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# STRUCTURE DETERMINATION

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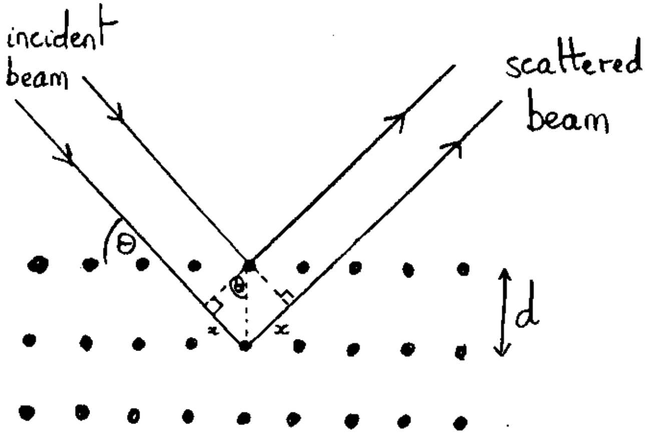
**A course of five lectures describing the techniques available for elucidating the structures of ceramic materials.**

During this course of five lectures I shall describe various techniques which can be used in structural studies of ceramic materials. The technique to be used in any particular case will be determined by the nature of the sample and the type of structural information that you wish to find out.

The most powerful technique available for structural studies of solids is single-crystal X-ray diffraction. However, as the name implies, use of this method requires the availability of good quality single crystals, with a typical linear dimension of ~0.5 mm, and these are not always available when a ceramic is to be characterised. We usually find that we are working with powdered, polycrystalline samples, and I shall, therefore, start by describing the sort of information that can be gleaned from X-ray powder diffraction (XRPD) measurements. Before I do that though, I want to say a few words about crystallography and the general principles of diffraction experiments. In any such experiment an incoming wave is scattered from a number of regularly spaced centres. In certain directions the scattered waves from all the centres will interfere constructively and these will be a maximum in the observed intensity. In other directions, destructive interference will lead to zero observed intensity. The positions of the maxima are determined by the separation of the scattering centres, and the width of the maxima is determined by the number of scattering centres (more centres, narrower maxima). The diffraction pattern is also modified by the relative size of the individual scattering centres compared to the wavelength of the incident radiation.

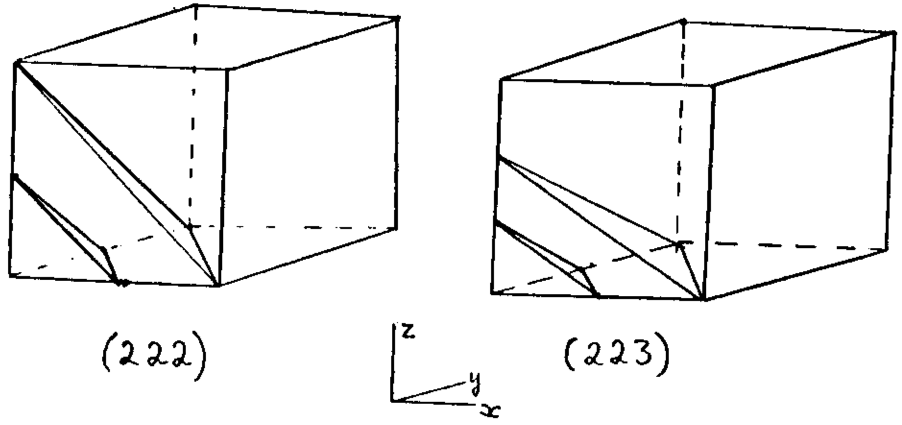
In an experiment which uses the regularly spaced atoms in a crystal as the diffraction grating, then the situation can be represented in the diagram:



The path difference between the wave scattered from the top plane of atoms and that scattered from the middle plane is $2x = 2d \sin\theta$, so that for constructive interference $\lambda = 2d \sin\theta$. This is BRAGGS'S LAW and it determines the angle at which diffraction maxima occur. Note that the angle between the incident beam and the scattered beam is $2\theta$, not $\theta$.

Knowing that $\sin\theta \leq 1$, it follows that the wavelength of the radiation used in a diffraction experiment must be of the same order of magnitude as the spacing between the planes of atoms in the crystal (or smaller).

Now I must introduce the system used to label the different sets of planes in a crystal structure. Such a structure can be thought of as being made up of a large number of small, 3-dimensional building blocks. The smallest block which, when repeated in 3 dimensions, can be used to build up the crystal structure is known as the unit-cell. The planes we are talking about in a diffraction experiment are defined within the unit cell. They cut the unit-cell axes in fractional parts (1/h, 1/k, 1/l) and are referred to as the (hkl) planes. The examples given below show the (222) and (223) planes in a crystal of cubic symmetry.



