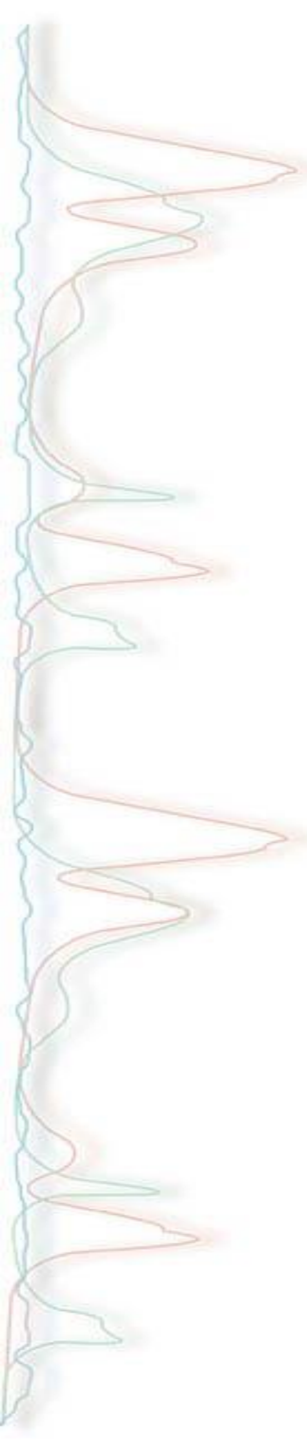

chem 5390

Advanced -ray Analysis

LECTURE 16

Dr. Teresa D. Golden
University of North Texas
Department of Chemistry

Application of Diffraction Data

XRD can be used for:

-Bravais lattice determination – phase determination (crystalline phases and orientation)

-Lattice parameter determination

-Determination of solvus line in phase diagrams (order-disorder transformation)

-Long range order

-Crystallite size and Strain

-Temperature factor – thermal diffuse scattering (thermal expansion)

-Thickness measurements of thin films and multilayers

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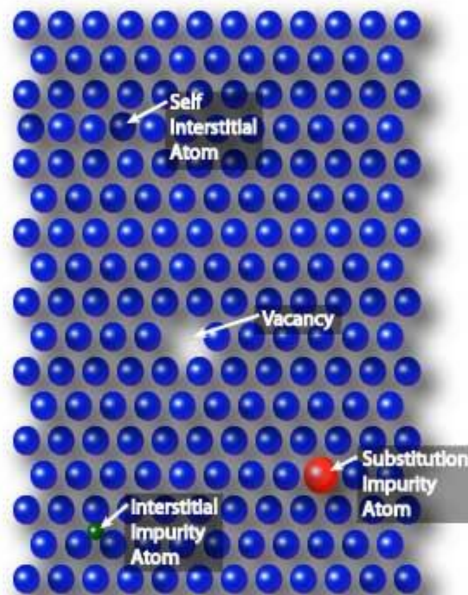
Application of Diffraction Data

Vectors and Planes

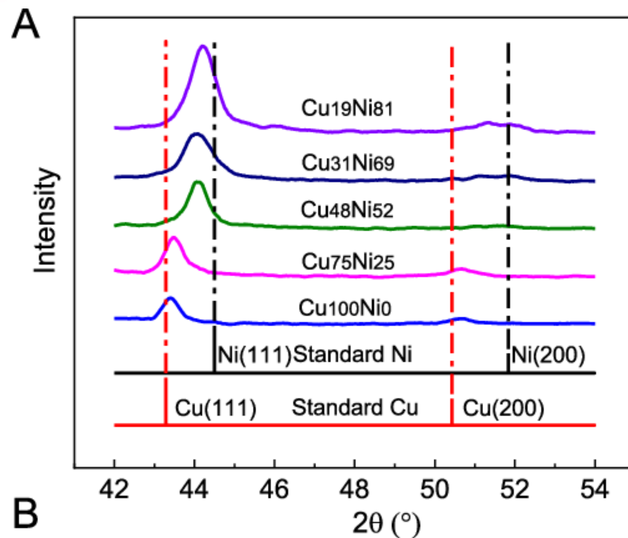
Crystal Defects

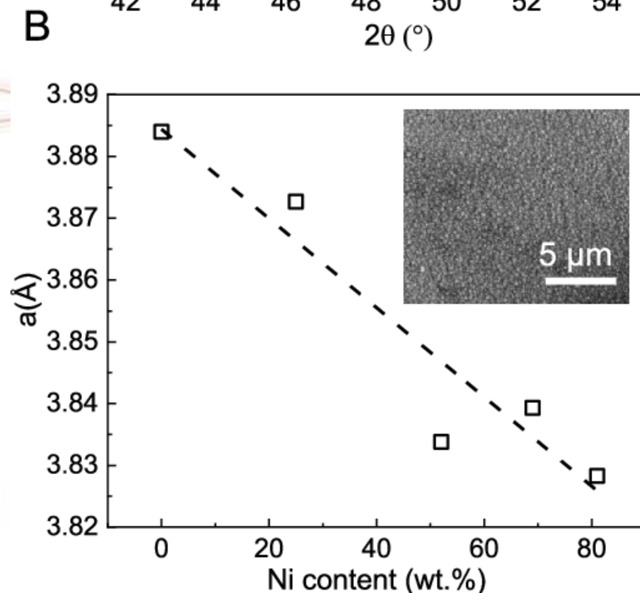
Point defects – substitutional or interstitial impurities.

Vegard's law – volume of unit cells in a substitutional solid solution is linearly proportional to the fraction of sites substituted.



Application of Diffraction Data





Vegard's law

In crystallography, Vegard's law is an empirical finding resembling the rule of mixtures. In 1921, Lars Vegard discovered that the lattice parameter of a solid solution of two constituents is approximately a weighted mean of the two constituents' lattice parameters at the same temperature.

Application of Diffraction Data

Phase Analysis - Vegard's Law

$$d_{hkl} = \sqrt{\frac{a^2}{h^2 + k^2 + l^2}}$$

Good for alloys with continuous solid solutions

Ex) Au-Pd

- **To create the plot on the right**
  - **Using the crystal structure of the alloy calculate "a" for each metal**
  - **Draw a straight line between them as shown on the chart to the left.**
- **To calculate the composition**
  - **Calculate "a" from d-spacings**
  - **"a" will be an atomic weighted fraction of "a" of the two metal**

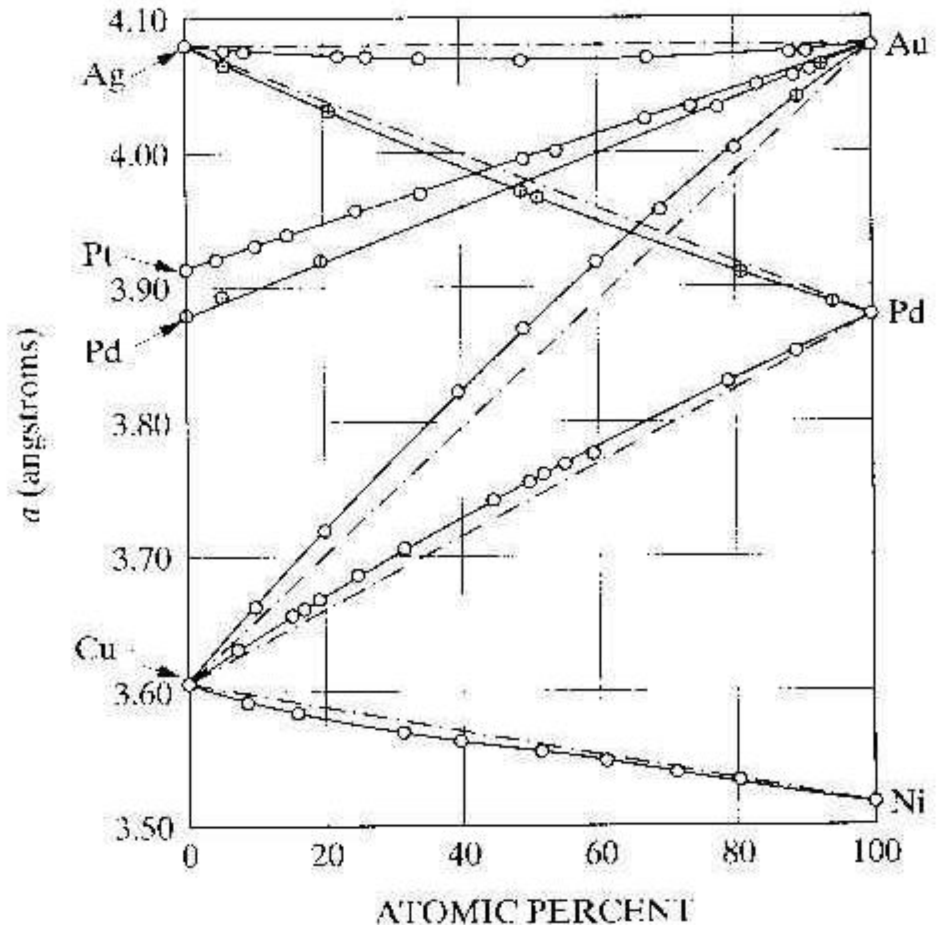
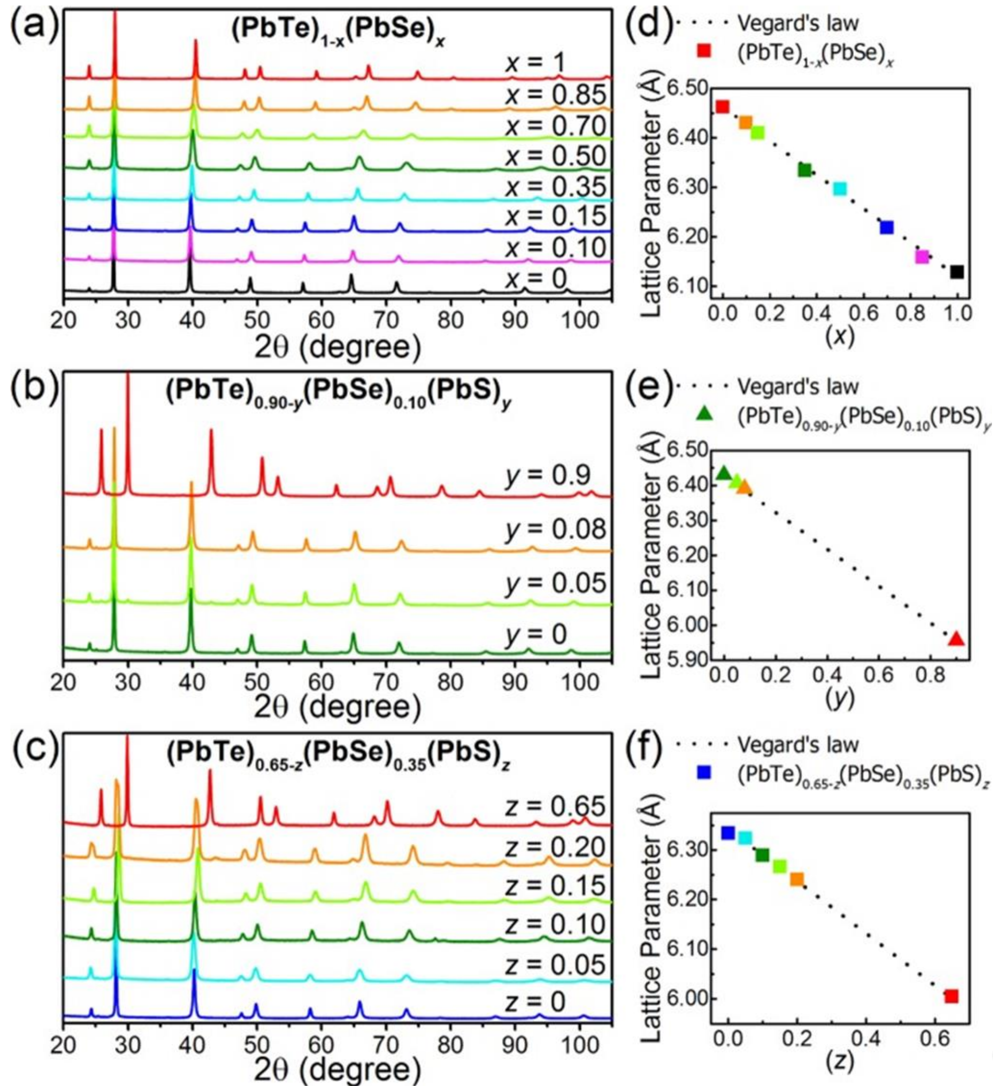
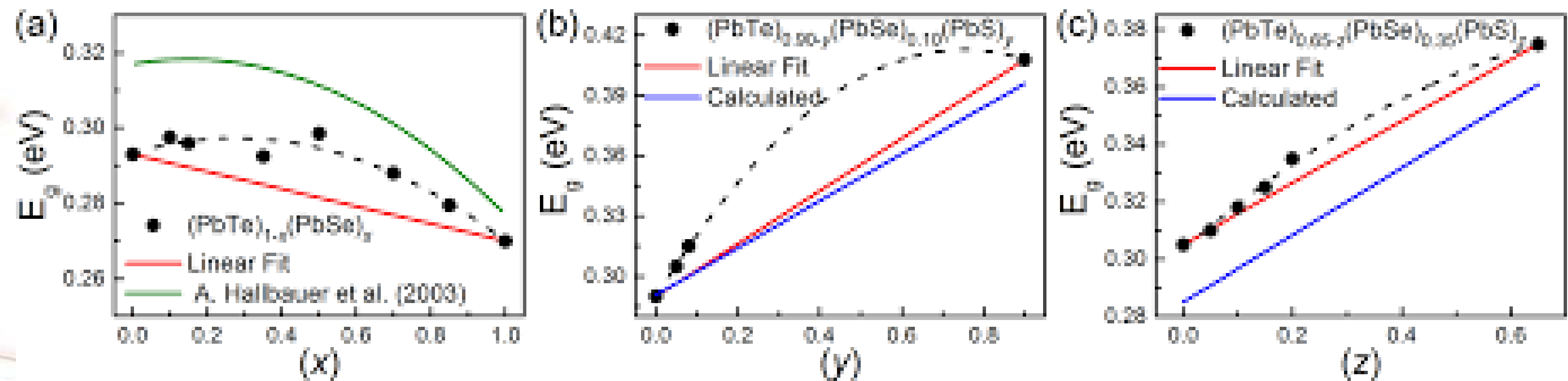


Figure 11-6 Lattice parameters of some continuous solid solutions. Dot-dash lines indicate Vegard's law. Barrett [1.7].

