

Symmetry, magnetism and phase coexistence in Superconducting Iron Chalcogenides $A_yFe_{2-x}Se_2$ ($A=K, Cs, Rb$)

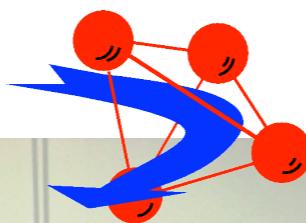
Vladimir Pomjakushin

Laboratory for Neutron Scattering, PSI, Switzerland

Laboratory for Neutron Scattering



LABORATORY
FOR D
EVELOPMENTS
AND M
ETHODS



Bosak, Krzton-Maziopa, Conder,
Pomjakushina, Pomjakushin

Svitlyk, Chernyshov

Ekaterina Pomjakushina, Anna Krzton-Maziopa, Kazimierz Conder *Laboratory for Developments and Methods, PSI, Switzerland*

Dmitry Chernyshov, Volodymir Svitlyk *Swiss-Norwegian Beam Lines at ESRF, France*

Alexey Bosak, *ESRF, France*

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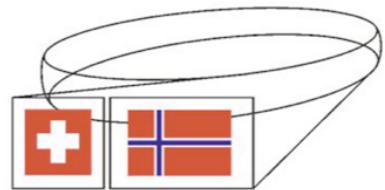
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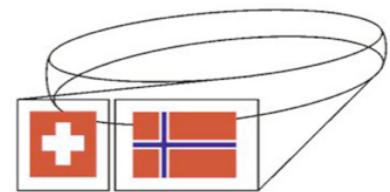
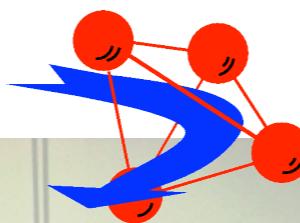
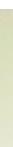


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Swiss-Norwegian Beam Lines
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High temperature iron arsenides and selenides/ telurides superconductors. T_c up to 55K

X-Fe-As pnictides¹ and X-Fe-Se chalcogenides²

where X= Li, LaO, Ba, none, ...

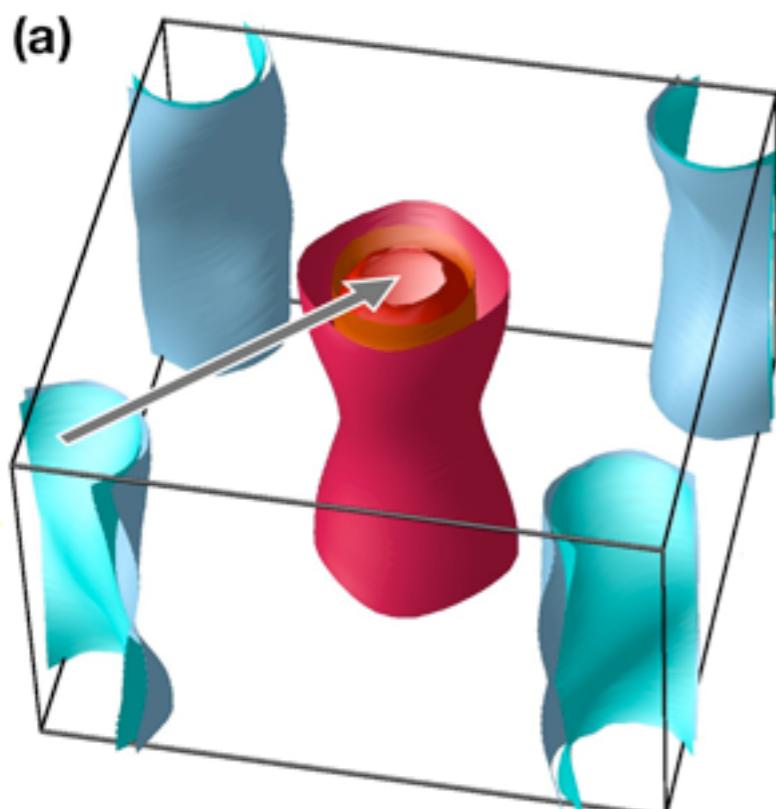
¹ compounds of P, As, Sb, Bi

² compounds of S, Se, Te

High temperature iron arsenides and selenides/tellurides superconductors. T_c up to 55K

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where X= Li, LaO, Ba, none, ...



I.Mazin, Physics 4, 26 (2011)

Iron-based high-temperature superconductors were discovered in January 2008

Towards the end of 2010: the $s\pm$ superconducting pairing

Calculated Fermi surfaces representative of $\text{Ba}(\text{Fe}_{1.94}\text{Co}_{0.06})_2\text{As}_2$
Experimentally observed spin excitation with the same wave vector
 $[1/2, 1/2, 0]$ or (π, π)

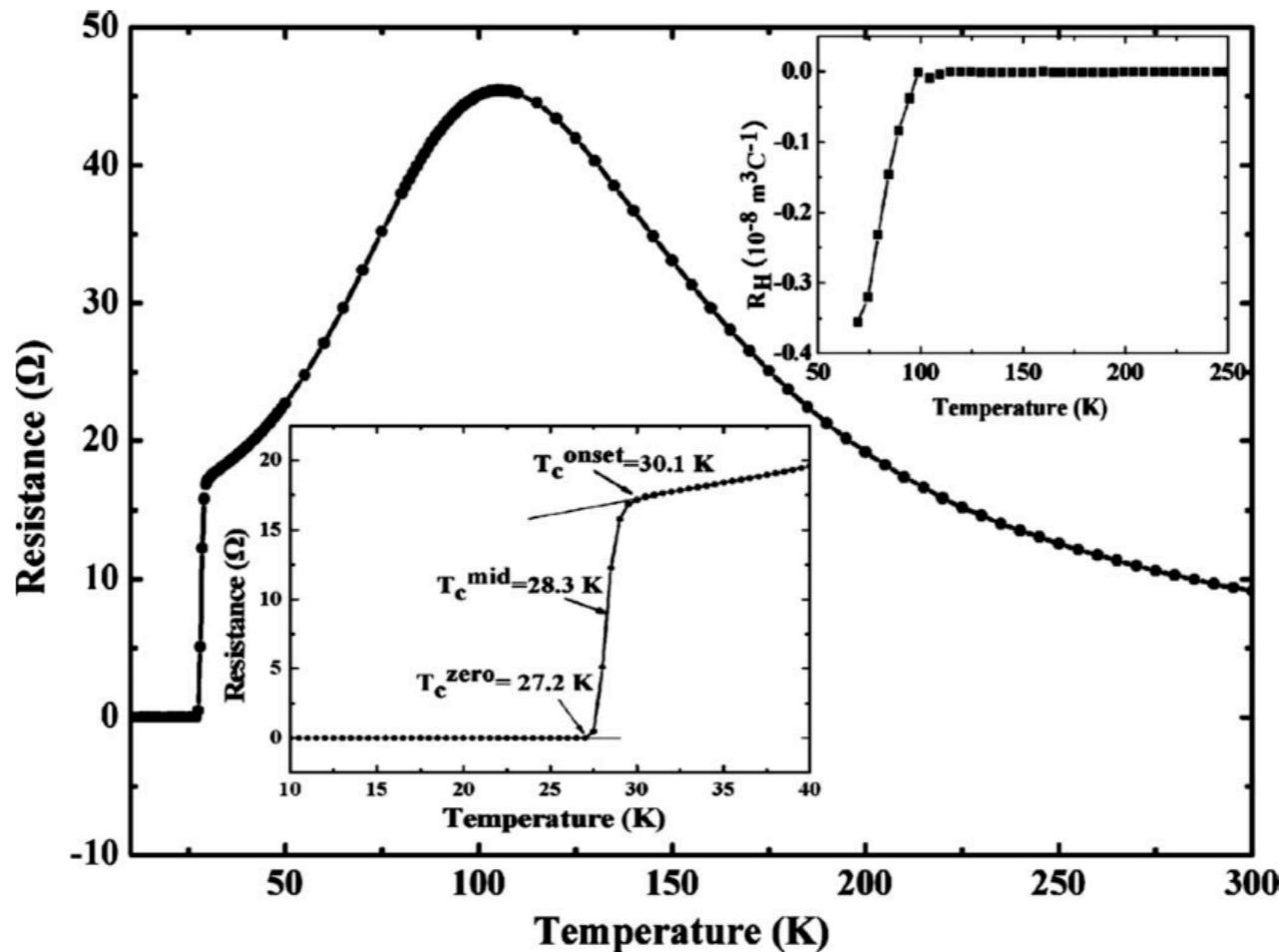
¹ compounds of P, As, Sb, Bi

² compounds of S, Se, Te

An unexpected surprise!

$K_yFe_{2-x}Se_2$ superconductor $T_c=30K$

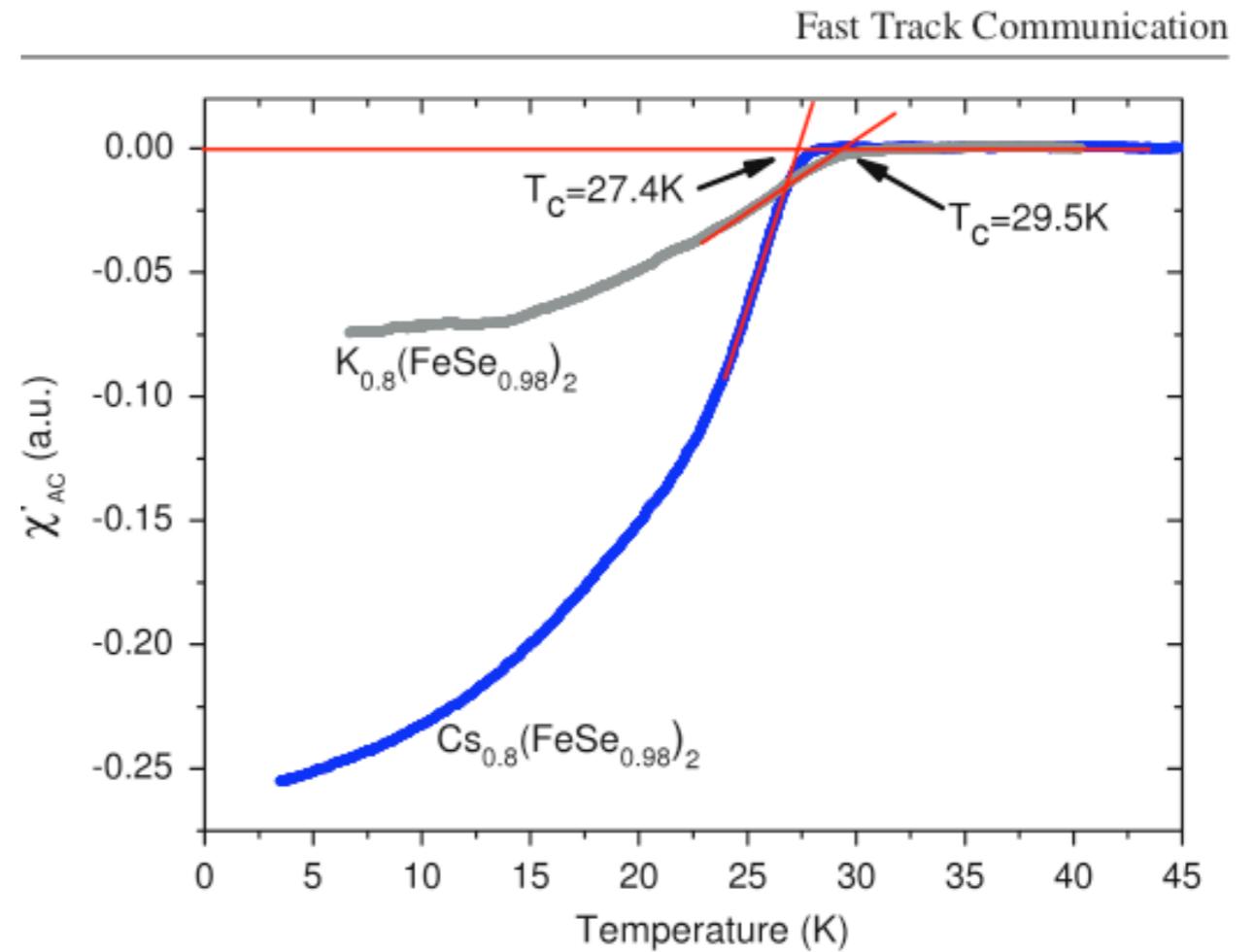
Jiangang Guo et al, (November 2010)



1. No (π,π) -resonance!
2. AFM at room T!

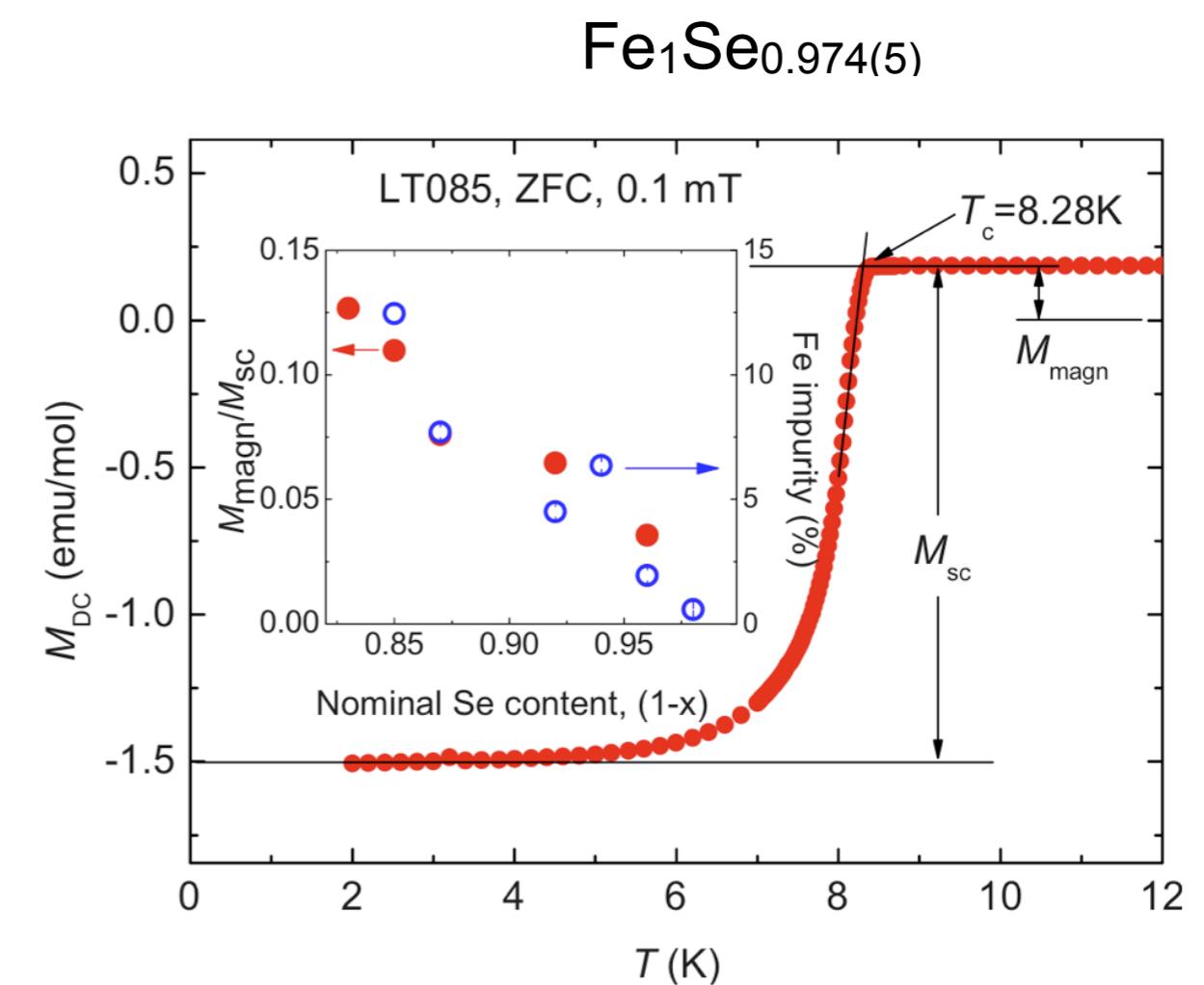
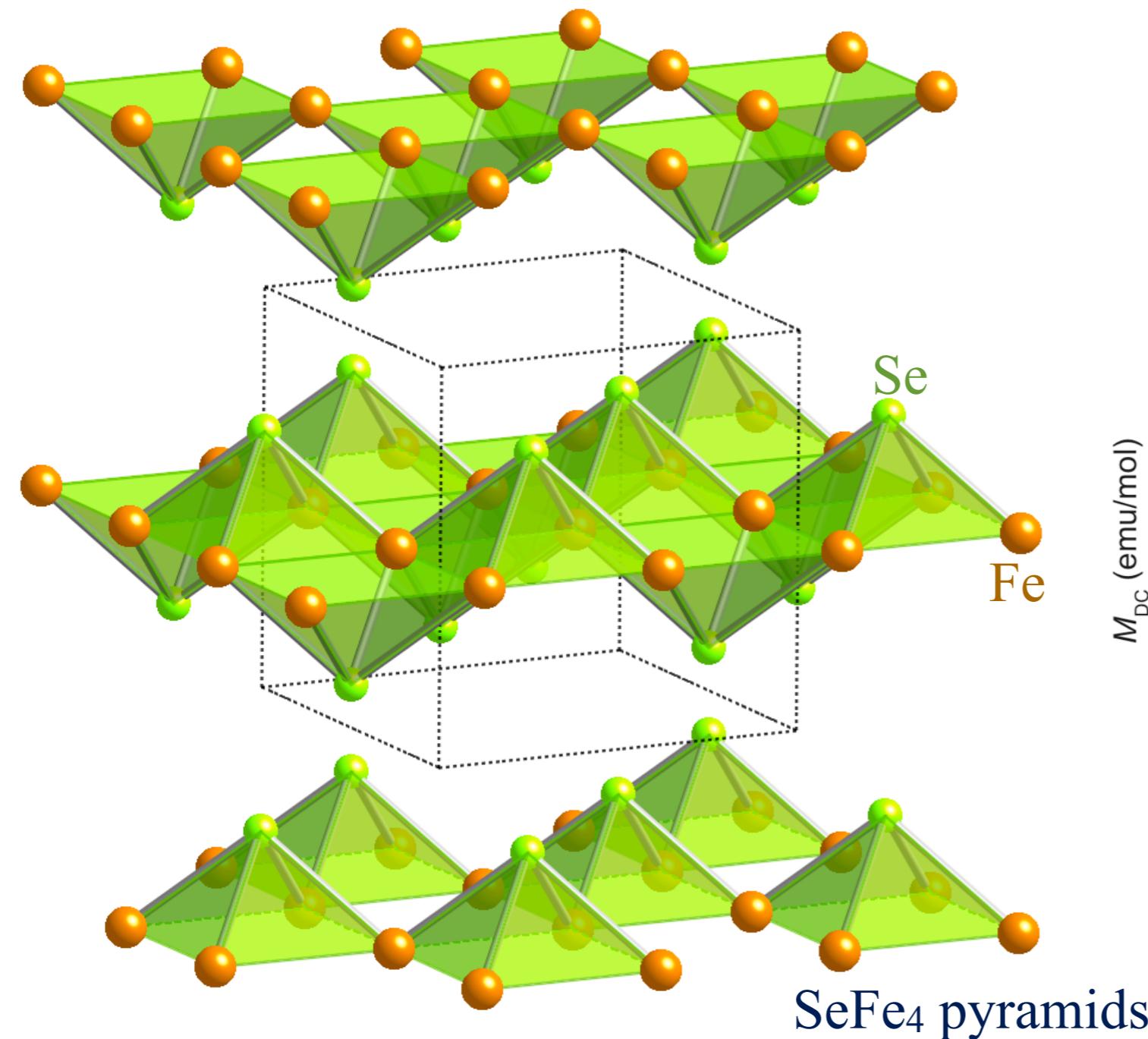
FIG. 3. The temperature dependence of electrical resistance for the $K_{0.8}Fe_2Se_2$ crystal sample. The lower inset shows the details of

Second member $Cs_yFe_{2-y}Se_2$ had been grown by A Krzton-Maziopa, E Pomjakushina, K.Conder (December 2010) *in Laboratory of Developement and Methods at Paul Scherrer institute PSI, Switzerland*



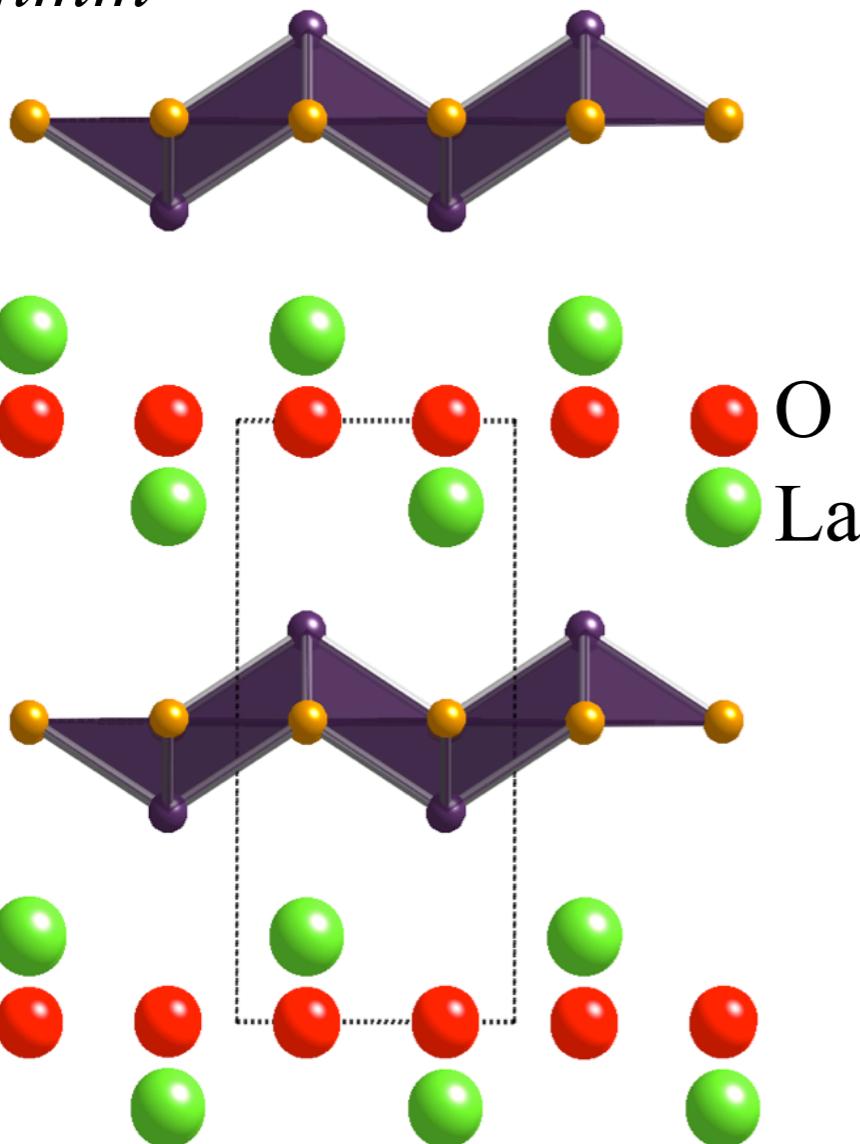
The simplest structure “11” FeSe, $T_c=8K$

$P4/nmm$. $T < 100K$ $Cmma$

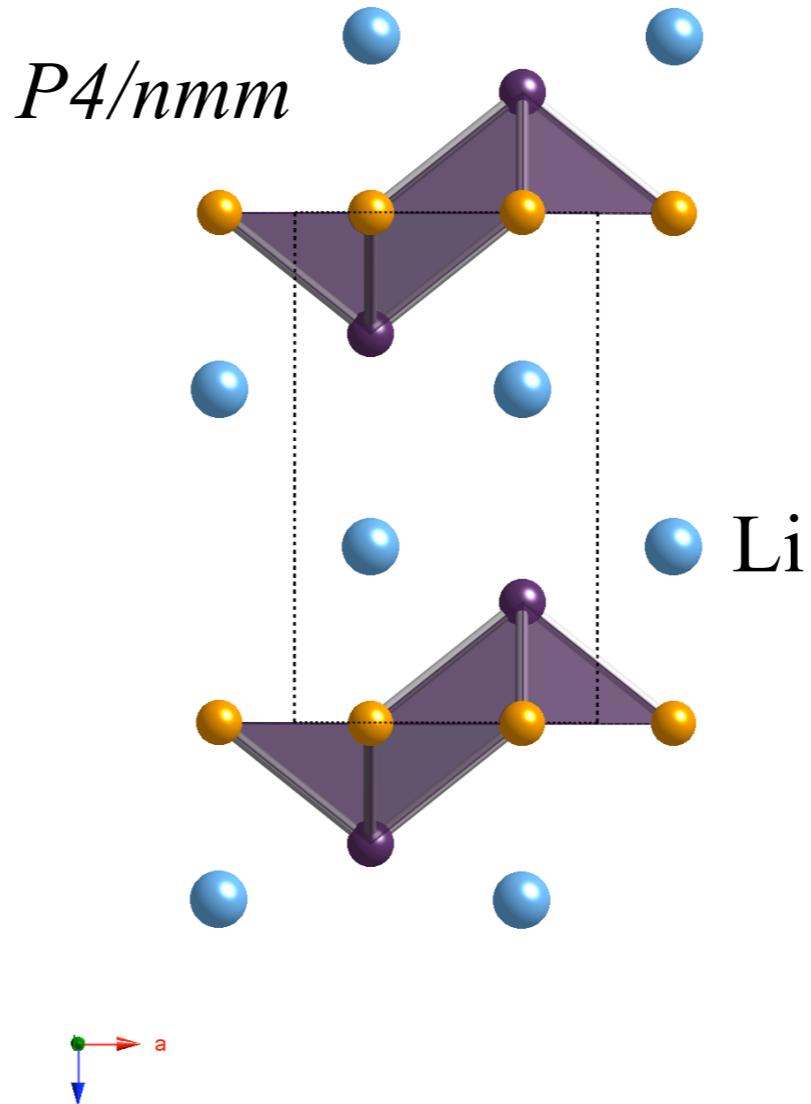


Nomenclature

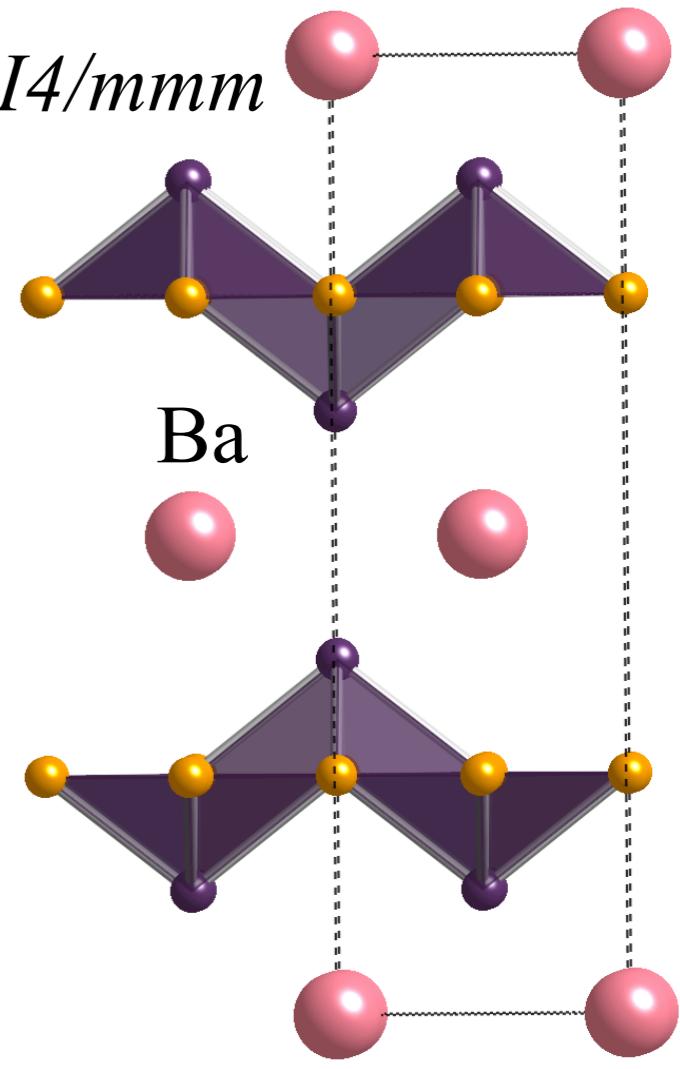
P4/nmm



P4/nmm



I4/mmm



11 $\text{Fe}_1\text{-}(\text{SeTe})_1$ ($T_c^{\max} = 14\text{K}$)

1111 $\text{La}_1\text{O}_1\text{-}\text{Fe}_1\text{As}_1$ ($T_c^{\max}=55\text{K}$)

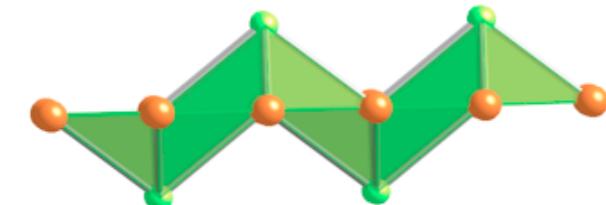
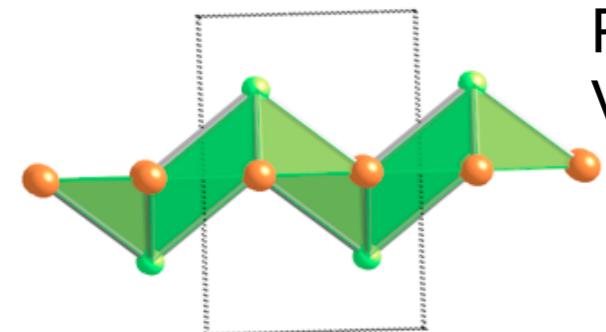
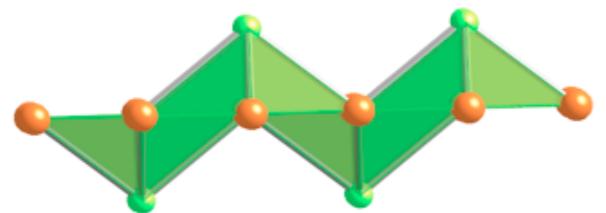
111 $\text{Li}_1\text{-}\text{Fe}_1\text{As}_1$ ($T_c^{\max} = 18\text{K}$)

122 $\text{Ba}_1\text{-}\text{Fe}_2\text{As}_2$ ($T_c^{\max} = 38\text{K}$)

$\text{Fe}_1\text{Se}_{0.974(5)}$

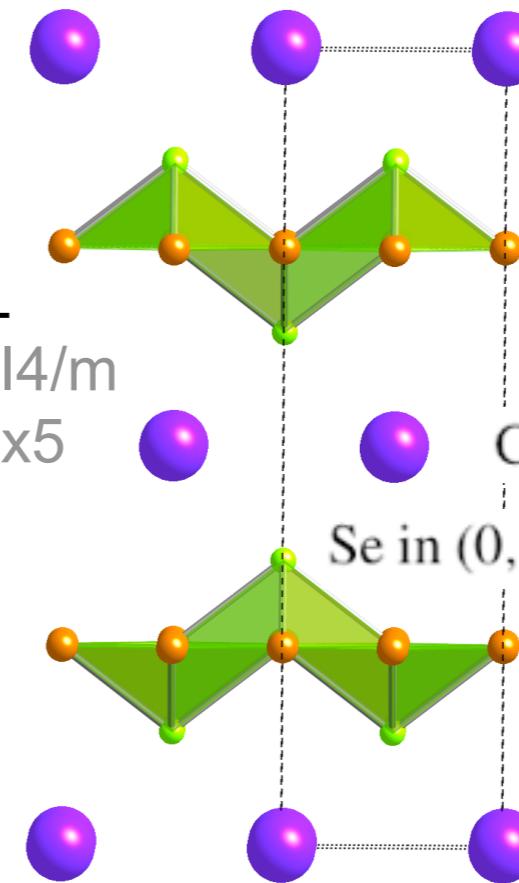


“ $\text{A}_1\text{Fe}_2\text{Se}_2$ ”: $\text{A}_y\text{Fe}_{2-x}\text{Se}_2$ ($\text{A}=\text{K}, \text{Cs}, \text{Rb}$)



P4/nmm
Volume

(1/2, 1/2, 1/2)+
 $\text{l}4/\text{mmm} \rightarrow \text{l}4/\text{m}$
x2

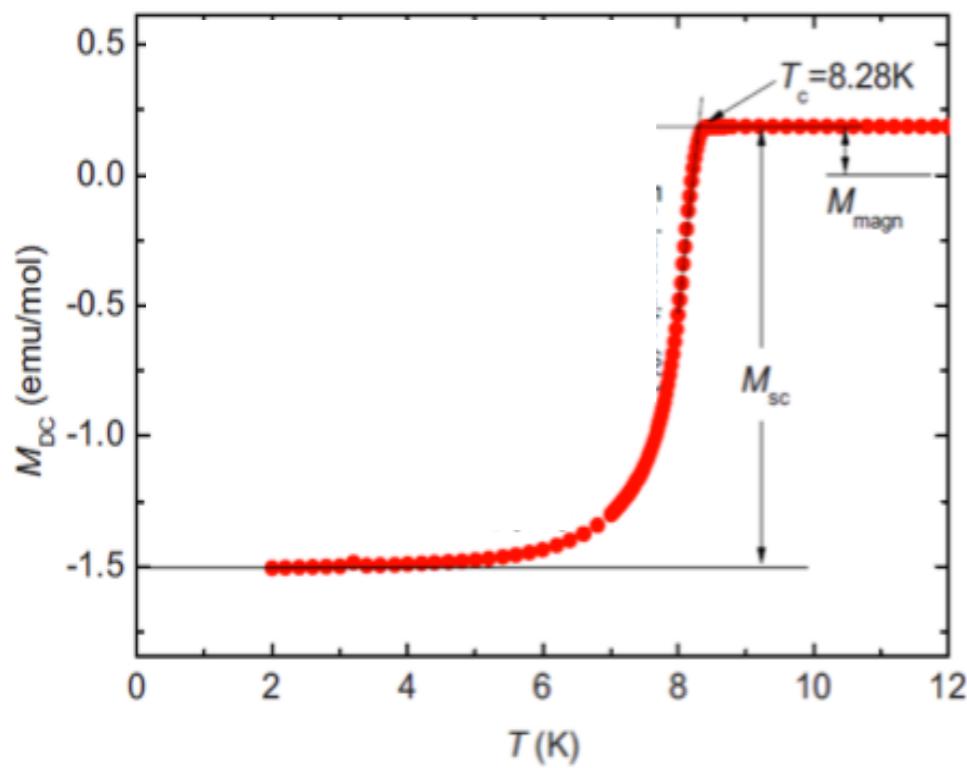


average crystal
structure $\text{l}4/\text{mmm}$

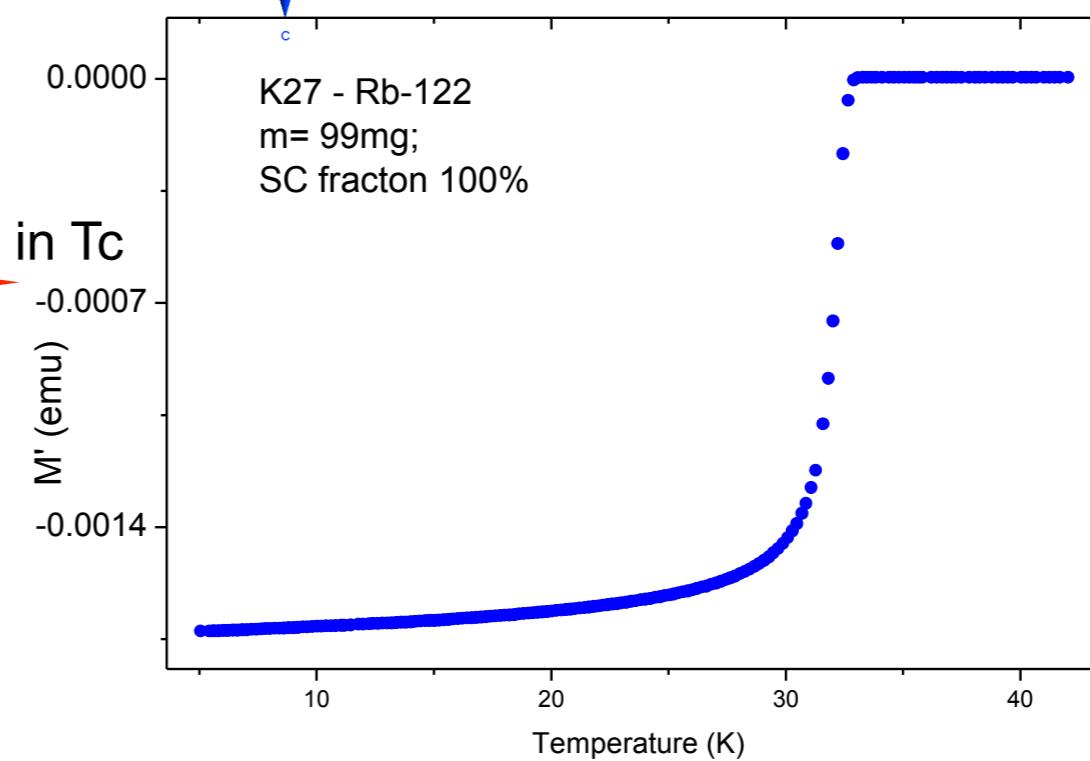
Cs in $(0,0,0)$ (2a)

Se in $(0,0,z)$ (4e)

Fe in $(0,\frac{1}{2},\frac{1}{4})$ (4d)



3 times
increase in T_c



Superconducting $A_yFe_{2-x}Se_2$ are fundamentally different from previously known 122

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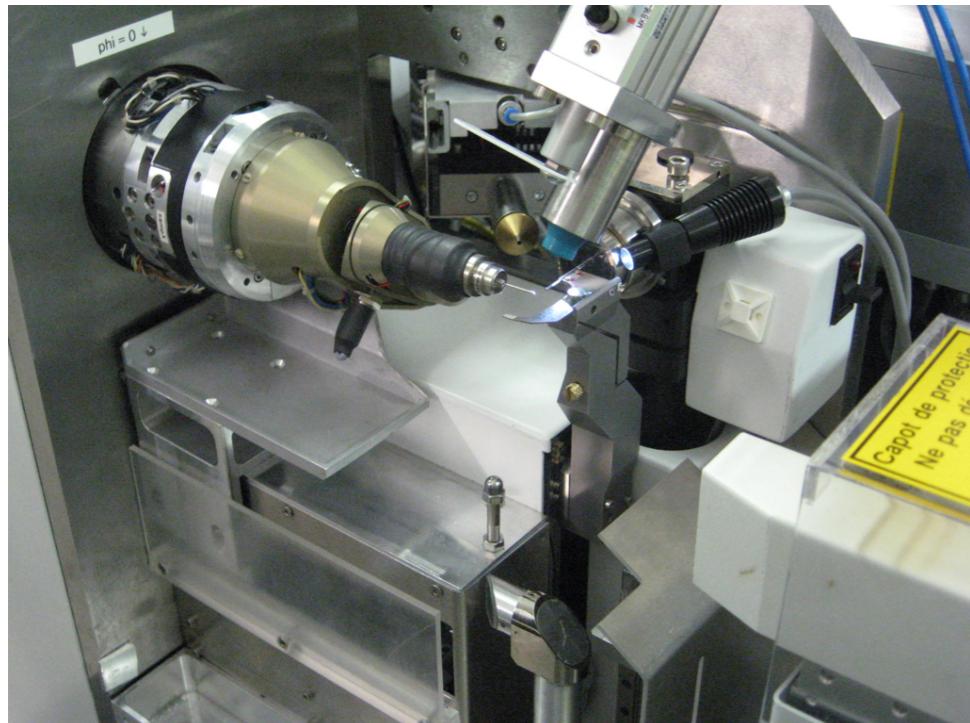
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 - There is a strong temptation to assign SC to one of the phases with “I4/mmm 122”-structure
-

Superconducting $A_yFe_{2-x}Se_2$ are fundamentally different from previously known I22

- Not single phase even in form of single crystal, opposite to all previously known I22 Ba-Fe₂As₂. From diffraction, uSR, microscopy,...
- Symmetry is lower than I4/mmm
- It possesses bulk AFM. Up to $3\mu_B/Fe$
- There is a strong temptation to assign SC to one of the phases with “I4/mmm I22”-structure
- Single phase I22 material $AyFe_{2-x}Se_2$ ($A=K,Rb,Cs$) does not exist at room temperature and below.

