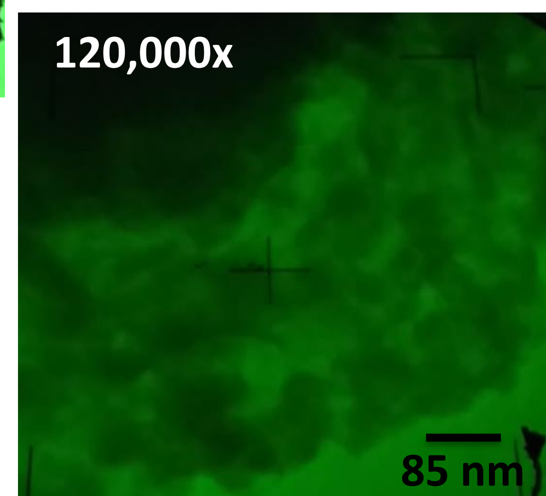
Morphology of $NaAlH_4$

Microstructure Feature
µm scale pore & particle size
µm scale pore & particle shape (smooth/rough surfaces)
nm scale pore & particle size
nm scale pore & particle shape
Striated Interconnects

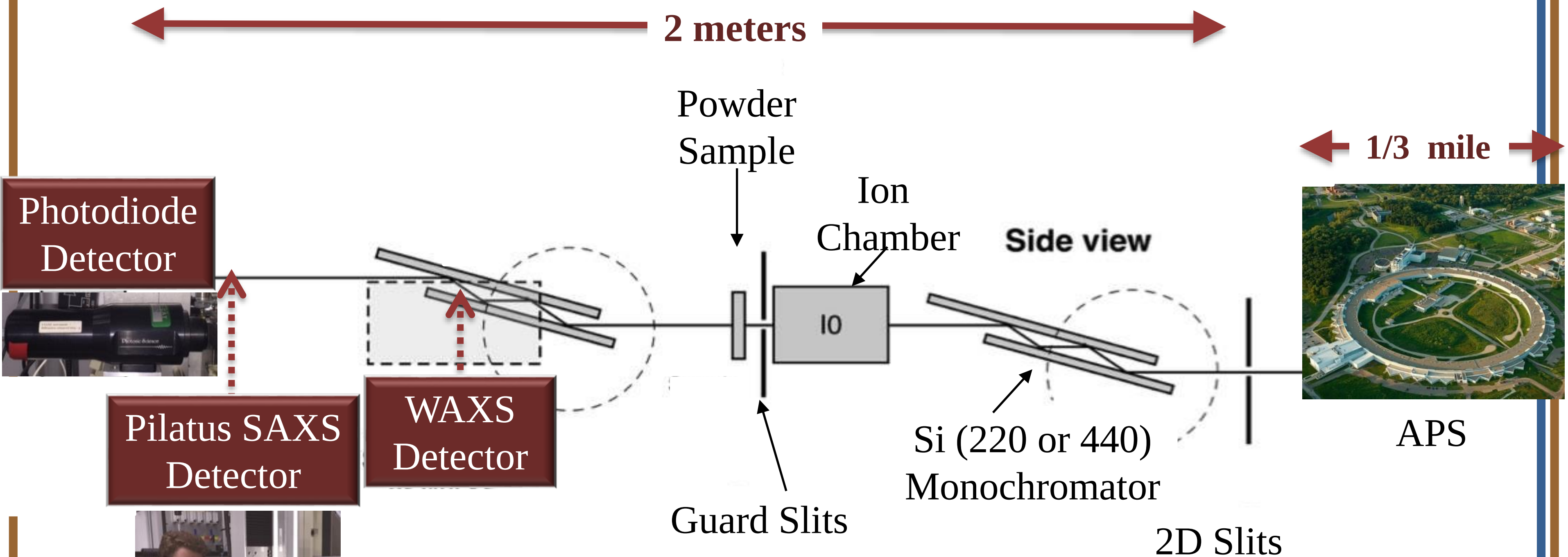


Striated interparticle interconnects





USAXS, PinSAXS, WAXS at Sector (9ID-C,D)



