Nb SRF Surfaces: XPS, XRD, and Laser Extraction

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Preface

- For the term of my internship, I worked with Arely Cano in the SQMS (Superconducting Quantum Material Sciences) Department on analyzing a group of new niobium superconducting cavities.
- Over the course of the 3 months, we performed GI-XRD analysis and ARXPS analysis, and I also designed a CO_2 gas cutting laser for a new extraction method for acquiring better samples of the cavities.
- The goals were to establish better methods of treatment for niobium cavities for increasing Q and maintaining Nb T_c , and a secondary goal was to find more accurate cutout extraction methods.

Figure 1: Nb SRF Cavities lined up and being tested with a magnetic field.

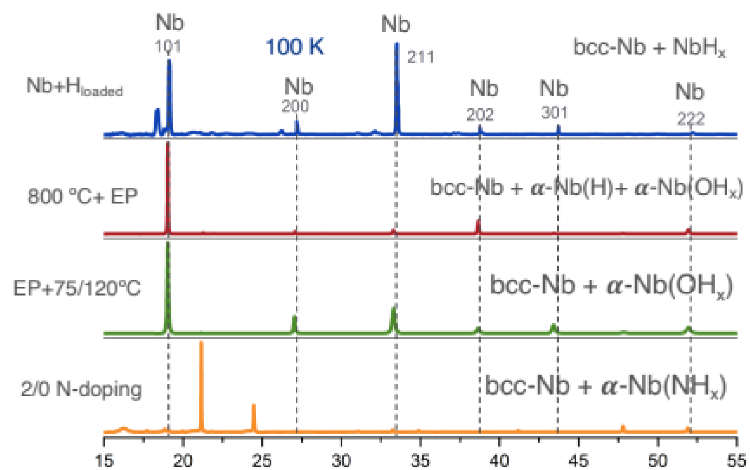


Figure 2: XPS spectra of some various treatment techniques on Nb cavities.

XPS

- In order to assess how oxygen forms on the surface of our niobium cavities, SQMS conducted ARXPS experiments on a cutout of the cavity at ESRF.
- ARXPS can be used to determine the chemical concentrations and chemical states of constituent elements.
- The experiment gained information to the chemical composition of the surface (0-10 nm deep) of the niobium cavity.
- Chemical compositions and chemical states of niobium, carbon, and oxygen were assessed.
  - Our use of XPS is primarily to find oxides in the cavity, a contaminant greatly responsible for lost Q and decreased T_c.

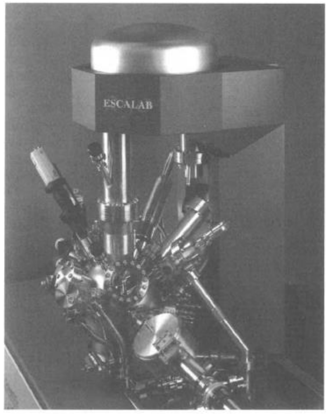
XPS Fundamentals

- XPS stands for "X-ray Photoelectron Spectroscopy."
- XPS uses x-rays to stimulate electrons into emission, each of which have unique energies required to emit them represented algebraically as binding energies.

$$Binding\ energy\ (BE) = Photon\ energy\ (\gamma E) - Photoelectron\ Kinetic\ Energy\ (KE)$$

- In XPS, BE is used to identify electrons of a material.
- XPS is used for analyzing the surface of materials because the x-rays best eject electrons to the anode electron detector from the surface.
  - Surface structure, while being a small portion of a material's volume, is critical to; chemical reactability, electrical conductivity, thermal conductivity, and friction. (J. Watts and co.)

Figure 3: A modern XPS machine. Adapted from *"An introduction to surface analysis by XPS and AES."*



O Layer with XPS

- XPS reaches 7-10 nm beyond the material surface, which is where the O layer forms.
- O concentration is inversely proportional to the superconducting temperature.
- At $T \cong 200℃$, the O layer of the Nb begins to irreversibly alter.
  - $Nb_2O_5 \rightarrow NbO_2 \rightarrow NbO$
- At $T \cong 1{,}000℃$, the O on the surface seems to completely disappear, only to reappear during cooling after $T \cong 900℃$.
  - The remaining O contamination migrates into the bulk at the former temperatures and seems to reform on the surface below the latter temperatures.
- Annealing at high temps is the method used to purify oxides out of the SRF cavities but does not completely eliminate the contamination.

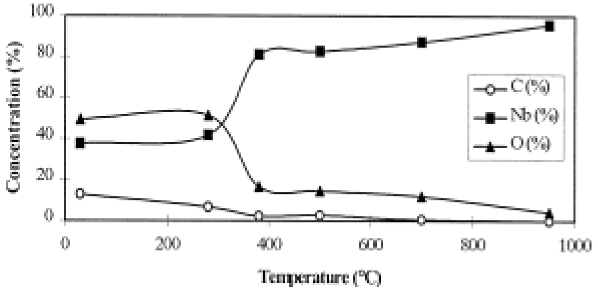


Fig. 5. Nb, O and C surface concentration vs. increasing temperature, for Nb anodized at 5 V (lines are a guide for the eyes).

Figure 4: Adapted from "XPS analysis of the surface composition of niobium for superconducting RF cavities" by Dacca and co.

Figure 5: Adapted from "XPS analysis of the surface composition of niobium for superconducting RF cavities" by Dacca and co.

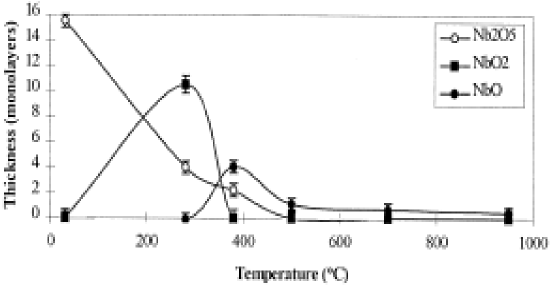


Fig. 6. Thickness of Nb_2O_5, NbO_2 and NbO layers on Nb surface vs. increasing temperature (lines are a guide for the eyes).

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ARXPS

- For the analysis of our niobium sample, we used ARXPS, or Angle-Resolved XPS.
- This is advantageous because changing the angle of the specimen in the experiment changes surface sensitivity to x-ray radiation, which allows for a more complete and accurate depiction of the surface.
- ARXPS can also give information about layers of the surface of the material.

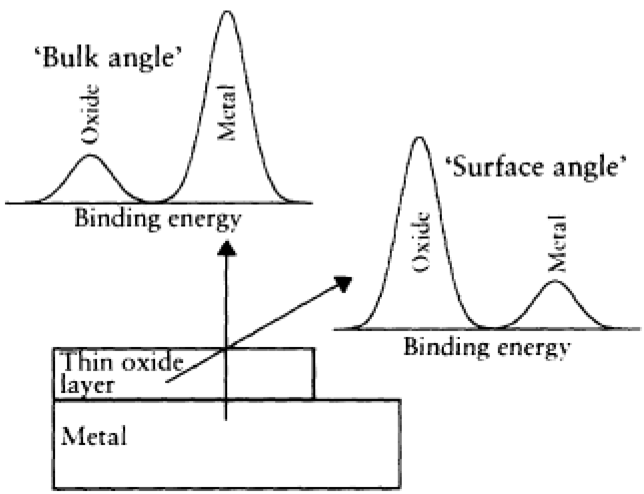

Figure 7: A representation of how altering experimental angle can alter CPS and perceived concentrations of the surface. Adapted from *"An introduction to surface analysis by XPS and AES."*

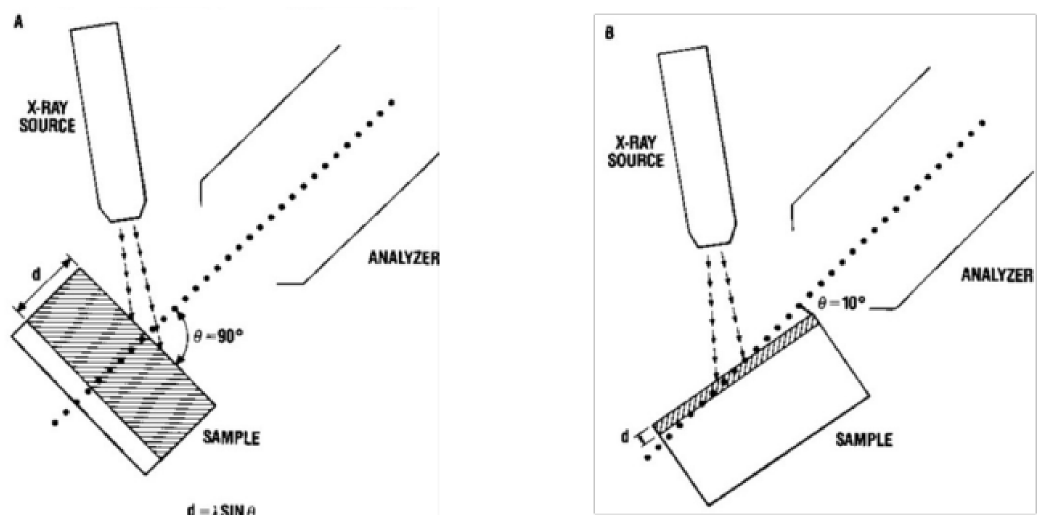

Figure 8: A visual demonstration of how altering the experimental angles relative to the analyzer results in deeper analysis. Clearly, $\theta \propto d$. Adapted from *"X-Ray Photoelectron Spectroscopy (XPS)-2" by Louis Scudiero.*

