Lesson 6
“How-To” Session

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Repetition: Refinement Strategies

- We control which parameters will be refined:
  - Fix / release for refinement («PARAM=»)
  - Set lower and upper limits

Question:

Why not **ALWAYS** refine **EVERYTHING**?

Answer:

Don’t try to get more information out of your data than it actually contains!

Refinements can become **unstable**

Correlations can spoil the results

Correlations

Effect in Diffraction Pattern	Origin in Crystal Structure Model
Wrong peak positions	Unit cell dimensions Sample height displacement Zero-shift
Wrong absolute intensities	Weight fraction (scaling)
Wrong relative intensities	Preferred orientation Atomic species / Substitutions Atomic coordinates Site occupancies Thermal displacement parameters
Wrong peak width →	Crystallite size Lattice strain

Only with good data we can distinguish the different broadening characteristics of size and strain!

Refinement Strategy: Words of Wisdom

Always refining everything
may lead to good fits,
but the results may be useless.

Release parameters one by one.
When the fit doesn't improve anymore,
don't try to extract more information.

Chose your refinement strategy wisely.
Ask yourself if the results make
physical sense.

Examples

Lesson 5: Example 1: Simple phase quantification

Lesson 5: Example 2: Phase quantification with size and micro-strain

Lesson 5: Example 5: Batch processing

Lesson 6: Example 1: Texture, preferred orientation

Lesson 6: Example 2: Anisotropic crystallite sizes

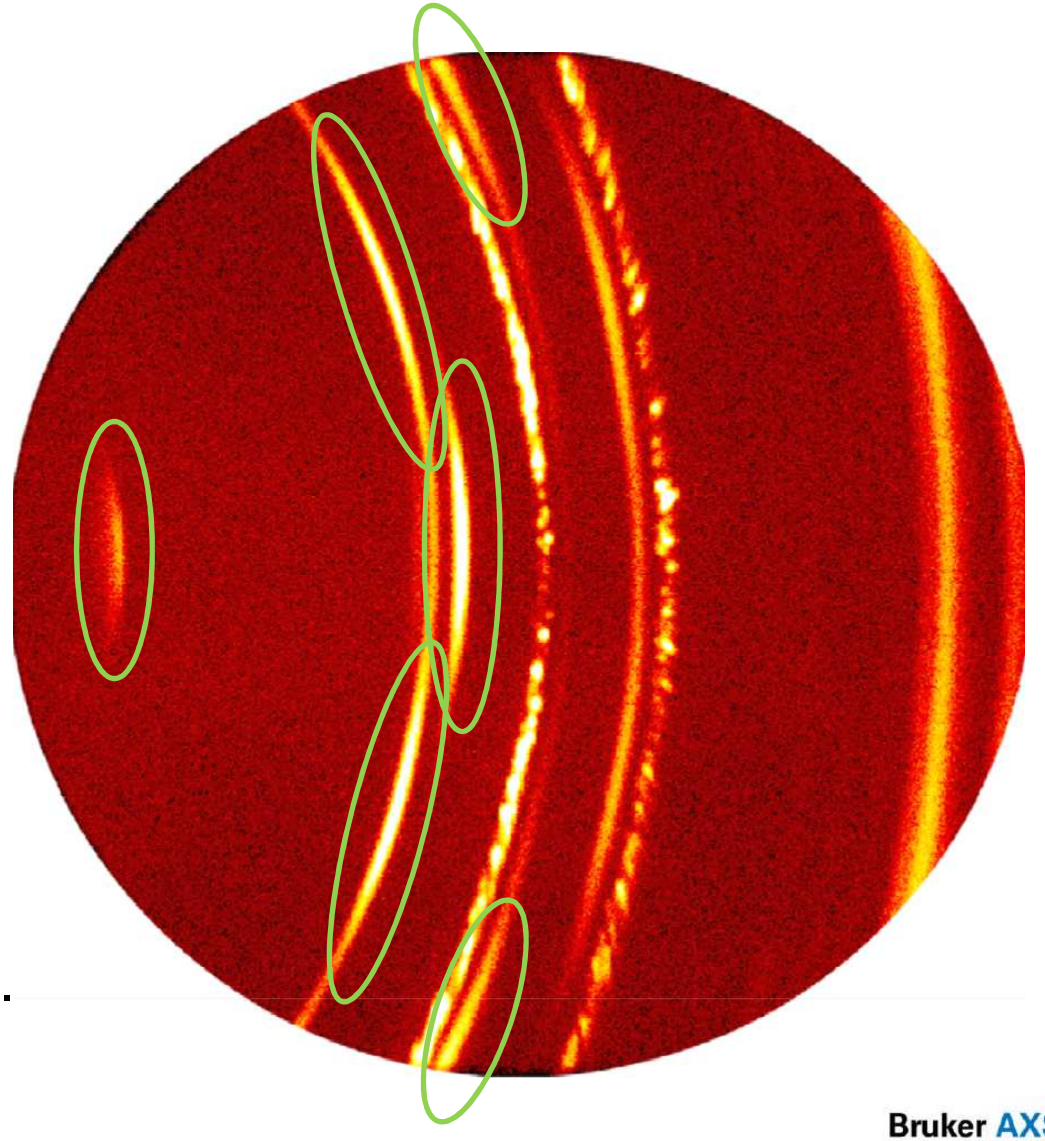
Lesson 6: Example 3: Non-existent phases

Lesson 6: Example 4: Micro-absorption and Brindley correction

Lesson 6: Example 5: Site occupancies

Texture, Preferred Orientation

Smooth, but non-continuous diffraction rings

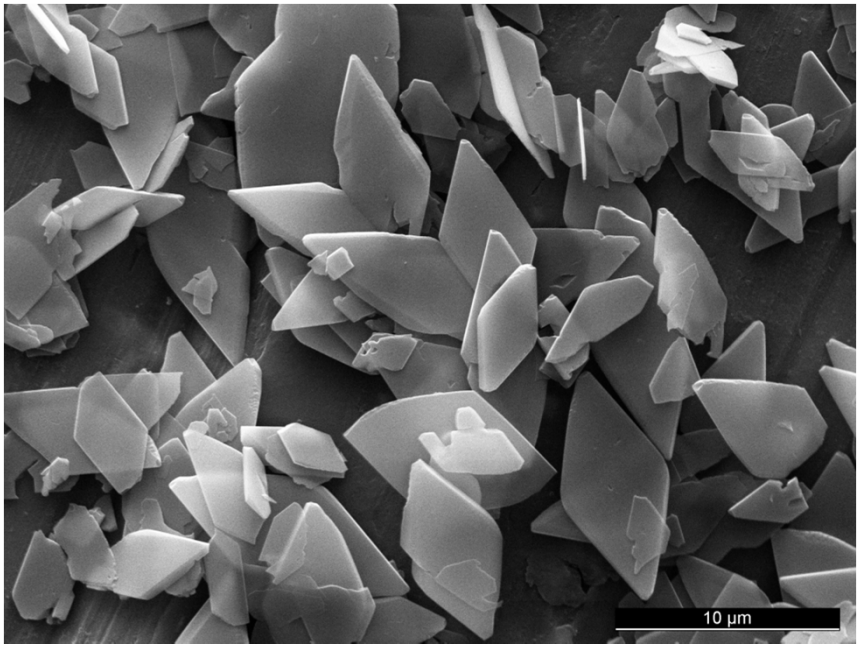


Reason:

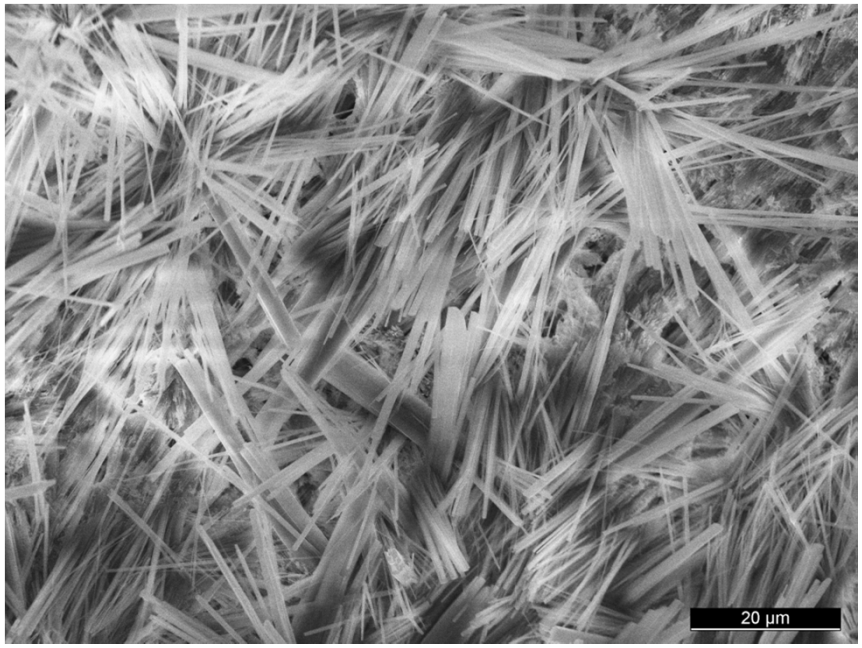
- Orientation of crystallites is not random.
- Some orientations are over-represented, others are under-represented.

Bruker AXS

Texture, Preferred Orientation



Platelets



Needles, Fibers, Whiskers

Random orientation

Preferred orientation

Images: L. Galea, RMS Foundation

Texture: Symmetrized Spherical Harmonics

In structure files (*.str) change:

PARAM=GEWICHT=0.1_0

to

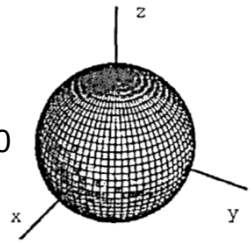
GEWICHT=SPHAR*n*

(n=0, 2, 4, 6, 8, 10)

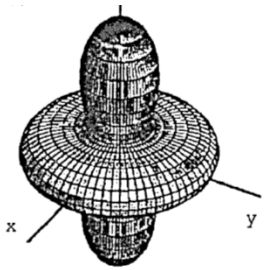
No preferred orientation:

PARAM=GEWICHT=0.1_0

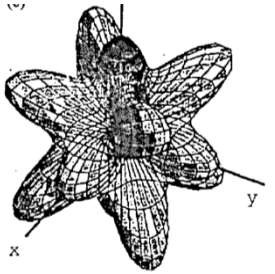
GEWICHT=SPHAR0



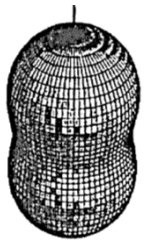
GEWICHT=SPHAR4



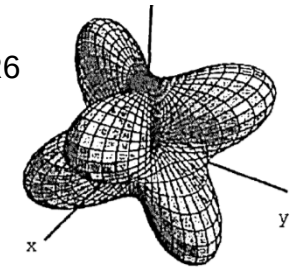
GEWICHT=SPHAR8



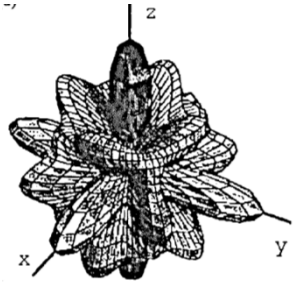
GEWICHT=SPHAR2



GEWICHT=SPHAR6



GEWICHT=SPHAR10



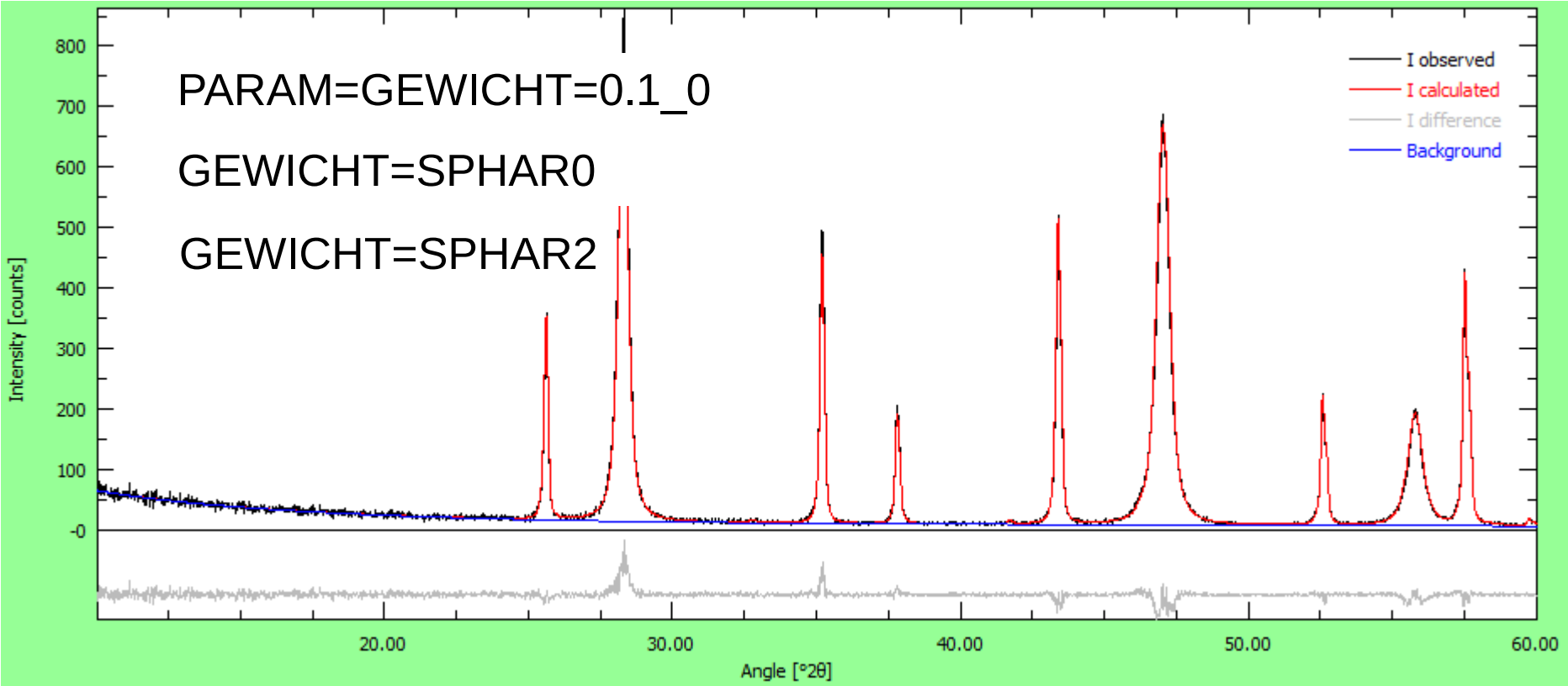
Järvinen, M. Materials Science Forum [278-281], 1998, 184-199.

