

Crystal Structure Determination II

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Diffraction Intensities

The integrated intensity, $I(hkl)$ (peak area) of each powder diffraction peak with *miller indices*, hkl , is given by the following expression:

$$I(hkl) = |F|^2 \times M_{hkl} \times LP(\theta) \times TF(\theta) \times A(\theta)$$

where

$|F|^2$ = Structure Factor

M_{hkl} = Multiplicity

$LP(\theta)$ = Lorentz and Polarization factors

$TF(\theta)$ = Temperature Factor (more correctly referred to as the displacement parameter)

$A(\theta)$ = Absorption Factor

This does not include effects that can sometimes be problematic such as preferred orientation and extinction.

Multiplicity Factor

In a powder diffraction experiment the d -spacings for related reflections are often equivalent. Consider the examples below:

Cubic

– (100), (010), (001), (-100), (0-10), (00-1) → Equivalent

Multiplicity Factor = 6

– (110), (-110), (1-10), (-1-10), (101), (-101), (10-1),
(-10-1), (011), (0-11), (01-1), (0-1-1) → Equivalent

Multiplicity Factor = 12

In general for a cubic system where the Miller indices are n_1 , n_2 and n_3 (all unequal) the multiplicity factors M_{hkl} are:

$n_1 0 0$ (i.e. 100) → $M = 6$

$n_1 n_1 0$ (i.e. 110) → $M = 12$

$n_1 n_1 n_2$ (i.e. 221) → $M = 24$

$n_1 n_1 n_1$ (ie 111) → $M = 8$

$n_1 n_2 0$ (ie 210) → $M = 24$

$n_1 n_2 n_3$ (ie 321) → $M = 48$

The multiplicities are lower in lower symmetry systems. For example in a tetragonal crystal the (100) is equivalent with the (010), (-100) and (0-10), but not with the (001) and the (00-1).

Scattering by an Atom

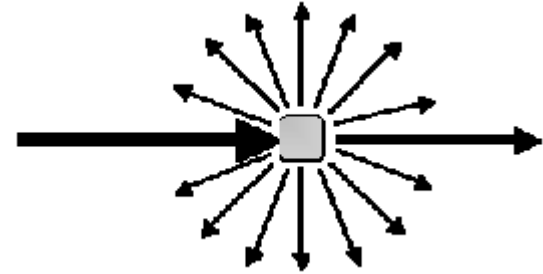
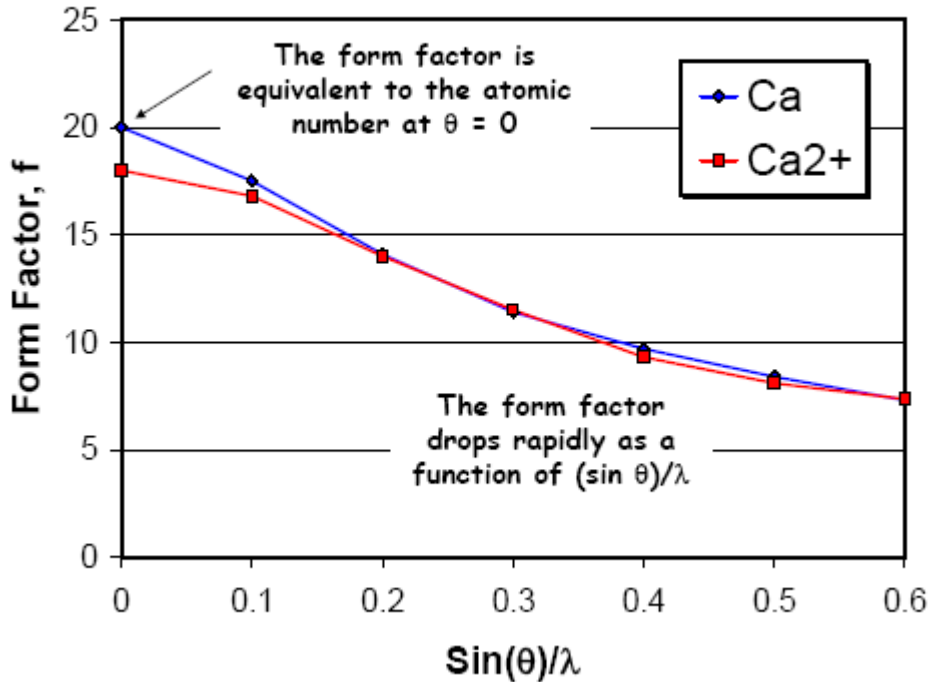
We can consider an atom to be a collection of electrons. The electrons around an atom scatter radiation in the manner described by Thompson. However, due to the coherence of the radiation we need to consider interference effects from different electrons within an atom. This leads to a **strong angular dependence** of the scattering. A quantity f , **the atomic scattering factor**, is used to describe the efficiency of scattering of a given atom in a given direction. It is defined as a ratio of amplitudes:

$$f = \frac{\text{amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by one electron}}$$

For any atom scattering in the forward direction f is equal to its atomic number Z , **$f = Z$** . As θ increases, the waves scattered by individual electrons become more and more out of phase and f decreases. The atomic scattering factor also depends on the wavelength of the incident beam: at fixed value of θ , f will be smaller with the shorter wavelength, since the path differences will be larger relative to the wavelength, leading to greater interferences between the scattered beams.

The actual calculation of f involves $\sin\theta$ rather than θ , so that the net effect is that f decreases as the quantity $(\sin\theta/\lambda)$ increases. The scattering factor is some times called the **form factor**, because it depends on the way in which the electrons are distributed around the nucleus.

X-ray Form Factors

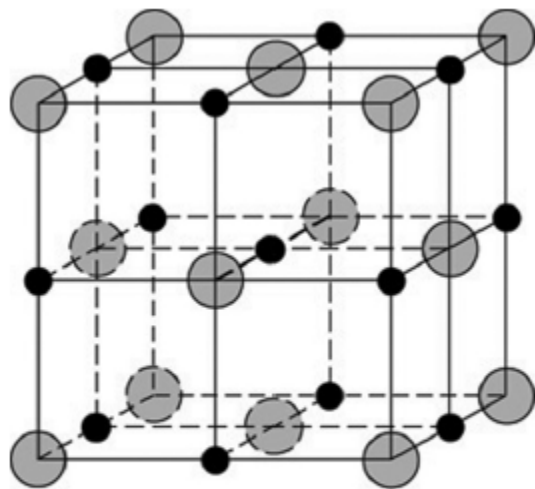


Structure Factor

The structure factor reflects the interference between atoms in the unit cell. All of the information regarding where the atoms are located in the unit cell is contained in the structure factor. The structure factor is given by the following summation over all atoms in the unit cell.

