A PERSONAL HISTORY OF EXAFS

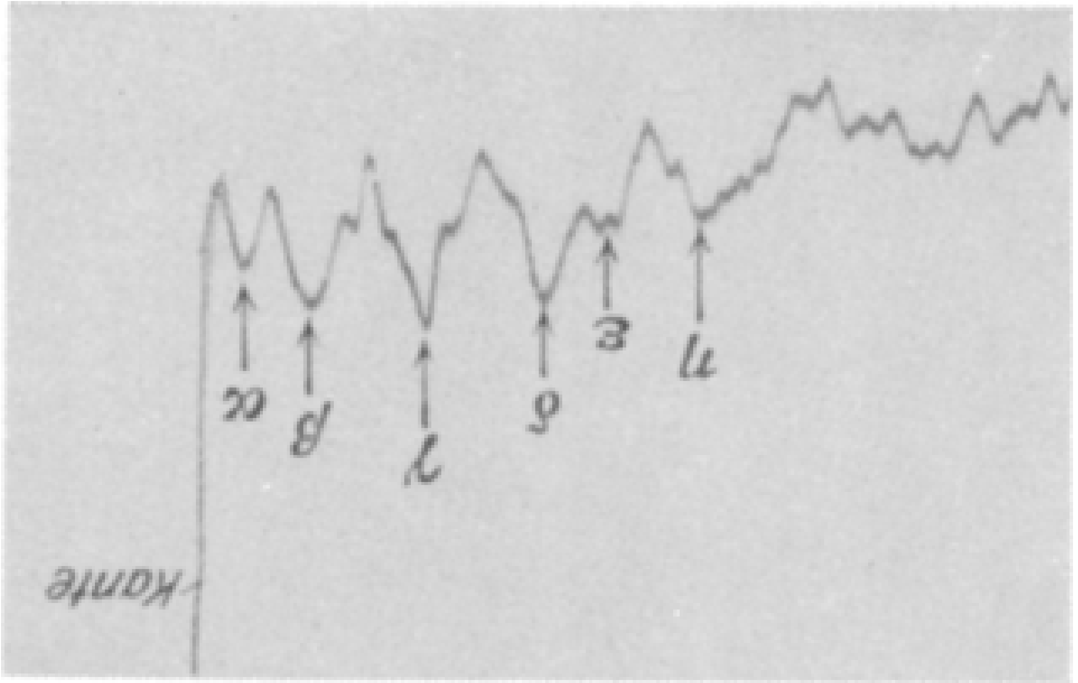
Riding the waves of synchrotron radiation and EXAFS

- A brief history of EXAFS
- The contribution of Ed Stern, Dale Sayers and Farrel Lytle 50 years ago
- My start at SSRP (now SSRL)
- The later generations of machines
  - NSLS
  - APS
- Doped Nb_3Sn: One of my research projects that spanned the generations

Argonne NATIONAL LABORATORY

Early film-based spectrometers were capable of obtaining reasonable quality fine structure

Lindh, Axel E. "Zur Kenntnis des K-Röntgenabsorptionsspektrums der Elemente Ni, Cu und Zn." *Zeitschrift für Physik* 63 (1930): 106-113.



Is EXAFS a result of short range or long range order?

The two theories coexisted for many years even though measurements showed structure in liquids

- Both ideas could qualitatively describe the fine structure
- The idea of electron bands and electrons diffracting in a lattice very appealing

For more details of the early work see:

Farrel W. Lytle, J. Synchrotron Rad. (1999). 6, 123-134
The EXAFS family tree: a personal history of the development of extended X-ray absorption fine structure

Von Bordwehr, R. S. (1989). A History of X-ray absorption fine structure. In Annales de Physique (Vol. 14, No. 4, pp. 377-465). EDP Sciences.

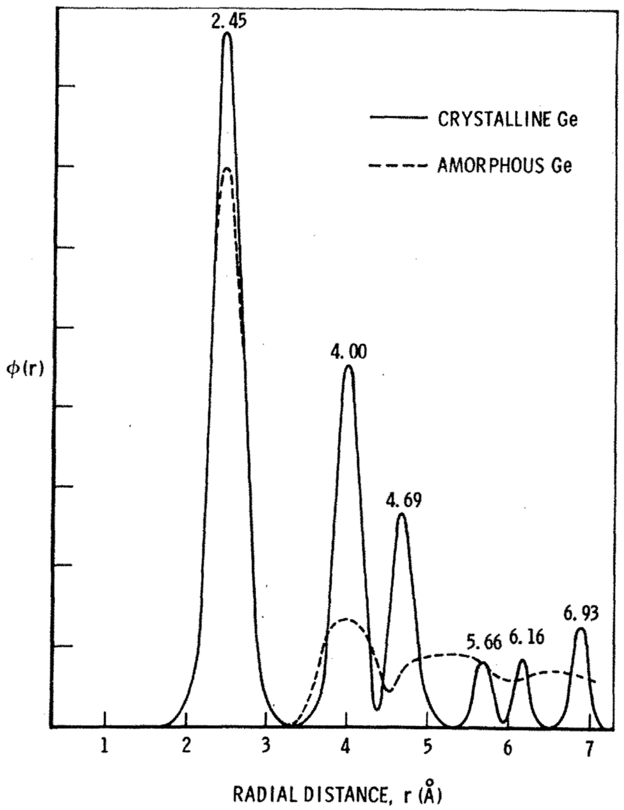
VOLUME 27, NUMBER 18 PHYSICAL REVIEW LETTERS 1 NOVEMBER 1971

New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray–Absorption Fine Structure*

Dale E. Sayers† and Edward A. Stern†‡
Department of Physics, University of Washington, Seattle, Washington 98105

and

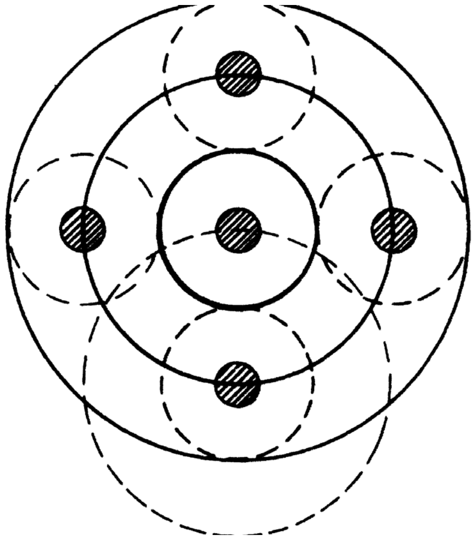
Farrel W. Lytle
Boeing Scientific Research Laboratories, Seattle, Washington 98124
(Received 16 July 1971)



PHYSICAL REVIEW B VOLUME 10, NUMBER 8 15 OCT

Theory of the extended x-ray-absorption fine structure*

Edward A. Stern
Department of Physics, University of Washington, Seattle, Washington 98195
(Received 14 March 1974)



PHYSICAL REVIEW B VOLUME 11, NUMBER 12 15 JUNE 1975

Extended x-ray-absorption fine-structure technique. III. Determination of physical parameters*

E. A. Stern and D. E. Sayers
Department of Physics, University of Washington, Seattle, Washington 98195

F. W. Lytle
The Boeing Company, Seattle, Washington 98124
(Received 23 December 1974)

PHYSICAL REVIEW B VOLUME 11, NUMBER 12 15 JUNE 1975

Extended x-ray-absorption fine-structure technique. II. Experimental practice and selected results

F. W. Lytle
The Boeing Company, Seattle, Washington 98124

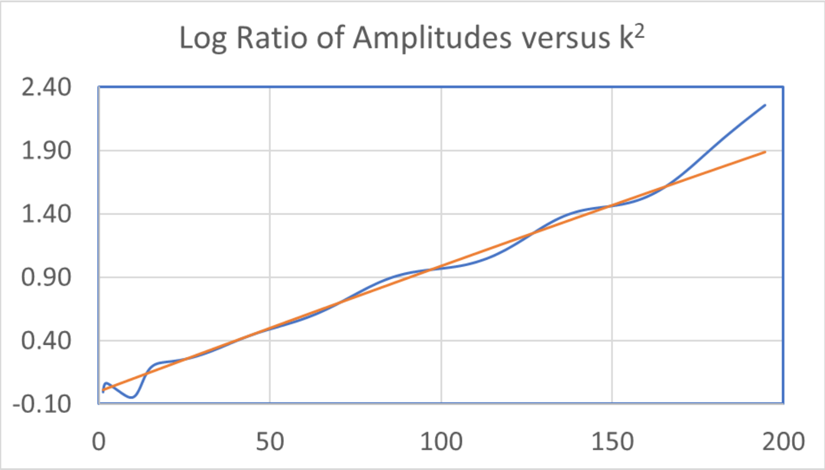
D. E. Sayers* and E. A. Stern
Department of Physics, University of Washington, Seattle, Washington 98195
(Received 23 December 1974)

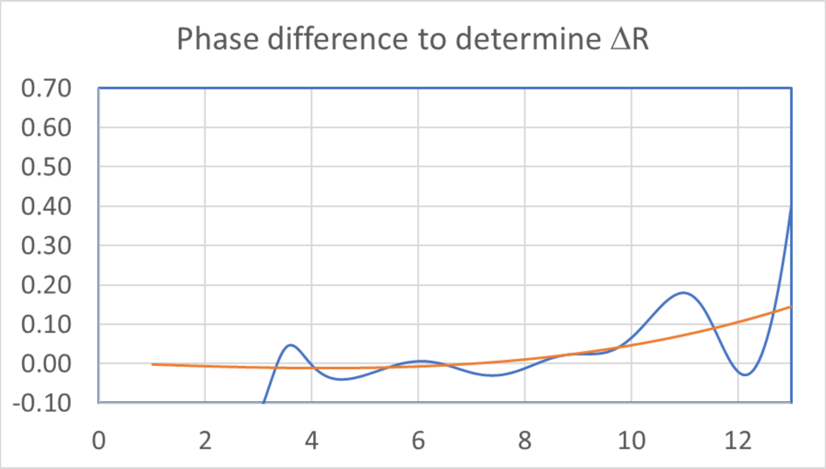
Warren award 1979

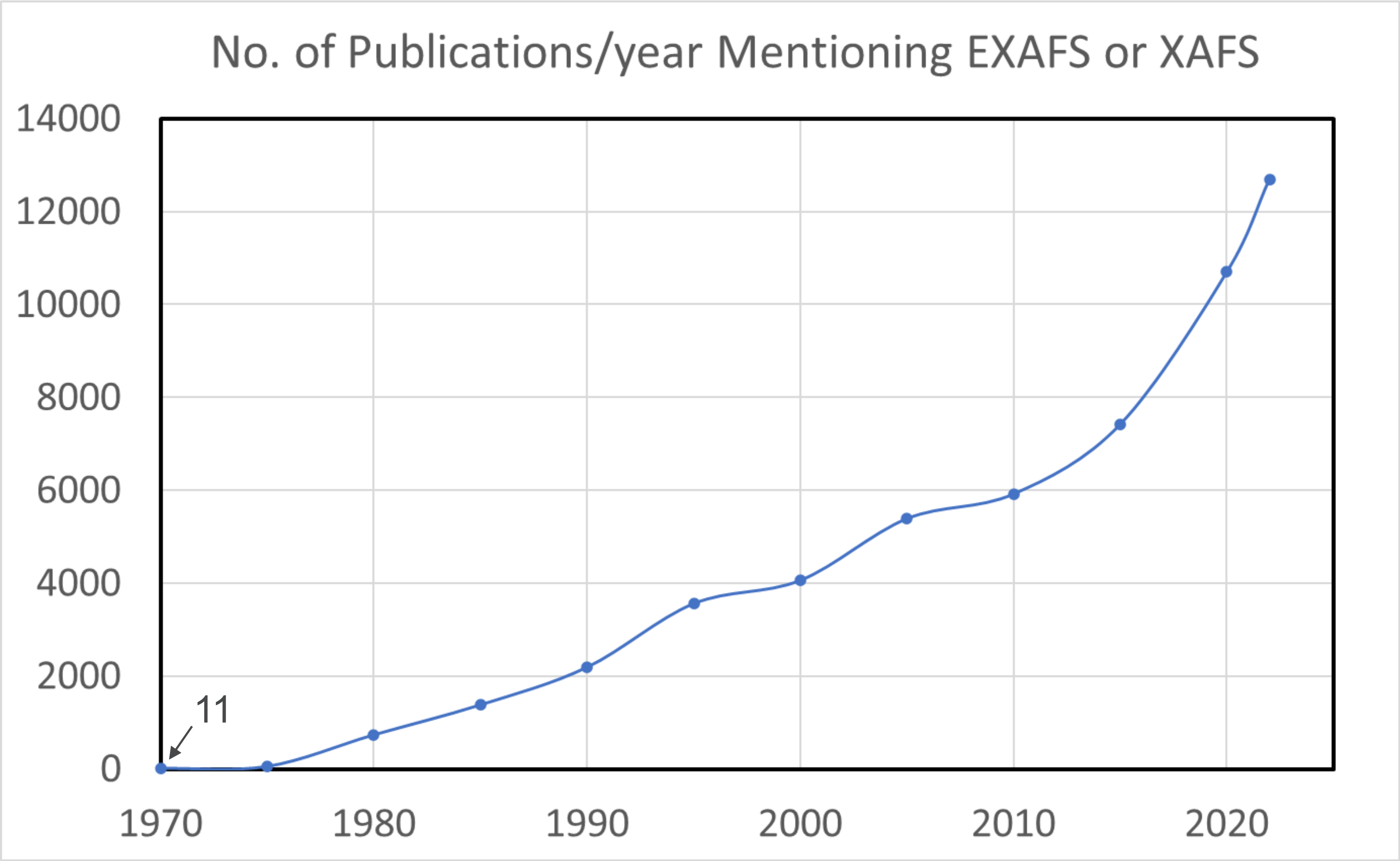
Edward Stern Dale Sayers Farrel Lytle

The Fourier transform was the key to unlocking EXAFS as a characterization method