Lesson 6: Example 1 - Texture

Instrument: pw1800-fds

Phases: Corundum, Fluorite

Both phases: RP=4 PARAM=k1=0_0^1 PARAM=k2=0_0 PARAM=B1=0_0^0.03 PARAM=GEWICHT=0.1_0 //



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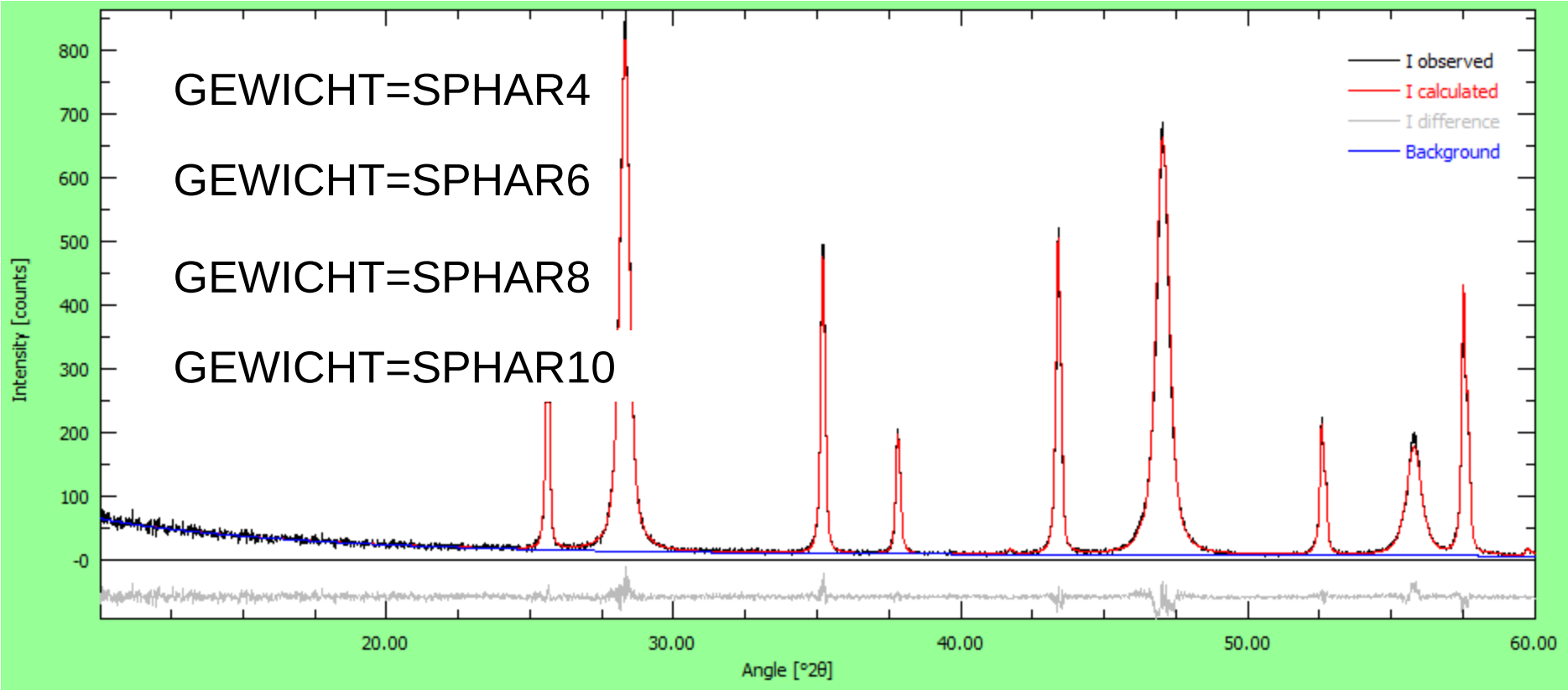
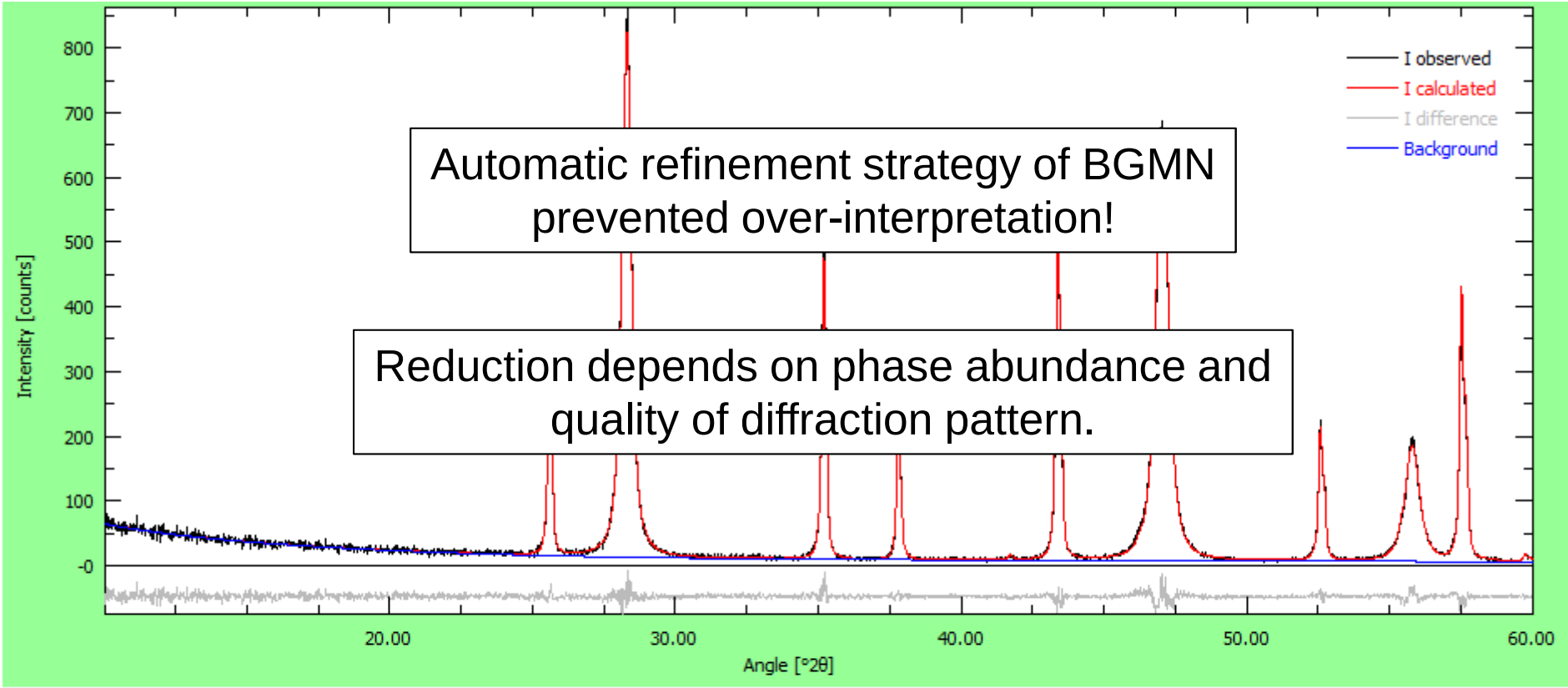


Lesson 6: Example 1 - Texture




```
--------------------------------------------------------------------------------
1. phase: texture reduced from SPHAR10 to SPHAR4 due to small contents
2. phase: texture reduced from SPHAR10 to SPHAR6 due to small contents
1. phase: initializing SPHAR4...OK
2. phase: initializing SPHAR6...
OK
```

!

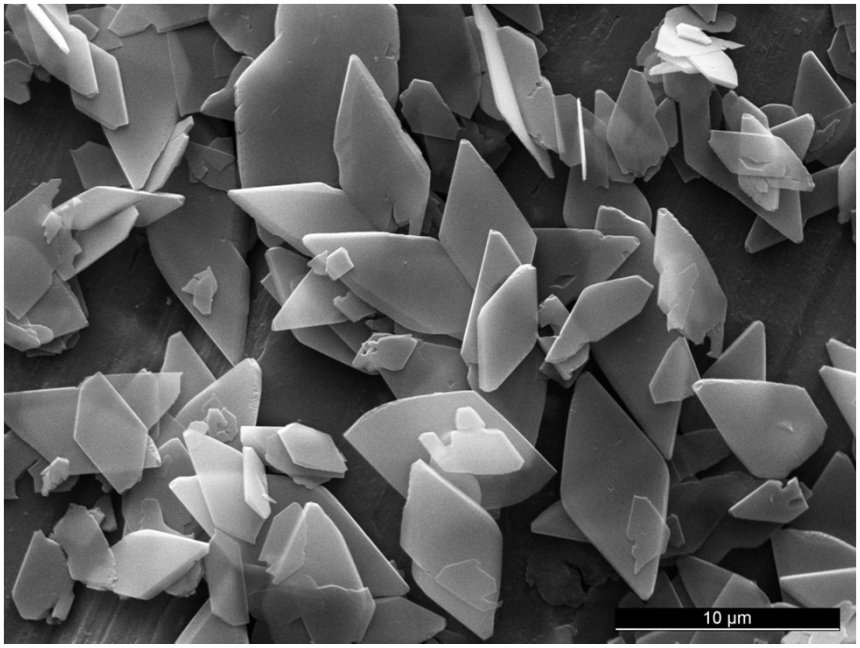
Lesson 6: Example 1 - Texture

- Refining «GEWICHT» with symmetrized spherical harmonics functions allows to model texture / preferred orientation.
- Complexity of the polynome can be set in structure file (SPHAR*n*).
- High order introduce large number of refined parameters. (→ slow refinement, may get unstable)
- Automatic refinement strategy will protect from over-interpretation.

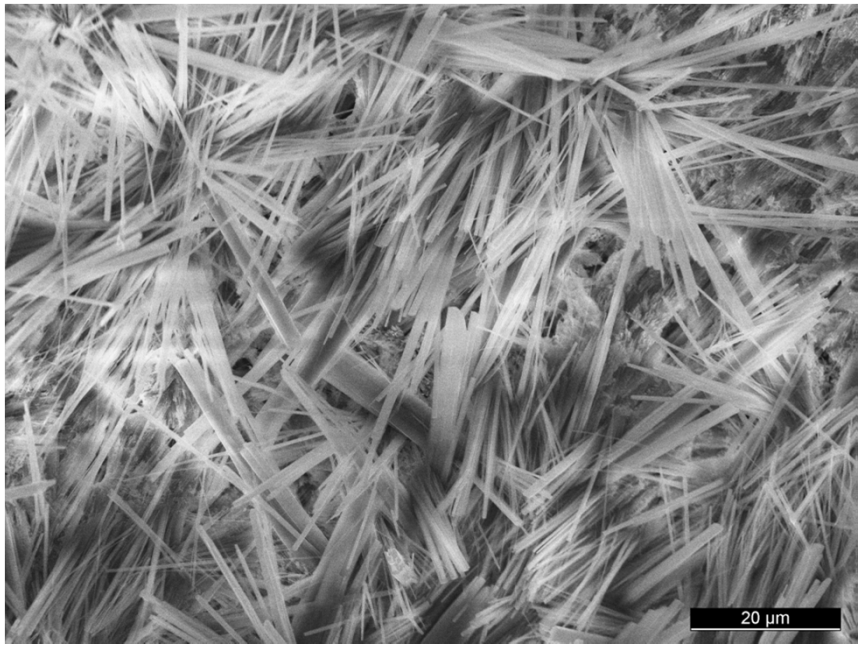
Recommendation:

- Use a moderate order of SPHAR polynomes in your structure files (e.g. SPHAR4)
- Let BGMN reduce the order if necessary
- Only increase the order if the fit really improves

