X-Ray Diffraction Based Phase Identification in NiTiHf Shape Memory Alloys with Variable Hf Content

(To B33, or Not To B33?)

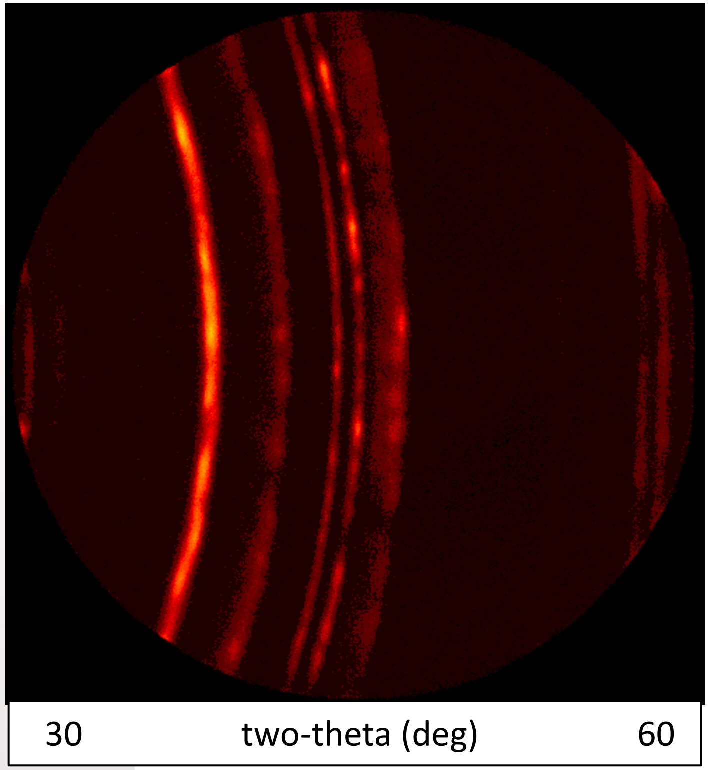
Laura Wilson[1],

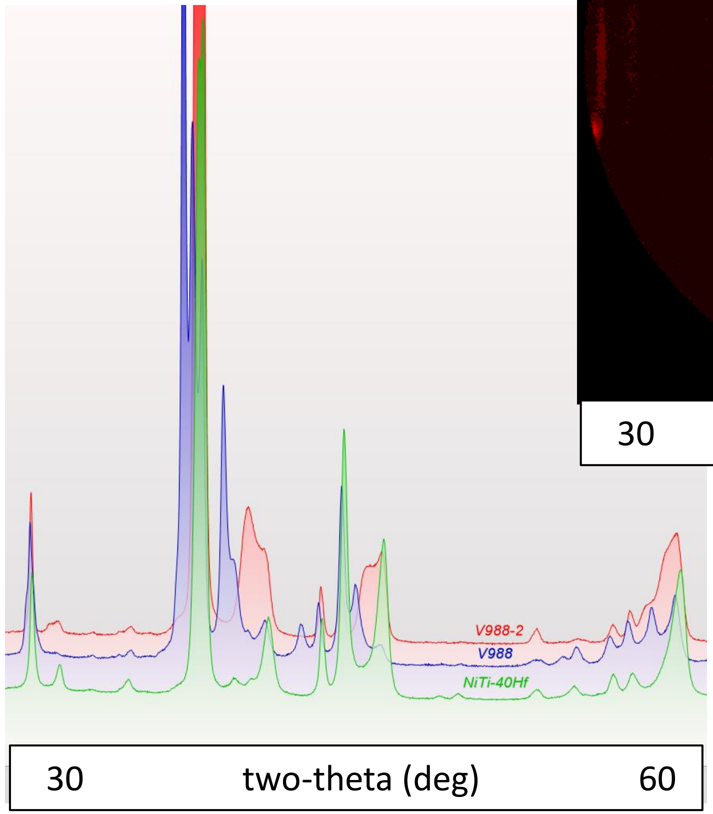
Elizabeth Young-Dohe[1], Othmane Benafan[1], Anita Garg[1&2], Richard Rogers[1], Peter Caltagirone[1&3]

[1]Materials and Structures Division, NASA Glenn Research Center, Cleveland, Ohio, USA
[2]University of Toledo, Ohio, USA
[3]Oak Ridge Associated Universities, Tennessee, USA

What are we going to cover?

- Introduction to Shape Memory Alloys (SMAs)
- High Temperature SMA – Why we even did this project
- What we did
  - The good stuff, about XRD!
- What it told us
- What still needs to be learned



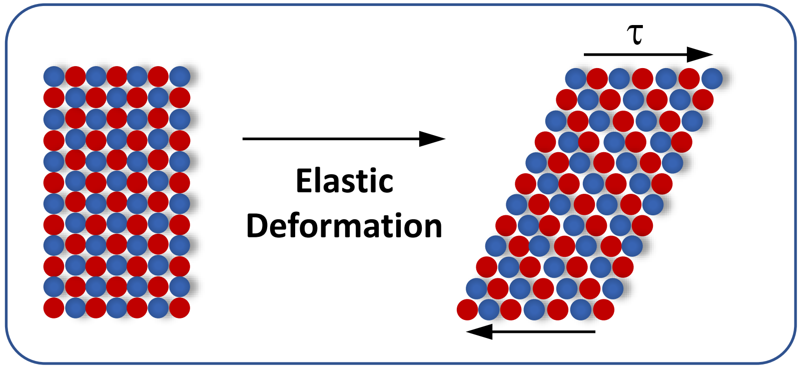


How do Shape Memory Alloys (SMAs) work?

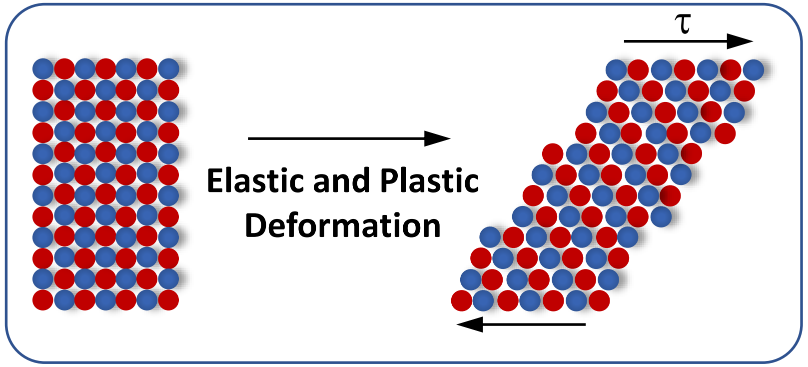
Conventional Metallic Materials

0.3% to 0.8% strain

Elastic Deformation (REVERSIBLE)



Plastic Deformation (PERMANENT)

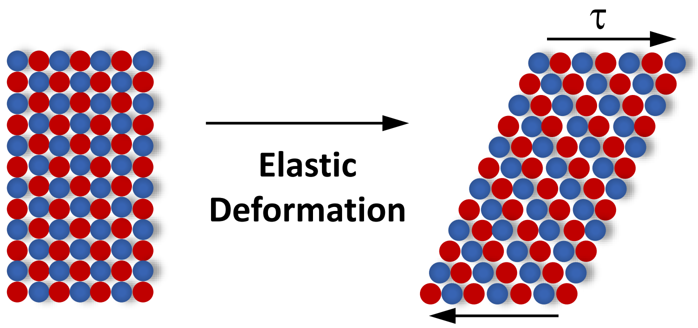


How do Shape Memory Alloys (SMAs) work?

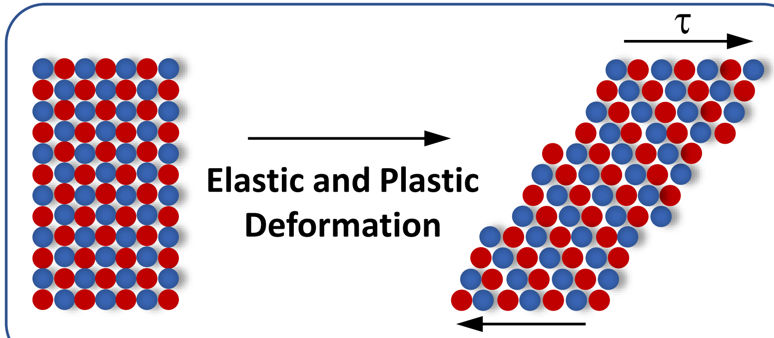
Conventional Metallic Materials

0.3% to 0.8% strain

Elastic Deformation (REVERSIBLE)



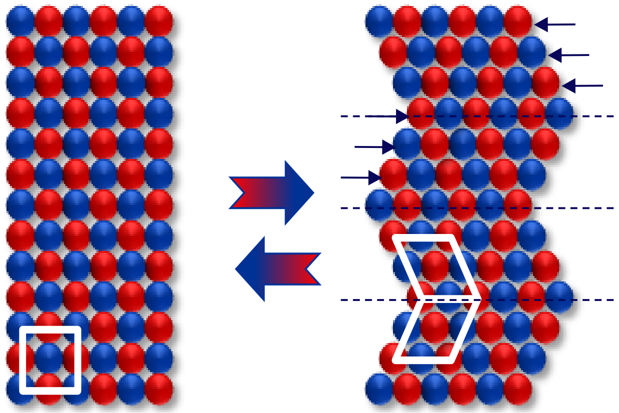
Plastic Deformation (PERMANENT)



Shape Memory Alloys

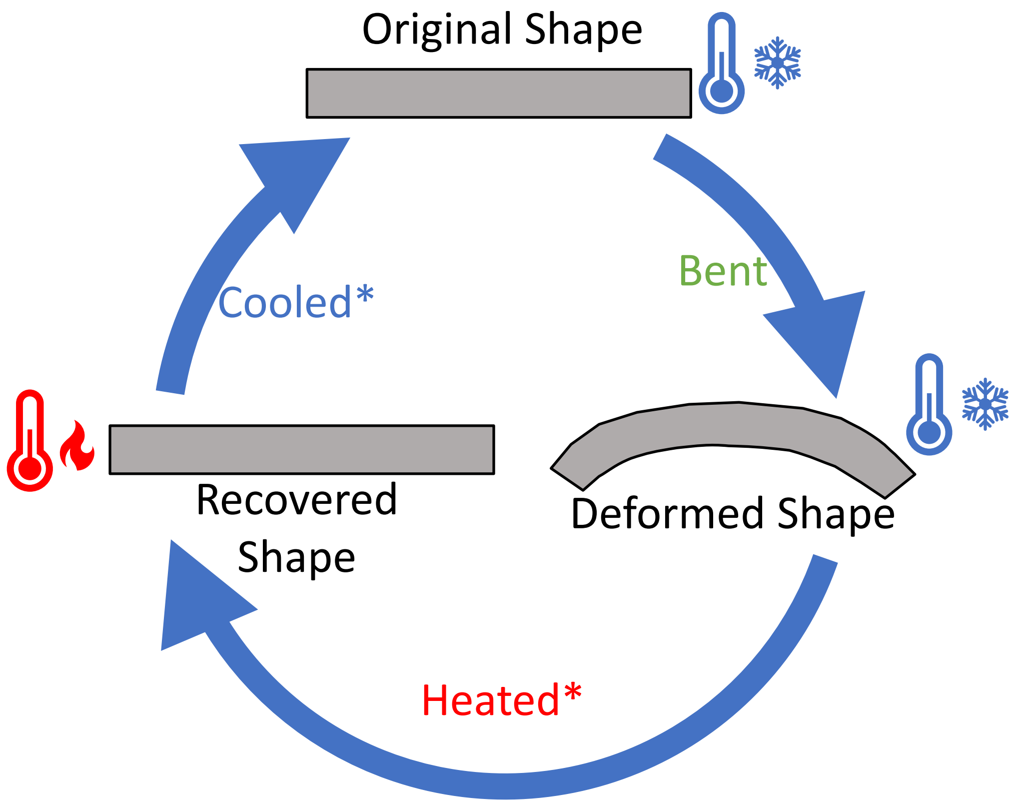
Up to 12% strain

Inelastic Deformation
(REVERSIBLE)—SMAs

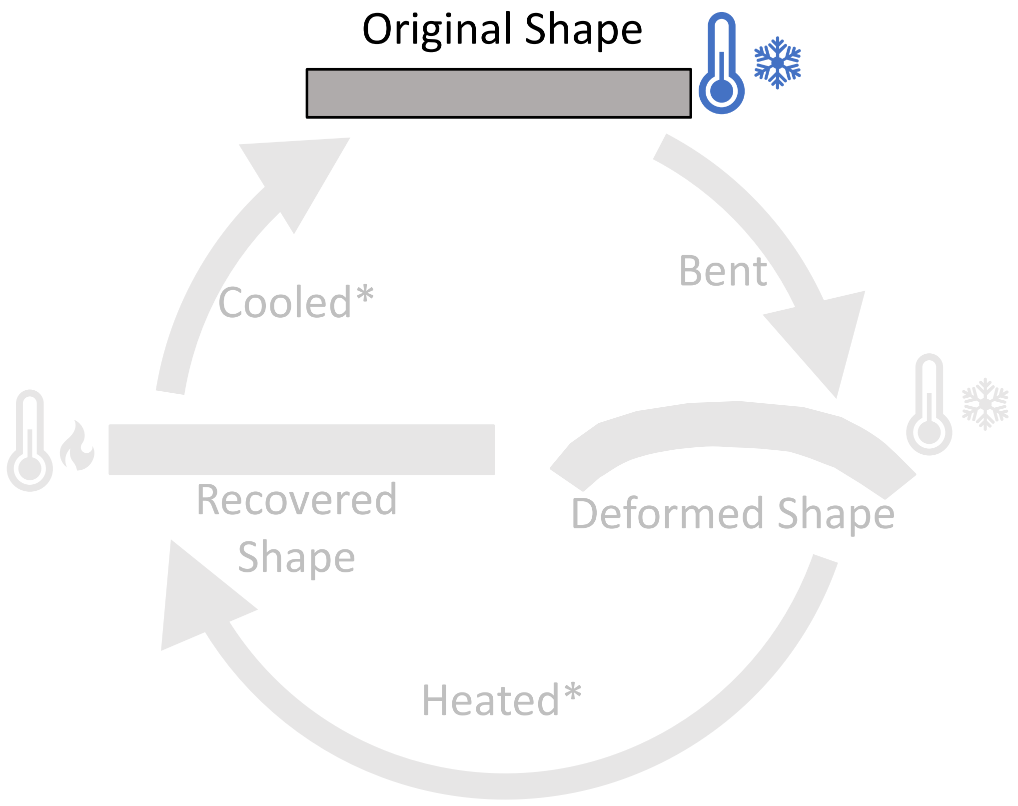


Deformed SMA wire + heat (hot water) = return to original shape!

