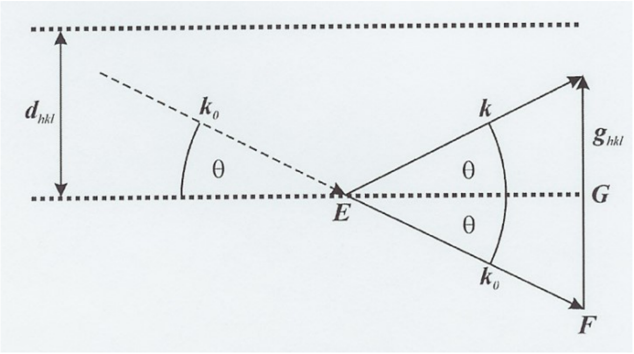
Evaluation of electron diffraction patterns

Evaluation of diffraction is based on elastic, kinematic (single) scattering

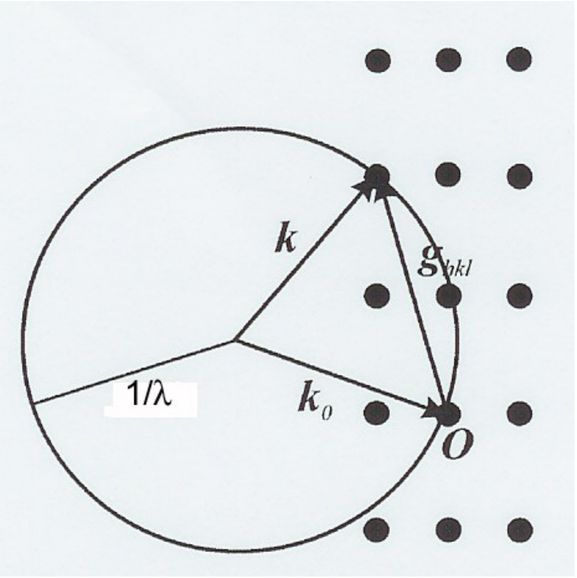
WH Bragg and WL Bragg noticed that when the diffraction condition is fulfilled, the geometry of the direct and scattered beams is like in reflection of light from planes.

The ***Bragg-equation*** expresses condition for the position (angle) of maximum intensities.



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

The above condition for maximum intensity is also expressed in the ***Ewald-construction***



In XRD **2π** is included in the definitions of all reciprocal lattice vectors, like K and g, in ED it is not.

Miller indices

Miller indices define the direction of a set of (real space) lattice planes.

Which set of planes can get Miller indices?

- The planes in the set must be parallel
- The planes must be equidistant (with distance *d* between them)
- All lattice points must lie on one of the planes

How to generate Miller indices for a plane set?

- Distances are measured in units of the base vectors. ⇒ Coordinates of lattice points are integer numbers.
- Select one plane of the set! Determine its intersections with the 3 axes!
  (You get 3 integer numbers.)
- Take the reciprocal of these 3 numbers (results are generally non-integers)!
- Apply a common multiplier to them to obtain integers. The resulting 3 integers are the ***Miller indices*** of the plane set.

Miller indices are also coordinates of reciprocal lattice vectors

If for each of the lattice planes above you draw a vector normal to the plane with length of *1/d*, you get another lattice, which is called the reciprocal lattice. Miller-indices are coordinates of these reciprocal lattice vectors.

The reciprocal lattice vector $\underline{g}_{hkl}=h\underline{b}_1+k\underline{b}_2+l\underline{b}_3$ is normal to the lattice planes of ***Miller indices*** (hkl) with plane-distance d_{hkl} and

$$\left|\underline{g}_{hkl}\right| = \frac{1}{d_{hkl}}$$

Number of symmetrically equivalent reflections

Why assignment of a Miller-index set to a measured d-value is ambiguous:
Symmetry operations of the crystal lattice bring a set of planes with a given d-value into a position, which cannot be distinguished from the original. Consequently, when you measure a d-value, any of the symmetry equivalent Miller indices are compatible with the measured value. However, the reciprocal lattice vectors, which correspond to these symmetry-equivalent Miller-indices point to different directions in space.

For instance, if you take a cube, the {1 0 0} Miller-index type denotes any faces of a cube with their normals pointing outward. Since there are 6 faces, which transform into each other by the symmetry operations of the cube (and cannot be distinguished from each other) the six Miller-indices given by (100), (-100), (010), (0-10), (001) and (00-1) are equivalent. Only one representative, 100 is found in the data sheet. You will need to generate the equivalents yourself when indexing patterns.

