X-ray Diffraction

applied to the study of polycrystalline materials

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Programme

Part I

- Powder Diffraction and reciprocal lattice
- Diffraction: theoretical elements

Part II

- Applications of powder diffraction: a survey

Part III

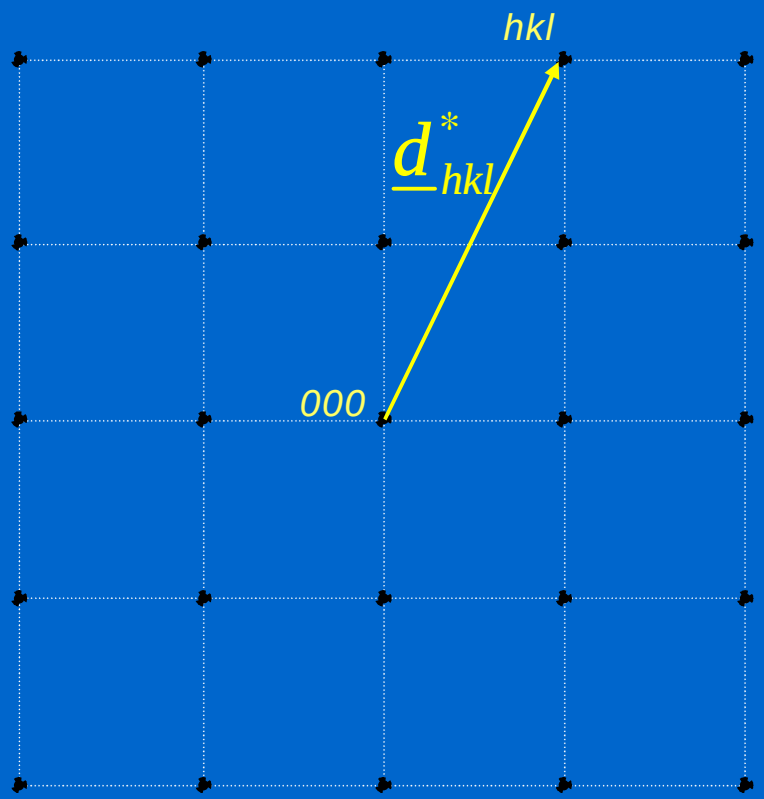
- Introduction to line profile analysis for the study of nanocrystalline and heavily deformed materials

DIFFRACTION AND RECIPROCAL SPACE

A vector drawn from the origin of the reciprocal lattice to the point (*hkl*), where *h*, *k*, *l* are the Miller indices (integer numbers) is given by:

$$\underline{d}^*_{hkl} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$$

where $\underline{a}^*$, $\underline{b}^*$, $\underline{c}^*$ are the reciprocal space vectors



The vector modulus is the inverse of the interplanar distance for the planes with indices (*hkl*):

$$d^*_{hkl} = \left|\underline{d}^*_{hkl}\right| = \frac{1}{d_{hkl}}$$

DIFFRACTION AND RECIPROCAL SPACE

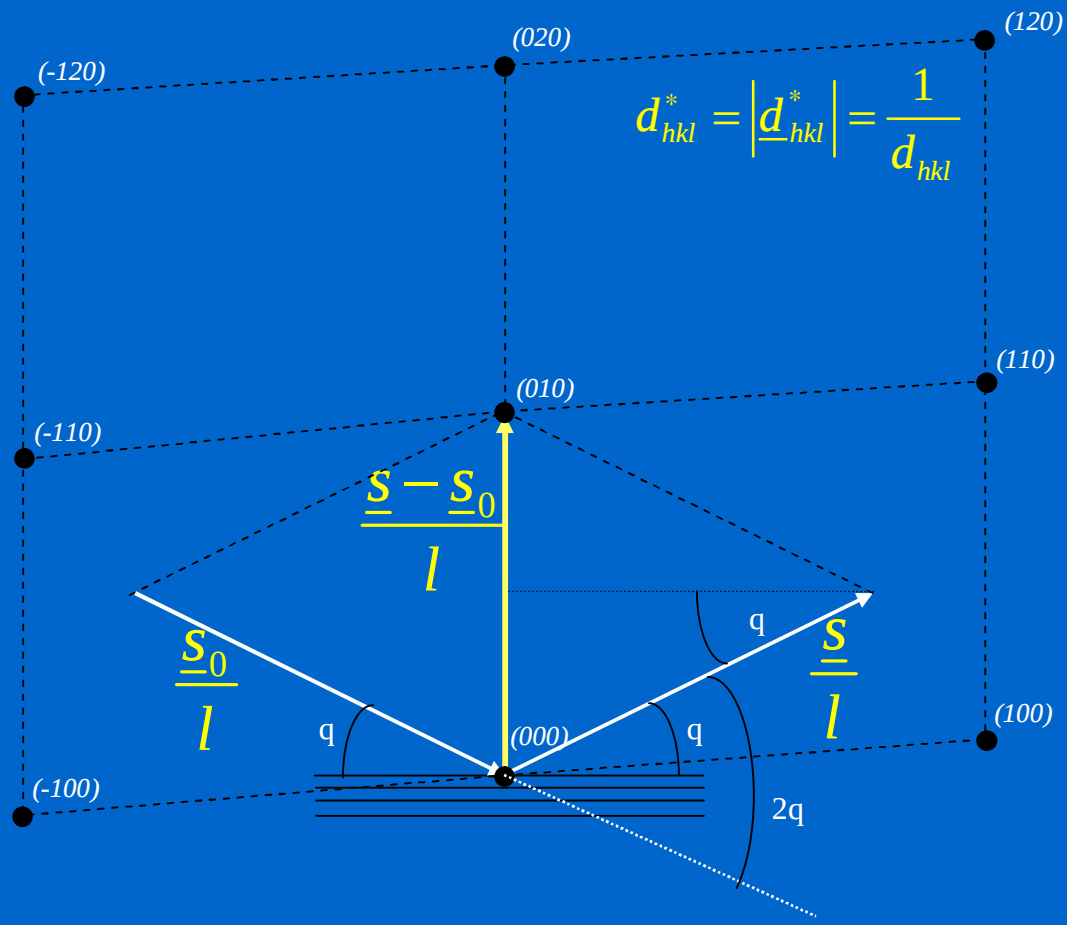
Versors $\underline{s}_0$ and $\underline{s}$ identify, respectively the incident and scattered beam

$$\left|\frac{\underline{s}-\underline{s}_0}{l}\right| = \frac{2\sin q}{l} = \frac{1}{d} = d^*$$

$\underline{d}^*$ = *scattering vector*

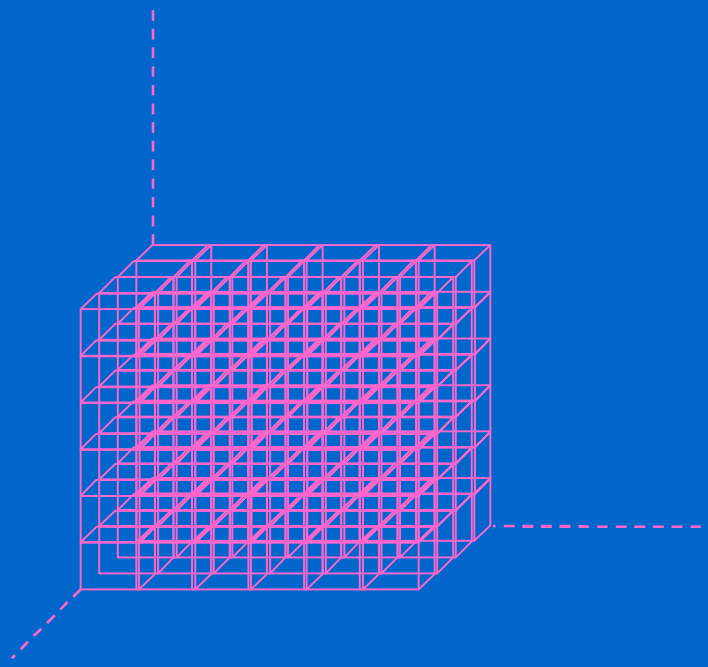
The Bragg law in reciprocal lattice is

$$\frac{\underline{s}-\underline{s}_0}{l} = \underline{d}^*_{hkl}$$

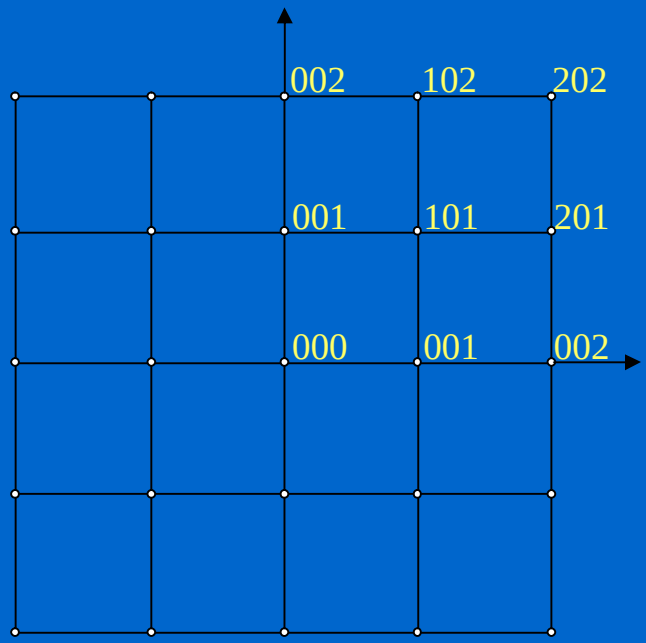


DIFFRACTION AND RECIPROCAL SPACE

For a *perfect (infinite) crystal*



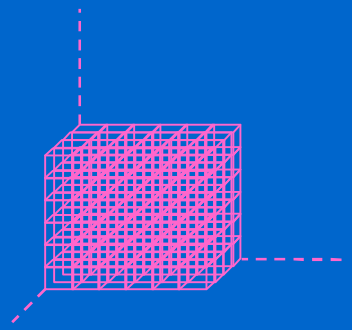
The *reciprocal lattice* is made of (infinitely small) points representing sets of planes of Miller indices *hkl*

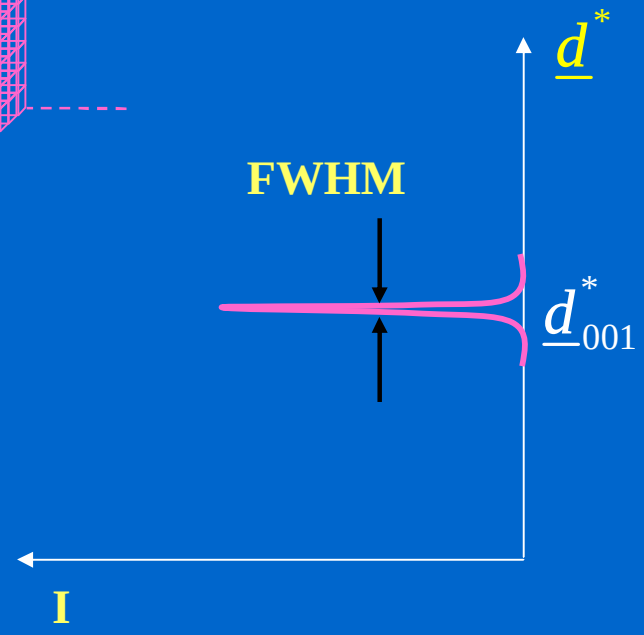


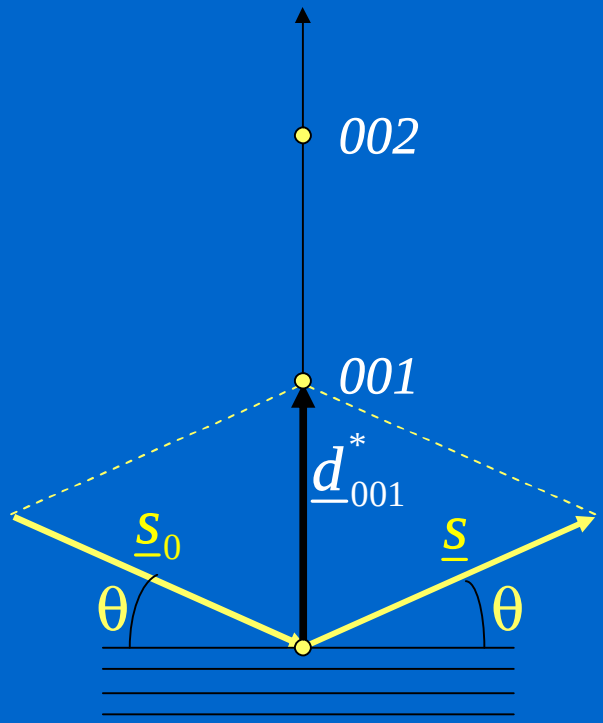
DIFFRACTION AND RECIPROCAL SPACE

For a *perfect (infinite) crystal* the peak width is determined by the instrumental resolution only:

$$|\underline{s} - \underline{s}_0| = \frac{2\sin q}{l} = \frac{1}{d_{hkl}} = d^*_{hkl}$$

