Materials Characterization using X-Ray Diffraction

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NASA Glenn Research Center

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John Carroll University

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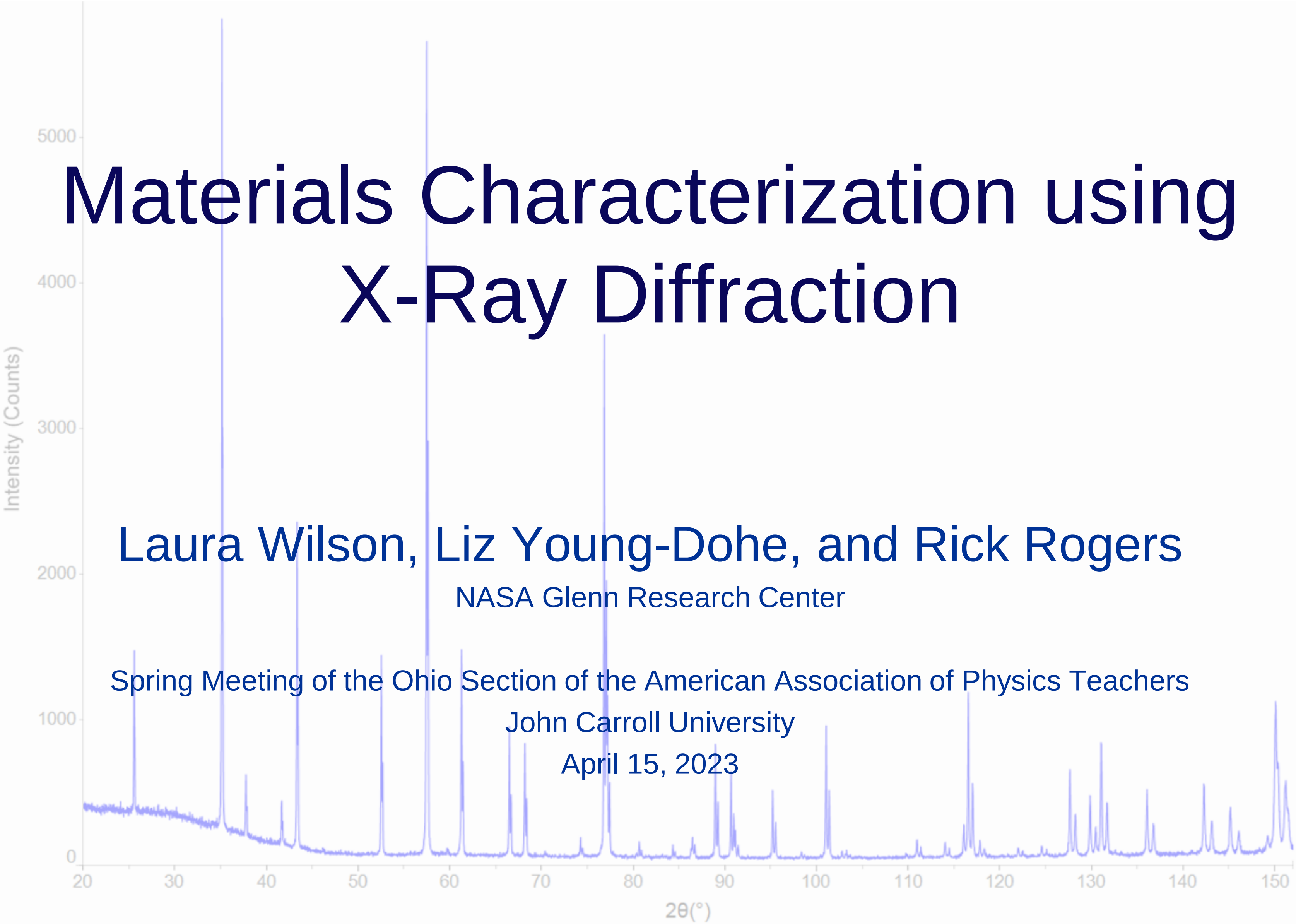
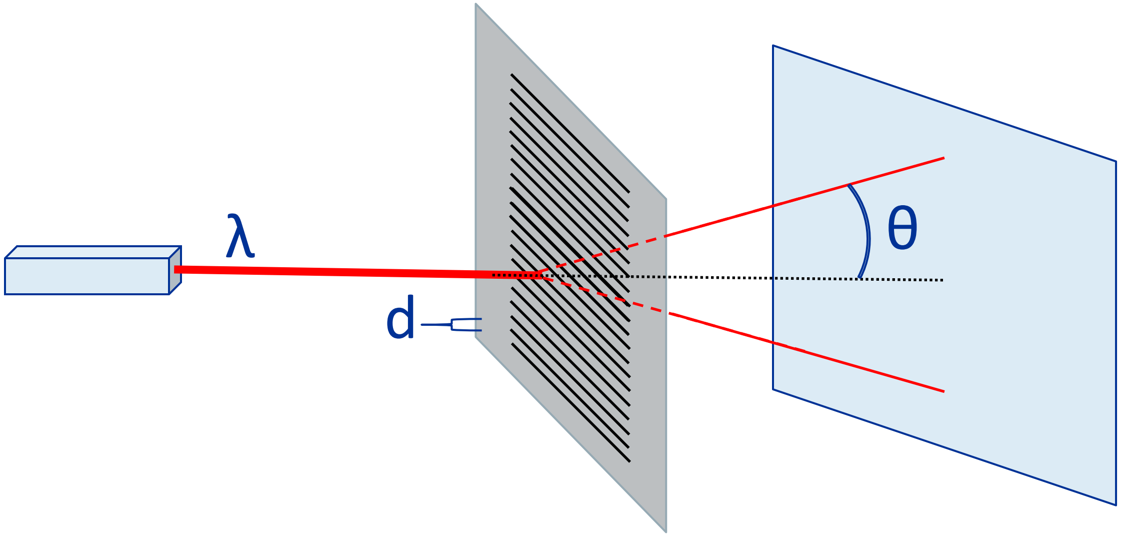


Presentation overview

- What is Diffraction?
- Basics of X-Ray Diffraction (XRD)
- What can be done with XRD?
- NASA Programs using XRD for materials development

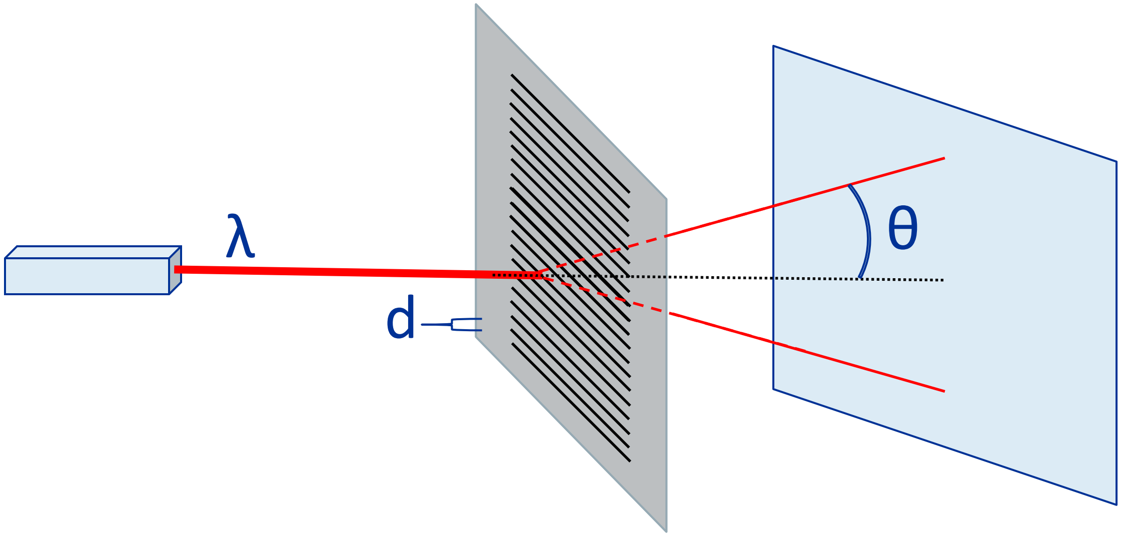
2D to 3D Diffraction
Grating Equation to Bragg's Law



$n\lambda = d * \sin(\theta)$

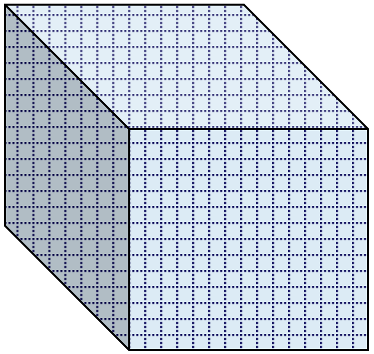
2D material diffraction

2D to 3D Diffraction
Grating Equation to Bragg's Law



$n\lambda = d * \sin(\theta)$

2D material diffraction, but crystals are 3D and have much smaller d-spacing…



Diffraction Equations
Relating Wavelength to d-Spacing

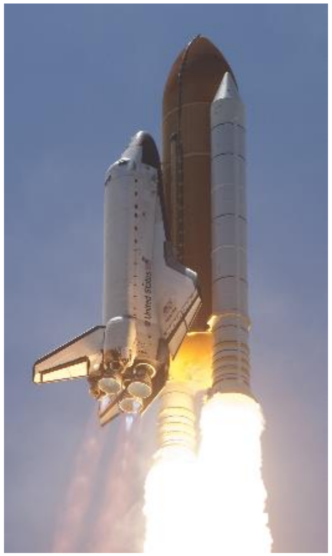
$$n\lambda = d*\sin(\theta)$$

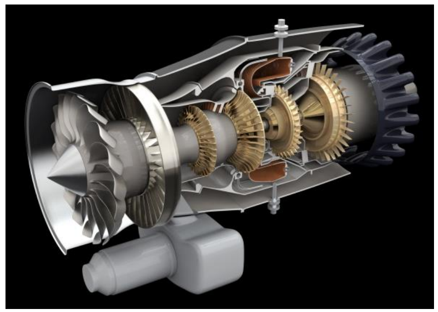
Direct relationship between wavelength and d-spacing

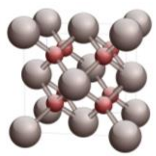
Use a LARGER/SMALLER wavelength to get diffraction in a LARGER/SMALLER material

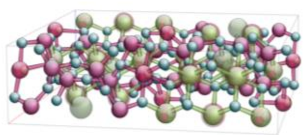
Probing the structure of materials with diffraction

X-ray length scales

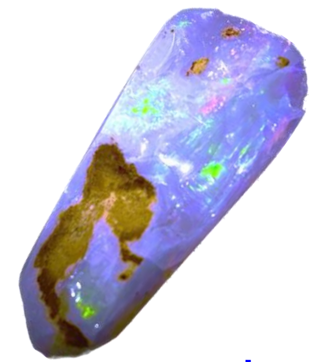


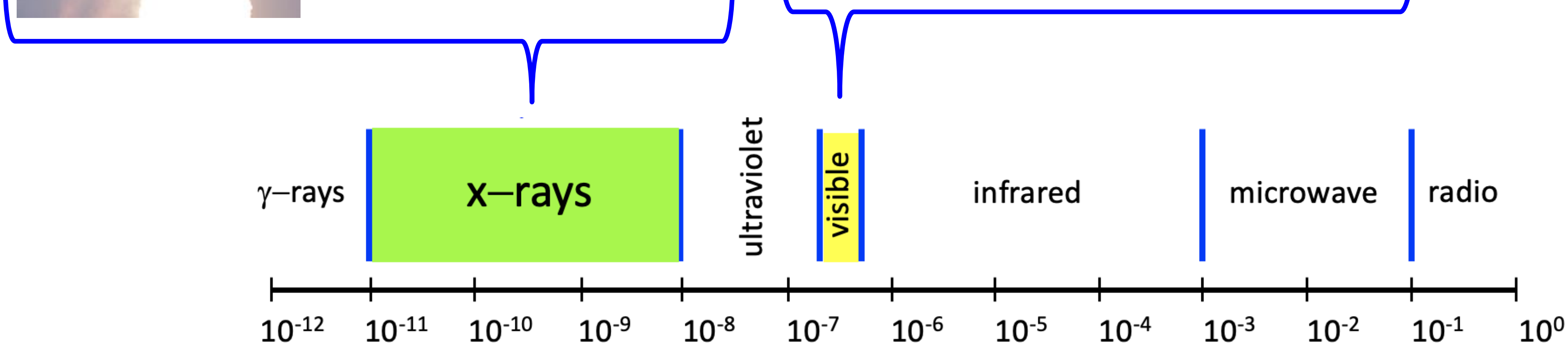




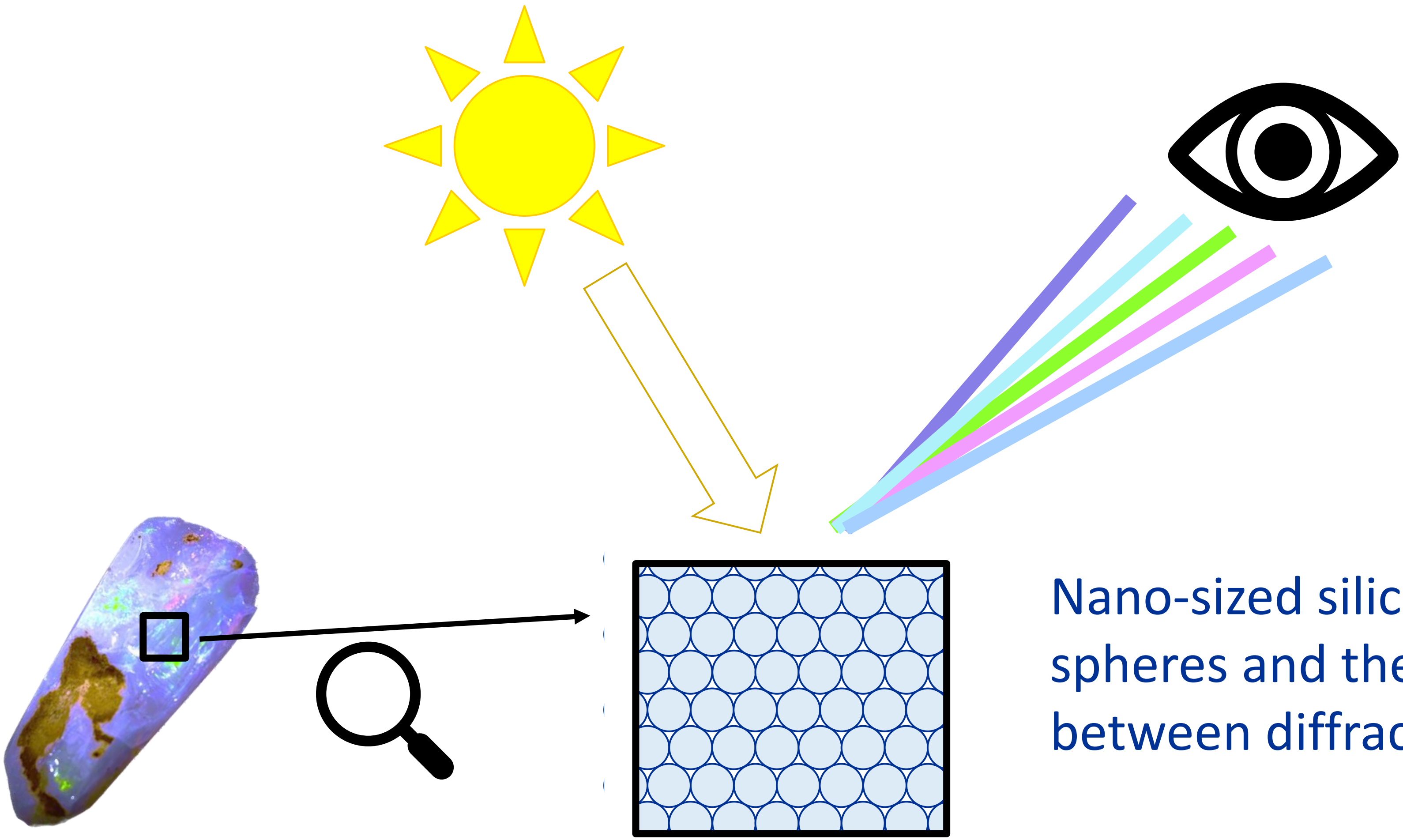


Optical length scales



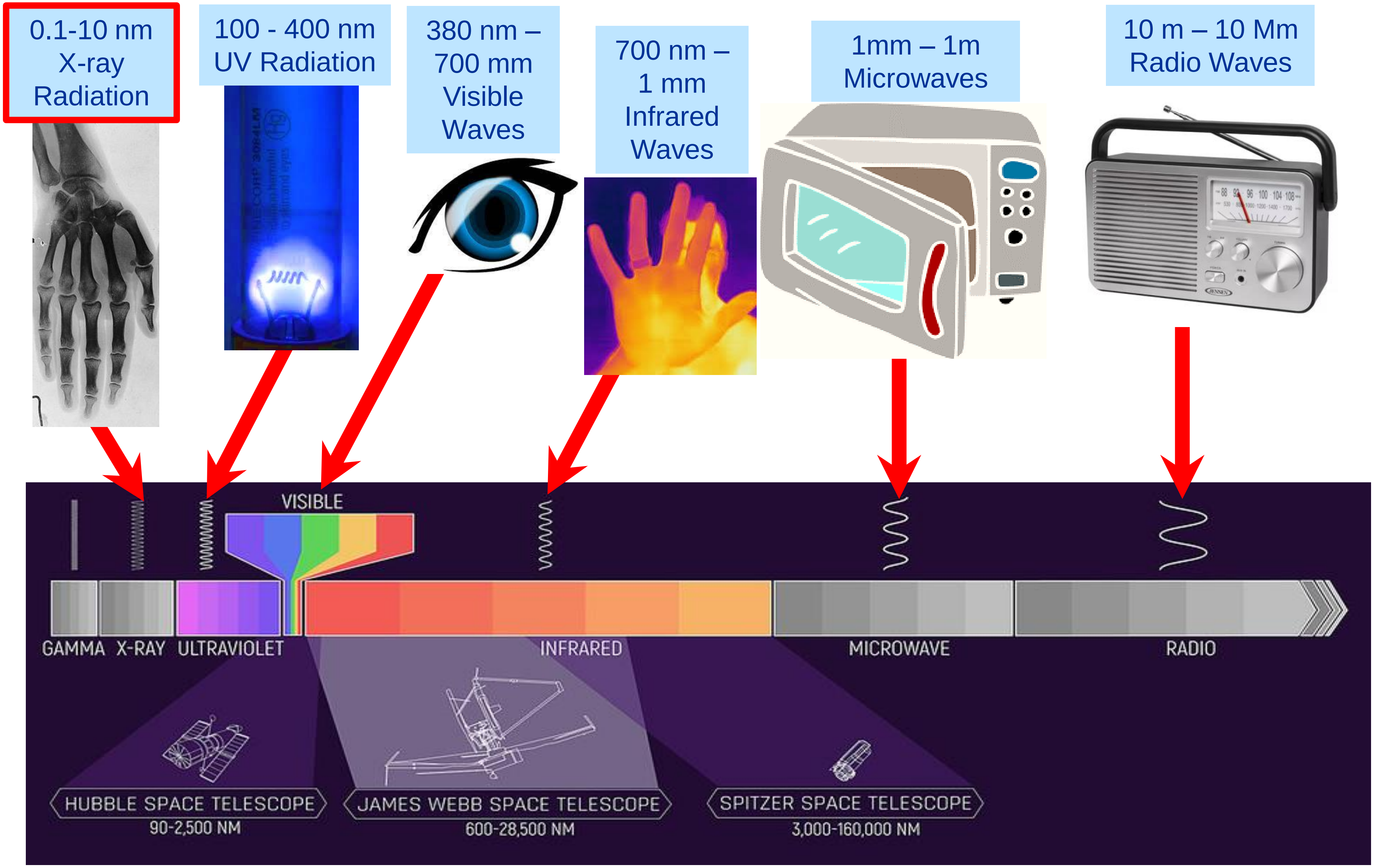


Speaking of opals, they diffract light!

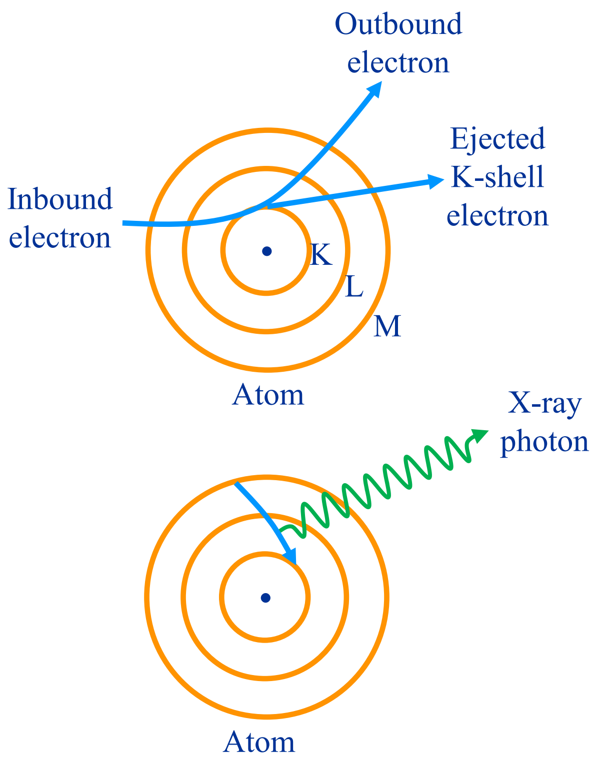


Nano-sized silica spheres and the spaces between diffract light

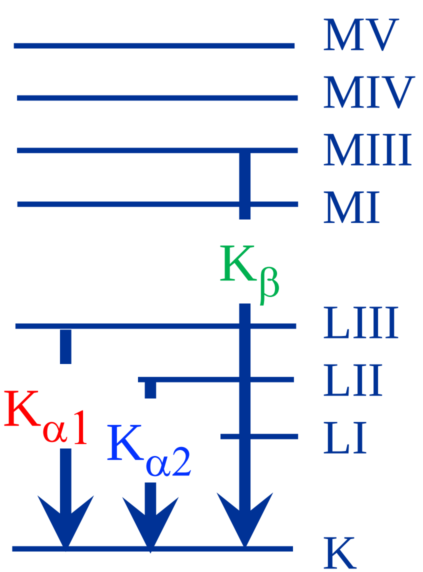
The Electromagnetic Spectrum – What are X-rays?

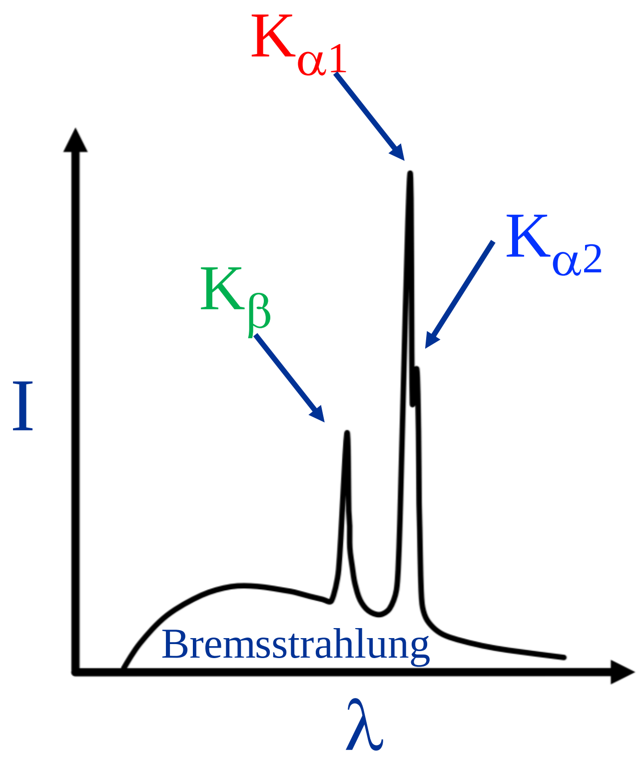


The wavelength of X-rays is determined by the anode of the X-ray source.



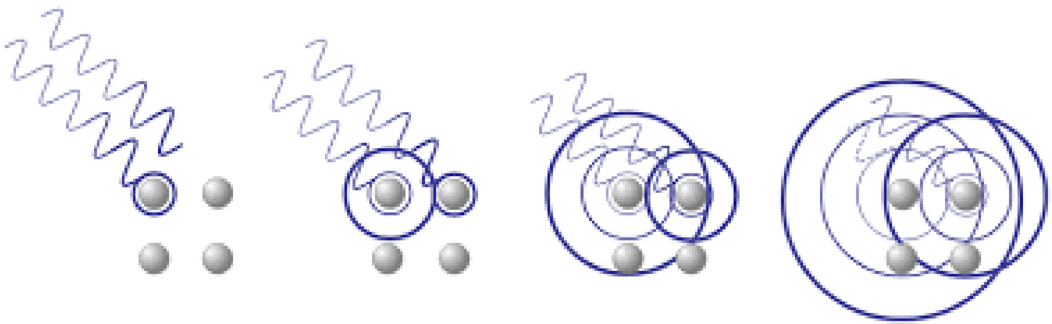
Inverse Photoelectric effect





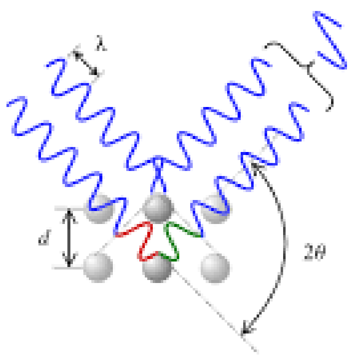
Why are X-rays Used to Analyze Materials?

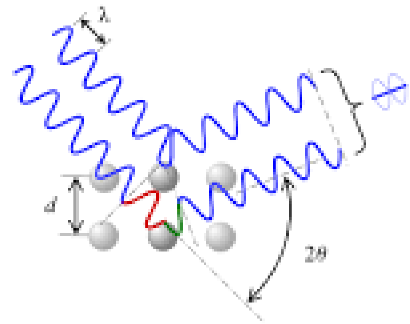
- X-rays λ ≈ size of atoms and crystallographic planes
- X-rays are scattered by atoms through interaction with the electrons



- If the X-ray encounters a regular array of atoms – like in a crystalline material – an array of spherical waves will be generated

Constructive interference



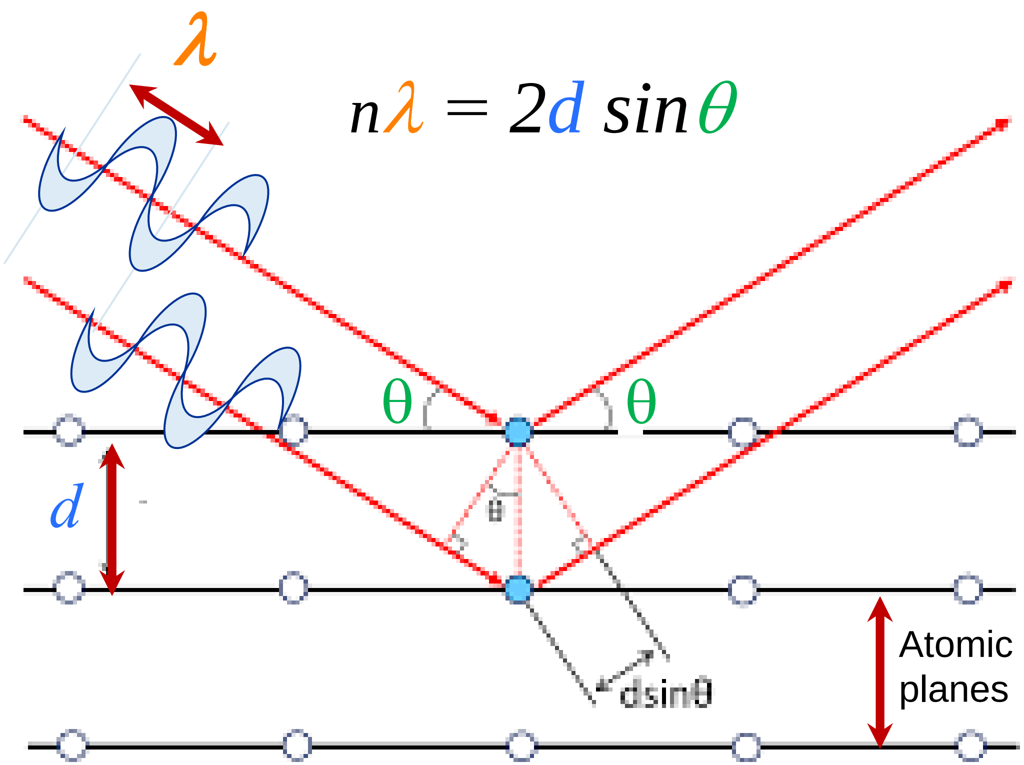


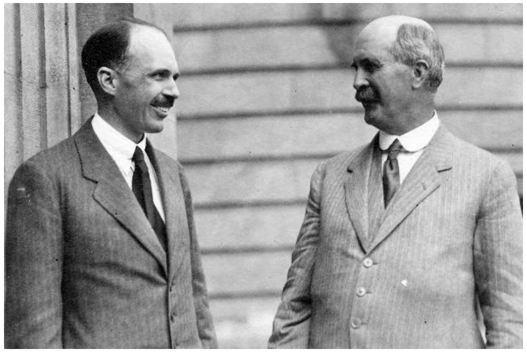
Destructive interference

Bragg's Law of Diffraction

Identify unknown materials based on crystal structure and elemental composition

A monochromatic wavelength of X-ray radiation interacts with the crystallographic planes of the materials - resulting in a pattern which can be matched to a database of materials or patterns obtained from previously tested samples.