(222) (223)

All the planes in a particular (hkl) set are parallel and therefore at a constant distance, $d_{hkl}$, apart. The Bragg equation is thus more fully written as $\lambda = 2d_{hkl} \sin \theta_{hkl}$, where the relection (ie diffraction maximum) from the (hkl) planes, separated from each other by a distance $d_{hkl}$, occurs at an angle of $2\theta_{hkl}$ to the incident beam. For a cubic crystal, with a unit-cell parameter (ie the length of the side of the unit-cell) equal to $a_o$, it can be shown that

$$d_{hkl} = \frac{a_o}{\sqrt{h^2+k^2+l^2}}$$

so substituting into the Bragg equation

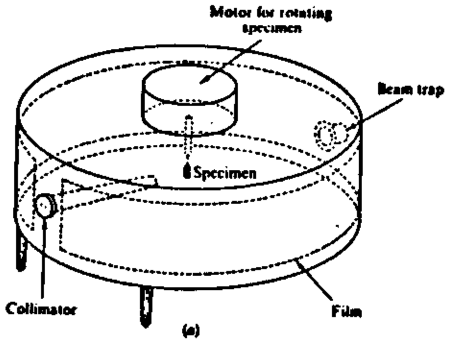
$$\lambda = 2 \frac{a_o}{\sqrt{h^2+k^2+l^2}} \sin \theta_{hkl}$$

or

$$\sin^2\theta_{hkl} = \frac{\lambda^2}{4a_o^2} (h^2+k^2+l^2)$$

The above treatment is applicable for all crystalline materials having cubic symmetry - it is in no way specific to X-ray diffraction, nor to neutron diffraction. The expression relating $d_{hkl}$ to the unit-cell parameters becomes more complex if the symmetry of the crystal is lower than cubic, but the general approach is still valid. (see D'eye and Wait p.135).

It is clear from the above equation that if we can measure experimentally the scattering angle $2\theta_{hkl}$ (and hence $\theta_{hkl}$) for a number of diffraction maxima and determine which set of (hkl) planes give rise to each maxima, then we can calculate the size of the unit cell of our sample material - the first stage of crystal structure determination. N.B. the size of the unit cell is determined from the positions of the diffraction maxima alone, not from their intensities. The experiment to determine the $2\theta$ values of the diffraction maxima is easily done using a polycrystalline sample of a ceramic. Indeed, it is one of the most basic measurements that are routinely done in solid state chemistry and ceramics. The apparatus used is either an X-ray powder diffractometer or an X-ray camera (eg Debye-Scherrer camera or Guinier camera). The Debye-Scherrer camera is very simple and will be used to illustrate the principle of the method, but for serious work a Guinier camera or a diffractometer is used nowadays. These have a higher resolution than the DS camera because their geometry is arranged so as to focus the diffracted X-ray beam. A Debye-Scherrer camera is shown in the diagram.



A finely ground polycrystalline sample is aligned along the axis of a cylindrical camera and rotated. An X-ray beam entering through the collimotor is scattered by the specimen, with maxima in the scattered intensity in those directions which satisfy the Bragg equation. These maxima are recorded on the film which lines the inner wall of the camera. The camera is made with a diameter of 114.6 mm such that 1 mm on the film corresponds to 1° of $2\theta$. Thus by measuring the postions of the maxima on the film, we can get $2\theta$ and hence $\sin^2\theta$ for each Bragg peak. Then we have to index the lines, ie determine which set of hkl planes gives rise to each maximum. Having done this we can then calculate the size of the unit cell, using the equation

$$\sin^2\theta_{hkl} = \frac{\lambda^2}{4a_o^2}(h^2+k^2+l^2)$$

Example

The first eight lines in the X-ray diffraction pattern of a polycrystalline material, known to possess cubic symmetry, correspond to the following values of $\sin^2\theta$:

0.0132 0.0256 0.0391 0.0514 0.0644 0.0769
0.1020 0.1150

Index the lines and determine the size of the unit cell. ($\lambda$ = 70.8 pm).

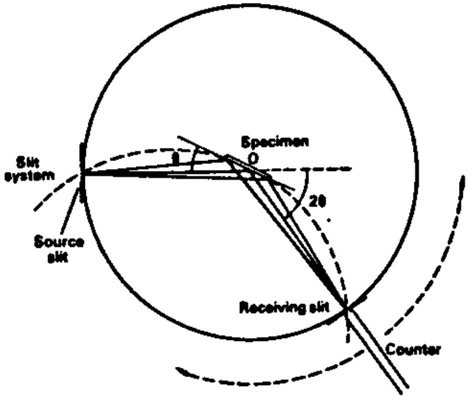
What you need to do is to look at the $\sin^2\theta$ values and try to spot the common factor. If you are dealing with real experimental data you must be prepared to allow for small discrepancies. Looking at those values, I hope you can see that there is a common factor of ~0.013. If you go through the eight lines and divide by 0.013 you get:

| line number | $\sin^2\theta/0.013$ | $h^2+k^2+l^2$ | (hkl) |
|---|---|---|---|
| 1 | 1.015 | 1 | (100) |
| 2 | 1.969 | 2 | (110) |
| 3 | 3.008 | 3 | (111) |
| 4 | 3.954 | 4 | (200) |
| 5 | 4.954 | 5 | (210) |
| 6 | 5.915 | 6 | (211) |
| 7 | 7.846 | 8 | (220) |
| 8 | 8.846 | 9 | (300) or (221) |