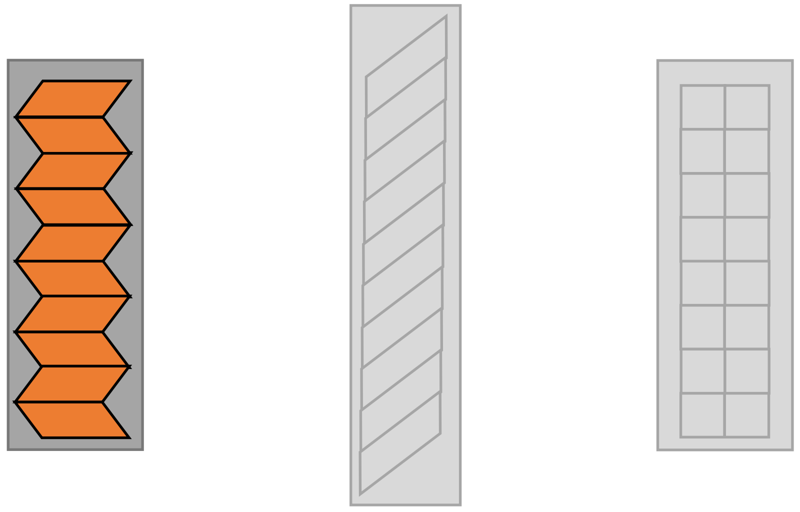
Phase Transformations Drive Shape Memory



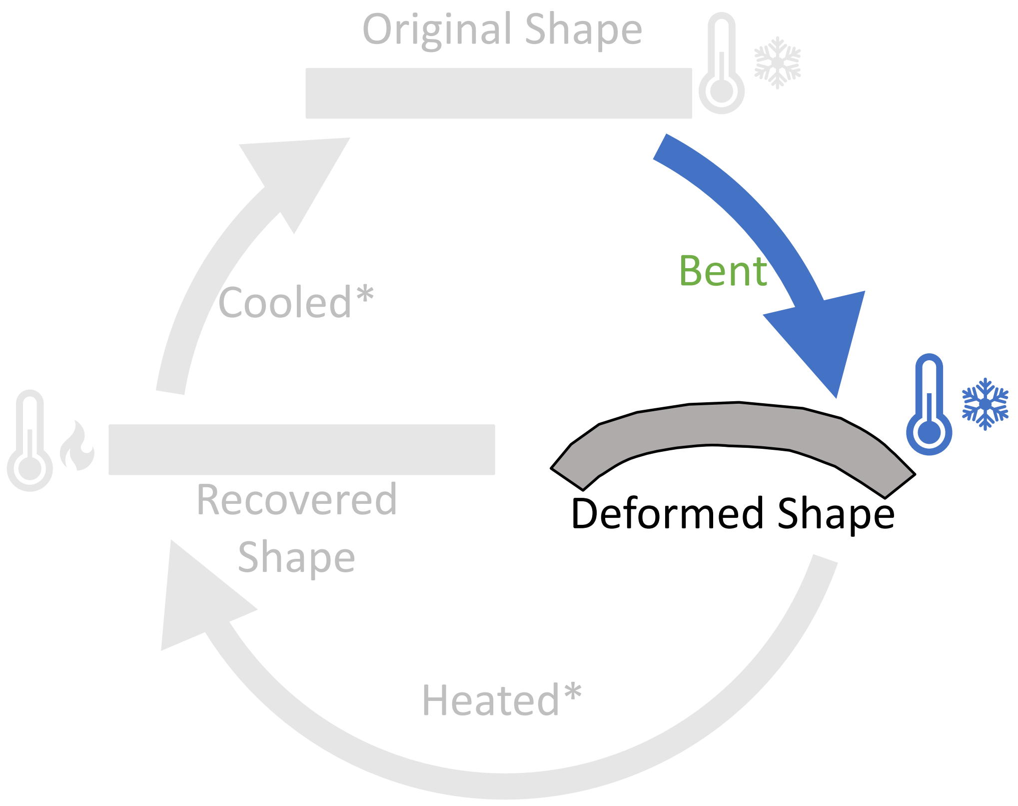
Phase Transformations Drive Shape Memory



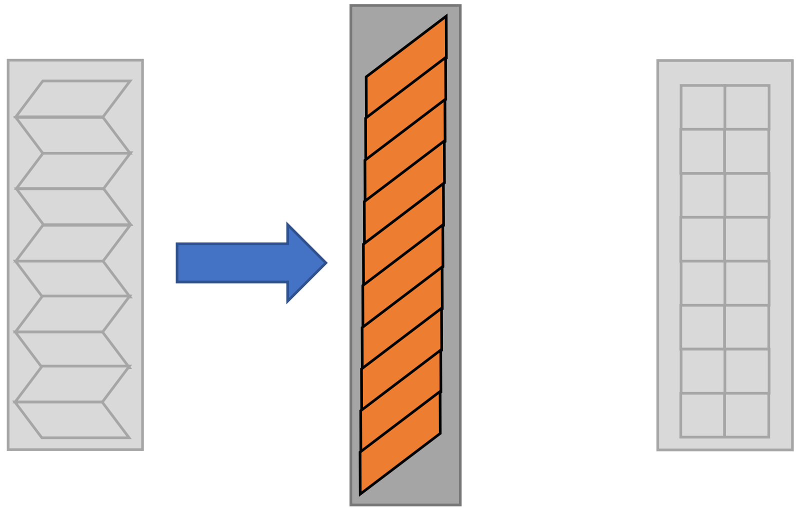
1. Original Material: twinned “Martensite”
2. Deformation de-twins the “Martensite”
3. Heating the material forms “Austenite”, restoring the original shape
4. Cooling the material forms the twinned “Martensite” again



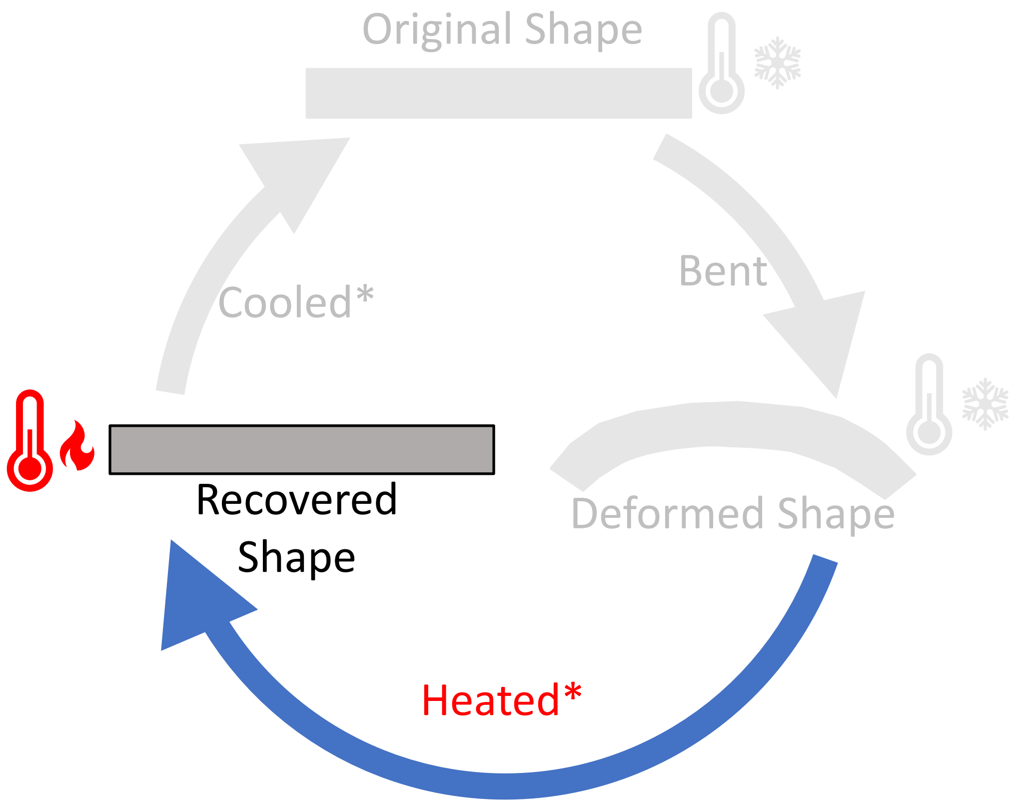
Phase Transformations Drive Shape Memory



1. Original Material: twinned “Martensite”
2. Deformation de-twins the “Martensite”
3. Heating the material forms “Austenite”, restoring the original shape
4. Cooling the material forms the twinned “Martensite” again

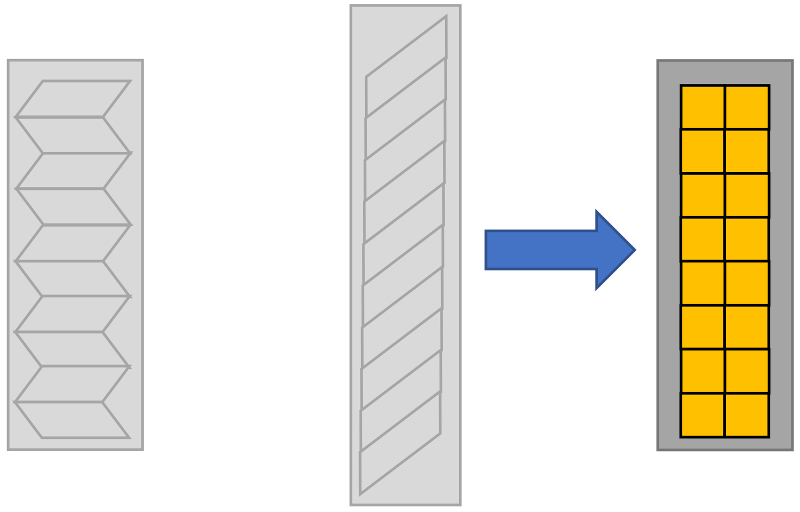


Phase Transformations Drive Shape Memory

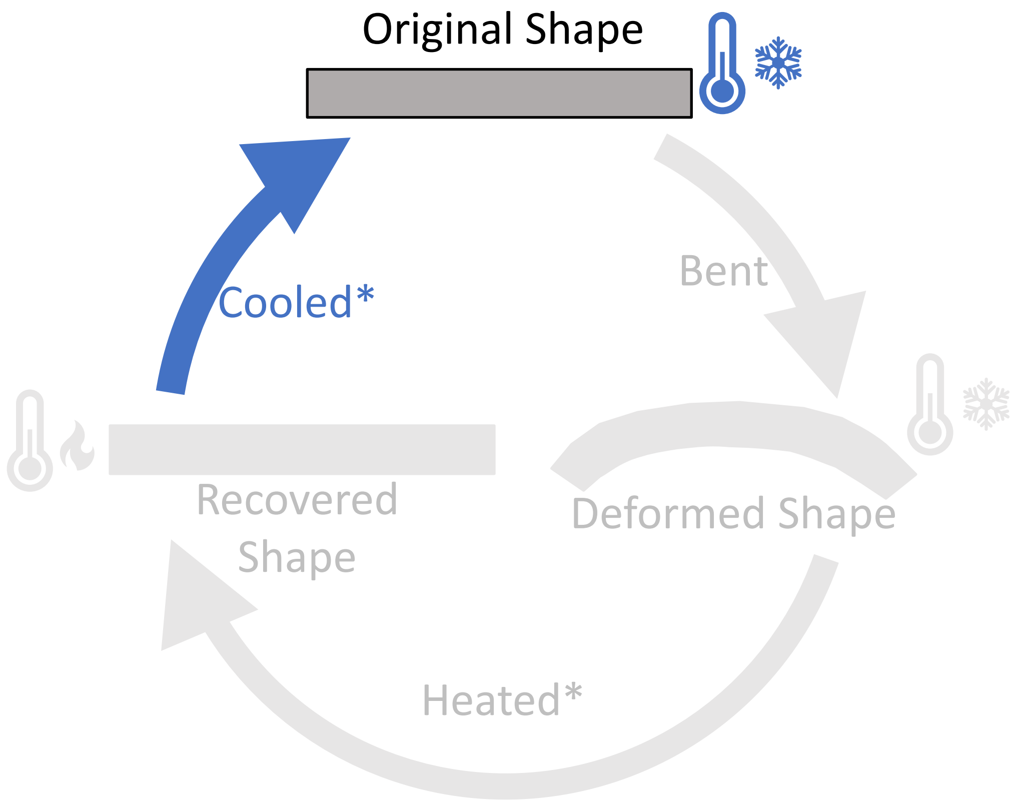


*external stimuli can include temperature, stress, magnetic fields, electric fields, or a few others

1. Original Material: twinned "Martensite"
2. Deformation de-twins the "Martensite"
3. Heating the material forms "Austenite", restoring the original shape
4. Cooling the material forms the twinned "Martensite" again

