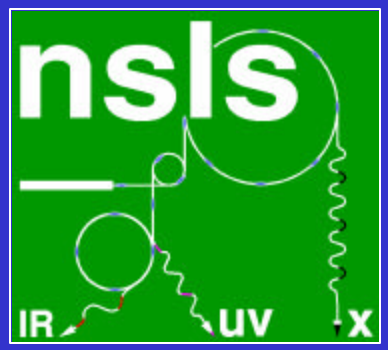
Powder Indexing of Difficult Cells using the Indexing Options within Topas

ACA, Orlando, May 28, 2005



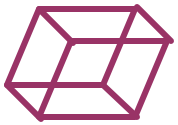
Thanks to Alen Coehlo and Arnt Kern for writing and fostering Topas, and for endless help in using it.

http://powder.physics.sunysb.edu
pstephens@sunysb.edu

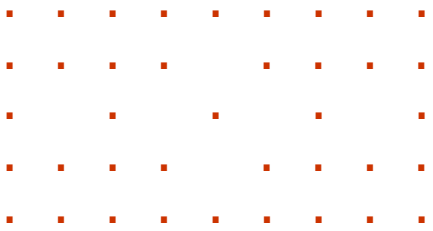
THEORY OF POWDER DIFFRACTION

(series of elementary recipes)

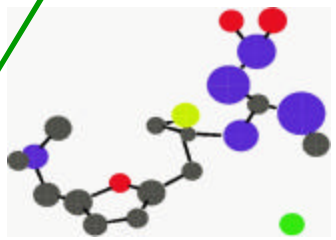
UNIT CELL



RECIPROCAL LATTICE,
SPACE GROUP



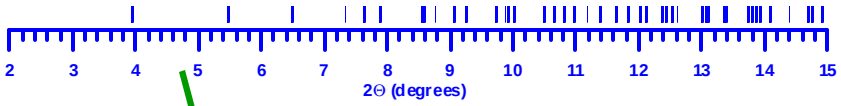
CONTENTS
OF UNIT CELL



INTENSITIES

$$I_{hkl} \sim \left| \sum f_j e^{2pi(hkl)\cdot(xyz)_j} \right|^2$$

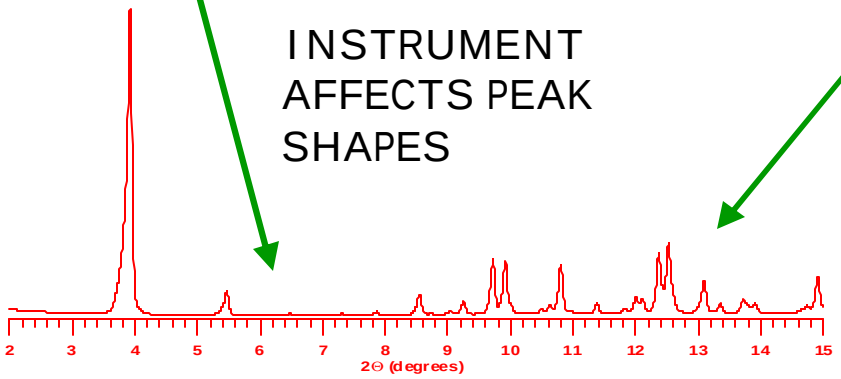
POWDER PEAK POSITIONS



PHYSICAL SAMPLE
AFFECTS LINESHAPES

INSTRUMENT
AFFECTS PEAK
SHAPES

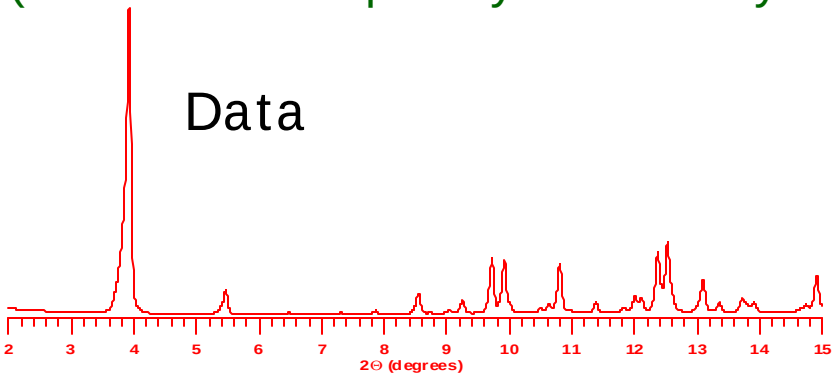
OTHER ARTIFACTS:
PREFERRED ORIENTATION, ETC.



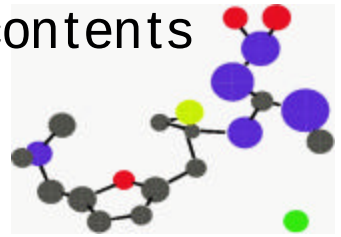
POWDER DIFFRACTION PATTERN

USE OF POWDER DIFFRACITON TO SOLVE A CRYSTAL STRUCTURE

(series of conceptually elementary recipes, depends on lots of computing)



Chemical knowledge of contents



1. Start with the best data you can get (but no better).
2. Get a list of accurate diffraction peak positions.
3. Figure out a lattice that explains the peaks.
4. Guess the space group (systematic absences, # molecules).
5. Search for the best place to put the molecule(s), best conformation of the molecule, best agreement data *vs.* model.
6. Refine, refine, refine, refine, refine, …

At any stage, you can be forced to jump back to any stage.

Indexing: The Problem

A crystal is defined by three translation vectors, $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, which produce a reciprocal lattice $\boldsymbol{a^*}$, $\boldsymbol{b^*}$, and $\boldsymbol{c^*}$.

Each possible reflection (hkl) is associated with a reciprocal lattice vector

$$\boldsymbol{Q} = h\boldsymbol{a^*} + k\boldsymbol{b^*} + l\boldsymbol{c^*},$$

such that the lattice planes which cause that reflection are separated by a distance $d = 1/|\boldsymbol{Q}|$.

In a powder experiment, one only measures the magnitude of $\boldsymbol{Q}$, so the 3D reciprocal lattice gets compressed into one dimension.

One can shuffle the equations around to a form that is more convenient,

$$1/d^2 = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk.$$

So the problem of indexing a powder diffraction pattern becomes:

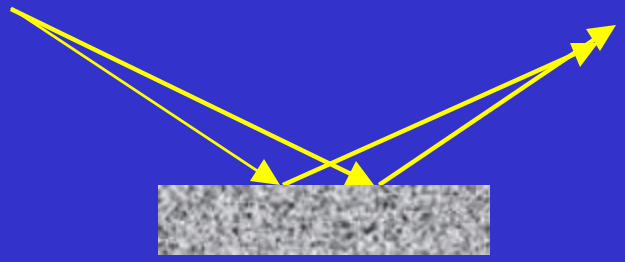
Given a list of *d* spacings, find a set of numbers {*A*,*B*,…,*F*} so that you can assign (*hkl*) to each *d*-spacing in the equation above…

(in the presence of experimental error, perhaps with some rogue extra *d*-spacings)

There is a pretty good collection of public domain programs for that purpose: TREOR, ITO, DICVOL, Crysfire suite.