- Emphasized the structural components
- Allowed more quantitative comparison to theory especially for 1st and 2nd shells by separating them from more complicated factors such as multiple scattering
- ‘Transferability’ of phases and amplitudes allowed extraction of accurate structural numbers
- Until theory improved isolated shells could be analyzed by the ratio method

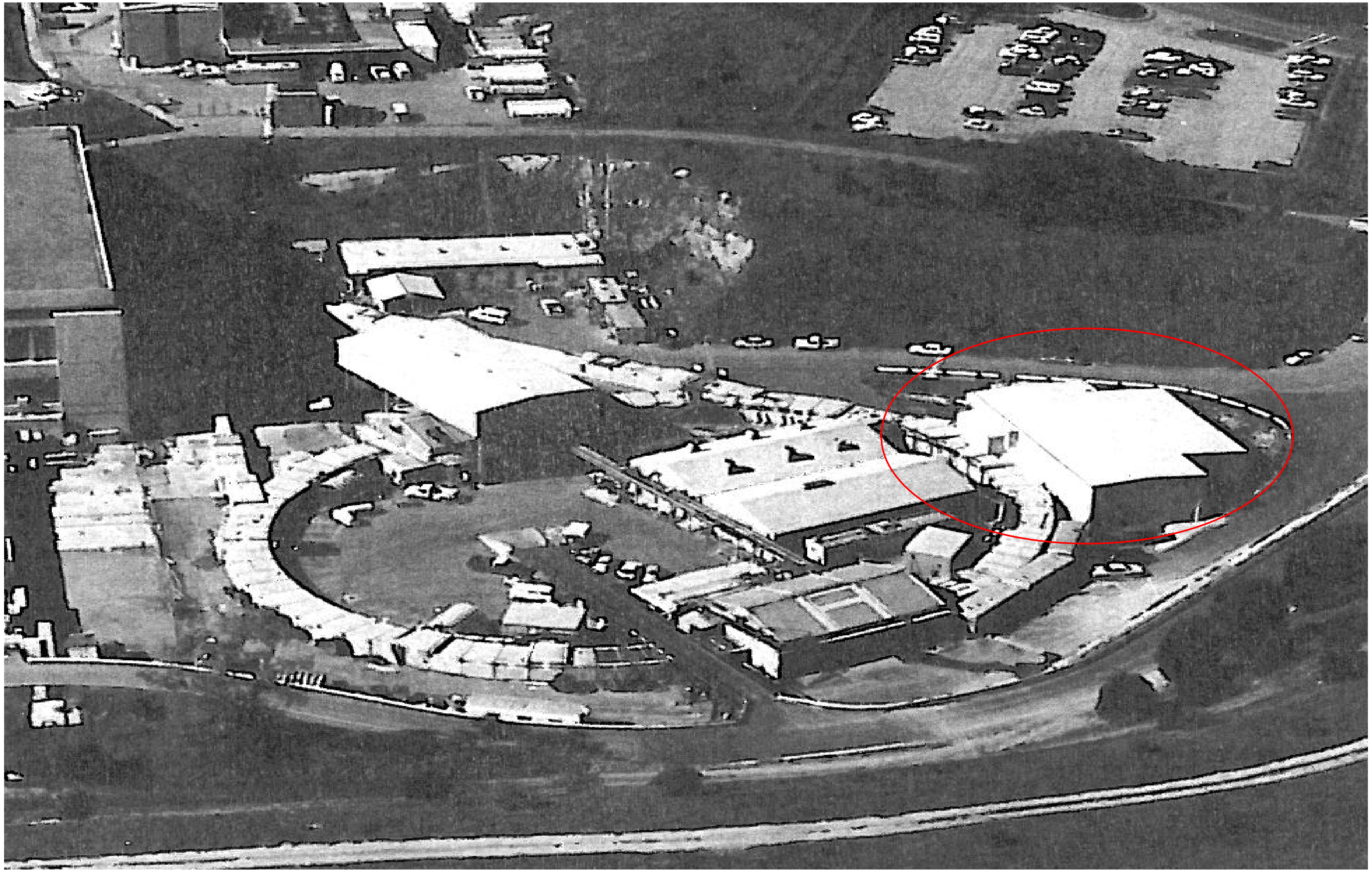






Note: the acronym EXAFS was introduced by Lytle in 1965

SSRP – the first US accelerator-based x-ray source 1974



The possibility of improved EXAFS measurements was an important justification for beamlines

My introduction to EXAFS

Finished my PhD thesis in 1976: ‘Thermal vacancies in Solid ^{3}He’

- Constructed a diffraction capable dilution refrigerator cryostat
- Precision x-ray diffraction measurements

These two backgrounds made me attractive post-doc candidate

- No one had EXAFS experience but at least I had an x-ray background
- Ed was looking to make low temperature measurements

The first 'hutches' at SSRP

Beamline 1-5

Beamline 2-3

My challenge was to design a He cryostat that fit through the bars

Exciting time with many new applications of EXAFS being tested

My first EXAFS paper:

Heald, Steve M., and Edward A. Stern. "Anisotropic X-ray absorption in layered compounds." Physical Review B 16, no. 12 (1977): 5549.

Had to understand thickness effects on the amplitude and the L edge polarization dependence

Other early topics included:

EXAFS of proteins (Ferritin)

Surface EXAFS (Br and Kr on graphite)

Fluorescence detection (the filter-slit detector)

The later generation storage rings greatly expanded the applications of EXAFS

- microXAFS (sub-micron resolution)
- Lower concentrations (sub ppm possible)
- Surfaces and interfaces
- Extreme conditions
- Time resolved (psec at storage rings, fsec at FEL’s)

1979 – Hired by BNL to be part of the X-11 PRT lead by Dale

NSLS - 1982

Rocky start see:

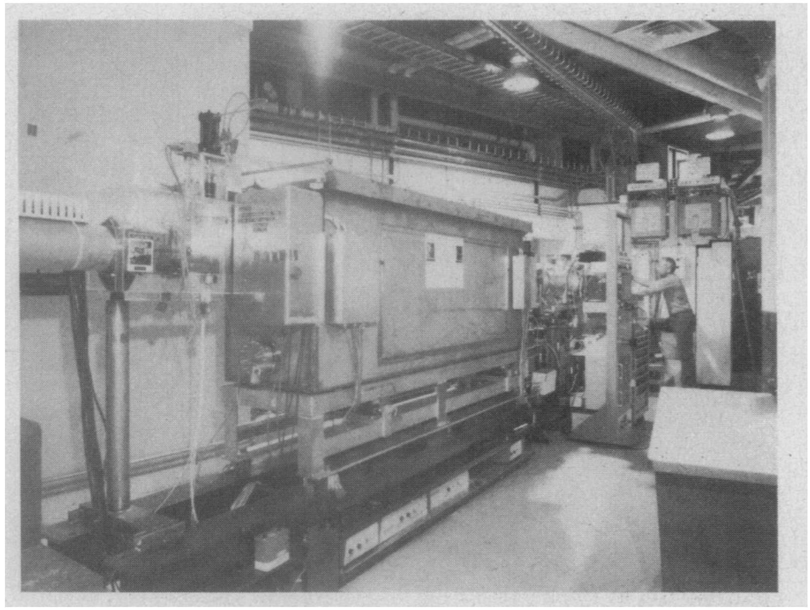
Crease, Robert P. "The national synchrotron light source, Part I: Bright idea." Physics in perspective 10 (2008): 438-467.

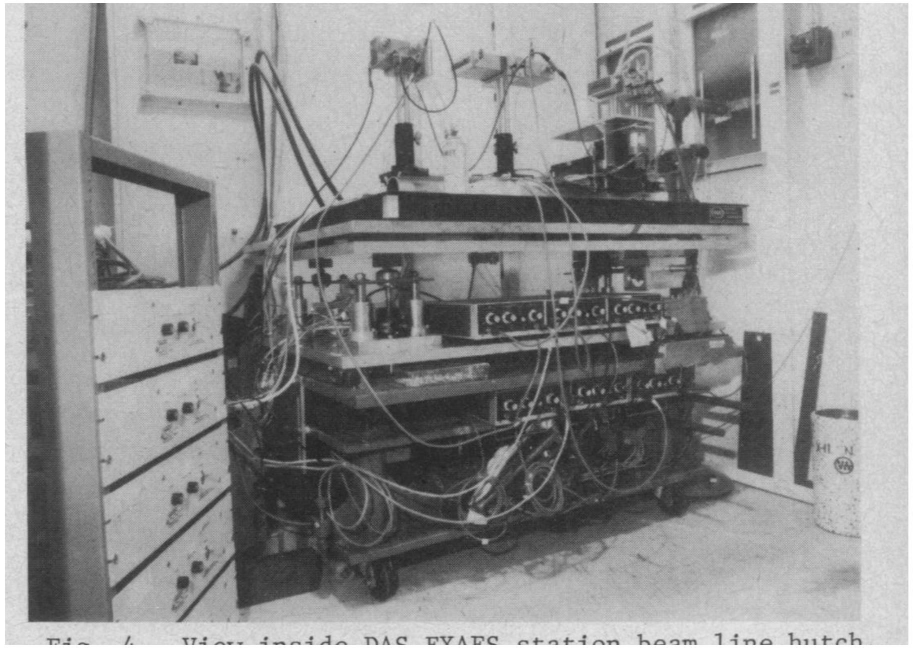
Crease, Robert P. "The national synchrotron light source, part II: the bakeout." Physics in Perspective 11 (2009): 15-45.

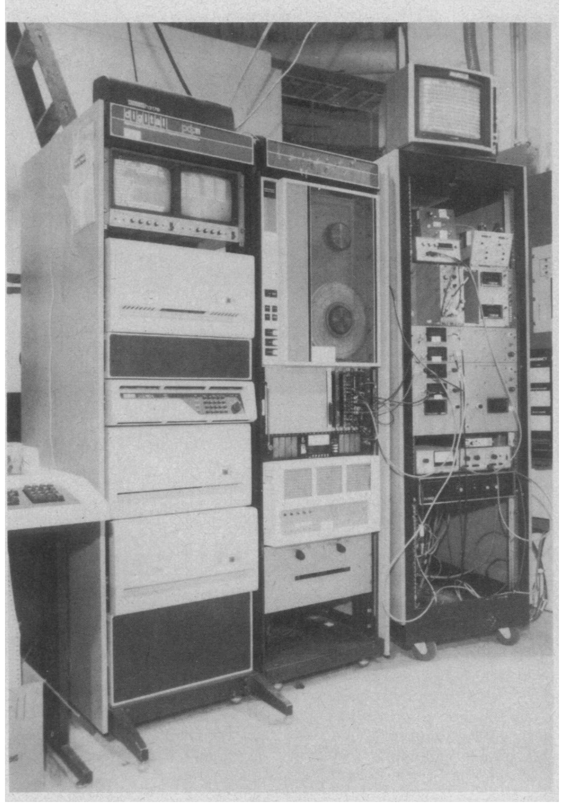
Operations started in 1985 – greatly expanding the opportunities for EXAFS along with a few other dedicated sources coming online in Europe and Japan

