

## X-Ray Diffraction

### Systematic absences

Examples: systematic absences in (hkl) occur for bcc (I) or fcc (F) lattices; the rules for the absences are:

bcc:  $h+k+l=\text{odd}$  are absent

fcc: only present if h,k,l all even or all odd

pc: no systematic absences

(Exercise to do once you've understood Structure Factors: PREDICT ALL OF THESE ABSENCES USING  $F(hkl)$  CALCULATIONS)

## Scattering of X-rays

Factors that affect the intensity,  $I(hk)$ , of diffracted X-rays?

- Atomic scattering factor (heavier elements have more electrons).
- Constructive interference (Bragg's law).
- Systematic absences (the Bragg condition is satisfied but symmetry leads to destructive interference).
- Other factors: thermal vibration; disorder; absorption & wavelength of X-rays

Now let us dot this equation with  $\hat{\mathbf{G}}$  to give

$$\begin{aligned}\hat{\mathbf{G}} \cdot \frac{2\pi}{\lambda}(\hat{\mathbf{k}} - \hat{\mathbf{k}}') &= \hat{\mathbf{G}} \cdot \mathbf{G} \\ \frac{2\pi}{\lambda}(\sin \theta - \sin \theta') &= |\mathbf{G}| \\ \frac{2\pi}{|\mathbf{G}|}(2 \sin \theta) &= \lambda \\ 2d \sin \theta &= \lambda\end{aligned}$$

which is the Bragg condition (in the last step we have used the relation between  $\mathbf{G}$  and  $d$ ). You may wonder why in this equation we got  $\lambda$  on the right hand side rather than  $n\lambda$  as we had in Eq. 10.3. The point here is that there if there is a reciprocal lattice vector  $\mathbf{G}$ , then there is also a reciprocal lattice vector  $n\mathbf{G}$ , and if we did the same calculation with that lattice vector we would get  $n\lambda$ . In other words, in the  $n\lambda$  case we are reflecting off of the spacing  $nd$  which necessarily also exists when there is a set of lattice planes with spacing  $d$ .

Thus we conclude that the Laue condition and the Bragg condition are equivalent. It is equivalent to say that interference is constructive (as Bragg indicates) or to say that crystal momentum is conserved (as Laue indicates).

## 10.2 Scattering Amplitudes

If the Laue condition is satisfied, we would now like to ask how much scattering we actually get. Recall in section 10.1.1 we started with Fermi's golden rule

$$\Gamma(\mathbf{k}', \mathbf{k}) = \frac{2\pi}{\hbar} |\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2 \delta(E_{\mathbf{k}'} - E_{\mathbf{k}})$$

and we found out that if  $V$  is a periodic function, then the matrix element is given by (See Eq. 10.1)

$$\langle \mathbf{k}' | V | \mathbf{k} \rangle = \left[ \frac{1}{L^3} \sum_{\mathbf{R}} e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}} \right] \left[ \int_{unit-cell} d\mathbf{x} e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{x}} V(\mathbf{x}) \right] \quad (10.4)$$

The first factor in brackets gives zero unless the Laue condition is satisfied, in which case it gives a constant (due to the  $1/L^3$  out front, this is now a nondivergent constant). The second term in brackets is known as the structure factor (compare to Eq. 9.6)

$$S(\mathbf{G}) = \int_{unit-cell} d\mathbf{x} e^{i\mathbf{G} \cdot \mathbf{x}} V(\mathbf{x}) \quad (10.5)$$

where we have used  $\mathbf{G}$  for  $(\mathbf{k}' - \mathbf{k})$  since this must be a reciprocal lattice vector or the first term in brackets vanishes.

Frequently, one writes

$$I_{(hkl)} \propto |S_{(hkl)}|^2 \quad (10.6)$$

which is shorthand for saying that  $I_{(hkl)}$ , the intensity of scattering off of the lattice planes defined by the reciprocal lattice vector  $(hkl)$ , is proportional to the square of the structure factor at this reciprocal lattice vector. Sometimes a delta-function is also written explicitly to indicate that the wavevector difference  $(\mathbf{k}' - \mathbf{k})$  must be a reciprocal lattice vector.

We now turn to examine this structure factor more closely for our main two types of scattering probes – neutrons<sup>8</sup> and x-rays.