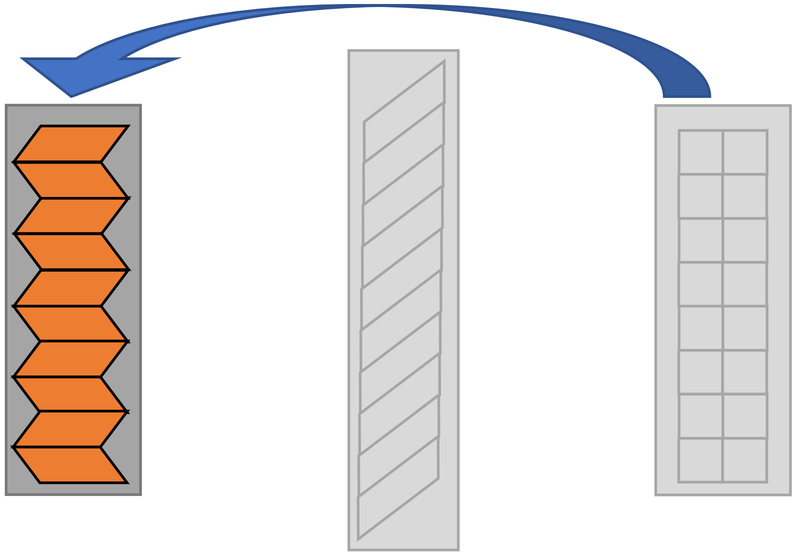


Phase Transformations Drive Shape Memory

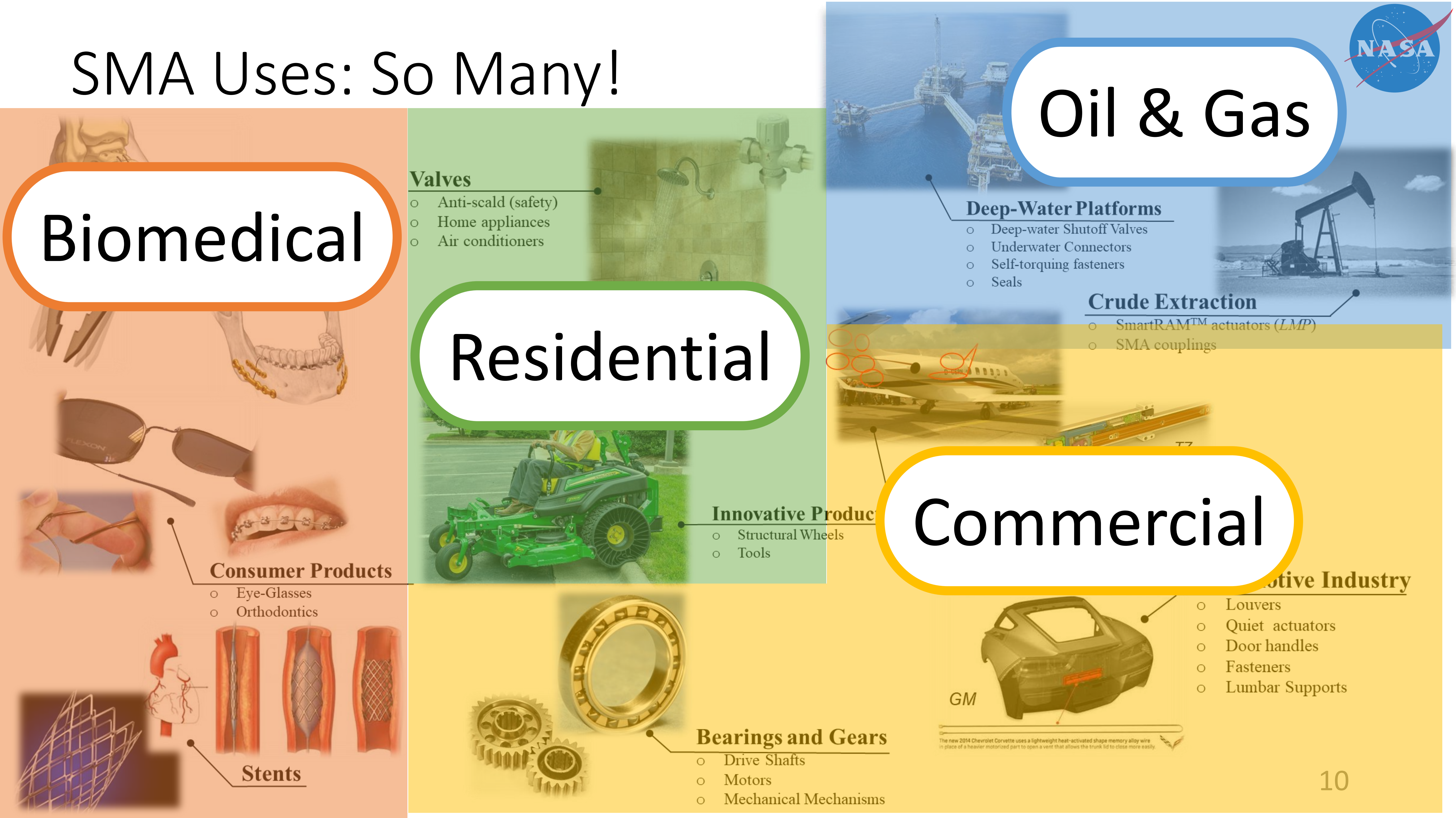


*external stimuli can include temperature, stress, magnetic fields, electric fields, or a few others

1. Original Material: twinned "Martensite"
2. Deformation de-twins the "Martensite"
3. Heating the material forms "Austenite", restoring the original shape
4. Cooling the material forms the twinned "Martensite" again



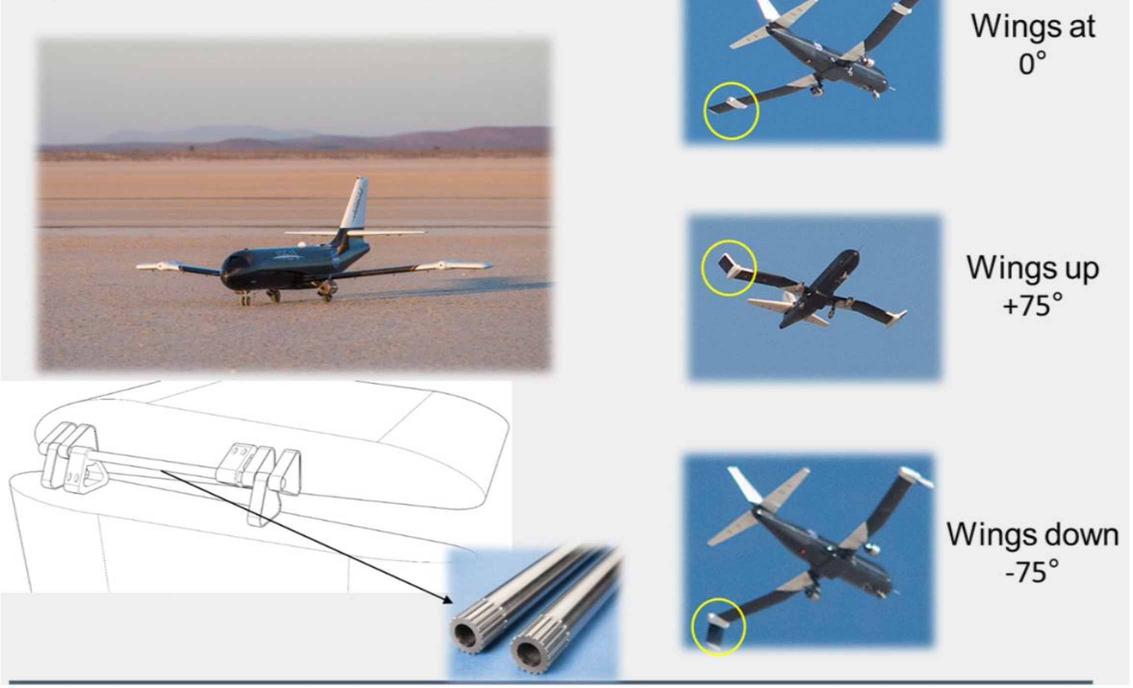
SMA Uses: So Many!

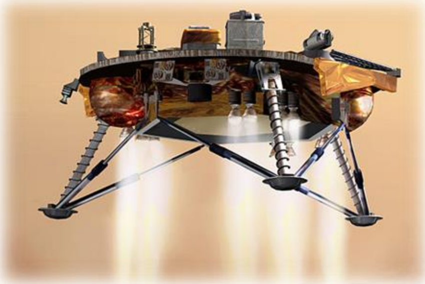


SMA Use at NASA

Wing-tip actuation using SMAs (Flight test)

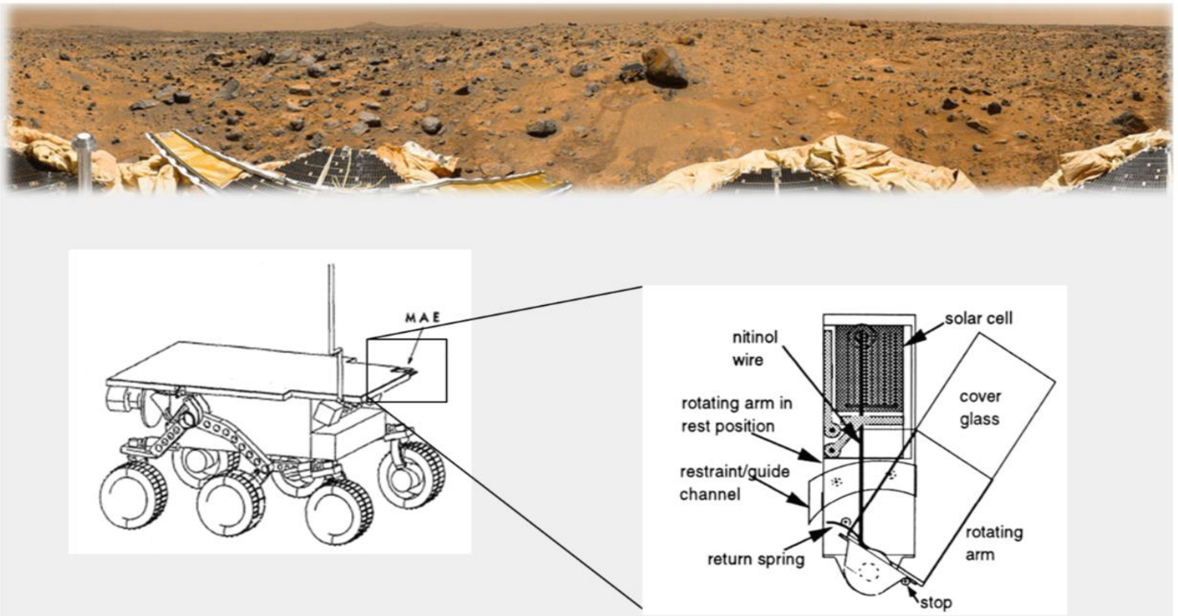
https://www.youtube.com/watch?v=9y1kkG2_QpE





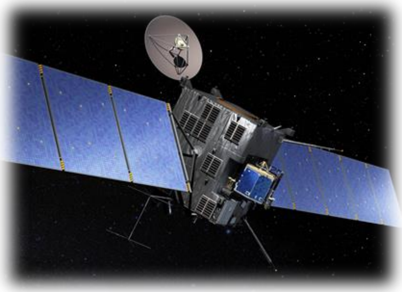
Deploy 12 critical instruments on PHOENIX (2008)

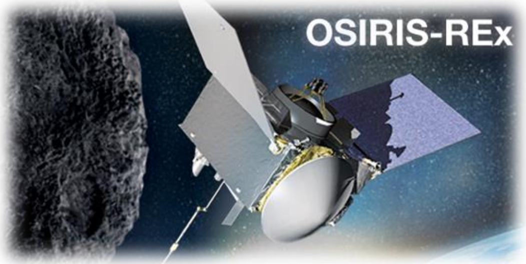
Release mechanism for ISS CUBESAT Deployer



The MAE demonstrated a shape-memory alloy rotating actuator (dust cover). This is the first multi-cycle SMA actuator used in a space application.

Deploy the Wide Angle Camera on ROSETTA



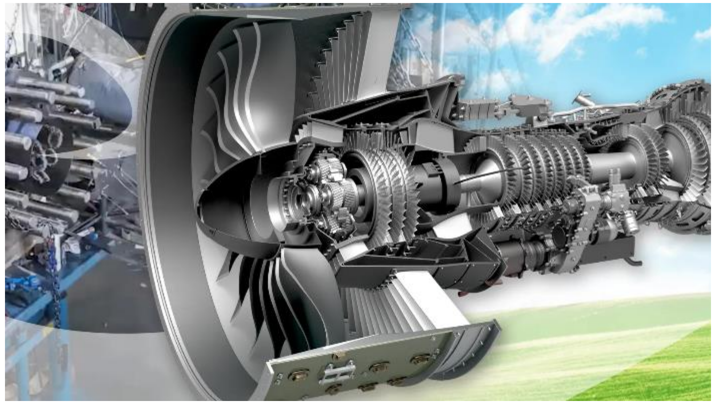


Deploy the sample capture mechanism

High-Temp and Ultra High-Temp SMAs

- Need to operate above 500 °C
- Potential Candidates:
  - NiHf alloys
  - TiPt or TiPd alloys
  - Ru-based alloys
  - Multi-component alloys (NiPdPy-TiTaZr)

Hypersonics



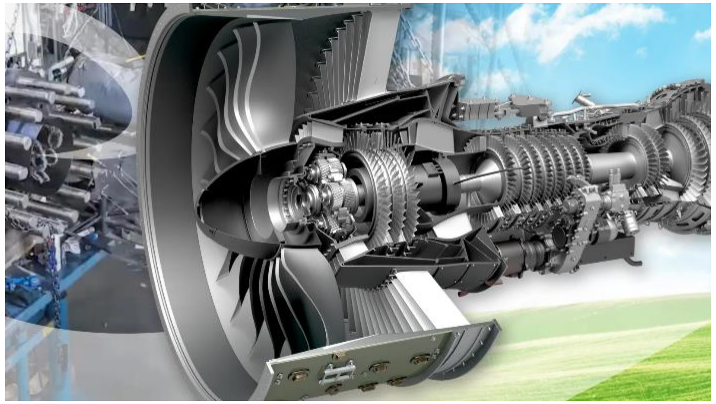
Jet Engines

Venus Probes/landers

High-Temp and Ultra High-Temp SMAs

- Need to operate above 500 °C
- Potential Candidates:
  - NiHf alloys
  - TiPt or TiPd alloys
  - Ru-based alloys
  - Multi-component alloys (NiPdPy-TiTaZr)

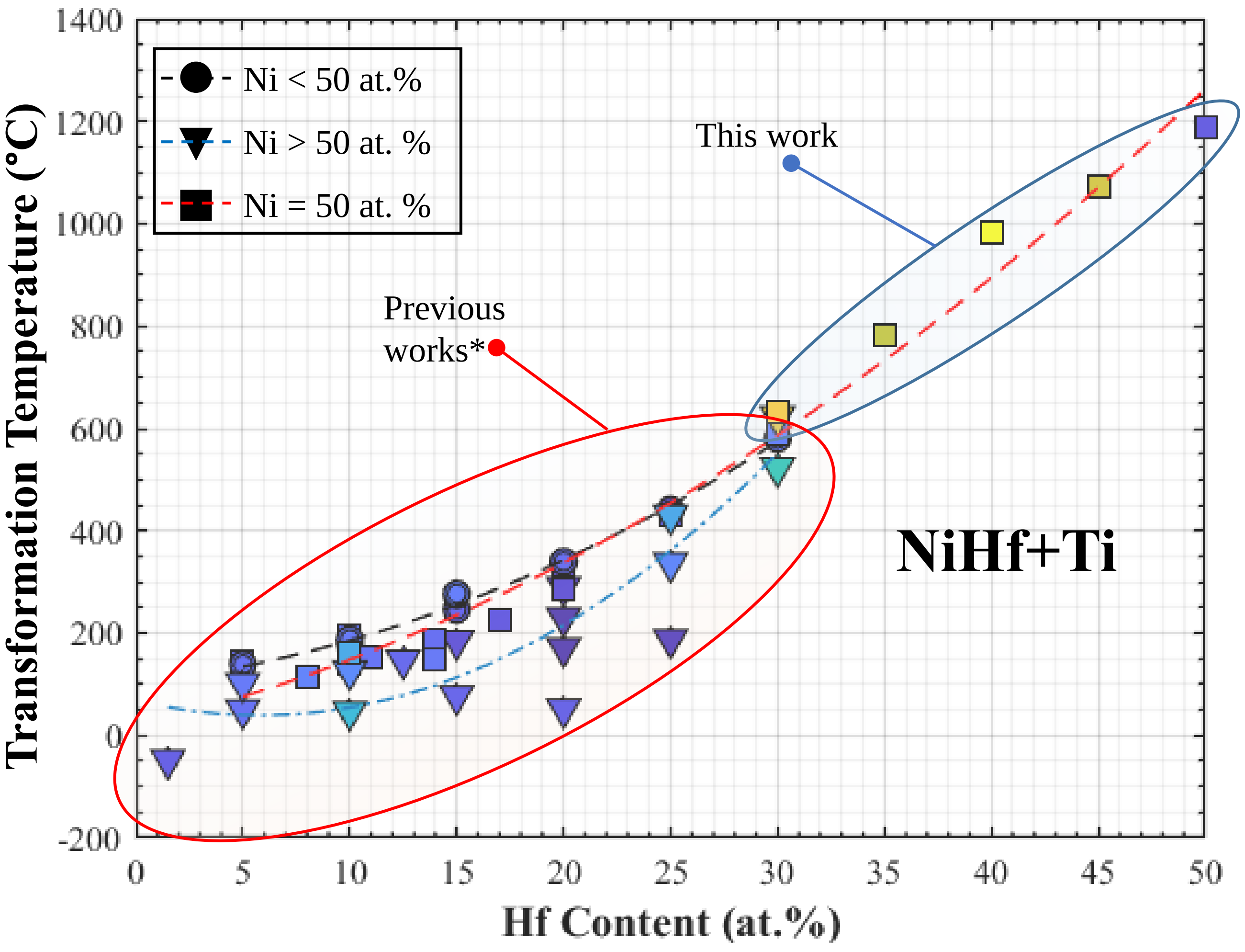

Hypersonics


Jet Engines


Venus Probes/landers

Previous Work Into Ni-Ti/Hf Alloys

- NiTi-based alloys + Hf = increased phase transformation temperatures, aka high-temperature SMAs
- Most previous work has focused on NiTi-20Hf alloys, with transformation temps as high as 330°C and SMA effects [1]



