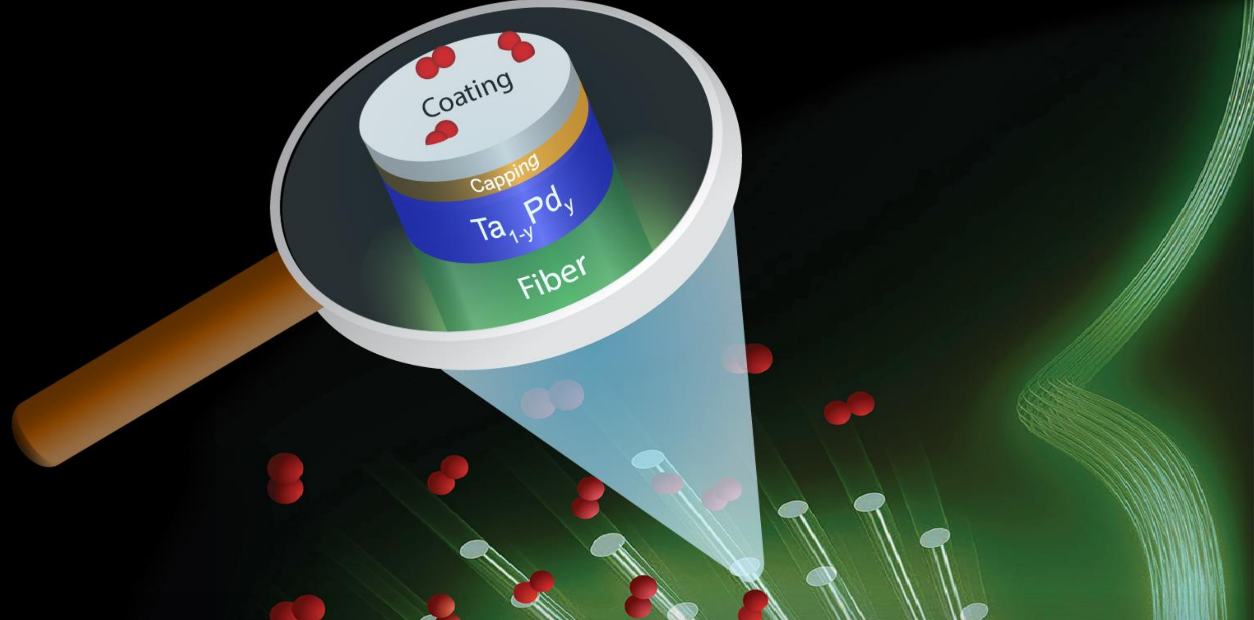

X-ray and Neutron Diffraction for (thin film) material characterization

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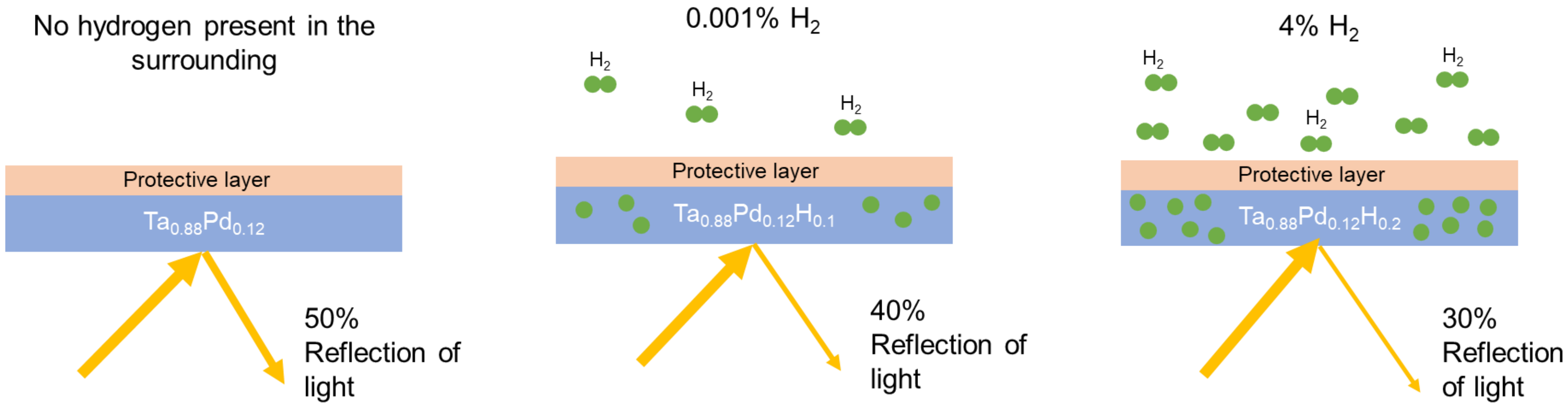
TU Delft

HfH_x - Optical hydrogen sensing material



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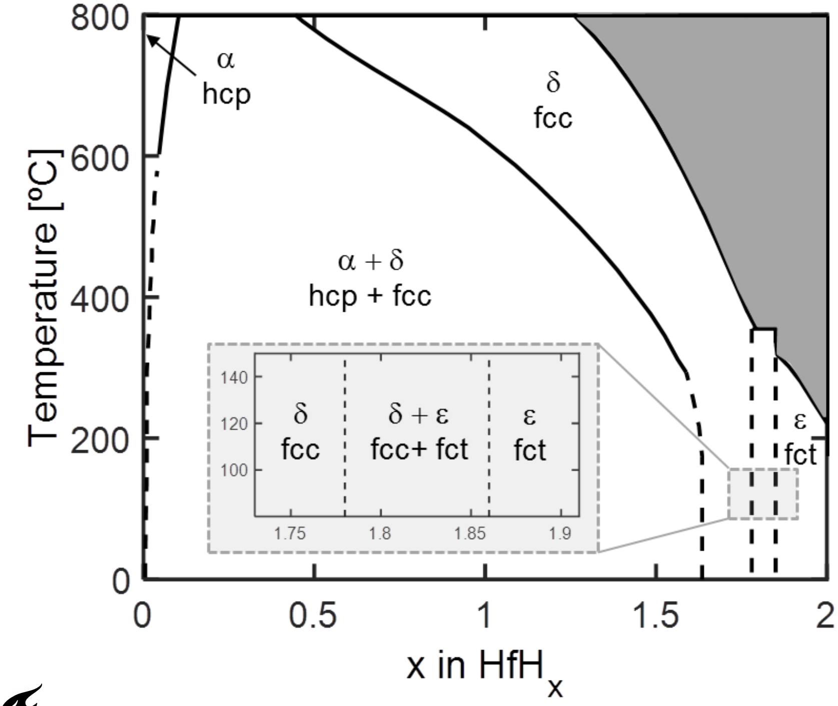
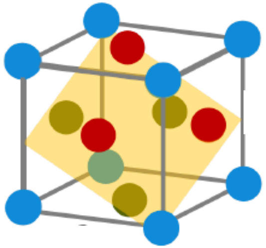
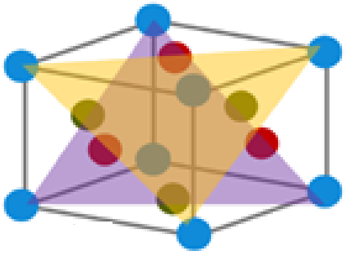
Why Hafnium?