### Neutrons

Since neutrons are uncharged, they scatter almost exclusively from nuclei (rather than electrons) via the nuclear forces. As a result, the scattering potential is extremely short ranged, and can be approximated as a delta-function. We thus have

$$V(\mathbf{x}) = \sum_{\text{atom } j \text{ in unit cell}} f_j \delta(\mathbf{x} - \mathbf{x}_j)$$

where  $\mathbf{x}_j$  is the position of the  $j^{\text{th}}$  atom in the unit cell. Here,  $f_j$  is known as the *form factor* or *atomic form factor*, and represents the strength of scattering from that particular nucleus. In fact, for the case of neutrons this quantity is proportional to the so-called “nuclear scattering-length”  $b_j$ . Thus for neutrons we frequently write

$$V(\mathbf{x}) \sim \sum_{\text{atom } j \text{ in unit cell}} b_j \delta(\mathbf{x} - \mathbf{x}_j)$$

Plugging this expression into Eq. 10.5 above, we obtain

$$S(\mathbf{G}) \sim \sum_{\text{atom } j \text{ in unit cell}} b_j e^{i(\mathbf{G}) \cdot \mathbf{x}_j} \quad (10.7)$$

### X-rays

X-rays scatter from the electrons in a system<sup>9</sup> As a result, one can take  $V(\mathbf{x})$  to be proportional to the electron density. We can thus approximate

$$V(\mathbf{x}) \sim \sum_{\text{atom } j \text{ in unit cell}} Z_j g_j(\mathbf{x} - \mathbf{x}_j)$$

where  $Z_j$  is the atomic number of atom  $j$  (i.e., its number of electrons) and  $g_j$  is a somewhat short-ranged function (i.e., it has a few angstroms range — roughly the size of an atom). Taking the Fourier transform, we obtain

$$S(\mathbf{G}) \sim \sum_{\text{atom } j \text{ in unit cell}} f_j(\mathbf{G}) e^{i(\mathbf{G}) \cdot \mathbf{x}_j} \quad (10.8)$$

where  $f_j \sim Z_j$ , the form factor has some dependence on the magnitude of the reciprocal lattice vector  $\mathbf{G}$ . Frequently, however, we approximate  $f_j$  to be independent of  $\mathbf{G}$  (which would be true if  $g$  were extremely short ranged), although this is not strictly correct.

Aside: As noted above,  $f_j(\mathbf{G})$  is just the Fourier transform of the scattering potential for atom  $j$ . This scattering potential is proportional to the electron density. Taking the density to be a delta function results in

<sup>8</sup>Brockhouse and Schull were awarded the Nobel prize in 1994 for pioneering the use of neutron scattering experiments for understanding properties of crystals. Schull’s development of this technique occurred around 1946 – making this the longest time-lag ever between a discovery and the awarding of the Nobel prize.

<sup>9</sup>The coupling of photons to matter is via the usual minimal coupling  $(\mathbf{p} - e\mathbf{A})^2/(2m)$ . The denominator  $m$  is why the nuclei are not important.

$f_j$  being a constant. Taking the slightly less crude approximation that the density is constant inside a sphere of radius  $r_0$  and zero outside of this radius will result in a Fourier transform

$$f_j(\mathbf{G}) \sim \frac{Z \sin(|\mathbf{G}|r_0)}{|\mathbf{G}|r_0} \quad (10.9)$$

(try showing this!). If the scattering angle is sufficiently small (i.e.,  $\mathbf{G}$  is small compared to  $1/r_0$ ), this function is roughly just  $Z$  with no strong dependence on  $\mathbf{G}$ .

### Comparison of Neutrons and X-rays

- For X-rays since  $f_j \sim Z_j$  the x-rays scatter very strongly from heavy atoms, and hardly at all from light atoms. This makes it very difficult to “see” light atoms like hydrogen in a solid. Further it is hard to distinguish atoms that are very close to each other in their atomic number (since they scatter almost the same amount). Also  $f_j$  is slightly dependent on the scattering angle.
- In comparison the nuclear scattering length  $b_j$  varies rather erratically with atomic number (it can even be negative). In particular, hydrogen scatters fairly well, so it is easy to see. Further, one can usually distinguish atoms with similar atomic numbers rather easily.
- For neutrons, the scattering really is very short ranged, so the form factor really is proportional to the scattering length  $b_j$  independent of  $\mathbf{G}$ . For X-rays there is a dependence of  $\mathbf{G}$  that complicates matters.
- Neutrons also have spin. Because of this they can be spin-polarized using a Stern-Gerlach-type setup<sup>10</sup>. One can then detect whether various electrons in the unit cell have their spins pointing up or down. We will return to this situations where the spin of the electron is spatially ordered in section 16.1.2 below.

