Grazing incidence XRD to investigate ion implantation induced damage

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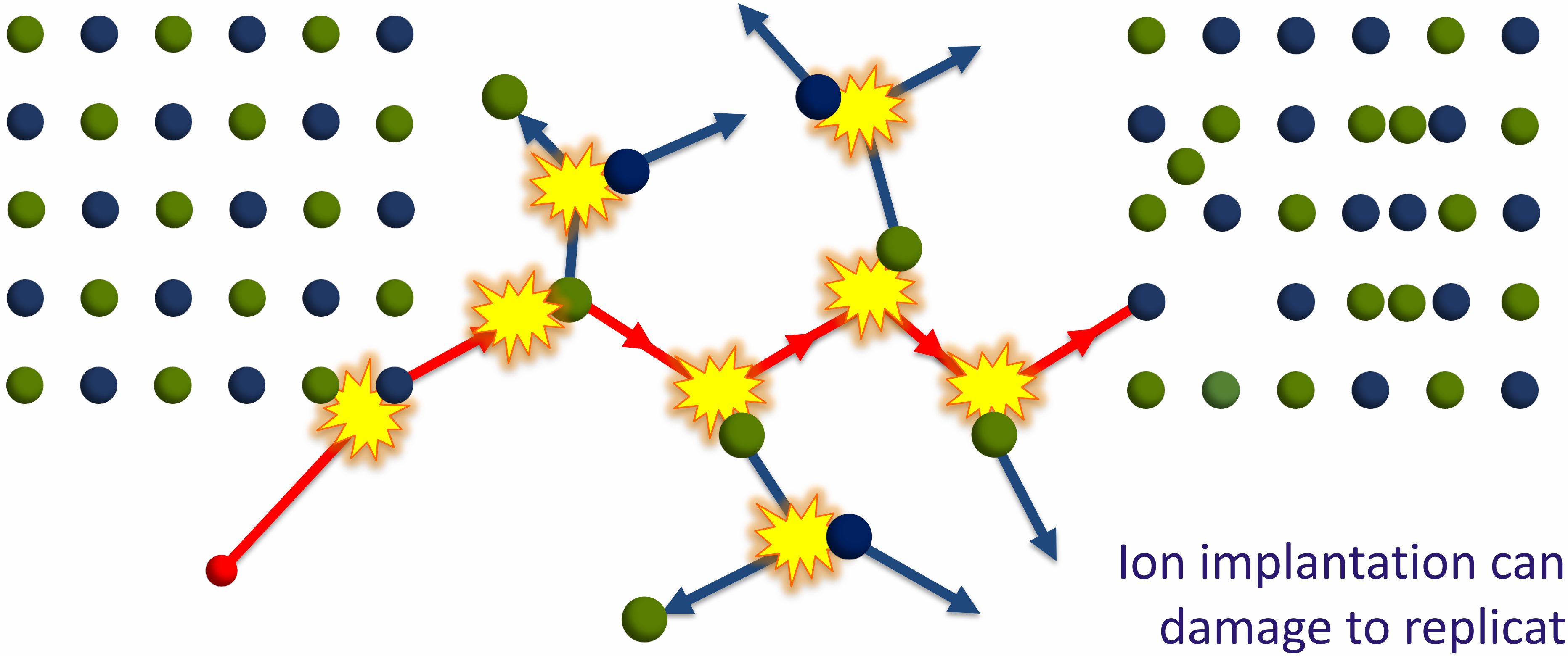
Ion Beam Irradiation and Characterisation: Best Practice
Manchester, March 2nd – 3rd 2023

Implantation induced damage



Ion implantation can induce displacement damage to replicate (ish!) the damage produced by nuclear reactions.

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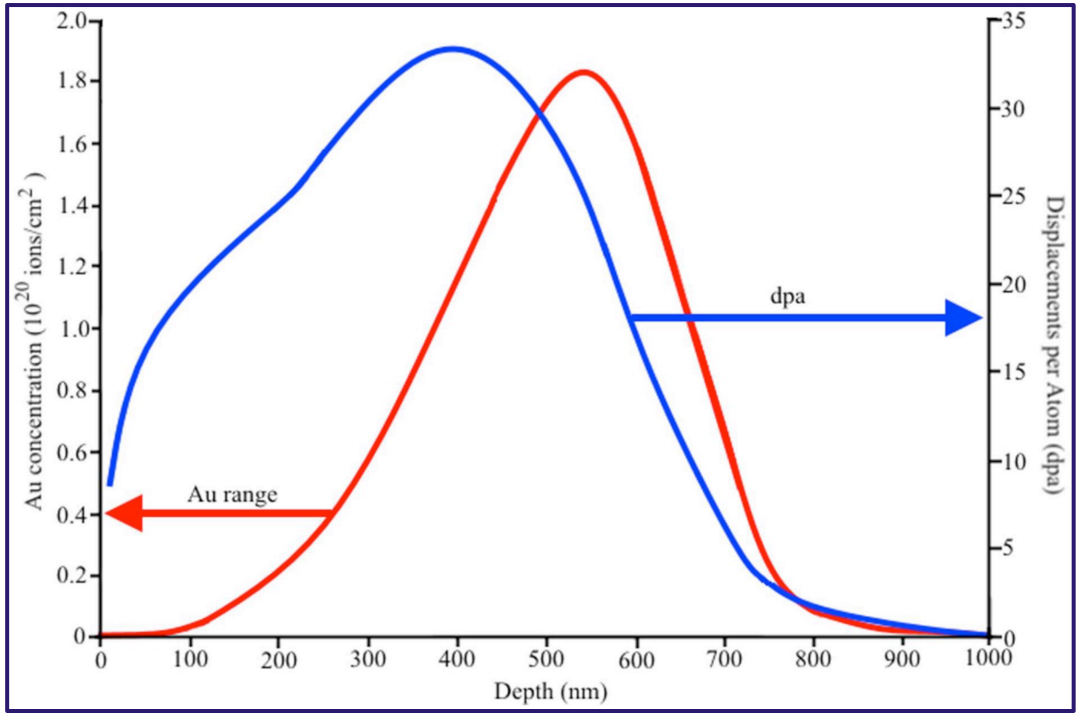
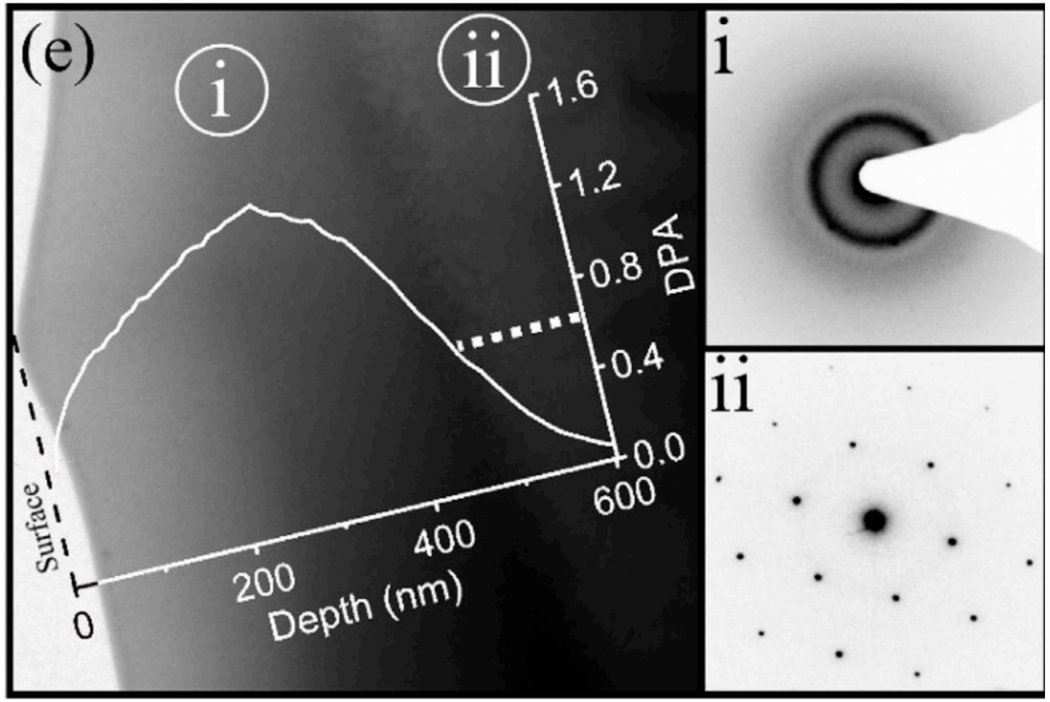
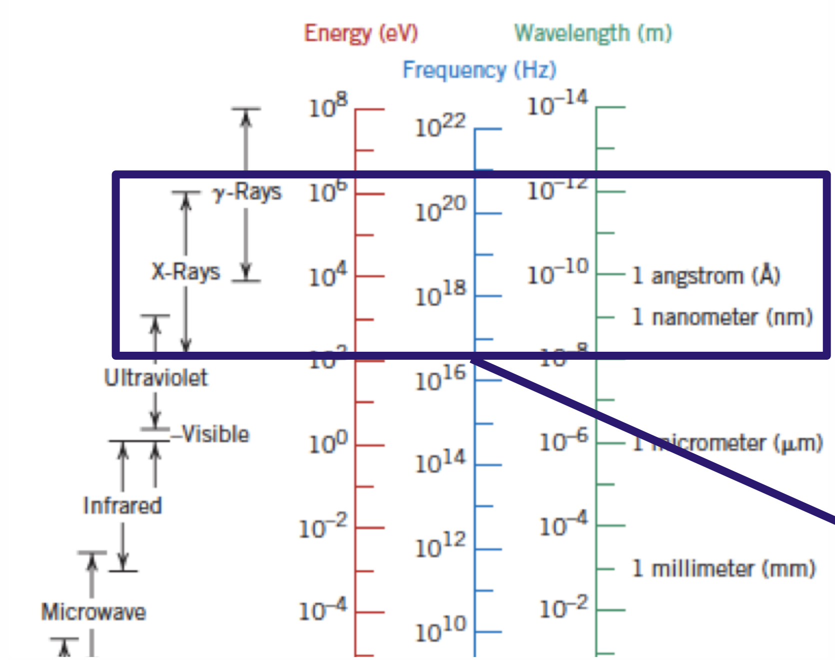


