



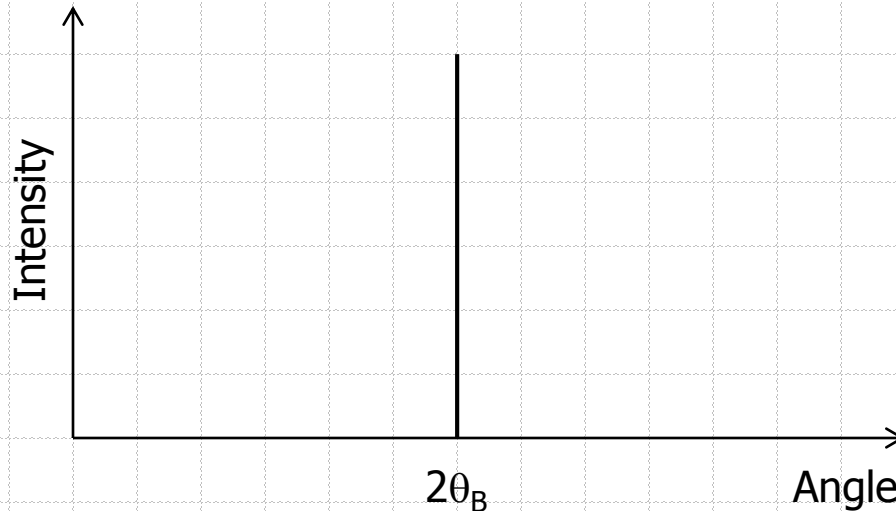
Diffraction: Real Samples Powder Method

Diffraction: Real Samples

- ◆ Up to this point we have been considering diffraction arising from infinitely large crystals that are strain free and behave like ideally imperfect materials (x-rays only scattered once within a crystal)
- ◆ Crystal size and strain affect the diffraction pattern
 - we can learn about them from the diffraction pattern
- ◆ High quality crystals such as those produced for the semiconductor industry are not ideally imperfect
 - need a different theory to understand how they scatter x-rays
- ◆ Not all materials are well ordered crystals

Crystallite Size

- ◆ As the crystallites in a powder get smaller the diffraction peaks in a powder pattern get wider.
- ◆ Consider diffraction from a crystal of thickness t and how the diffracted intensity varies as we move away from the exact Bragg angle
 - If thickness was infinite we would only see diffraction at the Bragg angle



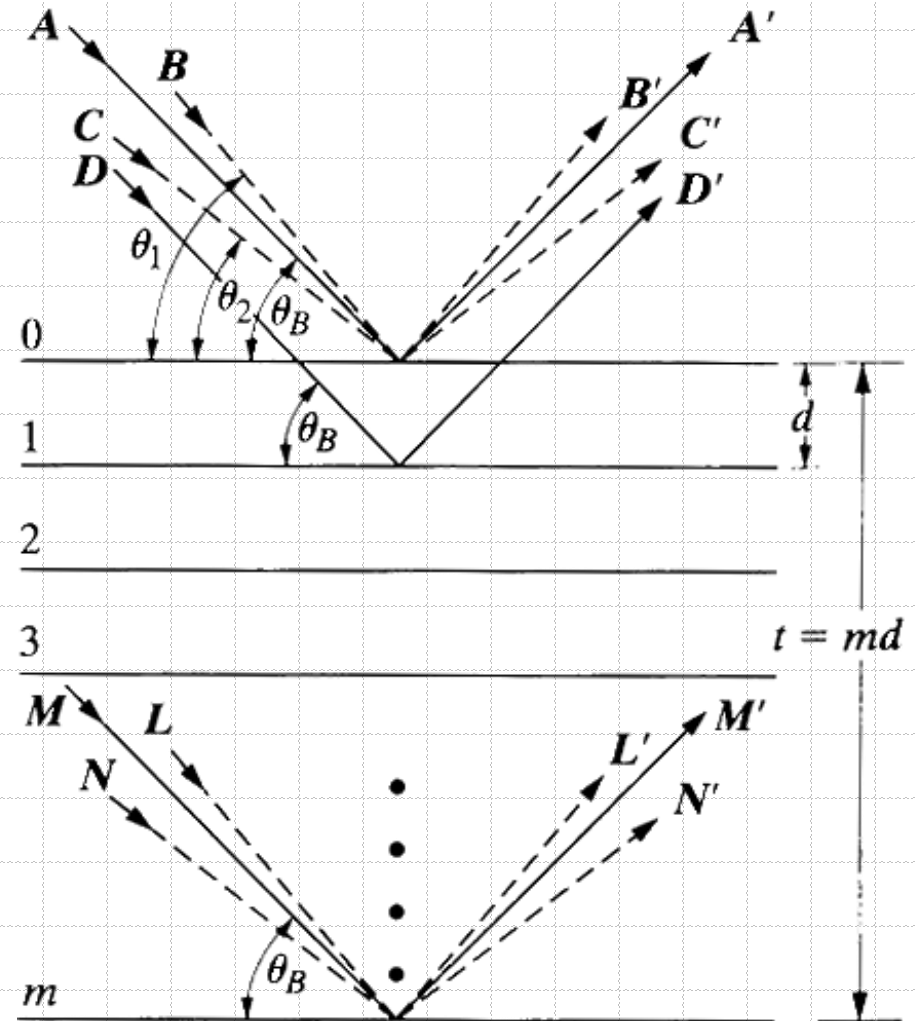
Crystallite Size

Suppose the crystal of thickness t has $(m + 1)$ planes in the diffraction direction.

Let say θ is variable with value θ_B that exactly satisfies Bragg's Law:

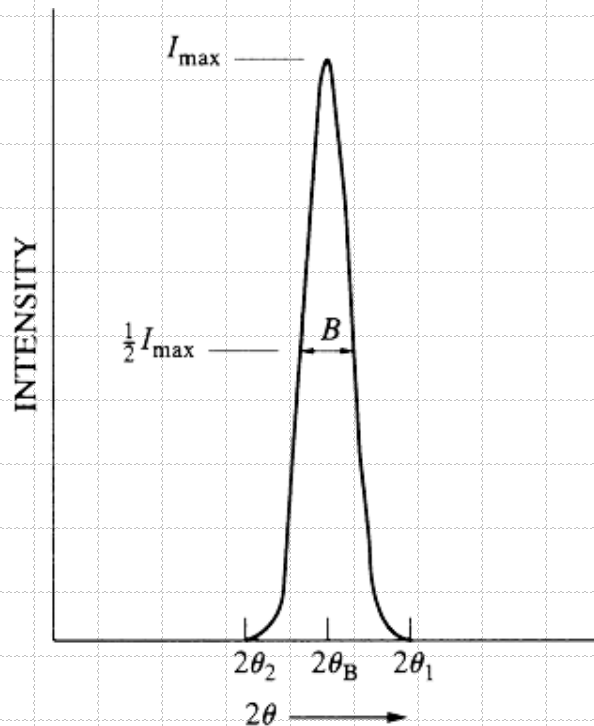
$$\lambda = 2d \sin \theta_B$$

- ◆ Rays **A**, **D**, ..., **M** makes angle θ_B
- ◆ Rays **B**, ..., **L** makes angle θ_1
- ◆ Rays **C**, ..., **N** makes angle θ_2

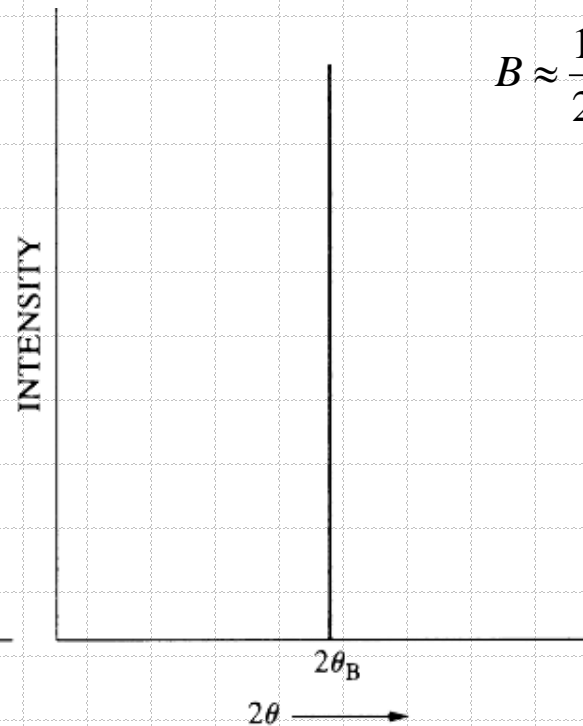


Crystallite Size

- ◆ For angle θ_B diffracted intensity is maximum
- ◆ For θ_1 and θ_2 – intensity is 0.
- ◆ For angles $\theta_1 > \theta > \theta_2$ – intensity is nonzero.



Real case



Ideal case

$$B \approx \frac{1}{2}(2\theta_1 - 2\theta_2) = \theta_1 - \theta_2$$

The Scherrer Equation

$$2t \sin \theta_1 = (m+1)\lambda,$$

$$2t \sin \theta_2 = (m-1)\lambda.$$

Subtracting:

$$t(\sin \theta_1 - \sin \theta_2) = \lambda,$$

$$2t \cos\left(\frac{\theta_1 + \theta_2}{2}\right) \sin\left(\frac{\theta_1 - \theta_2}{2}\right) = \lambda.$$

θ_1 and θ_2 are close to θ_B , so:

$$\theta_1 + \theta_2 \approx 2\theta_B,$$

$$\sin\left(\frac{\theta_1 - \theta_2}{2}\right) \approx \left(\frac{\theta_1 - \theta_2}{2}\right).$$

Thus:

$$2t \left(\frac{\theta_1 - \theta_2}{2}\right) \cos \theta_B = \lambda,$$

$$t = \frac{\lambda}{B \cos \theta_B}$$

The Scherrer Equation

**Instrument broadening
has to be subtracted**

◆ More exact treatment (see *Warren*) gives:

$$t = \frac{0.94\lambda}{B \cos \theta_B}$$

← Scherrer's formula

- Peak width B varies inversely with the crystallite size.
- The proportionality constant, K , is usually 0.94 and is valid for spherical crystals with cubic symmetry when B is taken as full width at half maximum (FWHM).
- The proportionality constant, K , is 0.89 for spherical crystals with cubic symmetry when B is taken as integral breadth.
- K sometimes is rounded up to 1.
- K might vary from 0.62 to 2.08.