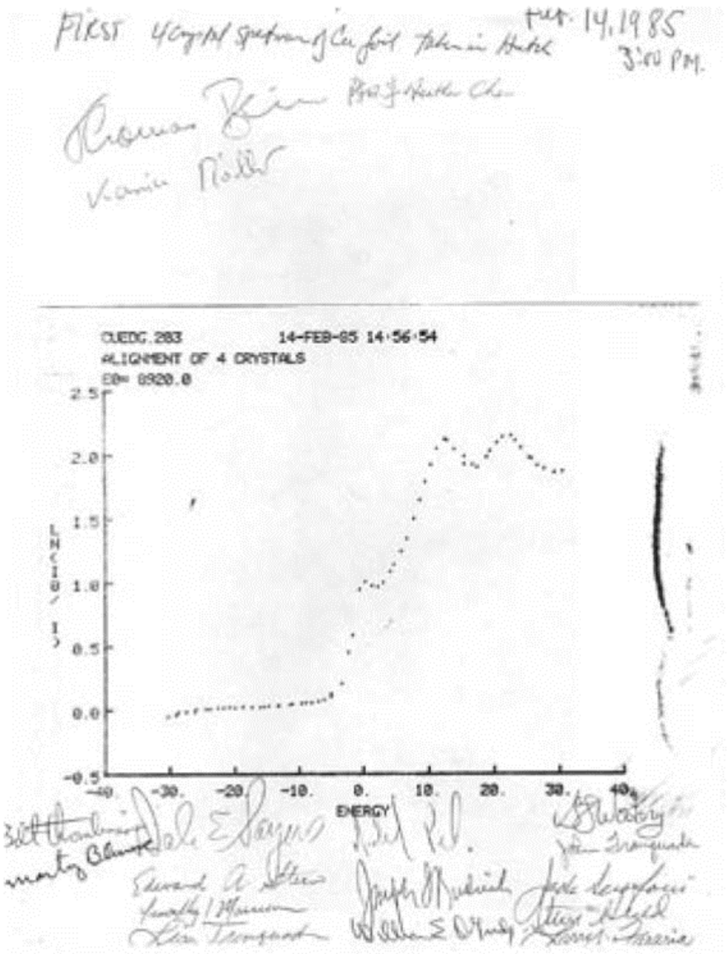
At the same time analysis methods improving: FEFF and EXCURVE allowed better analysis of higher shells

Beamline X-11A NSLS





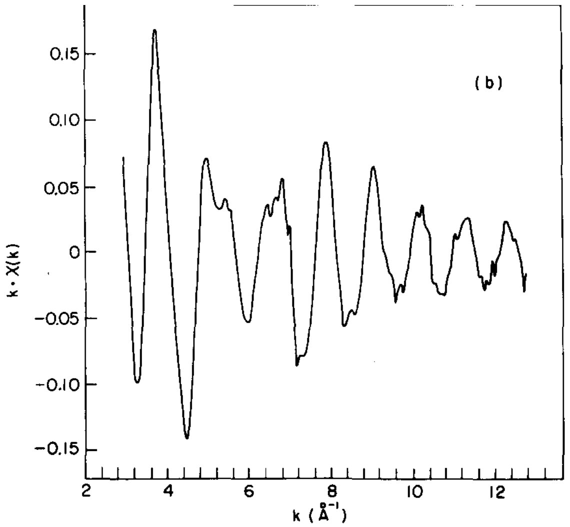




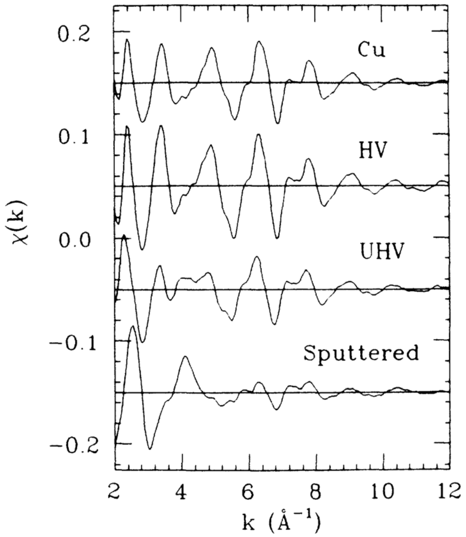
Working on the NSLS beamlines introduced me to x-ray optics

- Realized that combining reflection of x-rays with EXAFS a promising direction
  - Previous work looked at reflected beam – better option is fluorescence detection
  - Demonstrated sub-monolayer sensitivity
  - Buried interfaces
  - Multilayer interfaces using standing waves

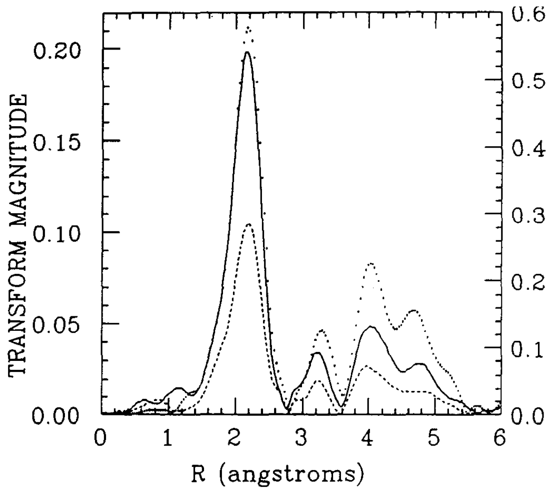
~ 1 monolayer Au
Physics Letters, 103A, 1984



Cu EXAFS at Cu/Al interface
Phys Rev B, 38, 1016 (1988)

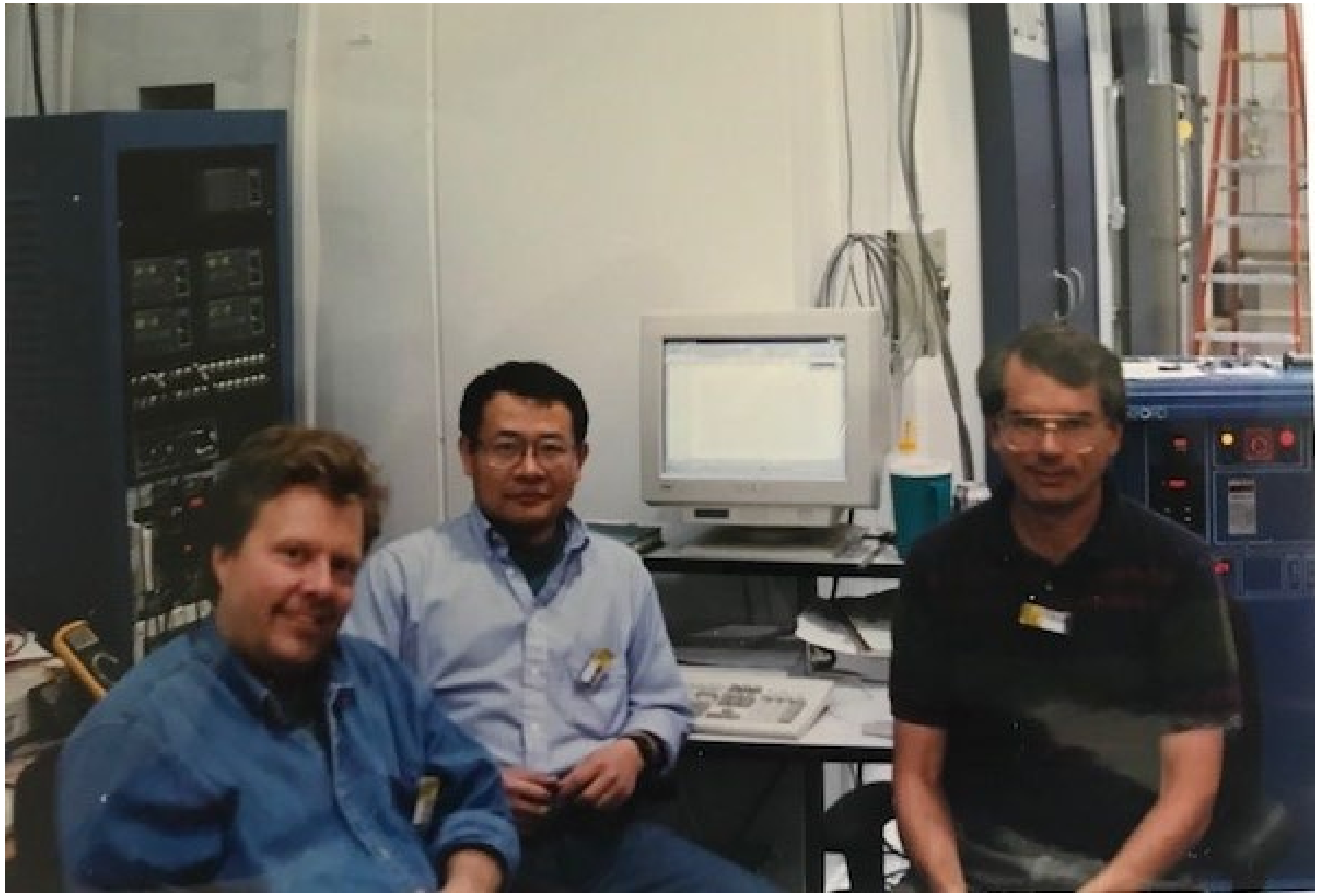


Ni EXAFS in a Ni/Ti multilayer
J. Appl. Phys., 65, 290 (1989)

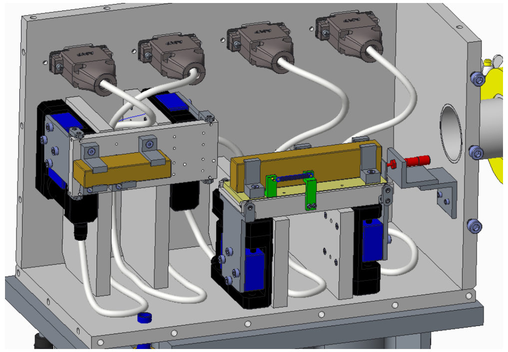


The third generation, the APS where I started in 1993 with the PNC-CAT headed by Ed

1997- Commissioning of beamline 20-ID-A
Dale Brewe, Detong Jiang, and myself



At APS my main new efforts were with microprobes and microXAFS



- Several microprobes commissioned (1-5 mm beams)
    - Tapered capillaries
    - KB mirrors

- Worked with PNNL on Hanford cleanup issues
    - microXAFS for speciation (primarily U and Tc)

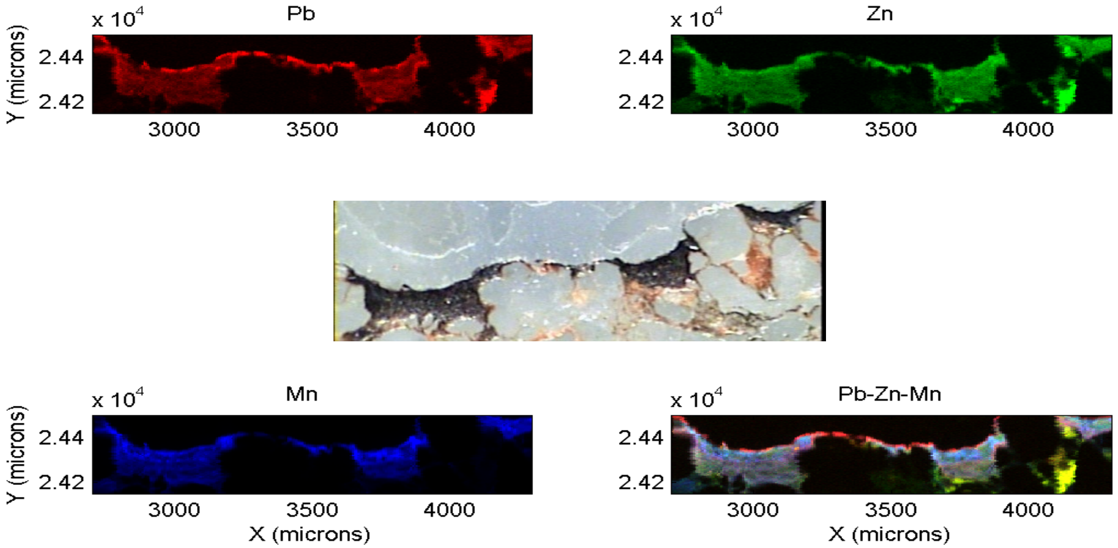
- Small beams allow for new detection options
    - More compact crystal analyzers

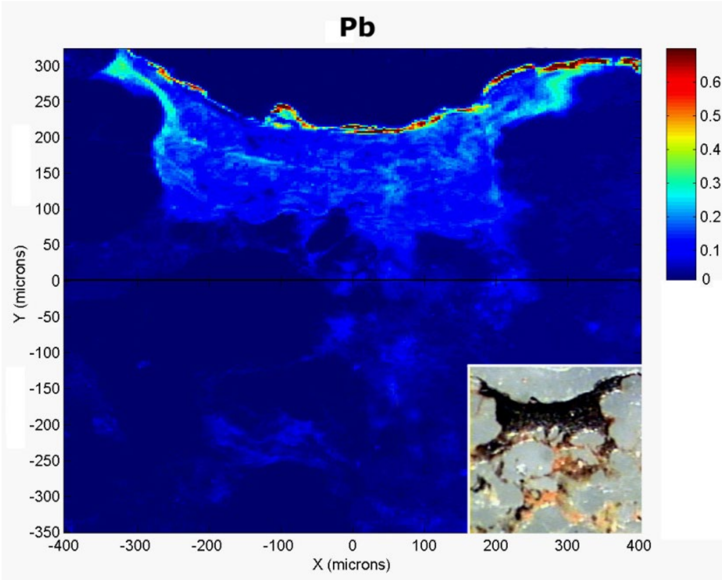
Can x-ray fluorescence date desert varnish (petroglyphs)?