Single crystal diffraction @ ESRF, France

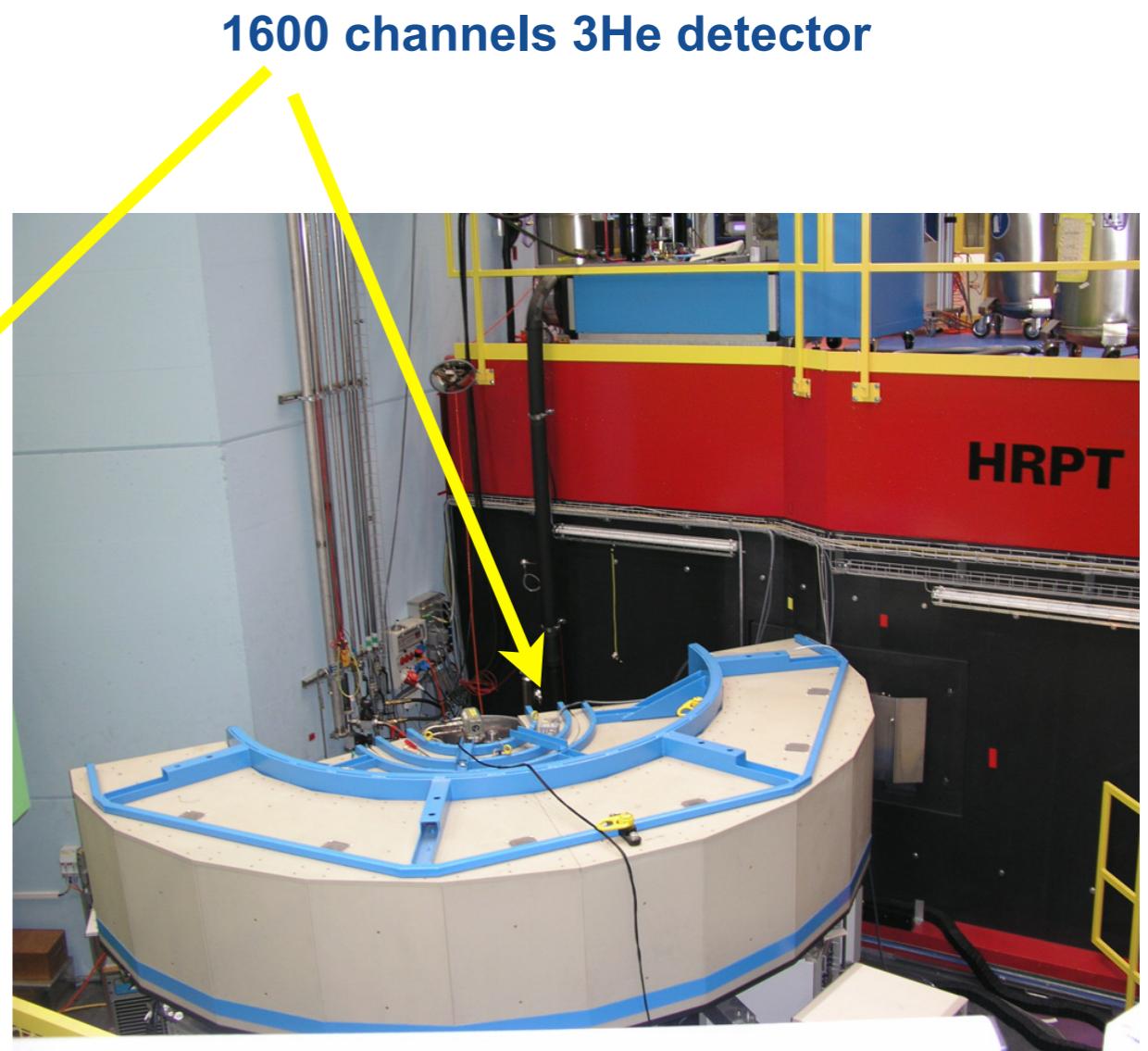
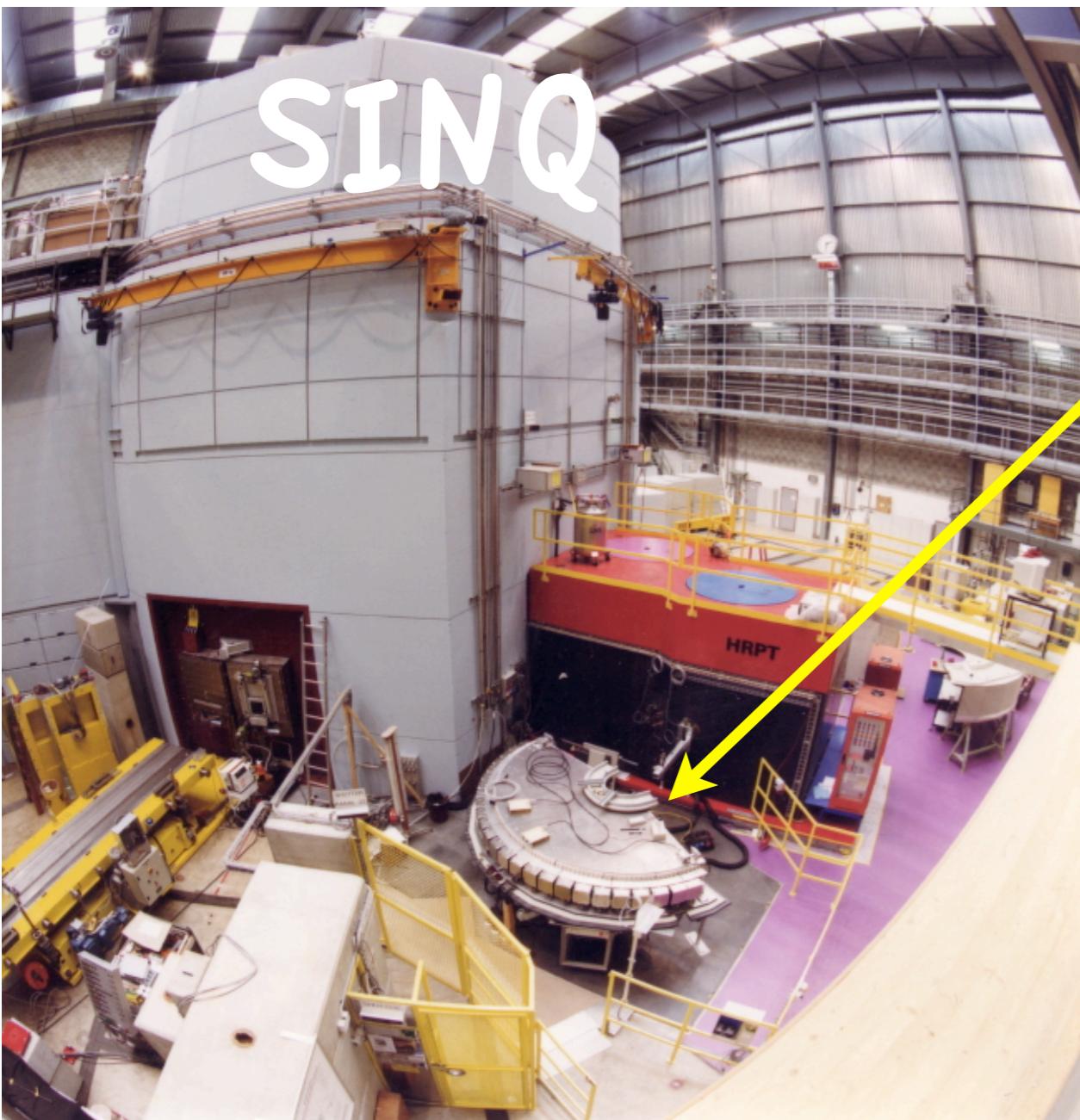
beamline ID29 PILATUS 6M



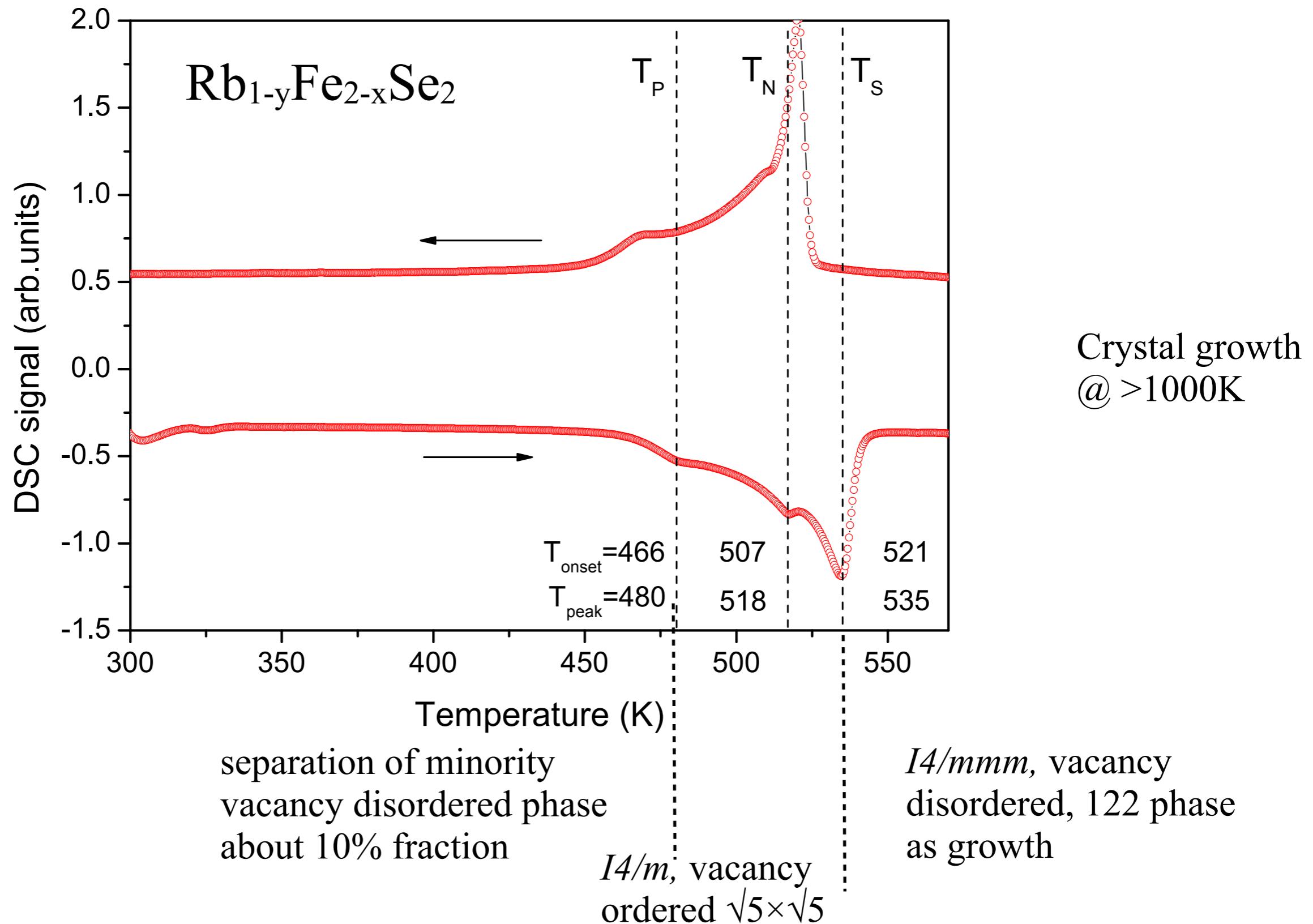
SNBL beamline BM1A with a MAR345 detector



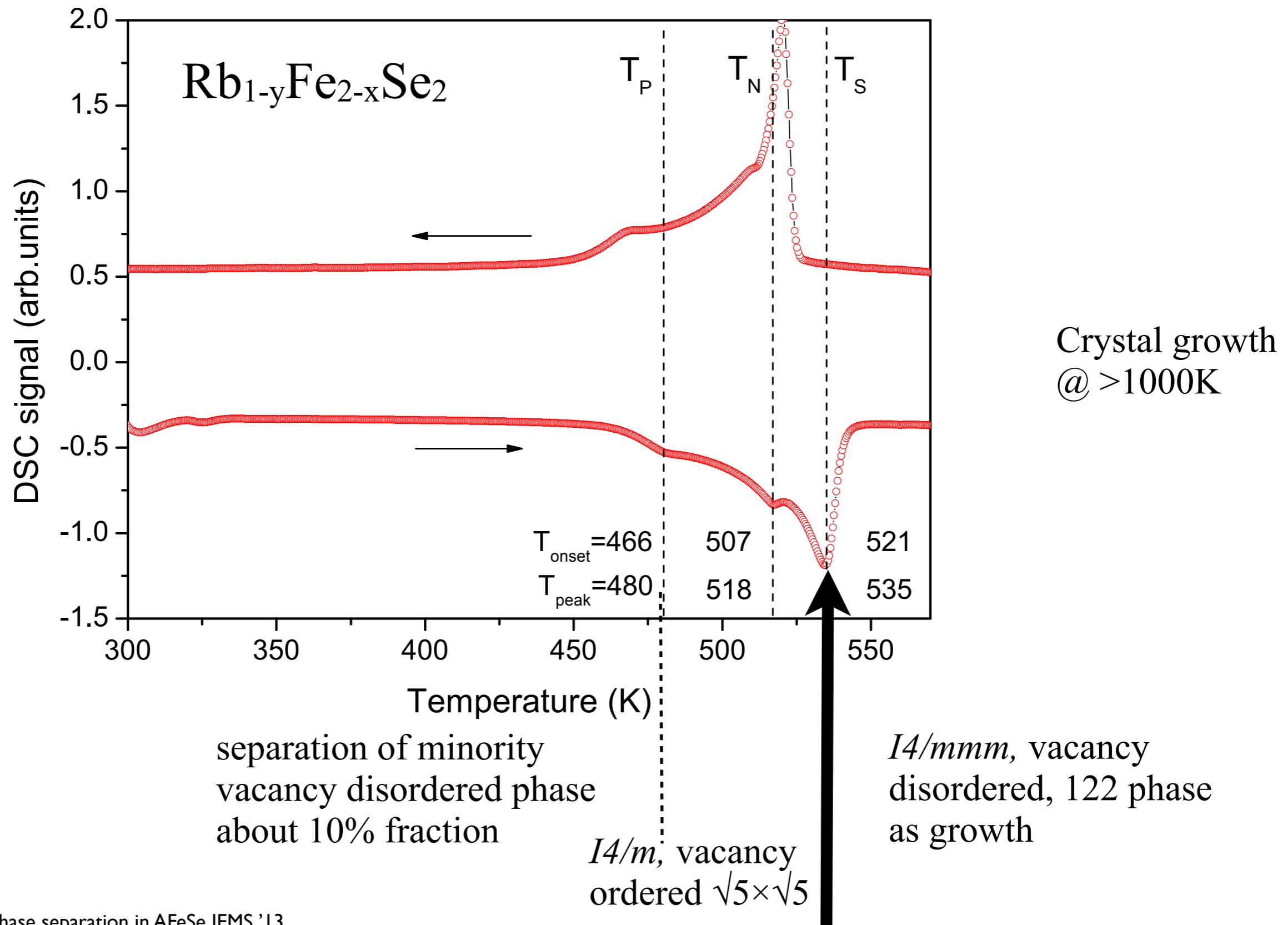
Powder neutron diffraction @ HRPT/SINQ, Paul Scherrer Institute, Switzerland



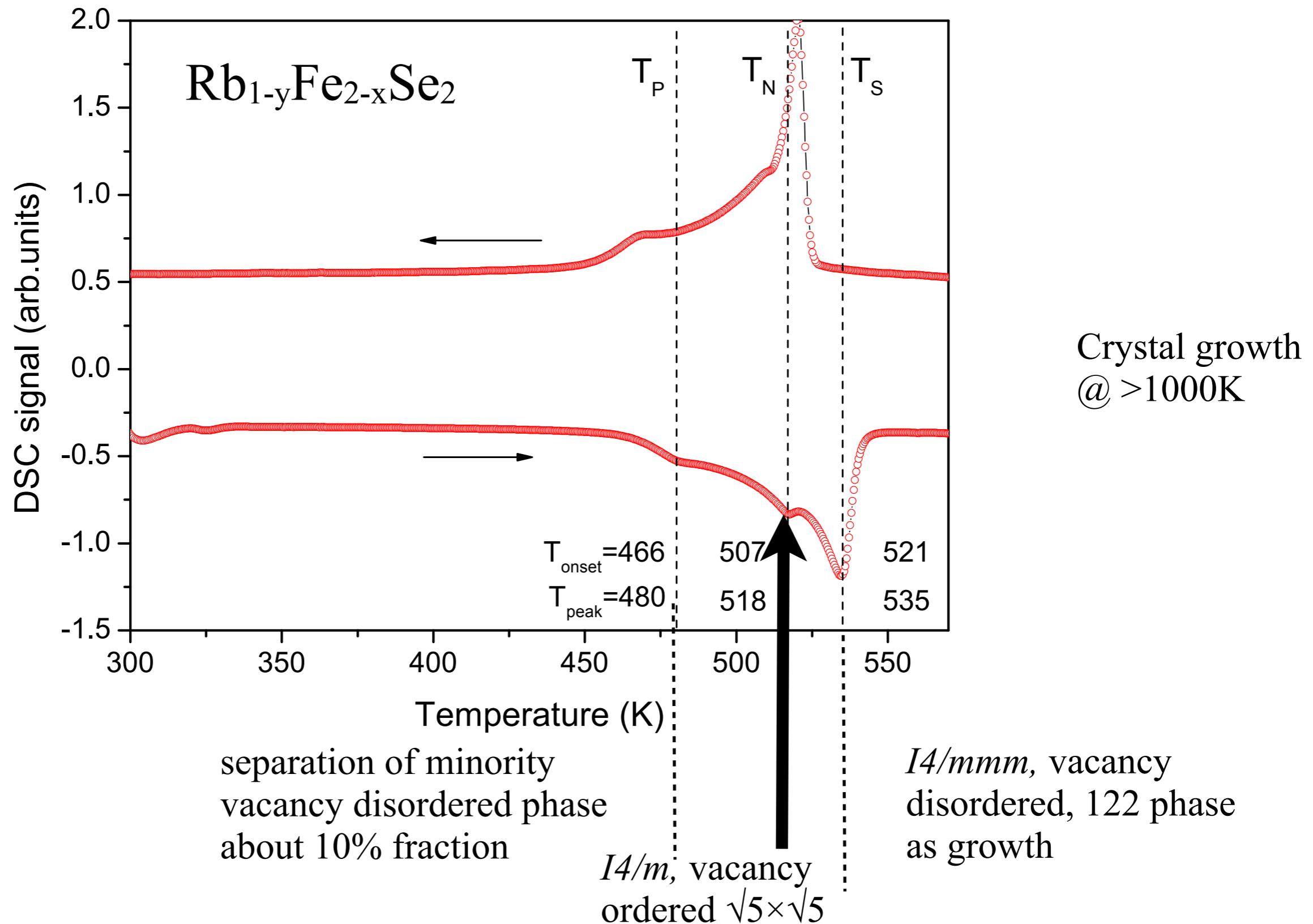
Differential scanning calorimetry. Identifying the transitions.



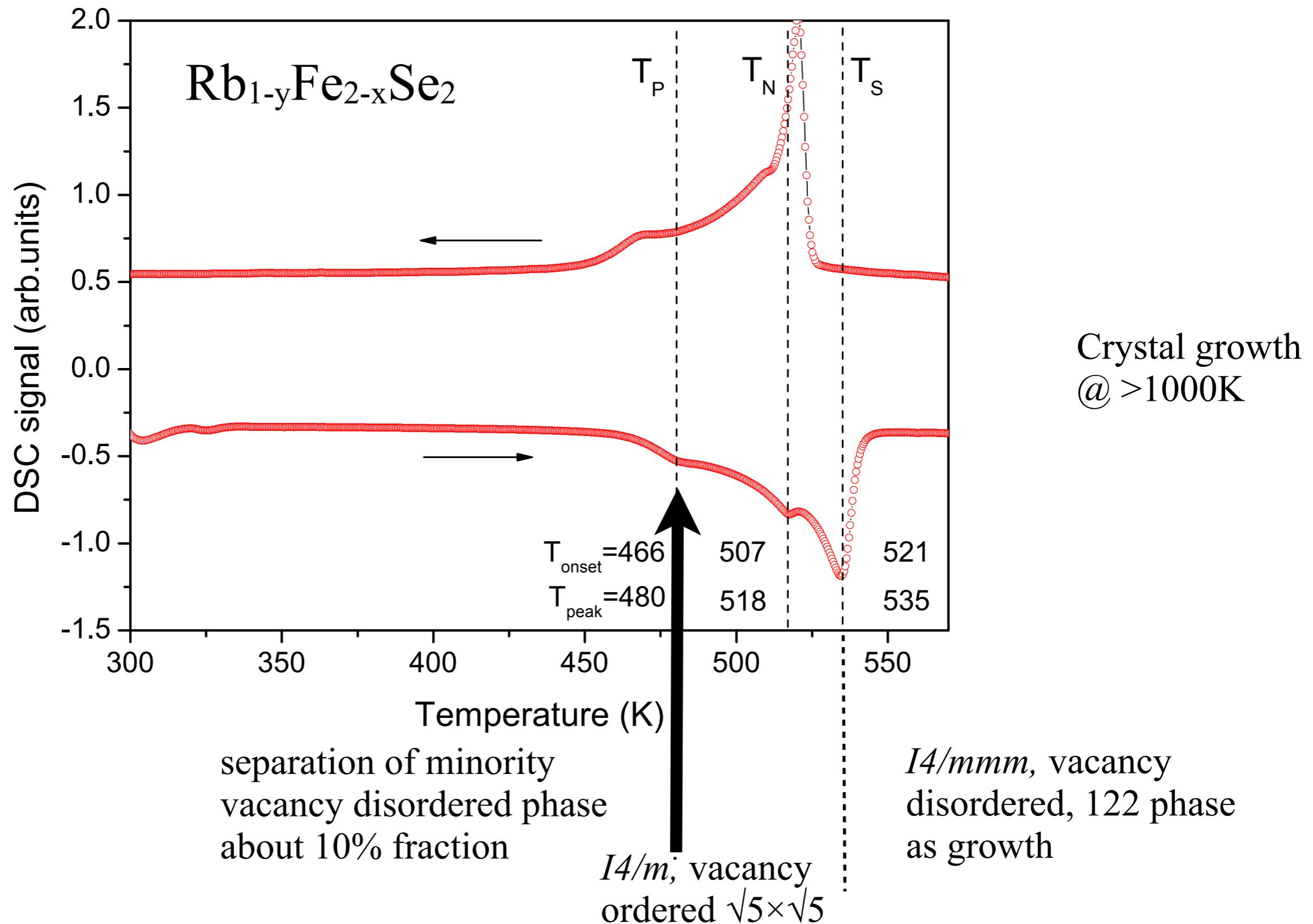
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Differential scanning calorimetry. Identifying the transitions.



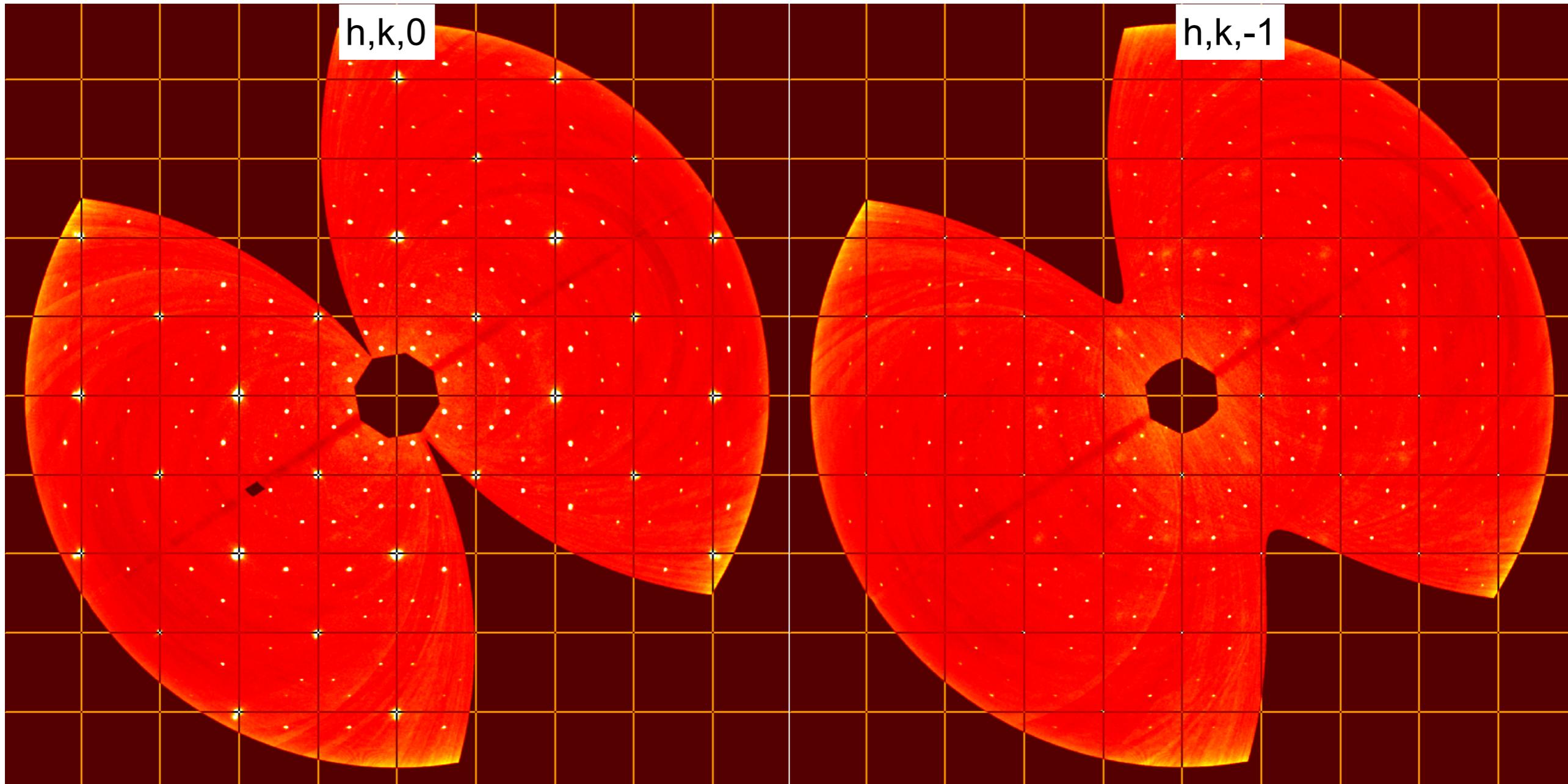
Differential scanning calorimetry. Identifying the transitions.



A diffraction view on phase separation:
I. Main (90%) phase (A)

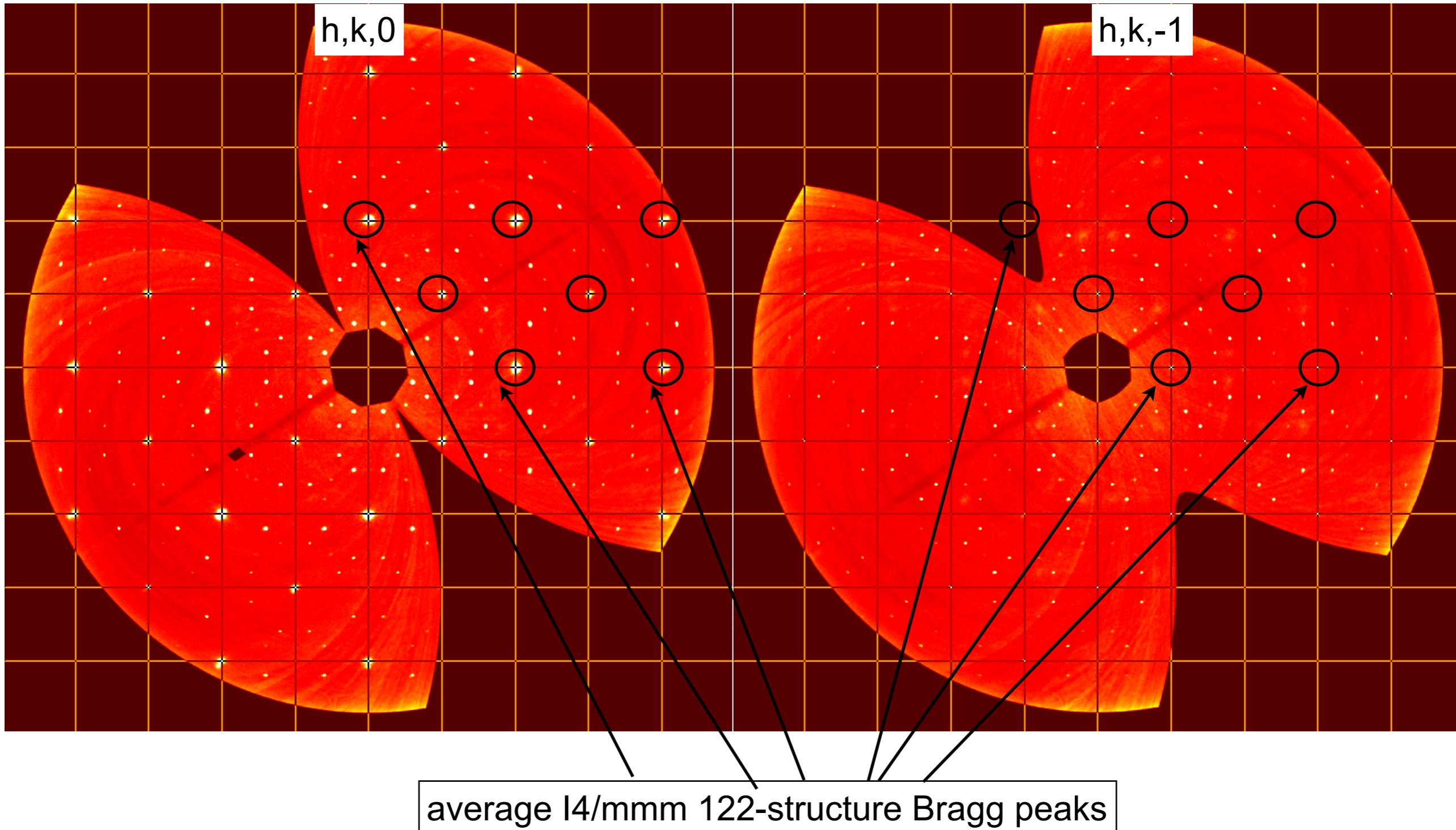
Reciprocal space reconstruction from single crystal x-ray @ SNBL/ESRF

the mesh is for the parent I4/mmm cell
T=300K, (hk0) plane of $\text{Cs}_y\text{Fe}_{2-x}\text{Se}_2$



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(hk0) slice of reciprocal space. indexing in average I4/mmm structure

4-arms k-vector stars

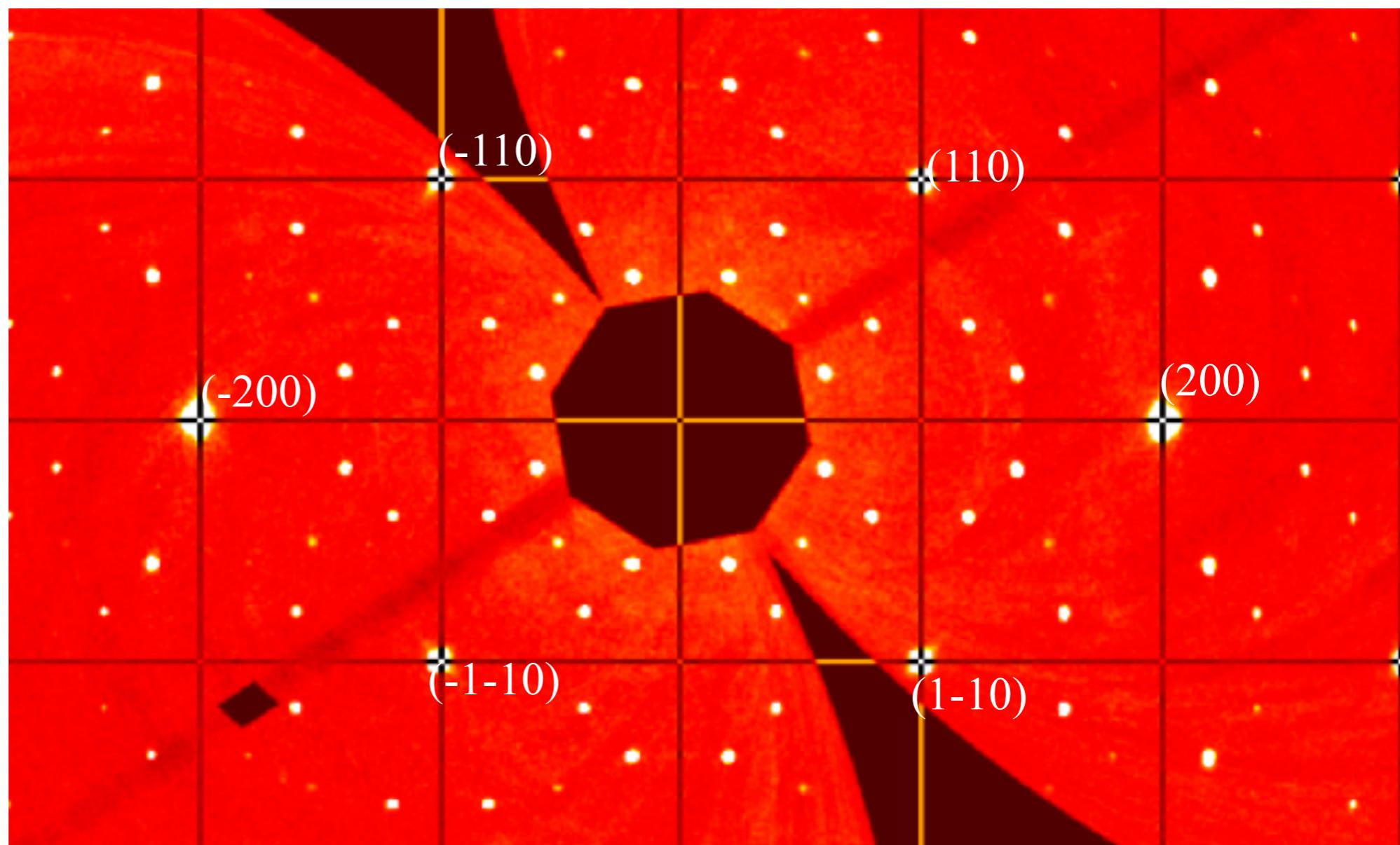
$$\{\mathbf{k}_1\} = \left\{ \left[\frac{2}{5}, \frac{1}{5}, 1 \right] \right\}$$

$$\{\mathbf{k}_2\} = \left\{ \left[\frac{1}{5}, \frac{2}{5}, \bar{1} \right] \right\}$$