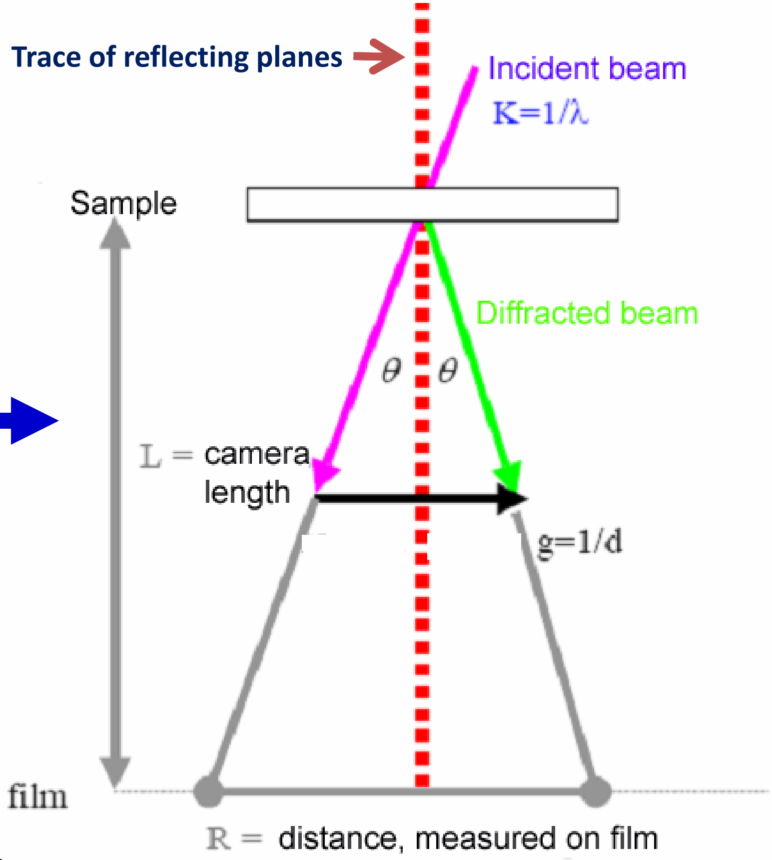
For cubic system you can get the symmetrically equivalent Miller indices by
- Creating permutations of the 3 indices
- Swapping the signs of the indices individually

High energy electron diffraction in TEM

Derivation of the calibration equation

Specialities:

- Thin sample ⇒ no backscattering
- In the smaller triangle (which in reciprocal space) you can recognize Ewald-construction. sinθ=g/(2K).
- The big triangle is in real space. tanθ=R/(2L)
- High energy (short wavelength; λ=0.00251nm @ 200 keV) ⇒ small (<5°) scattering angles ⇒ sinθ≅tanθ