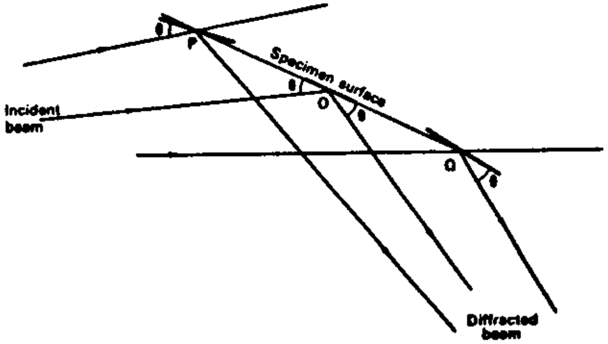
The result of this division is always close to an integer, particularly for the early lines. It is reasonable to expect greater deviation further down because 0.013 is not <u>that</u> accurate a value and the error begins to show through. The agreement here is good enough to suggest that you have found the common factor. You can then assign $h^2+k^2+l^2$ values, ie the nearest integer, to each line and it is comforting to see that 7 is missing - there are no three integers whose squares add up to 7. Then you can break the $h^2+k^2+l^2$ values down into (hkl) triplets. When you have done that you have indexed the lines. Now all that remains is to determine the size of the unit-cell. The most satisfactory method would be to plot a graph of $\sin^2\theta$ vs. $(h^2+k^2+l^2)$ and find the gradient which will equal $\lambda^2/4a_o^2$, and hence $a_o$. This is a very simple example based on a cubic material. The process gets more difficult, but is still possible, for materials of lower symmetry. There are now computer programs that can automatically index a diffraction pattern for you if you feed in sufficiently accurate $\sin^2\theta_{hkl}$ values. There are also computer programs that will refine the size of an approximate unit cell to optimise the agreement between observed and calculated $\sin^2\theta$ values.

As I said before, the Debye-Scherrer camera has a very simple geometry and is easy to understand, but most modern laboratories now use a focussing camera (eg a Guinier camera) or a powder diffractometer, which has a pseudo-focussing effect. The use of focussing means that a greater proportion of the incident intensity is useful in the experiment which consequently takes less time to perform. The basic principles of a powder diffractometer are shown in the diagram. The geometry is such that the incoming X-ray beam passes through a slit and subsequently diverges until it hits the specimen which is in the form of a flat plate, tangential to an arc which passes through both the source slit and the receiving slit. The X-rays are then diffracted and effectively focussed onto the receiving slit. In order for true focussing to take place, the specimen would have to be curved along the arc joining the two slit systems,

but as long as the sample is small compared to the length of the arc, there is a pseudo-focussing effect.



(a)



(b)

During the course of data collection, the counter rotates so as to sample the intensity at different 2θ values and the sample rotates by half as much so as to maintain vs

the correct geometry. The usual way to operate one of these instruments is simply to set the instrument up to scan from say 10° to 80° at a speed of perhaps 1°2θ per minute. The diffraction pattern is output onto a chart recorder 2θ vs. intensity. For accurate work - remember you are going to want to measure the angle 2θ, and from it calculate the unit-cell parameter, you need either a focussing camera or a diffractometer. Which you buy probably depends on whether you prefer to scrutinize short lengths of film, or spread 1 m lengths of chart recorder paper out over the floor and crawl around looking for peaks.

Until this point, I've talked only about the positions of the lines in the diffraction pattern - I've said nothing about their intensities. The scattered intensity for the (hkl) reflection in a powder diffraction experiment is given by

$$I_{hkl} = K(Lp)_{hkl} j_{hkl} F^2_{hkl} \; e^{-2w_{hkl}} \; A_{hkl}$$

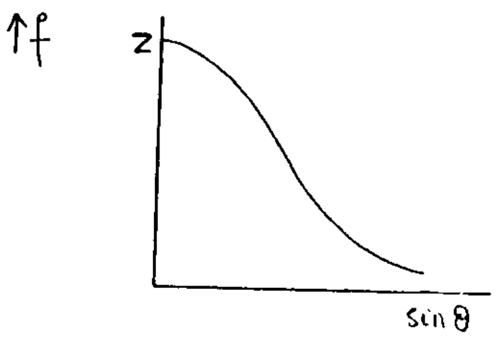
where

| | |
|---|---|
| $I_{hkl}$ | is the observed intensity of the (hkl) reflection |
| $(Lp)_{hkl}$ | is the Lorentz-polarisation factor |
| $j_{hkl}$ | is the multiplicity of the (hkl) planes |
| $F_{hkl}$ | is the structure factor of the (hkl) reflection |
| $W_{hkl}$ | is the Debye temperature correction factor |
| $A_{hkl}$ | is the absorption factor |
| $K$ | is a constant for all (hkl) values in a given experiment. It depends, among other things on the amount of sample used. |

$F_{hkl}$ - the structure factor for the (hkl) reflection contains all the information that chemists want to get at - ie the structure of the compound, where the atoms are within the unit cell, and hence how long the chemical bonds are, the shape of the molecule, how the molecules pack together to form a solid crystal etc. The structure factor can be expressed as follows:

$$F_{hkl} = \sum_{\substack{\text{all}\\ \text{lattice}\\ \text{points}}} \; \sum_{\text{basis}} \; f_i \cos 2\pi(hx_i+ky_i+lz_i)$$

where $f_i$ is the scattering factor (sometimes scattering length) of the $i^{th}$ atom, which has fractional coordinates $(x_i, y_i, z_i)$. In the case of X-ray diffraction, the scattering factor is related to the number of electrons that scatter the X-ray - and it falls off with increasing θ