<u>Bonse-Hart USAXS</u>

- **Dynamic Q-range from 0.0001A^{-1} to 0.3A^{-1}**

<u>Pinhole SAXS</u>

- **Dynamic Q-range from 0.05A^{-1} to 1.2A^{-1}**

<u>WAXS</u>

- **Dynamic Q-range from 1A^{-1} to 6A^{-1} (with 16.9 keV beam)**

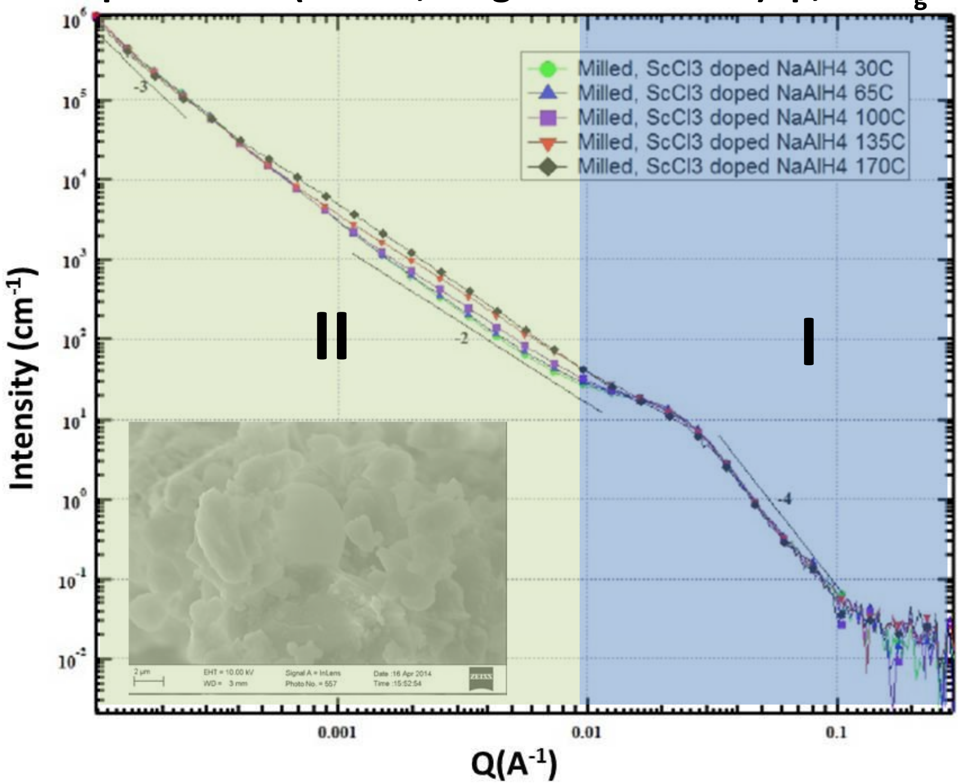
Ilavsky, J., F. Zhang, A. J. Allen, L. E. Levine, P. R. Jemian and G. G. Long. "Ultra-Small-Angle X-Ray Scattering Instrument at the Advanced Photon Source: History, Recent Development, and Current Status." *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science* **44A**, no. 1 (**2013**): 68-76.

http://usaxs.xray.aps.anl.gov/

Relationship of Scattering Data to $NaAlH_4$ Morphology

Data fitted using the "Unified Fit" with 2 populations:

- **Population I (High Q, Small Feature Size): p & R_g**
- **Population II (Low Q, Large Feature Size): p, no R_g**



$$I(Q) = G\exp\left(-\frac{Q^2 R_g^{\,2}}{3}\right) + B\left(\frac{\left(erf\left[\frac{QR_g}{\sqrt{6}}\right]\right)^3}{Q}\right)^p$$

Microstructure Feature		USAXS Parameter
~~μm scale pore & particle size~~		~~N/A (Pop II, no R_g)~~
Shape- μm scale pore & particle (smooth/rough surfaces)		p (Pop II)
Size-nm scale pore & particle		R_g (Pop I)
Shape-nm scale pore & particle		p~-4 (Pop I has smooth surfaces)
Number-relative amount of nm scale particles		B (Pop I)

G. Beaucage, "Approximations Leading to a Unified Exponential/Power-Law Approach to Small Angle Scattering" *J. Appl. Cryst.* **28** pp 717-728 (1995).

M^{x+}-doped $NaAlH_4$ Morphology

$$NaAlH_4 \overset{3.7wt\%}{\Leftrightarrow} 1/3Na_3AlH_6 + 2/3Al + H_2 \overset{1.9wt\%}{\Leftrightarrow} NaH + Al + 3/2H_2$$

Dopant Type	Desorption Rate (after 5 min.) – wt. % per hour	Desorption Rate (after 10 min.) – wt. % per hour
$TiCl_2$	3.98	2.38
$TiCl_3$	6.57	2.73
$ScCl_3$	-	-
VCl_3	1.80	0.95
$ZrCl_4$	1.50	1.40

Desorption rates from: D.L. Anton, *Journal of Alloys and Compounds*, **356-357** (2003) 400-404.