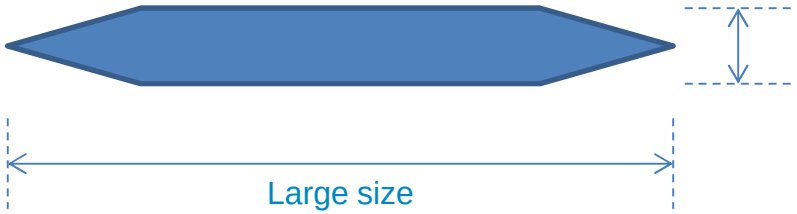
Anisotropic Crystallite Sizes



Platelets



Needles, Fibers, Whiskers

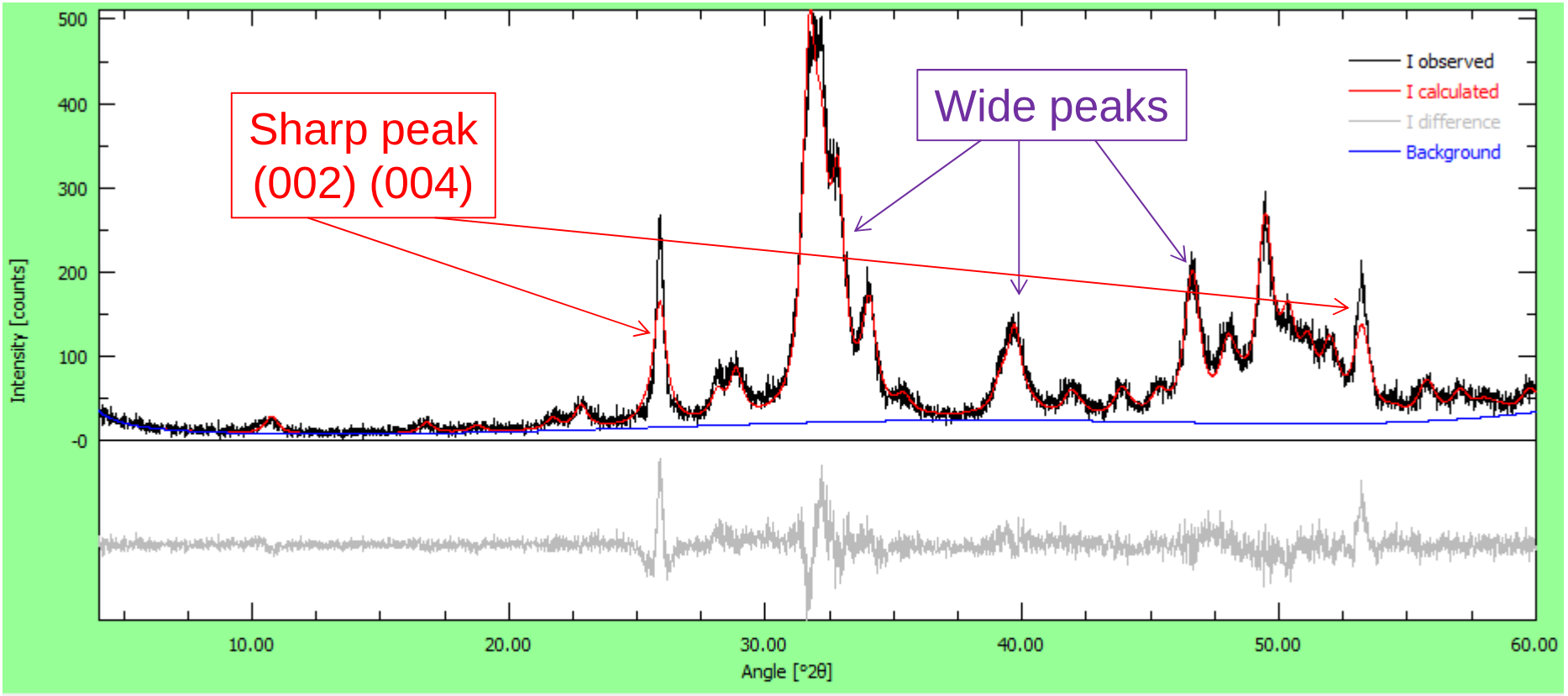


Small size
Strong peak broadening

Large size
Weak peak broadening

Images: L. Galea, RMS Foundation

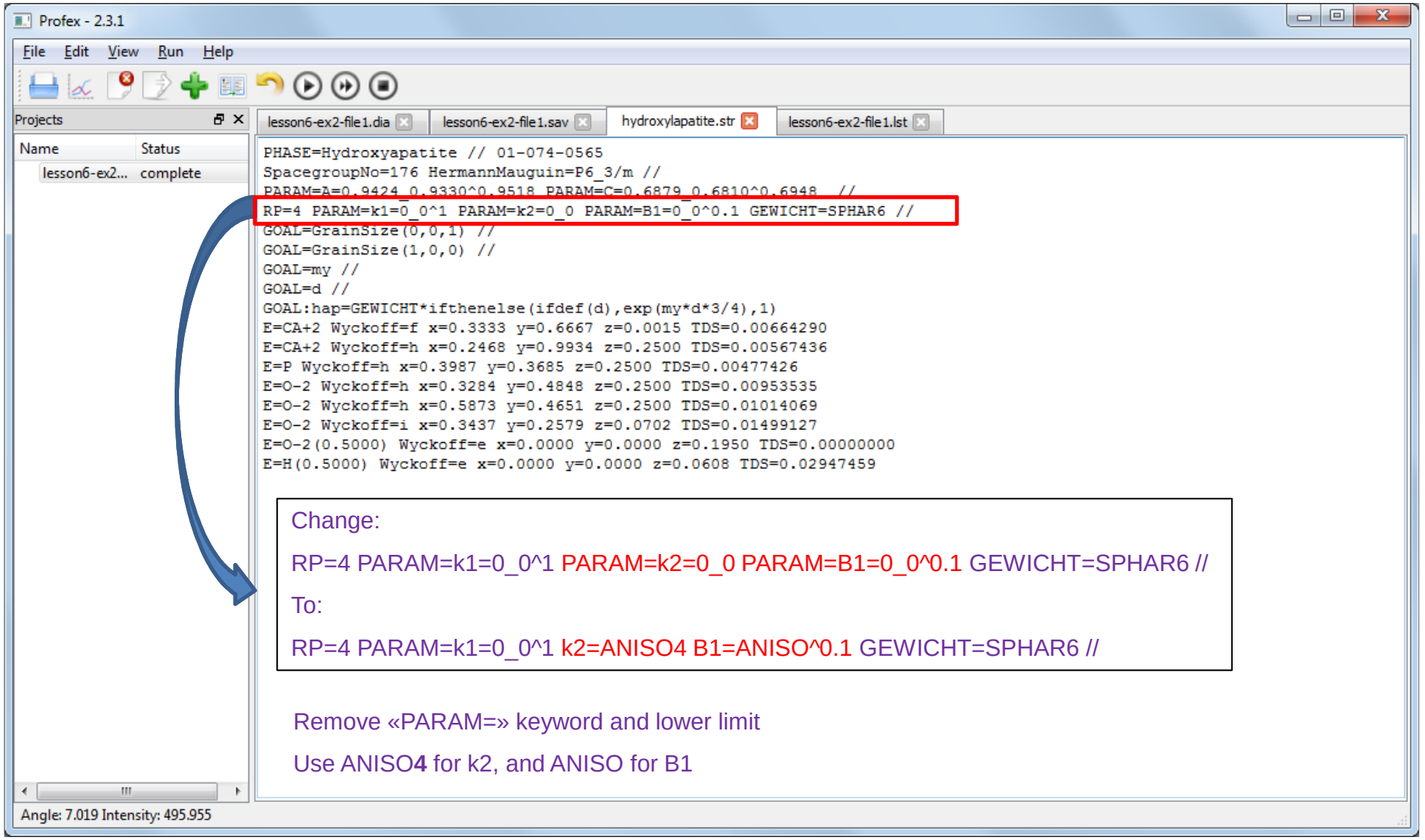
Lesson 6: Example 2 – Anisotropic Crystallite Size



Sample lesson6-ex2-file1 (C:/xrd/S12_0008/Examples/Lesson 6/Example 2/lesson6-ex2-file1.lst)

Phase	R_{Phase} [%]	Quantity [wt-%]	Mean Gewicht [a.u.]	Crystallite Sizes [nm]	Density [g/cm³]
Hydroxyapatite	14.91	100.00	0.044979	(0,0,1)14.22 (1,0,0)14.22	3.159

Lesson 6: Example 2 – Anisotropic Crystallite Size



Change:

RP=4 PARAM=k1=0_0^1 PARAM=k2=0_0 PARAM=B1=0_0^0.1 GEWICHT=SPHAR6 //

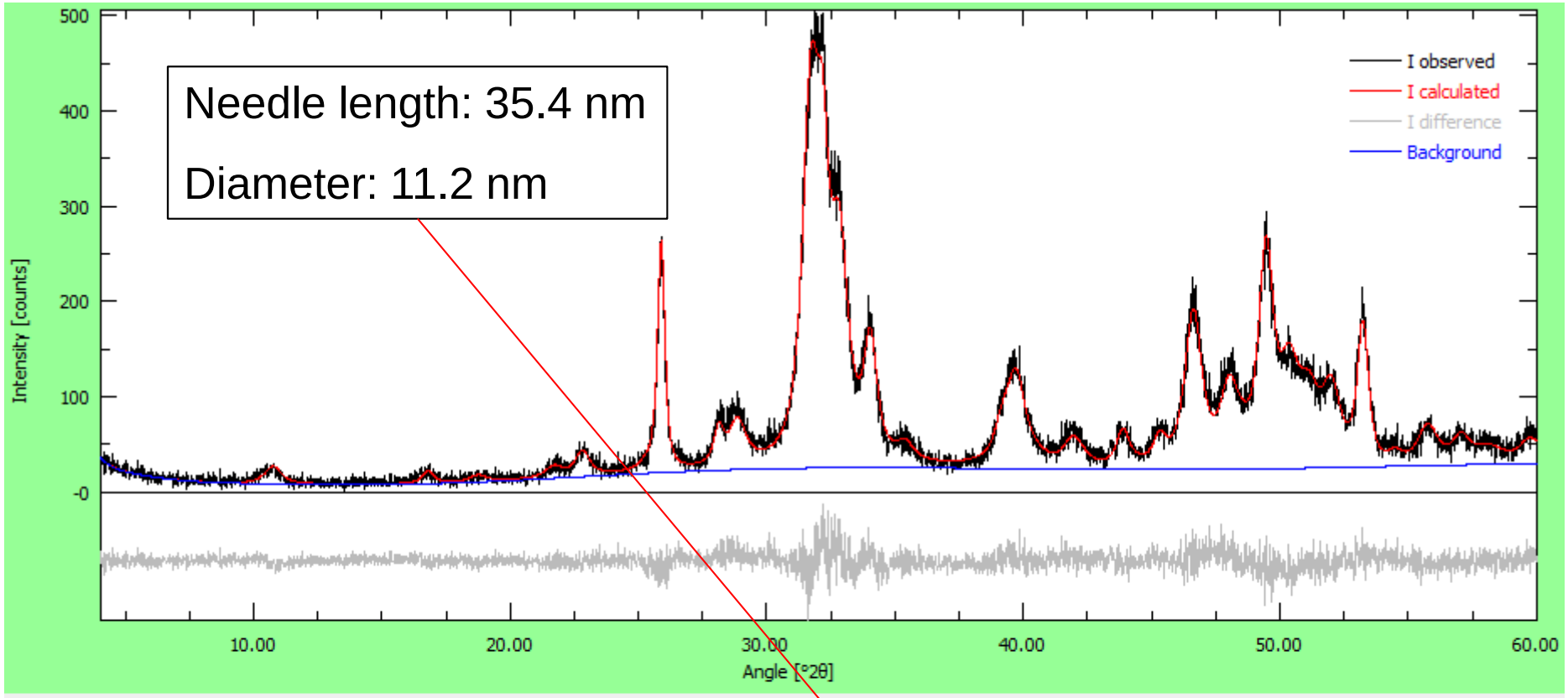
To:

RP=4 PARAM=k1=0_0^1 k2=ANISO4 B1=ANISO^0.1 GEWICHT=SPHAR6 //

Remove «PARAM=» keyword and lower limit

Use ANISO**4** for k2, and ANISO for B1

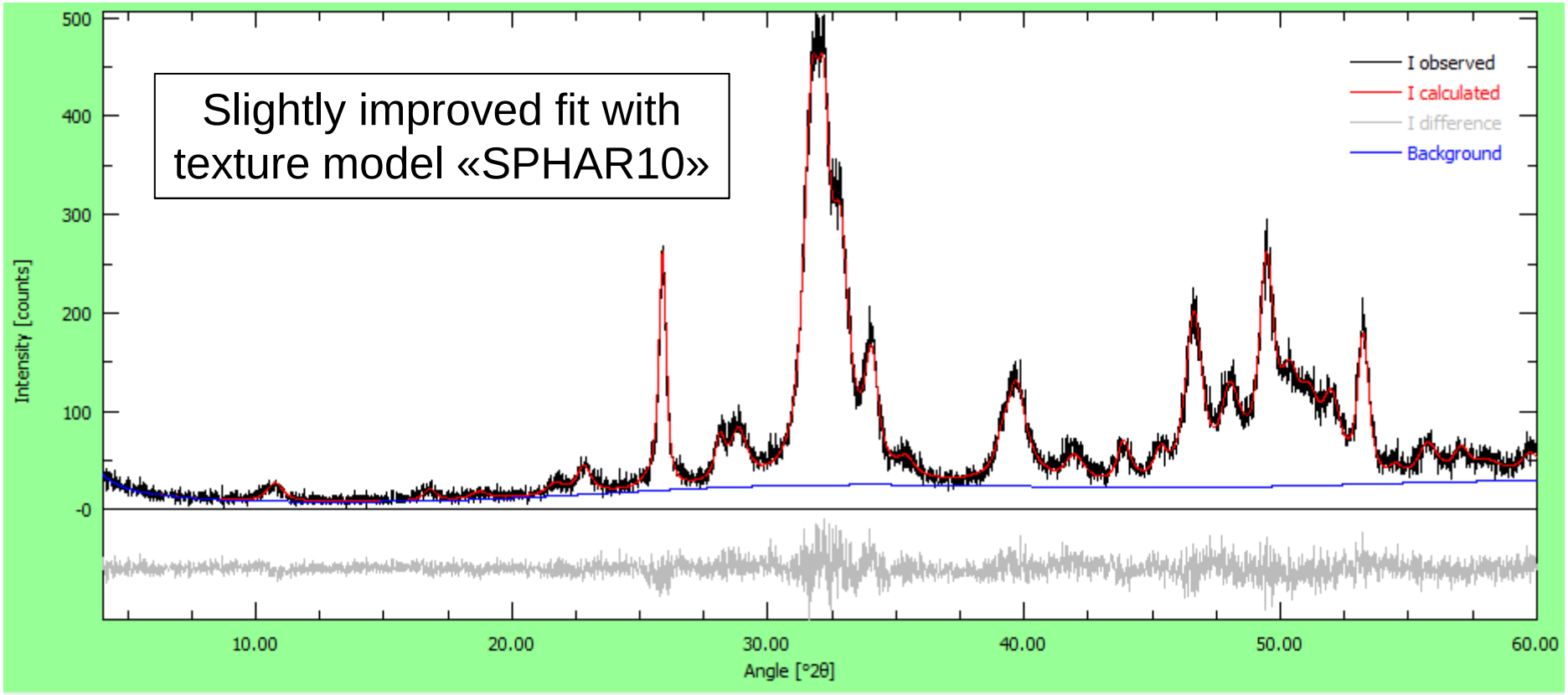
Lesson 6: Example 2 – Anisotropic Crystallite Size