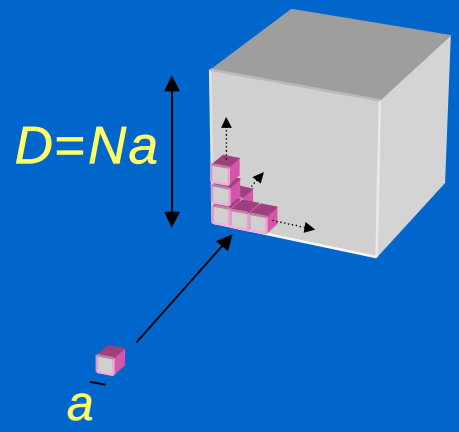




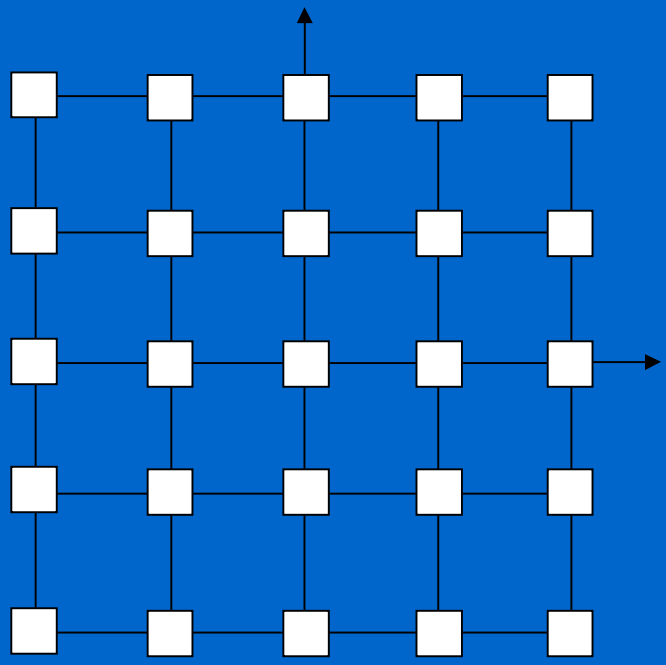


DIFFRACTION AND RECIPROCAL SPACE

For a *finite crystal* *(D<1mm)*

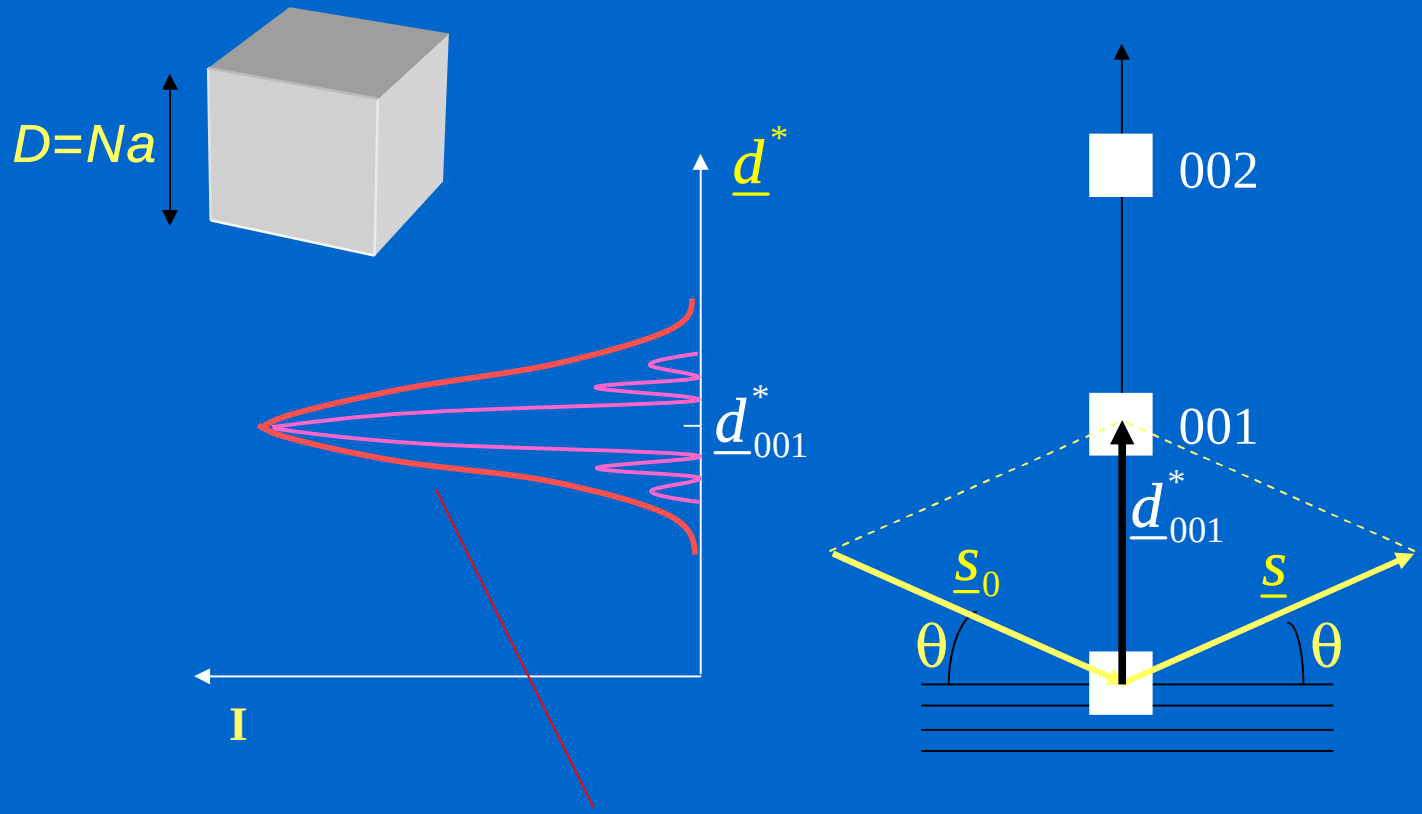


Reciprocal lattice points have finite extension. The shape is related to the crystal shape .



DIFFRACTION AND RECIPROCAL SPACE

Integral breadth: $b\left(d^*\right) = \dfrac{Peak\ Area}{Peak\ Maximum} = \dfrac{1}{D}$ *(Scherrer formula)*



Effect of instrument, domains with different shape/size

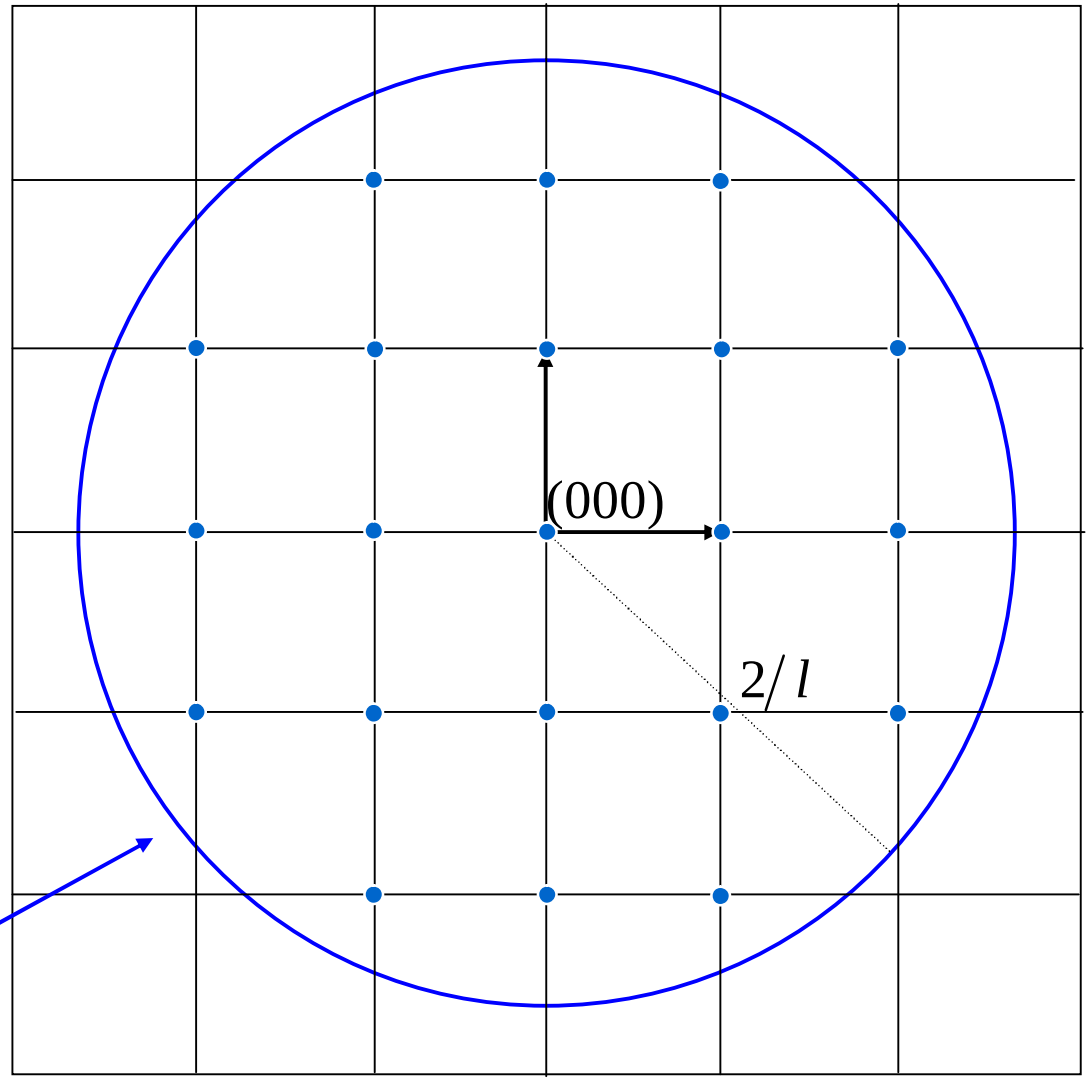
RECIPROCAL LATTICE: DIFFRACTION CONDITIONS

For a given wavelenght, the Bragg law sets a limit to the interplanar distances for which diffraction is observed:

$$\sin q = l/2d \leq 1$$

$$d^* \leq \frac{2}{l}$$

All points representing planes that can diffract are inside a sphere of finite radius, *2/l* *(limiting sphere)*

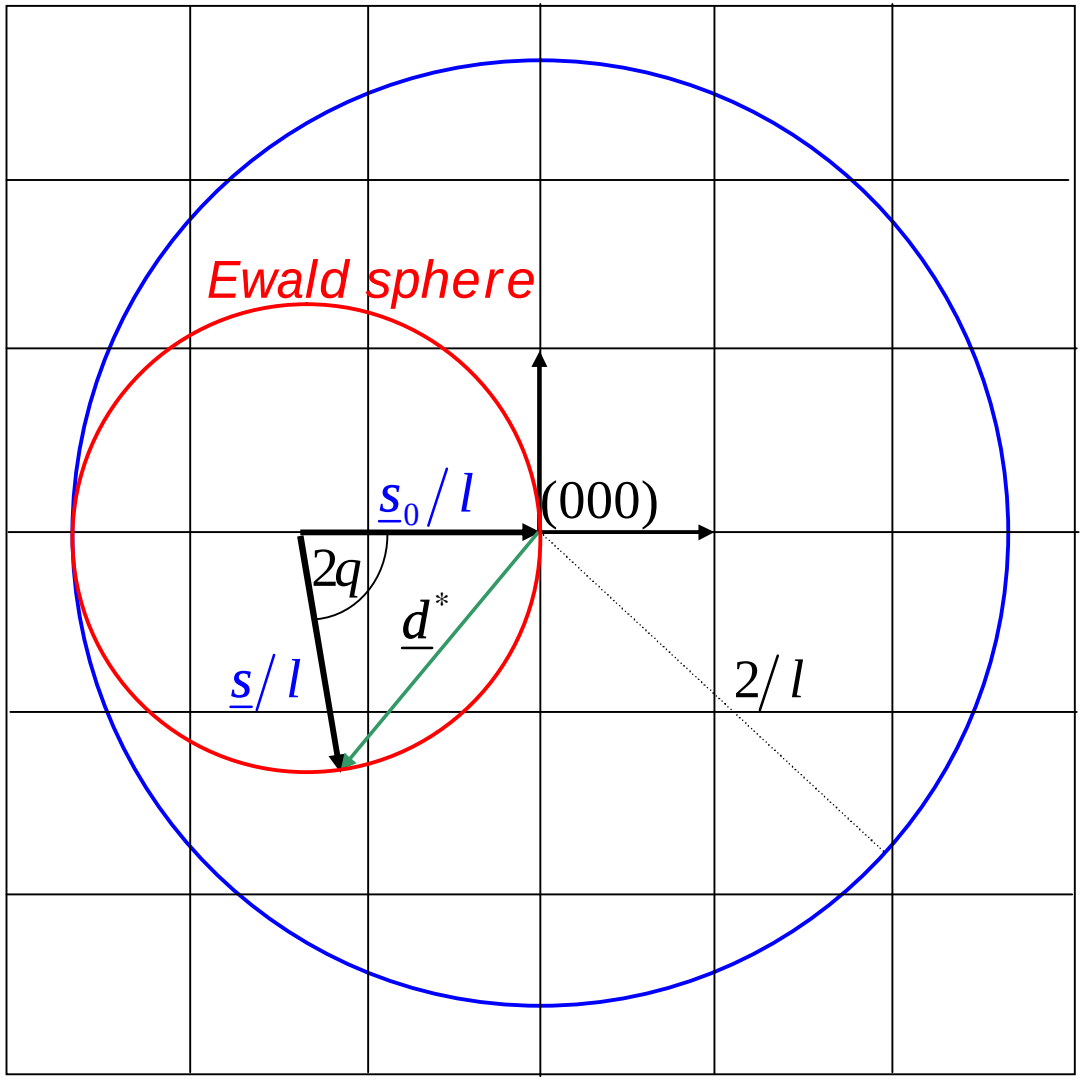


RECIPROCAL LATTICE: DIFFRACTION CONDITIONS

The diffraction condition occurs when the tip of the scattering vector *d** falls on a point of the reciprocal space.