Application of Diffraction Data



Application of Diffraction Data



Application of Diffraction Data

Measuring Changes In Phase Fraction

Using I/Icor

$$\frac{I_{\alpha-\exp}(hkl)}{I_{\beta-\exp}(HKL)} = \frac{I_{\alpha}(hkl) \times {}^{I}\!/_{Icor\,\beta}(hkl) \times w_{\beta}}{{}^{I}\!/_{Icor\,\alpha}(hkl) \times I_{\beta}(hkl) \times w_{\alpha}}$$

– Where

- $\frac{I}{I_{cor}} = \frac{\text{Intensity of sample's 100\% peak}}{\text{Intensity of Corundum's 100\% peak}}$
- ω= weight fraction
- I(hkl)=Reference's relative intensity
- I_{exp}(hkl)=Experimental integrated intensity

Application of Diffraction Data

Measuring Changes In Phase Fraction

Using Direct Comparison Method

$$\frac{I_{\alpha-\exp}(hkl)}{I_{\beta-\exp}(HKL)} = \frac{R_{\alpha} \times v_{\alpha}}{R_{\beta} \times v_{\beta}}$$

$$\mathrm{R} = \frac{1}{V}\left[\mathrm{pCL_P}\left[\mathrm{F_{hkl}}\right]^2\right]$$

$$\mathrm{I_{hkl}} = \mathrm{I_0 pCL_P}\left[\mathrm{F_{hkl}}\right]^2$$

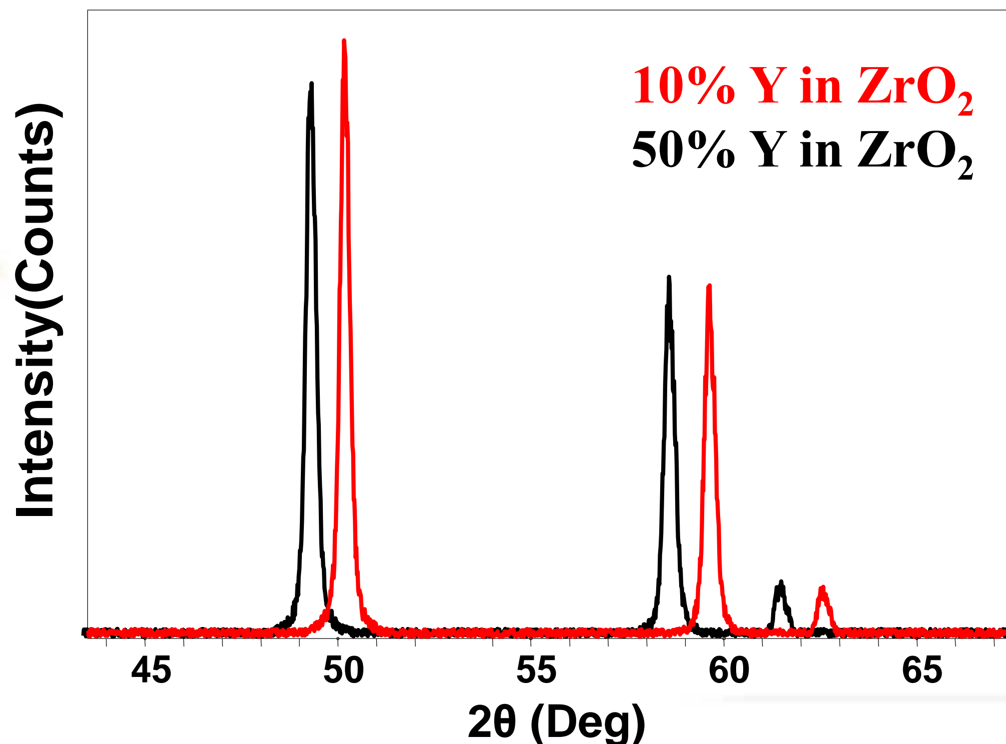
Because this is already a complicated method, many choose to go ahead and use **Rietveld Refinement**

Application of Diffraction Data

Measuring Changes In Phase Fraction

Substitutional doping can change bond distances, reflected by a change in unit cell lattice parameters

The change in peak intensity due to substitution of atoms with similar Z is much more subtle and may be insignificant



$R(Y^{3+}) = 0.104Å$

$R(Zr^{4+}) = 0.079Å$

Application of Diffraction Data

XRD can be used for:

-Bravais lattice determination – phase determination (crystalline phases and orientation)

-Lattice parameter determination

-Determination of solvus line in phase diagrams (order-disorder transformation)

-Long range order (Texture Analysis)

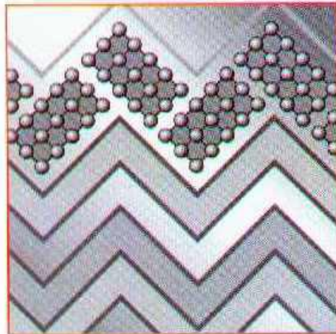
-Crystallite size and Strain

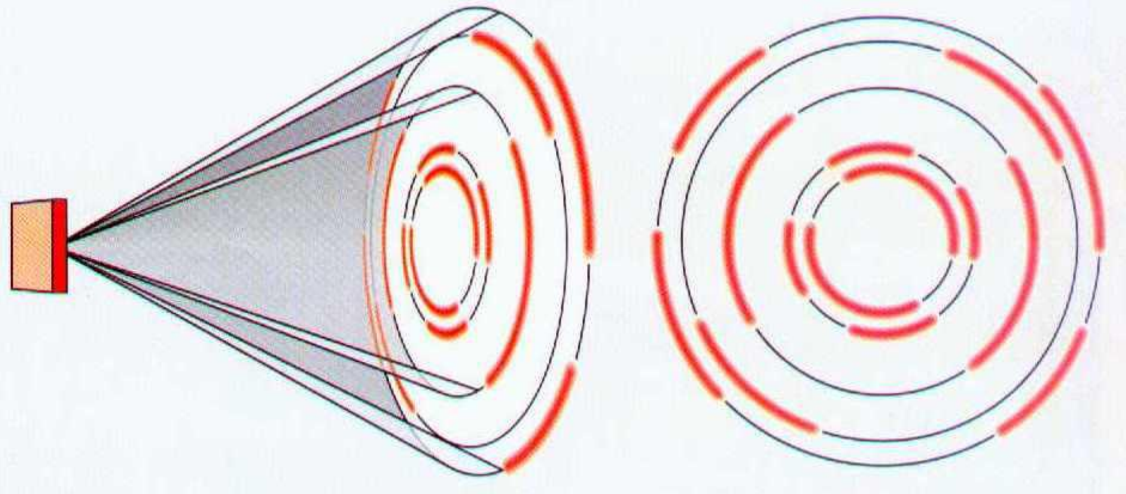
-Temperature factor – thermal diffuse scattering (thermal expansion)

-Thickness measurements of thin films and multilayers

Diffraction Theory

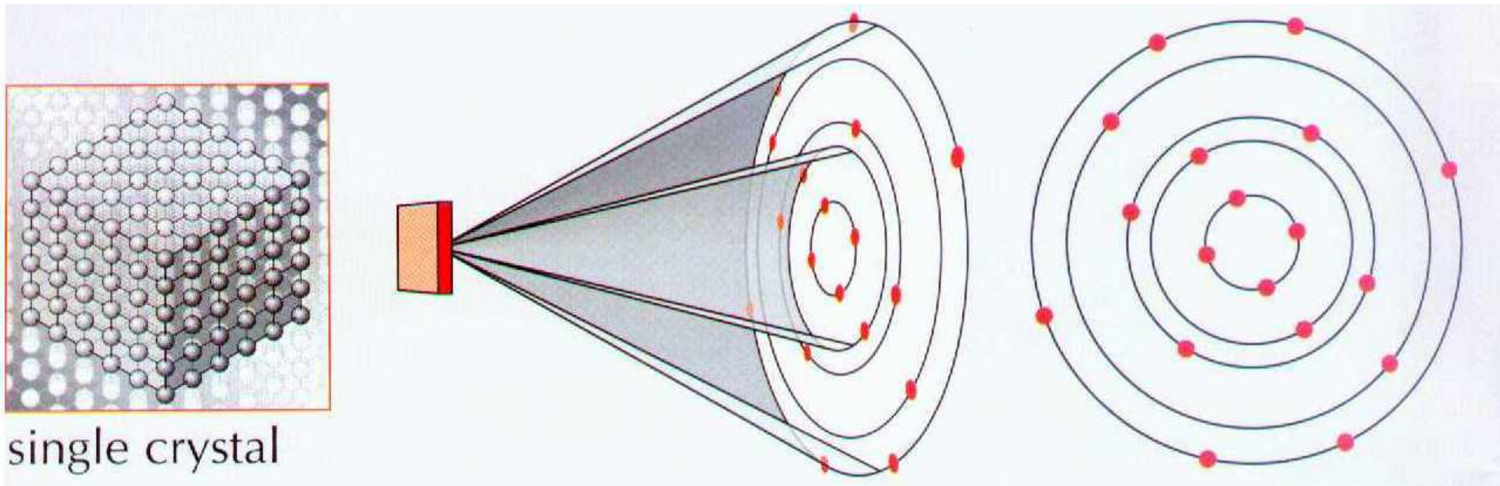
Texture analysis





Diffraction Theory

Single Crystal



Application of Diffraction Data

Orientations Matter in Single Crystals

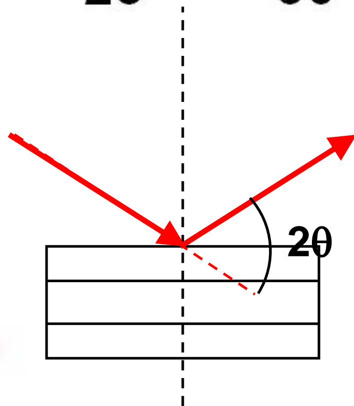
(a big piece of rock salt)

Intensity (AU)

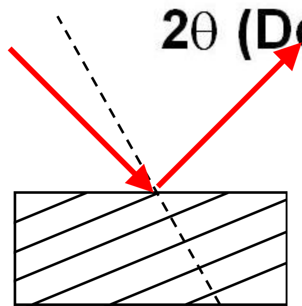
111 200 220 311 222

25 30 35 40 45 50 55 60

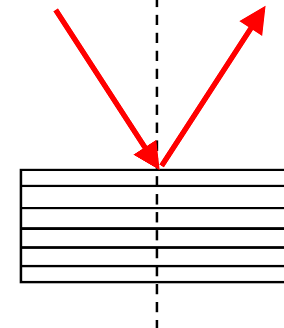
2θ (Degrees)



At 27.42 ° 2θ, Bragg's law fulfilled for the (111) planes, producing a diffraction peak.



The (200) planes would diffract at 31.82 ° 2θ; however, they are not properly aligned to produce a diffraction peak



The (222) planes are parallel to the (111) planes.

Application of Diffraction Data

Texture

Grains within a polycrystalline are not completely randomly distributed

There can be clustering of grains about some particular orientation(s) to a certain degree

Inducing texture in powder samples - causes peak intensities to vary

Large crystallite sizes and non-random crystallite orientations both lead to peak intensity variation

The measured diffraction pattern will not agree with that expected from an ideal powder

Application of Diffraction Data

Texture in samples is a common occurrence, and usually have more to do with how the samples are made.