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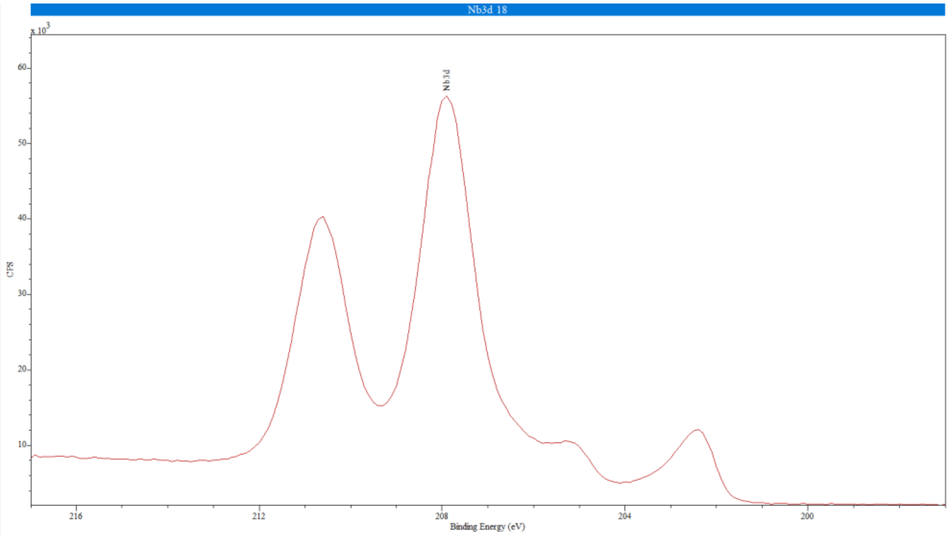
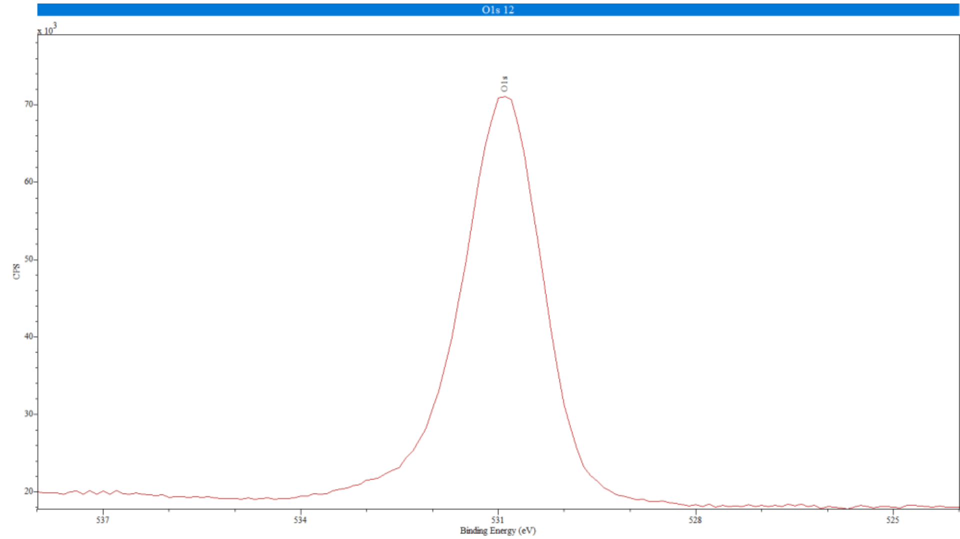
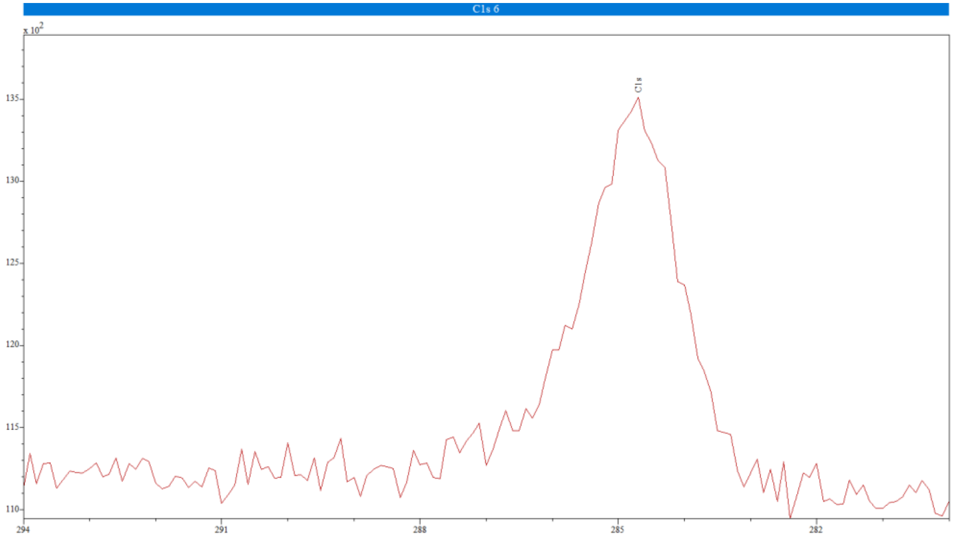
XPS Graphs @ 80⁰







43.26% Nb,
2.33% C,
41.84% O,
NbO_2 7.03%,
NbO 5.54%

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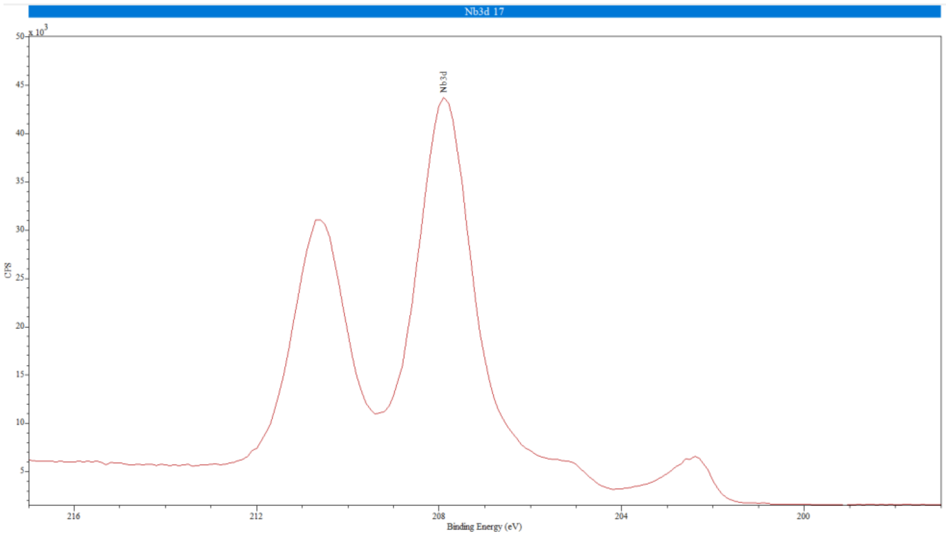
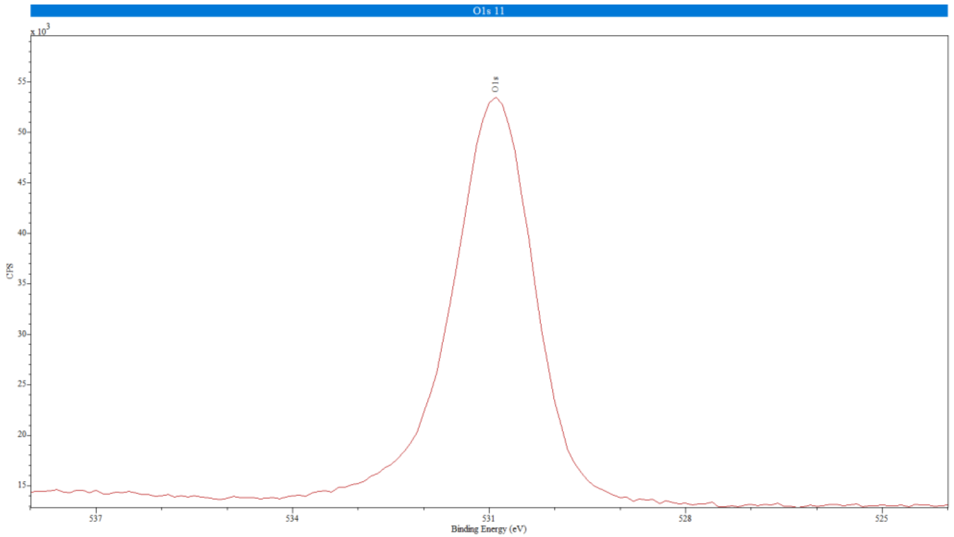
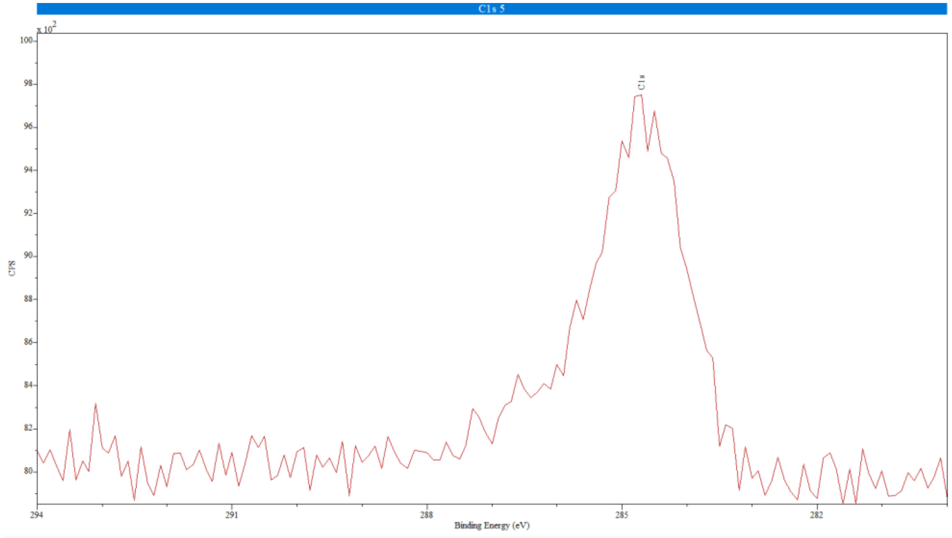
XPS Graphs @ 60⁰

