

# Neutron Powder Diffraction

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## 1. Introduction

### 1.1 A typical application of Neutron Powder Diffraction - High Tc Superconductors

For a few days in March 1987, all the world's major laboratories struggled to understand the structure of the 90K superconductor, using all possible techniques. The results at the end of the month can be summarised by figure 1. It shows a typical X-ray picture of the structure of the superconductor, obtained in this case by Bell laboratories [1], beside a typical neutron picture of the 'same' structure [2].

Both the X-ray and neutron pictures in figure 1 are technically correct. The obvious differences are simply because X-rays could not locate the light oxygen atoms with certainty. Even the chemical formula for the X-ray structure, given in the published title as  $\text{Ba}_2\text{YCu}_3\text{O}_{9-y}$ , was uncertain as to the precise number of oxygens, and the oxidation state of the copper ions was the question of crucial interest posed by Bednorz and Müller [3]. The formula given in the title of the neutron paper was  $\text{Ba}_2\text{YCu}_3\text{O}_7$ , and neutrons showed how oxygen could be extracted, destroying superconductivity.

Clearly the precise number and location of the light atoms is important for thinking about the structure. The X-ray structure implied that copper was co-ordinated by oxygen octahedrae, which Bednorz and Müller [3] had implied was necessary for superconductivity. The neutron structure claimed that there were no octahedra, and for this reason was hotly disputed. Instead it showed that the superconductor consisted of planes of copper oxide separated by chains, with the 2D and 1D elements joined by 'apical' oxygen.

This neutron paper [2] became the most cited experimental paper in the most competitive field of science in the following year. The neutron structure, which was simultaneously confirmed by many other neutron laboratories, strongly influenced the search for new superconductors based on either 1D or 2D copper oxide elements.

**Fig.1** Structures of the 90K superconductor

- (a)  $\text{YBa}_2\text{Cu}_3\text{O}_{9-x}$  obtained by X-rays [1] and of
- (b) ' $\text{YBa}_2\text{Cu}_3\text{O}_7$ ' obtained by neutrons [2].

Both structures are correct, but with X-rays it was not possible to determine the occupancy of the oxygen sites in the presence of the heavy atoms. Neutrons showed

that there were no octahedrae, but that the oxygens were ordered to form 1D CuO-chains connecting planes of CuO via apical 'bridging oxygens'.

## 1.2 Advantages of Neutron Diffraction for Single Crystals and Powders

This is an example where the extra 'details' provided by neutrons proved essential, leading directly to a fuller understanding of the chemistry, and even pointing the way to more interesting compounds.

But it is not too difficult to find other examples where thermal neutron diffraction has made unique contributions to the understanding of the chemistry and physics of important new materials. For example in the understanding of 'hard' magnetic materials, neutron diffraction was essential [8]. Neutron diffraction is becoming increasingly important for the study of in-situ reactions, such as oxidation-reduction, hydration-dehydration, chemical decomposition and adsorption, catalysis, electrolysis etc [9]. Our understanding of the stresses deep inside materials, around welds, cracks etc. has been much advanced by neutron diffraction, because of the great penetrating power of the neutron [10].

These are not academic problems, but in most cases are of immediate technological interest. Scientists using neutron diffraction are usually not 'neutron scattering specialists' but are using the technique in competition with all others available to them.

The advantages of neutrons, strong scattering from light atoms and no 'form factor' fall off with scattering angle, is best illustrated by the relative scattering factors for X-rays, electrons and neutrons for the atoms of high temperature superconductors.

**Fig. 2.** The scattering power for X-rays, electrons and neutrons of the different atoms in oxide superconductors. The circles are proportional to the scattering amplitude, and the areas to the intensity, for scattering at angles  $2\theta$  such that  $\sin\theta/\lambda = 1$ .

A list of neutron scattering "lengths" is given in table 1.

## 2. Design for a reactor based neutron powder diffractometer

### 2.1 The Simplest Neutron Diffraction Machines - Powder Diffractometers

Neutron diffraction conjures up ideas of the complicated and expensive equipment associated with a nuclear reactor. It is true that the neutron source itself is expensive, but if we already have such a source, the additional equipment for the simplest neutron diffraction measurements - those used to obtain most of the results described above - is actually simpler and cheaper than similar X-ray equipment. We will therefore start by describing the simplest of neutron diffractometers - the powder diffractometer [11, 12].

Figure 2 shows the essentials of a neutron powder diffractometer. The white beam of neutrons, extracted through a hole in the reactor, is collimated by  $\alpha_1$  to limit the spread of incident directions. The monochromator selects a band of wavelengths  $\Delta\lambda/\lambda$  and directs these neutrons to the powder sample, sometimes through a second collimator  $\alpha_2$ . The detector collects the neutrons, scattered in many directions by the sample, and records the scattered intensity as well as the angle  $2\theta$  of scattering. This angular detection is achieved using either a position sensitive detector (PSD) or a third collimator  $\alpha_3$ . In the latter case, the detector is scanned to cover the whole scattering range. The scale of the machine, related to the size of the sample and neutron beam, is larger than the usual laboratory X-ray machine, but may be smaller than a synchrotron powder diffractometer.

**Fig. 3.** The high resolution powder diffractometer D2B at ILL Grenoble [13]. A Söller collimator is used to define the incident beam direction to  $5^\circ$  or  $30^\circ$  of arc, and a (vertically focussing) monochromator crystal is used to select a particular wavelength, such as  $1.594\text{\AA}$ . Further  $5^\circ$  collimators in front of the  $64\text{ }^3\text{He}$  detectors define the scattered beam.

The intensity from the reactor is always smaller than desirable, and much smaller than from any X-ray source. The two design criteria for a neutron powder diffractometer are then to maximise the angular resolution but also to maximise the recorded intensity. These criteria are of course contradictory. The resolution can easily be increased by narrowing the collimators  $\alpha$ , but this naturally reduces the intensity. In finding a compromise we must of course make sure that we do not introduce errors in the data.

## 2.2 The Powder Sample and Environment

In order to gain intensity the samples are larger for neutrons, so positioning and alignment can be less precise. No need to keep the floor level to the nearest micron, nor to damp out vibrations caused by passing cars. The larger sample size is also a fundamental advantage for powder diffraction. The sample must represent all possible orientations of the constituent microscopic crystallites. This is often not true for the very small samples used with X-rays, where the high absorption limits sample size. Of course, the larger neutron samples are a disadvantage if only microscopic quantities of material can be prepared, but this is not usually a problem for modern neutron diffractometers on high flux reactors.

It is true that the much higher fluxes available with synchrotron sources permit higher line resolution than is possible for neutrons, even with a high flux neutron source. However, in practice resolution is limited by the particle size of the material.

But the resolution advantage of synchrotron powder diffraction is not so great as first appears from the narrow line width. This is because we are usually interested in the resolution in the spacing of atomic planes - the d-spacing - rather than the diffraction line width. The  $\Delta d/d$  resolution depends on the line width  $\Delta 2\theta$ , but also on the scattering angle  $2\theta$ , as shown by differentiating Bragg's equation  $2d\sin\theta=\lambda$  for scattering from the sample:

$$\Delta d/d = \Delta\theta \cdot \cot \theta$$

Clearly,  $\Delta d/d$  is small (high resolution) for high scattering angles  $2\theta$ . But neutrons have a fundamental advantage over X-rays at high scattering angles. Because scattering is from the almost point nucleus, and not from the much larger shells of atomic electrons as with X-rays, neutron scattering does not decrease with scattering angle. This means that usually lines can be measured at very high scattering angles with neutrons, so that even though the lines are broader, the  $\Delta d/d$  resolution with backscattered neutrons can rival that of X-ray machines [14, 15].

**Fig. 4.** Bragg's law is simply the condition for constructive interference for scattering by angle  $2\theta$  with wavelength  $\lambda$  from a set of planes of d-spacing  $d$ .

**Fig. 5.** The results of a high resolution neutron powder scan for the 12Å unit cell of yttrium iron garnet (YIG) on the D2B machine at ILL Grenoble [13]. Notice how sharp the Bragg reflexions are throughout the entire pattern, and how strong the peaks are at high scattering angle, where X-ray patterns fall off because of the 'form factor'.