-Plastically deformed metals (cold rolled, etc)

-Powders with particle shapes related to their crystal structure, particular planes form the faces

-Orientation in particular directions (Plates, needles, acicular, cubes, etc.)

Application of Diffraction Data

Orientation in particular directions (Plates, needles, acicular, cubes, etc.)

-Fiber Texture

A particular direction [uvw] for all grains is more or less parallel to the wire or fiber axis

e.g. [111] fiber texture in Al cold drawn wire

Double axis is also possible

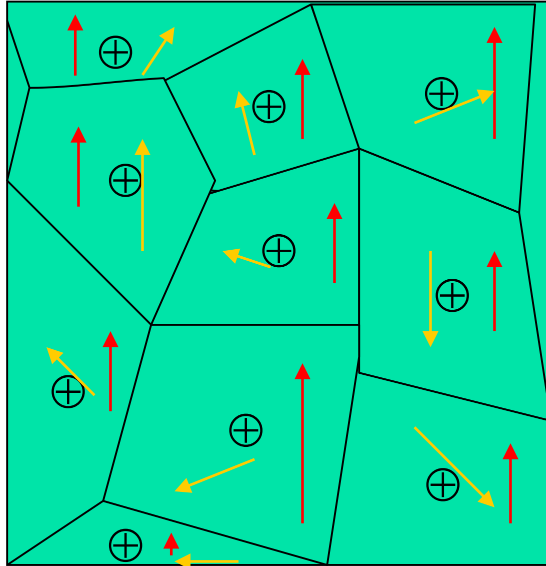
Example: [111] and [100] fiber textures in Cu wire

-Sheet Texture

Most of the grains are oriented with a certain crystallographic plane (hkl) roughly parallel to the sheet surface and certain direction [uvw] parallel to the rolling direction

Notation: (hkl)[uvw]

Application of Diffraction Data



Also, if the direction $[u_1v_1w_1]$ is parallel for all regions, the structure is like a single crystal

However, the direction $[u_1v_1w_1]$ is not aligned for all regions, the structure is like a mosaic structure, also called as **Mosaic Texture**

⊕ [uvw] i.e. perpendicular to the surface of all grains is parallel to a direction [uvw]

Orientation in particular directions (Plates, needles, acicular, cubes, etc.)

Application of Diffraction Data

Simple Means of Quantifying Texture

Lotgering degree of orientation (*f*)

- **A comparison of the relative intensities of a particular family of (hkl) reflections to all observed reflections in a coupled 2θ powder x-ray diffraction (XRD) Spectrum**
- ***f* is specifically considered a measure of the "degree of orientation" and ranges from 0% to 100%**
- **po is p of a sample with a random crystallographic orientation.**

$$f = \frac{p - p_o}{1 - p_o};$$

for (00l)

$$p = \frac{\sum I_{00l}}{\sum I_{00l} + \sum I_{non-00l}}$$

Jacob L. Jones, Elliott B. Slamovich, and Keith J. Bowman, "Critical evaluation of the Lotgering degree of orientation texture indicator," J. Mater. Res., Vol. 19, No. 11, Nov 2004

Application of Diffraction Data

Relative Texture Coefficient (RTC)

Relative peak intensities are analyzed by determining relative texture coefficients of the reflections present in the XRD pattern.

$$RTC_{hkl} = \frac{I_{p,hkl}/I^{\circ}_{p,hkl}}{\Sigma\, I_{p,hkl}/I^{\circ}_{p,hkl}} * 100\%$$

where $I_{p,hkl}$ is the intensity of the peak for each sample at each (hkl) reflection used.

$I^{\circ}_{p,hkl}$ is the intensity of those reflections for the standard reference (PDF# 00-000-0000) in the database.

The standard provides a random orientation pattern to compare against any preferred orientation found in the samples.

Application of Diffraction Data

Relative Texture Coefficient (RTC) Example: Golden et.al.

X-ray diffraction (XRD) of (a) pure Ni, (b) Ni CeO_2, and (c) Ni Fc-CeO_2 coatings

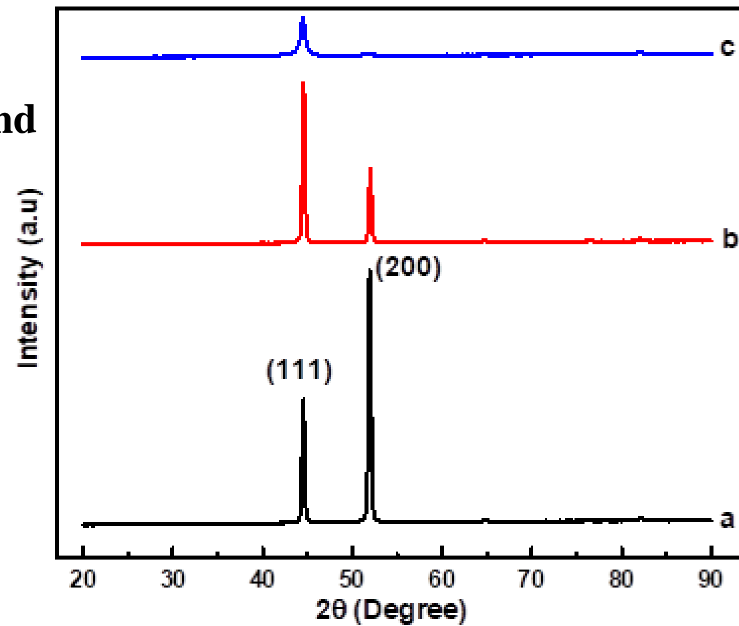
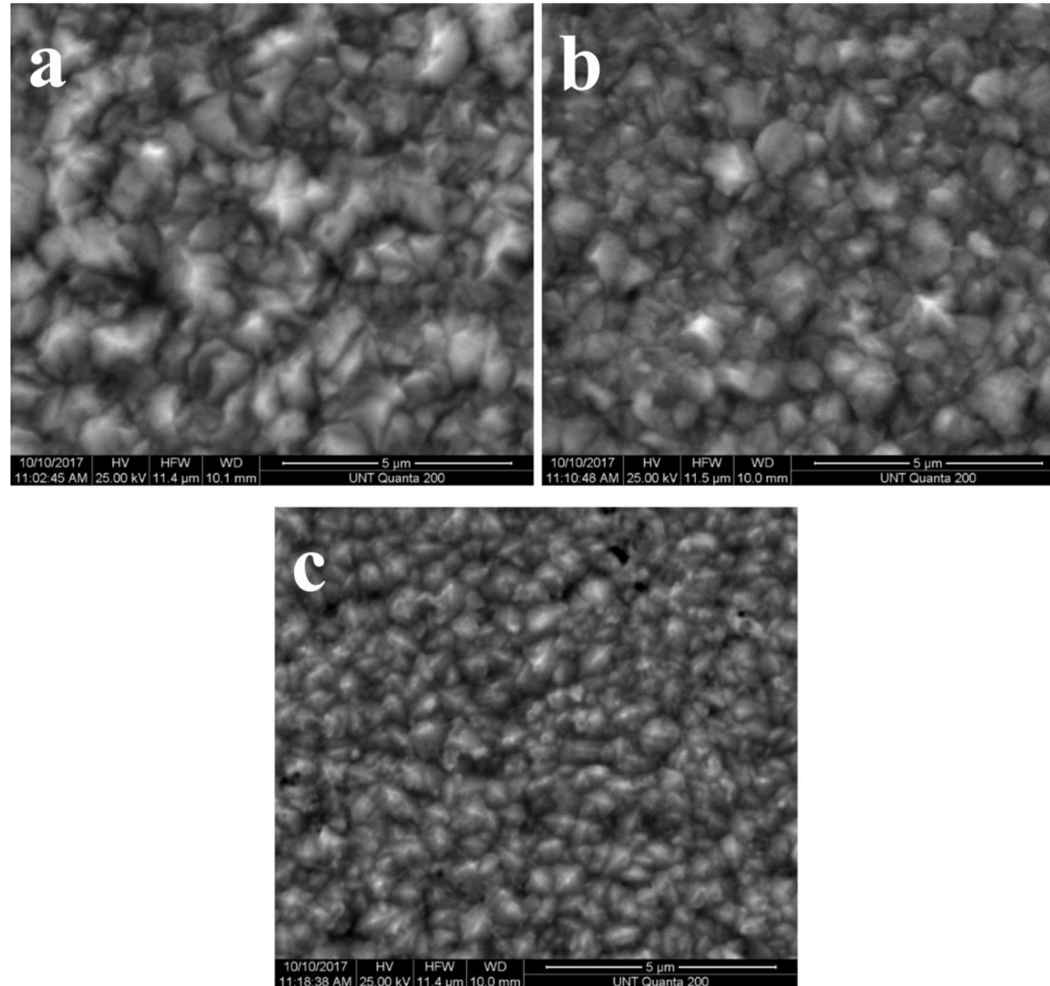


Table. XRD reflection intensities, relative texture coefficients, and crystallite sizes for Nickel, Ni CeO_2 and Ni Fc-CeO_2 electrodeposited coatings.

Coating (n=3)	$I(f)_{111}$	$I(f)_{200}$	$I(f)_{220}$	RTC_{111}	RTC_{200}	RTC_{220}	Crystallite size (nm)
PDF# 00-004-0850	100	42	21	---	---	---	---
Nickel	49	100	3	29.8	63.3	6.9	47.6 ± 5.0
Ni CeO_2	100	51	4	50.7	41.9	6.7	43.3 ± 6.3
Ni Fc-CeO_2	100	11	16	63.1	14.6	22.3	32.0 ± 5.5

Application of Diffraction Data

Relative Texture Coefficient (RTC) Example: Golden et.al.



Application of Diffraction Data

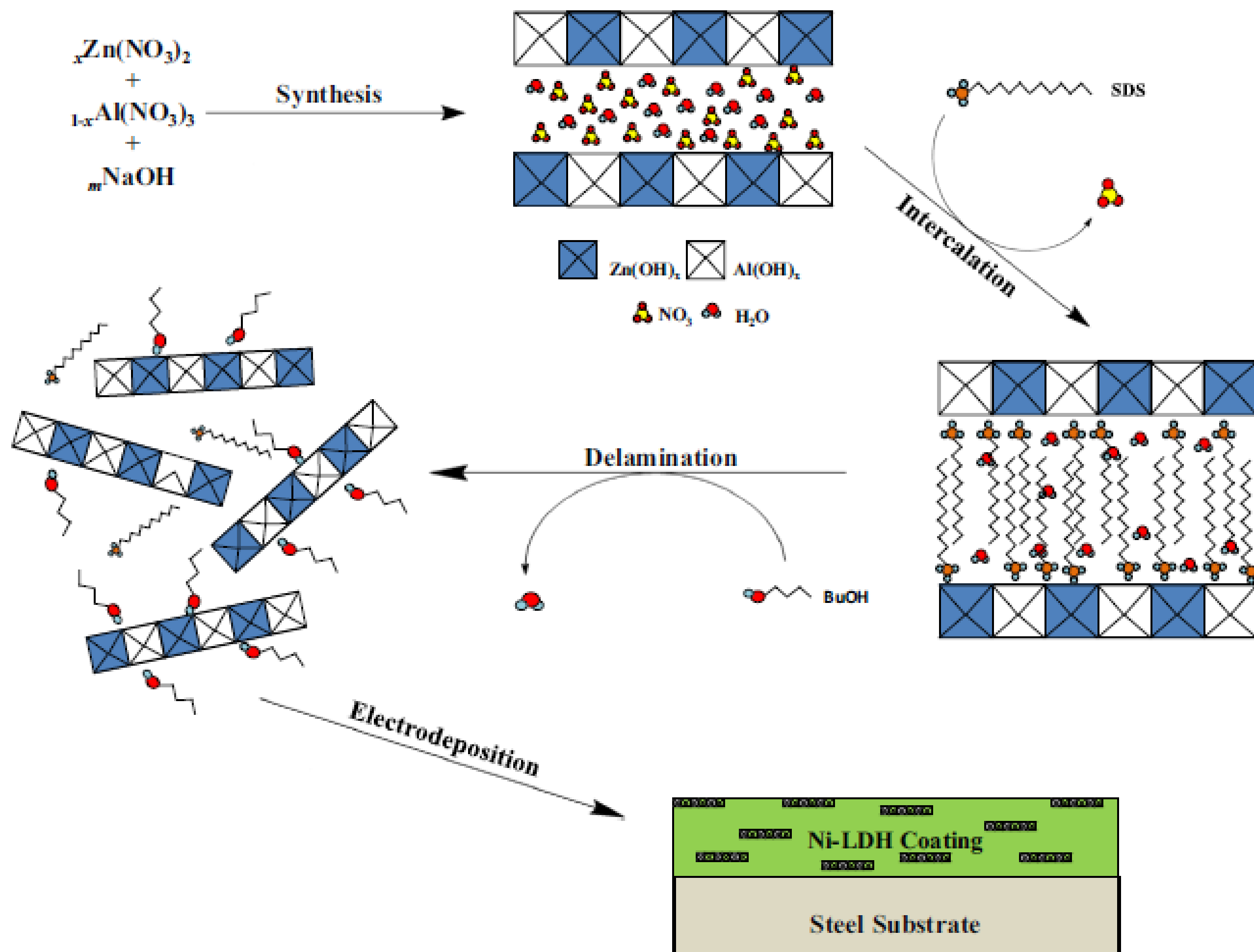


Fig. 1. Overview of the layered double hydroxide colloid synthesis and Ni-LDH metal matrix nanocomposite coating process.