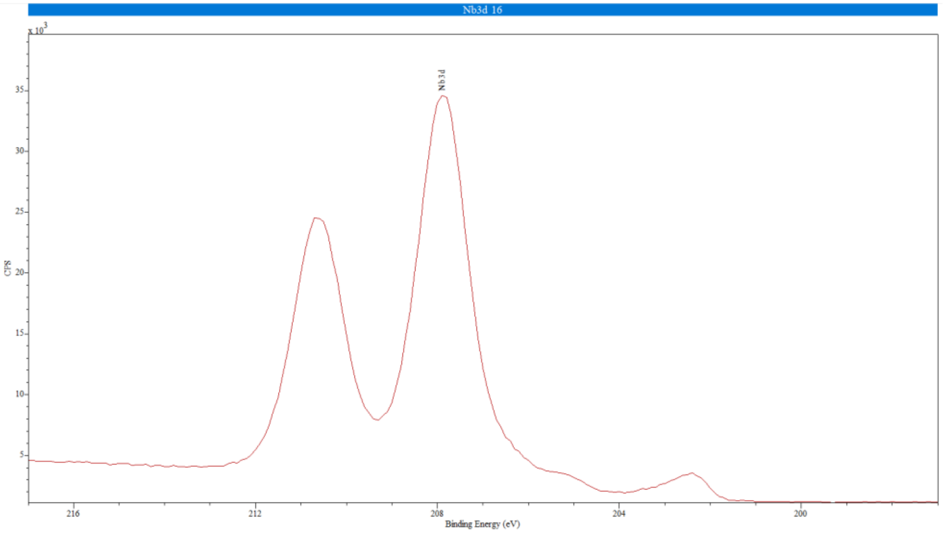


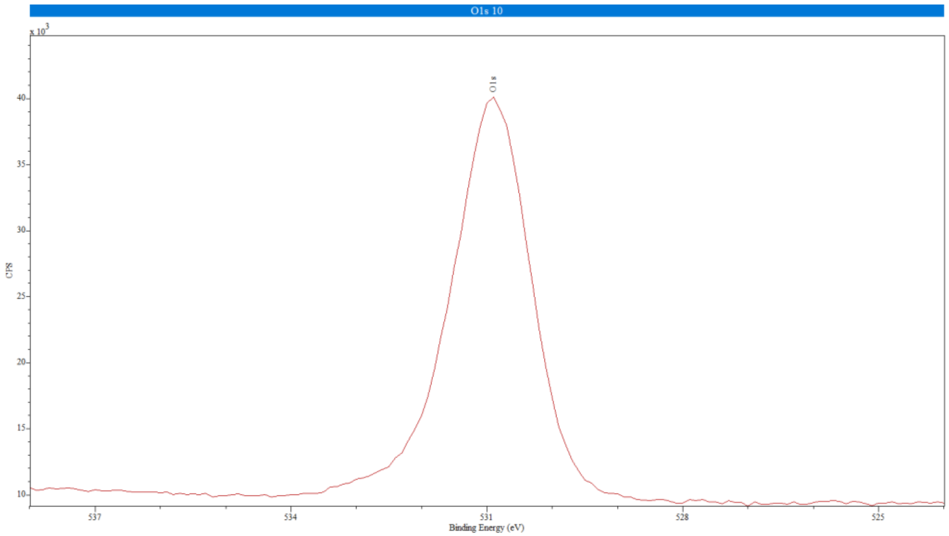


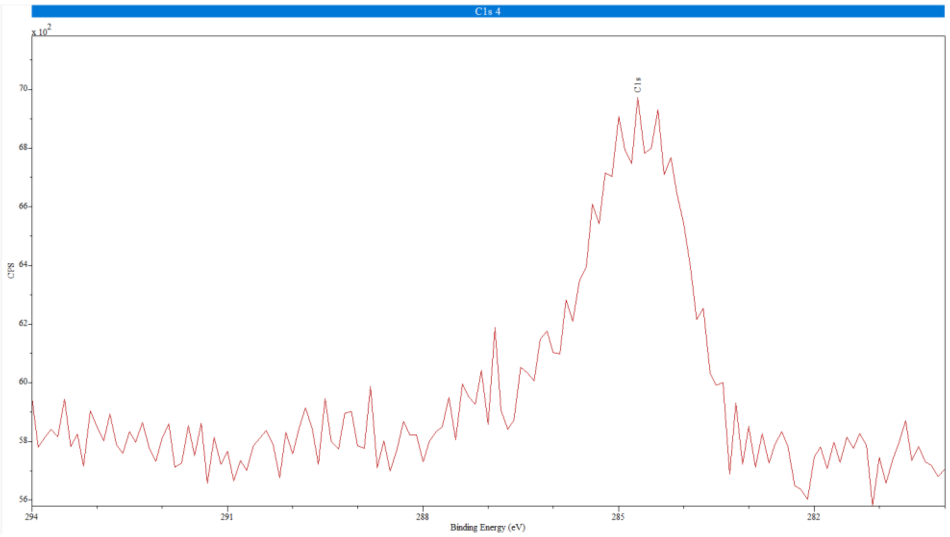


47.25% Nb,
1.99% C,
42.82% O,
NbO_2 4.07%,
NbO 3.87%

XPS Graphs @ 45⁰

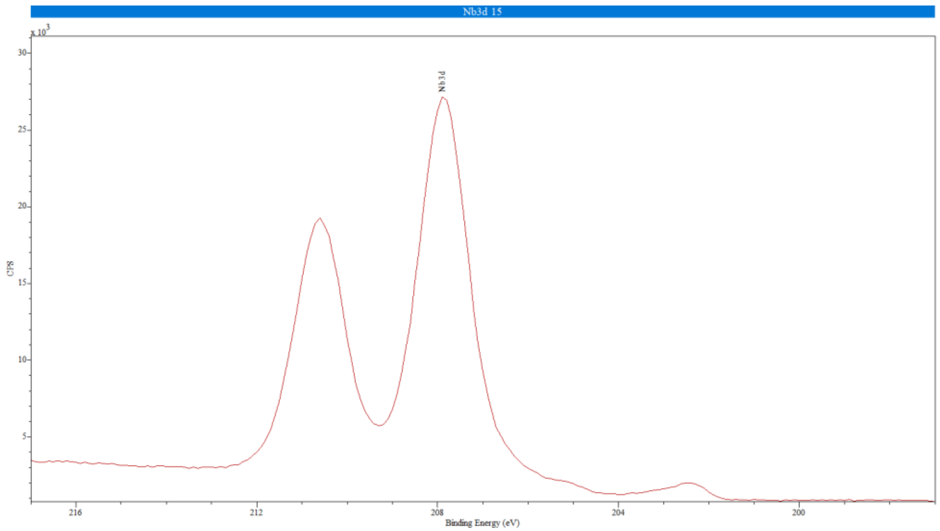


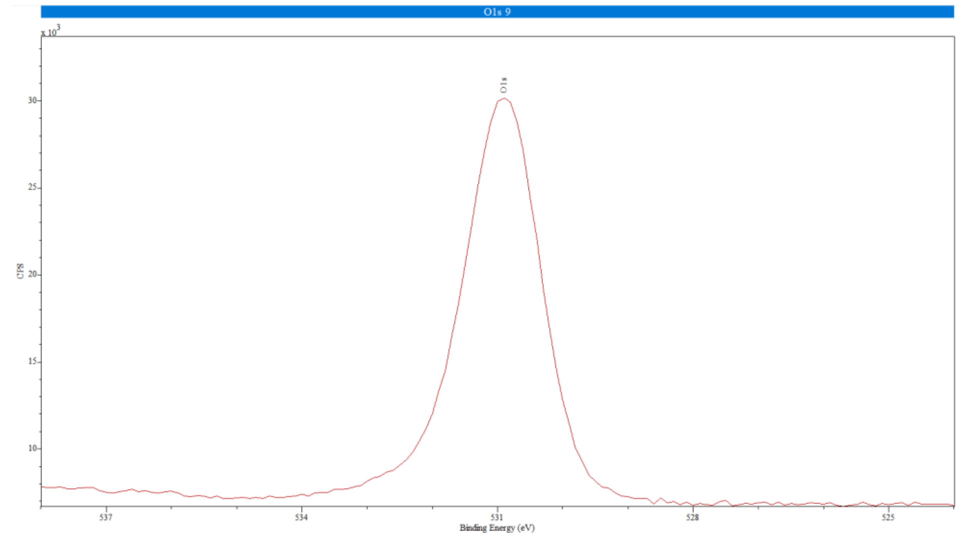




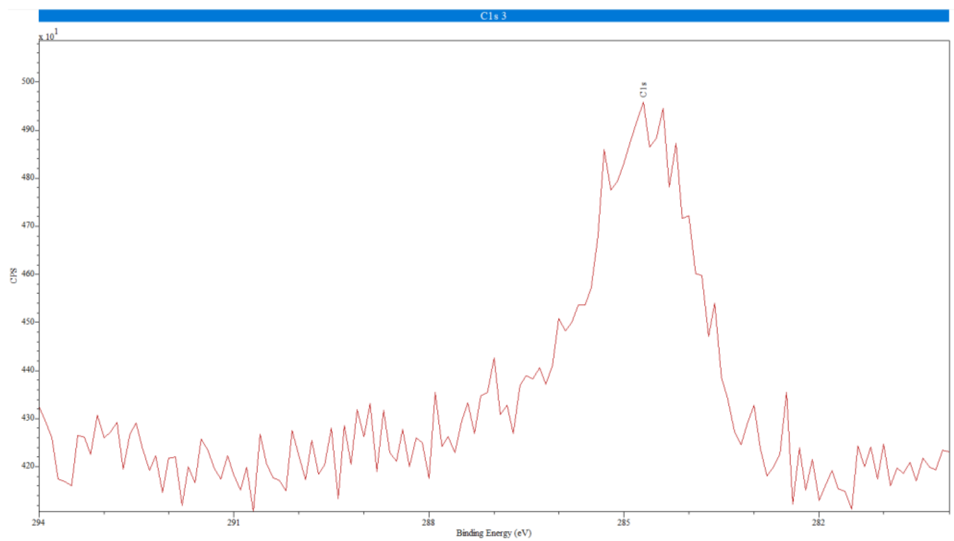
49.32% Nb,
2.01% C,
45.43% O,
NbO_2 1.95%,
NbO 1.29%

