Indexing powder X-ray diffraction data

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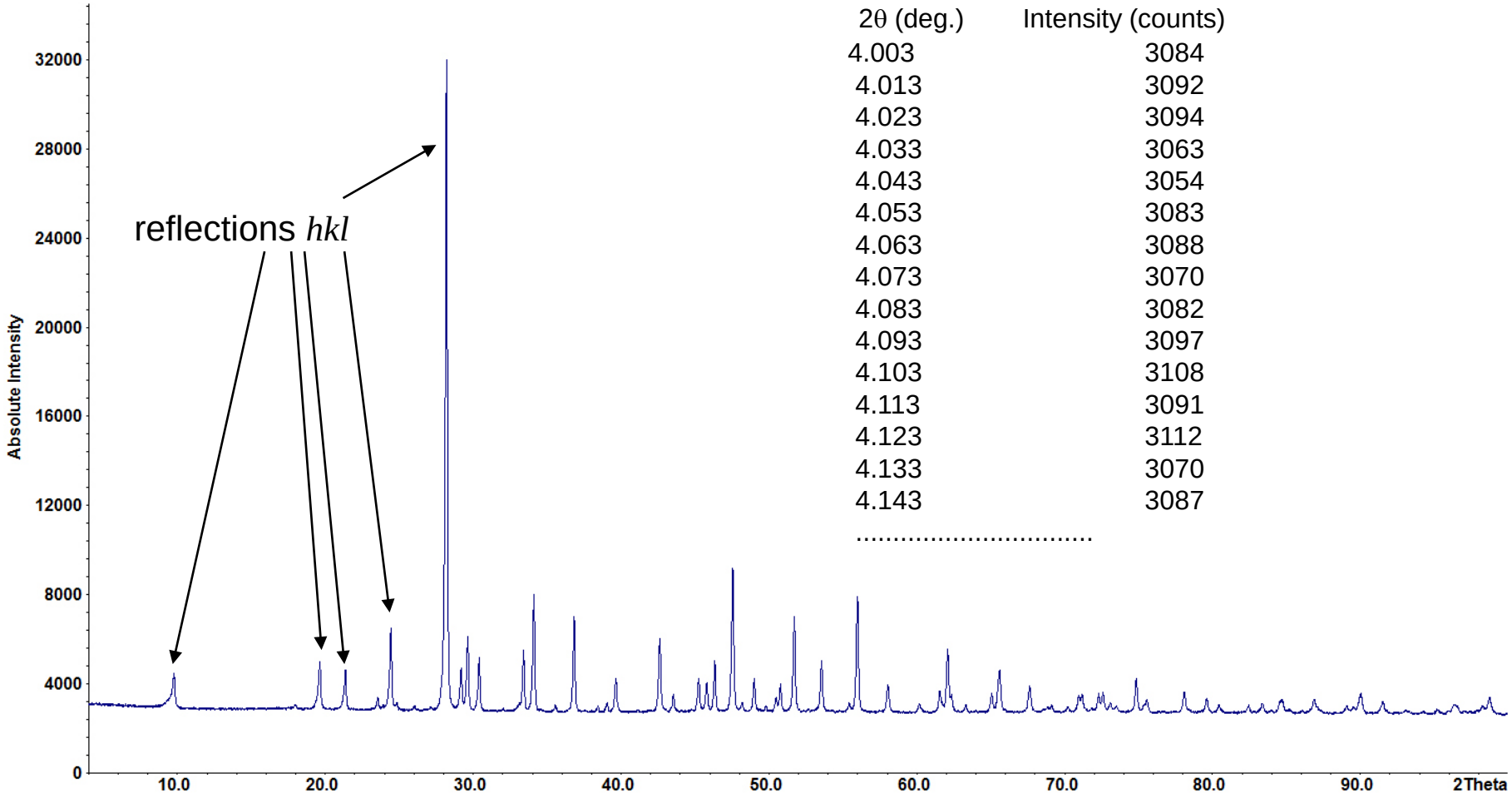
X-ray powder diffraction pattern



2θ (deg.)	Intensity (counts)
4.003	3084
4.013	3092
4.023	3094
4.033	3063
4.043	3054
4.053	3083
4.063	3088
4.073	3070
4.083	3082
4.093	3097
4.103	3108
4.113	3091
4.123	3112
4.133	3070
4.143	3087
.....	

$2d_{hkl} \sin\theta = n\lambda$

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d_{hkl} and the unit cell parameters $a,b,c,\alpha,\beta,\gamma$

triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90^o$

$$\frac{1}{d_{hkl}^2} = \frac{1}{s}\left[\left(\frac{h\sin\alpha}{a}\right)^2 + \left(\frac{k\sin\beta}{b}\right)^2 + \left(\frac{l\sin\gamma}{c}\right)^2 + 2\frac{hk}{ab}(\cos\alpha\cdot\cos\beta - \cos\gamma) + \right.$$
$$\left. + 2\frac{lh}{ca}(\cos\gamma\cdot\cos\alpha - \cos\beta) + 2\frac{kl}{bc}(\cos\beta\cdot\cos\gamma - \cos\alpha)\right]$$

$$s = 1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma$$

monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90^o$, $\beta \neq 90^o$

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2\sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2\sin^2\beta} - \frac{2hl\cos\beta}{ac\sin^2\beta}$$

hexagonal
$a = b \neq c$
$\alpha = \beta = 90^o\ \gamma = 120^o$

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\frac{h^2 + k^2 + hk}{a^2} + \frac{l^2}{c^2}$$

orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^o$

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90^o$

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

cubic
$a = b = c$
$\alpha = \beta = \gamma = 90^o$

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

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Indexing X-ray powder diffraction pattern

Indexing – assigning *hkl* indexes and calculating the lattice parameters

Problems:

- crystal system is not known: which formula to use?

- both *hkl* and $a,b,c,\alpha,\beta,\gamma$ are not known

the problem does not have a unique solution

> Indexing is more an art than a science
>
> A. Le Bail

Cubic structures

Everybody can manually index XRD pattern of a cubic structure

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \qquad \frac{10^4}{d_{hkl}^2} = \mathrm{Q}, \quad \frac{10^4}{a^2} = \mathrm{A} \qquad \mathrm{Q} = \mathrm{A}(h^2 + k^2 + l^2)$$

indexation is based on analyzing Q series

cubic lattice with a = 10 Å

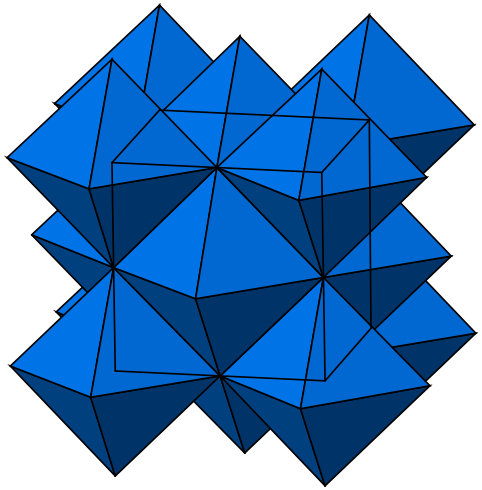
d, Å	Q	hkl (primitive)	Series	hkl (I-centered)	Series	hkl (F-centered)	Series
10.0000	100	100	1	-		-	
7.07106	200	110	2	110	2	-	
5.7735	300	111	3	-		111	3
5.0000	400	200	4	200	4	200	4
4.4721	500	210	5	-		-	
4.0824	600	211	6	211	6	-	
3.5355	800	220	8	220	8	220	8
3.3333	900	300, 221	9			-	
3.1622	1000	310	10	310	10	-	