Strictly, the line intensity falls with angle because of the smearing of the nucleus by atomic vibration. This Debye-Waller factor can however be greatly reduced by cooling the sample, which for technical reasons to do with the sample size, is usually easier with neutrons. Neutron samples are usually measured at low temperature, while X-ray measurements are often restricted to room temperature.

The ease with which neutron powder measurements can be performed at low temperature is also an advantage for studying the true crystal structure. A surprisingly large number of materials transform to a lower symmetry structure when cooled from room temperature. The most well known examples are the large family of perovskite structures - to which high Tc superconductors belong !

Finally, the larger sample size makes it easier to construct detectors for neutron powder diffraction. Powder samples naturally scatter in many directions simultaneously, so it is a big advantage to have a position sensitive detector (PSD), or a multidetector. The simplest form of PSD is of course the photographic plate, used from the beginning of X-ray diffraction. However, it is not ideally suited to precise measurements of intensity, which are necessary for structure determination. Electronic PSD's have only recently become practical for X-ray powder diffraction, while they have been used for more than 20 years with neutrons.

### 2.3 The Monochromator

The monochromator, with the detector, is the most important component determining the neutron intensity apart from the size of the sample. We want to use as wide a band of wavelengths  $\Delta\lambda/\lambda$  as possible, since this is directly proportional to the intensity. A wide wavelength band is simply achieved by having a large mosaic spread  $\Delta\theta_M$  for the monochromator, since again differentiating Bragg's equation  $2d\sin\theta_M = \lambda$  for scattering from the monochromator gives:

$$\Delta\lambda/\lambda = \Delta\theta_M \cdot \cot \theta_M$$

Since this equation for  $\Delta\lambda/\lambda$  is similar to the previous equation for  $\Delta d/d$ , it would appear that large  $\Delta\lambda/\lambda$  and high intensity implies large peak widths  $\Delta d/d$ . Fortunately this is not so. For the geometry shown in figure 2, the different wavelengths, leaving the monochromator in different directions, are brought back into the same direction when scattered a second time by the sample. This is strictly true only when the angle for scattering from the sample  $2\theta$  is equal to the monochromator ‘take-off’ angle  $2\theta_M$ , and is called ‘reciprocal space’ or wavelength focussing.

A small take-off angle  $\theta_M$  to increase  $\cot \theta_M$  would also increase  $\Delta\lambda/\lambda$  and intensity, but if we do that, we only have wavelength focussing at small scattering angles. In practice we want to focuss at large angles, so that we need an even larger monochromator mosaic to compensate. A monochromator mosaic of 15 minutes is not excessive for even the highest resolution neutron powder machine. In that case we should use a 30 minute wide collimator to allow all the wavelength band to reach the sample. In practice, we need no collimator at all, so that  $\alpha_3$  is determined by the size of the sample divided by the distance to the collimator.

A second kind of focussing, in real space, is also possible, since the instrument resolution does not depend much on the *vertical* divergence of the incident beam. We may use a vertical divergence of as much as 5 degrees on a machine which still has high resolution in the equatorial plane. Vertical divergence is obtained by placing the machine as close as possible to the source, and cutting a large hole in the reactor. But if this is not sufficient, we must use a vertically focussing monochromator.

Vertical focussing is achieved by cutting the monochromator into horizontal strips, and aligning the strips on a vertically curved backing plate to focus onto the sample. On D2B at ILL Grenoble, 30 x 1cm strips are used to focus a 30cm high neutron beam onto a 4cm high sample [13]. The focal length is constant, even though different wavelengths can be selected. This is made possible by the large fixed monochromator take-off angle.

Germanium in reflexion geometry is a good choice for the monochromator for several reasons. If the (h,h,l) (odd,odd,odd) reflexions are used, then both  $2\lambda$  and  $1/2\lambda$  harmonic contamination is avoided. Furthermore, with the high take-off angle, high order reflexions are used, and there is a useful choice of wavelengths for the same scattering angle. For example, (711), (533), (511), etc. all give different wavelengths. Since they all lie in the same crystallographic plane, changing the neutron wavelength is simply a matter of rotating the monochromator crystal by the small angle separating these high angle reflexions.

## 2.4 Söller Collimators

Söller collimators  $\alpha_1$  serve to define the direction of the beam incident on the monochromator. They consist of a stack of flat absorbing plates. The divergence is determined by the ratio of the distance between the plates and their length, and is therefore decoupled from the beam cross section, which is simply the cross section of

the stack. The ratio of the plate thickness to plate separation determines the neutron loss compared to a perfect collimator.

A big advance in neutron collimators was made when very thin stretched plastic foils were used as the plates [16]. For example, 25 $\mu$  thick foils, coated with another 25 $\mu$  of neutron absorber such as gadolinium oxide paint, give 90% efficiency even if the plate separation is only 0.5mm, as required for a 5 minute collimator 34cm long [17]. Such a collimator may have a beam cross section of 25x100 mm high or more. The beam width reflects the maximum width of the sample, while the beam height is important for obtaining high vertical divergence to increase intensity.

**Fig. 6.** The rocking curve for two 10' Söller collimators, representing the convolution of triangular functions, is equal to the line width at focussing, and is almost a perfect Gaussian.

## 2.5 The PSD Detector [18]

The neutron PSD is simpler to make, mainly because of the size of the sample and the scale of the diffractometer. If the sample is a cylinder of 5mm diameter, which is already small for neutrons, the position resolution of the detector may also be several mm. Neutron PSD's can be made simply from a stack of individual detectors, each 5mm wide [19]. The angular resolution of such a detector depends on the ratio of the sample/detector diameter to the distance between the two, so a 5mm diameter sample and detector separated by 1500mm means an angular resolution of 0.2 degrees. The line shape will then be at least 0.2  $\sqrt{2}$  degrees  $2\theta$ , since the detector resolution is folded with the resolution of the remainder of the diffractometer, as we shall see.

This would be a medium resolution powder diffractometer, provided that we could work at high scattering angles. Higher resolution with a PSD requires samples smaller than 5mm, and of course the intensity falls as the square of the sample diameter, usually making smaller samples impractical.

The D1B diffractometer at ILL Grenoble [20] was designed with these characteristics. Instead of individual 5mm detectors, a single BF<sub>3</sub> gas container was used, with individual wires spaced at 5mm intervals. This was the first, highly successful, PSD for neutron powder diffraction (Fig.3). 400 wires at 0.2 degree intervals covered an angular range of 80 degrees. Later the poisonous BF<sub>3</sub> gas was replaced by He<sup>3</sup> gas at higher pressure.

**Fig. 7.** The 'banana' on D1B at ILL was the first example of the use of a multiwire PSD for neutron powder diffraction.

Each wire of such a PSD produces one point on the diffraction pattern, so the number of points, or *definition* of the pattern, is low. This is a problem for the usual Rietveld refinement of the diffraction pattern profile. The definition of the profile can be increased, without changing the resolution, by displacing the whole detector by 0.1 degrees to collect another 400 points at intermediate angles. Indeed the PSD can be step-scanned to produce a profile with any desired definition.

The sample height can be much greater than the sample diameter, since vertical divergence does not much affect horizontal resolution. Vertical angles of 5 degrees or more can be tolerated, corresponding to samples as high as 125mm. Of course, the sample height is often limited by the available sample volume. The detector height could similarly be increased to 125mm or more, but is limited by the high gas pressures (5-10 bar) that must be supported over a correspondingly large detector window.

Larger samples could be used with larger PSD's to obtain more intensity if these mechanical problems can be solved, but such detectors would be expensive.

Inexpensive PSD's can consist of linear wire detectors, where the single wire is horizontal, and the position of the detected neutron is determined by timing the arrival of the resulting electrical pulse at both ends of the wire. This is the same technique used for X-ray powder PSD's. The X-ray detectors can be curved horizontally, but so far the neutron detectors use straight wires, which means that parallax errors must be corrected. A number of short straight sections can extend the angular range of the detector, and the vertical divergence can be increased by stacking several detector tubes [21].

