# Profile Refinement - The Rietveld Method

## Conventional crystal structure determination

- single crystal experiment
- measure Bragg reflection intensities $I_{hk\ell}$
- solve structure by Patterson function, Direct methods, etc.

What if you can't make suitable single crystals?

What if your material only displays interesting behaviour when in polycrystalline (powder) form?

Powder diffraction experiments

Extract integrated intensities

Peak overlap

Loss of information

## The Rietveld Method (H.M. Rietveld, 1967, 1969)

Individual step scanned intensities in a powder diffraction pattern used as data points

- Originally developed for constant λ neutron diffraction.
- Subsequently extended to X-ray diffraction (laboratory and synchrotron) and time-of-flight neutron diffraction

During Rietveld refinement the intensity at each point in the diffraction pattern is calculated using the expression

$$Y_{ic} = Y_{ib} + \sum_{k=k_1}^{k_2} G_{ik} I_k$$

where $Y_{ic}$ = calculated intensity at point i in the diffraction pattern
$Y_{ib}$ = background intensity at point i
$G_{ik}$ = value of normalised peak profile function at point i for reflection k
$I_k$ = Bragg intensity of reflection k
k = $k_1$ to $k_2$ are the reflections contributing intensity to point i

Note: many of the measured points in the diffraction pattern will have intensity contributions from several (overlapping) reflections

Intensities, $I_k$, proportional to square of structure factor:

$$F_{hk\ell} = \Sigma\, n_j f_j \exp[2\pi i(hx_j+ky_j+lz_j)] \,.\, \exp(-B_j \sin^2\theta / \lambda^2)$$

Peak profile function, $G_{ik}$, may be complicated.

BUT

- $I_k$ and $G_{ik}$ are both functions of several variables
- they can be differentiated

# Least Squares methods

- Minimise a function $X(p_1, p_2, p_3, ...)$
- Calculate partial derivatives wrt each of the variables and equate to zero

$$\left(\frac{\partial X}{\partial p_j}\right)_{p_{i:\, i \neq j}} = 0$$

structural, instrumental, peak shape, width, etc.

In the Rietveld method we minimise the (square of the) difference between the measured diffraction pattern and a calculated profile

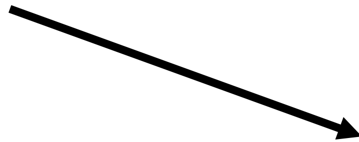
To calculate our profile we need to know:

- where the reflections are
- what their intensities are
- what their shapes are

(structural and instrumental information)

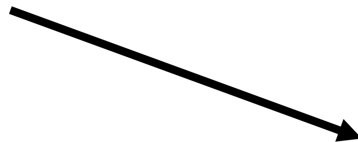
Crystal structure information

unit cell + space group



Bragg reflection positions (in *d*-spacing)

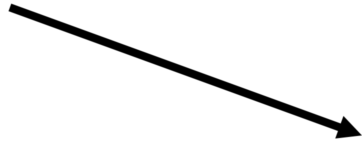
atomic coordinates, temperature factors,
site occupancies



Intensities

Diffractometer information

Detector flight paths and angles



Reflection positions (tof)

Peak shape

Other sample parameters

- preferred orientation
- absorption
- extinction

## Least Squares (revisited)

- Unfortunately *X* is <u>not</u> a linear function

$$\left(\frac{\partial X}{\partial p_j}\right)_{p_{i:\, i \neq j}} = f(p_1, p_2, p_3, \ldots)$$

- In order to evaluate the partial derivative wrt most parameters we need to know the value of that parameter itself!
- Need to have a good initial estimate, which we refine in an iterative process

The Rietveld method is a structure *refinement* method, NOT a structure *solution* method.

Sufficient knowledge of the crystal structure of the material being studied MUST be known in order to calculate a (partial) diffraction pattern.

## GSAS Instrument Parameter File

NBS silicon data collected on Polaris

high angle (backscattering) detectors - C bank

- $\langle 2\theta \rangle = 145°$
- $L_1$ = 12m
- $L_2$ = 0.8m