- hcp → fcc transition is irreversible under normal conditions
- Large potential sensing range from x in HfH_x of 1.5 – 2.0
- Is there phase coexistence/hysteresis?



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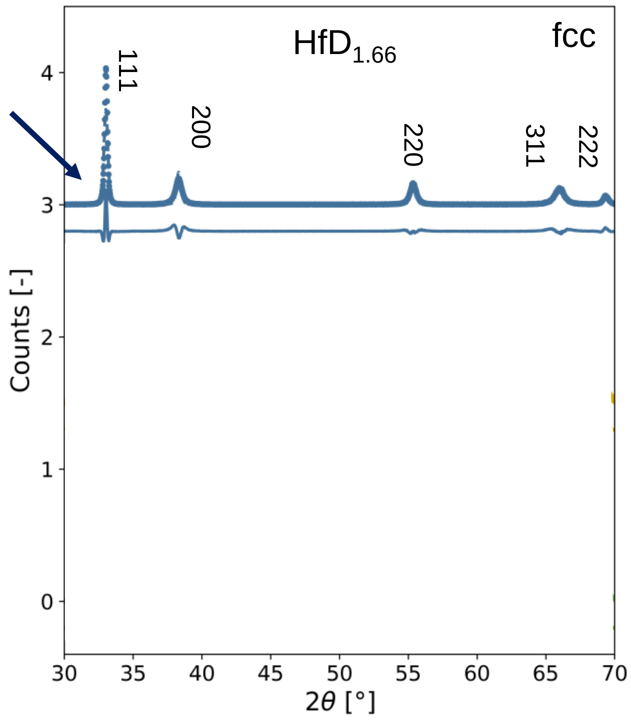
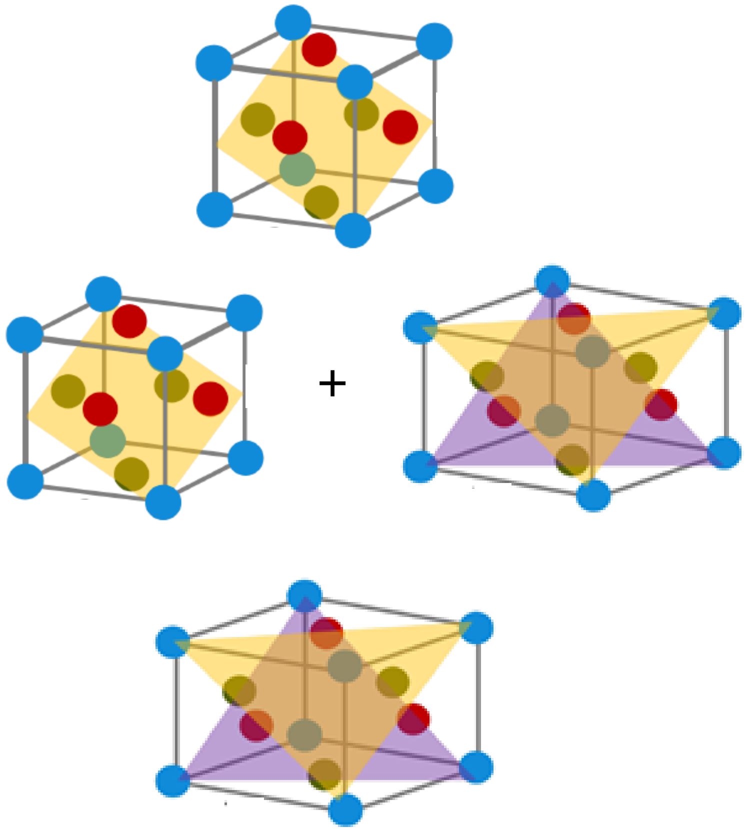
X-ray Diffraction

$$n\lambda = 2d \sin\theta$$





How about the hydrogen/deuterium atoms?

Structure and Form Factor

$$I_{hkl} \sim |F_{hkl}|^2$$

$$F_{hkl} = \sum_{j=1}^{N} f_j(\lambda, \theta) \exp[2\pi i(hx_j + ky_j + lz_j)]$$

Sum over all *N* atoms in unit cell

Form factor

Structure of the unit cell

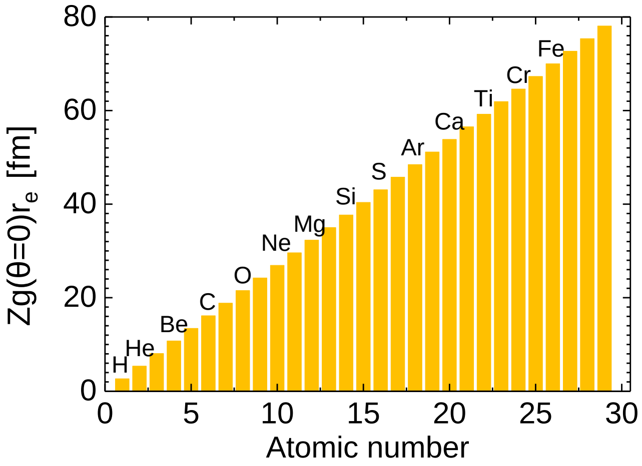
Form Factor

$$I_{hkl} \sim |F_{hkl}|^2$$

$$F_{hkl} = \sum_{j=1}^{N} f_j(\lambda, \theta) \exp[2\pi i(hx_j + ky_j + lz_j)]$$

X-rays

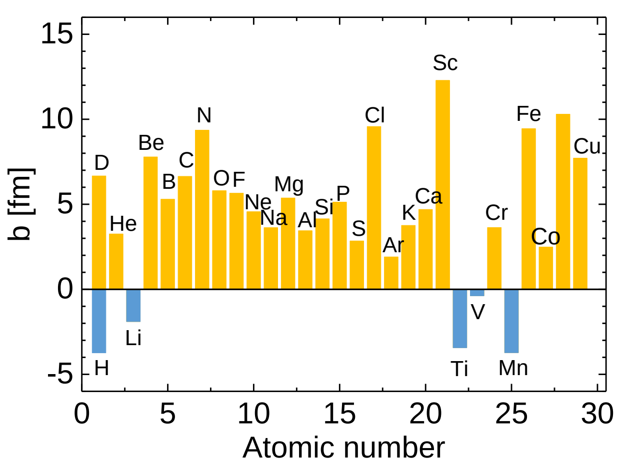
$$f_j(\lambda, \theta) = Zg\left(\frac{\sin\theta}{\lambda}\right) r_e$$