This is a data-driven enterprise, and that means that your diffractometer has to be well aligned, errors due to sample displacement, transparency have to be controlled.

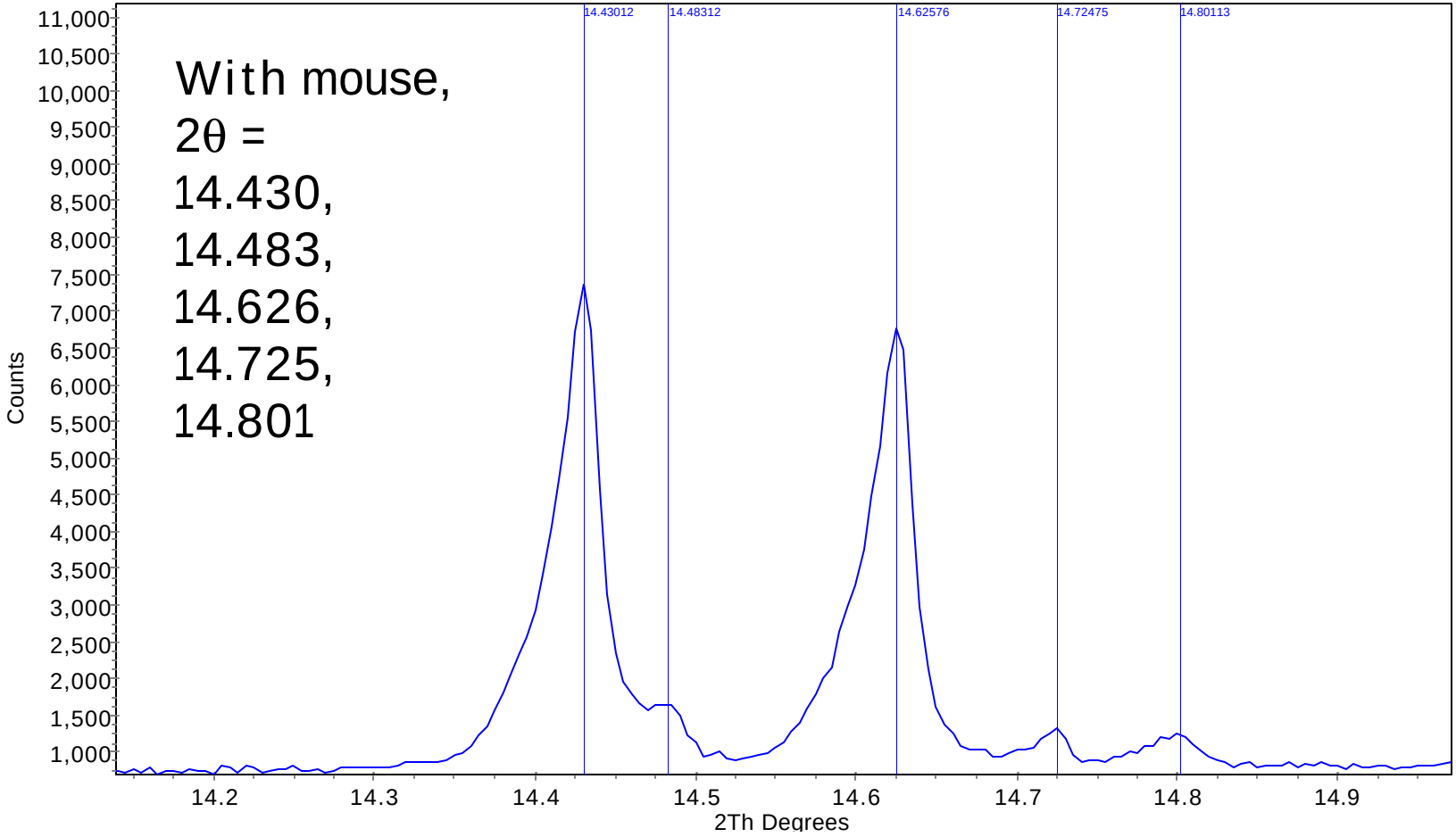
Bragg-Brentano

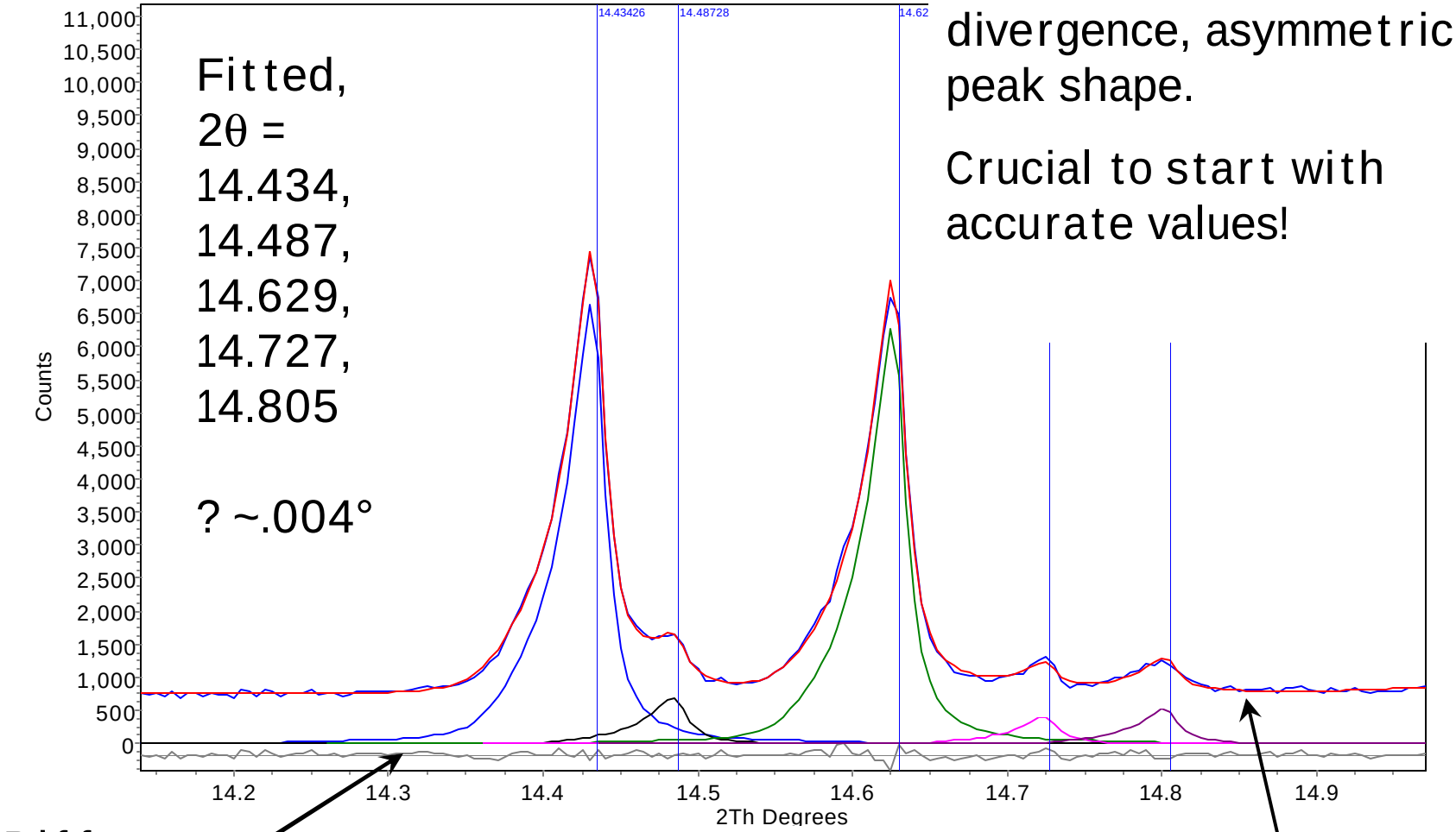


Focus diverging beam. Moderate resolution, sensitive to sample displacement, transparency