Golden at al

Application of Diffraction Data

Table 2
Crystallite size and strain measured from Williamson-Hall analysis and results of relative texture coefficient analysis of the XRD patterns of Ni and Ni-LDH coatings.

	Crystallite size (nm)	Strain	RTC_{111}	RTC_{200}	RTC_{220}	RTC_{311}
B1	37.54 ± 27	0.0228 ± 0.013	10.04 ± 5.5	5.84 ± 2.2	75.93 ± 9.0	8.19 ± 1.5
B2	60.20 ± 21	0.0192 ± 0.001	9.86 ± 6.0	8.66 ± 4.6	72.36 ± 12.0	9.12 ± 2.0
BL1	41.16 ± 2	0.0120 ± 0.007	6.25 ± 0.2	3.40 ± 1.0	84.94 ± 4.5	5.41 ± 3.3
BL2	25.10 ± 6	0.0158 ± 0.017	8.22 ± 1.8	5.88 ± 3.3	78.91 ± 8.6	6.99 ± 3.7

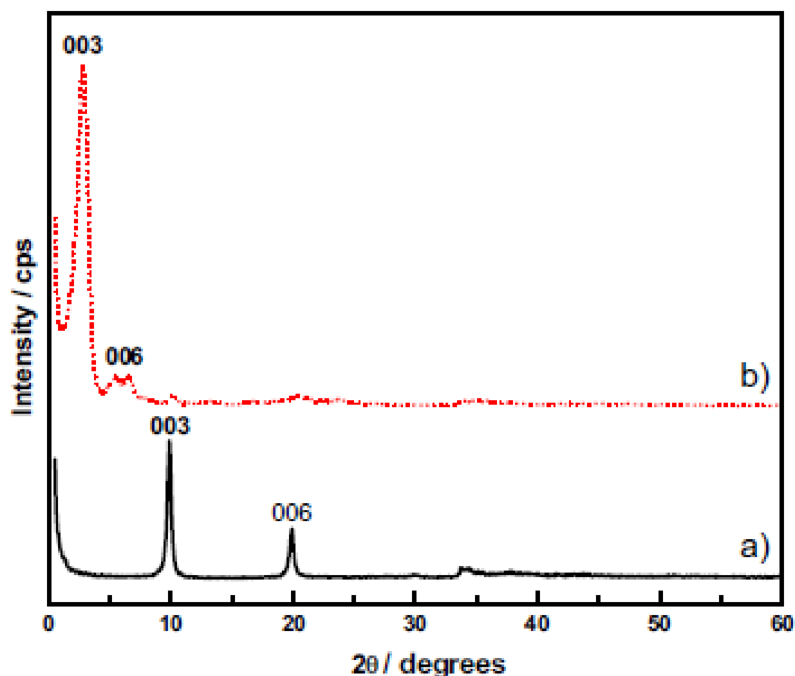


Fig. 3. Powder XRD patterns of a) LDH-NO_3 (solid line), and b) LDH-DS (dotted line) powders.

Application of Diffraction Data

Relative Texture Coefficient (RTC) Example: Golden et.al.

$$RTC_{hkl} = \frac{I_{p,hkl}/I^{\circ}_{p,hkl}}{\sum I_{p,hkl}/I^{\circ}_{p,hkl}} \times 100\%$$

where Ip,hkl is the intensity of the peak for each sample at (111), (200), (220), and (311) reflections and $I°$p,hkl is the intensity of those reflections for the nickel standard reference (PDF# 00-004-0850)

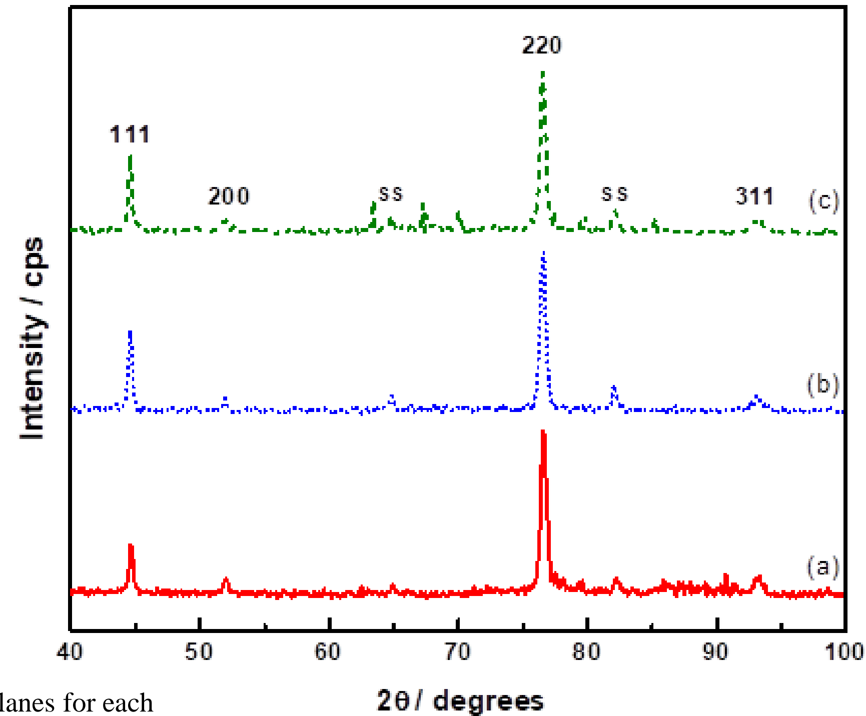


Table 2: Relative texture coefficients for (111), (200), (220), and (311) growth planes for each sample as measured with XRD.

Sample	RTC_{111}	RTC_{200}	RTC_{220}	RTC_{311}
A1	5.26	4.85	72.32	17.66
B1	8.09	4.32	71.84	15.74
B2	7.80	4.27	72.66	15.26

Application of Diffraction Data

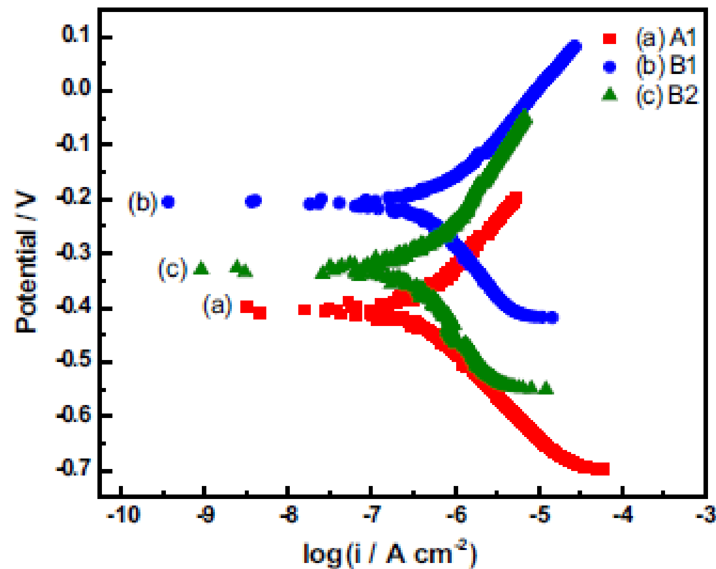


Fig. 7 Tafel polarization curves for each coating *a* A1 (*squares*), *b* B1 (*circles*), and *c* B2 (*triangles*) run in 3.5% NaCl after 14 days immersion in 3.5% NaCl

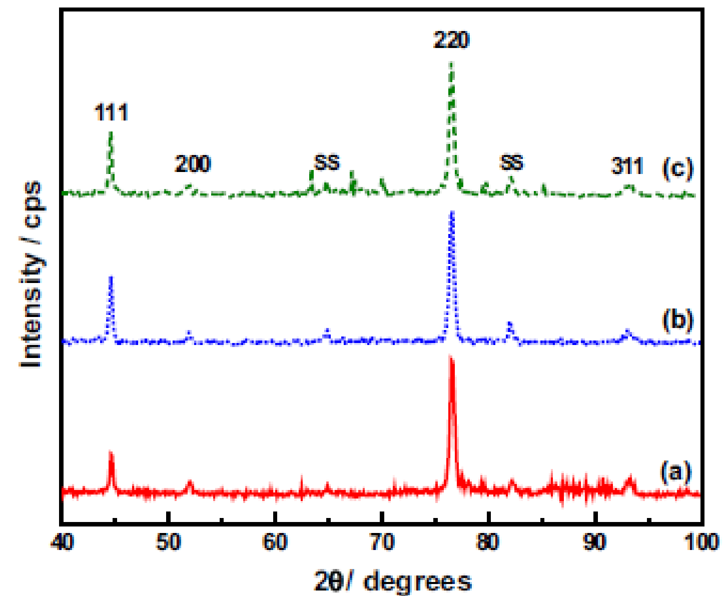


Fig. 2 X-ray diffraction patterns of each nickel coating *a* A1 (*solid line*), *b* B1 (*dotted line*), and *c* B2 (*dashed line*)

Table 2 Relative texture coefficients for (111), (200), (220), and (311) growth planes for each sample as measured with XRD

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Application of Diffraction Data

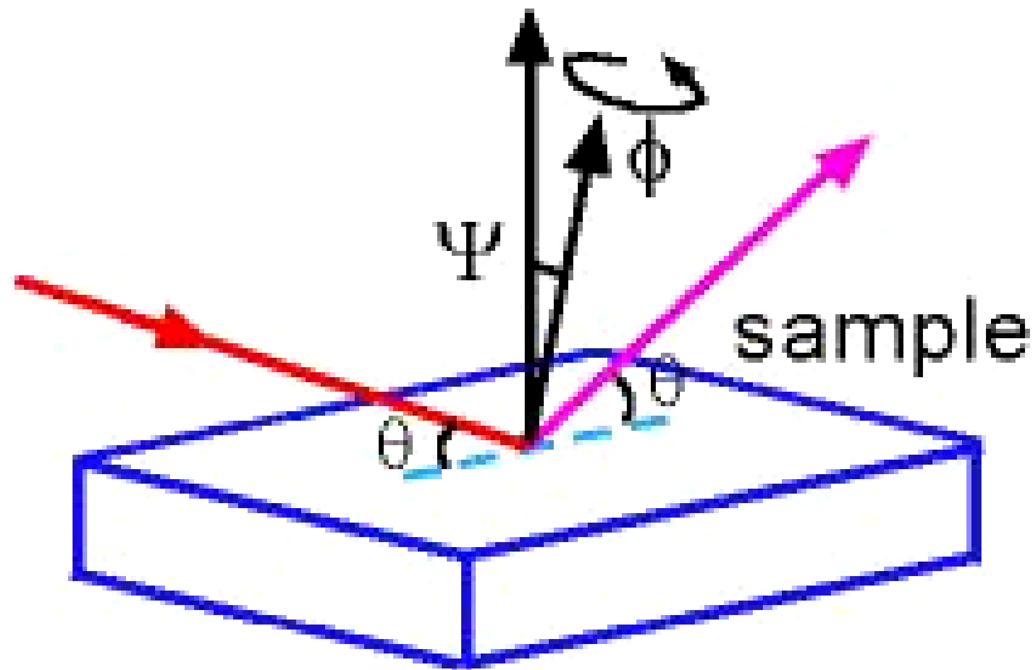
Pole Figure Analysis

Texture Analysis Experiment

Measurement of texture (the non-random or preferred orientation of crystallites) involves measurement of the variations in intensity of a single Bragg reflection as the sample is both tilted (psi) and rotated (phi).

