Rietveld method

method for refinement of crystal structures

what does this mean?

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Crystal structure considered known when atom positions known very precisely

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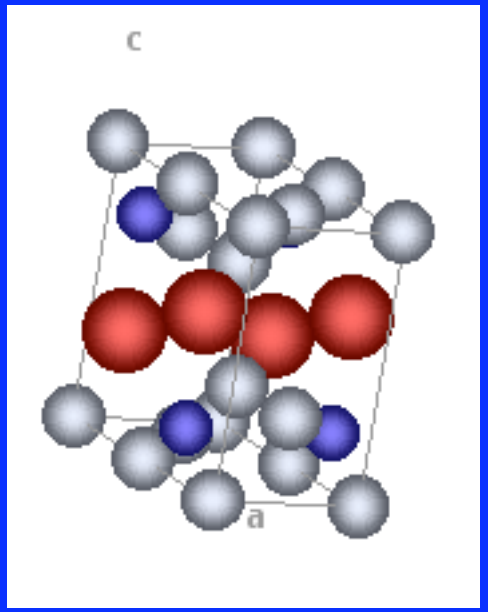
$LaCoAl_4$

Pmma

a = 7.701, b = 4.082, c = 7.023 Å

La 2e (1/4 0 0.388) ....
Co 2e (1/4 0 0.813) ....
Al_1 2a (0 0 0) ....
Al_2 2f (1/4 1/2 0.022) ....
Al_3 4f (0.061 1/2 0.708) ....



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X-ray diffraction data used for structure determination

reflection positions –-> cell size, space group symmetry

intensities –-> atom positions

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X-ray diffraction data used for structure determination

reflection positions –-> cell size, space group symmetry

intensities –-> atom positions

Thus precise lattice parameters & precise atom positions determined in 2 separate steps

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X-ray diffraction data used for structure determination

reflection positions –> cell size, space group symmetry

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$I_{hkl} \sim |F_{hkl}|^2$ $\quad F_{hkl} = \sum f_j e^{2\pi i (hx_j + ky_j + lz_j)}$

Rietveld method

method for refinement of crystal structures

what does this mean?

Initial values of atom positions obtained during structure analysis rarely the most precise values – & closest to truth

Values must be refined - use least squares procedure to make small adjustments in atom positions

Rietveld method

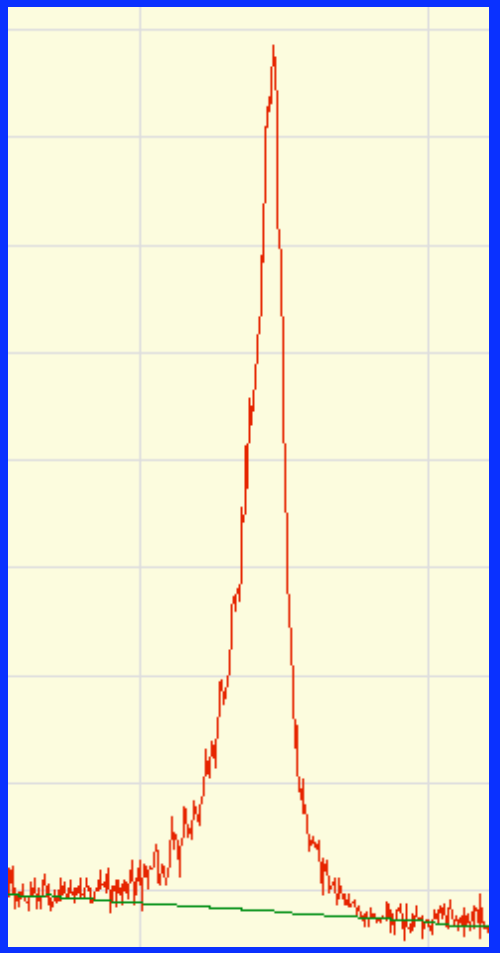
Previously:

Determine areas under
all observed Bragg peaks

Use these intensities to
get model for structure

Refine model on basis of
reflection intensities

Mostly single crystal intensities used,
but same procedure used for
“powder” patterns