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T=300K, (hk0) plane of $\text{Cs}_y\text{Fe}_{2-x}\text{Se}_2$

superstructure satellites



Note: the k-vectors are shown in projection. Their origin is at L=+/-1

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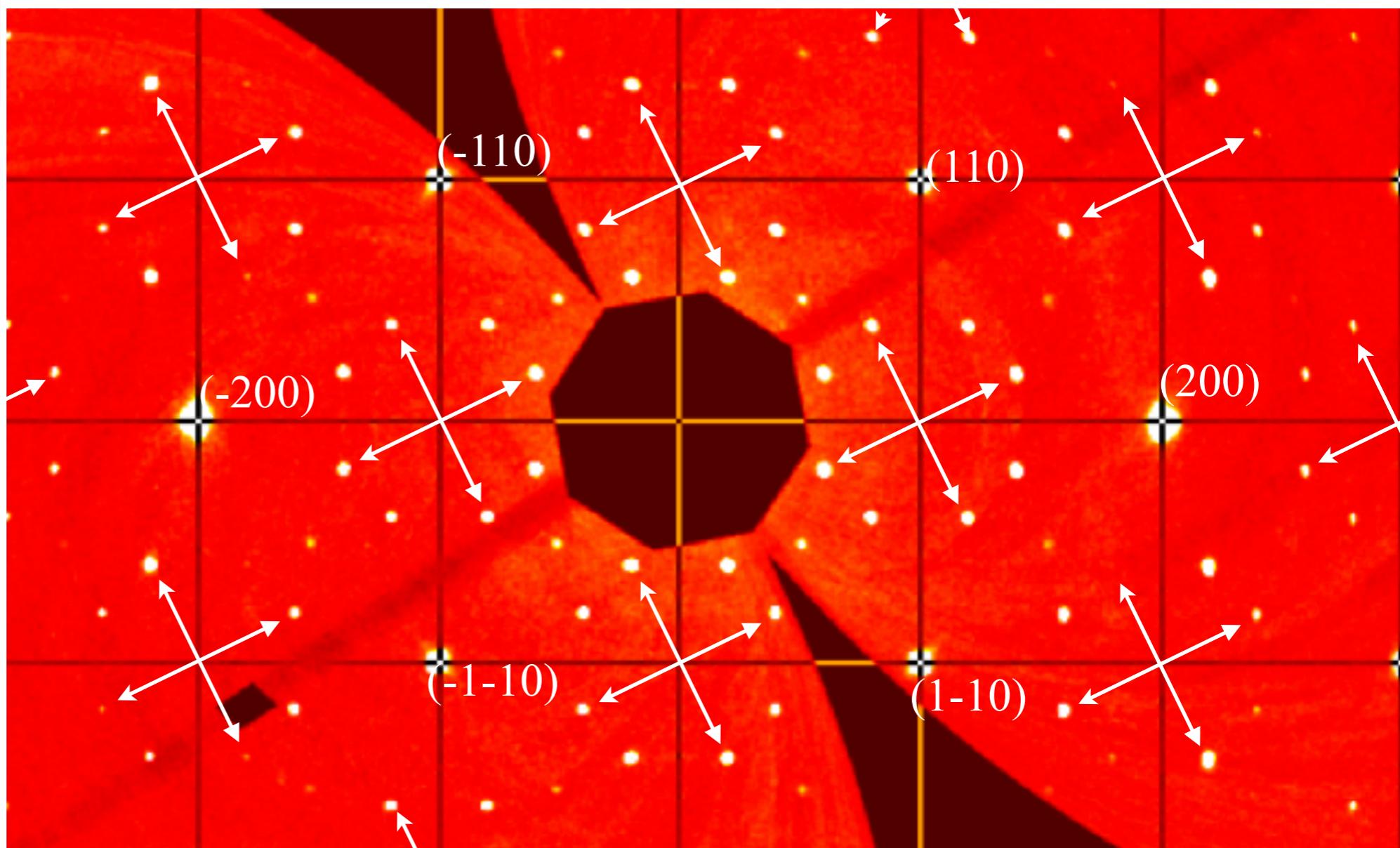
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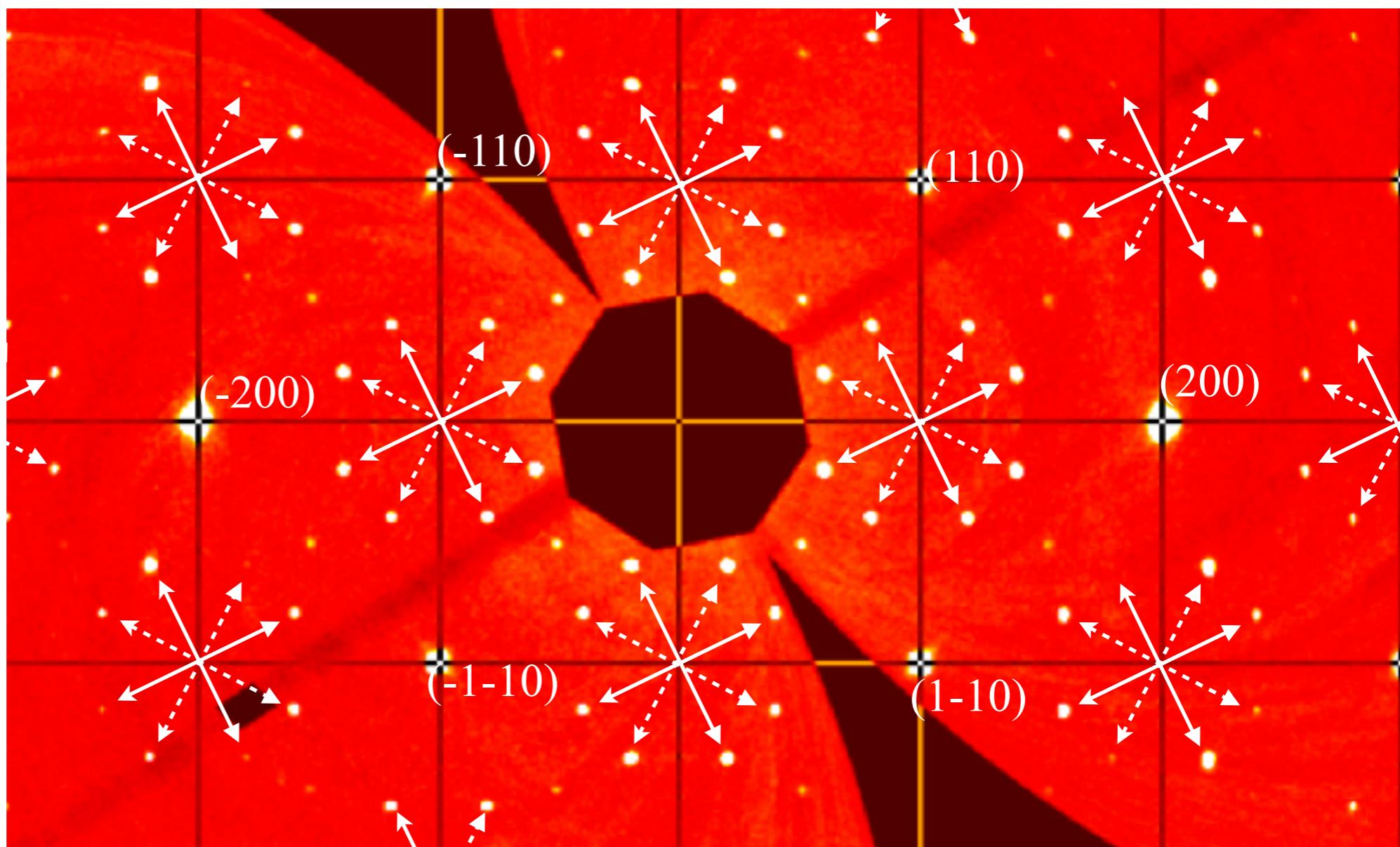
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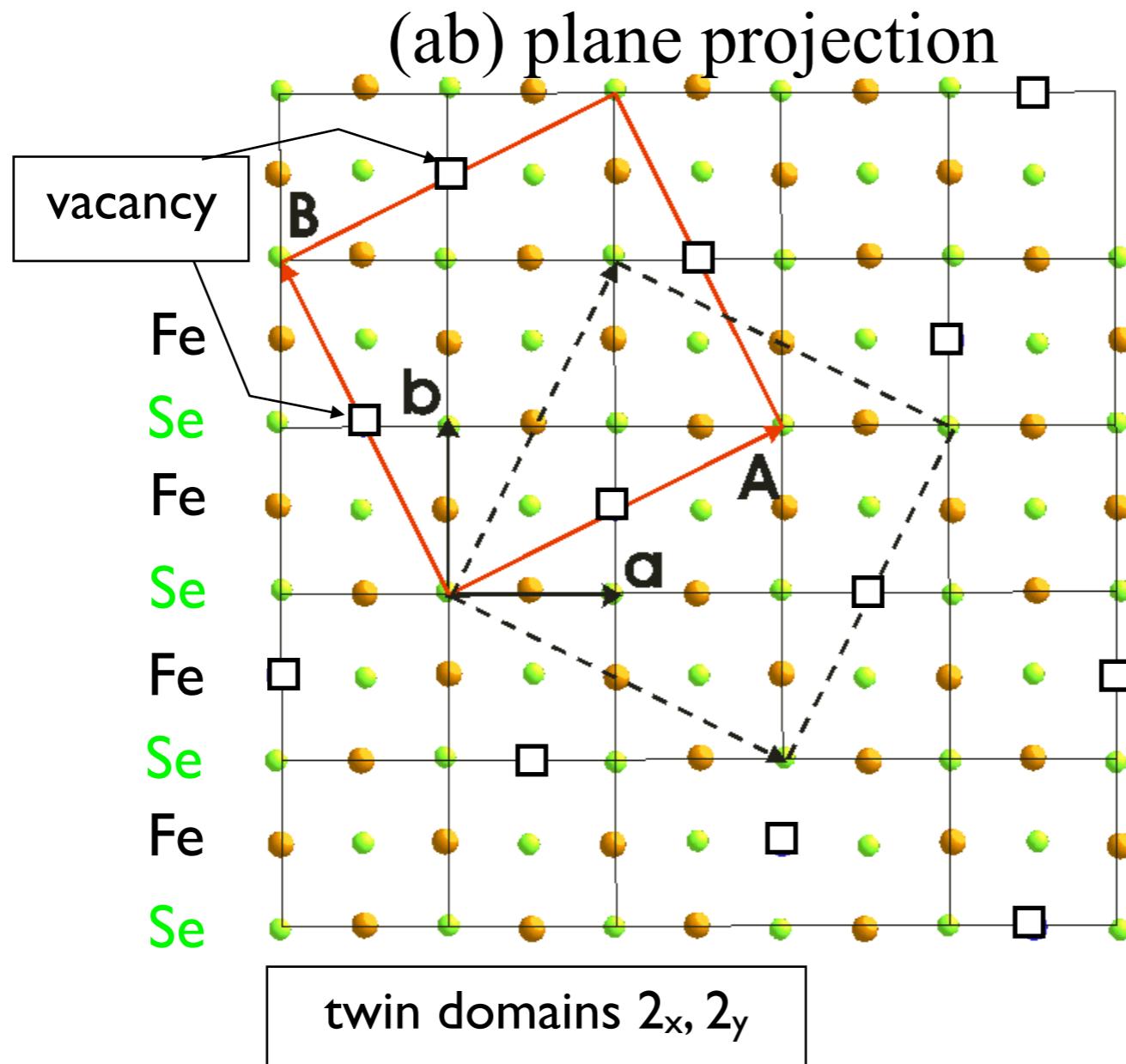
Note: the k-vectors are shown in projection. Their origin is at $L=+/-1$

I4/m structure of main phase A. Metrics. Two twins.

$$\{\mathbf{k}_1\} = \left\{ \left[\frac{2}{5}, \frac{1}{5}, 1 \right] \right\} \rightarrow \begin{aligned} \mathbf{A} &= 2\mathbf{a} + \mathbf{b} \\ \mathbf{B} &= -\mathbf{a} + 2\mathbf{b} \\ \mathbf{C} &= \mathbf{c} \end{aligned}$$

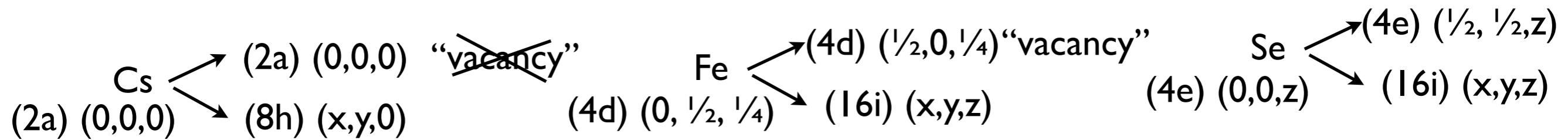
$$\{\mathbf{k}_2\} = \left\{ \left[\frac{1}{5}, \frac{2}{5}, \bar{1} \right] \right\} \rightarrow \begin{aligned} \mathbf{A} &= 2\mathbf{a} - \mathbf{b} \\ \mathbf{B} &= \mathbf{a} + 2\mathbf{b} \\ \mathbf{C} &= \mathbf{c} \end{aligned}$$

$$A \times B = \sqrt{5}a \times \sqrt{5}b$$



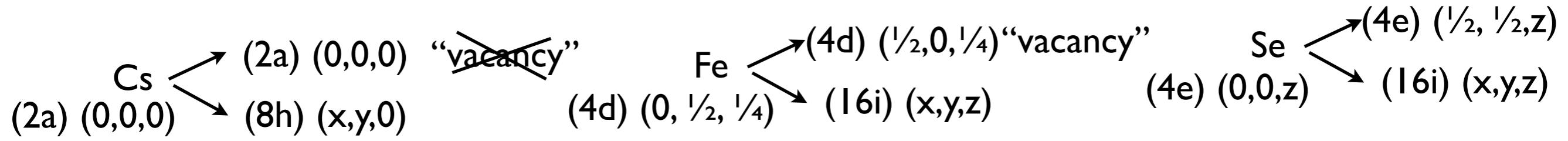
I4/mmm -> I4/m Structure details “245”

Position splitting



I4/mmm -> I4/m Structure details “245”

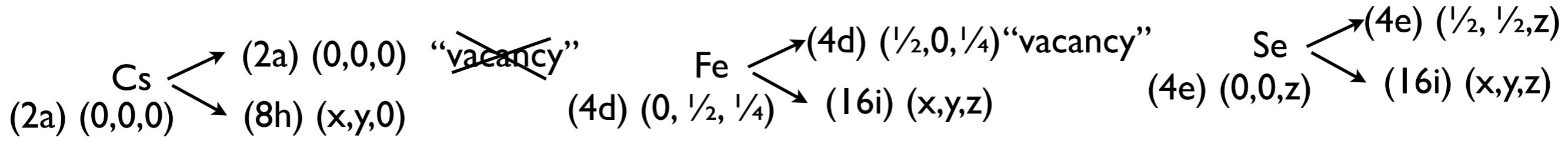
Position splitting



$$y=0.7-0.85, x=1.60-1.75$$

I4/mmm -> I4/m Structure details “245”

Position splitting

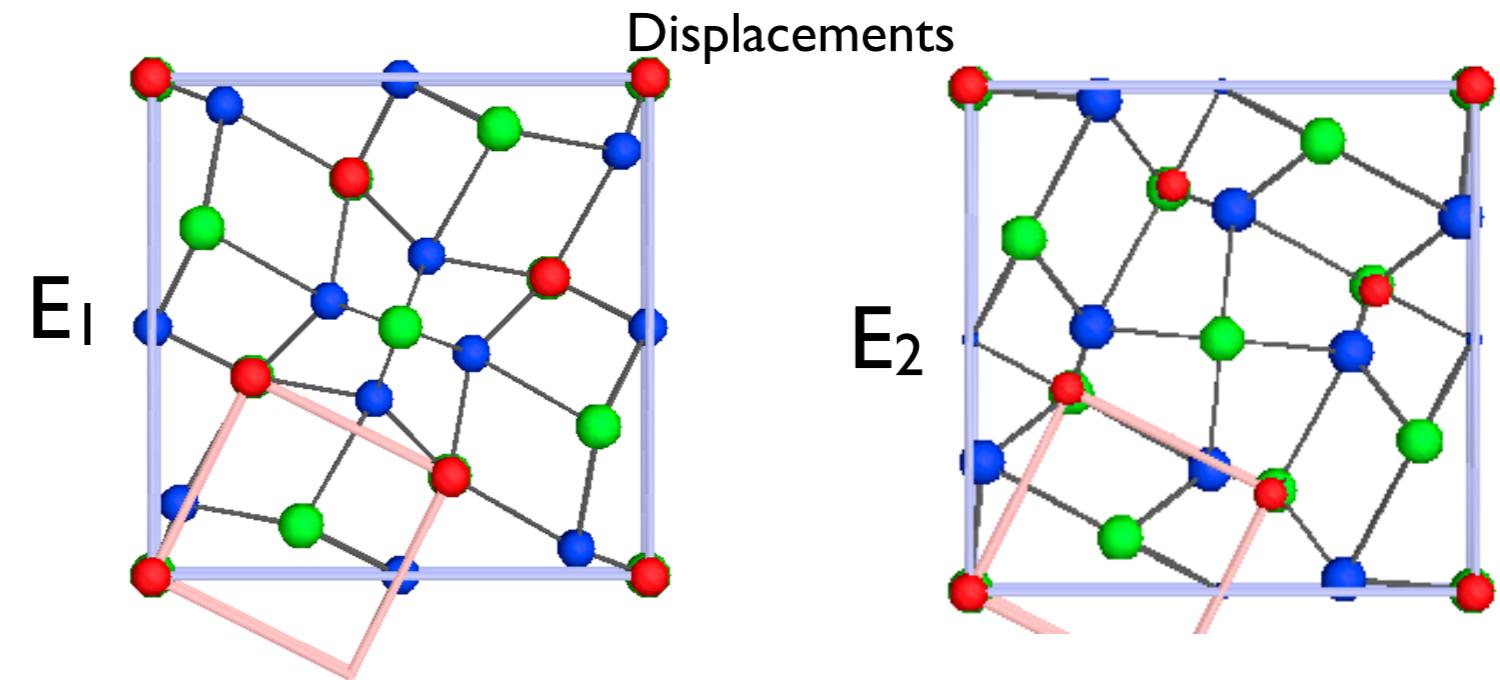
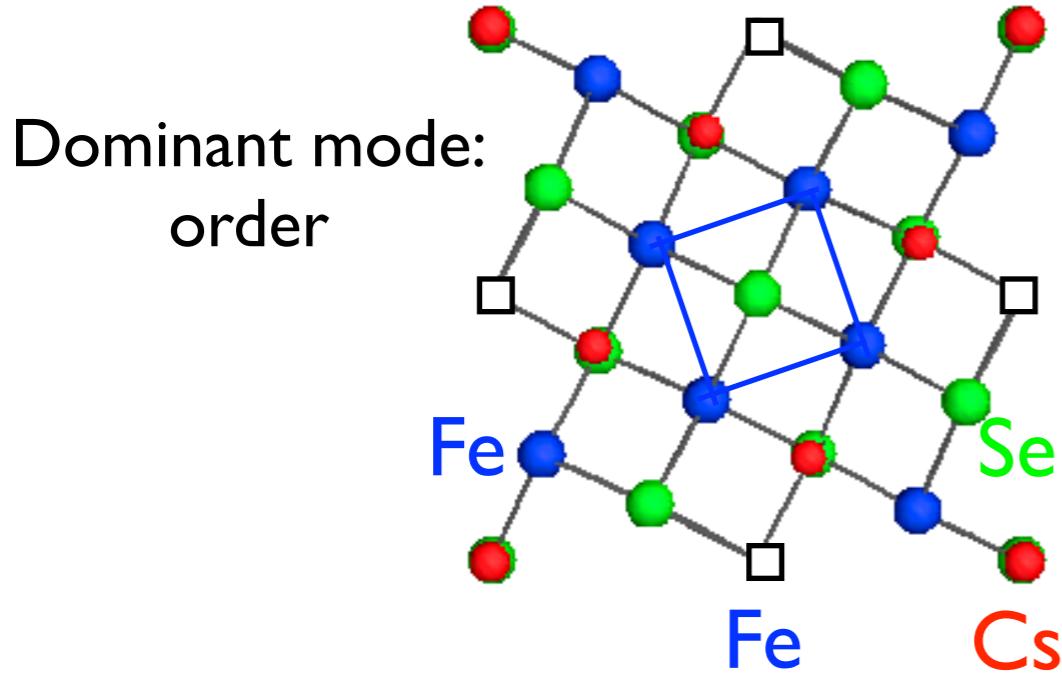


$$\text{Cs}_8\text{Fe}_{16}\text{Se}_{20} = \text{Cs}_2\text{Fe}_4\text{Se}_5 = \text{Cs}_{0.8}\text{Fe}_{1.6}\text{Se}_2 \quad \text{real: } A_y\text{Fe}_x\text{Se}_2$$

y=0.7-0.85, x=1.60-1.75

10 independent distortion modes: 2 order + 8 displacive

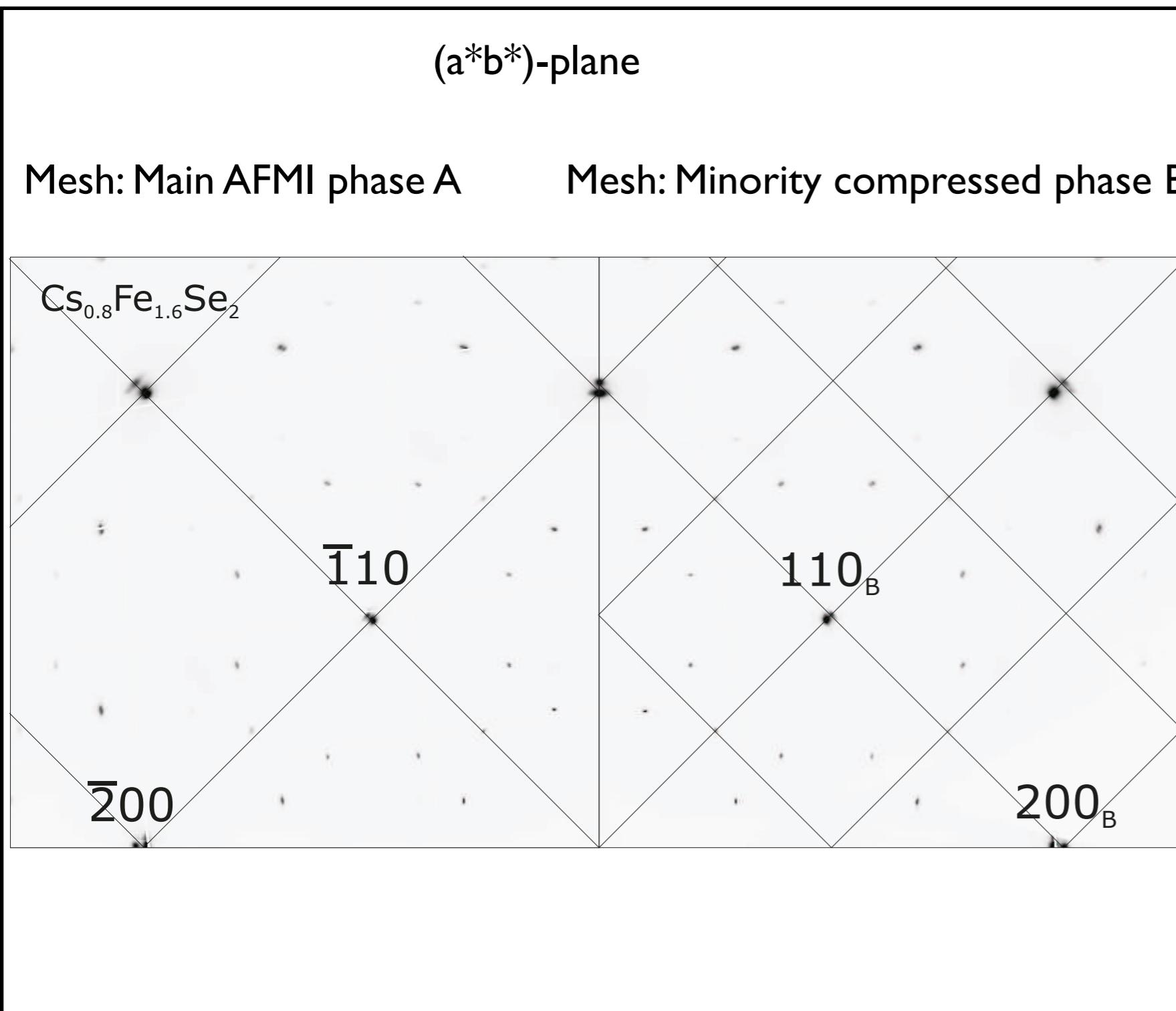
Example: distortions for Fe in (ab) plane



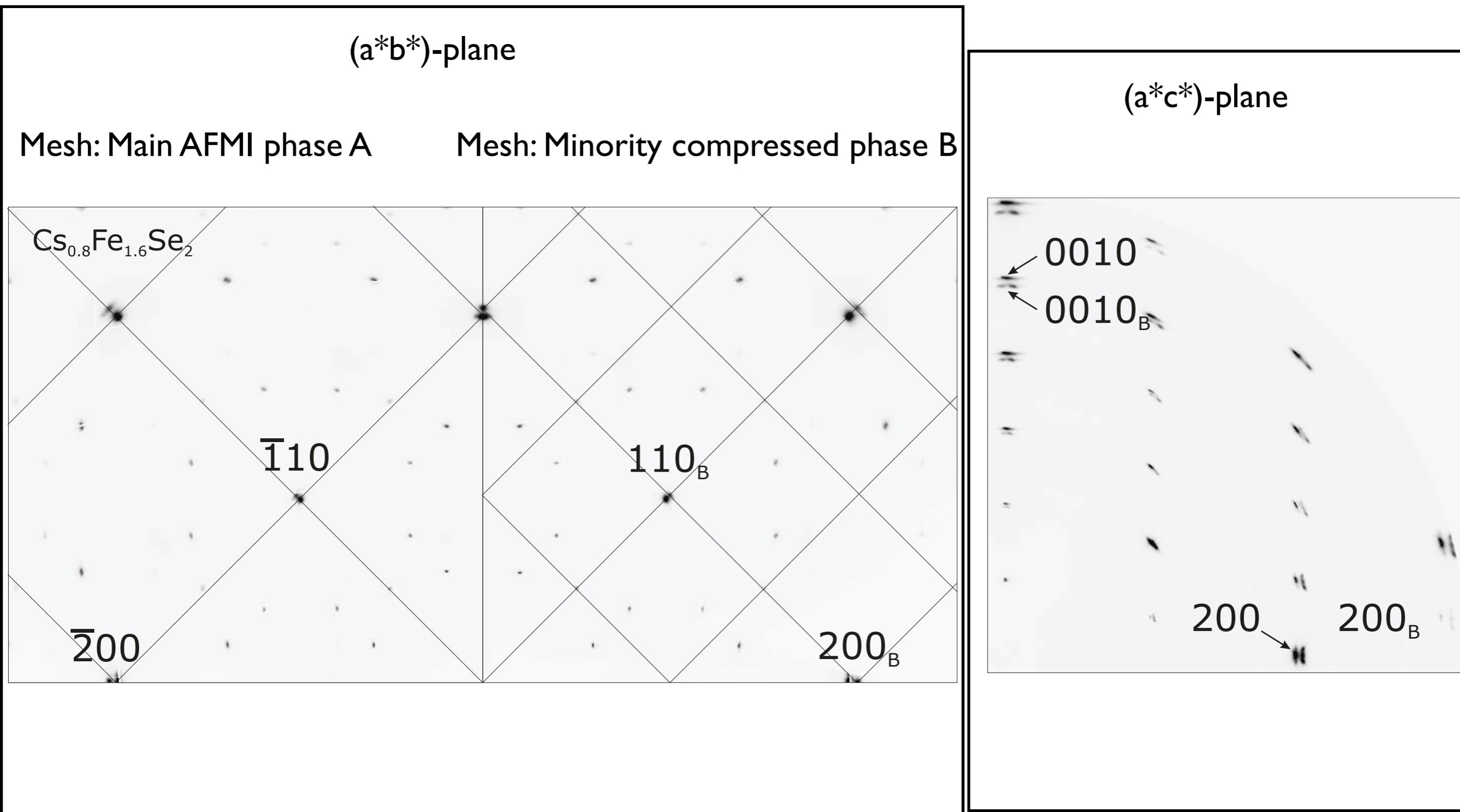
Fe displacements exaggerated for better visibility
 Calculated by ISODISTORT stokes.byu.edu/isotropy.html

**A diffraction view on phase separation:
II. Second minority (10%) phase (B) or (MCP)**

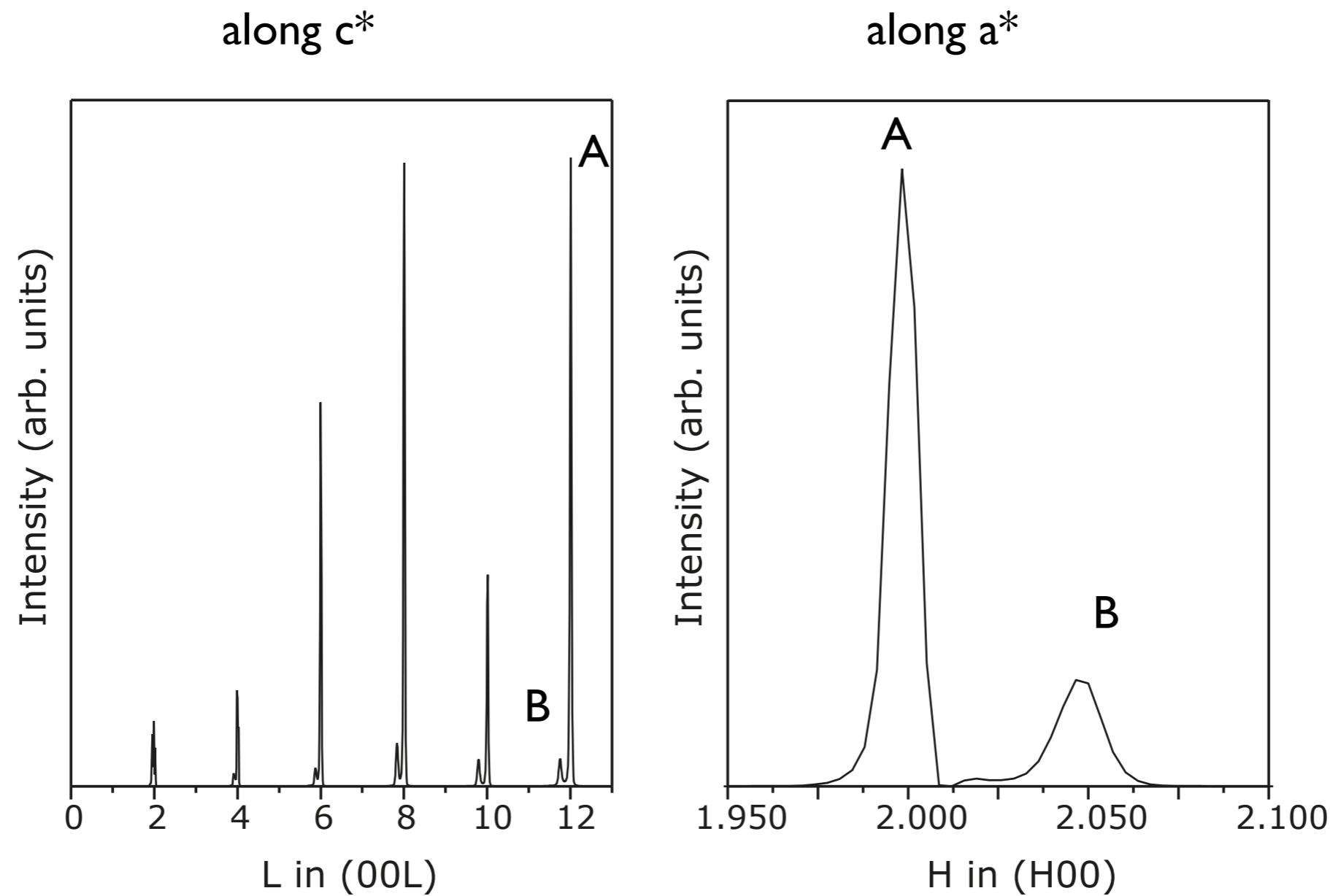
High resolution synchrotron x-ray, Slices of reciprocal space



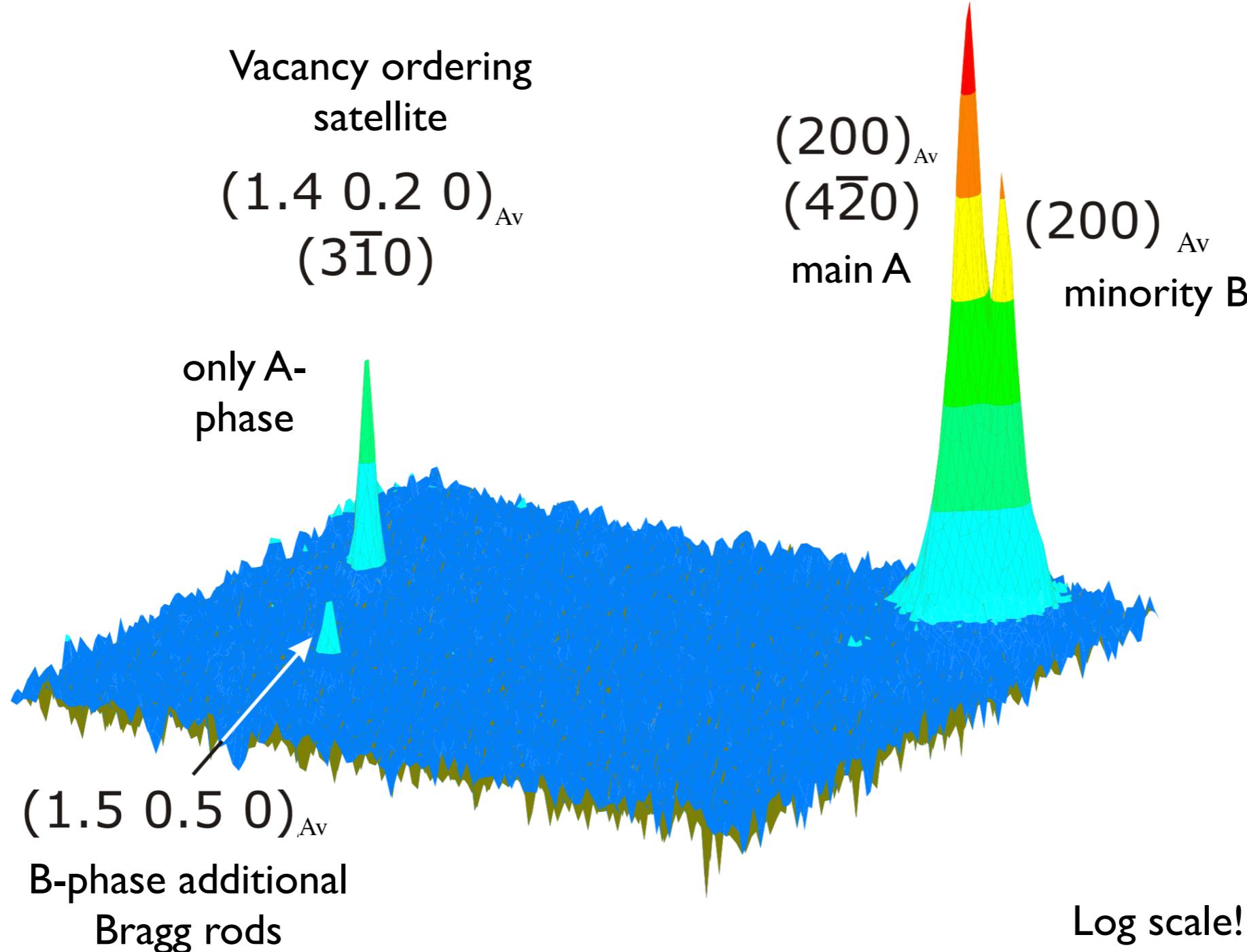
High resolution synchrotron x-ray, Slices of reciprocal space



Some projections



No vacancy ordered satellites from the second phase



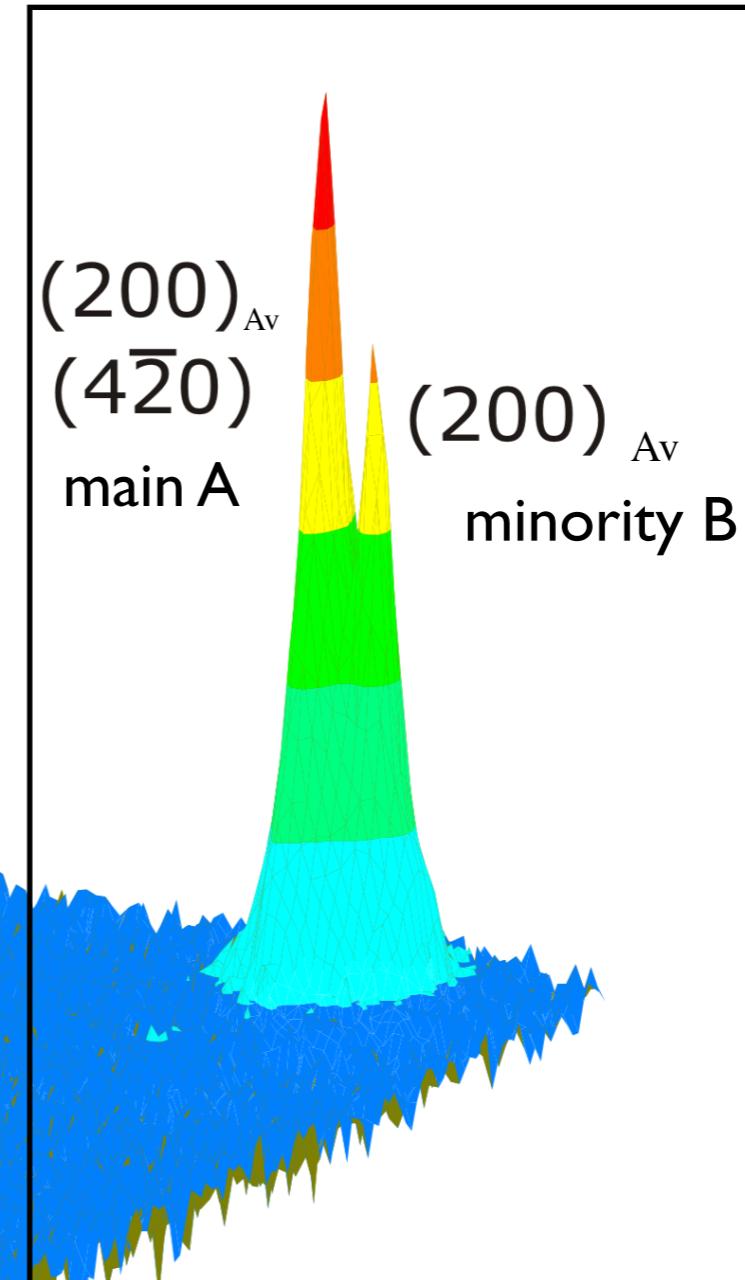
No vacancy ordered satellites from the second phase

Vacancy ordering satellite
 $(1.4 \ 0.2 \ 0)_{Av}$
 $(3\bar{1}0)$

only A-phase

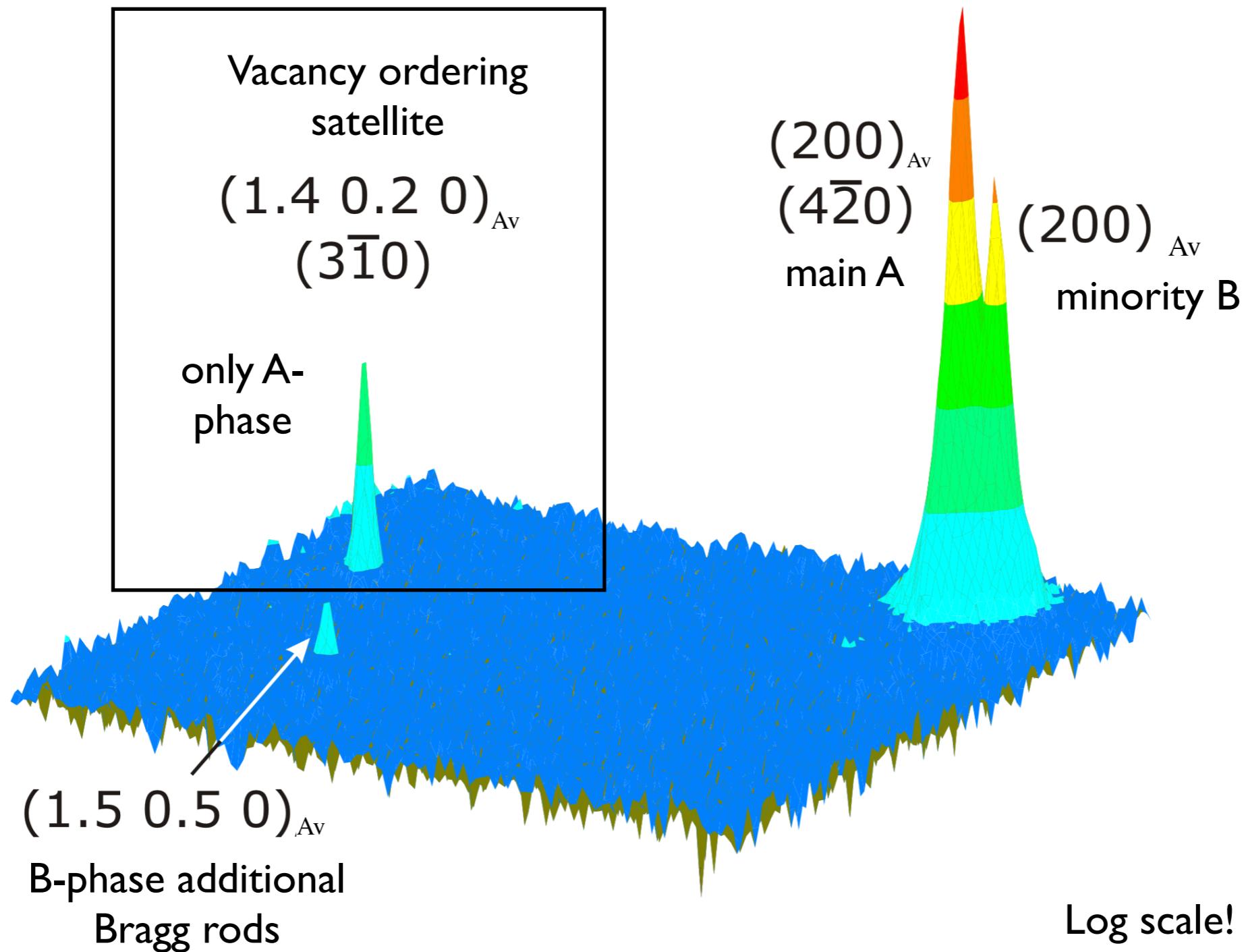
$(1.5 \ 0.5 \ 0)_{Av}$

B-phase additional Bragg rods

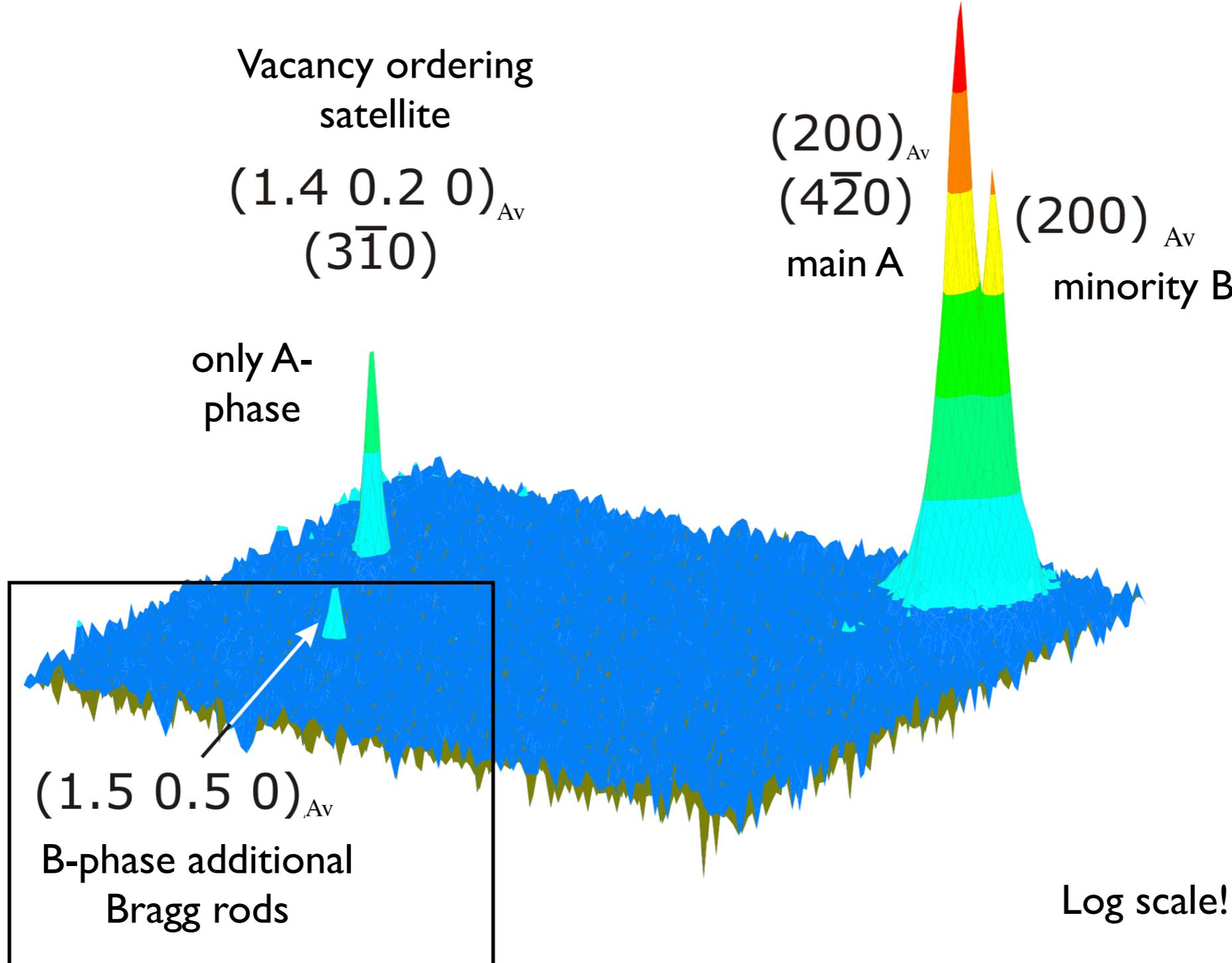


Log scale!