Use micro X-rays to understand and calibrate the field measurements

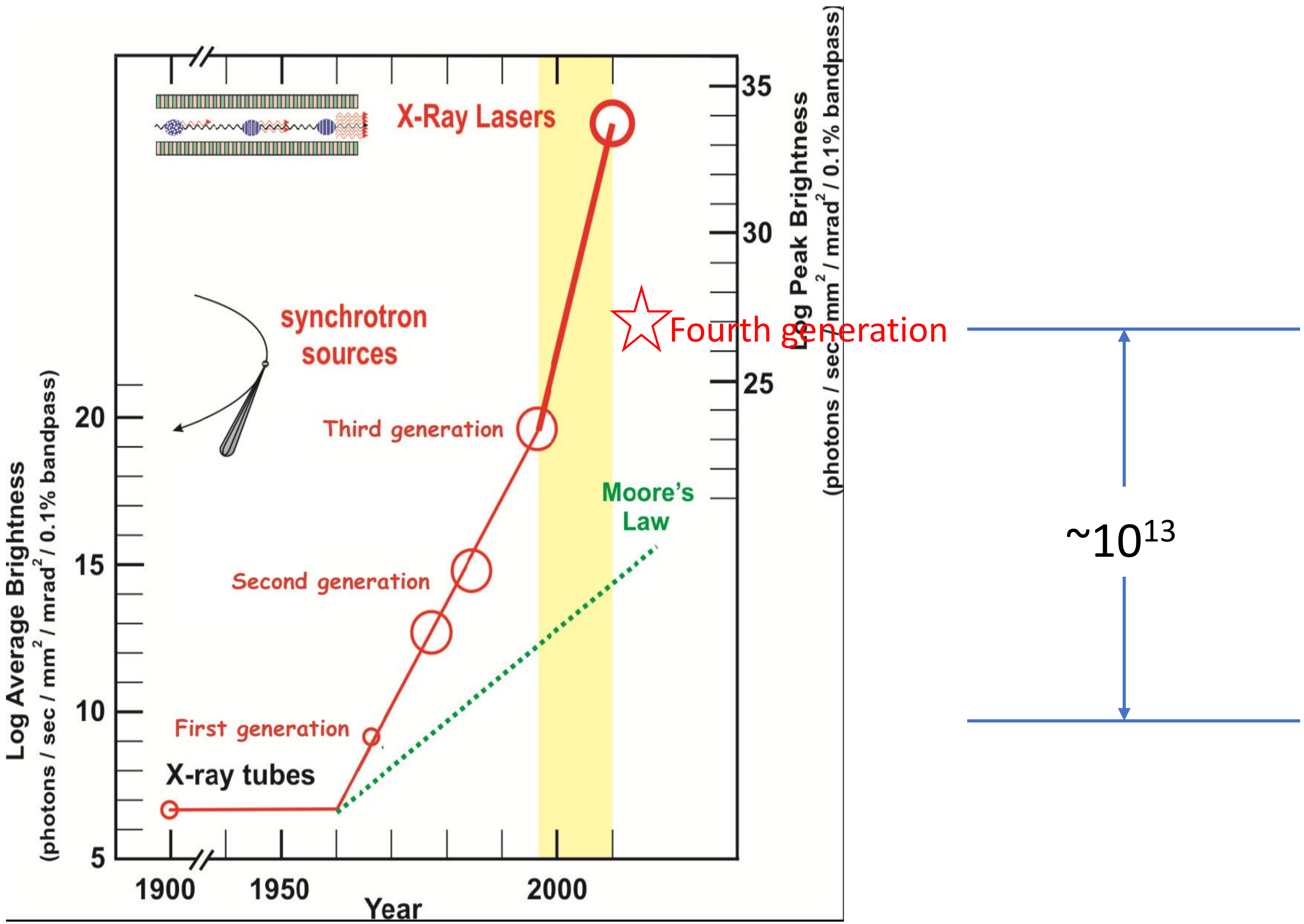
Farrel Lytle

Look at cross sections to understand depth dependence

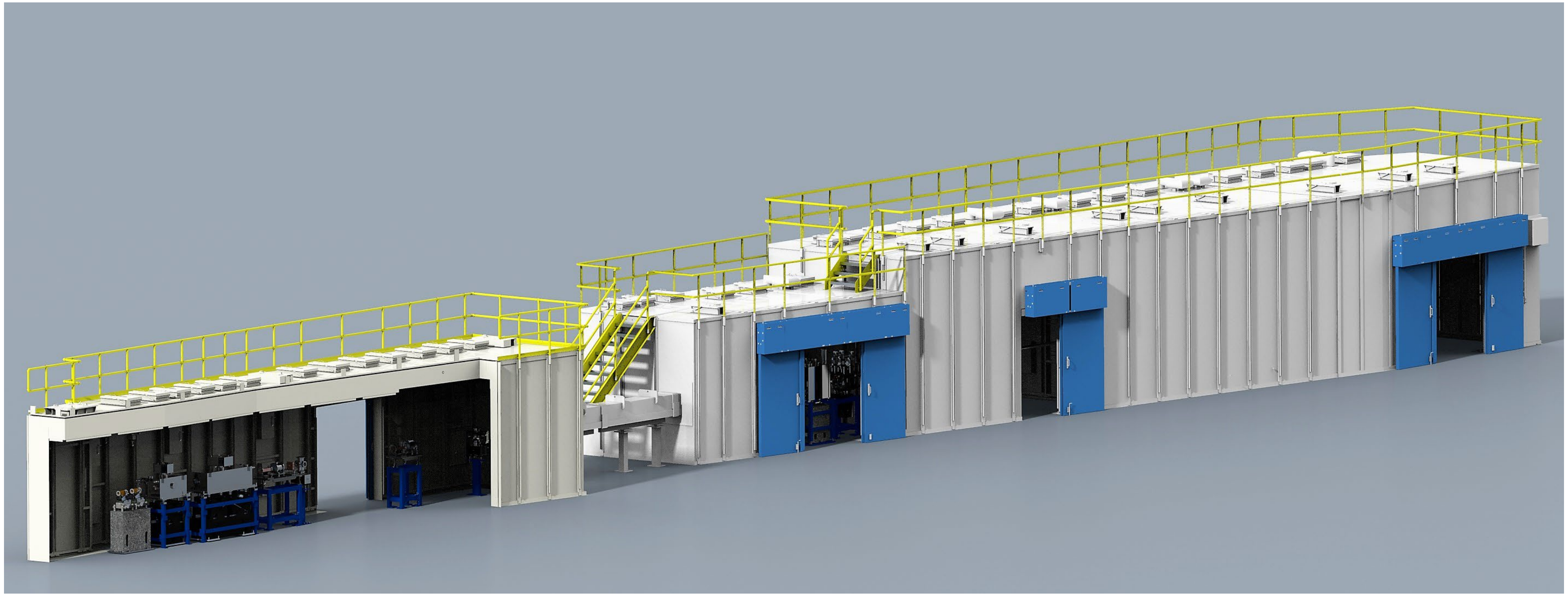




SSRP first generation x-ray facility – now starting the fourth generation



My last project – beamlines at sector 25 at the APS



Initial commissioning completed – ready for the new APS ring next summer

EXAFS STUDIES OF DOPED Nb_3Sn SUPERCONDUCTORS

Steve Heald

X-ray Science Division
Advanced Photon Source

Chiara Tarantini, Peter J. Lee, Michael Brown, and David Larbalestier

National High Magnetic Field Laboratory, Florida State University

IUCR 2017

Main Topics

- Some History – started in 1986!
  - Demonstrates some of the advances in EXAFS methods
- Motivation
- EXAFS of A15 compounds
- Results for Ta, Ti, and Hf doping
- Conclusions

For more details see:
Heald et al, "Evidence from EXAFS for Different Ta/Ti Site Occupancy in High Critical Current Density Nb3Sn Superconductor Wires," Sci. Rep. 8, 4798-1-4798-9 (2018). DOI: 10.1038/s41598-018-22924-3

Tarantini et al,, "Origin of the enhanced Nb_3Sn performance by combined Hf and Ta doping," Sci. Rep. 11, 17845 (2021). DOI: 10.1038/s41598-021-97353-w

Some History

1980's: Bronze process for making Nb_3Sn wires being developed at BNL
Explored the use of dopants such as Ti and Ta to improve magnetic properties

Tafto etal, J. Appl. Phys. 55 (12), 15 June 1984: Ti and Ta in Nb site from electron channeling

Heald etal, Adv. in Cryo. Eng. Mat., 471-478 (1986): EXAFS confirmed Ta in Nb site

Early 1986, High Tc materials discovered: Work on Nb_3Sn mostly ended

R. Flükiger et al. Cryogenics 48 (2008) 293–307: Ta on Nb sites and Ti on Sn sites based primarily on stoichiometry considerations

Recently: Interest in Nb_3Sn renewed with potential applications in large projects
LHC upgrade, Future Circular Collider (FCC), Fusion magnets (1000's of tons will be needed)
Expense and industrial capability for High Tc materials make them questionable

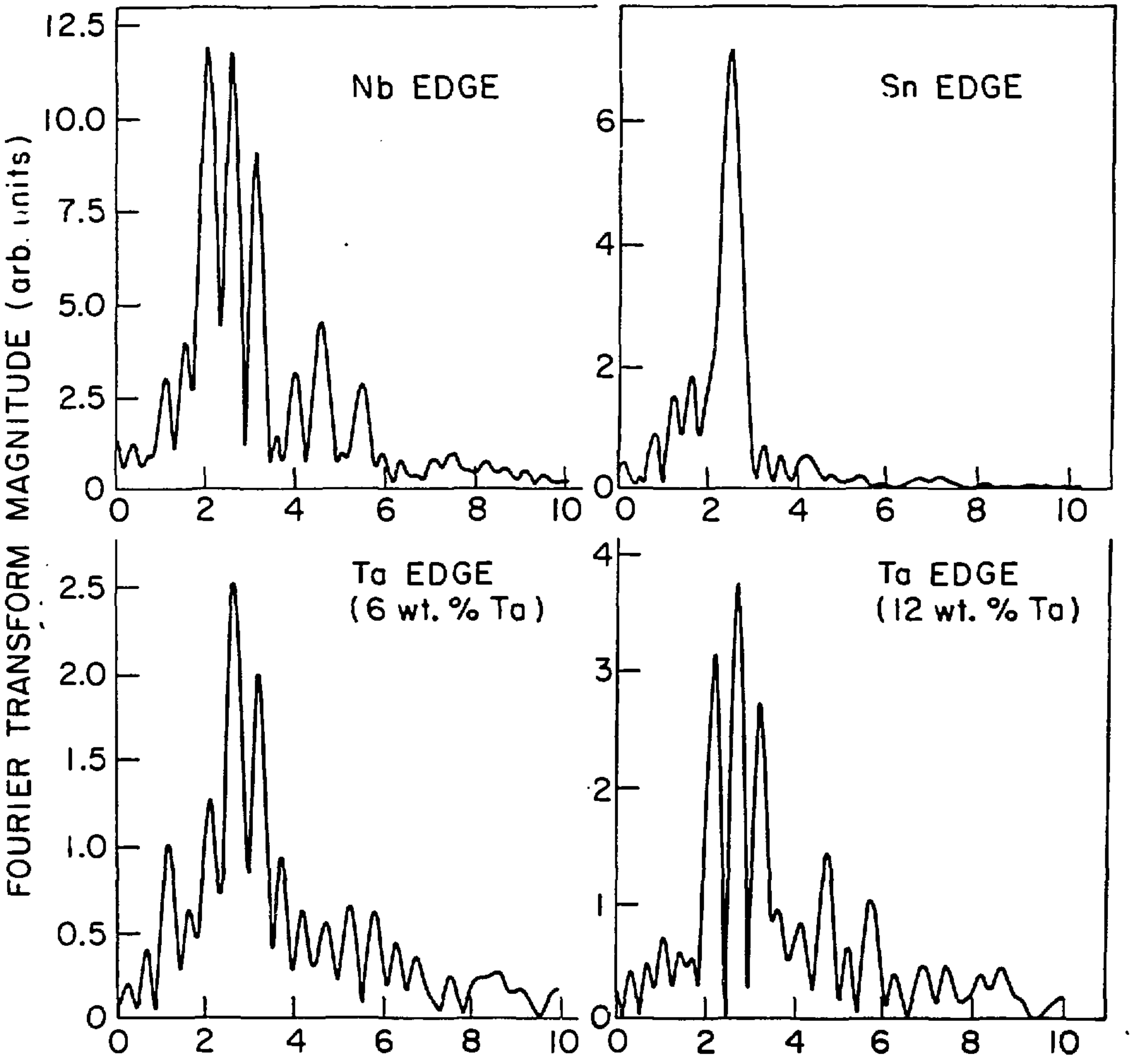
Ta doped Nb_3Sn

Early EXAFS data

Ribbon samples allowed transmission measurements after etching off the outer bronze layers