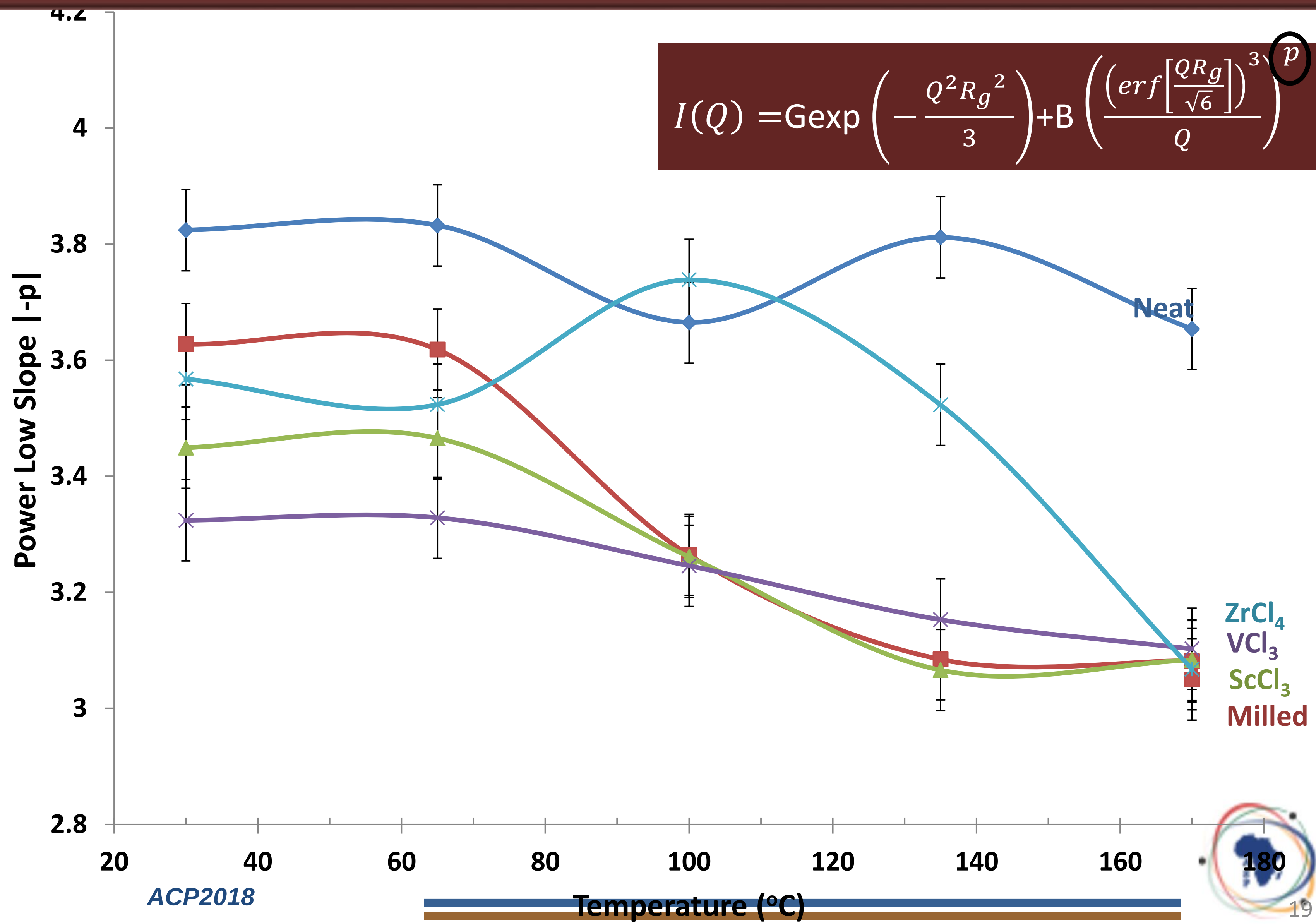
- Dopants were added at 3 mol % concentration by 10 minute high energy ball milling
- Comparisons were made also to "neat" (as-purchased $NaAlH_4$) and "milled"
- Overall goal is correlate parameter to well-performing dopants.
  - Population II (course) mapping : G=0; p(t,T)
  - Population I (fine) mapping: p=-4, Rg(t,T), B(t,T)

$$I(Q) = G\exp\left(-\frac{Q^2 R_g{}^2}{3}\right) + B\left(\frac{\left(erf\left[\frac{QR_g}{\sqrt{6}}\right]\right)^3}{Q}\right)^p$$