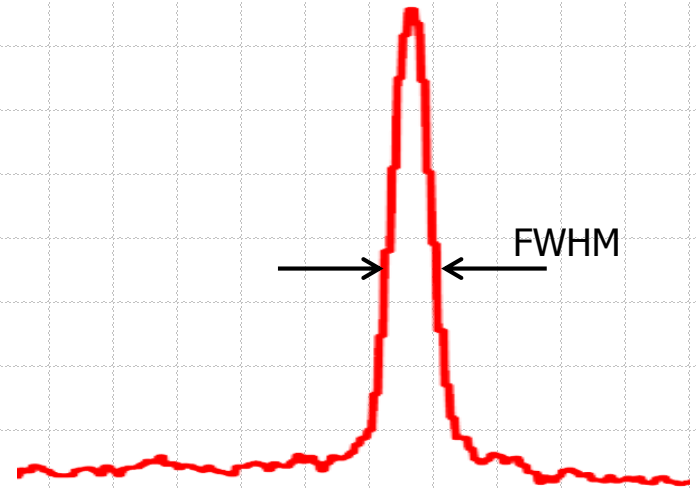
Suppose $\lambda = 1.54 \text{ \AA}$, $d = 1.0 \text{ \AA}$, and $\theta = 49^\circ$:

**for crystal size of 1 mm, $B = 10^{-5}$ deg.
for crystal size of 500 \AA , $B = 0.2$ deg.**

Peak Width

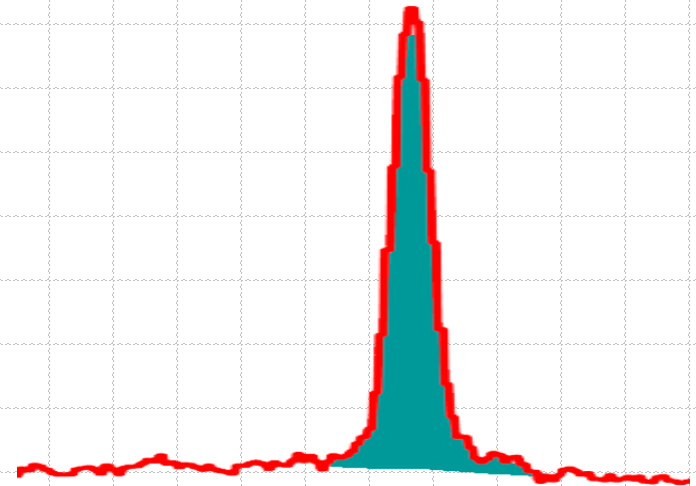
◆ Full Width at Half Maximum (FWHM):

- Width of the peak at half intensity value between background and peak maximum intensity.



◆ Integral Breadth:

- Total area under the peak divided by the peak height.
- Same as the width of a rectangle which has the same area and the same height as the peak



Strain

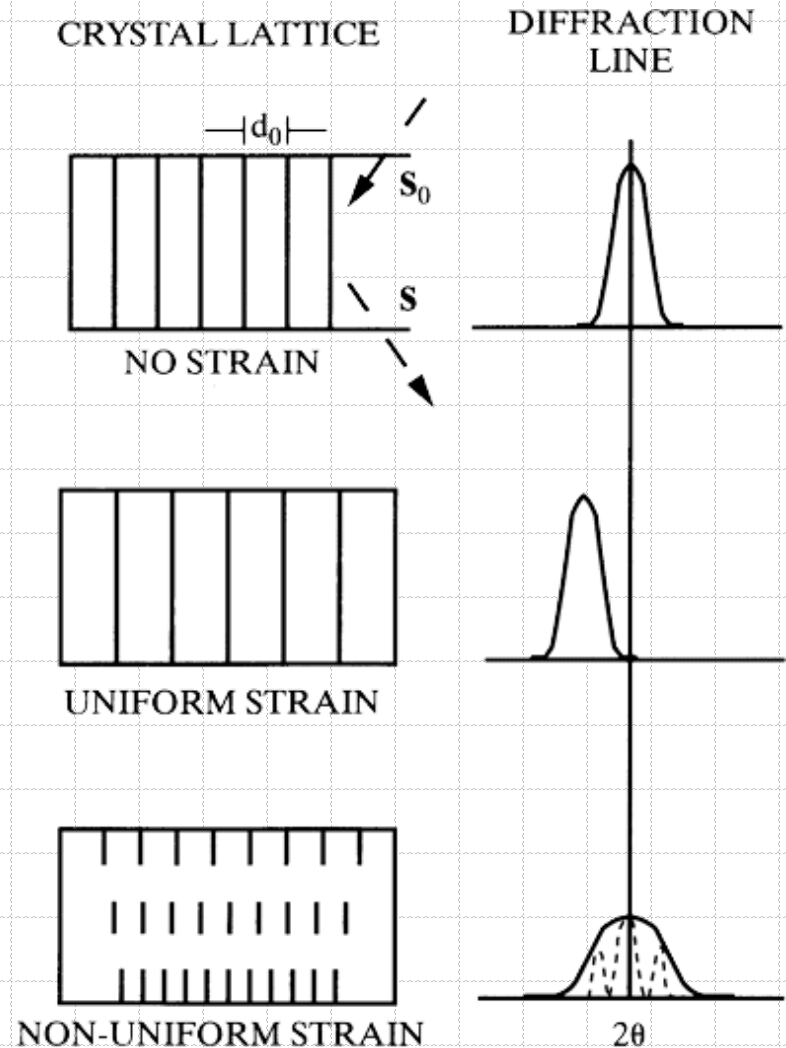
◆ Two types of stresses:

- microstresses – vary from one grain to another on a microscopic scale.
- macrostresses – stress is uniform over large distances.

◆ Usually:

- macrostrain is uniform – produces peak shift
- microstrain is nonuniform – produces peak broadening

$$b = \Delta 2\theta = -2 \frac{\Delta d}{d} \tan \theta$$

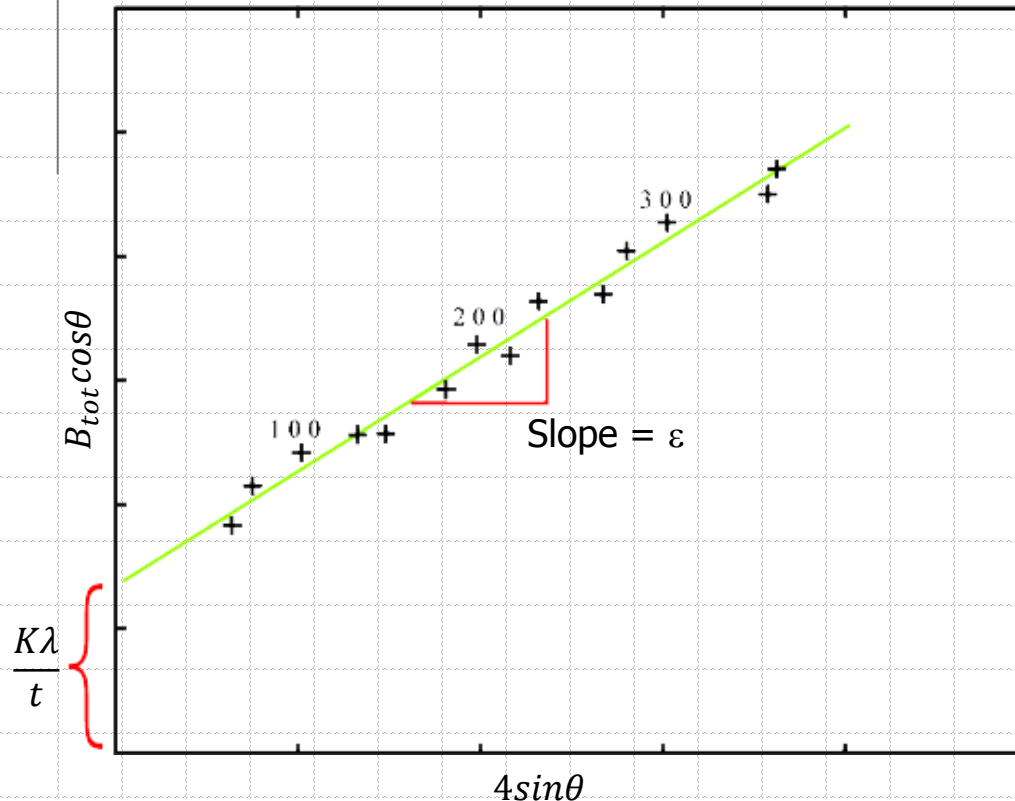


Williamson-Hall Plot

◆ Size broadening (Scherrer equation): $B_t(2\theta) = \frac{K\lambda}{t \cos\theta}$

◆ Strain broadening: $B_\varepsilon(2\theta) = 4\varepsilon \tan\theta$

◆ Convolved broadening: $B_{tot}(2\theta) = B_t(2\theta) + B_\varepsilon(2\theta) = \frac{K\lambda}{t \cos\theta} + 4\varepsilon \tan\theta$



$$B_{tot} \cos\theta = \frac{K\lambda}{t} + 4\varepsilon \sin\theta$$

**Instrument broadening
has to be subtracted**

Corrections for Instrumental Broadening

◆ There is a link between peak width and crystallite size/strain, but other sources of peak broadening have to be considered when analyzing diffraction data

■ Instrumental broadening:

- ◆ slit widths
- ◆ sample size
- ◆ penetration in the sample
- ◆ imperfect focusing
- ◆ unresolved α_1 and α_2 peaks
- ◆ or wavelengths widths where α_1 and α_2 peaks are resolved

◆ To correct for instrumental broadening:

- measure the sample
- measure under the same conditions the standard with unstrained particles large enough to eliminate particle-size broadening