→ Diffraction peak intensity increases with Z

Neutrons

$$f_j(\lambda, \theta) = f_j = -b$$



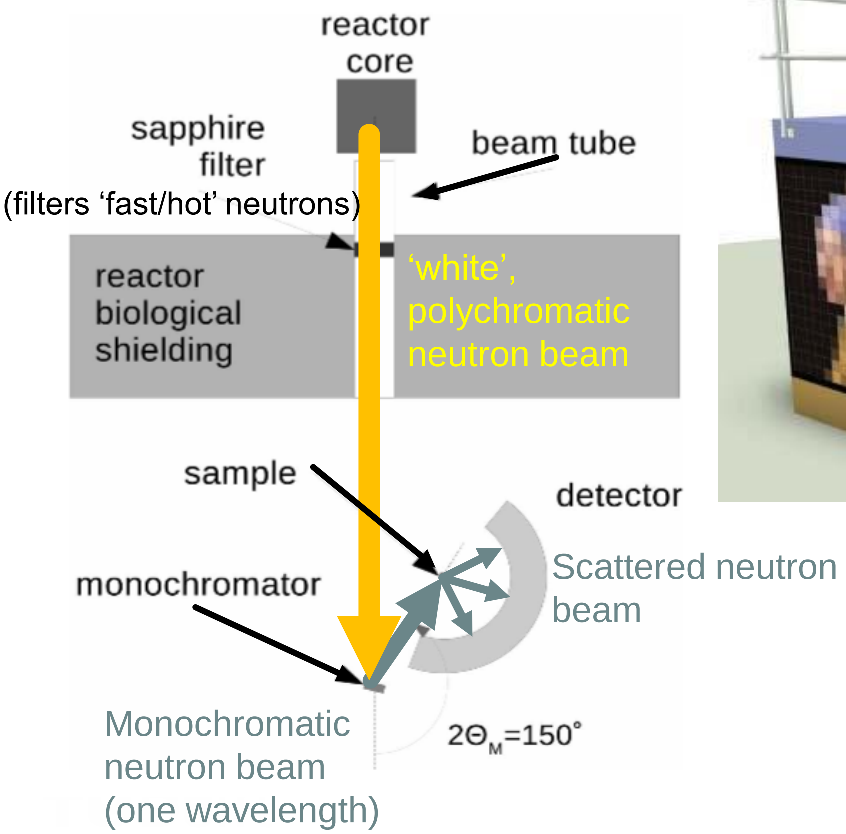
Neutron Diffraction

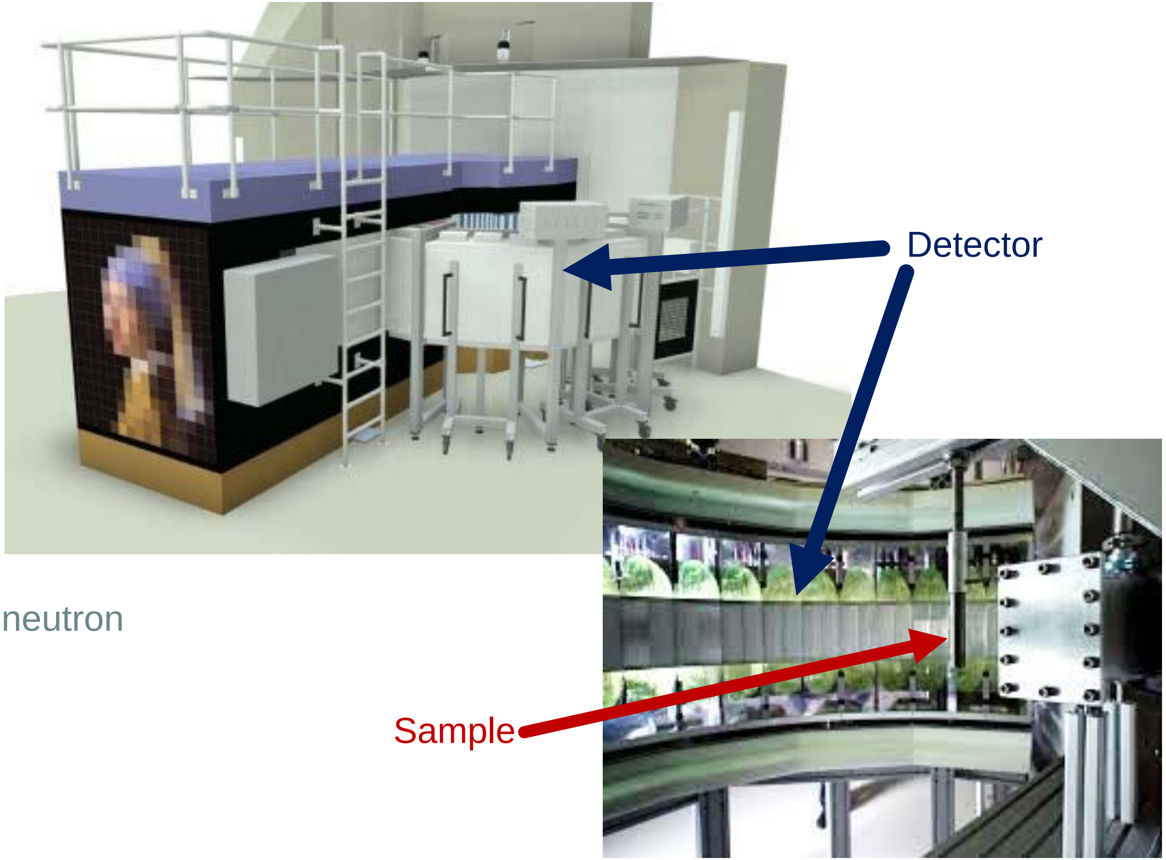
- Light atoms
- Atoms that are close in atomic number (e.g. Fe and Mn)
- Magnetic materials