The condition is fulfilled by all points on the *Ewald sphere*, a sphere of radius $1/\lambda$, tangent to the origin and to the $2/\lambda$ sphere.

In a powder diffraction measurement, the Ewald sphere can be thought as *rotating* inside the $2/\lambda$ sphere.



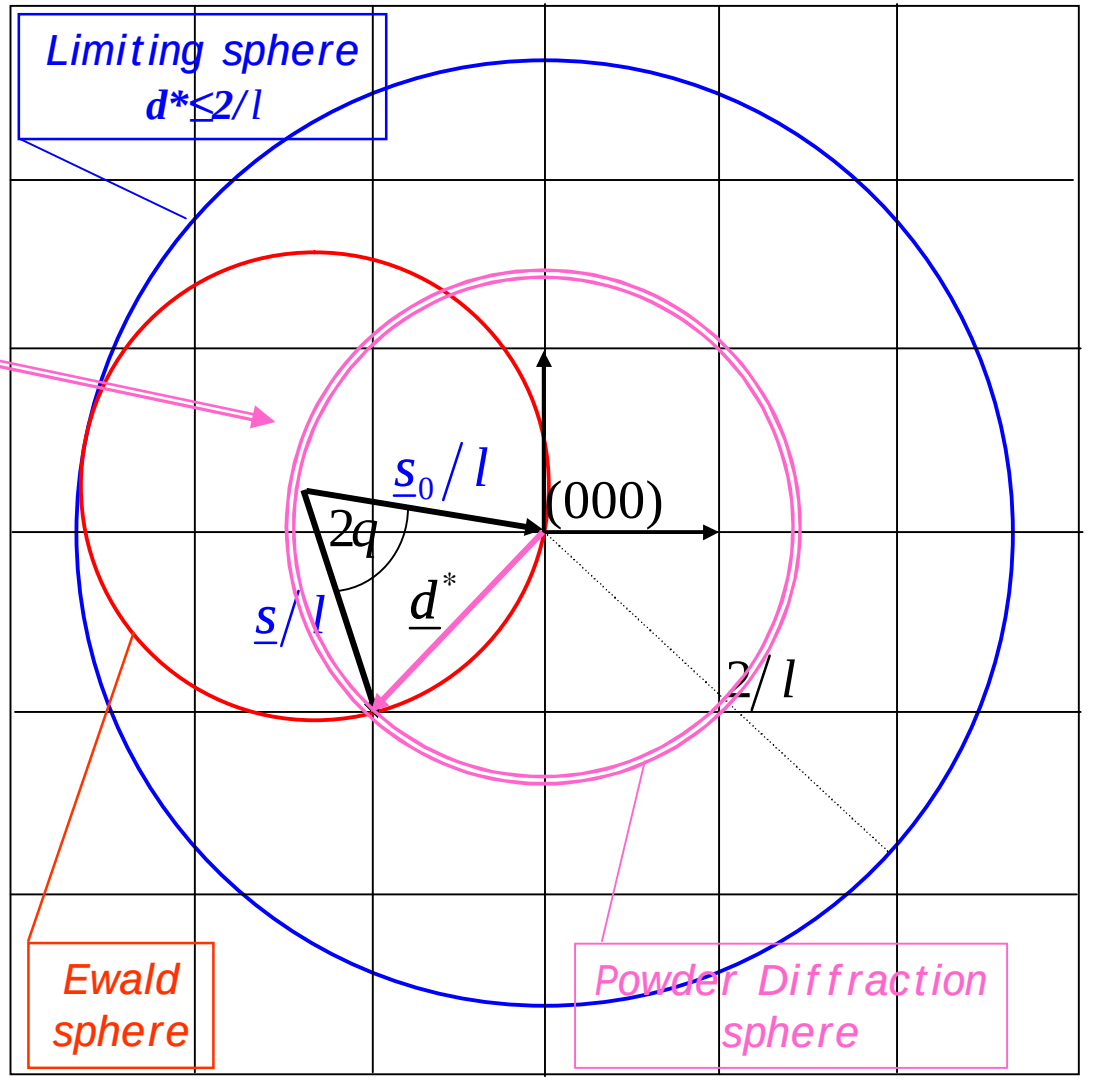
RECIPROCAL LATTICE: DIFFRACTION CONDITIONS

As a consequence, the tip of the scattering vector 'sweeps' the surface of a *sphere of radius d**

During a powder diffraction measurement, the sphere of radius *d** swells (for increasing 2θ) and sweeps the reciprocal space within the limits:

$$0 \le d^* \le \frac{2}{l}$$

$$(0 \le 2q \le 180°)$$

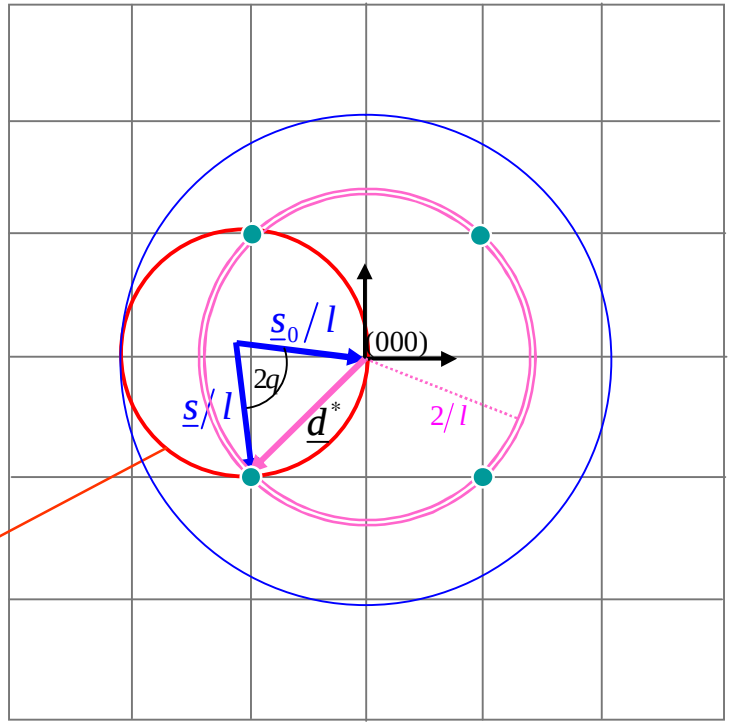


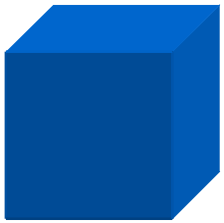
RECIPROCAL LATTICE: MULTIPLICITY

In a powder (polycrysta lline materials) measuremnt more than one point can be in diffraction condition *simultaneously*, i.e., for the same 2θ.

This property leads to the concept of *multiplicity* of a reflection, that is the number of equivalent planes.

In cubic structures:





Miller indices	*hkl*	*hhk*	*0kl*	*0kk*	*hhh*	*00l*
Multiplicity	48	24	24	12	8	6

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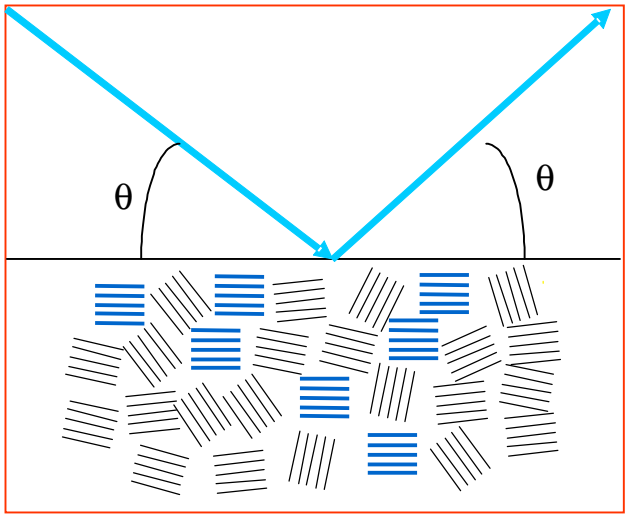
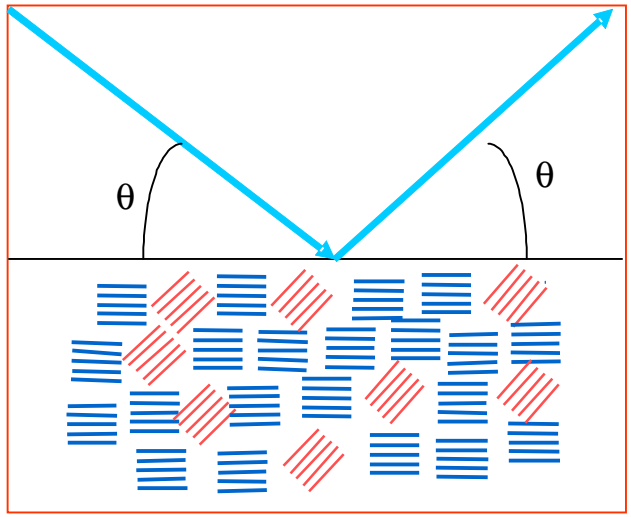
The concept of 'Powder'

An ideal powder is a polycrystalline sample (a true powder or a bulk specimen) such that for every possible orientation a sufficiently high number of grains (**à** *grain statistics*) has atomic planes in Bragg condition (*random orientation*).

If preferred orientation (*texture*) is present, suitable models are necessary to account for the 'non-ideal' conditions.



Random orientation

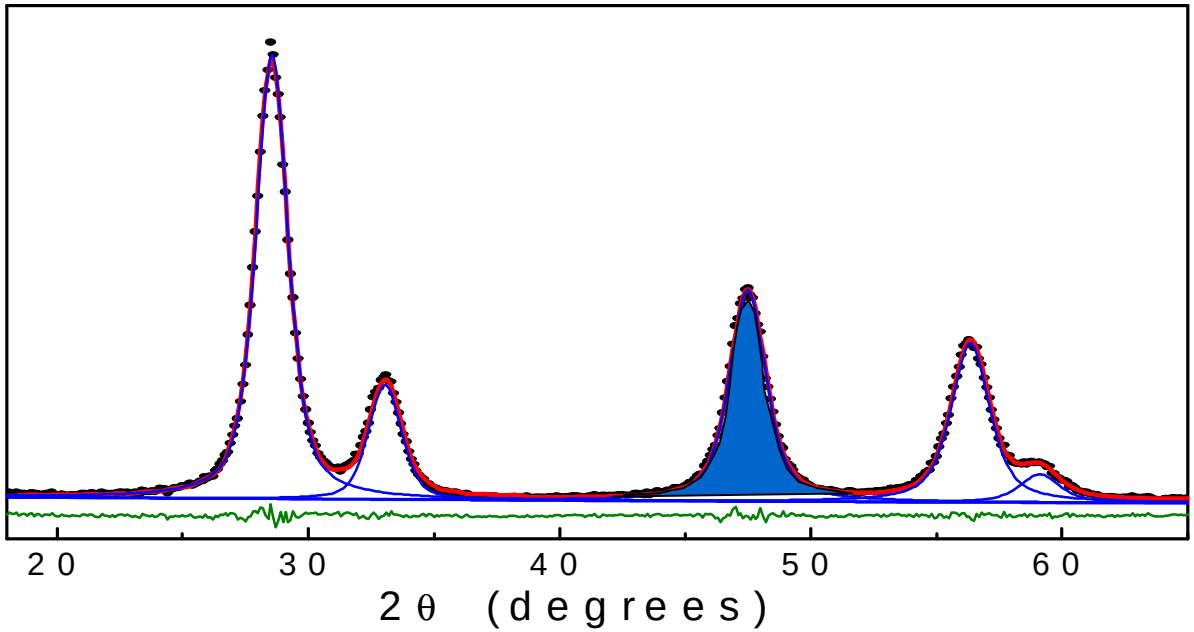


Preferred orientation

Integrated intensity

Intrinsic features of the sample, instrument and measurement geometry cause a dispersion of the scattered intensity across a finite angular range (*a peak*). The range (width) changes with $2q$.

The diffracted signal is better represented by the area of the diffraction peak (*integrated intensity)* than by maximum intensity.