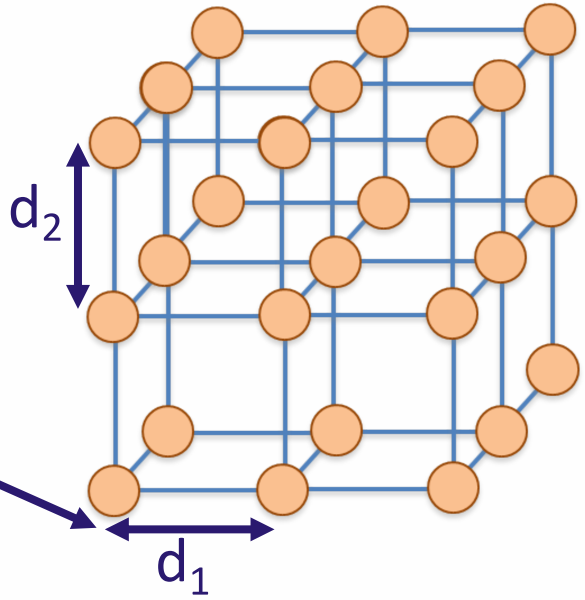
SRIM simulation of 5 MeV Au^{2+} ion implantation to a fluence of 5 x 10^{15} Au ions/cm^2 into a SiFeVCrMo alloy.

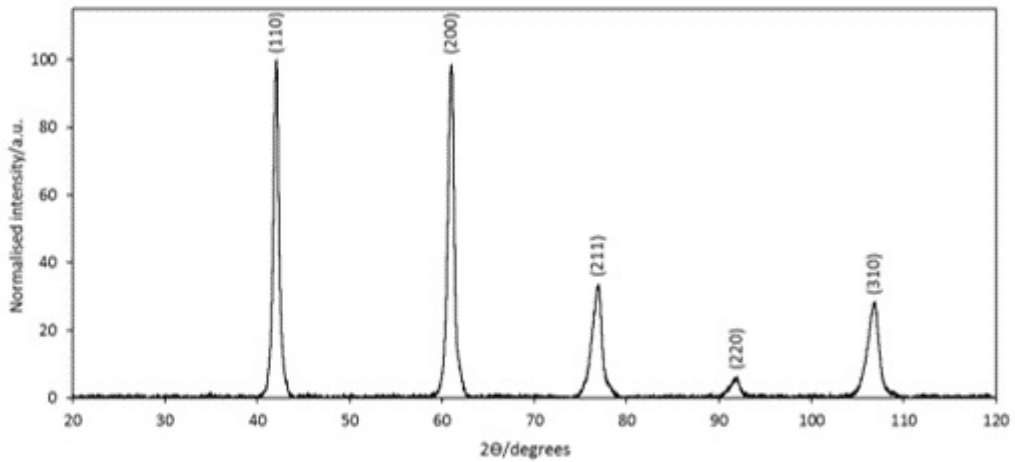


Cross-sectional TEM (XTEM) gives excellent information on implantation induced structural transformations, but requires extensive training!

X-ray Diffraction 101





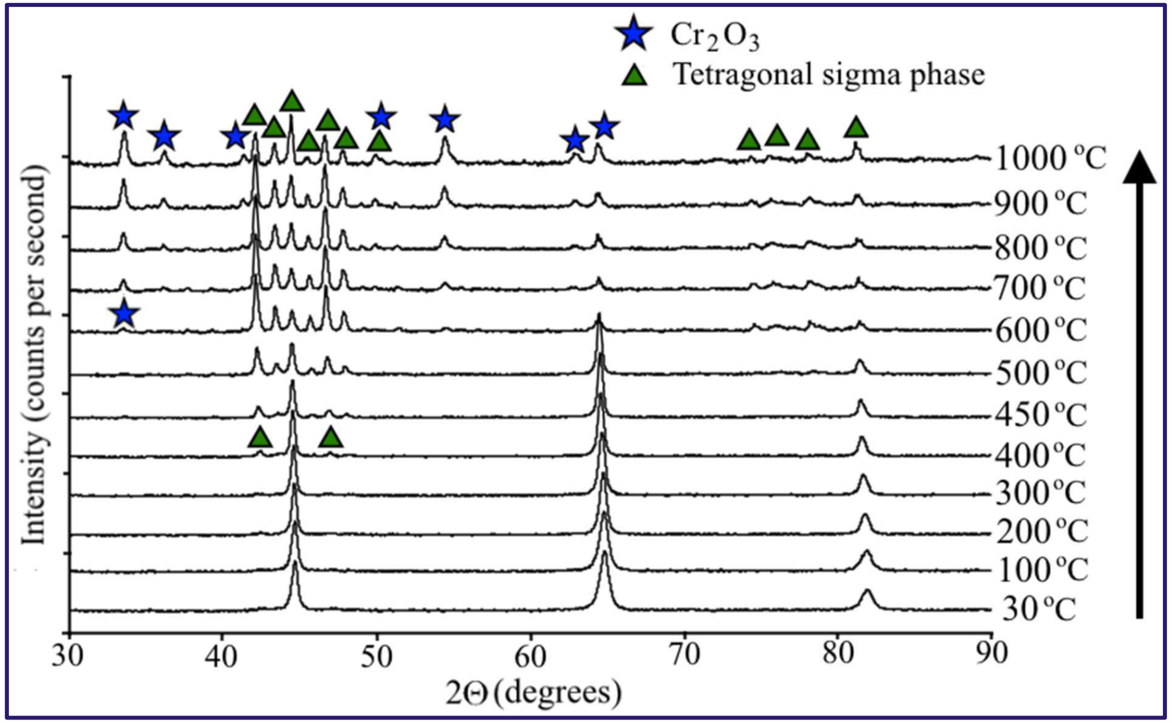


X-ray wavelength range $0.01 < \lambda < 100$ Å ≈ interatomic distances in a crystal.

X-ray Diffraction 101

XRD can be used to:

- Identify phases by comparison with data from known structures,
- Quantify changes in the cell parameters (e.g., cell volume, interatomic spacing),
- Determine crystallite size
- Determine crystallographic structure (cell parameters, space group, atomic coordinates) of novel or unknown crystalline materials.
- Determine temperature induced phase transformations.