Tetragonal and hexagonal structures

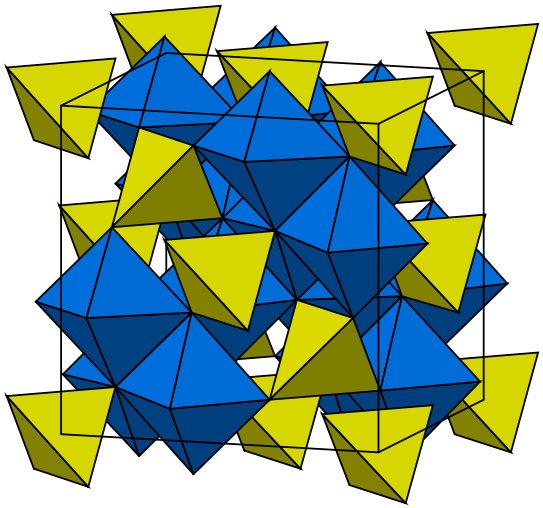
Q series for the tetragonal and hexagonal systems

$hk0$ (tetragonal)	h^2+k^2	$hk0$ (hexagonal)	h^2+k^2+hk	$00l$	l^2
100	1	100	1	001	1
110	2	110	3	002	4
200	4	200	4	003	9
210	5	210	7	004	16
220	8	300	9	005	25
300	9	220	12	006	36
310	10	310	13	007	49
320	13	400	16	008	64
400	16	320	19	009	81