XPS Graphs @ 34⁰

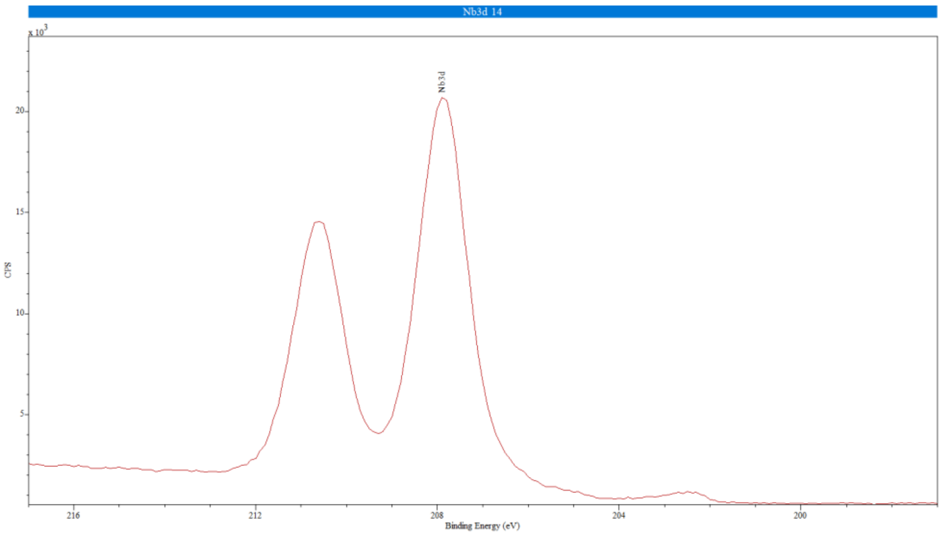


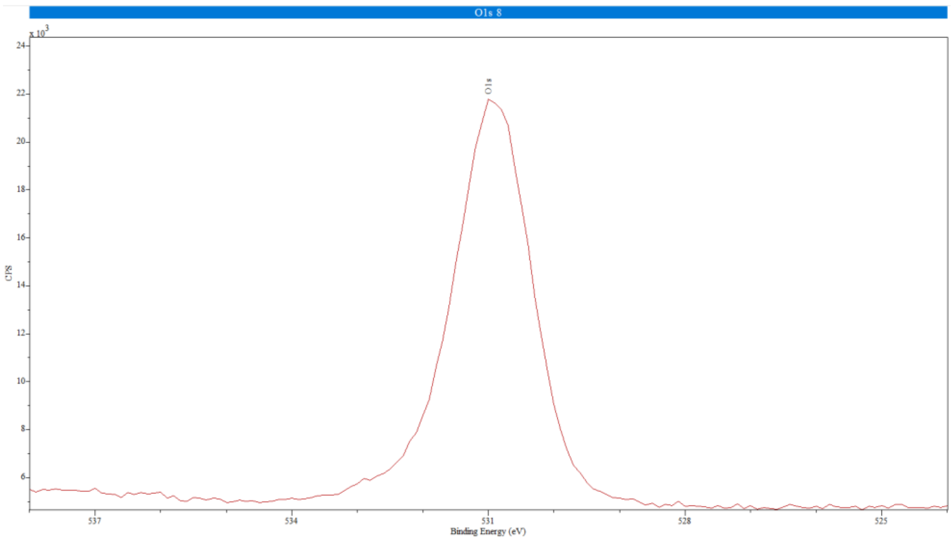


51.08% Nb,
2.00% C,
43.06% O,
NbO_2 1.31%,
NbO 2.55%

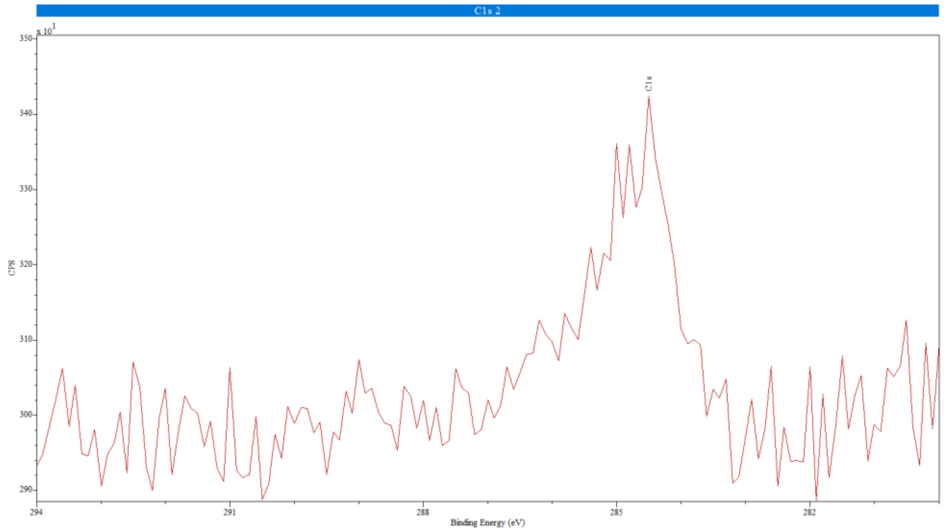


XPS Graphs @ 25.5⁰

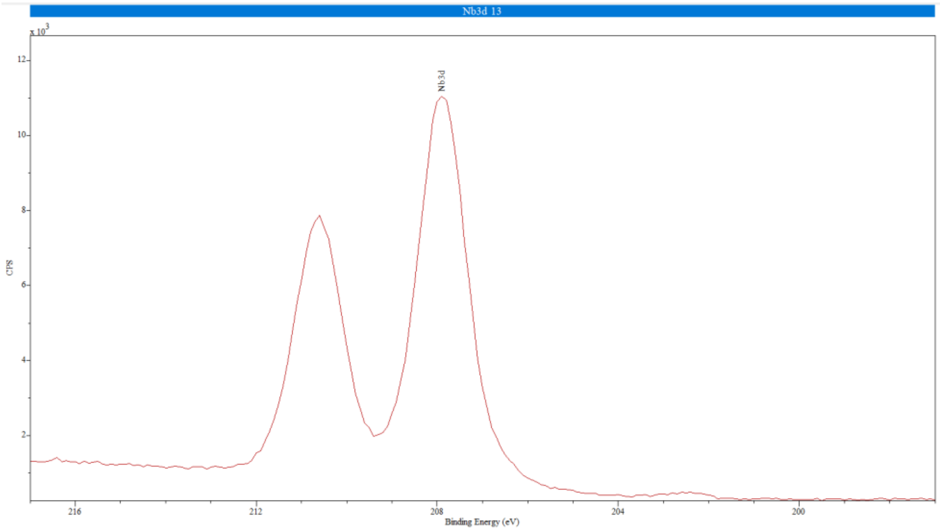


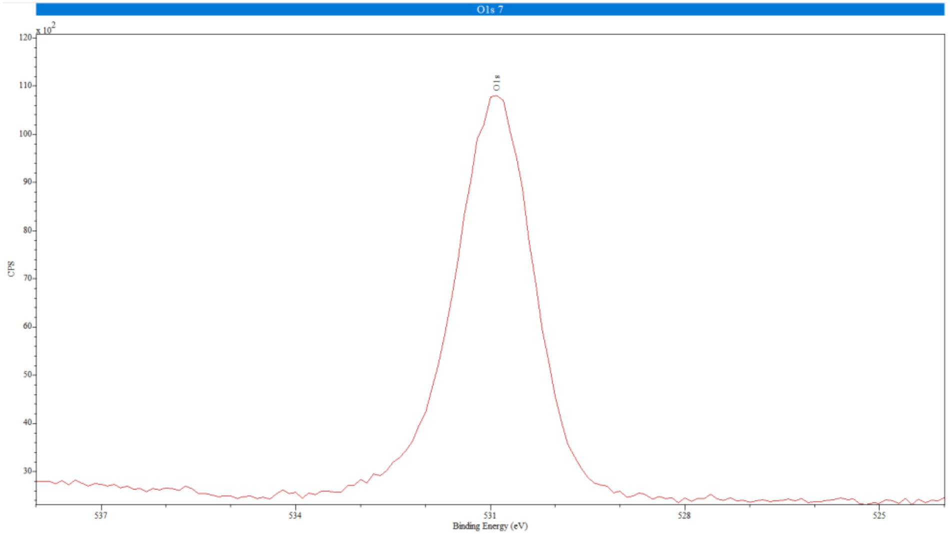


52. 92% Nb,
0.97% C,
43.95% O,
NbO_2 1.28%,
NbO 0.90%

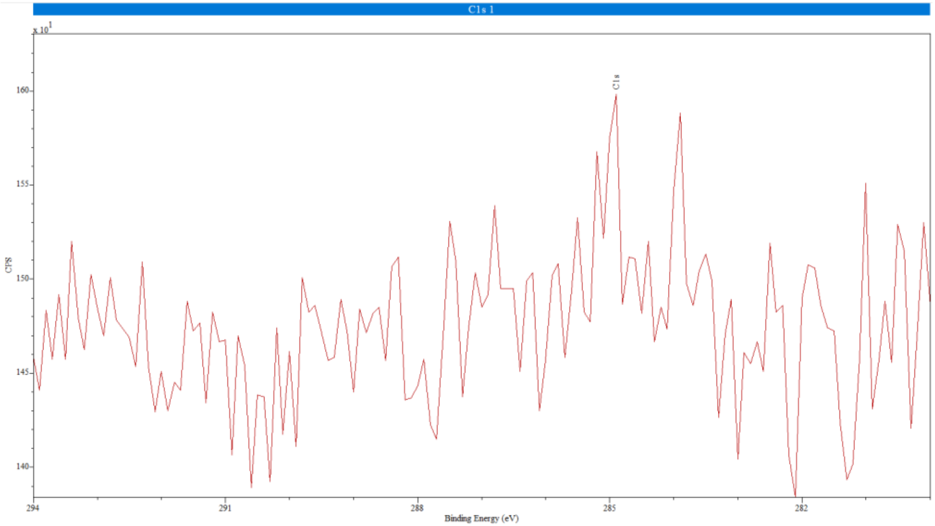


XPS Graphs @ 15^0





56.69% Nb,
0.233% C,
42.27% O,
NbO_2 .65%,
NbO .16%



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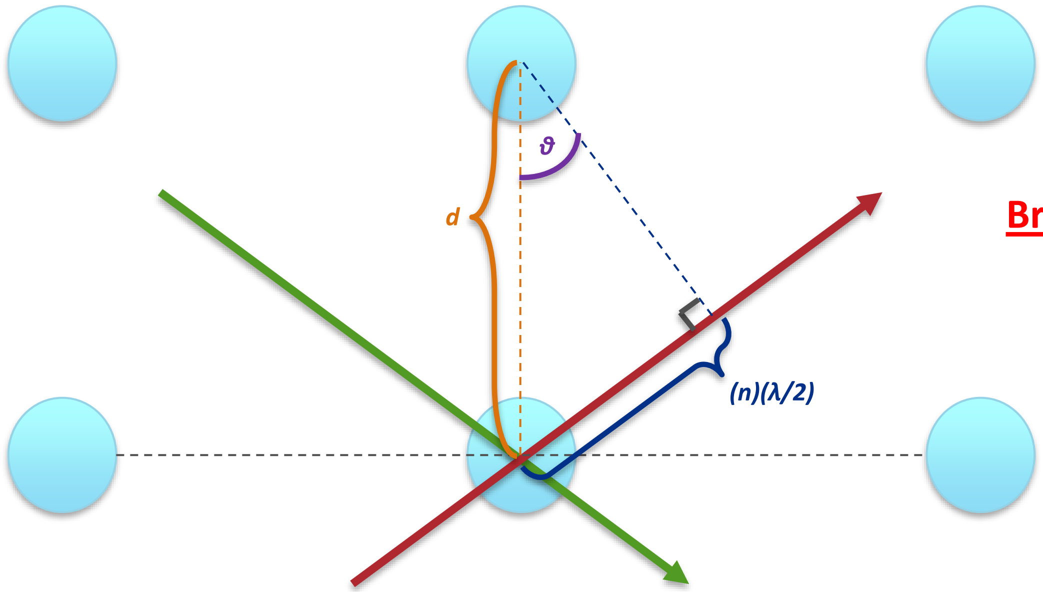
XPS Conclusion

- With the spectrums from the experiment, we found that there was a gradient of oxygen contamination that decreased with depth of analysis. We also found that carbon contamination was negligible and was probably caused by handling rather than cavity processing treatments.
- The greater the depth of the surface, the higher purity of niobium there was. The first layers of the surface are the most contaminated.
- This sample was the non-N-doped and non-degassed sample. A treatment involving N-doping and degassing as well as an annealing bake may improve future results.

GI-XRD Intro

- In addition to ARXPS for surface analysis, we used GIXRD.
