Cohen's method

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Abstract

I reproduce Cohen's method for determining lattice constants for cubic crystals, and show explicitly the analysis for hexagonal/rhombohedral crystals. In both cubic and hexagonal/rhombohedral cases we derive the normal equations and their analytic solutions. Cohen's derivation is slightly generalized to show how the analysis works with an arbitrary error function $F(\theta)$. An example Excel spreadsheet performing the analysis for hexagonal/rhombohedral crystals is shown.

INTRODUCTION

You have performed an x-ray diffraction experiment, and found diffraction peaks at angles θ_i. You've managed to index each peak to indices $(hkl)_i$, and for the moment we'll assume you've proven that your system is cubic. For each peak θ_i, you could then calculate a lattice parameter a_i according to

$$\frac{\lambda^2}{4a_i^2}\left(h^2+k^2+l^2\right)_i = \sin^2\theta_i \tag{1}$$

where λ is the wavelength of the incident radiation. Now you have a set of a_i, but how do you determine the best estimate of a from that set? You could just average the a_i, which would be a decent estimate, but that neglects the fact that the systematic uncertainty in your diffractometer is not constant, but dependent on θ. What one would like to do is find the lattice constant a that best fits the set of lattice constants from individual diffraction peaks a_i *weighted by the systematic uncertainty* in the diffraction experiment. That is, weight the a_i more strongly where the diffractometer is more accurate.

The problem at hand is then to find the lattice constant(s) that best fit the experimental data accounting for systematic error. The data in this case is presumed to be a table of $\sin^2\theta$ values for diffraction peaks along with their (hkl) indices. Cohen's method[1] starts by presuming angular-dependent systematic error in $\sin^2\theta$ values of $DF(\theta)$, where D is a (specimen-dependent) constant and $F(\theta)$ is the function describing the systematic error. Given the error function, the method performs a least-squares analysis to find the lattice constants.

ERROR FUNCTIONS

First, we need an error function. The simplest case is the error function of Bradley and Jay[2], who found theoretically that errors due to absorption and eccentricity of the sample dominate, and give an uncertainty in interplanar spacing of

$$\frac{\Delta d}{d} \propto \cos^2\theta \tag{2}$$

We can relate this to the uncertainty in the measured $\sin^2\theta$ values in the following way. First, square Bragg's law, and take the logarithm:

$$n^2\lambda^2 = 4d^2\sin^2\theta \qquad \text{or} \qquad \frac{n^2\lambda^2}{4} = 4d^2\sin^2\theta \tag{3}$$

$$2\log\frac{n\lambda}{2} = \log\sin^2\theta + 2\log d + 2\log 2 \tag{4}$$

Now differentiate (treating $u = \sin^2\theta$ as a variable, and $n\lambda$ as a constant), and

$$0 = \frac{\Delta\sin^2\theta}{\sin^2\theta} + \frac{2\Delta d}{d} \tag{5}$$

$$-2\frac{\Delta d}{d} = \frac{\Delta\sin^2\theta}{\sin^2\theta} \tag{6}$$

$$\text{or} \qquad \frac{\Delta d}{d} \propto \frac{\Delta\sin^2\theta}{\sin^2\theta} \tag{7}$$

Then we can write the uncertainty in $\sin^2\theta$ due to systematic uncertainties using Eq. 2 as

$$\Delta\sin^2\theta = \frac{\Delta d}{d}\sin^2\theta = \cos^2\theta\sin^2\theta \propto \sin^2 2\theta \equiv F(\theta) \tag{8}$$

A better error function was determined experimentally by Nelson and Riley:[3]

$$\frac{\Delta d}{d} \propto \frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \tag{9}$$

Proceeding as above, we can relate this to the uncertainty in $\sin^2\theta$ values:

$$\Delta \sin^2\theta = \frac{1}{2}\sin^2 2\theta \left(\frac{1}{\sin\theta} + \frac{1}{\theta}\right) \equiv F(\theta) \tag{10}$$

Given an error function $F(\theta)$, we can proceed. Which one to choose? For the experimental data in Fig. 1, covering an angular range of $\theta \in \{15, 50\}$, the difference in lattice constants determined by the two error functions above was about 0.03%. Unless you are doing very high precision work on single crystals, it probably doesn't matter. Nelson & Riley's paper does spell out the details and differences.[3]