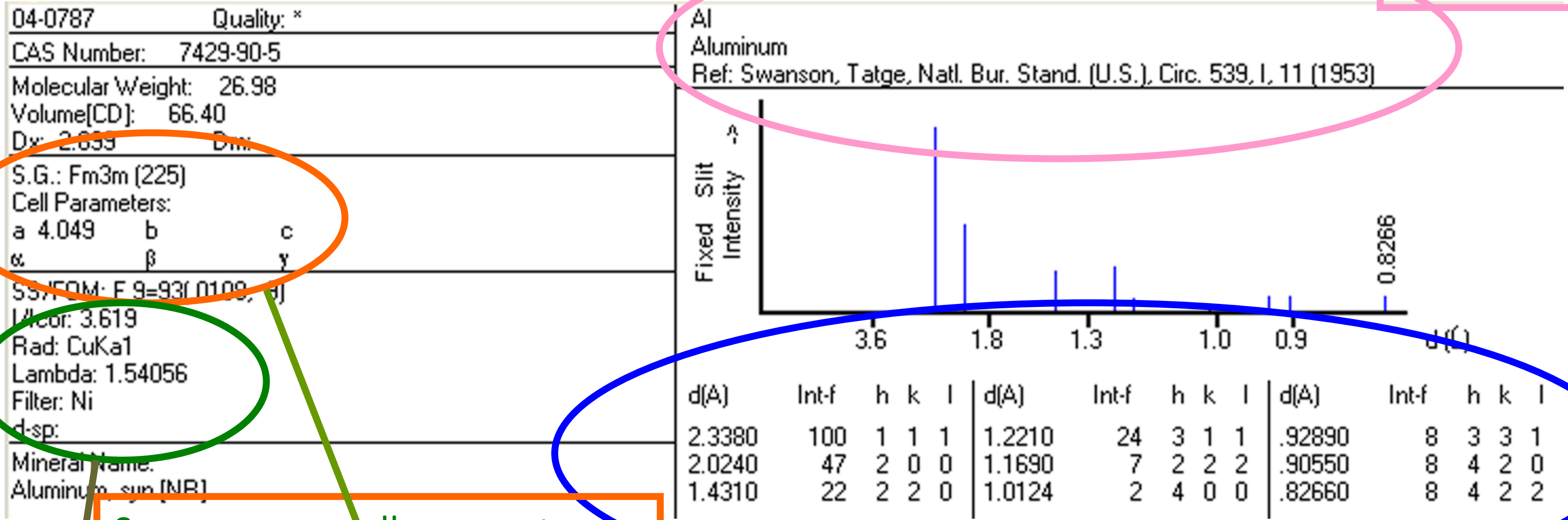


K>>g ==> $$\frac{R}{L} \cong \frac{g}{K} = \frac{\lambda}{d} \cong 2 \cdot \theta$$

Calibration with a known material:
Measure R, take d from datasheet ⇒
d, R ⇒ L

Indexing of unknown:
Take L from calibration, measure R ⇒
L, R ⇒ d

When you determine d-values, you get Miller-indices from XRD datasheets: Pdf-2 / Pdf-4+



04-0787 Quality: *

CAS Number: 7429-90-5

Molecular Weight: 26.98
Volume[CD]: 66.40
Dx: 2.699 Dm:

S.G.: Fm3m (225)
Cell Parameters:
a 4.049 b c
α β γ

SS/FOM: F 9=93(.0109, 9)
I/Icor: 3.619
Rad: CuKa1
Lambda: 1.54056
Filter: Ni
d-sp:

Mineral Name:
Aluminum, syn [NR]

Al
Aluminum
Ref: Swanson, Tatge, Natl. Bur. Stand. (U.S.), Circ. 539, I, 11 (1953)

d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l
2.3380	100	1	1	1	1.2210	24	3	1	1	.92890	8	3	3	1
2.0240	47	2	0	0	1.1690	7	2	2	2	.90550	8	4	2	0
1.4310	22	2	2	0	1.0124	2	4	0	0	.82660	8	4	2	2

Name & reference

Space group, cell parameters

The **first letter** of the SG gives the centering of the Bravais lattice (**P**: primitive, **F**: all face centered, **I**: body centered

d-values, X-ray intensities (irrelevant to SAED), **Miller-indices**

Radiation (X-ray), wavelength, filter (irrelevant data for SAED)

Indexing diffraction patterns from known materials

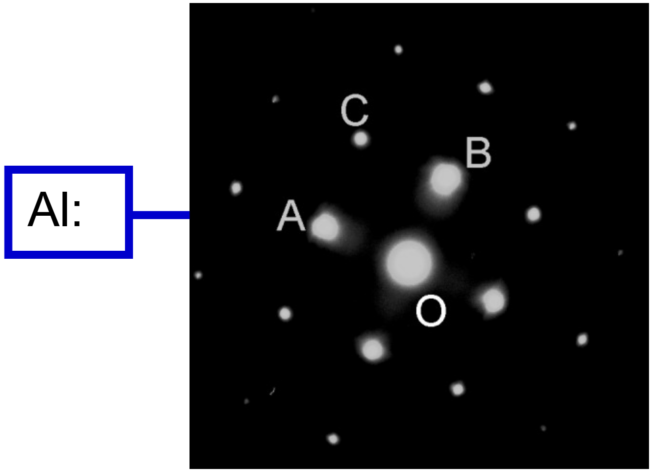
Calibration with a polycrystalline ***ring*** pattern:

- Measure ***radius***es of the consecutive rings (R_j).
- Pair them to the d-values (d_j) from the data-sheet of the material.
- Use $L \cdot \lambda = d_j \cdot R_j$ to determine the camera constant, $L \cdot \lambda$ in [mm·Å] units if you measure with a ruler from prints of the patterns.
- If you process the patterns electronically than distances are measured in pixels and the camera constant $L\lambda$ is in [pixels·Å] units.