  - GIXRD is “grazing incident x-ray diffraction.”
    - “Grazing incident” is important to keep analysis on the surface and encourage **elastic scattering.**
- This method uses constructive and destructive interference of elastic scattering to determine a material surface’s chemical composition, molecular unit cell structure, crystal phases and subphases, and surface contamination.

Figure 10: Illustration of Bragg’s Law derivation and XRD process



Bragg’s Law:

$$n\lambda = 2\, d \sin(\vartheta)$$

XRD for Nb Cavity Surface

- We used XRD for our purposes specifically because at niobium cryogenic temperatures required for operation, dissolved hydride contaminants segregate out of the metal in crystals.
- XRD can also be used to find oxides deeper than the surface as interstitial bulk oxygen migrates to the surface when the niobium slowly approaches cryogenic operating temperatures.
  - This is why most of the XRD signal comes from H and O.
- Our XRD experiments were conducted at ESRF with the BM25 Spline.

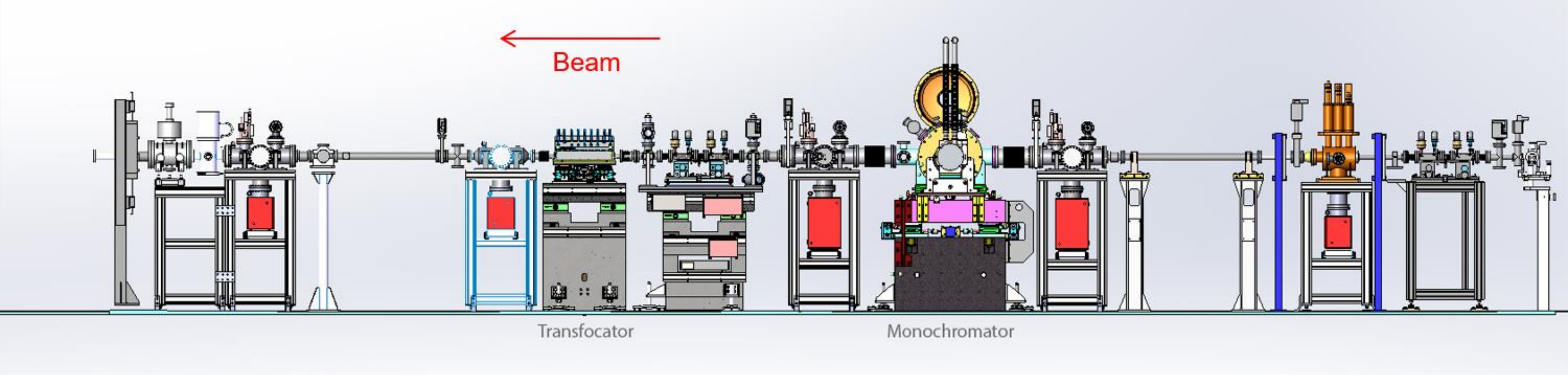
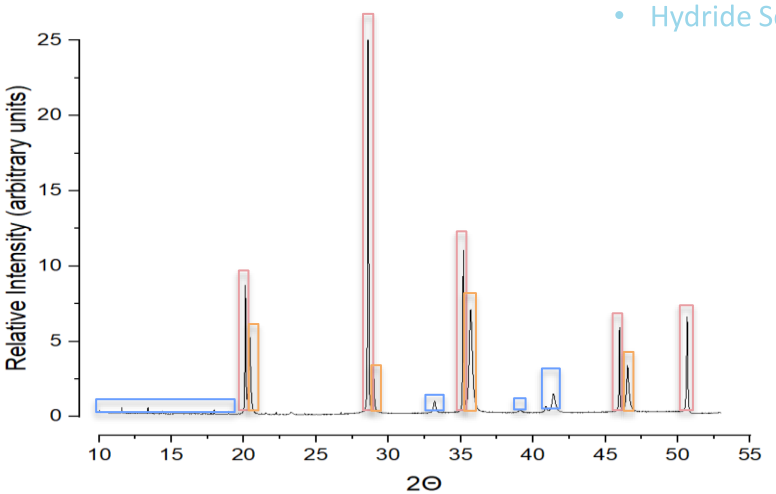


Figure 11: ID22 High Resolution Powder Diffraction XRD at ESRF. Retrieved from ESRF.fr.