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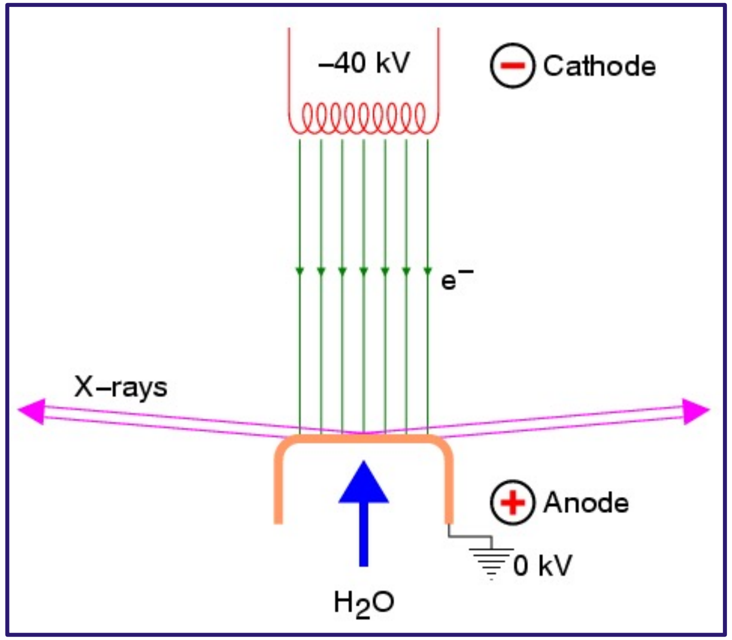
X-ray Diffraction 101



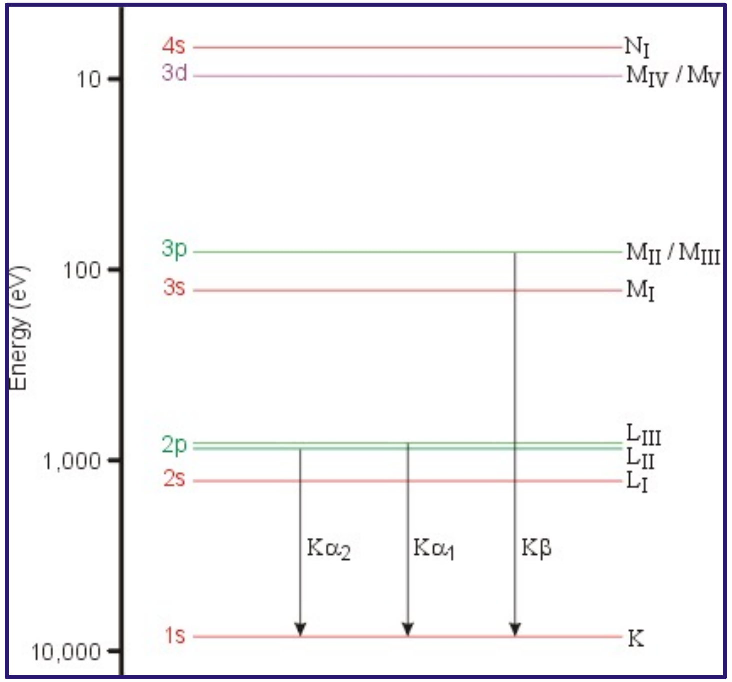
http://pd.chem.ucl.ac.uk/pdnn/inst1/xtube.htm

X-rays are generated by heating a filament (e.g., W) to emit electrons which are directed onto a target (e.g., Cu).

Interaction with core shell electrons in the target results in ionisation.

An electron from a higher energy level drops to the lower energy level, emitting a *characteristic X-ray*, with specific energy and wavelength.

$\Delta E = E_L - E_K$



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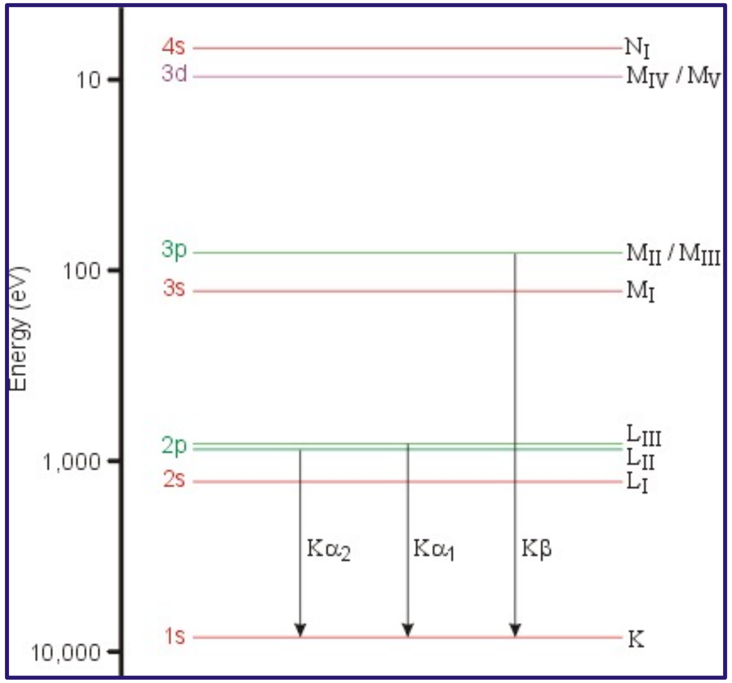
X-ray Diffraction 101



http://pd.chem.ucl.ac.uk/pdnn/inst1/xrays.htm

K_α L → K transitions

K_β M → K transitions

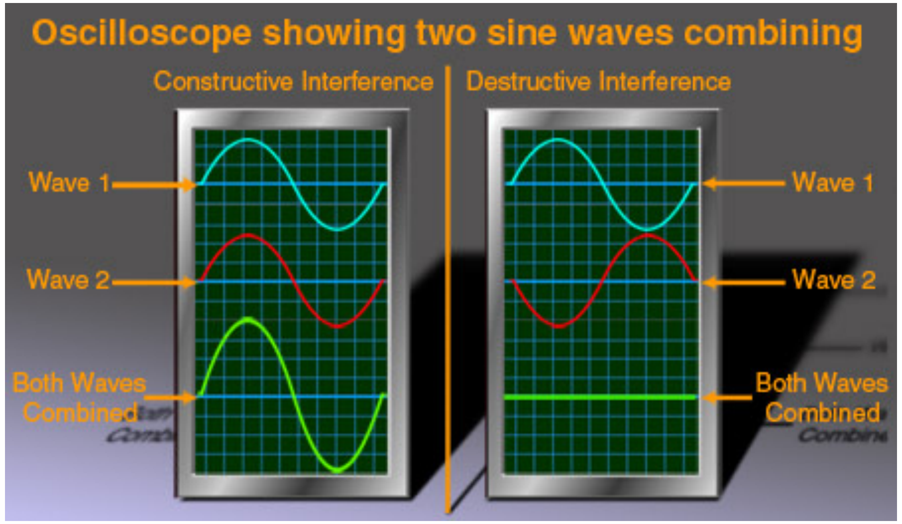
Cu source:

$K_\alpha = 1.54184$ Å

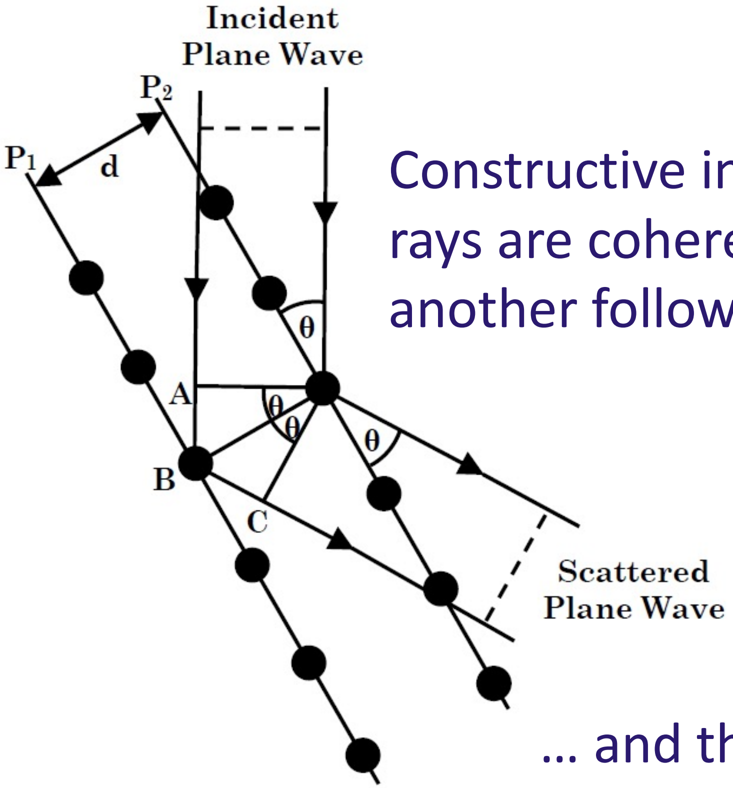
$K_\beta = 1.39222$ Å

Want monochromatic X-rays, so use a filter to supress Cu K_β transitions…

X-ray Diffraction 101



http://salfordacoustics.co.uk/sound-waves/superposition



Constructive interference only occurs if the X-rays are coherent and remain in phase with one another following diffraction…

Diffraction patterns are only produced when the diffracted X-rays interfere constructively.