*Data from: Shape Memory Materials Analysis and Research Tool (SM²ART) Database

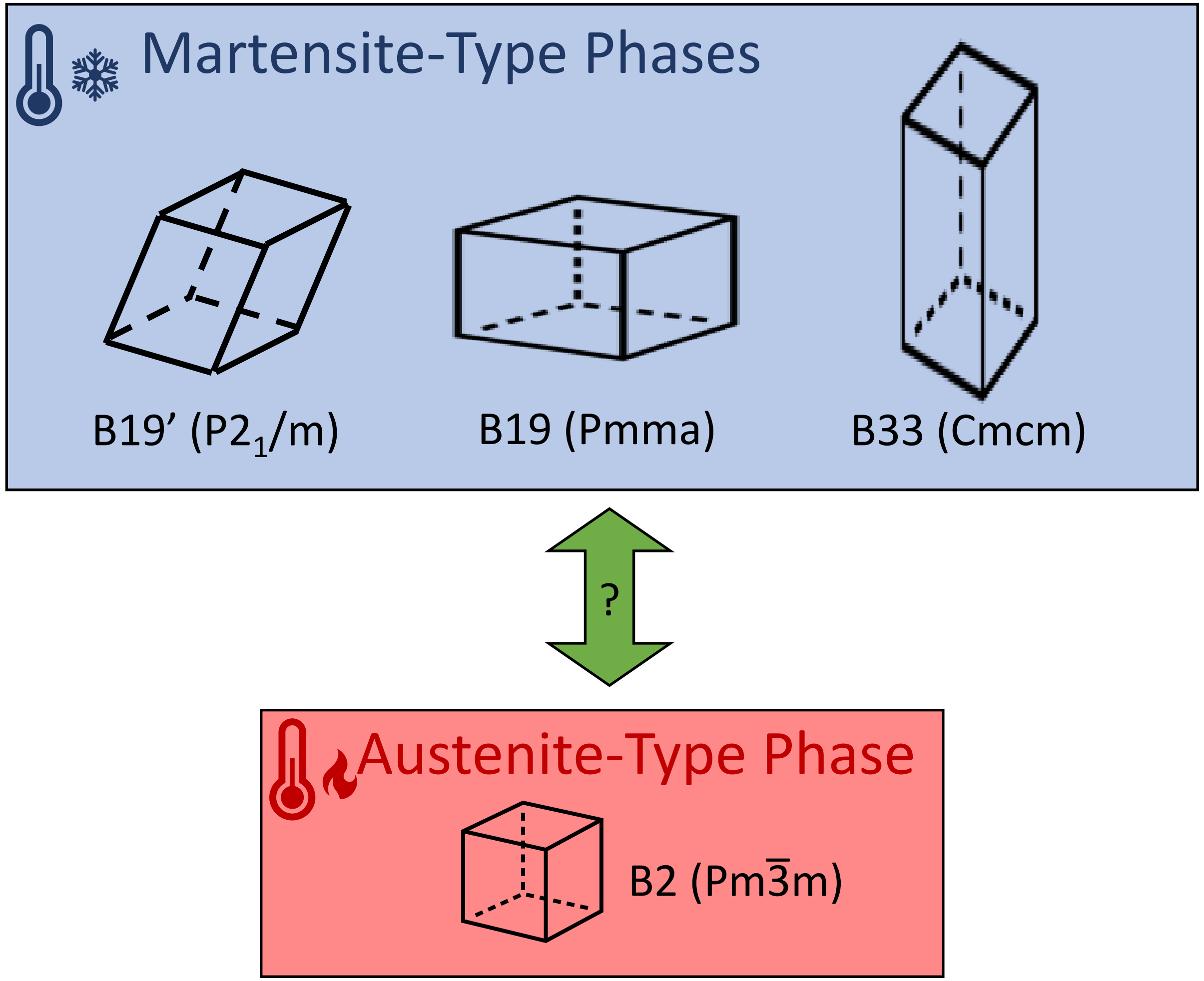
[1] Benafan O, Bigelow GS, Garg A, Noebe RD, Gaydosh DJ, Rogers RB (2021) Processing and scalability of NiTiHf high-temperature shape memory alloys. Shape Mem Superelast 7(1):109–165

Previous Work Looking for Phases in Ni-Ti/Hf

- Disagreements around:
    - what phases and crystal structures exist in NiTi- >20Hf alloys?
    - if there is a martensitic transformation?
    - If there is a shape memory behavior?

- Different phase geometries = different transformation strain accommodations and different properties

- This study [1] focused on answering those



[1] O. Benafan, G. S. Bigelow, A. Garg, L. G. Wilson, R. B. Rogers, E. J. Young-Dohe, D. F. Johnson, D. A. Scheiman, J. W. Lawson, Zhigang Wu (2024) Ultra-High Temperature Shape Memory Behavior in Ni–Ti–Hf Alloys. Shape Mem Superelast 10:55-69

Previous Work Looking for Phases in Ni-Ti/Hf

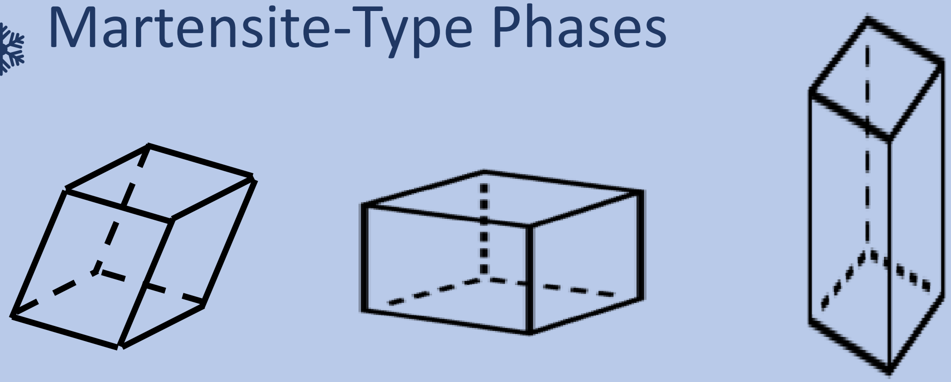
XRD!

- Disag
  - w es exist in
    N
  - i mation?
  - If there is a shape memory behavior?

- **Different phase geometries** = different transformation strain accommodations and different properties

- This study [1] focused on answering those

Martensite-Type Phases



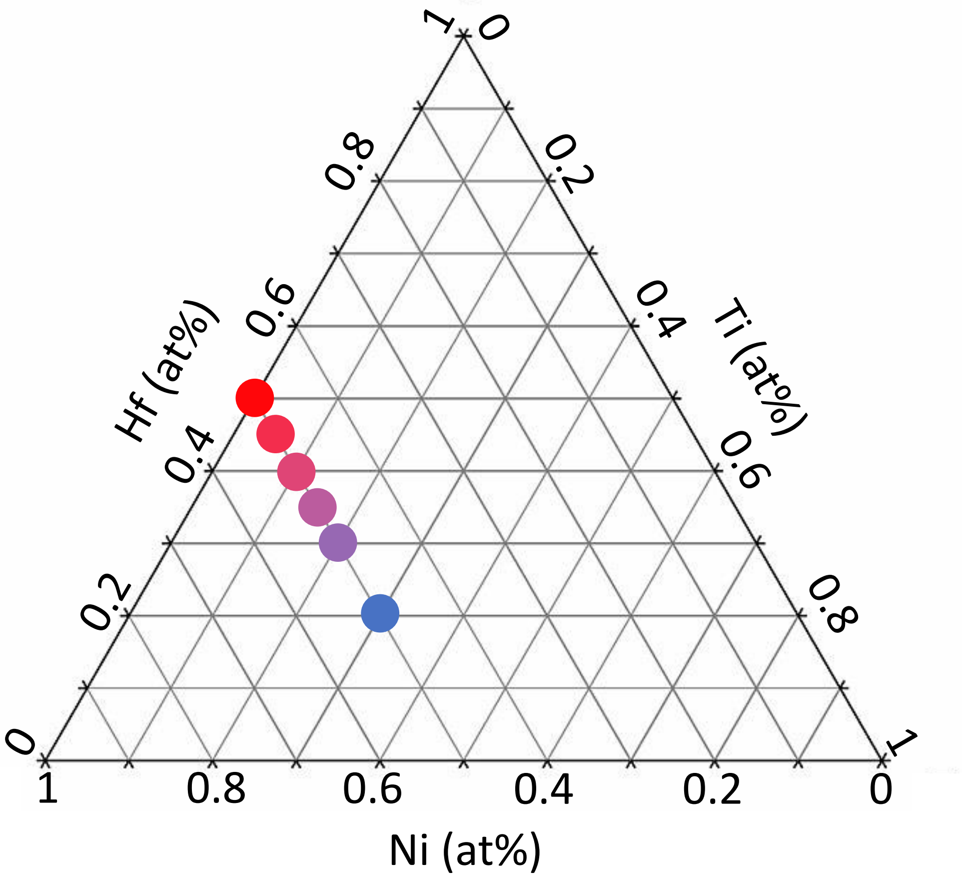
?

Austenite-Type Phase

[1] O. Benafan, G. S. Bigelow, A. Garg, L. G. Wilson, R. B. Rogers, E. J. Young-Dohe, D. F. Johnson, D. A. Scheiman, J. W. Lawson, Zhigang Wu (2024) Ultra-High Temperature Shape Memory Behavior in Ni–Ti–Hf Alloys. Shape Mem Superelast 10:55-69

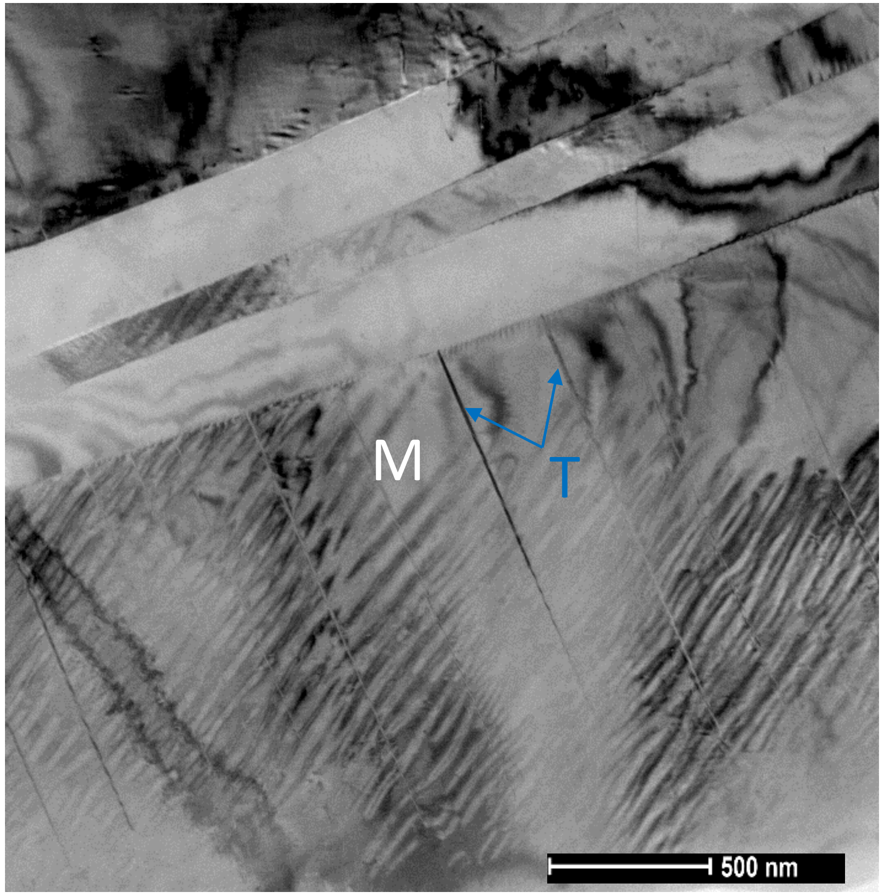
Samples

- 6 compositions of Ni-Ti/Hf:
  - $Ni_{50}Ti_{30}Hf_{20}$
  - $Ni_{50}Ti_{20}Hf_{30}$
  - $Ni_{50}Ti_{15}Hf_{35}$
  - $Ni_{50}Ti_{10}Hf_{40}$
  - $Ni_{50}Ti_{5}Hf_{45}$
  - $Ni_{50}Hf_{50}$
- Vacuum arc melting of pure components
- Buttons were melted and remelted x5 to homogenize
- Suction cast into rods