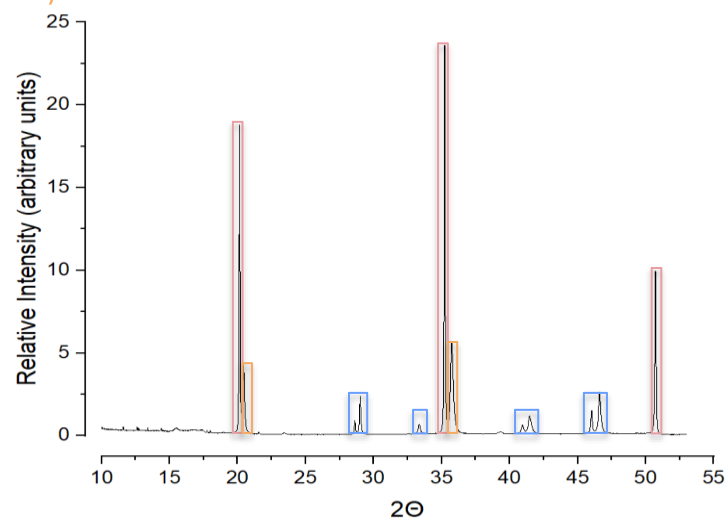
H under XRD Analysis

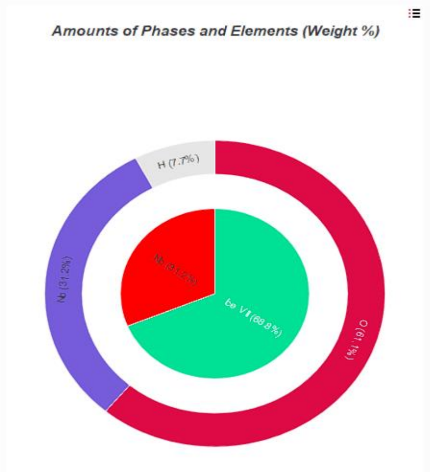
- H is one of the potential contaminants that can be present in our cavities.
  - This is primarly from the treatments (electropolishing, washing, etc.).
- Dissolved H contaminants will segregate out as crystals at ~175 K, which creates surface contamination that shows on some experimental composition analysis techniques like XRD.
  - When we cryogenically cool the Nb cutout to see the Nb crystal phases at operating temperature, we make these H surface segregates.

- Niobium Primary Phase
- Niobium Secondary Phase (subphase)
- Hydride Segregates

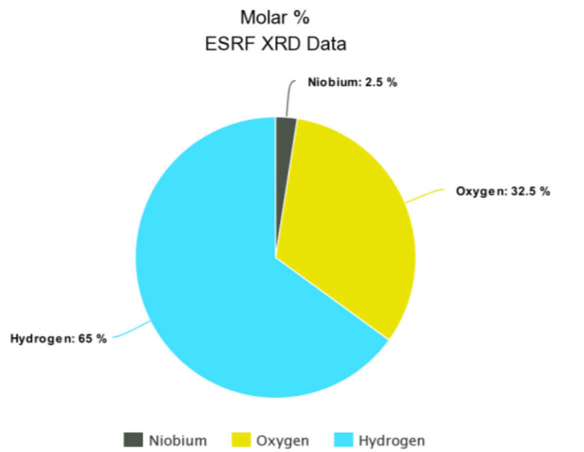


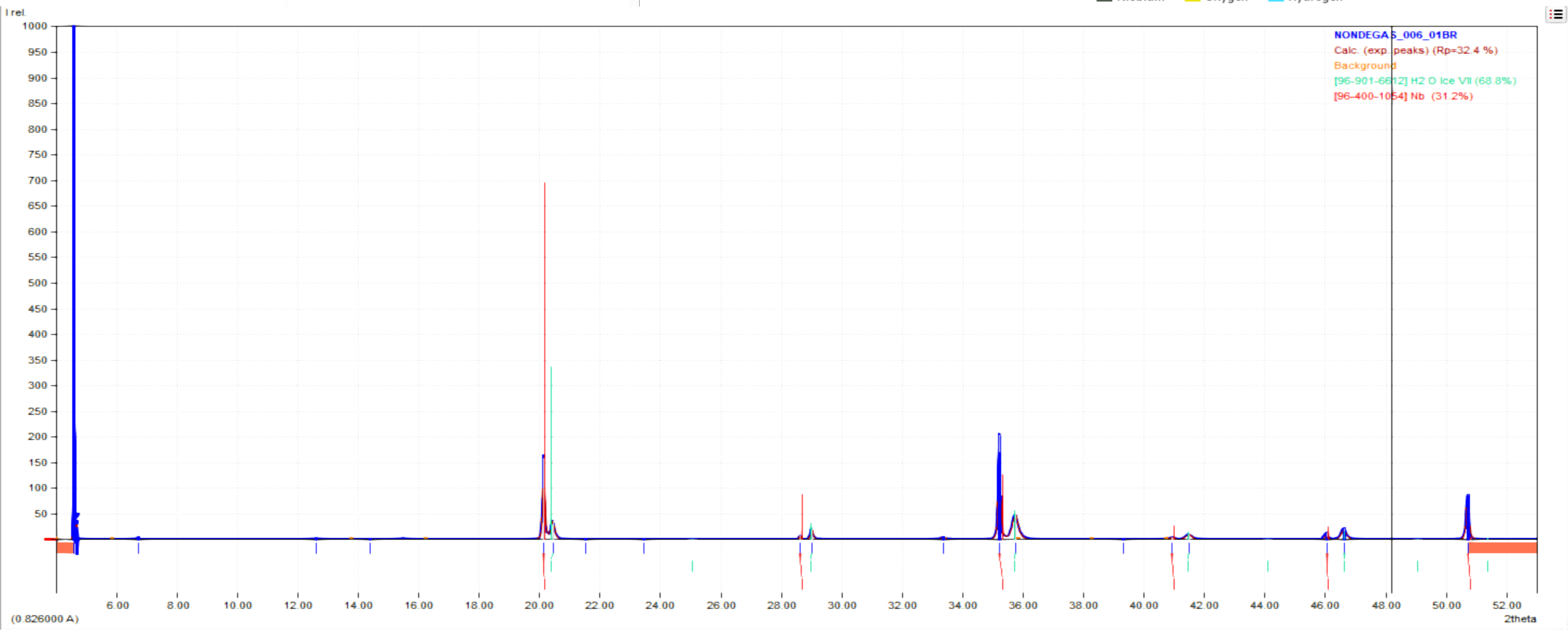
Figures 12 & 13: More XRD patterns revealing H segregates from the Nb sample. Graphed from data from ESRF.

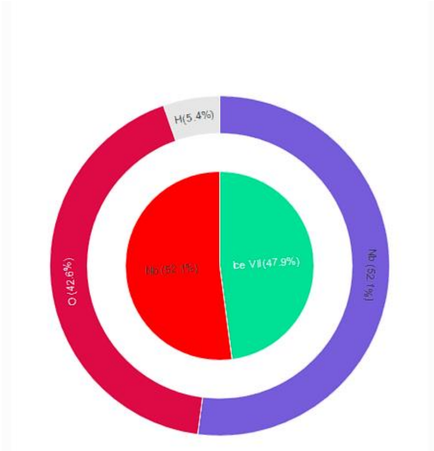




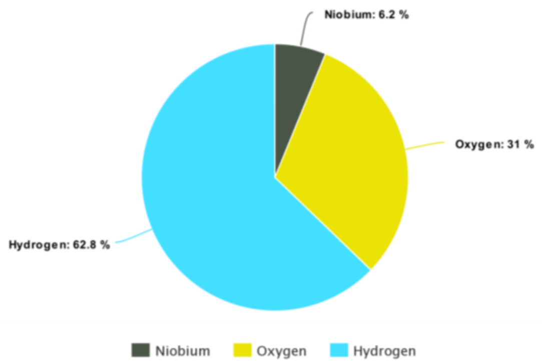
Incident Radiation: 5°
Temperature: 100 K