… and these conditions are only realised when the X-rays are diffracted through specific angles:

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

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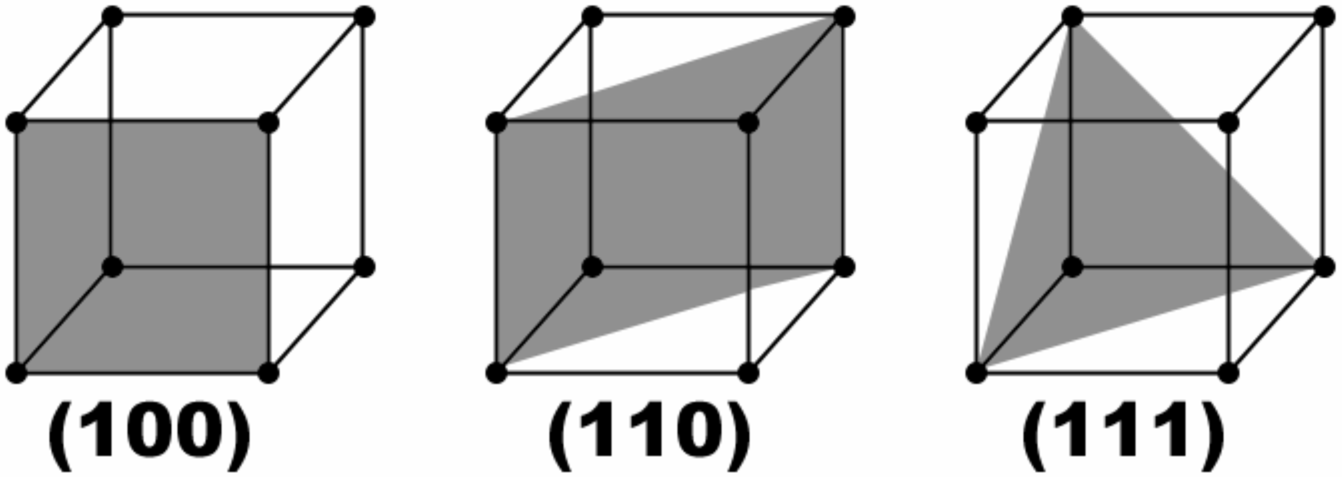
X-ray Diffraction 101

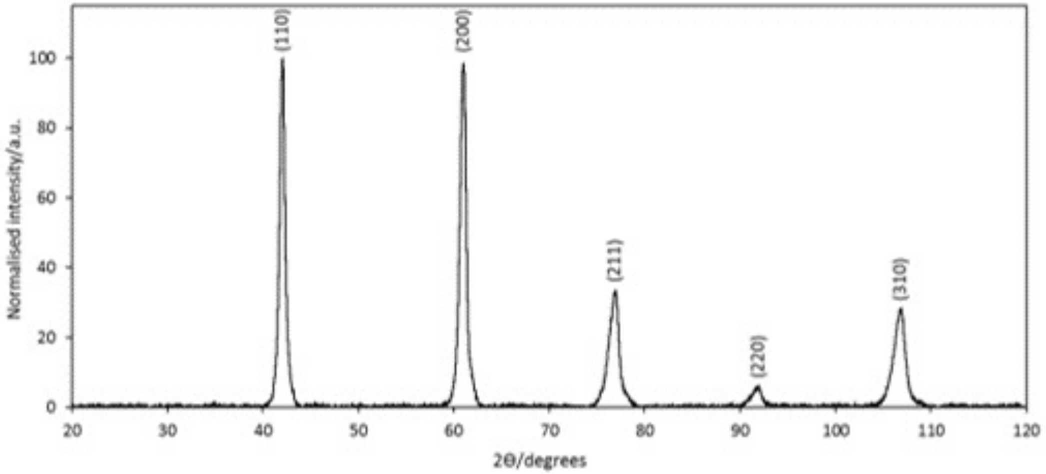


We use Bragg’s Law to predict the angles through which X-rays will be diffracted from a set of lattice planes.

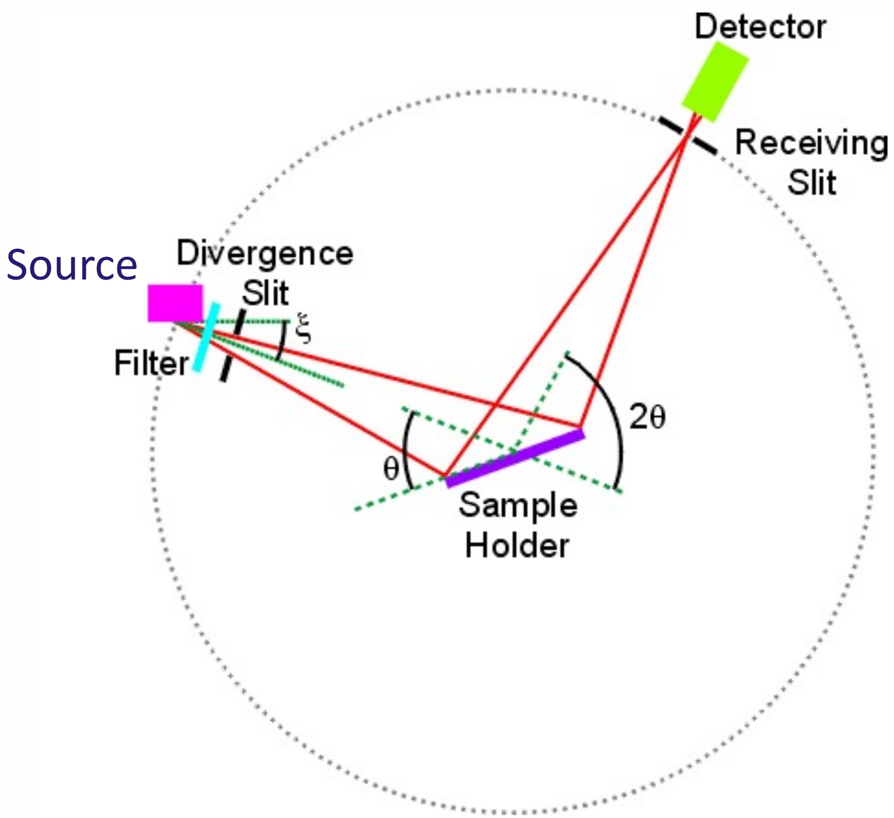
The diffracted angles are determined by the distances between parallel planes of atoms.

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

Recording the angles at which diffracted waves are observed gives a diffraction pattern which is unique to the material:



Reflection geometry



http://pd.chem.ucl.ac.uk/pdnn/inst1/optics1.htm

X-rays are divergent when produced.

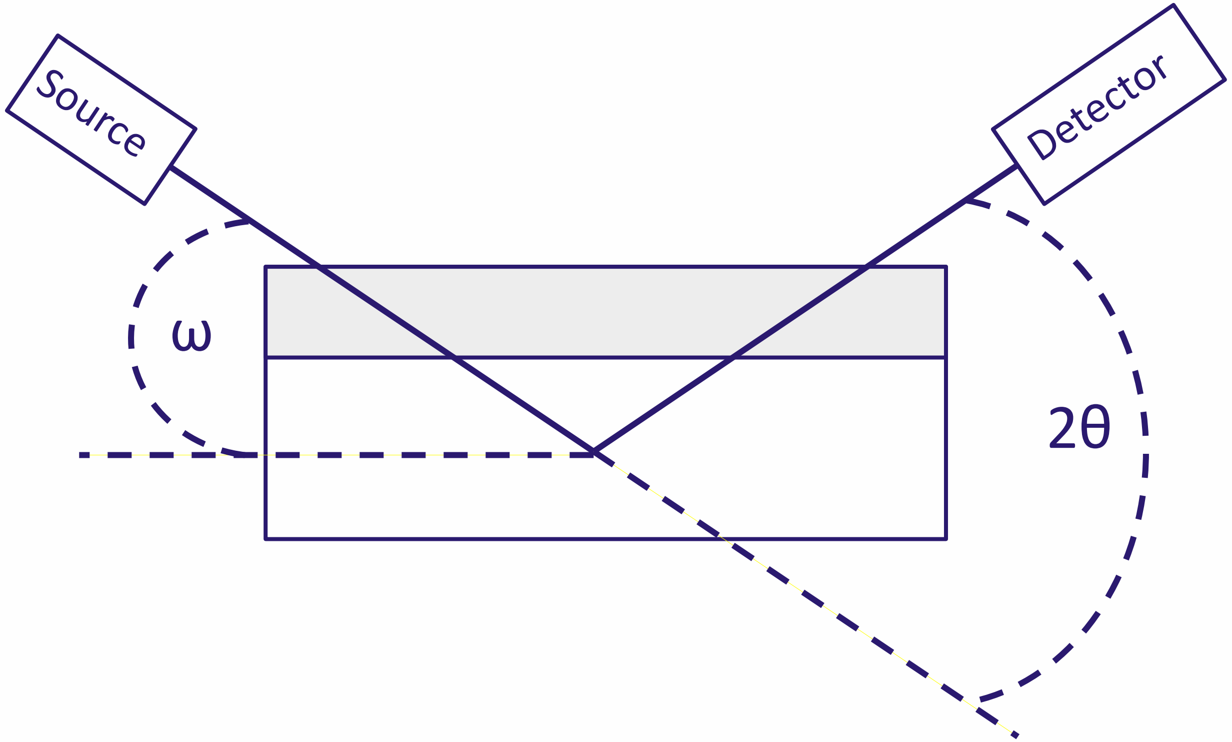
Bragg-Brentano geometry “focuses” the divergent and diffracted beams using Soller slits.