Need

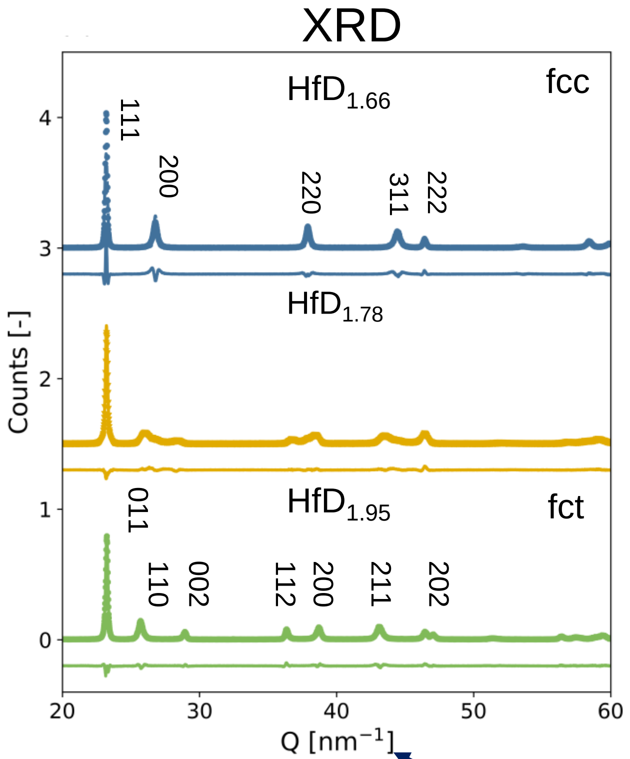
- Relatively large sample quantity (~ 1-5 grams)
- Relatively long measurement times (> 1h in Delft)