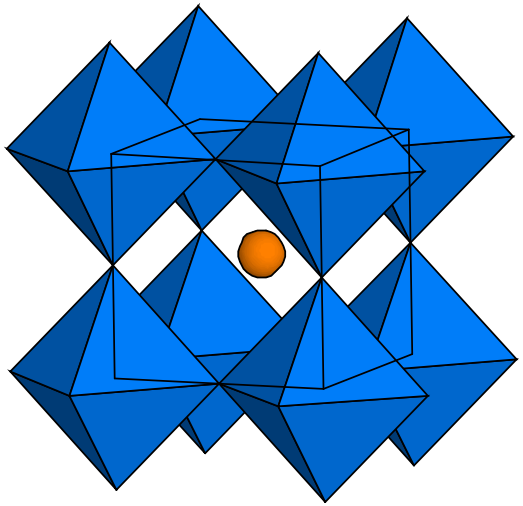
Prototype cubic structures



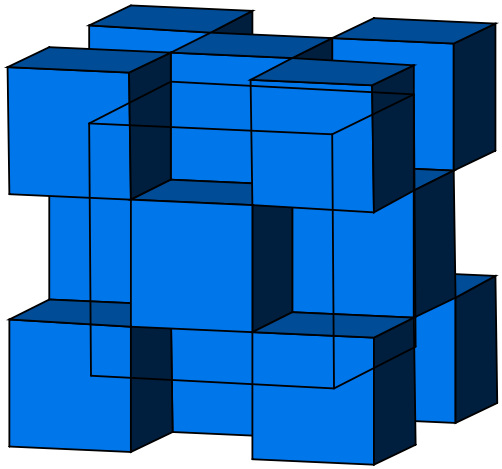
rock salt



spinel

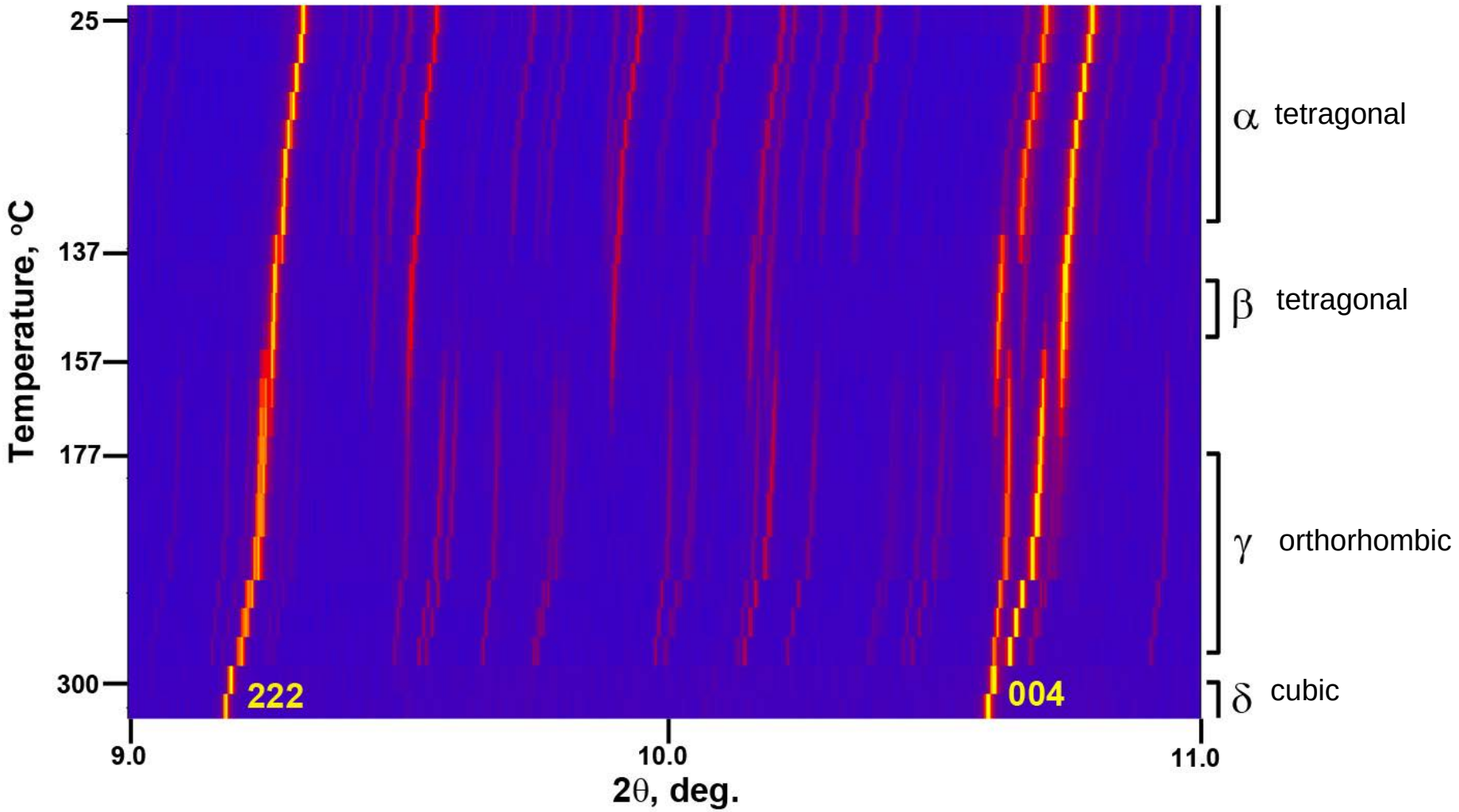


perovskite



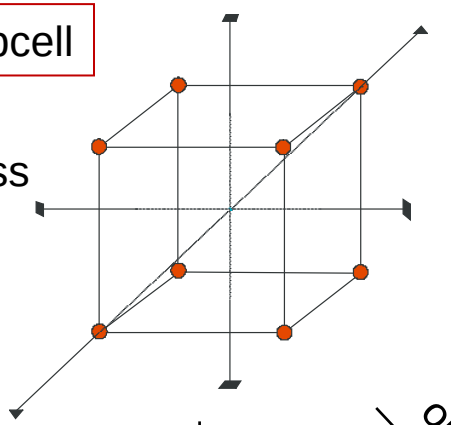
fluorite

Symmetry lowering and reflection splitting



Symmetry lowering and reflection splitting

cubic subcell

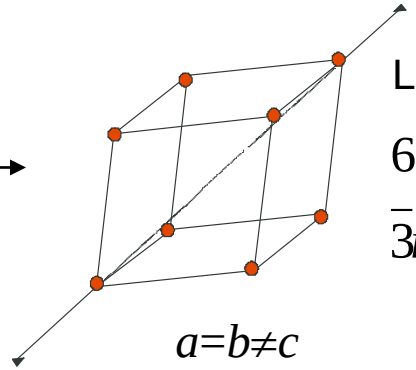


Laue class

$m\bar{3}m$

$m\bar{3}$

rhombohedral



Laue class

$6/mmm$, $6/m$

$\bar{3}m$, $\bar{3}$

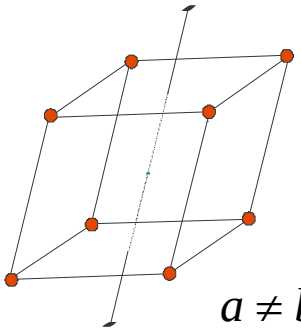
$a=b\neq c$

$\alpha=\beta=90°$; $\gamma=120°$

monoclinic

tetragonal

orthorhombic



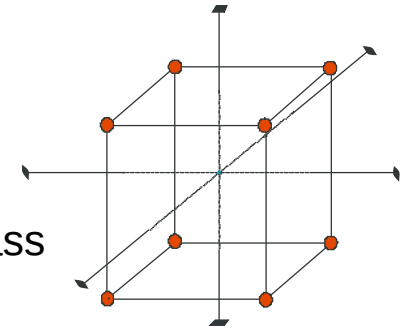
Laue class

$2/m$

$a \neq b \neq c$

$\alpha=\gamma=90°$

$\beta \neq 90^o$



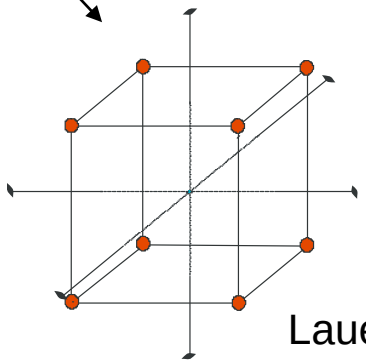
Laue class

$4/mmm$

$4/m$

$a=b\neq c$

$\alpha=\beta=\gamma=90°$



Laue class

mmm

$a \neq b \neq c$

$\alpha=\beta=\gamma=90°$

we keep the unit cell volume nearly the same

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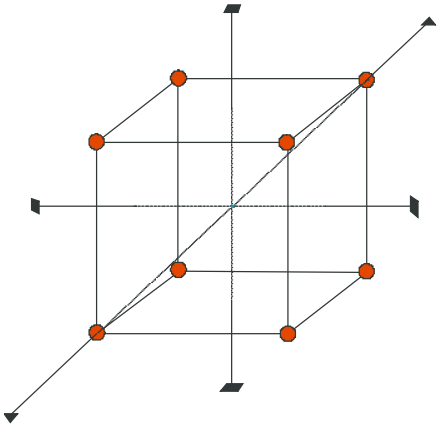
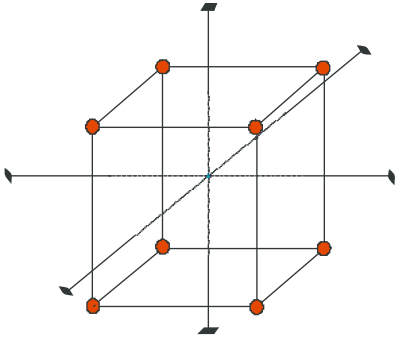
Symmetry lowering and reflection splitting



tetragonal distortion

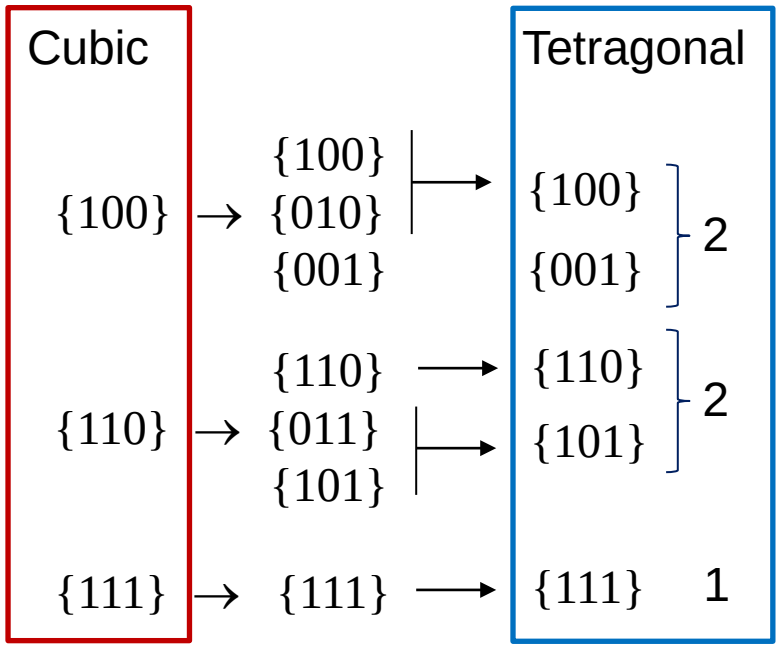


$a=b\neq c$

$\alpha=\beta=\gamma=90°$

Tetragonal distortion

$$\frac{1}{d_{hkl}^2}=\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}$$



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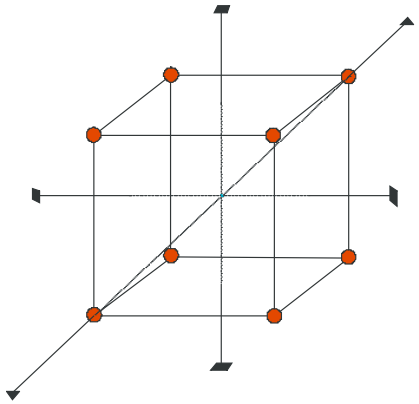
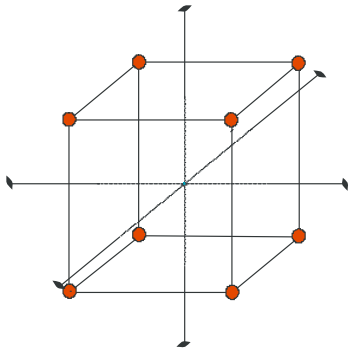
Symmetry lowering and reflection splitting