G. Beaucage, *J. Appl. Cryst.* **28** pp 717-728 (1995).

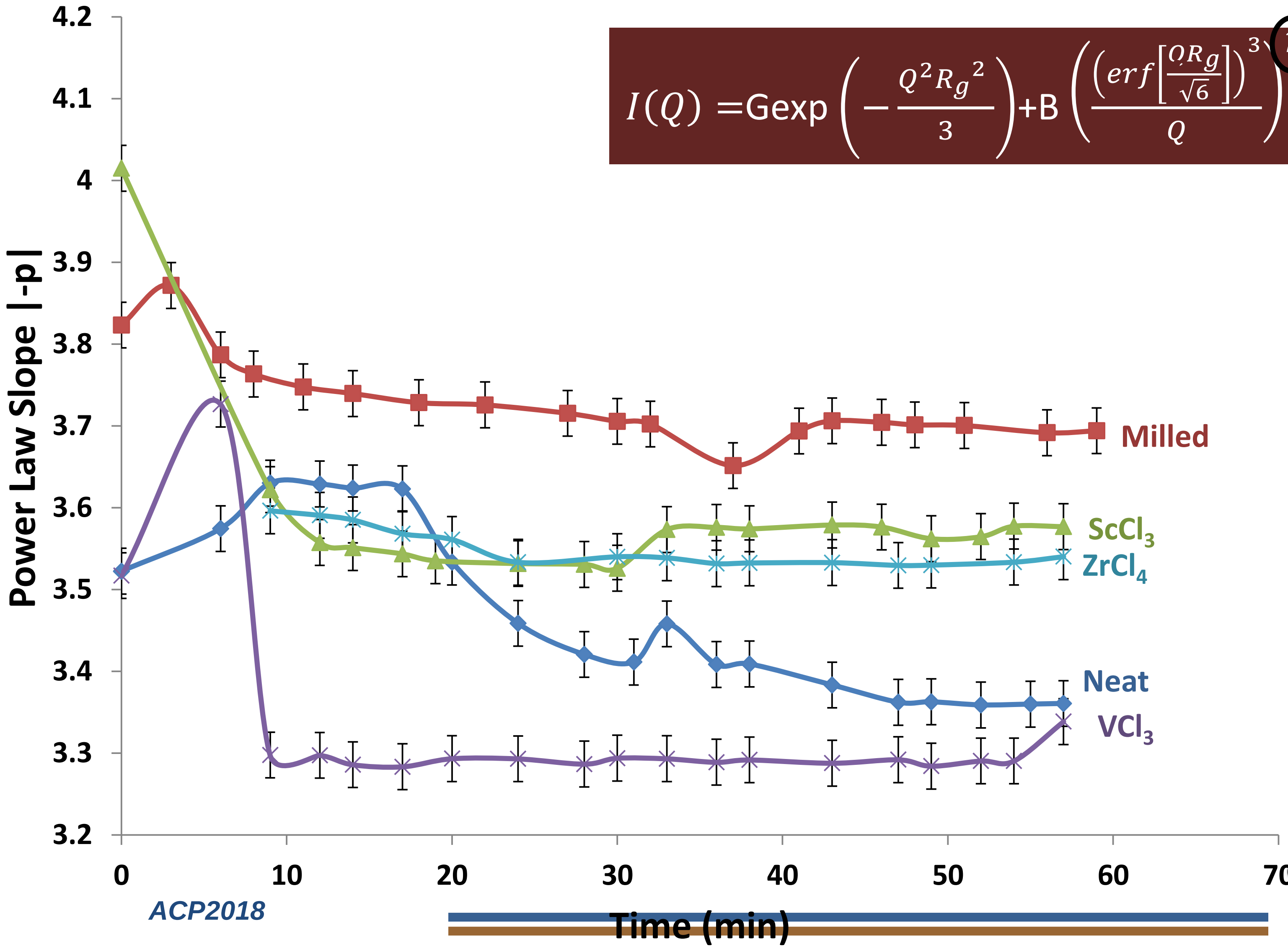
Agglomerate SA vs. Temperature

$$I(Q) = G\exp\left(-\frac{Q^2 R_g{}^2}{3}\right) + B\left(\frac{\left(erf\left[\frac{QR_g}{\sqrt{6}}\right]\right)^3}{Q}\right)^{p}$$



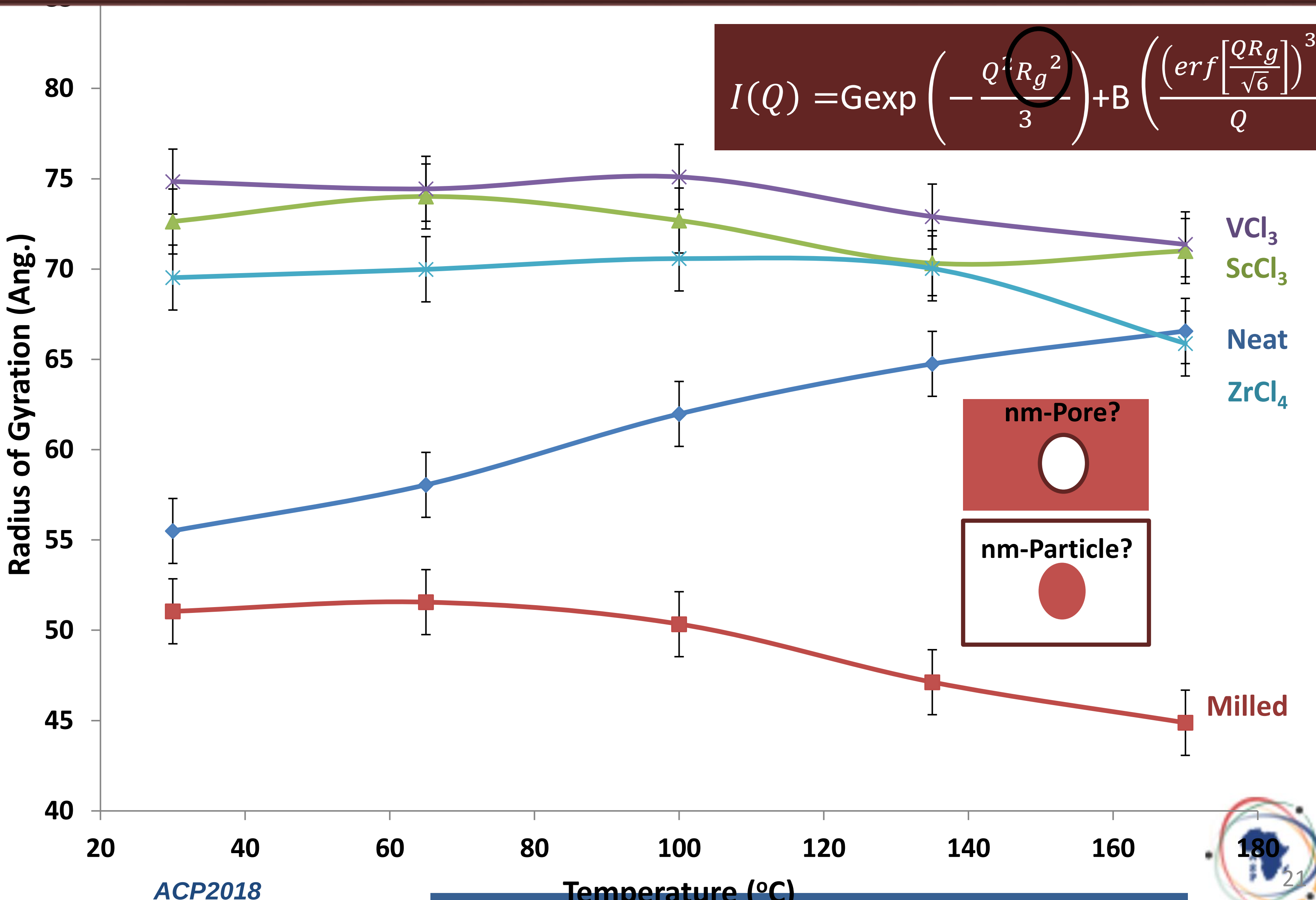
Agglomerate SA vs. Time

$$I(Q) = \text{Gexp}\left(-\frac{Q^2 {R_g}^2}{3}\right) + \text{B}\left(\frac{\left(erf\left[\frac{QR_g}{\sqrt{6}}\right]\right)^3}{Q}\right)^p$$