CUBIC CRYSTALS

The measured values of $\sin^2\theta$ can be related to the lattice constants and hkl indices accounting for the systematic error. For a cubic crystal, in the absence of errors, we have

$$A(h^2 + k^2 + l^2)_i = \sin^2\theta_i \tag{11}$$

for each peak i where $A = \lambda^2/4a_o^2$. Here the left-hand side is the predicted value from the lattice constant a_o and the (hkl) indices, while the right-hand side is the experimentally determined value of $\sin^2\theta_i$. Including the systematic errors means adding our systematic error to our prediction to better approximate the experimental data. That means adding a (specimen-dependent) constant D times our error function to the predicted values:

$$A(h^2 + k^2 + l^2)_i + DF(\theta_i) = \sin^2\theta_i \tag{12}$$

For convenience, we define $\alpha_i = (h^2+k^2+l^2)_i$ and $\delta_i = F(\theta_i)$. For the Bradley and Jay error function, $\delta_i = 10\sin^2 2\theta_i$, and for the Nelson-Riley function, $\delta_i = 10\sin^2 2\theta_i(1/\sin\theta_i + 1/\theta_i)$.[4] With these definitions we can write,

$$A\alpha_i + D\delta_i = \sin^2\theta_i \tag{13}$$

now the left-hand side is the predicted value of $\sin^2\theta$ including errors, and the right-hand side is the experimental value of $\sin^2\theta$. We wish to find the A and D that minimize the sum of the squared differences ϵ_i^2 between measurement (RHS) and prediction (LHS). That is, we should minimize

$$\sum_i (A\alpha_i + D\delta_i - \sin^2\theta_i)^2 = \sum_i \epsilon_i^2 \equiv \epsilon_t^2 \tag{14}$$

If ϵ_t^2 is minimal, then derivatives of ϵ_t^2 with respect to A or D should be zero.

$$\frac{d\epsilon_t^2}{dA} = \sum_i 2\alpha_i(A\alpha_i + D\delta_i - \sin^2\theta_i) = 0 \tag{15}$$

$$\frac{d\epsilon_t^2}{dD} = \sum_i 2\delta_i(A\alpha_i + D\delta_i - \sin^2\theta_i) = 0 \tag{16}$$

Simplifying gives the two normal equations:

$$A\sum_i \alpha_i^2 + D\sum_i \alpha_i\delta_i = \sum_i \alpha_i \sin^2\theta_i \tag{17}$$

$$A\sum_i \alpha_i\delta_i + D\sum_i \delta_i^2 + \sum_i \delta_i \sin^2\theta_i \tag{18}$$

The experimental data determines all but A and D. Solving these two equations simultaneously for A and D yields the lattice parameter a_o. With some tedium, one can show

$$A = \lambda^2/4a_o^2 = \frac{\left(\sum_i \alpha_i \sin^2\theta_i\right)\left(\sum_i \delta_i^2\right) - \left(\sum_i \alpha_i\delta_i\right)\left(\sum_i \delta_i \sin^2\theta_i\right)}{\left(\sum_i \alpha_i^2\right)\left(\sum_i \delta_i^2\right) - \left(\sum_i \alpha_i\delta_i\right)^2} \tag{19}$$

$$a_o = \frac{\lambda}{2}\sqrt{\frac{\left(\sum_i \alpha_i^2\right)\left(\sum_i \delta_i^2\right) - \left(\sum_i \alpha_i\delta_i\right)^2}{\left(\sum_i \alpha_i \sin^2\theta_i\right)\left(\sum_i \delta_i^2\right) - \left(\sum_i \alpha_i\delta_i\right)\left(\sum_i \delta_i \sin^2\theta_i\right)}} \tag{20}$$

HEXAGONAL CRYSTALS

For a hexagonal system, with no errors we have

$$A(h^2 + hk + k^2)_i + Cl_i^2 = \sin^2\theta_i \tag{21}$$

Where $A = \lambda^2/3a_o^2$ and $C = \lambda^2/4c_o^2$. As in the cubic case, we can simplify this further:

$$\alpha_i A + \gamma_i C = \sin^2\theta_i \tag{22}$$

where $\alpha_i = (h^2 + hk + k^2)_i$ and $\gamma_i = l^2$. Including errors as above, we have

$$\alpha_i A + \gamma_i C + \delta_i D = \sin^2\theta_i \tag{23}$$

with again $\delta_i = F(\theta_i)$. The sum of the squared differences between measurement and prediction are then

$$\sum_i (A\alpha_i + C\gamma_i + D\delta_i - \sin^2\theta_i)^2 = \sum_i \epsilon_i^2 \equiv \epsilon_t^2 \tag{24}$$