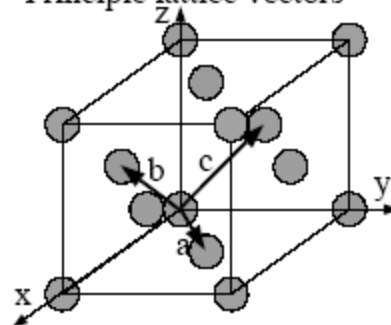
$$F_{(h,k,l)} = \sum_{j=1}^{\text{atoms}} f_{(j)} \exp[2\pi \cdot i(hx_{(j)} + ky_{(j)} + lz_{(j)})]$$

The value of this function is 1 for even multiples of 2π and -1 for odd multiples of 2π .



Face Centered Cubic (FCC)

Principle lattice vectors

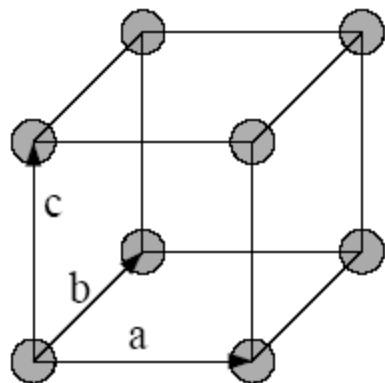


$$a = (x+y)/2$$

$$b = (x+z)/2$$

$$c = (y+z)/2$$

Cubic

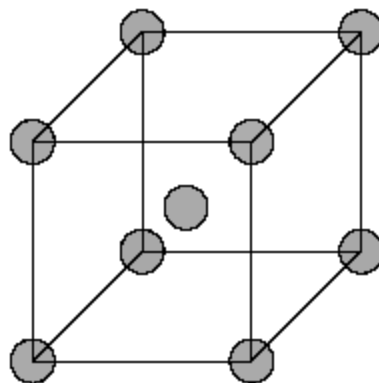


$$a = x$$

$$b = y$$

$$c = z$$

Body Centered Cubic

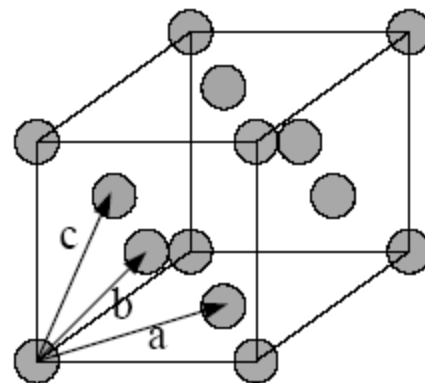


$$a = (x+y-z)/2$$

$$b = (-x+y+z)/2$$

$$c = (x-y+z)/2$$

Face Centered Cubic



$$a = (x+y)/2$$

$$b = (x+z)/2$$

$$c = (y+z)/2$$

Structure Factor Calculations

1. **Base-centered unit cell.** Two atoms of the same kind located at **0 0 0** and **1/2 1/2 0**

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

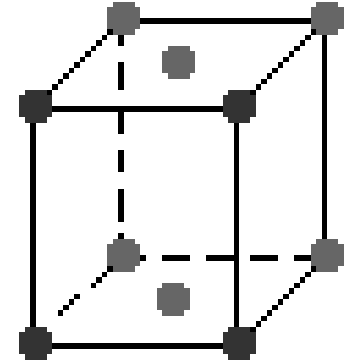
$$= f (1 + e^{\pi i(h+k)})$$

$$= 2f \text{ for } h \text{ and } k \text{ unmixed (both even or both odd)}$$

$$= 0 \text{ for } h \text{ and } k \text{ mixed (one even and one odd)}$$

➤ The value of l index has no effect on the structure factor

➤ Hence 111, 112, 113 all have the same value of F



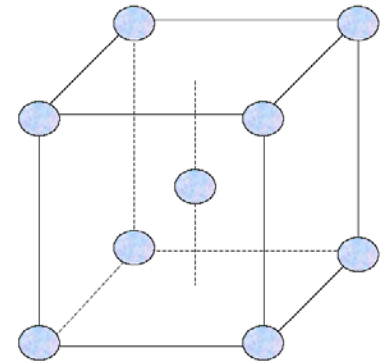
2. **Body-centered unit cell.** Two atoms of the same kind located at **0 0 0** and **1/2 1/2 1/2**.

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

$$= f (1 + e^{\pi i(h+k+l)})$$

$$= 2f \quad \text{when } (h+k+l) \text{ is even}$$

$$= 0 \quad \text{when } (h+k+l) \text{ is odd}$$



$$F_{(h,k,l)} = \sum_{j=1}^{\text{atoms}} f_{(j)} \exp[2\pi \cdot i(hx_{(j)} + ky_{(j)} + lz_{(j)})]$$

3. **Face-centered unit cell.** Four atoms of the same kind located at $0\ 0\ 0$, $1/2\ 1/2\ 0$, $1/2\ 0\ 1/2$ and $0\ 1/2\ 1/2$.

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

$$= f [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}]$$

If h , k , and l are unmixed, then the sums $(h+k)$, $(h+l)$ and $(k+l)$ are even integers and each term in the above equation has the value 1.

$F = 4f$ for unmixed indices;

If h , k and l are mixed, then the sum of the three exponentials is -1, whether two of the indices are odd and one even or two even and one odd. So

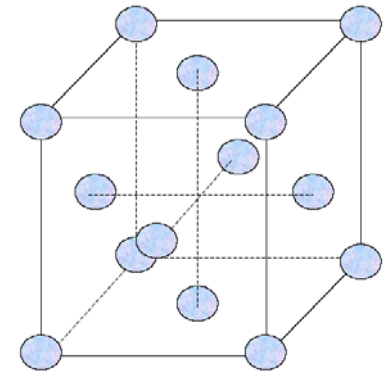
$F = 0$ for mixed indices

Thus, reflections may occur for such planes as (111), (200) and (220) but not for the planes (100), (210), (112) etc.

Note: Structure factor is independent of the *shape* and *size* of the unit cell. It means that rules of missing reflections apply to all kinds of unit cells of any dimension; cubic, tetragonal, orthorhombic etc.