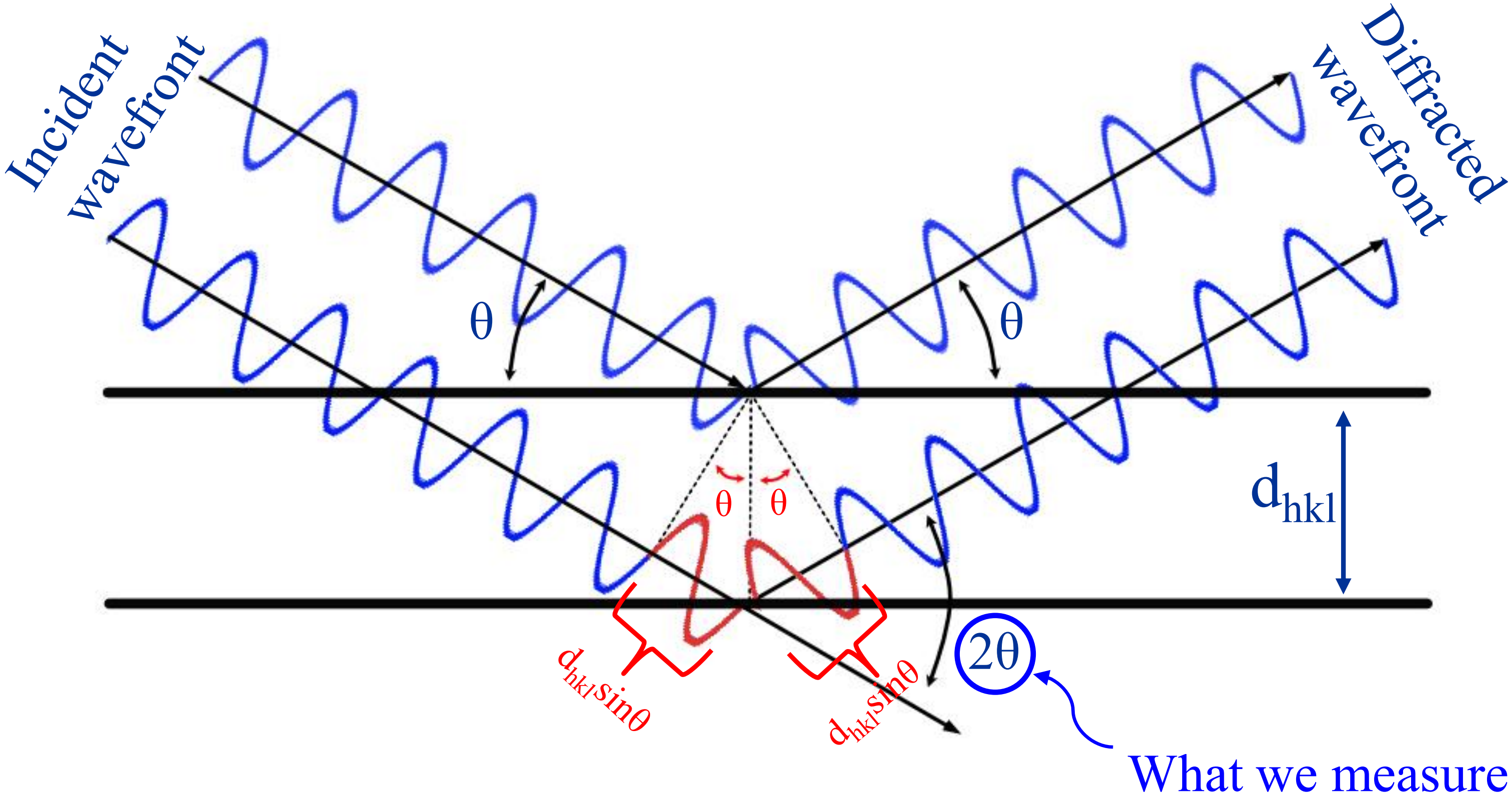


Credit: Smithsonian Institution Archives. Image # SIA2007-0340

In 1915, Lawrence Bragg and his father William Henry Bragg were awarded the Nobel Prize for their work in crystal structure determination.

Their work confirmed the existence of particles on the atomic scale – and provided a robust tool to study crystalline materials

Bragg's Law – the key equation in XRD

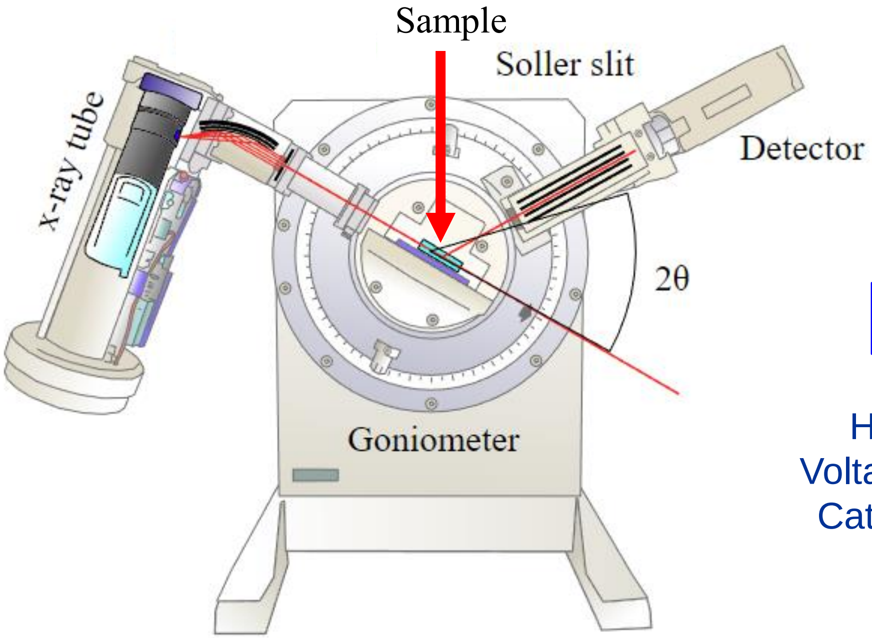


Bragg's Law: $n\lambda = 2d_{hkl}\sin\theta$

Bragg's Law applies not only to X-rays, but to all EM wavelengths

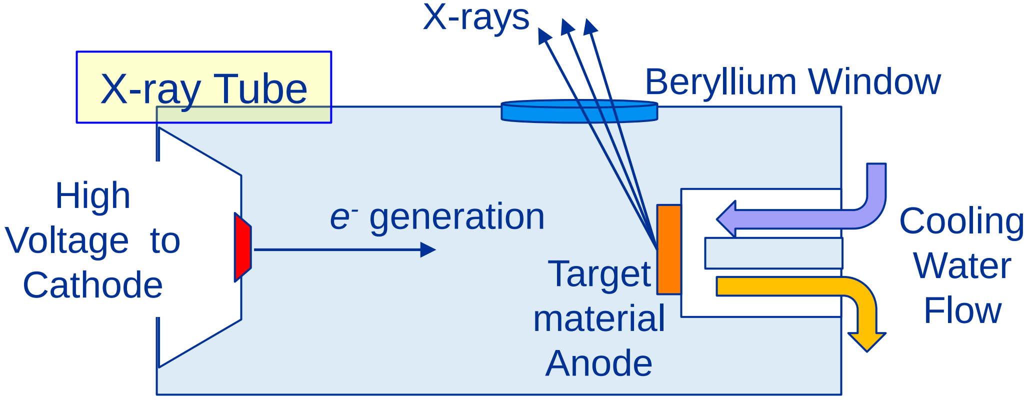
X-ray Diffraction System

- **Goniometer:** A device that precisely measures angle and permits the rotation of a sample to specific positions
- **X-ray tube:** Generates X-rays by converting electrical power into X-rays. The Cathode is energized by high voltage, causing it to emit electrons which then is accelerated by the anode voltage onto the target material. The wavelength of X-ray is dependent on the Anode material.
- **Detector:** Converts X-ray photon energy into electrical signals to generate the X-ray Pattern. Point Detectors are the most common, but area detectors are used for advanced characterization work.
- **Sample:** Material Under Test

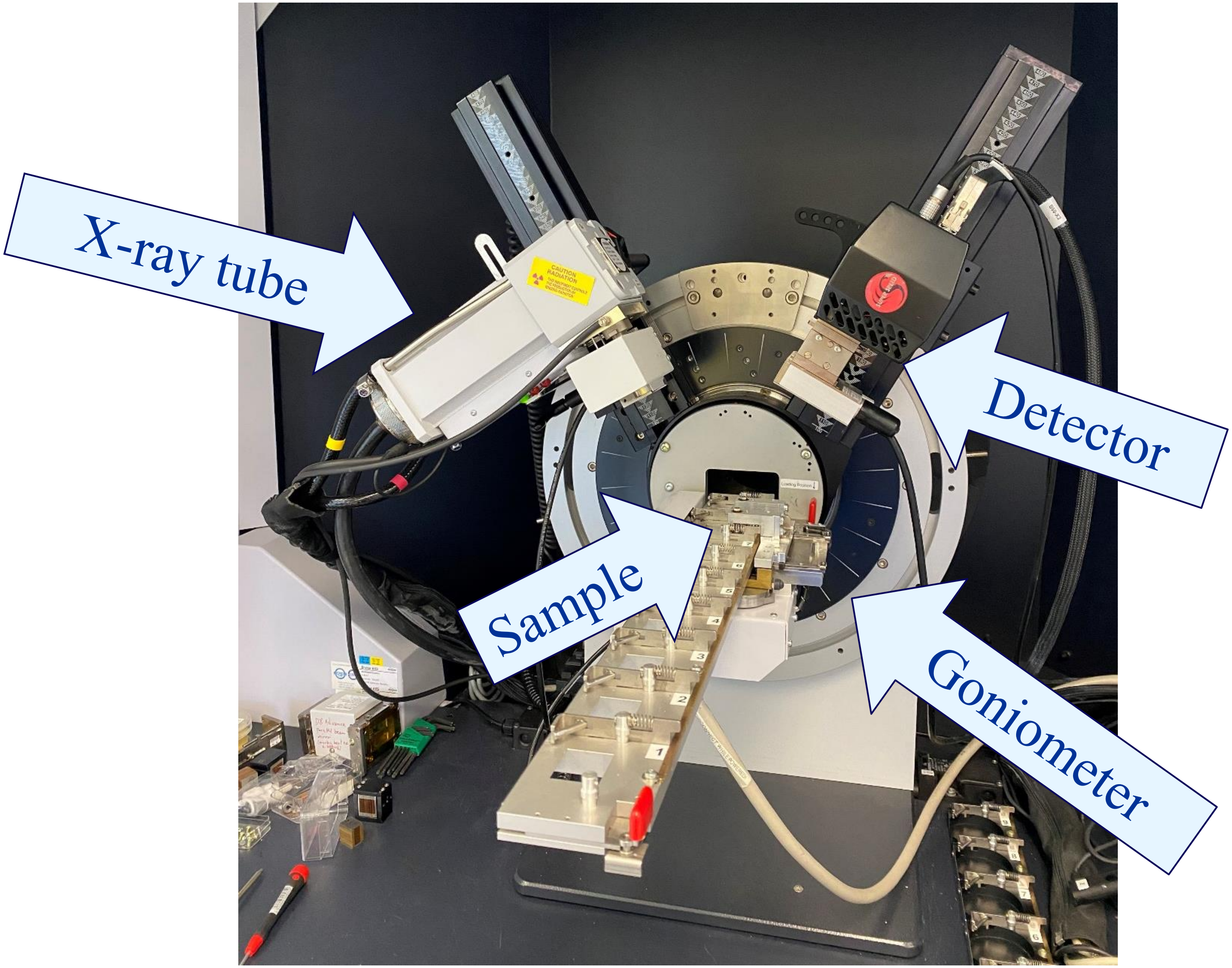


Some Common Anode Materials for X-Ray Diffraction:

Material	Wavelength (Å)
Molybdenum	0.71
Copper	1.5406
Cobalt	1.79
Iron	1.94
Chromium	2.29



Example diffractometer pic w/labels



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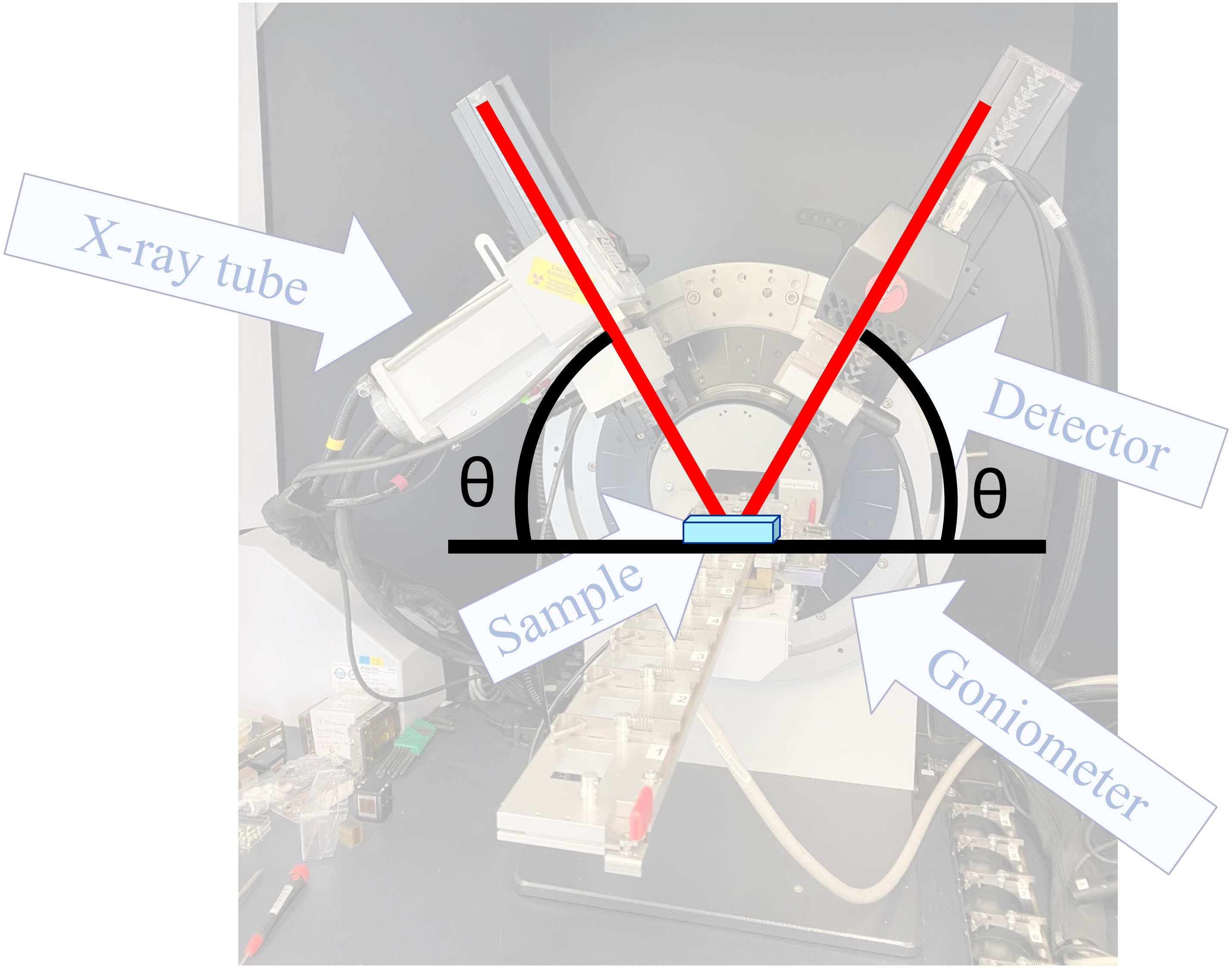
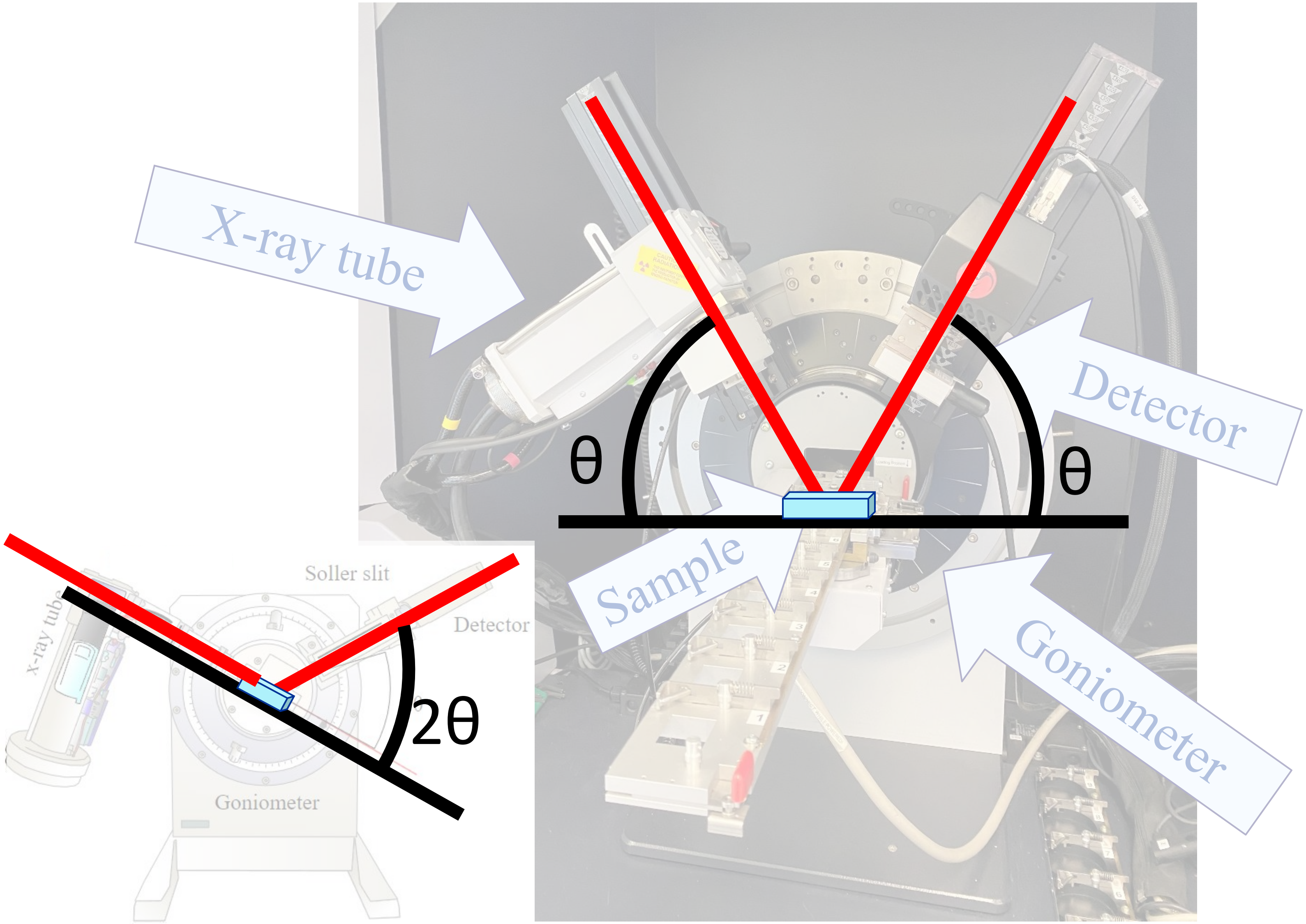
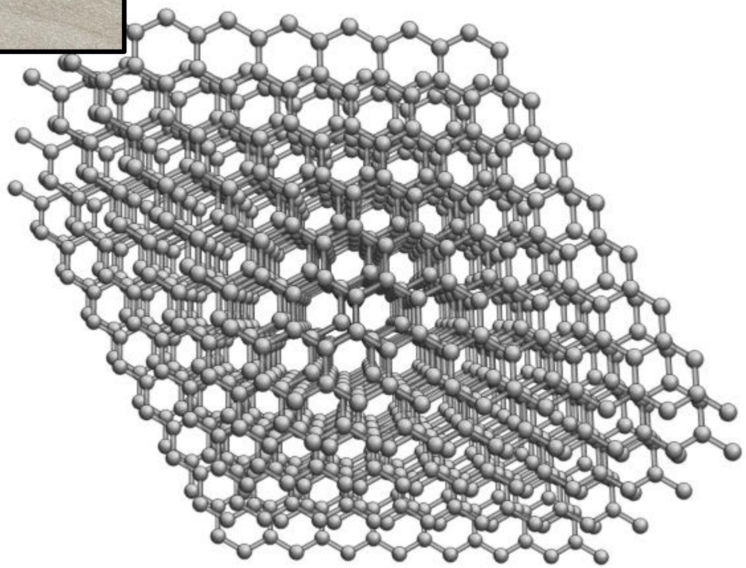


Example diffractometer pic w/labels

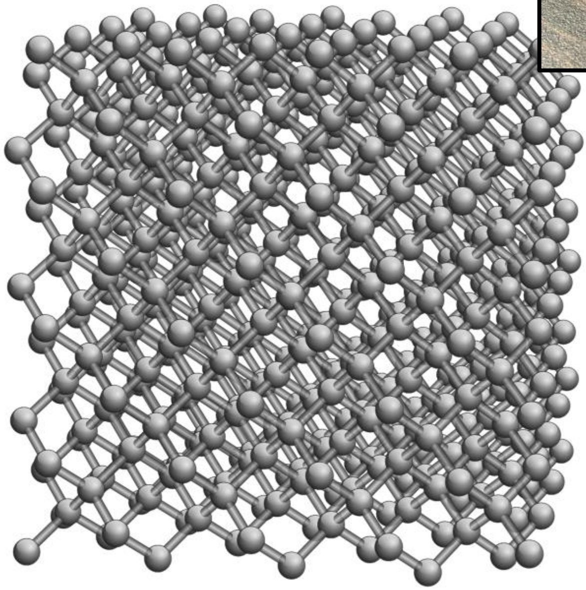


The relationship between structure and properties is a core focus of materials science and engineering

Graphite



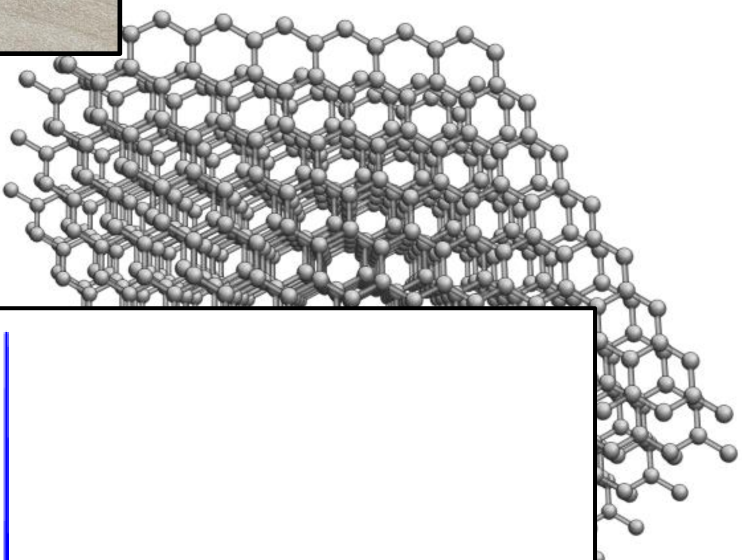
Diamond

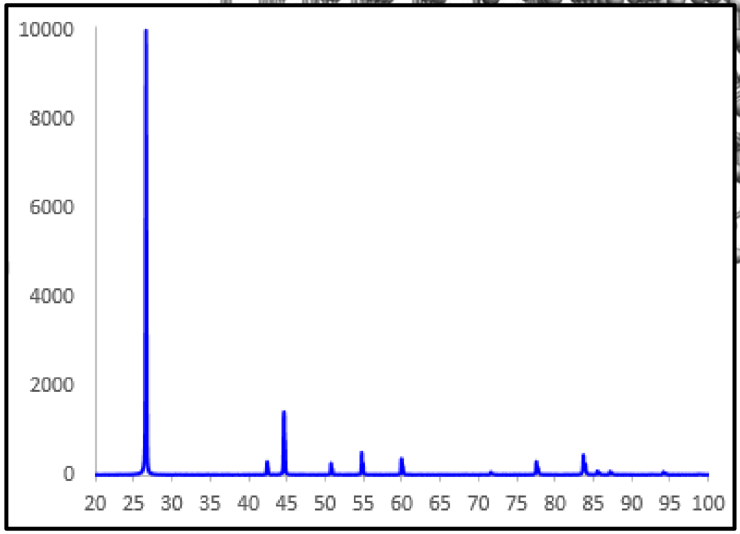


- Same element
- Extremely different physical properties, all due solely to differences in the arrangement of the C atoms.

XRD can distinguish between structures

Graphite





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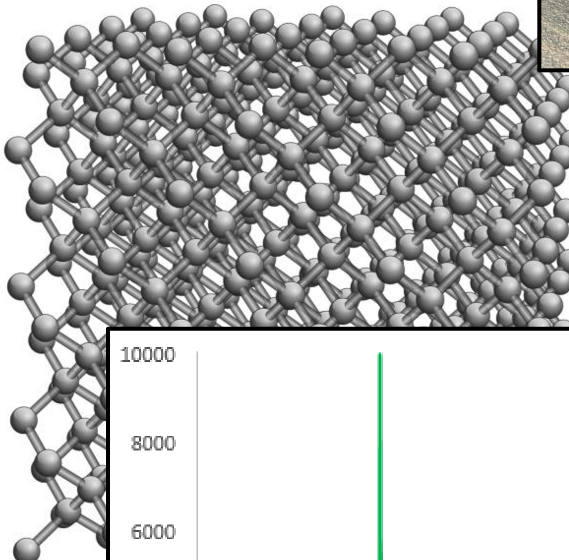
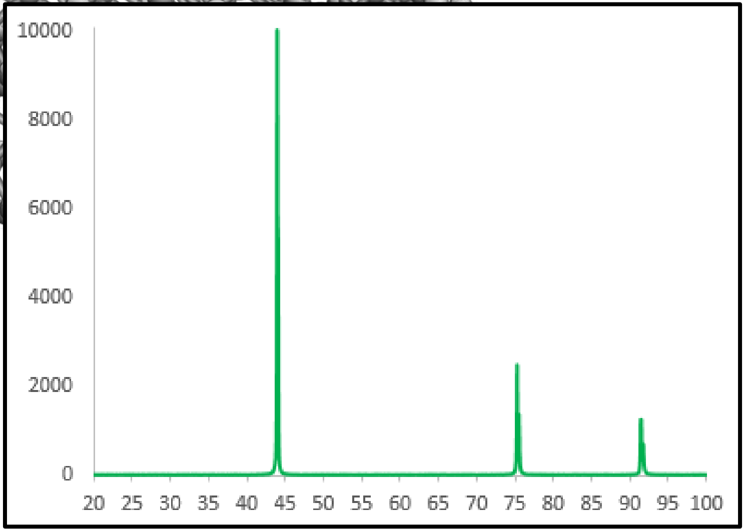
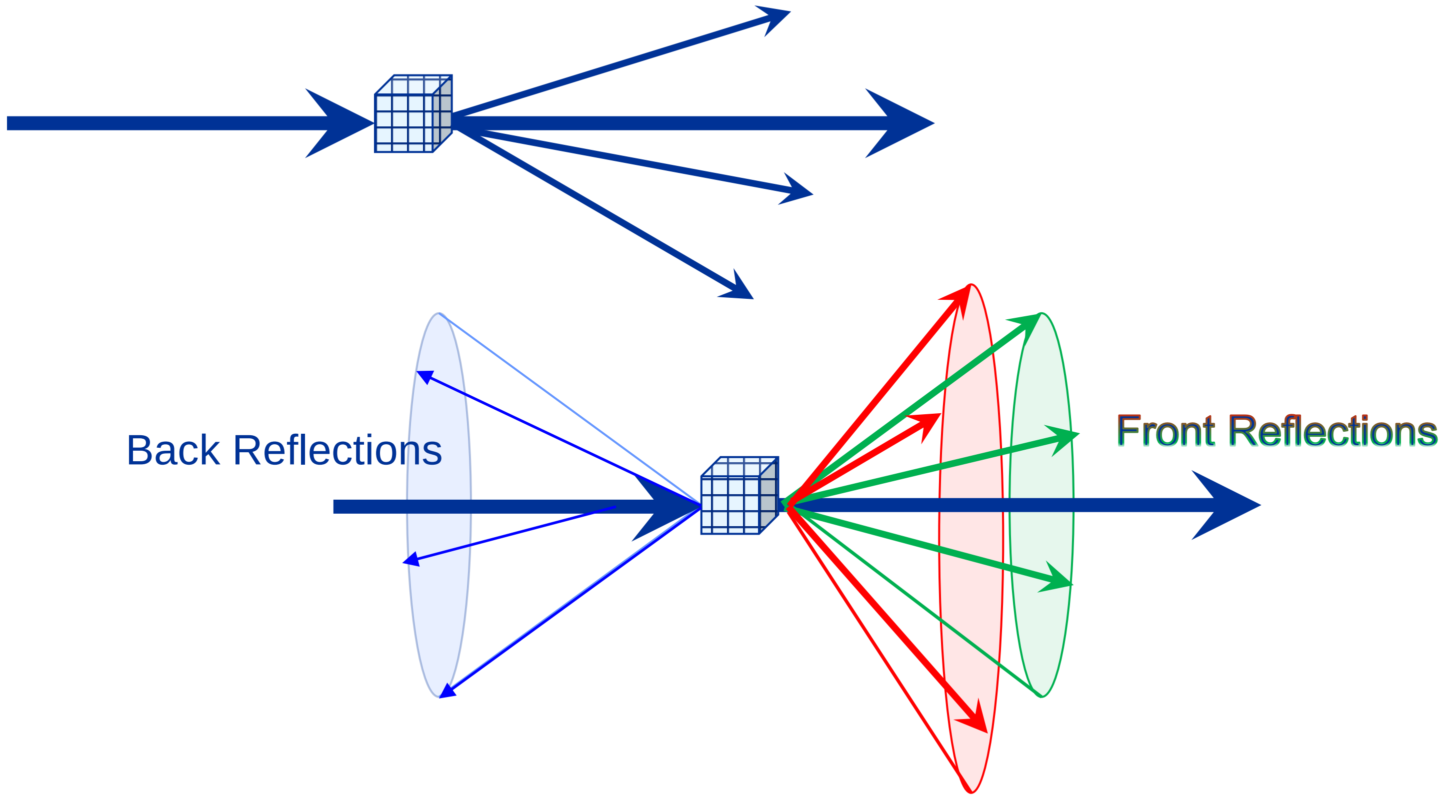
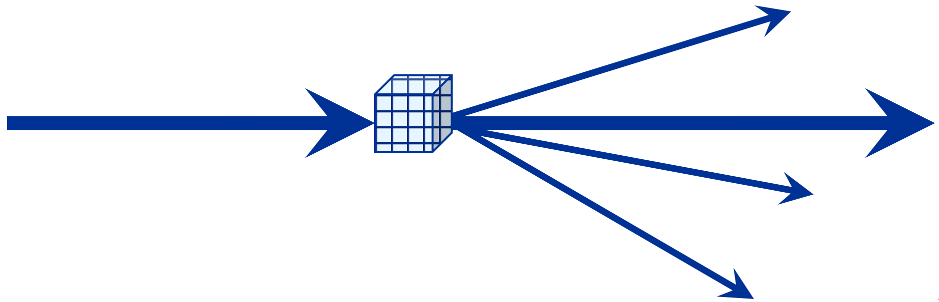
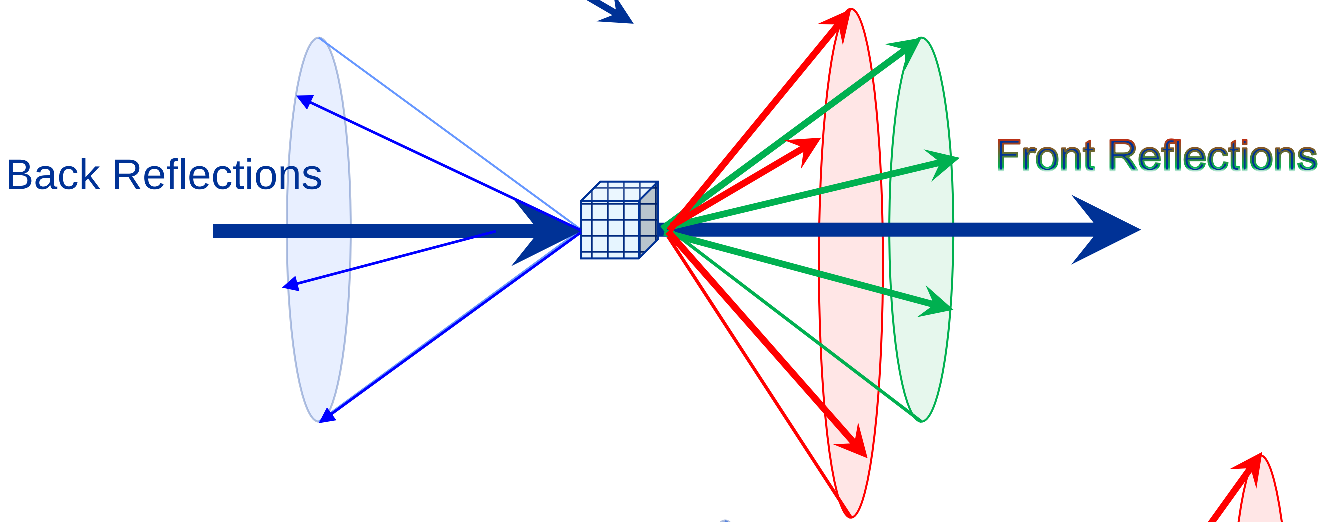
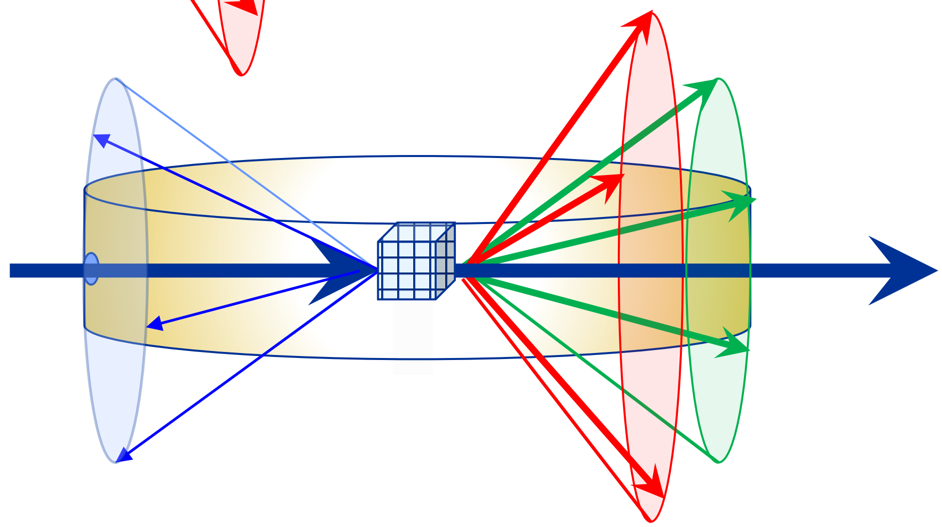