Neutron Diffractometer Pearl @ TU Delft

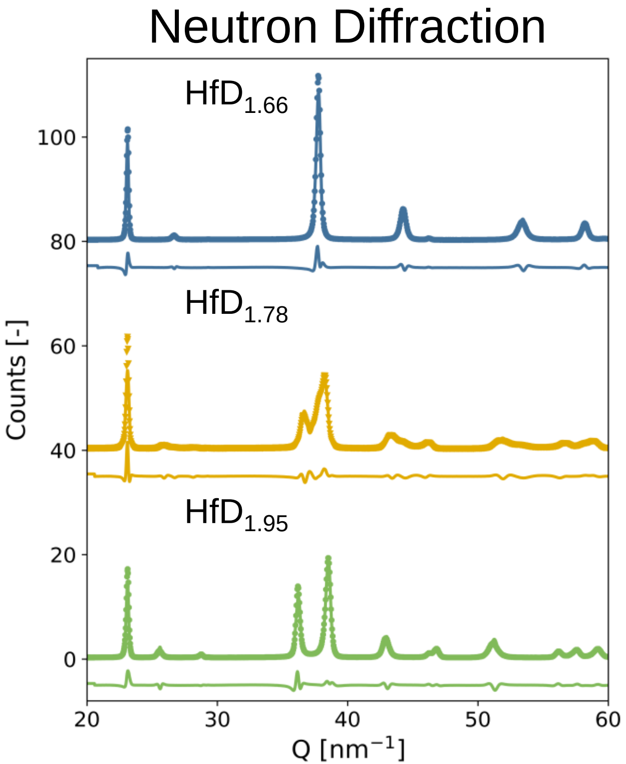


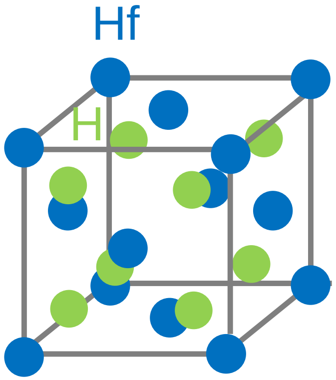


Neutron Diffraction



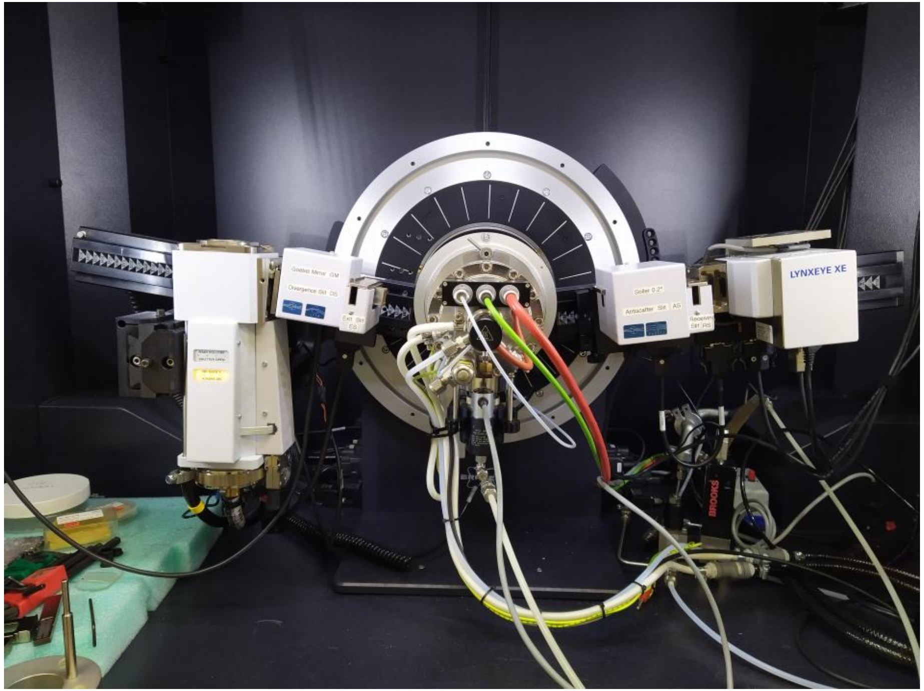
$$Q = \frac{4\pi \sin\theta}{\lambda}$$





Tetrahedral sites

In-situ XRD



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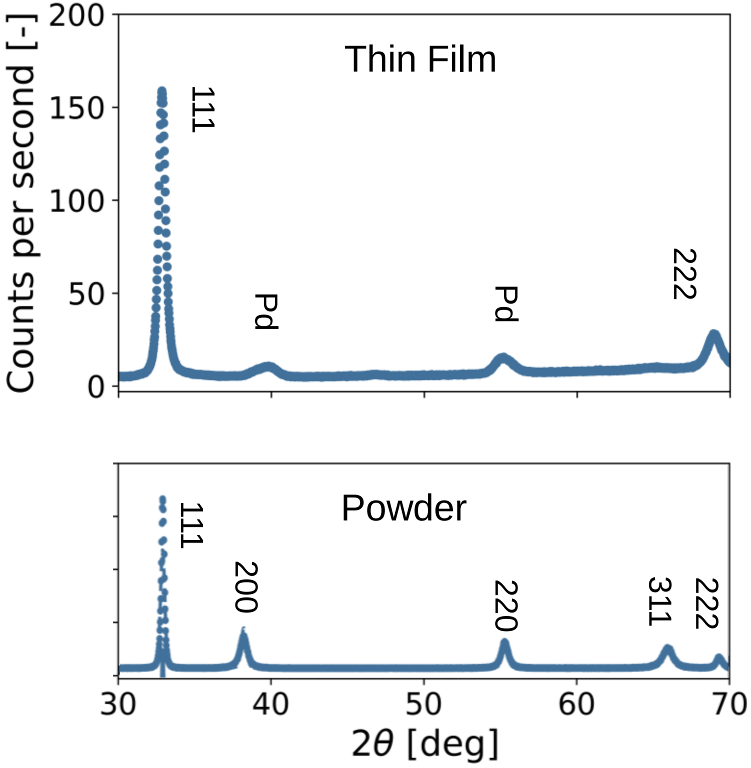
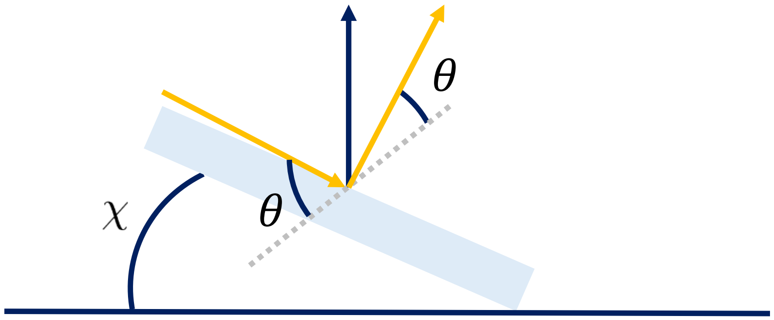
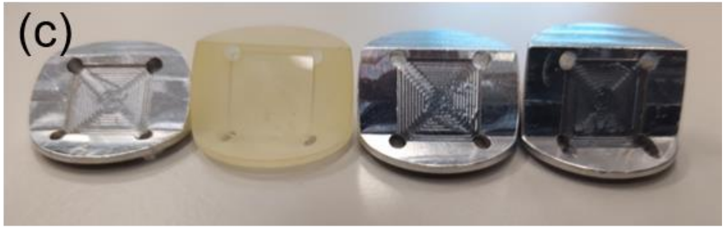
Thin Films – Textured!