4. **The Example of NaCl:** It has a cubic lattice with 4 Na and 4 Cl atoms per unit cell, located as follows:

Na	$0\ 0\ 0$	$1/2\ 1/2\ 0$	$1/2\ 0\ 1/2$	$0\ 1/2\ 1/2$
Cl	$1/2\ 1/2\ 1/2$	$1/2\ 0\ 0$	$0\ 1/2\ 0$	$0\ 0\ 1/2$



$$\begin{aligned}
 F &= f_{\text{Na}} e^{2\pi i(0)} + f_{\text{Na}} e^{2\pi i(h/2 + k/2)} + f_{\text{Na}} e^{2\pi i(h/2 + l/2)} + f_{\text{Na}} e^{2\pi i(k/2 + l/2)} + f_{\text{Cl}} e^{2\pi i(h/2 + k/2 + l/2)} + \\
 &\quad f_{\text{Cl}} e^{2\pi i(h/2)} + f_{\text{Cl}} e^{2\pi i(k/2)} + f_{\text{Cl}} e^{2\pi i(l/2)} \\
 &= f_{\text{Na}} [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}] + f_{\text{Cl}} [e^{\pi i(h+k+l)} + e^{\pi ih} + e^{\pi ik} + e^{\pi il}]
 \end{aligned}$$

In case of NaCl, the sodium-atom positions are related by the face centering translations and so are the chlorine-atom positions. Whenever a lattice contains common translations, the corresponding terms in the structure factor equation can always be factored out, leading to considerable simplification. In this case:

$$F = f_{\text{Na}} [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}] + f_{\text{Cl}} e^{\pi i(h+k+l)} [1 + e^{\pi i(-k-l)} + e^{\pi i(-h-l)} + e^{\pi i(-h-k)}]$$

The signs of the exponents in the second bracket may be changed:

$$F = f_{\text{Na}} [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}] + f_{\text{Cl}} e^{\pi i(h+k+l)} [1 + e^{\pi i(k+l)} + e^{\pi i(h+l)} + e^{\pi i(h+k)}]$$

As $e^{n\pi i} = e^{-n\pi i}$

$$F = [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}] [f_{\text{Na}} + f_{\text{Cl}} e^{\pi i(h+k+l)}]$$

Here the terms corresponding to the face-centering translations appear in the first factor; the second term contains the terms that describe the “basis” of the unit cell, namely, the Na atom at 0 0 0 and the Cl atom at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$. The first term have a total value of **zero** for mixed indices and **4** for unmixed indices as described earlier for face-centered unit cell. This shows at once that NaCl has a face-centered lattice and that:

$$F = 0 \quad \text{for mixed indices}$$

$$F^2 = 0$$

For unmixed indices

$$F = 4 [f_{\text{Na}} + f_{\text{Cl}} e^{\pi i (h+k+l)}]$$

$$F = 4 (f_{\text{Na}} + f_{\text{Cl}}) \quad \text{if } (h + k + l) \text{ is even;}$$

$$F^2 = 16 (f_{\text{Na}} + f_{\text{Cl}})^2$$

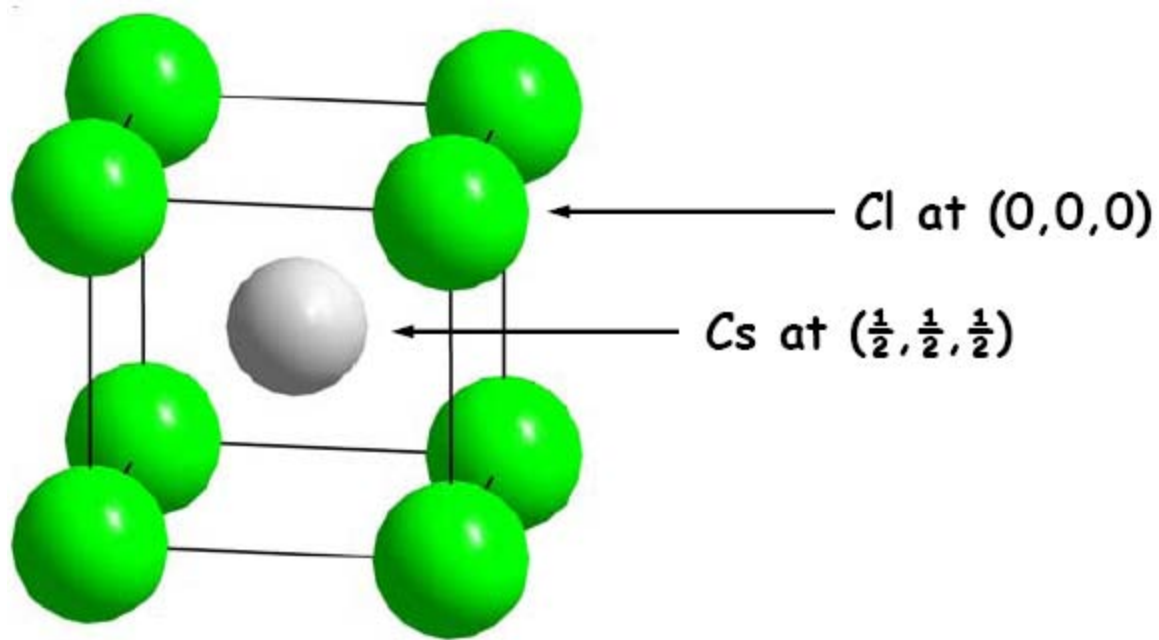
$$F = 4 (f_{\text{Na}} - f_{\text{Cl}}) \quad \text{if } (h + k + l) \text{ is odd;}$$

$$F^2 = 16 (f_{\text{Na}} - f_{\text{Cl}})^2$$

In this case, there are more than four atoms per unit cell (8), but the lattice is still face-centered. The introduction of additional atoms has not eliminated any reflections present in the case of the four-atom cell, but it has decreased some in intensity.

5. Example CsCl

- Let's calculate the structure factors for the first 6 peaks of CsCl. To do this we need to know the atomic positions and the Miller Indices.



$$F_{(h,k,l)} = \sum_{j=1}^{\text{atoms}} f_{(j)} \exp[2\pi \cdot i(hx_{(j)} + ky_{(j)} + lz_{(j)})]$$

$$F = f_{Cl} e^{2\pi i(0)} + f_{Cs} e^{2\pi i(h/2 + k/2 + l/2)}$$

$$F = f_{Cl} e^{2\pi i(0)} + f_{Cs} e^{\pi i(h+k+l)}$$

$$F = f_{Cl} - f_{Cs}$$

when $(h + k + l)$ is odd number

$$F = f_{Cl} + f_{Cs}$$

when $(h + k + l)$ is even number

$$F_{100} = f_{Cl} - f_{Cs}$$

$$F_{110} = f_{Cl} + f_{Cs}$$

$$F_{111} = f_{Cl} - f_{Cs}$$

$$F_{220} = f_{Cl} + f_{Cs}$$

$$F_{210} = f_{Cl} - f_{Cs}$$

$$F_{221} = f_{Cl} + f_{Cs}$$

Temperature Factor

The atoms in a crystal undergo thermal vibration about their mean positions and the amplitude of this vibration increases as the temperature is increased. For example at room temperature the average displacement of an atom of aluminum from its mean position is 0.17 Å, which is about 6 percent of the distance of closest approach of the mean atom positions in this crystal.