Corrections for Instrumental Broadening

◆ Lorentzian shape:

$$B_{obs} = B_{size} + B_{strain} + B_{inst}$$

$$(B_{obs} - B_{inst}) = B_{size} + B_{strain}$$

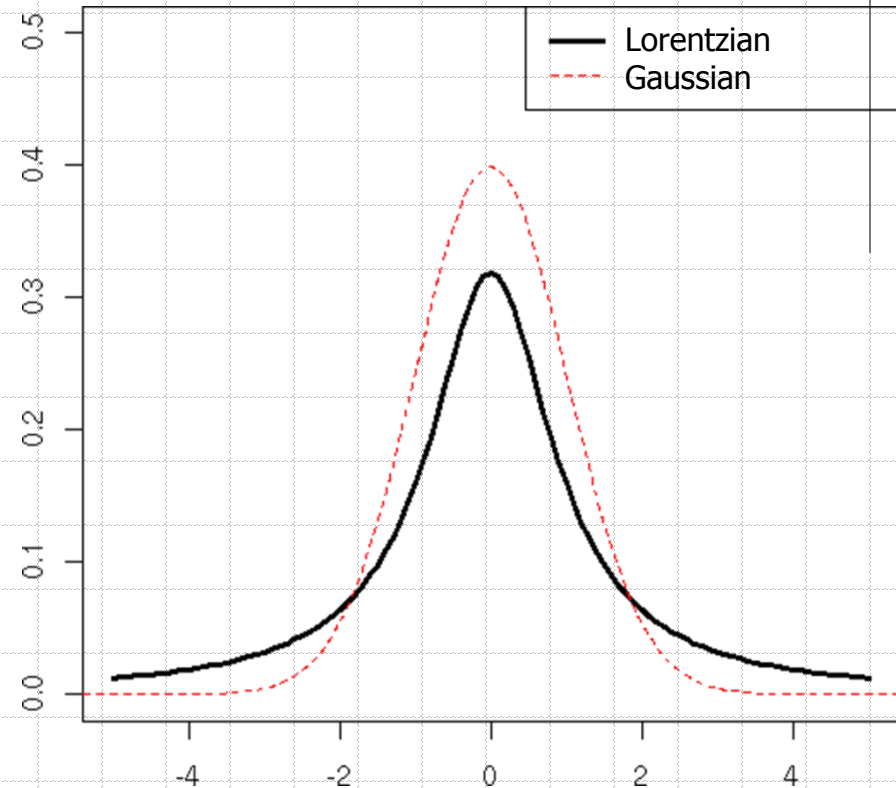
◆ Gaussian shape:

$$B_{obs}^2 = B_{size}^2 + B_{strain}^2 + B_{inst}^2$$

$$(B_{obs}^2 - B_{inst}^2) = B_{size}^2 + B_{strain}^2$$

◆ Voigt, Pseudo-Voigt:

- Deconvolute peaks into Gaussian and Lorentzian fractions and then subtract instrumental broadening.



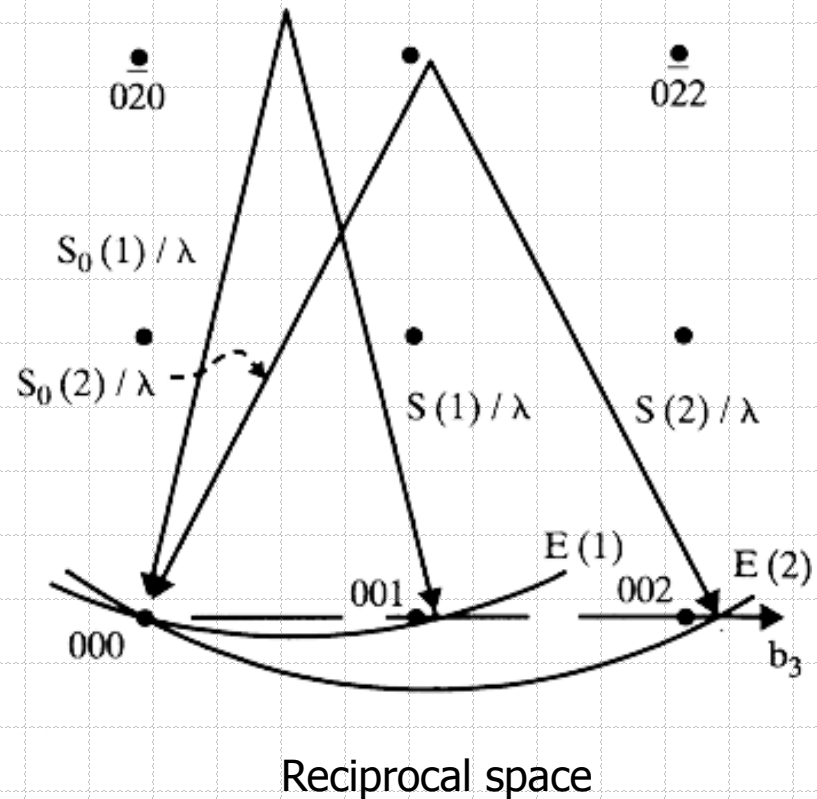
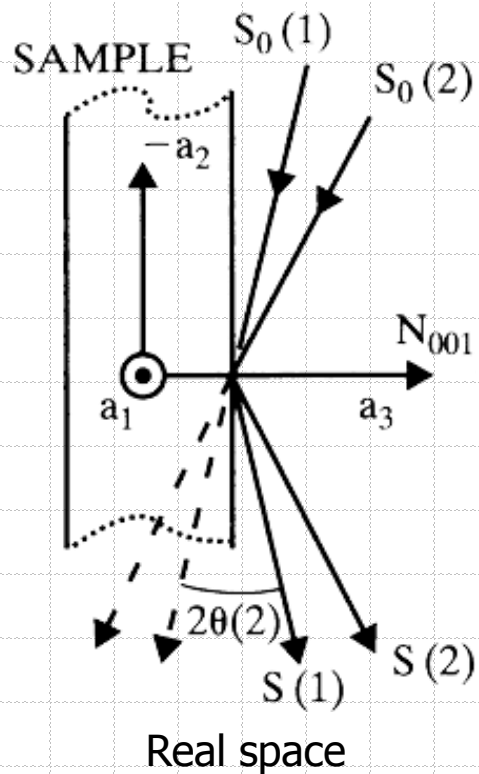
Interference Function

- ◆ We calculate the diffraction peak at the exact Bragg angle θ_B and at angles that have small deviations from θ_B .
- ◆ If crystal is infinite then at $\theta \neq \theta_B$ intensity = 0.
- ◆ If crystal is small then at $\theta \neq \theta_B$ intensity $\neq 0$. It varies with angle as a function of the number of unit cells along the diffraction vector ($\mathbf{s} - \mathbf{s}_0$).
- ◆ At deviations from θ_B individual unit cells will scatter slightly out of phase.
- ◆ Vector $(\mathbf{s} - \mathbf{s}_0)/\lambda$ no longer extends to the reciprocal lattice point (RLP).

$$\frac{(\mathbf{s} - \mathbf{s}_0)}{\lambda} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

Interference Function

- ◆ $\theta(1) > \theta_B(1)$ for 001 and $\theta(2) > \theta_B(2)$ for 002
- ◆ If $\mathbf{H}_{hkl} = \mathbf{H}$ is reciprocal lattice vector then $(\mathbf{s} - \mathbf{s}_0)/\lambda \neq \mathbf{H}$.

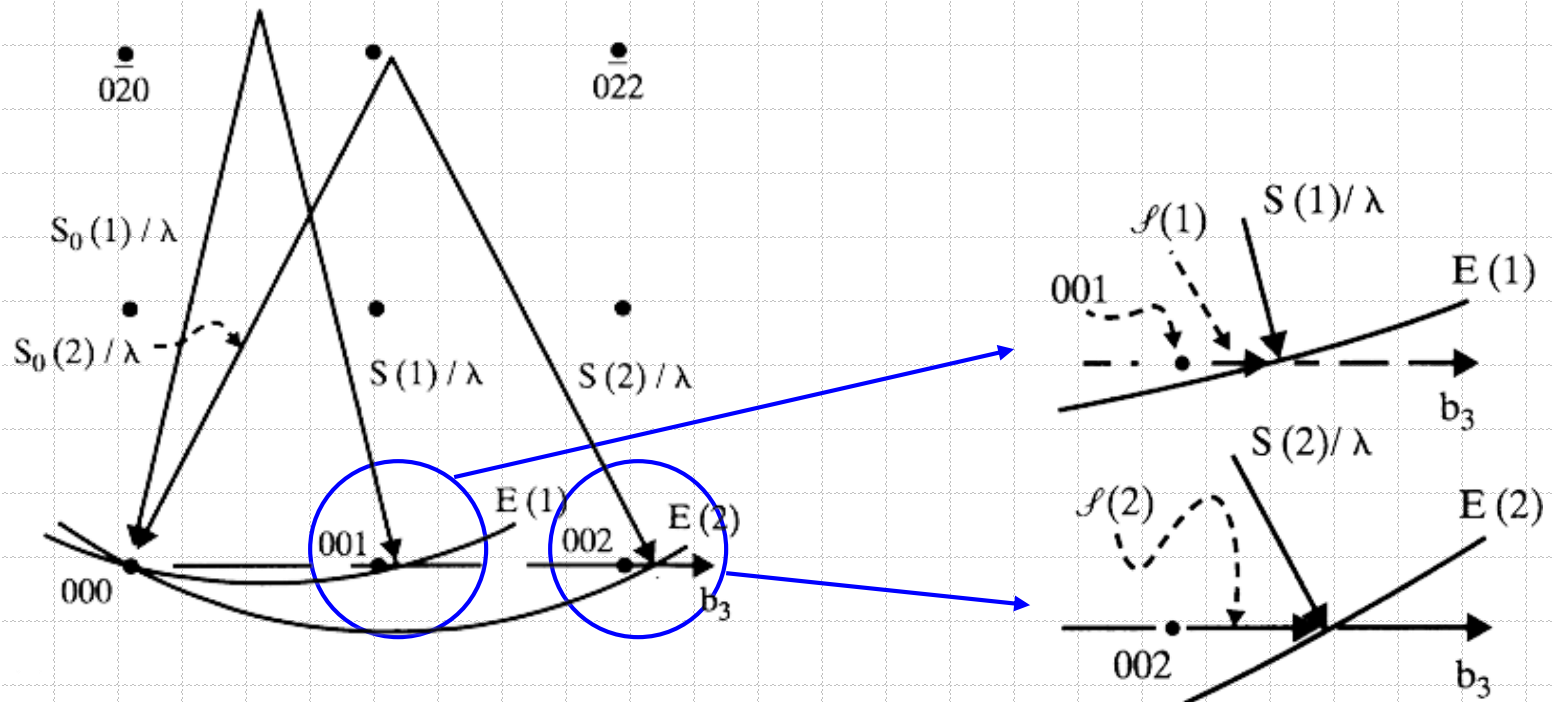


Interference Function

◆ We define:

$$(\mathbf{S} - \mathbf{S}_0) / \lambda - \mathbf{H} = \boldsymbol{\ell}$$

as deviation parameter



Interference Function

- ◆ In order to calculate the intensity diffracted from the crystal at $\theta \neq \theta_B$, the phase differences from different unit cells must be included.
- ◆ For three unit vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 :

$$A_{total} = \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} F \exp \frac{2\pi i}{\lambda} [(\mathbf{s} - \mathbf{s}_0) \cdot (n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3)]$$

n_i – particular unit cell

N_i – total number of unit cells along \mathbf{a}_i

From the definition of the reciprocal lattice vector:

$$(\mathbf{s} - \mathbf{s}_0) / \lambda = \mathbf{H} + \ell = (h_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + l_3 \mathbf{b}_3) + \ell$$