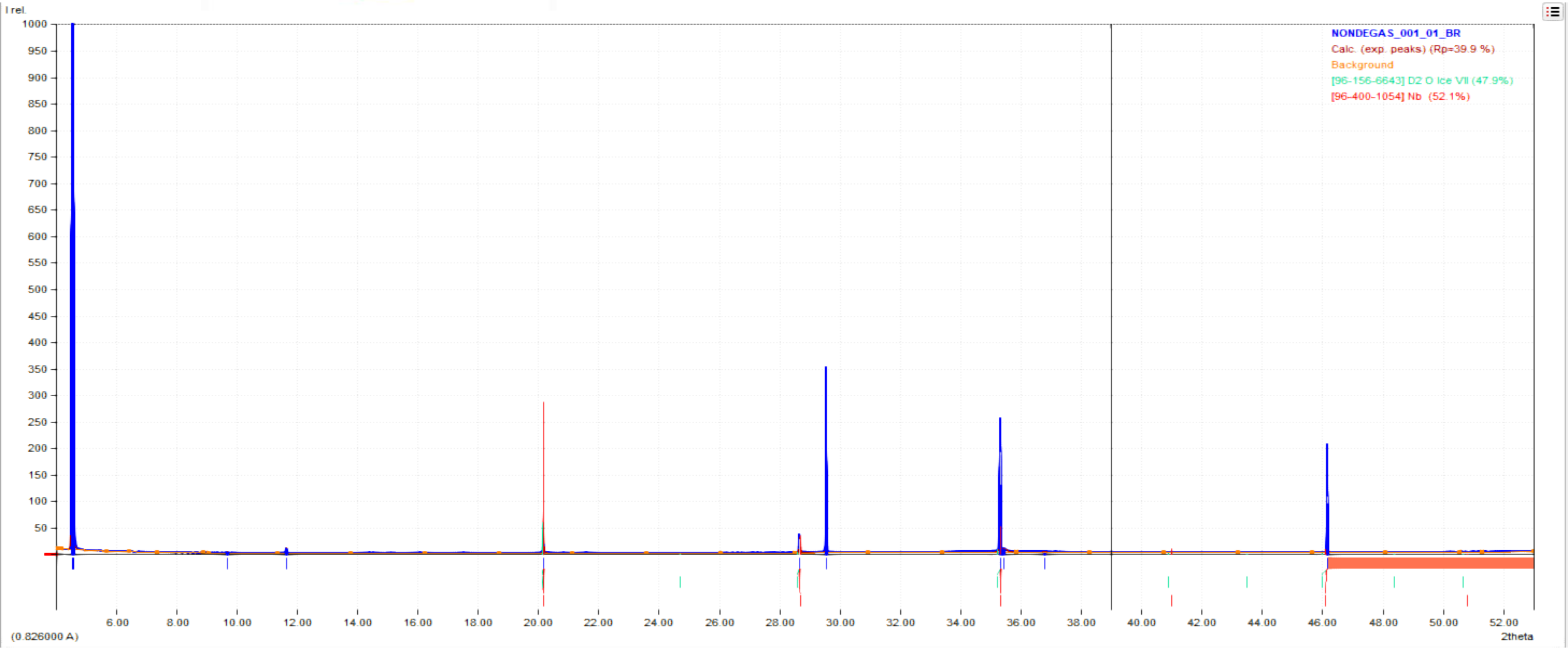






Incident Radiation: 4°
Temperature: 100 K





XRD Conclusion

- For the experiments conducted where the data returned was sensible and indicated a H signal, it was found that a minimum of 62.8%-65.0% of the first 2 nm of the surface was comprised of H crystal segregates at cryogenic operating temperatures.
- O was found possibly due to hydrides reacting with interstitial, molecularly-free oxygen which caused a reaction to create water/ice and precipitate out.

Laser Introduction

- For the development of accelerator technology, SRF and SQMS uses niobium superconducting cavities.
- In order to make better niobium superconducting cavities, the niobium must be purified.
  - Cutouts of the cavities are made to test for purity, because cavities are too big for the aforementioned analysis techniques.
- Current methods for acquisition of the cutouts results in less-than-preferable outcomes.
  - Nb cutouts are jagged on edges.
  - Nb can be contaminated by hydrogen, oxygen, and dissolved elements in high-pressure water milling.
  - Nb grain boundaries are affected, or dust particles are accumulated, making surface analysis with XPS and XRD very difficult and inaccurate.
- Laser cutting has been done on metals like steel for years but can be applied to niobium to meet SRF's/SQMS' needs.

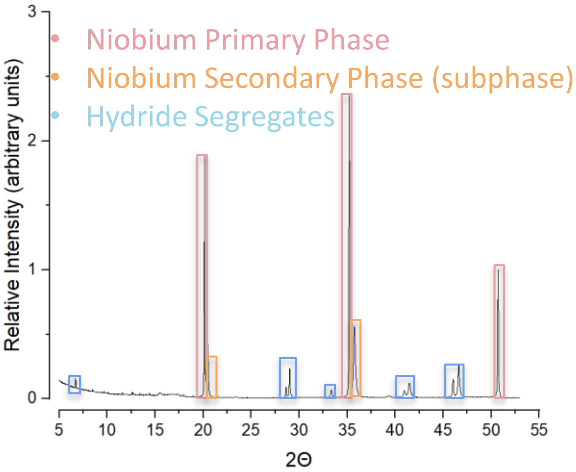
Figure 14: A laser beam being used to cut metal. Adapted from "How does a laser cutter work?" by Scultpeo, retrieved from https://www.sculpteo.com/en/3d-learning-hub/laser-cutting/how-does-a-laser-cutter-work/

Nb Surface Properties & Constraints

- Careful analysis of the surface is required, and therefore delicate treatment of the surface during sample cutouts for accurate assessment of our surface treatment techniques is made.
- We must make cutouts that leave clean, smooth edges, don't change the niobium microstructure, and don't change the chemical compositions of the niobium.
  - This means we must mitigate heat and abrasive edges.

Figure 15: A Nb cavity cutout. Notice the highly raised edges, making incident radiation analysis difficult. Retrieved from SQMS.

Figure 16: Hydride segregates found using XRD patterns. Because of hydro milling, we don't know if these H concentrations are from the Nb cavity treatment or the cutout procedure. Graphed from data from ESRF.



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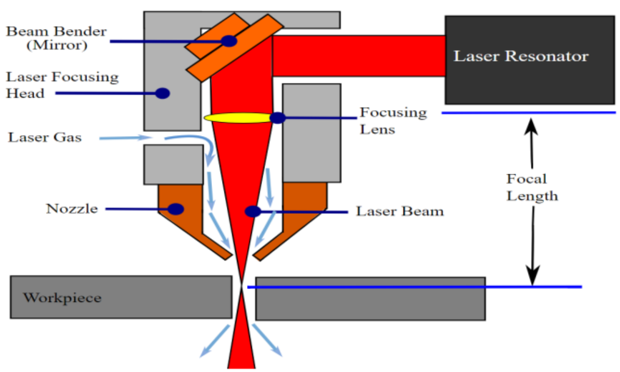
The Scope of Our Specific Laser Needs

- Small HAZ
  - As mentioned above, there needs to be minimal heat to the niobium to prevent reactions and subphase changes. A small **heat-affected zone** (**HAZ**) ensures that only the metal being cut is heated, not the surrounding metal.
- Clean cuts
  - The niobium cut by hydro milling is rough. This leads to a sample that can't be analyzed by incident radiation methods. The laser must leave no raised edges.

HAZ, Problems and Solutions

- Lasers use heat to cut. The laser design prototype will theoretically output 80-120 W of power. In order to use a laser for SRF/SQMS purposes, the laser must localize the heat **ONLY** to the cut.
- We need to reduce HAZ so that the niobium crystal structure nor the chemical compositions are altered.
- The HAZ can be reduced through optical and mechanical adjustments.
  - Using cold-gas jets around the laser cut can convect heat away from the area around the cut, reducing the temperature and area of the HAZ (*Review on HAZ in Laser Machining*, F. Abedin). Gas also plays a role is dissipating metallic liquid that melts in the cut.
  - Lenses can be used to focus light which can be used to create a focal point where the light is very intense and in a pinpoint spot. This intense energy increases cutting power and speed, as well as reduces the heat diffused away from the cut.
  - Making the cut very fast allows for completion of the procedure before the surrounding metal is heated.

Figure 17: A common design for a gas/focusing nozzle that can reduce HAZ. Adapted from "Laser Cutting" by Purdue University, retrieved from https://www.purdue.edu/bidc/resources/printing-and-prototyping/laser-engraving-and-cutting/



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Clean Cuts

- The laser must make clean, precise cuts without abrased or raised edges.
- Laser cutters excel at this, but only when properly focused.
- Using a laser with a short focal length on a deep cut can result in a messy cut.
- Other laser features such as a gas jet can make for clean edges.
  - A gas jet can blow away metallic melt that liquifies during the cut, which would otherwise result in a molten edge that has a deformed, amorphous shape.

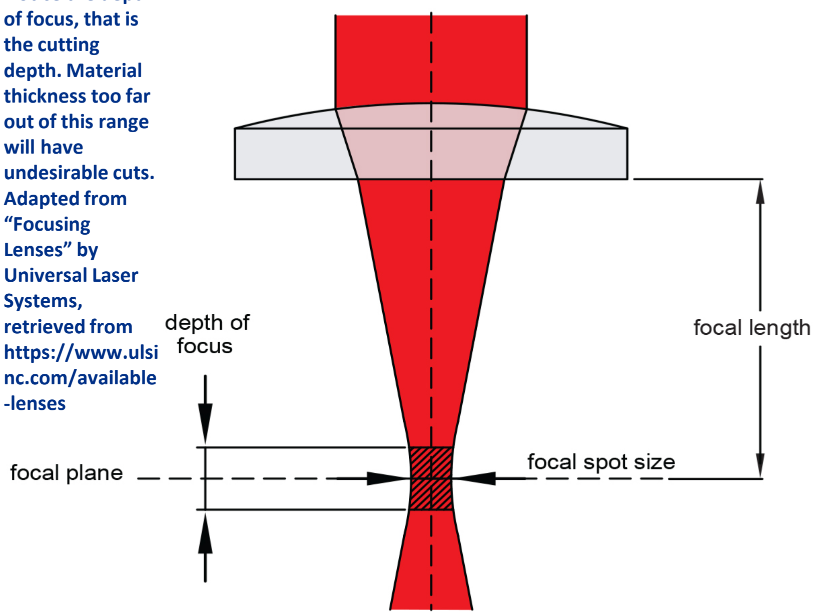


Figure 18: Focusing lens. Notice the depth of focus, that is the cutting depth. Material thickness too far out of this range will have undesirable cuts. Adapted from "Focusing Lenses" by Universal Laser Systems, retrieved from https://www.ulsinc.com/available-lenses