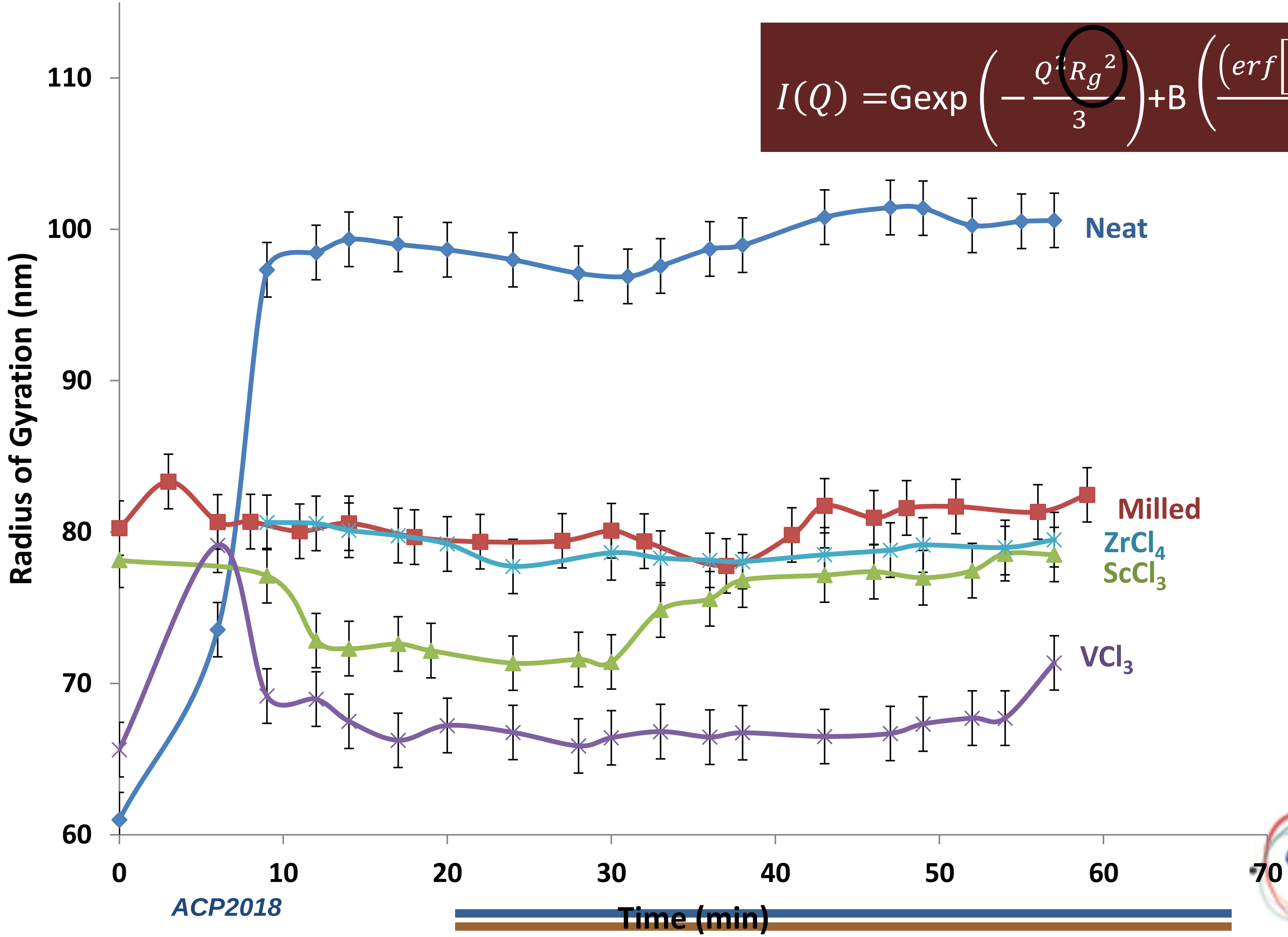
R_g vs. Temperature

$$I(Q) = G\exp\left(-\frac{Q^2 R_g^{\,2}}{3}\right) + B\left(\frac{\left(erf\left[\frac{QR_g}{\sqrt{6}}\right]\right)^3}{Q}\right)^p$$