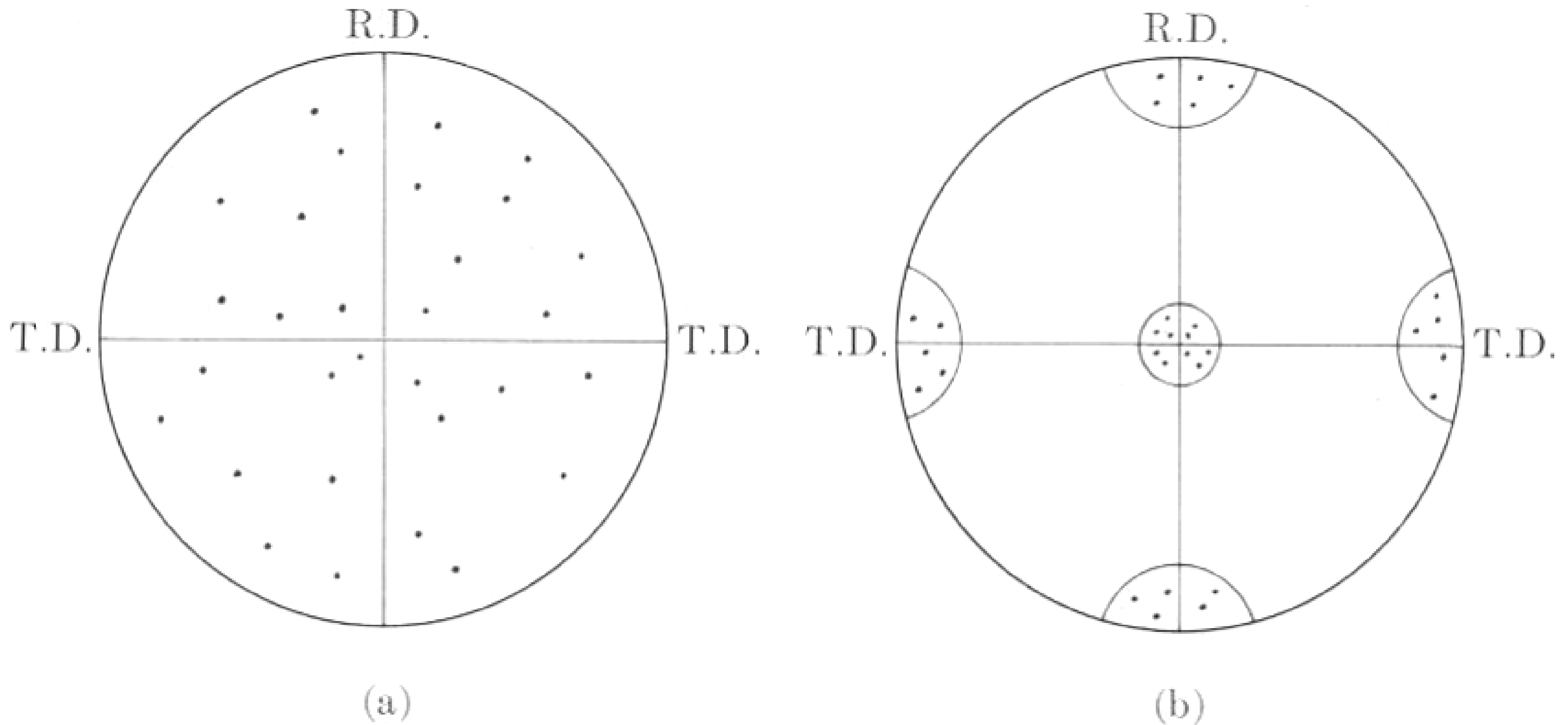
The result is plotted as a 'pole figure', in which the contours indicate intensity levels as a function of sample orientation.

Application of Diffraction Data



Pole Figure Measurement

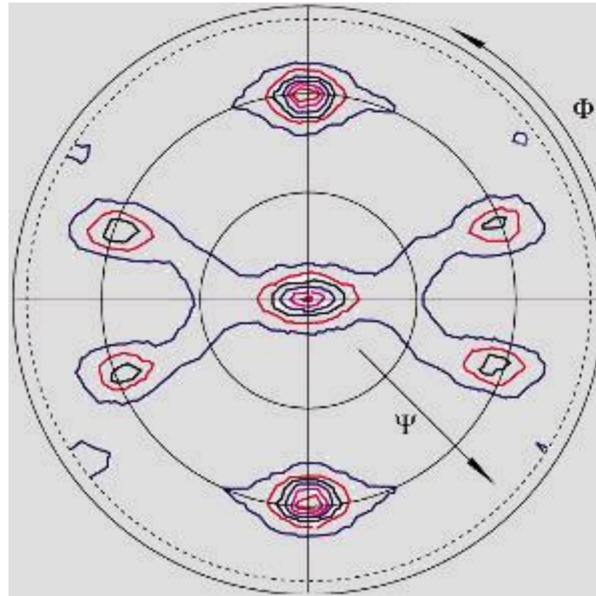
Application of Diffraction Data



(100) pole figures for a sheet material
(a) Random orientation (b) Preferred orientation

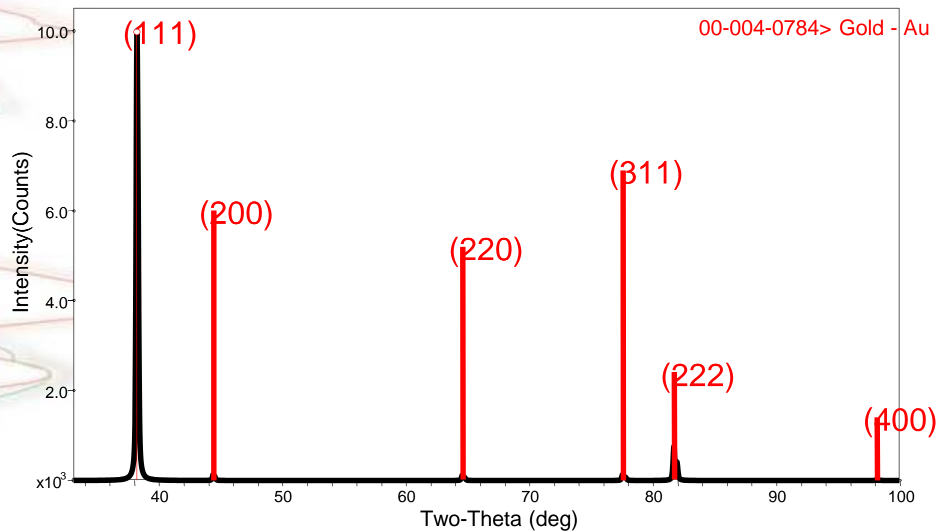
Application of Diffraction Data

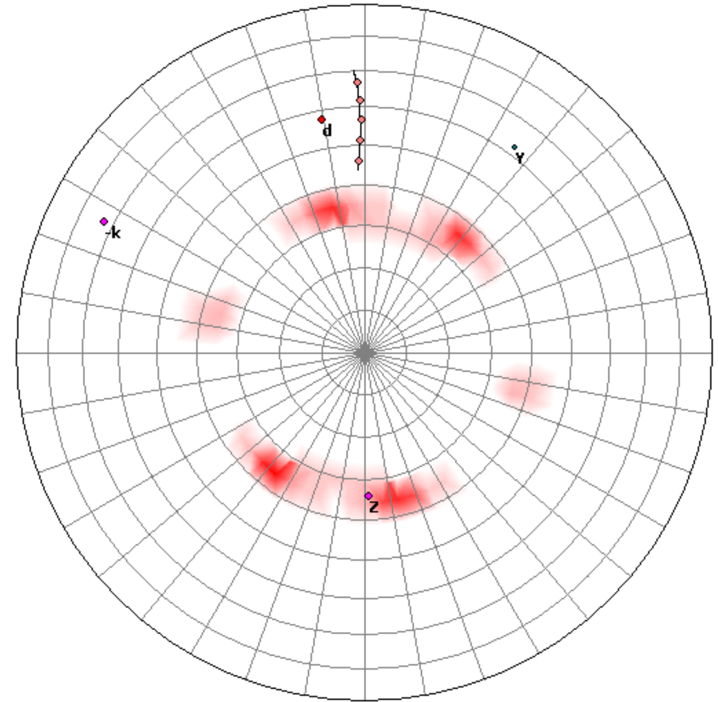
Texture Analysis



Application of Diffraction Data

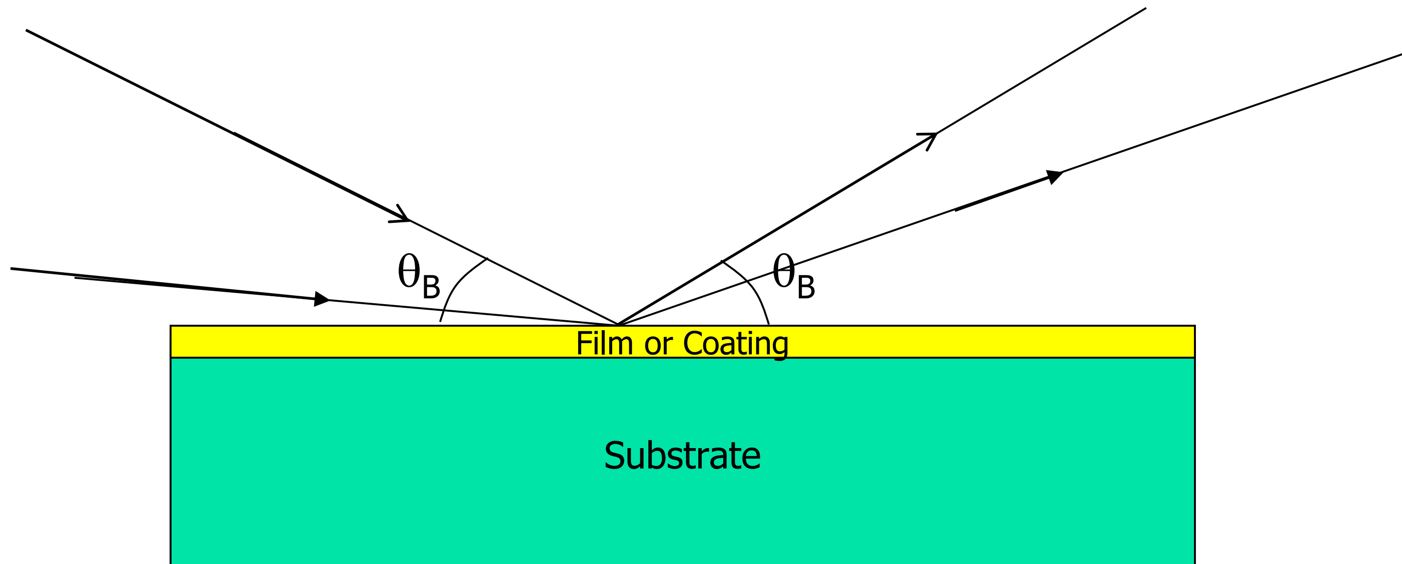
Texture Analysis





Application of Diffraction Data

Thin Film Analysis



Example – thin films grown epitaxially on top of a substrate.

Application of Diffraction Data

Epitaxial Films

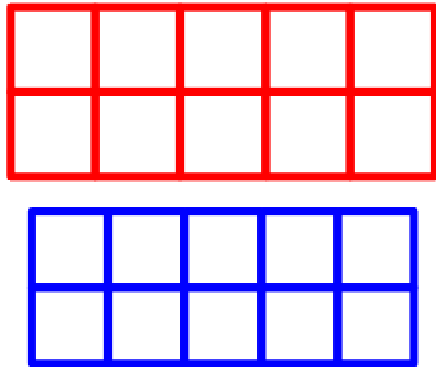
An epitaxial film is a lattice-matched thin film grown on usually a single crystal substrate

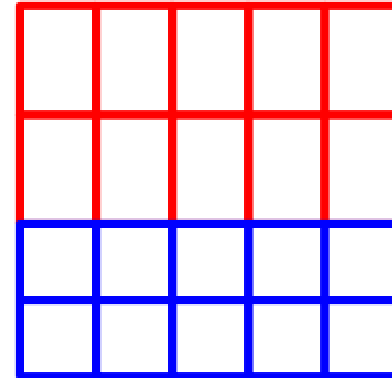
- **The lattice of the film is nearly identical to the lattice of the substrate**
- **When the film grows, its lattice changes (strains) in order to match the lattice of the substrate**
- **The atomic bonding across the substrate and film is "perfectly" matched**

Application of Diffraction Data

Epitaxial Films

An epitaxial film is a lattice-matched thin film grown on usually a single crystal substrate





The lattice of the film (red) is almost the same as the substrate (blue)

The lattice of the epitaxial film (red) distorts to minimize the strain energy where it bonds to the substrate (blue)