I'm illustrating with synchrotron data, which is not a particularly rigorous test of indexing algorithms.

Accurate peak positions require fitting model lineshape to observed data. (Here using Topas) (Data from NSLS X3B1)

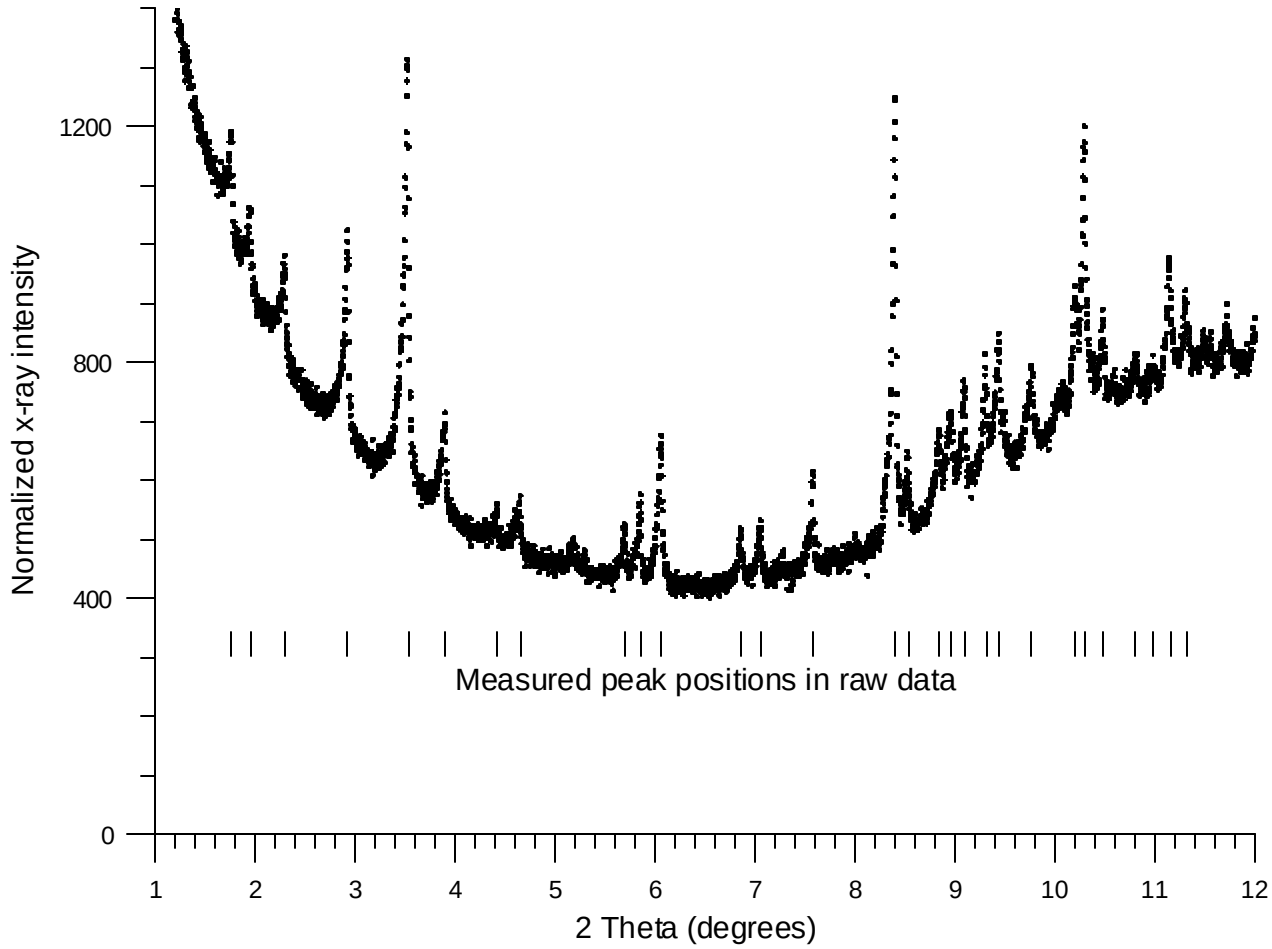




Note shifts due to axial divergence, asymmetric peak shape.

Crucial to start with accurate values!