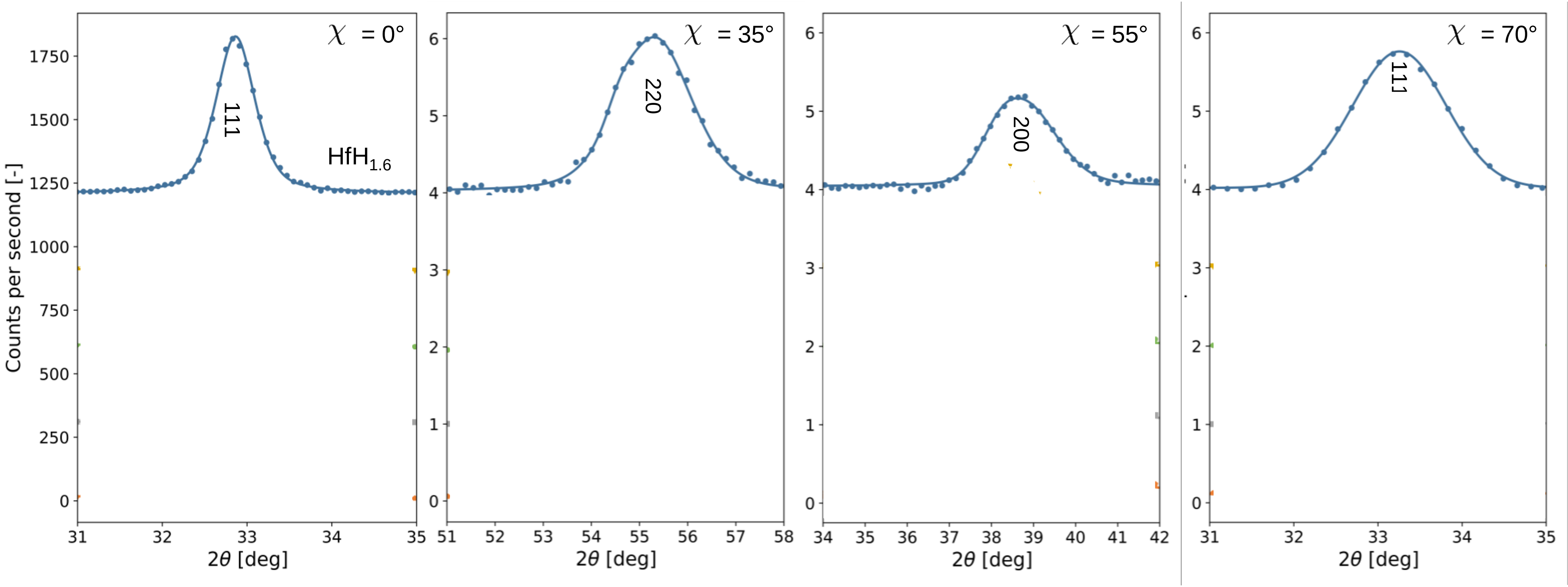




My apologies for my poor '3D' drawing skills

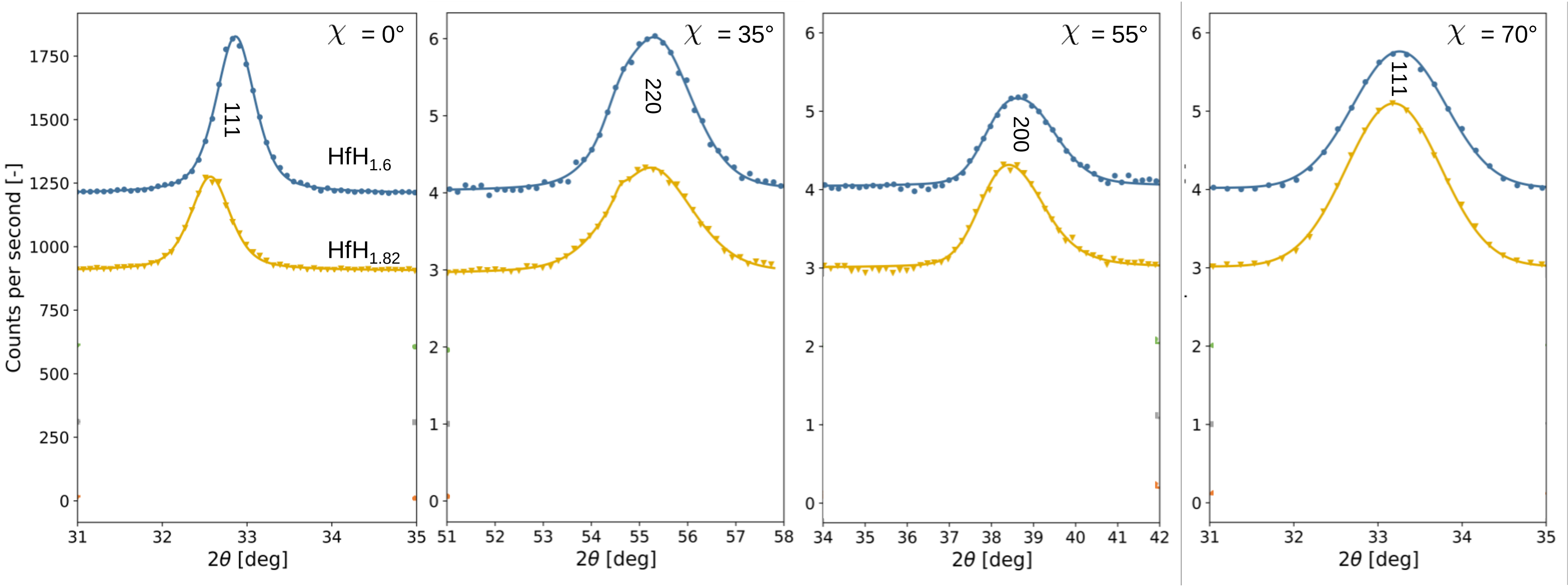


In situ XRD



χ = 0°
χ = 35°
χ = 55°
χ = 70°
111
220
200
111
HfH1.6
Counts per second [-]
2θ [deg]
2θ [deg]
2θ [deg]
2θ [deg]

In situ XRD



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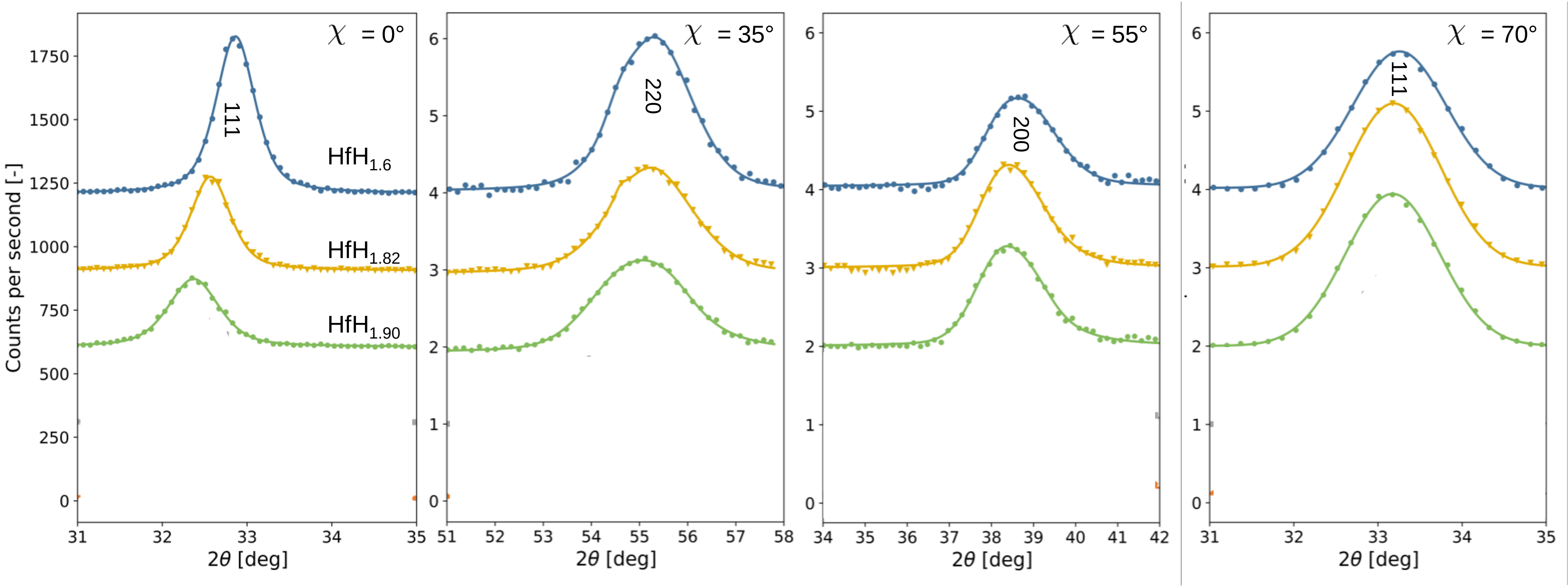
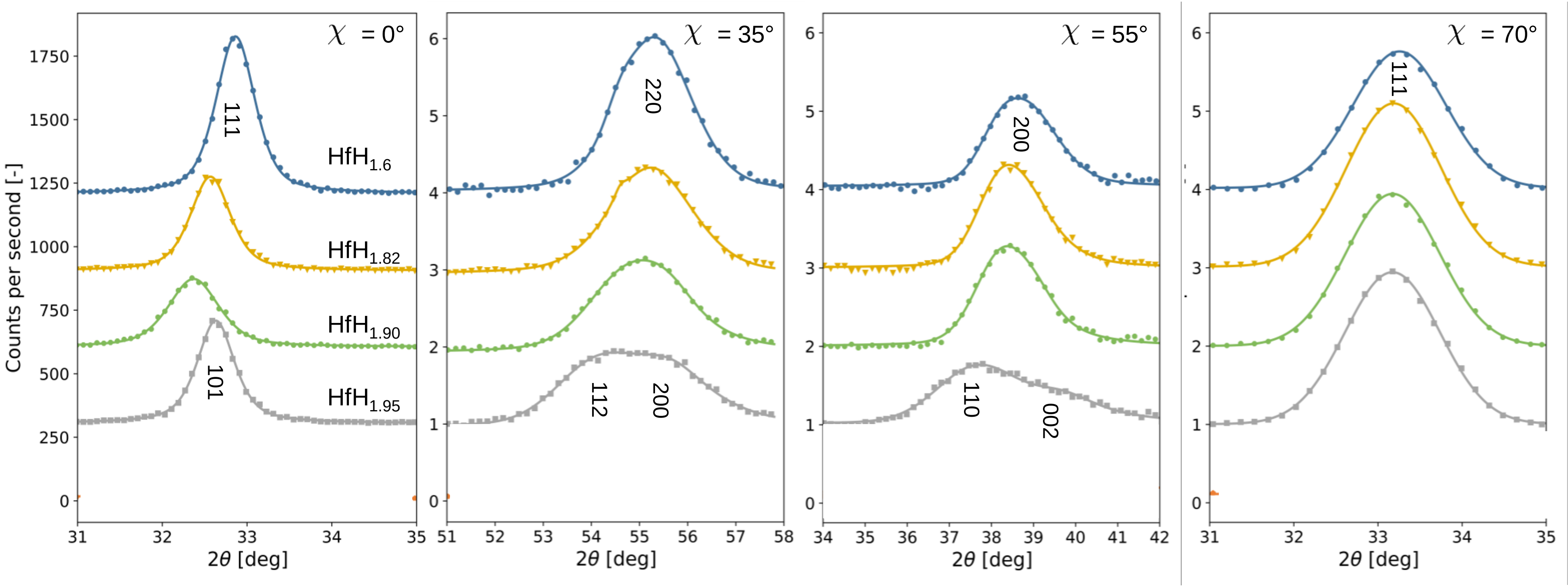
In situ XRD