### Simple Example

Generally, as mentioned above, we write the intensity of scattering as

$$I_{(hkl)} \propto |S_{(hkl)}|^2$$

Assuming we have orthogonal primitive basis vectors, we can then generally write

$$S_{(hkl)} = \sum_{\text{atom } j \text{ in unit cell}} f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad (10.10)$$

where  $[x_j, y_j, z_j]$  are the coordinates of atom  $j$  within the unit cell, in units of the three primitive basis vectors.

**Example 1: Caesium Chloride:** Let us now consider the simple example of CsCl, whose unit cell is shown in Fig. 10.3. This system can be described as simple cubic with a basis given by.<sup>11</sup>

<sup>10</sup>More Nobel history: Stern won the Nobel prize in 1943 without Gerlach. Stern had fled Germany before the war while Gerlach was suspected of contributing to the Nazi bomb effort.

<sup>11</sup>Do not make the mistake of calling this a lattice! Bcc is a lattice where all points must be the same.

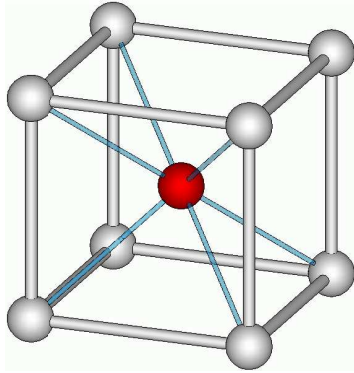


Figure 10.3: Cesium Chloride Unit Cell. Cs is white corner atoms, Cl is red central atom. This is simple cubic with a basis. Note that bcc Cs can be thought of as just replacing the Cl with another Cs atom.

Basis for CsCl	
Cs	Position= $[0, 0, 0]$
Cl	Position= $[a/2, a/2, a/2]$

Thus the structure factor is given by

$$\begin{aligned} S_{(hkl)} &= f_{Cs} + f_{Cl} e^{2\pi i(h,k,l) \cdot [1/2, 1/2, 1/2]} \\ &= f_{Cs} + f_{Cl} (-1)^{h+k+l} \end{aligned}$$

with the  $f$ 's being the appropriate form factors for the corresponding atoms. Recall that the scattered wave intensity is  $I_{(hkl)} \sim |S_{(hkl)}|^2$ .

### 10.2.1 Systematic Absences and More Examples

**Example 2: Caesium bcc:** Let us now consider instead a pure Cs crystal. In this case the crystal is bcc. We can think of this as simply replacing the Cl in CsCl with another Cs atom. Analogously we think of the bcc lattice as a simple cubic lattice with exactly the same basis, which we now write as

Basis for Cs bcc	
Cs	Position= $[0, 0, 0]$
Cs	Position= $[a/2, a/2, a/2]$

Now the structure factor is given by

$$\begin{aligned} S_{(hkl)} &= f_{Cs} + f_{Cs} e^{2\pi i(h,k,l) \cdot [1/2, 1/2, 1/2]} \\ &= f_{Cs} [1 + (-1)^{h+k+l}] \end{aligned}$$

Crucially, note that the structure factor, and therefore the scattering intensity vanishes for  $h+k+l$  being any odd integer! This phenomenon is known as a *systematic absence*.

To understand why this absence occurs, consider the simple case of the (100) family of planes (See Fig. 9.1). This is simply a family of planes along the crystal axes with spacing  $a$ . You might expect a wave of wavelength  $2\pi/a$  oriented perpendicular to these planes to scatter constructively. However, if we are considering a bcc lattice, then there are additional planes of atoms half-way between the (100) planes which then cause perfect *destructive* interference. We refer back to the **Important Complication** mentioned in section 9.1.5. As mentioned there, the plane spacing for the bcc lattice in this case is not  $2\pi/|\mathbf{G}_{(100)}|$  but is rather  $2\pi/|\mathbf{G}_{(200)}|$ . In fact in general, for a bcc lattice the plane spacing for any family of lattice planes is  $2\pi/|\mathbf{G}_{(hkl)}|$  where  $h + k + l$  is always even. This is what causes the selection rule.

**Example 3: Copper fcc** Quite similarly there are systematic absences in for scattering from fcc crystals as well. Recall from Eq. 8.4 that the fcc crystal can be thought of as a simple cubic lattice with a basis given by the points  $[0, 0, 0]$ ,  $[1/2, 1/2, 0]$ ,  $[1/2, 0, 1/2]$ , and  $[0, 1/2, 1/2]$  in units of the cubic lattice constant. As a result the structure factor of fcc copper is given by (plugging into Eq. 10.10)

$$S_{(hkl)} = f_{Cu} \left[ 1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)} \right] \quad (10.11)$$

It is easily shown that this expression vanishes unless  $h, k$  and  $l$  are either all odd or all even.