Interference Function

$$\begin{aligned} A_{total} &= F \sum_{n_1} \sum_{n_2} \sum_{n_3} \exp [2\pi i (\mathbf{H} + \ell) \cdot (n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3)] \\ &= F \sum_{n_1} \sum_{n_2} \sum_{n_3} \exp [2\pi i (h_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + l_3 \mathbf{b}_3 + \ell) \cdot (n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3)] \end{aligned}$$

since: $\mathbf{b}_j \cdot \mathbf{a}_i = \delta_{ij}$

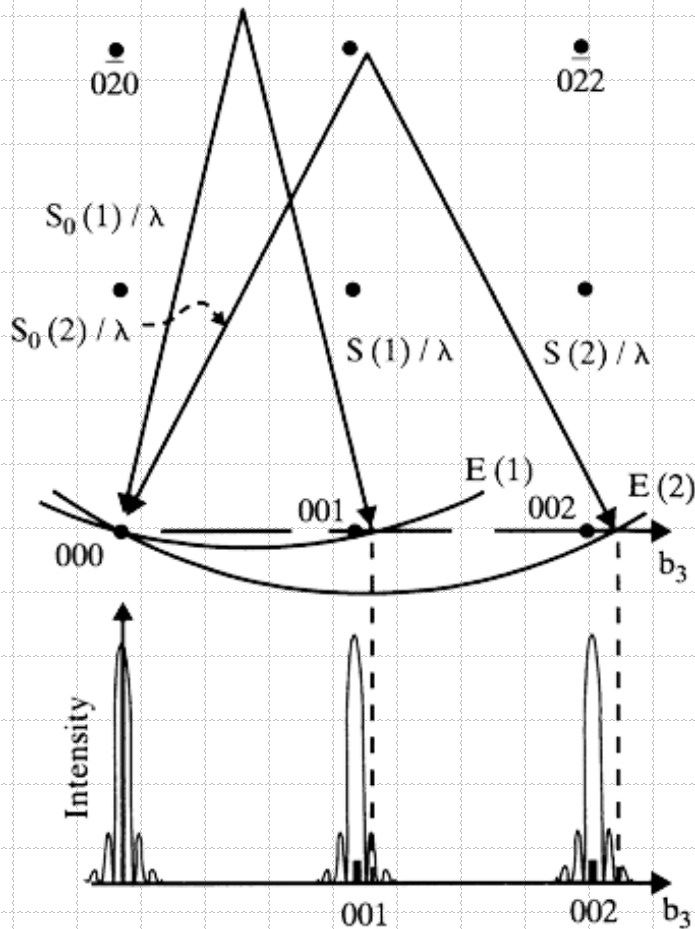
$$A_{total} = F \sum_{n_1} \exp(2\pi i l \cdot n_1 a_1) \sum_{n_2} \exp(2\pi i l \cdot n_2 a_2) \sum_{n_3} \exp(2\pi i l \cdot n_3 a_3)$$

Converting from exp to sines:

$$A_{total} = F \left[\prod_{i=1}^3 \frac{\sin \pi \lambda l \cdot N_i \mathbf{a}_i}{\sin \pi \lambda l \cdot \mathbf{a}_i} \right] \exp \left\{ \pi [(N_1 - 1) \mathbf{a}_1 + (N_2 - 1) \mathbf{a}_2 + (N_3 - 1) \mathbf{a}_3] \right\}$$

Interference Function

◆ Calculating intensity we lose phase information therefore:



$$I = |A_{total}|^2$$

$$I = F^2 \prod_{i=1}^3 \frac{\sin^2 \pi \lambda \ell \cdot N_i \mathbf{a}_i}{\sin^2 \pi \lambda \ell \cdot \mathbf{a}_i}$$

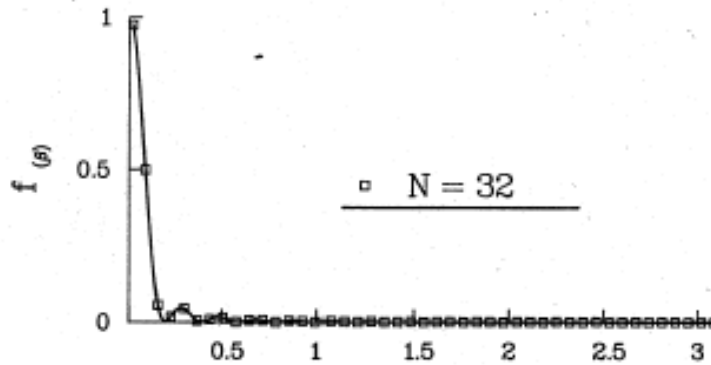
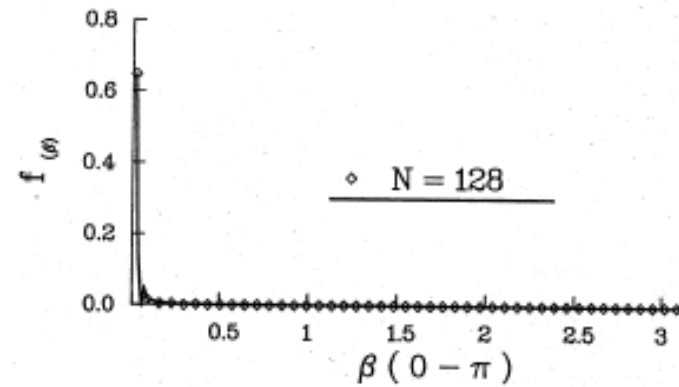
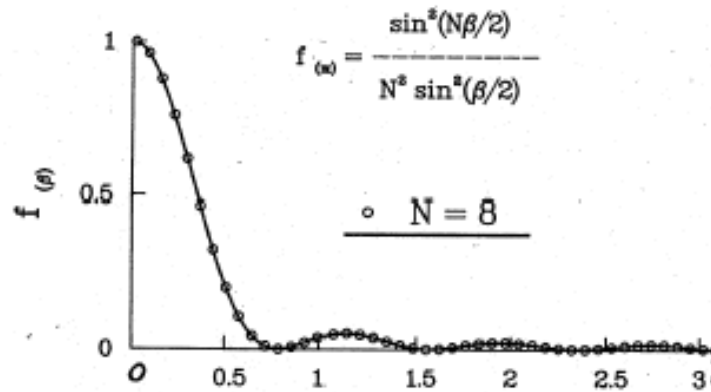
interference function

Maximum intensity at Bragg peak is $F^2 N^2$

Width of the Bragg peak $\propto 1/N$

N is a number of unit cells along $(\mathbf{s} - \mathbf{s}_0)$

Interference Function



For reasonable number of unit cells, ripples beyond main peak are very weak

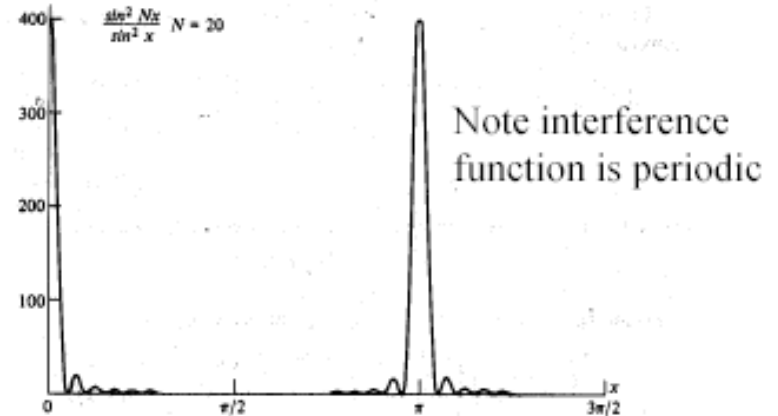
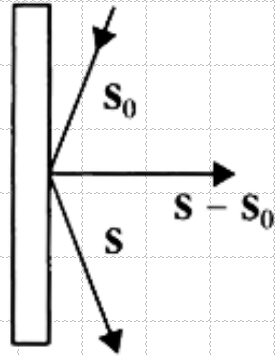


Fig. 3.2 The function $(\sin^2 Nx)/\sin^2 x$ for $N = 20$. The function peaks at values of x which are integral multiples of π , and it is essentially zero everywhere else.