Counts per second [-]
χ = 0°
111
$HfH_{1.6}$
$HfH_{1.82}$
$HfH_{1.90}$
χ = 35°
220
χ = 55°
200
χ = 70°
111
2θ [deg]

In situ XRD



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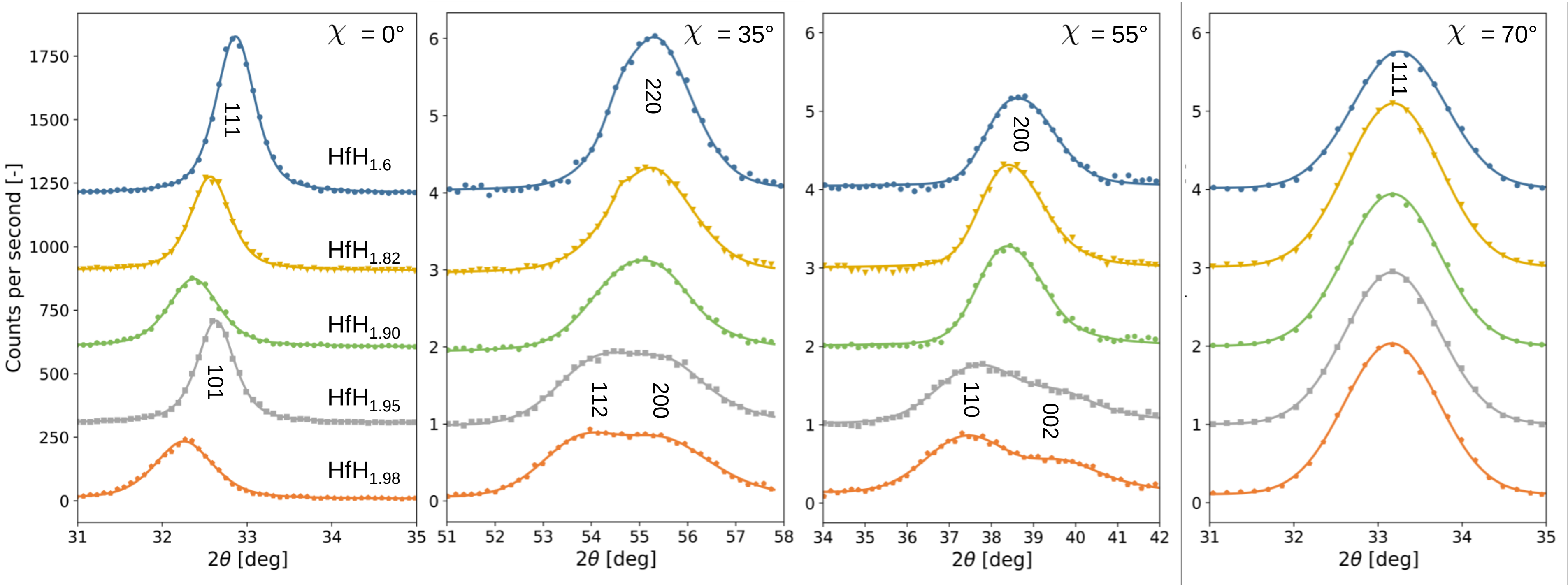
In situ XRD



FCC → FCT phase transition without phase coexistence

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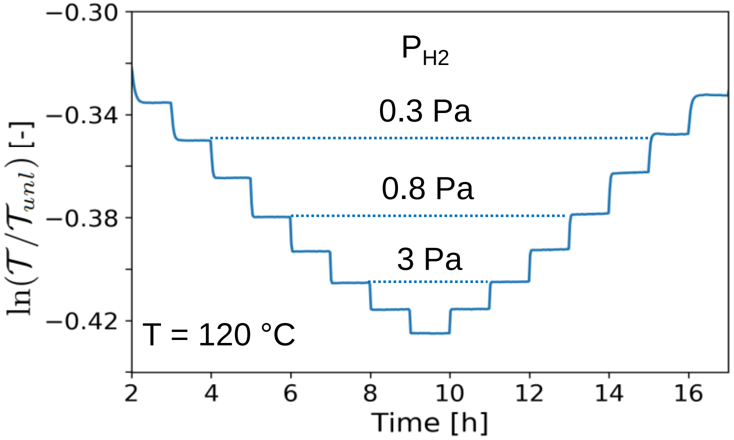
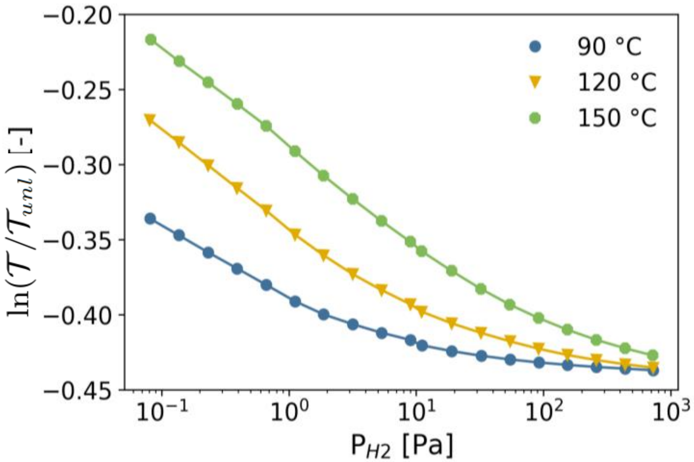
Hafnium as hydrogen sensor