Thermal vibration of the atoms has three main effects:

1. The unit cell expands, causing changes in periodicity of d and therefore in the 2θ positions of the diffraction lines.
2. The intensities of the diffraction lines decrease
3. The intensity of the background scattering between lines increases.

Thermal agitation decreases the intensity of diffracted beam because it degrades the periodicity of the lattice. In intensity calculations this effect is included by introducing the *temperature factor* e^{-2M} , which is a number by which the calculated intensity is to be multiplied to allow for thermal vibration of the atoms. ($f = f_0 e^{-M}$)

The quantity M depends on both the amplitude of thermal vibration and the scattering angle 2θ .

$$M = 8\pi^2 \bar{u}^2 (\sin \theta / \lambda)^2 = B (\sin \theta / \lambda)^2$$

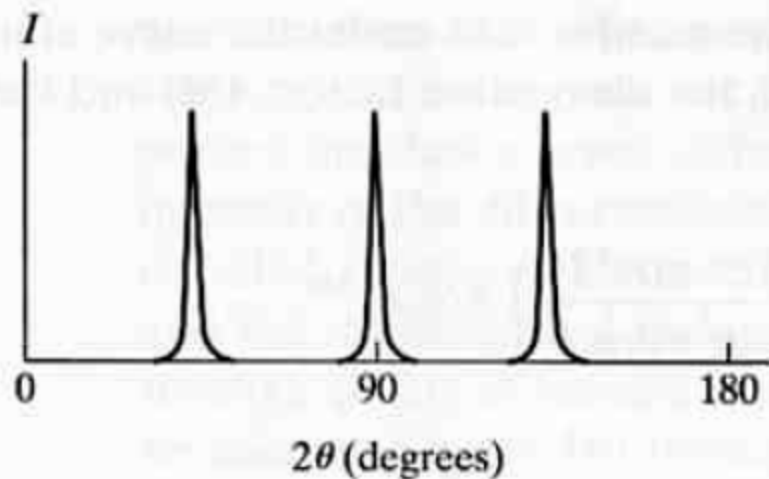
Where \bar{u} is the mean square displacement of the atom in a direction normal to the diffracting plane and the coefficient B is the isotropic temperature factor and is proportional to the mean squared displacement of the atoms.

More sophisticated treatments assume different values of B for each crystallographically independent atom and anisotropic vibrations (elliptical in shape rather than spherical).

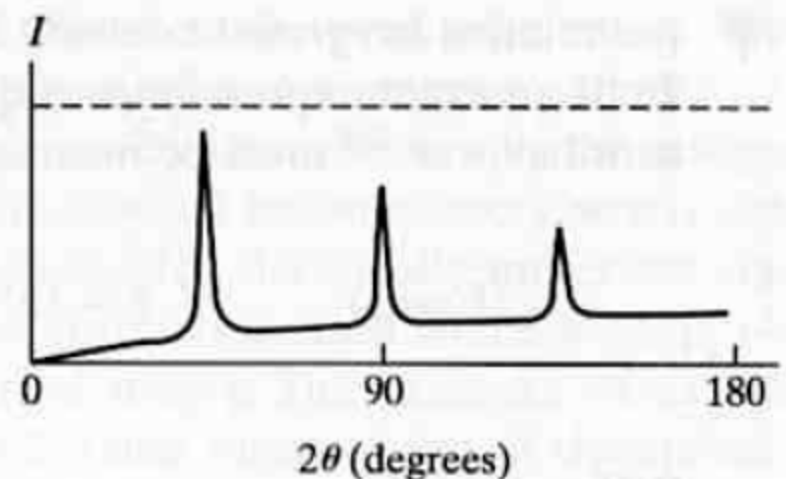
Isotropic factor: B or \bar{u}

Anisotropic factor: $B_{11}, B_{22}, B_{33}, B_{12}, B_{13}, B_{23}, \bar{u}_{11}, \bar{u}_{22}, \bar{u}_{33}, \bar{u}_{12}, \bar{u}_{13}, \bar{u}_{23}$

The thermal vibration of atoms has another effect on diffraction patterns. Besides decreasing the intensity of diffraction lines, it causes some general coherent scattering in all directions. This is called *temperature-diffuse scattering*; it contributes only to the general background of the pattern and its intensity gradually increases with 2θ .



(a) No thermal vibration



(b) Thermal vibration

Absorption Factor

According to Beer's law, absorption reduces the intensity of an X-ray beam travelling through a given material by an amount which depends on the material and the length of the path travelled by the radiation in it.

The intensity of the diffracted X-rays is reduced due to absorption by the factor:

$$I/I_0 = e^{-\mu x}$$

Here x is the total path length and μ is the linear absorption coefficient of the crystal.

Lorentz Factor

There are a number of factors that lead to angle dependence of the peak intensities (integrated intensities).

1. Diffraction can occur for angles slightly different from the value predicted by Bragg's Law $\rightarrow I \propto 1/\sin(2\theta)$.
2. The number of crystals oriented in such a way as to satisfy Bragg's Law is highest for low angles $\rightarrow I \propto \cos(\theta)$
3. The fraction of the diffraction cone that intersects the detector is highest at low angles $\rightarrow I \propto 1/\sin(2\theta)$

When combine these considerations and do some trigonometric manipulation we get the Lorentz Factor:

$$I \propto 1/(4\sin^2\theta \cos\theta)$$

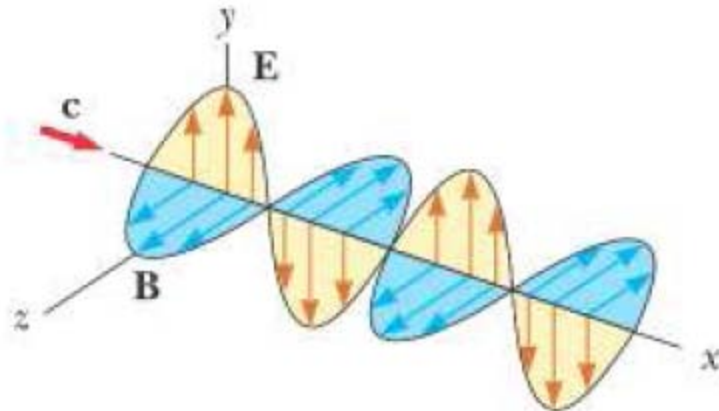
Polarization and the LP Factor

An X-ray propagating in the x-direction will have an electric vector oriented in the yz plane. The y and z components of the X-ray will be scattered differently because the angle between the scattered beam and the electric field gradient will differ, as derived by Thompson. This leads to the polarization factor:

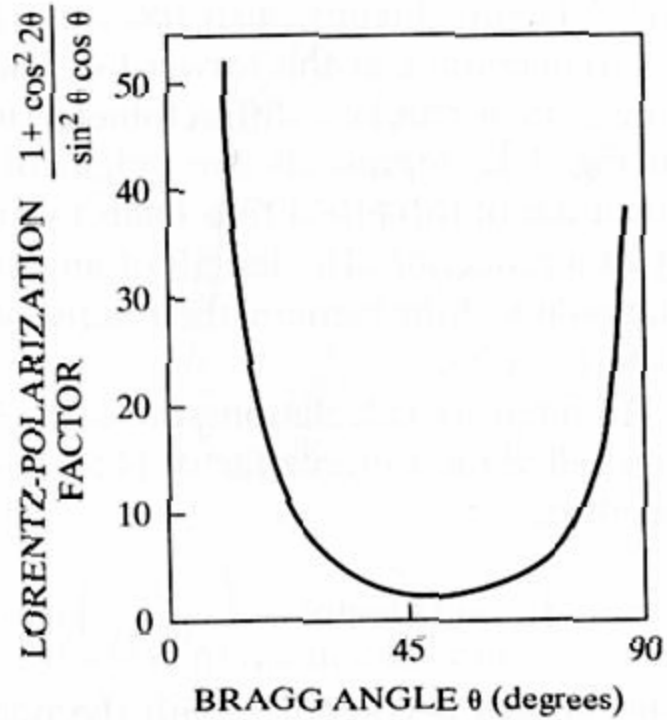
$$I \propto (1+\cos^22\theta)/2$$

Typically the Lorentz and Polarization terms are combined to give the Lorentz-Polarization (LP) factor.

$$I \propto (1+\cos^22\theta)/(8\sin^2\theta \cos\theta)$$

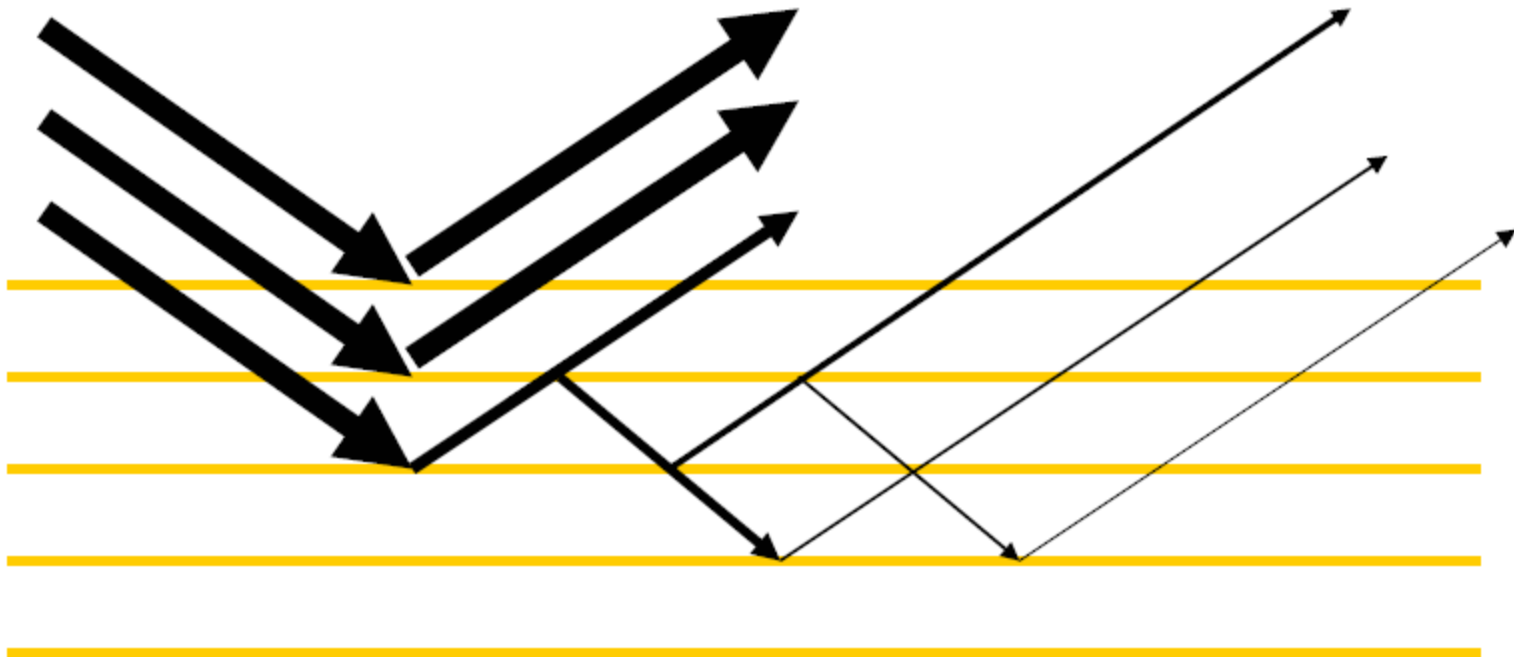


The overall effect of these geometrical factors is to decrease the intensity of the reflections at intermediate angle compared to those in forward or backward directions.



Extinctions

Intensity calculation formula is derived for “ideally imperfect” crystal, one consisting of quite small mosaic blocks which are randomly oriented. Such a crystal has maximum diffracting power. A crystal made up of large mosaic blocks is more nearly perfect and has a lower diffracting power. This decrease in the integrated intensity of the diffracted beam as the crystal becomes more nearly perfect is called extinction. Destructive interference from re-reflections within the crystals. The strong peaks appear weaker. The solution is to grind the powdered sample more.



Examples of Intensity Calculation

1. Peak Positions and Intensity Calculations for copper

Copper is an face-centered cubic with cell parameter $a = 3.615 \text{ \AA}$. Diffraction pattern is measured with Cu $K\alpha$ radiation.

1	2	3	4	5	6	7	8
Line	hkl	$h^2 + k^2 + l^2$	$\sin^2 \theta$	$\sin \theta$	θ	$\sin \theta / \lambda$	f_{Cu}
1	111	3	0.1365	0.369	21.7	0.24	22.1
2	200	4	0.1820	0.427	25.3	0.27	20.9
3	220	8	0.364	0.603	37.1	0.39	16.8
4	311	11	0.500	0.707	45.0	0.46	14.8
5	222	12	0.546	0.739	47.6	0.48	14.2
6	400	16	0.728	0.853	58.5	0.55	12.5
7	331	19	0.865	0.930	68.4	0.60	11.5
8	420	20	0.910	0.954	72.6	0.62	11.1

1	9	10	11	12	13	14
Line	F^2	M	LP	Cal. Intensity	Relative Intensity (%)	Obs. Intensity
1	7810	8	12.03	7.52×10^5	100	vs
2	6990	6	8.50	3.56×10^5	47	s
3	4520	12	3.70	2.01×10^5	27	s
4	3500	24	2.83	2.38×10^5	32	s
5	3230	8	2.74	0.71×10^5	9	m
6	2500	6	3.18	0.48×10^5	6	w
7	2120	24	4.81	2.45×10^5	33	s
8	1970	24	6.15	2.91×10^5	39	s

2. Peak Positions and Intensity Calculations ZnS

ZnS (zinc blende) is cubic and has a lattice parameter of 5.41 Å.