Back Reflections
Front Reflections

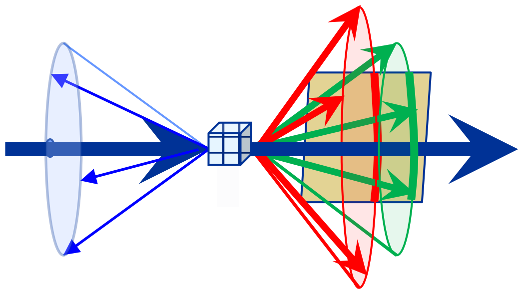


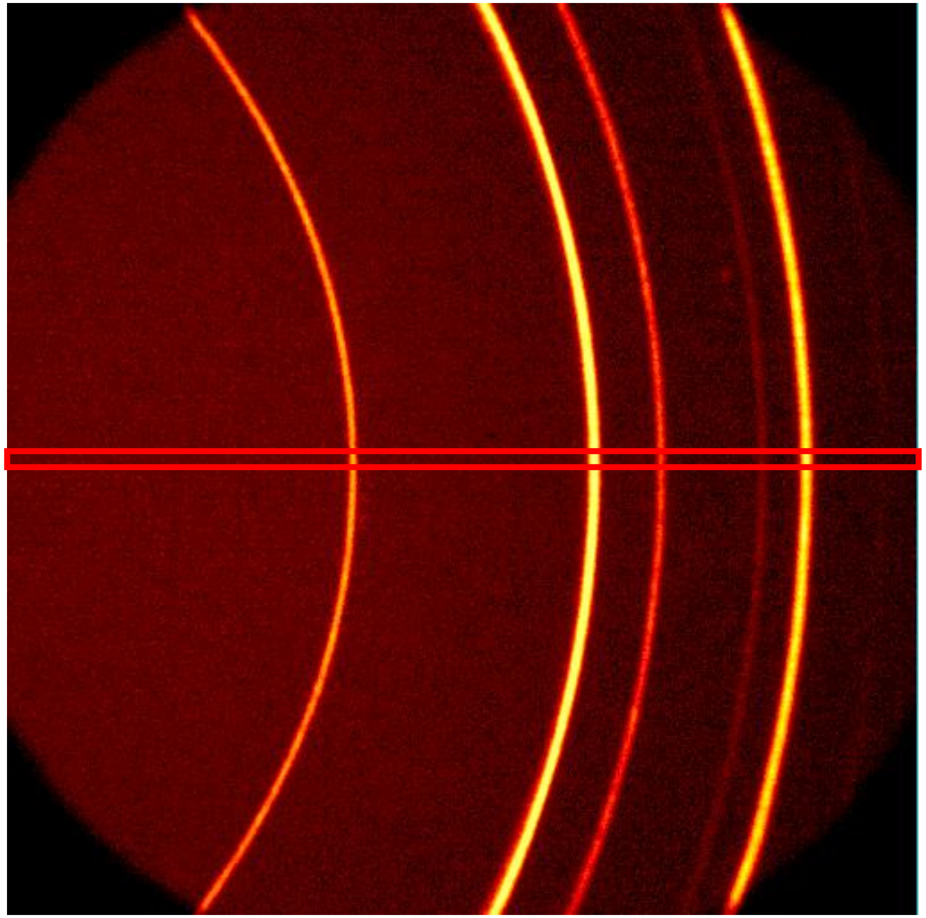


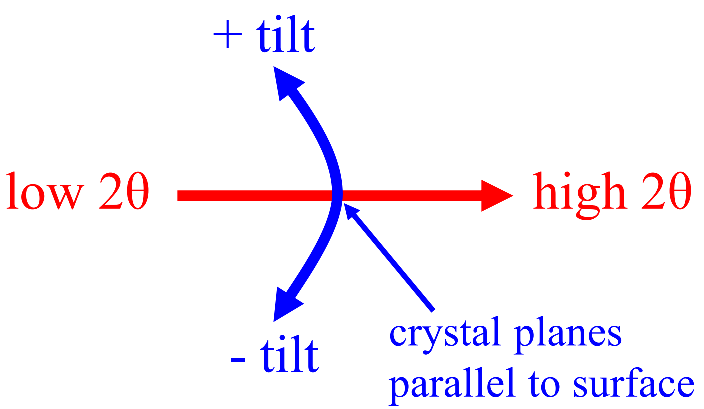


- Used to use film to detect ring intensities and positions
- Now use area or line detectors

Area Detector

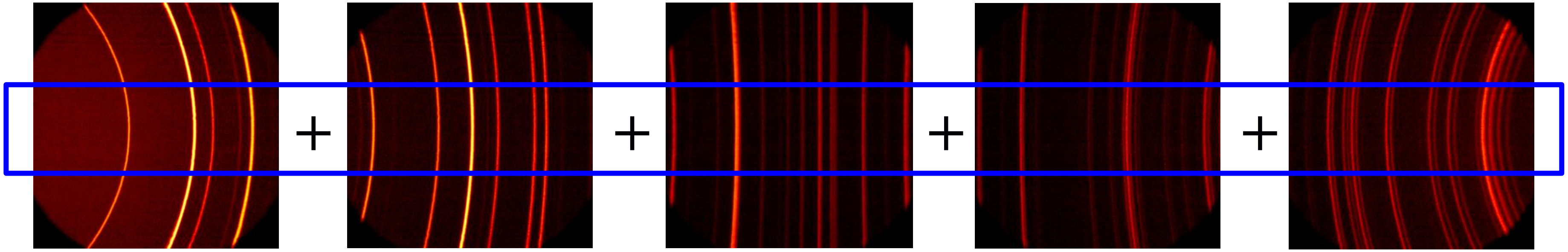


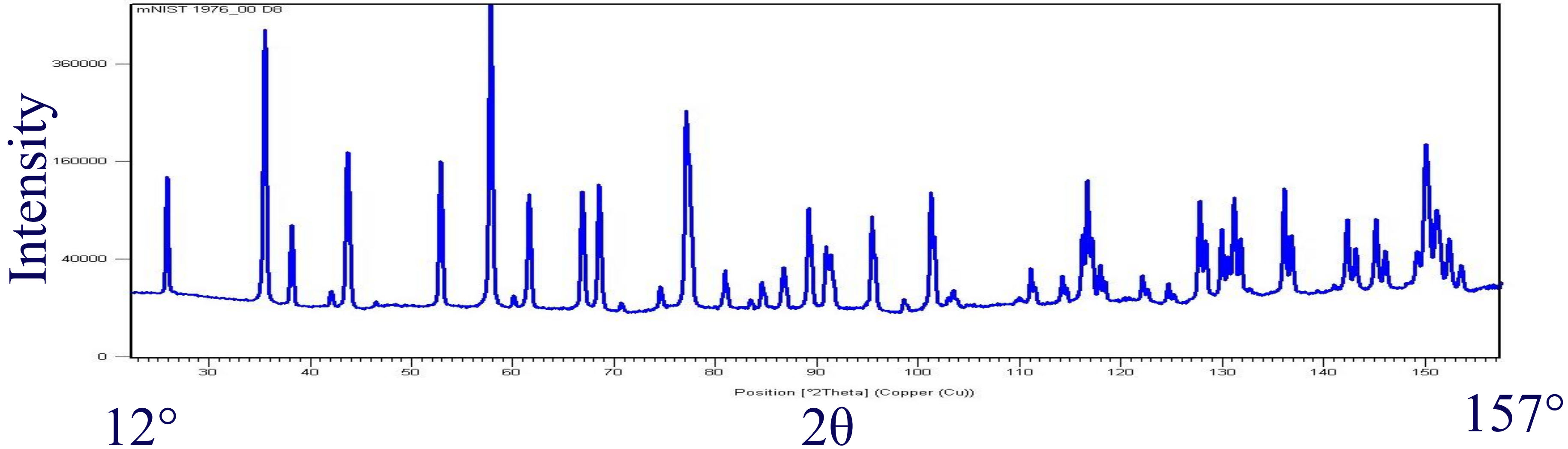




Data range covered by point detector & focusing geometry (Bragg-Brentano)

Building up a Data Scan





What you can do with X-ray diffraction (XRD)?

- Crystalline phase identification
  - XRD peak positions and intensities like a fingerprint
- Lattice parameter measurements
  - correlates with other important material properties
- Residual stress
  - essentially using crystal lattice as a strain gage
- Crystallographic texture (preferred orientation)
  - strong effect on physical properties
- Single crystal orientation and structure
  - extreme case of texture
- Crystallite size/strain
  - both affect peak with different θ-dependence

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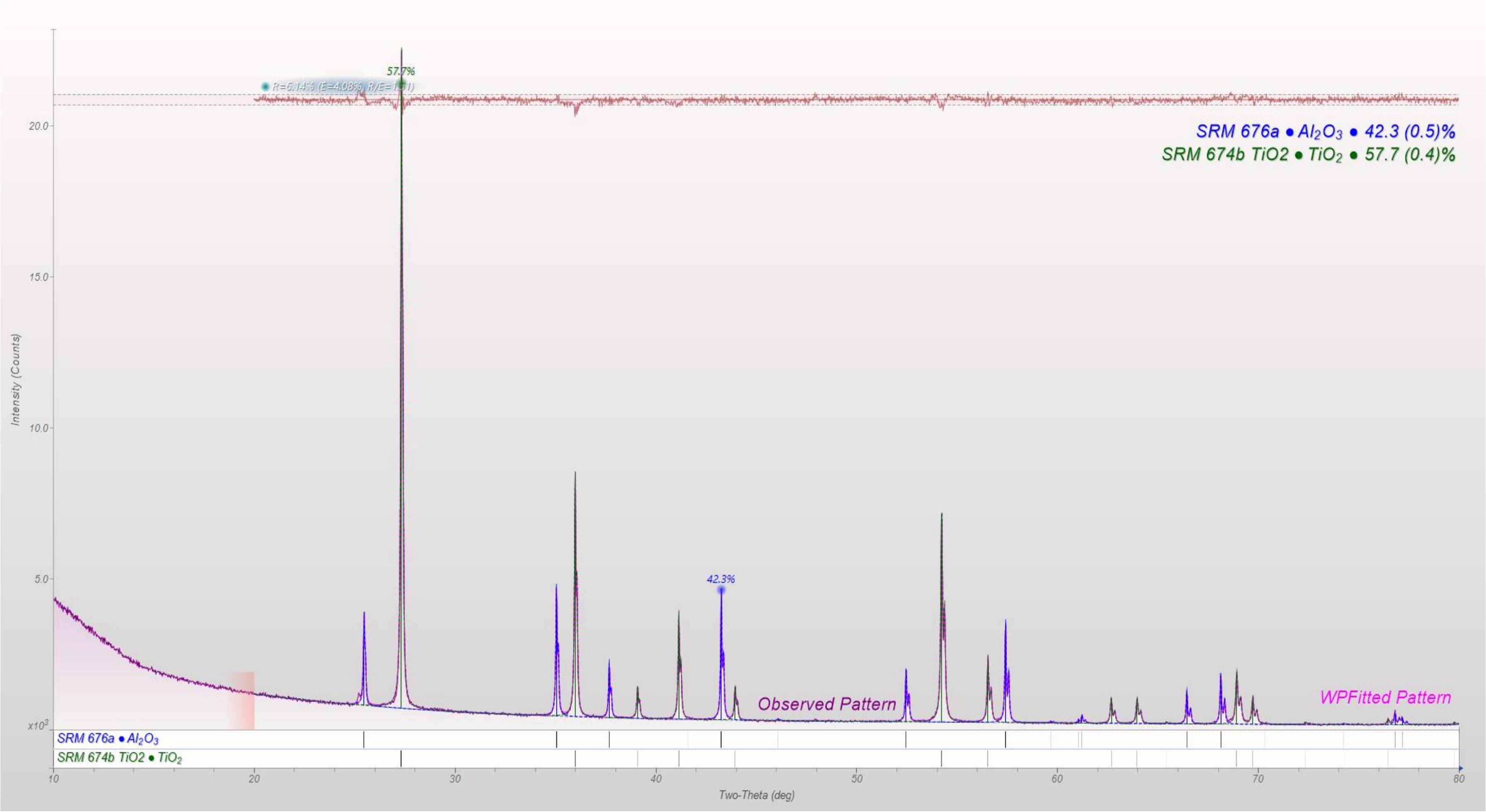
Phase ID

- What crystalline phases are present?
- How much of each phase?
- Crystalline vs. amorphous content

A pretty simple phase ID



A really complicated phase ID

RRCPE-3x Tim Gabb

Phase ID example: GEER

The Glenn Extreme Environment Rig (GEER) is a high-tech pressure vessel capable of simulating the temperature, pressure and atmospheric gas mix of many extreme environments in the Solar System and beyond.

Venus Conditions for GEER:

- Pressure: 94 bar (~93 atm)
- Temperature: 1000 °F
- Gases: 8 specialty gases + 1 liquid

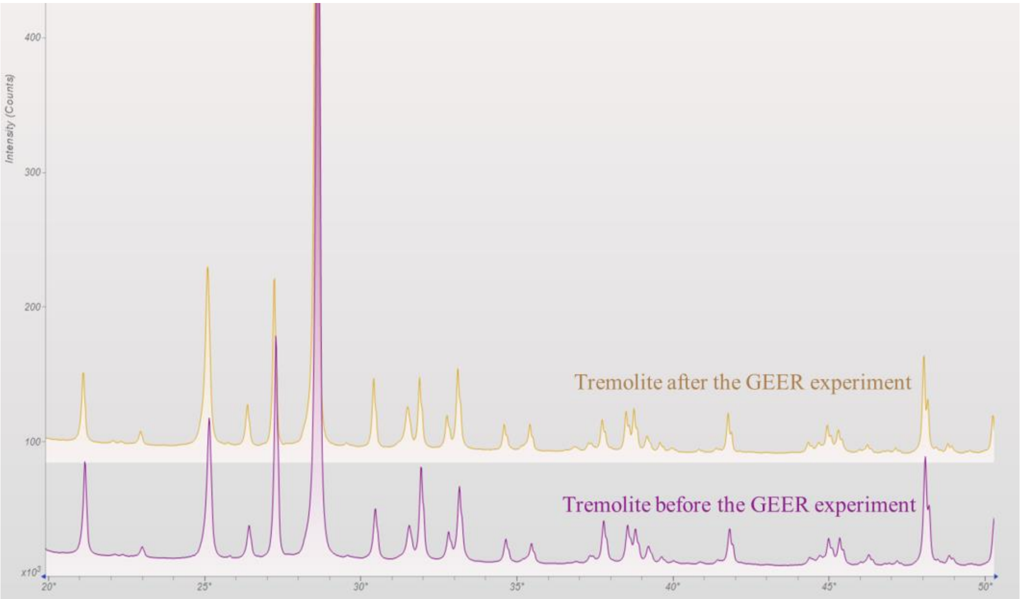
The End Cap weighs as much as a standard-size SUV

There is over 2 million pounds of force on the End Cap at our typical operating conditions

Minerals in GEER

Tremolite
($Ca_2Mg_5Si_8O_{22}(OH)_2$)

Before (left) and after (right) it was heated to Venus conditions for 60 days



- Was there water on Venus?
- Does HF replace the OH in the tremolite structure?

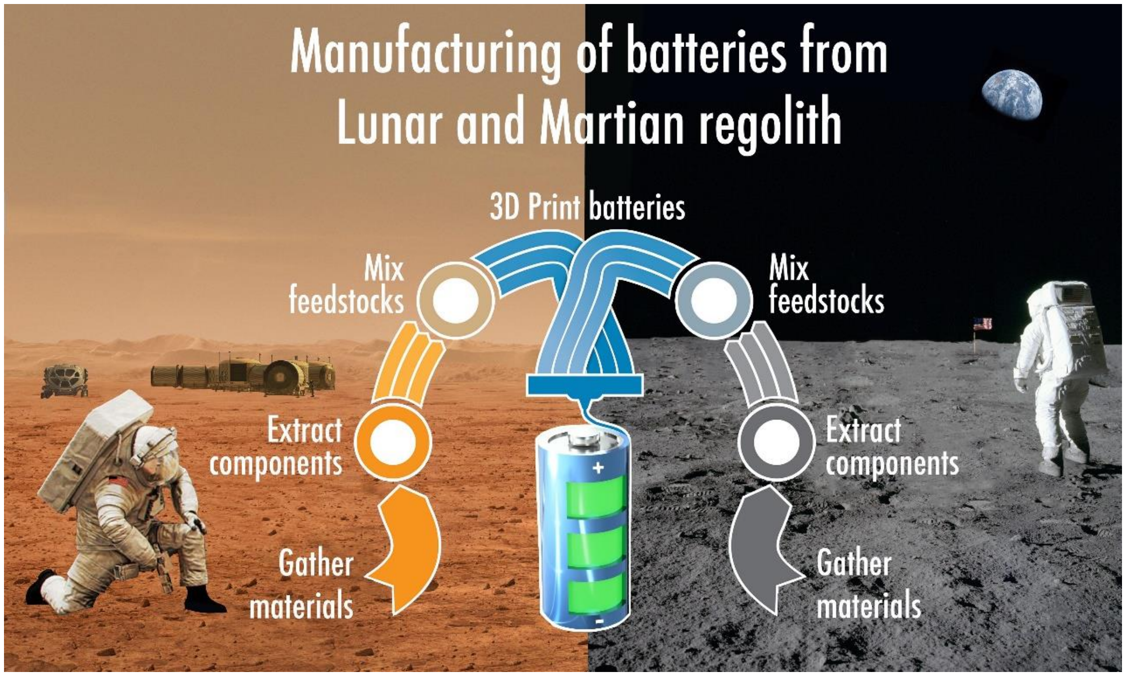
Port, S. T., Kremic, T., Hunter G. W. 2023. Experimental Investigations of Potential HCL and HF Mineral Buffers on Venus. LPSC LIV, abs. #2356.

Phase ID for Batteries

"What would battery manufacturing look like on the Moon and Mars?"

Open access paper: ACS Energy Lett. 2023, 8, 1042−1049

GRC POC's: Dr. Donald Dornbusch and Dr. William Huddleston



- In-situ resource utilization (ISRU)
- Sodium is more abundant than lithium on the Moon and Mars
- Goal: 3D print Sodium-ion batteries from ISRU materials
- Sodium-ion cathodes must balance:
    - Energy storage performance (energy density, voltage)
    - Elemental abundance (wt. % vs ppm)

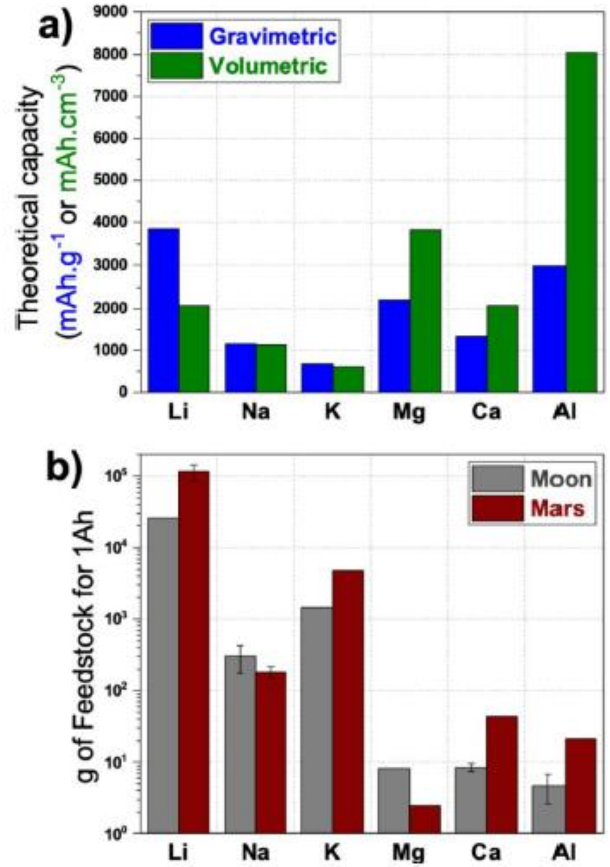
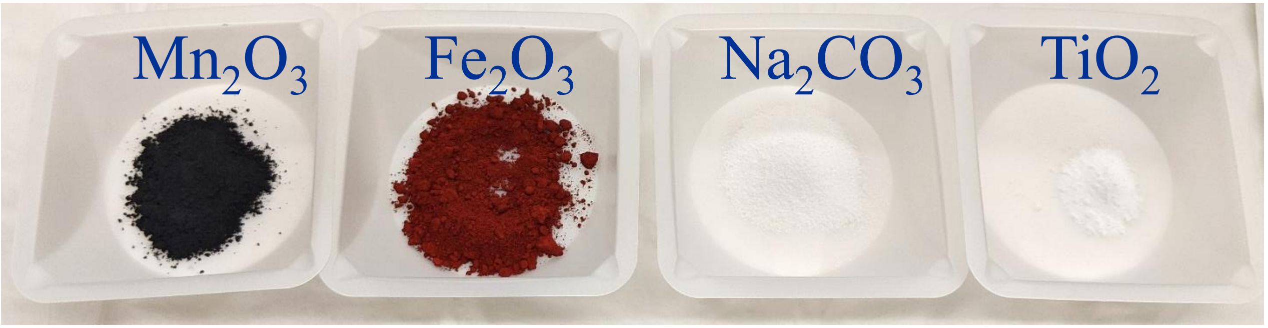
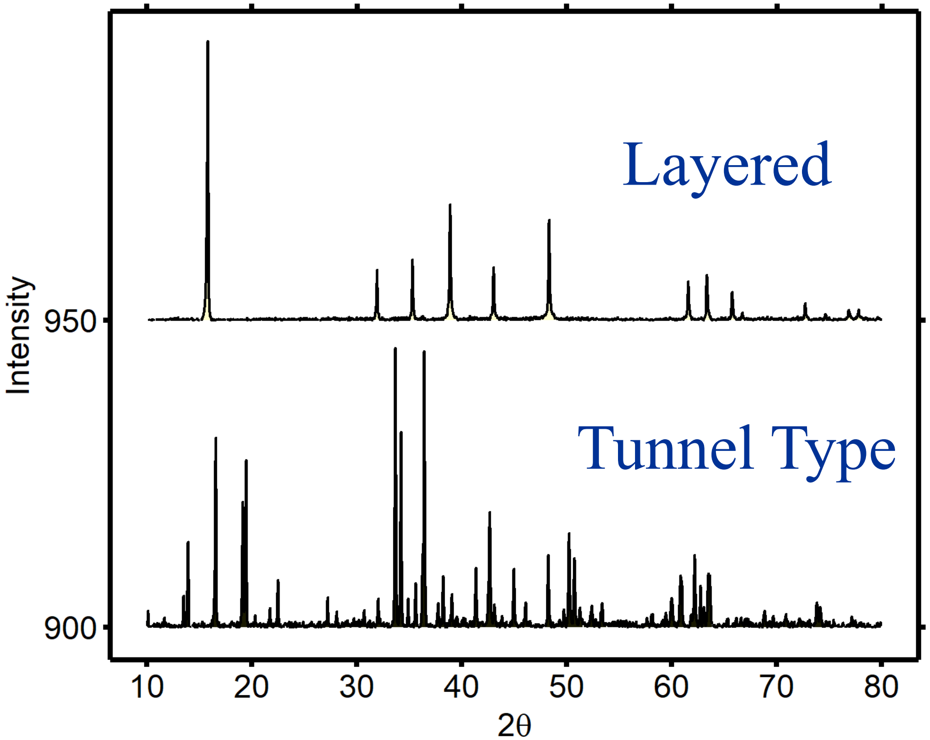
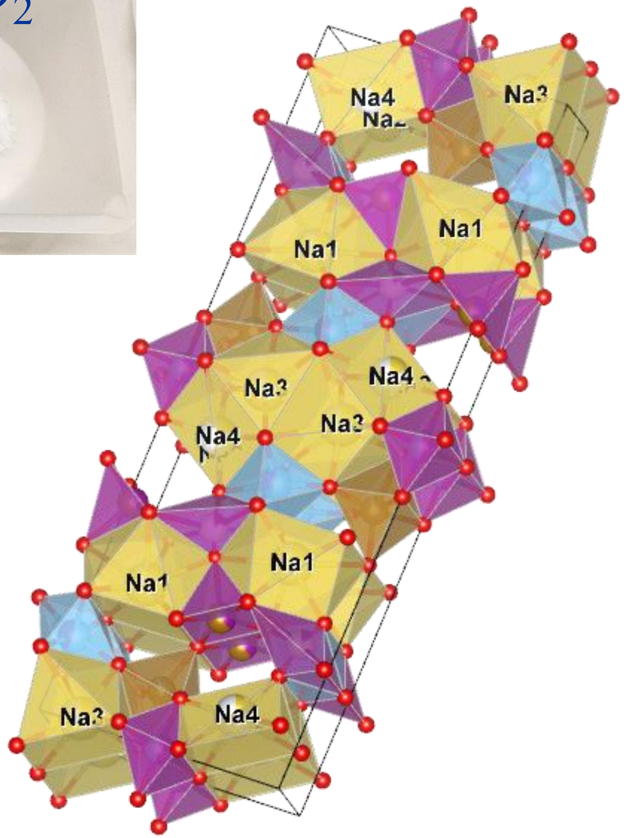


Figure 2. (a) Theoretical gravimetric or volumetric capacity values of relevant negative electrode materials. (b) Amount of lunar feedstock required to generate 1 Ah worth of negative electrode materials.

Pure precursor oxides







Example of "tunnel type" structure (orthorhombic - Pbam)

- Which composition, processing conditions, and structure provide the best balance between energy storage performance and elemental abundance?