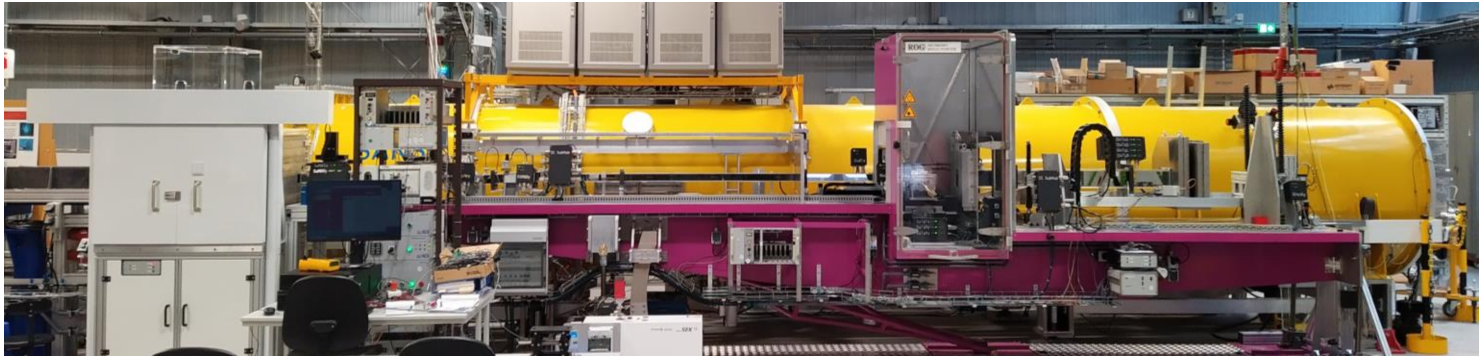
FCC → FCT phase transition without phase coexistence ensures a sensing response without hysteresis





Neutron Reflectometry

- How did we know the hydrogen concentration in the thin film? Neutron Reflectometry!
- X-ray and Neutron Reflectometry are techniques that provide information about the thickness, composition and roughness of flat samples with layer thicknesses of 2 - 200 nm.



Delft Neutron Reflectometer

Conclusions

- Hafnium (and other thin film metal hydrides) can be used as effective hydrogen sensing materials.
- The absence of a first-order phase transition in thin films
  - Consistent with the hysteresis-free sensing properties of hafnium-hydrogen thin films
  - Shows the profound influence of nanoconfinement
- Neutron diffraction can be a useful tool to study the atomic structure of materials with (i) light elements, (ii) elements that are close together in atomic number, (iii) magnetic materials.
- X-ray and Neutron Reflectometry are techniques that allows one to study the composition, thickness and roughness of thin layered structures.

Thanks to

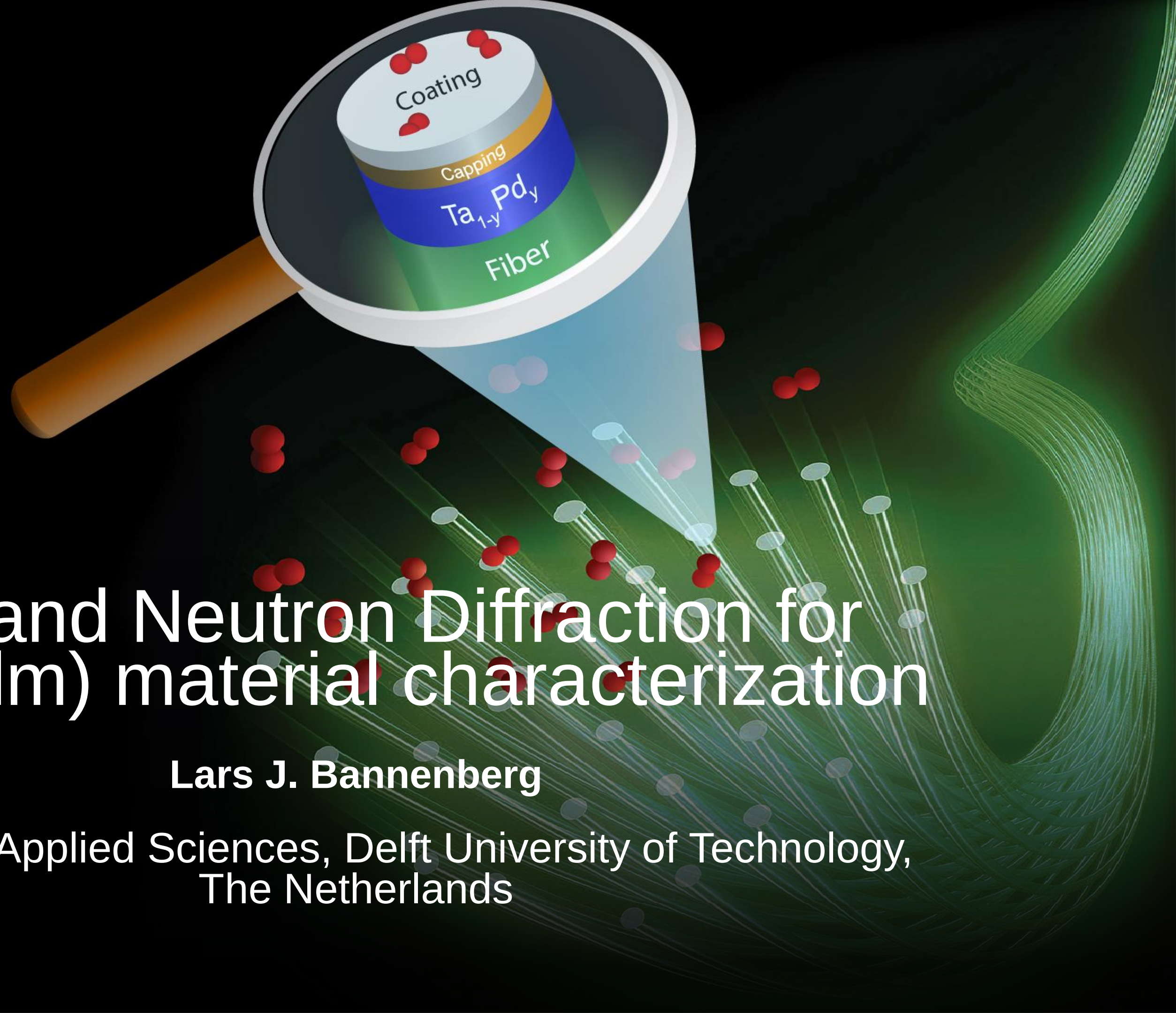
Herman Schreuders

Bernard Dam

Kohta Asano

and Christiaan Boelsma (now Tata Steel)

TU Delft



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