INTEGRATED INTENSITY

The *integrated intensity* of a powder diffraction peak is given by:

$$I(2q) = k' |F_T|^2 \; p \left(\frac{1+\cos^2(2q)}{\sin(q)\sin(2q)} \right)$$

Structure factor

Molteplicity

Lorentz-Polarization factor

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Structure factor

SCATTERING FROM A UNIT CELL: STRUCTURE FACTOR

The instant electric field scattered by a unit cell with N atoms is proportional to the

$$F = \sum_{n=1}^{N} f_n e^{2\pi i \frac{\underline{r}_n \cdot (\underline{s} - \underline{s}_0)}{l}}$$

Structure Factor

Phase term

Atomic scattering factor

$$F_{hkl} = \sum_{n=1}^{N} f_n e^{2\pi i \frac{\underline{r}_n \cdot (\underline{s} - \underline{s}_0)}{l}} = \sum_{n=1}^{N} f_n e^{2\pi i (u_n \underline{a} + v_n \underline{b} + w_n \underline{c}) \cdot (h\underline{a}^* + k\underline{b}^* + l\underline{c}^*)} = \sum_{n=1}^{N} f_n e^{2\pi i (u_n h + v_n k + w_n l)}$$

COHERENT AND INCOHERENT SCATTERING

Istantant electric field scattered by a unit cell

$$\propto F = \sum_{n=1}^{N} f_n e^{2\pi i(u_n h + v_n k + w_n l)}$$

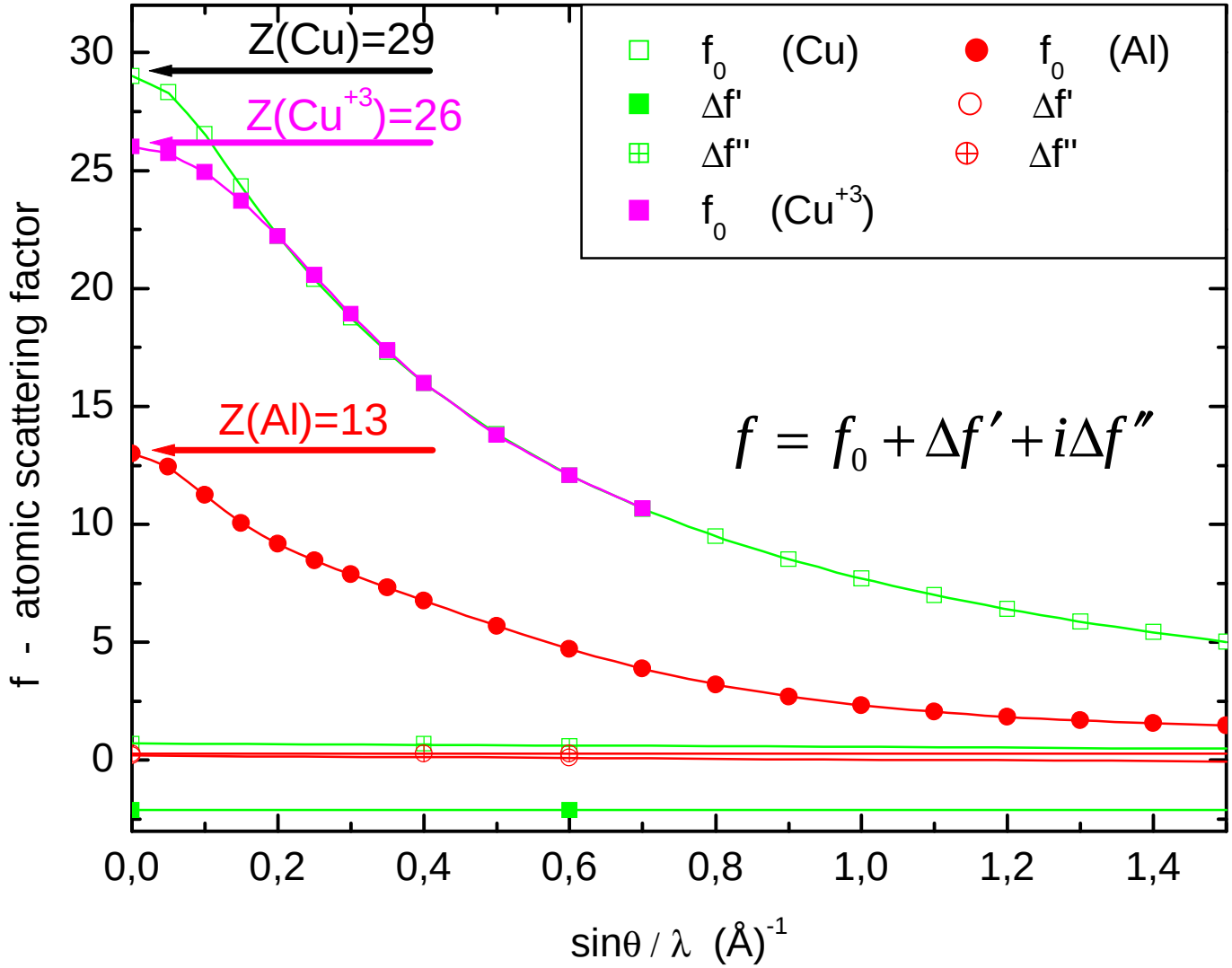
The diffracted intensity is proportional to: $|F|^2 = FF^*$

→ Phase problem

- For a totally constructive interference, the square of the sum of the amplitudes is considered: $I_P \propto (NF)^2$
- In absence of phase relation, the sum of the squared amplitudes (intensities) is considered: $I_P \propto \left(N|F|^2\right)$

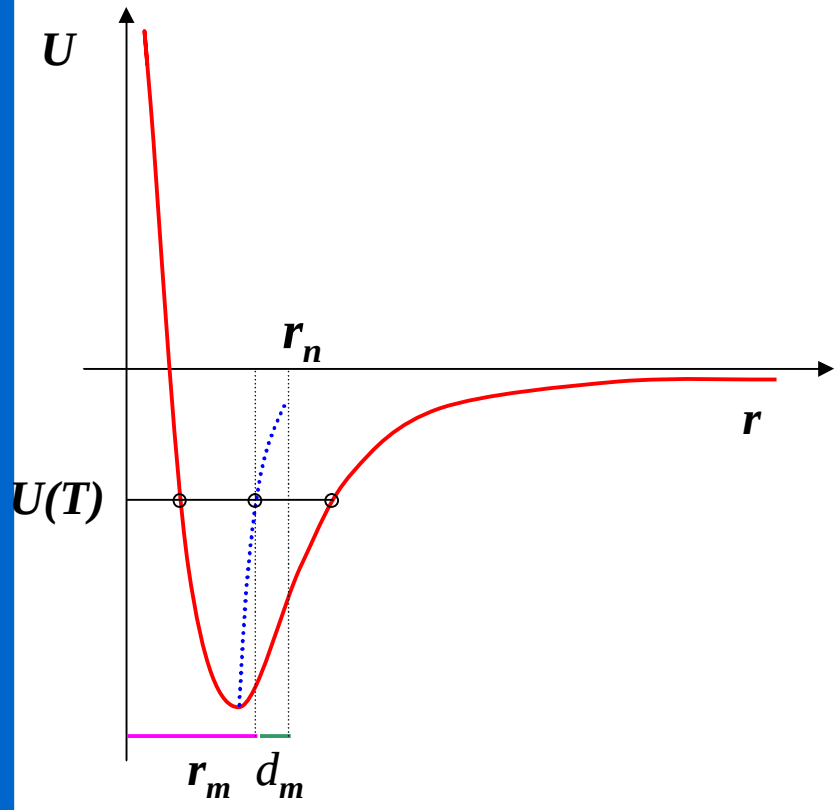
*Given the large number of unit cells in a crystal, the difference between **coherent** and **incoherent** signal is huge*

ATOMIC SCATTERING FACTOR AND DISPERSION CORRECTIONS



THERMAL VIBRATIONS: DEBYE-WALLER FACTOR

Owing to thermal vibrations, atoms and molecules oscillate about an equilibrium position. The instant position can be written as: $\underline{r}_n = \underline{r}_m + \underline{d}_m$ (average pos. + instant displacement)



instant displacement projected along the scattering vector direction

$\overline{d_{sm}^2}$

Thermal vibrations reduce the diffracted intensity by a factor

$$e^{-16p^2\overline{d_{sm}^2}\frac{\sin^2(q)}{l^2}} = e^{-2B\frac{\sin^2(q)}{l^2}} = e^{-2M_m}$$

B – Debye-Waller factor

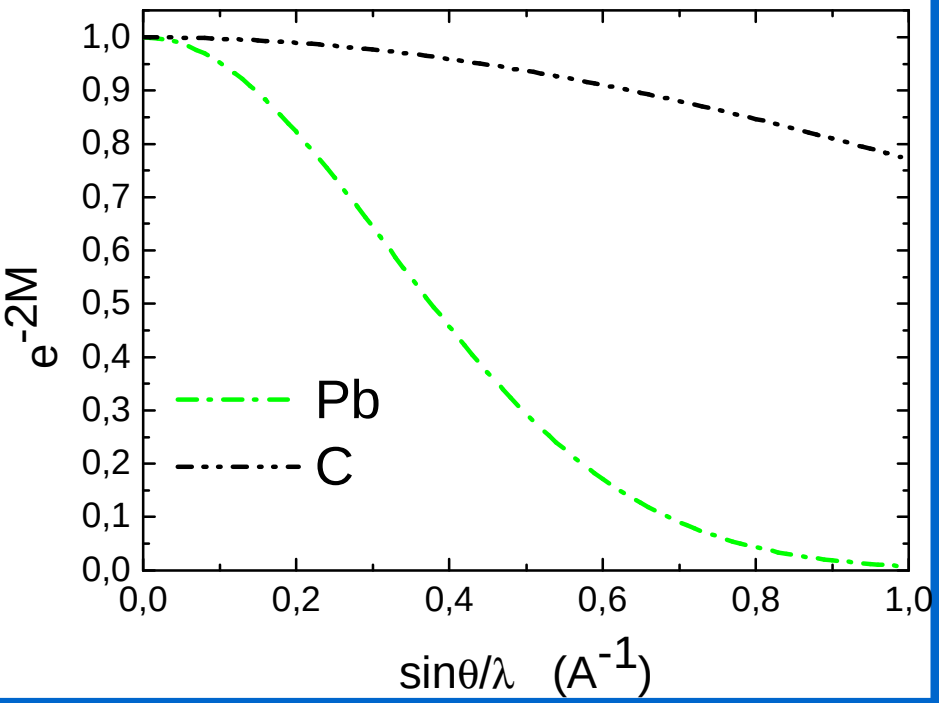
THERMAL VIBRATIONS: DEBYE-WALLER FACTOR

The effect on the Bragg component (coherent diffraction), for *one atomic species only*, assuming *isotropic oscillations*

$$I_P = I_e \left| \sum_{n=1}^{N} f_n e^{2\pi i(u_n h + v_n k + w_n l)} \right|^2 e^{-2M} = I_e |F|^2 e^{-2M} = I_e |F_T|^2$$

M is related to the elastic/ thermal properties of the material (atomic vibrations):

$$M = B \frac{\sin^2(q)}{l^2}$$



INTEGRATED INTENSITY

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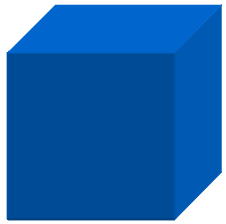
Molteplicity

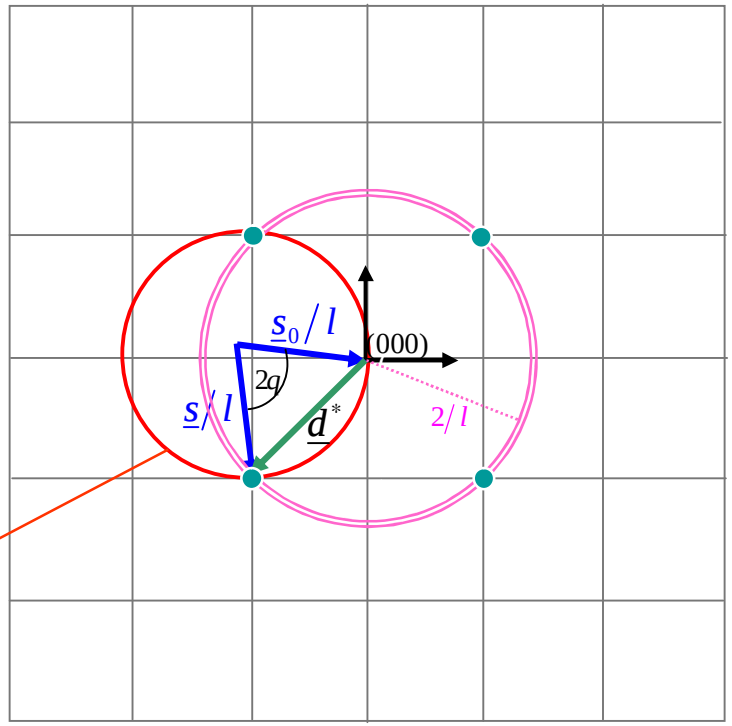
MULTIPLICITY

Multiplicity (*p*) : number of equivalent planes.