Indexing calibrated ***single crystalline spot patterns***:

- Use previously calibrated $L \cdot \lambda$.
- Measure the distances, corresponding to two linearly independent reciprocal vectors (pointing to your diffraction spots) R_j (j=1,2).
- If we could assign Miller indices unambiguously to these measurements, it would be enough, since all the other vectors could be obtained by linear combinations. Due to the presence of symmetry equivalents, we need to constrain selection.
- Measure length of the vector sum of the above two vectors (R_3).
- Determine d_j (j=1-3) for the 3 plane-sets corresponding to the above measured R_j values, using the same calibration equation $L \cdot \lambda = d_j \cdot R_j$.
- Use the data sheet of the material to get the Miller index types for these 3 reflections, $\{h_j\ k_j\ l_j\}$ (j=1,3) .
- Use the fact that you selected the 3rd vector as a vector-sum of the first two to constrain selection of Miller indices from the symmetrically equivalents (permutation and signs).
  i.e. $h_3=h_1+h_2$, $k_3=k_1+k_2$ and $l_3=l_1+l_2$.

Numerical example: Indexing of a single crystal pattern



Steps of indexing

- Calibrate camera constant!
- Select 3 points (A,B,C) which with form a parallelogram with the center (O)!
- Measure the distances OA, OB and OC and convert them to d-values [Angstrom].
- Look up the XRD card to see which Miller index-types correspond to these d-values!
- Select permutation and signs of indices to fulfill vector addition!

Example (Aluminum sample: diffraction pattern to the left and data sheet on the next slide):

d_A=2.03 [Å]; d_B=2.03 [Å]; d_C=1.43 [Å]

XRD card (above) $\Rightarrow$ A, B: {200} type; c: {220} type

Sum of vectors demands that

$h_A+h_B=h_C$; $k_A+k_B=k_C$ and $l_A+l_B=l_C$

$\Rightarrow$ A possible solution : (200)+(020)=(220)

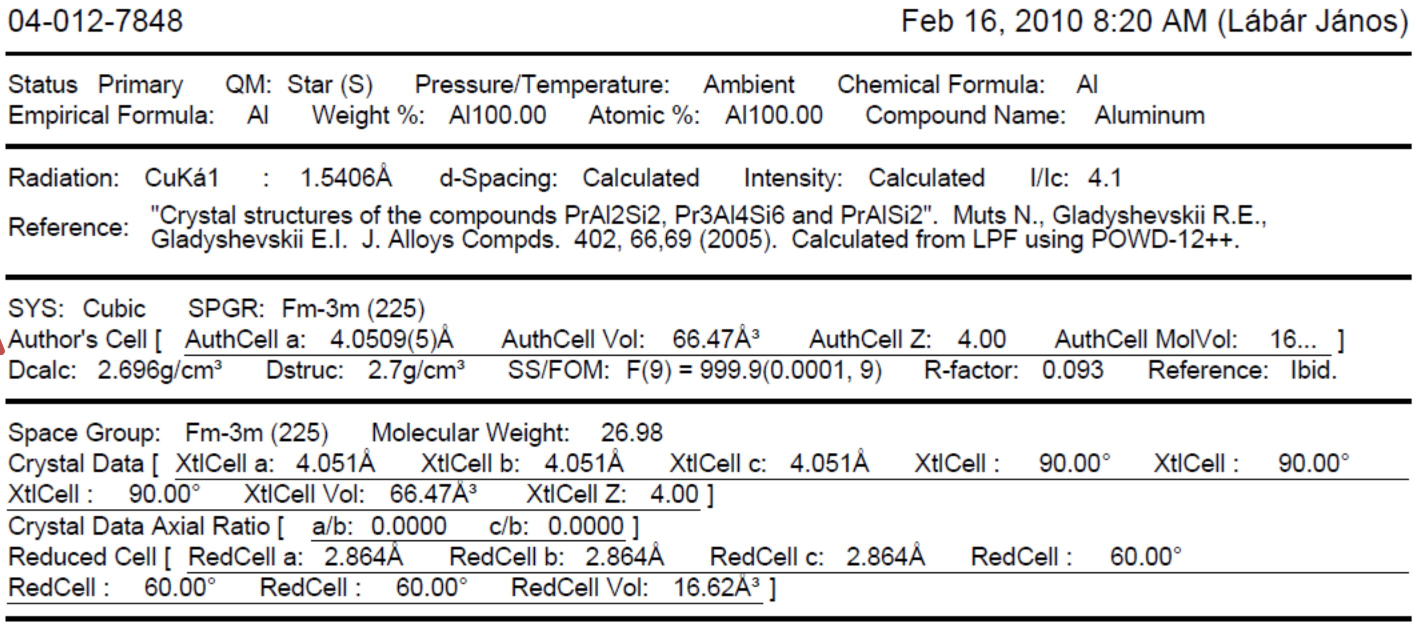
A similarly good other solution:

(0-20)+(002)=(0-22)

And so on...