Yet another kind of PSD can be constructed using neutron scintillators or other solid state techniques [22]. This has the advantage that the mechanical problems of containing high pressure gas are eliminated and large detectors can be made quite cheaply. The detection efficiency is not as high as for the best gas detectors, but may often be sufficient.

## 2.6 The Multicollimator Detector

An alternative to the PSD becomes attractive if large samples are available and the highest resolution is required. Instead of allowing the sample diameter to determine the resolution with a PSD, a soller collimator  $\alpha_3$  can be placed between the sample and detector to limit the horizontal divergence. Since soller collimators may have a divergence of less than 0.1 degrees, compared to the usual 0.2 degrees imposed by the sample size with a PSD, very high resolution is possible. Since this resolution is independent of sample size, samples up to 15mm diameter or more may be used, increasing the sample volume, and therefore intensity, by an order of magnitude. A bank of soller collimators and individual detectors can cover a wide angular range, of 160 degrees or more [13, 14].

A PSD simultaneously collects data over the whole of its range, while each collimator only collects data within the angle  $\alpha_3$ . If  $\alpha_3=0.1^\circ$  for example, then 64 collimators at  $2.5^\circ$  intervals covering  $160^\circ$  would be equivalent to a PSD covering an angle of only  $6.4^\circ$ . Alternatively, an  $\alpha_3$  of  $0.1^\circ$  could be achieved with a 2.5 mm diameter sample 1500 mm from a PSD covering  $160^\circ$  rather than  $6.4^\circ$ . The x25 larger PSD detector solid angle would be offset by the x36 larger volume of the 15mm diameter sample that could be used on the multicollimator machine.

**Fig. 8.** The multicollimator detector on D1A at ILL permits very high resolution, independent of the sample diameter, and excludes scattering from the sample environment..

The high resolution multicollimator is relatively inexpensive and easy to build, while a 160° PSD with a resolution of 0.1° would be very expensive. ILL has however been developing such a detector for a number of years.

The multicollimator machine has other practical advantages apart from cost. The  $\alpha_3$  collimators accept scattering from only a very small volume around the sample, while the PSD accepts scattering from all directions. This makes it much easier to use cryostats and furnaces with the multicollimator machine, and most experiments now require such sample environments. A radial collimator [23] can be used with a PSD detector to exclude scattering from much of the sample environment, but not to improve the resolution. It must be spun or rocked to average out the attenuation of the scattered radiation over the entire detector.

## 2.7 Bragg's Law and the Density of Bragg Peaks

Bragg's law is simply the condition for constructive interference for scattering by angle  $2\theta$  with wavelength  $\lambda$  from a set of planes of d-spacing  $d$  (figure 4).

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

For a cubic lattice of unit cell dimension  $a_0$ , the allowed values of  $n/d$  are:

$$n/d = \sqrt{h^2 + k^2 + l^2} \cdot 1/a_c$$

(h,k,l) are integer 'Miller indices' characteristic of a given Bragg angle  $\theta$ . Then

$$2\sin\theta = p^{1/2} \cdot \lambda/a_0$$

Bragg peaks are obtained for all allowed integer values of  $p = h^2 + k^2 + l^2$ . Differentiating with respect to  $\theta$  we obtain the density of Bragg peaks  $\partial p/\partial\theta$  as a function of scattering angle  $2\theta$ .

$$2\cos\theta = 1/2 \cdot p^{-1/2} \cdot \lambda/a_0 \cdot \partial p/\partial\theta$$

$$\partial p/\partial\theta = (2a_0/\lambda)^2 \cdot \sin 2\theta$$

The number of Bragg peaks in a given  $\sin 2\theta$  range then increases rapidly with  $a_0/\lambda$ , the size of the crystal structure relative to the neutron wavelength. Since the total scattered intensity depends on the number of atoms, and not the size of the crystal structure, the average intensity of a Bragg peak decreases as the number of peaks increases with  $a_0/\lambda$ . The wavelength  $\lambda$  of the neutrons must then be long for large structures, both to spread out the peaks and to increase the average peak intensity [24].

## 2.8 Caglioti's Equation and Diffractometer Resolution

The angle between adjacent Bragg peaks ( $\Delta p=1$ ) is, from the last equation:

$$\Delta 2\theta_B = 2\Delta\theta = (\lambda/2a_0)^2 \cdot 1/\sin 2\theta$$

This has a minimum at  $2\theta = 90^\circ$ . For a lattice of symmetry lower than cubic, this minimum is shifted to somewhat higher angles.

The FWHM (full width at half maximum) resolution of the diffractometer  $\Delta 2\theta_R$  also depends on scattering angle  $2\theta$  according to Caglioti's equation [25, 26]

$$\Delta 2\theta_R^2 = U \cdot \tan^2\theta + V \cdot \tan\theta + W$$

where  $U, V, W$  are constants for a given instrument geometry and depend in a complicated way on the collimators and the monochromator. This quadratic equation also has a minimum, for scattering angles near the monochromator take-off angle i.e. for  $2\theta \approx 2\theta_M$ . If this minimum is very shallow, the parameters  $U, V, W$  are highly correlated: the resulting instabilities in refinements can be eliminated by constraining the minimum in the resolution to occur at a scattering angle equal to the monochromator take-off angle. Differentiating Caglioti's equation gives this constraint as  $V = -2U \cdot \tan\theta_M$ .

A good diffractometer design will try to match instrument resolution,  $\Delta 2\theta_R$ , to the peak separation,  $\Delta 2\theta_B$ , over as large a range of  $2\theta$  as possible, and this means that the monochromator take-off angle must be large  $2\theta_M \geq 90^\circ$ .

Figure 9 shows how this match between  $\Delta 2\theta_R$  and  $\Delta 2\theta_B$  can be obtained in practice for a cubic cell of lattice dimension  $a_0 = 16\lambda$ . The vertical divergence of the incident neutron beam, which must be large to obtain high intensity, further broadens the instrument resolution, but these simple considerations, which are discussed more fully in [11], remain approximately valid.

**Fig. 9.** A good diffractometer design will try to match instrument resolution,  $\Delta 2\theta_R$ , to the peak separation,  $\Delta 2\theta_B$ , over as large a range of  $2\theta$  as possible, and this means that the monochromator take-off angle must be large  $2\theta_M \geq 90^\circ$ . This match between  $\Delta 2\theta_R$  and  $\Delta 2\theta_B$  can be obtained in principle on D2B for a cubic cell of lattice dimension of up to  $a_0 = 16\text{\AA}$ . [11].

## 2.9 Resolution in d-spacing and Backscattering

We have already seen that the resolution in d-spacing is given by  $\Delta d/d = \Delta\theta \cdot \cot\theta$ , and that since  $\cot\theta$  decreases rapidly with  $\theta$ , it is not difficult to achieve high resolution (small  $\Delta d/d$ ) at large scattering angles, provided  $\Delta\theta$  remains small. And we have seen that this is achieved if the diffractometer is designed to match the density of peaks and  $2\theta \approx 2\theta_M \geq 90^\circ$ .

The limiting case of  $2\theta \approx 180^\circ$  is called ‘backscattering’. It is particularly interesting because then  $\cot\theta \approx 0$ , and  $\Delta d/d \approx 0$ , meaning very high resolution of d-spacings, even if the detector acceptance angle ( $\approx 2\Delta\theta$ ) is large. This is the basis of the backscattering time-of-flight (TOF) machines [15]. Instead of scanning through the scattering angle  $2\theta$  for all Bragg reflexions at a fixed neutron wavelength  $\lambda$ , a stationary detector at  $2\theta \approx 180^\circ$  collects reflexions by scanning through  $\lambda$ . Figure 7 shows the HRPD machine at ISIS near Oxford [27].