Multiplicity for cubic structure powder specimens

Miller indices	*hkl*	*hhk*	0*kl*	0*kk*	*hhh*	00*l*
Multiplicity	48	24	24	12	8	6





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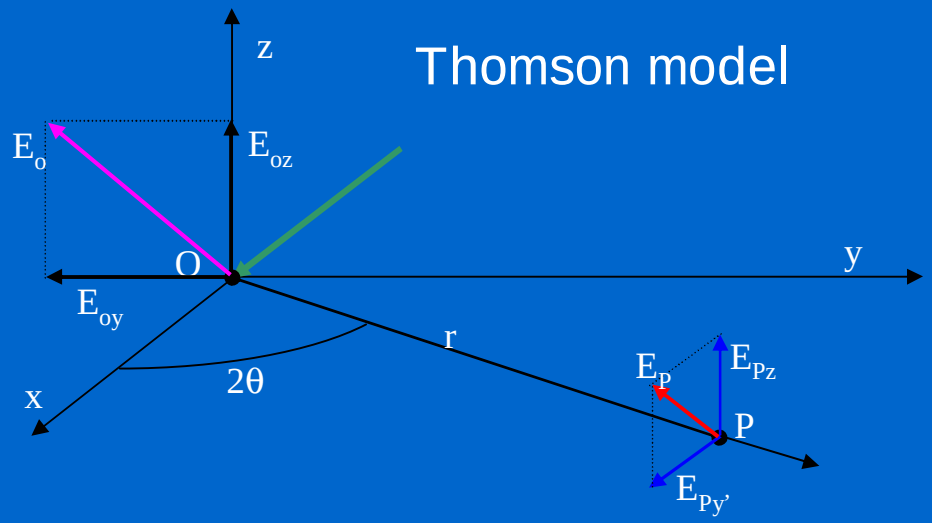
Lorentz-Polarization factor

X-RAY ELASTIC SCATTERING AND POLARIZATION



$$\left\langle E_{oy}^2 \right\rangle = \left\langle E_{oz}^2 \right\rangle = \frac{1}{2}\left\langle E_o^2 \right\rangle$$

$$E_{Pz} = \frac{e^2}{mc^2 r} E_{oz}$$

$$E_{Py'} = \frac{e^2}{mc^2 r} E_{oy} \cos(2q)$$

Mean square field:

$$\left\langle E_P^2 \right\rangle = \left\langle E_{Py'}^2 \right\rangle + \left\langle E_{Pz}^2 \right\rangle = \left\langle E_0^2 \right\rangle \frac{e^4}{m^2 c^4 r^2} \left[\frac{1+\cos^2(2q)}{2} \right]$$

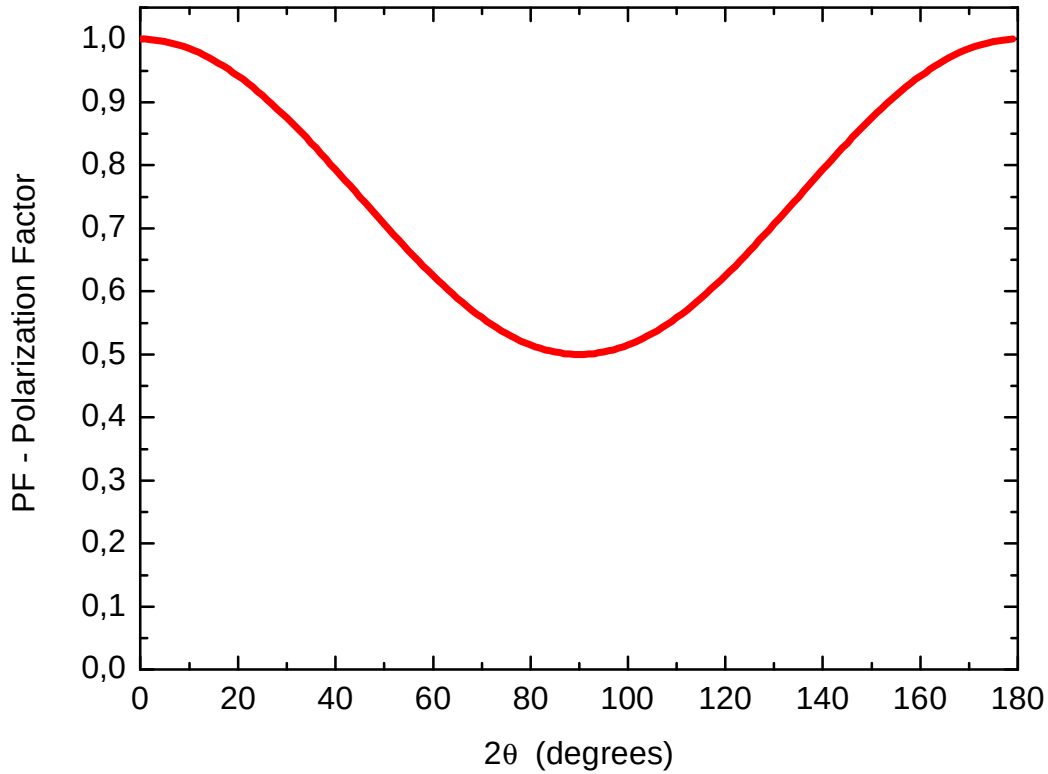
7.94×10^{-26} cm^2

Scattered intensity:

$$I_P = I_O \frac{e^4}{m^2 c^4 r^2} \left[\frac{1+\cos^2(2q)}{2} \right] = \frac{I_O K}{r^2} \left[\frac{1+\cos^2(2q)}{2} \right]$$

POLARIZATION FACTOR

$$PF = \left[1+\cos^2(2q)\right]/2$$



THE LORENTZ FACTOR

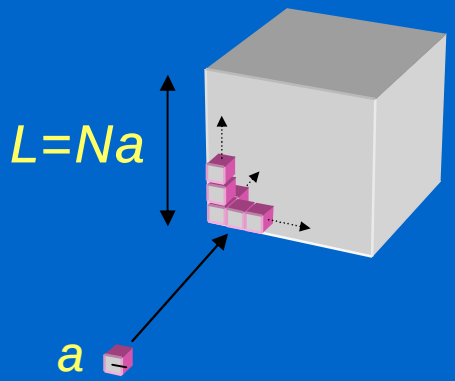
A diffraction measurement basically consists in a cross section through one or more reciprocal space (RS) points.

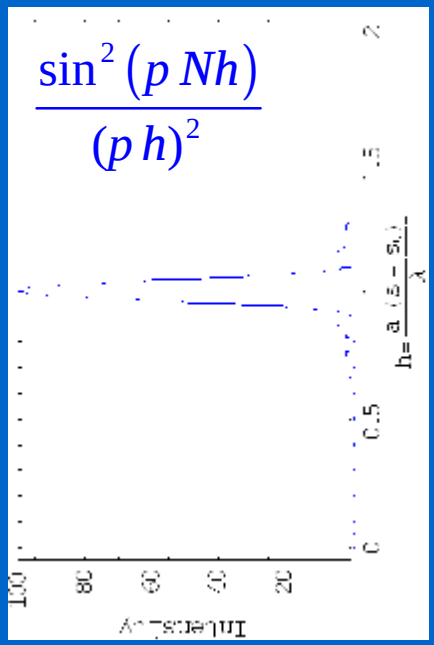
The measured intensity depends on:

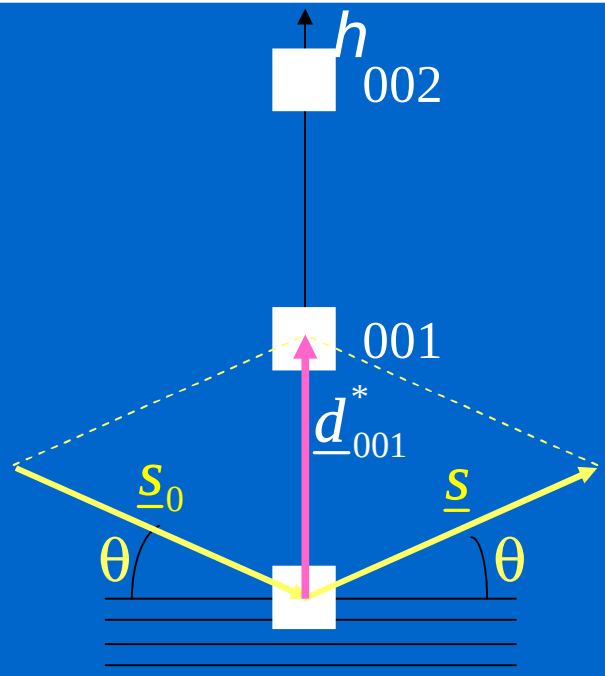
a) The way RS points are crossed;

b) The sampling in RS (considering measurements are in $2q$ space);

c) The fraction of diffracted signal collected by the detector.



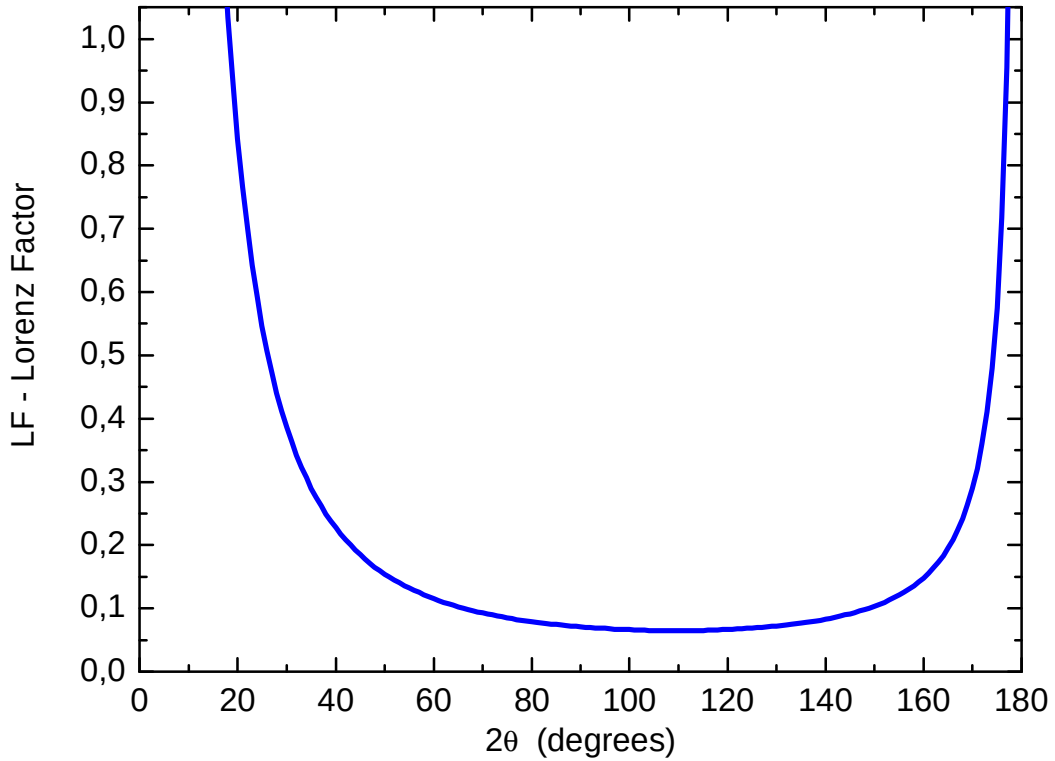




THE LORENTZ FACTOR

Putting together the trigonometric terms for the various contributions, the *Lorentz Factor* for the powder geometry is:

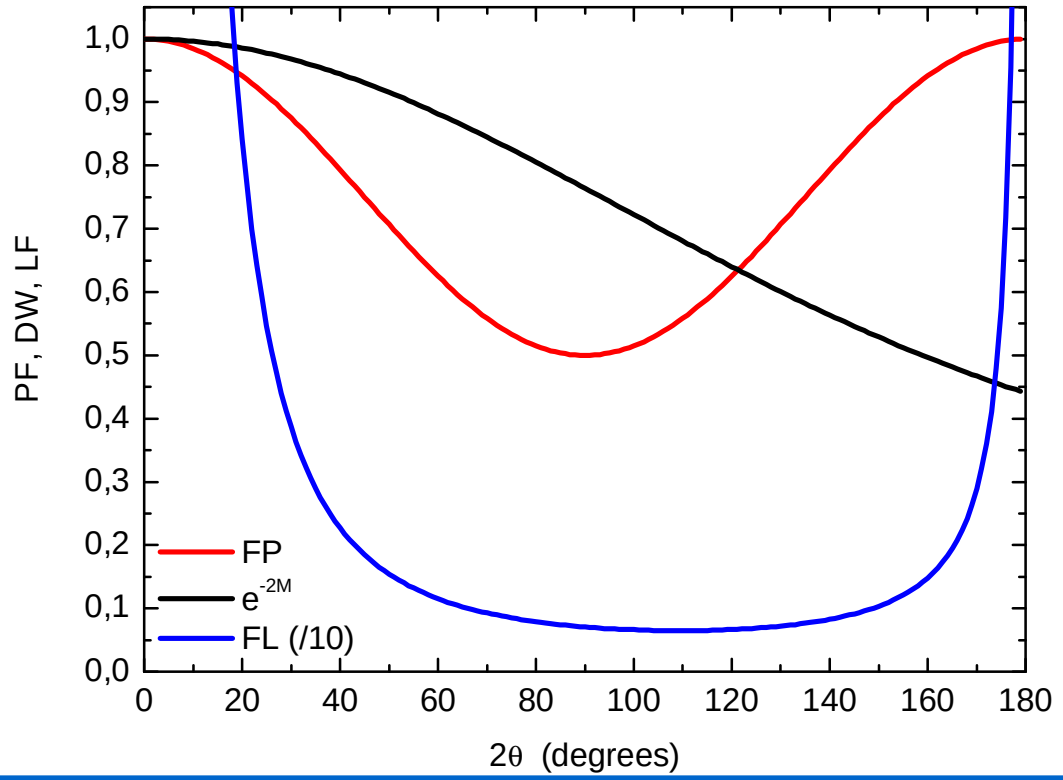
$$LF = \frac{1}{\sin 2q} \cdot \cos q \cdot \frac{1}{\sin 2q} = \frac{\cos q}{\sin^2 2q}$$