Application of Diffraction Data

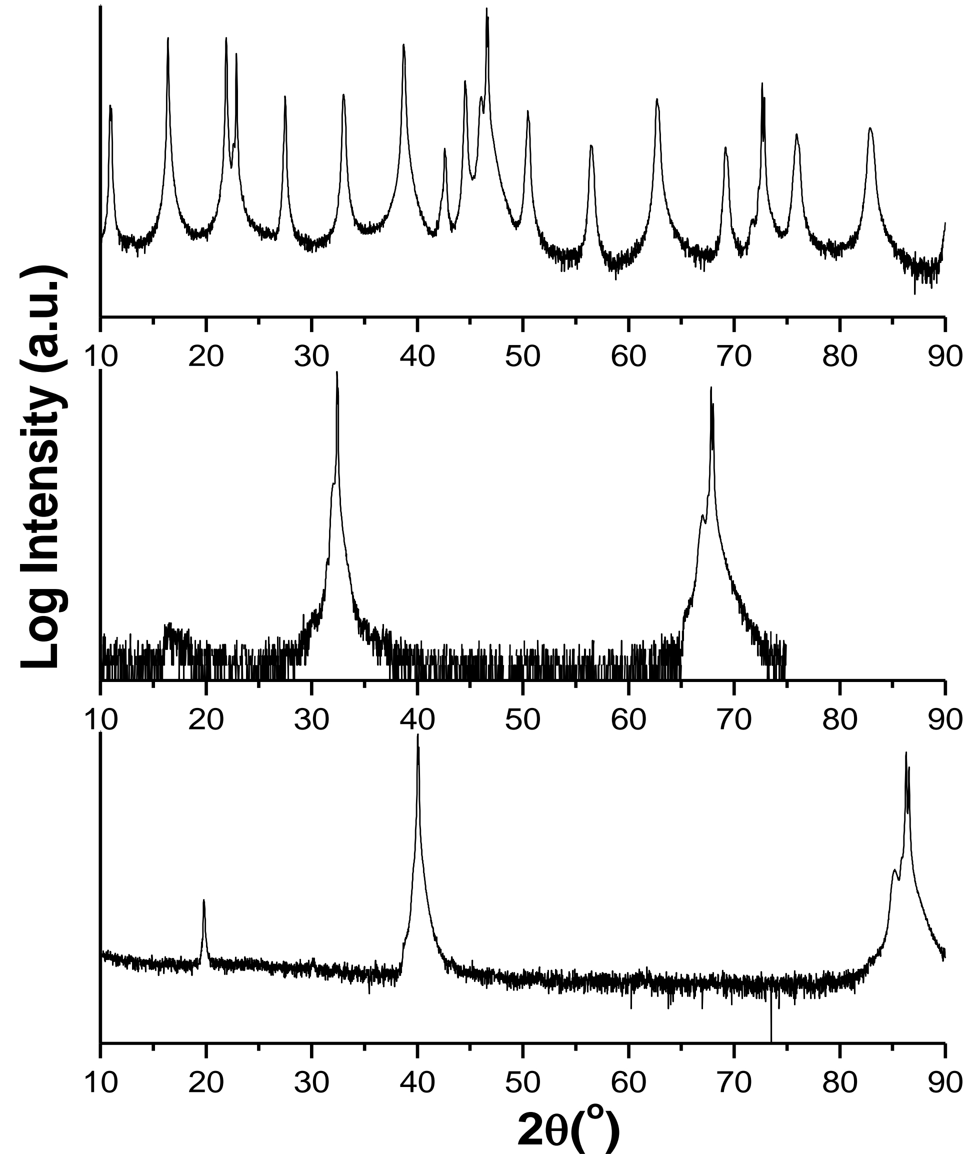
Example:

Bismuth Titanate thin films on oriented $SrTiO_3$ substrates

Only one type of peaks

It apparent that films are highly oriented

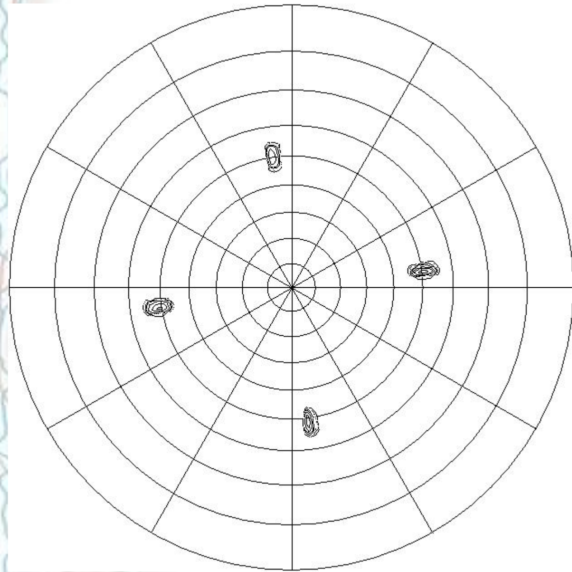
3 different examples



Application of Diffraction Data

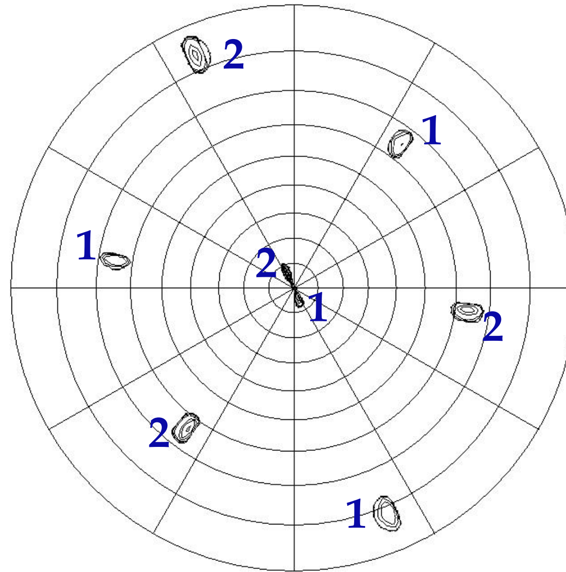
Pole Figure Analysis

$SrTiO_3$ (100)



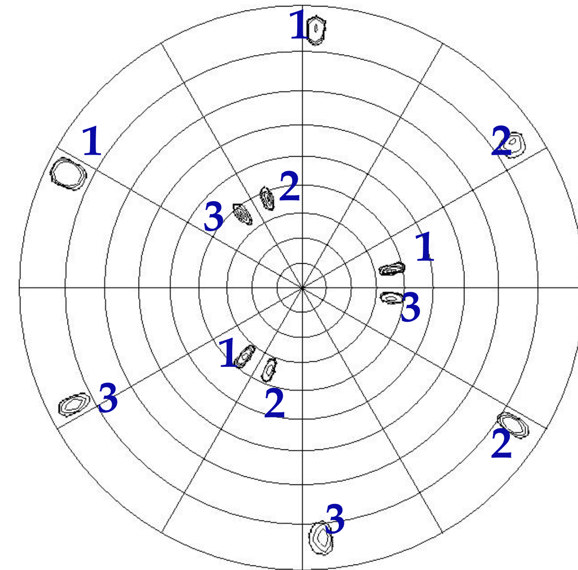
- 4 Peaks at ~50°
- Excellent in-plane orientation

$SrTiO_3$ (110)



- 2 sets of peaks at ~ 5, 65 and 85°
- Indicating a doublet or opposite twin growth

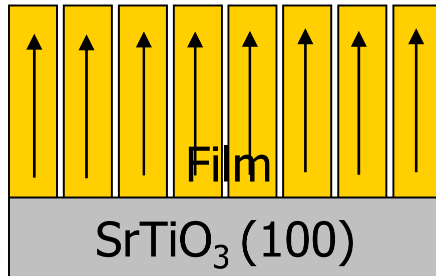
$SrTiO_3$ (111)

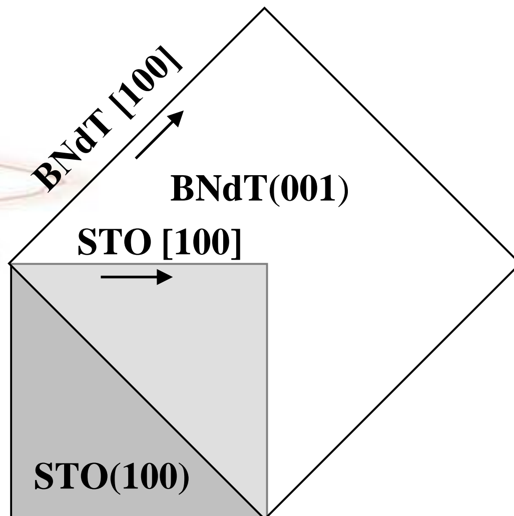


- 3 sets of peaks at ~ 35 and 85°
- indicating a triplet or triple twin growth

Application of Diffraction Data

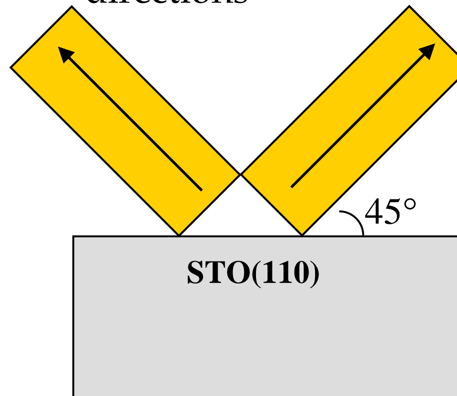
Texture Analysis Evolution





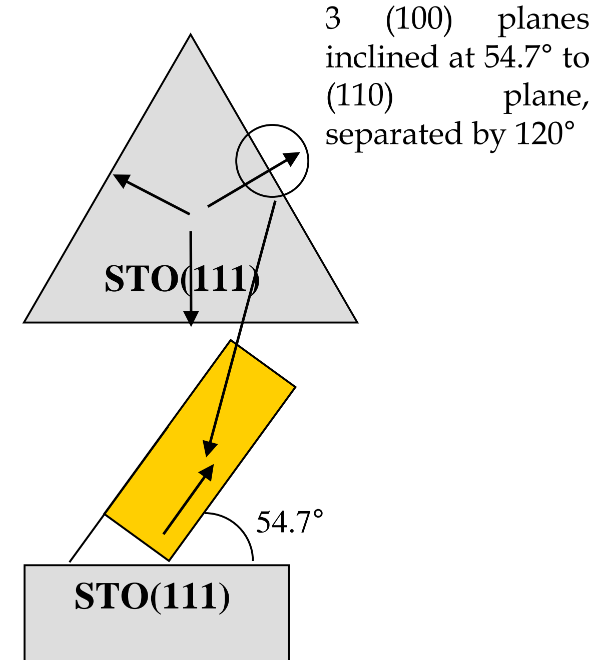
BNdT/SrTiO3 (100)

Two (100) planes inclined at 45° to (110) plane in opposite directions



BNdT/SrTiO$_3$ (110)

3 (100) planes inclined at 54.7° to (110) plane, separated by 120°



BNdT/SrTiO$_3$ (111)

Application of Diffraction Data

Rocking Curves

A useful method for evaluating the quality of oriented samples such as epitaxial films.

RC measurement reveals broadening of the diffraction peaks. The increase in the peak widths can be caused by:

-Mosaicity (misorientation of crystallites)

-Strain

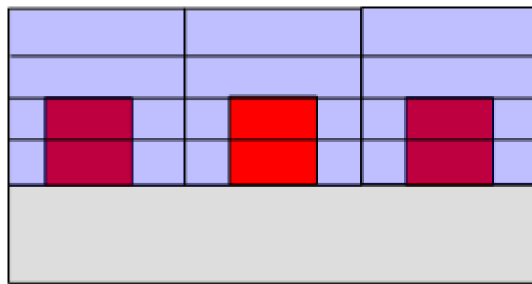
-Limited layer thickness

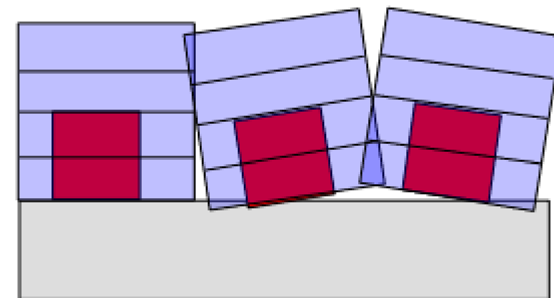
Application of Diffraction Data

Epitaxial Films – Mosaic Spread

Mosaicity is created by slight misorientations of different crystals as they nucleate and grow on the substrate.

When the crystals join, they form low energy domain boundaries.





Ideal case, each nuclei (red) is perfectly oriented. When the crystals grow and meet, there is perfect bounding between the crystallites and therefore there is no grain boundary

If the nuclei (red) are slightly misaligned, then low angle domain boundaries will be formed.

Application of Diffraction Data

Rocking Curves

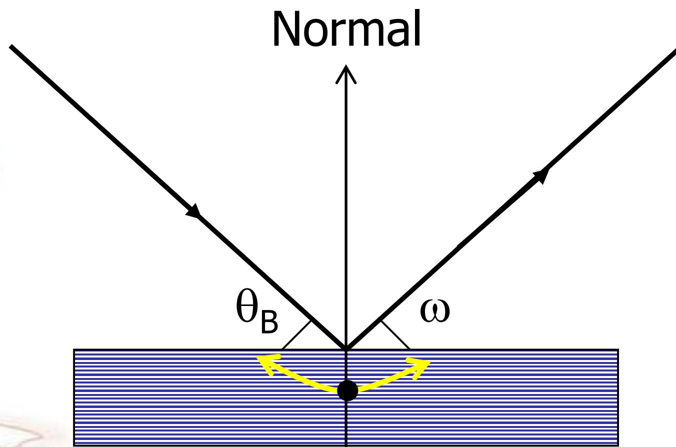
Typically XRD peak width is quantitatively described by Full-Width-at Half-Maximum (FWHM).