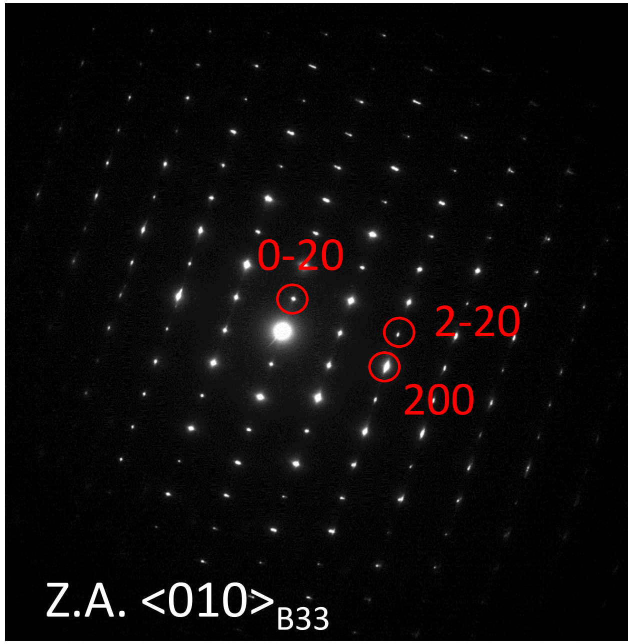
The Phases We Found with TEM

B33 + B19' phases are present in the 30-35 at.% Hf content

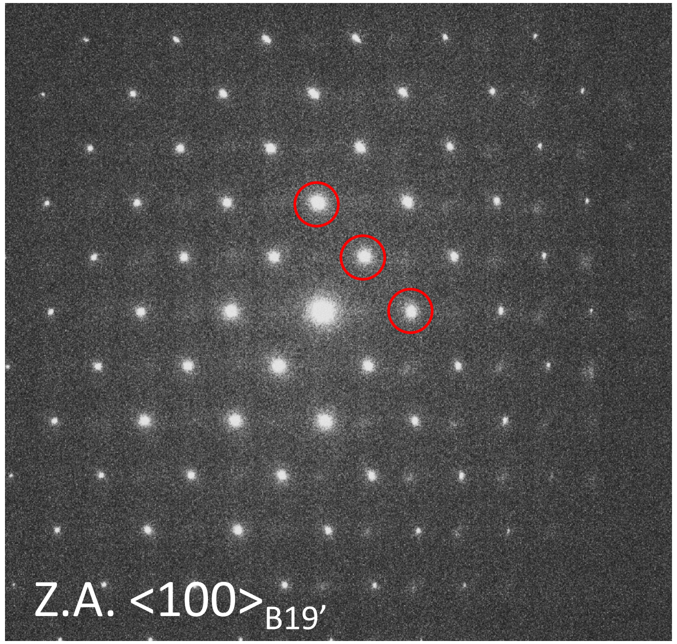


NiTi-30Hf

B33



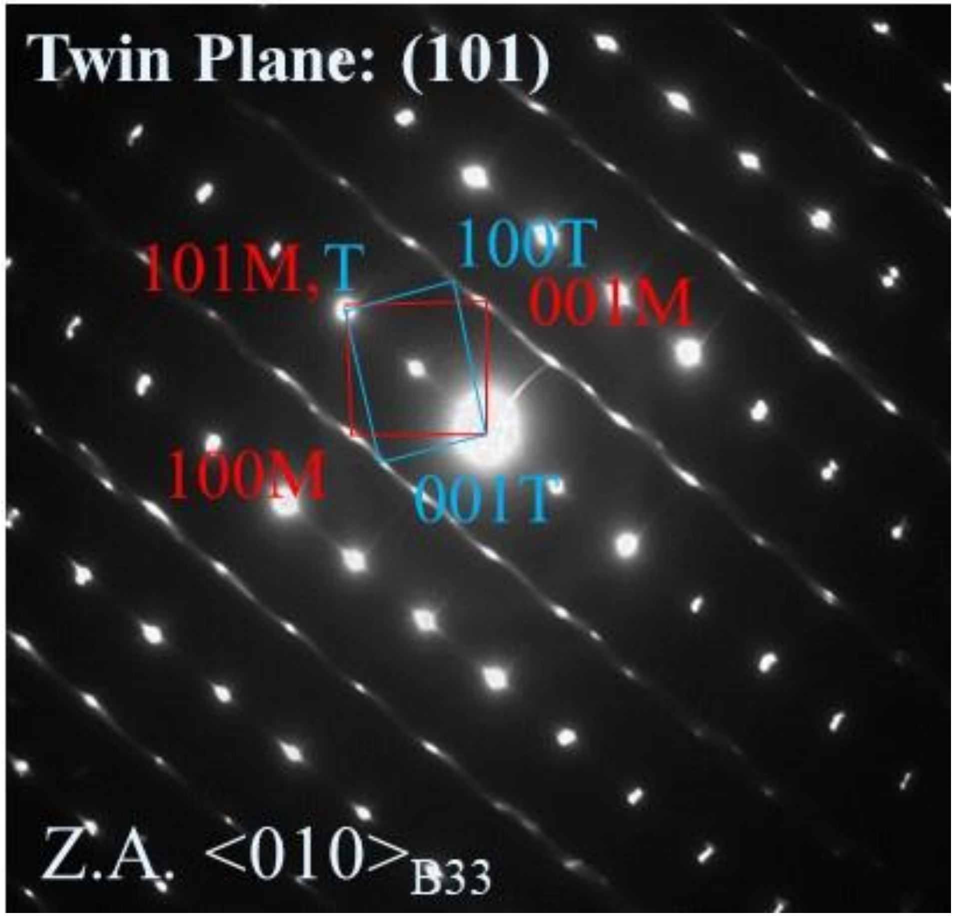
B19'



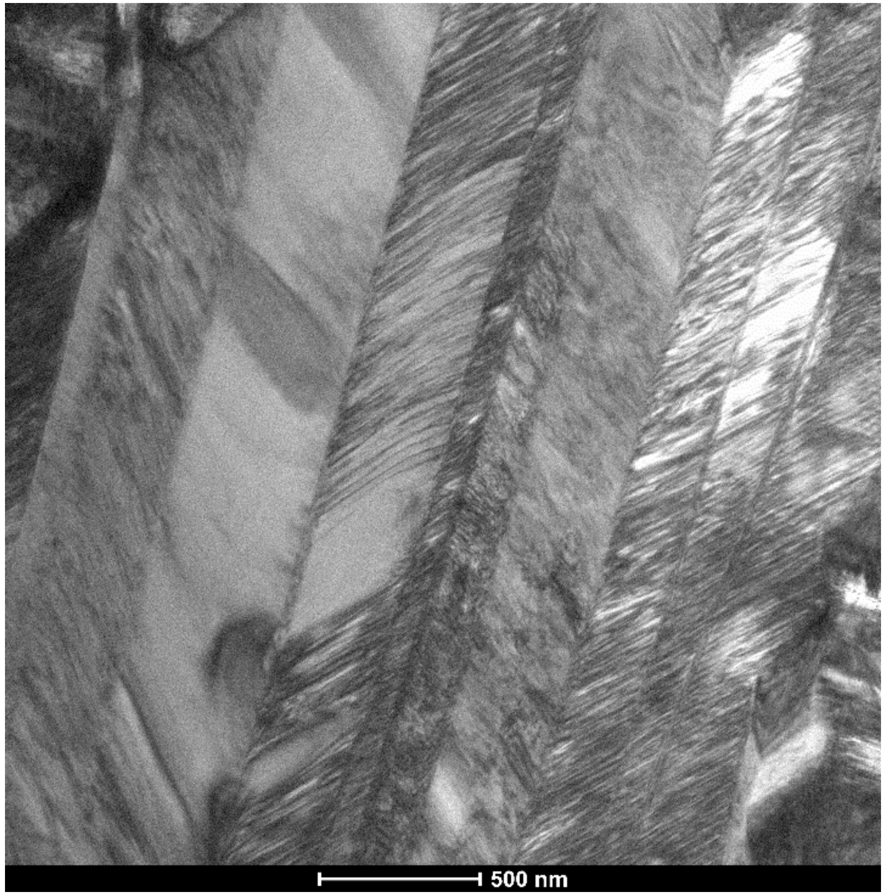
- Majority of the areas were indexed to an orthorhombic B33 phase
- A few areas were uniquely indexed to a monoclinic B19' phase

The Phases We Found and Didn't Find

Only B33 present in 40 to 50 Hf; B19' (or other structures) not detected



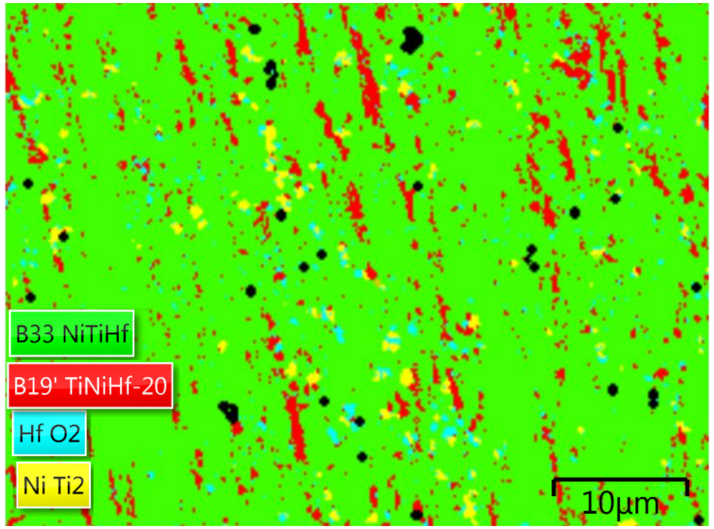
No direct evidence of the B19' phase



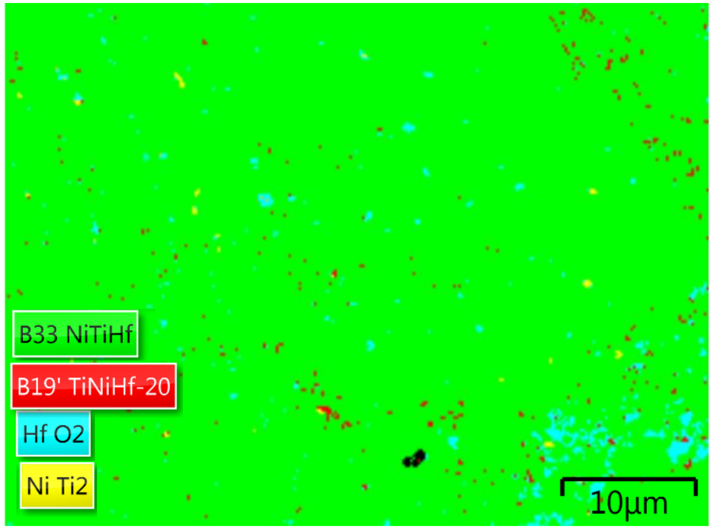
NiTi-40Hf

Can We Find The Phases in Bulk Samples?

Band contrast and EBSD crystallographic data show traces of B19’ on all compositions from 30 to 50 Hf

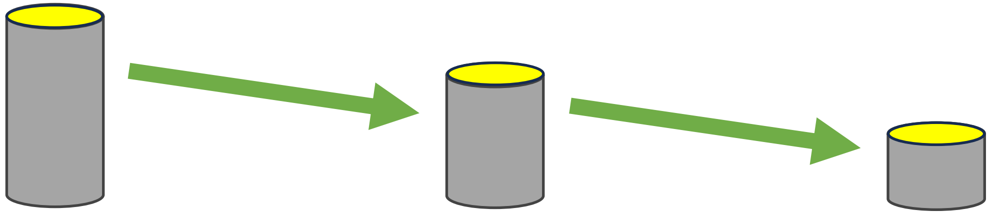


NiTi-30Hf

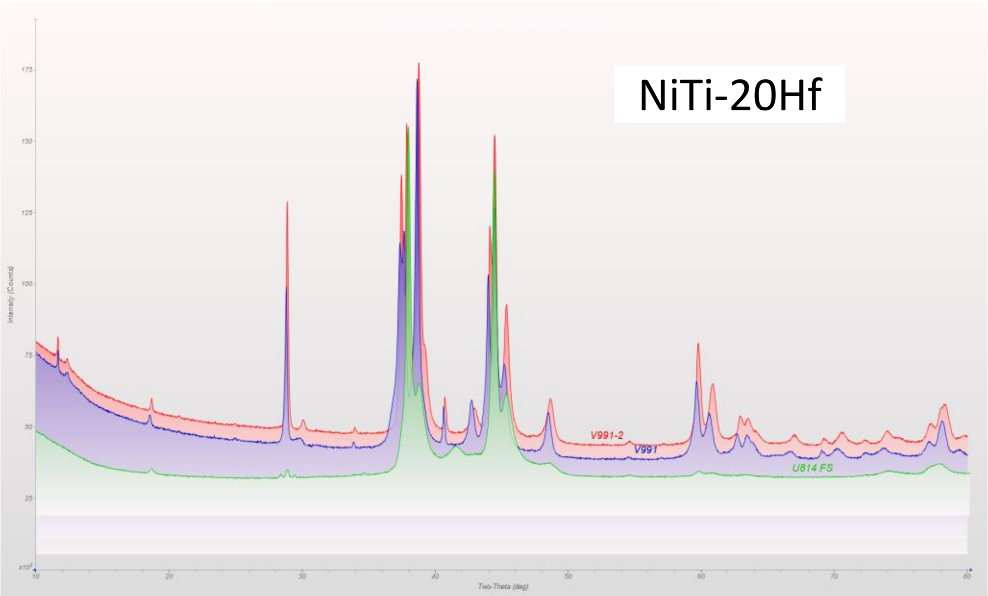


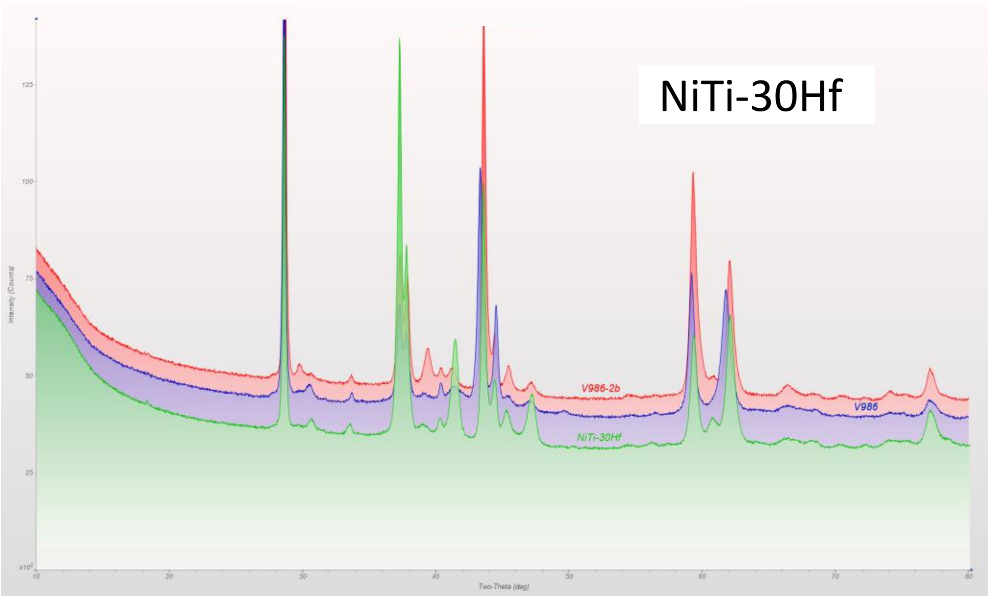
NiTi-50Hf

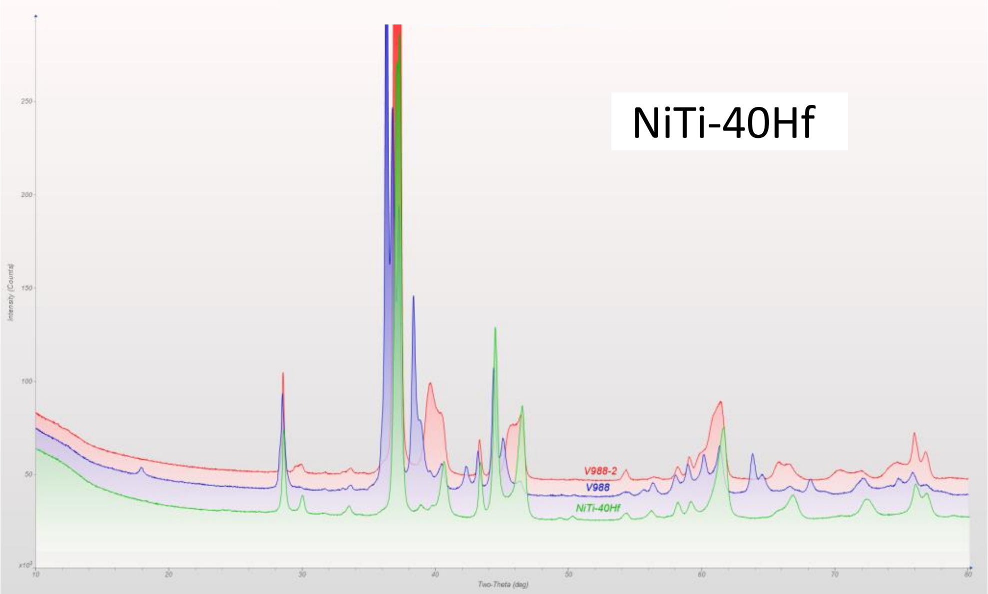
- Rod samples had large grains
- To increase sampling statistics, sliced and repolished x3
- 1D XRD, slice and repolish, 1D XRD, slice and repolish, 1D XRD