Since neutron detectors have poor  $\lambda$ -resolution, the neutron wavelengths are sorted by timing over a long (100m) flight path. The neutron source is pulsed (in this case from an accelerator rather than a reactor), and the faster neutrons arrive before the slower neutrons. The pulses  $\Delta t$  must be narrow compared to the total time-of-flight  $t$ , since

$$\Delta d/d \approx \Delta t/t$$

This means that although neutrons of all wavelengths are used, which is better than selecting a single  $\lambda$  with a monochromator, the source provides neutrons only during the short pulse, and not continuously as with the reactor based machine. The neutron pulse then spreads out in time over the incident flight path. In fact the time averaged flux on the sample is typically an order of magnitude lower than for a reactor machine with comparable resolution.

Fortunately the TOF machine has another advantage which compensates for the low time-averaged flux on the sample. We saw that resolution is high in backscattering even if  $2\Delta\theta$  is large. This means that the detector acceptance angle can be an order of magnitude greater than the array of fine collimators, and comparable to the solid angle of a PSD on a conventional diffractometer.

These advantages and disadvantages mean that for many purposes TOF and reactor machines are comparable in both resolution and speed. In table I, a comparison of D1A/ILL-GPPD/Argonne and D2B/ILL-HRPD/ISIS illustrates this [28].

### **3. Rietveld refinement of powder diffraction data**

#### **3.1 Principles of Rietveld Refinement**

However good the resolution of the diffractometer, many Bragg peaks will not be fully resolved. Initially this problem was solved by fitting a number of Gaussians to a group of overlapping peaks, to extract the individual Bragg intensities. The peak shape, being the convolution of a number of instrument parameters is closely approximated by a Gaussian, but more complex functions can be used to account for peak asymmetry, sample strain etc.

The difficulty is that a large number of parameters are required, four for each peak even for a simple Gaussian (position, height, width and background). In cases of severe peak overlap, these parameters are highly correlated, and the errors in the resulting Bragg intensities become important.

Rietveld [29] recognised that it was not necessary to extract the individual Bragg intensities, which was previously assumed by all crystallographers, but that the actual

structural parameters could be refined directly to fit the entire diffraction pattern. The structural parameters, having physical reality, are much less correlated among themselves, and there are far fewer of them.

The atom co-ordinates, which are the quantities we want anyway, determine the peak intensities, so they may as well be refined directly. Furthermore, all of the peak positions are determined by at most six lattice constants corresponding to the cell dimensions and angles (a,b,c,α,β,γ). The peak widths can be obtained from just three parameters U,V,W in Caglioti's formula, and the background can be measured in regions where there are no peaks, and be interpolated since it varies smoothly.

Then instead of four parameters for each of several hundred peaks, we typically have only a few tens of physically real parameters.

For each 2θ point in the diffraction pattern, the Rietveld refinement program [30] calculates the contributions from all of the Bragg peaks in the vicinity, and compares the total  $Y_i(\text{calc})$  with the observed count  $Y_i(\text{obs})$ . The structure parameters, which determine  $Y_i(\text{calc})$ , are then adjusted to minimize the 'chi-squared' quantity:

$$\chi^2 = \sum_i W_i \cdot |Y_i(\text{obs}) - 1/c \cdot Y_i(\text{calc})|^2$$

The summation is over all the 2θ points i and  $W_i \propto 1/\sigma_i^2 \approx 1/Y_i(\text{obs})$  is the weight allotted to the count  $Y_i(\text{obs})$  while c is a scale factor. Rietveld's weighting scheme can be justified in the following way [30].

Suppose that the counts  $Y_i(\text{obs})$  are samples of some population function  $Y_i(\text{calc})$ , which is completely defined by the crystal structure parameters. The probability  $p_i$  that a given sample count  $Y_i(\text{obs})$  will differ from  $1/c \cdot Y_i(\text{calc})$  is given by:

$$p_i \propto (1/\sigma_i) \cdot \exp \left\{ -(1/2\sigma_i^2) \cdot |Y_i(\text{obs}) - 1/c \cdot Y_i(\text{calc})|^2 \right\}$$

since each sample count comes from a normal distribution (a Gaussian peak) centred on  $1/c \cdot Y_i(\text{calc})$ , with standard deviation  $\sigma_i^2 = 1/c \cdot Y_i(\text{calc})$ . The probability P that all of the counts are samples of the population  $1/c \cdot Y(\text{calc})$  is the product  $\prod_i p_i$  of the individual probabilities:

$$P = \prod_i p_i \propto \left( \prod_i 1/\sigma_i \right) \cdot \exp \left\{ -\sum_i (1/2\sigma_i^2) \cdot |Y_i(\text{obs}) - 1/c \cdot Y_i(\text{calc})|^2 \right\} \propto \exp \left\{ -\chi^2 \right\}$$

This probability is maximized if the exponent factor  $\chi^2$  is minimized using the weighting scheme  $W_i \propto 1/\sigma_i^2 = 1/Y_i(\text{calc}) \approx 1/Y_i(\text{obs})$ . It should be noted that this statistical weight  $W_i$  is calculated from the raw data  $Y_i$  *including* the background contribution.

Since the background is a smooth function obtained from the average of many points, the statistical error introduced by background subtraction is usually neglected, as in single crystal measurements. Of course, *systematic* errors may occur; for example, an

underestimation of the contribution of thermal diffuse scattering will lead to an underestimation of the overall temperature factor.

### 3.2 The Weighting Scheme

The weighting scheme used for profile refinement, devised purely from statistical arguments, is to be contrasted with the different weighting schemes devised for conventional single crystal structure analysis. In the latter case, an attempt is usually made to give lower weights to those observations most affected by systematic errors such as extinction. With neutron powder measurements, such systematic errors are usually much less important.

However, if special care is taken to eliminate systematic errors, a purely statistical scheme can also be used for single crystal measurements. Sakata and Cooper [31, 32] propose that the weight for an integrated Bragg reflexion should again be inversely proportional to its integrated intensity. With this assumption they show that the calculated standard errors are different for the same data treated by profile refinement and by refinement of the integrated intensities. They conclude that the errors calculated by profile refinement must therefore be wrong. The details of this argument are correct, but the basic assumptions and conclusions are not.

In fact, each count is an independent estimate of the integrated Bragg intensity. Simply adding together these counts does not give the best possible estimate of integrated intensity, especially in the case of a weak peak on a strong background. It takes no account of the fact that a number of independent (but not equally good) estimates (a step scan) was made of a function that we know *a priori* to be a peak with rather well defined characteristics. Incidentally, it is not possible to argue that the observations are *not independent* because they all come from the same peak, nor to argue that the Bragg peaks are *not independent* because they come from the same structure. Measurements of the *same* object are said to be statistically independent.

Sakata and Cooper have then correctly demonstrated that, given their approximations, the calculated errors are not the same for integrated intensity refinement as for profile refinement. They correctly attribute this to the different weighting scheme used, especially for weak reflexions. However, the correct conclusion should be that profile refinement should be used for single crystal data, as shown long ago by [33].

### 3.3 R-factors, Statistical and Systematic Errors

Rietveld defined several R-factors, including an  $R_I$ -factor for integrated intensities, which was meant to be compared with the R factors quoted in conventional crystallography.

$$R_I \propto R_{\text{Nuclear}} = 100 \times \sum_i |F_i^2(\text{obs}) - F_i^2(\text{calc})| / \sum_i F_i^2(\text{obs})$$

Unfortunately, conventional crystallographers usually prefer to quote  $R_F$  since it is smaller than  $R_I$ .

$$R_F = 100 \times \sum_i |F_i(\text{obs}) - F_i(\text{calc})| / \sum_i F_i(\text{obs}) \approx 1/2 \cdot R_I$$

The conventional  $R_F$  should therefore be doubled before it is compared with the Rietveld  $R_I$ , though the latter is underestimated for the contributions of strongly overlapping peaks, when the relative contributions of different peaks is assumed to be simply the ratios of their *calculated* intensities.

The Rietveld profile R-factor is larger than either  $R_I$  or  $R_F$ , but is perhaps the most informative for profile refinement, being defined as:

$$R_{\text{Profile}} = 100 \times \sum_i |y_i(\text{obs}) - y_i(\text{calc})| / \sum_i y_i(\text{obs})$$

where  $y_i$  is the sum of the contributions of all Bragg peaks to the point  $i$ , *excluding* the background contribution.