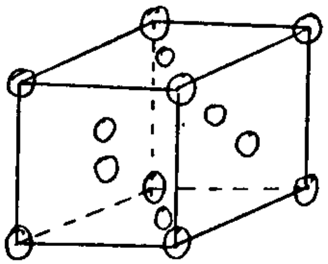


The equation I've given you for the structure factor is not really complete. There should be a term

$$+ j f_i \sin 2\pi(hx_i+ky_i+lz_i)$$

in addition to the cosine term, but I am going to ignore it so as not to complicate the arithmetic. For all centrosymmetric crystals, the sine term is zero, so I am not cheating - I'm just restricting this discussion to centrosymmetric materials. (A centrosymmetric material is one in which for every atom having coordinates (x,y,z) there is an identical atom at (-x, -y, -z)).

Let me show you an example of how you can use the structure factor. Consider a crystal of a metal which has a face centred cubic structure, eg Ca



There are 4 lattic points in this unit cell, at (000) (0½½) (½0½) and (½½0). The basis consists of one Ca atom located at each lattice point.

$$\therefore F_{hkl} = f_{ca}\cos 2\pi(h.0+k.0+l.0) + f_{ca}\cos 2\pi(h.0+k.\tfrac{1}{2}+l.\tfrac{1}{2})$$

$$+ f_{ca}\cos 2\pi(h.\tfrac{1}{2}+k.0+l.\tfrac{1}{2}) + f_{ca}\cos 2\pi(h.\tfrac{1}{2}+k.\tfrac{1}{2}+l.0)$$

$$= f_{ca}[\cos 0 + \cos \pi(k+l) + \cos \pi(h+l) + \cos \pi(h+k)]$$

$$\therefore F_{hkl} = 4f_{ca} \text{ if } h,k,l \text{ are all even or all odd}$$

$$= 0 \text{ otherwise}$$

So in a face-centred cubic material you only see a reflection for a fraction of (hkl) values. So when you are indexing your powder pattern, and looking at the value of $h^2+k^2+l^2$, instead of seeing the sequence 1,2,3,4,5,6,8,9 ...... as from a Primitive material, you will see 3,4,8,11,12,16 ....... You can do a similar calculation for a body centred material and hence show that only those reflections for which $h+k+l = 2n$ are observed, ie $h^2+k^2+l^2 = 2,4,6,8,10$ ....... The absent reflections are referred to as the systemic absences.

Until now I have really been talking about X-ray powder diffraction. If you want to reap the full benefit of X-ray diffraction and locate the atoms within the unit-cell, then it is usual to perform your experiments on single crystals. The equation I gave you for the intensity of the hkl reflection, $I_{hkl}$, is equally valid for single crystal diffraction. The geometry has changed so the Lp correction changes, but that is not a problem. The multiplicity also changes. Whereas the large number of randomly orientated crystallites in a polycrystalline sample give rise to a continuous distribution of intensity on the surface of a cone of angle $2\theta$, each particular crystallite gives rise to an individual spot. The line on a Debye-Scherrer film is thus made up from an apparently continuous distribution of spots. When you use a single crystal you see the individual spots.

The thing that does not change, even in a trivial way, on going from powder to single crystal is the structure factor. If you measure the intensity of the (hkl) reflection, you have a measure of the structure factor, or at least its square - an important point that I will come back to. Why is it important to know the structure factor? The electron density in a crystal, at a point (x,y,z), is given by

$$\rho(x,y,z) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F_{hkl}\, e^{2\pi i(hx+ky+lz)}$$

or, for centrosymmetric structures

$$\rho(x,y,z) = \frac{1}{V} \sum_{h,k,l} F_{hkl} \cos 2\pi(hx+ky+lz)$$

So, if you know V, the volume of the unit cell and you measure $F_{hkl}$ for as many (hkl) triplets as possible, then

you can calculate the electron density at every point (x,y,z) in the unit cell. Clearly, the electron density will have a maximum at the places where there is an atom, so what you are really doing is determining the locations of the atoms within the unit cell. The only problem is that you do not measure $F_{hkl}$, you measure $F^2_{hkl}$, and hence you can calculate $|F_{hkl}|$ but you don't know whether it has a + or - sign in front of it. This is known as "the phase problem in X-ray crystallography". You will realise that the calculated electron density will vary enormously depending on the sign associated with all the $F_{hkl}$ coefficients. What I want to do now is to go through the experimental procedure that is followed in order to get a set of X-ray single crystal diffraction data, and then I will go on to describe how to solve the phase problem.

The first thing you need to do is to grow a suitable crystal having a typical dimension of -0.2-0.3 mm. The next step is to determine the size of the unit cell and the space-group. (The space group is the formal, correct way for saying 'the symmetry of the crystal'.) Once this has been done you can use a computer controlled diffractometer to collect a set of intensity data, that is to measure $I_{hkl}$ for several (often 2000) (hkl) values. You then have to solve the phase problem.