No vacancy ordered satellites from the second phase



No vacancy ordered satellites from the second phase

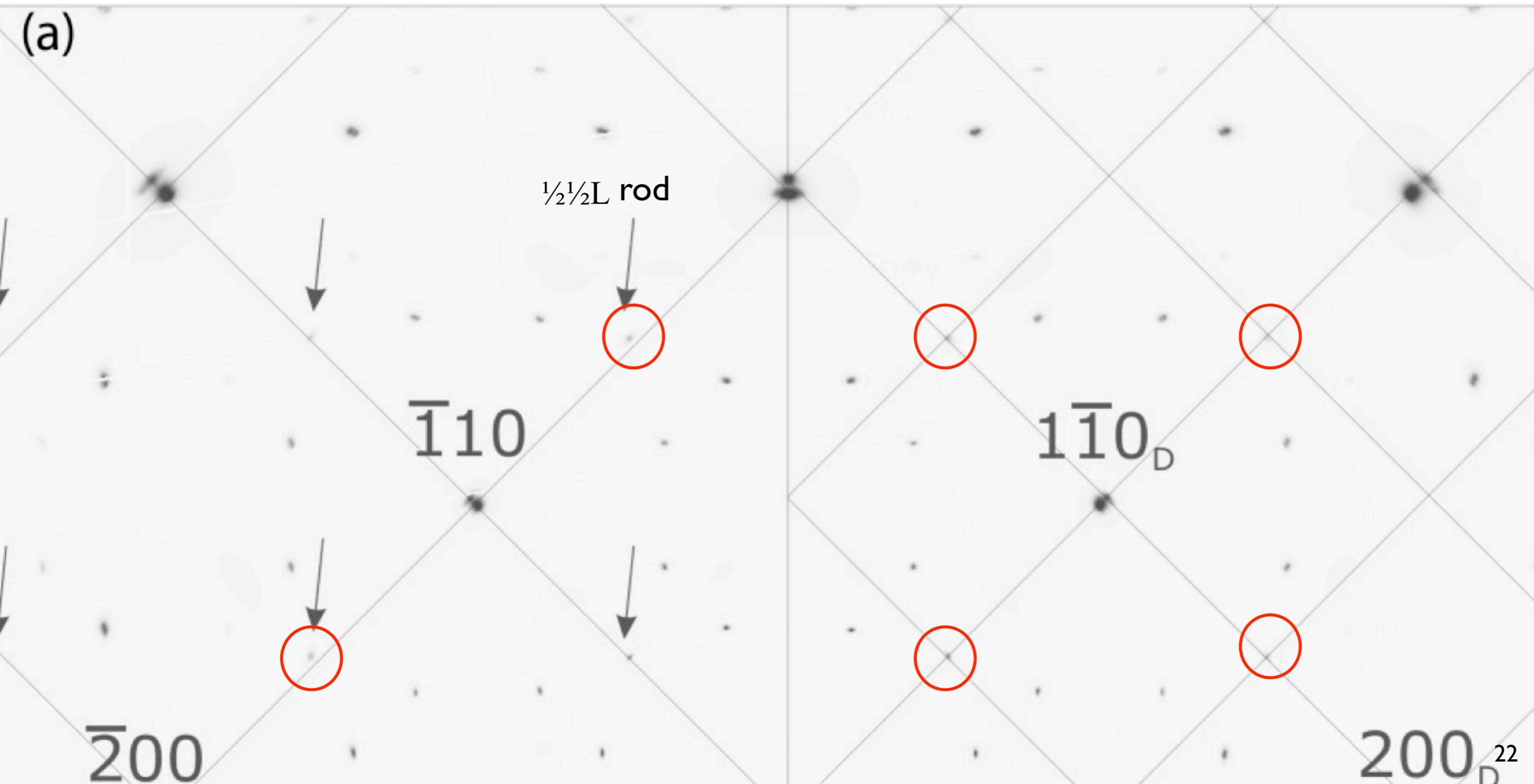


$(1/2, 1/2, L)$ rods from phase (B)

(a^*b^*) -plane

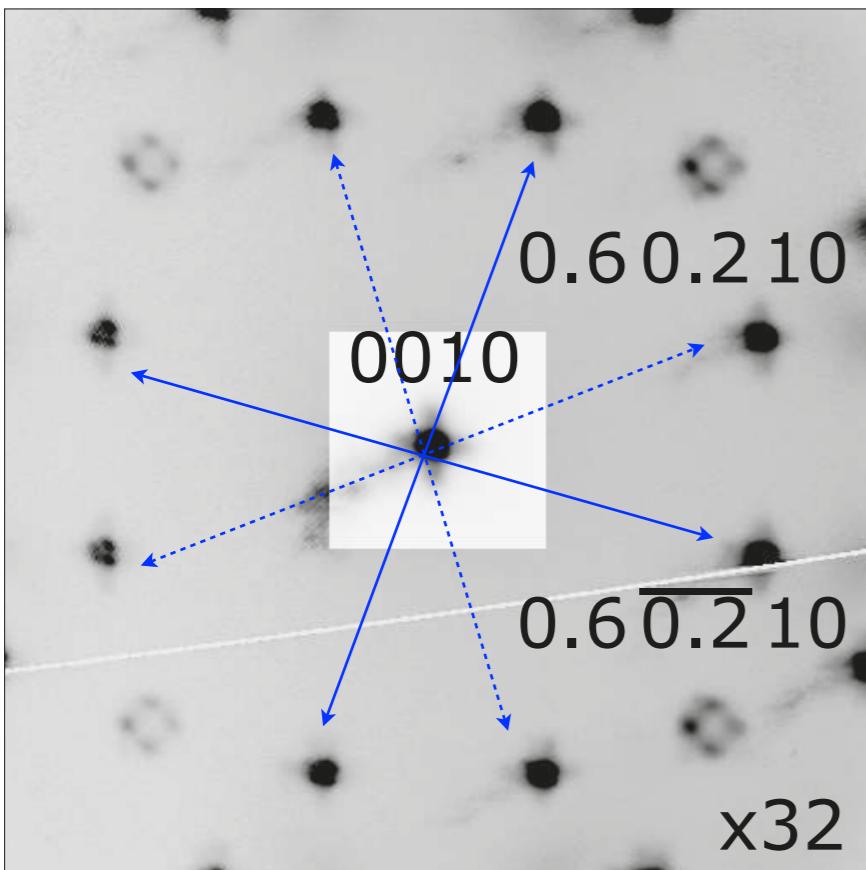
Mesh: Main AFMI phase A

Mesh: Minority compressed phase B

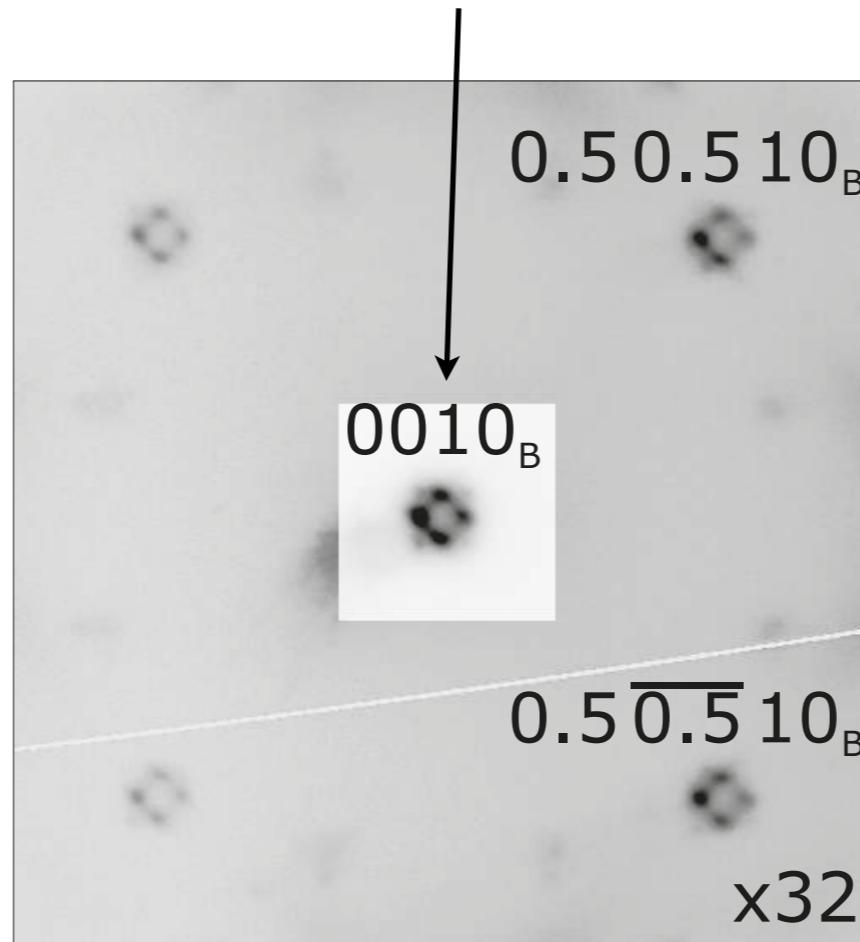


A specific four fold twinning of minority phase B

AFM phase A: I4/m with two twins in ab-plane



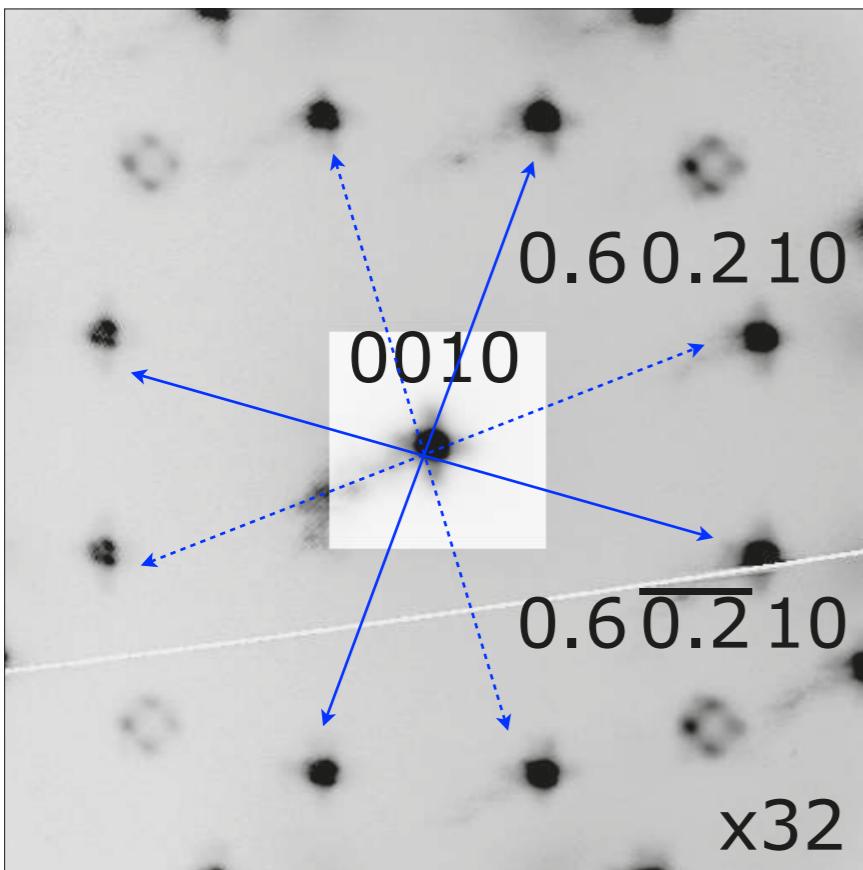
Minority phase B: four 100 rotational twins



(h, k, 10)-plane: best resolution

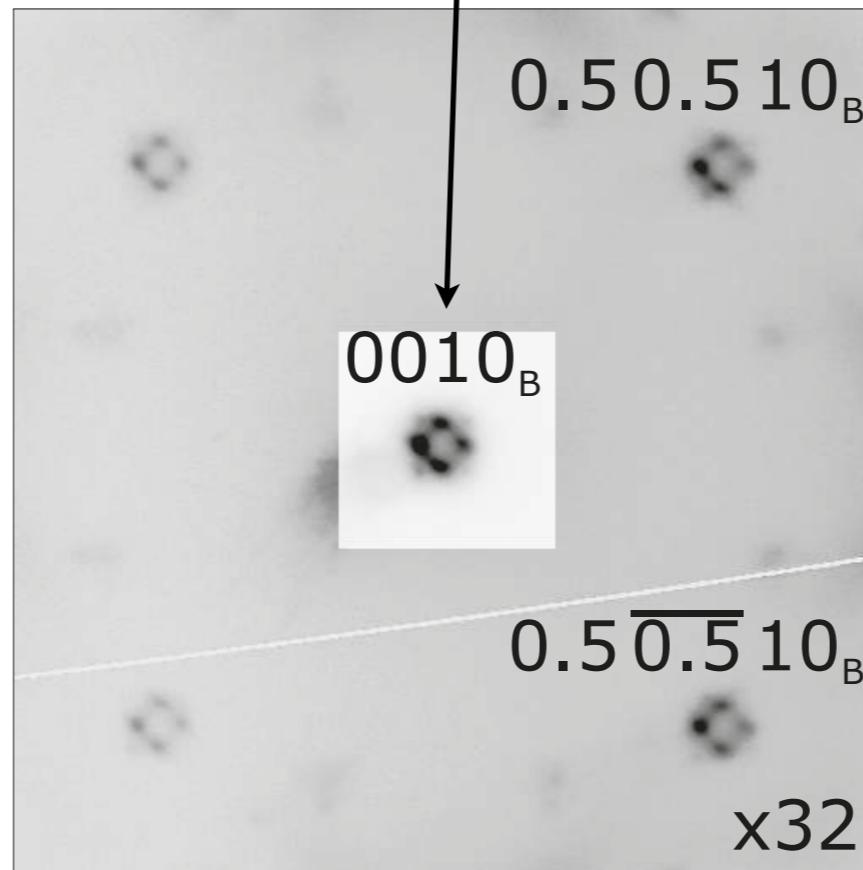
A specific four fold twinning of minority phase B

AFM phase A: I4/m with two twins in ab-plane

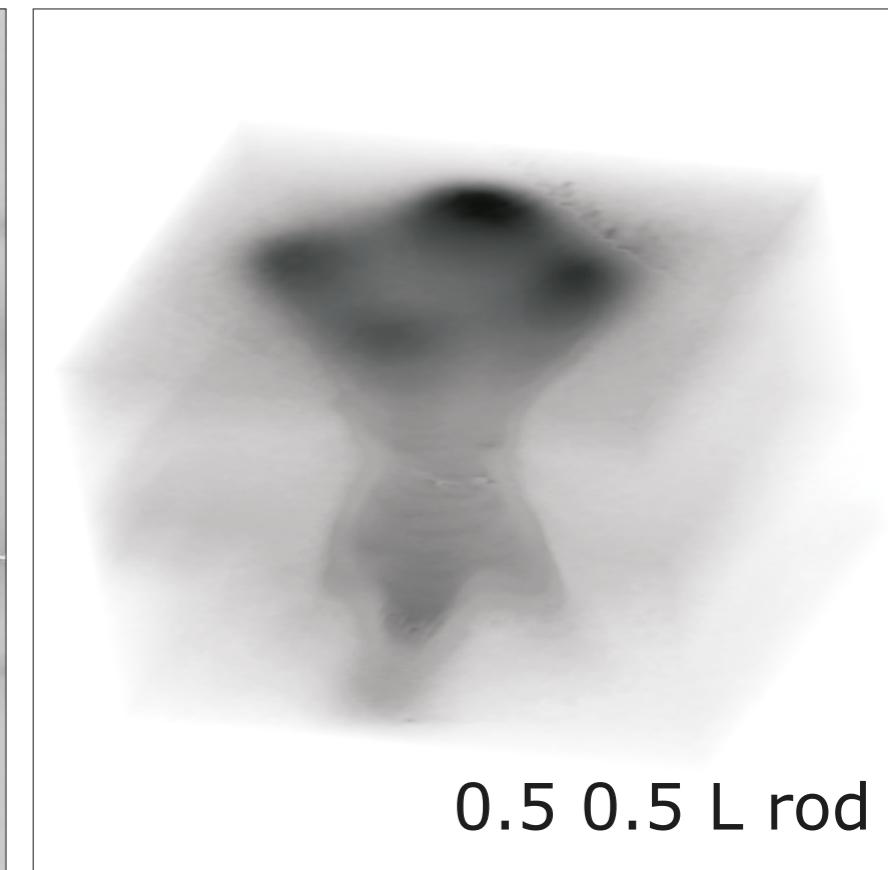


($h, k, 10$)-plane: best resolution

Minority phase B: four 100 rotational twins

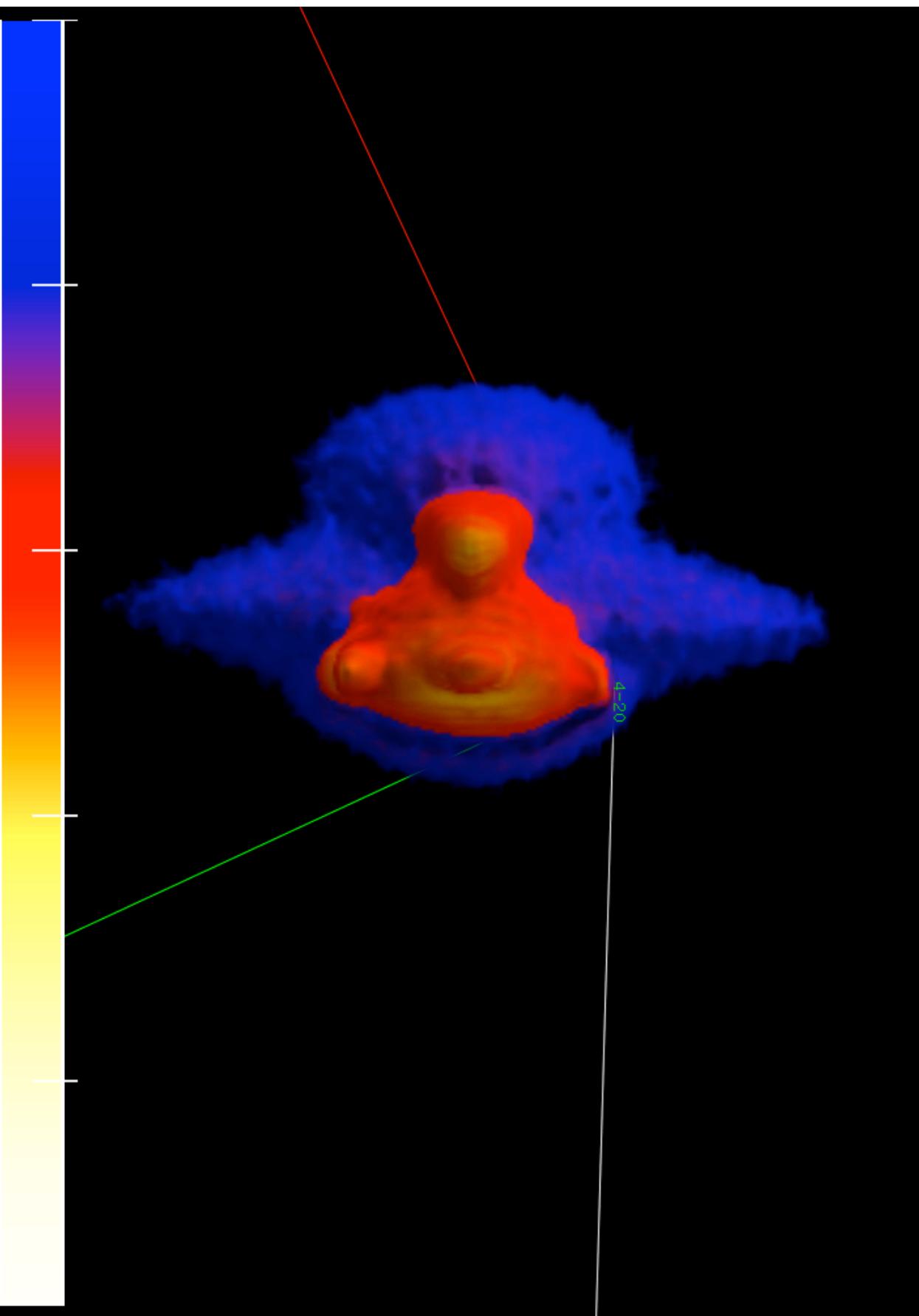


Diffraction rods of minority phase B. Also four twins! Log scale

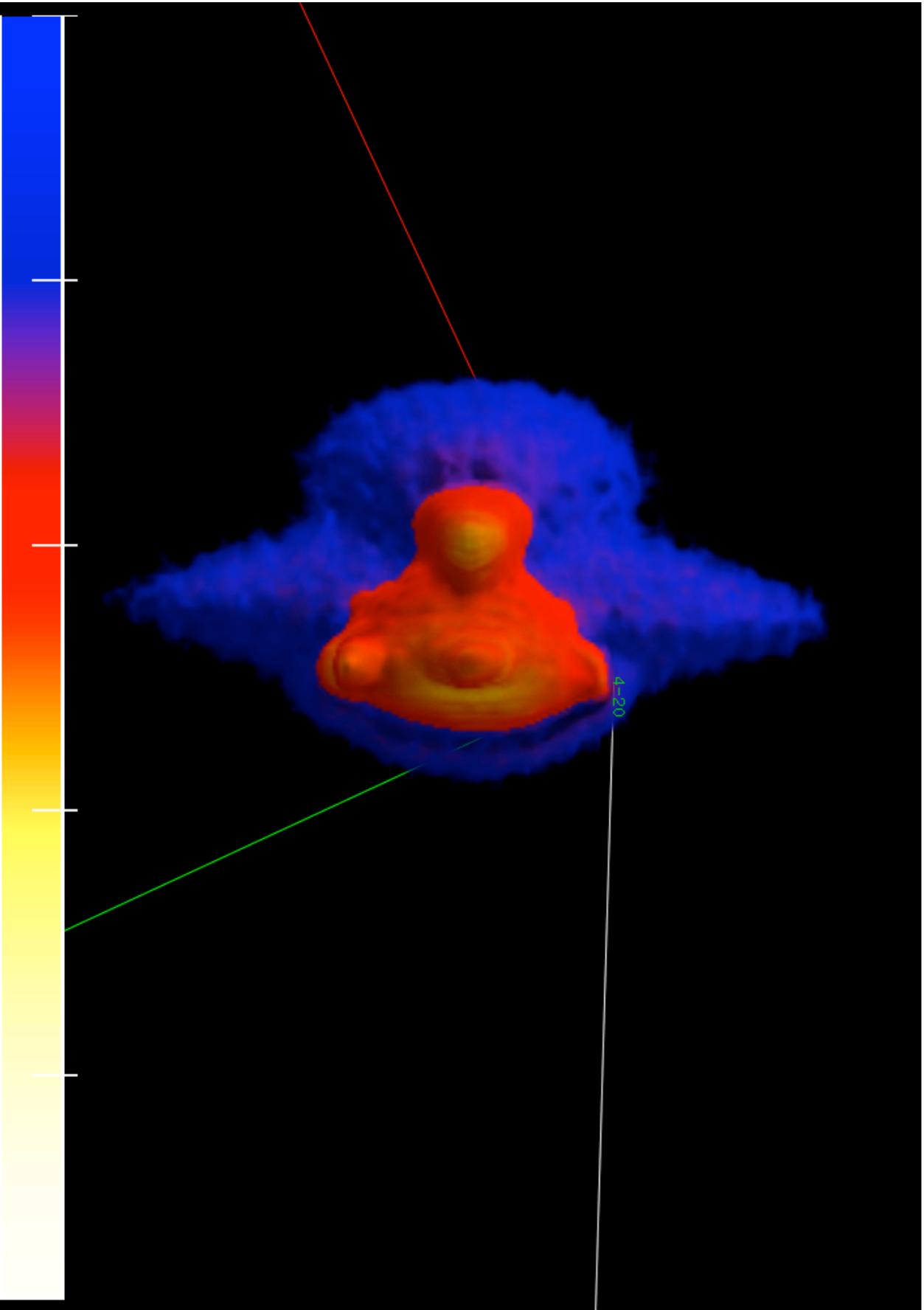


Origin: in plane 2D ordering of alkali-earth in $A_yFe_xSe_2$

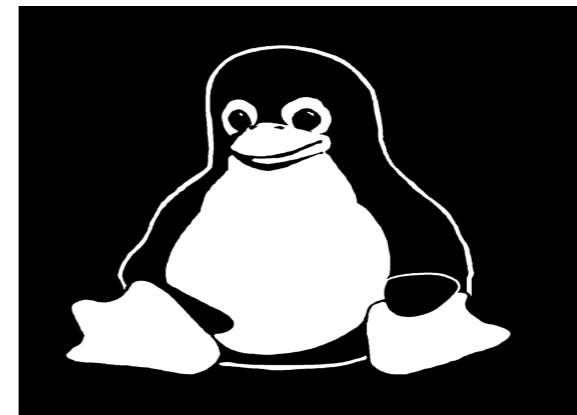
twinning of minority phase B



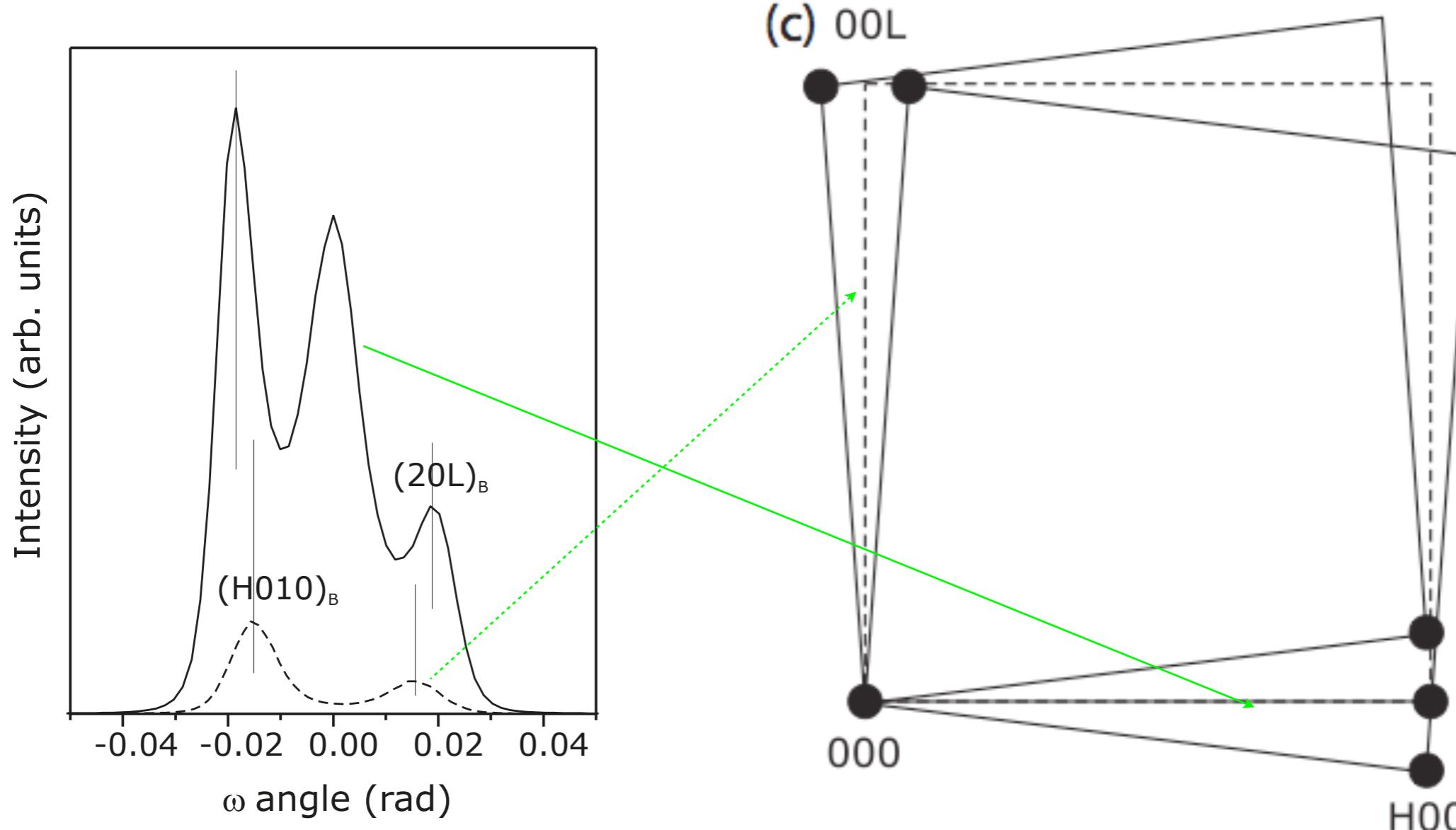
twinning of minority phase B



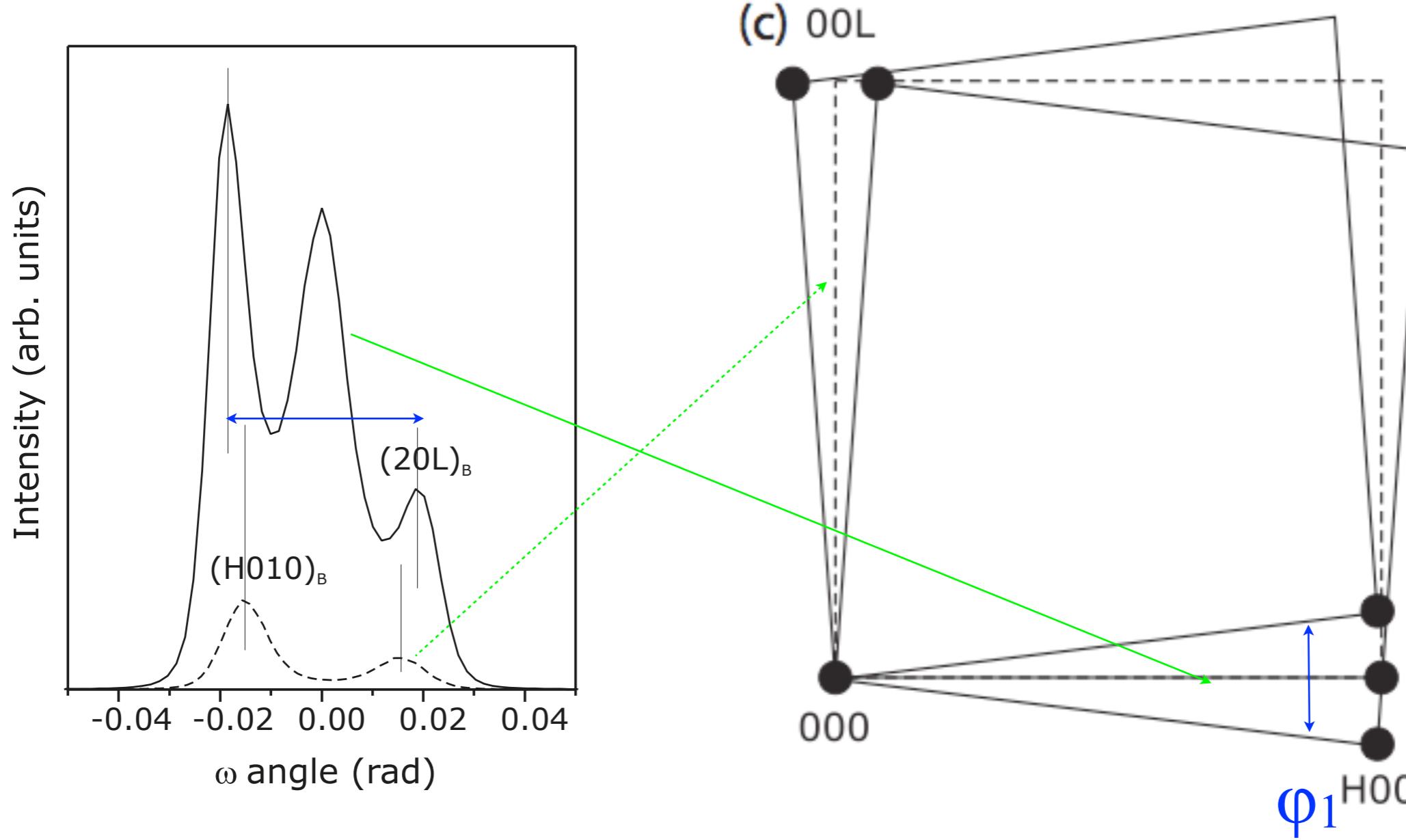
Looks like a penguin



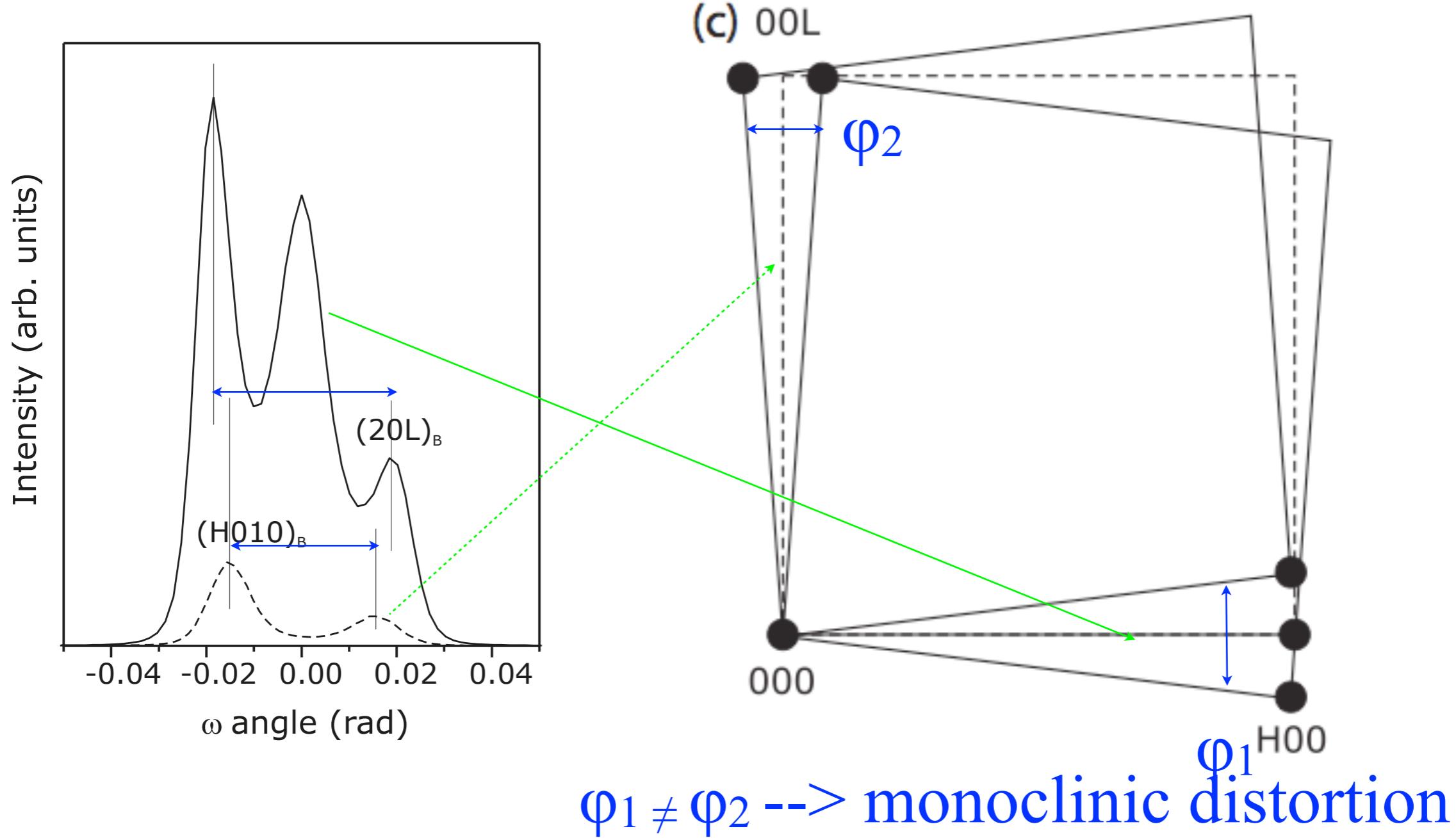
100 rotational twinning for the phase B



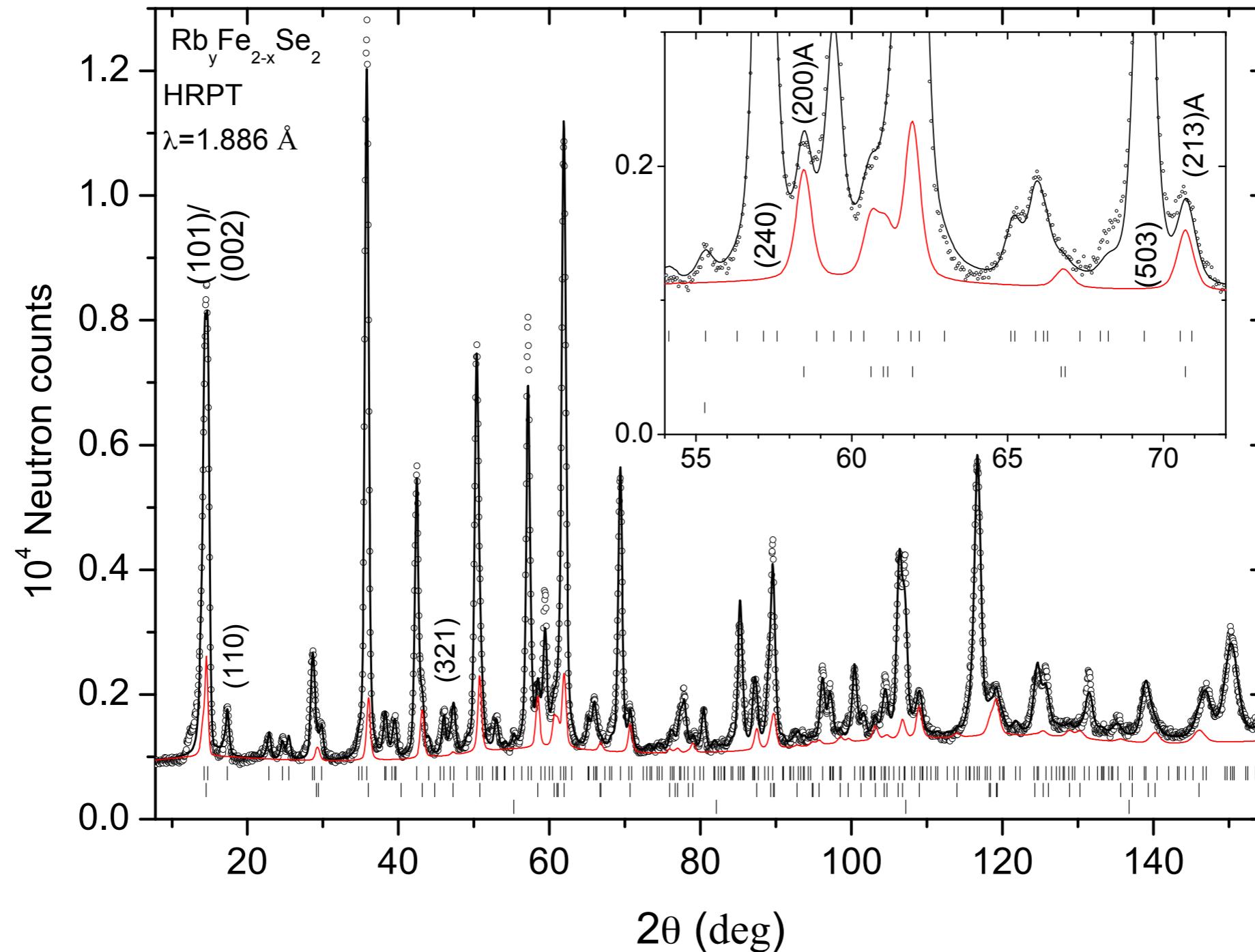
100 rotational twinning for the phase B



100 rotational twinning for the phase B



Powder neutron diffraction. Minority phase is shown by red line.