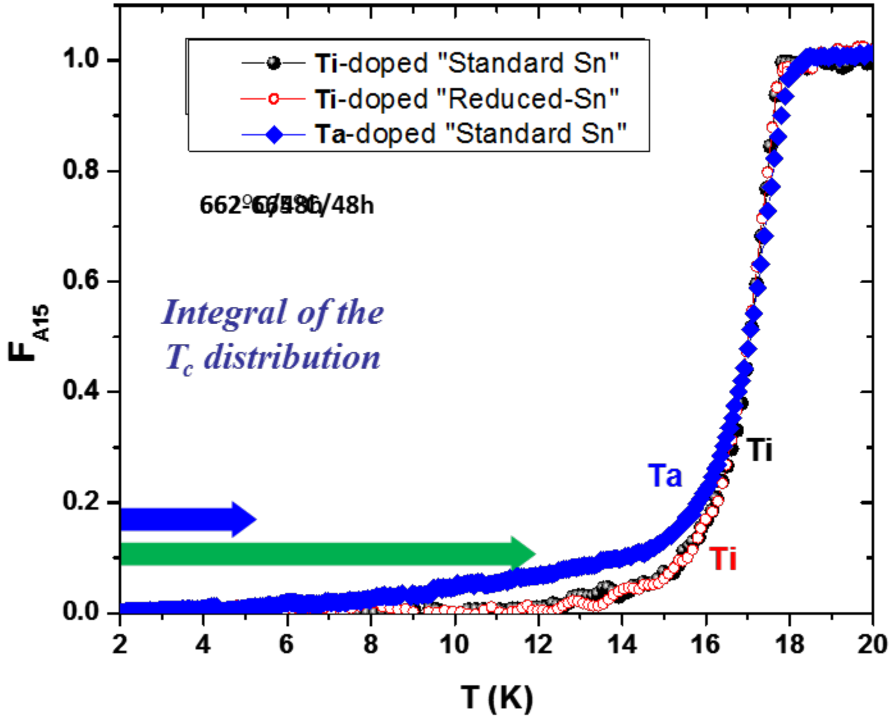
Clear much of Ta in Nb sites

Heald etal, Adv. in Cryo. Eng. Mat., 471-478 (1986):



Both Ta and Ti doping used to improve magnetic properties

Better understanding of the mechanism could lead to improved properties



- *Ti-doping*
  – *No A15 phase with T_c below ~12 K*

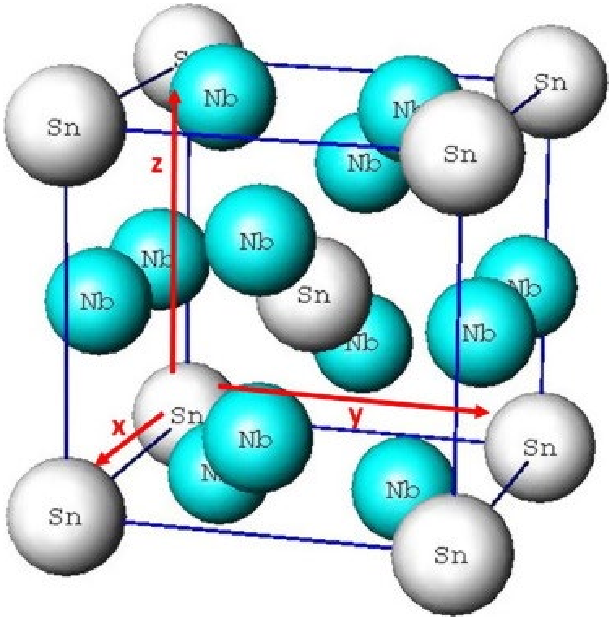
- ***Ta-doping***
  - A15 phase with T_c down to ~5-6 K

Ta homogeneity can be improved with higher T treatment but this caused other problems

Is the difference due to different lattice locations?

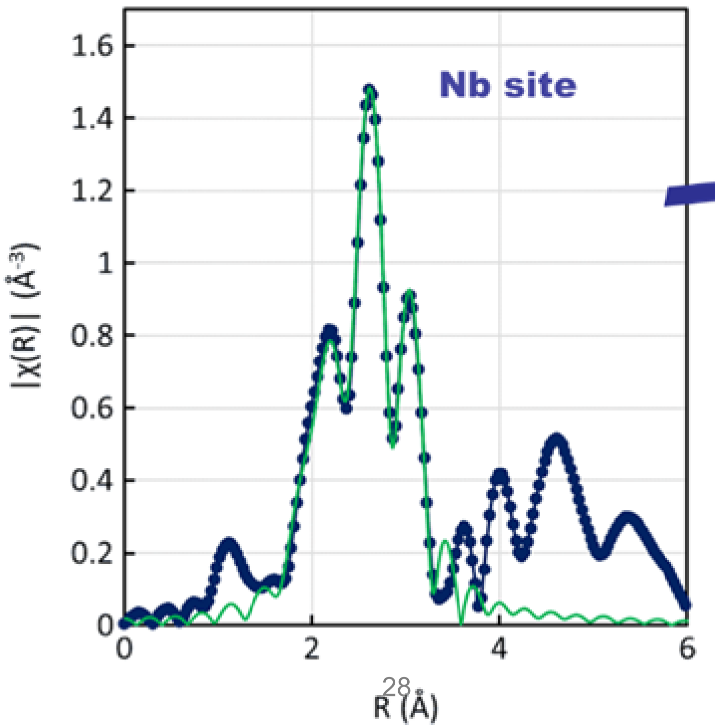
Should revisit EXAFS studies of Ta and Ti doped Nb_3Sn with modern methods and analysis

EXAFS from the A-15 structure



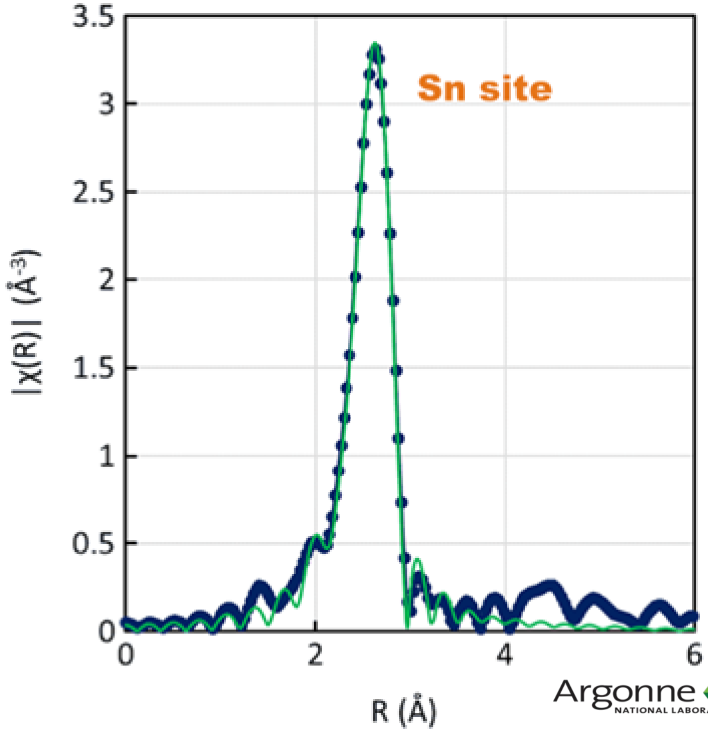
Nb EXAFS

Scattering Neighbors	N	R (Å)
Nb – Nb1	2	2.644
Nb – Sn	4	2.956
Nb – Nb2	8	3.238



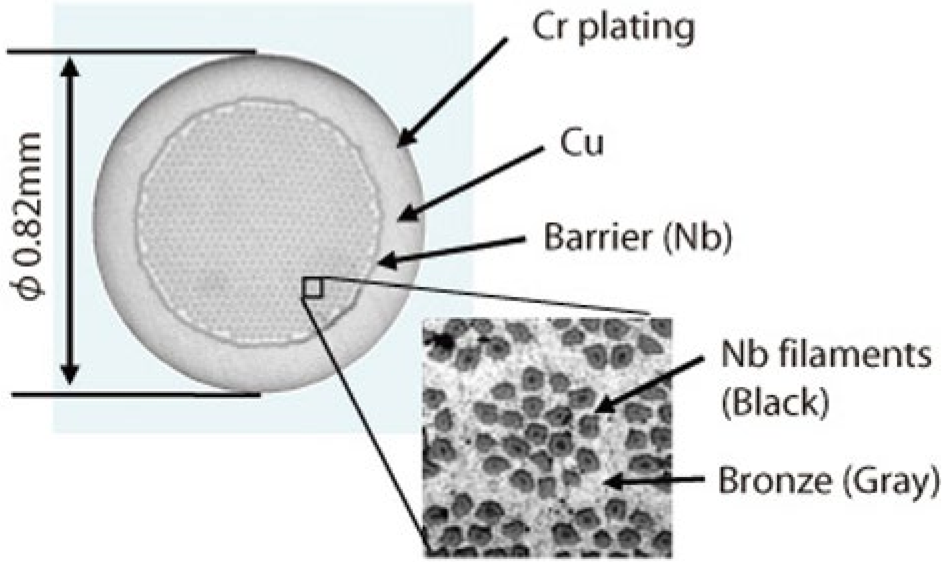
Sn EXAFS

Scattering Neighbors	N	R (Å)
Sn – Nb	12	2.956



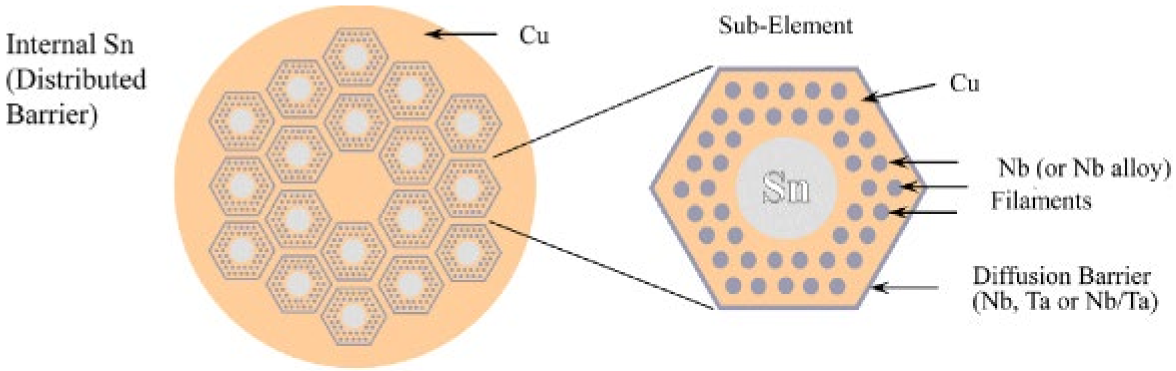
The Bronze process for making Nb_3Sn

Ductile wires of Nb in Cu-Sn bronze can be easily be drawn into wires – Nb_3Sn formed upon annealing



Okuno, K. et al., IEEE Transaction Superconductivity, vol.16, 2006, p.880-885

Internal Tin variation – doping for Ta by using Nb-Ta alloy for all strands
For Ti by adding some Nb-Ti strands