#### Summary of Systematic Absences

Systematic Absences of Scattering	
Simple Cubic	all $h, k, l$ allowed
bcc	$h + k + l$ must be even
fcc	$h, k, l$ must be all odd or all even

Systematic absences are sometimes known as *selection rules*.

It is very important to note that these absences, or selection rules, occur for any structure with the given Bravais lattice type. Even if a material is bcc with a basis of five different atoms per primitive unit cell, it will still show the same systematic absences as the bcc lattice we considered above with a single atom per primitive unit cell. To see why this is true we consider yet another example

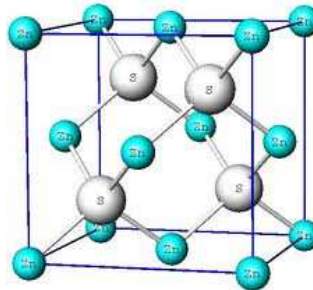


Figure 10.4: Zinc Sulfide conventional unit cell. This is fcc with a basis given by a Zn atom at  $[0, 0, 0]$  and a S atom at  $[1/4, 1/4, 1/4]$ .

**Example 4: Zinc Sulfide = fcc with a basis:** As shown in Fig 10.4, the Zinc Sulfide crystal is a an fcc lattice with a basis given by a Zn atom at  $[0, 0, 0]$  and an S atom at  $[1/4, 1/4, 1/4]$  (this is known as a zinblende structure). If we consider the fcc lattice to itself be a cubic lattice with basis given by the points  $[0, 0, 0]$ ,  $[1/2, 1/2, 0]$ ,  $[1/2, 0, 1/2]$ , and  $[0, 1/2, 1/2]$ , we then have the 8 atoms in the conventional unit cell having positions given by the combination of the two bases, i.e.,

Basis for ZnS				
Zn	Positions=	$[0, 0, 0]$ ,	$[1/2, 1/2, 0]$ ,	$[1/2, 0, 1/2]$ , and $[0, 1/2, 1/2]$
S	Positions=	$[1/4, 1/4, 1/4]$ ,	$[3/4, 3/4, 1/4]$ ,	$[3/4, 1/4, 3/4]$ , and $[1/4, 3/4, 3/4]$

The structure factor for ZnS is thus given by

$$S_{(hkl)} = f_{Zn} \left[ 1 + e^{2\pi i(hkl) \cdot [1/2, 1/2, 1/0]} + \dots \right] + f_S \left[ e^{2\pi i(hkl) \cdot [1/4, 1/4, 1/4]} + e^{2\pi i(hkl) \cdot [3/4, 3/4, 1/4]} + \dots \right]$$

This combination of 8 terms can be factored to give

$$S_{(hkl)} = \left[ 1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)} \right] \left[ f_{Zn} + f_S e^{i(\pi/2)(h+k+l)} \right] \quad (10.12)$$

The first term in brackets is precisely the same as the term we found for the fcc crystal in Eq. 10.11. In particular it has the same systematic absences that it vanishes unless  $h, k$  and  $l$  are either all even or all odd. The second term gives additional absences associated specifically with the ZnS structure.

Since the positions of the atoms are the positions of the underlying lattice plus the vectors in the basis, it is easy to see that the structure factor of a crystal system with a basis will always factorize into a piece which comes from the underlying lattice structure times a piece corresponding to the basis. Generalizing Eq. 10.12 we can write

$$S_{(hkl)} = S_{(hkl)}^{Lattice} \times S_{(hkl)}^{basis} \quad (10.13)$$

(where to be precise the form factors only occur in the latter term).

## 10.3 Methods of Scattering Experiments

There are many methods of performing scattering experiments. In principle they are all similar — one sends in a probe wave of known wavelength (an X-ray, for example) and measures the angles at which it diffracts when it comes out. Then using Bragg's laws (or the Laue equation) one can deduce the spacings of the lattice planes in the system.

### 10.3.1 Methods that are interesting and useful that you probably won't be tested on

#### Laue Method

Conceptually, perhaps the simplest method is to take a large single crystal of the material in question — fire waves at it (X-rays, say) at it from one direction, and measure the direction of the outgoing waves. However, given a single direction of incoming wave, it is unlikely that you precisely achieve the diffraction condition (the Bragg condition) for any given set of lattice planes. In order to get more data, one can then vary the wavelength of the incoming wave. This allows one to achieve the Bragg condition, at least at some wavelength.