Structure model for minority compressed phase B.

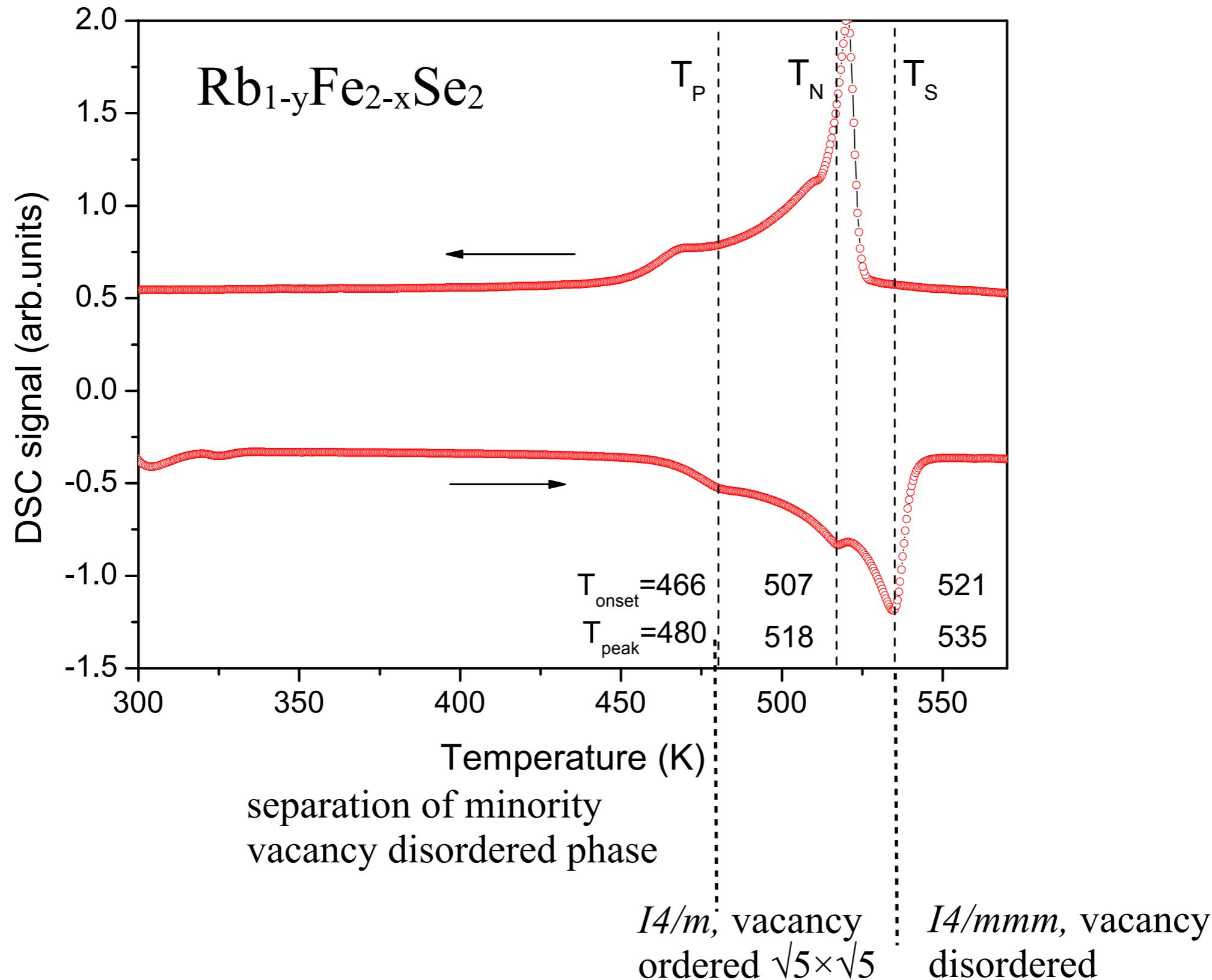
parent average vacancy disordered structure (*I*4/*mmm* space group)* with the refined stoichiometry $\text{Rb}_{0.60(5)}(\text{Fe}_{1.10(5)}\text{Se})_2$.

The minority phase amounts to 8–10% mass fraction.

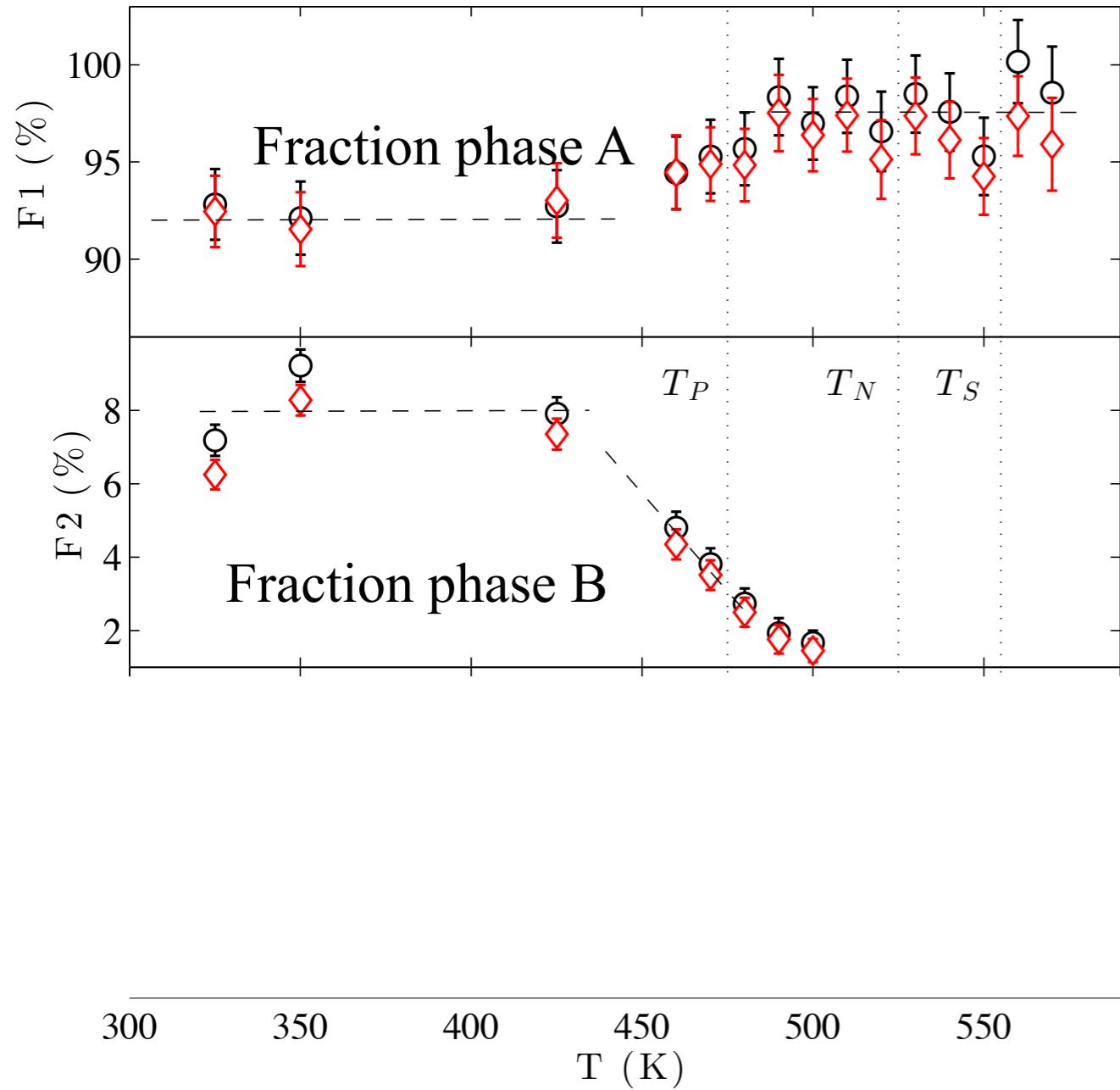
The unit cell volume of the minority phase is 3.2% smaller.

* we can not afford a better model for 10% of phase & powder diffraction data

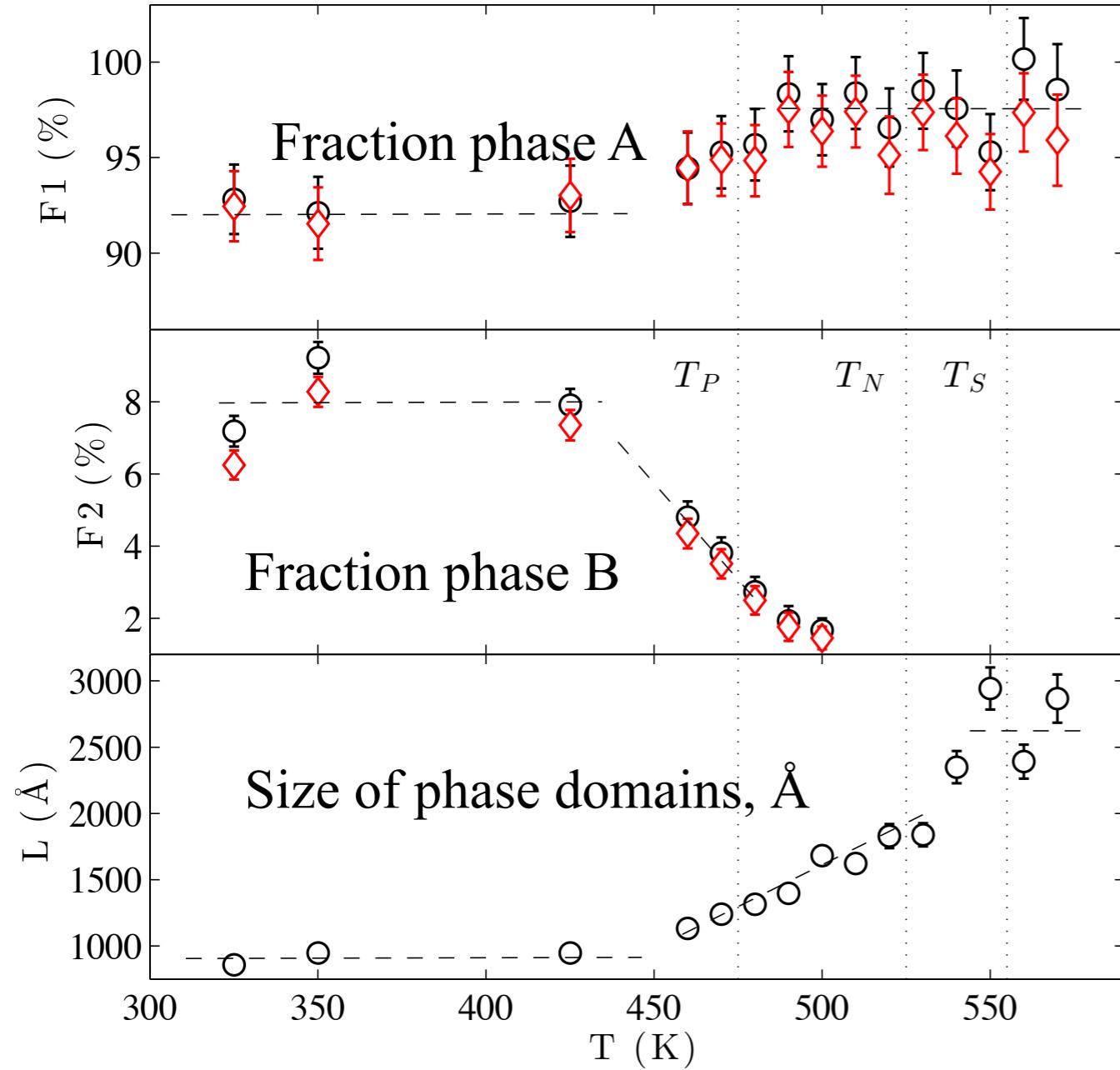
Differential scanning calorimetry



T-dependence of structure

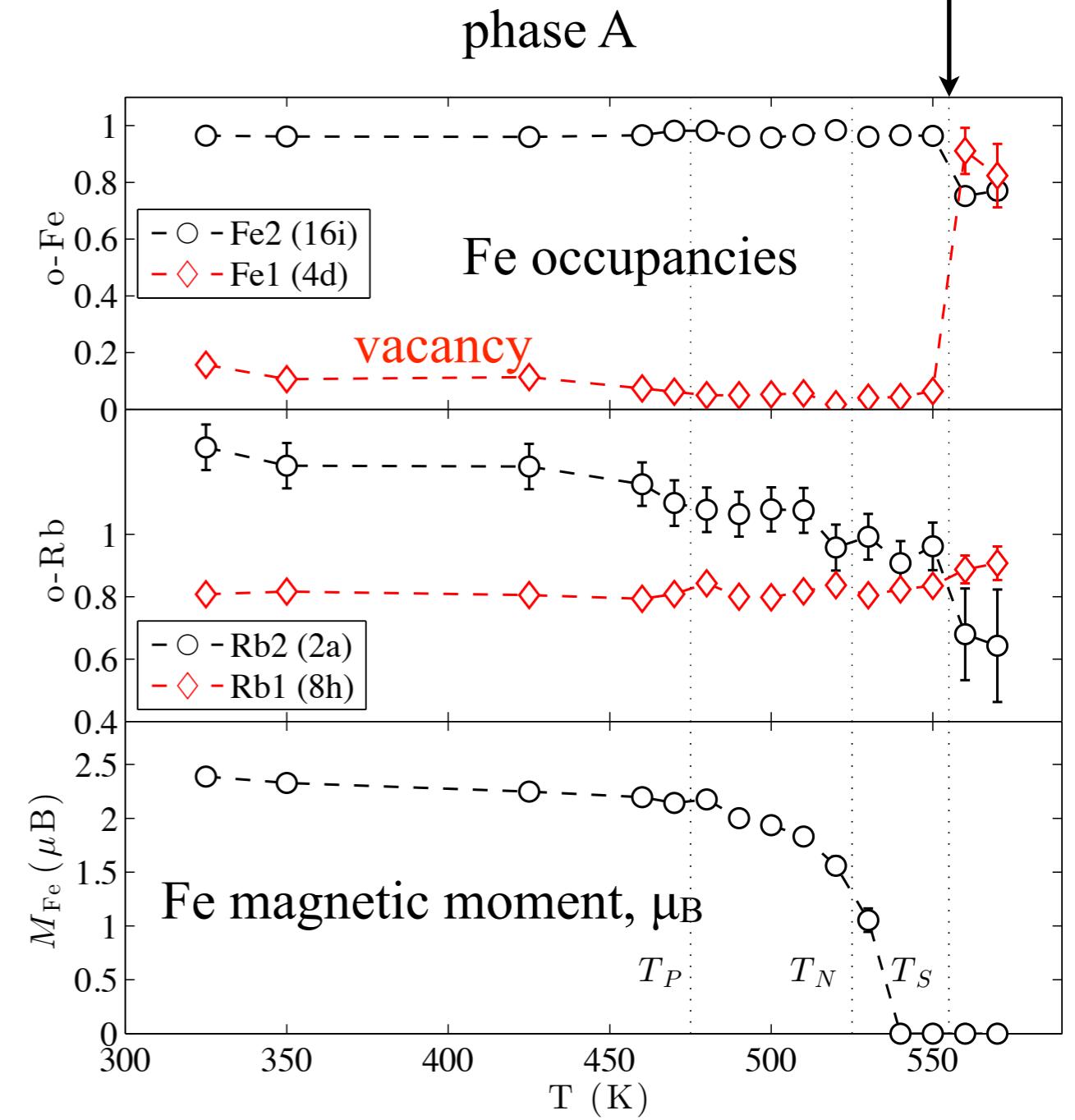
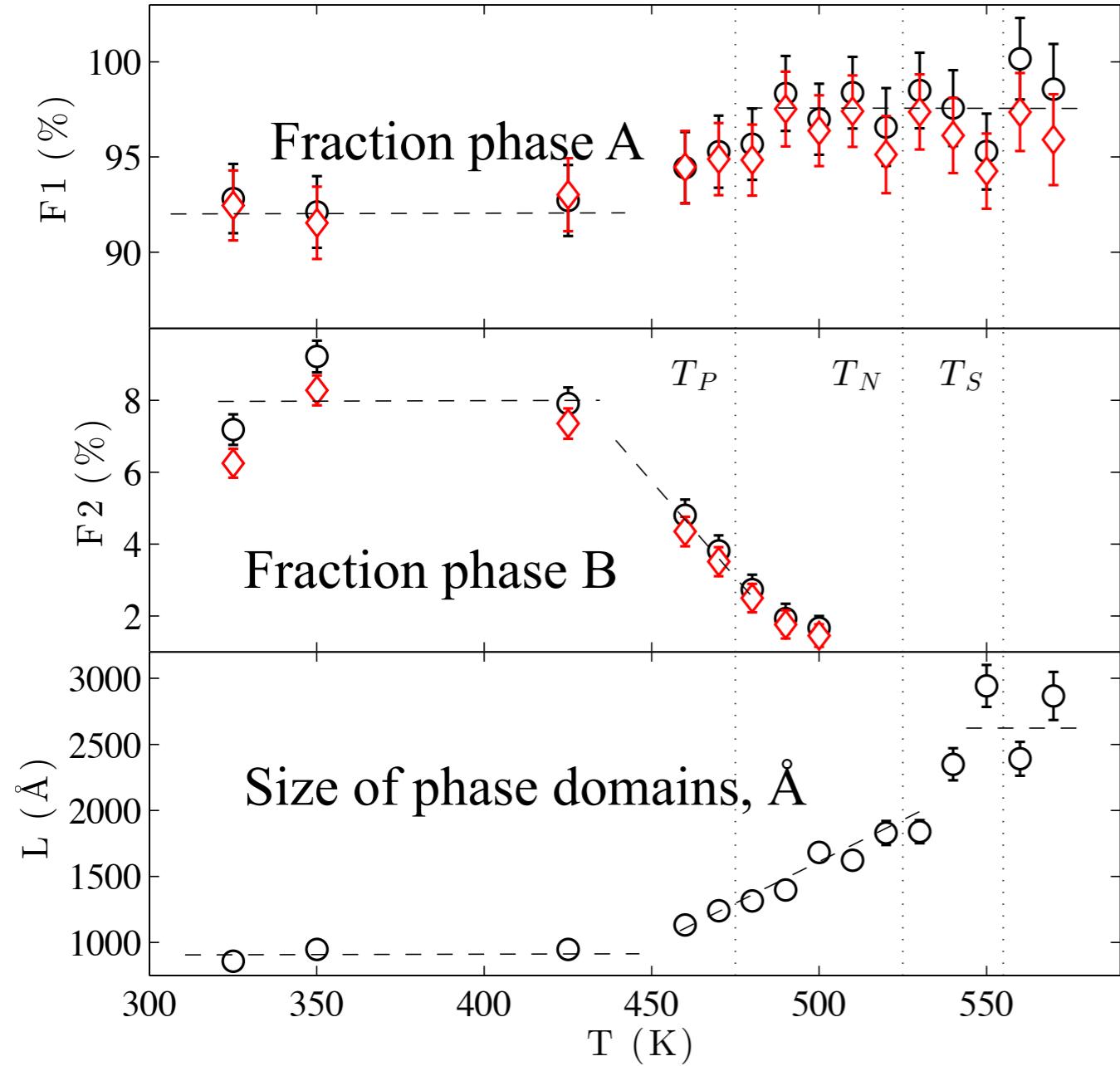


T-dependence of structure



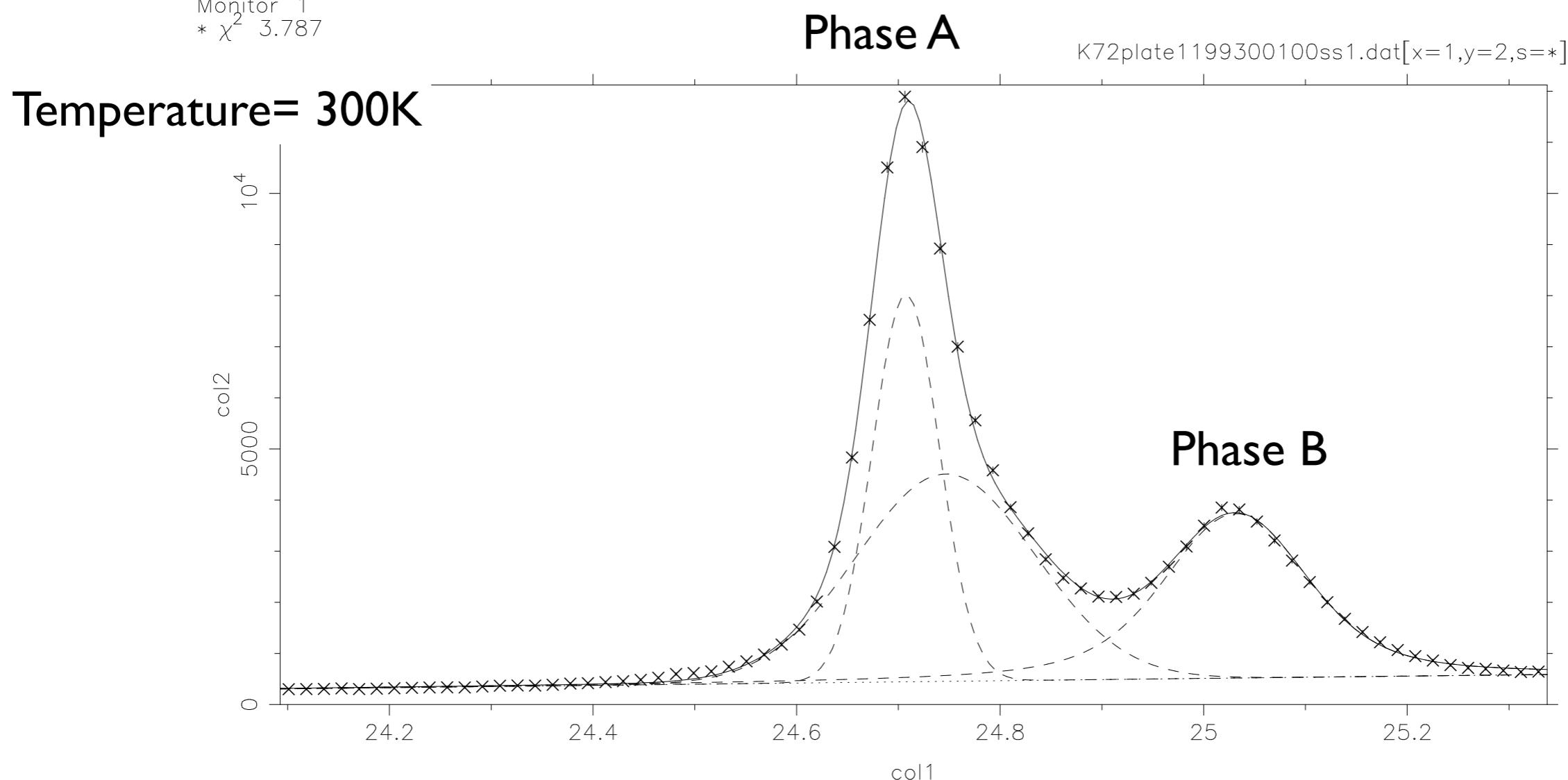
T-dependence of structure

$I4/m \rightarrow I4/mmm$



T dependence of phase separation. Single crystal synchrotron

Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.70748 ± 0.00058	7583.4	623.0 ± 6.8	0.0772 ± 9E-4	0.0000
24.74645 ± 0.00074	4057.9	892.5 ± 7.9	0.2066 ± 0.0013	0.0000
25.03181 ± 0.00082	3217.1	691.4 ± 5.4	0.1209 ± 0.0022	0.0775 ± 0.0019
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
2172.2 ± 6.9	444.8 ± 4.9	227 ± 13		
Monitor 1 * χ^2 3.787				

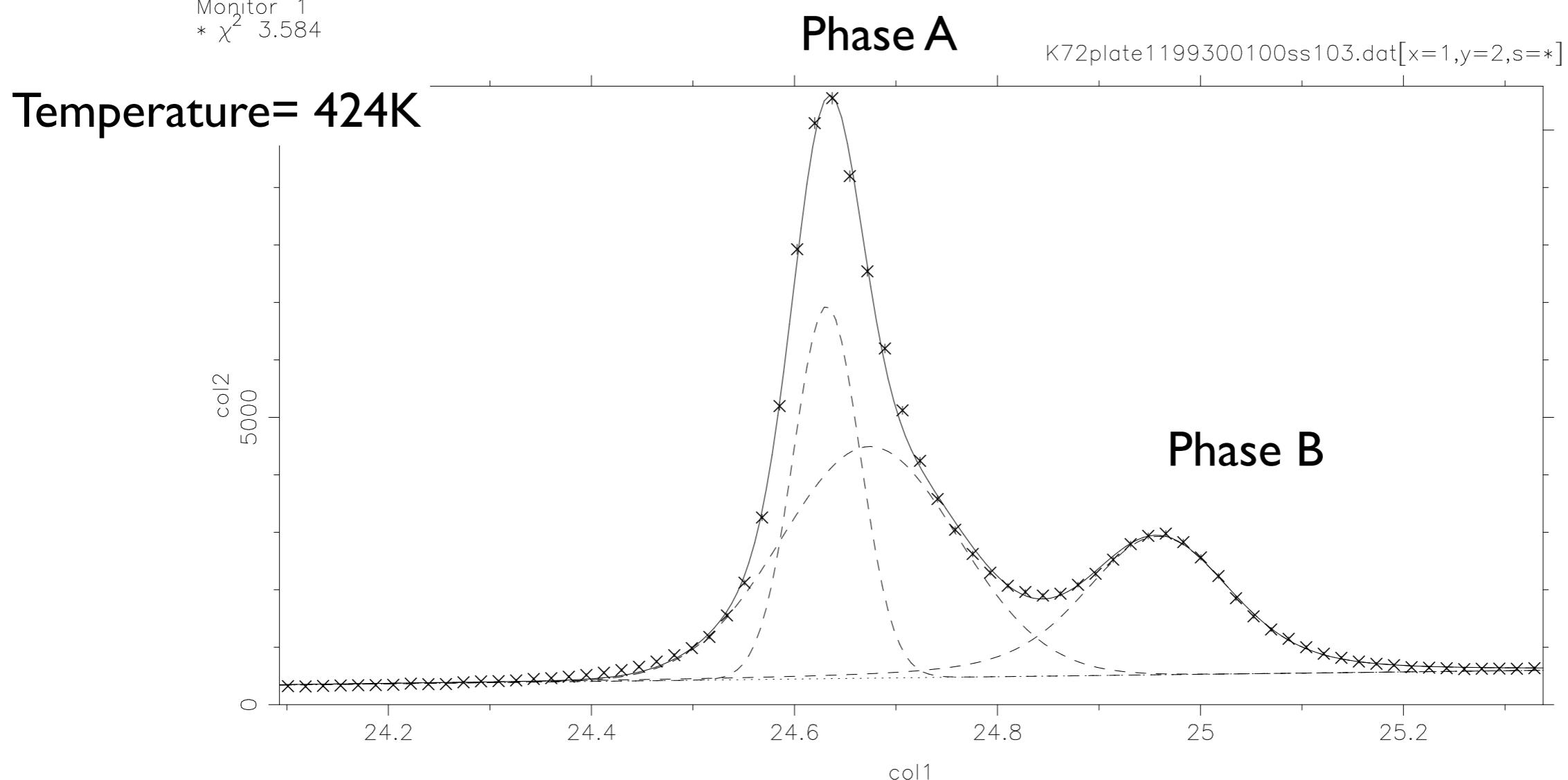


T dependence of phase separation. Single crystal synchrotron

Position	Max.Intensity
24.6318 ± 3E-4	6484.5
24.6738 ± 7E-4	4031.3
24.9578 ± 0.0011	2410.1
Int.Intens.Exp.	Bg(Pos)
1904.7 ± 6.6	452.3 ± 4.6
Monitor 1	
* χ^2 3.584	

Int.Intensity	fwhm (Gaussian)
531.8 ± 4.9	0.0770 ± 7E-4
876.6 ± 8.5	0.2043 ± 0.0019
514.3 ± 6.0	0.1304 ± 0.0021
dBg/dx	
207 ± 11	

fwhm (Lorentzian)
0.0000
0.0000
0.0681 ± 0.0022



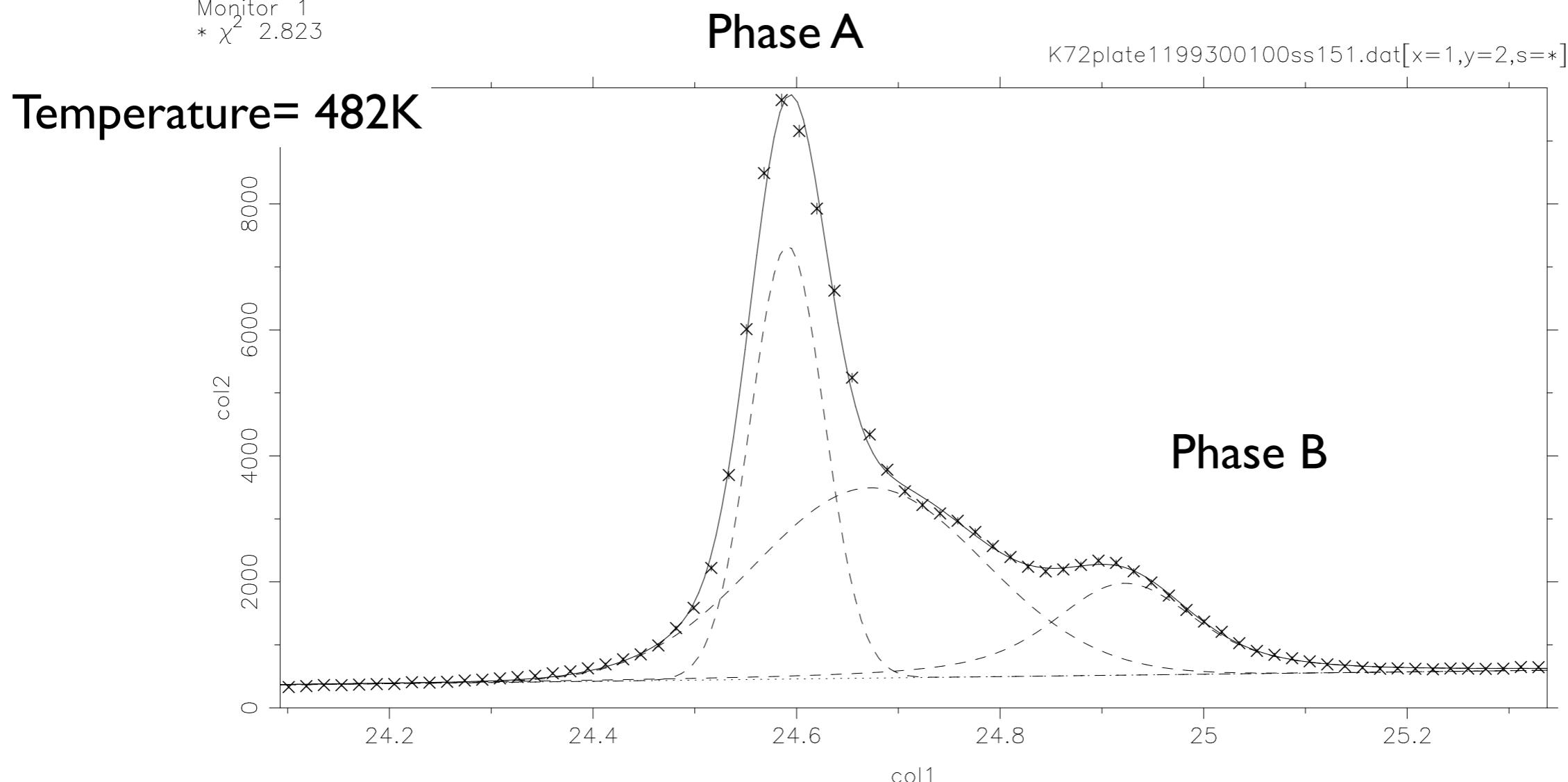
T dependence of phase separation. Single crystal synchrotron

Position	Max.Intensity
24.5912 ± 3E-4	6878.6
24.6719 ± 9E-4	3020.6
24.9224 ± 0.0013	1458.4
Int.Intens.Exp.	Bg(Pos)
1783.8 ± 6.4	457.3 ± 4.2

Monitor 1
* χ^2 2.823

Int.Intensity	fwhm (Gaussian)
622.7 ± 5.2	0.0850 ± 5E-4
850.5 ± 5.7	0.2645 ± 0.0018
326.1 ± 4.6	0.1056 ± 0.0052
dBg/dx	
187.4 ± 7.9	

fwhm (Lorentzian)
0.0000
0.0000
0.0966 ± 0.0024

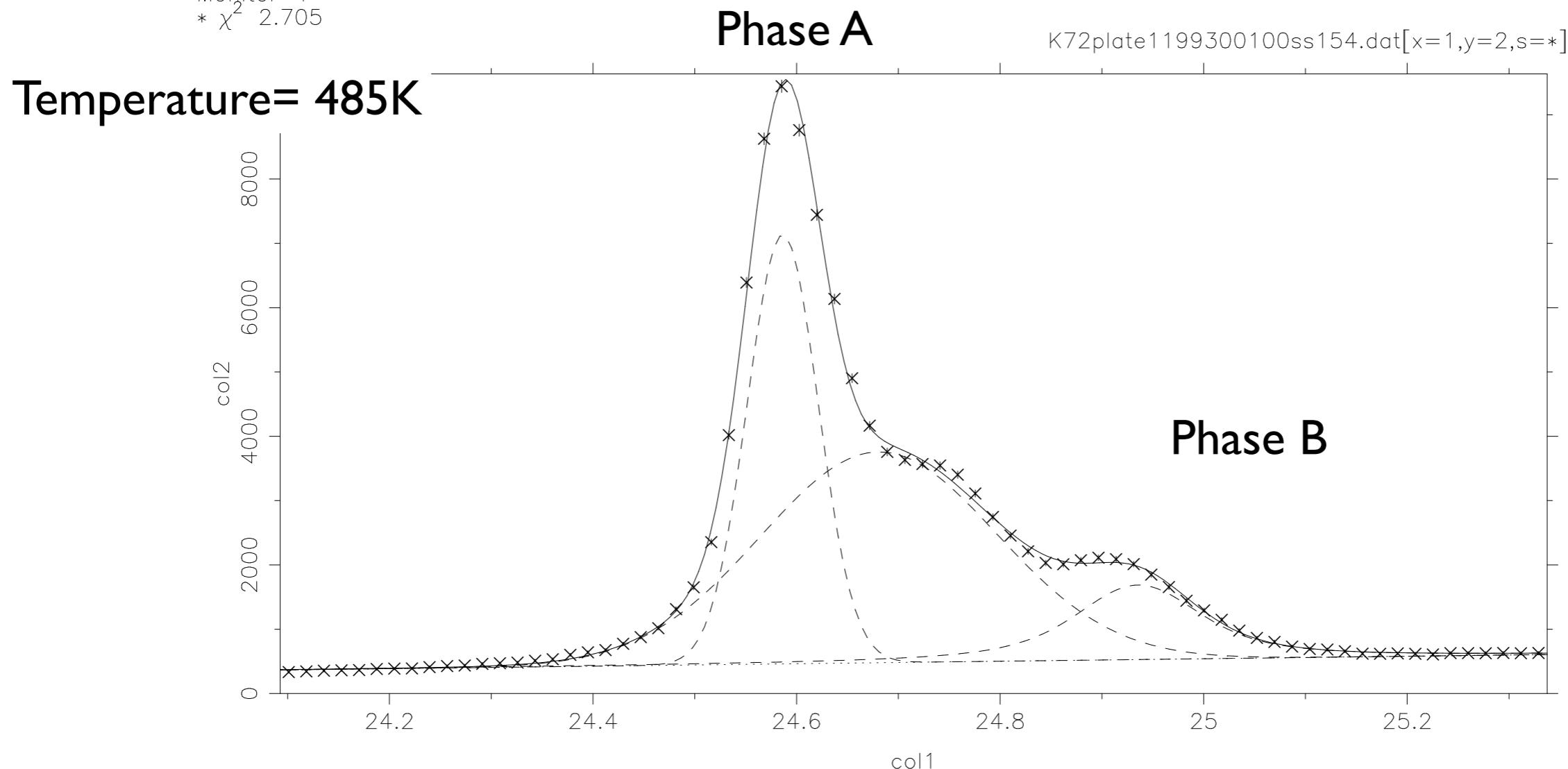


T dependence of phase separation. Single crystal synchrotron

Position	Max.Intensity
24.5864 ± 3E-4	6672.6
24.6804 ± 9E-4	3277.4
24.9355 ± 0.0019	1158.4
Int.Intens.Exp.	Bg(Pos)
1761.8 ± 6.4	461.0 ± 4.1
Monitor 1	
* χ^2 2.705	