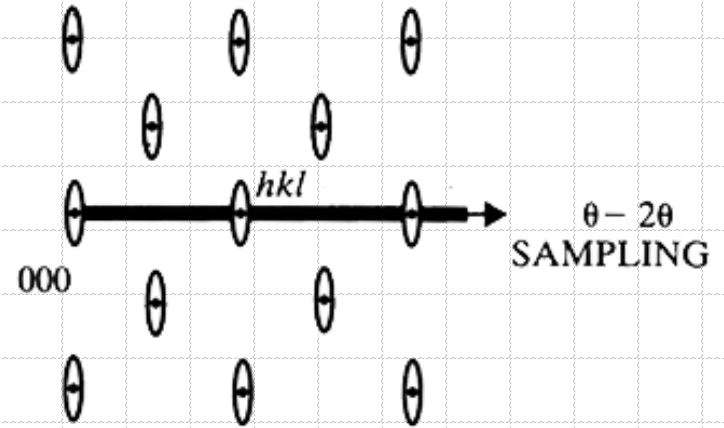
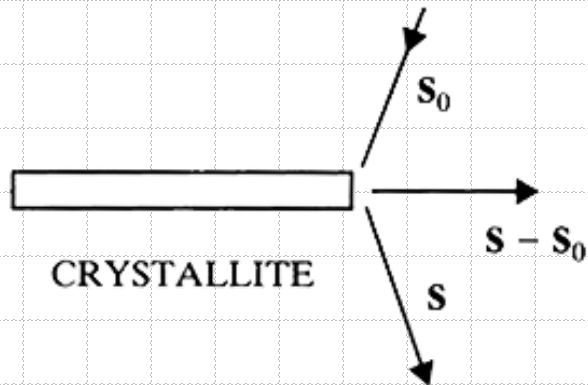
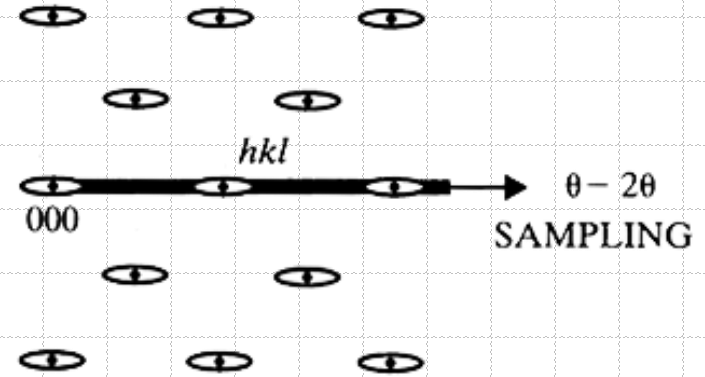
Crystallite Size

DIRECT SPACE

CRYSTALLITE



RECIPROCAL SPACE



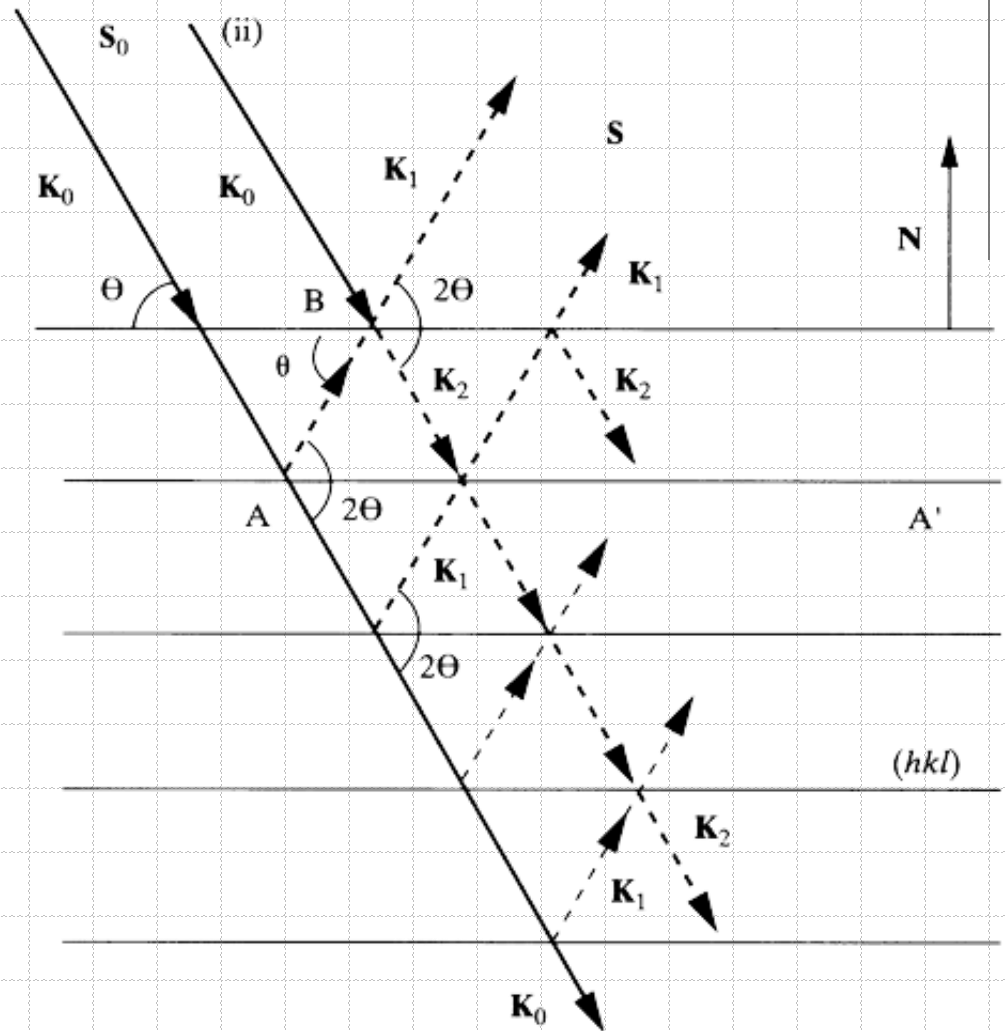
Perfect Crystals

- ◆ The diffracted intensity calculations make use of ideally imperfect crystals
- ◆ This is the “kinematical” theory of diffraction
- ◆ The integrated intensity from a perfect crystal – large and no mosaic blocks – is less than that from an ideally imperfect crystal
- ◆ Our consideration of Bragg peak width also has some problems. When we have very large perfect crystals the peak width is not zero. The width converges to a finite small value as the size of the crystal increases
- ◆ We need a better theory!
- ◆ Dynamical theory is used to treat diffraction in perfect crystals

Perfect Crystals

◆ Dynamical diffraction theory is complicated. It includes the possibility of multiple scattering in a crystal. Diffracted beam is phase shifted by 90° every time it is diffracted within the crystal (this is in addition to the 180° shift on scattering from an individual electron or atom)

- Scattering twice off a set of lattice planes K_0 to K_1 to K_2 , produces a diffracted beam in the direction of the incident beam but with a 180° phase shift. The resulting destructive interferences reduces the intensity of the beam in the incident direction
- This is PRIMARY EXTINCTION



Perfect Crystals

- ◆ A full mathematical treatment of dynamical theory uses differential equations that describe the transfer of energy between the forward and diffracted x-ray beams.
- ◆ This theory predicts that intensity from a perfect crystal with negligible absorption is

$$I = \frac{8}{3\pi} \left(\frac{e^2}{mc^2} \right) \frac{N\lambda^2 |F|}{\sin 2\theta} \left(\frac{1 + |\cos 2\theta|}{2} \right)$$

where N is the number of unit cells per unit volume.

Note the intensity depends on F not F²

Perfect Crystals

◆ The theory also predicts that the peak shape on rocking the crystal in the diffracted beam. The width of this rocking curve is called the Darwin width. Note that at the top of the curve the reflectivity is $\sim 100\%$.

◆ The width of the curve $2s$ is given by

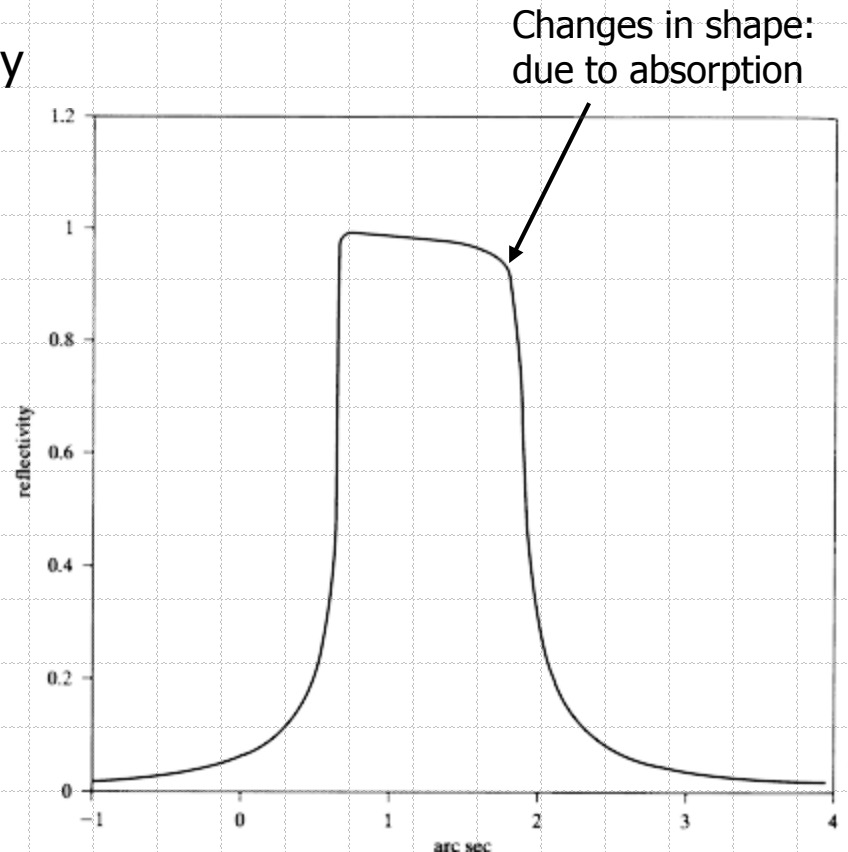
$$s = \left(\frac{e^2}{mc^2} \right) \frac{N\lambda^2 |F|}{\pi \sin 2\theta} \left(\frac{1 + |\cos 2\theta|}{2} \right)$$

FWHM, $\Delta\theta_0$, for Darwin curve = $2.12s$

For first order reflections:

$5 \text{ arcs} < \Delta\theta_0 < 20 \text{ arcs}$

Higher order reflections have considerably narrower rocking curves



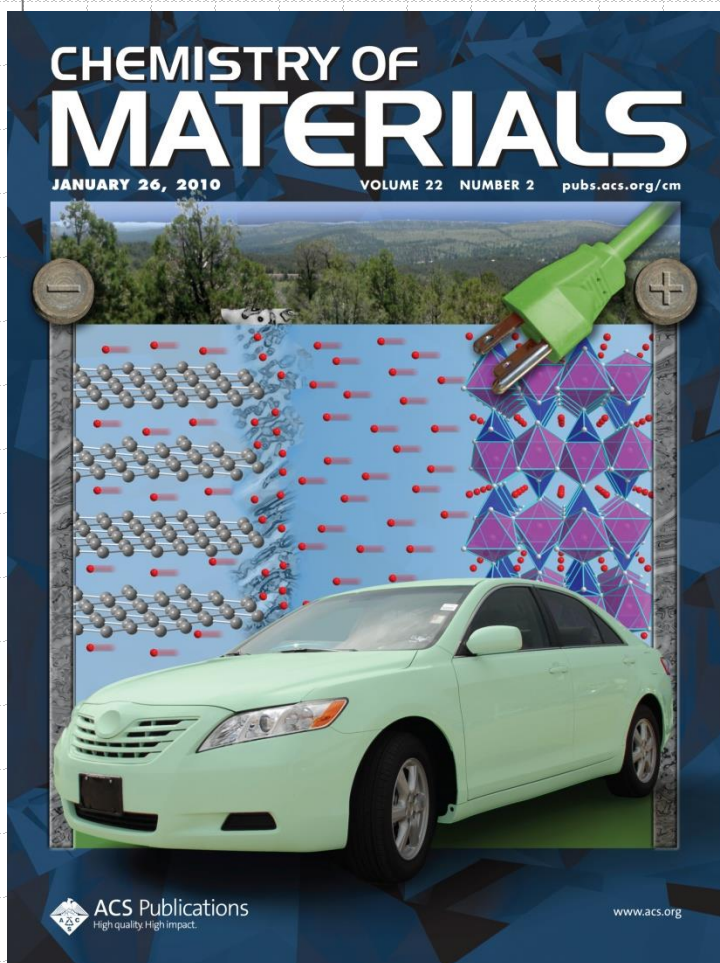
Whole Pattern Fitting - Example: LiFePO_4