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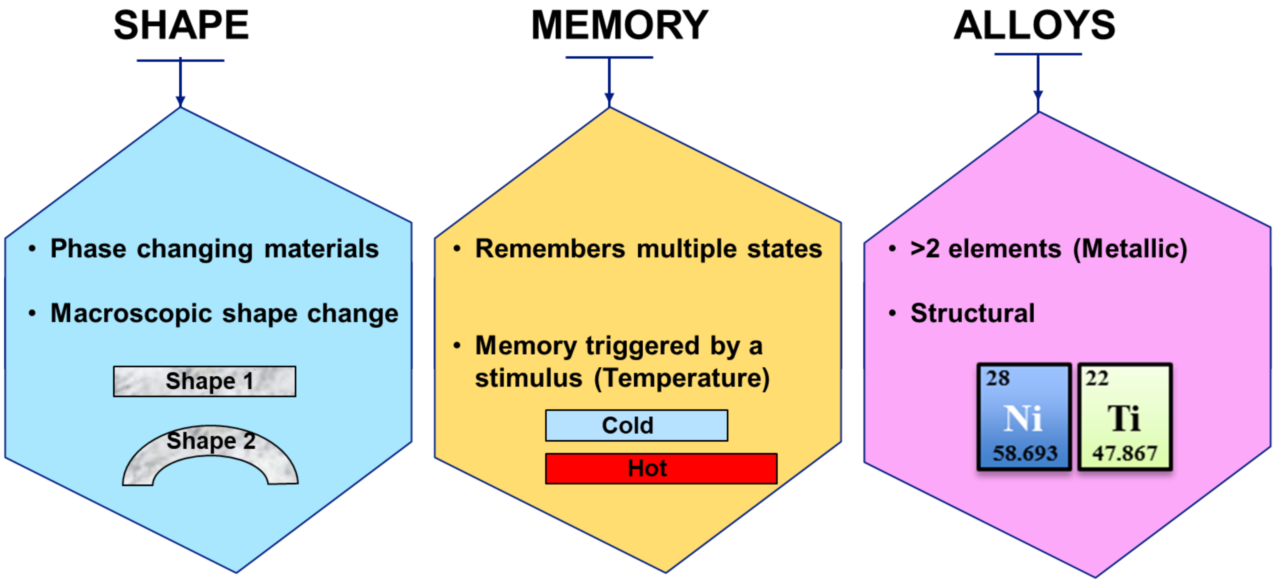
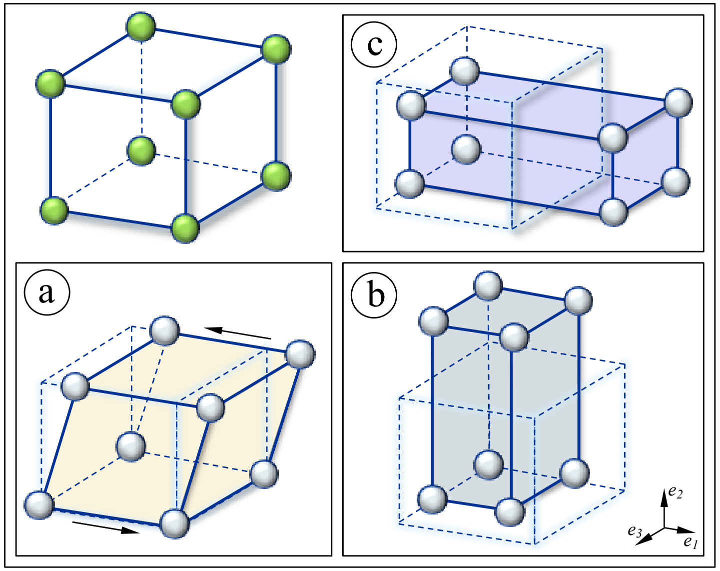
Lattice Parameter Example:

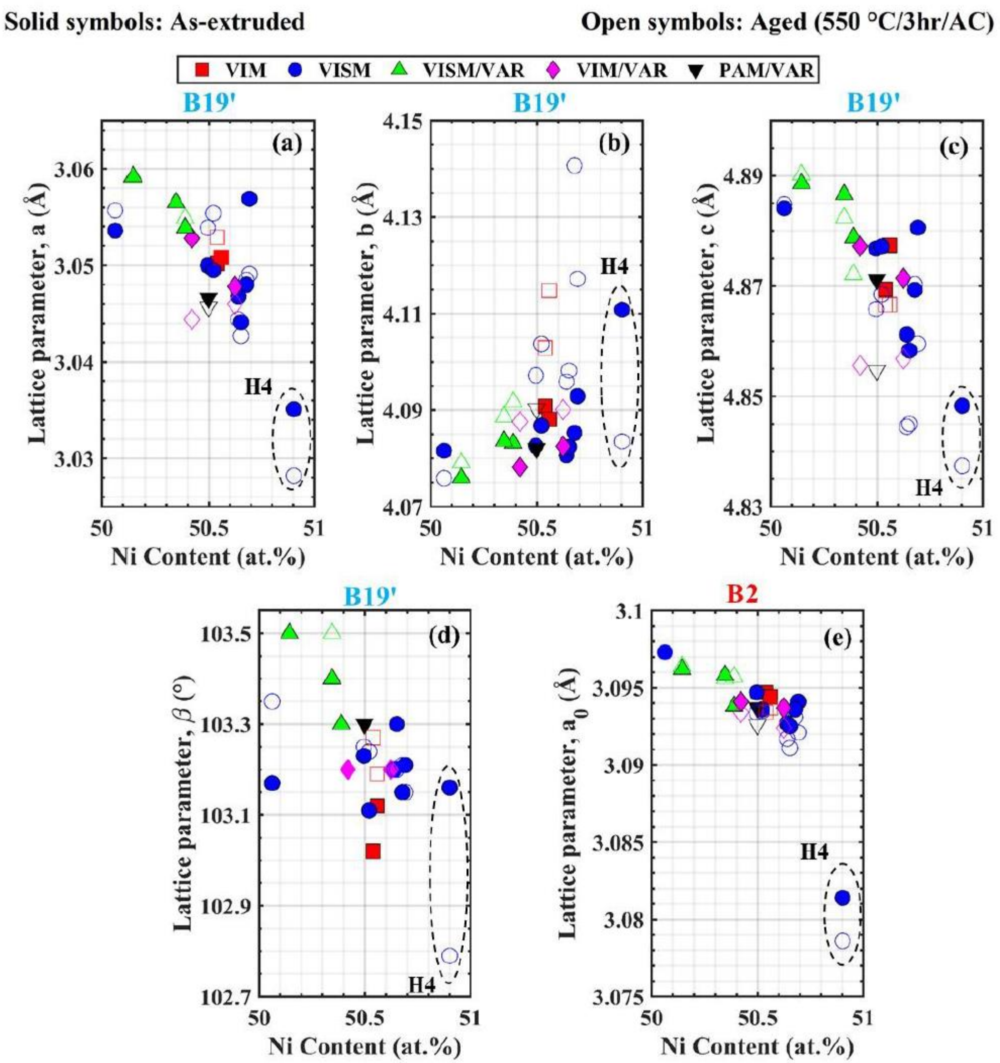


- Exhibit a solid-to-solid, reversible phase transformation
- Change in physical, mechanical, thermal properties
- Sense and actuate (multifunctional)

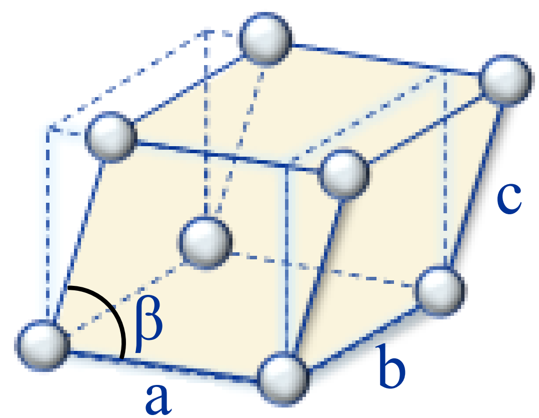



Shape Memory Alloys
National Aeronautics and Space Administration
Original Application of Shape Memory Alloys
Biomedical
Implants
Jaw Plates
Bone Staples
Hip Implants
Pedicle Screws
Stents
Medical Devices
Targeted Inhalers
Catheter Tubes
Instruments
Courtesy: Stefan Seelecke
Consumer Products
National Aeronautics and Space Administration
Shape Memory Alloys
Residential
Toys
RC Helicopter
Dolls
Robots
Valves
Anti-scald (safety)
Home appliances
Air conditioners
Consumer Devices
Antennas
Electronics
Computers
Switches
Latches
Couplings
Plumbing
Mechanical
Electrical
CryoFit Couplings
CryoFit Compatable
Innovative Products
Structural Wheels
Tools
Commercial Applications
Smart Fastening Systems
Latches
Oxygen masks
Seat configurations
Security Systems
TZ
GM
CORVETTE'S HEAT-ACTIVATED 'SMART MATERIAL'
Automotive Industry
Louvers
Quiet actuators
Door handles
Fasteners
Lumbar Supports
Valves
Fire Suppression
Fluid Flow
Safety Shutoff
Innovative Components
Structural Tires
Lattice Trusses
Bearings and Gears
Drive Shafts
Motors
Mechanical Mechanisms
Aerospace Applications
Adaptive Fan Blade
Embedded SMA actuators
Aerodynamic efficiency
Specific fuel consumption reduction
Shape change region
Variable Geometry Chevron
SMA actuators morph the chevron
Noise reduction at takeoff
Shock cell noise reduction at cruise
Boeing
SMA Spring Tire
Superelastic technology
Lunar & Martian rovers
Non-Pneumatic
SMA Docking Coupling
Cryogenic transfer coupling
Orbital propellant depots
Propellant handling/protection
LMT
NiTi Bearings
Corrosion resistant
Non-galling properties
High yield
Provides Drinking Water to Astronauts
www.nasa.gov

Lattice parameters correlate with many physical properties



- Transformation temperatures
- Young's modulus
- Microhardness
- Maximum strain
- Recovery ratio



Benafan, et al., Shape Memory and Superelasticity (2021) 7:109–165

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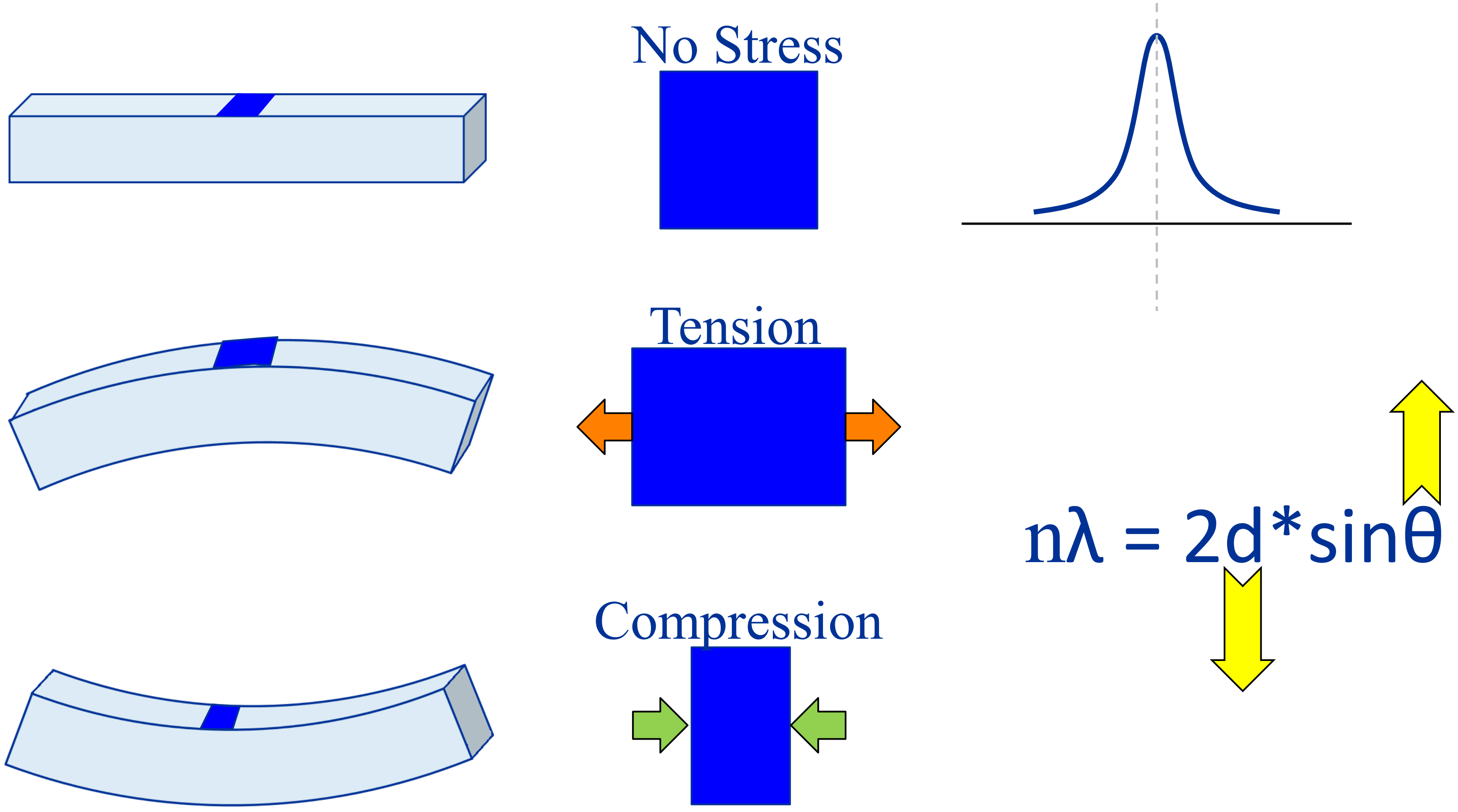
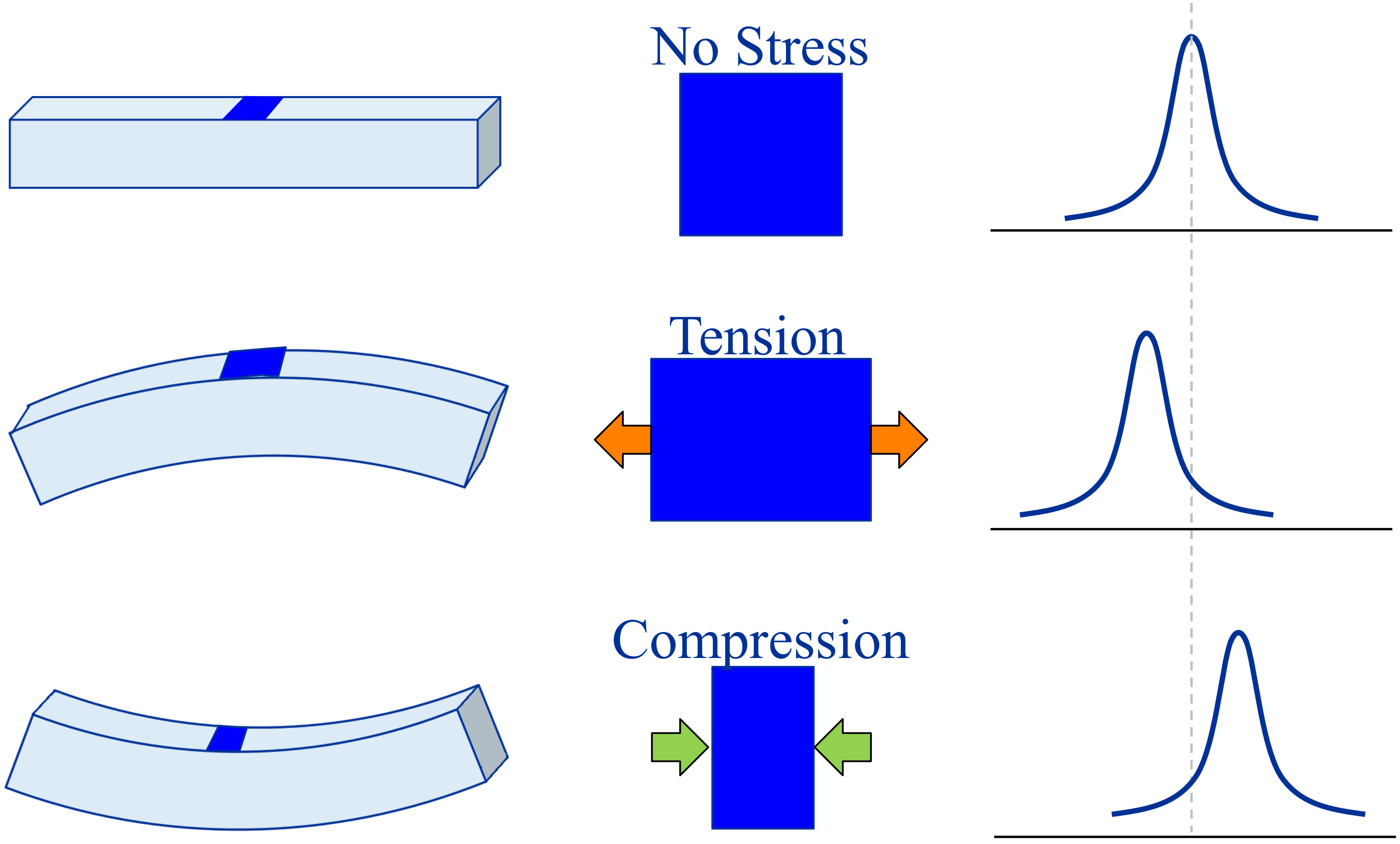
Residual Stress

Residual Stress



Crystal lattice acts as a strain gauge.

Residual Stress



Crystal lattice acts as a strain gauge.

Influences of Varied Electrical Discharge Machining Operations on Surface Conditions of Several Nickel-Based Superalloys

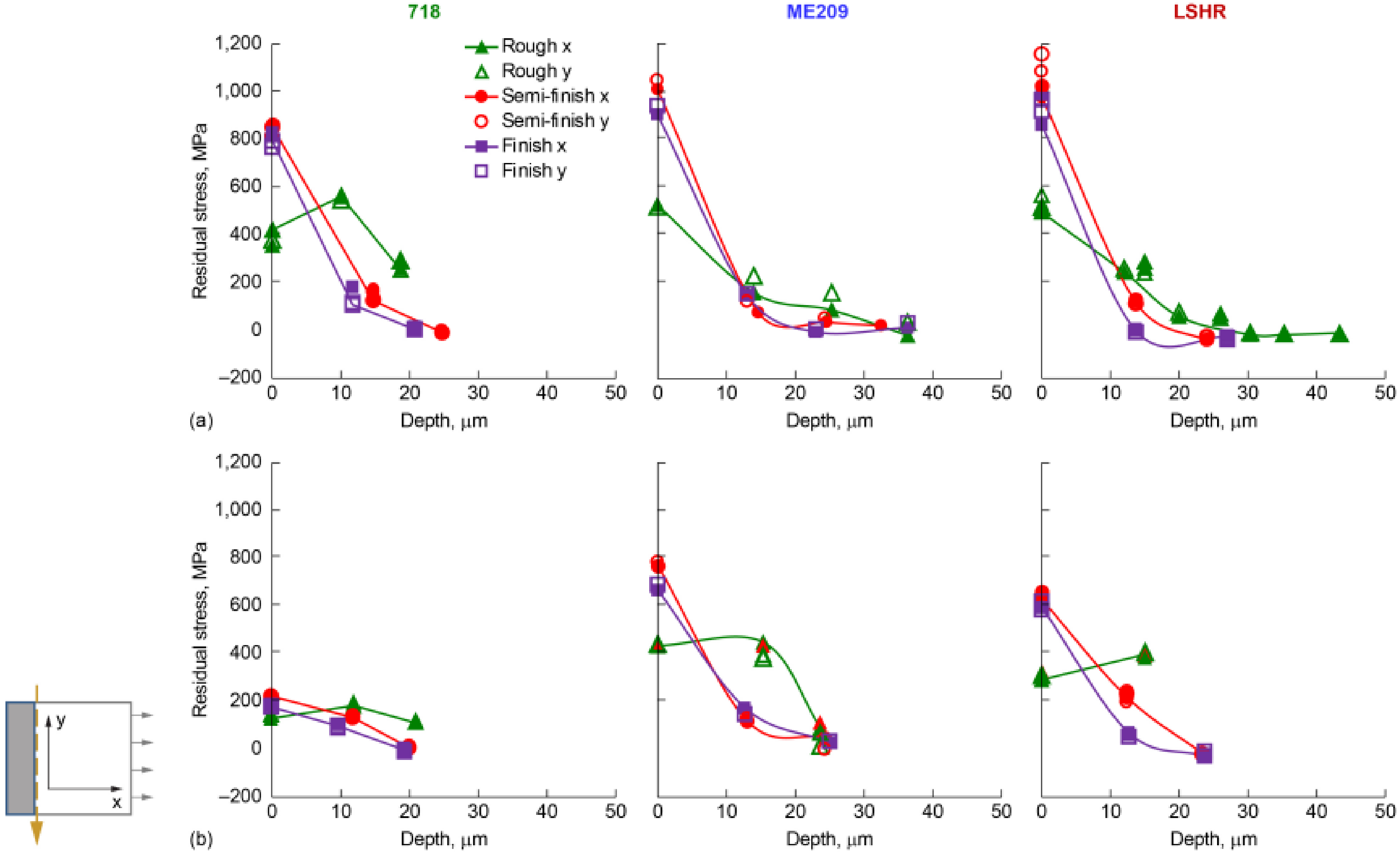


Figure 12.—Comparison of residual stress versus depth from the surface for superalloy 718, ME209, and LSHR after EDM using rough, semi-finish, and finish condition sets: (a) As-machined. (b) EDM plus heated at 704 °C for 24 h in vacuum.

What you can do with X-ray diffraction (XRD)?

- Crystalline phase identification
  - XRD peak positions and intensities like a fingerprint
- Lattice parameter measurements
  - correlates with other important material properties
- Residual stress
  - essentially using crystal lattice as a strain gage
- Crystallographic texture (preferred orientation)
  - strong effect on physical properties
- Single crystal orientation
  - extreme case of texture
- Crystallite size/strain
  - both affect peak with different θ-dependence

Crystallographic Texture

(Pole Figures)

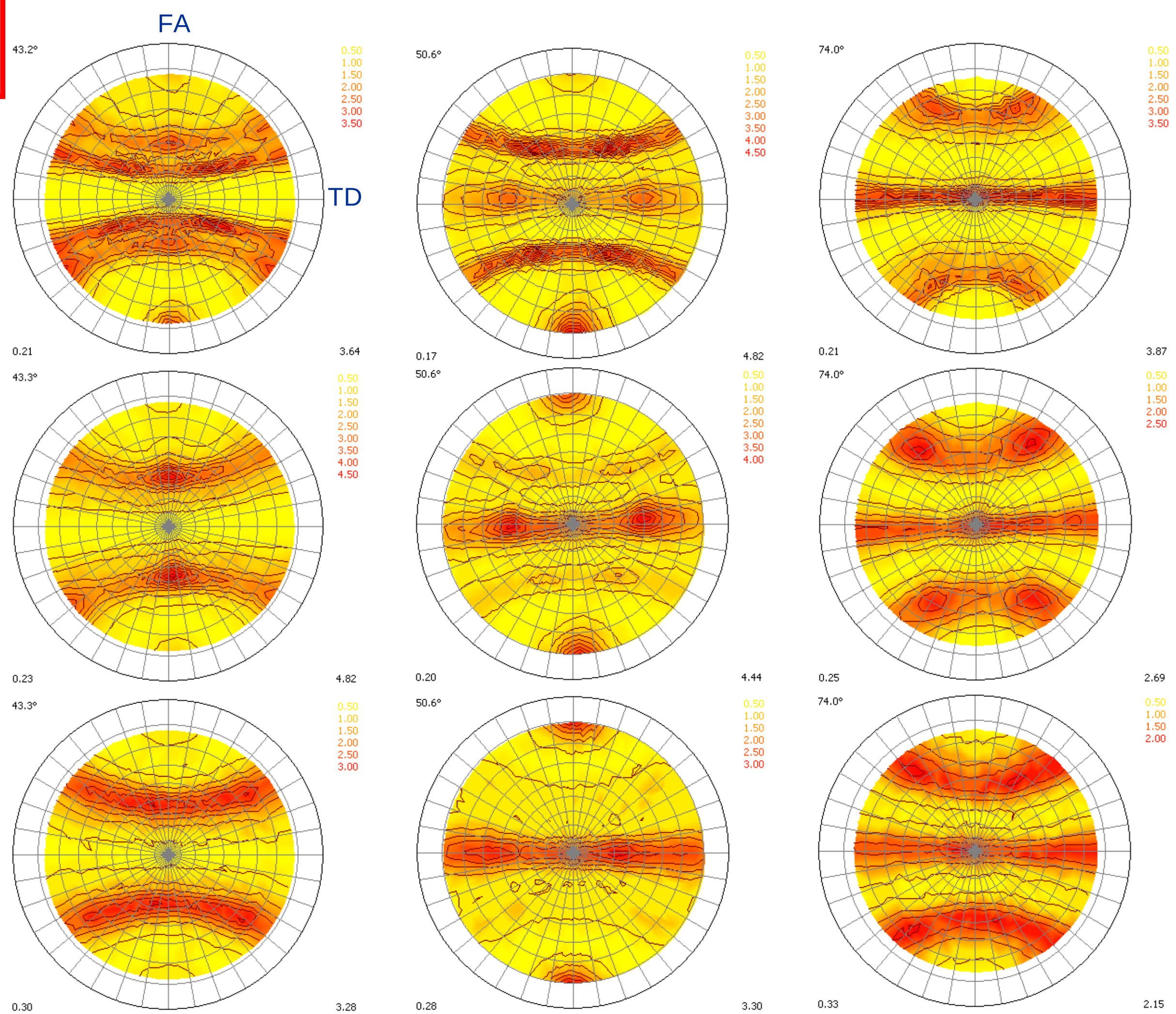
GRCop 84 – Dave Ellis and Chika Okuru

(111) pole | (200) pole | (220) pole

Sample 1

Sample 2

Sample 3



Increasing powder size

What you can do with X-ray diffraction (XRD)?

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- Single crystal orientation and structure
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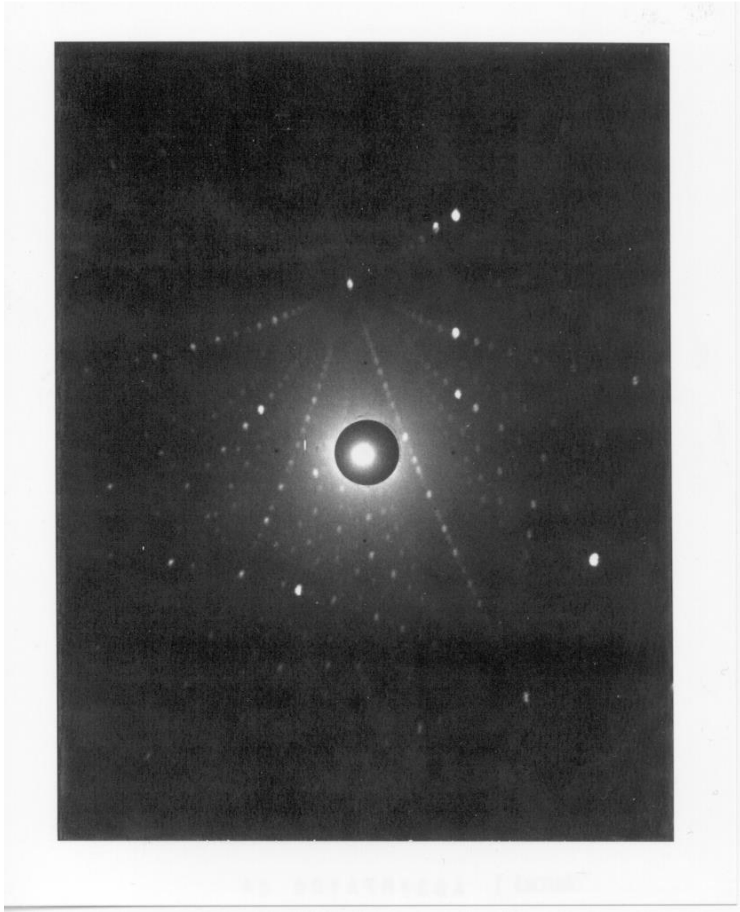
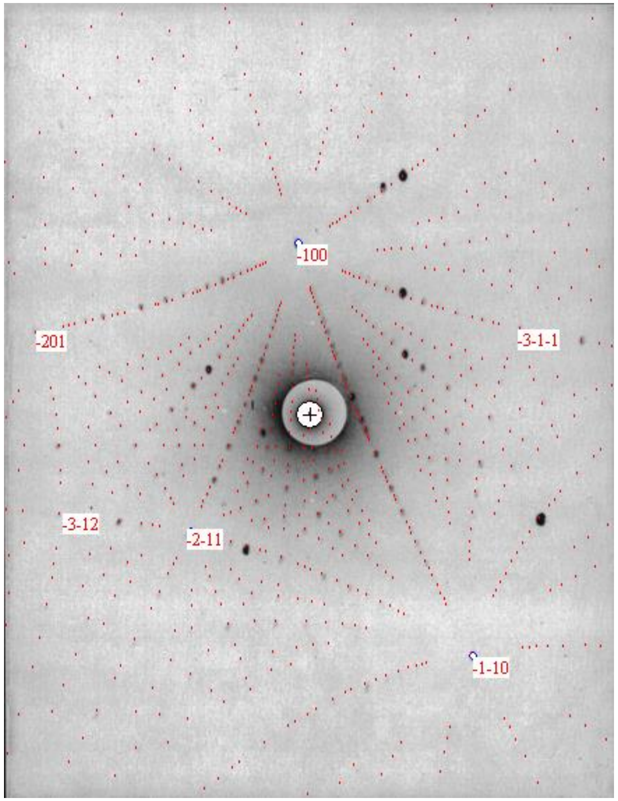
  - both affect peak with different θ-dependence

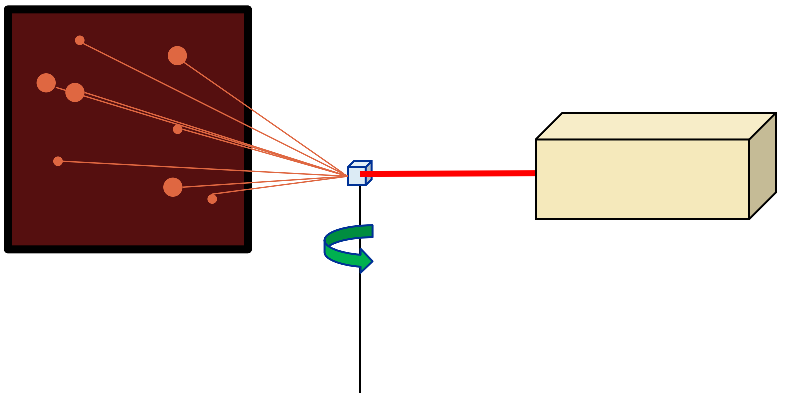
Single Crystal Orientation

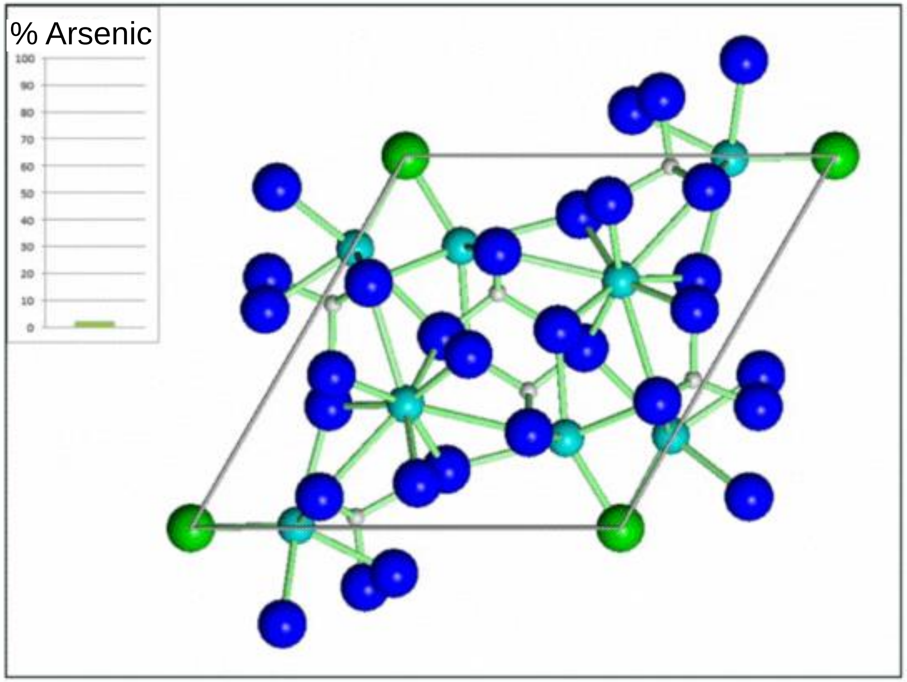
(Laue method)





Single Crystal XRD Structure Determination





- Unit Cell Structure
  - Bond lengths
  - Bond angles
  - Atom positions

What you can do with X-ray diffraction (XRD)?