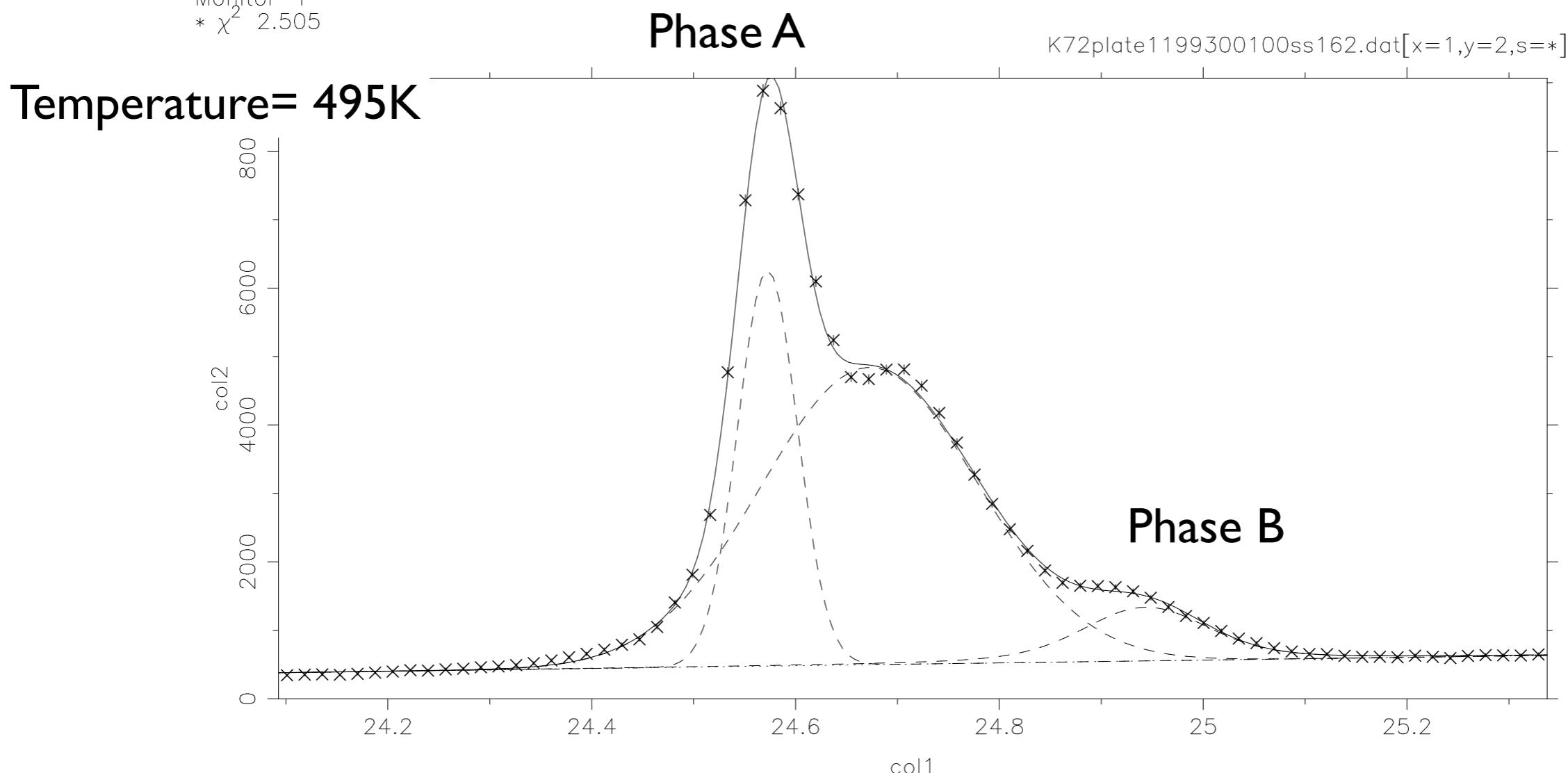
Int.Intensity	fwhm (Gaussian)
583.8 ± 5.0	0.0822 ± 6E-4
951.9 ± 6.3	0.2729 ± 0.0020
236.4 ± 4.3	0.0849 ± 0.0061
dBg/dx	
193.0 ± 10.6	

fwhm (Lorentzian)
0.0000
0.0000
0.0964 ± 0.0033



T dependence of phase separation. Single crystal synchrotron

Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.5725 ± 3E-4	5779.1	424.1 ± 3.0	0.0689 ± 7E-4	0.0000
24.6725 ± 6E-4	4342.0	1155.3 ± 7.1	0.2500 ± 0.0015	0.0000
24.9435 ± 0.0026	783.3	142.7 ± 3.4	0.1150 ± 0.0041	0.0550 ± 0.0038
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1720.3 ± 6.4	477.7 ± 3.8	204.3 ± 8.9		
Monitor 1 * χ^2 2.505				



T dependence of phase separation. Single crystal synchrotron

Position
24.5641 ± 3E-4
24.6626 ± 5E-4
24.9347 ± 0.0030

Int.Intens.Exp.
1698.1 ± 6.4

Max.Intensity
4947.1
5014.5
618.6

Bg(Pos)
481.7 ± 3.4

Int.Intensity
323.6 ± 3.0
1262.1 ± 6.1
109.7 ± 3.2

dBg/dx
214.4 ± 7.5

fwhm (Gaussian)
0.0615 ± 6E-4

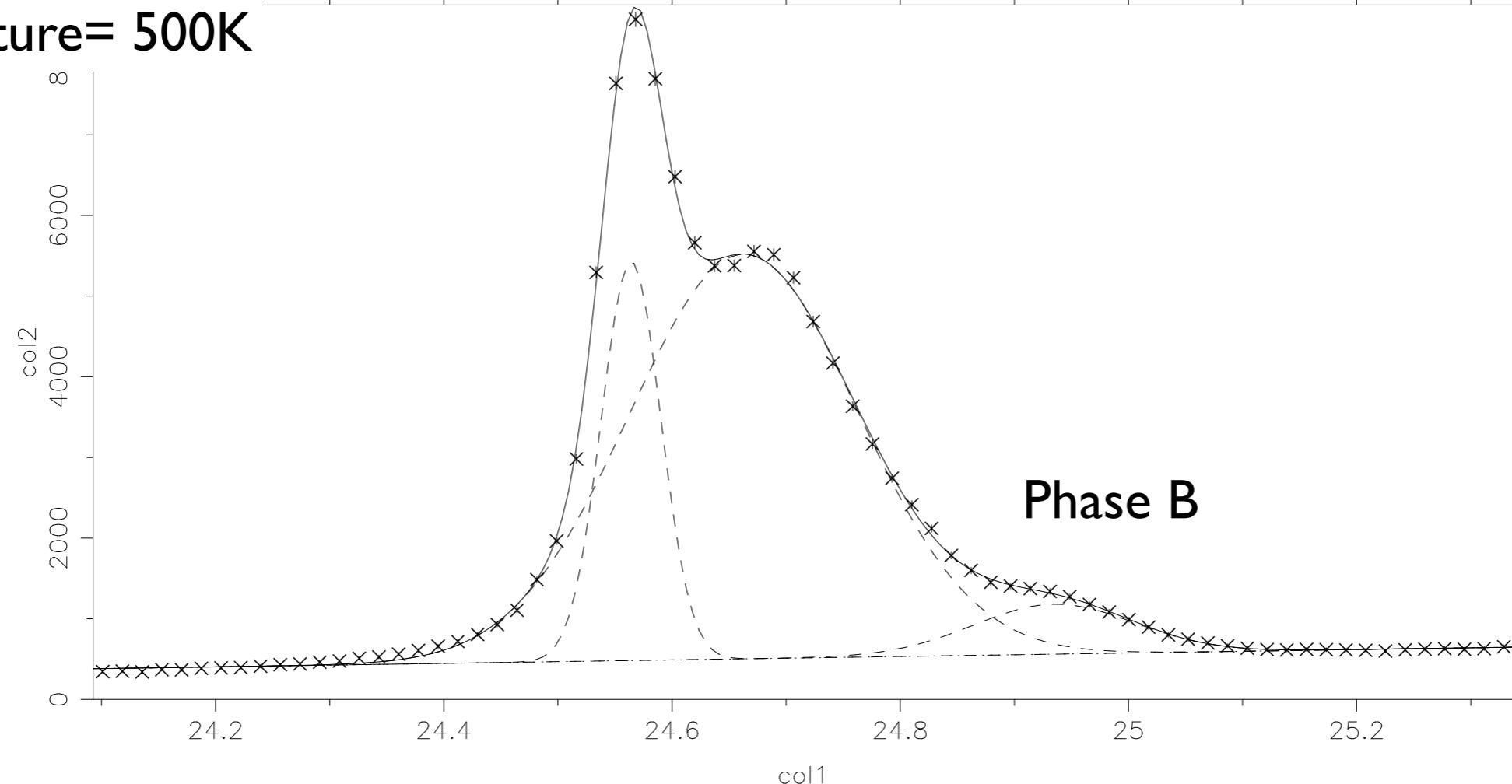
fwhm (Lorentzian)
0.000000
0.000000
0.001442 ± 0.005661

Monitor 1
* χ^2 2.091

Phase A

K72plate1199300100ss166.dat[x=1,y=2,s=**]

Temperature= 500K



T dependence of phase separation. Single crystal synchrotron

Position
24.5544 ± 6E-4
24.6483 ± 5E-4
24.8678 ± 0.0030
Int.Intens.Exp.
1673.2 ± 6.4

Max.Intensity
3711.7
5831.3
637.0
Bg(Pos)
480.9 ± 4.4

Int.Intensity
200.9 ± 3.6
1306.9 ± 7.6
161.2 ± 3.5
dBg/dx
201 ± 10

fwhm (Gaussian)
0.0509 ± 9E-4
0.2105 ± 0.0011
0.2377 ± 0.0045

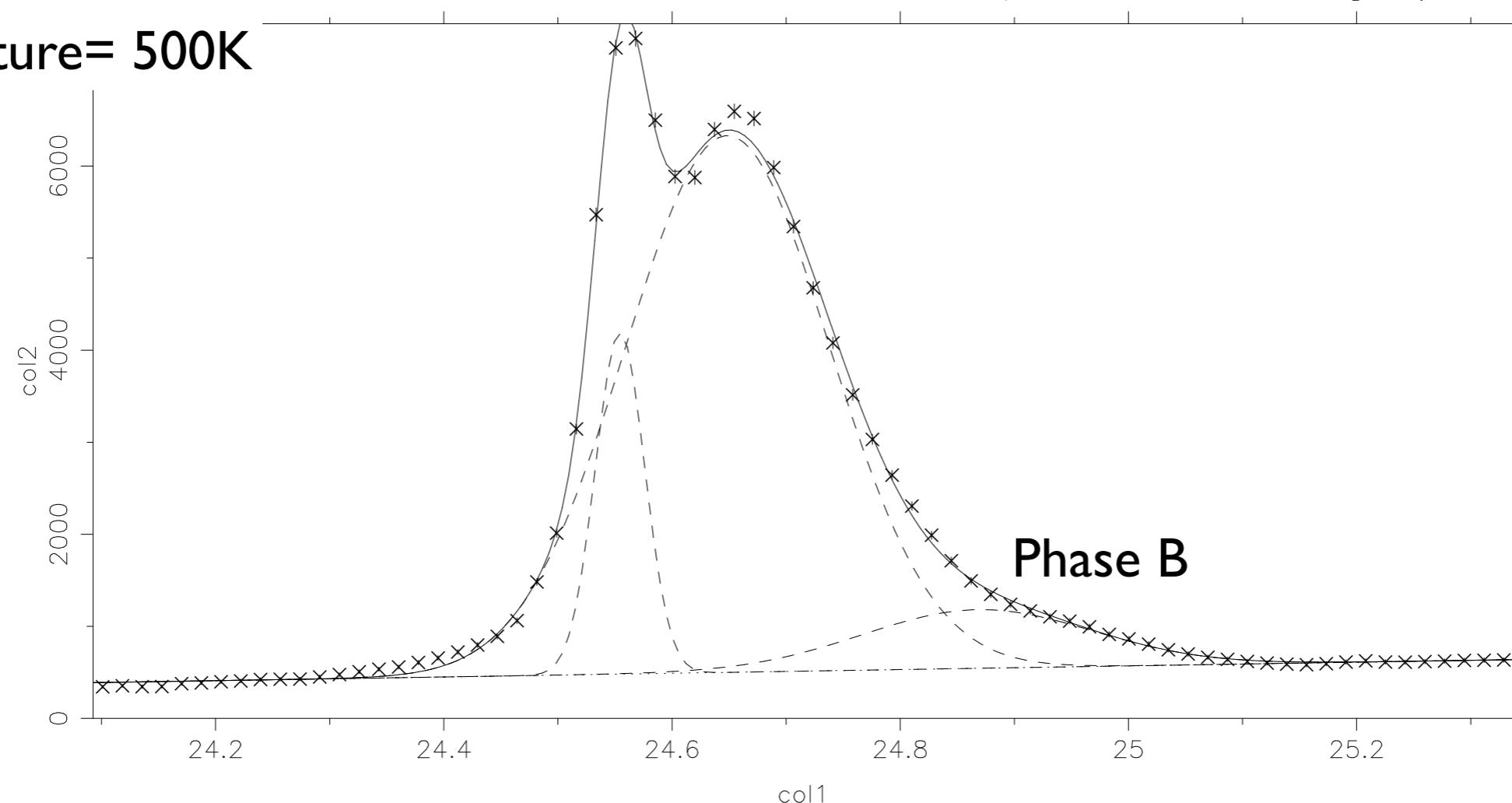
fwhm (Lorentzian)
0.0000000
0.0000000
3E-7 ± 0.0033014

Monitor 1
* χ^2 3.265

Phase A

K72plate1199300100ss182.dat[x=1,y=2,s=**]

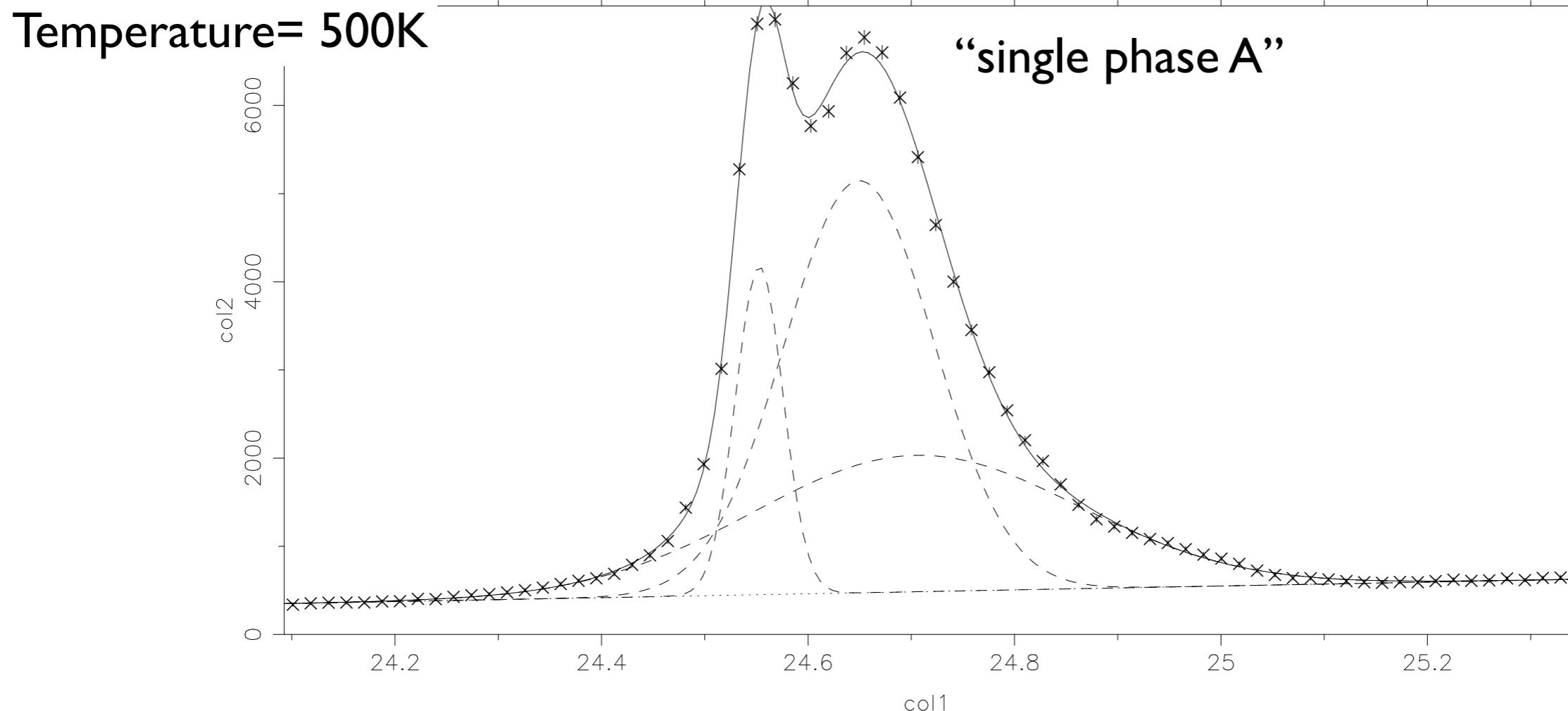
Temperature= 500K



T dependence of phase separation. Single crystal synchrotron

Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.55290 ± 0.00018	3721.6	214.6 ± 1.2	0.0542 ± 3E-4	0.000000
24.64952 ± 0.00026	4674.7	848.9 ± 2.7	0.1706 ± 5E-4	0.000000
24.70446 ± 0.00069	1546.8	611.2 ± 2.7	0.3707 ± 0.0014	0.000580 ± 0.001195
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1675.8 ± 6.3	451.0 ± 1.4	220.5 ± 2.3		
Monitor 1 * χ^2 1.3685				

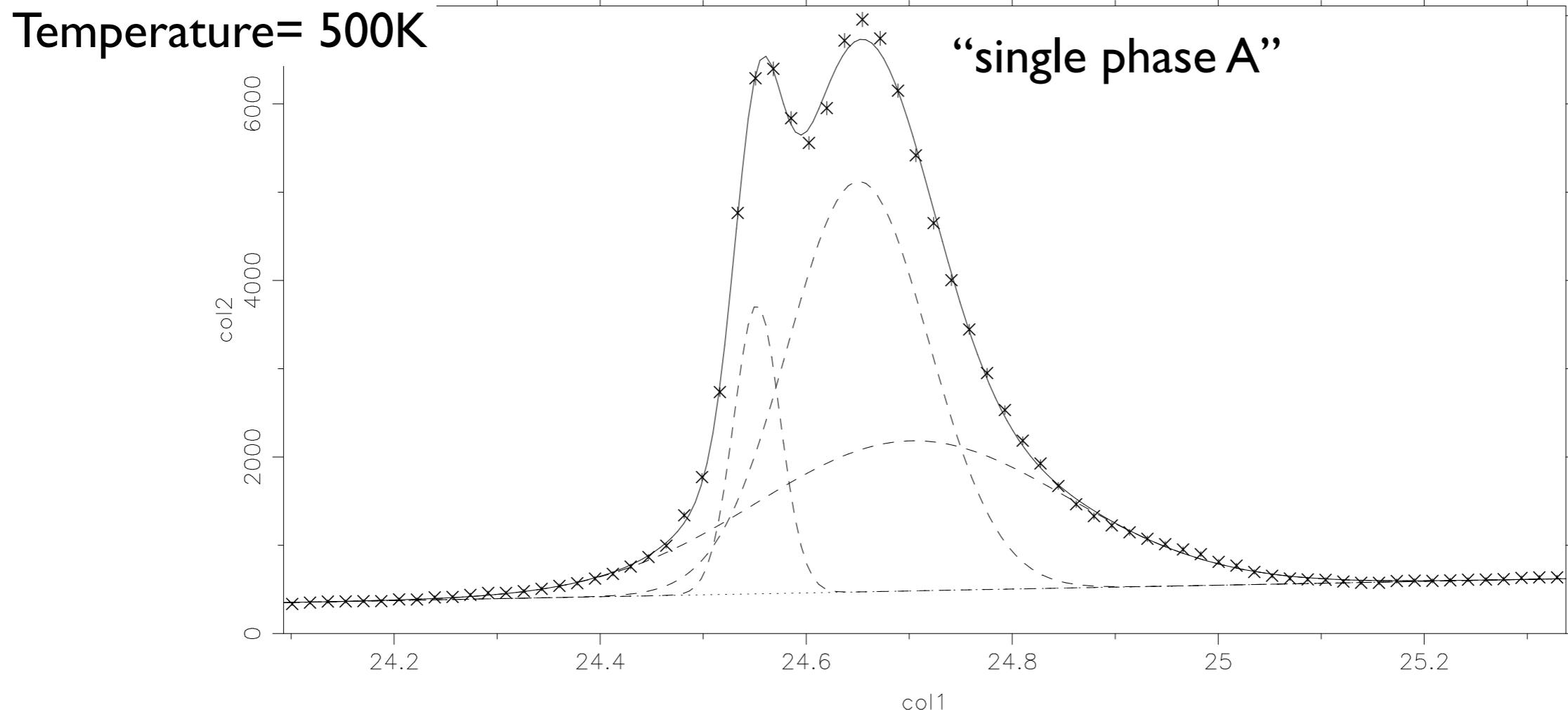
K72plate1199300100ss197.dat[x=1,y=2,s=**]



T dependence of phase separation. Single crystal synchrotron

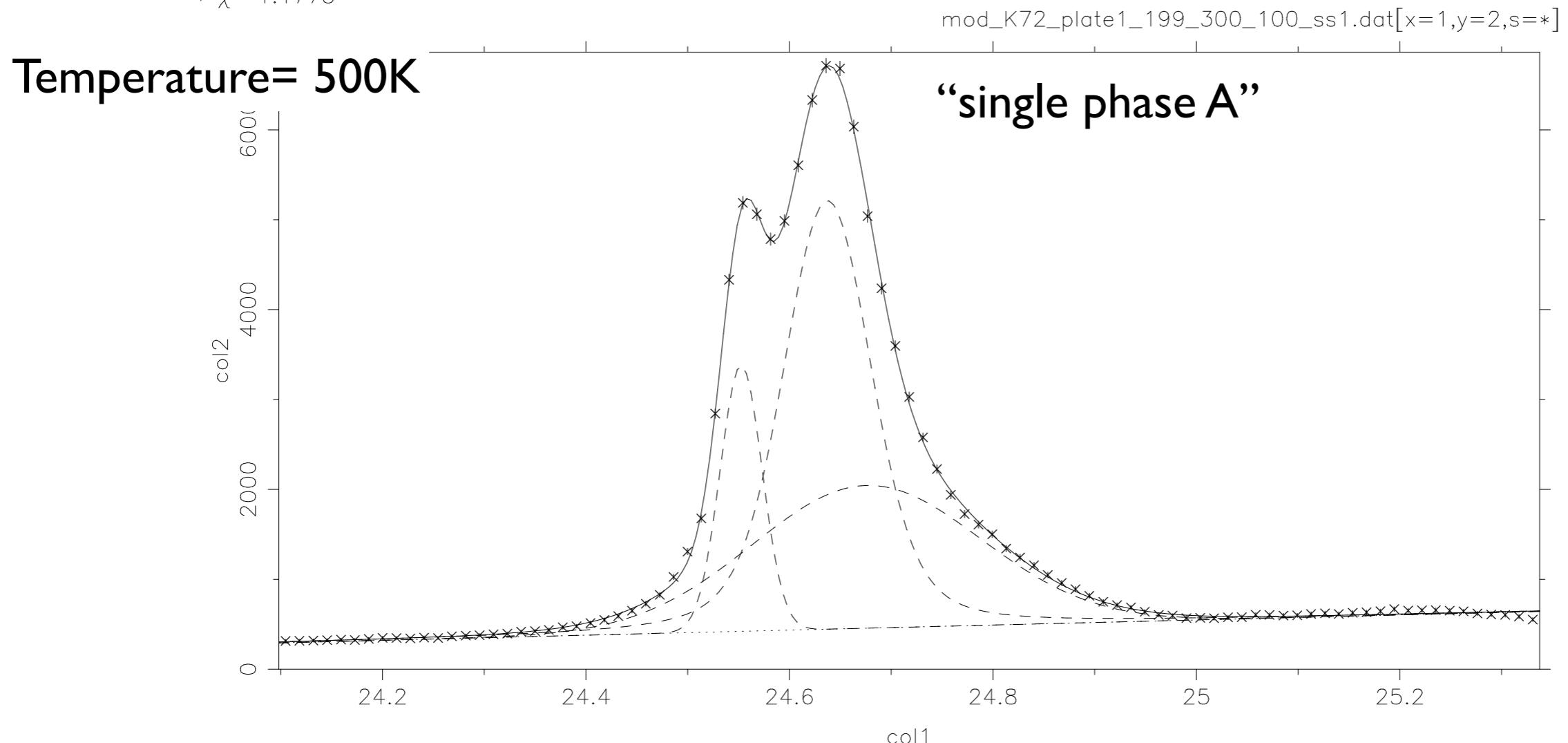
Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.55225 ± 0.00036	3274.5	184.7 ± 2.0	0.0530 ± 7E-4	0.0000000
24.65080 ± 0.00038	4651.7	795.9 ± 4.1	0.1607 ± 0.0010	0.0000000
24.70249 ± 0.00100	1700.7	642.2 ± 4.1	0.3546 ± 0.0024	0.0001565 ± 0.0013105
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1624.2 ± 6.2	450.3 ± 2.8	217.9 ± 6.5		
Monitor 1 * χ^2 1.3716				

K72plate1199300100ss244.dat[x=1,y=2,s=*]



T dependence of phase separation. Single crystal synchrotron

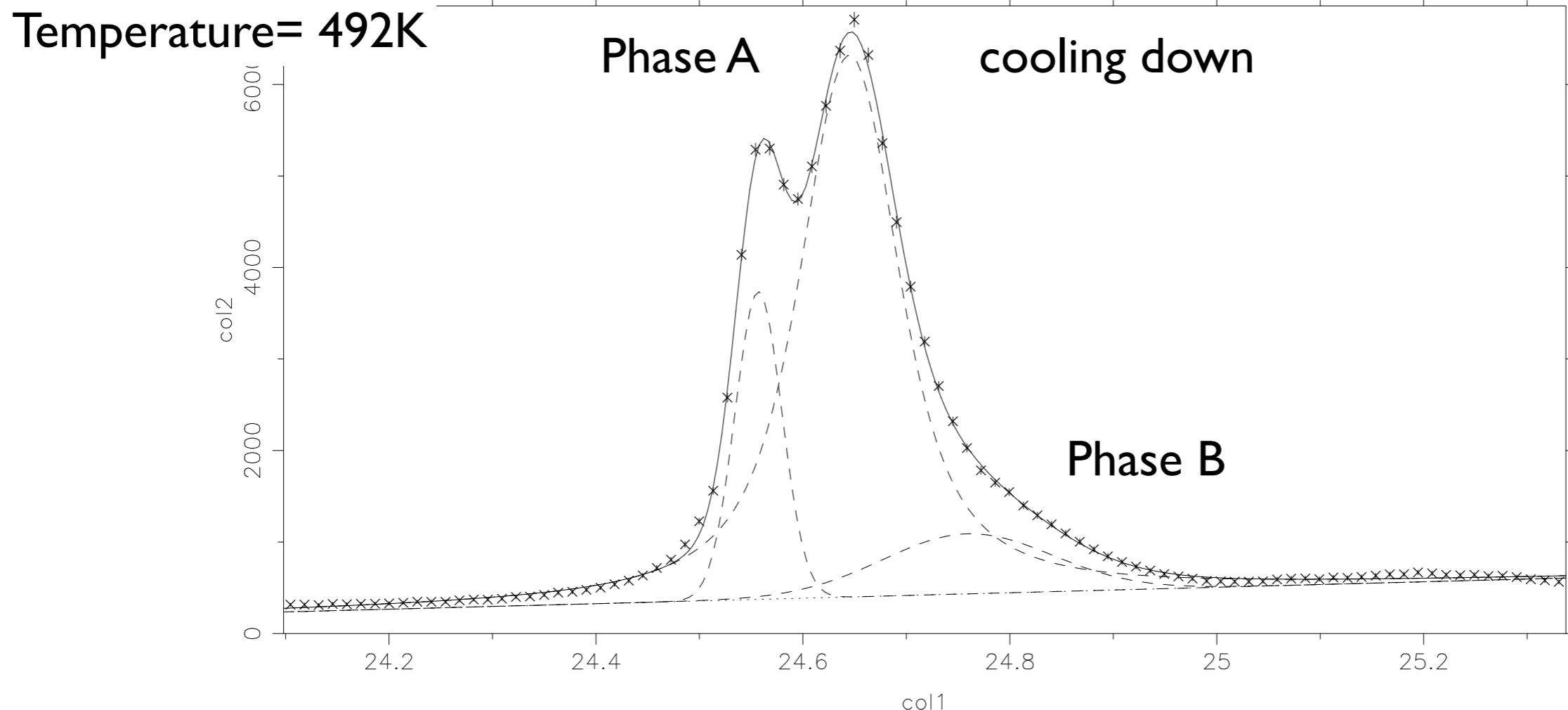
Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.55251 ± 0.00018	2959.6	153.4 ± 0.8	0.04868 ± 0.00036	0.00000
24.63731 ± 0.00015	4766.7	591.5 ± 1.3	0.08408 ± 0.00035	0.03229 ± 0.00034
24.67583 ± 0.00047	1587.6	446.3 ± 1.4	0.26407 ± 0.00084	0.00000
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1183.4 ± 4.9	421.6 ± 1.2	282.3 ± 3.1		
Monitor 1				
* χ^2 1.1773				



T dependence of phase separation. Single crystal synchrotron

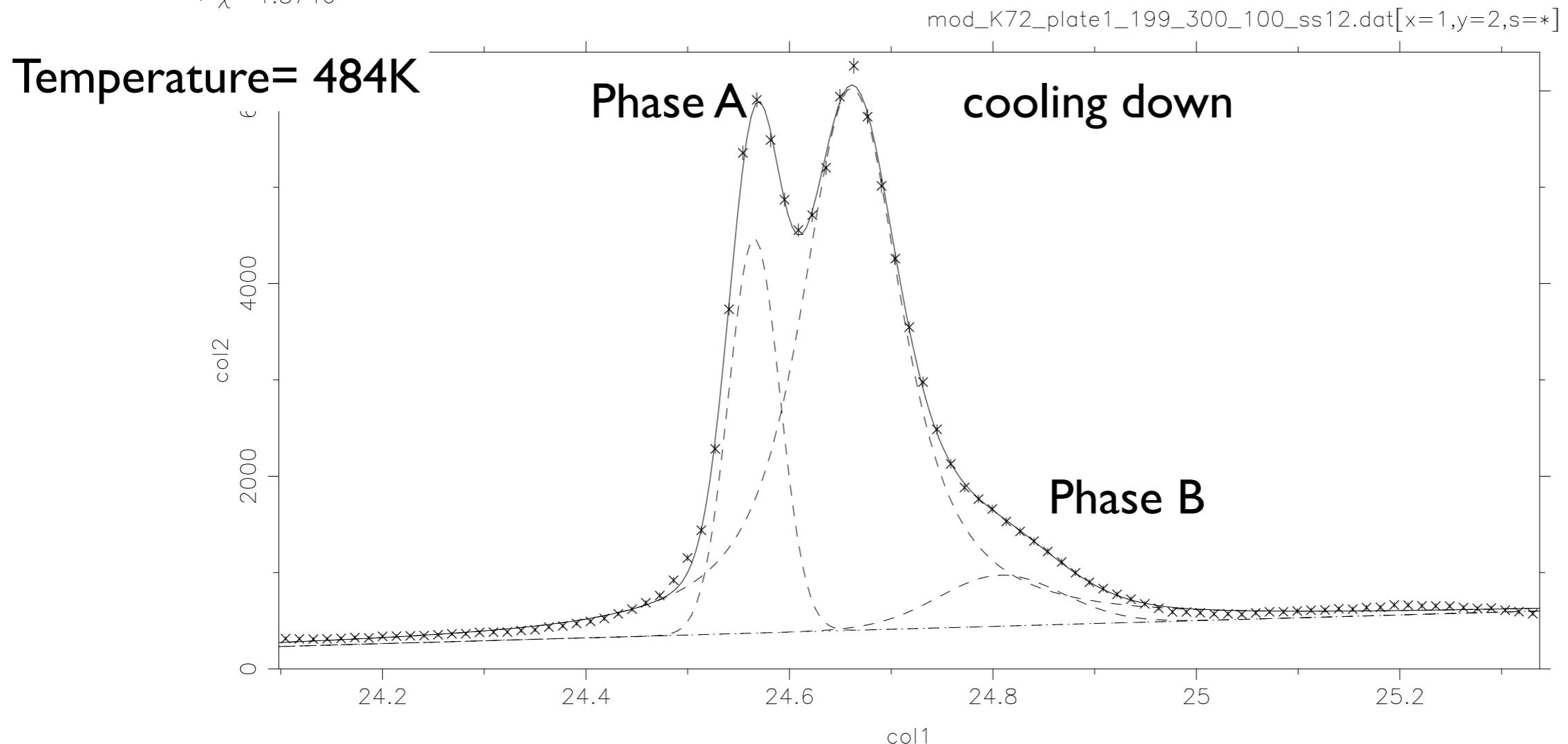
Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.5570 ± 4E-4	3362.5	191.2 ± 2.5	0.0534 ± 6E-4	0.00000
24.6450 ± 3E-4	5921.6	951.0 ± 3.8	0.0617 ± 1E-3	0.07936 ± 0.00048
24.7591 ± 0.0016	655.8	134.9 ± 2.0	0.1933 ± 0.0025	0.00000
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1239.2 ± 4.9	373.2 ± 2.7	299.4 ± 6.4		
Monitor 1				
* χ^2 1.7885				

mod_K72_plate1_199_300_100_ss5.dat[x=1,y=2,s=**]



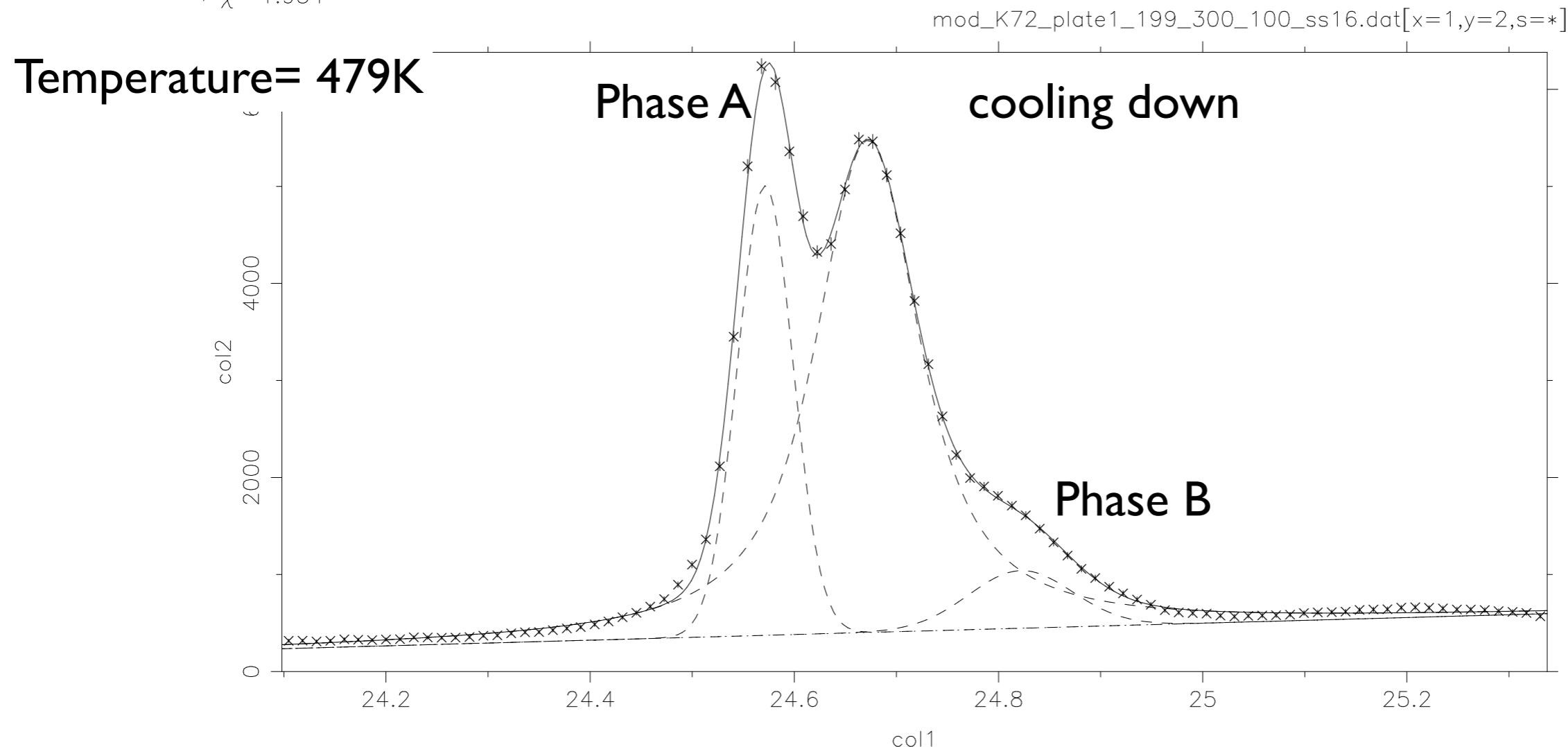
T dependence of phase separation. Single crystal synchrotron

Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.5654 ± 4E-4	4101.2	258.8 ± 2.6	0.0593 ± 6E-4	0.00000
24.6611 ± 3E-4	5631.3	950.6 ± 4.2	0.0571 ± 0.0011	0.08833 ± 0.00059
24.8075 ± 0.0017	529.9	80.8 ± 1.6	0.1433 ± 0.0027	0.00000
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1248.0 ± 4.9	370.9 ± 2.8	297.7 ± 5.5		
Monitor 1				
* χ^2 1.8746				



T dependence of phase separation. Single crystal synchrotron

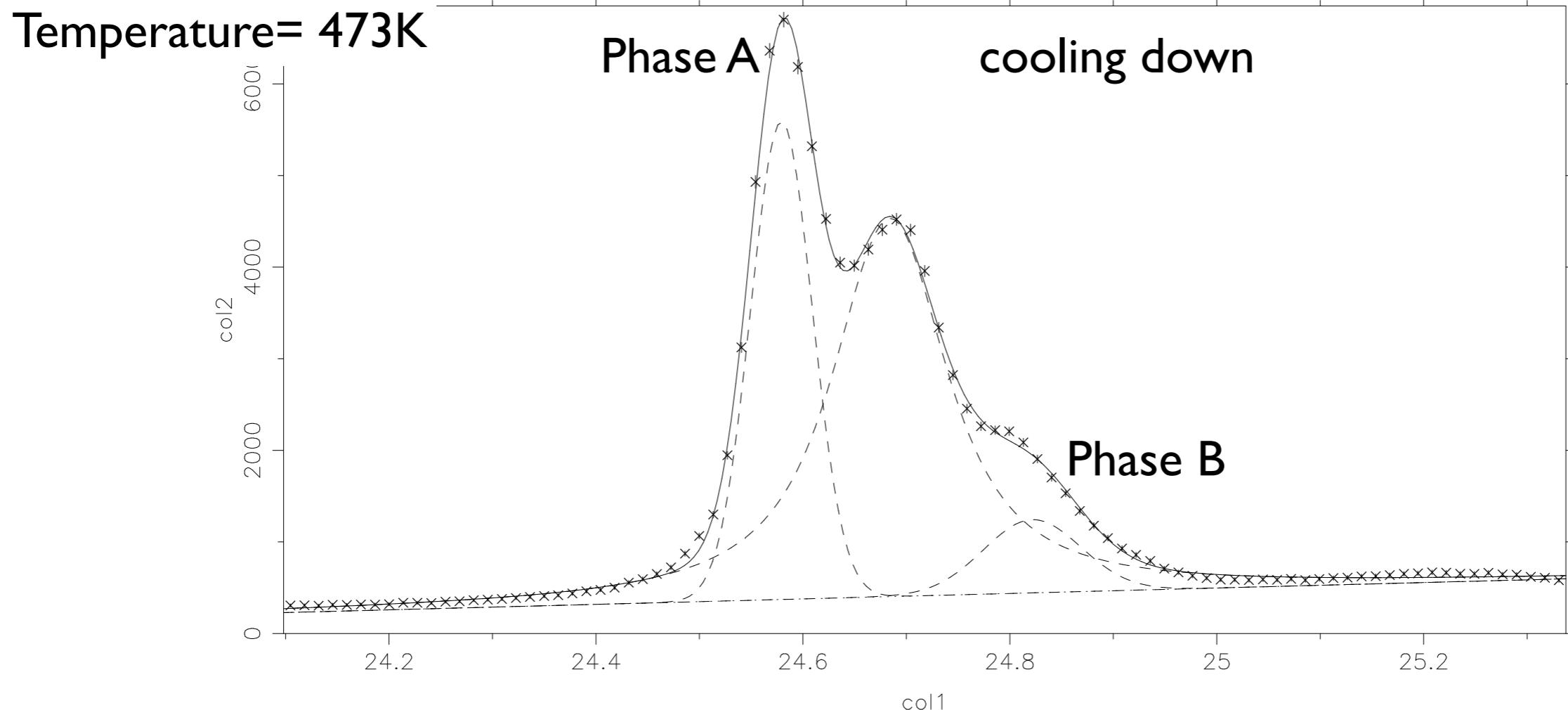
Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.5715 ± 3E-4	4633.1	315.4 ± 2.4	0.0640 ± 5E-4	0.00000
24.6720 ± 3E-4	5072.5	900.7 ± 3.8	0.0530 ± 0.0013	0.09702 ± 0.00063
24.8217 ± 0.0013	594.1	75.7 ± 1.4	0.1197 ± 0.0034	0.00000
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1248.0 ± 4.9	373.4 ± 2.7	291.8 ± 4.9		
Monitor 1 * χ^2 1.934				



T dependence of phase separation. Single crystal synchrotron

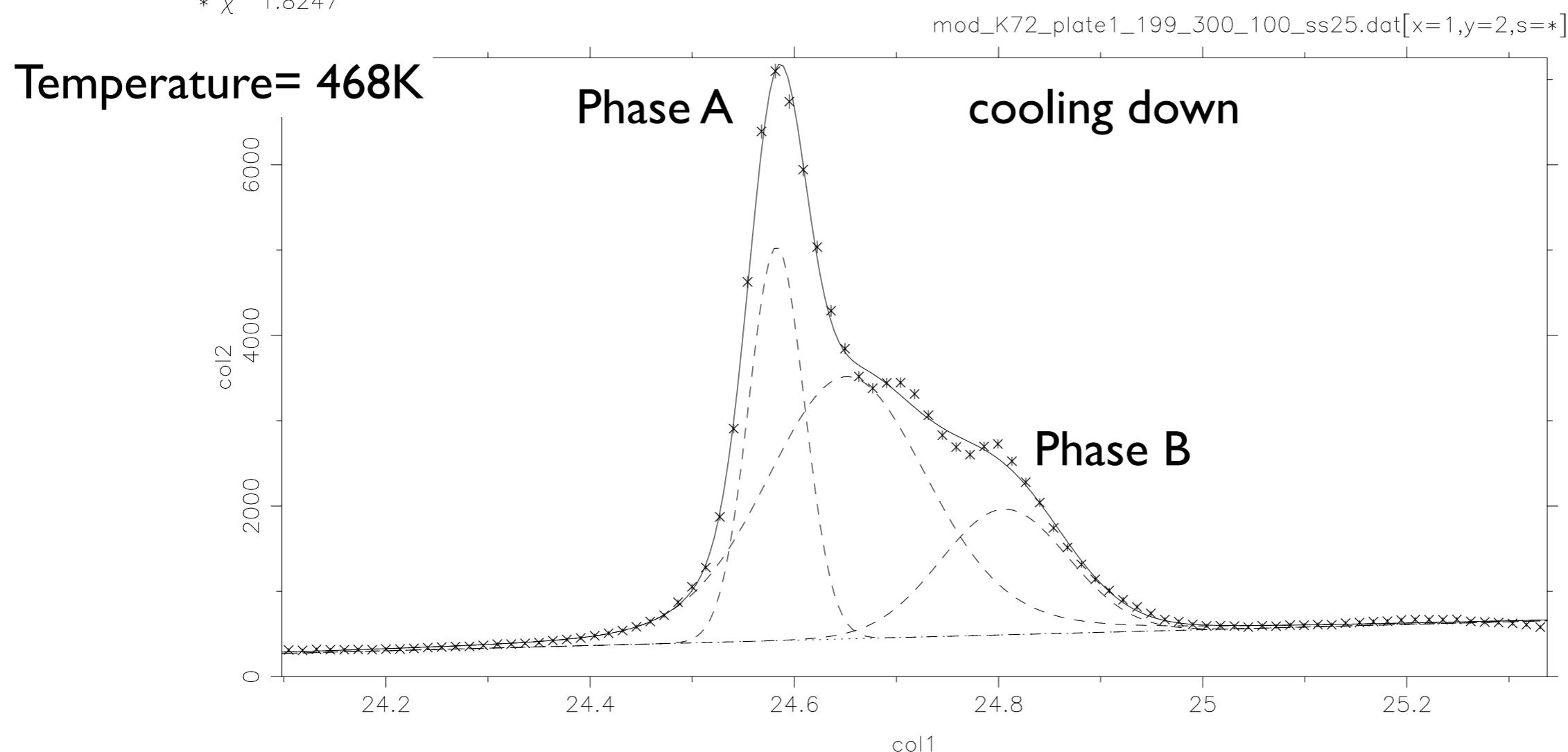
Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.5793 ± 3E-4	5217.7	390.6 ± 3.6	0.0703 ± 8E-4	0.00000
24.6842 ± 8E-4	4130.0	820.0 ± 4.5	0.0466 ± 0.0023	0.11490 ± 0.00082
24.8217 ± 0.0011	799.3	94.4 ± 1.7	0.1110 ± 0.0019	0.00000
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1258.2 ± 4.9	371.9 ± 3.1	297.9 ± 7.6		
Monitor 1 * χ^2 2.386				

mod_K72_plate1_199_300_100_ss21.dat[x=1,y=2,s=**]



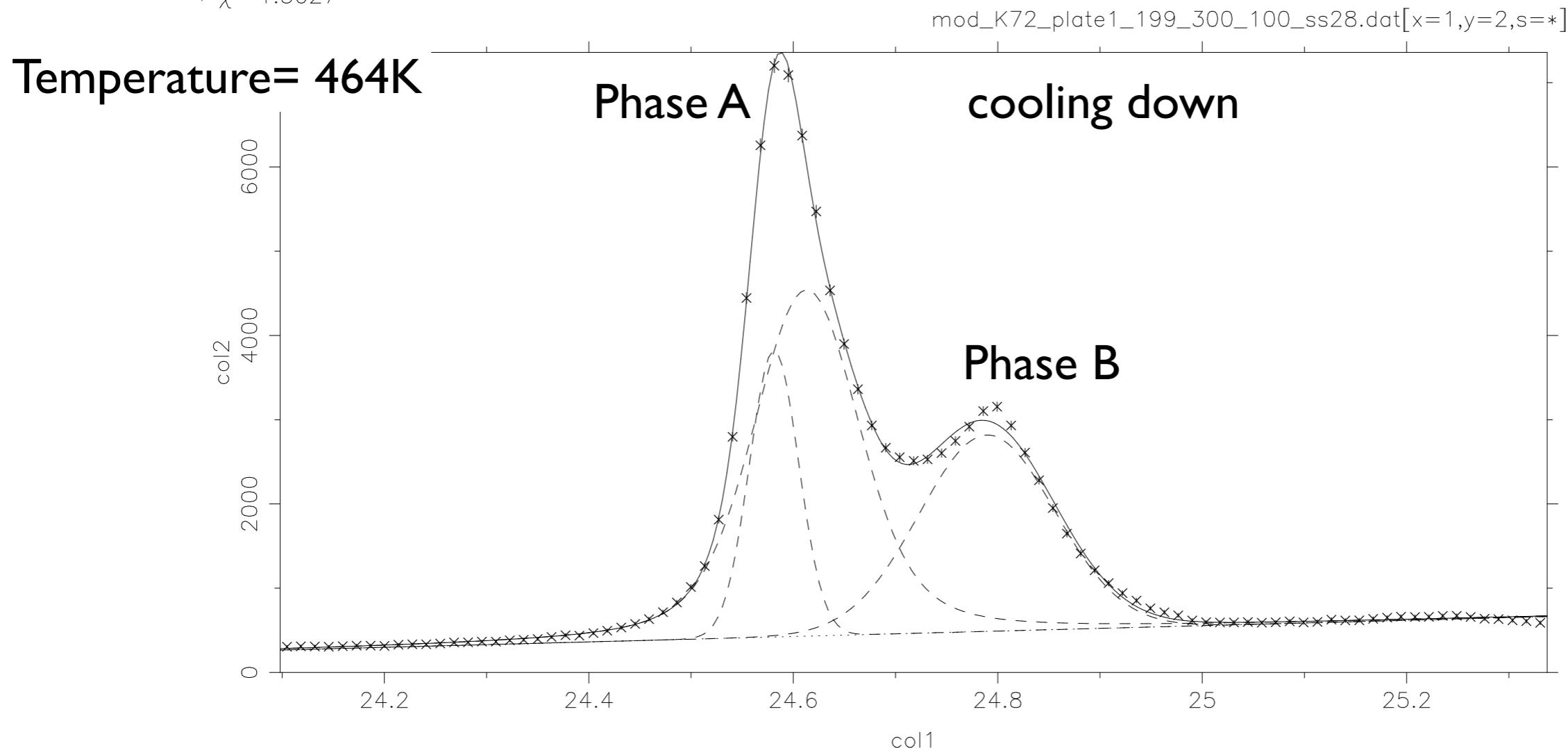
T dependence of phase separation. Single crystal synchrotron

Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.58256 ± 0.00028	4616.2	314.9 ± 3.5	0.0641 ± 9E-4	0.00000
24.65116 ± 0.00077	3075.1	672.5 ± 3.3	0.1619 ± 0.0011	0.04407 ± 0.00081
24.80557 ± 0.00061	1472.9	230.1 ± 1.9	0.1468 ± 9E-4	0.00000
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1204.3 ± 4.9	421.2 ± 2.6	309.2 ± 6.5		
Monitor 1 * χ^2 1.8247				



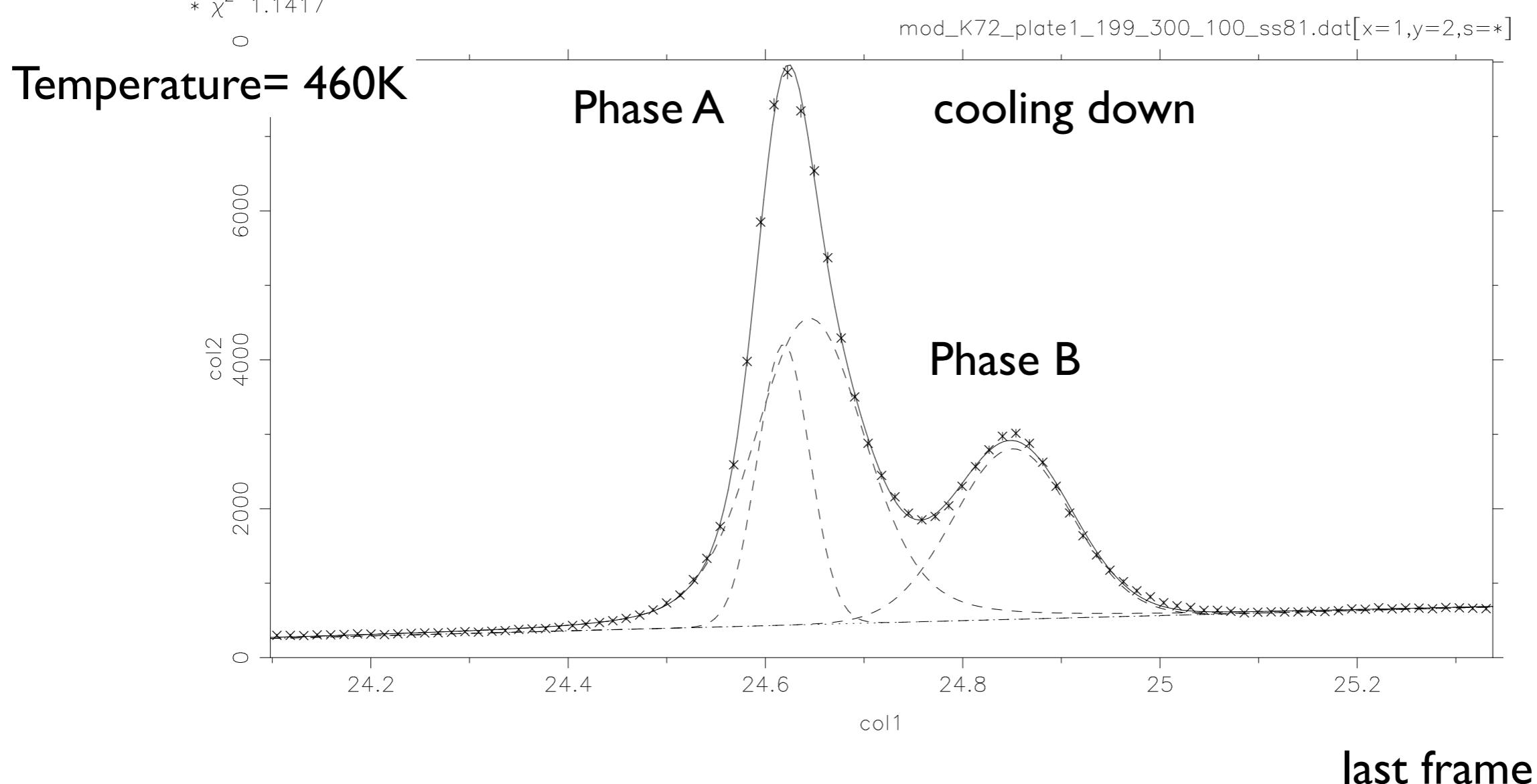
T dependence of phase separation. Single crystal synchrotron

Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.58118 ± 0.00020	3401.6	205.1 ± 1.4	0.05665 ± 0.00036	0.00000
24.61286 ± 0.00019	4109.3	622.1 ± 1.8	0.09702 ± 0.00052	0.04439 ± 0.00045
24.78935 ± 0.00036	2330.9	387.3 ± 1.4	0.15610 ± 0.00043	0.00000
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1201.9 ± 4.9	420.9 ± 1.5	321.2 ± 3.9		
Monitor 1 * χ^2 1.5027				



T dependence of phase separation. Single crystal synchrotron

Position	Max.Intensity	Int.Intensity	fwhm (Gaussian)	fwhm (Lorentzian)
24.61854 ± 0.00019	3775.9	249.0 ± 1.1	0.06196 ± 0.00026	0.00000
24.64470 ± 0.00017	4114.6	652.8 ± 1.9	0.11099 ± 0.00035	0.03805 ± 0.00034
24.85057 ± 0.00024	2289.9	343.3 ± 0.9	0.14083 ± 0.00031	0.00000
Int.Intens.Exp.	Bg(Pos)	dBg/dx		
1233.0 ± 5.0	434.8 ± 1.1	341.6 ± 3.4		
Monitor 1 * χ^2 1.1417				



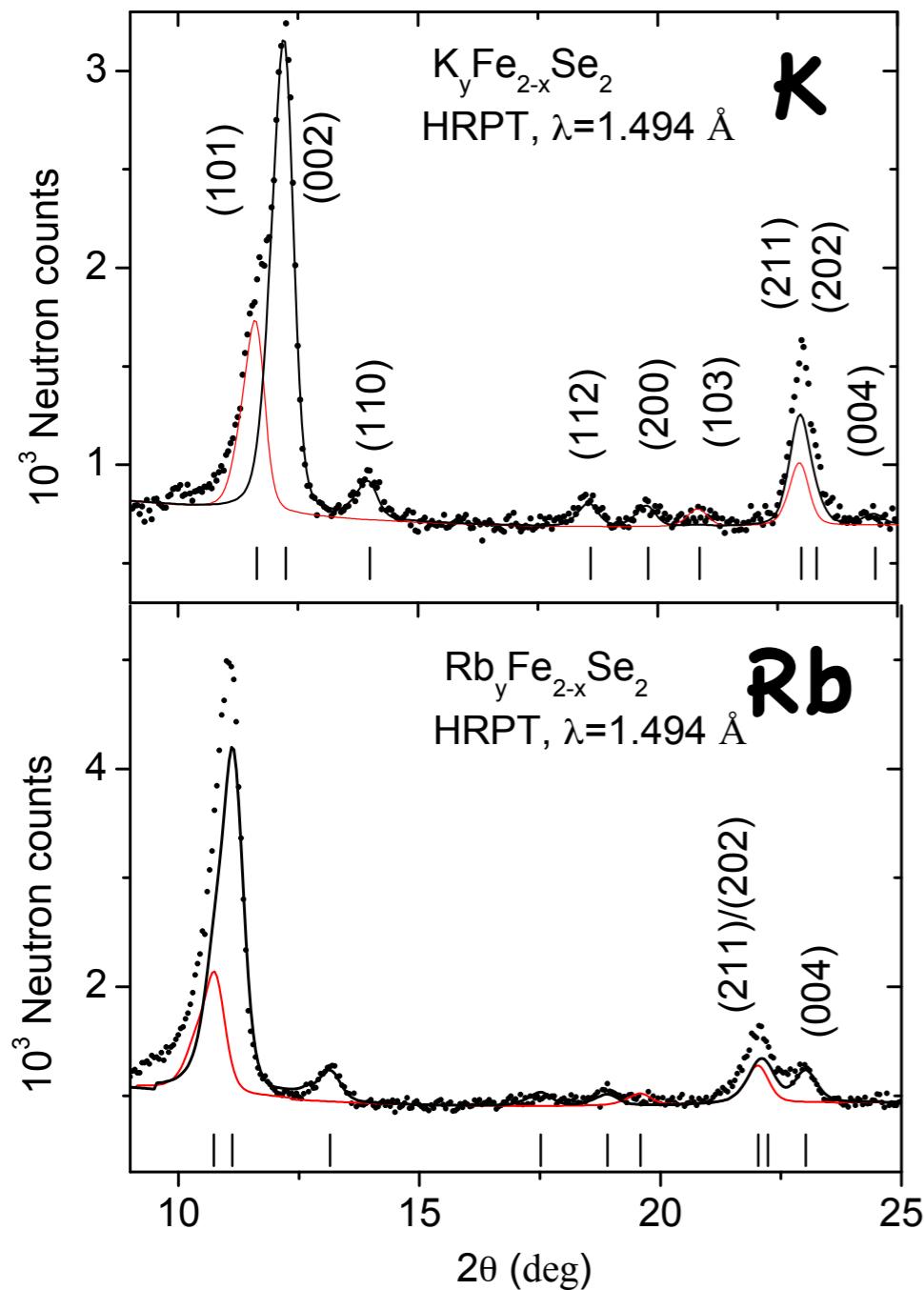
Summary on superconducting $A_{0.8}Fe_{1.7}Se_2$, $A=K$, Rb , Cs

- The ground state of the crystal is an intrinsically phase-separated state with two distinct-by-symmetry phases.
- The main phase has the iron vacancy ordered $\sqrt{5} \times \sqrt{5} I4/M$ -superstructure $Rb_{0.8}Fe_{1.5}Se_2$.
- The minority phase can be well approximated by $I4/mmm$ -disordered structure with the refined stoichiometry $Rb_{0.60(5)}(Fe_{1.10(5)}Se)_2$. True symmetry is lower with 2D (ab)-plane ordering $\sqrt{2} \times \sqrt{2}$
- The minority phase merges with the main vacancy ordered phase on heating above the phase separation temperature $T_P \approx 475K < T_S \approx 530K$ (to average I/mmm)

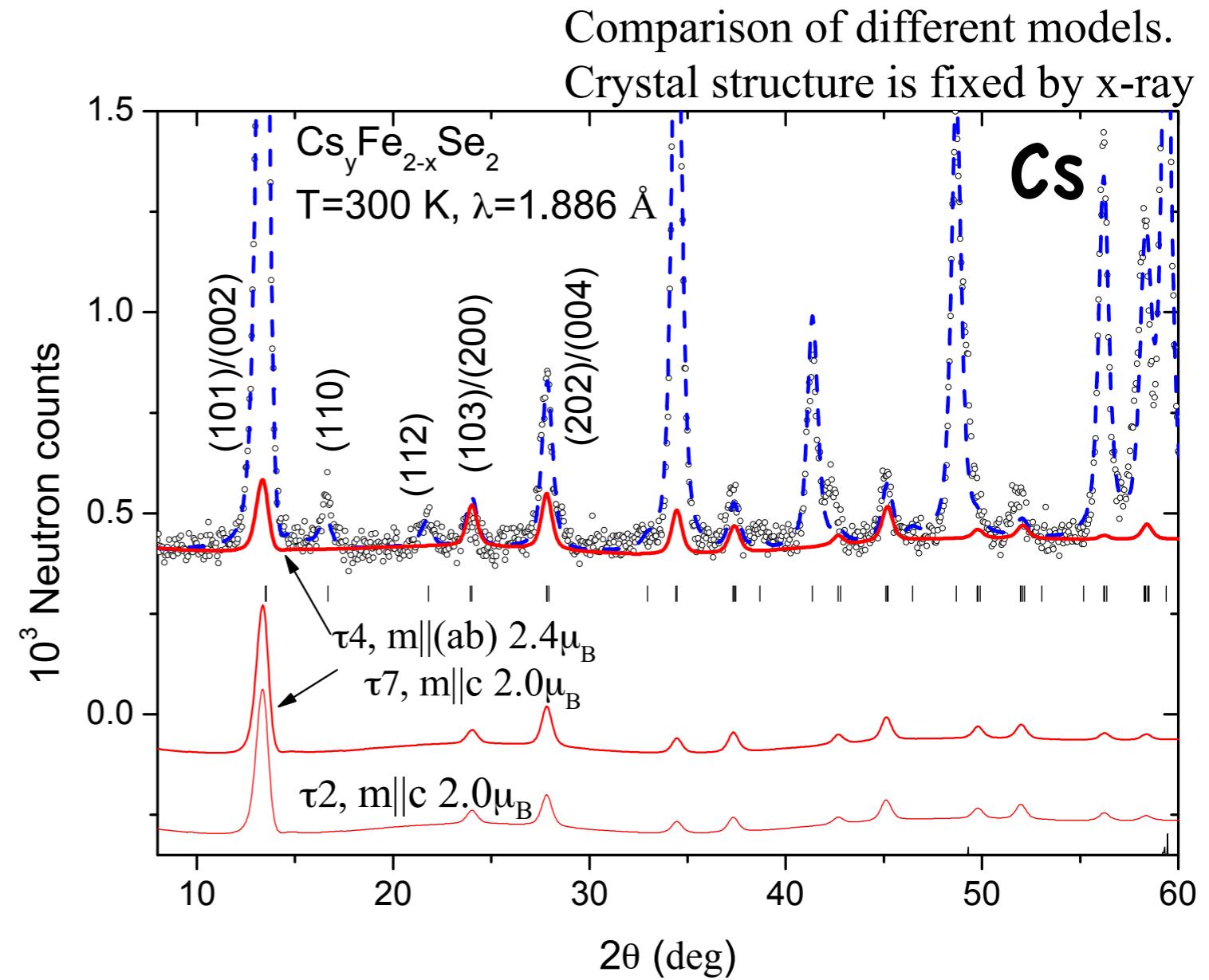
Thank you!

Neutron diffraction patterns Rb, K, Cs

Magnetic contribution is in red



τ_2 or τ_7 with spins along c



	K	Rb	Cs	
a =	8.7302	8.7996	8.8582 Å	is “difficult”
c =	14.1149	14.5762	15.2873 Å	for powder due
$(c/a)^2 =$	2.6140	2.7438	2.9783 = 3	to peak overlap

Magnetic representation. Symmetry adapted solutions.

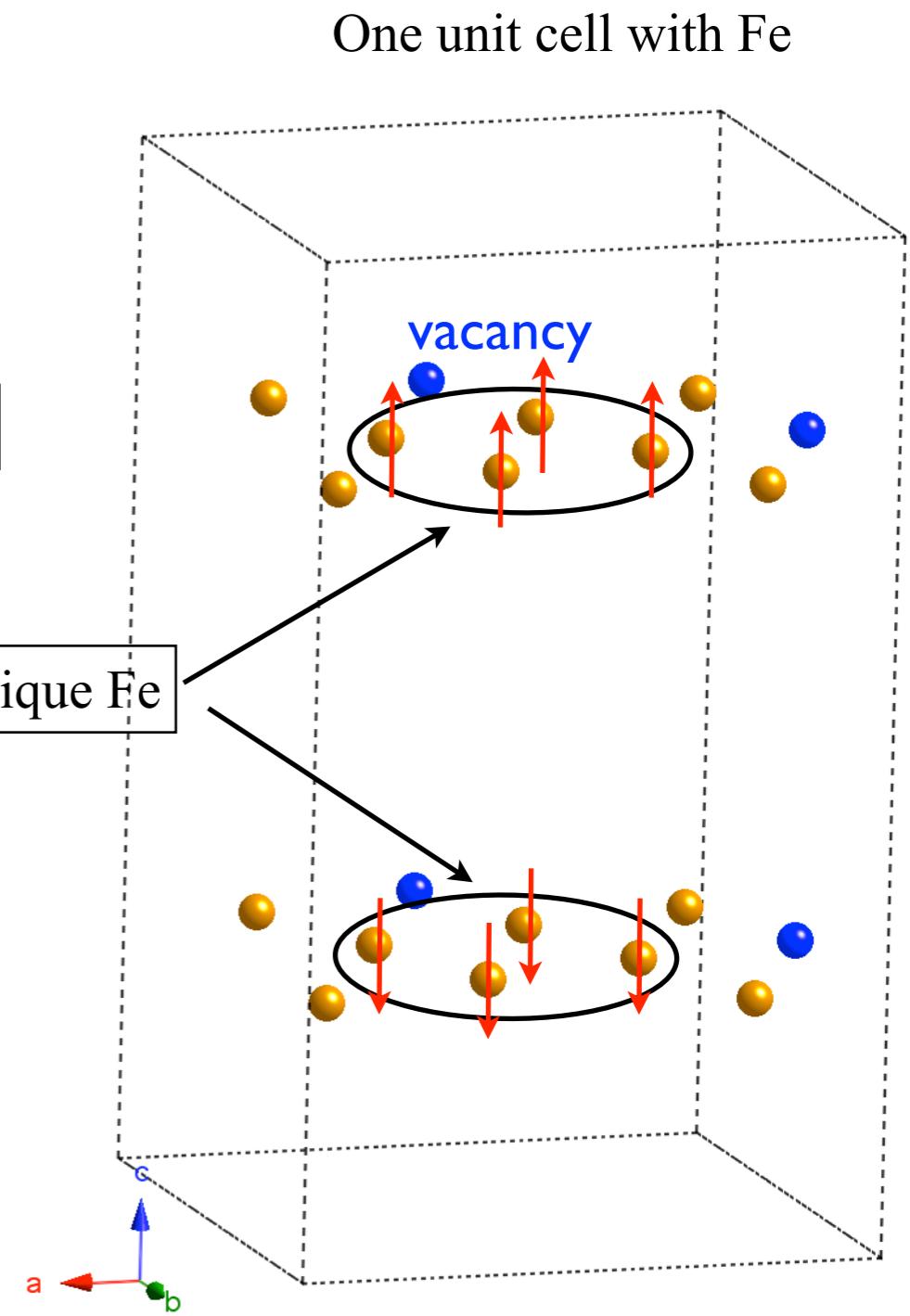
$I4/m$, $k=0$ has 8 1D irreps τ_1, \dots, τ_8 .

4 real irreps \leftrightarrow Shubnikov groups of $I4/m$

4 complex irreps

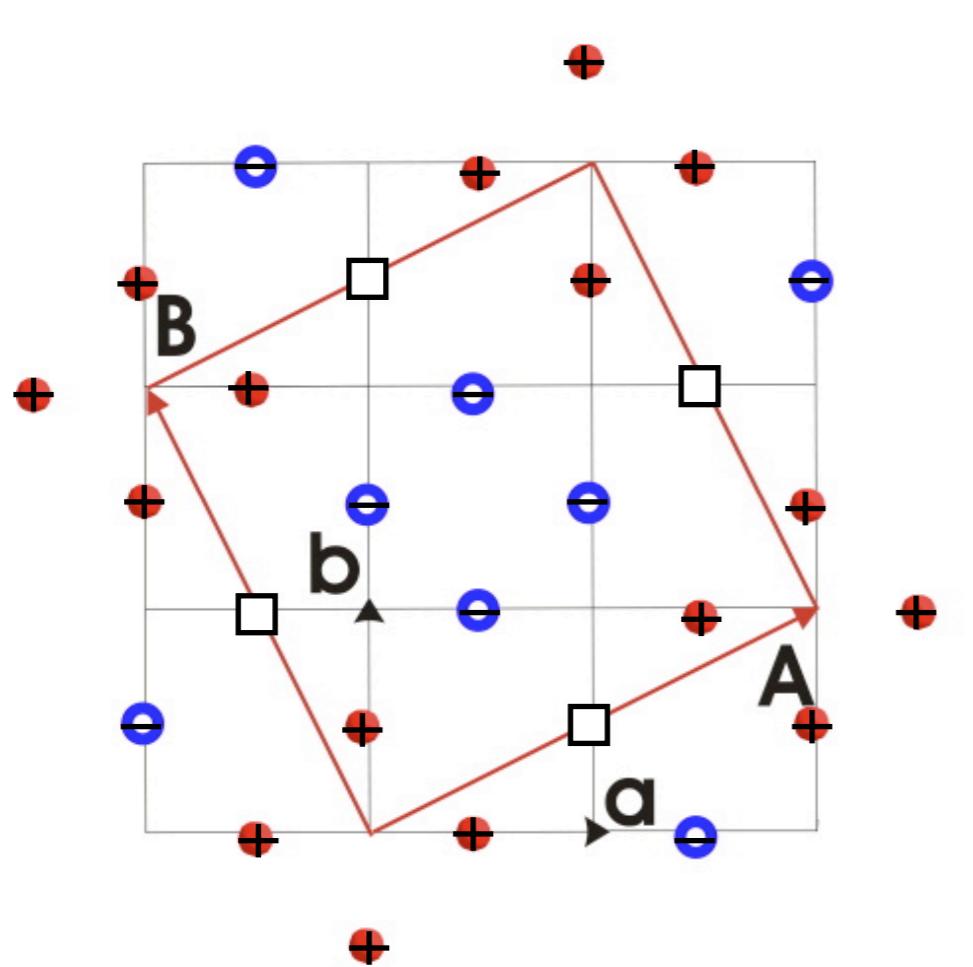
τ, ψ	h_1	h_{14}	h_4	h_{15}	h_{25}	h_{38}	h_{28}	h_{39}
	1	4_z^+	2_z	4_z^-	-1	-4_z^+	m_z	-4_z^-
$\tau_2 I4/m'$	1	1	1	1	-1	-1	-1	-1
τ_3	1	i	-1	$-i$	1	i	-1	$-i$
τ_5	1	-1	1	-1	1	-1	1	-1
τ_7	1	$-i$	-1	i	1	$-i$	-1	i

Fe Magnetic representation
 $(16i)$ (x,y,z) : all eight irreps
 $\Gamma = 3\tau_1 \oplus 3\tau_2 \oplus 3\dots \oplus 3\tau_8$

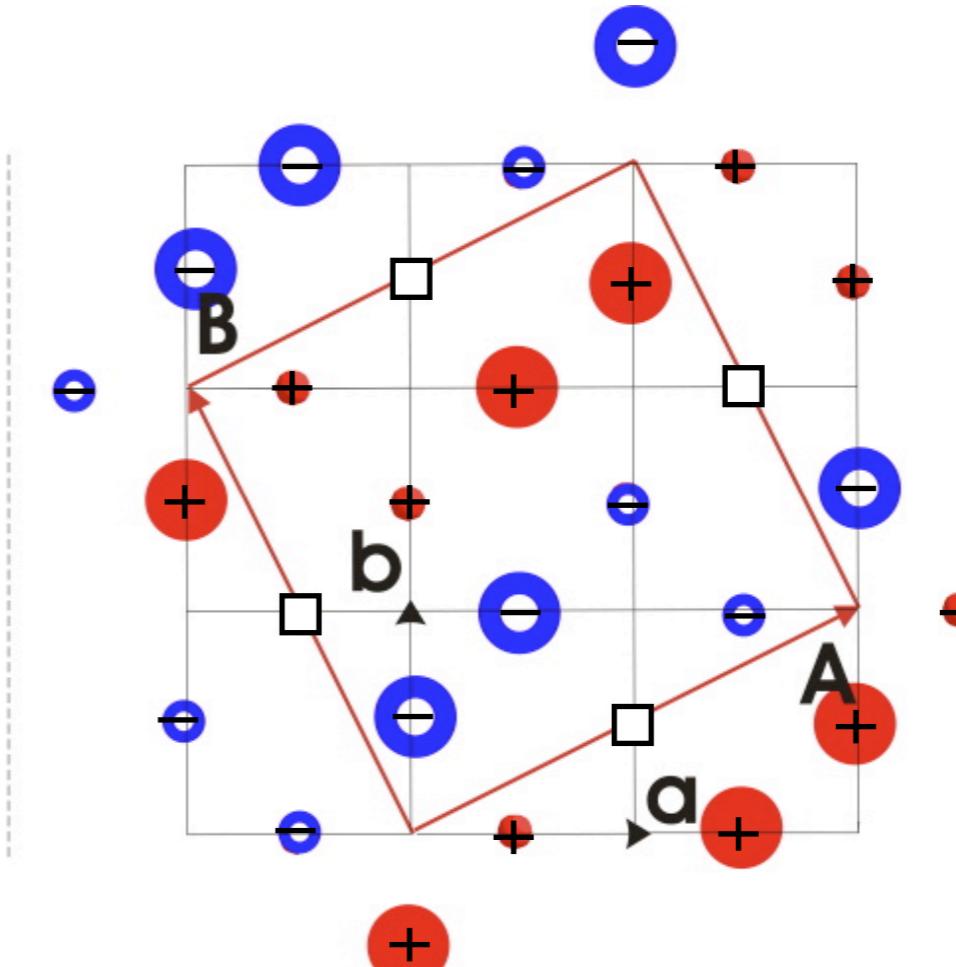


Magnetic structure of $X_{0.8}\text{Fe}_{1.6}\text{Se}_2$, $X=\text{K, Rb, Cs}$

I4/m cell shown by red square. One (*ab*) layer of Fe-atoms is shown. Fe spins are parallel (+) or antiparallel (-) to c-axis