### Rotating Crystal Method

A similar technique is to rotate the crystal continuously so that at some angle of the crystal with respect to the incoming waves, one achieves the Bragg condition and measures an outgoing diffracted wave.

Both of these methods are used. However, there is an important reason that they are sometimes impossible. Frequently it is not possible to obtain a single crystal of a material. Growing large crystals (such as the beautiful ones shown in Fig. 4.9) can be an enormous challenge<sup>12</sup> In the case of neutron scattering the problem is even more acute since one typically needs a fairly large single crystals compared to x-rays.

### 10.3.2 Powder Diffraction: you will almost certainly be tested on this!

Powder diffraction, or the *Debye-Scherrer method*<sup>13</sup> is the use of wave scattering on a sample which is not single crystalline, but is powdered. In this case, the incoming wave can scatter off of any one of many small crystallites which may be oriented in any possible direction. In spirit this technique is similar to the rotating crystal method in that there is always some angle at which a crystal can be oriented to diffract the incoming wave. A figure of the Debye-Scherrer setup is shown in Fig. 10.5. Using Bragg's law, given the wavelength of the incoming wave, we can deduce the possible spacings between lattice planes.

#### A Fully Worked Example. Study this!

Because this type of problem has historically ended up on exams essentially every year, and because it is hard to find references that explain how to solve these problems, I am going to work a powder-diffraction problem in detail here. As far as I can tell, they will only ever ask you about cubic lattices (simple cubic, fcc, and bcc).

Before presenting the problem and solving it, however, it is useful to write down a table of possible lattice planes and the selection rules that can occur for the smallest reciprocal lattice vectors

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<sup>12</sup>For example, high-temperature superconducting materials were discovered in 1986 (and resulted in a Nobel prize the next year!). Despite a concerted world-wide effort, good single crystals of these materials were not available for 5 to 10 years.

<sup>13</sup>Debye is the same guy from the specific heat of solids. Paul Scherrer was Swiss but worked in Germany during the second world war, where he passed information to the famous American spy (and baseball player), Moe Berg, who had been given orders to find and shoot Heisenberg if he felt that the Germans were close to developing a bomb.



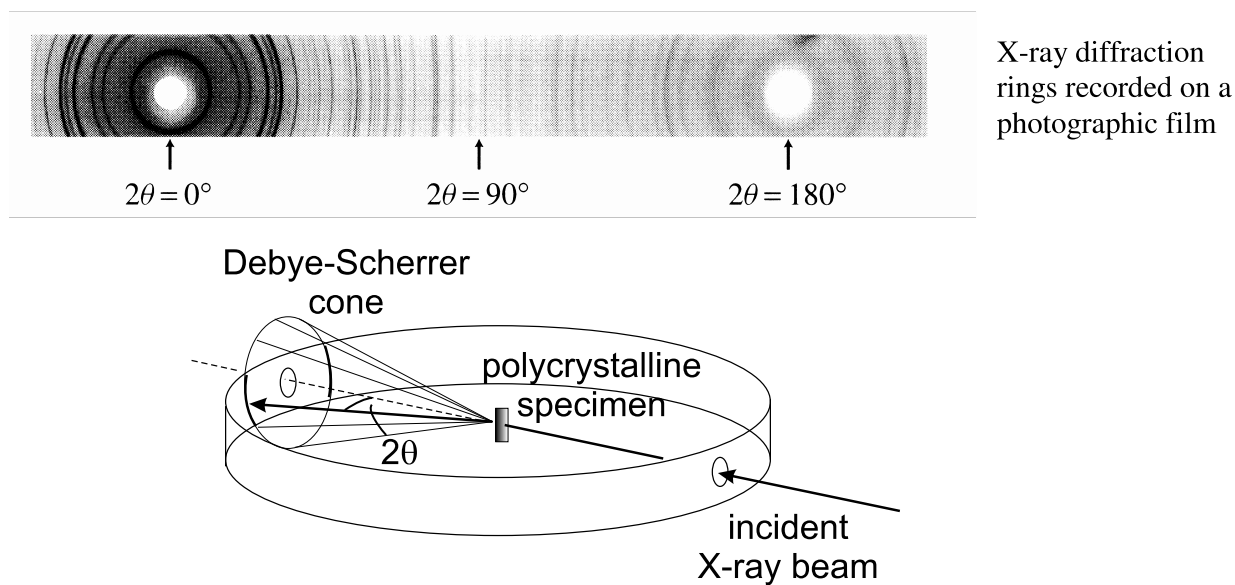


Figure 10.5: Debye-Scherrer Powder Diffraction.