The first step is to calculate the structure factor. ZnS has four zinc and four sulfur atoms per unit cell, located at the following positions.

Zn:	$\frac{1}{4} \frac{1}{4} \frac{1}{4}$	+ face-centering translations
S:	0 0 0	+ face-centering translations

Since structure is face-centered, the structure factor will be zero for planes of mixed indices. From example of NaCl, the terms in the structure factor equation corresponding to the face-centering translations can be factored out and the equation for unmixed indices written down at once:

$$F = 4[f_s + f_{Zn} e^{(\pi i/2)(h + k + l)}]$$

$|F|^2$ is obtained by multiplication of the above by its complex conjugate:

$$|F|^2 = 16[f_s + f_{Zn} e^{(\pi i/2)(h + k + l)}] [f_s + f_{Zn} e^{-(\pi i/2)(h + k + l)}]$$

This reduces to the following form:

$$|F|^2 = 16[f_s^2 + f_{Zn}^2 + 2f_s f_{Zn} \cos(\pi/2)(h + k + l)]$$

Further simplification is possible for various special cases:

$$|F|^2 = 16[f_s^2 + f_{Zn}^2]$$

when $(h + k + l)$ is odd

$$|F|^2 = 16[f_s - f_{Zn}]^2$$

when $(h + k + l)$ is an odd multiple of 2

$$|F|^2 = 16[f_s + f_{Zn}]^2$$

when $(h + k + l)$ is an even multiple of 2

The intensity calculations are carried out in the table below:

1	2	3	4	5	6
Line	<i>hkl</i>	θ	$\sin\theta/\lambda$	f_s	f_{Zn}
1	111	14.3	0.16	12.3	25.8
2	200	16.6	0.19	11.4	24.6
3	220	23.8	0.26	9.7	22.1
4	311	28.2	0.30	9.0	20.7
5	222	29.6	0.32	8.8	20.0
6	400	34.8	0.37	8.2	18.4

1	7	8	9	10	11
Line	F^2	M	LP	Relative Intensity (%) (Calc.)	Obs. Intensity
1	13070	8	30	100	vs
2	2790	6	21.7	12	w
3	16180	12	9.76	61	vs
4	8150	24	6.64	41	vs
5	2010	8	5.95	3	vw
6	11320	6	4.19	9	w

Determination of Atom Positions

The observed relative intensities are determined by the atom positions in the unit cell. However, there is no known procedure of directly calculating atom positions from observed intensities.

Atom positions are rather calculated by trial and error method. A set of atom positions is assumed, the intensities corresponding to these positions are calculated and the calculated intensities are compared with the observed ones, the process being repeated until satisfactory agreement is reached. This trial method is further aided by the accumulated knowledge of previously known structures. From these known structures a few likely candidates may be selected as a starting point.

There are many complex structures which can not be solved by this simple approach. Two powerful methods of *space group theory* and *Fourier series* are used in these cases. For example if a given substance is known to be tetragonal and to have n atoms in its unit cell, then space-group theory lists all possible arrangements of n atoms which will have tetragonal symmetry. This listing of possible arrangements is further aided by the knowledge of systematic absences.

A *Fourier series* is a type of infinite trigonometric series by which any kind of periodic function may be expressed. Now the one essential property of a crystal is that its atoms are arranged in space in a periodic fashion. This means that density of electrons is also a periodic function of position in the crystal, rising to maximum at the point where an atom is located and dropping to a low value in the region between atoms. Since the electron density is a periodic function of position of atoms, a crystal may be described analytically by means of the *Fourier series*.

Example of Structure Determination

Consider an intermediate phase which occurs in the cadmium-tellurium system. Chemical analysis of the specimen showed that it contains 46.6 weight percent Cd and 53.4 weight percent Te. This is equivalent to 49.8 atomic percent Cd and can be represented by the formula CdTe. Powder X-ray diffraction pattern was collected by using Cu K_{α} radiation.

The observed values of $\sin^2\theta$ for the first 16 lines are listed in the Table 1, together with the visually estimated relative line intensities. This pattern can be indexed on the basis of a cubic unit cell and the indices of the observed lines are given in the Table 1. The lattice parameter, calculated from the $\sin^2\theta$ value for the highest line, is 6.46 Å.

The density of the specimen, as determined by weighing a quantity of the powder in a pycnometer bottle was 5.82 g/cm³.

The sum of atomic weights can be calculated as:

$$\sum A = \frac{(5.82)(6.46)^3}{1.66042} = 945$$

Since the molecular weight of CdTe is 240.02, the number of molecules per unit cell is $945/240.02 = 3.94$, or 4 within experimental error.

Knowing the unit cell of CdTe is cubic and that it contains 4 molecules of CdTe, i.e., 4 atoms of Cd and 4 atoms of Te, possible arrangement of these atoms in the unit cell can be evaluated.

Examination of the indices listed in Table 1 reveals that the indices of the observed lines are all unmixed and that the Bravais lattice must be *face-centered*. Not all possible of sets of unmixed indices are present, however: 200, 420, 600, 442, 622 and 640 are missing from the pattern. These reflections may be too weak to be observed. Now there are two common face-centered cubic structures of AB type i.e., containing two different atoms in equal proportions and both contain four molecules per unit cell: these are the NaCl structure and the zinc-blende form of ZnS. Both these are logical possibilities.

The next step is to calculate relative diffracted intensities for each structure and compare them with experiment, in order to determine whether or not one of these structures is correct one. If CdTe has the NaCl structure, then its structure factor for unmixed indices is given by:

$$F = 4 (f_{Cd} + f_{Te}) \quad \text{if } (h + k + l) \text{ is even;}$$

$$F^2 = 16 (f_{Cd} + f_{Te})^2$$

$$F = 4 (f_{Cd} - f_{Te}) \quad \text{if } (h + k + l) \text{ is odd;}$$

$$F^2 = 16 (f_{Cd} - f_{Te})^2$$

On the other hand, if the ZnS structure is correct, then the structure factor for unmixed indices is given by:

$$|F|^2 = 16[f_{Cd}^2 + f_{Te}^2] \quad \text{when } (h + k + l) \text{ is odd}$$

$$|F|^2 = 16[f_{Cd} - f_{Te}]^2 \quad \text{when } (h + k + l) \text{ is an odd multiple of 2}$$

$$|F|^2 = 16[f_{Cd} + f_{Te}]^2 \quad \text{when } (h + k + l) \text{ is an even multiple of 2}$$

Even before making a detailed calculation of relative diffracted intensities, the NaCl structure can almost be eliminated as a possibility simply by inspection of above equations. The atomic numbers of Cd and Te are 48 and 52 respectively, so the value of $[f_{Cd} + f_{Te}]^2$ is several hundred times greater than the value of $[f_{Cd} - f_{Te}]^2$ for all values of $(\sin \theta)/\lambda$. Then, if CdTe has the NaCl structure, the 111 reflection should be very weak and the 200 reflection very strong. Actually, 111 is strong and 200 is not observed.