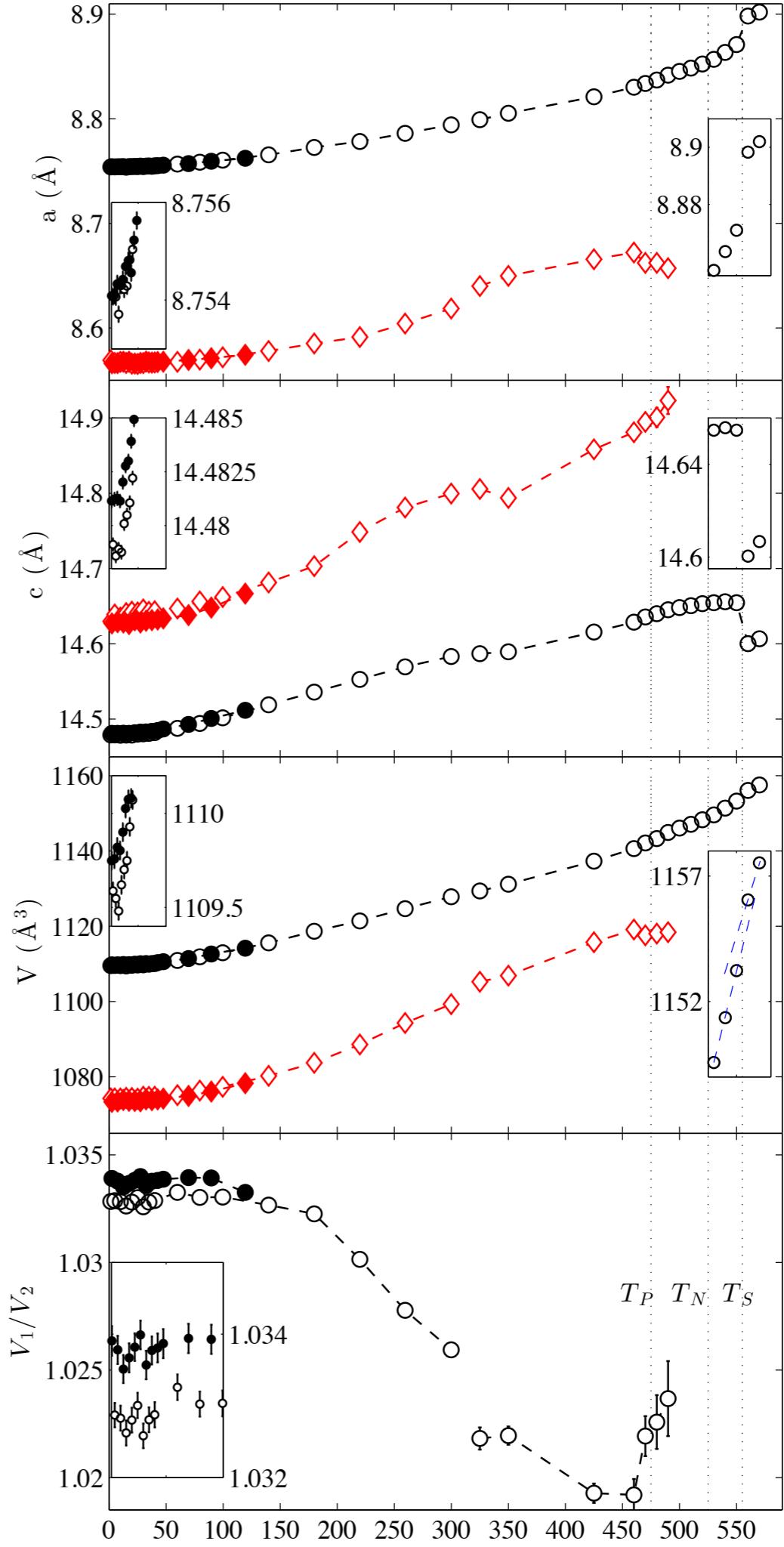


block checkerboard AFM
irrep τ_2 , ($\Gamma 1^-$) $I4/m'$



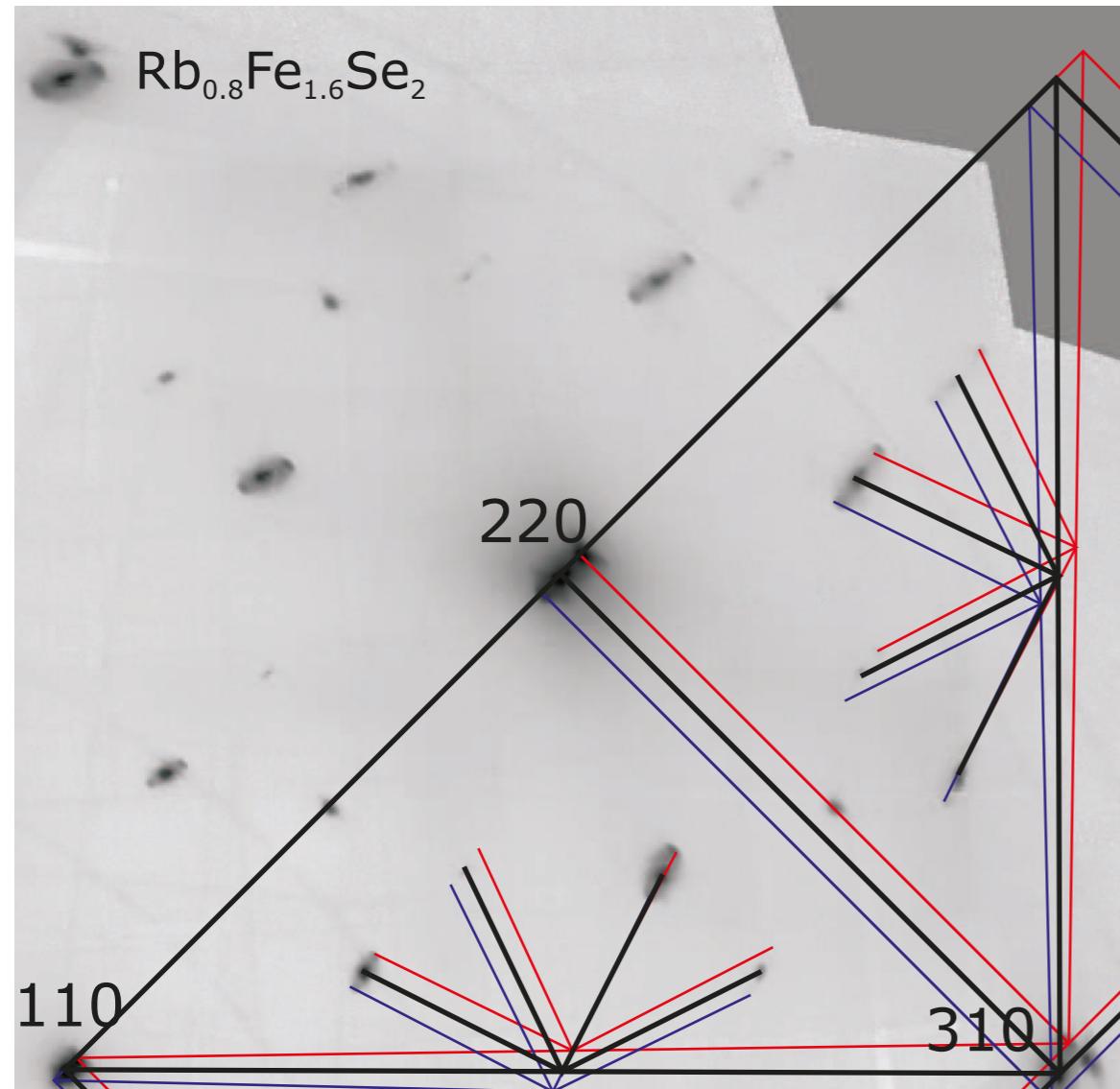
zig-zag AFM
irrep τ_7/τ_3 , ($\Gamma 4^+/\Gamma 3^+$), $C2'/m'$

Metric(τ)



Yet another phase

Higher resolution: third phase (C) identification



HK0 plane: logarithmic intensity

each reflection of main phase A is surrounded by weaker spots, corresponding to orthorhombic distortion in the basis $a' = (a+b)$, $b' = (a-b)$

- the symmetry of minority phase C is not higher than orthorhombic
- $a_c \sim 1.02a_0 2^{1/2}$, $b_c \sim 0.98a_0 2^{1/2}$, $c_c \sim c_0$
- vacancies ordering is similar to that of main phase
- no disorder-related component is present
- component C is more pronounced in Rb system

twinning motif recovery from 2D images is difficult

Different choice of equivalent propagation k-vectors in I4/mmm

arm of $\{k_1\}$: $k_1 = [\frac{2}{5}, \frac{1}{5}, 1]$

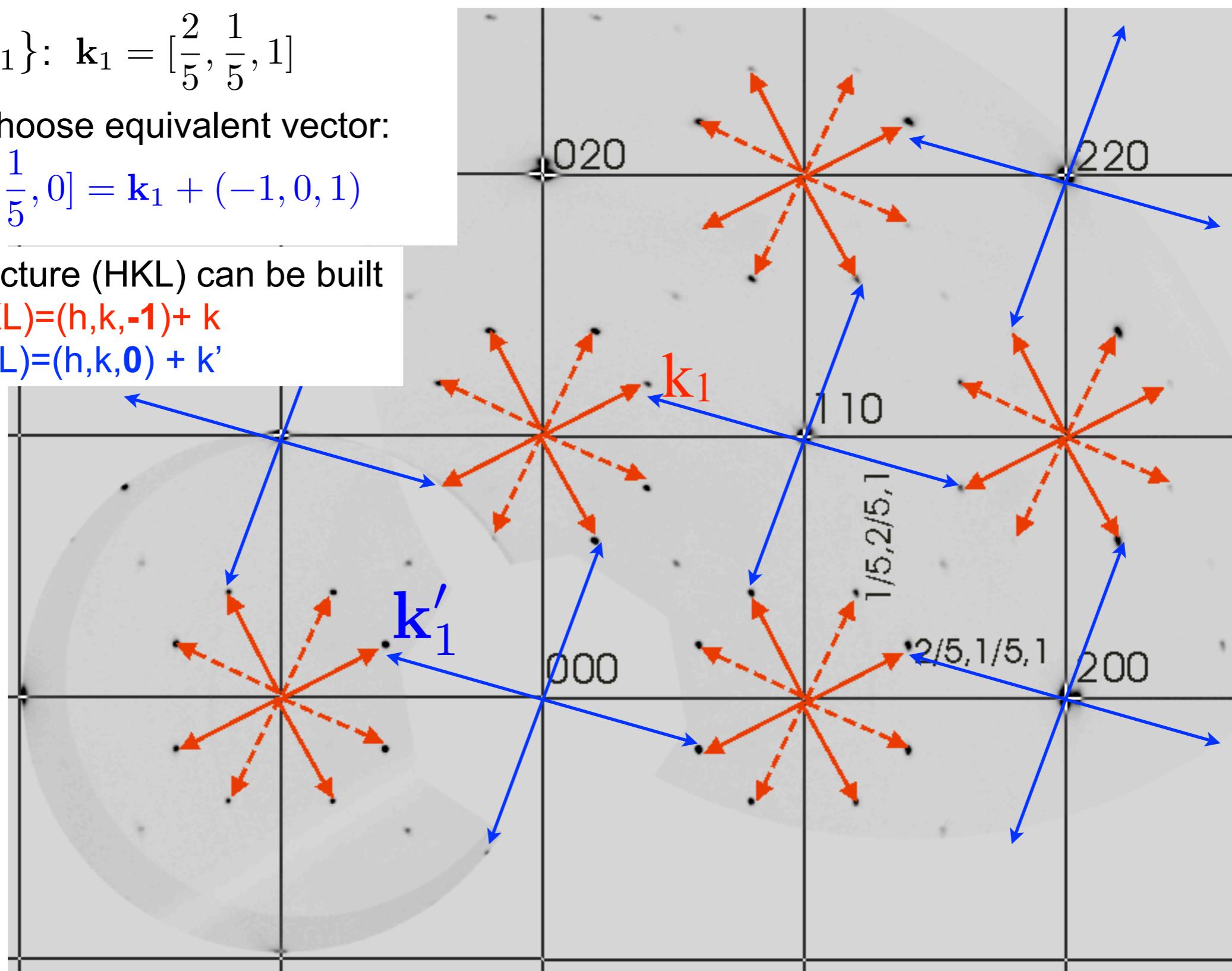
one can choose equivalent vector:

$$k'_1 = [-\frac{3}{5}, \frac{1}{5}, 0] = k_1 + (-1, 0, 1)$$

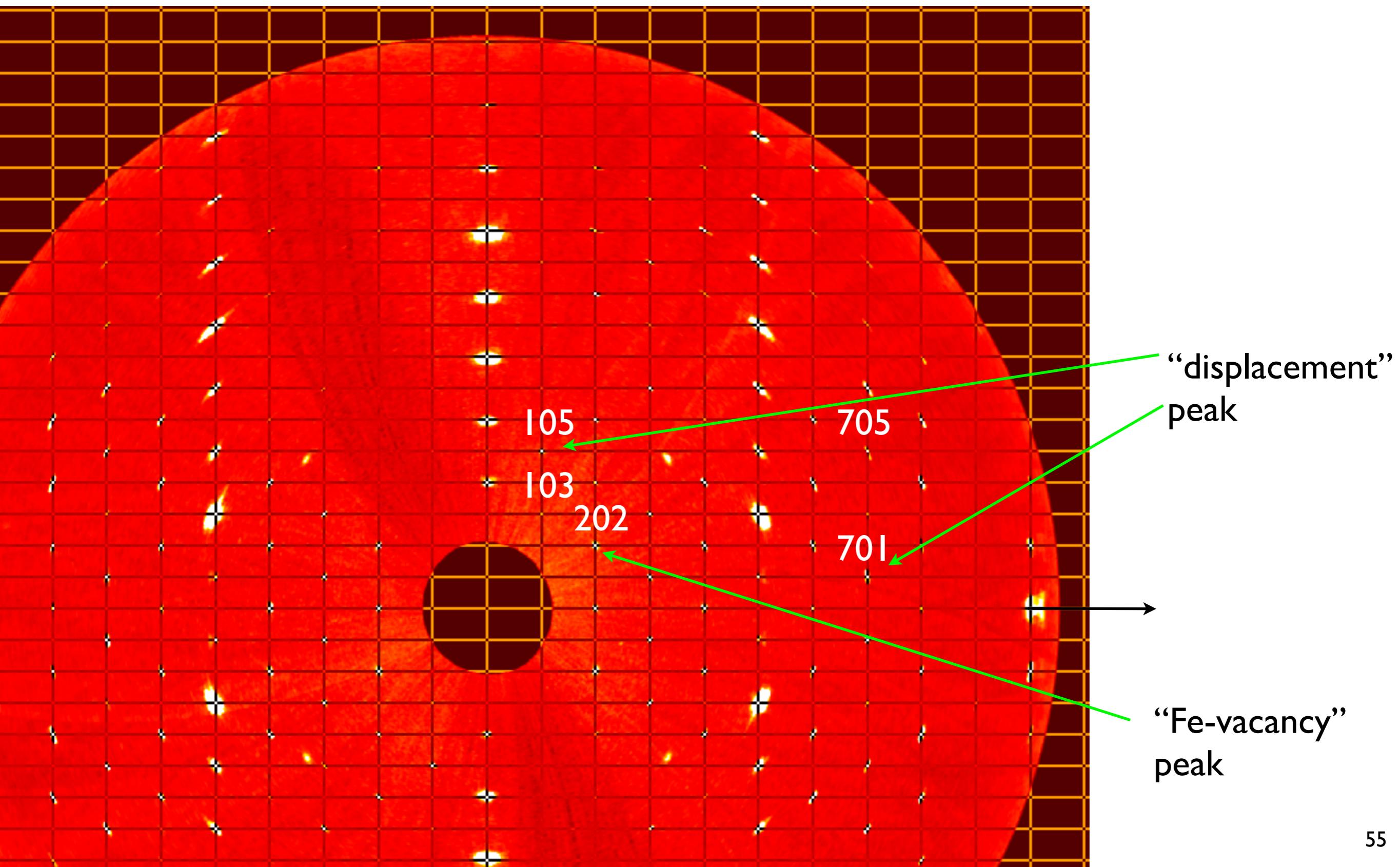
Superstructure (HKL) can be built

Red: $(HKL) = (h, k, -1) + k$

Blue: $(HKL) = (h, k, 0) + k'$

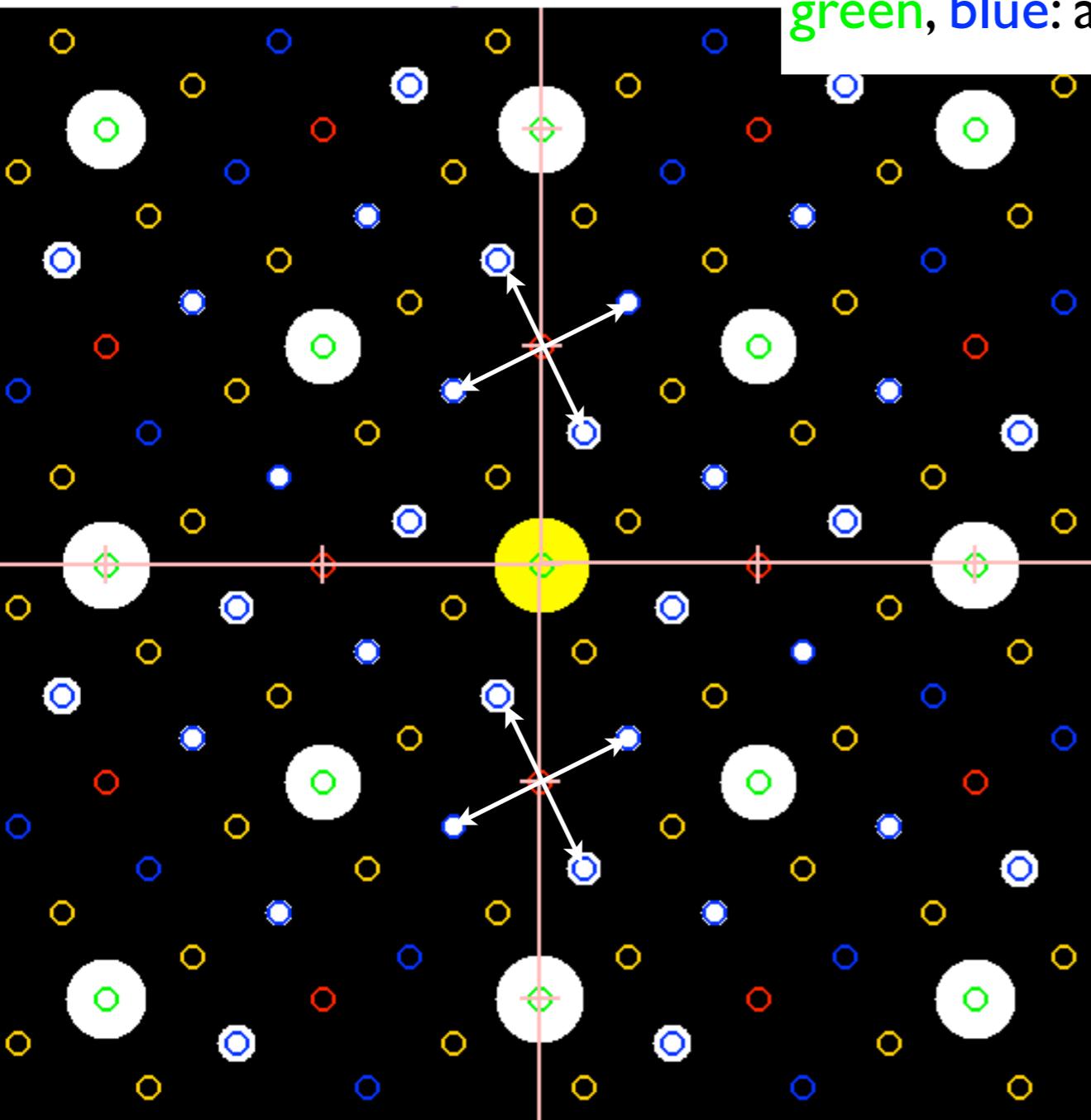


HOL slice. Supercell. Soft classification of peaks

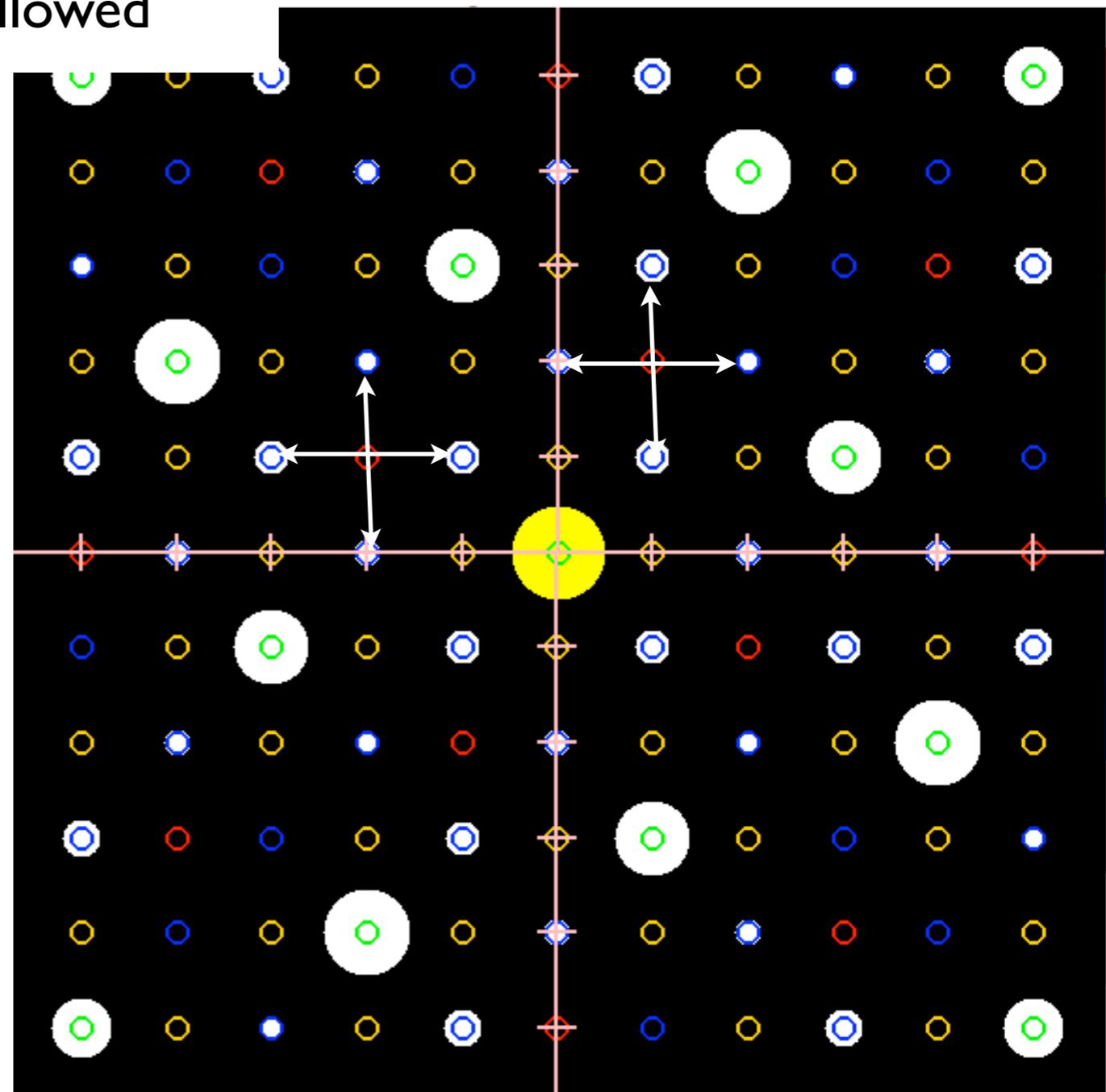


Crystal structure distortion in L=0 plane according to refined structure parameters

(HK0) parent cell

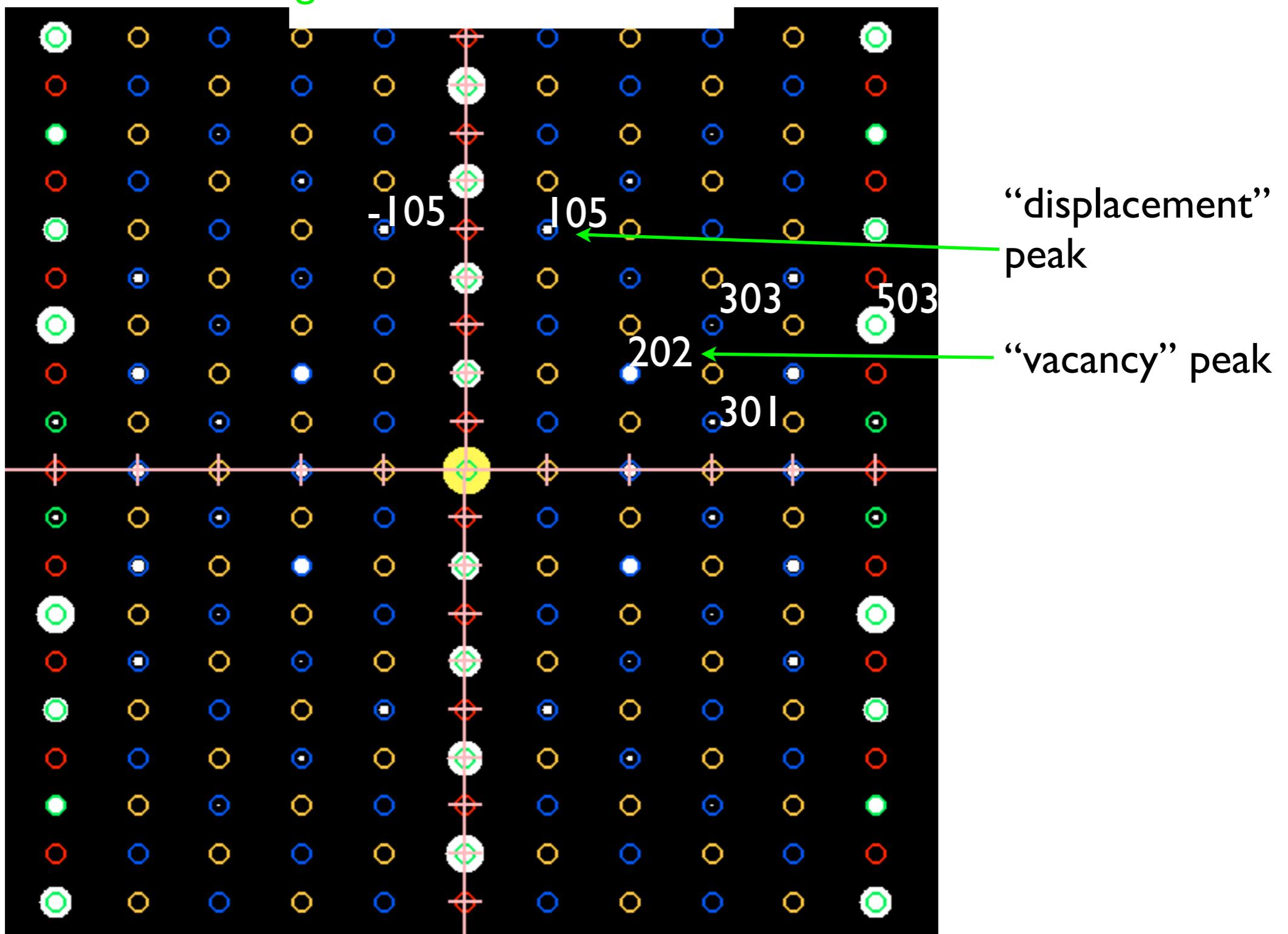


(HK0) supercell

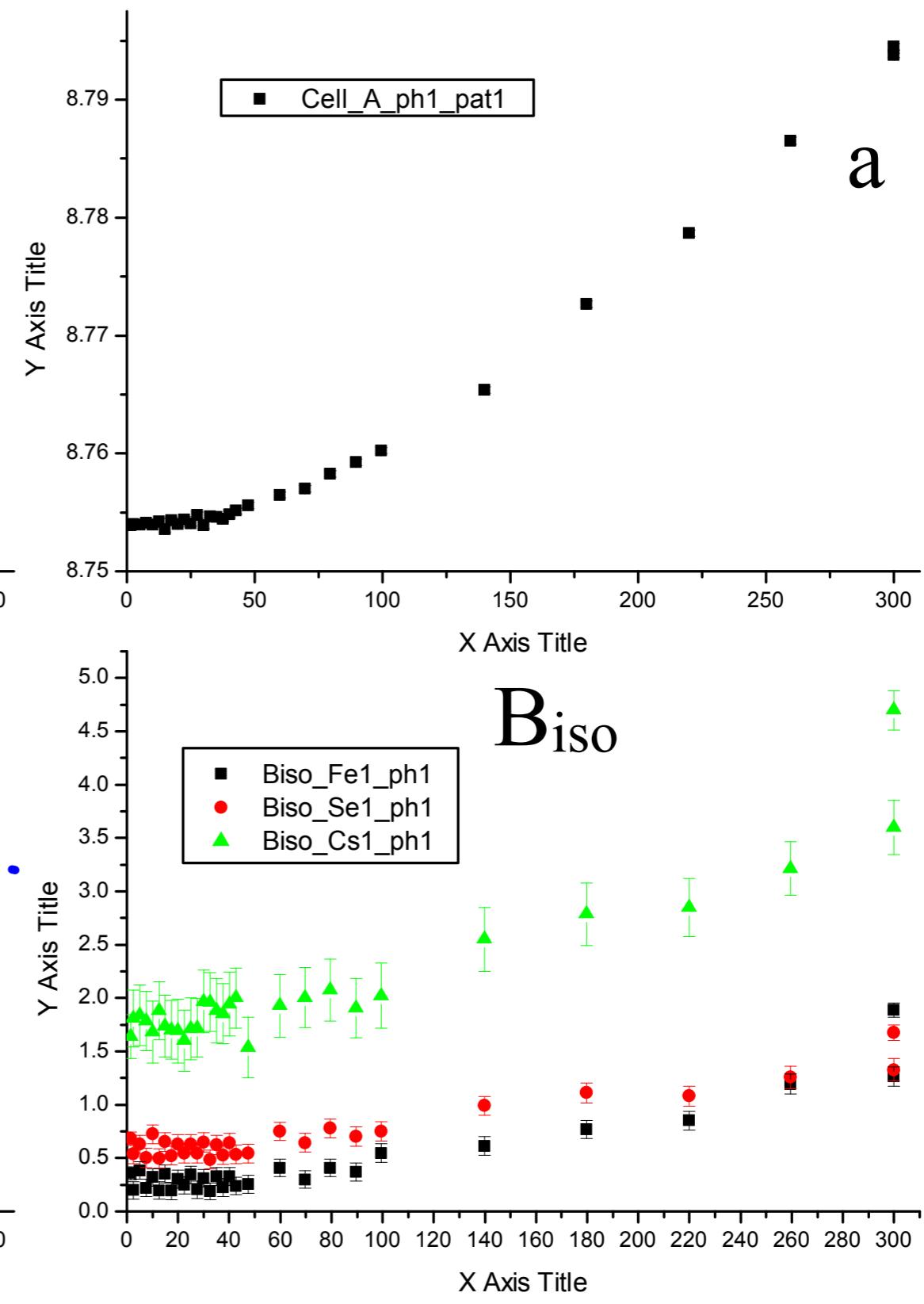
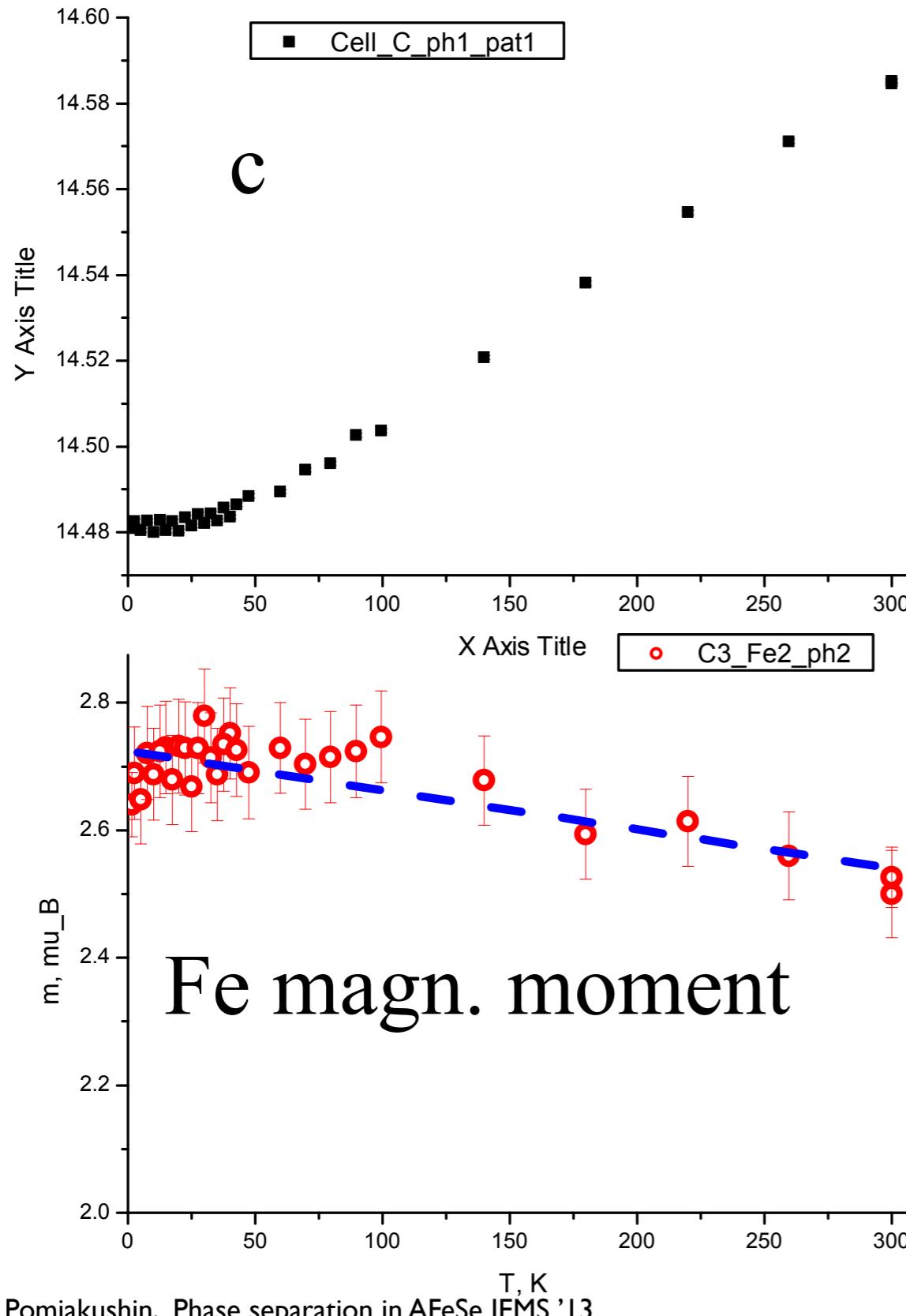


Crystal structure distortion in $\kappa=0$ plane (H0L) supercell

red, orange: forbidden
green, blue: allowed



No visible anomaly at T_c



Fe magn. moment

Parent compounds. FeSe/Tl_y(Fe_{2-x}Se₂)

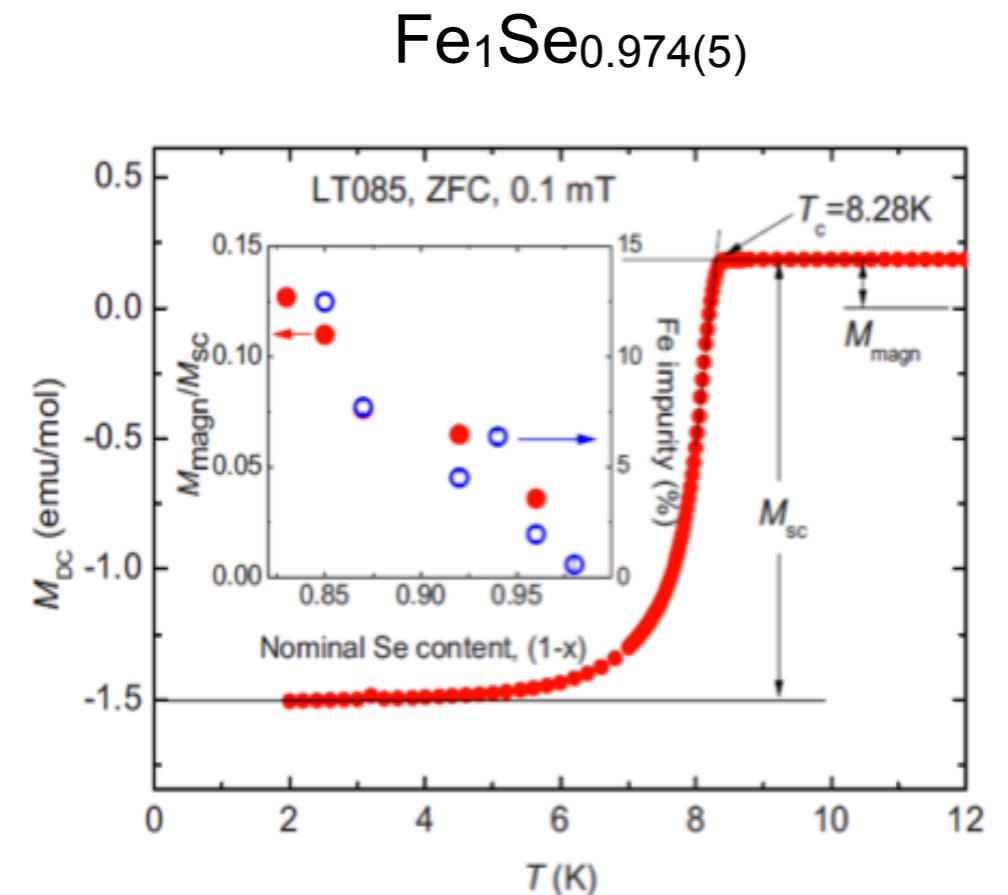
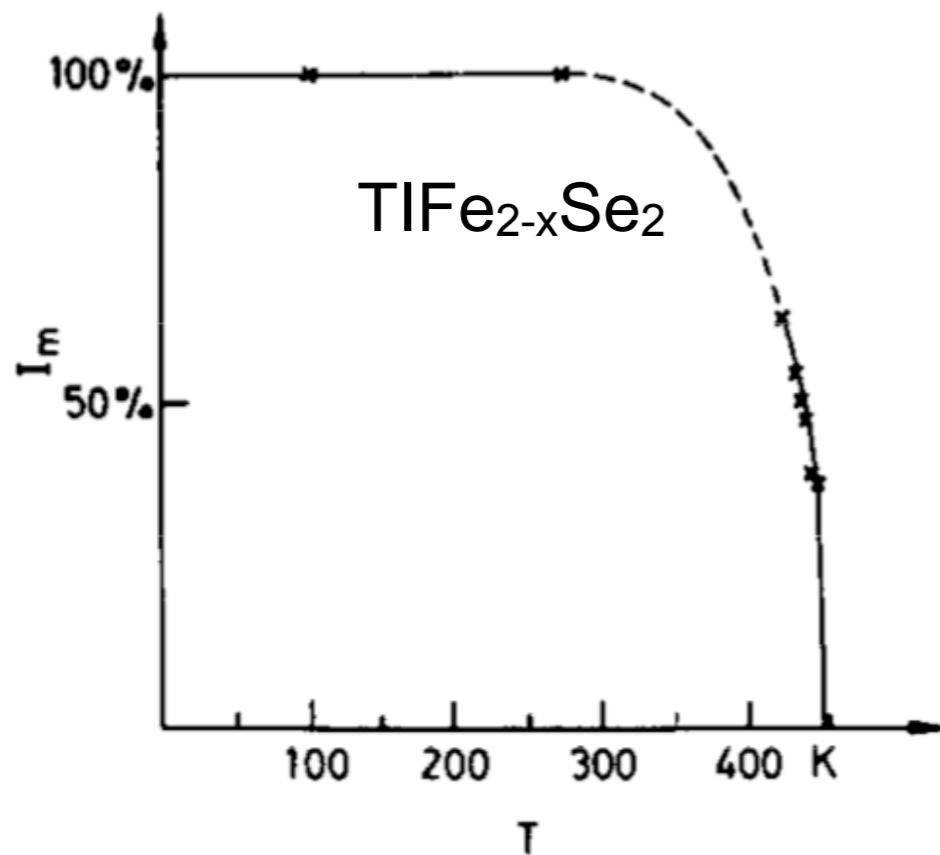


FIG. 5. Relative intensity of the magnetic main component as a function of temperature.

E. Pomjakushina et al (2009)

L. HÄGGSTRÖM, et al (1986)
H. Sabrowsky et al (1986)

Mossbauer and x-ray studies on a mosaic of single crystals of $\text{TlFe}_{2-x}\text{Se}_2$