orthorhombic distortion



$a \neq b \neq c$

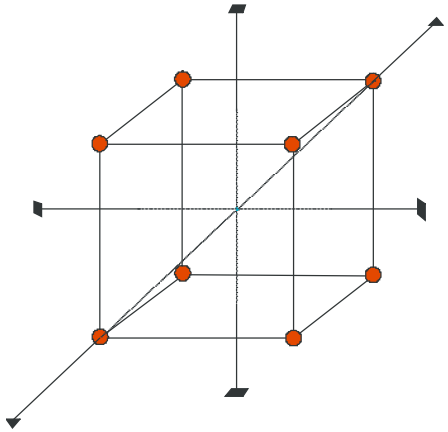
$\alpha=\beta=\gamma=90°$

Orthorhombic distortion

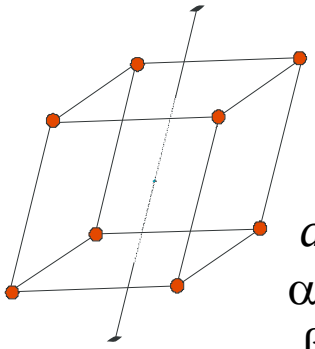
$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Cubic		Orthorhombic	
{100}	→ {100}	{100}	3
	→ {010}	{010}	
	→ {001}	{001}	
{110}	→ {110}	{110}	3
	→ {011}	{011}	
	→ {101}	{101}	
{111}	→ {111}	{111}	1

Symmetry lowering and reflection splitting



monoclinic distortion



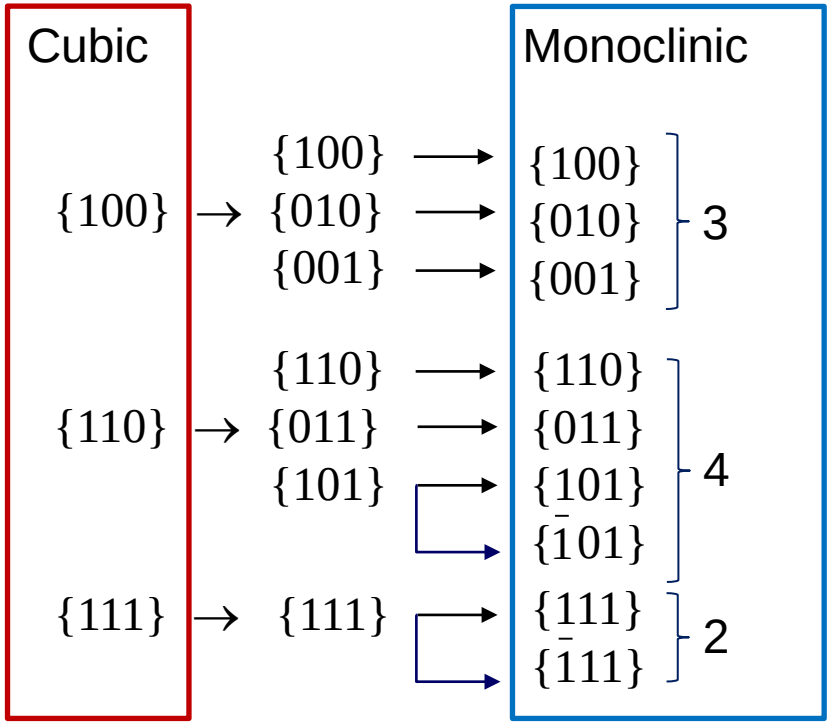
$a \neq b \neq c$

$\alpha=\gamma=90°$

$\beta \neq 90^{o}$

Monoclinic distortion

$$\frac{1}{d^2_{hkl}} = h^2a^{*2}+k^2b^{*2}+l^2c^{*2}+2lhc^*a^*\cos\beta^*$$



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Intensities of split reflections

We assume that the structure distortion does not significantly change the intensities of the reflections.

Relative intensities of the split reflections depend on their multiplicities.

Multiplicity is the number of reflections which superimpose in the same diffraction peak and can not be principally resolved.

In the cubic system:

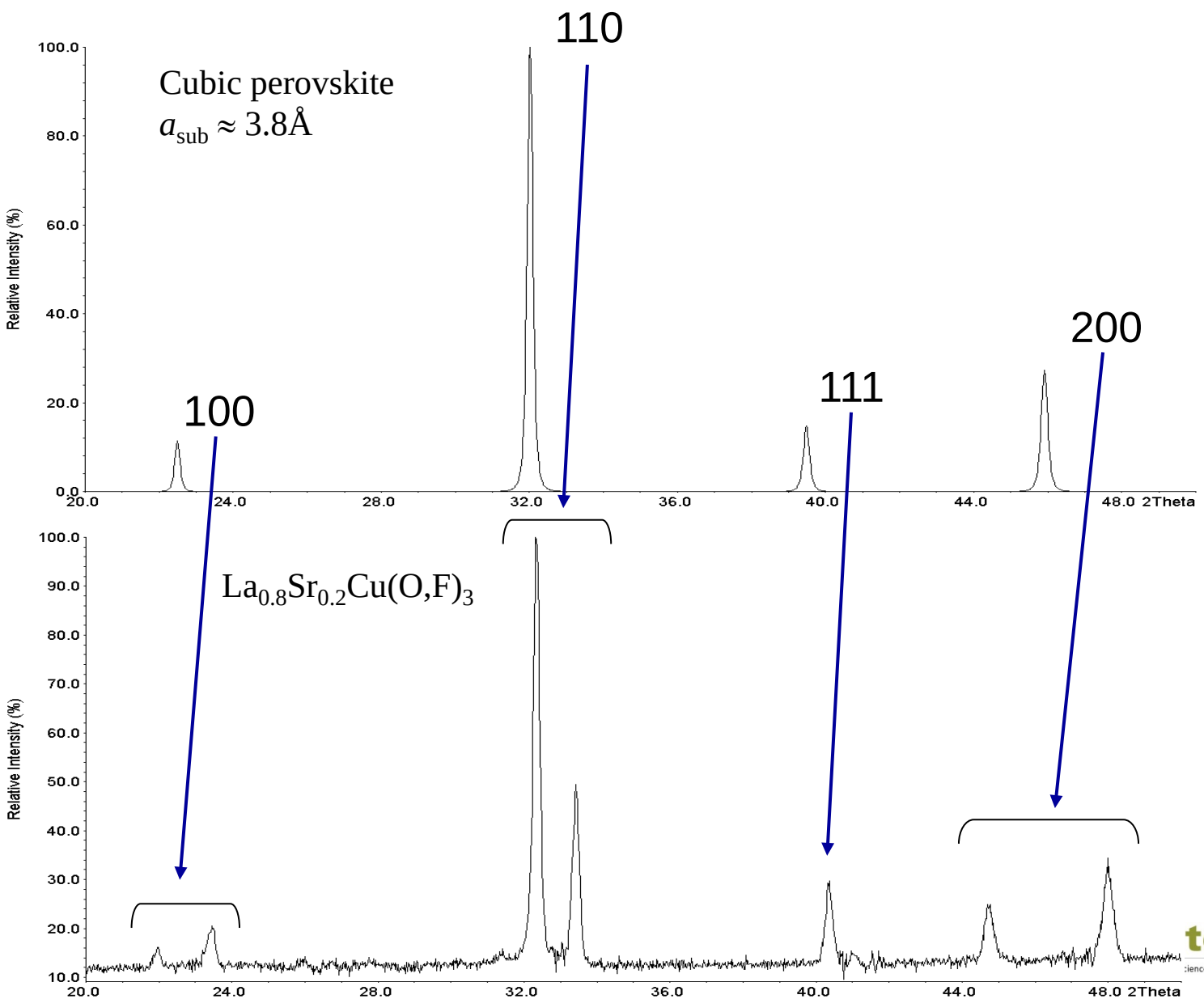
{100} = 100, 010, 001, $\bar{1}00$, $0\bar{1}0$, $00\bar{1}$ – multiplicity 6