If you have a set of X-ray single crystal diffraction data on a compound, ie a set of hkl:$I_{hkl}$ values, and you know nothing about the compound other than its empirical formula, then there are two ways of solving the crystal structure. The first is the Patterson, or heavy-atom method. The X-ray scattering power of an atom is proportional to the number of electrons it has. This means that if a compound contains one element that is much heavier than the rest, then that atom will tend to dominate the X-ray scattering. So if we can locate the heavy atom, and using the formula

$$F_{hkl}^{calc} = \cos 2\pi(hx_i+ky_i+lz_i)$$

calculate the structure factor, both modulus and sign, which would be correct if <u>only</u> the heavy atom was in the unit cell, then for a large fraction of the reflections we will have found the correct sign, or phase, for $F_{hkl}$. This will be true in particular for the strongest reflections. So how do we locate this heavy atom, and hence get into a position where we can assign a phase to each of the reflections? We calculate the Patterson function

$$p(u,v,w) = \frac{1}{V} \sum_{h=-\infty} \sum_{k=-\infty} \sum_{l=-\infty} |F_{hkl}^{obs}|^2 \cos 2\pi(hu+kv+lw)$$

for $0 < u,v,w < 1$. This function relies on $|F_{hkl}^{obs}|^2$, which we can measure in the experiment. Patterson showed that the maxima in this function correspond to interatomic vectors, ie if the Patterson function has a maximum at (u,v,w) then

there are two atoms in the structure at $(x_1,y_1,z_1)$ and $(x_2,y_2,z_2)$ such that

$$U = x_1 - x_2$$

$$V = y_1 - y_2$$

$$W = z_1 - z_2$$

You have to look at the list of peaks in the Patterson function and attempt to assign them to the correct atom pairs. Remember that the strongest peaks will correspond to vectors between heavy atoms.

So now we know where the heavy atom is - what next? We calculate $F_{hkl}^{calc}$ for each reflection assuming only the heavy atom contributes - this gives us $F_{hkl}^{calc}$, complete with its sign. We then assign the same sign to $|F_{hkl}^{obs}|$, ie the square root of $I^{obs}$, and so we have both $F_{hkl}^{obs}$ and $F_{hkl}^{calc}$ for each reflection. They will be different because the calculated structure factor only includes the contribution from the heavy atom whereas the observed structure factor contains contributions from all the atoms. The idea now is to find the rest of the atoms so that when we include them in the calculation agreement between $F_{hkl}^{obs}$ and $F_{hkl}^{calc}$ improves as much as possible. How do we find the rest of the atoms? Some time ago I told you that what we are really doing in an X-ray diffraction experiment is determining the electron denisty at every point in the unit cell

$$\rho(x,y,z) = \frac{1}{V} \sum_{hkl} F_{hkl} \cos 2\pi(hx+ky+lz)$$

let me now be more specific and write

$$\rho^{obs}(x,y,z) = \frac{1}{V} \sum F^{obs}_{hkl} \cos 2\pi(hx+ky+lz)$$

and

$$\rho^{calc}(x,y,z) = \frac{1}{V} \sum F^{calc}_{hkl} \cos 2\pi(hx+ky+lz)$$

So if we calculate the difference function

$$\rho^{obs}(x,y,z) - \rho^{calc}(x,y,z) = \frac{1}{V} \sum_{hkl} (F^{obs}_{hkl} - F^{calc}_{hkl}) \cos 2\pi(hx+ky+lz)$$

this Difference Fourier function should have maxima at the positions of the missing atoms. In practice this is a good way of finding the next heaviest atoms. It is then necessary to vary the positions of the located atoms slightly to maximise the agreement between $F^{obs}_{hkl}$ and $F^{calc}_{hkl}$, ie the positions that come from Patterson and Difference Fourier calculations are close to being correct, but not quite. Computers are used to do all these calculations using packages of standard programs. The atomic positions are refined using the method of least squares until the agreement between $F^{obs}$ and $F^{calc}$ is optimised. The level of agreement is judged using the R-factor

$$R = \frac{\sum |(|F^{obs}| - |F^{calc}|)|}{\sum (|F^{obs}|)}$$

Once the R-factor has been minimised, $F^{calc}_{hkl}$ is recalculated and another Difference Fourier is calculated. Hopefully

this will reveal the next heaviest atoms. The Fourier/least squares sequence is repeated until there are no major features left in the difference map and the R-factor is down to ~5%. At that stage you can regard the structure as solved and fully refined, and you can start to calculate bond distances and bond angles, and you can begin to ask "Why does it have this structure? What factors dominate the chemical bonding in this material?" When asking this sort of question, you should always remember that the final atomic coordinates (x,y,z) will have a standard deviation associated with them, and you must never interpret your results more deeply than the errors permit.

Well, that's one way to solve a crystal structure, and it works well when one or two atoms dominate the scattering. What happens when all the atoms in the unit cell have roughly the same X-ray scattering power, as is the case in many organic materials containing only C, N, O and H? In that case we use the technique known as Direct methods to solve the structure. This is a statistical method for predicting the phases of the different reflections and it ideally requires (i) that all the atoms have the same X-ray scattering power and (ii) that the distribution of atoms within the unit cell is quasi-random. The mathematical basis of the method was developed by Hauptmann and Karle in ~1950; they were rewarded with the Nobel Prize for Chemistry in 1986. The method is little used in the study of ceramics and I shall say no more about it now.