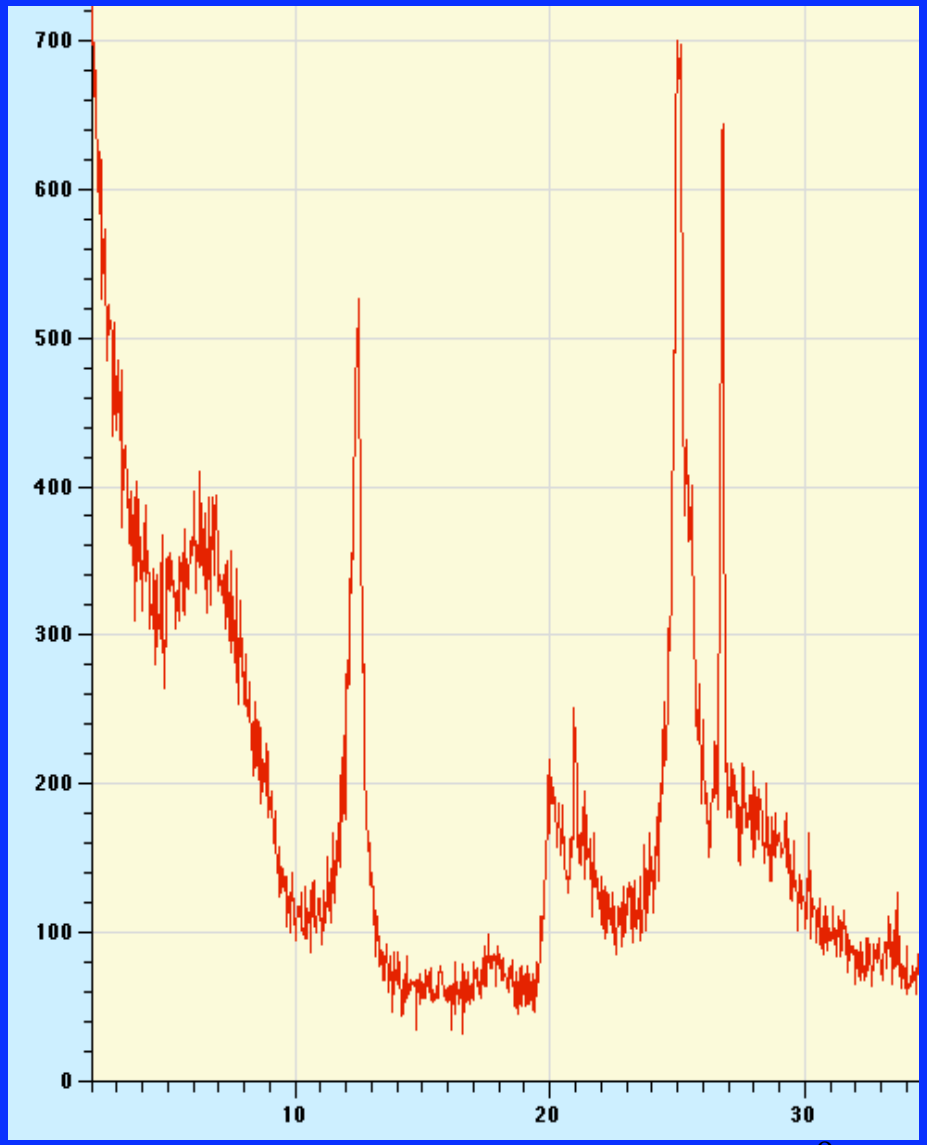


Rietveld method

Problems wrt powder patterns:

Loss of information -

peak shape, width, tails



Rietveld method

Problems wrt powder patterns:

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background

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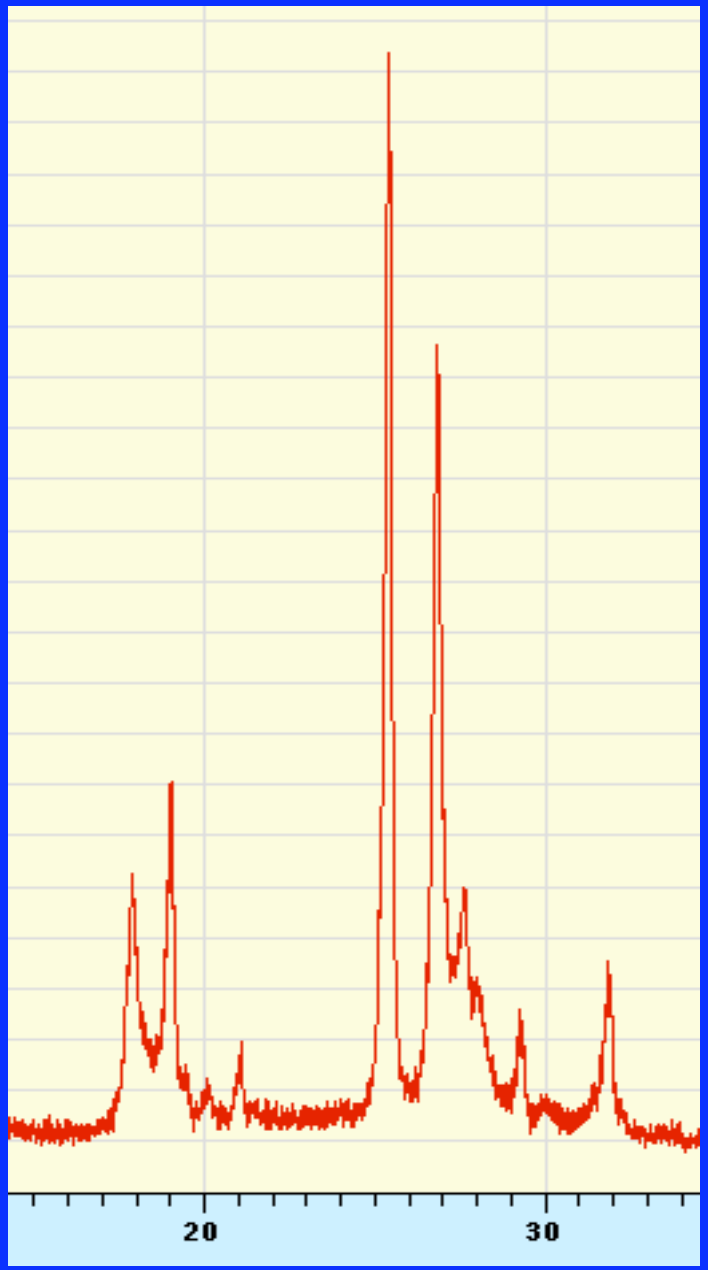
Peak overlap problems



Rietveld method

Problems wrt powder patterns:

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Peak overlap problems

Other things:

Preferred orientation gives wrong intensities

What about multiple phase patterns?

Rietveld method

Uses every datum (y_{obs}) collected, individually

Each y_{obs} compared with a corresponding calculated value (y_{calc})

Must be able to calculate y_{calc}

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Models all involve parameters

Herein lies the complexity of the method

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Change parameters according to the least squares criterion

Minimize

$$R = \sum_i w_i (y_i^{obs} - y_i^{calc})^2$$

Rietveld method

Rietveld algorithms - 1966+

Development of automated diffractometry - early 1980s

Increased computing power

Rietveld method

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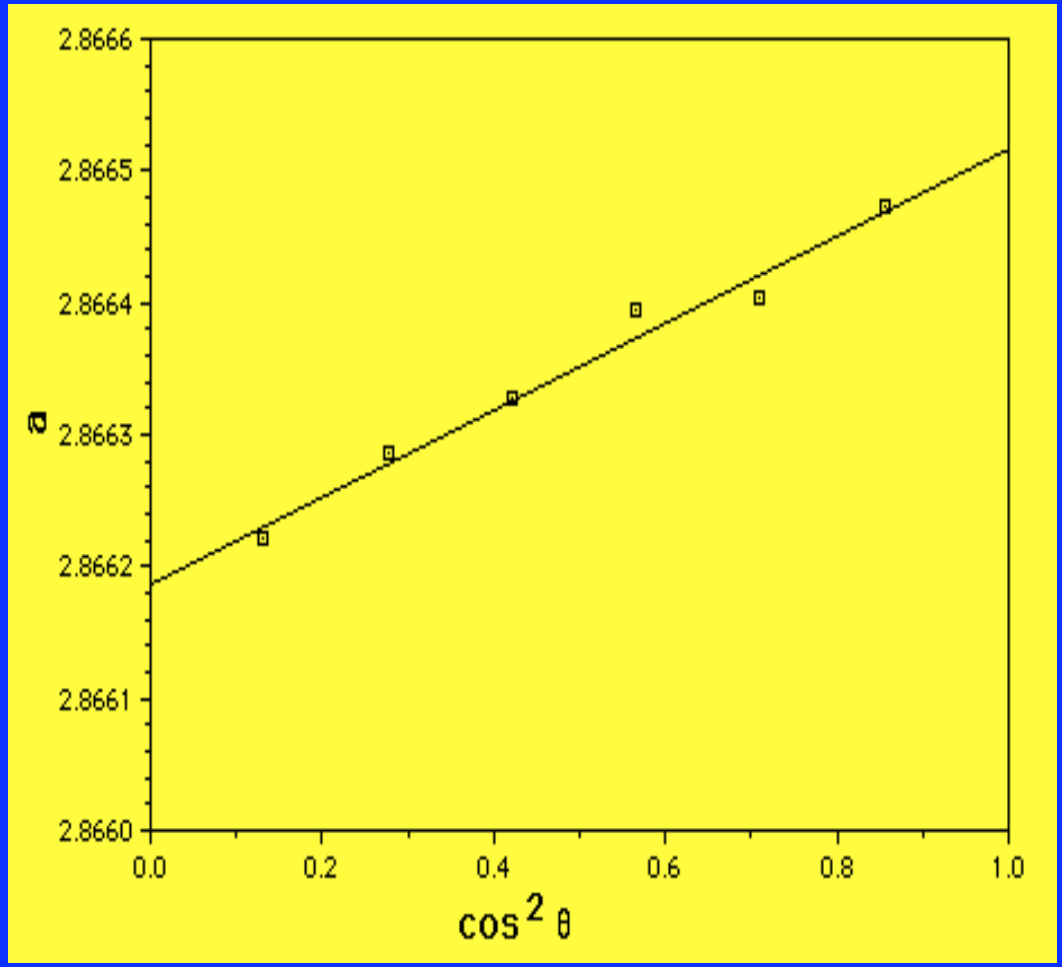
Rise of demand for information contained in peak shapes, background