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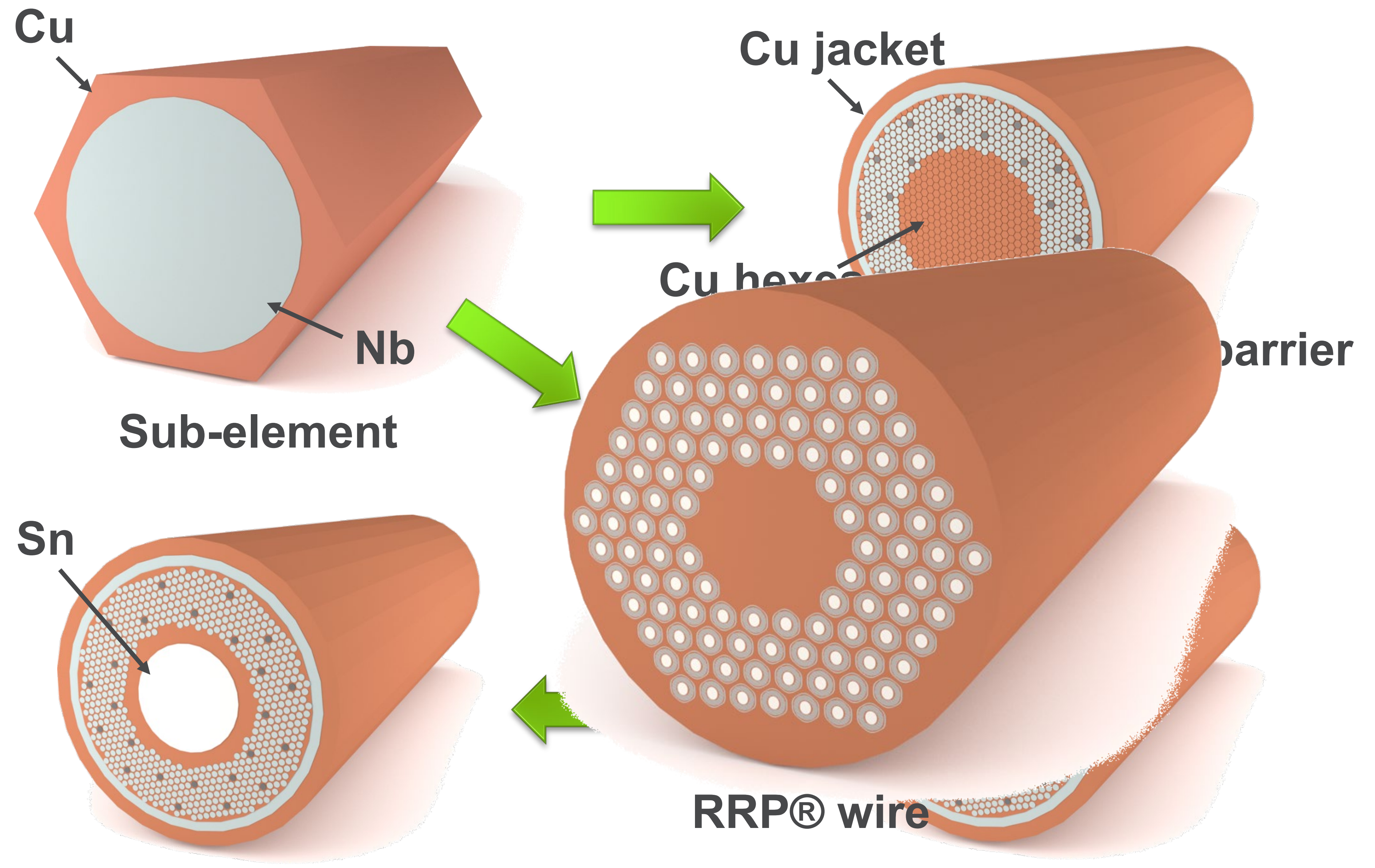
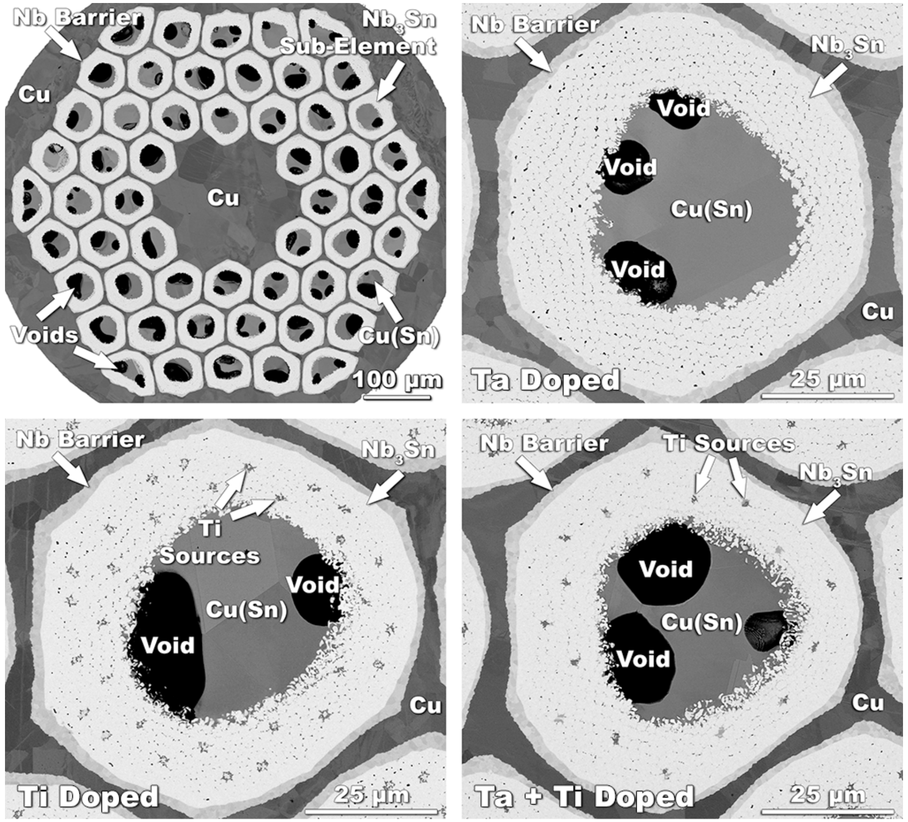


WIRES PROPERTIES AFTER REACTION



Final heat treatment at 40 h at 640°C forms a continuous A15-phase annulus

- Ta-doped samples use Nb-Ta diffusion barrier and Nb-Ta rods
- Ti-doped samples use Nb barrier, mostly Nb rod and few Nb-Ti rods as Ti source
- Note correlation of at%

Sample ID	Dopant	Billet ID	Design Subs/Stack	Final HT	Nb at %	Sn at %	Ta at %	Ti at %	$T_{c,Onset}$ K	$\mu_0 H_k$ T	Non-Cu J_c(12T,4.2K) A/mm²	A15 layer J_c(12T,4.2K) A/mm²
Ta	4 at. %Ta	8781	54/61	640°C/40h	72.46	25.17	2.37		18.4	22.66	2712	4860
Ta+Ti	4 at. %Ta +1 at%Ti	9362-5	54/61	640°C/40h	71.41	24.64	2.60	1.35	17.9	24.59	2622	4528
Ti#1	2 at%Ti	9415-BE	54/61	640°C/40h	74.87	23.40		1.73	18.1	23.75	2872	5065
Ti#2	2 at%Ti	14895FE	108/127	662°C/48h	75.59	23.10		1.31	17.9	25.45	3035	4896

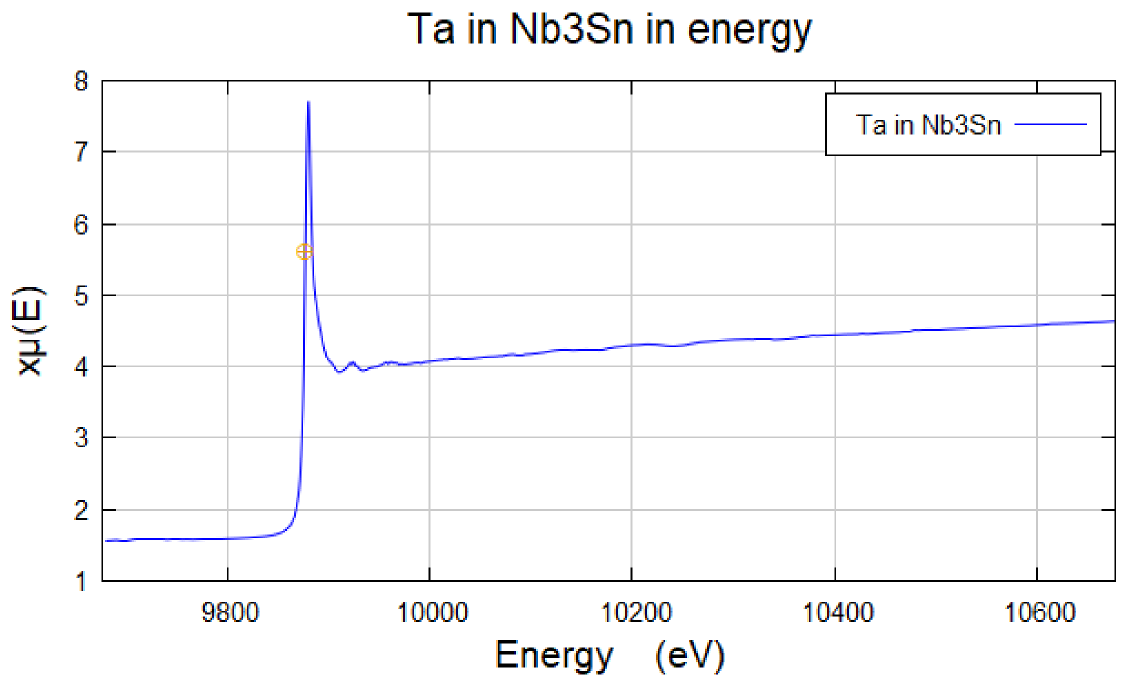
DIFFICULTIES FOR EXAFS MEASUREMENTS

- Hf, Cu, and Ta fluorescence overlap (Hf:7.85 and 7.90, Cu:8.04, Ta:8.09 and 8.15 keV)
  - Cu surrounds the thin filaments
- Typical filament width ~10 micron
- EXAFS fairly weak and need data to high k for good discrimination of sites
- Diffraction from small grains

Solution

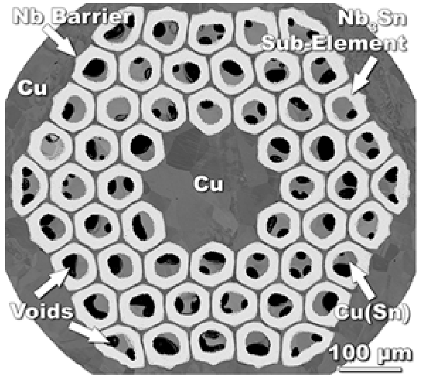
Bent Laue detector

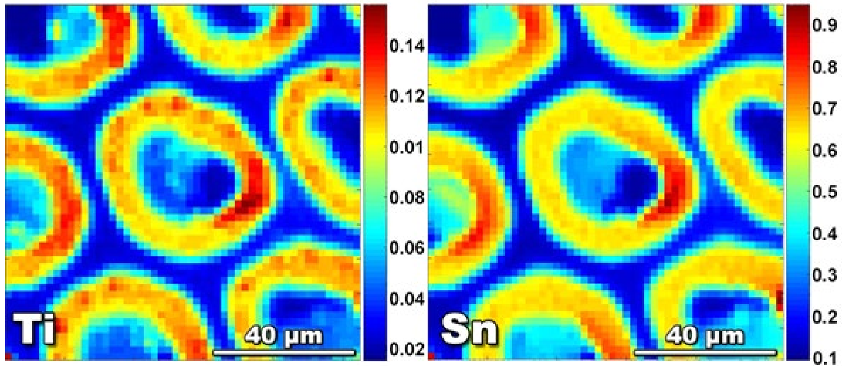
2 micron beam at 20ID microprobe



EXAFS DATA

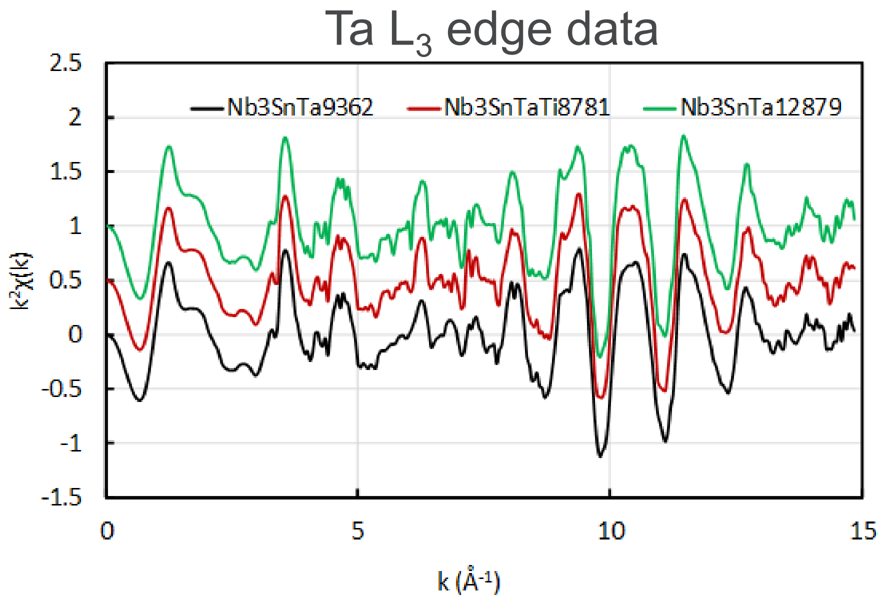
20-ID microprobe station – 2 µm beam size

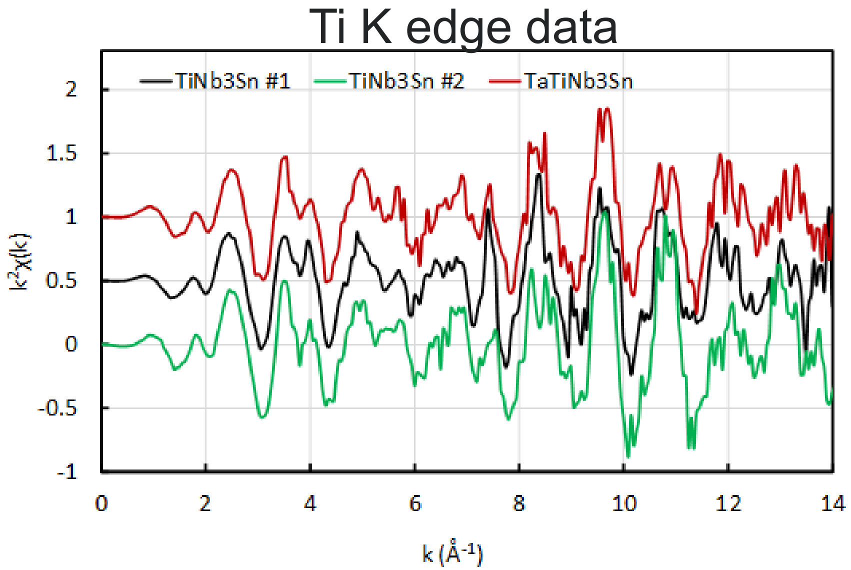




Ti data – standard fluorescence (4 element vortex)