Divergence slit determines the X-ray “footprint” on the sample.

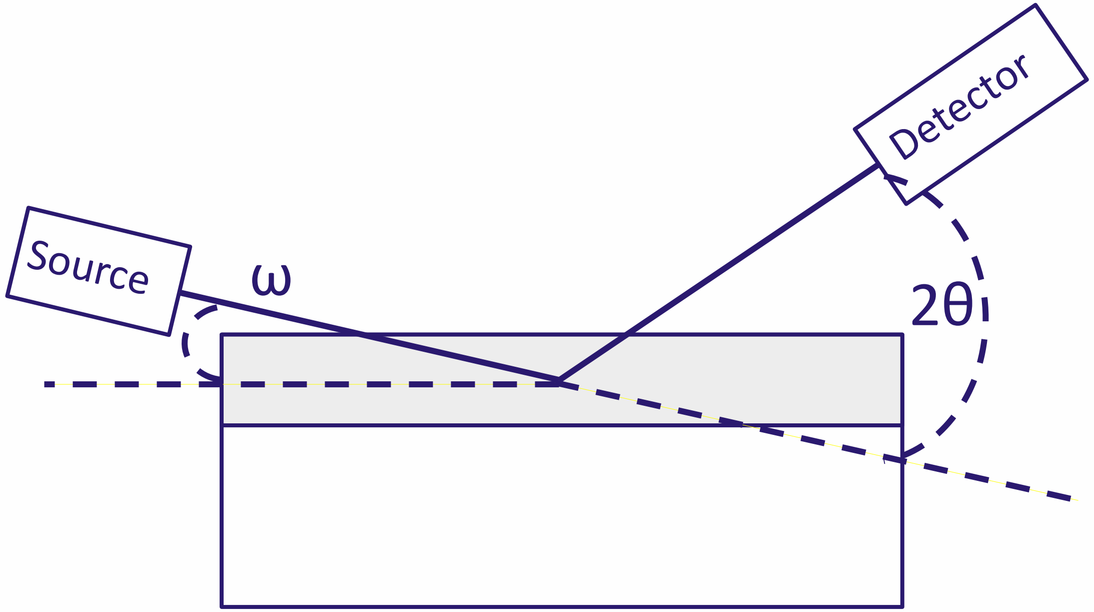
Both the source and the detector move by – θ and θ in this geometry.

The X-ray may probe too deeply to study ion implantation induced damage.

Grazing Incidence geometry



X-ray source and detector move



X-ray source does not move → ω is small and constant.

Detector moves through 2θ.

X-ray penetration depth

The angle, ω, required for the X-rays to penetrate into a specific region beneath the surface is calculated by:

$$\omega = \ sin^{-1}\left(\frac{x}{3\mu}\right)$$

Where x is the thickness of the region (i.e., the implanted region), and μ in the attenuation length of the material, which is **dependant on the density and composition of the material and X-ray energy.**

μ measures the exponential decay of X-ray intensity as it passes through a material.

X-ray penetration depth

μ is defined as the length travelled before the X-ray intensity falls to 1/e of its original value.

Aim to probe a depth of 3 μ, where there has been > 95 % attenuation of incident X-rays in the defined thickness.

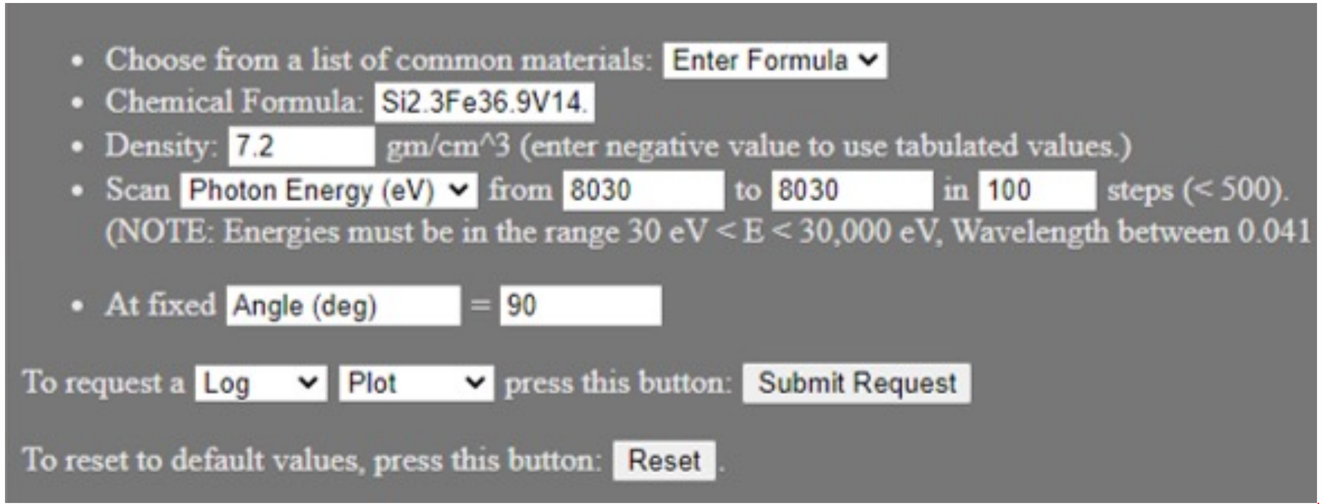
Calculation of a compounds attenuation length is determined through addition of μ values of each individual element, multiplied by a weight fraction term.

μ for your material can be calculated using for example the Hephaestus software package, or: https://henke.lbl.gov/optical_constants/atten2.html

X-ray penetration depth

Si 2.3at% - Fe 36.9 at% - V 14.79 at% - Cr 35.09 at% - Mo 10.92 at%; Density = 7.2 gcm^{-3}

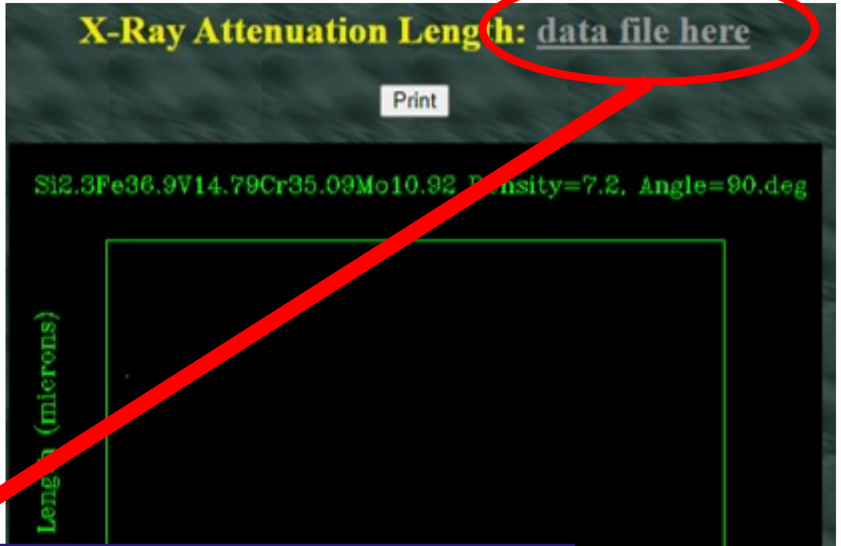
Cu K$_\alpha$ = 1.544 Å = 8.03 KeV = 8030 eV



- Choose from a list of common materials: Enter Formula
- Chemical Formula: Si2.3Fe36.9V14.
- Density: 7.2 gm/cm^3 (enter negative value to use tabulated values.)
- Scan Photon Energy (eV) from 8030 to 8030 in 100 steps (< 500).
  (NOTE: Energies must be in the range 30 eV < E < 30,000 eV, Wavelength between 0.041
- At fixed Angle (deg) = 90

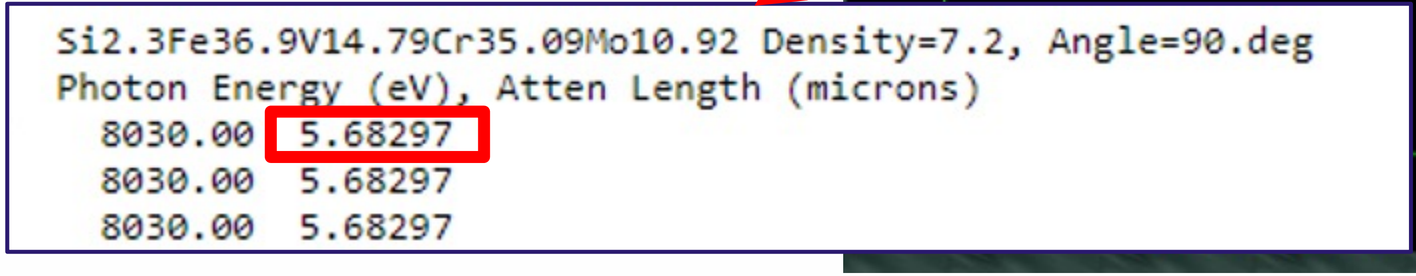
To request a Log Plot press this button: Submit Request

To reset to default values, press this button: Reset.