- Crystalline phase identification
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  - correlates with other important material properties
- Residual stress
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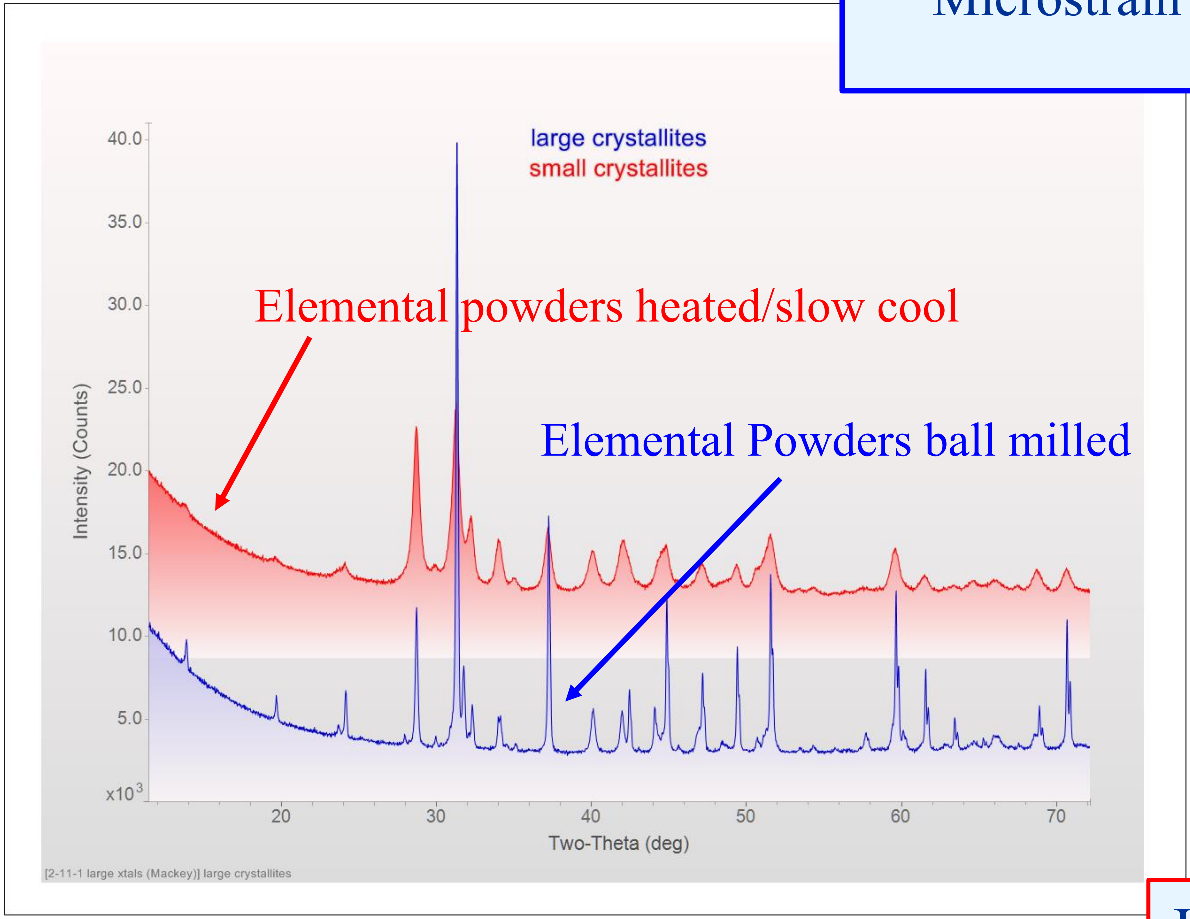
- Single crystal orientation and structure
  - extreme case of texture
- Crystallite size/strain
  - both affect peak with different θ-dependence

Crystallite Size

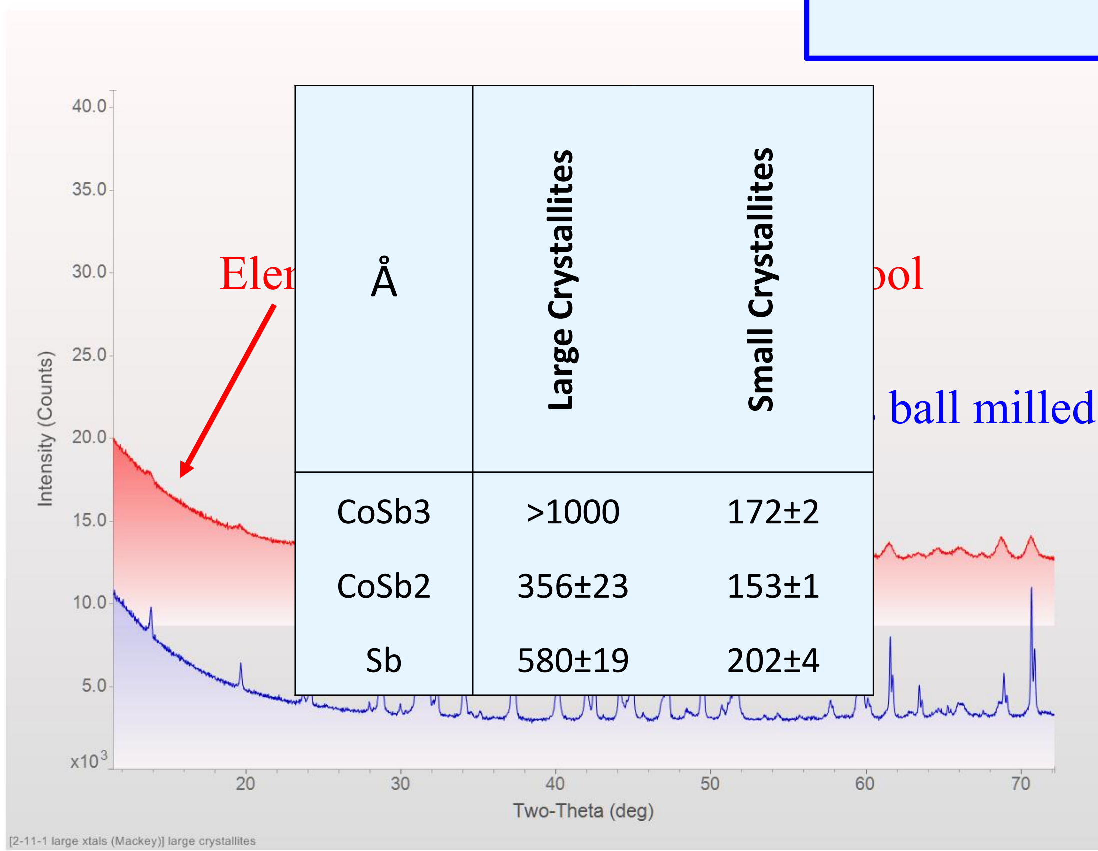
Crystallite size → 1/Cos θ
Microstrain → Tan θ



J. Mackey

Crystallite Size

Crystallite size → 1/Cos θ
Microstrain → Tan θ



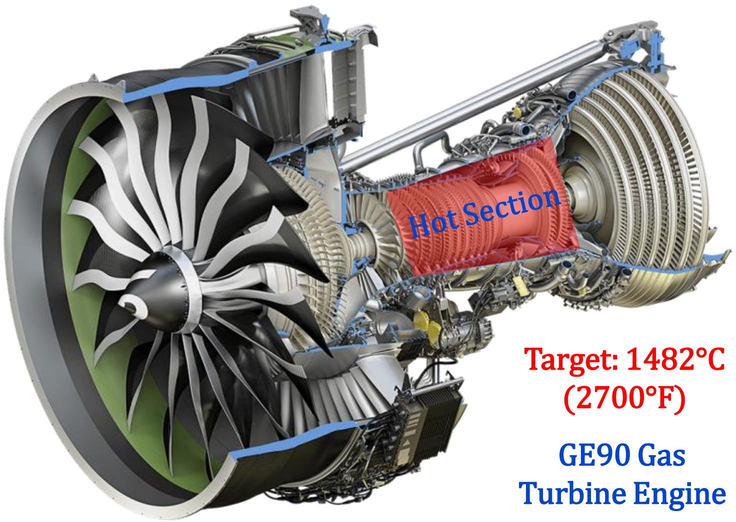
Å	Large Crystallites	Small Crystallites
CoSb3	>1000	172±2
CoSb2	356±23	153±1
Sb	580±19	202±4

J. Mackey

Presentation overview

- What is Diffraction?
- Basics of X-Ray Diffraction (XRD)
- What can be done with XRD?
- NASA Programs using XRD for materials development

Protective Coatings for Gas Turbine Engines

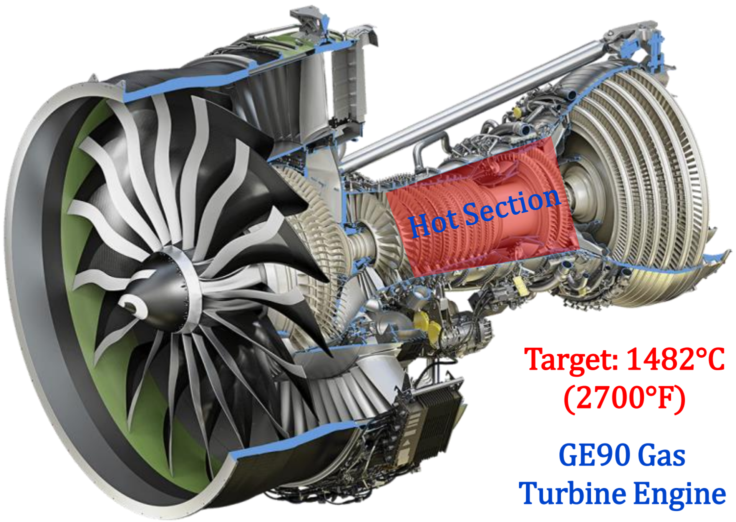


- Multi-decade development push to replace metallic airplane components with **lightweight composite materials**
  - Boeing 787 Dreamliner – Carbon-fiber composite fuselage
- Replacement of Ni-based superalloy engine components with SiC-based ceramic matrix composites (CMCs) to **increase turbine engine efficiency**
  - Lower (1/3) density than conventional metal-based components
  - Allow for higher operating temperatures (>1200°C)

$$\varepsilon = 1 - \frac{T_c}{T_H}$$

- **6% increase in fuel efficiency savings of ~$400,000 per plane per year**

Protective Coatings for Gas Turbine Engines

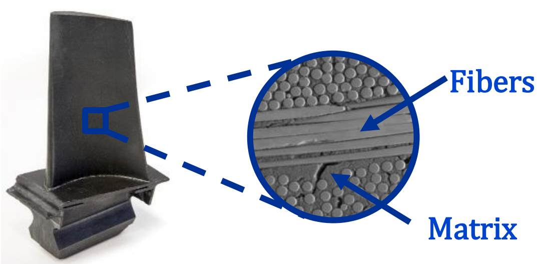


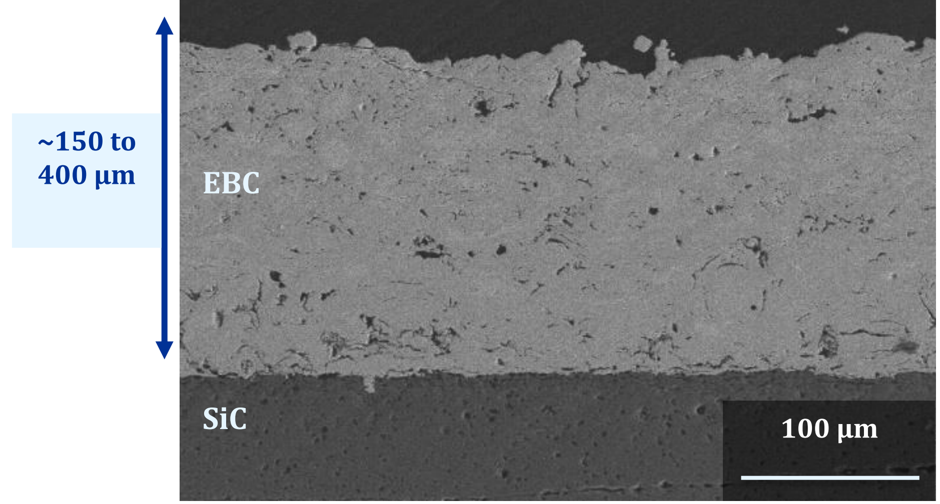
Target: 1482°C (2700°F)

GE90 Gas Turbine Engine

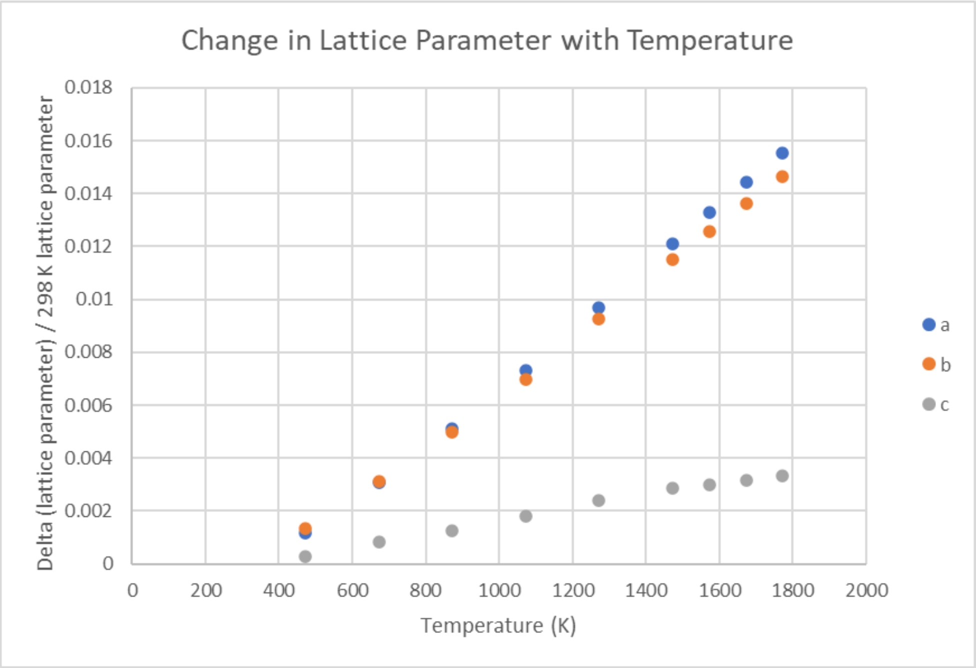
- Silicon carbide (SiC) CMCs susceptible to environmental attack at temperatures >800°C in oxygen and water vapor
  - Silica (SiO_2) scale formation that volatilizes in H_2O environment
  - Surface recession
- Require **environmental barrier coatings (EBCs)** to protect CMC component from harsh environment

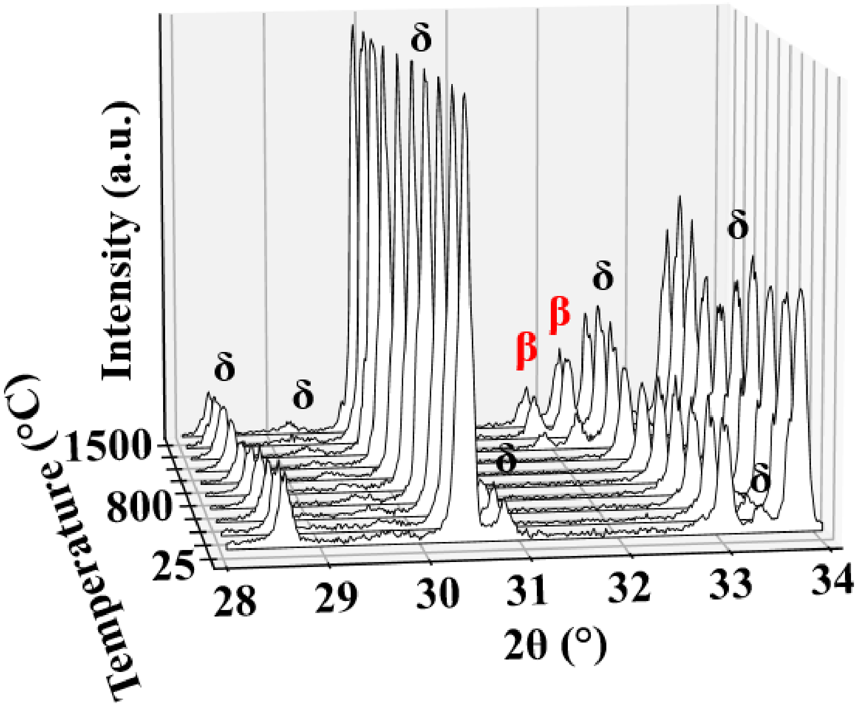
CMC Turbine Blade



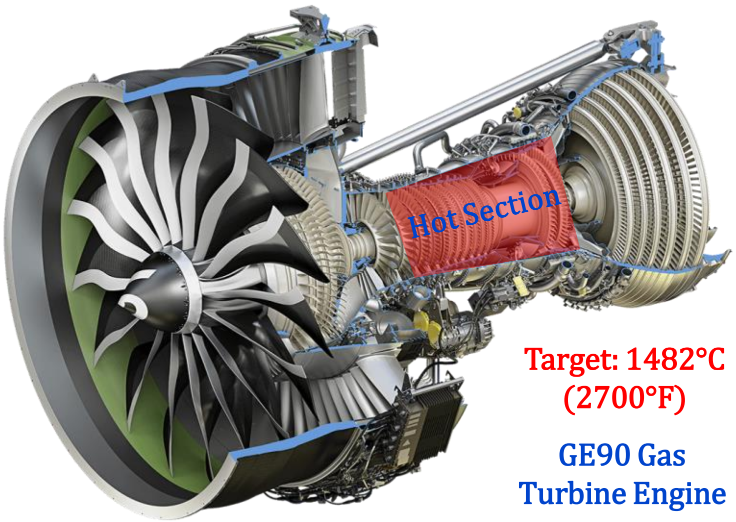


XRD Data for CTE determination





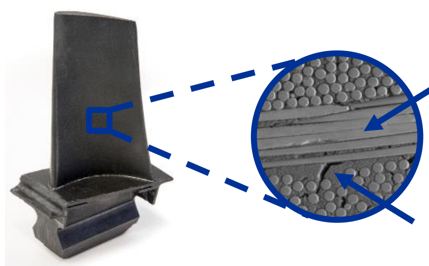
Protective Coatings for Gas Turbine Engines



Target: 1482°C (2700°F)

GE90 Gas Turbine Engine

CMC Turbine Blade



Fibers

Matrix

Properties	$Y_2Si_2O_7$ Yttrium Disilicate	$Yb_2Si_2O_7$ Ytterbium Disilicate
CTE (x 10^{-6}/K)	3.9	4.0
Elastic Modulus (GPa)	155	168
Fracture Toughness ($MPa \cdot m^{1/2}$)	2.12	2.8

Intrinsic Material Selection Criteria

- Coefficient of thermal expansion (CTE)
- Sintering resistance
- Low H_2O and O_2 diffusivity/solubility
- Phase Stability
- Low Modulus
- Limited coating interaction

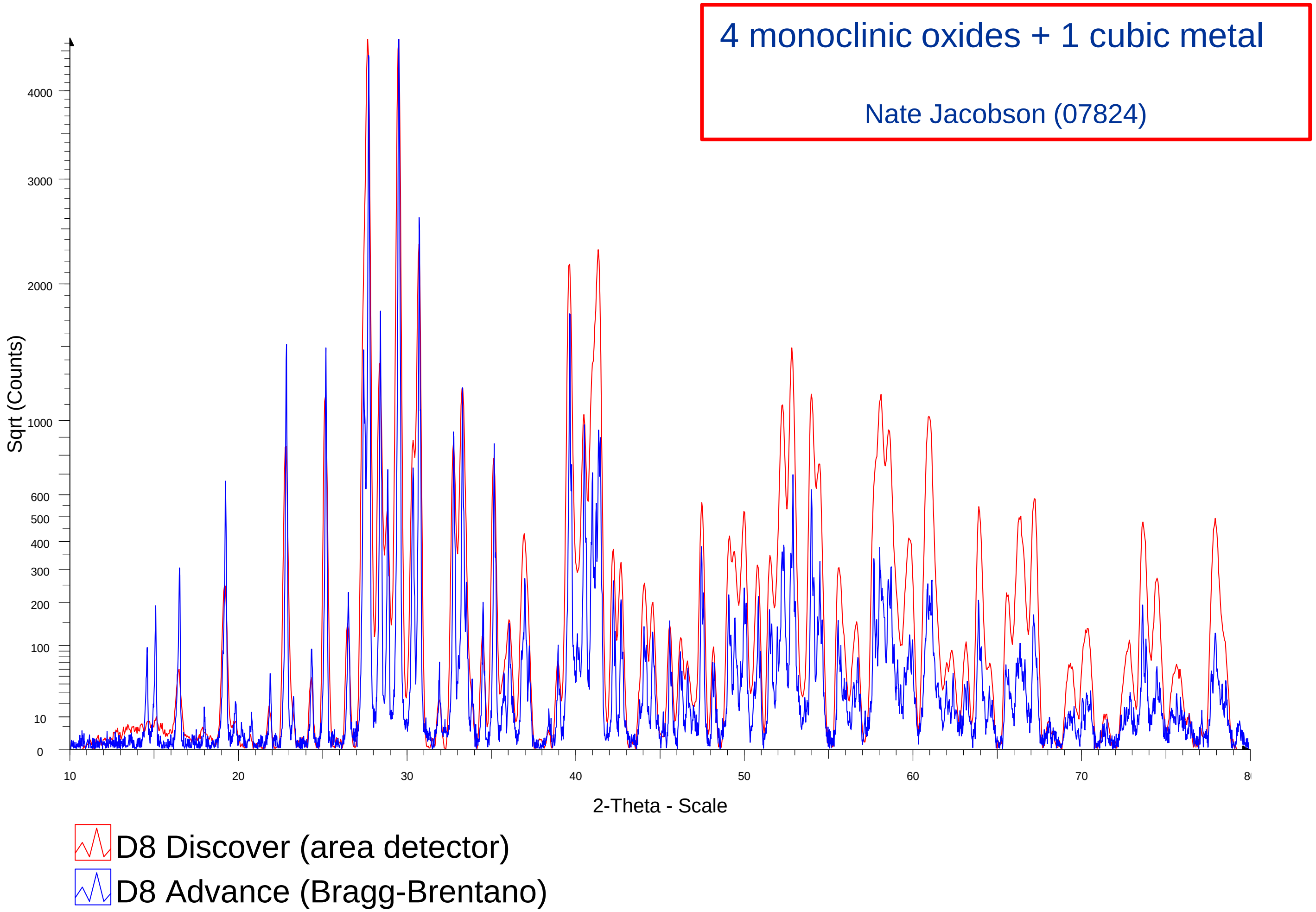
Thank you for your time today.

Questions???

Laura Wilson	Rick Rogers	Liz Young-Dohe
laura.g.wilson@nasa.gov	richard.b.rogers@nasa.gov	elizabeth.j.young-dohe@nasa.gov