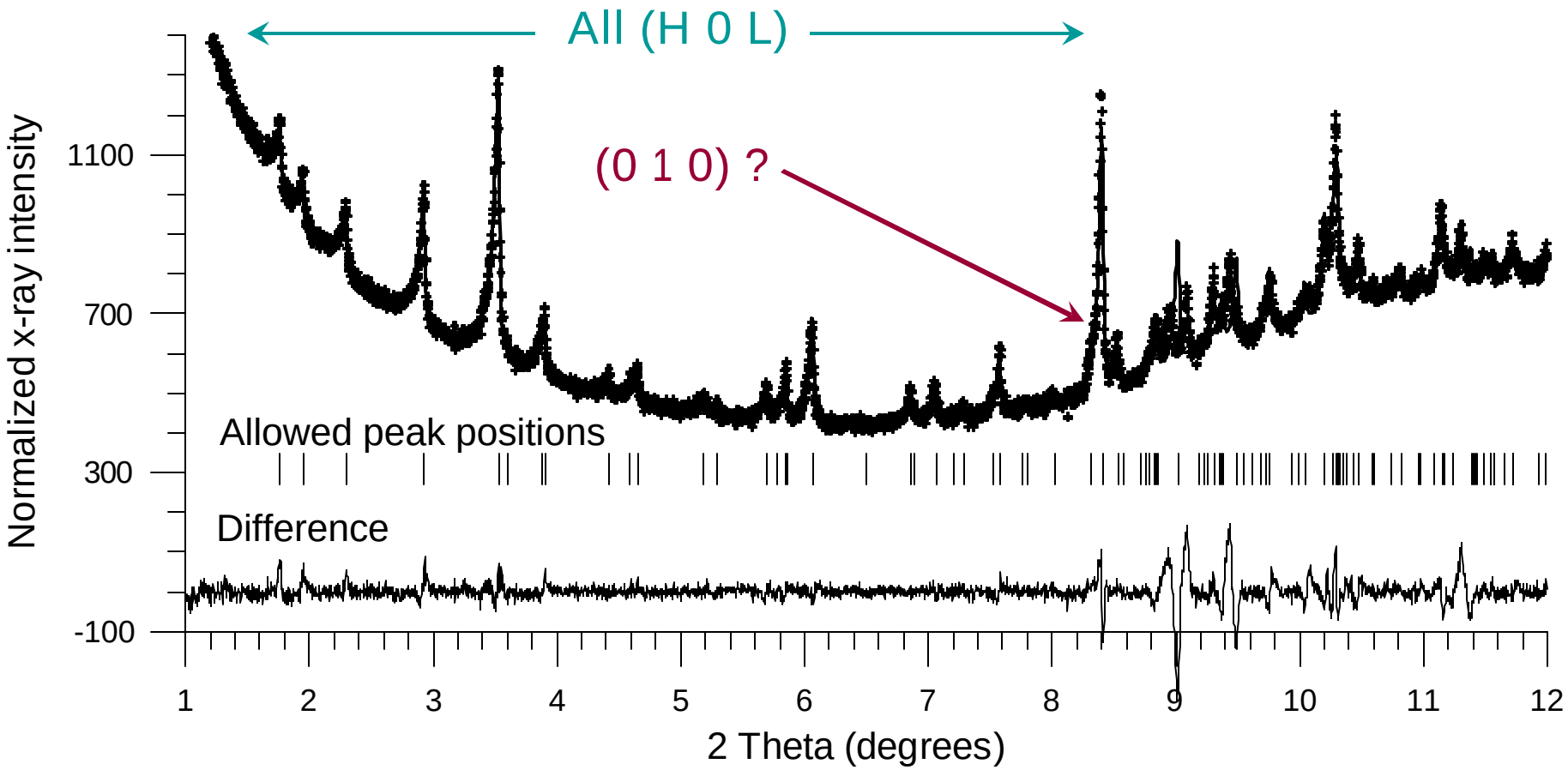
1st Example. Amyloid analog from lab of D. Eisenberg, UCLA. (six peptides, Cd, unknown amount of water)



First tried with ITO. Serious dominant zone problem.

The first 15 observed peaks are fit by a single zone
(2D slice of reciprocal space): *a* = 23.413 Å, *c* = 21.190 Å, ß = 103.86°

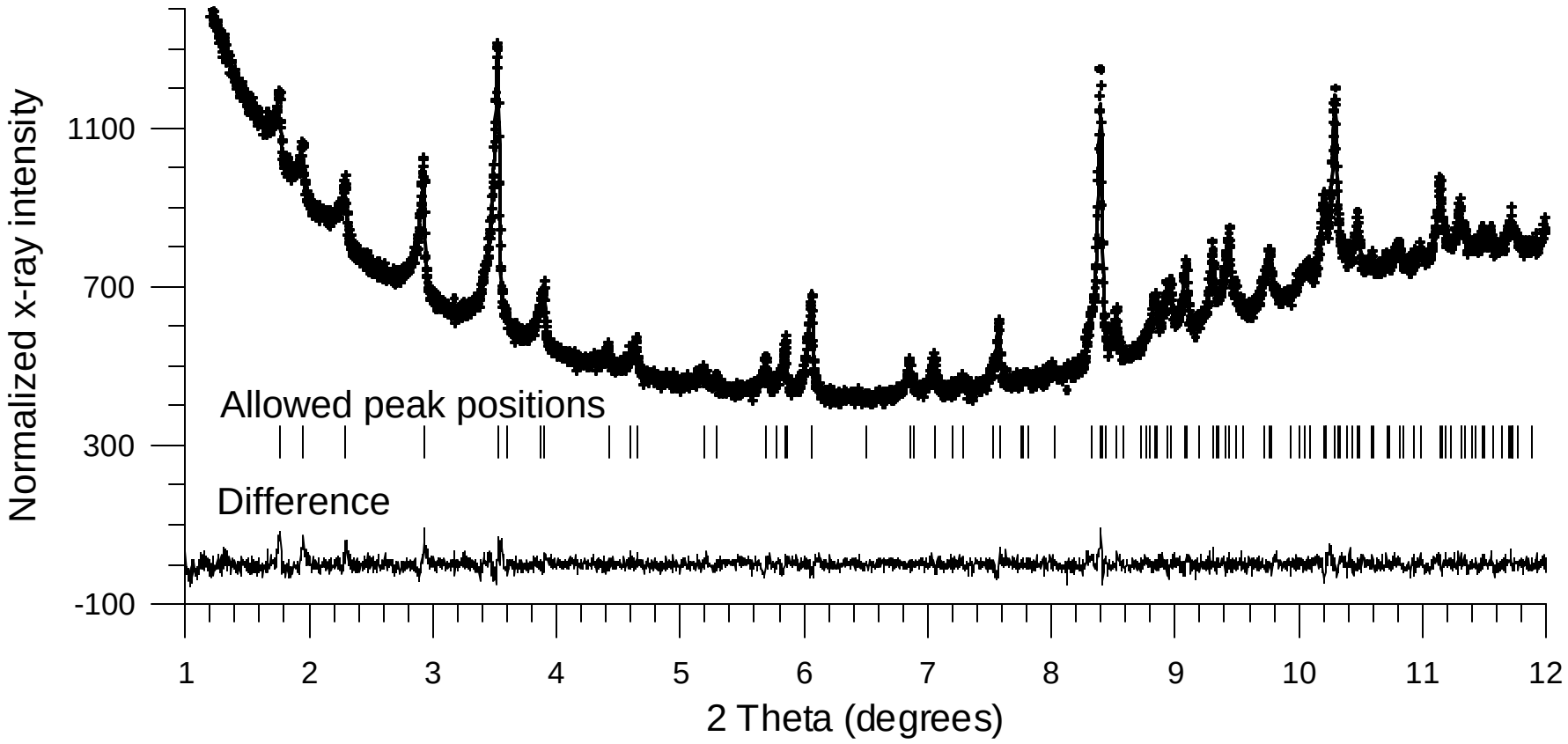
Is it monoclinic with b = 4.707 Å? No.



Is the peak at *d* = 4.707 Å? the (-1 1 1)?