{110} = 110, 101, 011, $\bar{1}10$, $10\bar{1}$, $0\bar{1}1$, $1\bar{1}0$, $\bar{1}01$, $01\bar{1}$, $\bar{1}\bar{1}0$, $\bar{1}0\bar{1}$, $0\bar{1}\bar{1}$ – multiplicity 12

{111} = $\bar{1}11$, $1\bar{1}1$, $11\bar{1}$, $\bar{1}\bar{1}1$, $\bar{1}1\bar{1}$, $1\bar{1}\bar{1}$, $\bar{1}\bar{1}\bar{1}$, 111 – multiplicity 8

If the reflection with multiplicity m = q + p splits into two reflections with multiplicities q and p, the ratio between their intensities will be nearly equal to q/p.

Example 1


110
Cubic perovskite
$a_{sub} \approx 3.8$Å
200
111
100
Relative Intensity (%)
100.0
80.0
60.0
40.0
20.0
0.0
20.0
24.0
28.0
32.0
36.0
40.0
44.0
48.0 2Theta
$La_{0.8}Sr_{0.2}Cu(O,F)_3$
Relative Intensity (%)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
20.0
24.0
28.0
32.0
36.0
40.0
44.0
48.0 2Theta

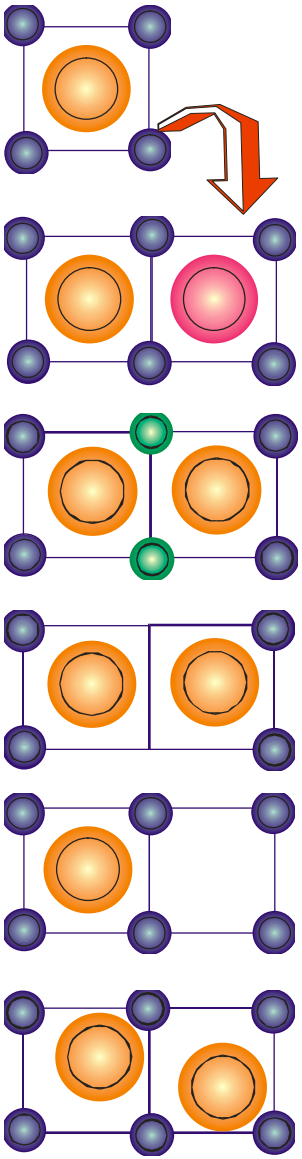
Example 1

d, Å	I, %	Q	$Q_{subcell}$	$hkl_{subcell}$	Splitting	hkl
4.0453	4.4	611	653	100	001	001
3.7931	10.8	695			100, 010	100
2.7661	100.0	1307	1350	110	101, 011	101
2.6791	41.2	1393			110	110
2.2332	18.1	2005	2005	111	111	111
2.0242	13.8	2440	2613	200	002	002
1.8940	23.1	2787			200, 020	200

1. Analyzing Q series for the subcell gives sublattice type – cubic primitive
2. Splitting type corresponds to tetragonal distortion of the subcell
3. Intensity ratio between the split reflections allows assigning the multiplicity factors and *hkl* indexes
4. Refinement of the lattice parameters:

   a = 3.7893(7)Å, c = 4.048(1)Å

Superstructure



periodic perturbation of the parent structure due to different reasons reducing the translational symmetry

1. Cation ordering

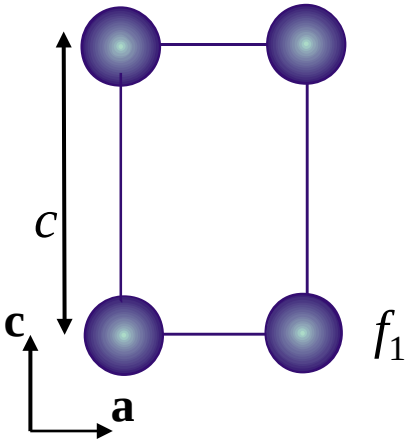
2. Anion ordering

3. Ordering of anion vacancies

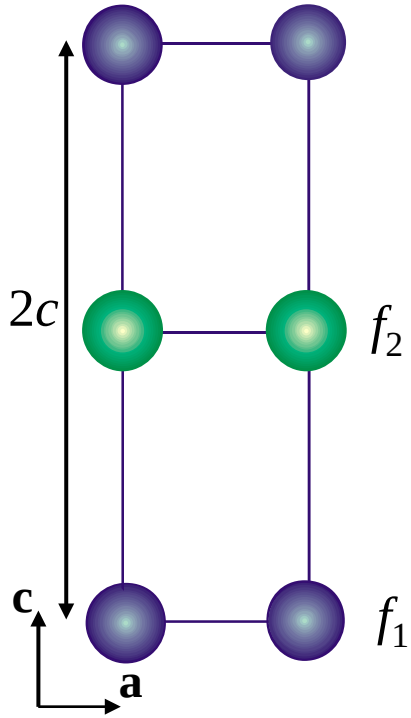
4. Ordering of cation vacancies

5. Atomic displacements

Subcell and supercell reflections



parent structure: the atom with the scattering factor f_1 at 0,0,0



superstructure: the atom with the scattering factor f_1 at 0,0,0 and the atom with the scattering factor f_2 at 0,0,1/2

$$F(\mathbf{H}_{hkl}) = \sum_{j=1}^{N} f_j e^{i2\pi \mathbf{H}_{hkl}\cdot\mathbf{r}_j} =$$