BACKUP SLIDES

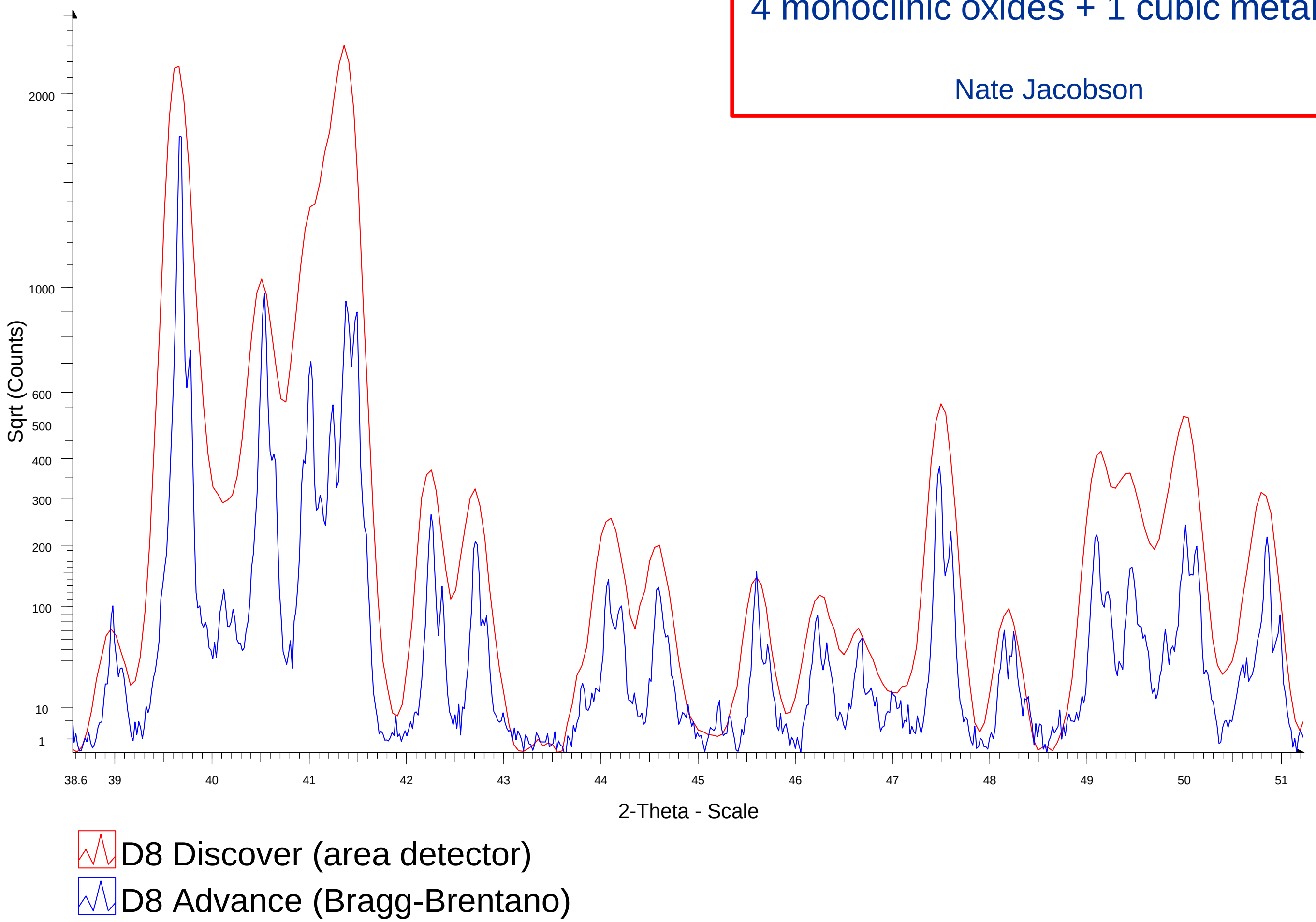
Instrument Peak Width Comparison



Instrument Peak Width Comparison

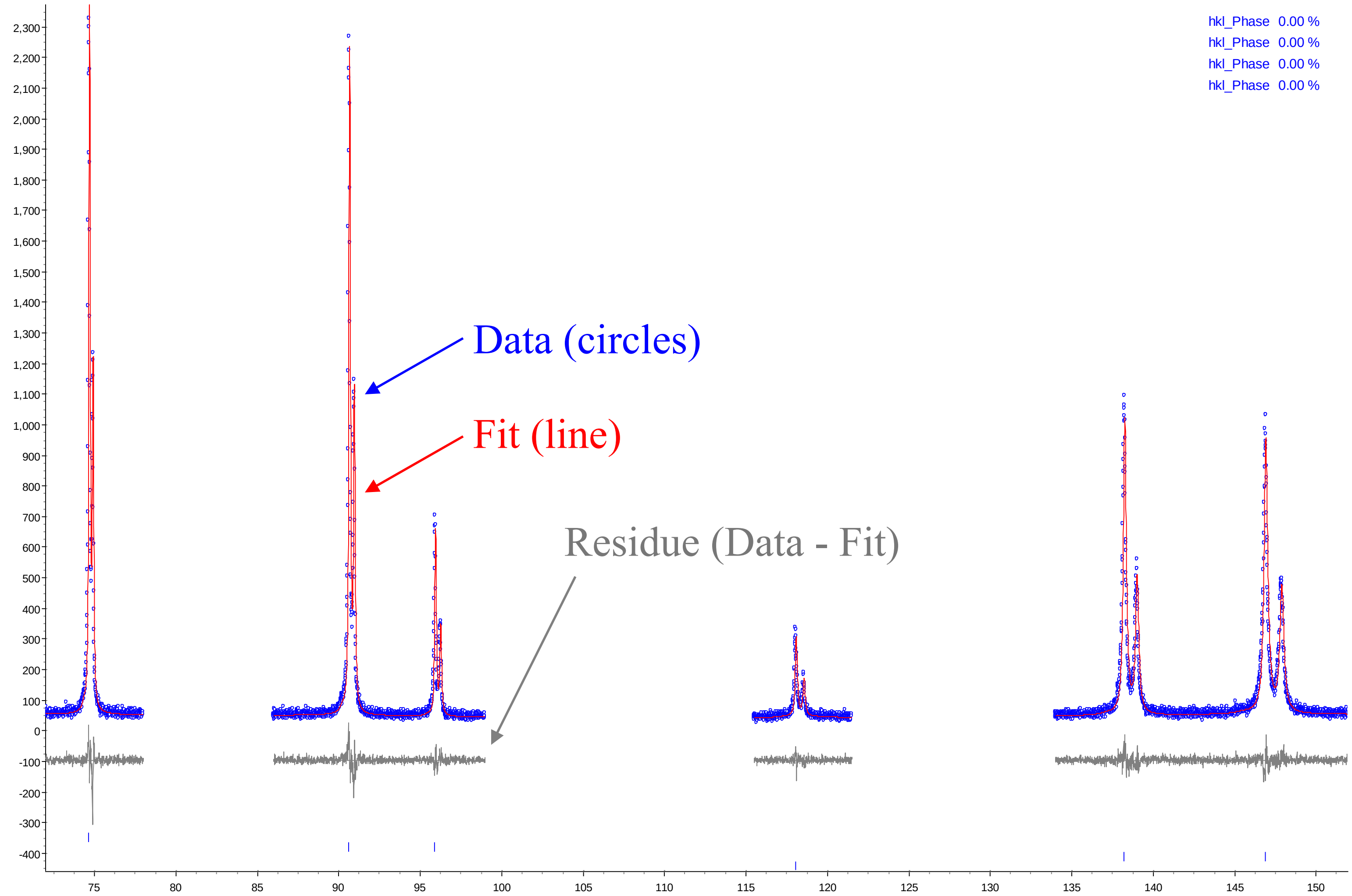
4 monoclinic oxides + 1 cubic metal

Nate Jacobson



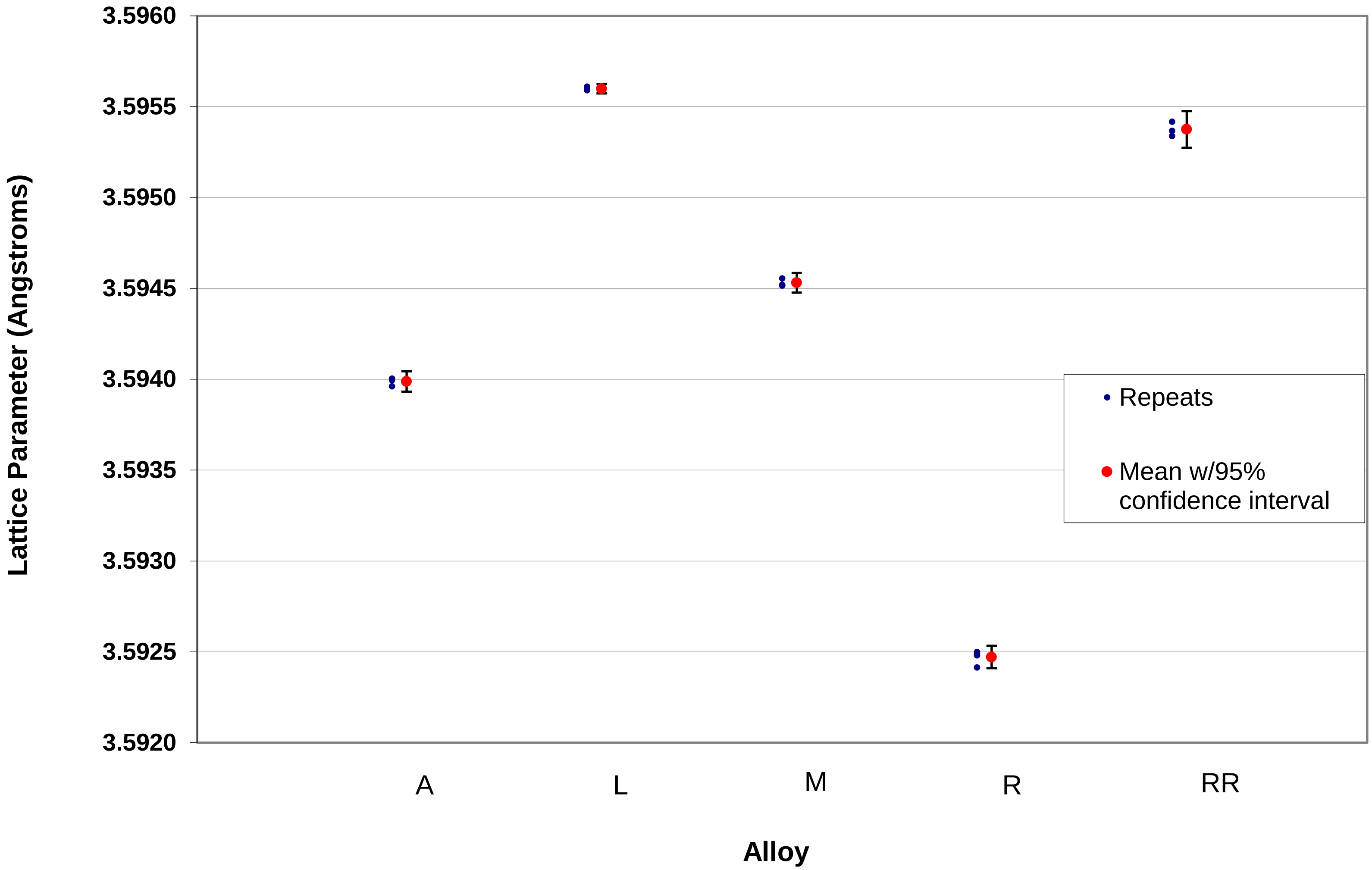
Lattice Parameter Measurement

TG 8045-001a GP-1x

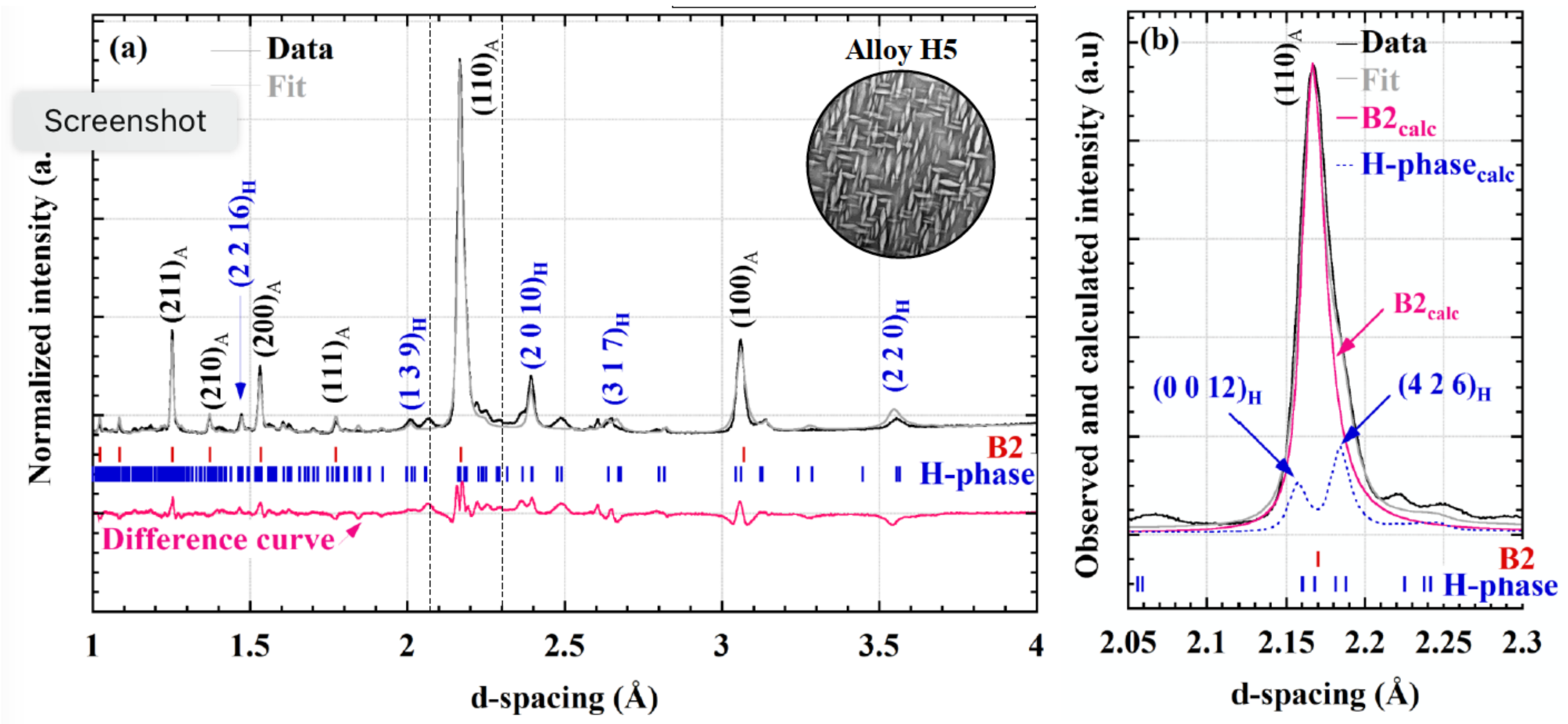


Gamma Prime Lattice Parameter

(Nickel-based Superalloy Tim Gabb)



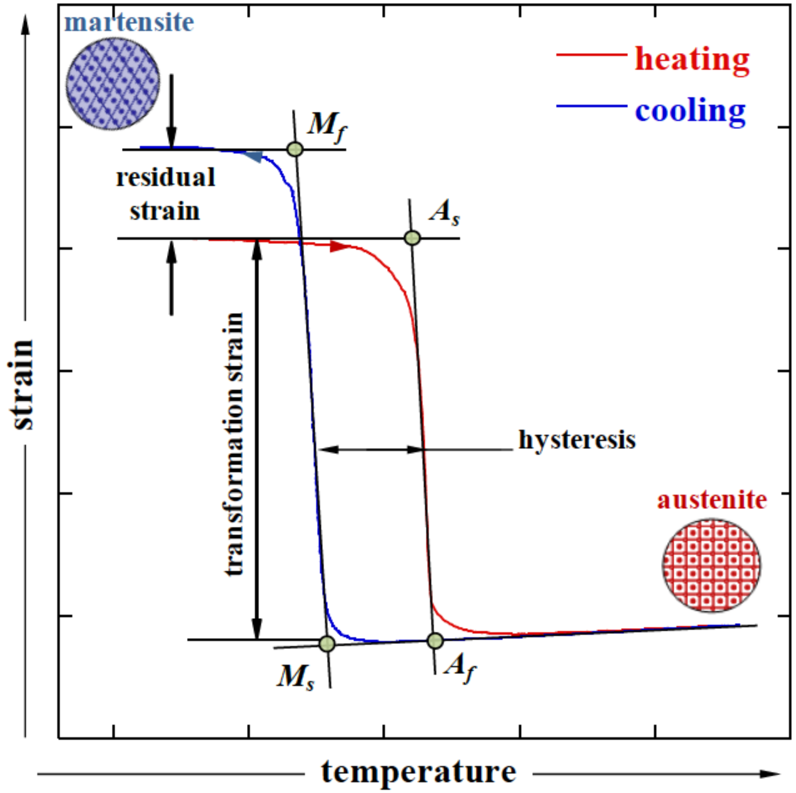
SMA Phase ID



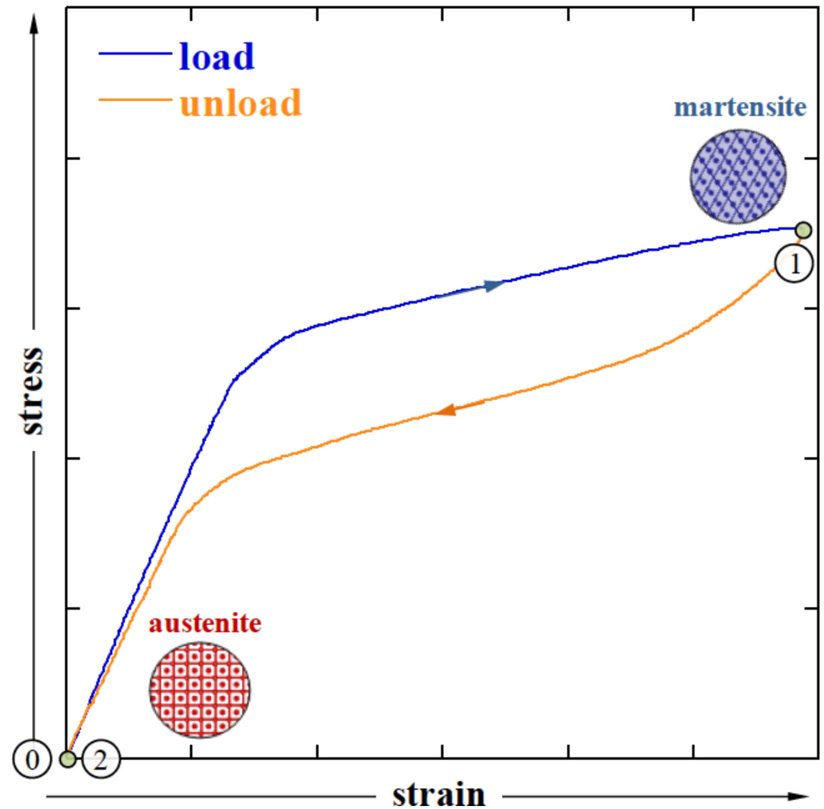
Benafan, et al., Shape Memory and Superelasticity (2021) 7:109–165

Two important SMA properties

Thermally-induced phase transformation



Superelastic effect

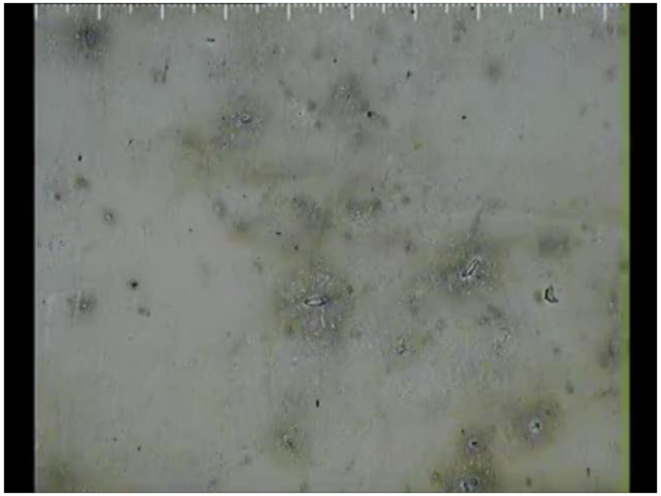


Benafan – NASA TM 2012-217741

What is a Shape Memory Alloy (SMA)?

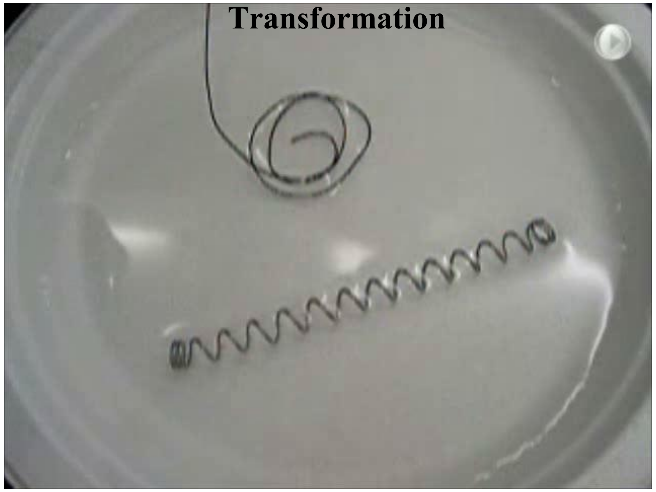
Alloys that have a "memory." These materials have the ability to remember and recover their original shapes with load or temperature.

Mechanically Induced Transformation



Courtesy of NWU

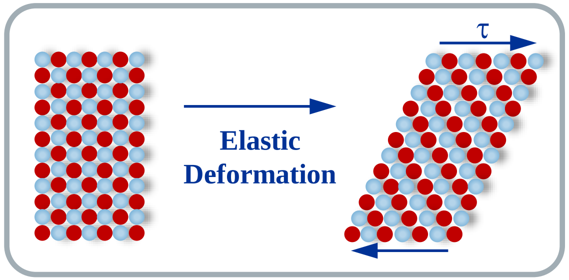
Thermally Induced Transformation



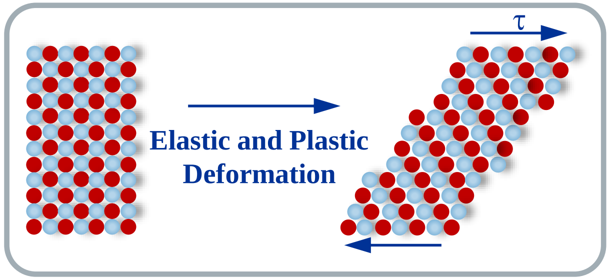
Courtesy of UCF

Shape Memory Alloy, How Does it Work?

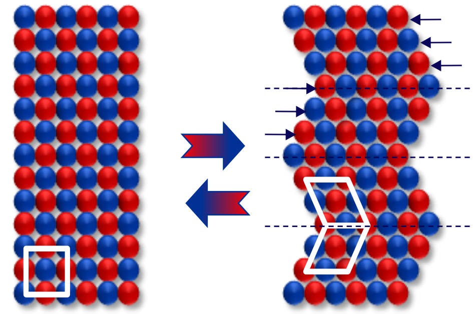
1. Elastic Deformation (REVERSIBLE)



2. Plastic Deformation (PERMANENT)



3. Inelastic Deformation (REVERSIBLE)—SMAs



Shape Memory Alloy, How Does it Work?

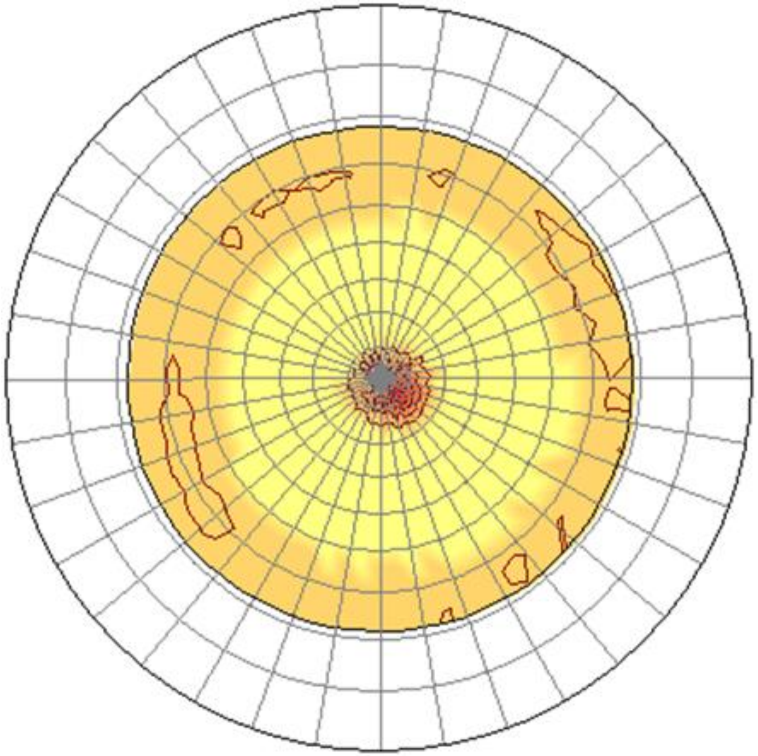
Cold state:
Also referred to as "*Martensite*"

Hot state:
Also referred to as "*Austenite*"

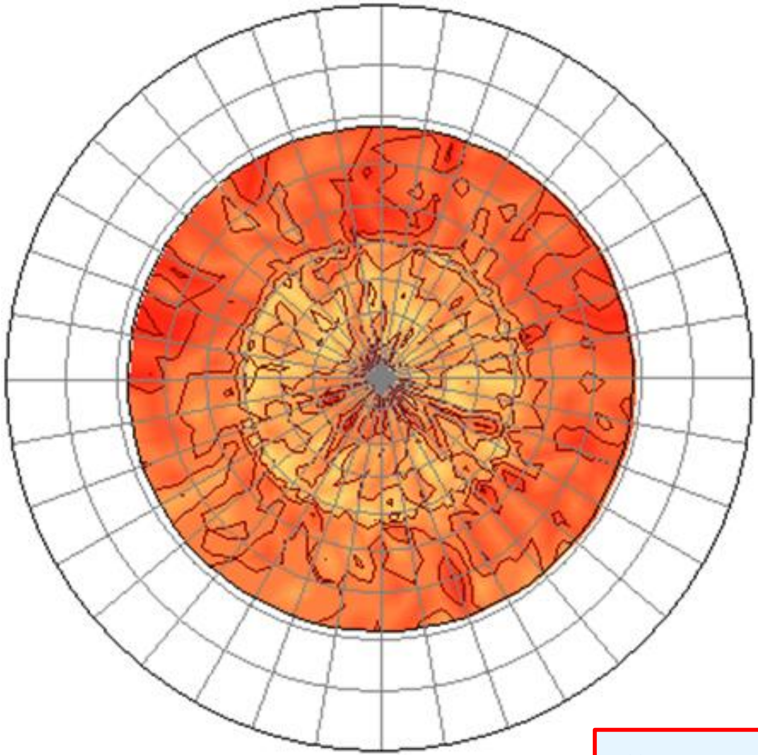
Phase Transformation:
Solid-to-solid, martensitic phase transformation between a high temperature, high symmetry austenite phase (generally cubic) and a lower temperature, low symmetry martensite phase (e.g., monoclinic, tetragonal, or orthorhombic).

Texture
Additively mfg. Ti-6-4 (002) pole

(002) Fiber texture

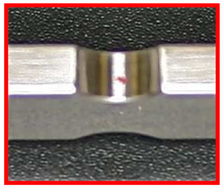


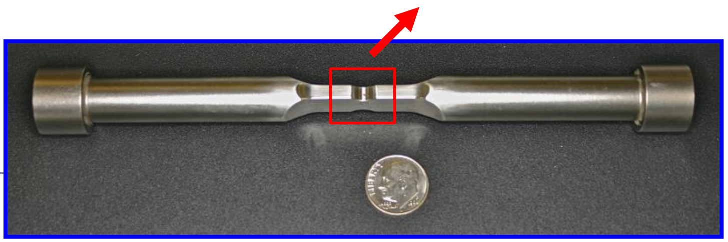
No Texture

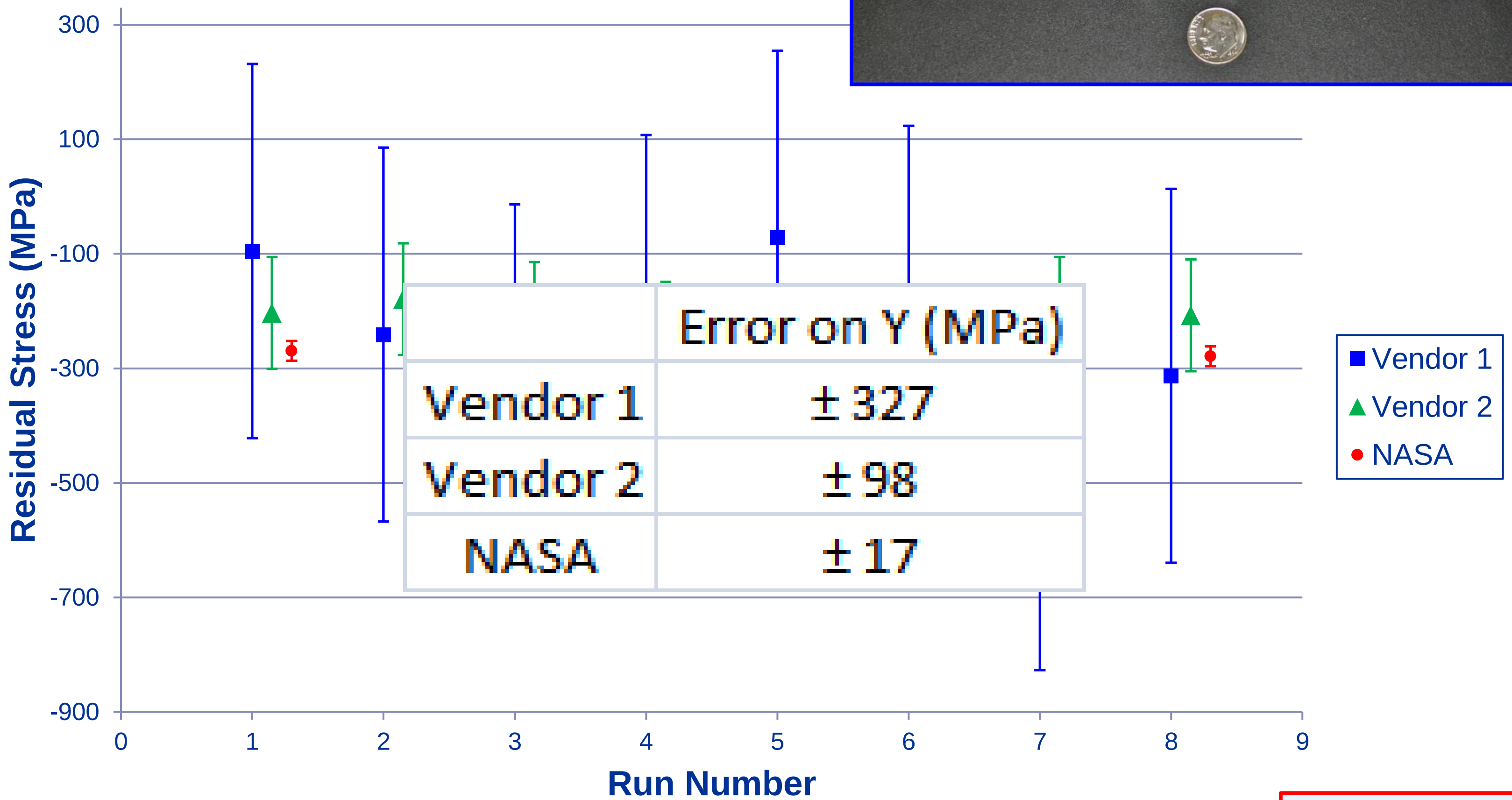


S. Draper

Residual Stress
Superalloy notch specimen



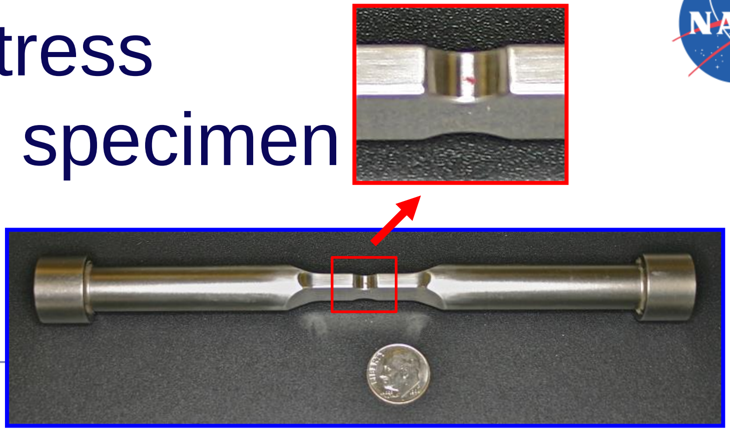


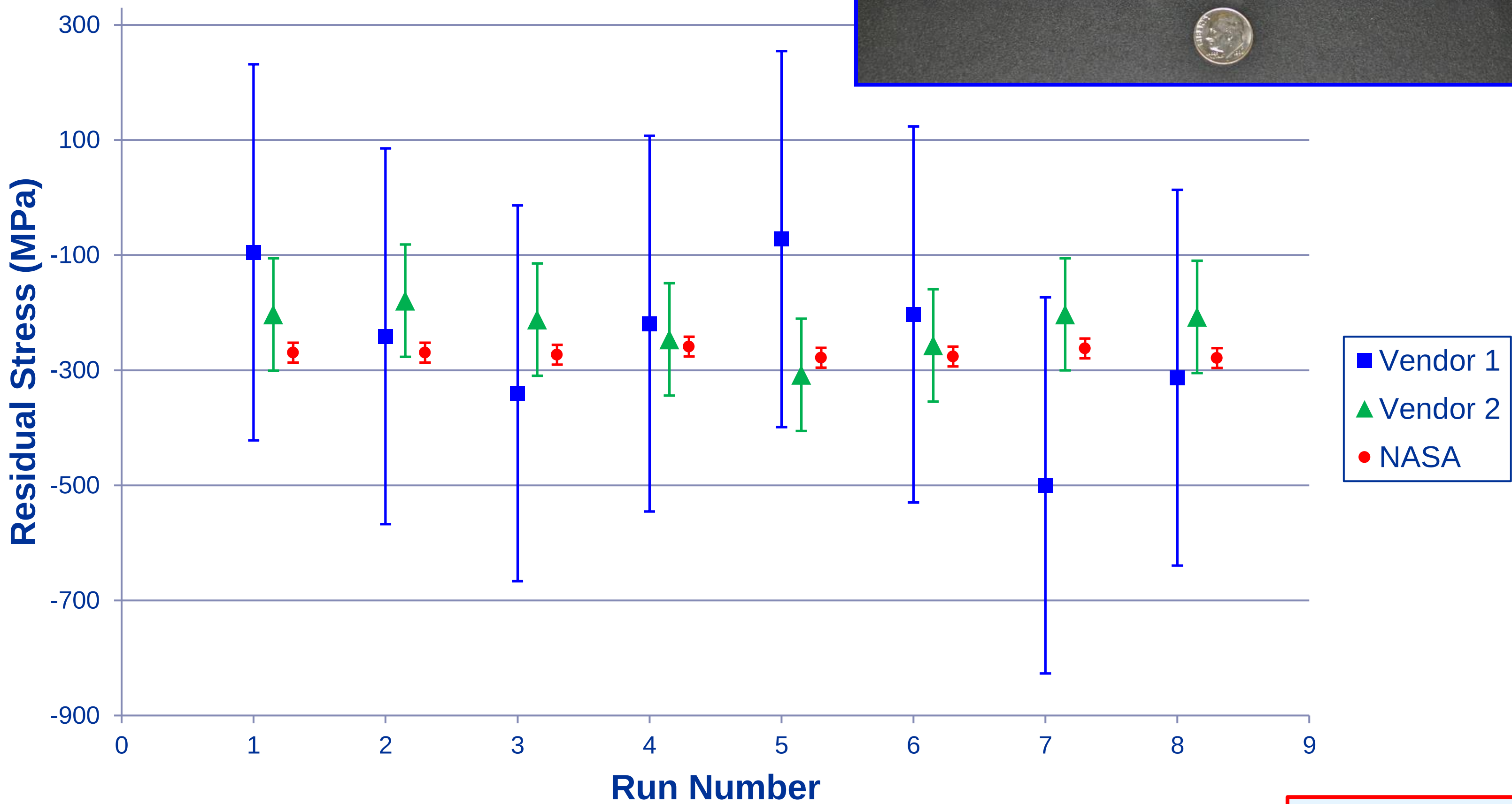


	Error on Y (MPa)
Vendor 1	± 327
Vendor 2	± 98
NASA	± 17

T. Gabb &
J. Telesman

Residual Stress
Superalloy notch specimen





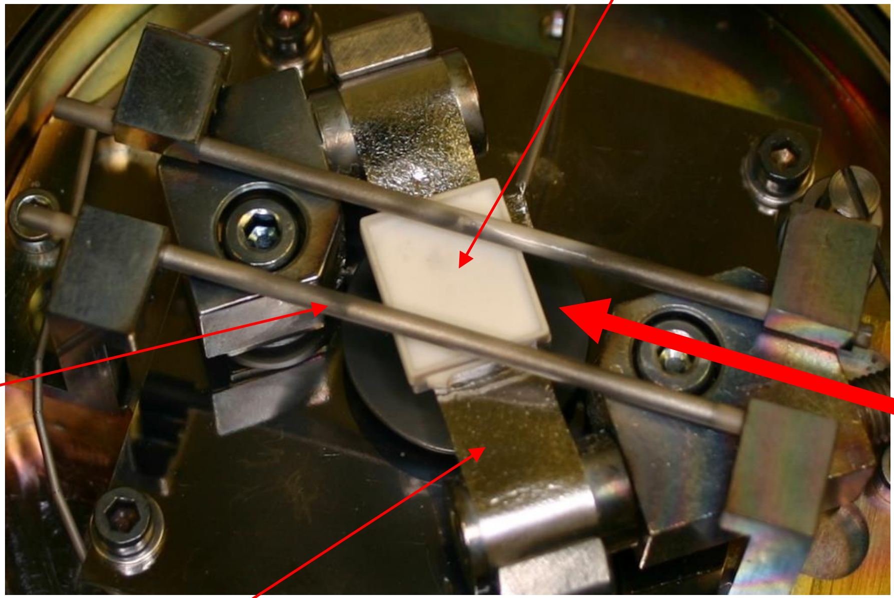
T. Gabb &
J. Telesman

High temperature stage

1100°C max in air, argon, or vacuum (10^{-7} mbar)