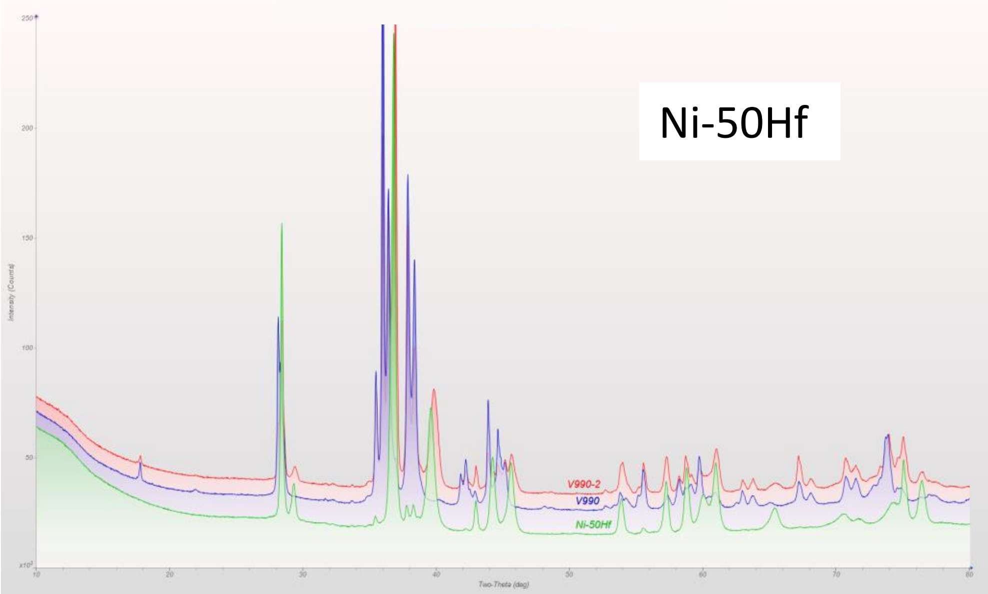


1D XRD of NiTi -#Hf Comparisons

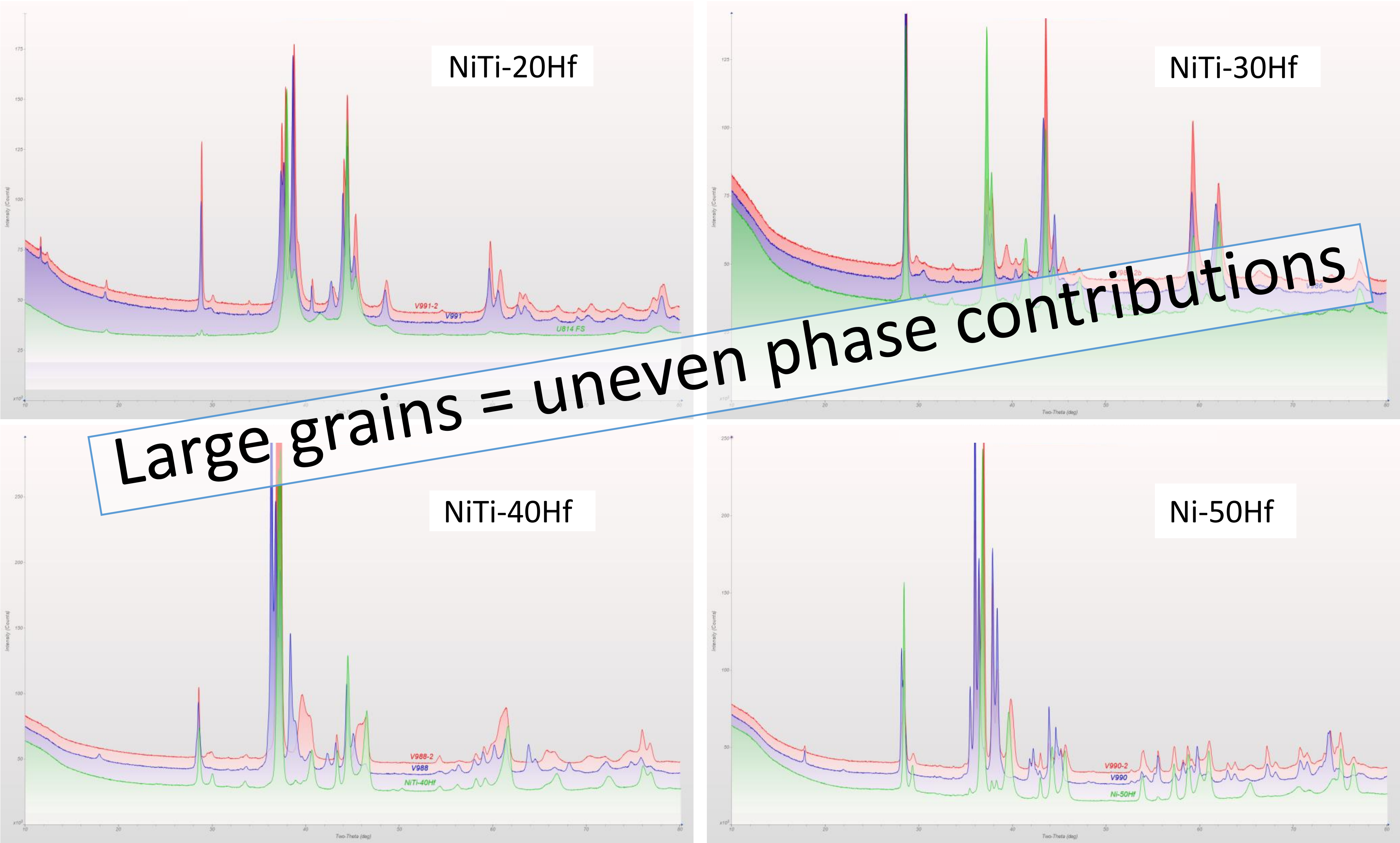






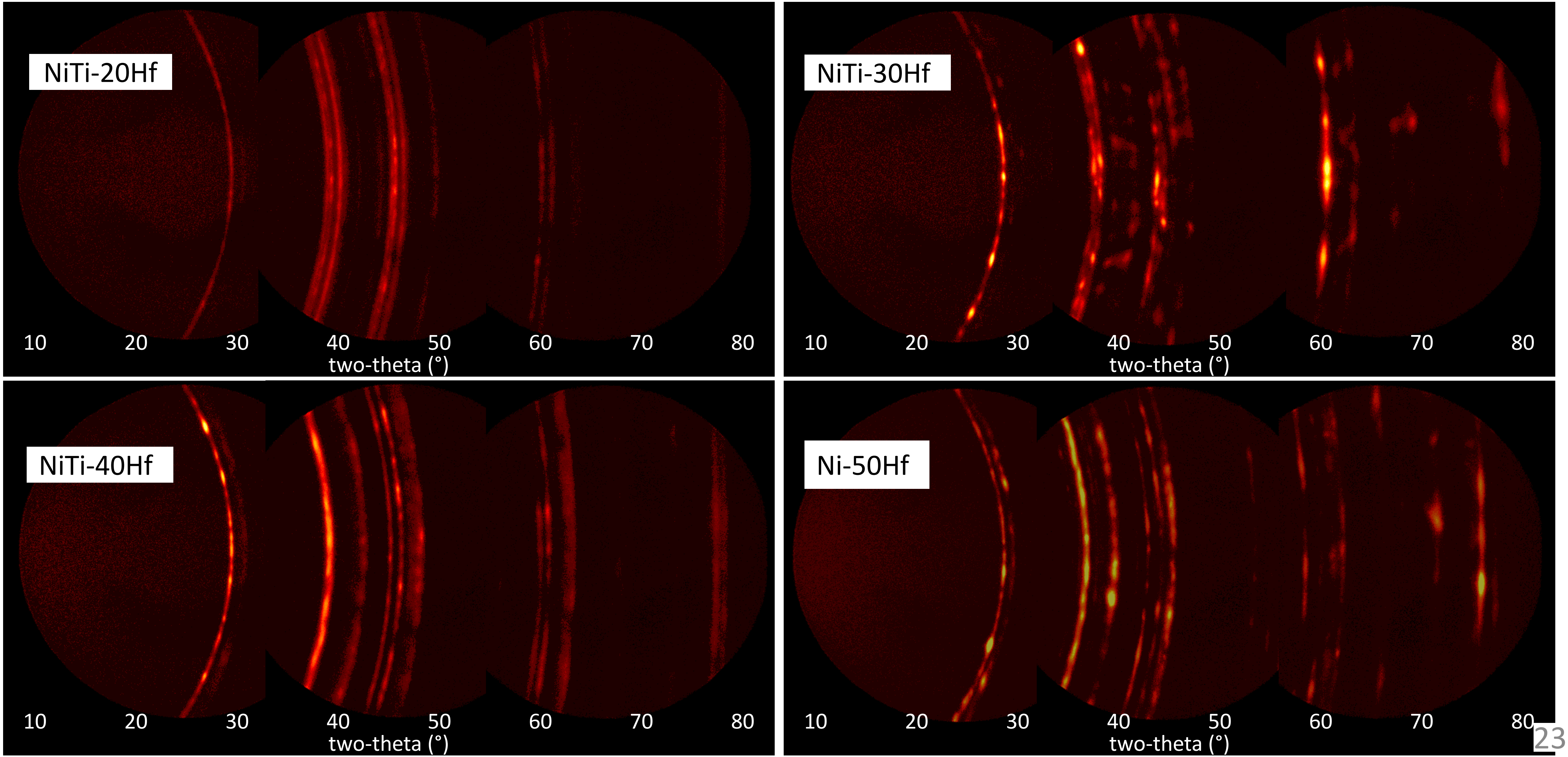


1D XRD of NiTi -#Hf Comparisons

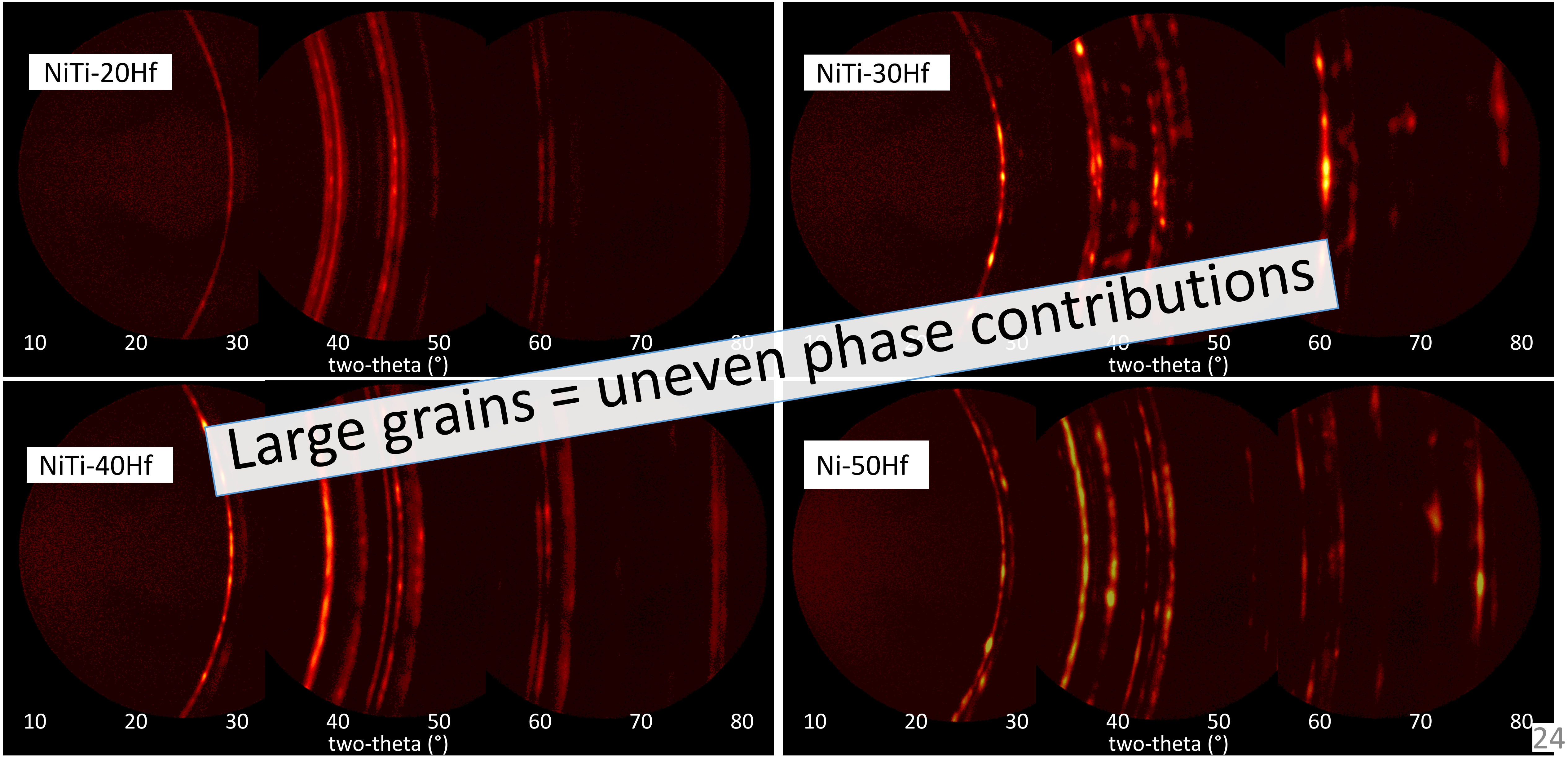


Large grains = uneven phase contributions

2D XRD of NiTi -30Hf to -50Hf

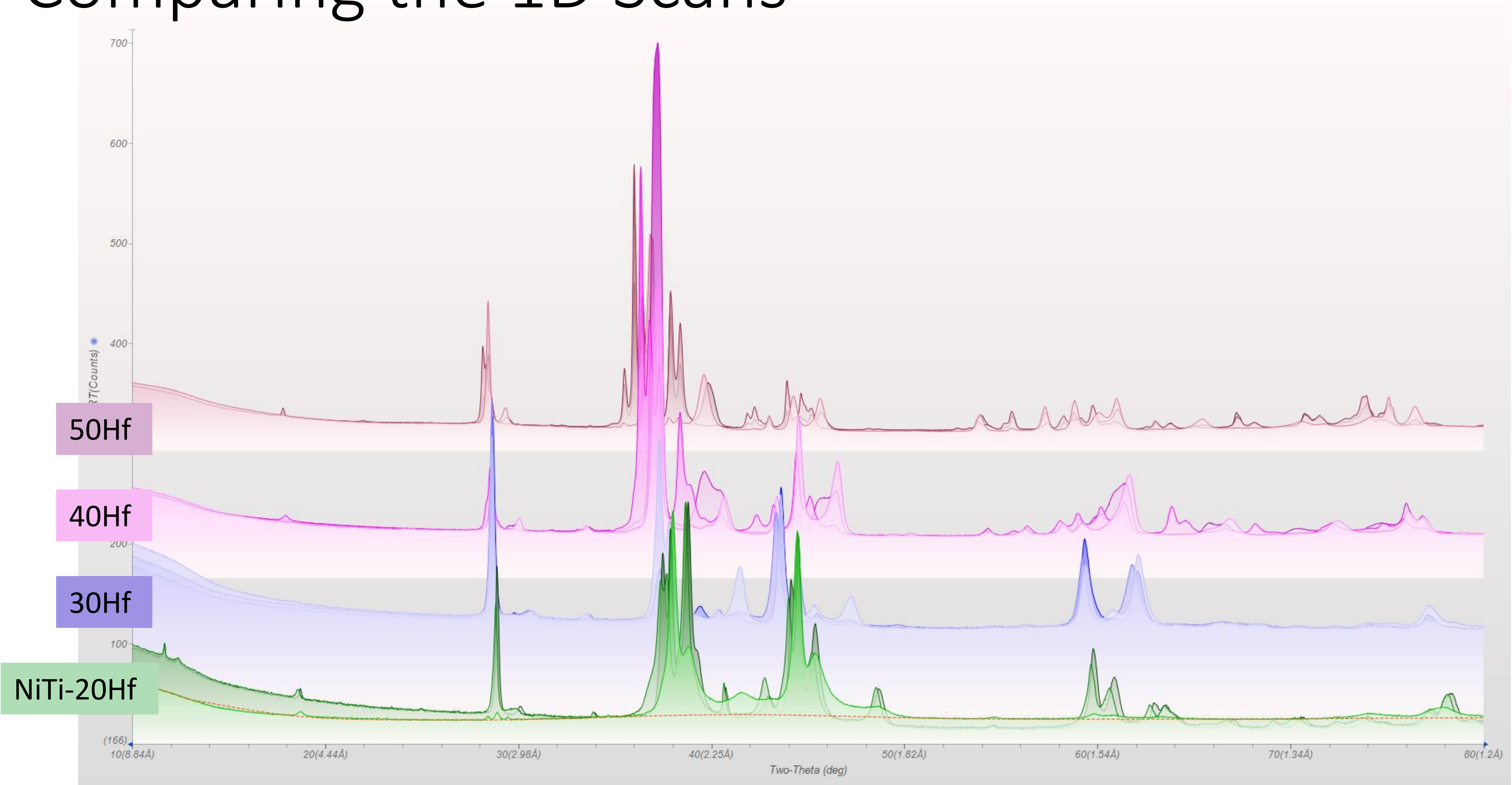


2D XRD of NiTi -30Hf to -50Hf

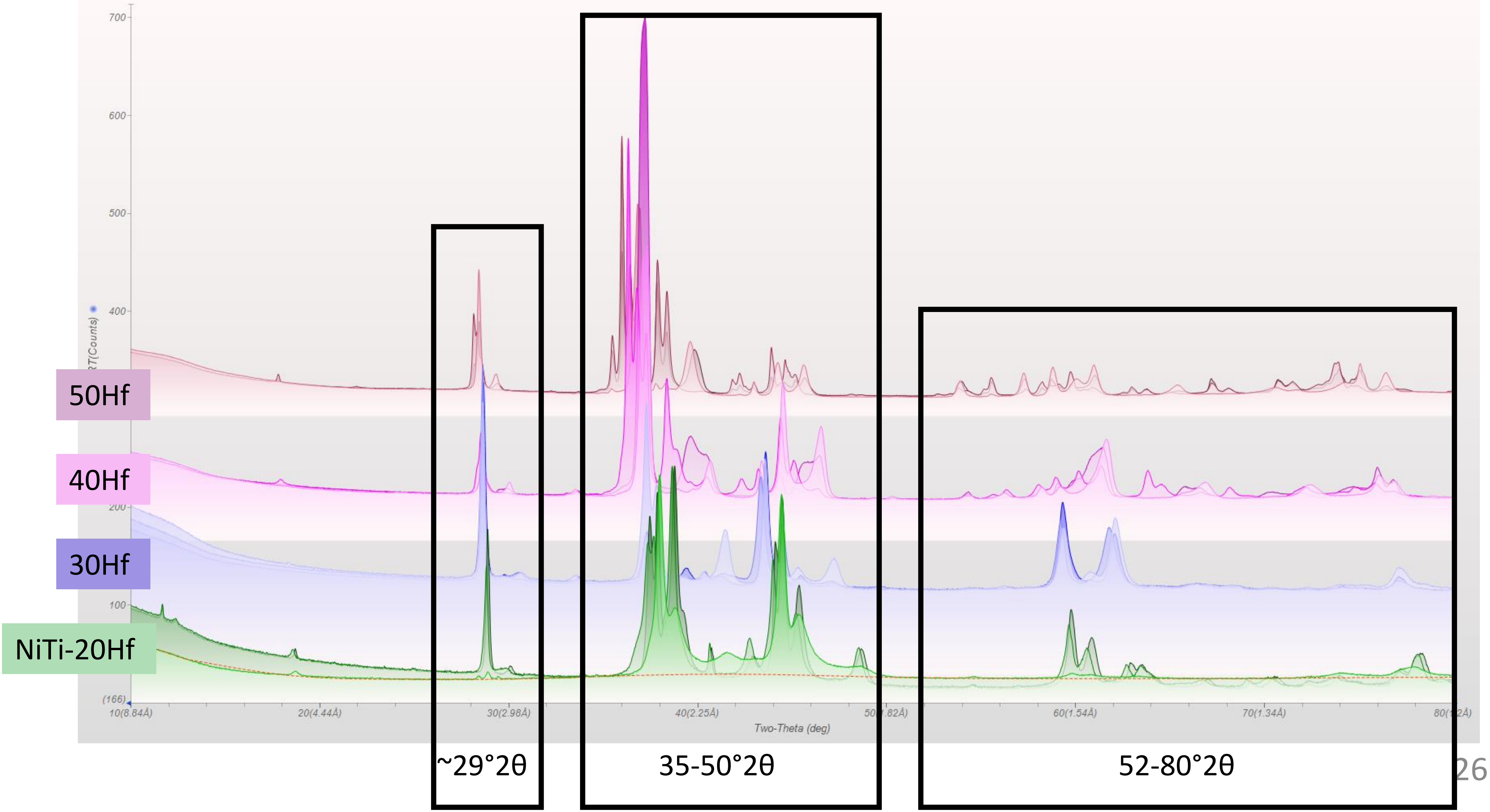


Large grains = uneven phase contributions

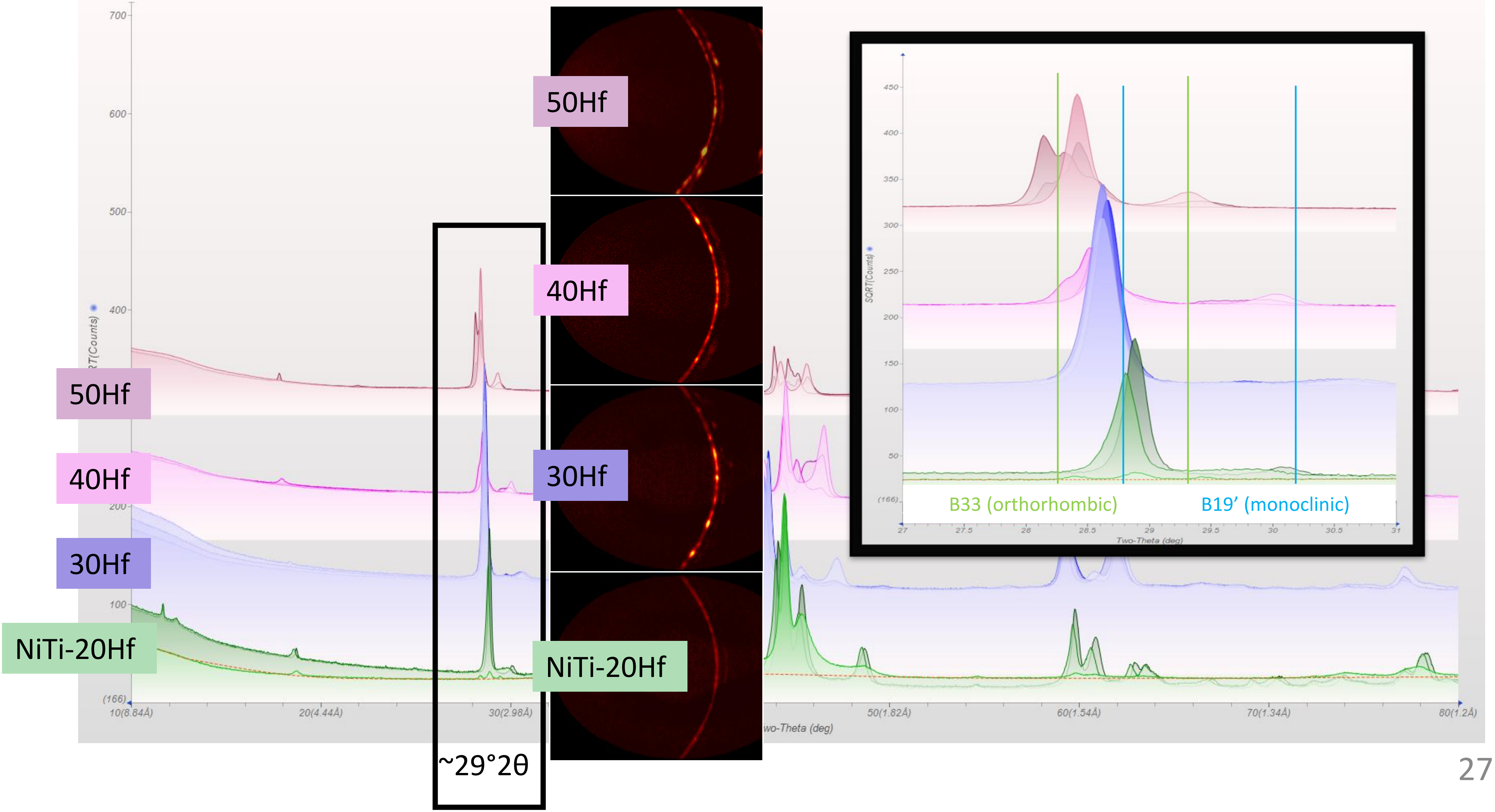
Comparing the 1D Scans