$$= f_1 + f_2 e^{i\pi l} = f_1 + (-1)^l f_2$$

hkl: $l = 2n$ $\quad F(\mathbf{H}_{hkl}) = f_1 + f_2$ - subcell reflections

hkl: $l \neq 2n$ $\quad F(\mathbf{H}_{hkl}) = f_1 - f_2$ - supercell reflections

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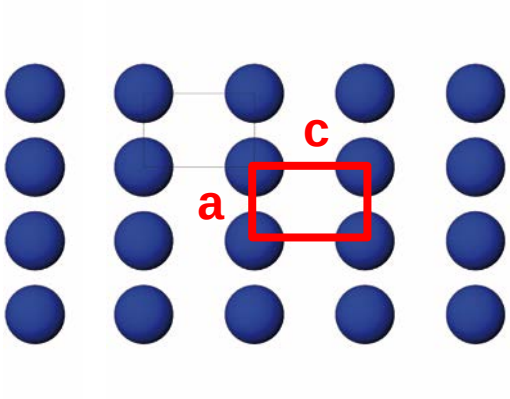
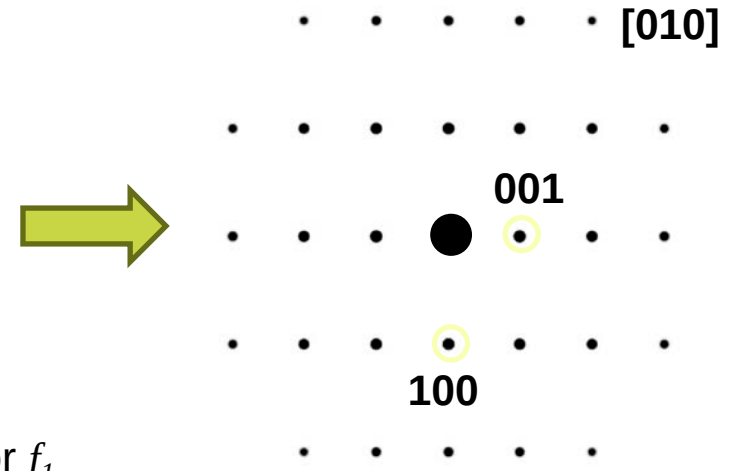
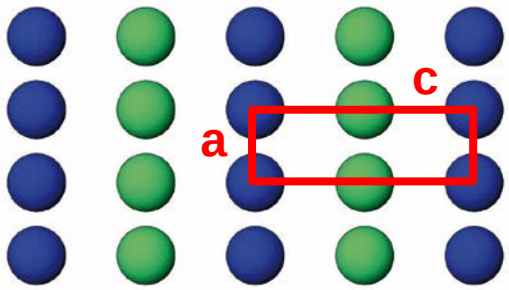
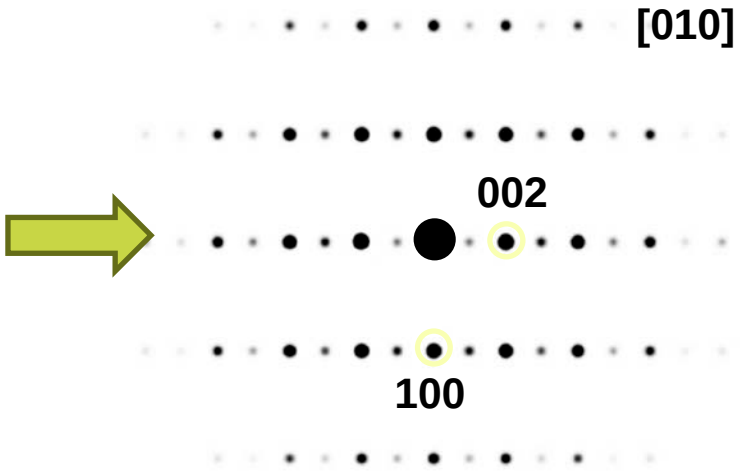
Subcell and supercell reflections





One atom with the scattering factor f_1





Alternation of atoms with f_1 and f_2

Subcell and supercell reflections

1. Superstructure is generally related to multiple increase of the unit cell volume:
- determinant of the transformation matrix > 1

2. Intensities of superlattice reflections depend strongly on the degree of deviation from the substructure.

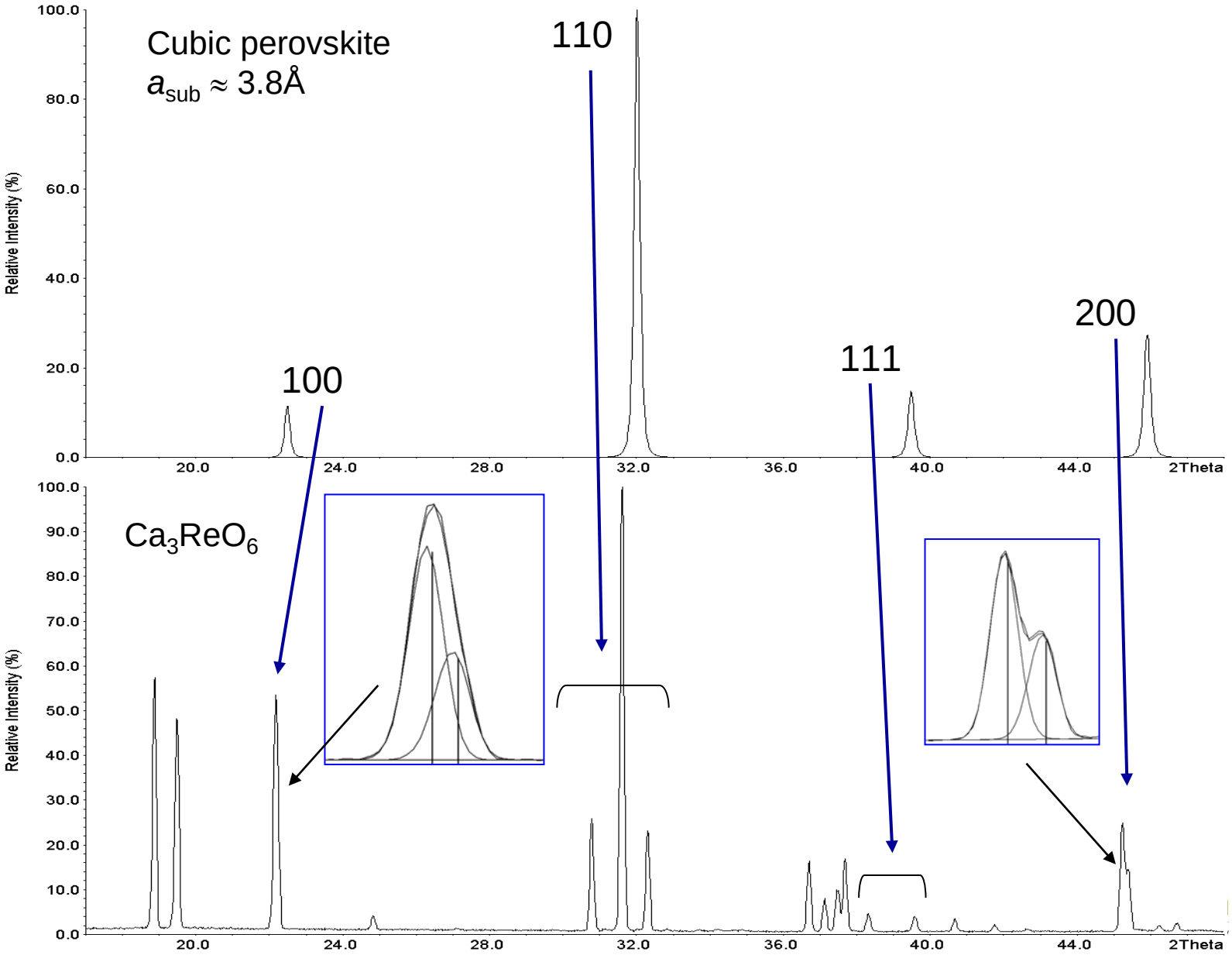
3. Transformation matrix shows the relationships between the subcell and supercell vectors