Computer programs such as that of Wiles & Young [34] later replaced  $y_i$  in the definition of  $R_{\text{Profile}}$  by  $Y_i$ , the count *including* the background contribution. Either definition can be used of course, but the Rietveld  $R_{\text{Profile}}$  is independent of the background, while an R-factor defined in terms of  $Y_i$  decreases when the background increases ! For samples with strong backgrounds, such as from samples containing hydrogen, low R-factors can be obtained by fitting the background even when the structure itself might be quite wrong. This difference in the definition of  $R_{\text{Profile}}$  accounts for the lower R-factors obtained with some refinement programs, compared with those based on the original Rietveld refinement.

The R-factor  $\chi^2$  which is the quantity minimised in Rietveld refinement is well known in statistics, and should be quoted in addition to  $R_{\text{Profile}}$  and  $R_I$ . Indeed the “chi-squared test” can be used to test the significance of the initial hypothesis that the  $Y_i(\text{obs})$  are samples of the  $Y_i(\text{calc})$ , i.e. that the observations are consistent with the model.

### 3.4 Peak Shape and Background

In the original Rietveld refinement, the background was assumed to be a smoothly varying function, and was interpolated between measurements at points for which there were no Bragg contributions. Some programs attempt to fit the background. For example, the Wiles-Young program [34] expands the background in a series of arbitrary transcendental functions. This has the advantage that the refinement can be made completely automatic, but if the background parameters are not related to physical variables, systematic errors are just as likely. In some cases, where the background is strongly structured, such methods will not even succeed in fitting the background modulations, and will therefore introduce systematic errors, especially in the Debye-Waller factors.

Rietveld’s peak shape was a simple Gaussian, modified for the peak asymmetry that occurs at low (and high) angles due to relatively large vertical aperture intersecting the diffraction cone. For neutron diffraction this is often a good approximation, provided the resolution is not so high that particle size/strain broadening contributes significantly. The neutron line shape is then determined mainly by the convolution of triangular collimator functions, and the convolution of two triangles is nearly a

gaussian; when other components are folded in, the approximation becomes even better.

With high resolution diffractometers, the line broadening due to the finite particle size of the sample and the lattice strain, must also be folded in. Particles of size  $D$  produce Bragg spots in reciprocal space of size  $\Delta k \approx D^{-1}$  where according to Bragg's law,  $k = d^{-1} = 2\lambda^{-1} \sin\theta$  is the scattering vector. Then differentiating the scattering vector with respect to  $\theta$  we find that the angular broadening due to finite particle size is

$$\Delta 2\theta_{\text{Size}} = K\lambda/D\cos\theta$$

The Scherrer constant  $K$  takes into account unknown factors such as particle shape.

Differentiating Bragg's law  $\lambda = 2d\sin\theta$  again with respect to  $d$ -spacing, we obtain the broadening due to the variation  $\Delta d/d$  due to lattice strain

$$\Delta 2\theta_{\text{Strain}} = 2(\Delta d/d) \tan\theta$$

If both these components are Gaussian, then when they are folded with the Gaussian instrument resolution the total broadening is the RMS value of the individual contributions i.e.

$$\begin{aligned} \Delta 2\theta_G^2 &= \Delta 2\theta_R^2 + \Delta 2\theta_{\text{Size}}^2 + \Delta 2\theta_{\text{Strain}}^2 \\ &= \Gamma_G^2 = U \tan^2\theta + V \tan\theta + W + Z/\cos^2\theta \end{aligned}$$

The Gaussian approximation is no longer sufficient for very high resolution neutron, X-ray and especially synchrotron powder diffraction because the strain and especially the particle size and shape distributions are no longer strictly Gaussian. Suortti et al. [35] and De Keijser et al. [36] folded a Lorentzian with the Gaussian component to give the Voigt function. The Lorentz FWHM is simply the sum of the strain and size components

$$\Delta 2\theta_L = \Delta 2\theta_{\text{Size}} + \Delta 2\theta_{\text{Strain}} = \Gamma_L = X/\cos\theta + Y \tan\theta$$

With synchrotron radiation, the instrument broadening may be small compared to the particle strain and size effects, and Thompson, Cox and Hastings [37] have found that to a good approximation  $\Gamma_G \approx V \tan\theta$  and  $\Gamma_L \approx X/\cos\theta$ . In order to simplify least squares refinement further, Wertheim et al [38] have shown that the Voigt function can be closely approximated a pseudo-Voigt function, which is a linear combination of the Lorentzian  $L$  and Gaussian  $G$  components, and has been much used in Rietveld refinement (eg Young and Wiles [39]).

$$PV = \eta L + (1-\eta).G$$

However, Ahtee et al [40] and David & Matthewman [41] have shown how the Voigt function itself may be used in least squares refinements. The advantages are that the different angular dependences of the Gaussian and Lorentzian components may be

included, and the parameters obtained have physical significance in terms of particle size and strain.

### 3.5 Absorption Corrections

Except for a few isotopes (for example, the most common isotopes of H, B, Cd, Gd, Eu and other transuranics), the effect of absorption for neutrons is very much smaller than it is for X-rays. Cylindrical samples of less than 1 cm radius are usual. This means that a large sample can be used, greatly simplifying the geometry, and providing a true bulk average of the crystal structure. However, even this small absorption can cause systematic errors in the temperature factors, which will then be underestimated. The error in the Debye-Waller factor  $B_{ij}$  can be calculated directly if  $\mu r < 1$ , where  $\mu$  is the absorption coefficient and  $r$  the sample radius [42].

The quantity  $\Delta B \cos \gamma^*$  must be added to all the  $B_{ij}$  where  $\gamma^*$  is the angle between the reciprocal lattice axes  $i$  and  $j$  and

$$\Delta B = \lambda^2 |b_1 \mu r + b_2 (\mu r)^2| / 2$$

For a cylindrical sample  $b_1 = -0.0368$  and  $b_2 = -0.3750$ . There are printing errors in the formulae given in the original paper which have been corrected here.

### 3.6 Rietveld Computer Programs

Most of the Rietveld refinement routines are directly descended from the original Rietveld code [29], which was brought to Harwell and modified in 1972 [30]. This program was further modified at Oxford and taken to the USA by von Dreele, where it was rewritten as the GSAS package [43], one of the most widely used systems for both X-ray and neutron powder refinement. Further copies were sent from Harwell to Brookhaven, where it was modified by Khattak and Cox [44], and to Georgia Tech., where it was modified by Wiles and Young [34]. In Oxford, modifications were made by Murray, Fitch and Cockcroft, and served as the basis of a new program by the latter author at ILL. The Wiles and Young program was later rewritten by Sakthivel, and is popular in its current version called DBW3.2S [45]. The earlier DBW1.9 version was modified in turn by Hill and Howard to give LHPM8 [46], and PC versions were produced by J. Schneider (PC/WYRIET) and J. Rodriguez-Carvajal [47]. The latter program, called FullProf, is now perhaps the most popular in Europe.

A number of independent Rietveld programs also appeared, the first of which was as early as 1970 by J.C. Taylor in Australia. Other more recent programs include those of Malmros and Thomas [48], EDINP a constrained molecule Rietveld refinement by Pawley [49], XRS-82 by Baerlocher [50], a program based on the X-ray system of Stewart, RIETAN by F. Izumi in Japan [51], ARIT-1/4 by Le Bail, MRIA-PC by Antson etc. The review of the Rietveld refinement intercomparison by Hill [52] gives some indication of the frequency of usage of these different programs.

## 4. Other methods of profile refinement and direct methods

### 4.1 Parrish-Will refinement

An alternative use of profile refinement for separating overlapping peaks in X-ray powder diffraction data was developed by Parrish, Huang and Will [53, 54]. The positions of all peaks, as well as their intensities, are refined as independent parameters, instead of constraining the positions to depend on the refined lattice constants and the intensities on the refined structure as in Rietveld refinement. The computer program "POWLS" is based on these methods.