Apparently so.

a = 23.413 Å
b = 4.889 Å
c = 21.190 Å
β= 103.86°
P 2_1 ?
beta-sheet

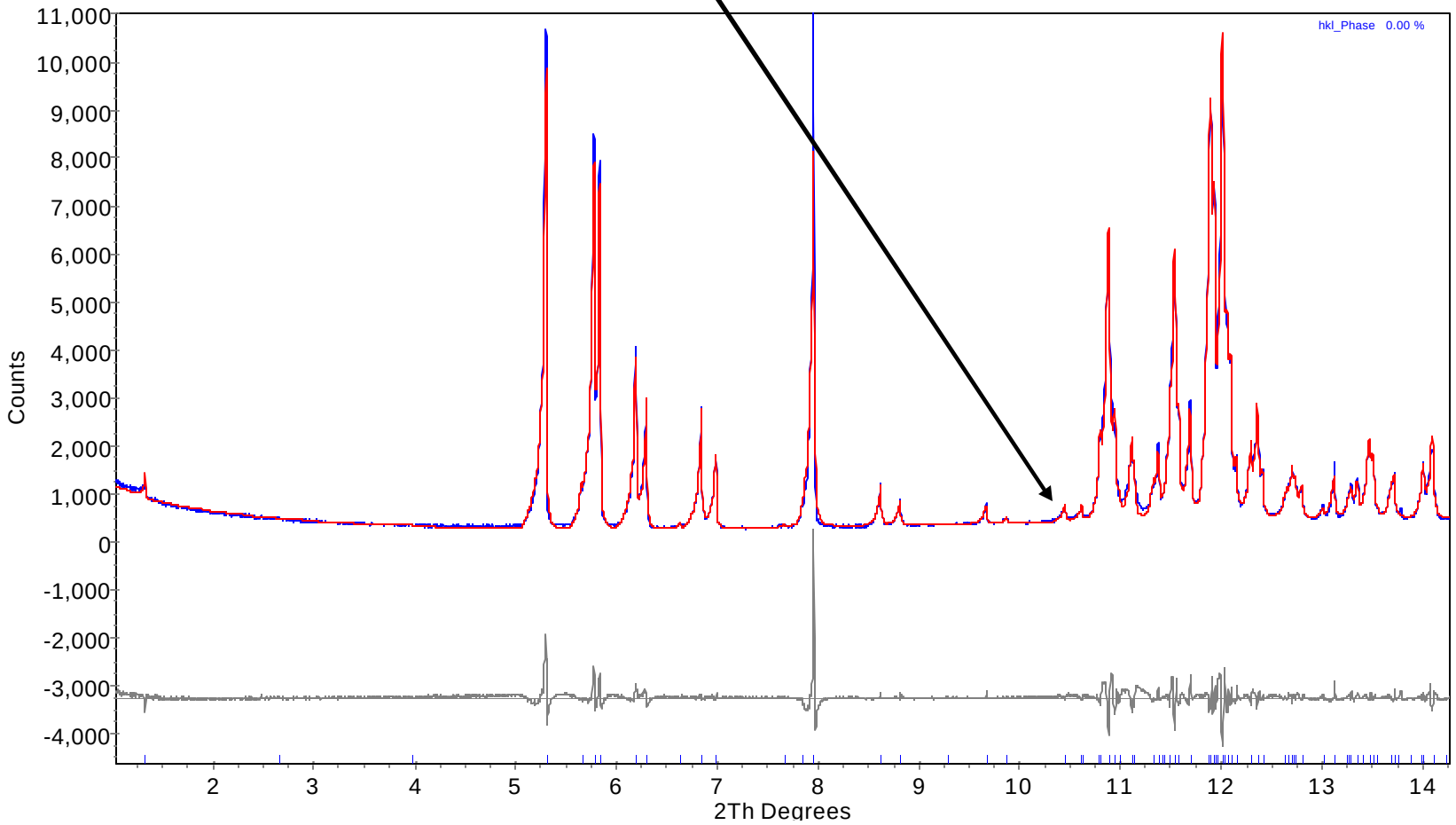


Some months later, at a conference I bumped into Arnt Kern and Frank Stowasser, who popped my diffraction lines into Topas.

It decisively spit out the answer in a few seconds!

2nd example. Small molecule from Sara Wishkerman, BGU Israel.
One form known from single crystal, 2nd polymorph only powder.

Index everything up to here with a single zone,
31.223Å x 7.093Å, ß = 104.4º

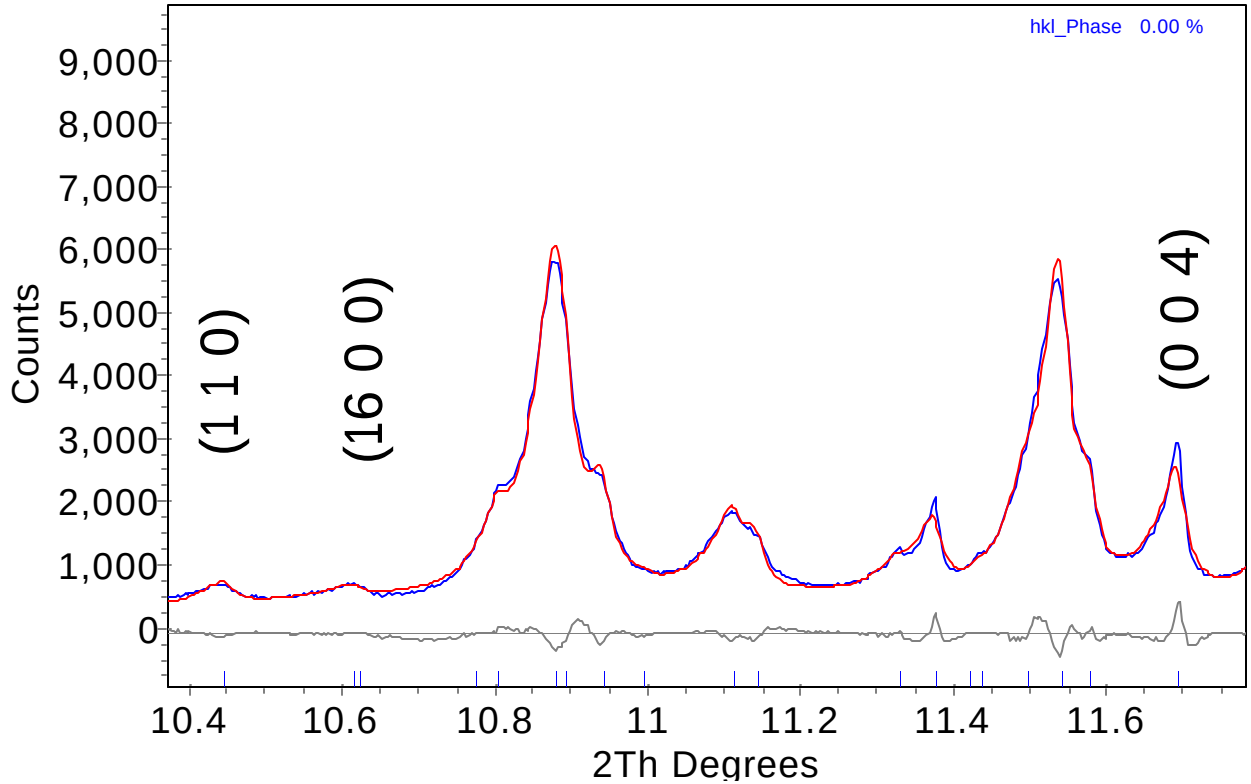


But attempts to find the third axis by hand failed.