First Reported:

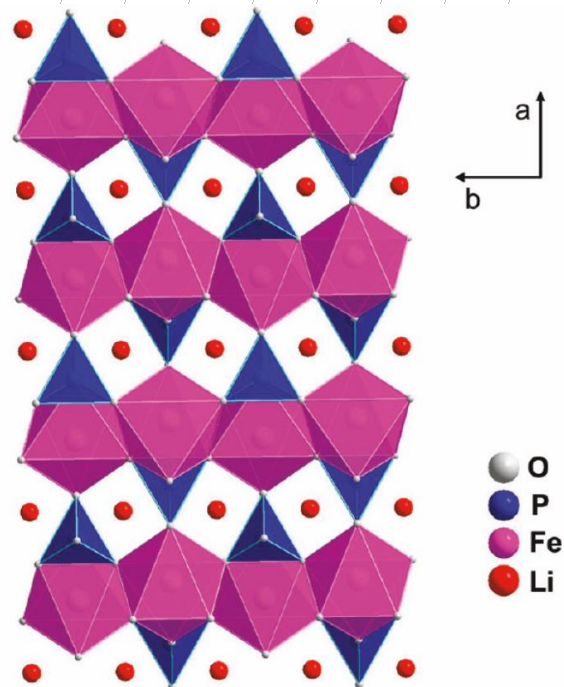
" LiFePO_4 : A Novel Cathode Material for Rechargeable Batteries",

A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *Electrochemical Society Meeting Abstracts*, **96-1**, May, 1996, pp 73.

Excellent candidate for the cathode of rechargeable lithium battery that is inexpensive, nontoxic, and environmentally benign.



Structure of LiFePO_4



Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. *J. Electrochem. Soc.* 1997, **144**, 1188

Whole Pattern Fitting - Example: LiFePO_4

- When a lithium-based cell is discharging, the lithium is extracted from the anode and inserted into the cathode.
- When the cell is charging, the reverse occurs.

Cathode (Li_xCoO_2 : $0 < x < 1$)

Anode (Li_xC_6 : $0 < x < 1$)

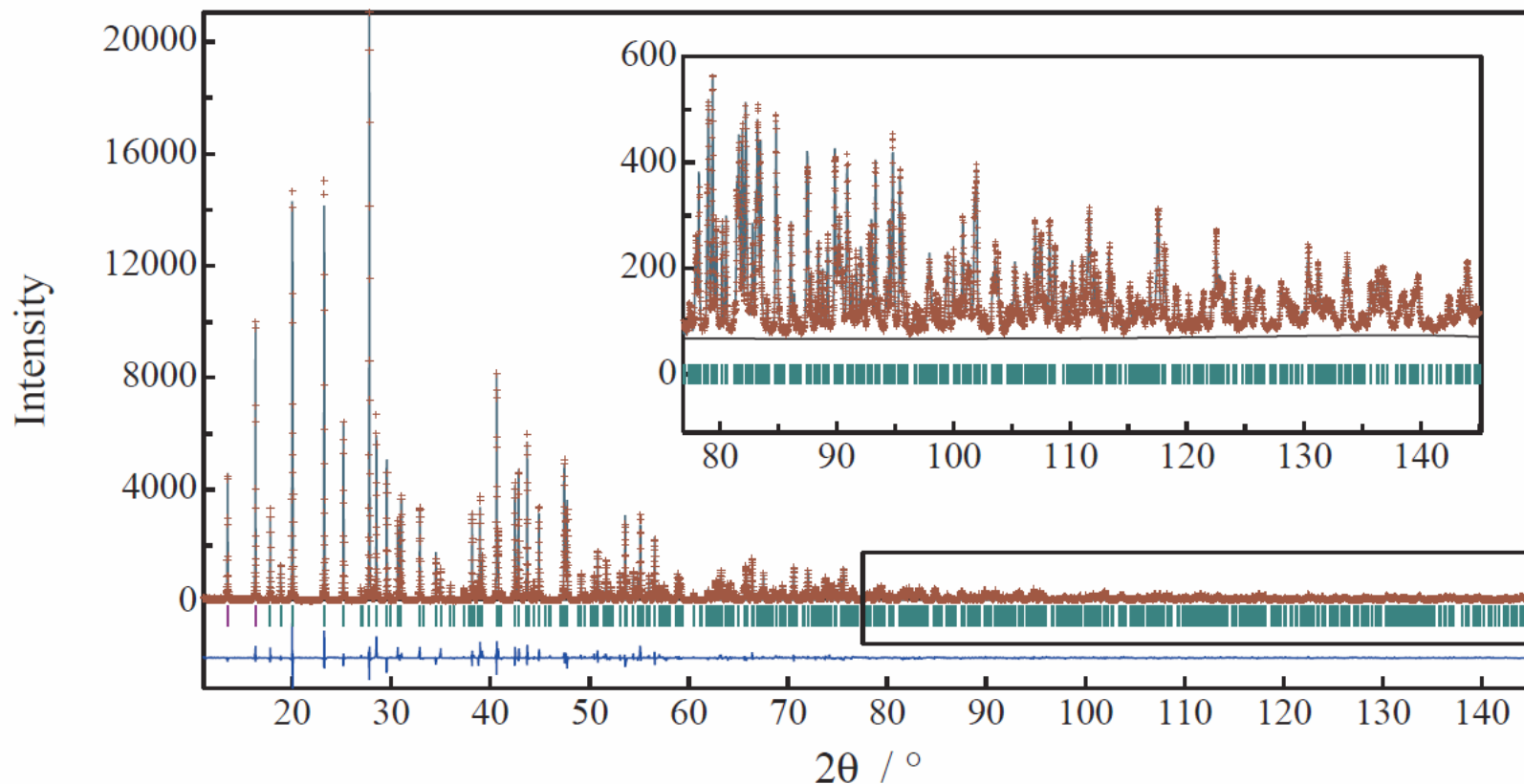
Commercialized by Sony Corp. in 1991

Limits for the large scale applications:

1. Safety
2. Cost (Co)



Whole Pattern Fitting - Example: LiFePO_4



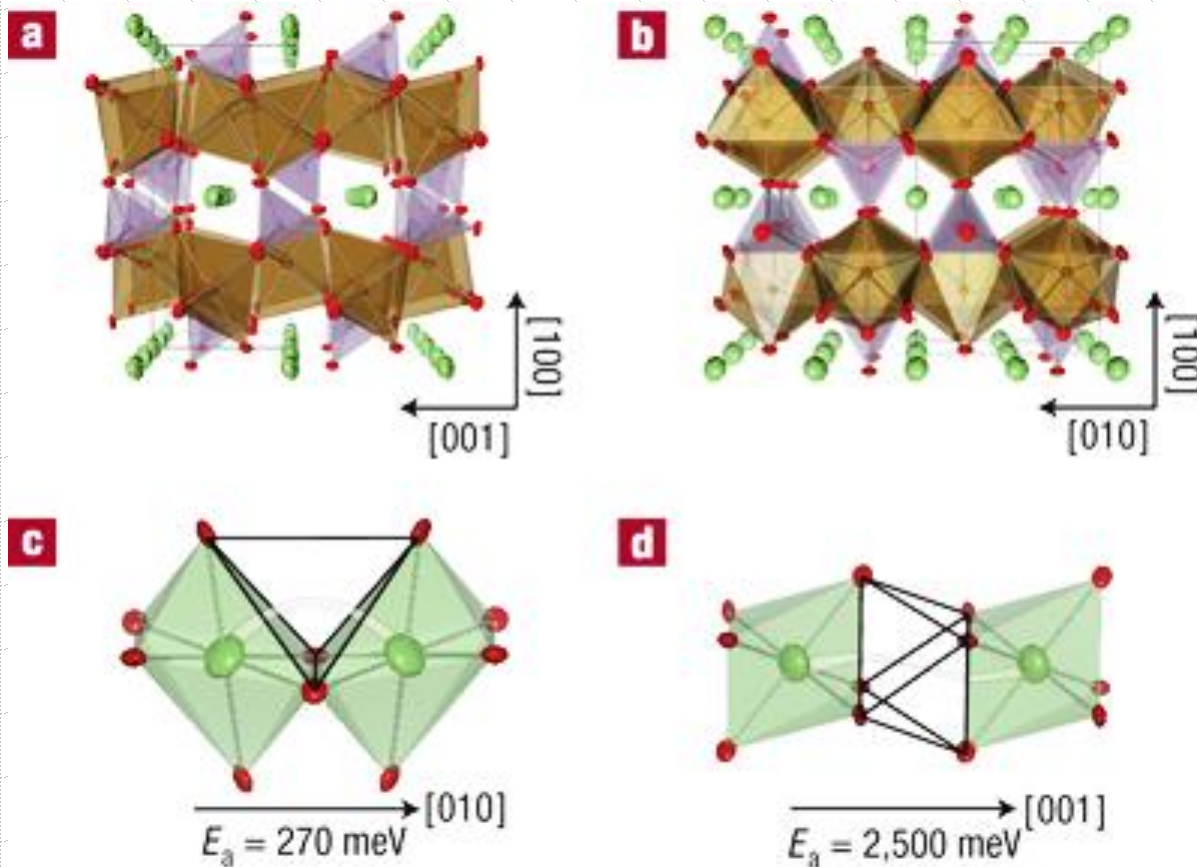
Maximum entropy method (MEM)-based whole-pattern fitting of room temperature high-resolution synchrotron X-ray diffraction data for LiFePO_4 . The incident beam from the bending magnet source was monochromated by a double-crystal Si (111) monochromator, and the diffraction data were collected by a multiple-detector system with flat Ge (111) analysis crystals and scintillation counters. The wavelength was calibrated as 1.206353 \AA by powder diffraction data from NIST SRM640c.