THE LORENTZ-POLARIZATION FACTOR

The Lorentz and Polarization factors can be combined in a single trigonometric term: the *Lorentz-Polarization* factor:

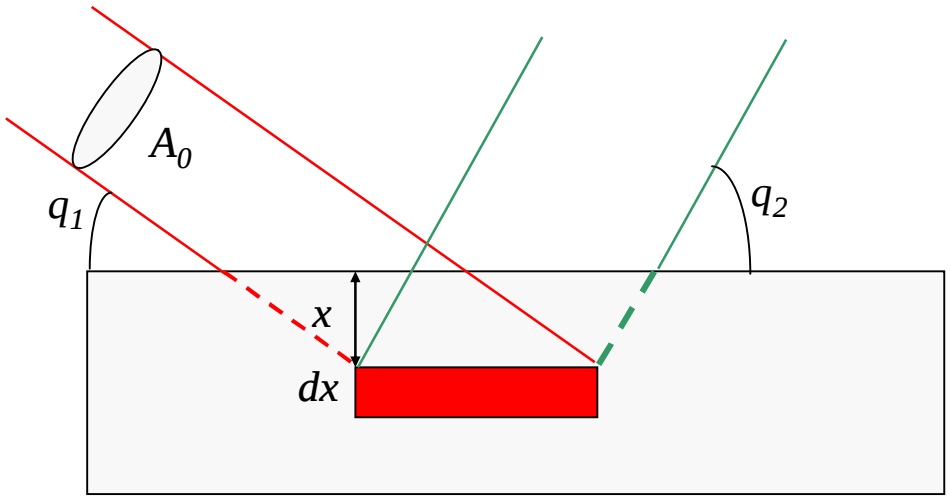
$$LF = \frac{\cos q}{\sin^2 2q} \qquad PF = \left[1+\cos^2(2q)\right]/2 \Longrightarrow \boxed{LP = \frac{1+\cos^2(2q)}{\sin(q)\sin(2q)}}$$



ABSORPTION

An advantage of the traditional Bragg-Brentano powder diffraction geometry: no need for q-dependent correction terms for absorption

Beam cross section A_0, intensity I_0 impinging with angle q_1. A small volume dV (thickness dx, surface $A_0/\sin(q_1)$) diffracts at the angle q_2



$$dI = I_0 e^{-mx(1/\sin q_1 + 1/\sin q_2)} dV = \frac{I_0 A_0}{\sin q_1} e^{-mx(1/\sin q_1 + 1/\sin q_2)} dx$$

ABSORPTION

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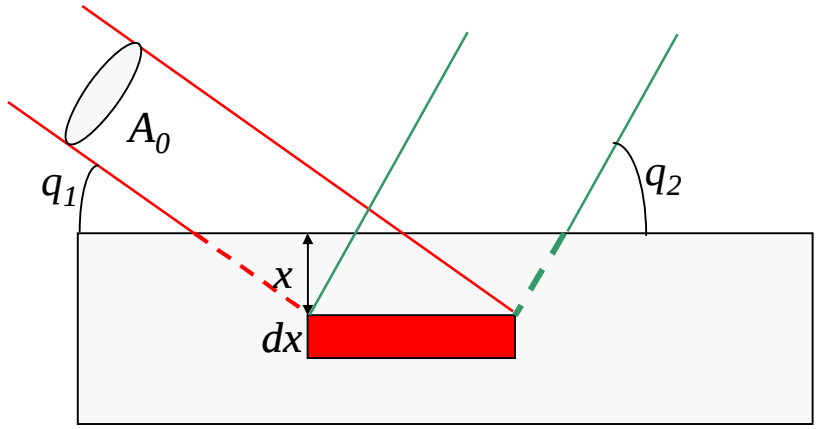
In the traditional powder geometry: $q_1 = q_2 = q$

By integrating on the sample thickness: $I = \frac{I_0 A_0}{\sin q} \int_0^\infty e^{-2mx/\sin q} dx = \frac{I_0 A_0}{2m}$



Indipendent of q

INTEGRATED INTENSITY

The *integrated intensity* of a powder diffraction peak is given by:

If terms for absorption (m), cell volume (v_a), goniometer radius (r) and wavelenght (l) are written explicitly,

$$I(2q) = k \frac{l^3}{m r v_a^2} |F_T|^2 \, p \left(\frac{1+\cos^2(2q)}{\sin(q)\sin(2q)} \right)$$

Structure factor

Molteplicity

Lorentz-Polarization factor

Absorption

INTEGRATED INTENSITY

If the secondary circle of a crystal monochromator (analyzer) is present at q_m, the polarization factor must be written as:

$$I(2q) = k' \frac{|F_T|^2 \, l^3 p}{mrv_a^2} \left(\frac{1 + \cos^2(2q_m)\cos^2(2q)}{\sin(q)\sin(2q)} \right)$$

Structure factor

Absorption

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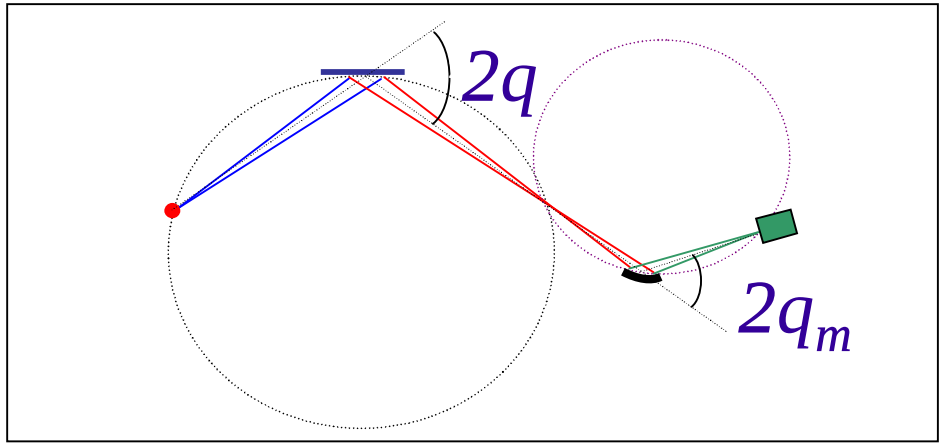
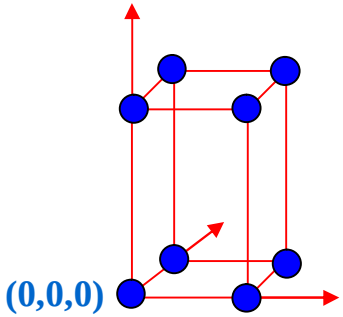
Lorentz-Polarization factor



STRUCTURE FACTOR CALCULATION

Primitive unit cell (*P*) (Z=1) with one atomic species



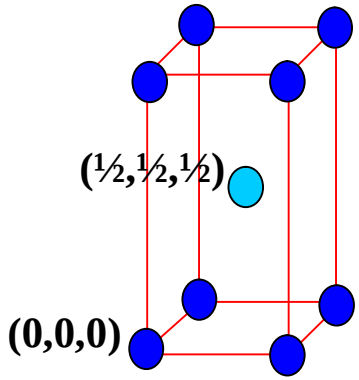
$$F = fe^{2\pi i(0\cdot h+0\cdot k+0\cdot l)} = f$$

$$I \propto |F|^2 = f^2$$

The structure factor is the same for all (hkl) reflections

STRUCTURE FACTOR CALCULATION

Body centred lattice (*I*) (Z=2) with one atomic species in (0,0,0) and (½,½,½)

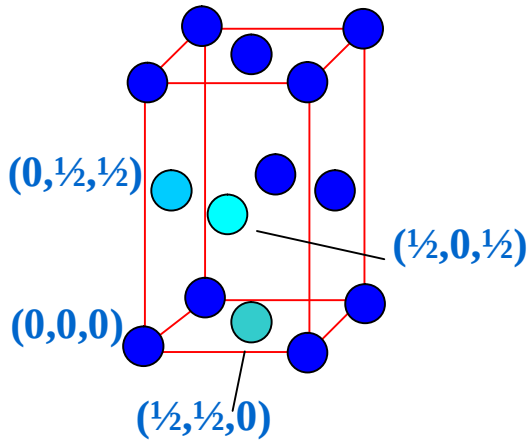


$$F = fe^{2\pi i(0)} + fe^{2\pi i(h/2+k/2+l/2)} = f\left[1+e^{\pi i(h+k+l)}\right] = \begin{cases} 0 & h+k+l \quad odd \\ 2f & h+k+l \quad even \end{cases}$$

The intensity is proportional to $4f^2$ for reflections with whose indices have sum even, and it is *zero* for sum odd

STRUCTURE FACTOR CALCULATION

Face centred lattice (*F*) (Z=4) with one atomic species in (0,0,0), (0,½,½), (½,0,½) e (½,½,0)



$$F = fe^{2\pi i(0)} + fe^{2\pi i(0+k/2+l/2)} + fe^{2\pi i(h/2+0+l/2)} + fe^{2\pi i(h/2+k/2+0)}$$

$$= f\left[1+e^{\pi i(k+l)}+e^{\pi i(h+l)}+e^{\pi i(h+k)}\right] = \begin{cases} 0 & h,k,l \quad mixed \\ 4f & h,k,l \quad unmixed \end{cases}$$

The intensity is proportional to $16f^2$ for reflections with unmixed indices and is *zero* for mixed indices

STRUCTURE FACTOR CALCULATION

P	*I*	*F*
(100)	-	-
(110)	(110)	-
(111)	-	(111)
(200)	(200)	(200)
(210)	-	-
(211)	(211)	-
(220)	(220)	(220)
(300)/(221)	-	-
(310)	(310)	-
(311)	-	(311)
(222)	(222	(222)
(320)	-	-
(321)	(321)	-
(400)	(400)	(400)

The structure factor is independent of shape and size of the unit cell.

Rules derived in previous examples hold for any *P*, *I* or *F* unit cell.

EXAMPLE

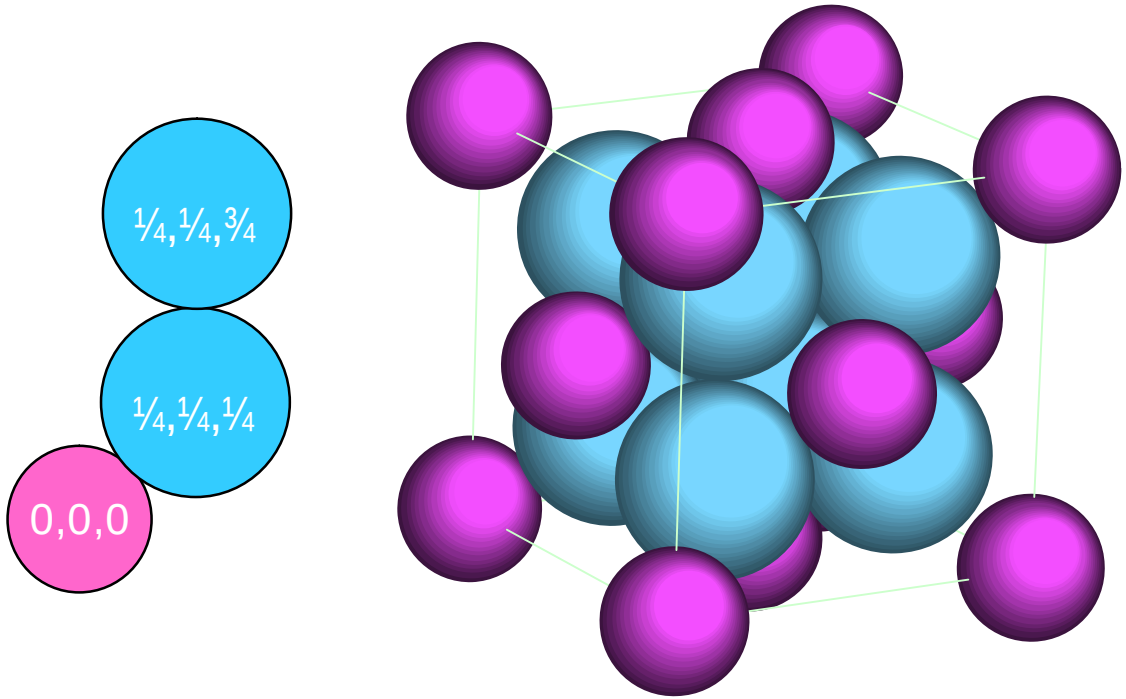
Calculated integrated intensity
for the reflections of Fluorite

FLUORITE POWDER PATTERN

Fluorite (CaF_2): *fcc* (Z=4) unit cell.