Lattice Plane Selection Rules					
$\{hkl\}$	$N = h^2 + k^2 + l^2$	Multiplicity	cubic	bcc	fcc
100	1	6	✓		
110	2	12	✓	✓	
111	3	8	✓		✓
200	4	6	✓	✓	✓
210	5	24	✓		
211	6	24	✓	✓	
220	8	12	✓	✓	✓
221	9	24	✓		
300	9	6	✓		
310	10	24	✓	✓	
311	11	24	✓		✓
222	12	8	✓	✓	✓
⋮	⋮				

The selection rules are exactly those listed above: simple cubic allows scattering from any plane, bcc must have  $h + k + l$  be even, and fcc must have  $h, k, l$  either all odd or all even.

We have added a column  $N$  which is the square magnitude of the reciprocal lattice vector.

We have also added an addition column labeled “multiplicity”. This quantity is important

for figuring out the amplitude of scattering. The point here is that the (100) planes have some particular spacing but there are 5 other families of planes with the same spacing: (010), (001), ( $\bar{1}00$ ), ( $0\bar{1}0$ ), ( $00\bar{1}$ ). (Because we mean all of these possible families of lattice planes, we use the notation  $\{hkl\}$  introduced at the end of section 9.1.5). In the powder diffraction method, the crystal orientations are random, and here there would be 6 possible equivalent orientations of a crystal which will present the right angle for scattering off of one of these planes, so there will be scattering intensity which is 6 times as large as we would otherwise calculate — this is known as the multiplicity factor. For the case of the 111 family, we would instead find 8 possible equivalent planes: (111), (11 $\bar{1}$ ), (1 $\bar{1}$ 1), (1 $\bar{1}\bar{1}$ ), ( $\bar{1}$ 11), ( $\bar{1}$ 1 $\bar{1}$ ), ( $\bar{1}\bar{1}$ 1), ( $\bar{1}\bar{1}\bar{1}$ ). Thus, we should replace Eq. 10.6 with

$$I_{\{hkl\}} \propto M_{\{hkl\}} |S_{\{hkl\}}|^2 \quad (10.14)$$

where  $M$  is the multiplicity factor.

Note: calculating the actual intensity of scattering works very well for neutron scattering, but is much harder for x-ray scattering because the form factor for X-rays depends on  $\mathbf{G}$ . I.e, since in Eq. 10.7 the form factor (or scattering length  $b_j$ ) is a constant independent of  $\mathbf{G}$ , it is easy to calculate the expected amplitudes of scattering based only on these constants. For the case of X-rays you need to know the functional forms of  $f_j(\mathbf{G})$ . At some *very* crude level of approximation it is a constant. More precisely we see in Eq. 10.9 that it is constant for small scattering angle but can vary quite a bit for large scattering angle.

### The Example

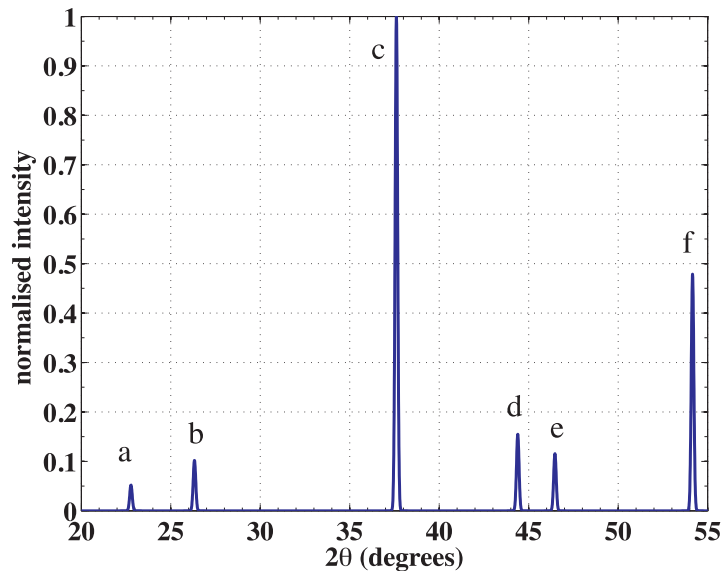


Figure 10.6: Powder Diffraction of Neutrons from  $\text{PrO}_2$ . The wavelength of the neutron beam is  $\lambda = .123 \text{ nm}$

Consider the powder diffraction data from  $\text{PrO}_2$  shown in Fig. 10.6. (Exactly this data was presented in the 2009 Exam, and we were told that the lattice is some type of cubic lattice). Given the wavelength .123 nm, we first would like to figure out the type of lattice and the lattice constant.