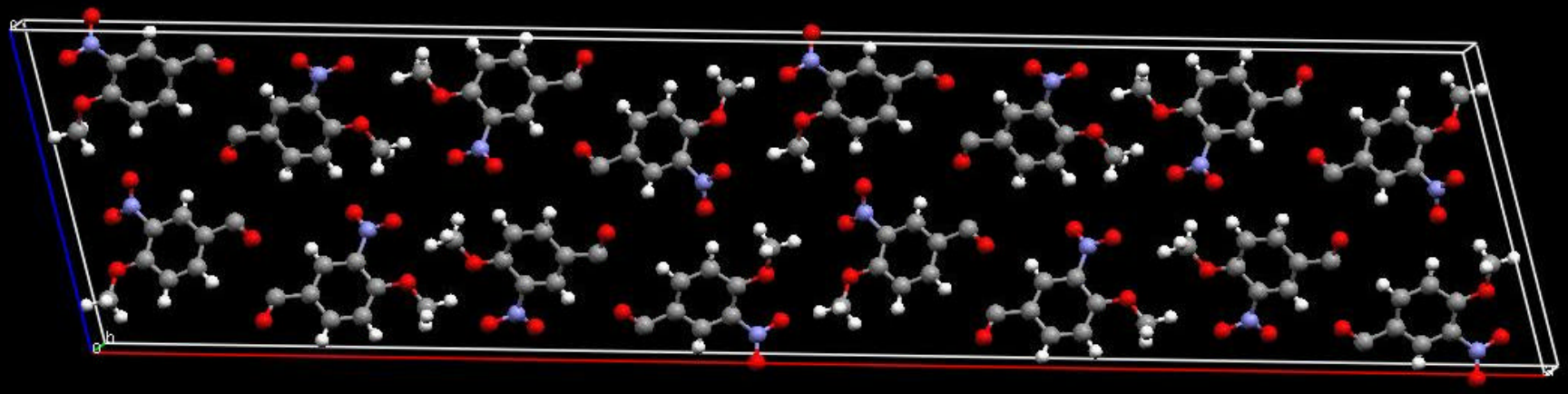
(This is the last time I'll bother to index anything without Topas.)

Without hesitation, Topas spits out space group C2/c

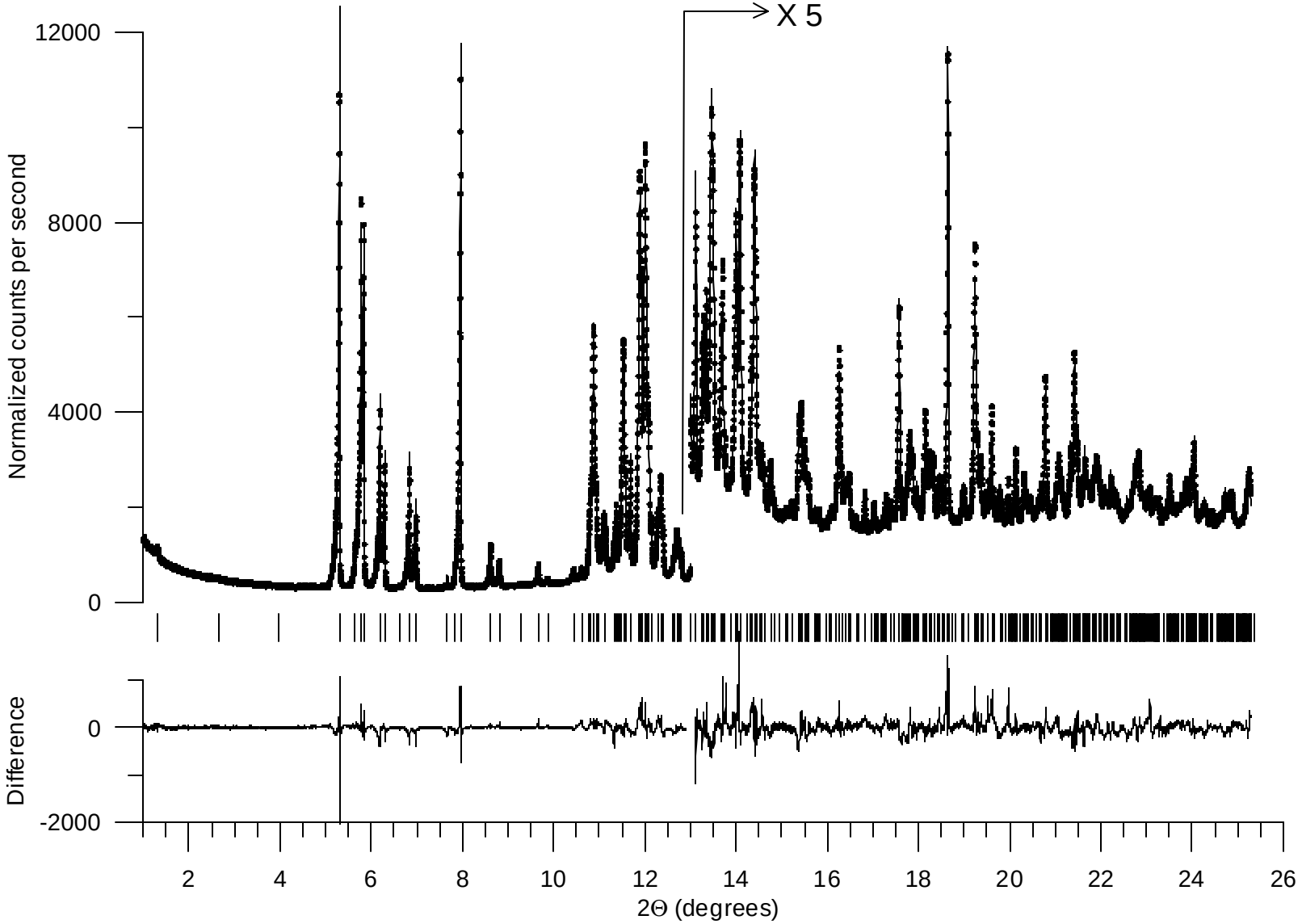
a = 62.424Å, *b* = 3.849Å, *c* = 14.180Å, ß = 104.40°