Sample lesson6-ex2-file1 (C:/xrd/S12_0008/Examples/Lesson 6/Example 2/lesson6-ex2-file1.lst)

Phase	R_{Phase} [%]	Quantity [wt-%]	Mean Gewicht [a.u.]	Crystallite Sizes [nm]	Density [g/cm³]
Hydroxyapatite	11.43	100.00	0.043704	(0,0,1)35.4 (1,0,0)11.18	3.159

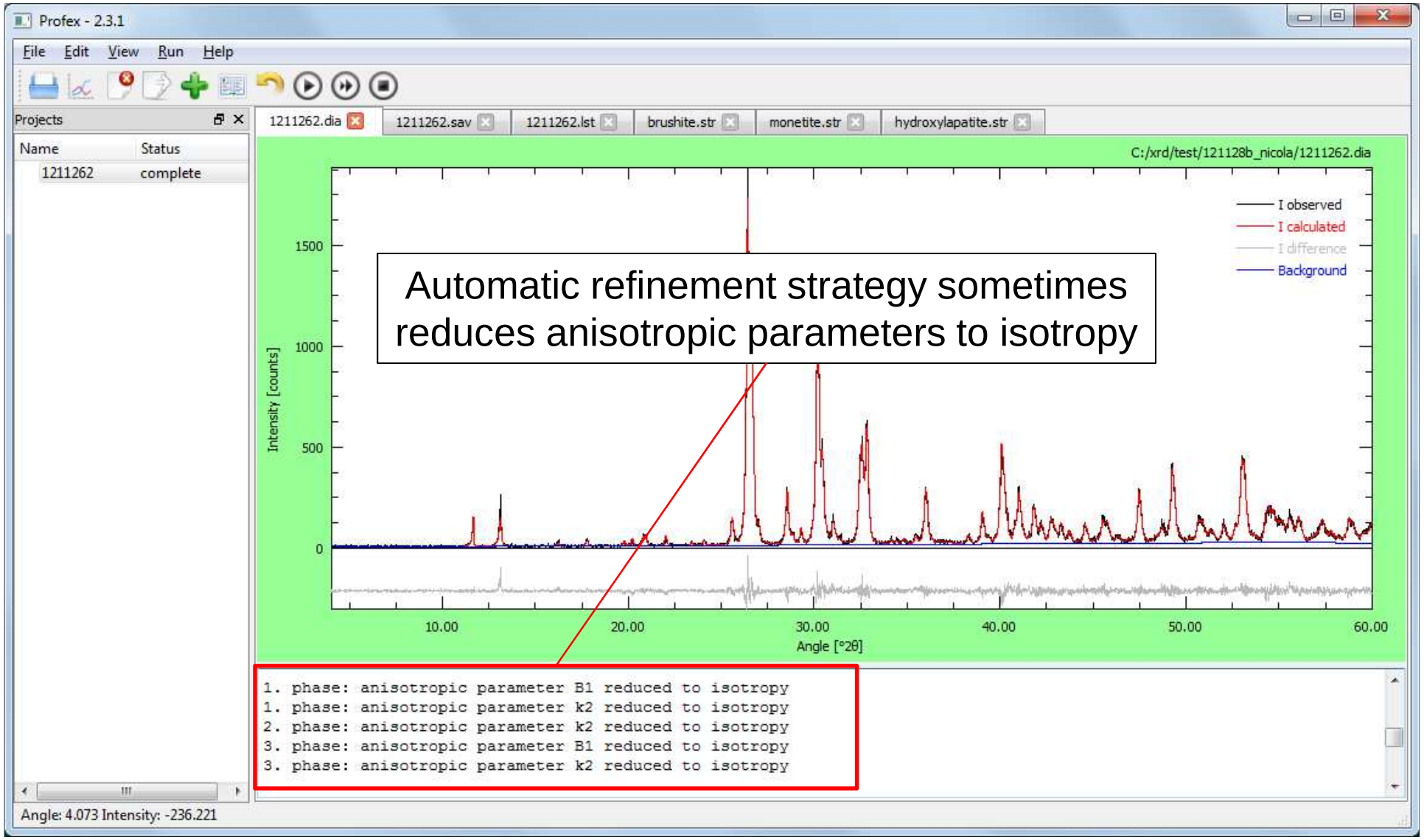
Lesson 6: Example 2 – Anisotropic Crystallite Size



Sample lesson6-ex2-file1 (C:/xrd/S12_0008/Examples/Lesson 6/Example 2/lesson6-ex2-file1.lst)

Phase	R_{Phase} [%]	Quantity [wt-%]	Mean Gewicht [a.u.]	Crystallite Sizes [nm]	Density [g/cm³]
Hydroxyapatite	11.14	100.00	0.045248	(0,0,1)35.0 (1,0,0)11.18	3.16

Lesson 6: Example 2 – Anisotropic Crystallite Size



Lesson 6: Example 2 – Anisotropic Crystallite Size

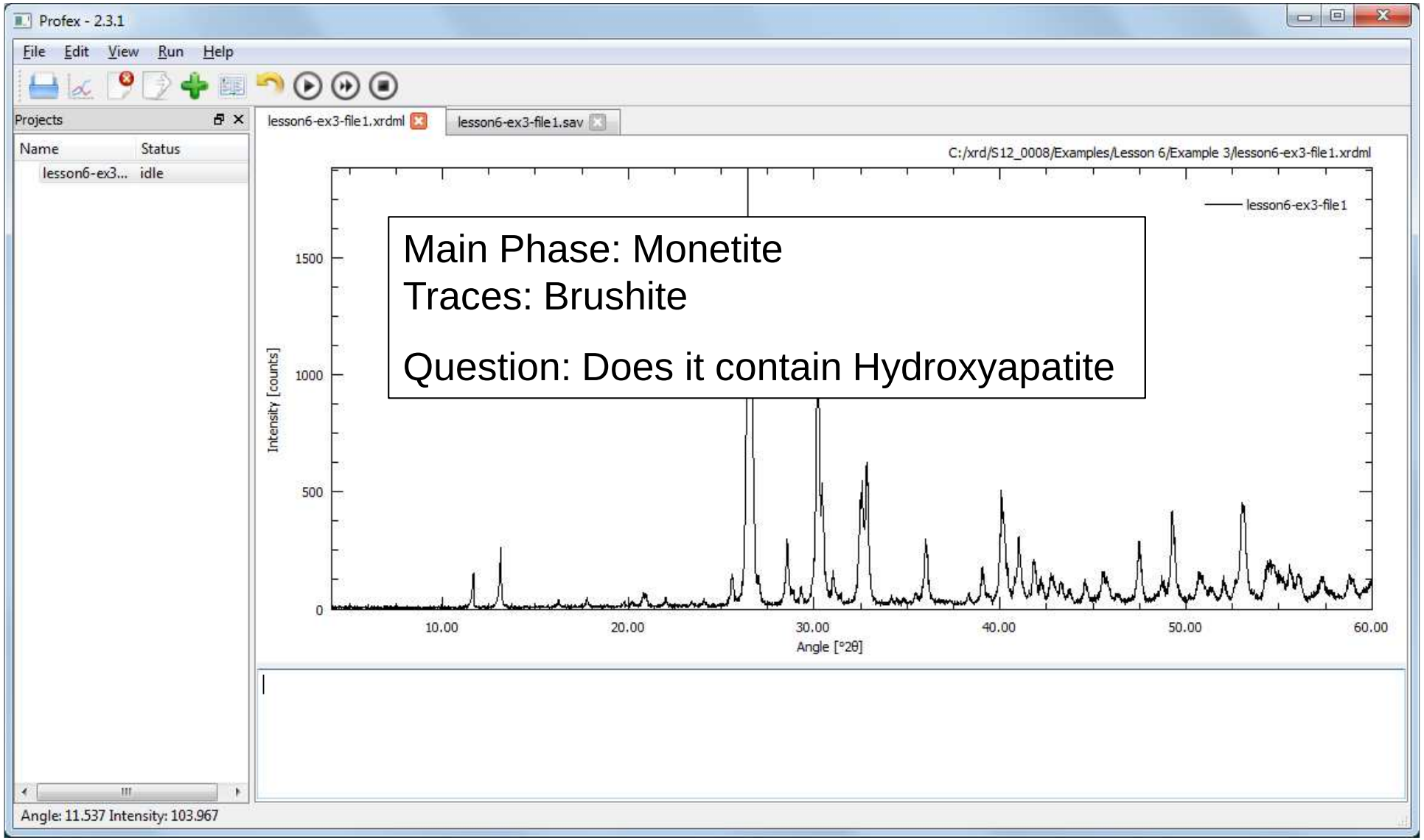
Refine anisotropic crystallite sizes with «B1=ANISO»

Refine anisotropic micro-strain with «k2=ANISO4»

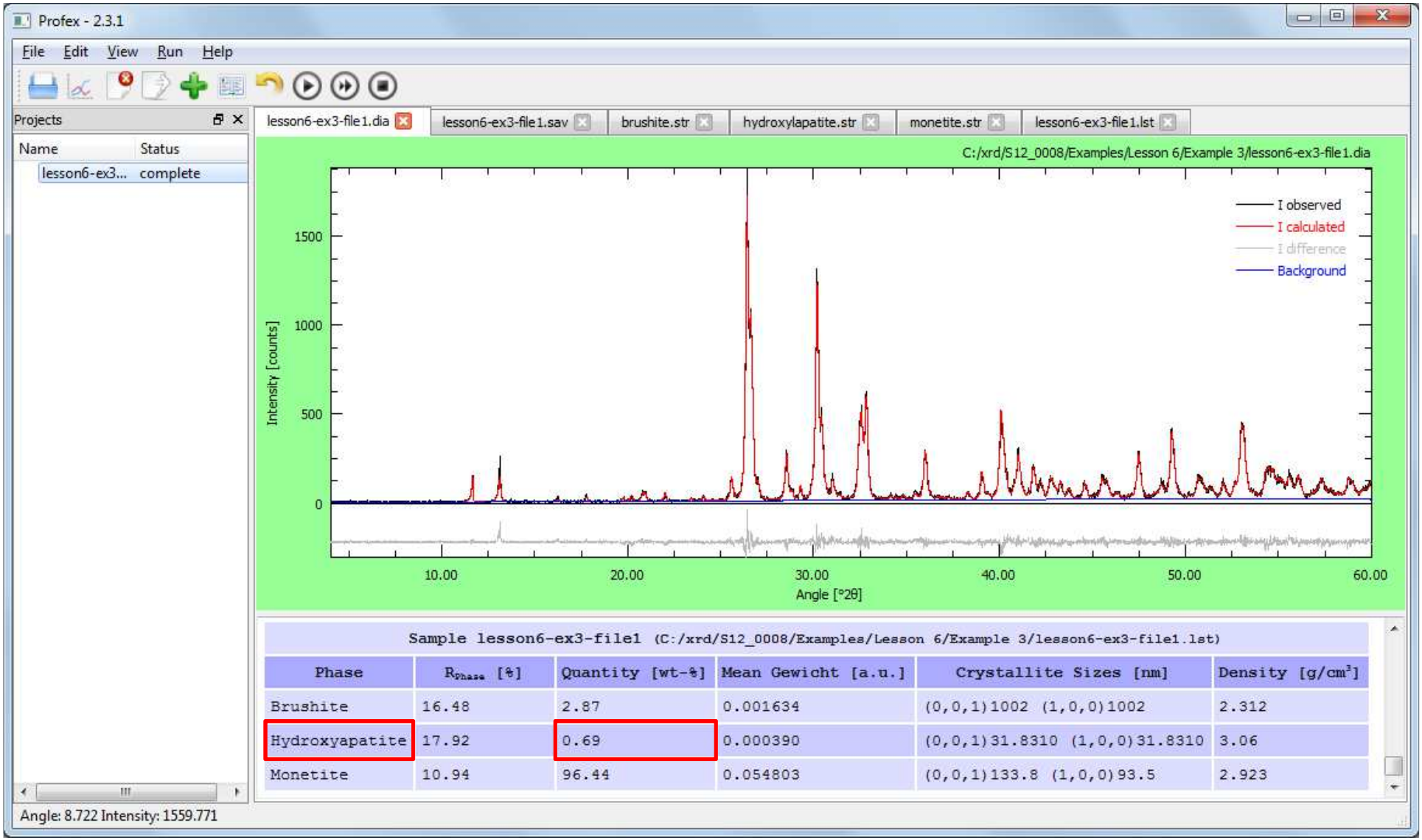
Recommendation:

- Do not refine micro-strain anisotropically unless it improves the fit
- Refine peak broadening anisotropically
  (PARAM=k1=0_0^1 B1=ANISO^0.01)
  let BGMN handle the reduction to isotropy
- Check if the upper limit of B1 was reached. If yes:
  - increase the limit…
  - … or see next example (non-existent phases)

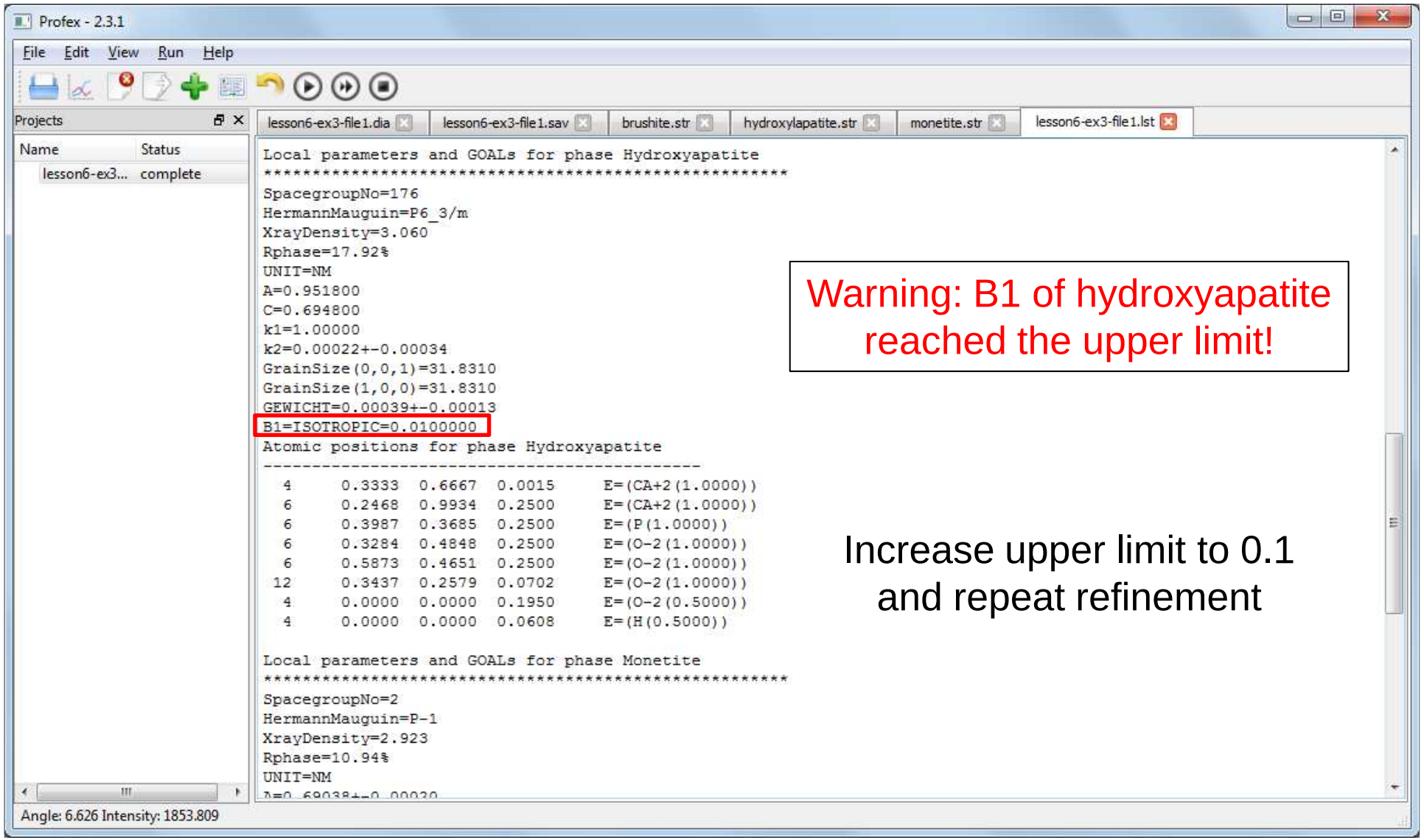
Lesson 6: Example 3 – Non-existent Phases



Lesson 6: Example 3 – Non-existent Phases



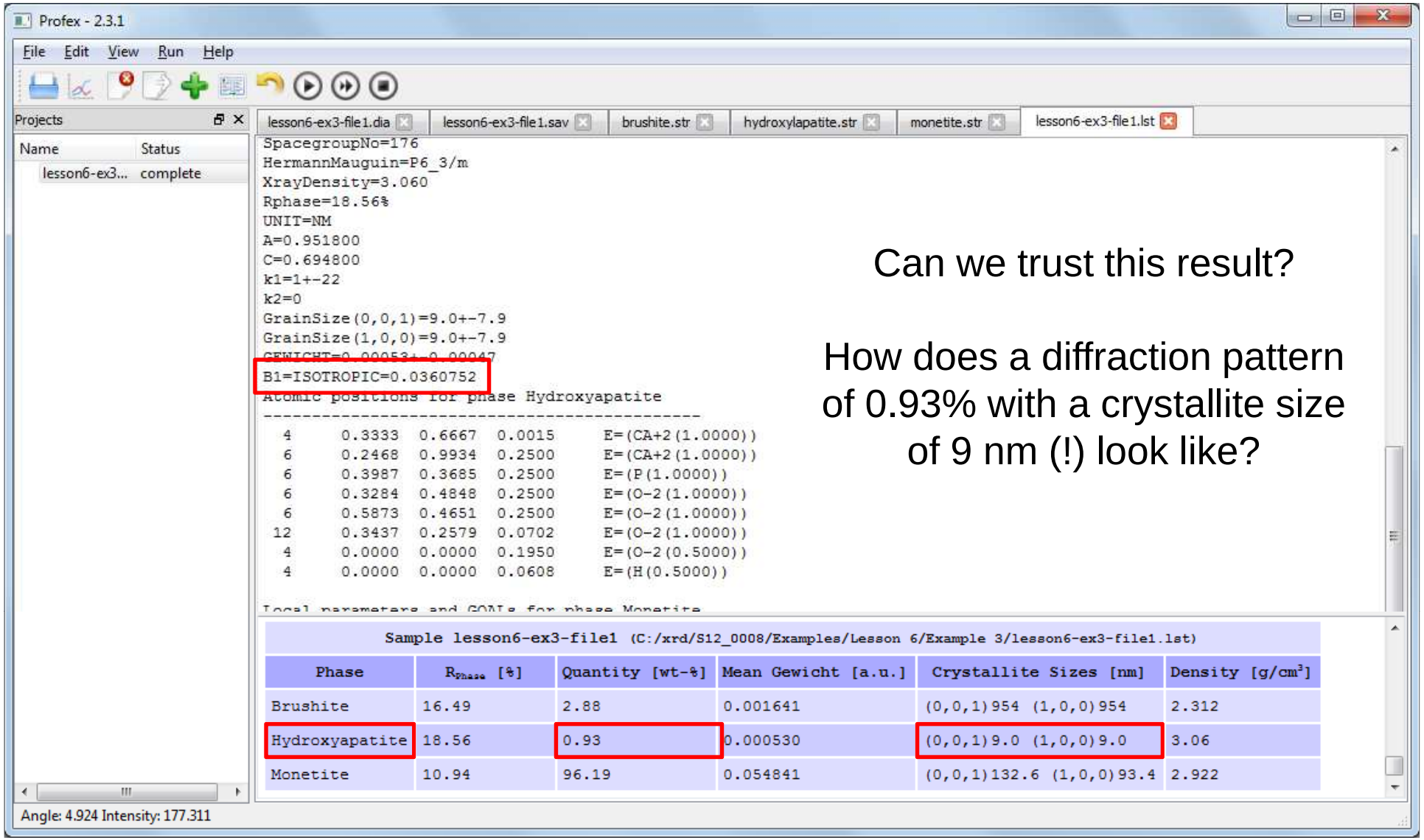
Lesson 6: Example 3 – Non-existent Phases



Warning: B1 of hydroxyapatite reached the upper limit!

Increase upper limit to 0.1 and repeat refinement

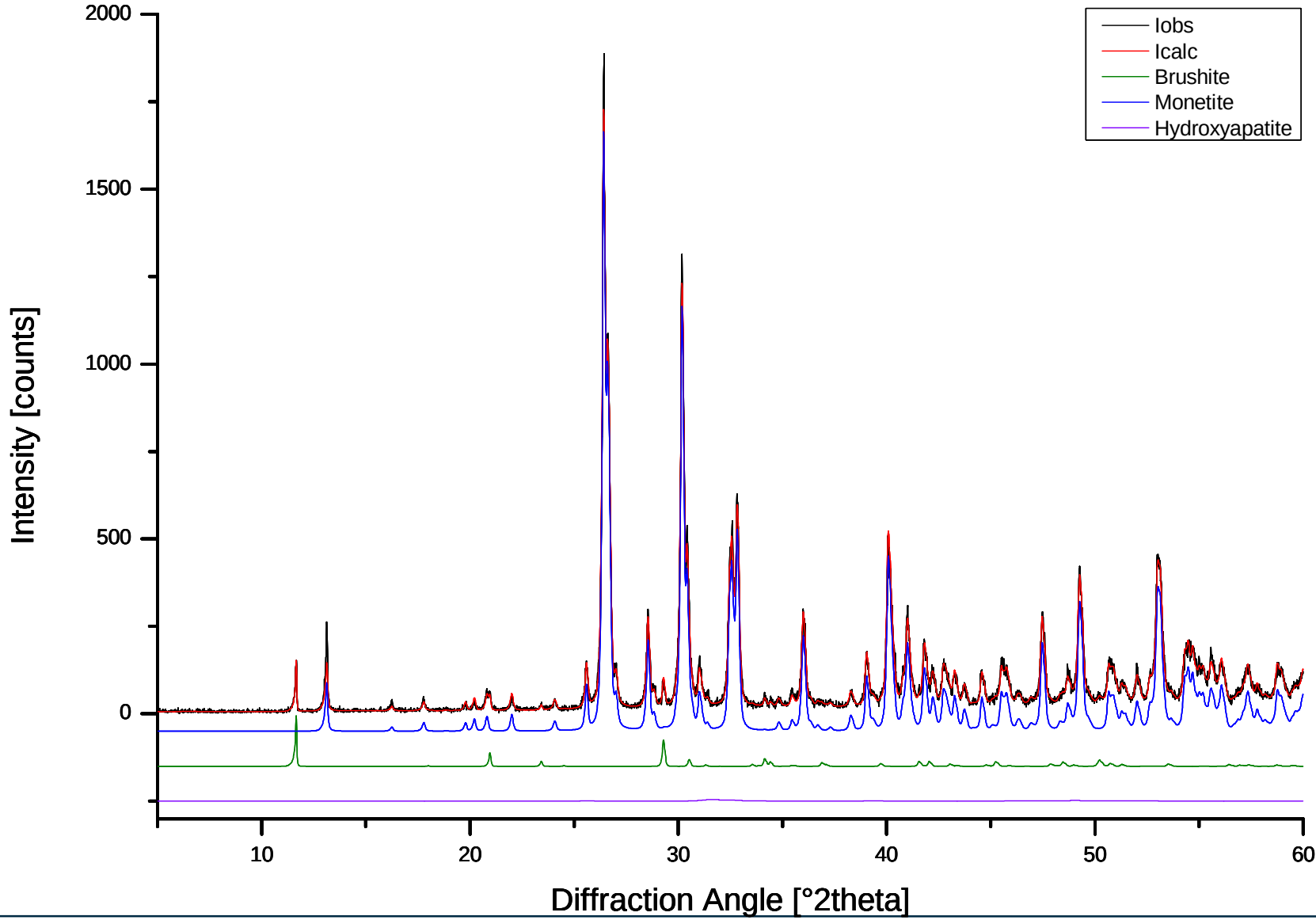
Lesson 6: Example 3 – Non-existent Phases