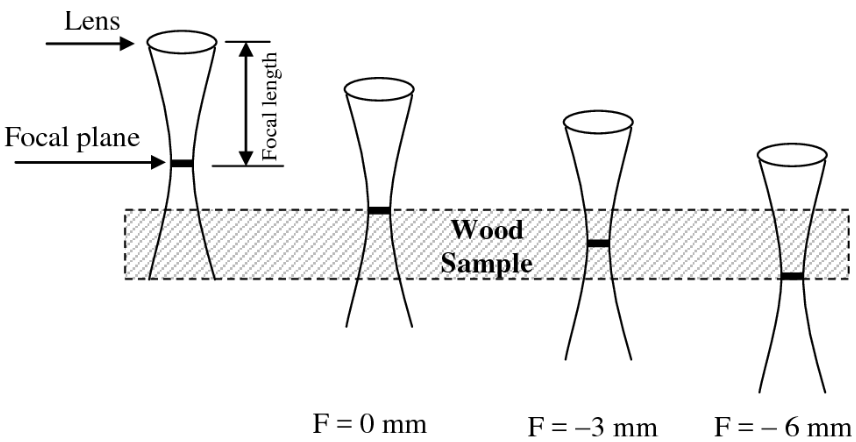
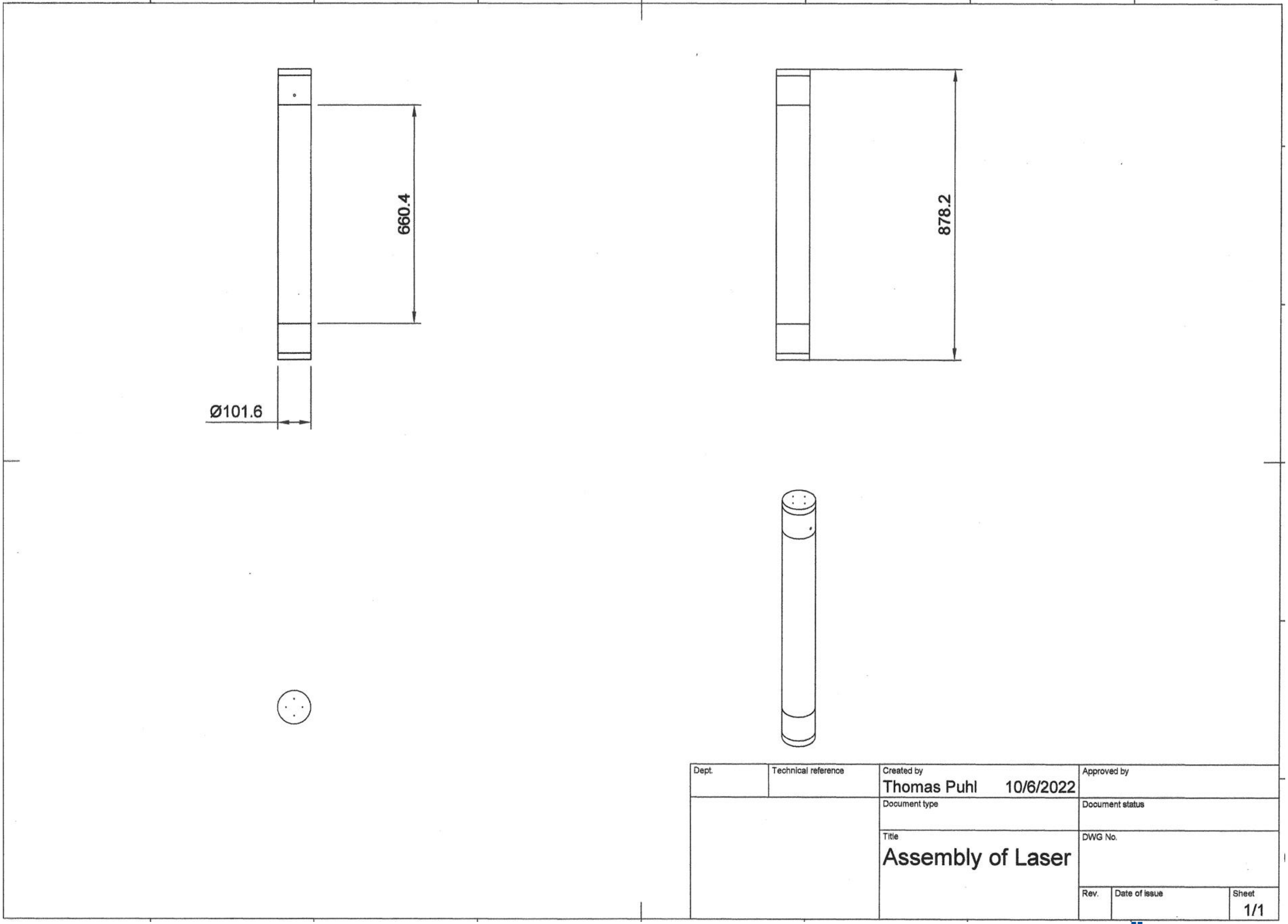


Figure 19: Various depths of the focus in a wood workpiece. Notice the areas covered by the cutting beam throughout the material. Adapted from "Investigating the CO2 laser cutting parameters of MDF wood composite material" by Eltawahni and co., retrieved from https://www.semanticscholar.org/paper/Investigating-the-CO2-laser-cutting-parameters-of-Eltawahni-Olabi/3565d2397705f06f4cc6caac66ade4cbc2b2fed2

Laser Design


660.4
878.2
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Technical reference
Created by
Thomas Puhl 10/6/2022
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Assembly of Laser
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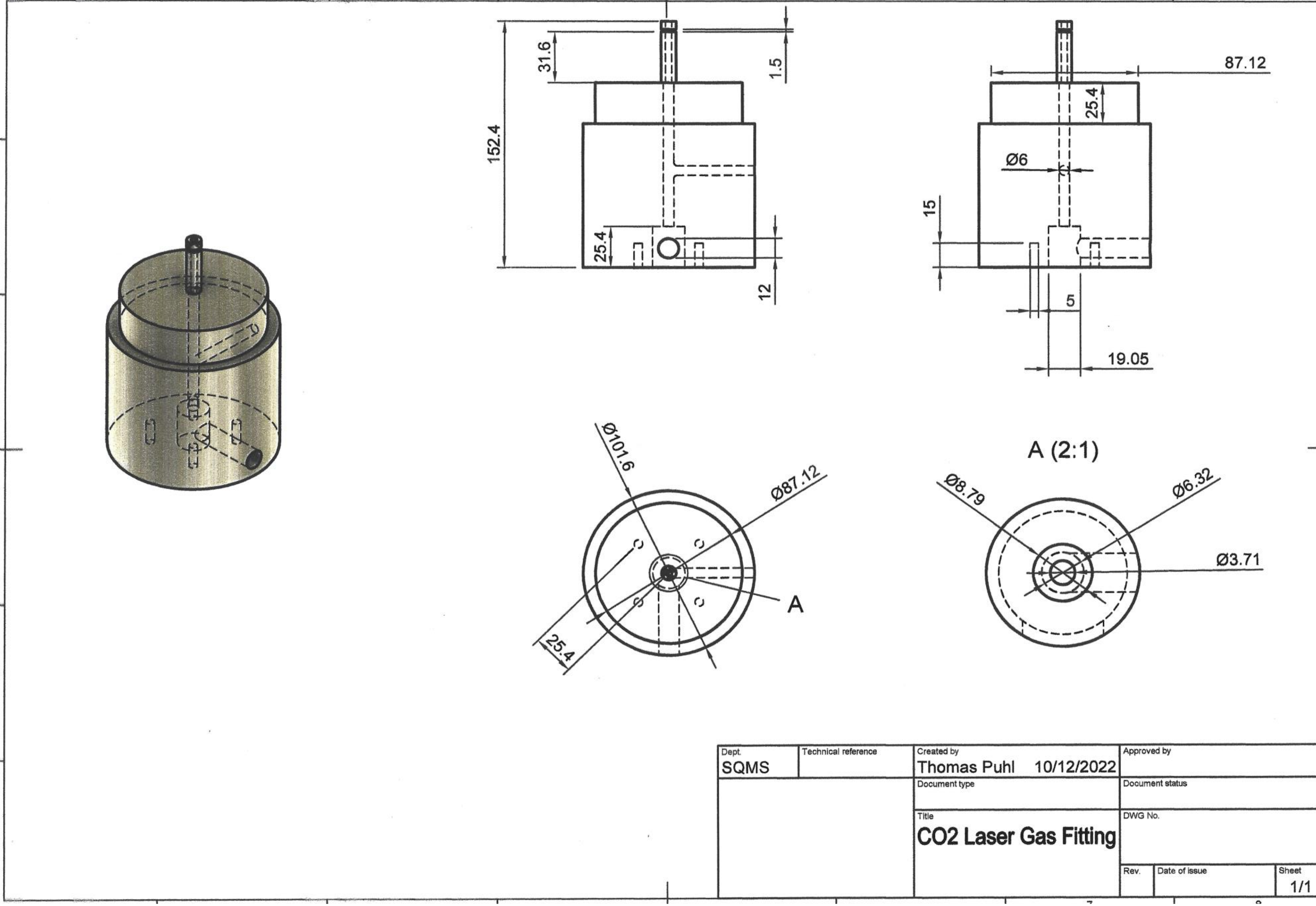
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1.5
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25.4
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87.12
25.4
Ø6
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Ø101.6
Ø87.12
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Ø6.32
Ø3.71
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SQMS
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Thomas Puhl 10/12/2022
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Laser Conclusion

- The laser idea was deemed to be inappropriate for development because of the remote work arrangements (remote workers cannot do any builds of any sort for Fermilab while at home due to safety risks).
- The laser design was considerable, however, since the design put forth was cheaper than commercially available laser resonators.
  - Complete resonator w/ SULI design = ~$700
  - Complete resonator commercially available for purchase = ~$1000
- The laser was never built or tested but was considered a future possibility.

Conclusion

- With the research I helped conduct at Fermilab the past few months with XPS and XRD, we hope to develop even better SRF technology by establishing better treatment methods for niobium metal.
- Next steps include reducing surface oxides and hydride contaminants that decrease Q.
  - Suggestion: New annealing method. Annealing in the past has been the technique used to turn ordinary Nb cavities into LHC-qualifier cavities, a new generation of thermo-treatments could be what takes SRF cavities into a new generation of purity.
    - Suggestion: A thermo-treatment that includes the use of a chemical wash like that of electropolishing can chemically react out dissolved oxides near the surface and cause a precipitate out of the cavity, further driving purity.

References

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