Vacuum or inert gas - Be dome

Sample

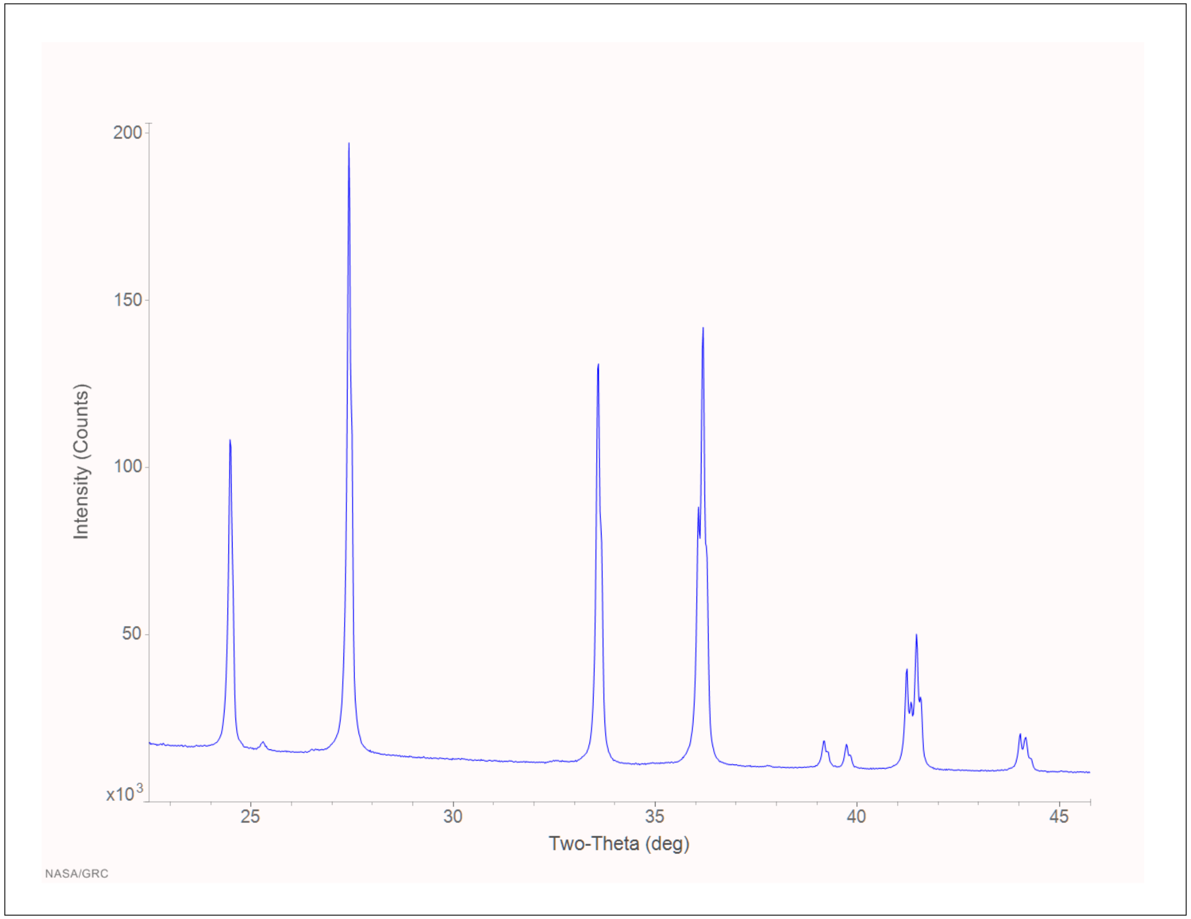


Alumina rods and spring loaded sample provides top reference To maintain alignment

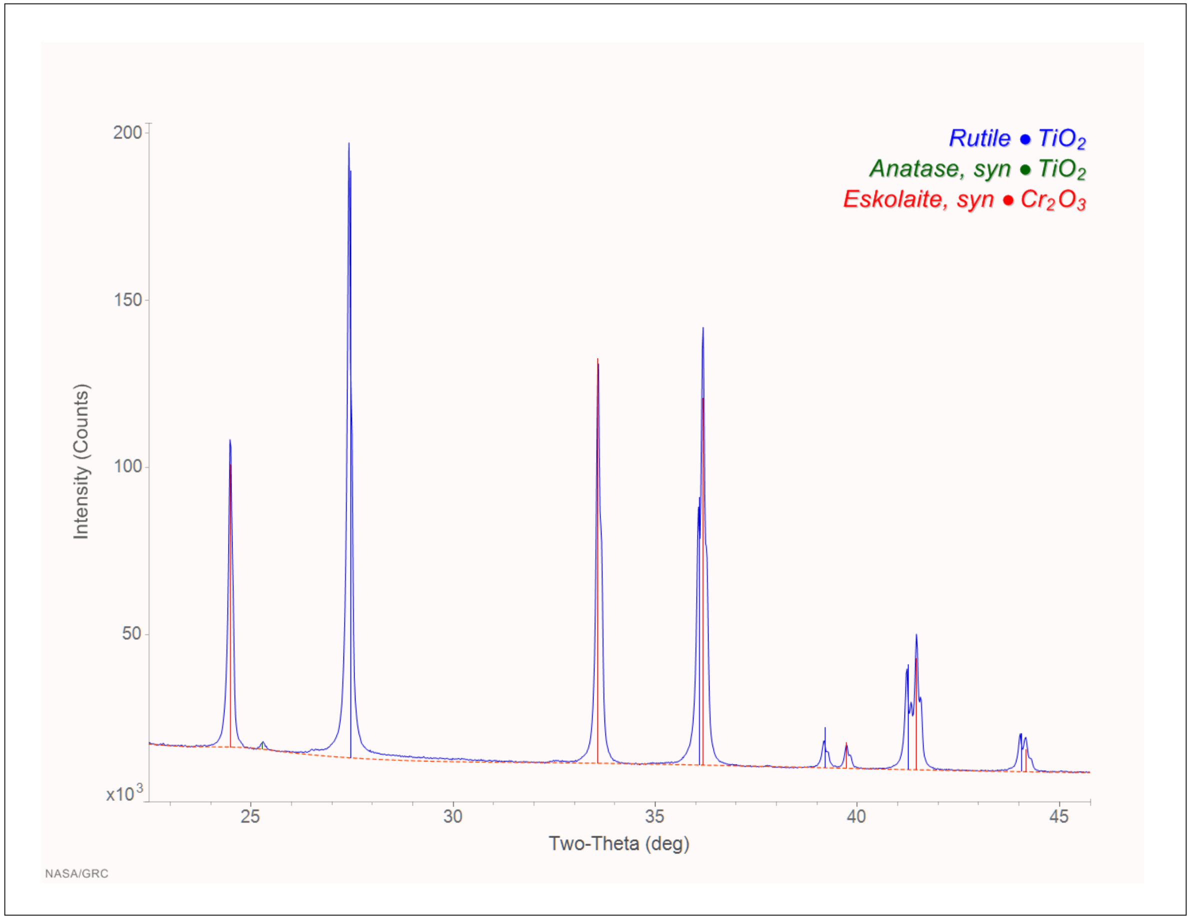
Platinum strip heater

X-ray path parallel to alumina rods

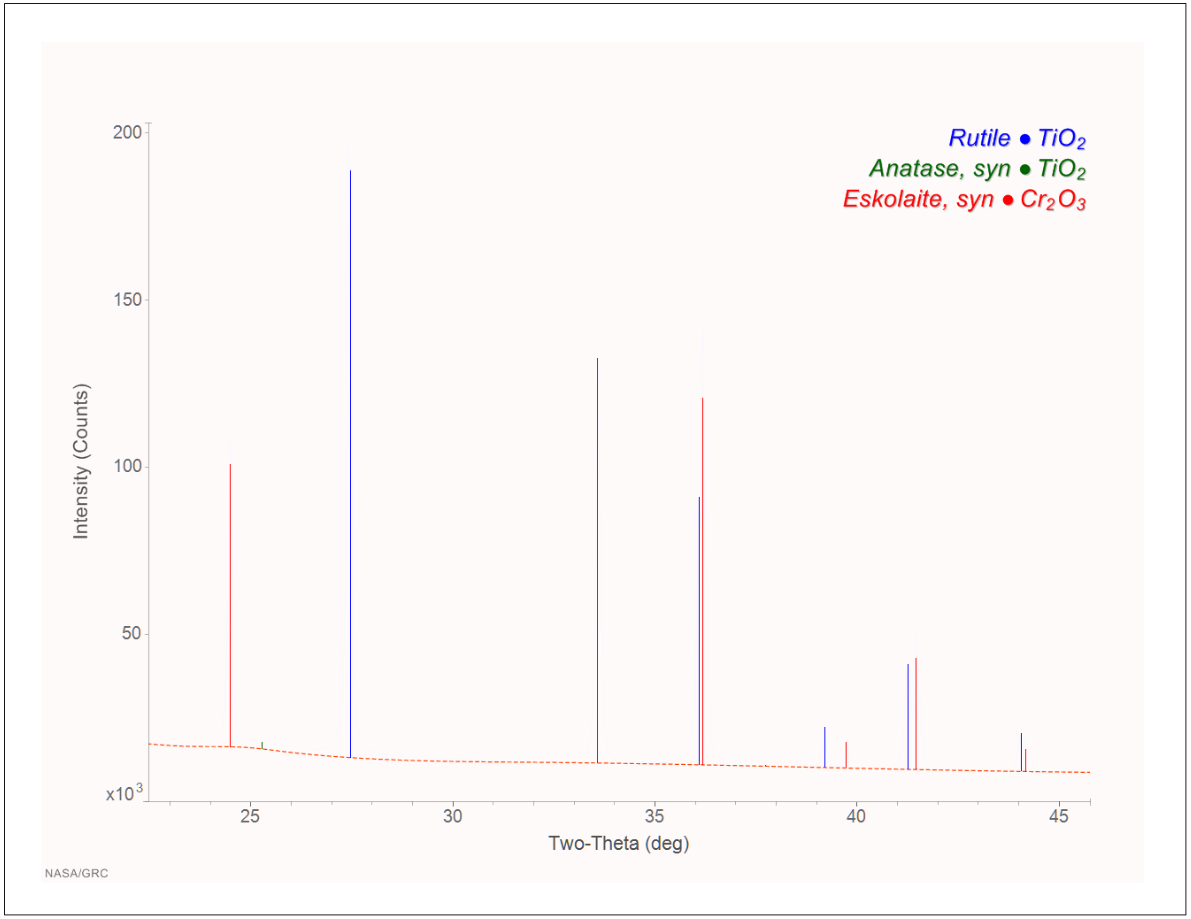
Quantitative Phase ID
Historical vs. Modern Methods



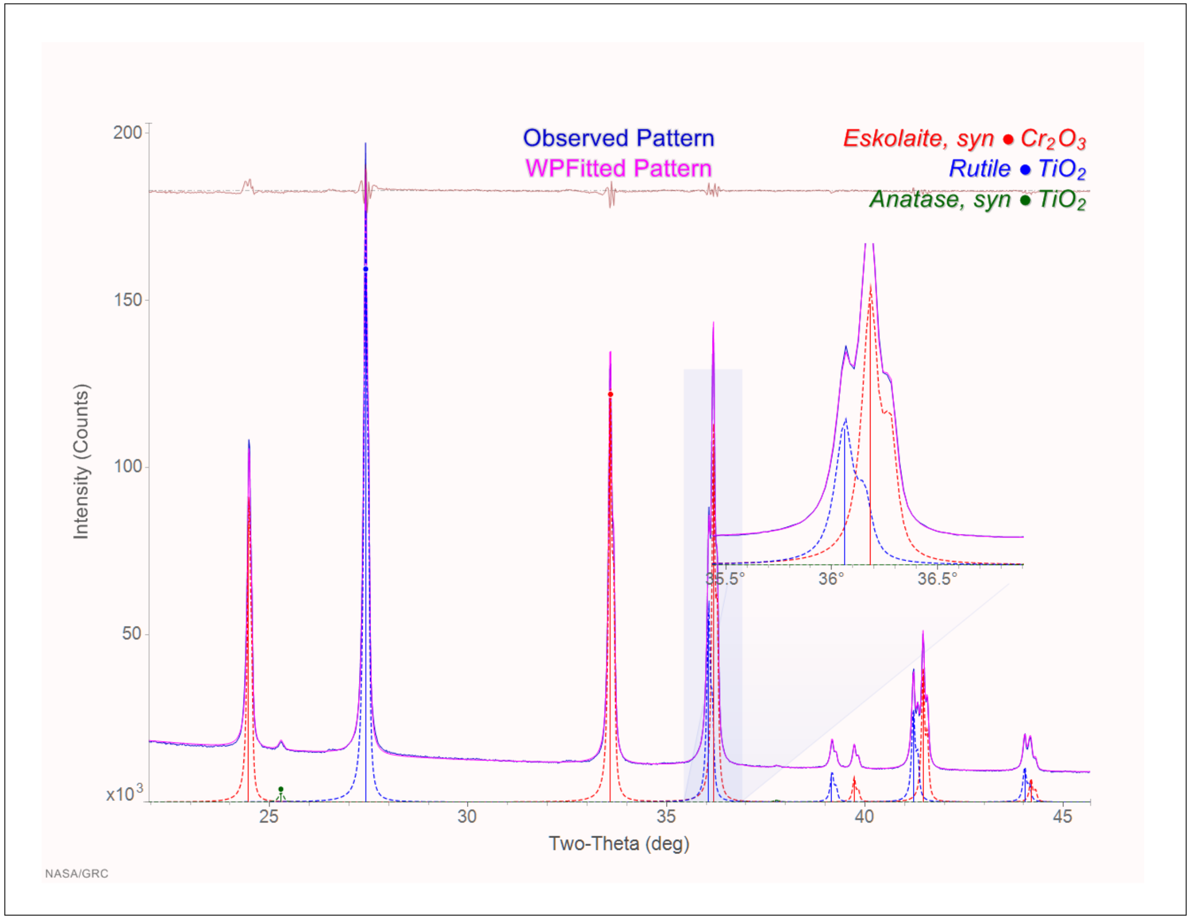
Historical and Modern Methods Identify Phases



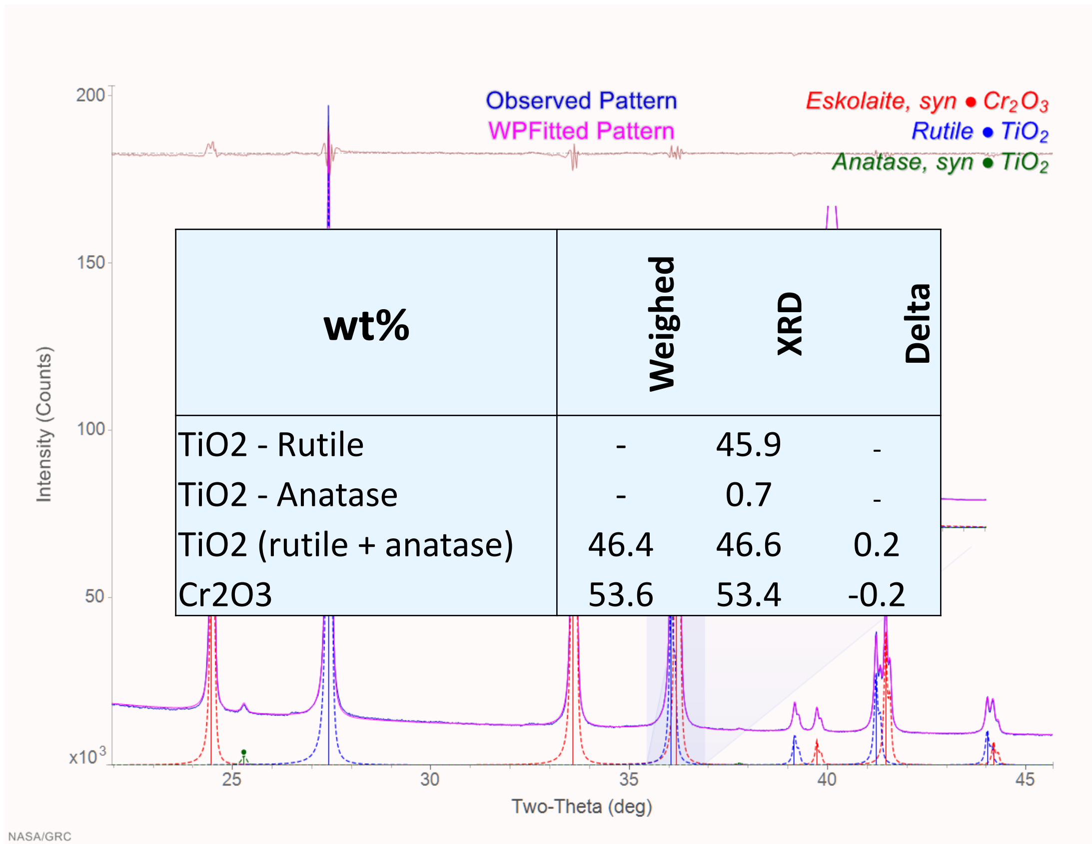
Historical Methods
Reduce data to peak positions and intensities



Modern Methods
Fit entire XRD dataset

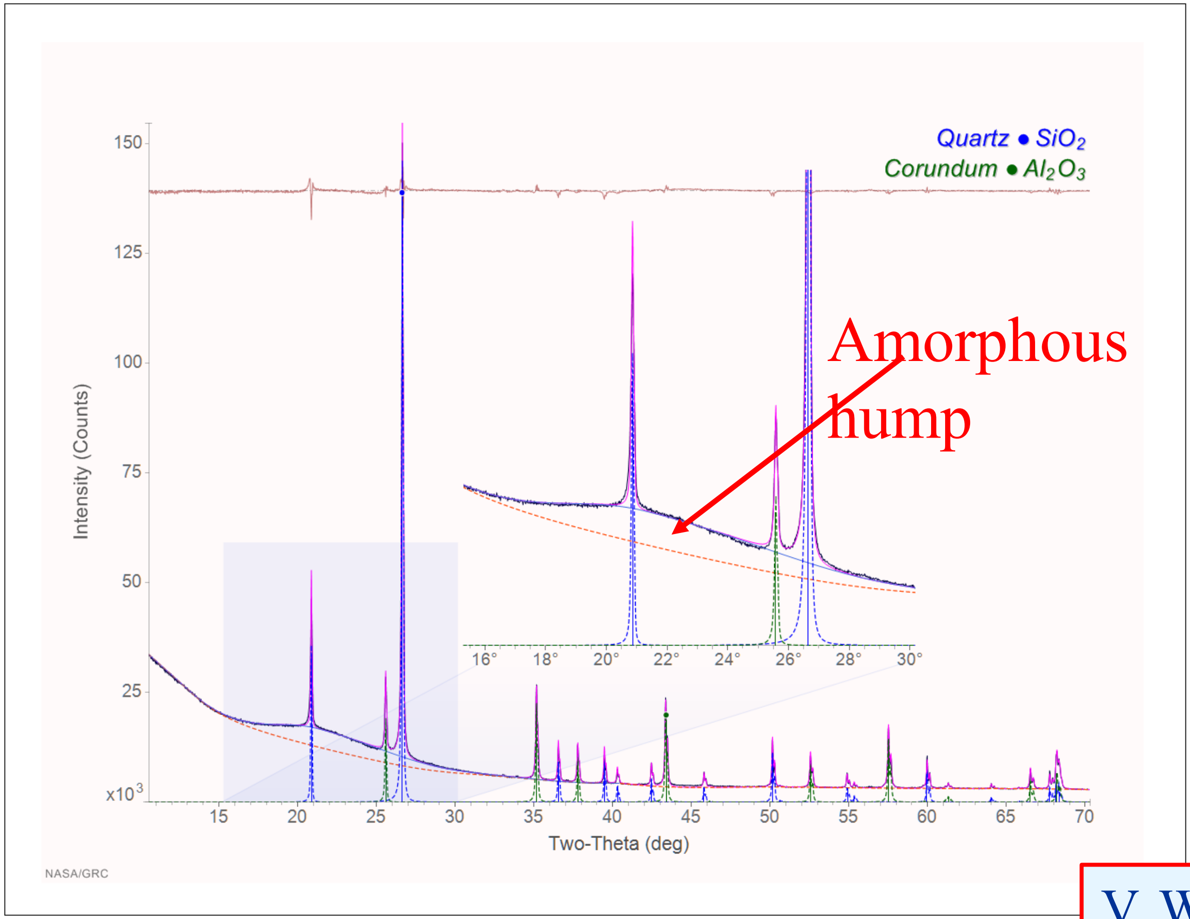


Modern Methods
Fit entire XRD dataset



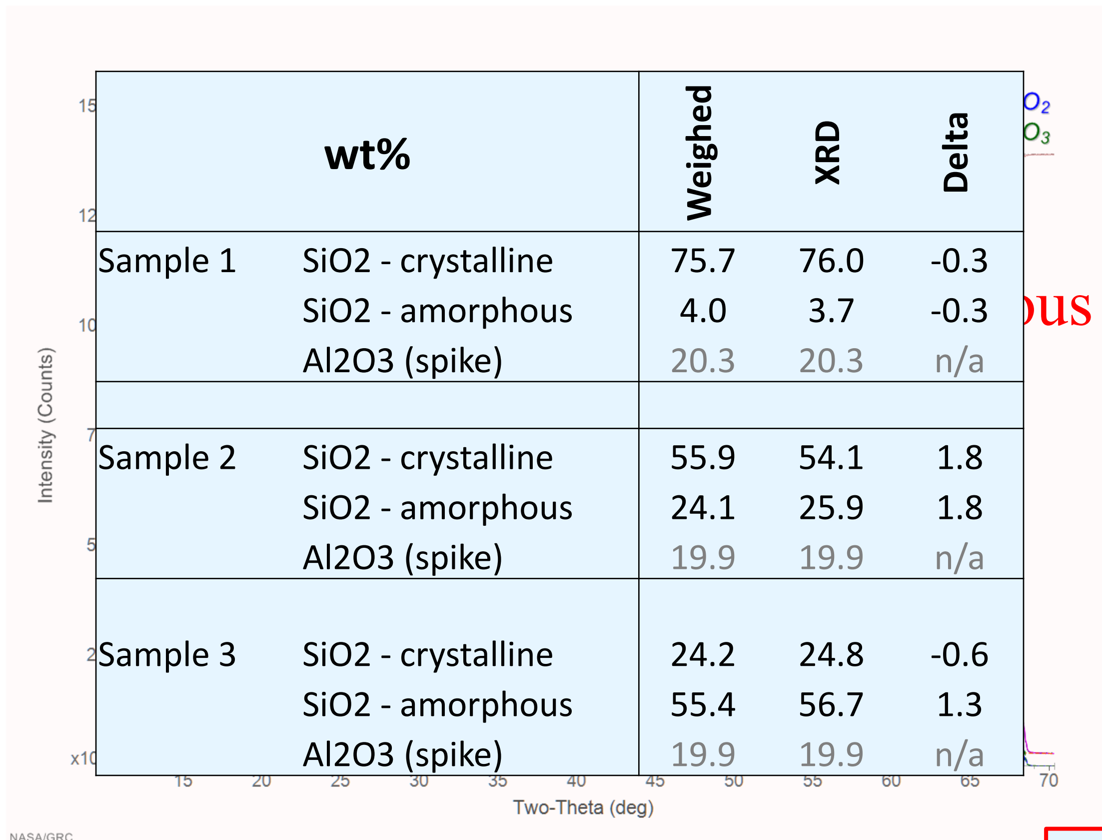
wt%	Weighed	XRD	Delta
TiO2 - Rutile	-	45.9	-
TiO2 - Anatase	-	0.7	-
TiO2 (rutile + anatase)	46.4	46.6	0.2
Cr2O3	53.6	53.4	-0.2

Quantitative Phase ID
Amorphous vs. crystalline content



V. Wiesner and G. Costa

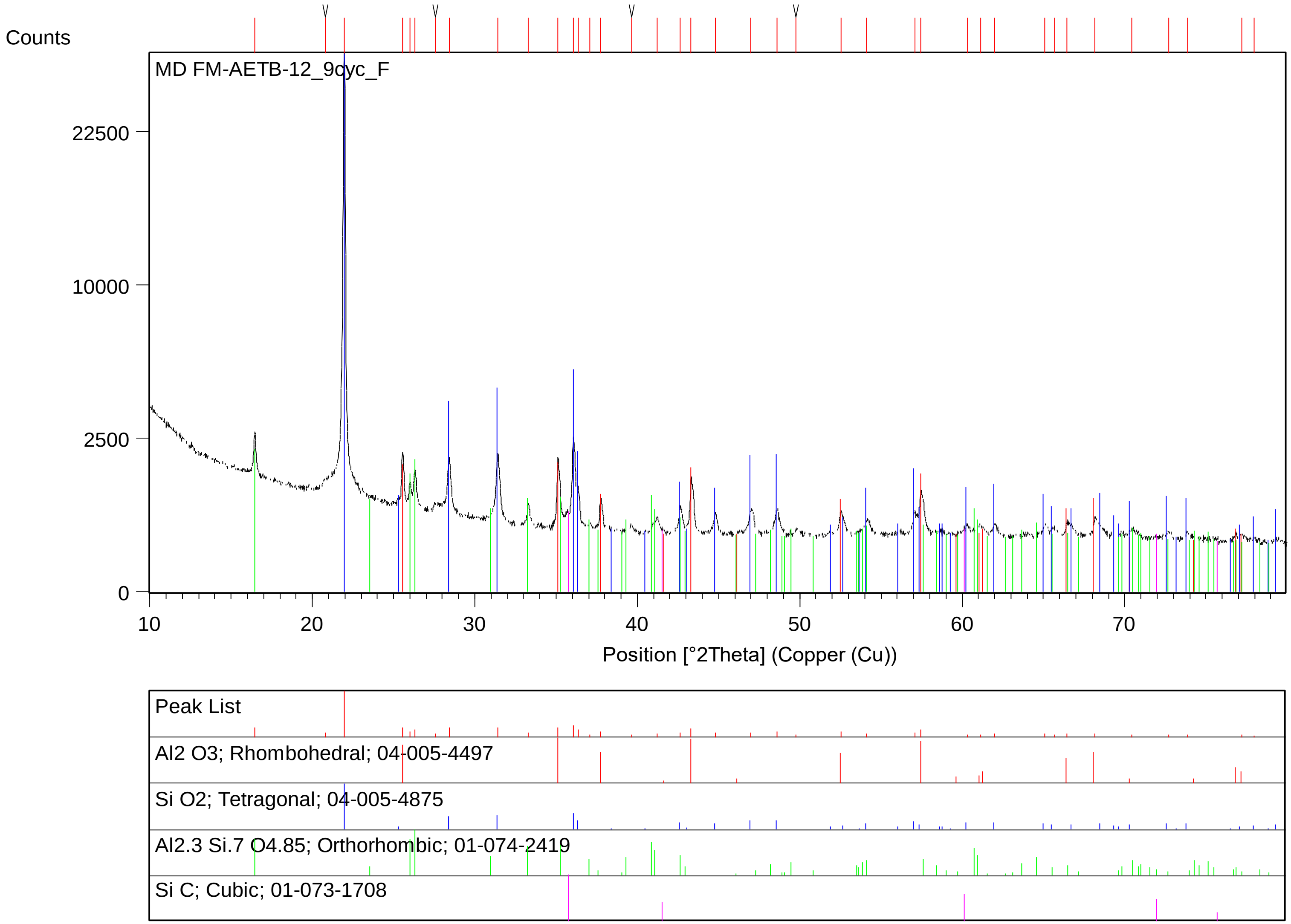
Quantitative Phase ID
Amorphous vs. crystalline content



wt%		Weighed	XRD	Delta
Sample 1	SiO2 - crystalline	75.7	76.0	-0.3
	SiO2 - amorphous	4.0	3.7	-0.3
	Al2O3 (spike)	20.3	20.3	n/a
Sample 2	SiO2 - crystalline	55.9	54.1	1.8
	SiO2 - amorphous	24.1	25.9	1.8
	Al2O3 (spike)	19.9	19.9	n/a
Sample 3	SiO2 - crystalline	24.2	24.8	-0.6
	SiO2 - amorphous	55.4	56.7	1.3
	Al2O3 (spike)	19.9	19.9	n/a