Cations (Ca^{+2}, r=0.99 Å) in the origin and positions equivalent by *fcc* Translations.

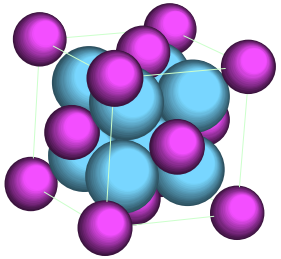
Anions (F^{-1}, R=1.33 Å) in (¼,¼,¼), (¼,¼,¾) and positions equivalent by *fcc* Translations.



FLUORITE POWDER PATTERN

Ca^{+2} (0,0,0) + *fcc*

F^{-1} (¼,¼,¼), (¼,¼,¾) + *fcc*.



$$F = 4\left[f_{Ca} + f_F e^{\frac{ip}{2}(h+k+l)} + f_F e^{\frac{ip}{2}(h+k+3l)} \right] = 4\left[f_{Ca} + f_F \left(e^{\frac{ip}{2}(h+k+l)} + e^{\frac{ip}{2}(h+k-l)} \right) \right] =$$

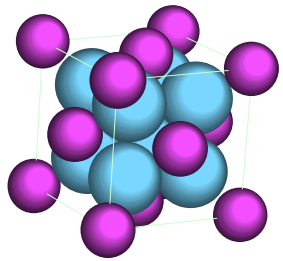
$$= 4\left[f_{Ca} + 2 f_F e^{\frac{ip}{2}(h+k)} \cos\left(\frac{pl}{2}\right) \right]$$

$$|F|^2 = 16\left\{ f_{Ca}^2 + 4 f_F^2 \cos^2\left(\frac{pl}{2}\right) + 2 f_{Ca} f_F \left[e^{\frac{ip}{2}(h+k)} + e^{-\frac{ip}{2}(h+k)} \right] \cos\left(\frac{pl}{2}\right) \right\} =$$

$$= 16\left\{ f_{Ca}^2 + 4 f_F^2 \cos^2\left(\frac{pl}{2}\right) + 4 f_{Ca} f_F \cos\left[\frac{p}{2}(h+k)\right] \cos\left(\frac{pl}{2}\right) \right\}$$

FLUORITE POWDER PATTERN

$$|F|^2 = 16\left\{ f_{Ca}^2 + 4 f_F^2 \cos^2\left(\frac{p\,l}{2}\right) + 4 f_{Ca} f_F \cos\left[\frac{p}{2}(h+k)\right]\cos\left(\frac{p\,l}{2}\right)\right\}$$



The expression simplifies consideraning that *h,k,l* are integers:

$$|F|_A^2 = 16 f_{Ca}^2 \qquad l \text{ odd}$$

$$|F|_B^2 = 16\left(f_{Ca} - 2 f_F\right)^2 \qquad (h+k) \textit{ or } l \text{ odd } \textit{multiple} \text{ of } 2$$

$$|F|_C^2 = 16\left(f_{Ca} + 2 f_F\right)^2 \qquad (h+k) \text{ and } l, \text{ both odd or both even multiple of } 2$$

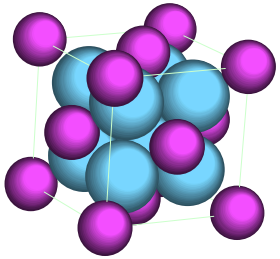
(111)	(200)	(220)	(311)	(222)	(400)	(331)	(420)	(422)	(333)	(511)	(440)	(531)	(600)
$\|F\|_A^2$	$\|F\|_B^2$	$\|F\|_C^2$	$\|F\|_A^2$	$\|F\|_B^2$	$\|F\|_C^2$	$\|F\|_A^2$	$\|F\|_B^2$	$\|F\|_C^2$	$\|F\|_A^2$	$\|F\|_A^2$	$\|F\|_C^2$	$\|F\|_A^2$	$\|F\|_B^2$

FLUORITE POWDER PATTERN

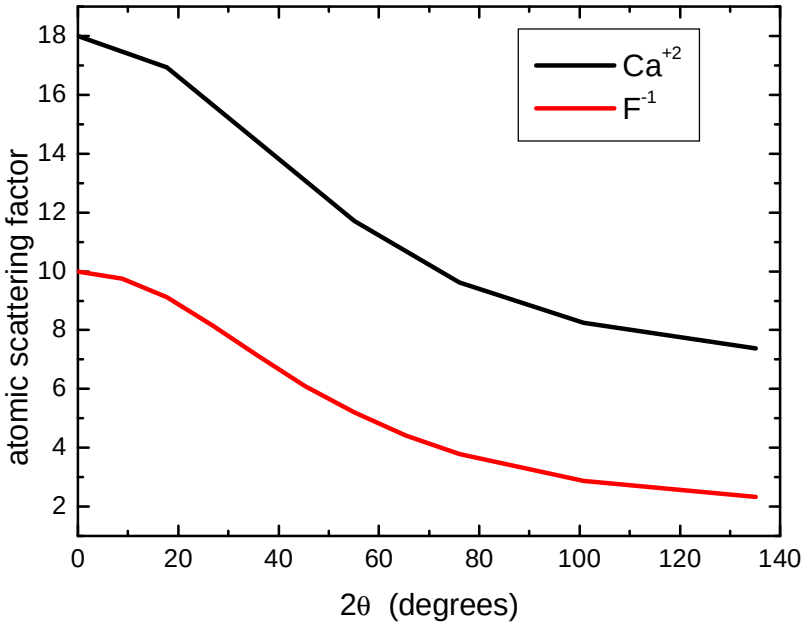
$$|F|_A^2 = 16 f_{Ca}^2 \qquad l \text{ odd}$$

$$|F|_B^2 = 16(f_{Ca} - 2f_F)^2 \qquad (h+k) \textit{ or } l \text{ odd } \textit{multiple} \text{ of } 2$$

$$|F|_C^2 = 16(f_{Ca} + 2f_F)^2 \qquad (h+k) \text{ and } l, \text{ both odd or both even multiple of } 2$$



Atomic scattering factor (*f*):



Dispersion corrections:

	Ca	F
$\Delta f'$	0.3	0.0
$\Delta f''$	1.4	0.1

à $(f+Df')+iDf''$

Debye-Waller factors:

$$B(Ca) = 0.47 \text{ Å}^2, B(F) = 0.67 \text{ Å}^2$$

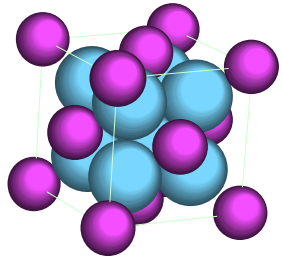
FLUORITE POWDER PATTERN

$|F|_A^2 = 16 f_{Ca}^2$ l odd

$|F|_B^2 = 16(f_{Ca} - 2f_F)^2$ $(h+k)$ *or* l odd *multiple* of 2

$|F|_C^2 = 16(f_{Ca} + 2f_F)^2$ $(h+k)$ and l, both odd or both even multiple of 2

(f+Df')+iDf''



$$|F_T|_A^2 = 16 f_{Ca}^2 e^{-2M_{Ca}} = 16\left[\left(f_{0,Ca} + \Delta f'_{Ca}\right)^2 + \left(\Delta f''_{Ca}\right)^2\right] e^{-2M_{Ca}}$$

$$|F_T|_B^2 = 16\left(f_{Ca} e^{-M_{Ca}} - 2 f_F e^{-M_F}\right)^2 =$$

$$= 16\left\{\left[\left(f_{0,Ca} + \Delta f'_{Ca}\right) e^{-M_{Ca}} - 2\left(f_{0,F} + \Delta f'_F\right) e^{-M_F}\right]^2 + \left(\Delta f''_{Ca} e^{-M_{Ca}} - 2\Delta f''_F e^{-M_F}\right)^2\right\}$$

$$|F_T|_C^2 = 16\left(f_{Ca} e^{-M_{Ca}} + 2 f_F e^{-M_F}\right)^2 =$$

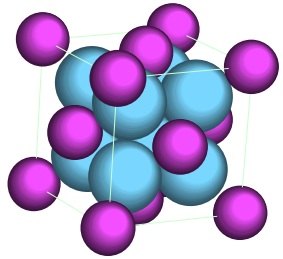
$$= 16\left\{\left[\left(f_{0,Ca} + \Delta f'_{Ca}\right) e^{-M_{Ca}} + 2\left(f_{0,F} + \Delta f'_F\right) e^{-M_F}\right]^2 + \left(\Delta f''_{Ca} e^{-M_{Ca}} + 2\Delta f''_F e^{-M_F}\right)^2\right\}$$

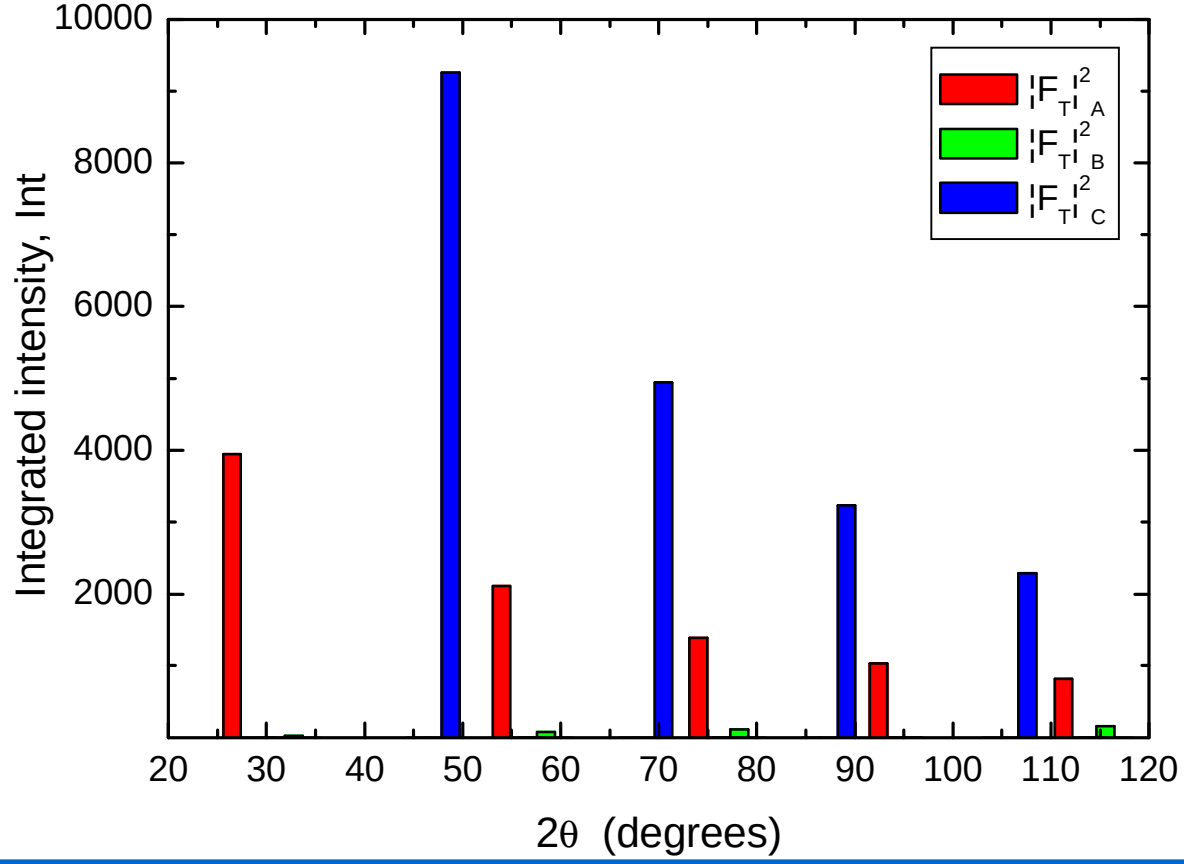
FLUORITE POWDER PATTERN

$$|F|_A^2 = 16 f_{Ca}^2 \qquad l \text{ odd}$$

$$|F|_B^2 = 16(f_{Ca} - 2f_F)^2 \qquad (h+k) \text{ or } l \text{ odd } \textit{multiple} \text{ of } 2$$

$$|F|_C^2 = 16(f_{Ca} + 2f_F)^2 \qquad (h+k) \text{ and } l, \text{ both odd or both even multiple of } 2$$



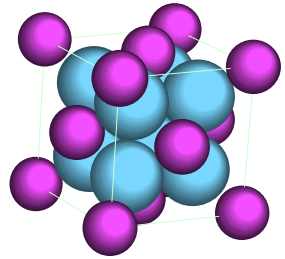


FLUORITE POWDER PATTERN

$|F|_A^2 = 16 f_{Ca}^2$ l odd

$|F|_B^2 = 16(f_{Ca} - 2f_F)^2$ $(h+k)$ *or* l odd *multiple* of 2

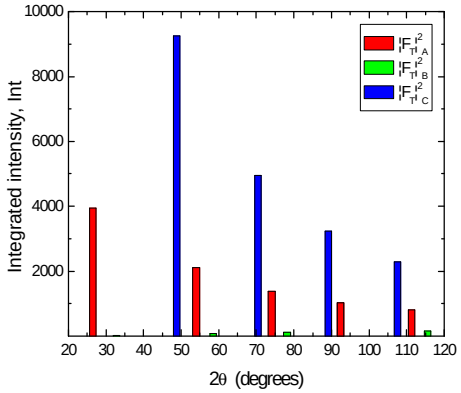
$|F|_C^2 = 16(f_{Ca} + 2f_F)^2$ $(h+k)$ and l, both odd or both even multiple of 2