On the other hand, if the ZnS structure is assumed, intensity calculations lead to the values listed in the fifth column. The agreement between these values and the observed intensities is excellent, except for a few minor inconsistencies among the low-angle reflections and these are due to neglect of the absorption factor. In particular, note that the ZnS structure satisfactorily accounts for all the missing reflections (200, 420, etc), since the calculated intensities of these reflections are all extremely low. Therefore this example of CdTe has the structure of the zinc-blende form of ZnS.

After a given structure has been shown to be in accord with the diffraction data, it is advisable to calculate the interatomic distances involved in that structure. This calculation not only is of interest in itself but also to disclose any gross errors that may have been made, since there is obviously something wrong with the proposed structure if it brings certain atoms impossibly close together. In the present structure, the nearest neighbour to the Cd atom at 0 0 0 is the Te atom at $\frac{1}{4} \frac{1}{4} \frac{1}{4}$. The Cd-Te interatomic distance is therefore $a/4 = 2.80 \text{ \AA}$ which is quite reasonable.

Table 1

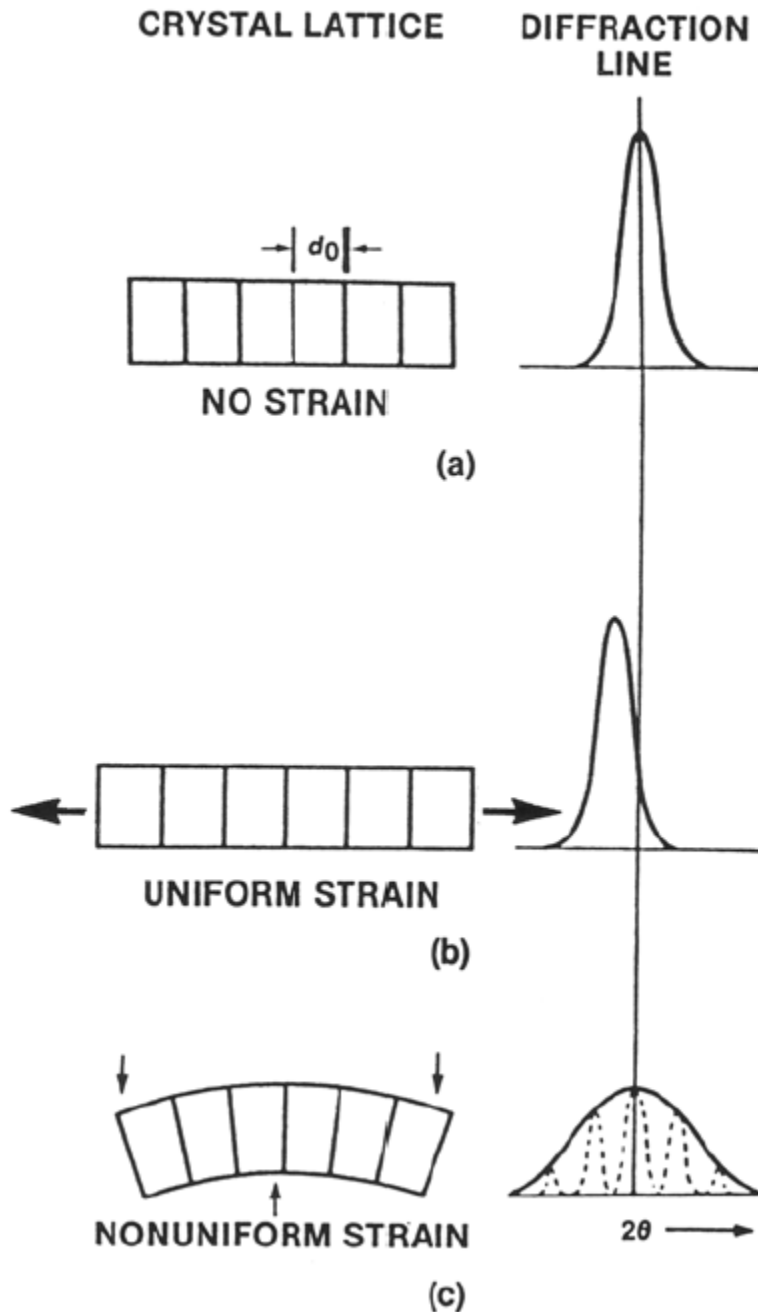
Line	Intensity	sin²θ	<i>hkl</i>
1	s	0.0462	111
2	vs	0.1198	220
3	vs	0.1615	311
4	vw	0.1790	222
5	m	0.234	400
6	m	0.275	331
7	s	0.346	422
8	m	0.391	511, 233
9	w	0.461	440
10	m	0.504	531
11	m	0.575	620
12	w	0.616	533
13	w	0.688	444
14	m	0.729	711, 551
15	vs	0.799	642
16	s	0.840	731, 553

Table 2

Line	<i>hkl</i>	Obs. Intensity	Cal. I (NaCl)	Cal. I (ZnS)
1	111	s	0.05	12.4
	200	nil	13.2	0.03
2	220	vs	10.0	10
3	311	vs	0.02	6.2
4	222	vw	3.5	0.007
5	400	m	1.7	1.7
6	331	m	0.01	2.5
	420	nil	4.6	0.01
7	422	s		3.4
8	511, 233	m		1.8
9	440	w		1.1
10	531	m		2.0
	600, 442	nil		0.005
11	620	m		1.8
12	533	w		0.9
	622	nil		0.004
13	444	w		0.6
14	711, 551	m		1.8
	640	nil		0.005
15	642	vs		4.0
16	731, 553	s		3.3

*Calculated intensities have been adjusted so that the 220 line has an intensity of 10.0 for both structures.

Residual Stress and Strain



Strain in a material can produce two types of diffraction effects. If the strain is uniform (either tensile or compressive) it is called *macrostrain* and the unit cell distances will become either larger or smaller resulting in a shift in the diffraction peaks in the pattern. Macrostrain causes the lattice parameters to change in a permanent (but possibly reversible) manner resulting in a peak shift. Macrostrains may be induced by heating of clay minerals.