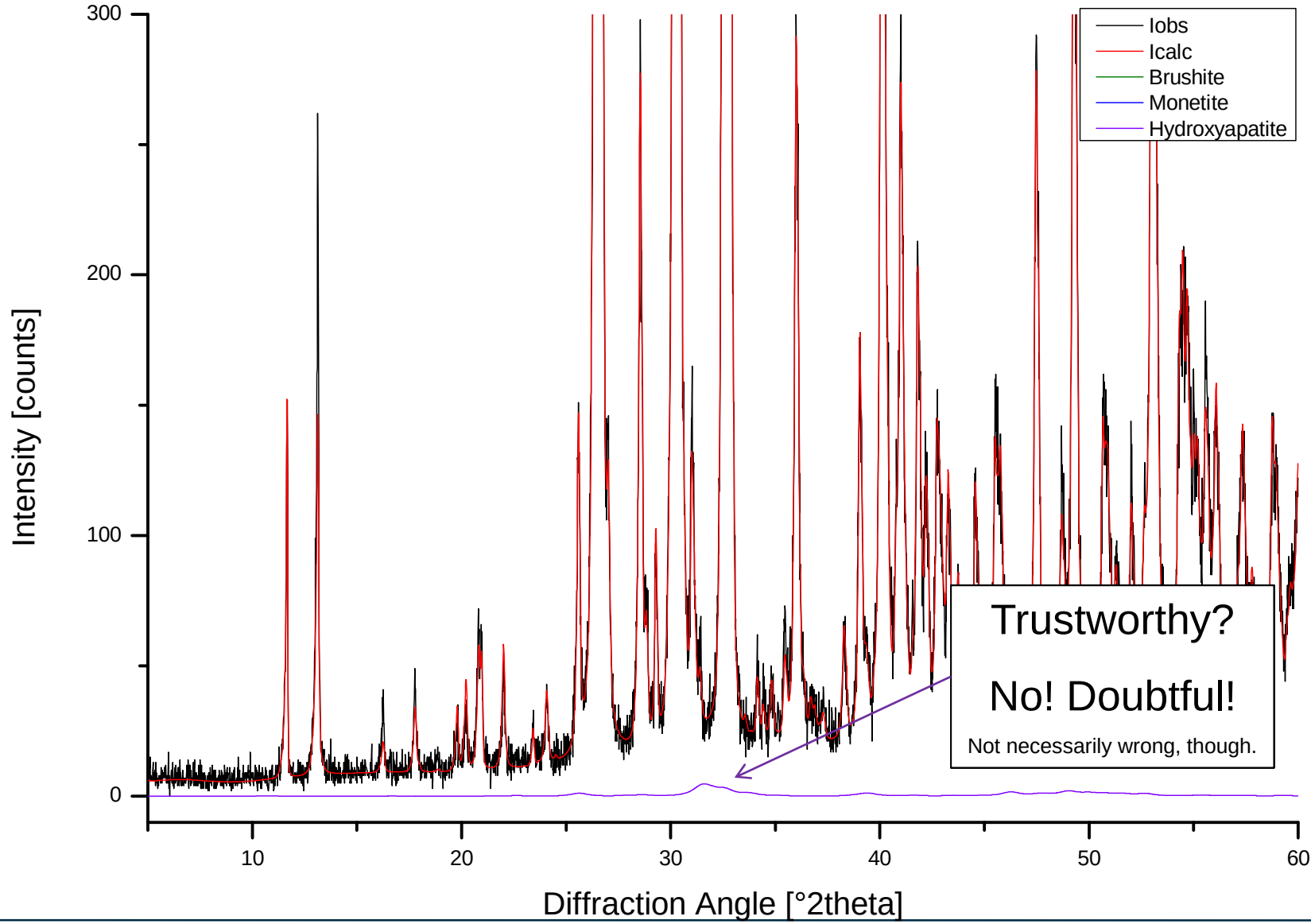
Can we trust this result?

How does a diffraction pattern of 0.93% with a crystallite size of 9 nm (!) look like?

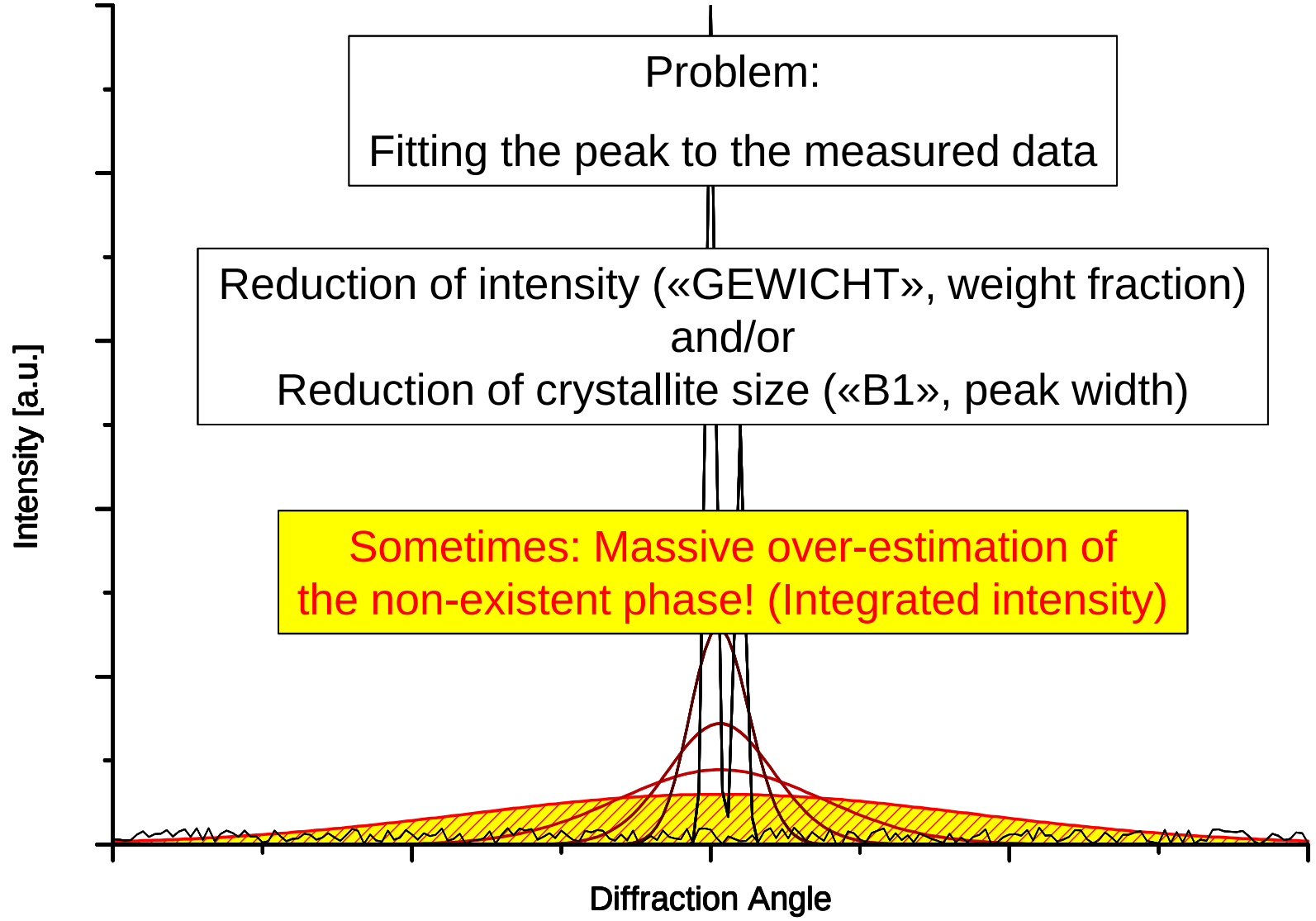
Lesson 6: Example 3 – Non-existent Phases



Lesson 6: Example 3 – Non-existent Phases



Lesson 6: Example 3 – Non-existent Phases



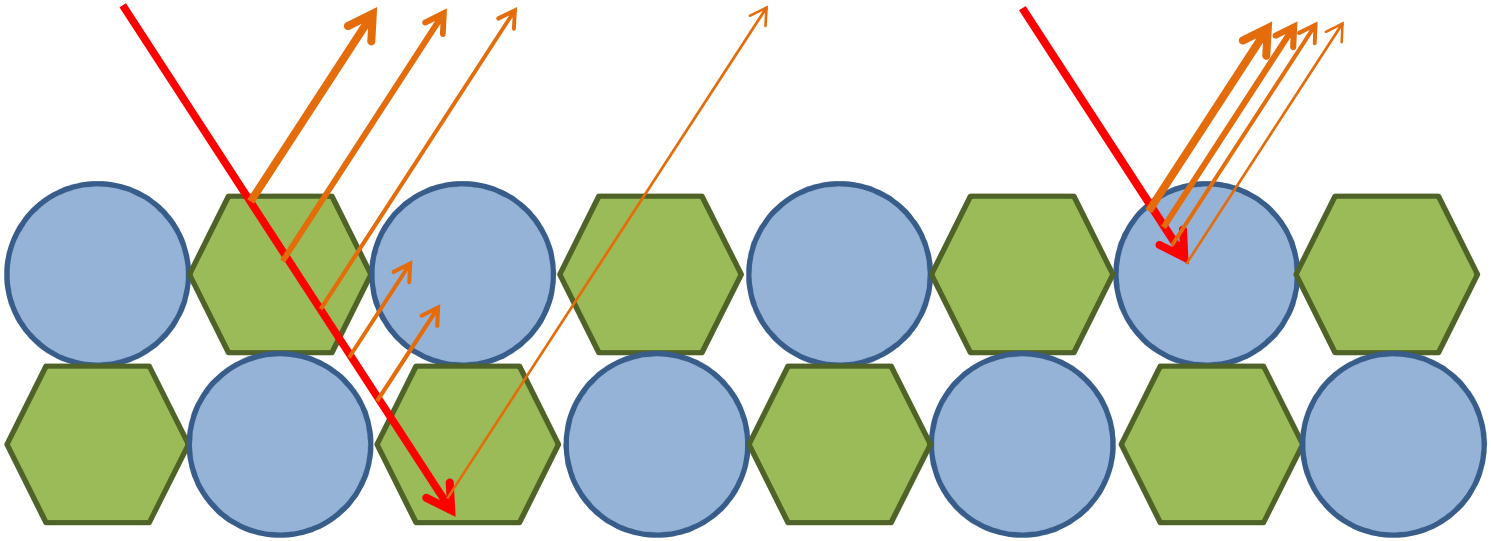
Lesson 6: Example 3 – Non-existent Phases

Solutions:

- Use a reasonable upper limit for B1 (peak broadening, crystallite size)
- Don’t trust very small crystallite sizes (e.g. < 20 nm)
- Repeat the refinement without the questionable phase
  (Does the fit really look worse? Or just as good?)
- Use additional information to limit B1:
  - Sintered samples: very small crystallites are unlikely
  - Cement samples: very small crystallites are reasonable

Trying to identify very poorly crystalline precipitated phases in cements?
Good luck!

Micro-absorption and Brindley Correction



Weak attenuation by phase 2

→ Large volume of interaction

Strong attenuation by phase 1

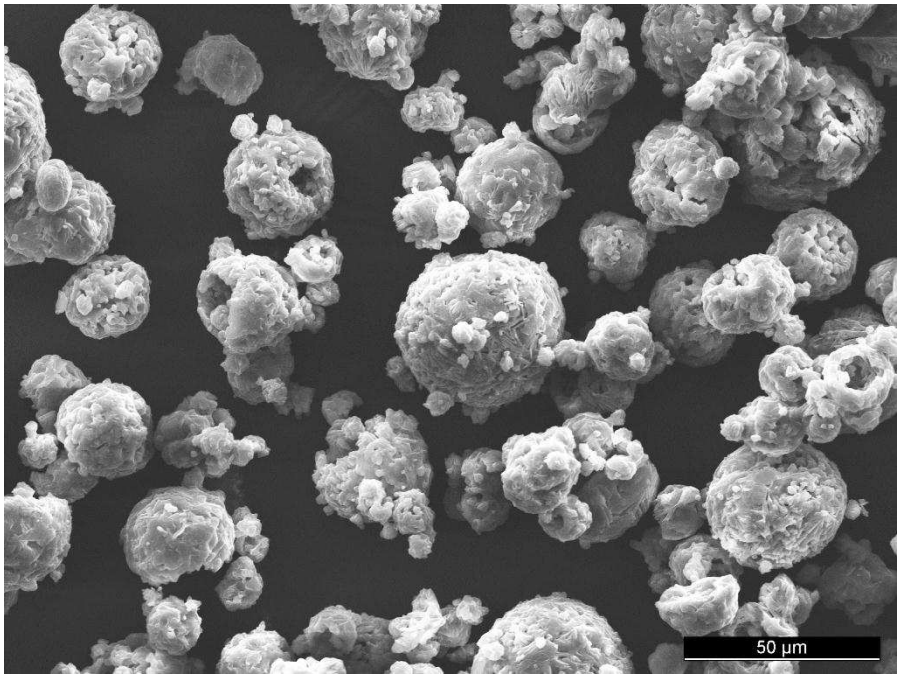
Large particles absorb significant part of the radiation.

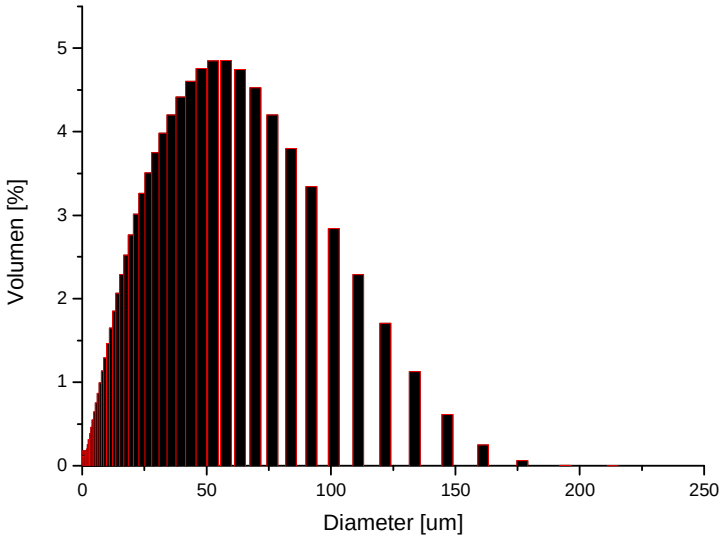
→ Small volume of interaction

Phase quantification biased for phase 2!

Micro-absorption and Brindley Correction

Micro-absorption can be corrected,
but mean particle* size must be known.