The advantage of Parrish-Will refinement is that the structure factors can be extracted without the need for a structure model, and that the errors are therefore independent of such a model. The estimated errors for any refinement are only meaningful if the model contains no systematic errors; the Parrish-Will refinement should therefore reduce the bias due to the structure model assumed as the basis of Rietveld refinement.

The disadvantage of Parrish-Will refinement is that the number of parameters is greatly increased, and the correlation between some of these parameters means that they are poorly determined. For example, in the case of strongly overlapping peaks, the peak positions will be strongly correlated with their widths and intensities, and the refinement may be underdetermined; by requiring the peak positions to correspond to **some** set of lattice constants, and the peak heights to **some** structure, Rietveld refinement introduces physical constraints which reduce the number of parameters and the correlation between them.

#### **4.2 Pawley Refinement and other Constraints**

With the line profile analysis of Parrish et al. we assume nothing at all about the structure; this technique is particularly useful for a preliminary analysis of unknown structures or even the analysis of a mixture of unknown materials. The positions and strengths of the strong lines can be obtained automatically and compared with a computer file to identify the different phases. However, if model structures are already known, it is better to use the Rietveld technique to reduce the number of parameters to those few that are physically meaningful, thereby reducing the correlation between parameters.

Intermediate types of profile refinement can also be envisaged. Pawley [55] has written the program ALLHKL to refine the individual peak intensities, so that the structure need not be known a priori. The peak positions however, are determined by the lattice constants, greatly reducing the number of parameters and the correlations between them. The Pawley program is very useful for checking the unit cell obtained by indexing programs.

The Pawley program can be regarded as a 'constrained refinement'; the positions of the individual peaks, which would be free parameters for line profile analysis, are constrained to correspond to the positions predicted for a unit cell, and the only free parameters are the unit cell dimensions and angles. Rietveld refinement is another type of constrained refinement where the peak intensities are constrained to correspond to those predicted for the model structure, in which the atom positions are the only free parameters.

Even greater constraints can be imposed to reduce the number of parameters, and therefore refine ever larger structures from the relatively small amount of information contained in powder data. Pawley [49] has written a program to constrain whole groups of atoms or molecules, refining them as rigid units with the only free parameters being the position and orientation of the group.

Other non-Rietveld profile refinement programs include the program by Toraya [56], where, as in ALLHKL, the structure factors are first extracted by profile refinement, so that the structure itself may be obtained by direct methods, and refined by conventional crystallographic programs.

### **4.3 Fourier Techniques with Powder Diffraction**

The Rietveld program refines the structure to fit the diffraction pattern, without first extracting the structure factors needed for Fourier synthesis. However, if a large part of the structure is already known, for example from X-ray work, it is possible to use this part to find the remainder from a difference Fourier synthesis. These techniques have been used for example to find hydrocarbon molecules absorbed into known zeolite structures.

The scale factor, lattice constants etc are refined for the incomplete structure, and even though the fit will not be very good, the experimental structure factors are extracted approximately by dividing up the intensities of overlapping peaks according to the ratios of the calculated structure factors. The phases are also calculated from the model of the incomplete structure. A difference Fourier is then constructed between the incomplete model and the extracted structure factors, and searched in the usual way for features that might be identified with the missing parts of the structure.

Some of the unknown atoms can then be placed, and the whole procedure repeated to find any remaining unknown atom positions. Finally, the atom positions obtained with this approximate procedure are refined together with all the others with the usual Rietveld procedure. This difference Fourier technique works well when no more than about one quarter of the atom positions are unknown, and of course when the structure is centro-symmetric, so that the phases are simply  $0^\circ$  or  $180^\circ$ .

### **4.4 Direct Methods of Structure Solution with Powders**

For centro-symmetric structures, good results have been obtained in solving unknown structures by direct methods from high resolution neutron powder data (e.g. Christensen et al. [57]). However, X-rays have a clear advantage over neutrons for this because with X-rays the few heavy atoms can be found and then the remainder of the structure filled in by difference Fourier techniques. Werner et al. [58] have been most prolific at solving structures from X-ray powder data in this way. With neutrons, all of the atoms scatter with similar power, so the problem to be solved is always more complex. Very high resolution neutron powder diffractometers and new mathematical techniques based on maximum entropy methods may improve the success rate for neutrons (David et al. [59]), but even then it is difficult to see neutrons competing with X-rays for the solution of completely unknown structures.

There are of course exceptional cases where neutrons are needed. Materials that are liquids or gases under normal conditions may be easier to handle with neutrons, especially when they contain light atoms. For example, even the structures of materials as simple as solid methane have not been fully determined because of practical problems with X-ray measurements.

## 5. Applications to Chemical Crystallography

Rietveld and his co-workers used his method mainly for the determination and refinement of magnetic structures, and this remains an important application. But the "Rietveld Method" is now applied to many different branches of solid state chemistry and physics, as listed in table

<b>Suited to Powders</b>	<b>and Suited to Neutrons</b>	<b>Other applications</b>
<b>Structural transitions</b>	<b>Magnetic structures</b>	<b>Minerals</b>
<b>Solid liquids &amp; gases</b>	<b>Heavy metal compounds</b>	<b>Polymers &amp; biological</b>
<b>Zeolites</b>	<b>Hydrides &amp; H<sub>2</sub> storage</b>	<b>Other structures</b>
<b>Intercalates</b>	<b>Hydrogen bonding</b>	<b>High pressure</b>
<b>Catalysts</b>	<b>Other bonding</b>	<b>Thermal expansion</b>
<b>Solid electrolytes</b>	<b>Mixed valence</b>	<b>Texture &amp; stress</b>
<b>Other disorder/defects</b>		<b>Techniques</b>
<b>Superconductors</b>		<b>Synchrotron papers</b>
<b>Ceramics</b>		
<b>Other X-ray applications</b>		

Table II. Applications of powder diffraction [60].

The first column lists those areas for which powders have natural advantages over single crystals. For example, materials which undergo phase transitions often break up on cooling, or at least form multi-domain crystals less suitable for conventional crystallographic study - the sample is more naturally available in powder form. In particular, solid liquids and gases are easier to prepare and handle as powders. Other materials, such as zeolites, may be only available as powders and some materials may break up on intercalation. Catalysts are usually powders, and the purification process of crystal growth may be undesirable for the study of solid electrolytes (ionic conductors and electrode materials). Other defected or disordered structures and nonstoichiometric compounds may also be changed by single crystal growth.

Oxide superconductors already formed an important category in 1984 and included materials such as partially oxidized Chevrel phases, where the transition temperature is sensitive to the stoichiometry. Finally 'ceramics' includes those other oxides,

nitrides, etc., which are usually produced in powdered ceramic form - for example, as dielectrics.

The second column in table I lists powder-diffraction subjects that are particularly suited to neutron diffraction. Magnetic structures are, of course, the typical example, since unlike X-rays, neutrons see the magnetic moments on the atoms. Because the neutron scattering factor is of similar magnitude for all nuclei, heavy metal compounds such as transuranics, on the one hand, and hydrides and hydrogen bonds, on the other, usually require neutron diffraction. Metal hydrides were studied for their potential applications for hydrogen gas storage.

The study of other types of bonding, and of mixed valence compounds, may also be better done with neutron powder diffraction. This is simply because systematic errors in X-ray powder diffraction are more important, reducing the precision with which bond lengths can be determined: for example, quite precise bond lengths are required to distinguish between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  using the Zachariasen/Brown-Shannon rules. This is a technique that has since proved especially valuable for the study of the new oxide superconductors, as we shall see.

The third column of Table I lists other subjects for which powders have been used with advantage, ranging from mineral structures to polymers and biological materials. High-pressure structures can sometimes best be done with powders, and of course systematic measurements, as a function of temperature, may be less time-consuming with powders.

Finally, we have a category for texture, stress and strain measurements. This is a well-established subject for X-rays, but has acquired new applications with neutron powder diffraction; the greater penetrating power of the neutron permits non-destructive testing of the interior of objects of  $\text{cm}^2$  dimensions - welds, pressure-vessels, rolled and worked metal, prestressed composite superconducting wires, etc.