R_g vs. Time

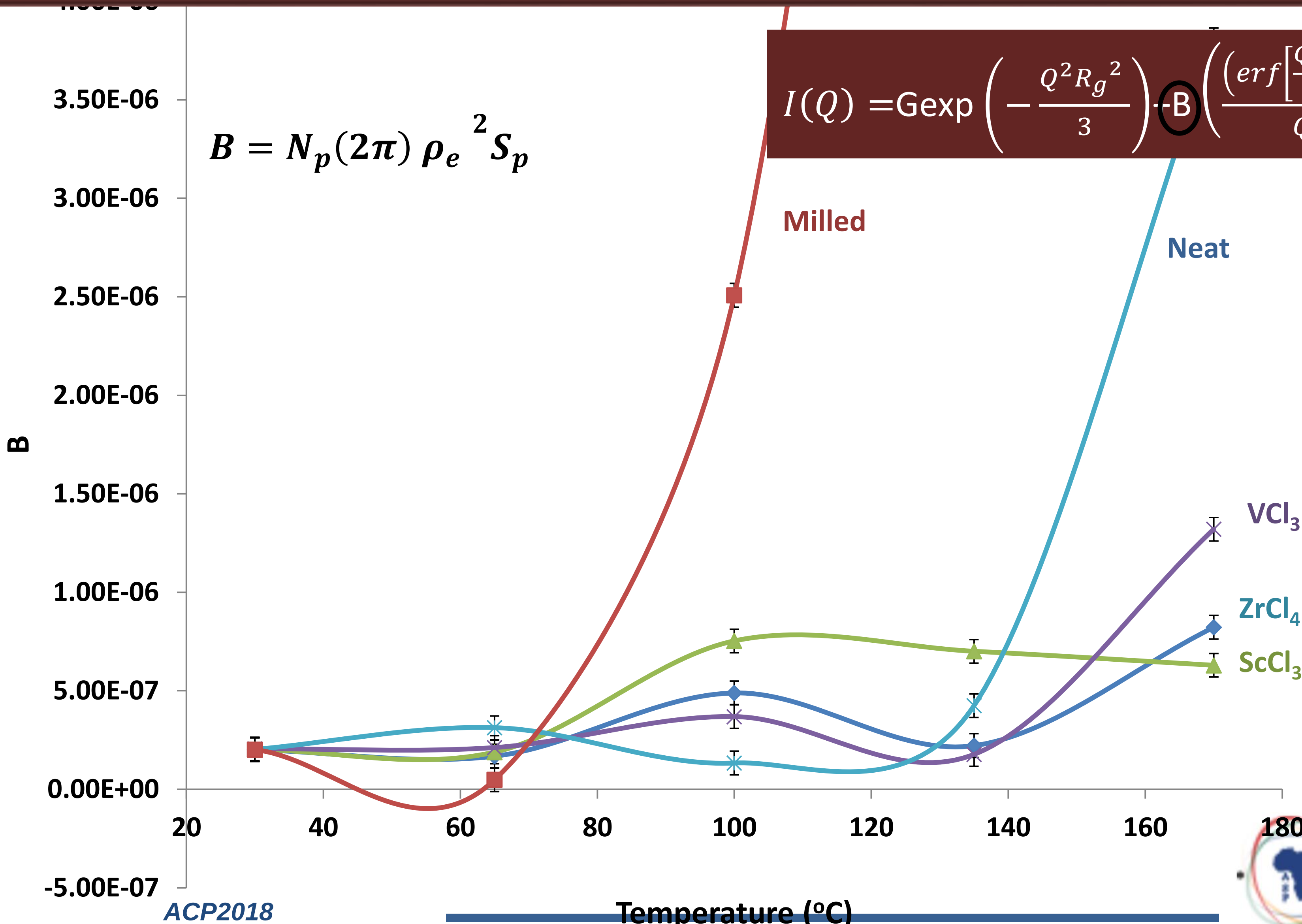
$$I(Q) = G\exp\left(-\frac{Q^2 R_g^2}{3}\right) + B\left(\frac{\left(erf\left[\frac{QR_g}{\sqrt{6}}\right]\right)^3}{Q}\right)^p$$



Number of nm-objects N_p vs. Temperature

$$I(Q) = G\exp\left(-\frac{Q^2 {R_g}^2}{3}\right) + B\left(\frac{\left(erf\left[\frac{QR_g}{\sqrt{6}}\right]\right)^3}{Q}\right)^p$$