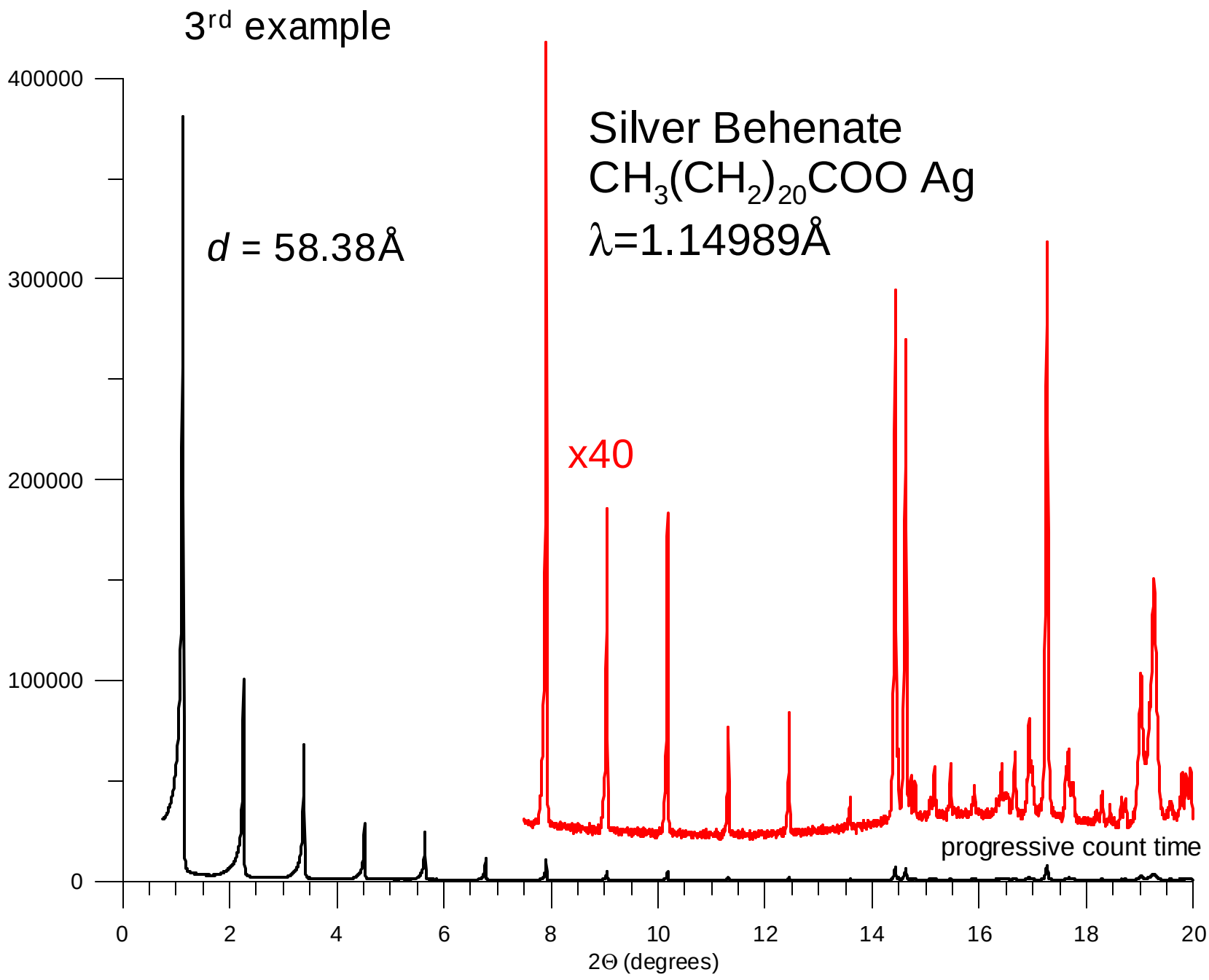


4-methoxy 3-nitro benzaldehyde Form II



4-methoxy 3-nitro benzaldehyde Form II




3rd example
Silver Behenate
CH3(CH2)20COO Ag
λ=1.14989Å
d = 58.38Å
x40
progressive count time
400000
300000
200000
100000
0
0
2
4
6
8
10
12
14
16
18
20
2Θ (degrees)

```
seed
index_lam 1.149854

Bravais_Triclinic_sg
s

load index_th2 {
1.129713
2.259535
3.389577
4.51994944
5.6507616
6.782125
7.91415071
9.04695034
10.1806364
11.3153229
    (51 more lines)
21.3459
21.4153
21.5917301
}
```

```
1)       P-1 0 2245.4 183.47 5.4220 7.1597 58.4694 86.558 88.194
     97.316
2)   . . . . .
8282) P2 7 4185.9 1.00 18.3416 58.3182 3.9316 90.000 84.489 90.000
. . . . . .
1   0  -6    4.626
1   0   7    4.599
1  -1   0    4.577    4.577   -0.000   14.433   14.433    0.001
1  -1  -1    4.566
1  -1   1    4.560    4.560    0.000   14.487   14.487   -0.000
1  -1  -2    4.527
1  -1   2    4.516    4.516    0.000   14.629   14.629   -0.000
0   0  13    4.486    4.486   -0.000   14.727   14.727    0.000
1  -1  -3    4.463    4.462   -0.001   14.803   14.805    0.002
1  -1   3    4.447
1   0  -7    4.437    4.437    0.000   14.892   14.892   -0.000
1   0   8    4.410    4.410   -0.000   14.983   14.983    0.000
0   1  11    4.383
1  -1  -4    4.377    4.377    0.001   15.096   15.095   -0.002
0  -1  10    4.367
1  -1   4    4.357    4.357    0.000   15.166   15.166   -0.000
1  -1  -5    4.272    4.272    0.000   15.468   15.467   -0.001
1  -1   5    4.249
```