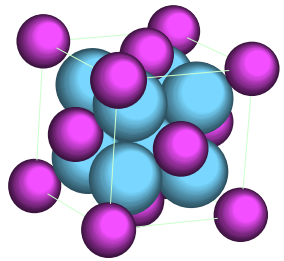
hkl	2*q*	sin*q*/*l*	*LP*	*p*	$e^{-B(Ca)\frac{\sin^2 q}{l^2}}$	$e^{-B(F)\frac{\sin^2 q}{l^2}}$	$f_{0,Ca^{+2}}$	$f_{0,F^{-1}}$	$\|F_T\|_A^2$	$\|F_T\|_B^2$	$\|F_T\|_C^2$	*Int* (§)
111	28.27	0.1585	15.00	8	0.988	0.983	15.53	7.99	3947			**86.3**
200	32.76	0.1830	10.94	6	0.984	0.978	14.87	7.49		24		**0.3**
220	47.00	0.2588	4.94	12	0.969	0.956	12.77	5.93			9259	**100.0**
311	55.76	0.3035	3.36	24	0.958	0.940	11.61	5.12	2109			**31.0**
222	58.48	0.3171	3.02	8	0.954	0.935	11.28	4.90		79		**0.3**
400	68.67	0.3661	2.14	6	0.939	0.914	10.22	4.18			4950	**11.6**
331	75.85	0.3989	1.77	24	0.928	0.899	9.62	3.79	1382			**10.7**
420	78.18	0.4093	1.68	24	0.924	0.894	9.45	3.68		114		**0.8**
422	87.37	0.4483	1.45	24	0.910	0.874	8.87	3.31			3228	**20.5**
333 511	94.22	0.4756	1.38	8 24	0.899	0.859	8.52	3.07	1032 1032			**2.1** **6.2**
440	105.8	0.5177	1.39	12	0.882	0.836	8.03	2.71		0	2288	**7.0**
531	113.06	0.5415	1.49	48	0.871	0.822	7.76	2.50	812			**10.6**
600	115.57	0.5492	1.54	6	0.868	0.817	7.67	2.44	0	155		**0.3**

$a_0 = 5.463$Å $q_m = 13.28°$ $M = B(\sin q/l)^2$ $l = 1.540598$Å

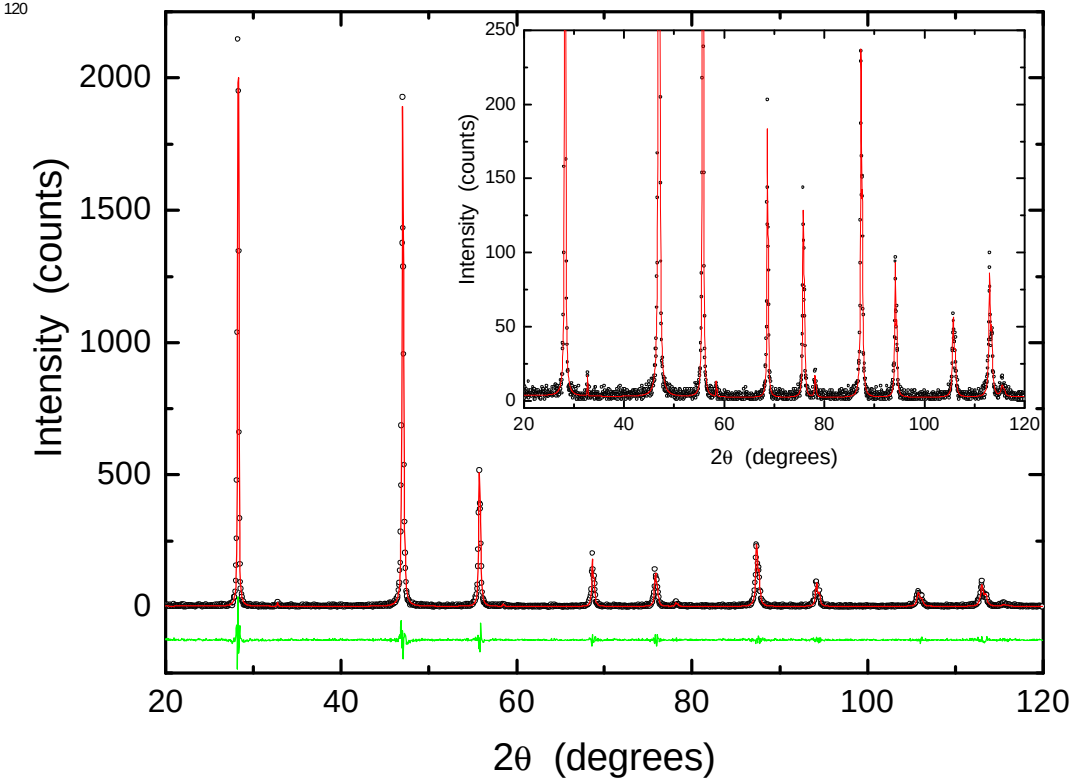
FLUORITE POWDER PATTERN



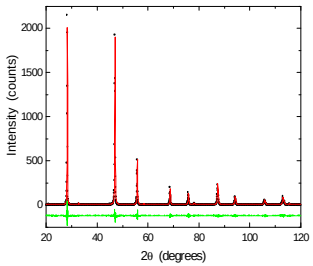
Experimental pattern of fluorite powder



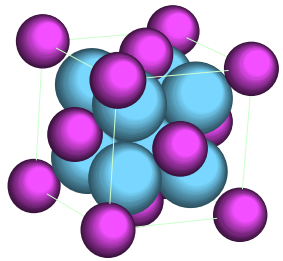
a_0	*sd*	R_{wp}	R_{exp}	*GoF*
5.4639 (1) Å	11 μm	23.98 %	22.33	1.074



FLUORITE POWDER PATTERN



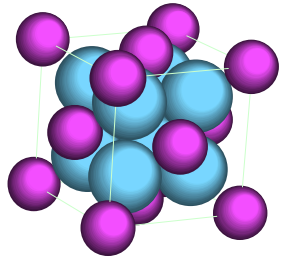
Experimental pattern of fluorite powder: profile fitting results



(hkl)	$2q$	d_{hkl}	I_{max}	*Area*	*Int*
111	28.267	3.1546	1676 (25)	318.5	**83.66**
200	32.754	2.7320	12 (3)	1.7	**0.44**
220	47.000	1.9318	1688 (21)	379.9	**100**
311	55.754	1.6474	453 (13)	124.2	**32.68**
222	58.467	1.5773	10 (2)	1.5	**0.41**
400	68.654	1.3660	167 (7)	48.6	**12.78**
331	75.833	1.2535	117 (6)	42.7	**11.23**
420	78.171	1.2218	14 (2)	4.6	**1.22**
422	87.364	1.1153	221 (7)	83.6	**22.01**
333	94.201	1.0515	21 (1)	8.5	**2.24**
511			64 (14)	25.6	**6.73**
440	105.784	0.9659	50 (3)	28.0	**7.37**
531	113.033	0.9236	79 (4)	44.3	**11.65**
600	115.532	0.9107	7 (2)	5.4	**1.42**

FLUORITE POWDER PATTERN

Comparison between calculated and measured integrated intensities:

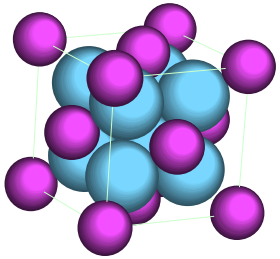


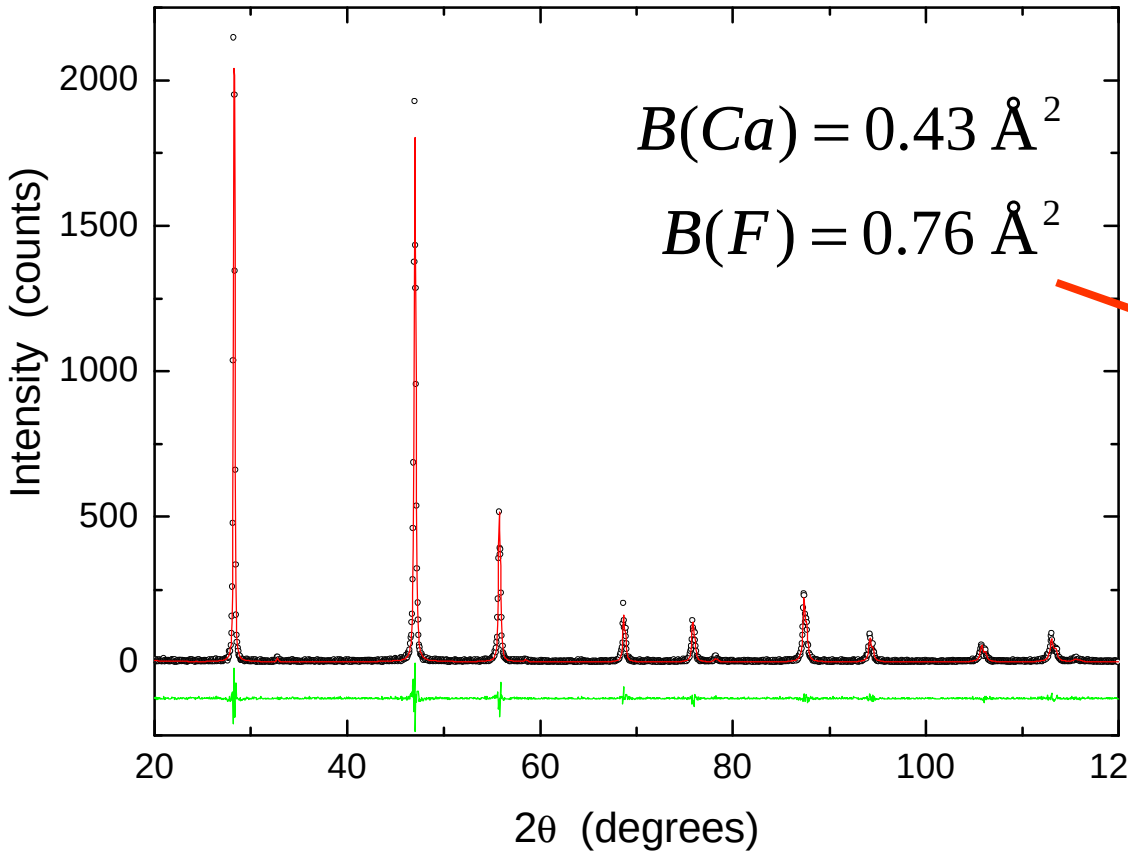
hkl	2*q*	**Calculated** Integ. Int.	**Experimental** Integ. Int.	s_P (%)
111	28.27	**86.3**	**83.7**	**1.0**
200	32.76	**0.3**	**0.4**	**23.0**
220	47.00	**100.0**	**100.0**	**1.0**
311	55.76	**31.0**	**32.7**	**1.7**
222	58.48	**0.3**	**0.4**	**12.7**
400	68.67	**11.6**	**12.8**	**2.9**
331	75.85	**10.7**	**11.2**	**3.0**
420	78.18	**0.8**	**1.2**	**4.3**
422	87.37	**20.5**	**22.0**	**2.1**
333 511	94.22	**2.1** **6.2**	**2.2** **6.7**	**3.5**
440	105.8	**7.0**	**7.4**	**4.1**
531	113.06	**10.6**	**11.6**	***3.0***
600	115.57	**0.3**	**1.4**	***3.1***

$$s_P = \frac{\sqrt{N_T + N_B}}{N_T - N_B} x100$$

FLUORITE POWDER PATTERN

Result using the Rietveld method (TOPAS ©) :





Literature values:

$B(Ca) = 0.47$ Å^2

$B(F) = 0.67$ Å^2

REFERENCES

REFERENCES

[1] B.E. Warren, *X-ray Diffraction*, Addison-Wesley, Reading, MA, 1969.

[2] R.A.Young, *The Rietveld method*, Oxford University Press, Oxford, 1993.

[3] B.D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley, reading Ma, 1978.

[4] H.P. Klug & L.E. Alexander, *X-ray Diffraction procedures*, Wiley, New York, 1974.

[5] International Tables for X-ray Crystallography, 3rd series. Kluwer Academic Publishers, Dordrecht, Boston, London. Vol.A (1983), Vol.B (1993), Vol.C (1992), "Brief Teaching Edition of Volume A" (1985).

[6] P.P. Ewald, *Fifty years of X-ray Diffraction*, Reprinted in pdf format for the IUCr XVIII Congress, Glasgow, Scotland. Copyright © 1962, 1999 International Union of Crystallography, Chester, UK.

[7] International Union of Crystallography: http://www.iucr.org

[8] International Centre for Diffraction Data, Newtown Square, PA, USA. http://www.icdd.com

[9] CCP14 : http://www.ccp14.ac.uk/ ; http://www.iucr.org/sincris-top/logiciel/index.html