Note that the full deflection angle is  $2\theta$ . We will want to use Bragg's law and the expression for the spacing between planes

$$d_{(hkl)} = \frac{\lambda}{2 \sin \theta} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where we have also used the expression Eq. 9.12 for the spacing between planes in a cubic lattice given the lattice constant  $a$ . Note that this then gives us

$$a^2/d^2 = h^2 + k^2 + l^2 = N$$

which is what we have labeled  $N$  in the above table of selection rules. We now make a table. In the first two columns we just read the angles off of the given graph *Note, you should try to make the measurements of the angle from the data as carefully as possible. It makes the analysis much easier if you measure the angles right!*

peak	$2\theta$	$d = \lambda/(2 \sin \theta)$	$d_a^2/d^2$	$3d_a^2/d^2$	$N = h^2 + k^2 + l^2$	$\{hkl\}$	$a = d\sqrt{h^2 + k^2 + l^2}$
a	22.7°	0.313 nm	1	3	3	111	.542 nm
b	26.3°	0.270 nm	1.33	3.99	4	200	.540 nm
c	37.7°	0.190 nm	2.69	8.07	8	220	.537 nm
d	44.3°	0.163 nm	3.67	11.01	11	311	.541 nm
e	46.2°	0.157 nm	3.97	11.91	12	222	.544 nm
f	54.2°	0.135 nm	5.35	16.05	16	400	.540 nm

In the third column of the table we calculate the distance between lattice planes for the given diffraction peak using Bragg's law. In the third fourth column we have calculated the squared ratio of the lattice spacing  $d$  for the given peak to the lattice spacing for the first peak (labeled a) as a reference. We then realize that these ratios are pretty close to whole numbers divided by three, so we try multiplying each of these quantities by 3 in the next column. If we round these numbers to integers (given in the next column), we produce precisely the values of  $N = h^2 + k^2 + l^2$  expected for the fcc lattice (According to the above selection rules we must have  $h, k, l$  all even or all odd). The final column calculates the lattice constant from the given diffraction angle. Averaging these numbers gives us a measurement of the lattice constant  $a = .541 \pm .002$  nm.

The analysis thus far is equivalent to what one would do for X-ray scattering. However, with neutrons, assuming the scattering length is independent of scattering angle (which is typically a good assumption) we can go a bit further and analyze the the intensity of the scattering peaks.

In the problem given on the 2009 Exam, it is given that the basis for this crystal is a Pr atom at position  $[0,0,0]$  and O at  $[1/4,1/4,1/4]$  and  $[1/4,1/4,3/4]$ . Thus, the Pr atoms form a fcc lattice and the O's fill in the holes as shown in Fig. 10.7.

Let us calculate the structure factor for this crystal. Using Eq. 10.13 we have

$$S_{(hkl)} = \left[ 1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)} \right] \left[ b_{Pr} + b_O \left( e^{i(\pi/2)(h+k+l)} + e^{i(\pi/2)(h+k+3l)} \right) \right]$$

The first term in brackets is the structure factor for the fcc lattice, and it gives 4 for every allowed scattering point (when  $h, k, l$  are either all even or all odd). The second term in brackets is the structure factor for the basis.

The scattering intensity of the peaks are then given in terms of this structure factor and the peak multiplicities as shown in Eq. 10.14. We thus can write for all of our measured peaks

$$I_{\{hkl\}} = CM_{\{hkl\}} \left| b_{Pr} + b_O \left( e^{i(\pi/2)(h+k+l)} + e^{i(\pi/2)(h+k+3l)} \right) \right|^2$$

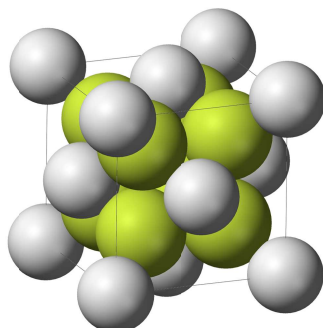


Figure 10.7: The fluorite structure. This is fcc with a basis given by a white atom (Pr) atom at  $[0, 0, 0]$  and yellow atoms at  $[1/4, 1/4, 1/4]$  and  $[1/4, 1/4, 3/4]$ .

where the constant  $C$  contains other constant factors (including the factor of  $4^2$  from the fcc structure factor). Note: We have to be a bit careful here to make sure that the bracketed factor gives the same result for all possible  $(hkl)$  included in  $\{hkl\}$ , but in fact it does. Thus we can compile another table showing the predicted relative intensities of the peaks.