No such thing as c-centered triclinic, so a quick adjustment gives ->

Reduce to primitive triclinic

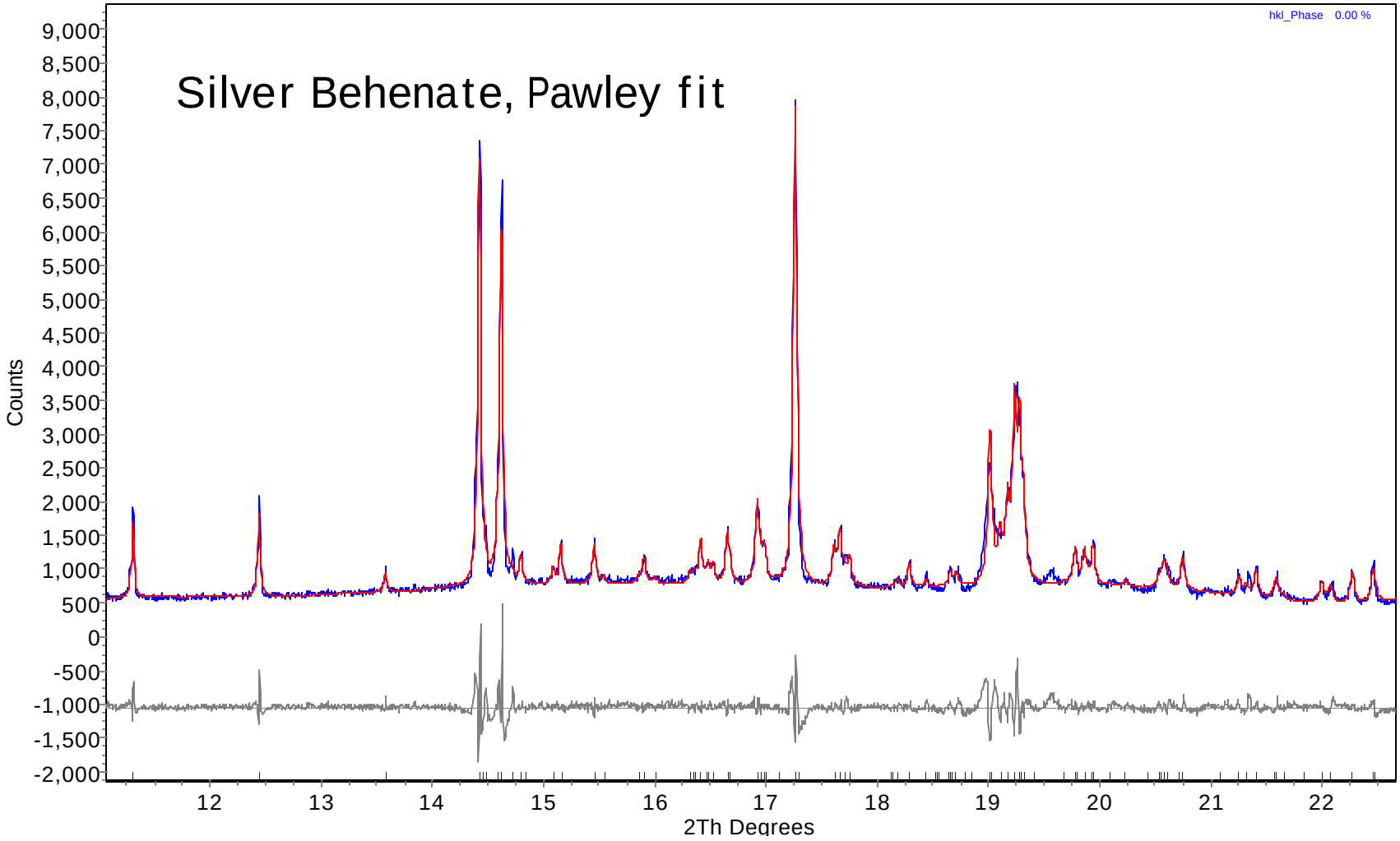
a = 4.2225Å, b = 4.7725Å, c = 58.547Å

a = 91.707º, ß = 85.527º, ? = 106.344º

cf. V. Vand *et al.* (1949), using a Frevel focusing camera

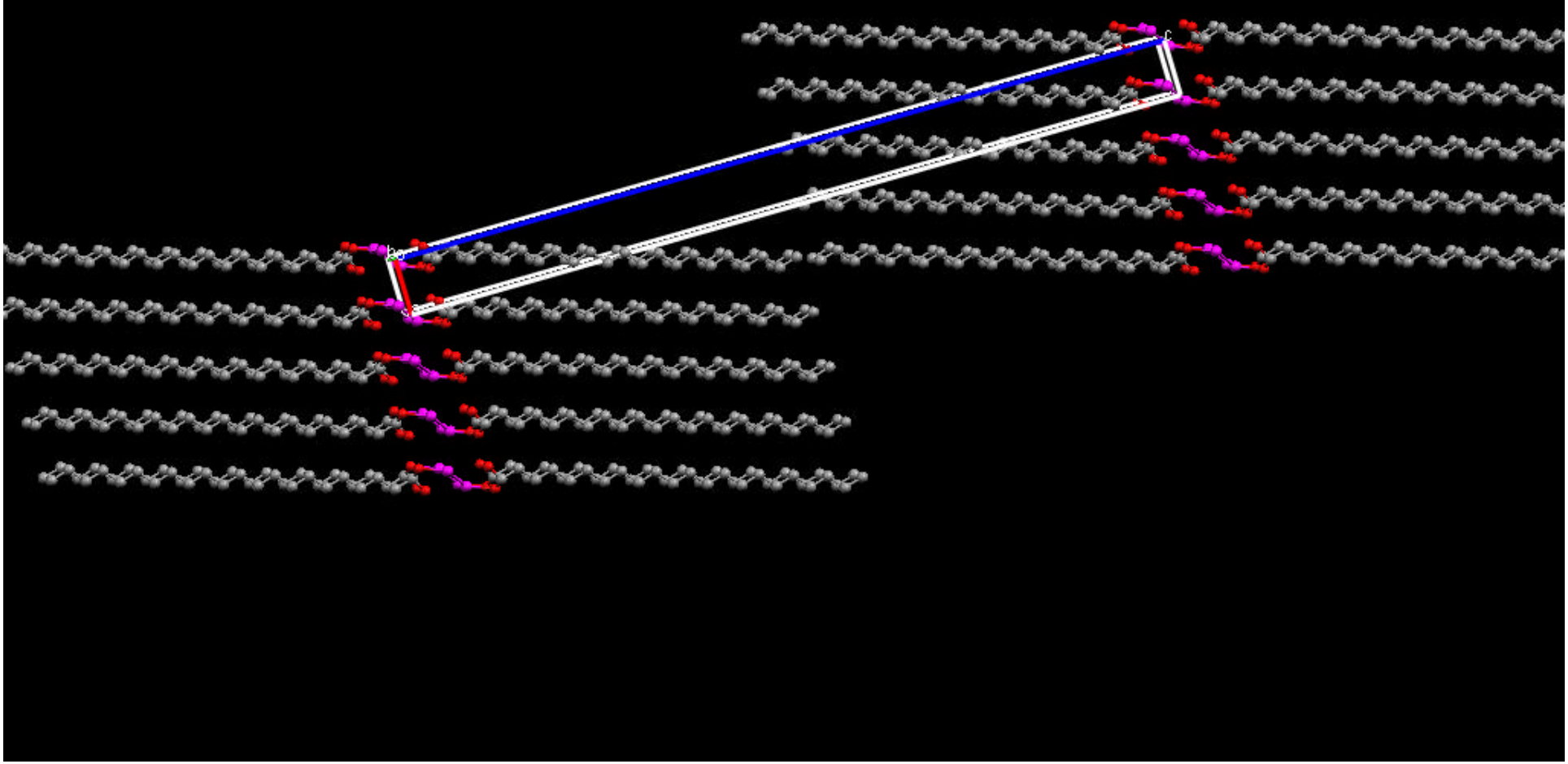
Table 4. *Silver soaps: parameters of the unit cell at* 20° C.

Soap	Silver caproate	Silver caprylate	Silver caprate	Silver laurate	Silver myristate	Silver palmitate	Silver stearate
A^*	0·2213	0·2200	0·2193	0·2198	0·2189	0·2192	0·2196
B^*	0·2528	0·2493	0·2502	0·2496	0·2489	0·2486	0·2502
c^*	0·05056	0·04078	0·03396	0·02920	0·02562	0·02277	0·02054
α^*	80° 16′	78° 42′	77° 53′	77° 1′	76° 32′	76° 23′	76° 1′
β^*	81° 11′	84° 11′	85° 22′	86° 35′	87° 39′	88° 58′	89° 28′
γ (mean)	80° 4′	79° 38′	78° 57′	77° 53′	78° 23′	77° 3′	76° 1′
a (A.)	4·588	4·621	4·646	4·653	4·663	4·682	4·693
b (A.)	4·016	4·078	4·072	4·097	4·102	4·128	4·120
c (A.)	20·41	25·24	30·31	35·33	40·30	45·32	50·35
α	101° 12′	102° 23′	103° 9′	103° 51′	104° 9′	104° 13′	104° 35′
β	102° 28′	97° 48′	96° 57′	95° 59′	95° 3′	94° 7′	93° 59′


Silver Behenate, Pawley fit
hkl_Phase 0.00 %
Counts
9,000
8,500
8,000
7,500
7,000
6,500
6,000
5,500
5,000
4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
-500
-1,000
-1,500
-2,000
12
13
14
15
16
17
18
19
20
21
22
2Th Degrees

Structure solved with PSSP.

I'm not ready to discuss it in detail.



Conclusions:

1) Get the best data you can.

2) Use the best software you can.