- crystallite size
- microstress
- thermal motion
- stacking faults
- amorphous content
- other atomic disorder

Least squares

Simple example – straight line fit

What is best straight line to represent these data?



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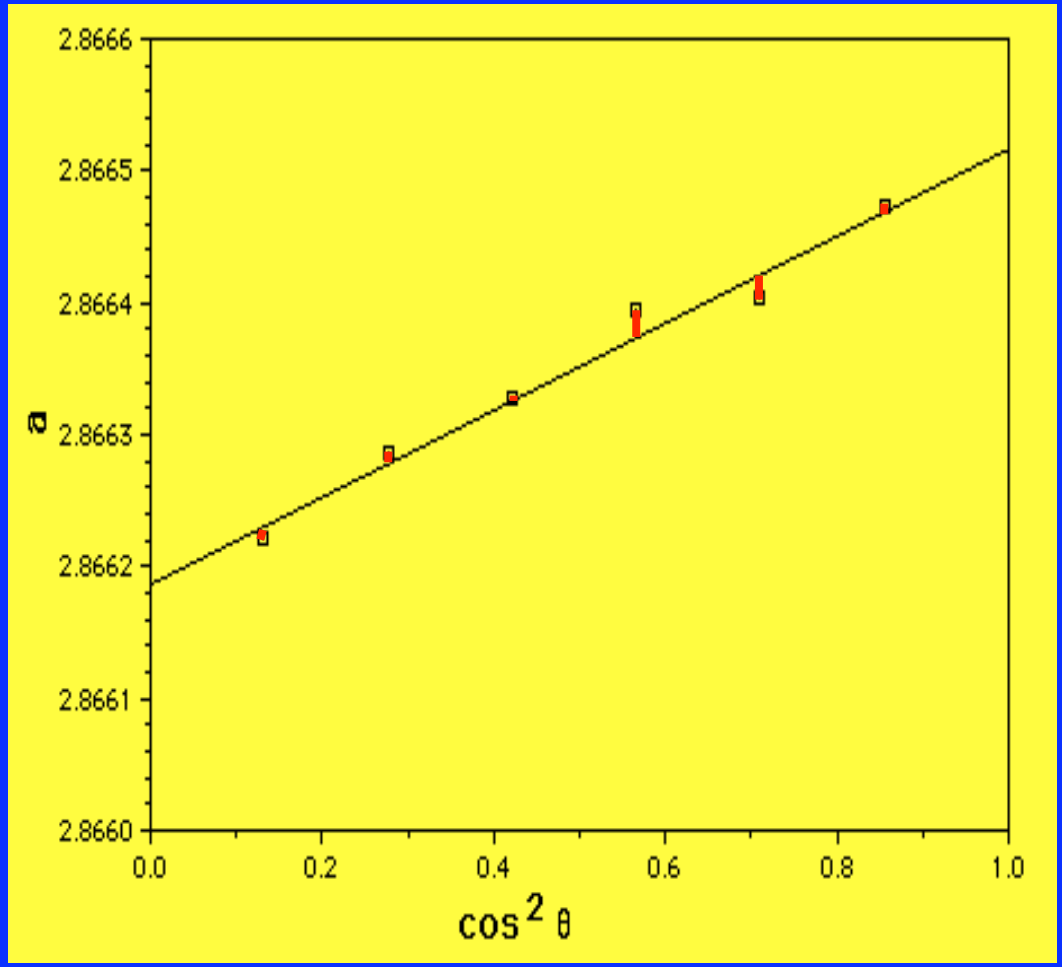