Tetragonal *a*<*c*

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

Subcell	Supercell
	001
100	
002	
	101
110	
102	
	111
	103
112	
	113

Example 2


Cubic perovskite
$a_{sub} \approx 3.8$Å
110
100
111
200
Relative Intensity (%)
2Theta
Ca_3ReO_6

Example 2

d, Å	I, %	Q	$Q_{subcell}$	$hkl_{subcell}$	Splitting	hkl_{sub}
4.6935	56.8	454				
4.5473	50.5	484				
4.0057	44.8	623	626	100	100, 001	100, 001
3.9920	23.1	628			010	010
3.5803	3.2	780				
2.9008	25.1	1188	1248	110	101	101
2.8270	100.0	1251			011, 110, $\bar{1}10$, $01\bar{1}$	011, 110
2.7676	22.9	1305			$10\bar{1}$	$10\bar{1}$
2.4460	15.1	1671				
2.4190	6.9	1709				
2.3972	9.7	1740				
2.3845	16.0	1759				
2.3465	3.8	1816	1874	111	111	111
2.2745	3.4	1932			$11\bar{1}$	$11\bar{1}$
2.2160	2.6	2036				
2.1609	1.4	2141				
2.1180	0.6	2229				
2.0026	24.4	2493	2502	200	200, 002	200, 002
1.9957	13.8	2511			020	020

1. Sublattice type – cubic primitive
2. Splitting type corresponds to monoclinic distortion of the subcell (111 reflection is split)
3. Indexing the reflections according to their multiplicity factors

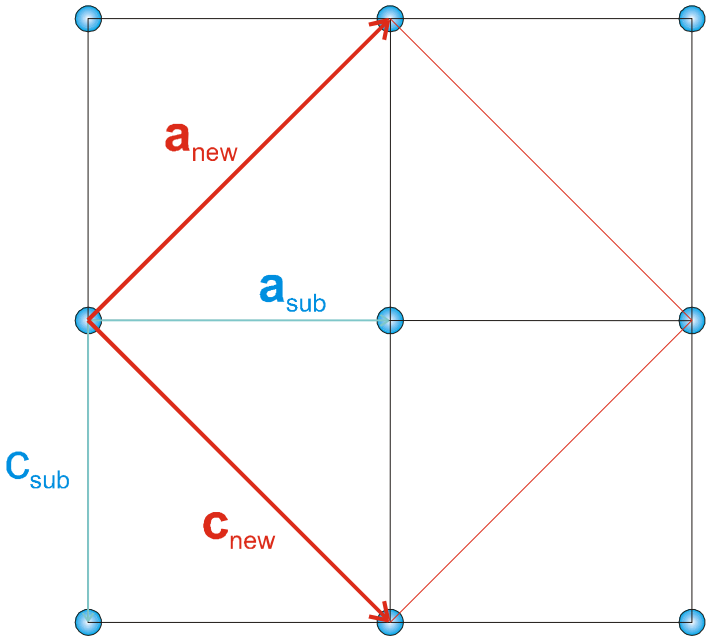
   ⇓

   monoclinic unit cell (*b*-setting) with *a*=*c*
4. Refinement of the lattice parameters:

   a = 4.0099(8)Å,
   b = 3.9917(4)Å
   c = 4.0095(7)Å
   β = 92.695(6)°

Example 2

For the monoclinic unit cell with *a*=*c* we can always find an orthorhombic unit cell of larger volume



monoclinic *P* $\Rightarrow$ orthorhombic *B*

$$\begin{pmatrix} \mathbf{a}_{new} \\ \mathbf{b}_{new} \\ \mathbf{c}_{new} \end{pmatrix} = \begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_{sub} \\ \mathbf{b}_{sub} \\ \mathbf{c}_{sub} \end{pmatrix}$$

$$\det = 2$$

$$\mathbf{a}_{new} = \mathbf{a}_{sub} - \mathbf{c}_{sub}$$
$$\mathbf{b}_{new} = \mathbf{b}_{sub}$$
$$\mathbf{c}_{new} = \mathbf{a}_{sub} + \mathbf{c}_{sub}$$

Example 2

d, Å	I, %	Q	$Q_{subcell}$	$hkl_{subcell}$	Splitting	hkl_{sub}	hkl_{new}
4.6935	56.8	454					
4.5473	50.5	484					
4.0057	44.8	623	626	100	100, 001	100, 001	101
3.9920	23.1	628			010	010	010
3.5803	3.2	780					
2.9008	25.1	1188	1248	110	101	101	002
2.8270	100.0	1251			011, 110, $\bar{1}10$, $01\bar{1}$	011, 110	111
2.7676	22.9	1305			$10\bar{1}$	$\bar{1}01$	200
2.4460	15.1	1671					
2.4190	6.9	1709					
2.3972	9.7	1740					
2.3845	16.0	1759					
2.3465	3.8	1816	1874	111	111	111	012
2.2745	3.4	1932			$11\bar{1}$	$11\bar{1}$	210
2.2160	2.6	2036					
2.1609	1.4	2141					
2.1180	0.6	2229					
2.0026	24.4	2493	2502	200	200, 002	200, 002	202
1.9957	13.8	2511			020	020	020

Lattice parameters of the new *B*-centered orthorhombic unit cell:

a_{new} = 5.5363(3)Å,

b_{new} = 3.9921(3)Å

c_{new} = 5.8022(4)Å

What to do with other unindexed reflections?

We will treat them as supercell reflections.

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Example 2

d, Å	I, %	Q	$Q_{subcell}$	$hkl_{subcell}$	Splitting	hkl	hkl_{new}	hkl_{ss}
4.6935	56.8	454						011
4.5473	50.5	484						110
4.0057	44.8	623	626	100	100, 001	100, 001	101	101
3.9920	23.1	628			010	010	010	020
3.5803	3.2	780						111
2.9008	25.1	1188	1248	110	101	101	002	002
2.8270	100.0	1251			011, 110, $\bar{1}10$, $01\bar{1}$	011, 110	111	121
2.7676	22.9	1305			$10\bar{1}$	$\bar{1}01$	200	200
2.4460	15.1	1671						112
2.4190	6.9	1709						031
2.3972	9.7	1740						130
2.3845	16.0	1759						211
2.3465	3.8	1816	1874	111	111	111	012	022
2.2745	3.4	1932			$11\bar{1}$	$11\bar{1}$	210	220
2.2160	2.6	2036						131
2.1609	1.4	2141						122
2.1180	0.6	2229						221
2.0026	24.4	2493	2502	200	200, 002	200, 002	202	202
1.9957	13.8	2511			020	020	020	040

Searching for the supercell is not trivial.

Low angle reflections are the most important.

Check possible multiplication of subcell axes lengths.

Check different possibilities of simple *hkl* for low angle reflections.

Check relationships between the low angle and subcell reflections.