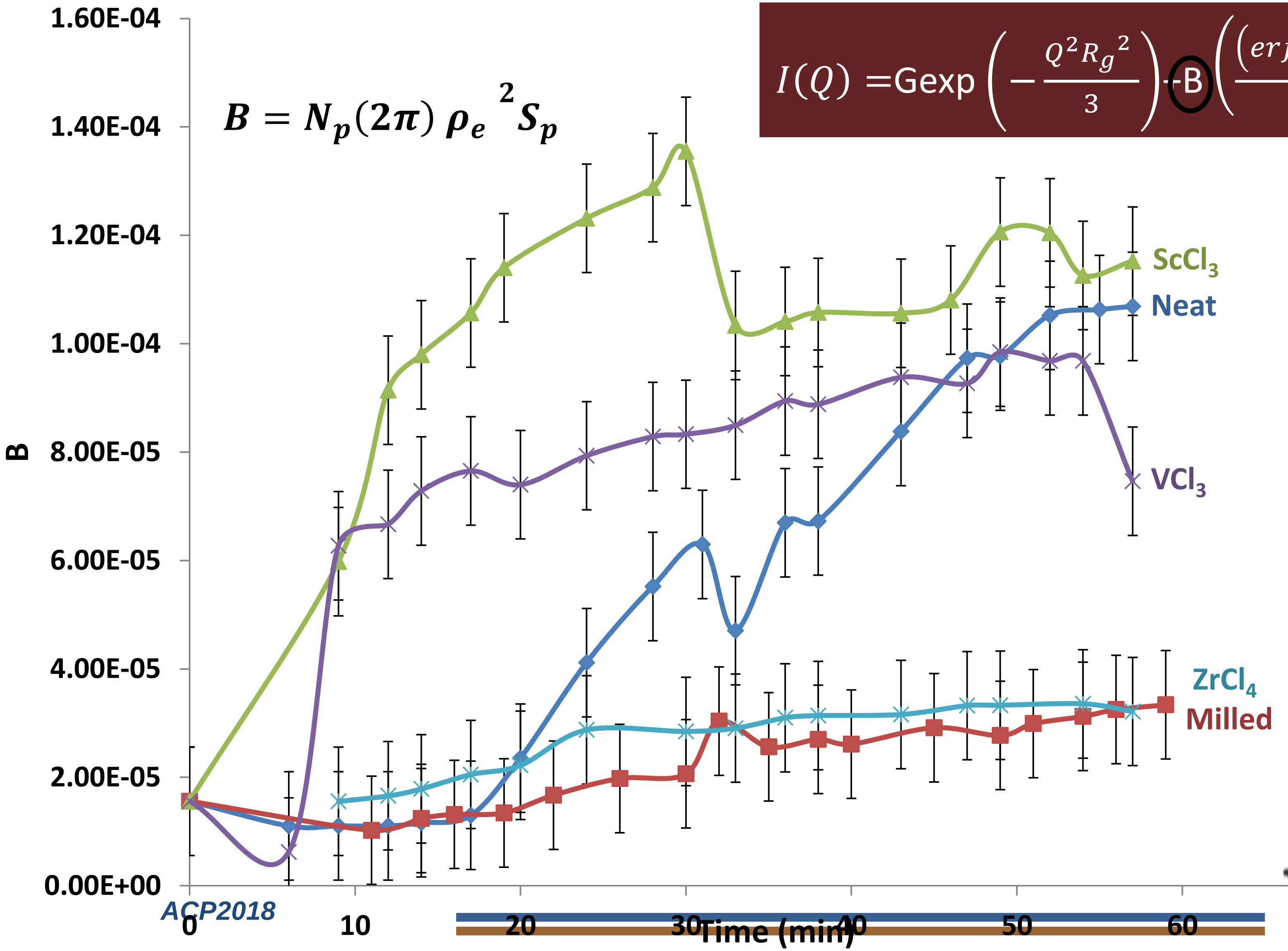
$$B = N_p(2\pi)\,{\rho_e}^2 S_p$$



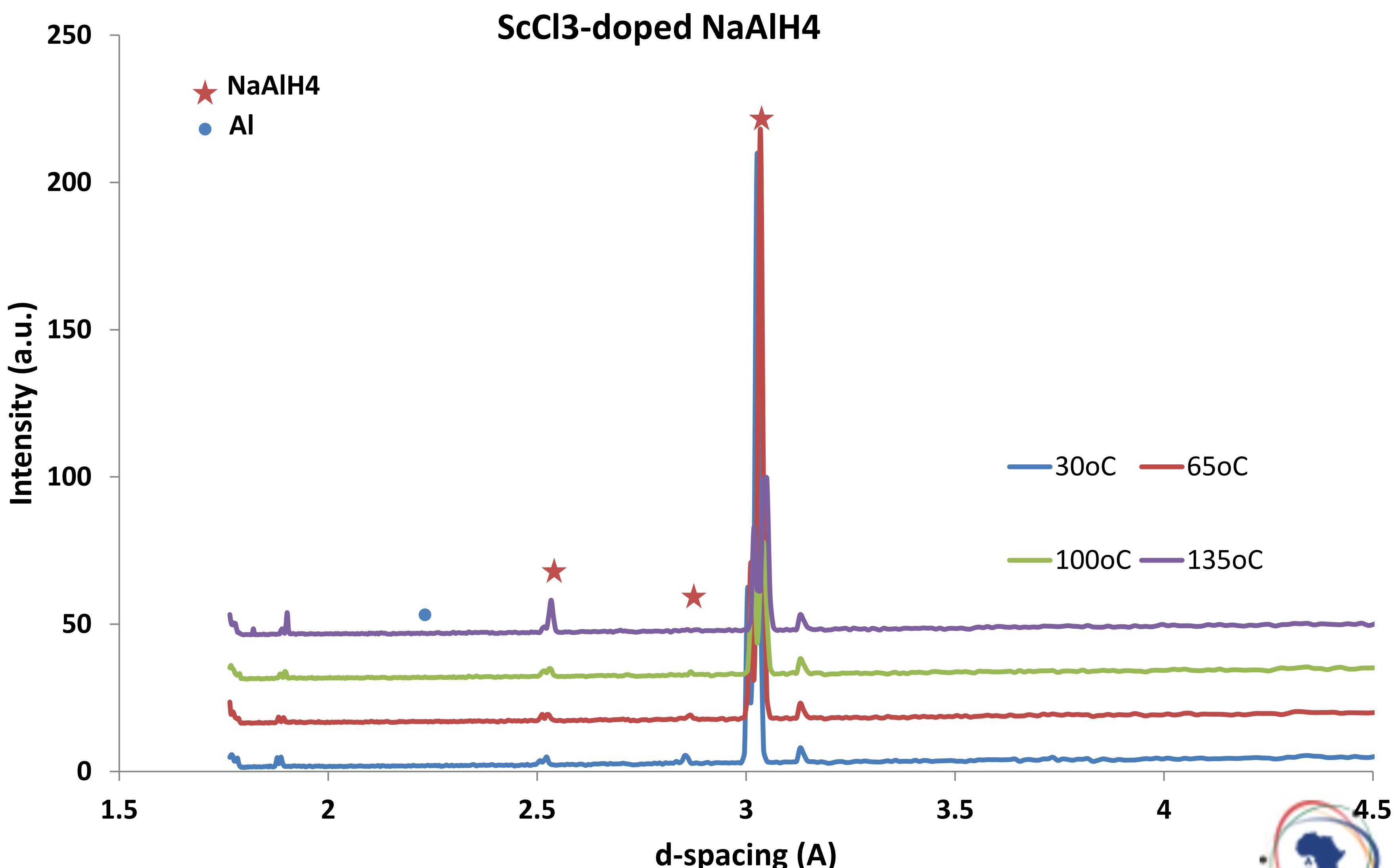
Number of Particles N_p vs. Time

$$I(Q) = G\exp\left(-\frac{Q^2 R_g{}^2}{3}\right) + B\left(\frac{\left(erf\left[\frac{QR_g}{\sqrt{6}}\right]\right)^3}{Q}\right)^p$$

$$B = N_p (2\pi)\, \rho_e{}^2 S_p$$



WAXS


ScCl3-doped NaAlH4
NaAlH4
Al
Intensity (a.u.)
250
200
150
100
50
0
1.5
2
2.5
3
3.5
4
4.5
d-spacing (A)
30oC
65oC
100oC
135oC

Summary : SCATTERING

New understandings of morphology changes leading to desorption in hydrides:

- Increased SA as temperature increased for all doped samples (and milled).
- Size remains *relatively* constant with temperature. Doped samples show 70-80nm size while milled is smaller.
- At 135°C, little change in SA or R_g with time.
- N_p for 50-70nm size increases with both T and t. These scattering objects are likely pores
    - WAXS data shows no increase in product phase formation associated with increasing N_p

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Shathabish NaraseGowda (Nanohydrides)
James Torres (USAXS/SAXS/WAXS)