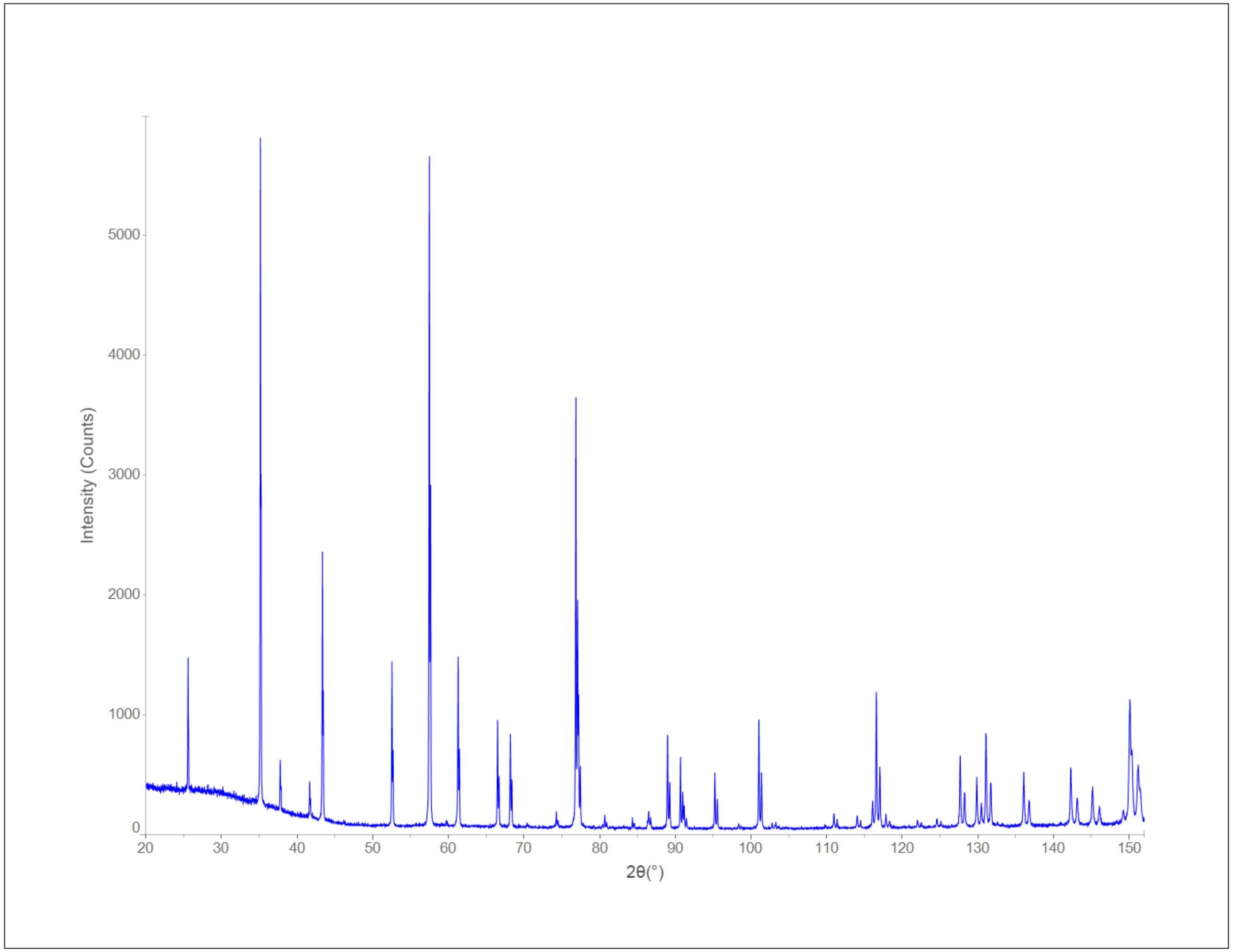
V. Wiesner and G. Costa

Crystalline Phase ID – a Composite 4-Phase Material

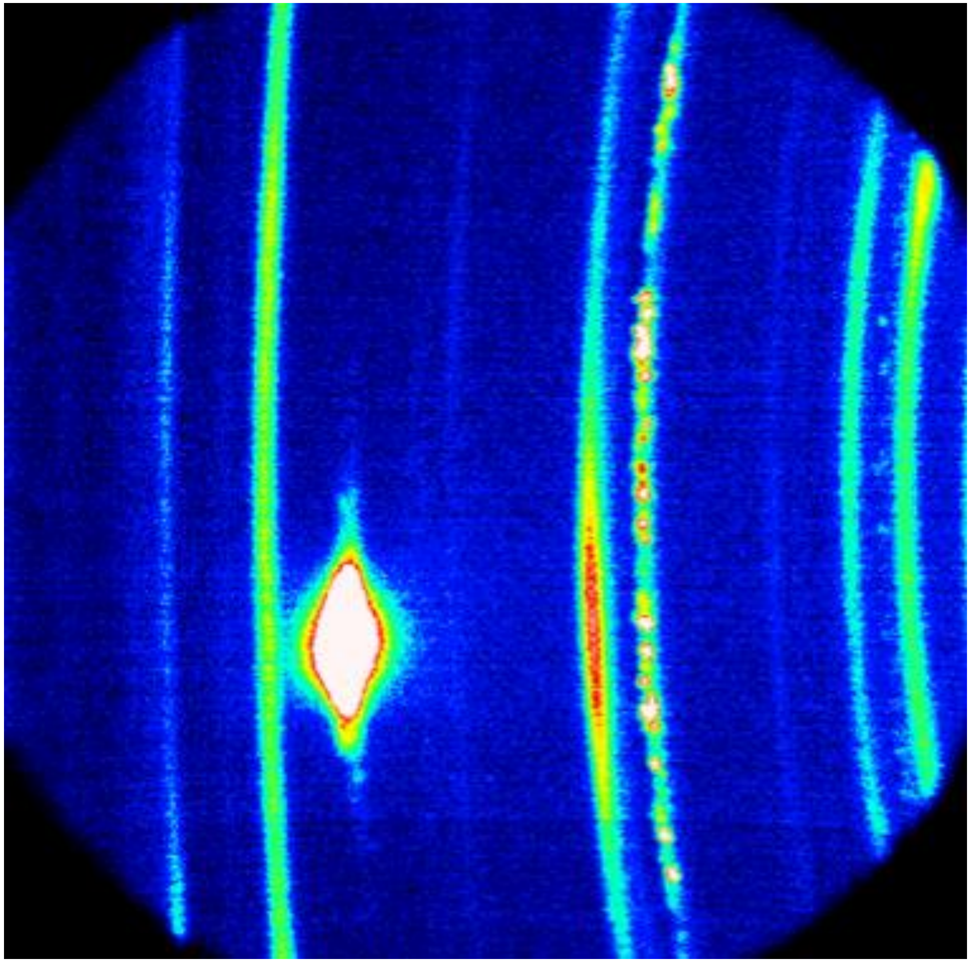


XRD pattern of Al_2O_3

NIST SRM 1976a

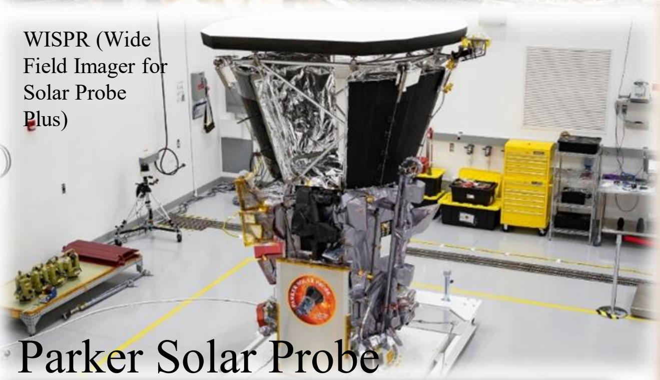


Qualitative Phase ID
Area Detector



Oxidized SX nickel-based superalloy (J. Smialek)

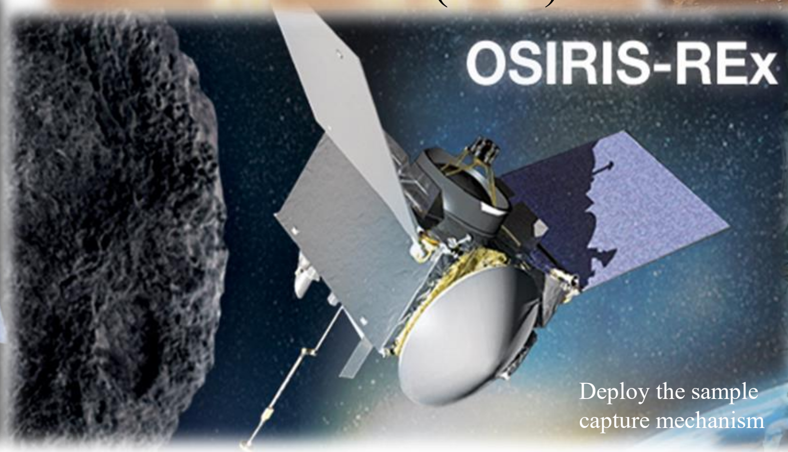

MARS Pathfinder (1996)


WISPR (Wide Field Imager for Solar Probe Plus)
Parker Solar Probe


PHOENIX (2008)

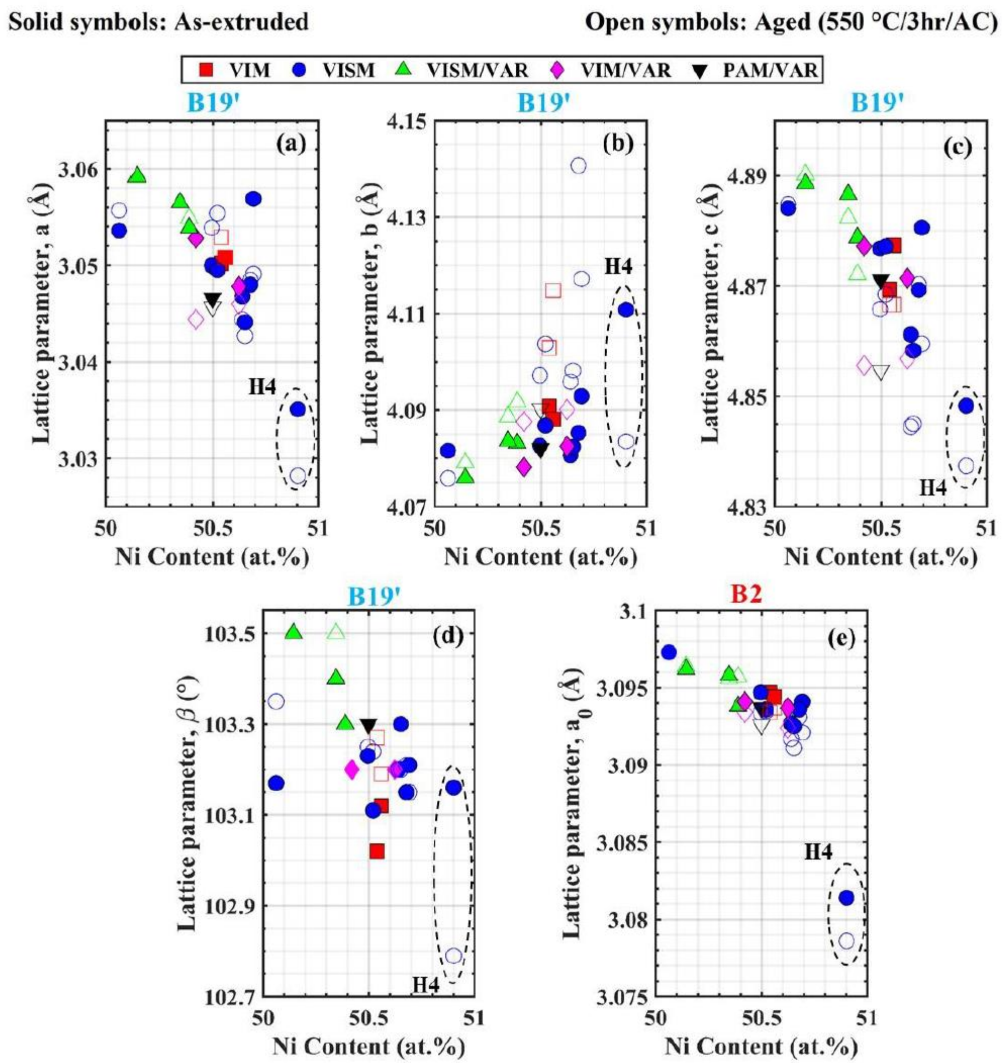

INSIGHT (2018)


ROSETTA
Deploy the Wide Angle Camera

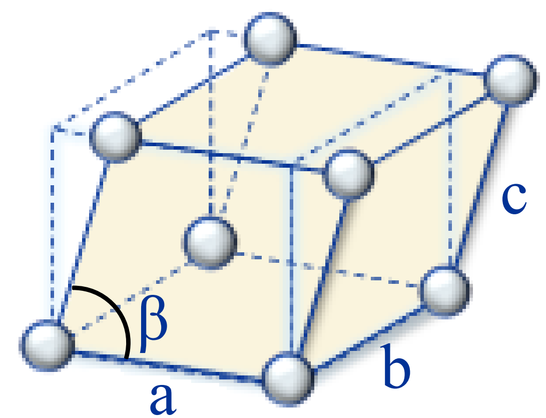

OSIRIS-REx
Deploy the sample capture mechanism


Isolation valves
ISS BEAM

Lattice parameters correlate with many physical properties



- Transformation temperatures
- Young's modulus
- Microhardness
- Maximum strain
- Recovery ratio



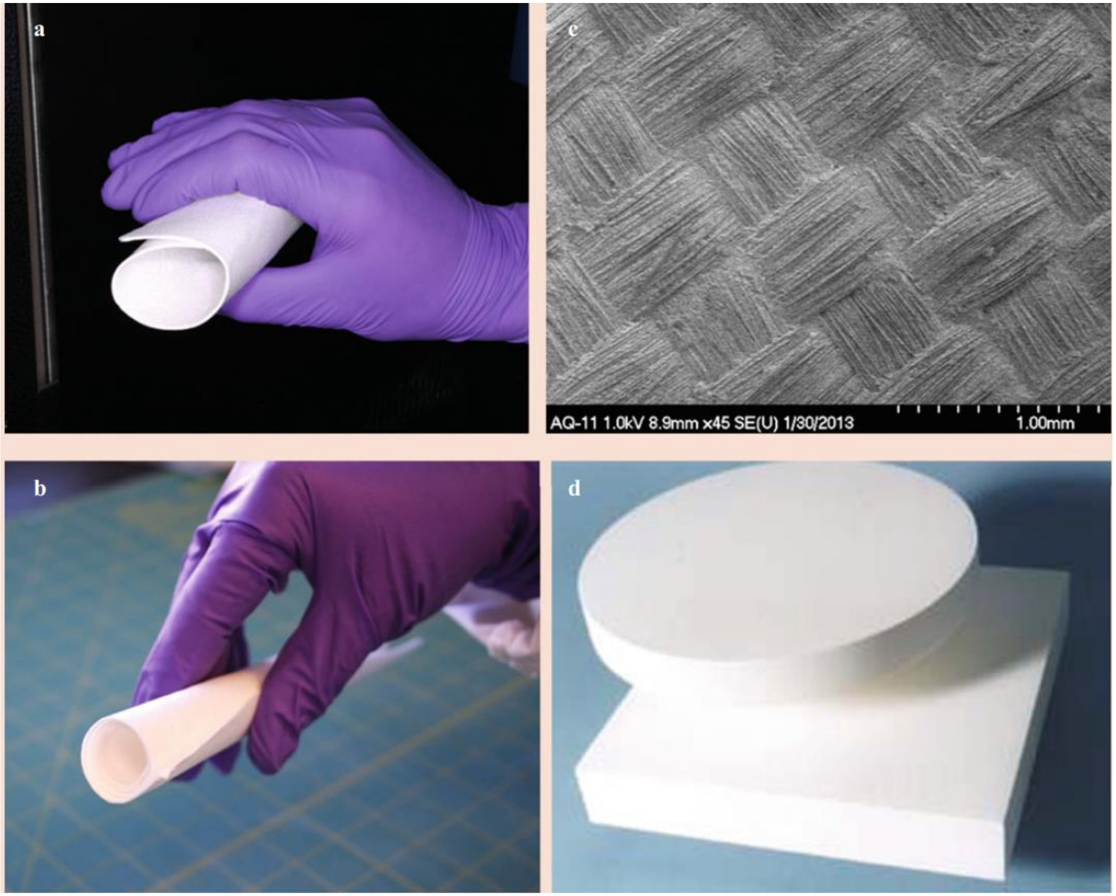
Benafan, et al., Shape Memory and Superelasticity (2021) 7:109–165

Aerogel processing and applications

Hydrogel

↓ CO_2 citical point drying

Aerogel



Selected aerogel composites: (a) reinforced with alumina paper, (b) reinforced with alumina-silica paper, (c) aerogel impregnated into woven fabric, and (d) aerogel impregnated alumina foam.

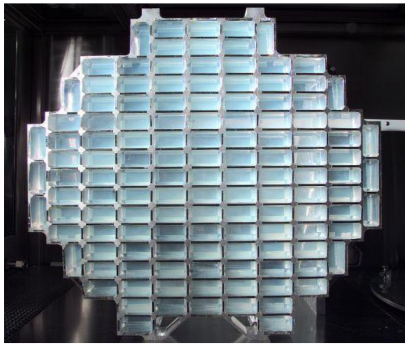
Hurwitz, et al., "High Temperature Aerogels" in Springer Handbook of Aerogels (in press)

Aerogels

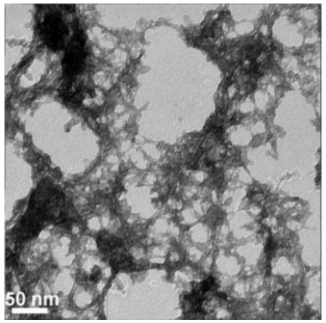
- High specific surface area (SSA), high porosity, and low density
  - **SSA**: 200 – 1000 m^2/g
  - **Porosity**: 90 – 99.9%
- Low thermal conductivity
  - Low as 0.009 W/(m•K) in atmosphere and 0.003 W/(m•K) under vacuum
  - Low density = Low solid conductivity
  - Pore sizes ≤ mean free path of gas = Low gas convection
- Versatile synthesis adaptable to a wide array of metal oxide

Highly porous structure of aerogel is responsible for its extremely low thermal conductivity.

Bunsen burner applied to aerogel



STARDUST mission used aerogels to capture interstellar dust

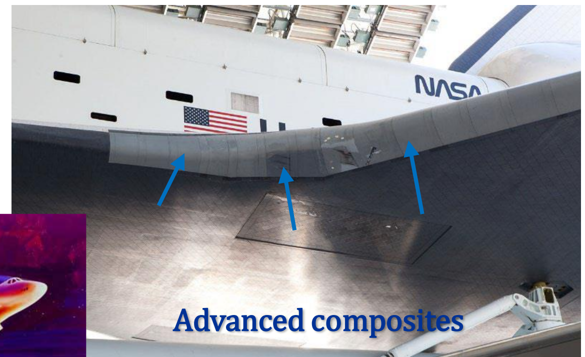


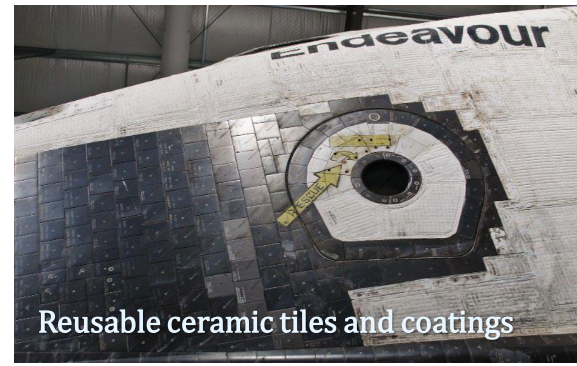
Highly porous network of interconnected nanoparticles

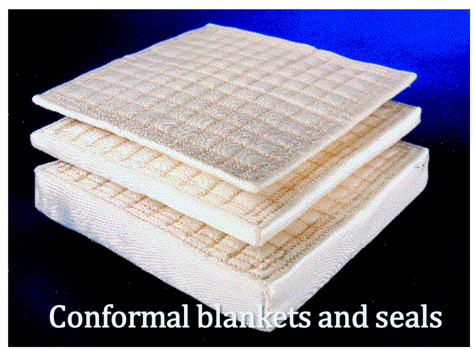
Thermal protection for Mars rovers' electronic boxes from temperature fluctuations between day and night

Thermal Protection Systems

- Development of lightweight, high-performance aerospace thermal protection systems







<u>TPS Needs</u>

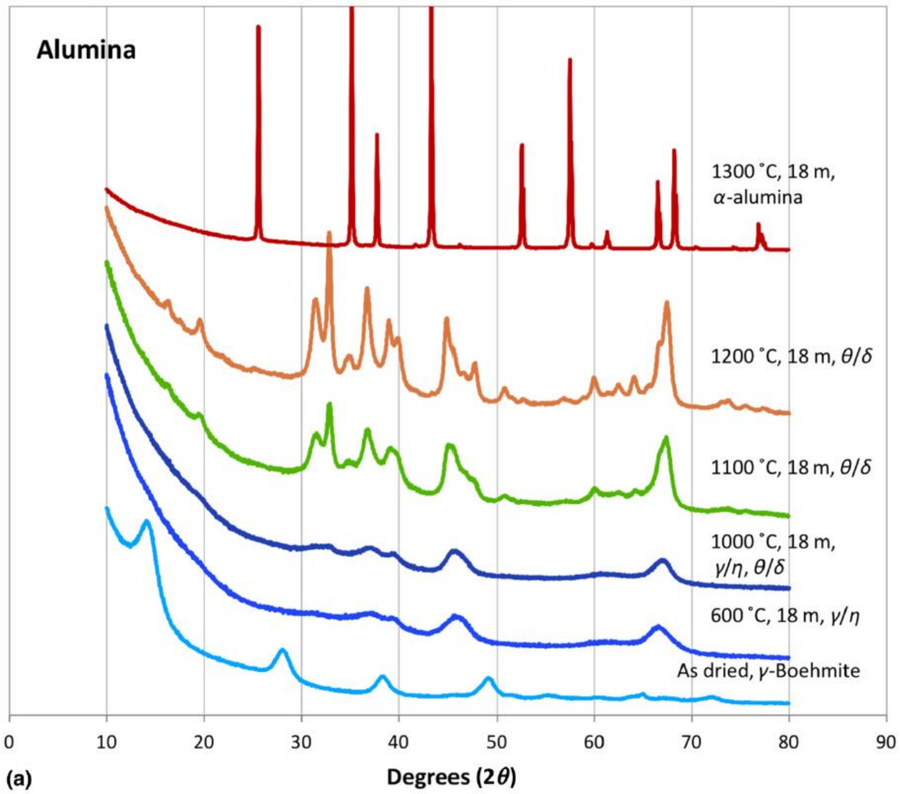
Thermal management
Mechanical durability
Lightweight
Reusable when possible

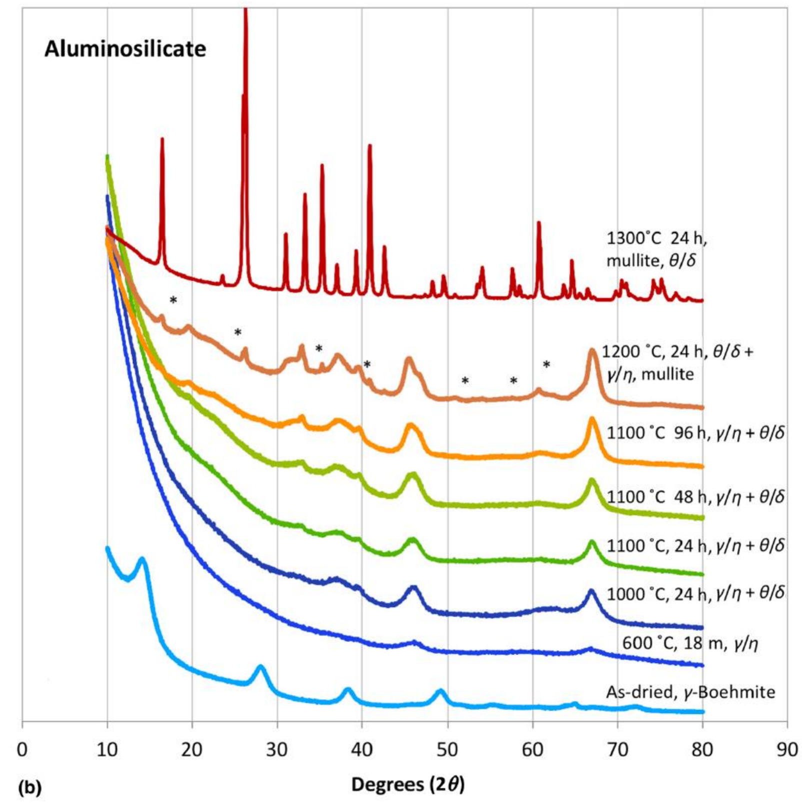
<u>Our Goals</u>

Reduce thermal conductivity to improve performance

Reduce mass/volume to lower costs

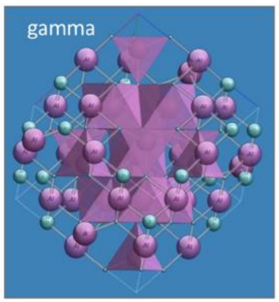
Aerogel phase transitions

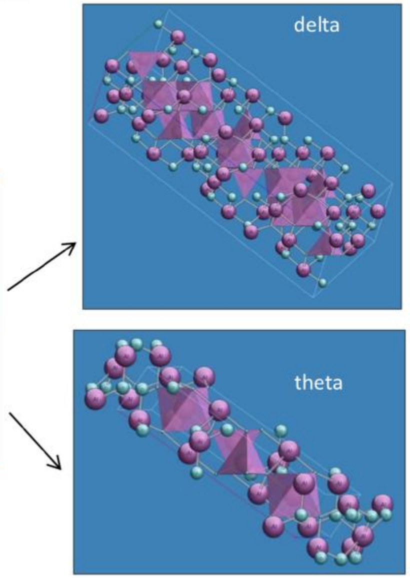




Hurwitz, et al., MRS Communications, Vol. 7, No. , (2017) , pp. 642 – 650.

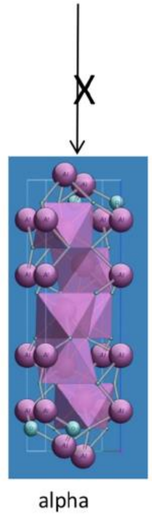
Aerogel phase transitions

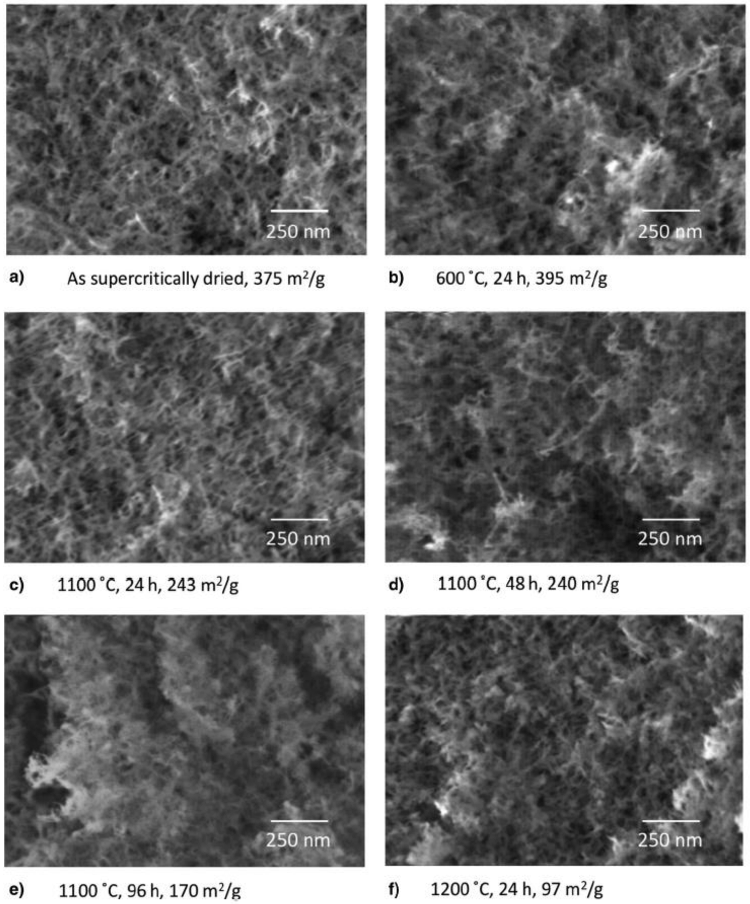




Displacive transformation (mix of TETRAHEDRAL and OCTAHEDRAL bonding)

Reconstructive transformation (all OCTAHEDRAL bonding) takes place in all-alumina but not aluminosilicate gels





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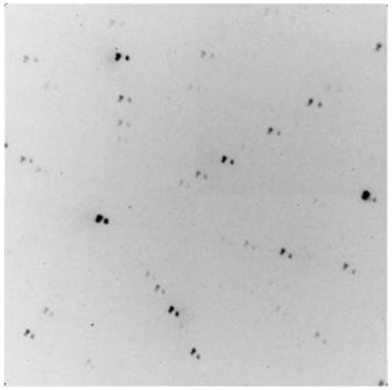
Single Crystal Orientation



- Two possible objectives with a SX sample:
- What is the crystallographic orientation of a sample relative to its physical geometry?
- Manipulate a sample such that crystallographic directions are aligned in a prescribed manner.