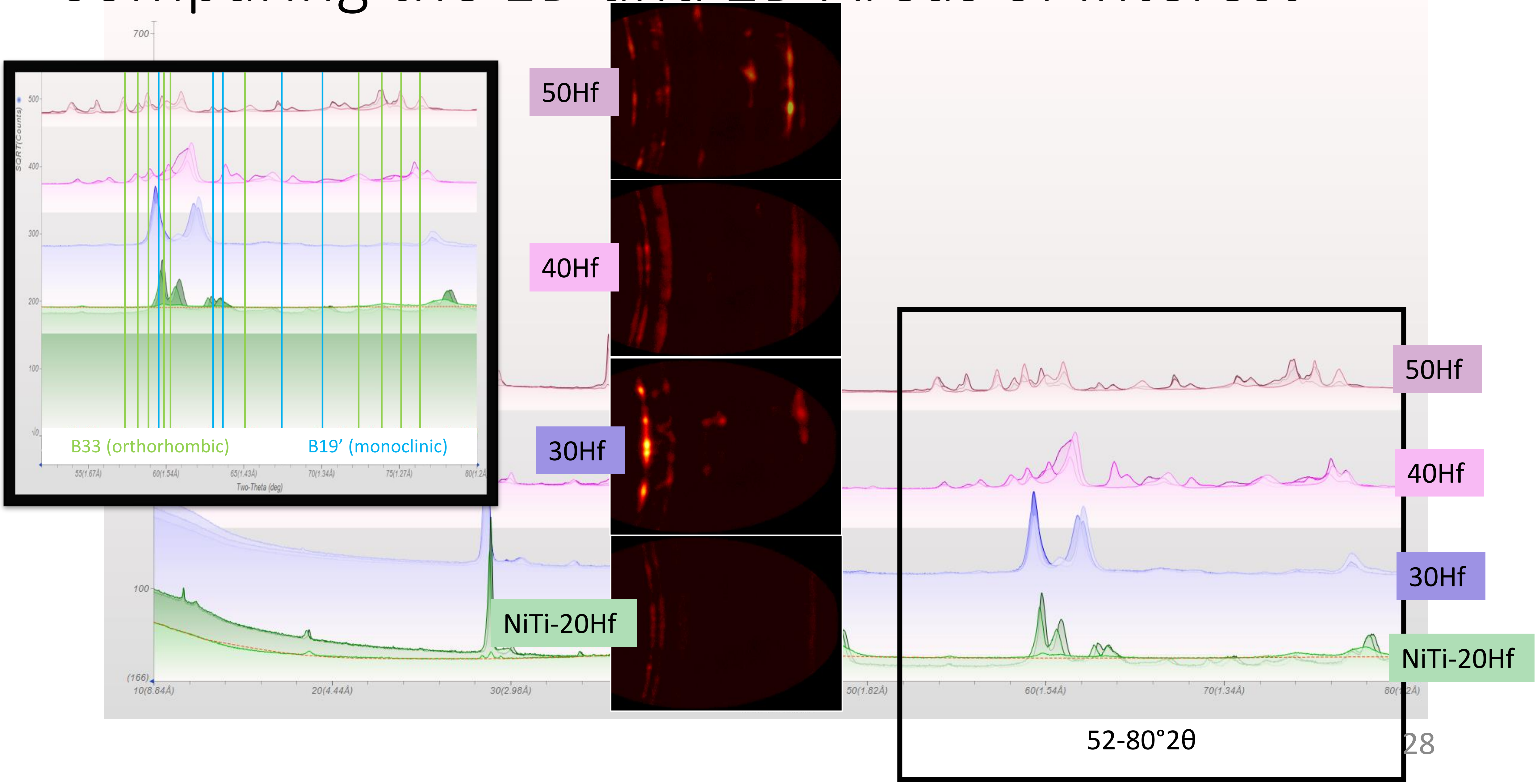
Comparing the 1D Areas of Interest



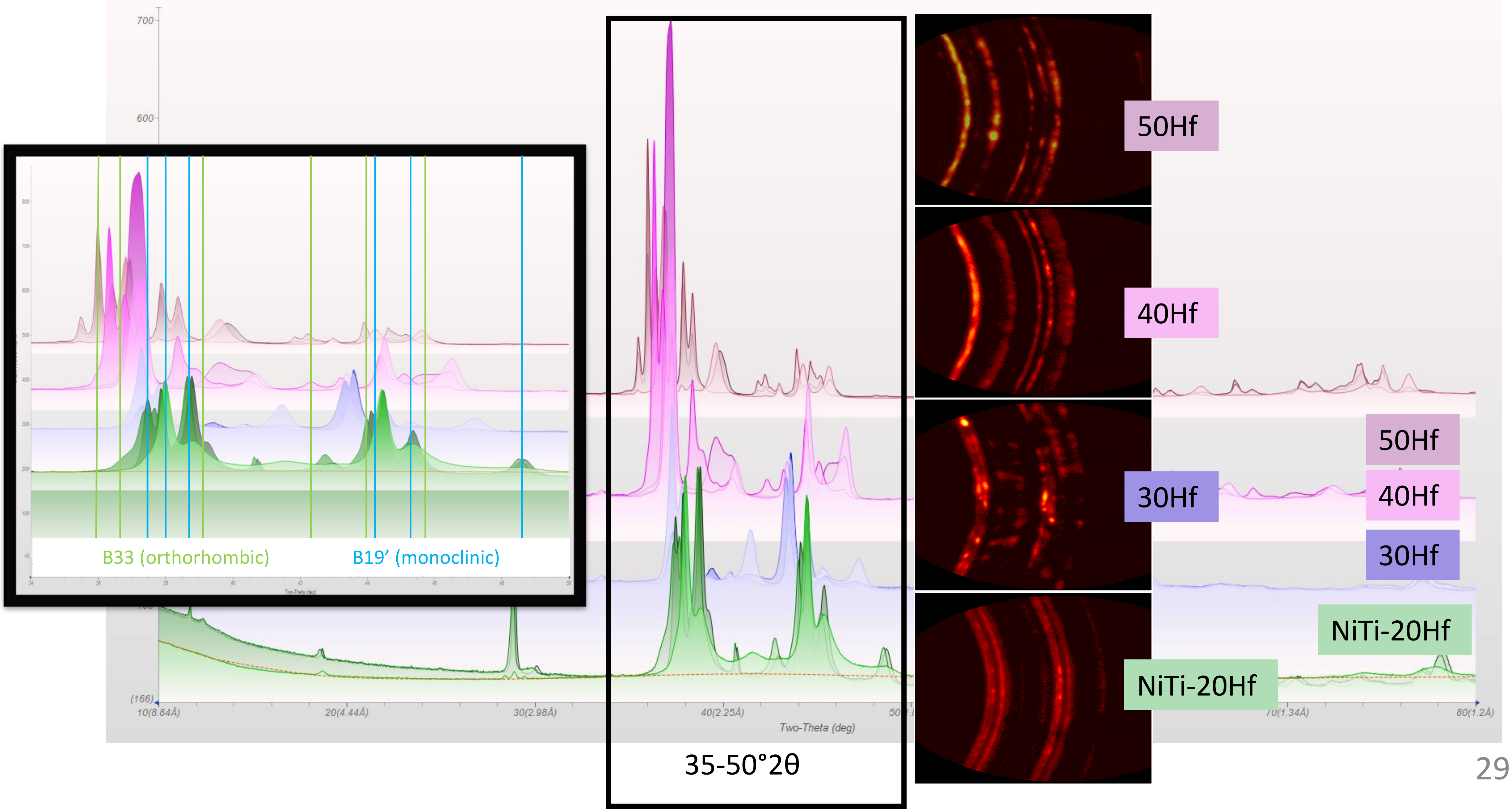
Comparing the 1D and 2D Areas of Interest



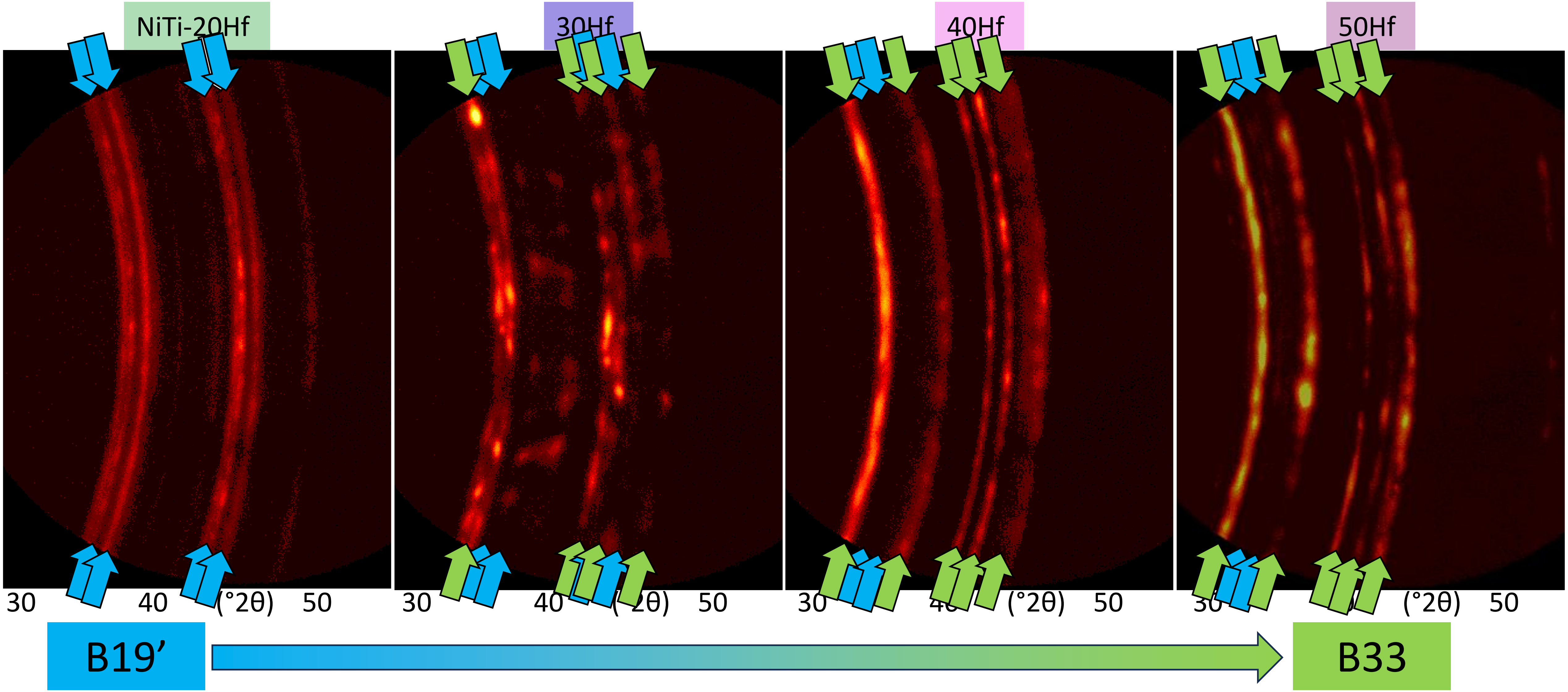
Comparing the 1D and 2D Areas of Interest



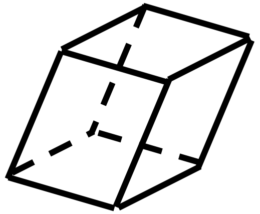
Comparing the 1D and 2D Areas of Interest



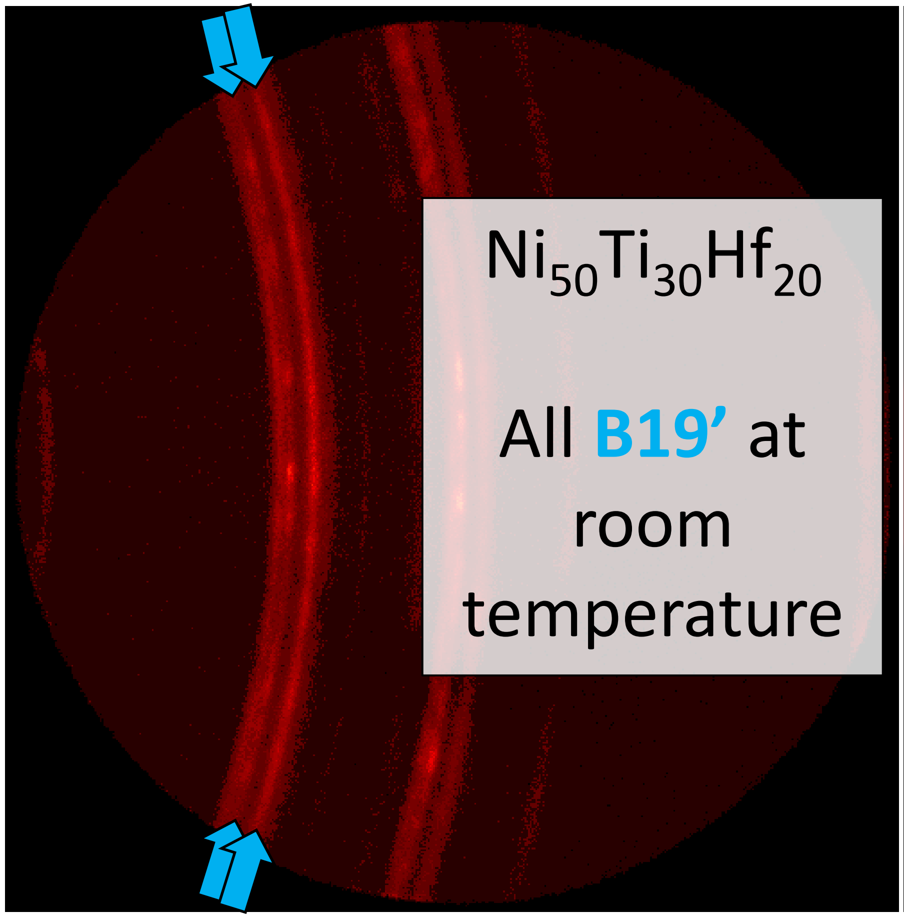
35-50 °2θ 2D XRD Comparisons



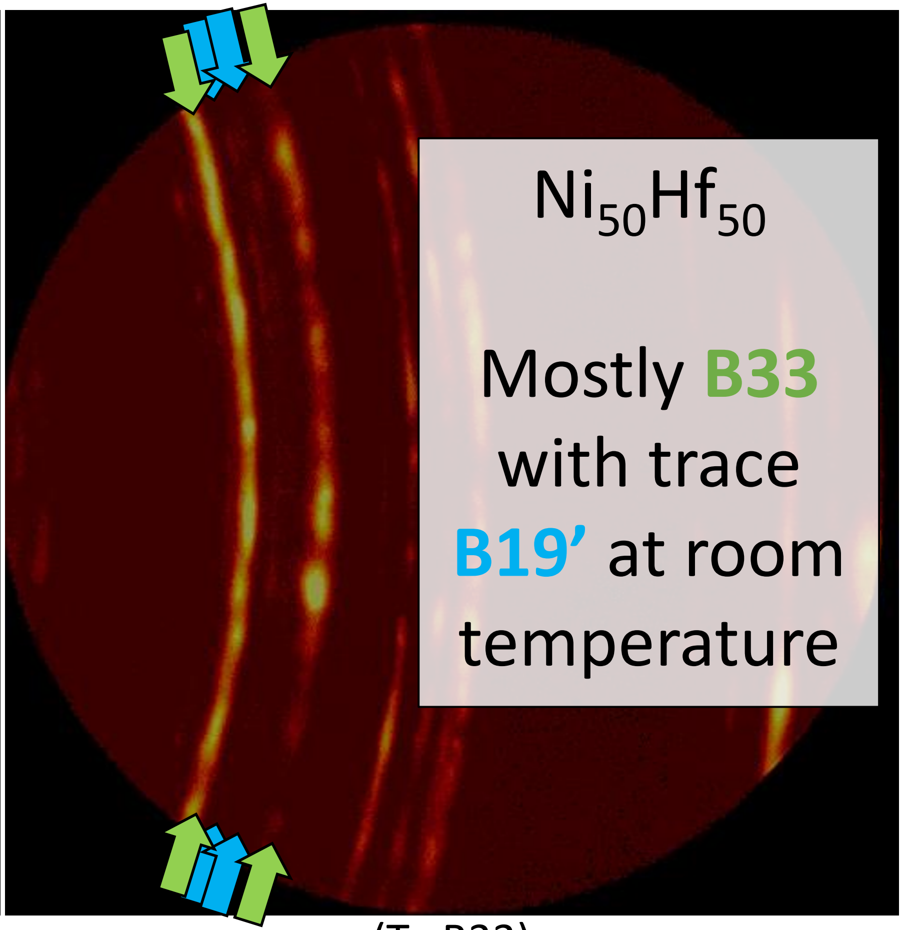
2D XRD Solves the Case!



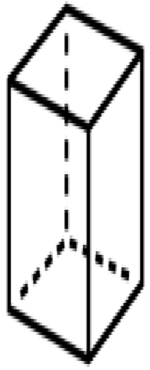
B19' ($P2_1/m$)



(Not to B33)



(To B33)