Whole Pattern Fitting - Example: LiFePO_4

"Experimental visualization of lithium diffusion in Li_xFePO_4 "

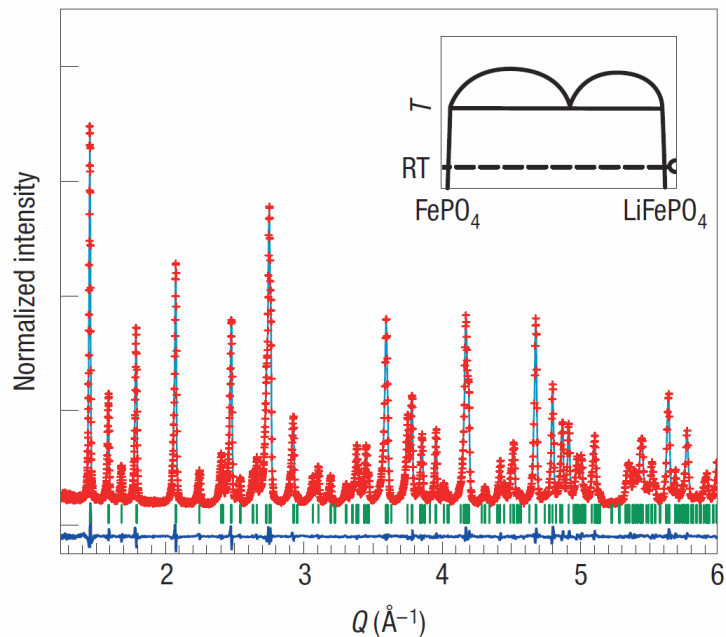
Shin-ichi Nishimura, Genki Kobayashi, Kenji Ohoyama, Ryoji Kanno, Masatomo Yashima & Atsuo Yamada

Nature Materials **7**, 707 (2008) Published online: 10 August 2008



Whole Pattern Fitting - Example: LiFePO₄

a



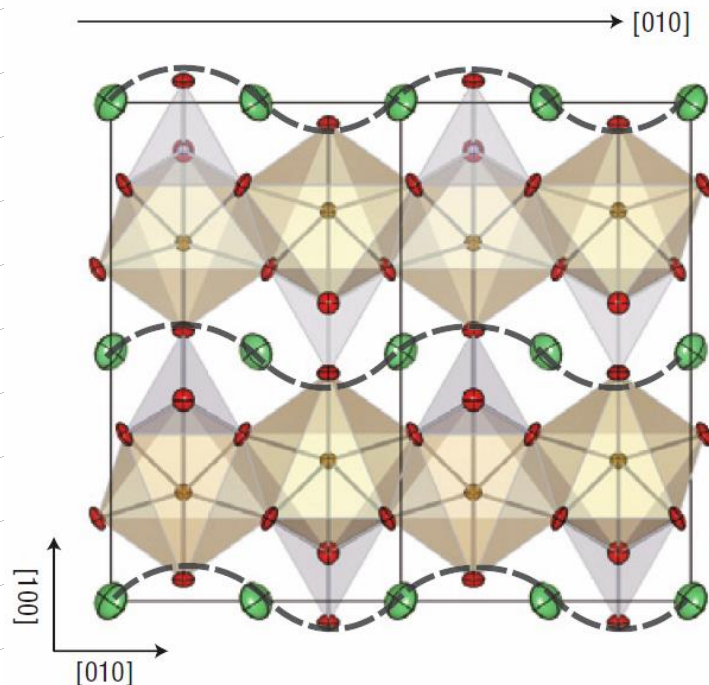
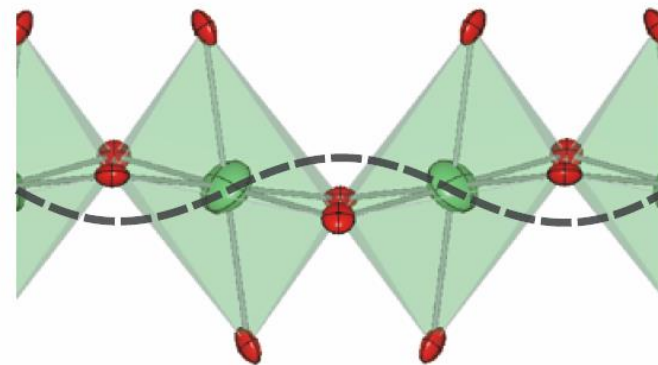
Atom	Wyckoff	g	x	y	z
Li	4a	1	0	0	0
Fe	4c	1	0.28210(6)	1/4	0.97535(19)
P	4c	1	0.09512(12)	1/4	0.4180(3)
O (1)	4c	1	0.09709(12)	1/4	0.7418(3)
O (2)	4c	1	0.45693(11)	1/4	0.2060(3)
O (3)	8d	1	0.15474(9)	0.04636(14)	0.28508(16)

Atom	$U_{11} / \text{Å}^2$	$U_{22} / \text{Å}^2$	$U_{33} / \text{Å}^2$	$U_{12} / \text{Å}^2$	$U_{13} / \text{Å}^2$	$U_{23} / \text{Å}^2$	B_{eq}
Li	0.022(2)	0.0190(18)	0.0156(19)	-0.0027(15)	-0.002(2)	-0.0053(19)	1.51
Fe	0.0043(4)	0.0045(4)	0.0062(4)	0	0.0003(3)	0	0.40
P	0.0036(6)	0.0036(6)	0.0035(7)	0	0.0007(6)	0	0.28
O (1)	0.0084(6)	0.0075(7)	0.0029(7)	0	-0.0005(5)	0	0.49
O (2)	0.0038(7)	0.0080(6)	0.0065(7)	0	0.0003(5)	0	0.48
O (3)	0.0085(5)	0.0048(4)	0.0064(5)	0.0034(4)	0.0011(4)	-0.0005(4)	0.52

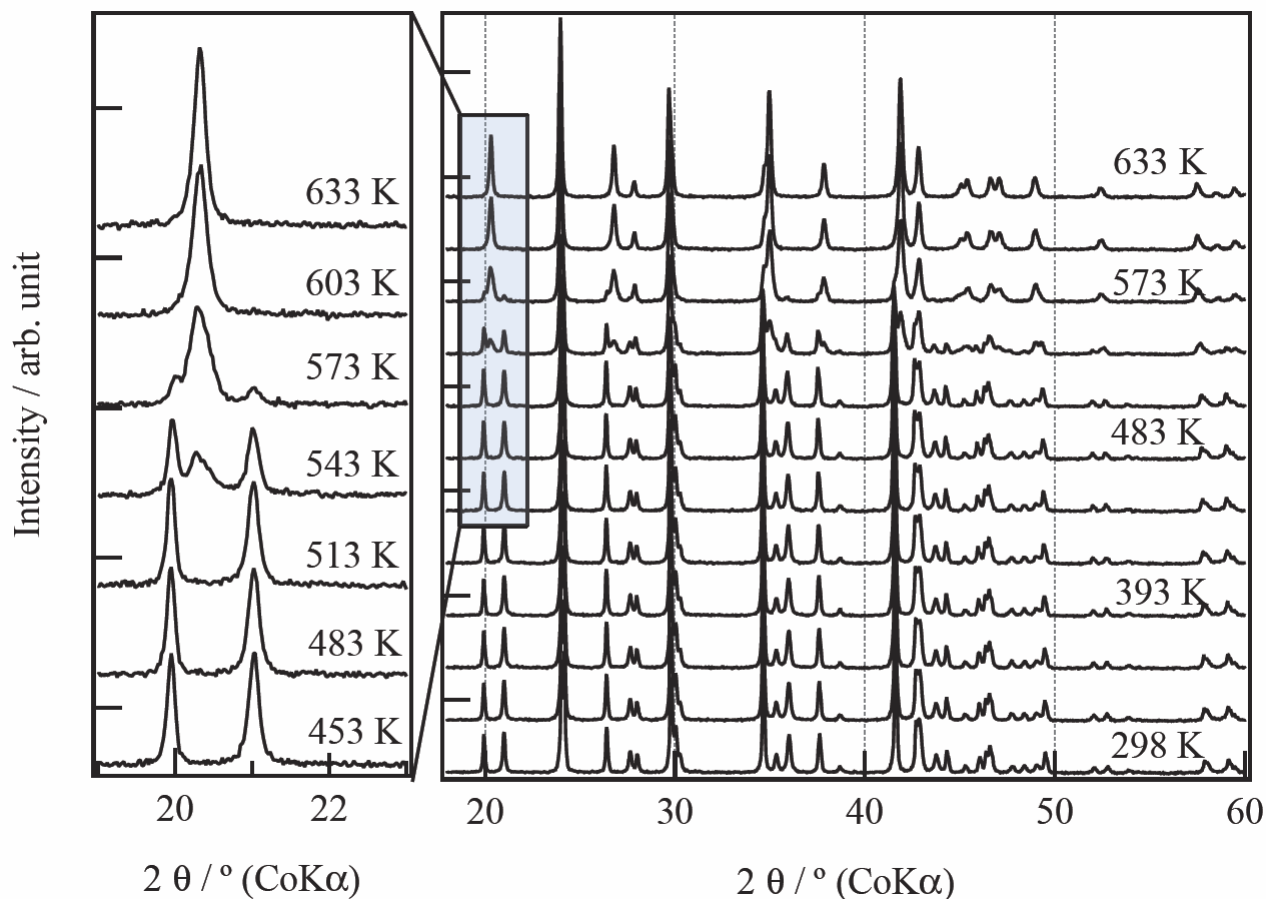
$a = 10.32884(19) \text{ \AA}$, $b = 6.00684 \text{ \AA}$, $c = 4.69236(8) \text{ \AA}$, $V = 291.131(9) \text{ \AA}^3$

$R_{\text{wp}} = 2.66\%$, $R_p = 2.17\%$, $S = 1.34$, $R_I = 0.46\%$, $R_F = 0.47\%$

Rietveld refinement results for LiFePO₄ with neutron diffraction data measured at room temperature in air.