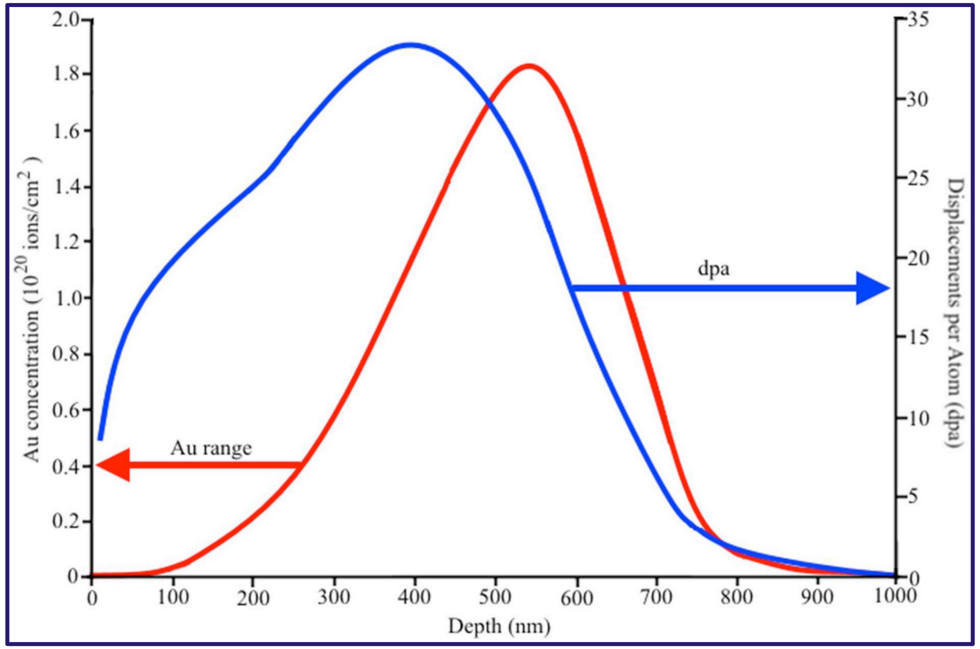
X-Ray Attenuation Length: data file here

Si2.3Fe36.9V14.79Cr35.09Mo10.92 Density=7.2, Angle=90.deg



```
Si2.3Fe36.9V14.79Cr35.09Mo10.92 Density=7.2, Angle=90.deg
Photon Energy (eV), Atten Length (microns)
  8030.00  5.68297
  8030.00  5.68297
  8030.00  5.68297
```

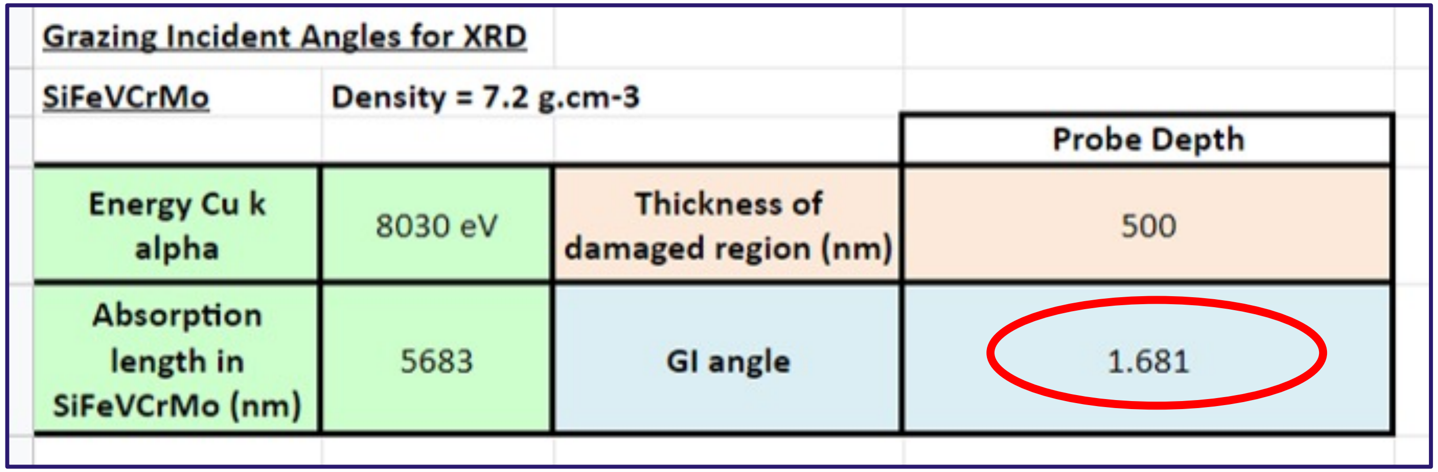
X-ray penetration depth



SRIM simulation of 5 MeV Au^{2+} ion implantation to a fluence of 5 x 10^{15} Au ions/cm^2 into a SiFeVCrMo alloy.

$$\omega = sin^{-1}\left(\frac{x}{3\mu}\right)$$

$$\omega = sin^{-1}\left(\frac{500}{3\times5683}\right)$$



Grazing Incident Angles for XRD			
SiFeVCrMo	**Density = 7.2 g.cm-3**		
			Probe Depth
Energy Cu k alpha	8030 eV	**Thickness of damaged region (nm)**	500
Absorption length in SiFeVCrMo (nm)	5683	**GI angle**	1.681

PANalytical X'Pert3

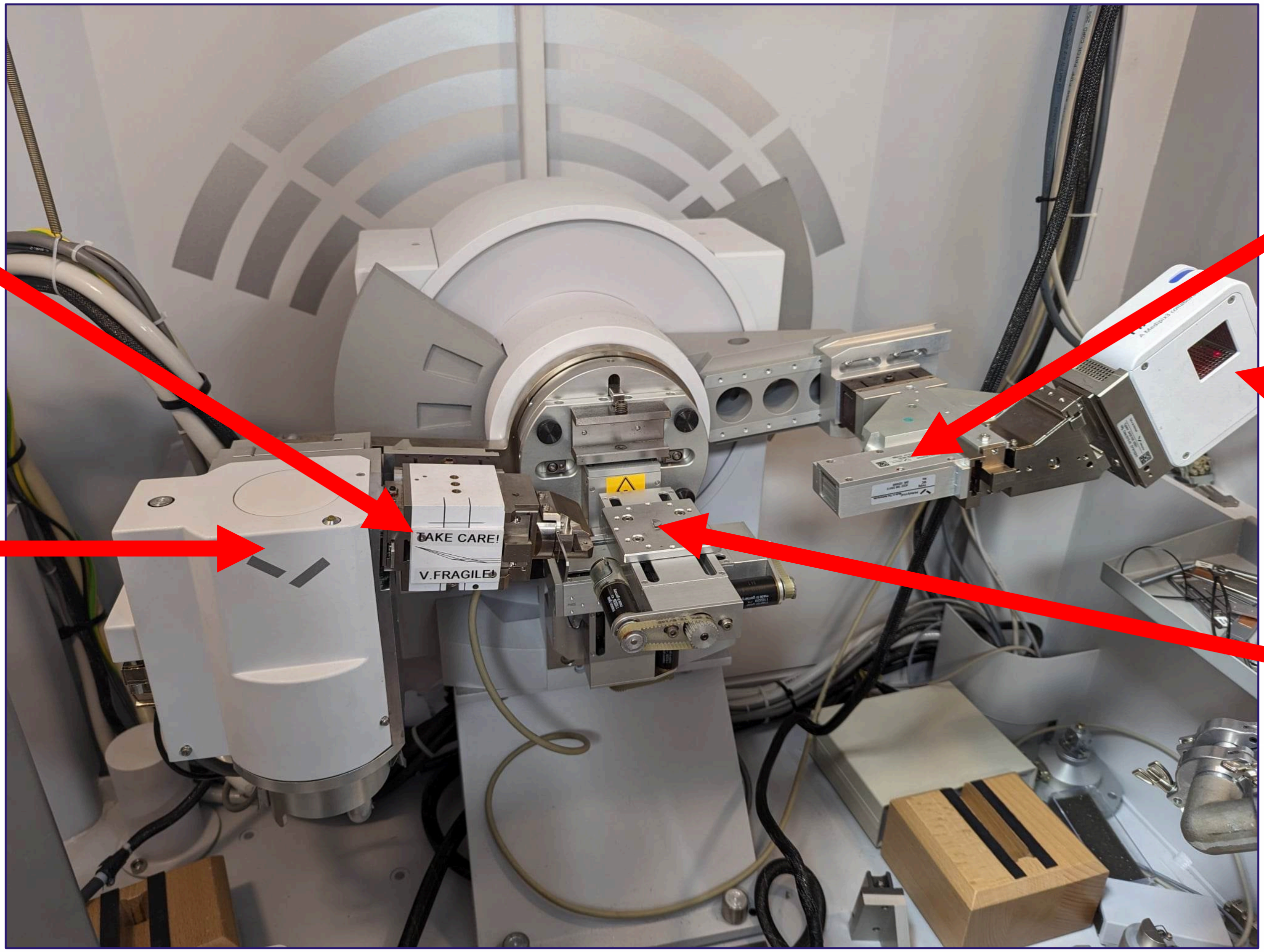
Instrument details:

- Cu X-ray source (1.544 Å).
- Ni Kbeta filter.
- Programmable divergence and acceptance slit.
- Goebel mirror.
- PIXcel1D detector.
- 0.27 parallel plate collimator with secondary beam monochromator.
- 45 position sample changer.

Applications:

- Grazing incidence XRD (GIXRD).
- X-ray reflectometry (XRR).
- Texture and stress analysis.
- High temperature XRD.

Grazing Incidence XRD



Parallel beam mirror

Fixed ω at e.g., 1.681º

Parallel plate collimator

Detector moves through 2θ

Sample

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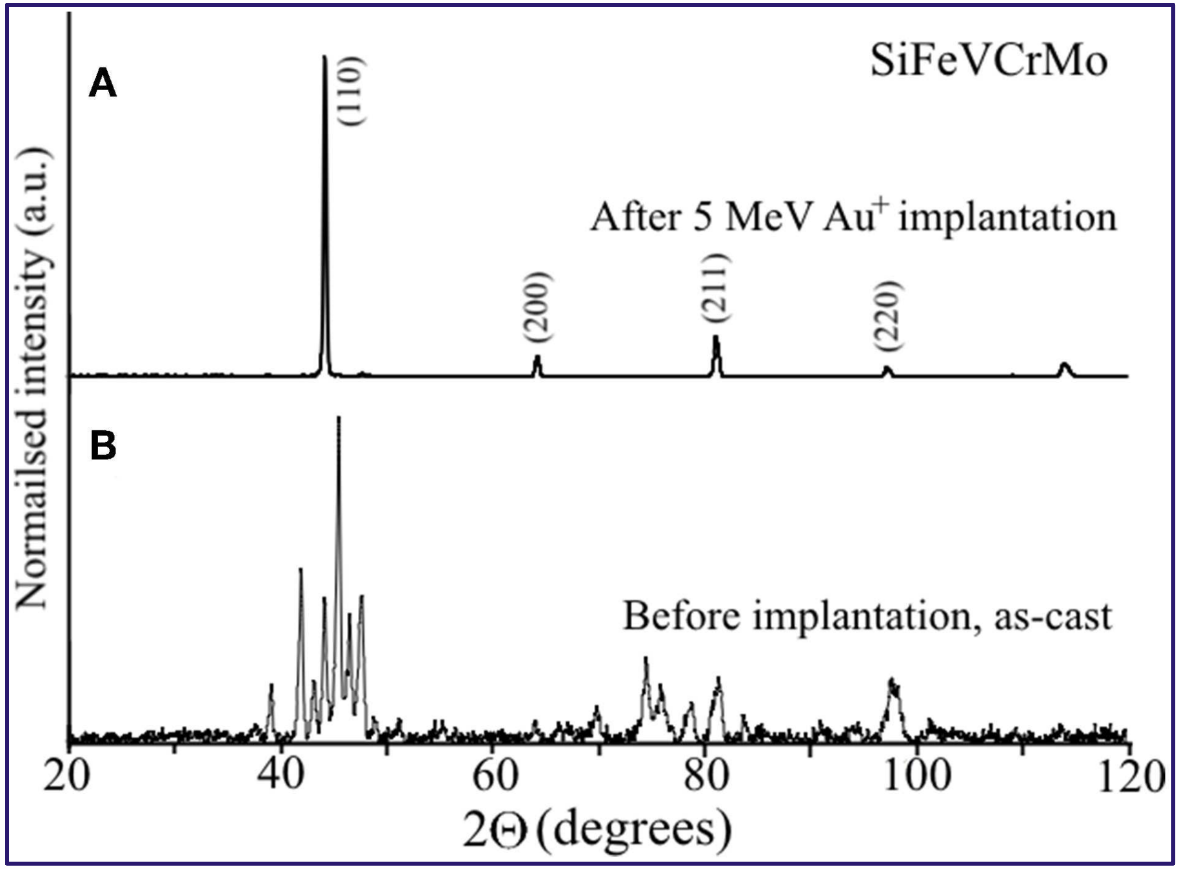
Damage recovery in HEAs



Room temperature grazing incidence XRD patterns from SiFeVCrMo, (B) before and (A) after room temperature ion implantation with 5 Mev Au^{2+} ions, to a fluence of 5x10^{15} Au^{2+} ions/cm$^{2.}$

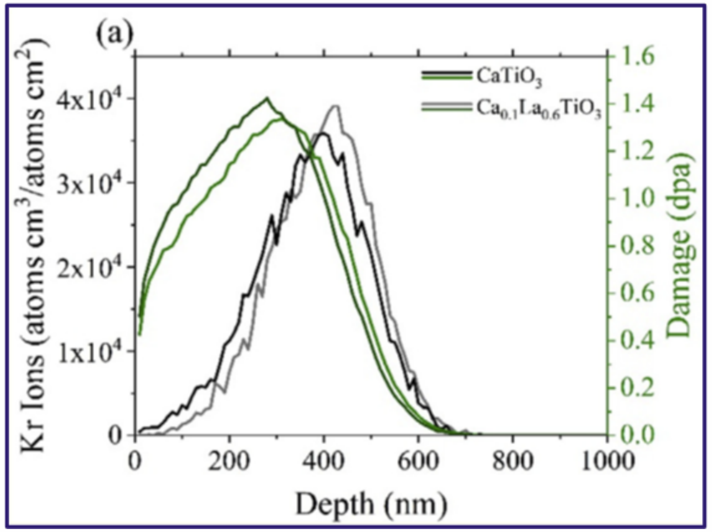
GIXRD patters show a transformation from tetragonal to BCC structure following ion implantation.