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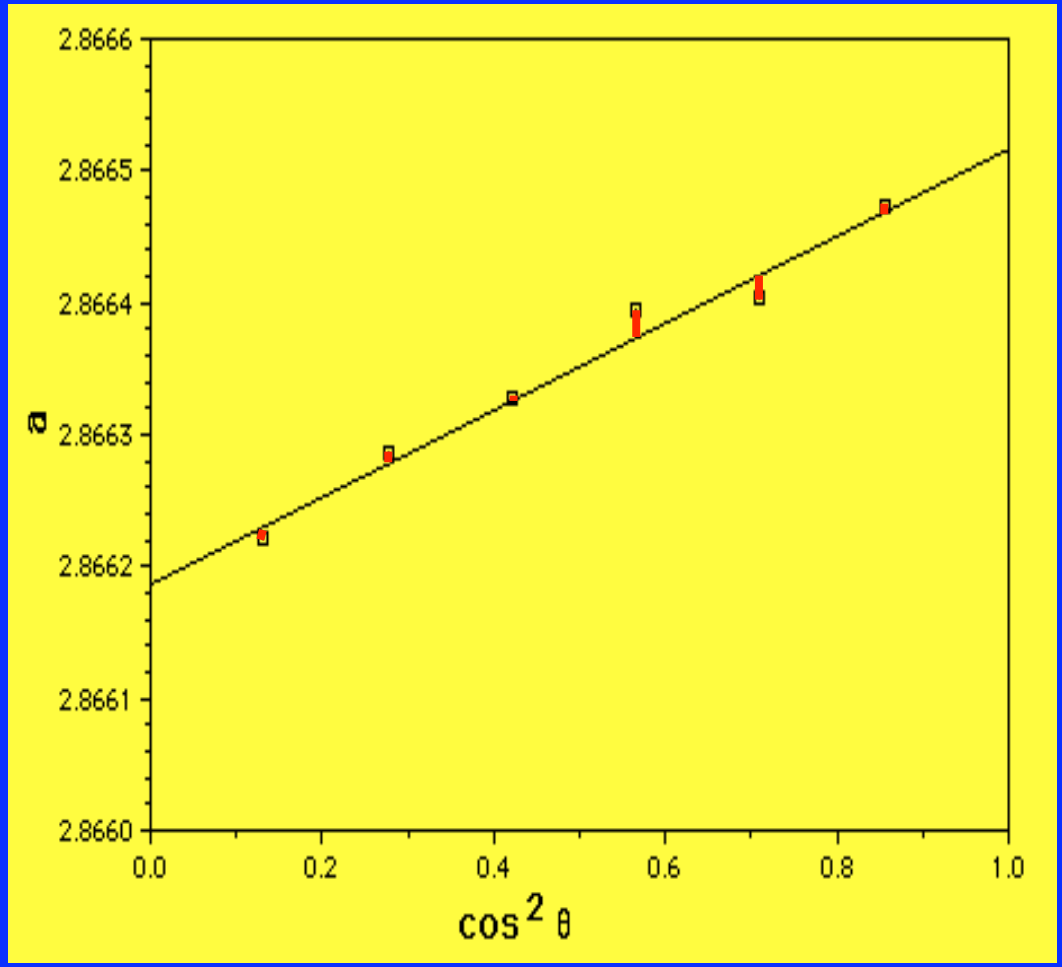
y_i^{calc} values unknown except

$y = mx + b$
(straight line)



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Then

$$R = \sum_i (y_i^{obs} - (mx_i + b))^2$$

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$$R = \sum_i (y_i^{obs} - y_i^{calc})^2$$

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Then

$$R = \sum_i (y_i^{obs} - (mx_i + b))^2$$

Minimize R

$$\partial R/\partial m = \partial R/\partial b = 0$$

$$-2\Sigma (y^{obs} - (mx + b))x = 0$$

$$-2\Sigma (y^{obs} - (mx + b)) = 0$$

Least squares

Simple example – straight line fit

$$-2\Sigma\,(y^{obs} - (mx + b))x = 0 \rightarrow \sum_i x_i y_i^{obs} = m \sum_i x_i^2 + b \sum_i x_i$$

$$-2\Sigma\,(y^{obs} - (mx + b)) = 0 \rightarrow \sum_i y_i^{obs} = m \sum_i x_i + b \sum_i 1$$

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These are the *normal equations*

Insert data (x, y values) & solve for m, b