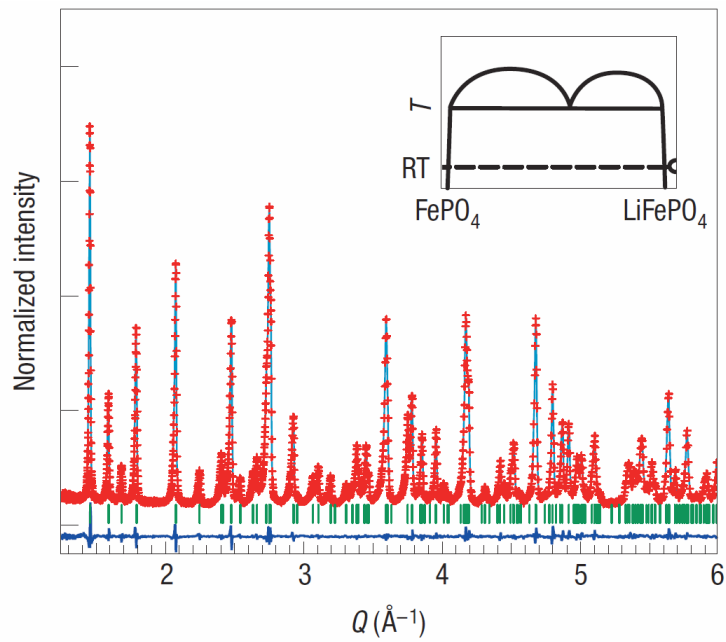
Whole Pattern Fitting - Example: LiFePO_4



X-ray diffraction patterns of a mixture of 0.6 LiFePO_4 and 0.4 FePO_4 recorded at 30 K steps from 298 K to 633 K with magnification of 200 reflections. Bruker AXS D8 ADVANCE powder diffractometer was used with Co-K α radiation and linear position-sensitive detector Vantec-1. Measurement ranges were from 15° to 100°. The measurements were conducted under a high-purity He atmosphere in an Anton Paar HTK 450 temperature-controlled chamber.

Whole Pattern Fitting - Example: LiFePO_4

a



Atom	Wyckoff	g	x	y	z
Li	4a	1	0	0	0
Fe	4c	1	0.28210(6)	1/4	0.97535(19)
P	4c	1	0.09512(12)	1/4	0.4180(3)
O (1)	4c	1	0.09709(12)	1/4	0.7418(3)
O (2)	4c	1	0.45693(11)	1/4	0.2060(3)
O (3)	8d	1	0.15474(9)	0.04636(14)	0.28508(16)

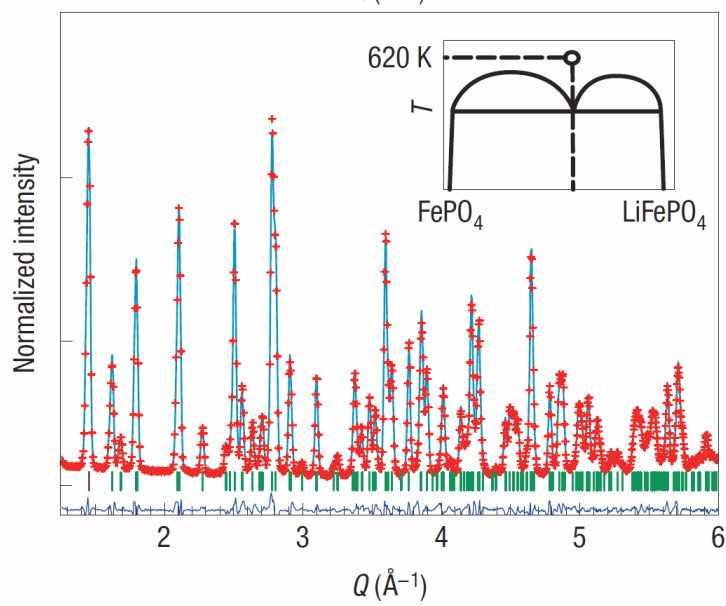
Atom	$U_{11} / \text{Å}^2$	$U_{22} / \text{Å}^2$	$U_{33} / \text{Å}^2$	$U_{12} / \text{Å}^2$	$U_{13} / \text{Å}^2$	$U_{23} / \text{Å}^2$	B_{eq}
Li	0.022(2)	0.0190(18)	0.0156(19)	-0.0027(15)	-0.002(2)	-0.0053(19)	1.51
Fe	0.0043(4)	0.0045(4)	0.0062(4)	0	0.0003(3)	0	0.40
P	0.0036(6)	0.0036(6)	0.0035(7)	0	0.0007(6)	0	0.28
O (1)	0.0084(6)	0.0075(7)	0.0029(7)	0	-0.0005(5)	0	0.49
O (2)	0.0038(7)	0.0080(6)	0.0065(7)	0	0.0003(5)	0	0.48
O (3)	0.0085(5)	0.0048(4)	0.0064(5)	0.0034(4)	0.0011(4)	-0.0005(4)	0.52

$a = 10.32884(19) \text{ \AA}$, $b = 6.00684 \text{ \AA}$, $c = 4.69236(8) \text{ \AA}$, $V = 291.131(9) \text{ \AA}^3$

$R_{\text{wp}} = 2.66\%$, $R_p = 2.17\%$, $S = 1.34$, $R_I = 0.46\%$, $R_F = 0.47\%$

Rietveld refinement results for LiFePO_4 with neutron diffraction data measured at room temperature in air.

b



Atom	Wyckoff	g	x	y	z	$B_{\text{iso}} / \text{Å}^2$
Li	4a	0.6	0	0	0	3.4(3)
Fe	4c	1	0.28059(13)	1/4	0.9706(3)	-
P	4c	1	0.0954(3)	1/4	0.4184(5)	-
O (1)	4c	1	-0.8898(3)	1/4	0.7343(4)	-
O (2)	4c	1	0.4542(3)	1/4	0.1806(5)	-
O (3)	8d	1	0.16810(18)	0.0477(3)	0.2792(4)	-

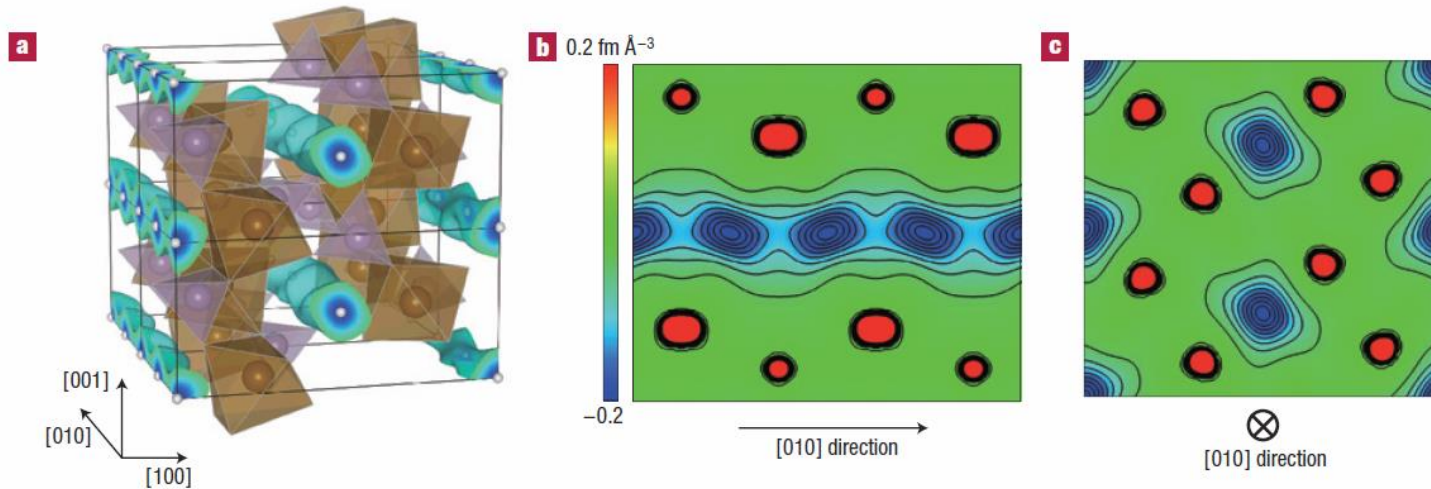
Atom	$U_{11} / \text{Å}^2$	$U_{22} / \text{Å}^2$	$U_{33} / \text{Å}^2$	$U_{12} / \text{Å}^2$	$U_{13} / \text{Å}^2$	$U_{23} / \text{Å}^2$	B_{eq}
Li	-	-	-	-	-	-	-
Fe	0.0150(9)	0.0119(8)	0.0133(9)	0	-0.0010(7)	0	1.06
P	0.0173(18)	0.0164(14)	0.0060(15)	0	0.0005(13)	0	1.04
O (1)	0.0271(18)	0.0256(15)	0.074(15)	0	-0.0018(15)	0	1.58
O (2)	0.0176(17)	0.0262(16)	0.0131(16)	0	0.0050(10)	0	1.50
O (3)	0.0181(11)	0.0187(8)	0.0211(11)	0.0018(9)	0.0059(9)	-0.0071(10)	1.53

$a = 10.1763(9) \text{ \AA}$, $b = 5.9683(5) \text{ \AA}$, $c = 4.7733(4) \text{ \AA}$, $V = 289.91(4) \text{ \AA}^3$

$R_{\text{wp}} = 3.65\%$, $R_p = 2.75\%$, $S = 3.37$, $R_I = 0.66\%$, $R_F = 0.32\%$

Rietveld refinement results for $\text{Li}_{0.6}\text{FePO}_4$ using neutron diffraction data measured at 620 K in Ar.

Whole Pattern Fitting - Example: LiFePO_4



Nuclear distribution of lithium calculated by the Maximum Entropy Method (MEM) using neutron powder diffraction data measured for $\text{Li}_{0.6}\text{FePO}_4$ at 620 K.

- (a) Three-dimensional Li nuclear density data shown as blue contours. The brown octahedra represent FeO_6 and the purple tetrahedra represent PO_4 units.
- (b) Two-dimensional contour map sliced on the (001) plane at $z = 0.5$; lithium delocalizes along the curved one-dimensional chain along the [010] direction, whereas Fe, P and O remain near their original positions.
- (c) Two-dimensional contour map sliced on the (010) plane at $y = 0$; all atoms remain near their original positions.