Christopher Bennett (USAXS/SAXS/WAXS)

Collaborators:

- CAMD (EXAFS/XANES) SYNCHROTRON LABORATORY: Amitava Roy and Greg Merchan
- ADVANCED PHOTON SOURCE: Jan Ilavsky and Ivan Kuzmenko

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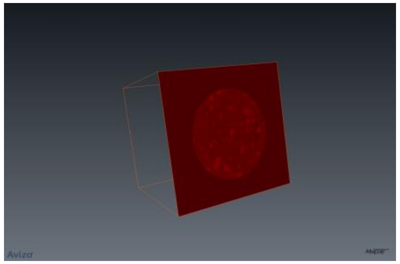
- AFRICAN LIGHT SOURCE STEERING COMMITTEE
- LAAAMP
- REDI-SPARC Initiative



3D Tomographic Imaging

Synchrotron Courses

http://users.rowan.edu/~dobbins/

PAN AFRICAN CONFERENCE ON CRYSTALLOGRAPHY (PCCr)

Joint Conference of the Pan African Conference on Crystallography (PCCr2) And The African Light Source (AfLS2)

28th January-2nd February 2019
in Accra, Ghana

Bio Crystallography Crystal Engineering Industrial Materials Inorganic Materials	Plenary Talks Large Scale Facilities Strategies for Africa Guided tour of Ghana and Cape Coast Castle	Spectroscopy 3D Tomographic Imaging Light Sources of the Future Mineralogy Paleontology

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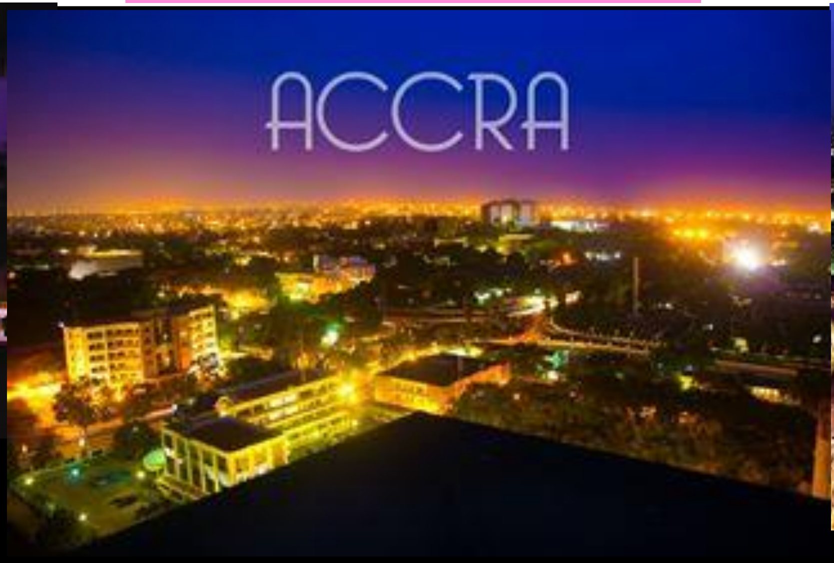

Questions

?

http://users.rowan.edu/~dobbins

dobbins@rowan.edu

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