*not crystallite size

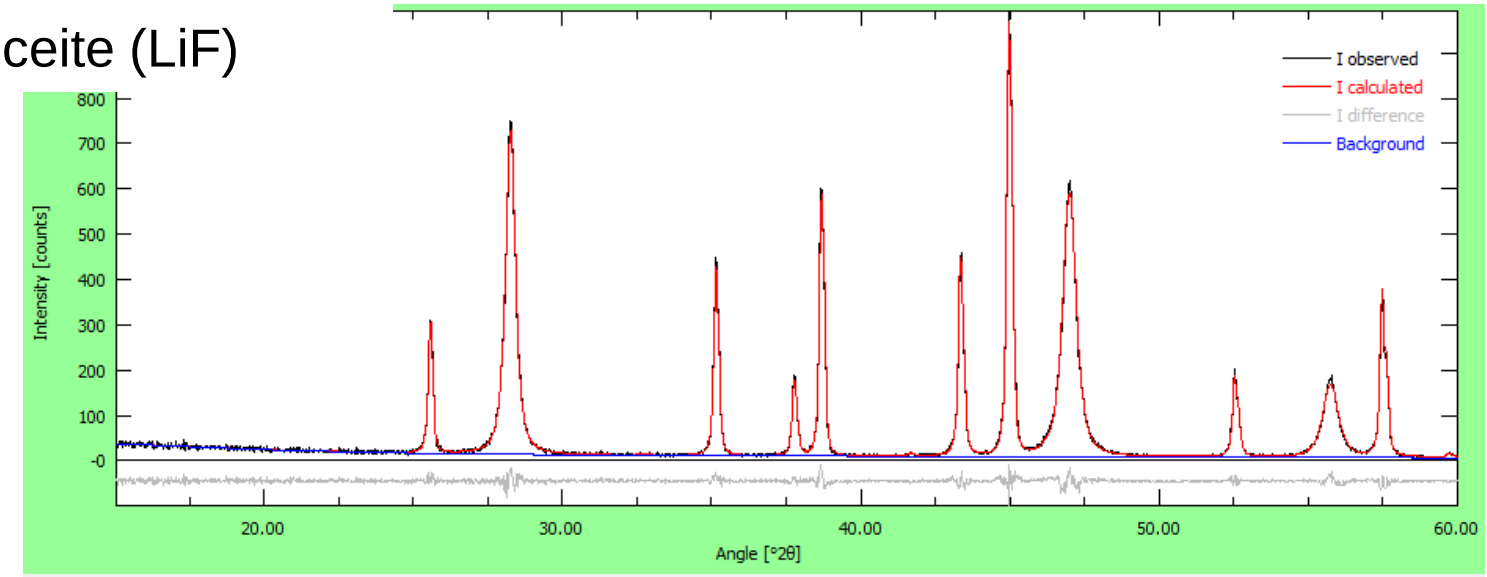
Lesson 6: Example 4 – Micro-Absorption

Reference mixture:

33.33 wt-% Corundum (Al_2O_3)

33.33 wt-% Fluorite (CaF_2)

33.33 wt-% Griceite (LiF)



Sample lesson5-ex4-file1 (C:/xrd/S12_0008/Examples/Lesson 6/Example 4/lesson5-ex4-file1.lst)

Phase	R_{Phase} [%]	Quantity [wt-%]	Mean Gewicht [a.u.]	Crystallite Sizes [nm]	Density [g/cm³]
Corundum_Al2O3	6.05	33.48	0.022075	(1,1,1)118.5	3.981
Fluorite	5.49	30.01	0.019786	(1,1,1)36.8	3.172
LiF	4.36	36.51	0.024073	(1,1,1)185	2.633

Wrong phase quantities

Lesson 6: Example 4 – Micro-Absorption

Add mean particle diameter (µm) to structure files:

lesson5-ex4-file1.dia | lesson5-ex4-file1.sav | lesson5-ex4-file1.lst | Corundum.str | Fluorite.str | LiF.str

```
PHASE=Corundum_Al2O3 // 04-004-2852
SpacegroupNo=167 Setting=1 HermannMauguin=R-32/c //
PARAM=A=0.4760_0.4712^0.4808 PARAM=C=1.2993_1.2863^1.3123  //
RP=4 PARAM=k1=0_0^1 k2=ANISO4 B1=ANISO^0.01 GEWICHT=SPHAR8 //
GOAL=GrainSize(1,1,1) //
d=12 //
GOAL=d //
GOAL=my //
GOAL:corundum=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
E=AL Wyckoff=c x=0.0000 y=0.0000 z=0.3522 TDS=0.00224764
E=O-2 Wyckoff=e x=0.3062 y=0.0000 z=0.2500 TDS=0.00271875
```

Corundum: 12 µm
Fluorite: 10 µm
LiF: 9 µm

If d is defined:

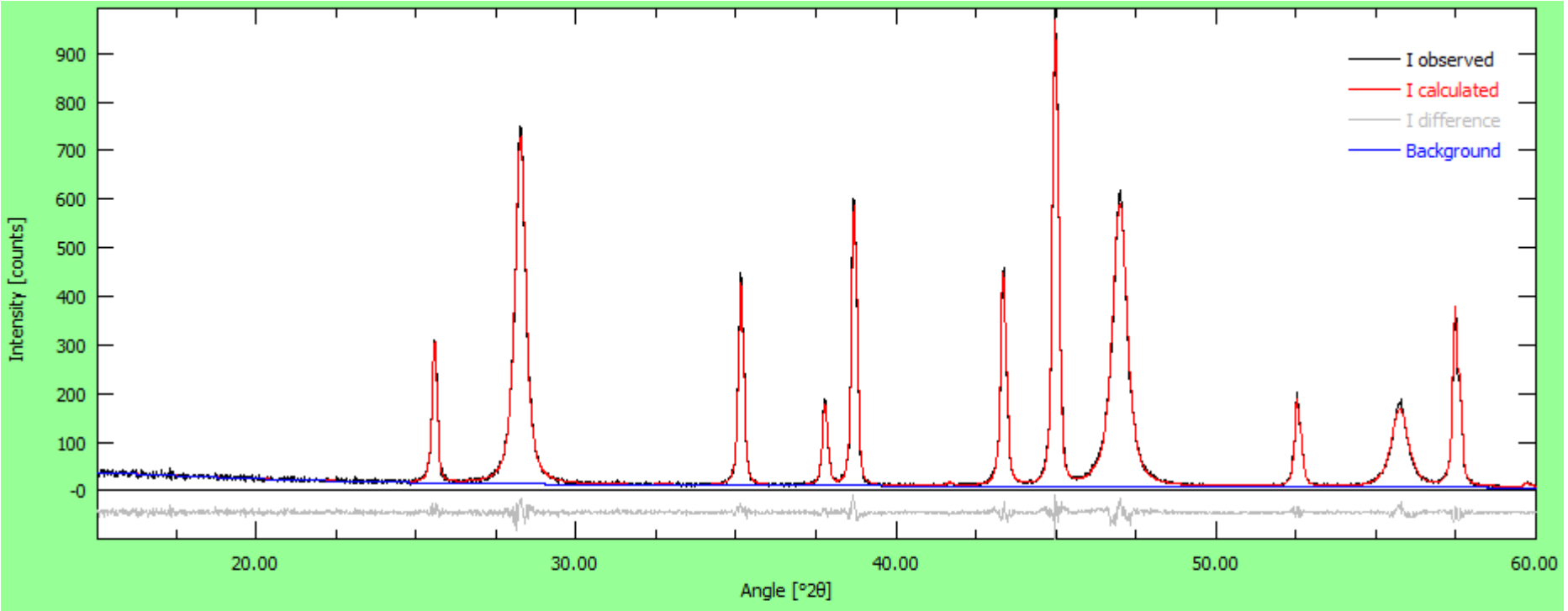
GEWICHT=GEWICHT*exp(my*d*3/4)

else

GEWICHT= GEWICHT*1

my (µ) = mass absorption coefficient
(calculated automatically by BGMN)

Lesson 6: Example 4 – Micro-Absorption



Sample lesson5-ex4-file1 (C:/xrd/S12_0008/Examples/Lesson 6/Example 4/lesson5-ex4-file1.lst)

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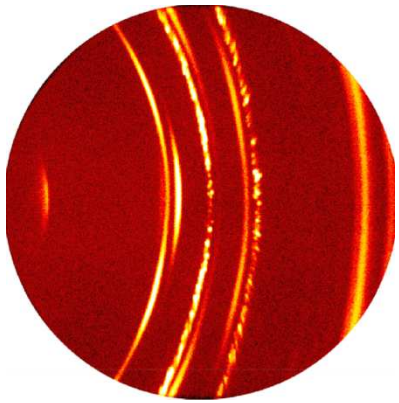
Fluorite	5.49	33.47	0.024800	(1,1,1)36.8	3.172
LiF	4.36	33.17	0.024579	(1,1,1)185	2.633

Lesson 6: Example 4 – Micro-Absorption

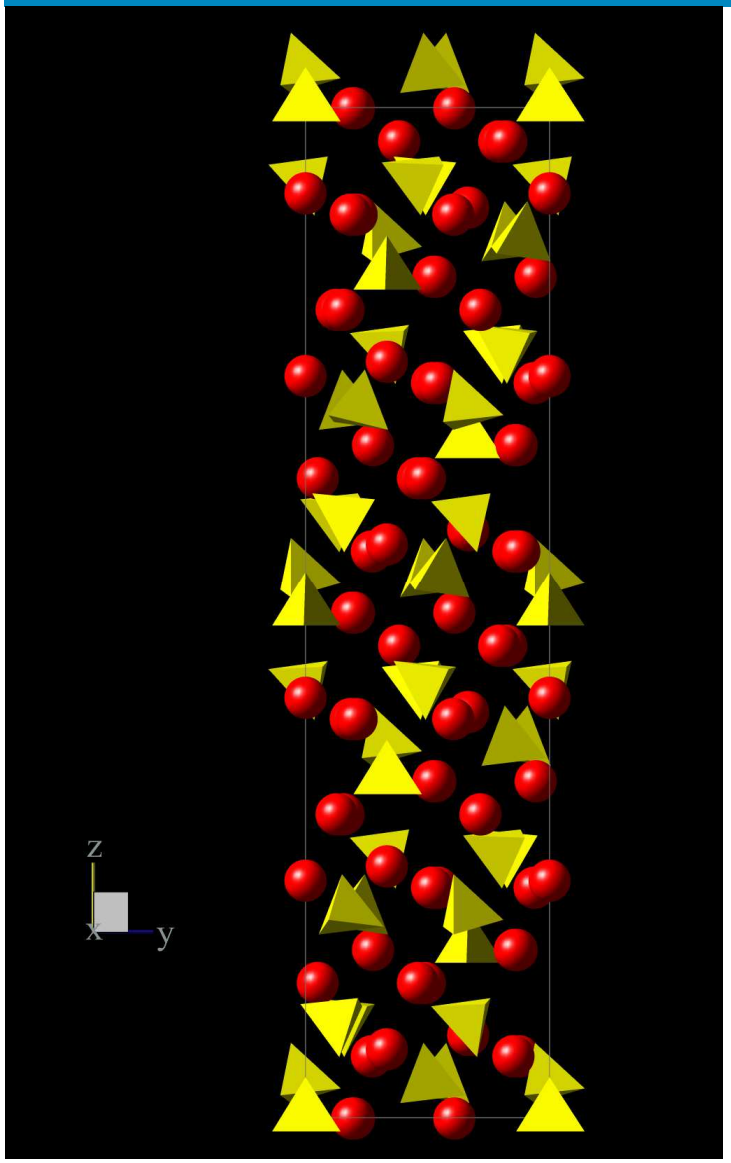
Micro-Absorption and Brindley correction:

- Try to avoid the problem in the first place (keep particle size close to 1 µm)
- Additional information (particle size from SEM, PSD analysis) required for all refined phases!
- Large particles still lead to grainy diffraction patterns. Brindley-correction does **not** solve this problem!



Bruker AXS

Refinement of Site Occupancies



β-TCP: β-$Ca_3(PO_4)_2$

PO_4^{3-}

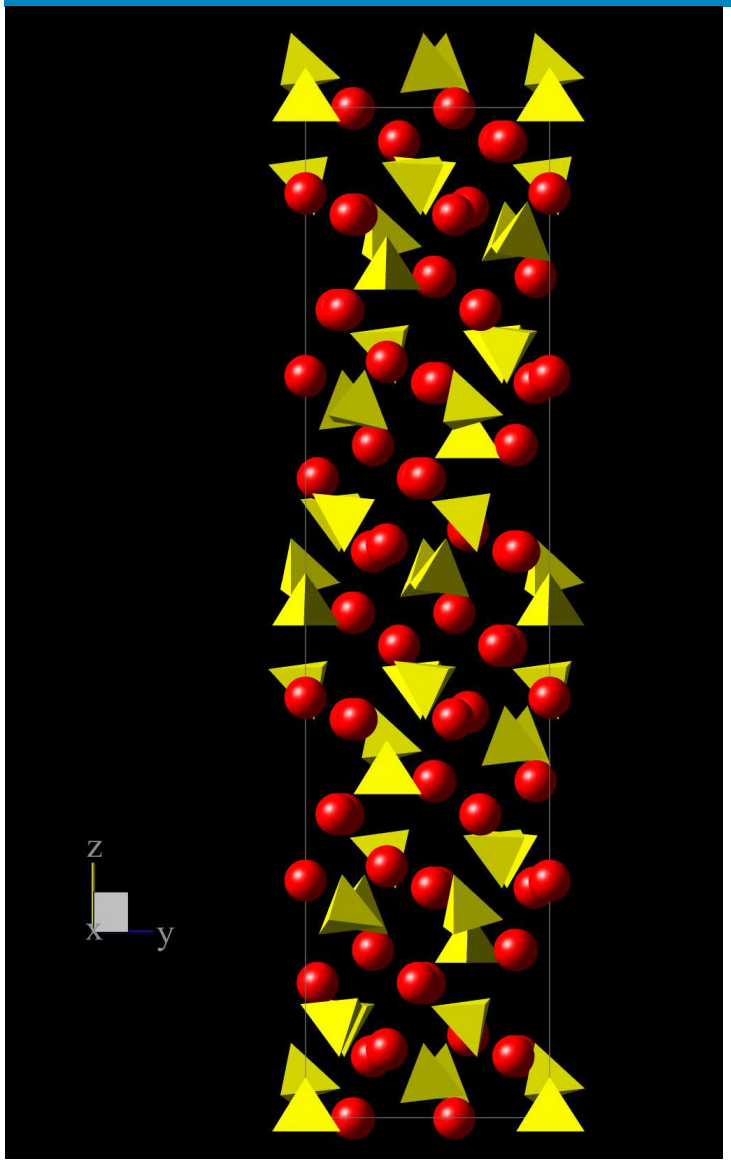
Ca^{2+}

X-radiation interacts with electron shell.