The normal equations are found from derivatives of ϵ_t^2 with respect to A, C, and D:

$$\frac{d\epsilon_t^2}{dA} = \sum_i 2\alpha_i \left(\alpha_i A + \gamma_i C + \delta_i D - \sin^2\theta_i\right) = 0 \tag{25}$$

$$\frac{d\epsilon_t^2}{dC} = \sum_i 2\gamma_i \left(\alpha_i A + \gamma_i C + \delta_i D - \sin^2\theta_i\right) = 0 \tag{26}$$

$$\frac{d\epsilon_t^2}{dD} = \sum_i 2\delta_i \left(\alpha_i A + \gamma_i C + \delta_i D - \sin^2\theta_i\right) = 0 \tag{27}$$

Simplifying,

$$A\sum_i \alpha_i^2 + C\sum_i \alpha_i\gamma_i + D\sum_i \alpha_i\delta_i = \sum_i \alpha_i \sin^2\theta_i \tag{28}$$

$$A\sum_i \alpha_i\gamma_i + C\sum_i \gamma_i^2 + D\sum_i \gamma_i\delta_i = \sum_i \gamma_i \sin^2\theta_i \tag{29}$$

$$A\sum_i \alpha_i\delta_i + C\sum_i \gamma_i\delta_i + D\sum_i \delta_i^2 = \sum_i \delta_i \sin^2\theta_i \tag{30}$$

Using the experimental values for the sums involving α_i, δ_i, γ_i and $\sin^2\theta_i$, we are left with a system of 3 equations and 3 unknowns. Solving them gives A and C, which can be used to obtain a_o and c_o. One can solve these equations analytically for A and C with a great deal of effort better spent by a computer. Here are the results for A and C in case you are curious:

$$A = \frac{A'}{A_D} \tag{31}$$

$$\begin{aligned} A' = {} & \sum_i \alpha_i \sin^2\theta_i \sum_i \gamma_i^2 \sum_i \delta_i^2 + \sum_i \alpha_i\gamma_i \sum_i \gamma_i\delta_i \sum_i \delta_i \sin^2\theta_i + \sum_i \alpha_i\delta_i \sum_i \gamma_i \sin^2\theta_i \sum_i \gamma_i\delta_i \\ & - \sum_i \alpha_i\delta_i \sum_i \gamma_i^2 \sum_i \delta_i \sin^2\theta_i - \sum_i \alpha_i\gamma_i \sum_i \gamma_i \sin^2\theta_i \sum_i \delta_i^2 - \sum_i \alpha_i \sin^2\theta_i \sum_i \gamma_i\delta_i \sum_i \gamma_i\delta_i \end{aligned} \tag{32}$$

$$A_D = \sum_i \alpha_i\gamma_i \sum_i \gamma_i^2 \sum_i \delta_i^2 + 2\sum_i \alpha_i\gamma_i \sum_i \alpha_i\delta_i \sum_i \gamma_i\delta_i - \sum_i \gamma_i^2 \sum_i \alpha_i\delta_i^2 - \sum_i \delta_i^2 \sum_i \alpha_i\gamma_i^2 - \sum_i \alpha_i^2 \sum_i \gamma_i\delta_i^2 \tag{33}$$

$$C = \frac{C'}{A_D} \tag{34}$$

$$\begin{aligned} C' = {} & \sum_i \alpha_i^2 \sum_i \gamma_i \sin^2\theta_i \sum_i \delta_i^2 + \sum_i \alpha_i \sin^2\theta_i \sum_i \gamma_i\delta_i \sum_i \alpha_i\delta_i + \sum_i \alpha_i \sin^2\theta_i \sum_i \alpha_i\gamma_i \sum_i \delta_i \sin^2\theta_i \\ & - \sum_i \alpha_i \sin^2\theta_i \sum_i \gamma_i \sin^2\theta_i \sum_i \alpha_i\delta_i - \sum_i \alpha_i \sin^2\theta_i \sum_i \alpha_i\gamma_i \sum_i \delta_i^2 - \sum_i \alpha_i^2 \sum_i \gamma_i\delta_i \sum_i \delta_i \sin^2\theta_i \end{aligned} \tag{35}$$

$$A_D = \sum_i \alpha_i\gamma_i \sum_i \gamma_i^2 \sum_i \delta_i^2 + 2\sum_i \alpha_i\gamma_i \sum_i \alpha_i\delta_i \sum_i \gamma_i\delta_i - \sum_i \gamma_i^2 \sum_i \alpha_i\delta_i^2 - \sum_i \delta_i^2 \sum_i \alpha_i\gamma_i^2 - \sum_i \alpha_i^2 \sum_i \gamma_i\delta_i^2 \tag{36}$$

