Precise Parameter measurements

Introduction

- The change in solute concentration or temperature produce only a small change in lattice parameter→ **precise parameter measurements is needed to measure these quantities with any accuracy.**
- The parameter "a" of **cubic substances** is directly proportional to the spacing "d" of any particular set of lattice planes:

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

- Measuring Bragg-angle θ for this set of planes→determining "d" → calculating "a"
- But Sinθ not θ appears in Bragg law → **precision in "d" or "a" depends on precision in sinθ (a derived quantity) and not precision in θ (measured quantity).**

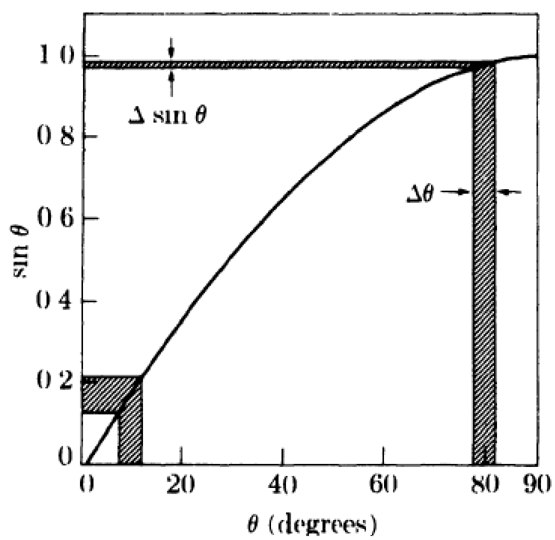


Fig. 1 The error in sin θ cussed by a given error in θ decreases as θ increases

- Angular position in more sensitive to a given change in plane spacing "d" when θ is large compared to small θ.

In cubic system:

$$\frac{\Delta \boldsymbol{a}}{\boldsymbol{a}} = \frac{\Delta \boldsymbol{d}}{\boldsymbol{d}} = -\boldsymbol{cot\theta}\,\Delta\boldsymbol{\theta}$$

If θ --> 90° (**backward-reflected)** then cot θ --> 0

$\frac{\Delta a}{a}$ is the fractional error in a

→precision in parameter in the use of **backward-reflected** beam having 2θ at near 180° (not possible to see reflection at this angle of 180°)

- Not possible to see reflection at 2θ = 180° → **extrapolating** to 2θ=180° on plot of 2θ vs. "a"
- **certain function of 2θ ($sin^2θ$ or $cos^2θ$) with "a" will be linear**
- By selecting the parameter from highest-angle line → precision ~ 0.01Å →since "a" for most substances is around 3-4Å then precision ~ 0.3 %
- **With a good experimental technique and extrapolation function→ the precision will be ~ 0.001 Å or 0.03% without much difficulty.**
- The general approach in finding an **extrapolation function**: considering the various effects leading to **errors in measured values of θ** and how these errors in θ vary with the angle θ itself.

Errors in the measurements of a lattice parameter

- two kinds of errors are involved: **systematic and random**
- **Systematic errors**: vary in a regular manner with some particular parameter
  → film shrinkage, incorrect radius, off-center specimen and absorption are all systematic errors
  →they vary in regular way with θ
- **Random errors**: are the ordinary chance errors involved in any direct observation
  →error in measuring the position of the various lines on the film
  →they may be positive or negative and do not vary in any regular manner with the position of the line on the film.
- The systematic errors in "a" approach zero as θ approach 90°
  → the magnitude of these errors is proportional to slop of the extrapolation line (see Fig 2a)
- The random errors are responsible for deviation of the various points from the extrapolation line (see Fig. 2b).

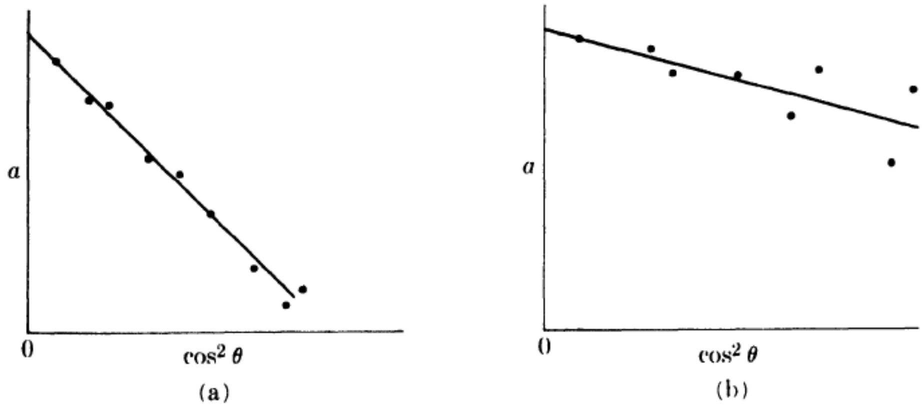
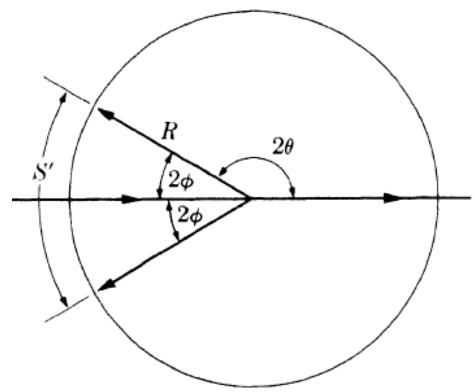