In the above example: 6 variants can be selected for the first vector, and for each of them 4 selections are possible for the second vector => 24 equivalent solutions.

XRD data sheet of Aluminum



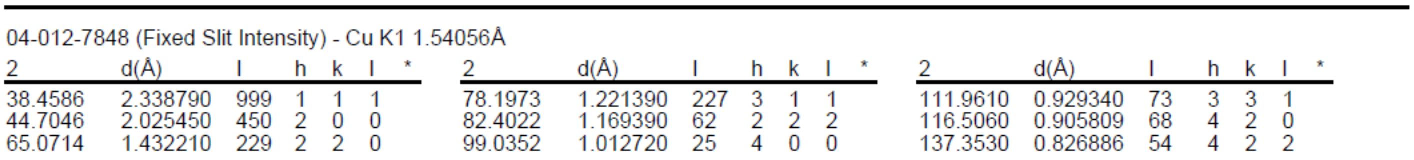
04-012-7848 Feb 16, 2010 8:20 AM (Lábár János)

Status Primary QM: Star (S) Pressure/Temperature: Ambient Chemical Formula: Al
Empirical Formula: Al Weight %: Al100.00 Atomic %: Al100.00 Compound Name: Aluminum

Radiation: CuKá1 : 1.5406Å d-Spacing: Calculated Intensity: Calculated I/Ic: 4.1
Reference: "Crystal structures of the compounds PrAl2Si2, Pr3Al4Si6 and PrAlSi2". Muts N., Gladyshevskii R.E., Gladyshevskii E.I. J. Alloys Compds. 402, 66,69 (2005). Calculated from LPF using POWD-12++.

SYS: Cubic SPGR: Fm-3m (225)
Author's Cell [AuthCell a: 4.0509(5)Å AuthCell Vol: 66.47Å^3 AuthCell Z: 4.00 AuthCell MolVol: 16...]
Dcalc: 2.696g/cm^3 Dstruc: 2.7g/cm^3 SS/FOM: F(9) = 999.9(0.0001, 9) R-factor: 0.093 Reference: Ibid.

Space Group: Fm-3m (225) Molecular Weight: 26.98
Crystal Data [XtlCell a: 4.051Å XtlCell b: 4.051Å XtlCell c: 4.051Å XtlCell : 90.00° XtlCell : 90.00°
XtlCell : 90.00° XtlCell Vol: 66.47Å^3 XtlCell Z: 4.00]
Crystal Data Axial Ratio [a/b: 0.0000 c/b: 0.0000]
Reduced Cell [RedCell a: 2.864Å RedCell b: 2.864Å RedCell c: 2.864Å RedCell : 60.00°
RedCell : 60.00° RedCell : 60.00° RedCell Vol: 16.62Å^3]



04-012-7848 (Fixed Slit Intensity) - Cu K1 1.54056Å

2	d(Å)	I	h	k	l	*
38.4586	2.338790	999	1	1	1	
44.7046	2.025450	450	2	0	0	
65.0714	1.432210	229	2	2	0	
78.1973	1.221390	227	3	1	1	
82.4022	1.169390	62	2	2	2	
99.0352	1.012720	25	4	0	0	
111.9610	0.929340	73	3	3	1	
116.5060	0.905809	68	4	2	0	
137.3530	0.826886	54	4	2	2	

fcc

Zone axis determination for an indexed spot pattern

All planes that have a common direction belong to the same ***zone***.
Their common direction is the ***zone axis***.

If we have a periodic 2D spot pattern than it was recorded from a zone axis orientation!

Proof: The diffraction spots represent reciprocal lattice points. The vector from the spot of the direct beam to a diffraction spot is a reciprocal lattice vector. There is a set of planes in real space lattice normal to this vector. All reciprocal lattice vectors in your patterns are located within a single plane, so all the relevant real space lattice plane-sets are normal to the plane of the pattern. ⇒ Their common direction (the zone axis) is also normal to the pattern.

To determine the direction (=indices) of the zone axis (which is a real space lattice vector)

- Index the pattern! (Permutations and signs of the indices must be correct!)
- Create a cross product of two, non-collinear reciprocal vectors (right hand rule to point towards you)! Cross product can be calculated with coordinates. You can omit a common multiplier!

In the above example OBxOA gives the vector pointing to you (consult figure, use your right hand). $\begin{matrix} 0 & 2 & 0 & 0 & 2 & 0 \\ 2 & 0 & 0 & 2 & 0 & 0 \end{matrix}$ ⇨ $0 \quad 0 \quad -4$, so the zone is [0 0 -1].