## 5.2 Di-electric and Ferro-electric Ceramics and Structural Transitions

This is an early example of the use of Rietveld refinement which is of particular relevance to the study of oxide superconductors, because many of the same types of material (oxide perovskites) were studied, and many similar phenomena (small displacements of atoms) were of interest. In the classical ferro-electric  $\text{BaBiO}_3$  the electrical dipole is created by a structural transition involving small displacements of positively charged cations in opposite directions to the displacements of the negative oxygen ions. The dipole moment requires the measurement of the magnitude of these displacements, and this is the objective of Rietveld refinement.

The idea is to measure the powder diffraction pattern at a number of temperatures, and to obtain the atom co-ordinates at each temperature.

**Fig. 11** The diffraction patterns obtained for  $\text{KNbO}_3$  at temperatures corresponding to the (a)tetragonal, (b)orthorhombic and (c)rhomboidal phases. Even though the atomic displacements are small, large changes are produced in the neutron diffraction patterns. These patterns, collected at Harwell [61], represent the first example of the application of the Rietveld method to such problems; modern diffractometers produce much better resolution, and the changes are even more striking.

The resulting atomic co-ordinates obtained with Rietveld refinement are in this case much more reliable than those obtained with classical single crystal methods, because in fact it is very difficult to obtain good single crystals. When such crystals are grown at high temperature, they are in the cubic phase. When they are cooled to the orthorhombic phase, there are several possibilities for the **a**, **b**, and **c** axes, and the crystal breaks up into microscopic domains corresponding to each possibility. 'Single' crystals can be obtained by applying a very strong electric field to the crystal as it is cooled from the cubic phase, but even then the resulting strains in the material effect different reflexions in different ways.

The powder experiment is also much easier and faster, and because of this the structure can be determined at many different temperatures, instead of the one or two temperatures usual with classical crystallography. The proof of the success of the method in this case was the fact that the polarisation obtained by measuring the microscopic displacements of the ions agreed well with macroscopic measurements.

### 5.3 Magnetic Structures and Magneto-Resistive Materials

Neutron diffraction is of course unique for the determination of magnetic structures, and again real materials are first produced as powders. In fact the first uses of Rietveld refinement were to magnetic structures in the 1970's, and since then magnetic structure determination has always been an important application of the method. In the early 1980's a Nd-Fe-B alloy was found to have remarkably good magnetic properties up to 585K, with an energy product of up to 360 J/m<sup>3</sup>. Even the chemical formula of this new phase, Nd<sub>2</sub>Fe<sub>14</sub>B, was not known until the crystal and magnetic structures were established [8, 62]. The Nd and B atoms were found to occupy layers, separated by Fe-layers. The strong anisotropic magnetic properties of these materials up to room temperature and above, due to the rare earth ions, and the relatively large proportions of common iron compared to expensive rare-earth-cobalt magnets such as SmCo<sub>5</sub>, make these hard magnet materials particularly attractive.

Most recently Giant Magneto-Resistive manganates (GMR) have excited much interest because large changes in electrical conductivity as a function of temperature are associated with magnetic phase transitions. This leads to interesting applications, for example in high capacity hard disks for computers. Several groups have used neutron and synchrotron powder diffraction to understand the subtle charge and magnetic ordering associated with the magneto-elastic transition.

For example, Fernández-Díaz et al. (1999, Phys.Rev.B59, 1277) have shown how at low temperatures the Mn<sup>+4</sup> and Mn<sup>+3</sup> of La<sub>1/3</sub>Ca<sub>2/3</sub>MnO<sub>3</sub> order on different atomic sites (fig. 12a).

**Fig. 12a.** Ordering of the Mn<sup>+4</sup> and Mn<sup>+3</sup> in La<sub>1/3</sub>Ca<sub>2/3</sub>MnO<sub>3</sub> at low temperature (Fernández-Díaz et al. 1999) determined by neutron powder diffraction.

It is possible to obtain this ordering by measuring the Mn-O distances, because Mn<sup>+4</sup> and Mn<sup>+3</sup> have slightly different sizes. As well, the magnetic order of the material

was determined from the super-lattice peaks that appear in the low temperature neutron powder pattern (fig. 12b).

**Fig. 12b.** Observed and calculated neutron powder patterns of  $\text{La}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$  at low temperature (Fernández-Díaz et al. 1999) The first set of ticks indicate nuclear reflections, and the second set magnetic reflections. The inset shows the temperature dependence of the ordered magnetic moment.

**Fig. 12c.** The proposed anti-ferromagnetic structure of  $\text{La}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$  at low temperature (Fernández-Díaz et al. 1999) showing just the moments on the Mn ions in the  $z=0$  plane.

This is a very nice example of the power of neutron powder diffraction to obtain both subtle changes in the atomic structure, which results from valence charge ordering at 270K, and as well the details of the ordering of the magnetic moments on the different Mn-ions at the anti-ferromagnetic transition at 170K.

## 5.4 Interfaces and Catalysts, in particular Zeolites

The active surface of a catalyst makes up a large part of its volume, so neutron scattering from the bulk material can provide information about the catalytic interface. For example, Zeolites are important catalysts in the petrochemical industry, and it would be interesting to know how absorbed molecules are attached and interact within the zeolite channels. Again, classical crystallography is difficult because all synthetic zeolites are polycrystalline materials.

The basic zeolite structure can be obtained with X-rays, but neutrons are much better for seeing the light atoms of the hydrocarbon. Hydrogen itself has a large negative scattering length, and even greater contrast can be obtained by comparison with deuterated materials, since the deuterium hydrogen isotope has a large positive scattering length. For example, Fitch et al. [63]. have shown that relatively small numbers of molecules such as benzene adsorbed into sodium Y-zeolite can be located.

**Fig. 13.**(a) The neutron diffraction pattern of the de-hydrated zeolite  $\text{Na}_{56}\text{Si}_{136}\text{Al}_{56}\text{O}_{384}$ .  
(b) The quite different pattern obtained with adsorbed benzene [63].

The diffraction pattern of the bare de-hydrated zeolite  $\text{Na}_{56}\text{Si}_{136}\text{Al}_{56}\text{O}_{384}$  was first obtained (figure 13a), and the the earlier single crystal structure confirmed by Rietveld refinement. Diffraction patterns were then obtained at 4K (to reduce disorder) with two different coverages of benzene: 1.1 and 2.6 molecules per supercell. The patterns obtained with benzene are clearly different (figure 13b) to that of the bare zeolite.

These differences then served to obtain the positions of the benzene molecules using 'Fourier difference' techniques, which essentially produce a contour map of the differences between the bare and benzene loaded samples (figure 13c). The benzene positions were then refined using the Rietveld technique. In this way one can identify which atoms of the hydrocarbon interact with which atoms in the zeolite channels.

**Fig. 13.** (c) A Fourier map of the differences between the bare and benzene loaded samples.  
(d) Small angle neutron scattering showed that the benzene molecules clump together in the zeolite channels [63].

Figure 13c shows a simple example of such a difference Fourier map, showing benzene in sodium Y-zeolite [63]. In figure 13d this information has been used to show schematically how the benzene molecules pack into the zeolite channels.

Since these channels and molecules are of a size that can be investigated by neutron small angle scattering, a further simple experiment can be performed. Neutron small angle scattering patterns are collected, again for the anhydrous and the loaded zeolite. In this case, the difference gives a direct measure of the size of hydrocarbon aggregates within the zeolite channels.

These measurements showed that at low coverages, benzene was distributed evenly throughout the supercages, with the molecule bonded by its  $\pi$ -electron density to one of the sodium atoms. At higher coverages, clusters formed by aggregation of the molecules in adjacent supercages and occupation of the windows connecting them (figure 13b).

The discovery of clustering of molecules, and their interaction with certain sites in the zeolite cages, should help our understanding of how zeolites catalyse chemical reactions of adsorbed hydrocarbons.