On Ca^{2+} sites we detect 18 electrons.

If Ca^{2+} was replaced by Mg^{2+}, we would detect 10 electrons.

Refinement of Site Occupancies



If we measure scattering from 16 electrons?

2 Solutions:

- 89 % Ca^{2+} ions + 11 % vacancies
- 75 % Ca^{2+} ions + 25 % Mg^{2+} ions

From chemical analysis & synthesis route:
Mg substitutions expected

Refinement of Ca site occupancies:

$x * Ca^{2+} + (1-x) * Mg^{2+}$
x = refined parameter

Lesson 6: Example 5 – Site Occupancies

```
PHASE=betaTCP // 04-008-8714
SpacegroupNo=161 HermannMauguin=R3c //
PARAM=A=1.0439_1.0235^1.0643 PARAM=C=3.7375_3.7001^3.7749  //
RP=4 PARAM=k1=0_0^1 k2=ANISO4 B1=ANISO^0.1 GEWICHT=SPHAR8 //
GOAL=GrainSize(1,1,1) //
GOAL=my //
GOAL=d //
GOAL:betaTCP=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
PARAM=pCa4=0.5_0^0.5
PARAM=pCa5=1_0^1
E=CA+2 Wyckoff=b x=-0.2766 y=-0.1421 z=0.1658 TDS=0.00686924
E=CA+2 Wyckoff=b x=-0.3836 y=-0.1775 z=-0.0336 TDS=0.00673765
E=CA+2 Wyckoff=b x=-0.2721 y=-0.1482 z=0.0606 TDS=0.01873909
E=(CA+2(pCa4),MG+2(0.5-pCa4)) Wyckoff=a PARAM=z=-0.0850 PARAM=TDS=0.01105396_0
E=(CA+2(pCa5),MG+2(1-pCa5)) Wyckoff=a PARAM=z=-0.2658 PARAM=TDS=0.01150138_0
E=P Wyckoff=a z=0.0000 TDS=0.00886948
E=O-2 Wyckoff=b x=0.0070 y=-0.1366 z=-0.0136 TDS=0.02092356
E=O-2 Wyckoff=a z=0.0400 TDS=0.02031823
E=P Wyckoff=b x=-0.3109 y=-0.1365 z=-0.1320 TDS=0.00802728
E=O-2 Wyckoff=b x=-0.2736 y=-0.0900 z=-0.0926 TDS=0.02473981
E=O-2 Wyckoff=b x=-0.2302 y=-0.2171 z=-0.1446 TDS=0.02316067
E=O-2 Wyckoff=b x=-0.2735 y=0.0053 z=-0.1523 TDS=0.00752722
E=O-2 Wyckoff=b x=-0.4777 y=-0.2392 z=-0.1378 TDS=0.01652830
E=P Wyckoff=b x=-0.3465 y=-0.1537 z=-0.2333 TDS=0.00526379
E=O-2 Wyckoff=b x=-0.4031 y=-0.0489 z=-0.2211 TDS=0.01118555
E=O-2 Wyckoff=b x=-0.4246 y=-0.3056 z=-0.2152 TDS=0.01184353
E=O-2 Wyckoff=b x=-0.1814 y=-0.0805 z=-0.2233 TDS=0.01076445
E=O-2 Wyckoff=b x=-0.3696 y=-0.1748 z=-0.2735 TDS=0.01381745
```

2 new refined parameters pCa4, pCa5

Structural limitation: $SOF_{Ca4} = 0.5$

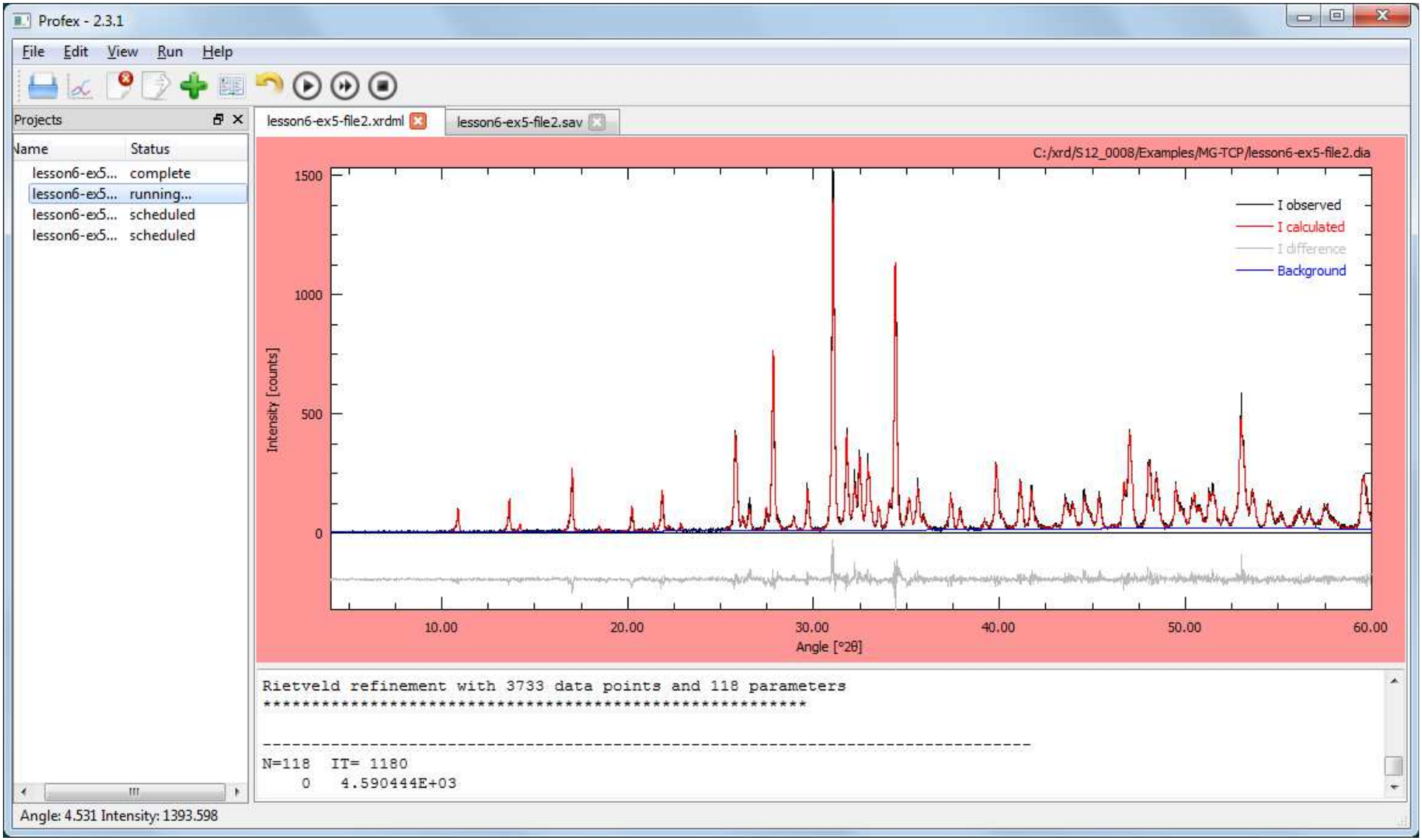
Models for SOF:

Ca4: *pCa4* * Ca^{2+} + (0.5-*pCa4*) * Mg^{2+}

Ca5: *pCa5* * Ca^{2+} + (1-*pCa5*) * Mg^{2+}

Also refine z coordinates and TDS (may be different for Mg^{2+} and Ca^{2+})

Lesson 6: Example 5 – Site Occupancies



Lesson 6: Example 5 – Site Occupancies

```
Local parameters and GOALs for phase betaTCP
****************************************************
SpacegroupNo=161
HermannMauguin=R3c
XrayDensity=3.081
Rphase=13.05%
UNIT=NM
A=1.03907+-0.00022
C=3.73189+-0.00078
k1=1.00000
GrainSize(1,1,1)=301+-33
my=0.025897+-0.000067
d=ERROR
pCa4=0.500000
pCa5=0.596+-0.038
GEWICHT=SPHAR8, MeanValue(GEWICHT)=0.0378133
B1=ANISOLIN, MeanValue(B1)=0.00109941, sqrt3(det(B1))=0.00109664
k2=ANISO4, MeanValue(k2)=0.00000394388
Atomic positions for phase betaTCP
-------------------------------------------
18 -0.2766 -0.1421 0.1658 E=(CA+2(1.0000))
18 -0.3836 -0.1775 -0.0336 E=(CA+2(1.0000))
18 -0.2721 -0.1482 0.0606 E=(CA+2(1.0000))
6 0.0000 0.0000 -0.0807 E=(CA+2(0.5000),MG+2(0.0000))
z=-0.08071+-0.00054
TDS=0.0014+-0.0063

6 0.0000 0.0000 -0.2659 E=(CA+2(0.5956),MG+2(0.4044))
z=-0.26585+-0.00043
TDS=0.0076+-0.0046

6 0.0000 0.0000 0.0000 E=(P(1.0000))
18 0.0070 -0.1366 -0.0136 E=(O-2(1.0000))
…
```

Total unit cell content

(consider site multiplicities):

Site	Site Multipl.	SOF	Element
Ca1	18	1	Ca
Ca2	18	1	Ca
Ca3	18	1	Ca
Ca4	6	0.5	Ca
Ca4	6	0	Mg
Ca5	6	0.5956	Ca
Ca5	6	0.4044	Mg

Lesson 6: Example 5 – Site Occupancies

Site	Site Multipl.	SOF	Element	Total
Ca1	18	1	Ca	18
Ca2	18	1	Ca	18
Ca3	18	1	Ca	18
Ca4	6	0.5	Ca	3
		0	Mg	0
Ca5	6	0.5956	Ca	3.5736
		0.4044	Mg	2.4264

60.5736 Ca^{2+}

2.4264 Mg^{2+}

42.0000 P^{5+}

168.0000 O^{2-}

$Z = 21$

$Ca_{2.8845}Mg_{0.1155}(PO_4)_2$

Mg/(Ca+Mg) = 3.85%

Lesson 6: Example 5 – Site Occupancies

	A	B	C	D	E	F	G	H
1	Sample	Mg/(Ca+Mg) [%] mixed	pCa4 refined	pCa5 refined	Mol Ca	Mol Mg	Mg/(Ca+Mg) [%] refined	Formula
2	120925-1	**0.0**	0.5	1	3.000	0.000	**0.00**	Ca3Mg0(PO4)2
3	120925-2	**1.0**	0.5	0.891	2.969	0.031	**1.04**	Ca2.969Mg0.031(PO4)2
4	120925-3	**2.0**	0.5	0.84	2.954	0.046	**1.52**	Ca2.954Mg0.046(PO4)2
5	120925-4	**4.0**	0.5	0.5956	2.884	0.116	**3.85**	Ca2.884Mg0.116(PO4)2
6								
7								
8								
9								
10								
11								

What I mixed (solid state reaction)

21 wt-% hydroxyapatite show that raw materials were not stoichiometric

What we refined

In the β-TCP structure

Lesson 6: Example 5 – Site Occupancies

Refinement of Site Occupancy Factors (SOF)

- Differences in electron density can be refined (expected vs. found)
- With an appropriate chemical model (consider charge balance):
  - Locate & quantify substitutions
  - Locate & quantify vacancies
- Very good data quality needed!
- Additional information (from synthesis, chemical analysis) can be helpful

Summary

Confused?

Wednesday & Thursday morning:

- Work with your own data sets
- I will assist
- Use the examples from this «How-To» session

Thank you!

Lesson 6: Example 4 – Micro-Absorption

Note for Profex:

lesson5-ex4-file1.dia | lesson5-ex4-file1.sav | lesson5-ex4-file1.lst | Corundum.str | Fluorite.str | LiF.str

```
PHASE=Corundum_Al2O3 // 04-004-2852
SpacegroupNo=167 Setting=1 HermannMauguin=R-32/c //
PARAM=A=0.4760_0.4712^0.4808 PARAM=C=1.2993_1.2863^1.3123  //
RP=4 PARAM=k1=0_0^1 k2=ANISO4 B1=ANISO^0.01 GEWICHT=SPHAR8 //
GOAL=GrainSize(1,1,1) //
d=12 //
GOAL=d //
GOAL=my //
GOAL:corundum=GEWICHT*ifthenelse(ifdef(d),exp(my*d*3/4),1)
E=AL Wyckoff=c x=0.0000 y=0.0000 z=0.3522 TDS=0.00224764
E=O-2 Wyckoff=e x=0.3062 y=0.0000 z=0.2500 TDS=0.00271875
```

These two lines are required by Profex

Otherwise the summary will show uncorrected results:

This formula is hard-coded in Profex

Sample lesson5-ex4-file1 (C:/xrd/S12_0008/Examples/Lesson 6/Example 4/lesson5-ex4-file1.lst)

Phase	R_{Phase} [%]	Quantity [wt-%]	Mean Gewicht [a.u.]	Crystallite Sizes [nm]	Density [g/cm³]
Corundum_Al2O3	6.05	33.37	0.024727	(1,1,1)118.5	3.981
Fluorite	5.49	33.47	0.024800	(1,1,1)36.8	3.172
LiF	4.36	33.17	0.024579	(1,1,1)185	2.633