Before I leave X-ray crystallography, there are two points I want to make. The first concerns the time taken to do an experiment. The way I just described it, the answer is 3 or 4 days. However, it is possible to ask the question in a much more fundamental way - how long does it take for an atom to scatter an X-ray photon? This is what is properly referred to as the timescale of the experiment. It is easily calculated in this case: the X-ray photon travels with the velocity of light, $c = 3 \times 10^{8}$ $ms^{-1}$. The distance travelled by the photon during the scattering process is equal to the atomic diameter, $10^{-10}$ m. Therefore

$$\tau = \frac{\text{distance}}{\text{speed}} = \frac{10^{-10}}{3\text{x}10^{8}}$$

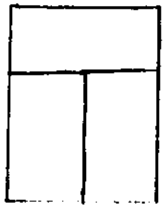
$$\therefore \quad \tau = 0.33 \times 10^{-18} \text{ s.}$$

Every experimental technique has a timescale associated with it. If the system changes between two states with a frequency greater than $1/\tau$, then the experiment cannot resolve the two states, but instead sees an average. The X-ray timescale is very short - cf $\tau_{nmr}$ $-10^{-4}$ s.

The second point I want to raise concerns the question "How big does a crystal have to be before I see a diffraction pattern". Imagine a polycrystalline sample where each grain of powder consisted of only, say, 2 unit cells - would I see an X-ray diffraction pattern? The answer is no. Each crystallite must be several wavelengths in diameter - you won't see an X-ray diffraction pattern if the crystallite size is less than about 200Å (20,000 pm). This constraint arises because of the coherence length of the X-ray wave packet - a piece of physics that I do not want to go into in any depth. Just remember that when you say "there is no impurity in this sample because I X-rayed it and didn't see any extra diffraction lines" what you are really saying is "any impurity in this sample has a crystallite size of less than 20,000 pm". Another way to look at this is to say that the X-ray experiments take a structural average over a distance of 200Å. If there is no coherent structure over this distance, then you don't see any Bragg peaks.

There is one intermediate caase which is being recognised in more and more materials, that is when structural micro-domains occur. Consider a material with an orthorhombic unit cell

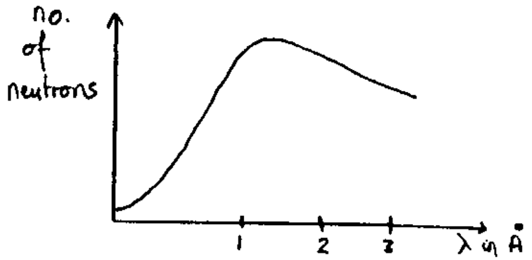
You can imagine small regions within this unit cell, packing together as follows



ie with small (<200Å) orthorhombic regions packed together in a disordered way. The <u>local</u> symmetry is everywhere orthorhombic, but over a distance of ~200Å, the average structure, as seen by an X-ray beam, is cubic, because of the disordered way in which the orthorhombic regions (or microdomains) are packed together. So you do see an X-ray diffraction pattern, but it will show cubic rather than the true orthorhombic symmetry. If you were to use a radiation with a shorter wavelength, and hence a shorter coherence length, you could see the true orthorhombic symmetry. This is the case in an electron microscope.

I am going to leave X-ray diffraction now to look at neutron diffraction. The neutron is a particle which can be regarded as a wave according to the de Broglie equation $\lambda = h/mv$. If you want to do an X-ray diffraction experiment you simply walk down the corridor and there's a diffractometer waiting to be used. If you want to do a neutron diffraction experiment you need a 60MW nuclear reactor. The neutrons are produced in nuclear reactions in the core of the reactor. Their energies are moderated by a volume of heavy water that surrounds the core. The neutrons are thus brought into equilibrium at a temperature T, characteristic of the heavy water. Their kinetic energy is thus given by $\frac{1}{2}mv^2 = \frac{3}{2}k_BT$. Substituting from de Broglie's equation $\lambda^2 = h^2/3mk_BT$ so for T = 0°C, λ = 1.55; T = 100°C, λ = 1.33Å, ie wavelengths suitable for diffraction experiments. The actual profile

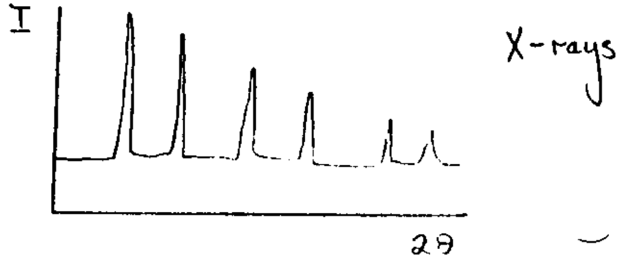
of number of neutrons vs. wavelength look something like this:



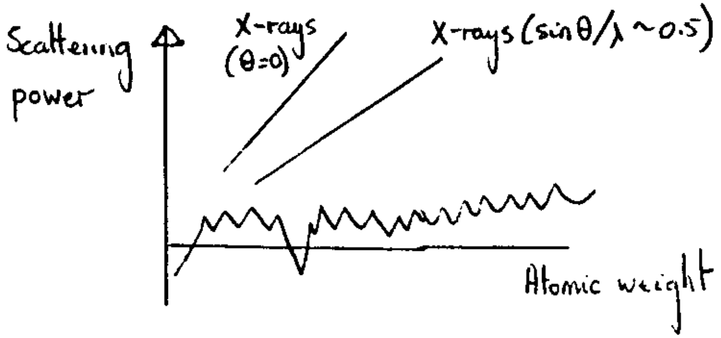
de Broglie: $\lambda = \frac{h}{mv}$

because of moderator temperature, these are known as 'thermal neutrons'

A monochromatic beam is produced from this distribution by allowing the neutrons to hit a single crystal monochromator, often germanium. In a neutron diffraction experiment the neutrons are scattered by the atomic nuclei. This has two important consequences, firstly in the X-ray case the size of the scatterer - the electron cloud of an atom - is of the same typical dimension, ~2Å, as the wavelength of the radiation. This means that the atom does not act as a point scatterer and consequently the scattered intensity falls off quite rapidly with increasing 2θ. In the neutron case, the scatterer is a nucleus, several orders of magnitude smaller than the wavelength of the radiation and therefore acting as a point scatterer. The scattering does not fall off rapidly with increasing 2θ. So the diffraction pattern from a metal might look something like this in the two cases:

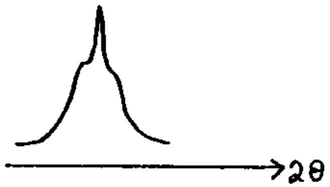


The consequence of this is that you often see more observable reflections in a neutron diffraction pattern than you do in an X-ray pattern, and if you are trying to solve a structure, then the more reflections you see the better. The second consequence of the difference in scattering mechanism concerns the relative ability of X-rays and neutrons to distinguish between different types of atom. The scattering power of an atom with respect to X-rays is directly proportional to the number of electrons that it has, ie uranium scatters much more strongly than hydrogen. On the other hand, the neutron scattering power depends on nuclear properties which change only over a very small range throughout the periodic table, ie the neutron scattering power of hydrogen is roughly the same as that of uranium. Furthermore, the variations that do occur are essentially random. This is summarised in the following graph:



I've plotted atomic weight on the horizontal axis, rather than atomic number, to help make the point that isotopes of the same element can have different neutron scattering powers, for example deuterium is a better neutron scatterer than hydrogen. Their X-ray scattering power is, of course, identical. The graph shows clearly why neutrons are preferred to X-rays when the problem is to locate light atoms in the presence of heavy ones. The X-ray scattering from a rare-earth hydride would be dominated by the rare earth to such an extent that the scattering from the protons would be lost in the experimental noise. On the other hand, in a neutron experiment the two species would contribute almost equally to the scattering. Although all elements scatter neutrons to roughly the same extent, the random variations in scattering power can often be useful. For example, in the compound $NiCo_2O_4$, X-rays could locate the metal atoms but they could not tell which were nickel and which were cobalt - they are next to each other in the periodic table and $Ni^{3+}$ and $Co^{2+}$ are isoelectronic -they have the same number of electons. Fortunately, the neutron scattering power of nickel happens to be four times greater than that of cobalt, so there is no difficulty in distinguishing the two types of atoms in a neutron diffraction experiment. This sharp contrast in the scattering power of neighbouring atoms is particularly marked in the first transition series.

There are two further factors which can, on occasion, make it preferrable to use neutron diffraction rather than X-ray diffraction. Firstly, the absorption of a neutron beam by most materials is very low. This means that it is much easier to do experiments at low temperature with the sample mounted in a cryostat, or at high temepratures with the sample mounted in a furnace. The housing of the furnace or cryostat will not absorb the neutron beam to any great extent. The absorption of X-rays is much greater and measurements at temperatures other than ambient are far from routine. Secondly, the neutron has a magnetic moment which, during the course of the scattering process, can interact with any magnetic moment that the sample may possess, ie you can probe the magnetic properties of transition metal compounds and look at the properties of ferromagnets and antiferromagnets. The X-ray photon does not have a magnetic moment and so only very weak magnetic scattering, too weak to be of any use, is seen in the X-ray diffraction pattern. These then are the fundamental differences between X-ray and neutron diffraction. The most obvious practical difference is the inconvenience and high cost of doing a neutron diffraction experiment compared to an X-ray experiment. Consequently it is usual to use X-rays whenever possible. If you make a new compound in the form of a single crystal, the way to begin its structural characterisation is by single crystal X-ray diffraction. That will probably enable you to locate all the atoms. If it cannot locate the lighter atoms, and their positions are crucial to the understanding of the material, for example if you cannot find the protons when you are making a study of hydrogen bonding, then you might do a single crystal neutron diffraction experiment in order to locate the all important hydrogen atoms. If you can only make your new compound in polycrystalline form then you can study it by X-ray powder diffraction and hopefully find the unit-cell parameters. However, it is difficult to get structural information, ie atomic coordinates, out of a powder pattern, but what success there has been has been achieved largely, though not entirely with neutrons; if you cannot grow single crystals and have to rely on powder diffraction, you may be better off using neutrons rather than X-rays. Let me first explain why it is difficult to determine structures from powder data alone. It is essentially because all the data have to be represented in one dimension in a powder pattern, so that in a cubic crystal for example the (221) reflection lies directly on top of the (300). Thus, you cannot assign an intensity to each individual reflection. In a single crystal experiment the two reflections would occur at the same $2\theta$ value of course, but at different points in space - there is always a loss of information when you go to a powder sample. There are, perhaps, two reasons why powder diffraction has been more successful with neturons than with X-rays. Firstly, because neutron scattering does not fall off with increasing scattering angle in the way that X-ray scattering does - there is no form factor in the neutron case - you can record diffraction maxima out to higher 2θ values in the neutron case (~160°) and hence get a larger data set. Secondly, because the data set is compressed into one dimension, for compounds having all but the highest symmetry and the smallest unit cells, there is a considerable degree of reflection overlap. I don't just mean the unavoidable overlap of cubic (221) and (300) reflections, but if you have an orthorhombic material with say a = 5.50, b = 5.47, c = 7.75 then you will find that the (200), (020) and (112) reflections occur at 2θ values of 32.56, 32.74 and 32.66 °. Given that the instrumental linewidth is about 0.3° (2θ) you cannot resolve these three reflections - you observe something like this:



If you have a diffraction pattern that is full of overlapping peaks like that and you want to analyse the intensities of the Bragg reflections then you have to be able to aportion the intensity under a broad, unresolved maximum into the individual peaks that contribute to the maximum. You (or your computer) can do this if you know the shape of the individual Bragg peaks. This is where neutrons have scored over X-rays, because the peaks in a neutron diffraction pattern have a Gaussian shape that is easily modelled, whereas those in an X-ray diffraction pattern have a more complex shape which is difficult to model mathematically. The convenient Gaussian peak shape has led to the development and widespread use of the Rietveld profile analysis technique in structure refinements based on neutron powder diffraction data. However, you must remember that this is a technique for structure refinement rather than structure solution. You need to know the basic structure of the material, and then you can fine-tune it using profile analysis. If you know the positions for all but one atom you can probably locate that missing atom, or you can determine the magnetic structure (ferromagnetic or antiferromagnetic) if you know the crystal structure already. Profile analysis is a very powerful technique, but I only know of two crystal structures that have actually been solved, as against refined, from powder neutron data. The loss of information in the one-dimensional data set is generally too great for Patterson and direct methods to work.

Having said that X-ray refinements using powder data have lagged behind those done with neutrons, I should point out that the situation is beginning to change with the increasing availability of X-ray powder diffractometers on high intensity beam lines at synchrotron radiation sources, such as that at Daresbury in Cheshire, England. These instruments have a resolution ~30x better than a neutron powder diffractometer (~10x better than a laboratory X-ray diffractometer) and so the extent of peak overlap is minimised. It then becomes possible to assign intensity to individual Bragg peaks and to actually solve structures by Patterson methods. People have also been putting a lot of effort into characterising the X-ray peak shape, and with some success. At the moment it seems that if you have to work with powders, then you might be better off using X-rays to solve the structure, particularly if a heavy metal atom is present, but neutron diffraction with its larger data set spread over a wider angular range is probably still superior for structure refinement. The first real structure determination done using a polycrystalline sample and a synchrotron X-ray source was that of $\alpha$-$CrPO_4$ by Attfield, Sleight and Cheetham (Nature 322, 620 (1986)). Another example is $MnPO_4.H_2O$ done by Lightfoot, Sleight and Cheetham (Inorg. Chem. 26, 3544 (1987)).

Finally, on the subject of neutron diffraction, I want to introduce you to a technique which has only been available for the last five years, but which holds a lot of promise for the future. This is time-of-flight neutron scattering. If we go back to Bragg's Law, $\lambda = 2d_{hkl} \sin \theta_{hkl}$, then all the experiments I've desribed so far have involved holding $\lambda$ constant and varying $\theta$ to detect the maxima in the scattered intensity. You can do it the other way round by holding $\theta$ constant and varying $\lambda$. In the experimental arrangement, protons are accelerated in a synchrotron to something like 500 MeV and they are then allowed to collide with a heavy metal target to produce a burst of neutrons in a spallation process. This pulse of neutrons is then guided to the sample, without any form of monochromator. The sample is thus bombarded by a pulse of neutrons with a continuous distribution of wave-lengths. Each set of (hkl) planes in the sample will diffract different wavelengths to maxima at different angles. So if you sit with your detector at one particular angle you will receive maxima from all the different sets of (hkl) planes, but the maxima will be at different wavelengths for each set of planes. This means that the neutrons arriving at the fixed detector after scattering from the (111) planes will have a different wavelength from those arriving after scattering by the (200) planes. They will, therefore, have a different velocity, from de Broglies's Law, and they will, therefore, take a different length of time to get to the detector. So if you measure the time of flight between sample and detector you can calculate the wavelength and hence the d-spacing. This tof neutron scattering promises a new generation of high intensity, high resolution diffractometers. A facility based on this technique opened at Rutherford Appleton Laboratory in Oxfordshire during 1985.

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