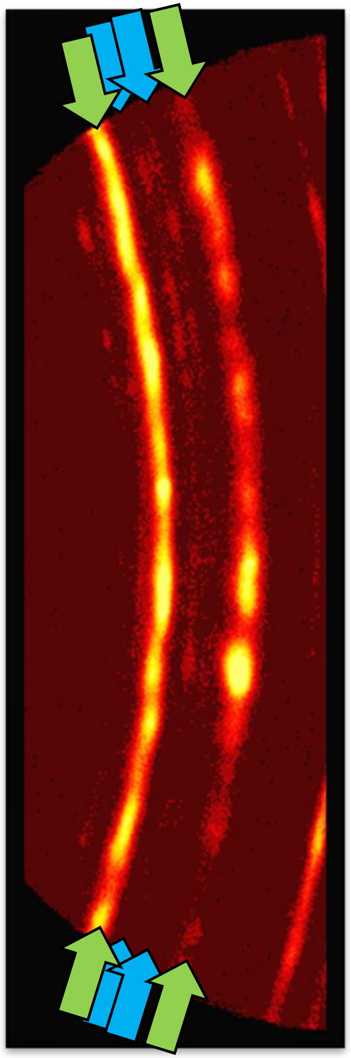


B33 (Cmcm)

(This can be seen in 1D XRD spectra also, but it is easier to visualize with 2D)

What We Learned and What we Still Have to Learn

- TEM only showed B33 in $Ni_{50}Hf_{50}$
- SEM/EBSD showed trace B19' in $Ni_{50}Hf_{50}$
- 1D + 2D XRD confirmed mostly B33 with trace B19' in $Ni_{50}Hf_{50}$
- Future work to increase shape memory effects in $Ni_{50}Hf_{50}$ at high temperatures



Questions?


NASA
Glenn Research Center
Lewis Field
RESEARCH AND TECHNOLOGY
NASA
Glenn
Research
Center
FOR THE BENEFIT OF ALL