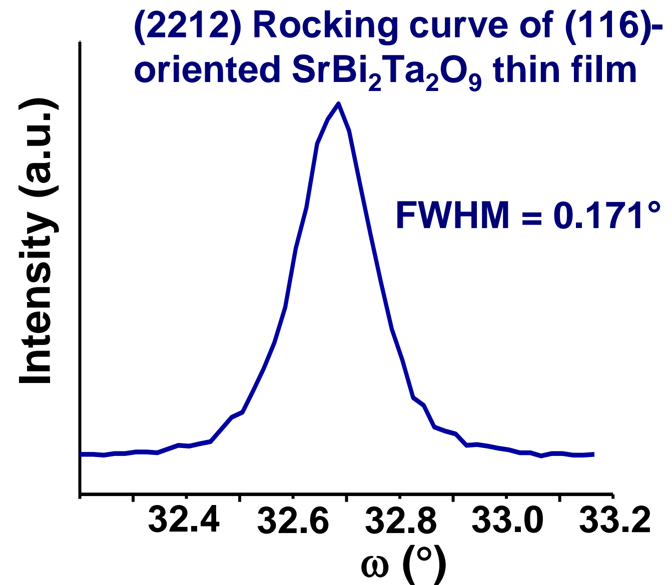
ω is changed by rocking the sample but θ_B is held constant

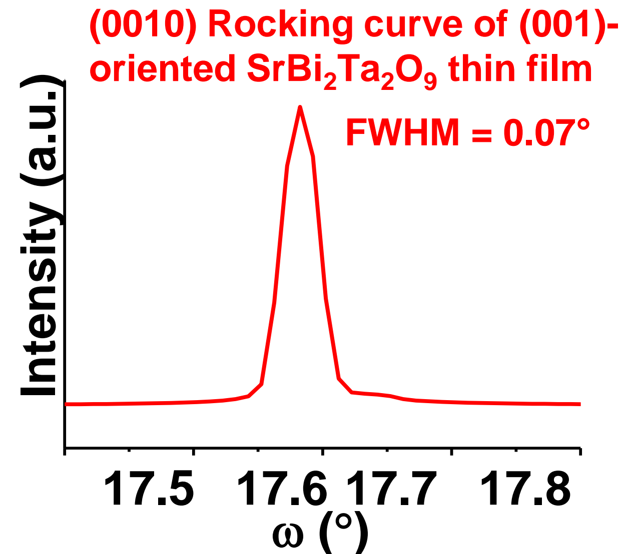
Width of Rocking curve is a direct measure of the range of orientation present in the irradiated area of the crystal

Application of Diffraction Data

Rocking Curves







Summary

Perfect Epitaxy	Single crystal film in perfect registry with a substrate. There are no defects in the film or the substrate.
Nearly perfect epitaxy	Single crystal film in nearly perfect registry with a substrate. Both film and substrate contain a low concentration of defects. Most defects are dislocations in the film.
Textured epitaxial*	Film consists of mosaic domains in nearly perfect registry with the substrate. All domain boundaries are very low angle/low energy. There is nearly perfect bonding across domain boundaries.
Strongly textured polycrystalline	Film consists of grains with nearly perfect preferential orientation of all principle axes. This orientation is often strongly correlated to the substrate. Misorientation parameter for texture is small.
Textured polycrystalline	Film consists of grains with a preferred orientation for 3 principle axes or only along 1 axis out-of-plane.
Polycrystalline	Film consists of randomly oriented grains.
Amorphous	Film does not have long-range crystalline order.

Application of Diffraction Data

Summary

	Thickness	Composition	Lattice Strain/ Relaxation	Defects	Orientation	Residual Stress	Crystallite Size
Perfect Epitaxy	XRR, HRXRD	HRXRD, RC	Assume 100%	Assume none	HRXRD	--	--
Nearly perfect epitaxy	XRR, HRXRD	HRXRD, RC	HRXRD	RC	HRXRD	--	--
Textured epitaxial*	XRR, HRXRD	HRXRD	HRXRD, IP-GIXD	RC	HRXRD	--	--
Strongly textured polycrystalline	XRR	XRPD, IP-GIXD	IP-GIXD	XRPD, IP-GIXD	IP-GIXD, PF	IP-GIXD	XRPD, IP-GIXD
Textured polycrystalline	XRR	XRPD, GIXD or IP-GIXD	--	XRPD, GIXD OR IP-GIXD	PF	Psi	XRPD, GIXD
Polycrystalline	XRR	XRPD, GIXD	--	XRPD, GIXD	PF	Psi	XRPD, GIXD
Amorphous	XRR	--	--	--	--	--	--

XRR- X-Ray Reflectivity
HRXRD- High Resolution XRD using coupled scan or RSM

RC- Rocking Curve
XRPD- Bragg-Brentano powder diffraction
GIXD- grazing incidence XRD

IP-GIXD- in-plane grazing incidence XRD
PF- pole figure
Psi- $\sin^2$psi using parellel beam

Application of Diffraction Data

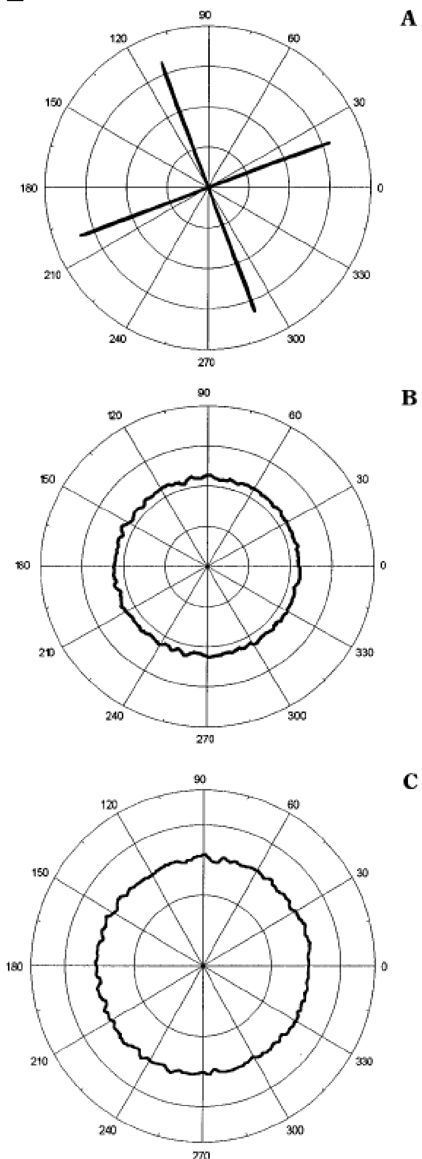


Figure 7. Rotational scans for (A) [100] silicon single crystal, (B) silicon powder, and (C) a 5 μm thick [100] Tl_2O_3 film. X-ray diffraction is from the {111} planes.

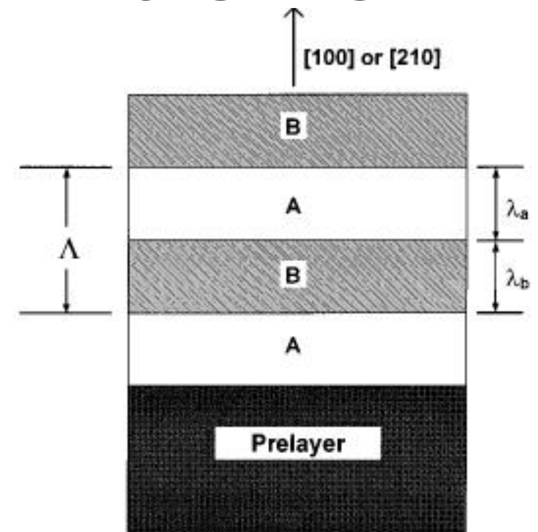


Figure 8. Idealized superlattice grown on an oriented prelayer. The orientation of the prelayer is maintained through the superlattice. The thickness of layer a is λ_a, and the thickness of layer b is λ_b.

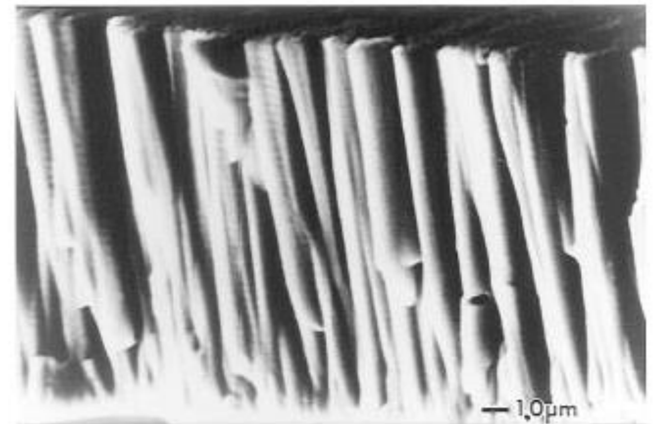


Figure 9. Scanning electron micrograph of an electrodeposited columnar superlattice structure. The individual layer thicknesses are approximately 0.5 μm. The bar marker is 1.0 μm.

Application of Diffraction Data

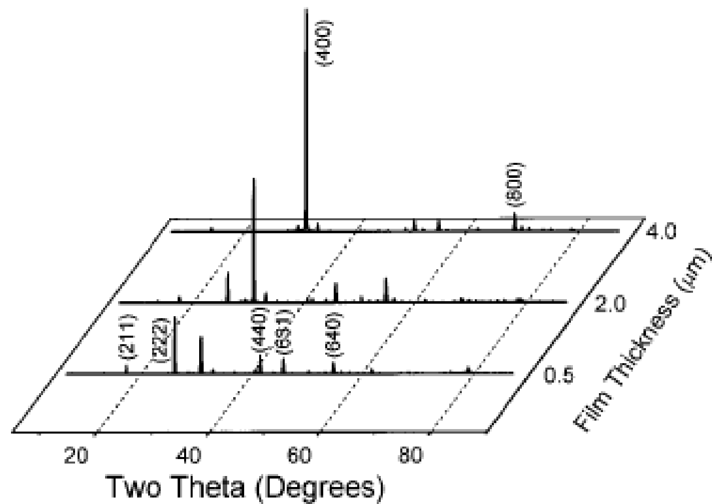


Figure 3. Dependence of the prelayer texture on the film thickness for a Tl_2O_3 prelayer. The texture increased with film thickness. A current density of 5 mA/cm^2, and a stirred solution of 0.1 M $TlNO_3$ in 5 M NaOH was used to deposit the prelayers.

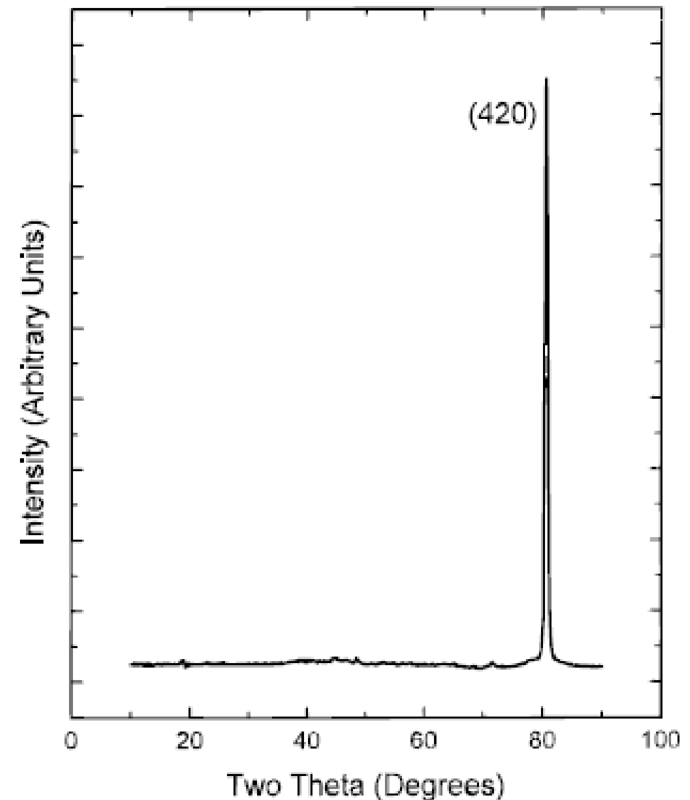


Figure 4. Highly oriented 20 μm Pb−Tl−O prelayer with a [210] texture. A current density of 5 mA/cm^2, and a stirred solution of 0.005 M $TlNO_3$, 0.1 M $Pb(NO_3)_2$ in 5 M NaOH was used to deposit the Pb−Tl−O film.