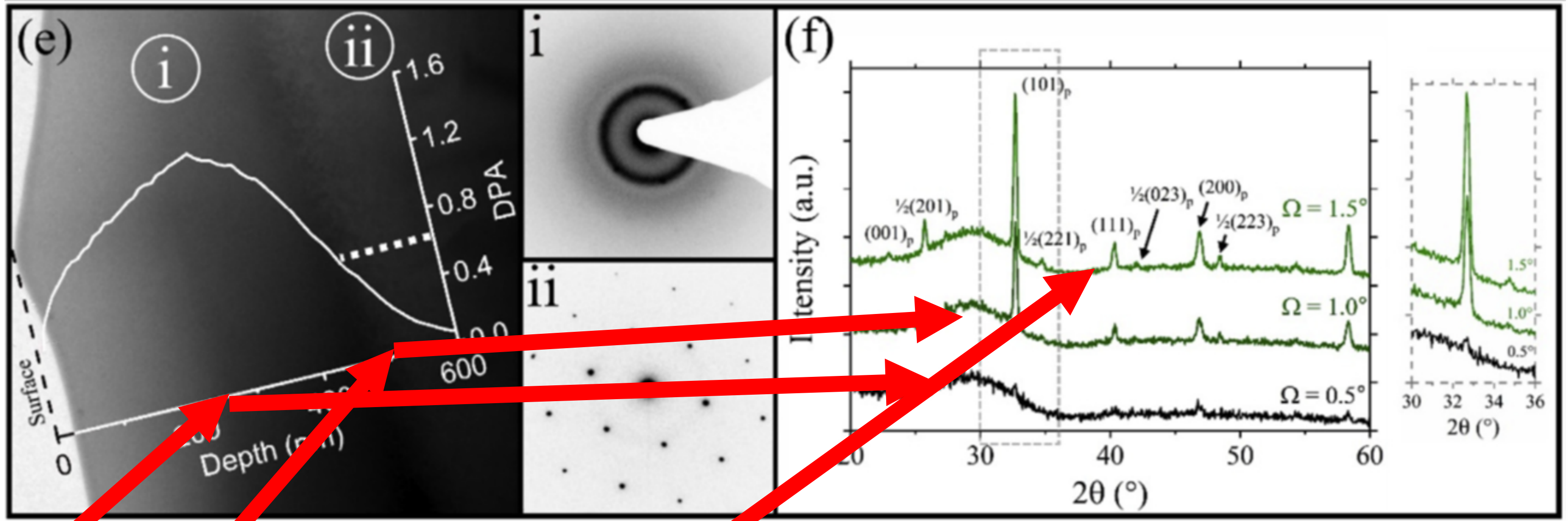
Phase analysis used the International Center for Diffraction Data's (ICDD) PDF-4+ database.

A S. Gandy, B Jim, G Coe, D Patel, L Hardwick, Sh Akhmadaliev, N Reeves-McLaren, R Goodall; High temperature and ion implantation induced phase transformations in novel reduced activation Si-Fe-V-Cr (-Mo) high entropy alloys, Frontiers in Materials (2019)

Implantation induced amorphisation

$Ca_{1-x}La_{2x/3}TiO_3$ ceramic system used to determine the link between cation vacancies in perovskites and radiation damage resistance (from 1 MeV Kr^+ ions).





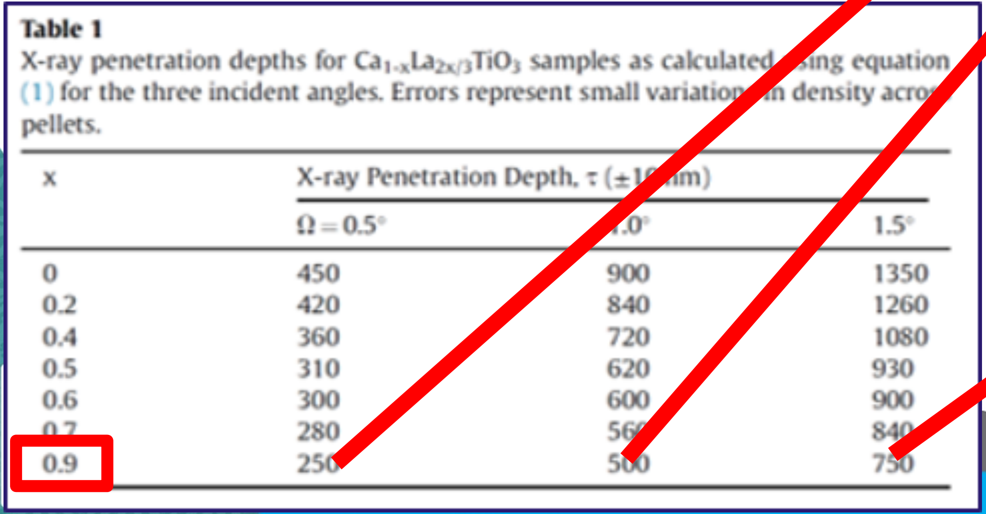


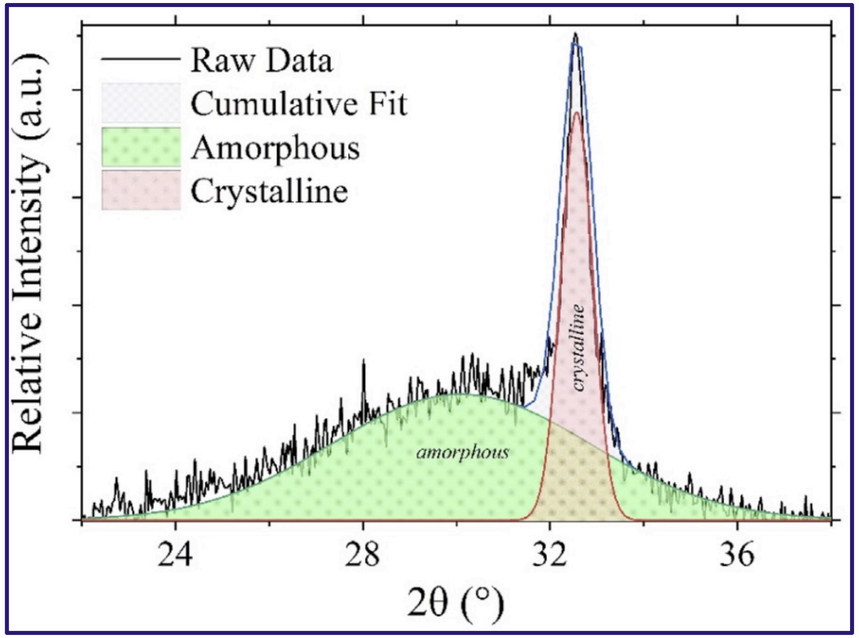
Table 1

X-ray penetration depths for $Ca_{1-x}La_{2x/3}TiO_3$ samples as calculated using equation (1) for the three incident angles. Errors represent small variations in density across pellets.

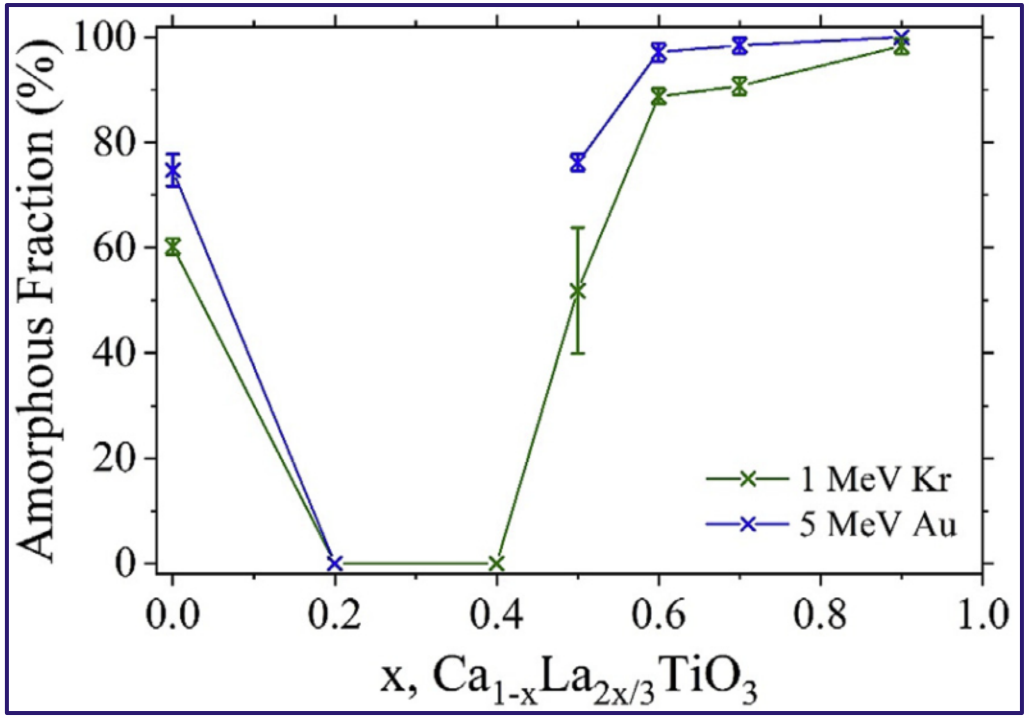
x	X-ray Penetration Depth, τ (±10 nm)		
	Ω = 0.5°	1.0°	1.5°
0	450	900	1350
0.2	420	840	1260
0.4	360	720	1080
0.5	310	620	930
0.6	300	600	900
0.7	280	560	840
0.9	250	500	750

S M Lawson, N C Hyatt, K R Whittle, A S Gandy; Resistance to amorphisation in $Ca_{1-x}La_{2x/3}TiO_3$ perovskites – a bulk ion-irradiation study, Acta Materialia (2019)

Implantation induced amorphisation



A pseudo-Voigt peak fit to determine crystalline and amorphous fractions produced in ion implanted materials.



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Other machines are available through Royce:

https://www.sheffield.ac.uk/royce-institute/x-ray