Microstrains are produced by a distribution of tensile and compressive forces resulting in a broadening of the diffraction peaks. In some cases, some peak asymmetry may be the result of microstrain. Microstress in crystallites may come from dislocations, vacancies, shear planes, etc; the effect will generally be a distribution of peaks around the unstressed peak location, and a crude broadening of the peak in the resultant pattern.

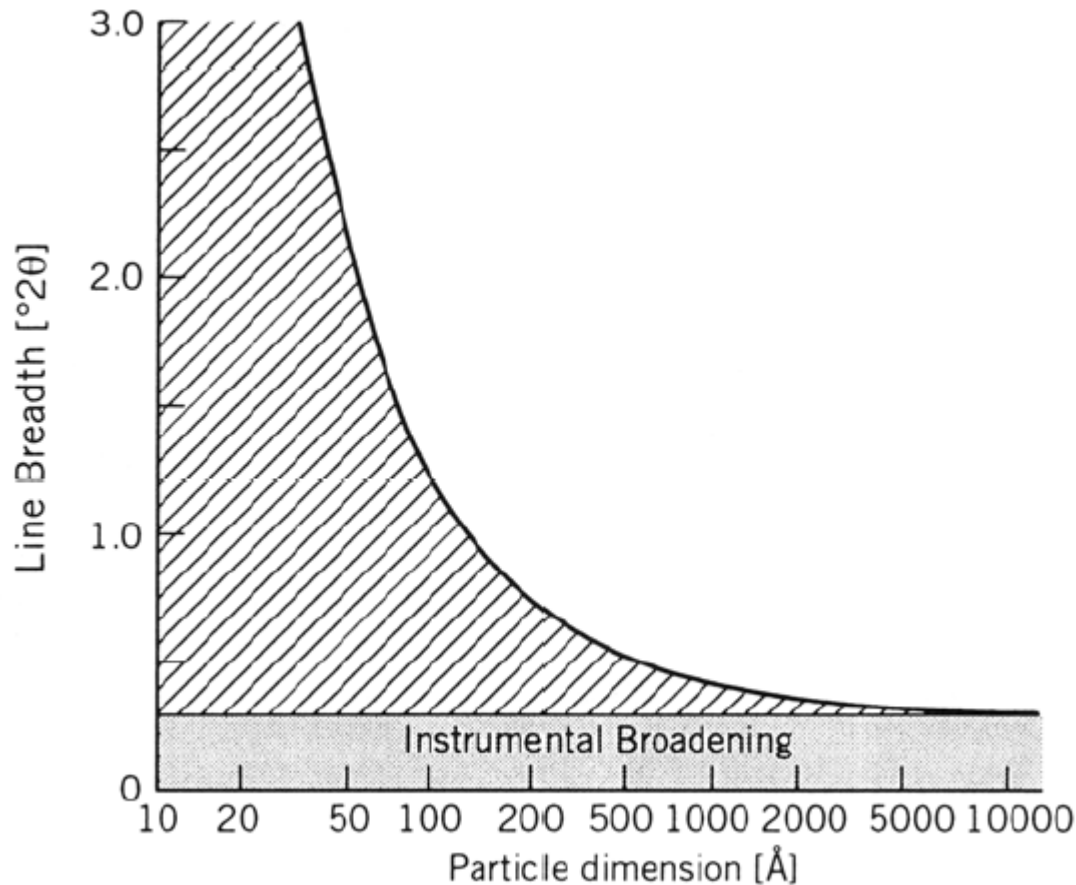
Crystallite Size

- For large crystallites (i.e., thousands of unit cells), diffraction will result in “*sharp*” diffraction peaks only at the precise location of the *Bragg angle*.
- If the particle size is smaller (such that there are insufficient lattice planes to effectively cancel all incoherent scattering at angles close to the Bragg angle) the net result will be a broadening of the diffraction peak around the Bragg angle. This phenomenon of widening of diffraction peaks is related to incomplete “canceling” of small deviations from the Bragg angle in small crystallites is known as *particle size broadening*.
- Particle size broadening is differentiated from the normal width of diffraction peaks related to instrumental effects. In most cases, particle size broadening will not be observed with crystallite sizes larger than 1 μm . The crystallite size broadening (β_τ) of a peak can usually be related to the mean crystallite dimension (τ) by the *Scherrer equation*:

$$\tau = \frac{K\lambda}{\beta_\tau \cos \theta}$$

where β_τ is the line broadening due to the effect of small crystallites and is given by $(B - b)$, B being the breadth of the observed diffraction line at its half-intensity maximum, and b the instrumental broadening or breadth of a peak that exhibits no broadening beyond the inherent instrumental peak width.

- Note that β_τ is given in radians, and that K is the shape factor which typically has a value of about 0.9.
- As shown below, particle size broadening is not significant at sizes above 10,000 Å (1 μm). When instrumental parameters are known (i.e., FWHM values for crystallites larger than 1 μm), the relationship above may be used to calculate crystallite sizes as small as 10 Å if the structures are unstrained.



It is interesting to think of particle size broadening when considering the diffraction pattern obtained from many amorphous materials. Typically these materials (like glass and plastics) will give an extremely broad peak over an angular range of perhaps $2\theta \sim 5^\circ - 10^\circ$ that will look like a “hump” in the background. One can think of this “hump” as an extreme example of particle size broadening where the short range ordering is on the order of a several angstroms.

Lanthanum hexaboride (LaB_6) has the narrowest peaks of any material and for all practical purposes one can consider all measured peak broadening as being due to instrumental factors.

Resolving Power of Diffractometer

The sensitivity of change of the 2θ angle for a reflection with change in d_{hkl} -spacing is the measure of the resolving power of the diffraction technique. The resolving power or the limit of resolution, $\delta d / d$, can be obtained by differentiating Bragg's law with respect to d and θ (λ fixed), i.e.

$$\lambda = 2d \sin\theta$$

differentiating

$$0 = 2d \cos\theta \delta\theta + 2\sin\theta \delta d$$

hence

$$\delta d/d = -\cot\theta \delta\theta$$

For a given value of $2\delta\theta$, which may be expressed in terms of the minimum resolved distance between two reflections, and for the smallest limit of resolution we want $\cot\theta$ values to be as small as possible, or for a given value of $\delta d/d$, we want the angular separation of the reflections $2\delta\theta$ to be large, and hence again $\cot\theta$ values to be as small as possible.

As we know that $\cot\theta$ values are high at low angles and rapidly decrease towards zero as θ approaches 90° . Hence d_{hkl} -spacing measurements are most accurate using high angle reflections.