Ta data – bent Laue crystal analyzer to reduce Cu interference

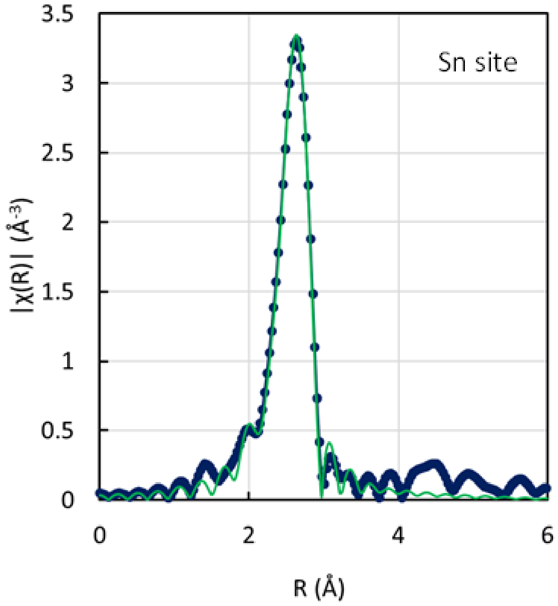


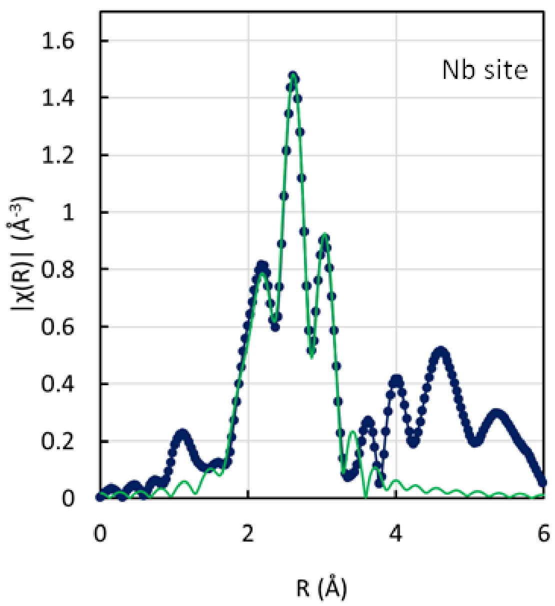


EXAFS ANALYSIS

Demeter analysis package used

Check modeling by fitting the Nb and Sn edges in pure Nb_3Sn





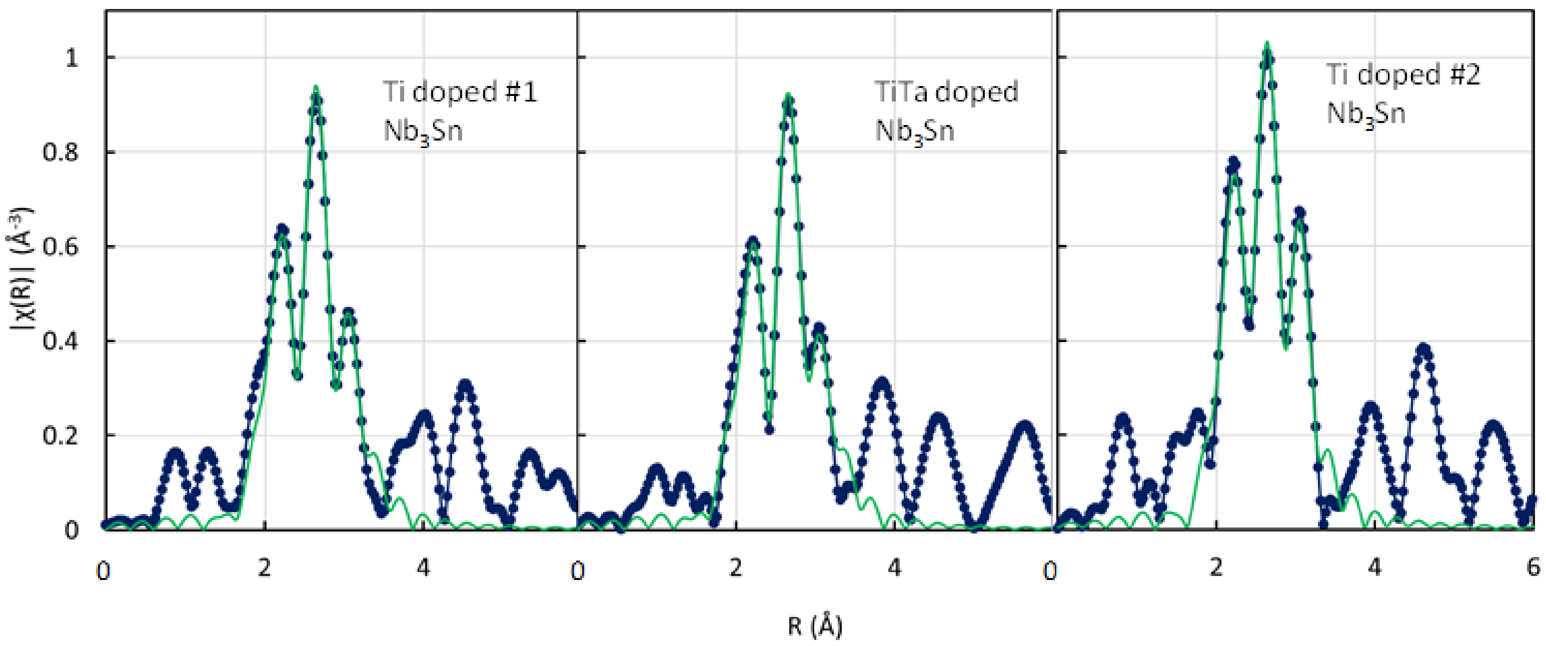
Fitting parameters:
Note those marked in bold are independent measurements of the same parameters

Scattering Path	N	R (Å)	R (fit)	σ^2 (Å^2)	S_0^2	E_0 (eV)
Nb – Nb1	2	2.644	2.65 (0.010)	0.0060 (0.0008)	1.06	-1.80
Nb – Sn	4	2.956	**2.95 (0.010)**	**0.0044 (0.0006)**	1.06	-1.80
Nb – Nb2	8	3.238	3.24 (0.010)	0.0100 (0.001)	1.06	-1.80
Sn – Nb	12	2.956	**2.95 (0.010)**	**0.0049 (0.0005)**	0.96	1.02

Ti ANALYSIS

Allow for both sites
Fix coordination numbers

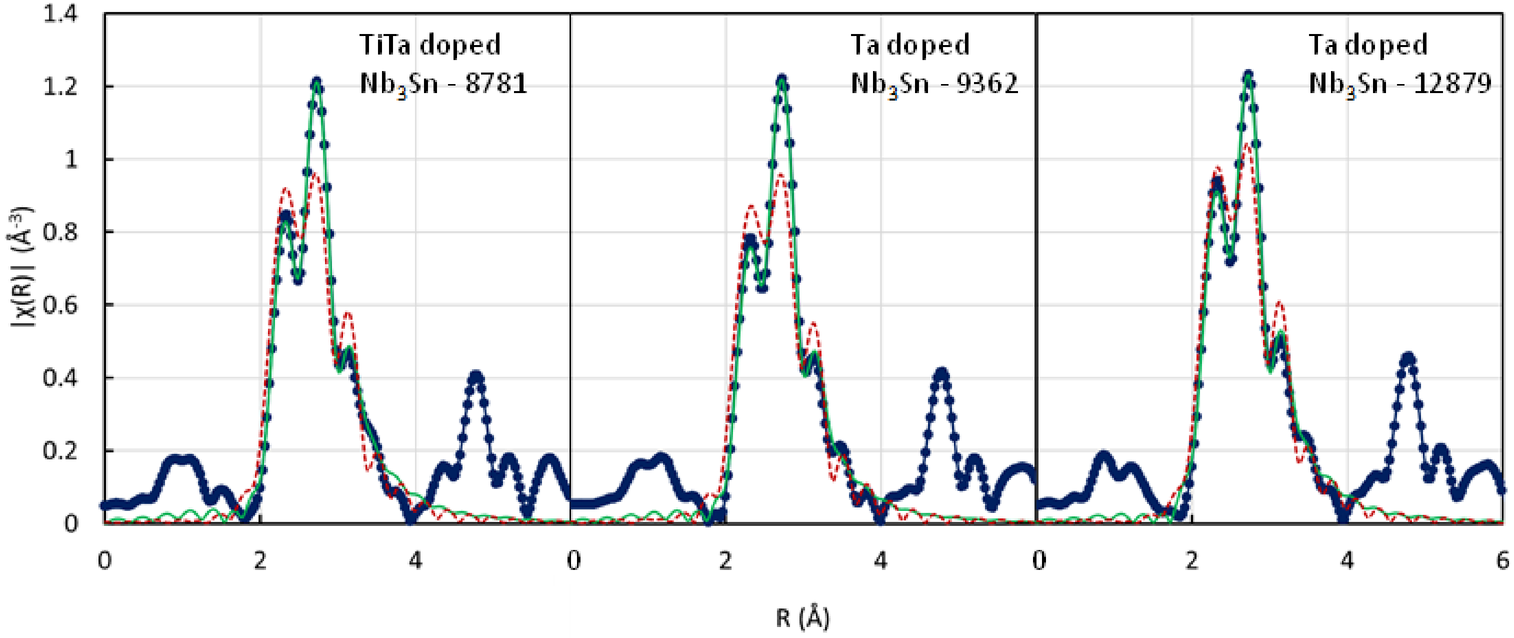
All fits refined only Nb site occupancy



Sample	Scattering Path	N (Fixed)	R (Å)	σ^2 (Å^2)	Site Occupancy
Ti #1 doped	Ti – Nb1	2	2.67 (0.02)	0.0096 (0.002)	1.0
	Ti – Sn	4	2.91 (0.01)	0.0066 (0.001)	1.0
	Ti – Nb2	8	3.25 (0.02)	0.0164 (0.003)	1.0
Ti #2 doped	Ti – Nb1	2	2.66 (0.02)	0.0054 (0.002)	1.0
	Ti – Sn	4	2.93 (0.02)	0.0059 (0.002)	1.0
	Ti – Nb2	8	3.24 (0.03)	0.0110 (0.003)	1.0
TaTi doped	Ti – Nb1	2	2.66 (0.01)	0.0079 (0.002)	1.0
	Ti – Sn	4	2.92 (0.01)	0.0062 (0.001)	1.0
	Ti – Nb2	8	3.24 (0.02)	0.00147 (0.002)	1.0

Ta ANALYSIS

Red curves assume Nb site only



Allow for both sites
Fix coordination numbers

All fits refined to combined Nb and Sn sites (~30% Sn site)

Sample	Scattering Path	N (Fixed)	R (Å)	σ^2 (Å^2)	Site Occupancy
Ta9362	Ta – Nb1	2	2.64 (0.02)	0.0042 (0.002)	**0.68 (0.08)**
	Ta – Sn	4	2.96 (0.02)	0.0095 (0.002)	**0.68 (0.08)**
	Ta – Nb2	8	3.24 (0.02)	0.0084 (0.002)	**0.68 (0.08)**
	Ta – Nb	12	2.96 (0.02)	0.0095 (0.002)	**0.32 (0.08)**
Ta12879	Ta – Nb1	2	2.67 (0.03)	0.0044 (0.005)	**0.79 (0.10)**
	Ta – Sn	4	2.95 (0.02)	0.0078 (0.001)	**0.79 (0.10)**
	Ta – Nb2	8	3.24 (0.02)	0.0091 (0.004)	**0.79 (0.10)**
	Ta – Nb	12	2.95 (0.02)	0.0078 (0.003)	**0.21(0.10)**
TaTi8781	Ta – Nb1	2	2.68 (0.03)	0.0042 (0.002)	**0.70 (0.12)**
	Ta – Sn	4	2.96 (0.02)	0.0097 (0.003)	**0.70 (0.12)**
	Ta – Nb2	8	3.24 (0.02)	0.0087 (0.003)	**0.70 (0.12)**
	Ta – Nb	12	2.96 (0.02)	0.0097 (0.003)	**0.30 (0.12)**

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What does this mean? Antisite disorder?

Original supposition of site preference based on correlation between Nb and Ta concentration and Sn and Ti concentration

Antisite disorder known to be common in A15 compounds

Is the doping correlated with antisite disorder?

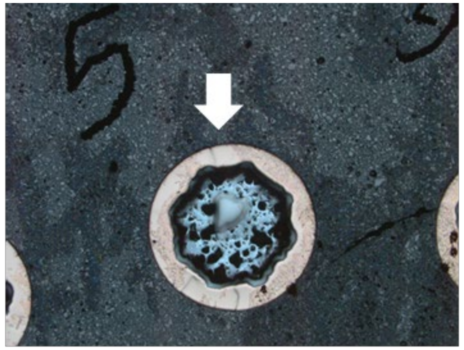
- EXAFS not very sensitive to antisite disorder of few percent
- Maybe diffraction studies needed?