Scattering Intensity			
peak	$\{hkl\}$	$I_{\{hkl\}}/C \propto M S ^2$	Measured Intensity
a	111	$8b_{Pr}^2$	0.05
b	200	$6[b_{Pr} - 2b_O]^2$	0.1
c	220	$12[b_{Pr} + 2b_O]^2$	1.0
d	311	$24b_{Pr}^2$	0.15
e	222	$8[b_{Pr} - 2b_O]^2$	0.1
f	400	$6[b_{Pr} + 2b_O]^2$	0.5

where the final column are the intensities measured from the data in Fig. 10.6.

From the analytic expressions in the third column we can immediately predict that we should have

$$I_d = 3I_a \quad I_c = 2I_f \quad I_e = \frac{4}{3}I_b$$

Examining the fourth column of this table, it is clear that the first two of these equations are properly satisfied. However the final equation does not appear to be correct. This points to some error in constructing the plot. Thus we suspect some problem in either  $I_e$  or  $I_b$ . Either  $I_e$  is too small or  $I_b$  is too large<sup>14</sup>.

To further home in on this problem with the data, we can look at the ratio  $I_c/I_a$  which in the measured data has a value of about 20. Thus we have

$$\frac{I_c}{I_a} = \frac{12[b_{Pr} + 2b_O]^2}{8b_{Pr}^2} = 20$$

<sup>14</sup>Another possibility is that the form factor is not precisely independent of scattering angle, as is the case for X-ray scattering. However, the fact that all the peaks are consistent but for this one peak suggests a transcription error.

with some algebra this can be reduced to a quadratic equation with two roots, resulting in

$$b_{Pr} = -.43b_O \quad \text{or} \quad .75b_O \quad (10.15)$$

Let us suppose now that our measurement of  $I_b$  is correct. In this case we have

$$\frac{I_b}{I_a} = \frac{6[b_{Pr} - 2b_O]^2}{8b_{Pr}^2} = 2$$

which we can solve to give

$$b_{Pr} = .76b_O \quad \text{or} \quad -3.1b_O$$

The former solution being reasonably consistent with the above. However, were we to assume  $I_e$  were correct, we would have instead

$$\frac{I_e}{I_a} = \frac{8[b_{Pr} - 2b_O]^2}{8b_{Pr}^2} = 2$$

we would obtain

$$b_{Pr} = .83b_O \quad \text{or} \quad -4.8b_O$$

which appears inconsistent with Eq. 10.15. We thus conclude that the measured intensity of  $I_e$  given in Fig. 10.6 is actually incorrect, and should be larger by about a factor of 4/3.

## 10.4 Still more about scattering

Scattering experiments such as those discussed here are *the* method for determining the microscopic structures of materials. One can use these methods (and extensions thereof) to sort out even very complicated atomic structures such as those of biological molecules.

Aside: In addition to the obvious work of von Laue and Bragg that initiated the field of X-ray diffraction (and Brockhouse and Schull for neutrons) there have been about half a dozen Nobel prizes that have relied on, or further developed these techniques. In 1962 a chemistry Nobel prize was awarded to Perutz and Kendrew for using X-rays to determine the structure of the biological proteins hemoglobin and myoglobin. The same year, Watson and Crick were awarded the prize in Biology for determining the structure of DNA — which they did with the help of X-ray diffraction data taken by Rosalind Franklin<sup>15</sup>. Two years later in 1964, Dorothy Hodgkin<sup>16</sup> won the prize for determination of the structure of penicillin and other biological molecules. Further Nobels were given in chemistry for determining the structure of Boranes (Lipscomb, 1976) and for the structure of photosynthetic proteins (Deisenhofer, Huber, Michel 1988).

### 10.4.1 Variant: Scattering in Liquids and Amorphous Solids

A material need not be crystalline to scatter waves. However, for amorphous solids or liquids, instead of having delta-function peaks in the structure factor at reciprocal lattice vectors (as in Fig. 10.6), the structure factors (which is again defined as the fourier transform of the density) will have smooth behavior — with incipient peaks corresponding to  $2\pi/d$  where  $d$  is roughly the

<sup>15</sup>There remains quite a controversy over the fact that Watson and Crick, at a critical juncture, were shown Franklin's data without her knowledge! Franklin may have won the prize in addition to Watson and Crick and thereby received a bit more of the appropriate credit, but she tragically died of cancer at age 37 in 1958, two years before the prize was awarded.

<sup>16</sup>Dorothy Hodgkin was a student and later a fellow at [Somerville College, Oxford](#). Yay!