Fig. 2 The schematic of extrapolation curves. (a): larger symmetric errors , small random errors. (b): small systematic errors, large random errors.

Debye-Scherrer camera



The sources of error in θ are:

- Film shrinkage
- Incorrect camera radius
- Absorption in specimen
- The overall error is given by

$$\Delta\phi_{S',R,C,A} = \left(\frac{\Delta S'}{S'} - \frac{\Delta R}{R}\right)\phi + \frac{\Delta x}{R} sin\phi\ cos\phi$$

Where, S' is the distance on the film between two corresponding back-reflection lines. 2ϕ is supplement of 2θ and $\phi = S'/4R$. Δx is displacement of the specimen from the camera center in parallel to the incident beam. R is the camera radius.

$\phi = 90° - \theta$, $\Delta\phi = -\Delta\theta$, sinϕ =cosθ and cosϕ=sinθ

- After some calculation ….→

$$\frac{\Delta \boldsymbol{d}}{\boldsymbol{d}} = \boldsymbol{Kcos^2\theta}$$

where K is constant $K = \left(\frac{\Delta S'}{S'} - \frac{\Delta R}{R} + \frac{\Delta x}{R}\right)$

➔ **Fractional error in "d" are directly proportional to $\boldsymbol{cos^2\theta}$**

- In cubic system →

$$\frac{\Delta a}{a} = \frac{\Delta d}{d} = \frac{a - a_0}{a_0} = K\cos^2\theta$$

$$\boldsymbol{a = a_0 + a_0 k\cos^2\theta} \qquad \textbf{(1)}$$

- The true value of "a" can be found by extrapolating the straight line to $\cos^2\theta$ =0
- From various approximation involved in the derivation of this Equation (1) it is clear that this Equation is true for large values of θ. (the angles larger than 60° should be used in extrapolation).
- **Nelson- and Riley analyzed the various sources of error, particularly absorption, and showed that the relation**

$$\boldsymbol{\frac{\Delta d}{d} = k\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)}$$

holds quite accurately down to very low values of θ and not just at high angles.
the bracketed terms are called the **Nelson-Riley function**.

- The value of "a_0" can be found by plotting "a" against the N-R function, which approaches zero as θ approaches 90°.

Diffractometres

Source of systematic errors:

1. Misalignment; 2. Use of flat specimen instead of specimen curved to conform to the focusing circle; 3. Absorption; 4. displacement of the sample from diffractometer axis.

Ab error in d given by :

$$\boldsymbol{\frac{\Delta d}{d} = \left(-\frac{D}{R}\frac{\cos^2\theta}{\sin\theta}\right)}$$

- Where D is the specimen displacement parallel to the reflecting-plane normal and R is the diffractometer radius

Method of least squares

- The accuracy of measuring lattice parameter depends on the **accuracy of a straight line** drawing through a set of experimental points, each of which is subject to random errors.
  →an analytical method is needed to find the best fitted line
  → **method of least squares**
- **If a number of measurements are made of the same physical quantity and if these measurements are subject only to random errors, then the theory of least squares**

states that the most probable value of the measured quantity is that which makes the sum of the squares of the errors a minimum.

- Suppose: the various points have coordinates x_1 y_1, x_2 y_2,….and x and y are related by an Equation of : $\boldsymbol{y = a + bx}$

  →The first experimental point has a value of $y=y_1$

  →the error in the first point: $e_1=(a+bx_1) - y_1$

  → the sum of the squares of these errors:

$$\sum(e^2) = (a + bx_1 - y_1)^2 + (a + bx_2 - y_2)^2 + \cdots$$

- The theory of least squares

  →the best *a* from differentiating with respect to *a*

$$\frac{\partial \sum(e^2)}{\partial a} = 2(a + bx_1 - y_1)^1 + 2(a + bx_2 - y_2)^1 + \cdots = 0$$

$$\sum a + b\sum x - \sum y = 0$$

  →the best *b* from differentiating with respect to *b*

$$a\sum x + b\sum x^2 - \sum xy = 0$$

  These are normal equations.

  Simultaneous solution of these two Equations → give *a* and *b*

- The normal equation are :

$$\sum y = \sum a + b\sum x$$

$$\sum xy = a\sum x + b\sum x^2$$