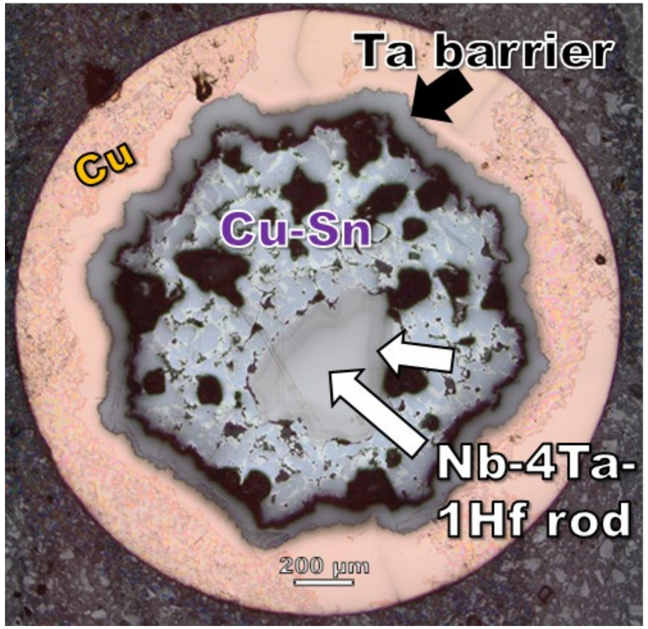
Sample ID	Dopant	Billet ID	Design Subs/Stack	Final HT	Nb at %	Sn at %	Ta at %	Ti at %	$T_{c,Onset}$ K	$\mu_0 H_k$ T	Non-Cu J_c(12T,4.2K) A/mm²	A15 layer J_c(12T,4.2K) A/mm²
Ta	4 at. %Ta	8781	54/61	640°C/40h	**72.46**	**25.17**	**2.37**		18.4	22.66	2712	4860
Ta+Ti	4 at. %Ta +1 at%Ti	9362-5	54/61	640°C/40h	**71.41**	**24.64**	**2.60**	**1.35**	17.9	24.59	2622	4528
Ti#1	2 at%Ti	9415-BE	54/61	640°C/40h	**74.87**	**23.40**		**1.73**	18.1	23.75	2872	5065
Ti#2	2 at%Ti	14895FE	108/127	662°C/48h	**75.59**	**23.10**		**1.31**	17.9	25.45	3035	4896

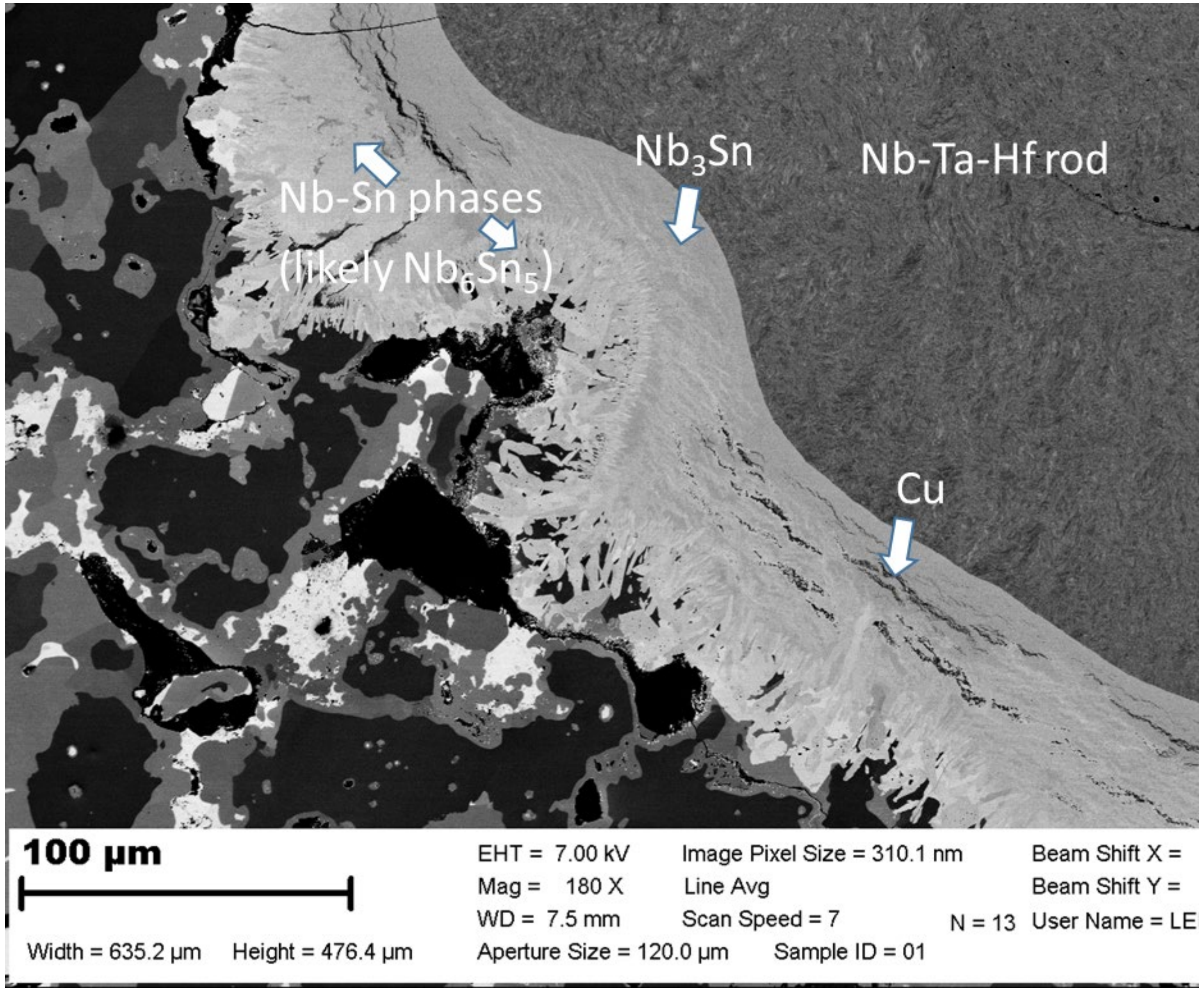
Hf DOPED Nb_3Sn

- High field magnetic properties can be improved by adding pinning centers
- ZrO_2 formed by adding Zr to Nb and SnO_2 as an oxygen source
  - Improved pinning but hurt other properties
- New work combining Ta with Zr and Hf
- Best properties with Ta + Hf additions but no SnO_2

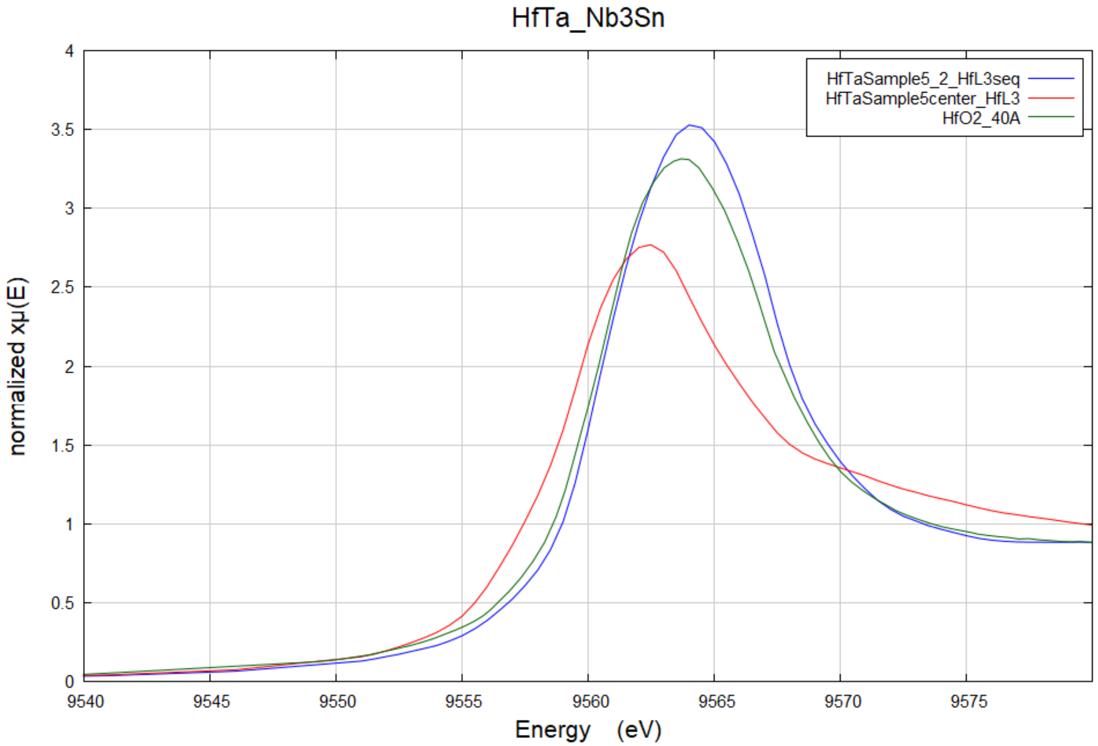
TA-HF SAMPLE

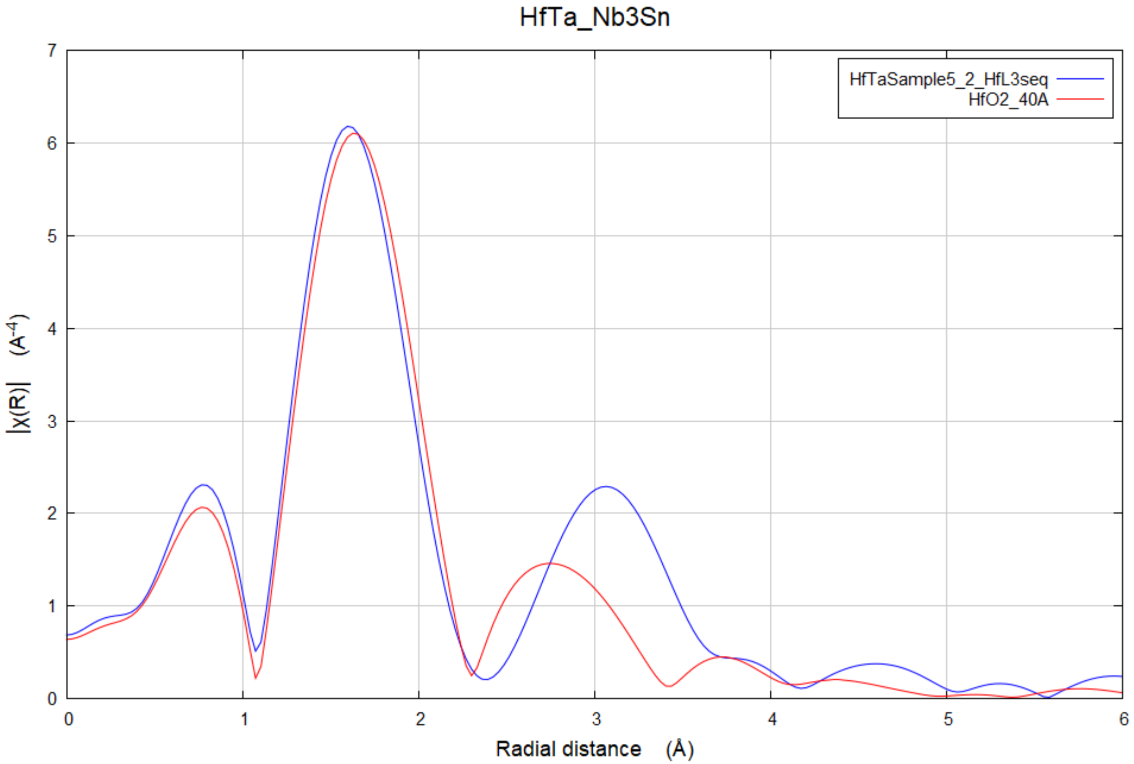



Ta barrier
Cu
Cu-Sn
Nb-4Ta-1Hf rod
200 µm


Nb-Sn phases
(likely Nb_6Sn_5)
Nb_3Sn
Nb-Ta-Hf rod
Cu
100 µm
Width = 635.2 µm
Height = 476.4 µm
EHT = 7.00 kV
Mag = 180 X
WD = 7.5 mm
Aperture Size = 120.0 µm
Image Pixel Size = 310.1 nm
Line Avg
Scan Speed = 7
Sample ID = 01
N = 13
Beam Shift X =
Beam Shift Y =
User Name = LE

Hf LOOKS OXIDIZED





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CONCLUSIONS

- EXAFS a good tool for looking at the lattice location of dopants
- Ti exclusively in Nb sites
- Ta mostly in Nb sites but also in Sn sites
- Hf oxidized even without an oxygen source

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