Application of Diffraction Data

XRD can be used for:

-Bravais lattice determination – phase determination (crystalline phases and orientation)

-Lattice parameter determination

-Determination of solvus line in phase diagrams (order-disorder transformation)

-Long range order (Texture Analysis)

-Crystallite size and Strain

-Temperature factor – thermal diffuse scattering (thermal expansion)

-Thickness measurements of thin films and multilayers

Application of Diffraction Data

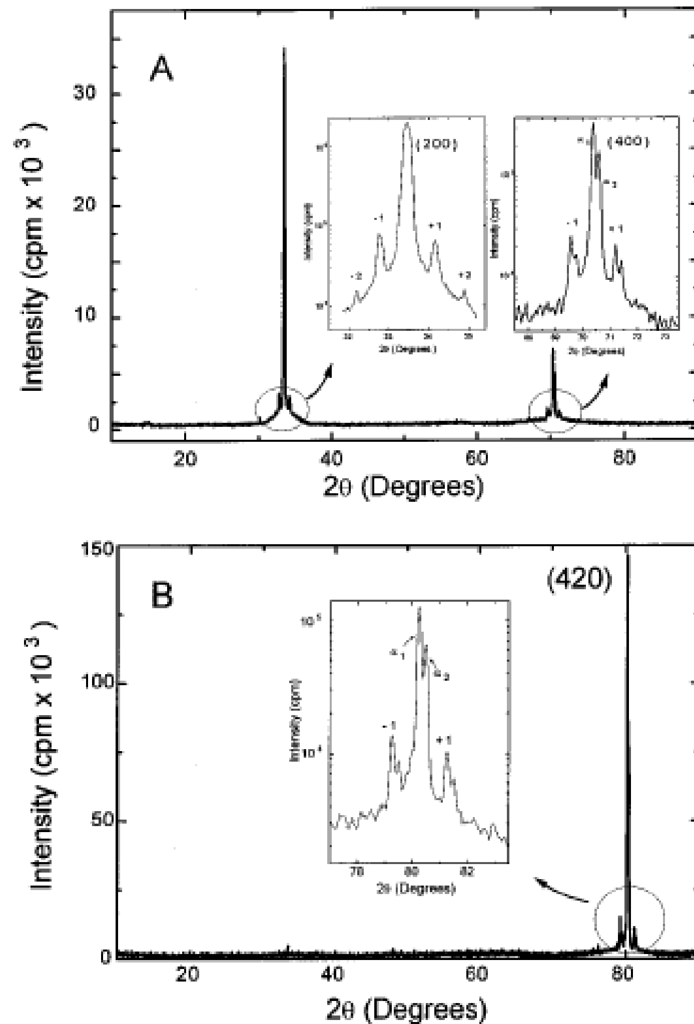


Figure 12. (A) [100]-textured superlattice in the Pb–Tl–O system. The modulation wavelength was calculated as Λ_F = 13.2 nm by Faraday's law and measured by X-ray diffraction as Λ_x = 13.3 nm. (B) [210]-textured superlattice with Λ_F = 12 nm and Λ_x = 11.8 nm. Both superlattices were deposited by pulsing the current between 0.05 mA/cm² (82 s) and 5 mA/cm² (1.2 s).

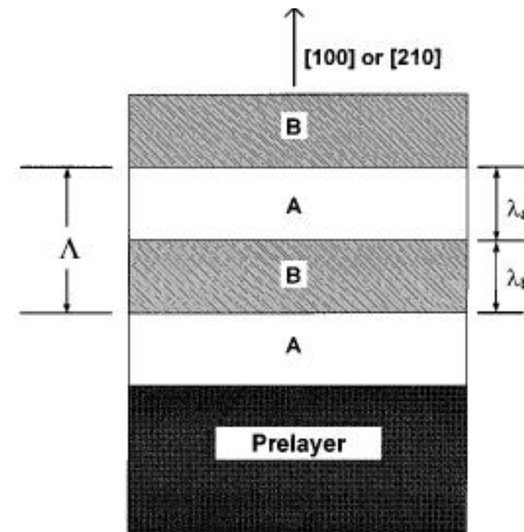


Figure 8. Idealized superlattice grown on an oriented prelayer. The orientation of the prelayer is maintained through the superlattice. The thickness of layer a is λ_a, and the thickness of layer b is λ_b.

Application of Diffraction Data

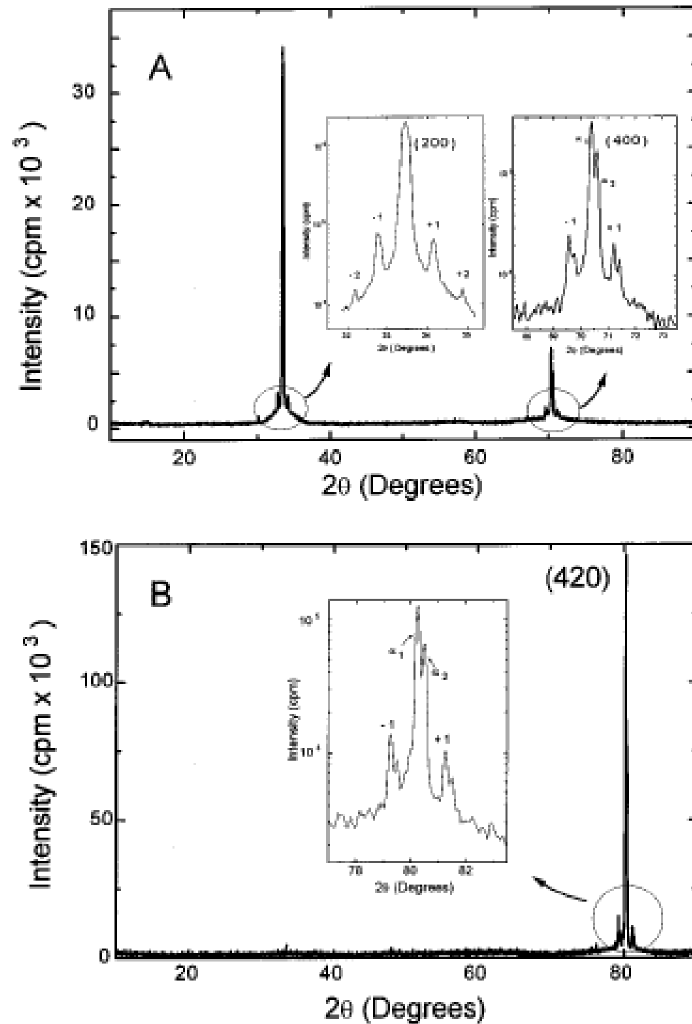


Figure 12. (A) [100]-textured superlattice in the Pb–Tl–O system. The modulation wavelength was calculated as Λ_F = 13.2 nm by Faraday's law and measured by X-ray diffraction as Λ_x = 13.3 nm. (B) [210]-textured superlattice with Λ_F = 12 nm and Λ_x = 11.8 nm. Both superlattices were deposited by pulsing the current between 0.05 mA/cm² (82 s) and 5 mA/cm² (1.2 s).

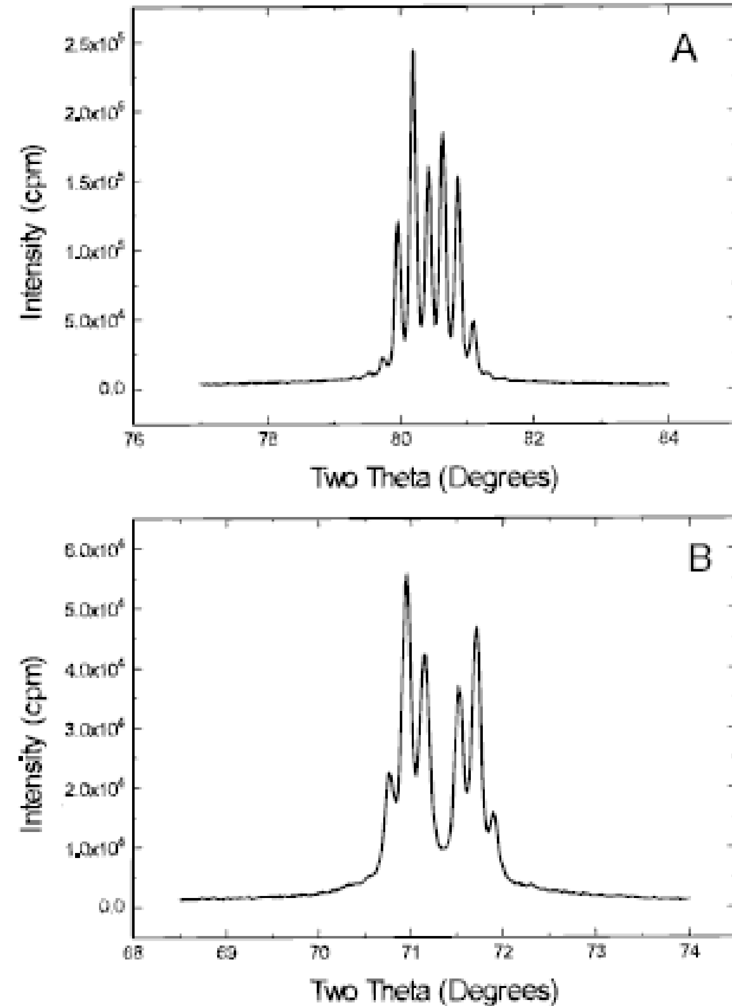
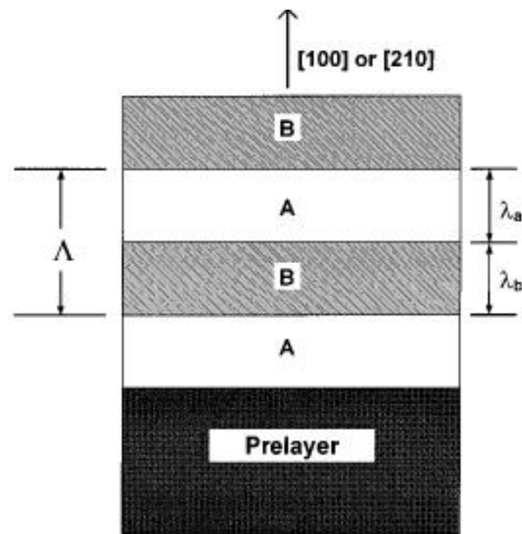


Figure 14. (A) X-ray diffraction pattern of a [210]-textured superlattice in the Pb–Tl–O system using Cu Kα radiation as the X-ray source. The modulation wavelength was calculated as Λ_F = 50 nm by Faraday's law. (B) Same as (A), except using Cu Kβ radiation for the X-ray source.

Application of Diffraction Data



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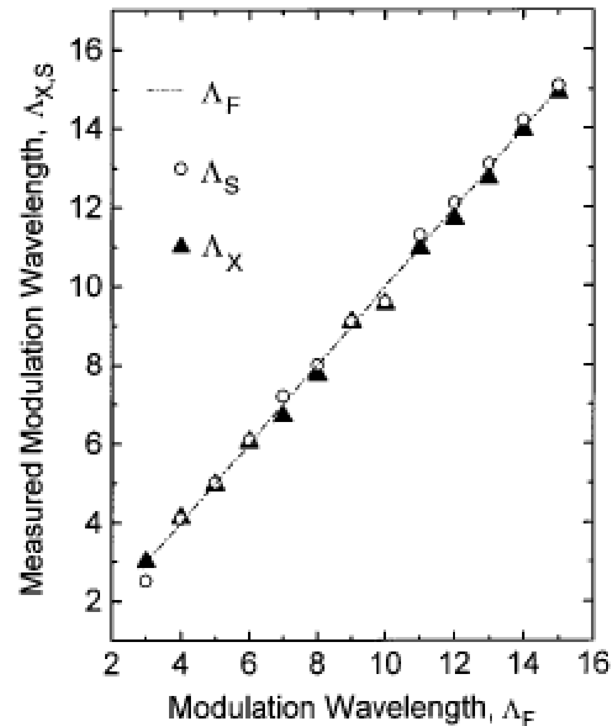

Figure 13. Comparison of the Pb–Tl–O superlattice modulation wavelength in nanometers calculated by Faraday's law (Λ_F) with those measured by scanning tunneling microscopy (Λ_S) and X-ray diffraction (Λ_X).

Homework Assignment: Phase Diagram Calculations

Due Tuesday 11-19-24

Read Chapter 8 from:

-X-ray Diffraction Procedures by Klug and Alexander

Read Chapter 3-7, 9-11 and 13 from:

-Introduction to X-ray powder Diffractometry by Jenkins and Synder

Read Chapter 3, 4, 6, 13, and 14 from

-Elements of X-ray Diffraction by Cullity and Stock

Read Chapter 2 from Norton