In this case – doubling of *b*-parameter:
Q_{010} = 628/4 = 157
Q_{011} = 157 + 1188/4 = 454 – first low angle reflection
Q_{110} = 157 + 1305/4 = 483 – second low angle reflection

Final refinement of the lattice parameters:

a = 5.5366(3)Å,
b = 7.9845(4)Å
c = 5.8022(3)Å

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Subcell and supercell

Transformation matrix

$$\mathbf{A'} = \mathbf{M} \times \mathbf{A}$$

$$\begin{pmatrix} \mathbf{a}_{ss} \\ \mathbf{b}_{ss} \\ \mathbf{c}_{ss} \end{pmatrix} = \begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_{sub} \\ \mathbf{b}_{sub} \\ \mathbf{c}_{sub} \end{pmatrix}$$

$$\mathbf{H'} = \mathbf{M} \times \mathbf{H}$$

$$\begin{pmatrix} h_{ss} \\ k_{ss} \\ l_{ss} \end{pmatrix} = \begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} h_{sub} \\ k_{sub} \\ l_{sub} \end{pmatrix}$$

Transformation of the atomic coordinates - inverse transpose of the transformation matrix

$$\mathbf{X'} = (\mathbf{M^T})^{-1} \times \mathbf{X}$$

$$\begin{pmatrix} x_{ss} \\ y_{ss} \\ z_{ss} \end{pmatrix} = \begin{pmatrix} 1/2 & 0 & 1/2 \\ 0 & 1/2 & 0 \\ -1/2 & 0 & 1/2 \end{pmatrix} \begin{pmatrix} x_{sub} \\ y_{sub} \\ z_{sub} \end{pmatrix}$$

You get a starting set of atomic coordinates in the superstructure unit cell for further work.

You can limit the choice of possible space groups by the subgroups of the space groups of the parent structure.

In addition to standard figure-of-merit criteria, the correctness of indexation is confirmed by a clear crystallographic relationship with the prototype structure

Indexing the subcell does not require the peak positions to be very precise – you can do it even if a zero shift is present. Then use the subcell reflections as a reference to refine the zero shift, correct your data and continue.

Splitting patterns

Primitive cubic (*P*)

№	Symmetry	Number of split reflections					
		100	110	111	200	210	211
I	tetragonal	2	2	1	2	3	2
II	trigonal	1	2	2	1	2	3
III	orthorhomb.	3	3	1	3	6	3
IV	orthorhomb.	2	3	2	2	4	4
V	monoclinic	3	4	2	3	8	6
VI	monoclinic	2	4	3	2	6	7
VII	triclinic	3	6	4	3	12	12

Face-centered cubic (*F*)

№	Symmetry	Number of split reflections					
		111	200	220	311	222	400
I	tetragonal	1	2	2	2	1	2
II	trigonal	2	1	2	3	2	1
III	orthorhomb.	2	2	3	4	2	2
IV	orthorhomb.	1	3	3	3	1	3
V	monoclinic	2	3	4	6	2	3
VI	monoclinic	3	2	4	7	3	2
VII	triclinic	4	3	6	12	4	3

Body-centered cubic (*I*)

№	Symmetry	Number of split reflections					
		110	200	211	220	310	222
I	tetragonal	2	2	2	2	3	1
II	trigonal	2	1	3	2	2	2
III	orthorhomb.	3	3	3	3	6	1
IV	orthorhomb.	3	2	4	3	4	2
V	monoclinic	4	3	6	4	8	2
VI	monoclinic	4	2	7	4	6	3
VII	triclinic	6	3	12	6	12	4

Automatic indexing

- trial-and-error method (*TREOR*):

1) assigning *hkl* indexes to a basis set of minimum required number of low angle reflections;
2) attempt to index all other reflections (or at least a fraction of them)

- zone axis search (*ITO*):

1) search for *hkl* indexes belonging to specific zone axes (*hk*0, 00*l* etc, as in the manual method);
2) attempt to index all other reflections (or at least a fraction of them)

Quality assessment criteria:

de Wolff

Q-value for the refl. #20

$$M_{20} = \frac{Q_{20}}{2\bar{\varepsilon} N_{20}}$$

number of possible refl.

$average\ |Q_{exp} - Q_{calc}|$

problem with anysotropic unit cell

Smith & Snyder

number of refl.

$$F_N = \left(\frac{1}{|\Delta 2\theta|}\right)\left(\frac{N}{N_{poss}}\right)$$

average $\Delta 2\theta$

number of possible refl.

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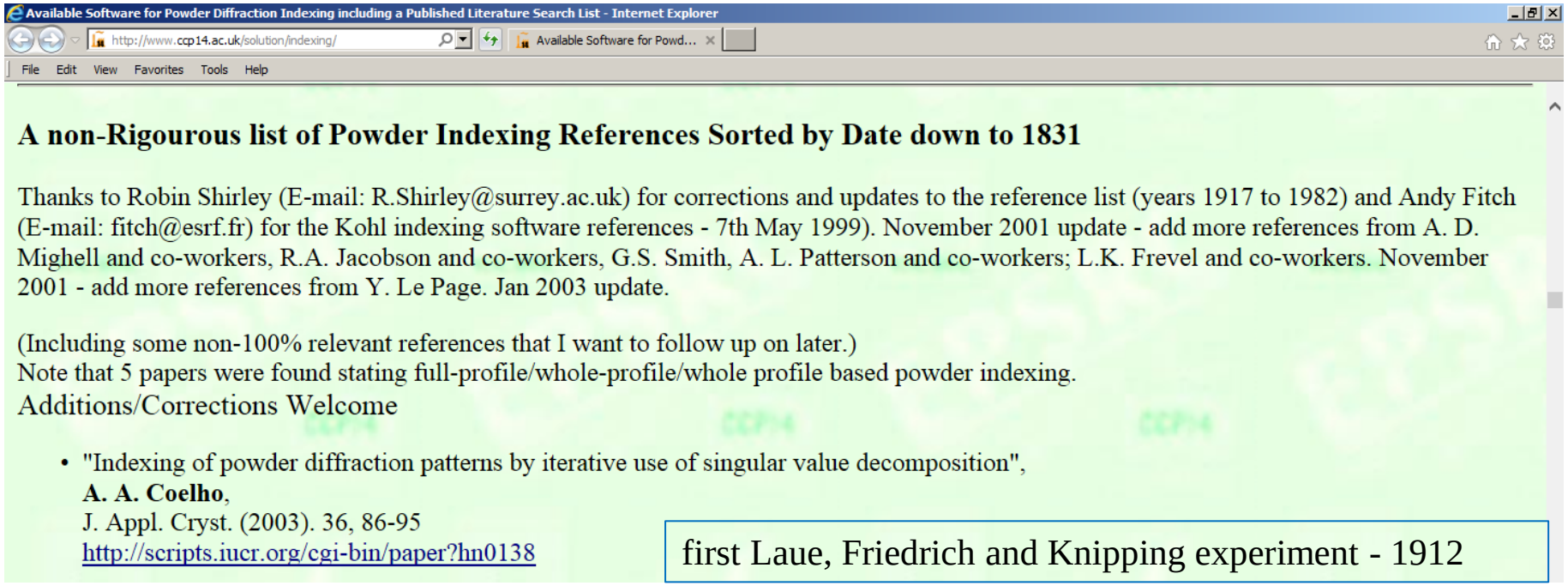
Indexing X-ray powder diffraction pattern



first Laue, Friedrich and Knipping experiment - 1912

Automatic indexing programs:

ITO	J.Visser, J.Appl.Cryst. **2**, 89-95 (1969)
TREOR	P.-E. Werner et. al, J.Appl.Cryst. **18**, 367-370 (1985)
DICVOL	A.Boultif & D.Louèr, J.Appl.Cryst. **24**, 987-993 (1991)