As you can see above, it is far too tedious to write down a general solution in terms of the various sums. After arriving at the normal equations, it is much more sensible to use numerical matrix methods to solve for A and D. Figure 1 shows how to do the calculations in Excel using matrix methods, given a list of peak angles, hkl indices, and the incident radiation wavelength.

Alternatively, one can start by considering the $\sin^2\theta_i$ values to be a three-dimensional function and use standard curve fitting methods. Our function is

$$f(\theta_i) = \sin^2\theta_i = \alpha_i A + \gamma_i C + \delta_i D \tag{37}$$

From the experimental data, construct columns of data $(\alpha_i, \gamma_i, \delta_i, \sin^2\theta_i) = (x, y, z, f)$ and fit the data to a linear function $f = Ax + Cy + Dz$. This has the advantage that most fitting routines (e.g., in OriginLab) will include uncertainty in the estimated parameters and covariances. [5]

FIG. 1: Example excel sheet

Fe2MnGe sample (900C/23D anneal), Co K-α

			α	γ	δ													
h	k	l	h^2+hk+k^2	l^2	10*sin^2(2θ)	2θ	θ	sin^2(2θ)	α*sin^2(θ)	γ*sin^2(θ)	δ*sin^2(θ)	α^2	γ^2	δ^2	αγ	αδ	γδ
1	0	1	1	1	3.05920463	33.58	16.79	0.08344282	0.08344282	0.08344282	0.25526866	1	1	9.358732973	1	3.05920463	3.05920463
2	0	0	4	0	5.28607768	46.64	23.32	0.15670995	0.6268398	0	0.82838097	16	0	27.94261726	0	21.1443107	0
0	0	2	0	4	5.86136479	49.96	24.98	0.17833887	0	0.71335549	1.04530919	0	16	34.35559719	0	0	23.4454592
2	0	2	4	4	8.90433359	70.67	35.335	0.33449574	1.33798296	1.33798296	2.97846165	16	16	79.28715676	16	35.6173344	35.6173344
3	0	0	9	0	9.13147476	72.86	36.43	0.35264624	3.17381615	0	3.22018023	81	0	83.38383128	0	82.1832728	0
2	0	3	4	9	9.86629558	96.64	48.32	0.55781531	2.23126125	5.02033782	5.50357076	16	81	97.34378847	36	39.4651823	88.7966602
							SUM -->		7.45334298	7.1551191	13.8311715	130	114	331.6717239	53	181.469305	150.918658

λ 1.789

AX = B

	130	53	181.469		7.4533
A = coeff	53	114	150.9187	B = RHS	7.1551
normal eq	181.469	150.919	331.672		13.8312

A matrix (all are sums)

αα	αγ	αδ
αγ	γγ	γδ
αδ	γδ	δδ

B matrix (sums)

α sin^2(θ)
γ sin^2(θ)
δ sin^2(θ)

to get A, C, D: =MMULT(MINVERSE(F14:H16),L14:L16) (select 3 col cells and ctrl+enter)

A	0.039225	-->	a	5.2151731 Å
C	0.044598	-->	c	4.2356626 Å
D	########			

results Origin fit to data below

A	0.03923	a	5.2148348 Å
C	0.0446	c	4.2355803 Å
D	-5.92E-05		
dA	8.39E-05	da	5.57E-03 Å
dC	6.90E-05	dc	3.28E-03 Å
dD	7.49E-05		

[1] M. U. Cohen, Review of Scientific Instruments **6**, 68 (1935).
[2] A. J. Bradley and A. H. Jay, Proceedings of the Physical Society **44**, 563 (1932).
[3] J. B. Nelson and D. P. Riley, Proceedings of the Physical Society **57**, 160 (1945).

[4] The factor 10 is to make all terms of comparable size.
[5] Don't forget to propagate uncertainties when going from A to a. Since $a = \lambda/\sqrt{3A}$, the uncertainty in a is related to the uncertainty in A by $\delta a = \frac{1}{2}\frac{\delta A}{A}a$.