## 6. High Temperature Superconductors

### 6.1 Oxide Superconductors

Neutron powder diffraction has proved important for understanding the structures of the new oxide superconductors because of the lack of single crystals, and because of the need to locate oxygen atoms in the presence of heavy metal atoms such as barium and bismuth.

In fact, one of the first uses in the US of the Rietveld method for the analysis of neutron powder diffraction patterns was for an oxide superconductor. Cox & Sleight [64] in 1976 showed that in  $\text{BaBiO}_3$  the bismuth atoms were distributed over two sites of different size: the bismuth valence was dissociated into  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  (Fig.14). This required the precise location of oxygen atoms, and the determination of Bi-O bond lengths. In  $\text{BaPbO}_3$ , there is only one site for  $\text{Pb}^{4+}$ , and when  $\text{BaBiO}_3$  is doped with  $\text{Pb}^{4+}$  the two (Bi,Pb)-sites become equivalent, with the  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  disordered over this single site. The resulting material is a superconductor with  $T_c$  up to 13K.

More recently, Cava et al.[65] have shown that  $T_c$  can be increased to 30K if instead Ba is replaced by K. Again the symmetry of the  $\text{BaBiO}_3$  structure is increased, and  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  are distributed over a single site.

**Fig. 14.** Ordering of  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  on sites of different size in  $\text{BaBiO}_3$ . With Pb/Bi (or K/Ba) doping  $\text{Bi}^{3+}/\text{Bi}^{5+}$  is distributed over a single site, and the material becomes superconducting. (The arrows and +,- signs indicate the directions of tilting of the  $\text{BiO}_6$  octahedra.)

## 6.2 The First High Temperature Superconductor.

However, the most exciting developments in oxide superconductors had to wait ten years for the ideas of Bednorz and Müller [3]. They proposed that valence fluctuations could provide the electron-phonon coupling necessary for superconductivity. For example, just as  $\text{Bi}^{3+}$  requires a larger site than  $\text{Bi}^{5+}$ ,  $\text{Cu}^{2+}$  requires a larger site than  $\text{Cu}^{3+}$  (Fig.15). The apical Cu-O distances will be large for  $\text{Cu}^{2+}$  due to the ‘Jahn-Teller’ distortion, but these oxygens should move toward copper if it becomes  $\text{Cu}^{3+}$ .

**Fig. 15.** Expected effect of  $\text{Cu}^{2+}/\text{Cu}^{3+}$  fluctuations on the disorder of apical oxygen O1 in the superconductor  $(\text{La,Sr})_2\text{CuO}_4$ .

Neutron powder diffraction by Jorgensen et al. [66] showed no evidence for such Cu-O ‘breathing’ displacements, but there was a structural transition involving displacement of the apical oxygen associated with tilting of the  $\text{CuO}_6$  octahedra (Fig.16). Such transverse displacements would not be strongly coupled to the electronic structure of copper, since the Cu-O distance changes only to second order.

**Fig. 16.** Observed disorder of apical oxygen in  $(\text{La,Sr})_2\text{CuO}_4$  due to tilting of the  $\text{CuO}_6$  octahedra resulting in low temperature structural transitions.

## 6.3 The 90K 123-Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$

There are no obvious low temperature structural transitions in the 90K superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , but Capponi et al. [2] showed that the oxygens along the CuO-chain (Fig.1) appear to be disordered perpendicular to the chain axis even at low temperature. François et al. [67] proposed that these CuO-chains may zig-zag for short distances, with tilting of the  $\text{CuO}_4$  squares similar to tilting of  $\text{CuO}_6$  octahedra in normal perovskites. Again, such transverse O4 displacements would not couple strongly to the electronic state of copper.

Jorgensen et al. [68] have shown that there is a structural transition at *high* temperature to a tetragonal non-superconducting phase as oxygen is removed from the CuO-chains (Fig.17). Rodriguez et al. [69] have shown how the kinetics of this process can be followed by neutron powder diffraction.

Cava et al. [70] showed that as oxygen is removed,  $T_c$  decreases, but with a plateau corresponding to  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  (Fig.18). Using the neutron powder measurements of Santoro et al. [71], they demonstrated that a sharp *drop* in  $T_c$  was associated with a sharp *increase* of the Cu2-O1 apical oxygen distance.

**Fig. 17.** Structures of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  showing the displacement of the bridging oxygen O1 associated with a decrease in  $T_c$  on removal of the chain oxygen O4.

**Fig. 18.** Variation of  $T_c$  with oxygen loss in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  showing two plateau regions followed by a sharp drop to the non-superconducting phase.

Cava et al. [72] used neutron powder diffraction to measure all Cu-O distances in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  as a function of oxygen loss  $x$  from the Cu-O chains (Fig.6). Their samples were very well ordered, since they were prepared by low temperature ‘gettering’ to remove precise amounts of oxygen.

The Cu-O distances *within* the planes and chains varied little with oxygen loss, in striking contrast to the the apical oxygen O1 bridging planes and chains. As oxygen was removed from the CuO-chains, reducing  $T_c$ , this bridging oxygen moved away from Cu2 in the planes toward Cu1 in the chains.

**Fig. 19.** Cu2-O1 distances in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , mirroring the changes in  $T_c$ , with an initial plateau and a sharp increase with the loss of superconductivity. The other Cu-O distances hardly change.

The Cu2-O1 distance (Fig.19) seems to remain constant, as does  $T_c$  (Fig.18), for small losses of oxygen ( $x < 0.2$ ). It then increases, but starts to level out again between  $0.4 < x < 0.6$ , corresponding to the plateau in  $T_c$ , before increasing abruptly with the loss of superconductivity. Since this distance is only the average of Cu2-O1 distances for more complex intermediate superstructures, an exact correspondence cannot be expected.

These increases can however be associated with loss of  $\text{Cu}^{3+}$  (or more precisely, electron holes) from the CuO-planes, implying a direct relation between the number of  $\text{Cu}^{3+}$  in these planes and  $T_c$ . The ideas of Bednorz and Müller (Fig.15) appear then to be supported by the results of these neutron powder diffraction measurements.

## 7. Applications to in-situ chemical reactions

### 7.1 Oxidation-Reduction

Because neutrons are highly penetrating, it is possible to study physical and chemical reactions in large volumes in real time. For example we have already seen that when  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is heated, it loses oxygen and its superconductivity as it transforms to  $\text{YBa}_2\text{Cu}_3\text{O}_6$ . These structural changes (Fig.26) can be monitored directly because of the changes on the neutron diffraction pattern and the strong neutron scattering power of oxygen [69]: with X-rays, scattering is instead dominated by the heavy metals. It is possible to study the effect of oxidising and reducing atmospheres, of quenching from different temperatures, and of aging the resulting material at room temperature.

**Fig. 26.** The occupancy of the alternative oxygen chain sites O(4) and O(5) as a single oxygen is lost from  $\text{YBa}_2\text{Cu}_3\text{O}_7$  can be plotted in real time as the temperature is varied on the ILL D1B PSD [69].

### 7.2 Hydration-Dehydration

Another example is provided by the hydration of Portland cement (a mixture of calcium silicates and aluminates), resulting in solidification. Christensen et al. [82]

used neutron diffraction to investigate the reactions between water and the constituent oxides of cement. They showed that the hardening process for  $\text{Ca}_3\text{SiO}_5$  consists of three stages: initialisation, induction and reaction. During the first stage there is a rapid dissolution of  $\text{Ca}_3\text{SiO}_5$ . The induction period may be due to the formation of a protective layer surrounding the grains until it too is dissolved. Precipitation of  $\text{Ca}(\text{OH})_2$  the only crystalline product, marks the beginning of the final reaction stage, where all dissolved silicon goes into producing an amorphous gel, with a neutron diffraction pattern quite different from the crystalline phases.

Since both hydrogen and oxygen scatter neutrons strongly, the detection of water is relatively easy. Chemical reactions which proceed through hydrated (or hydroxylated) precursors are then ideal for study by neutron diffraction. For example figure 27 illustrates the thermal dehydration of  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$  [83]. At low temperature ( $160^\circ\text{C}$ ) the high background level is due to incoherent scattering from water: as the temperature is increased, the decrease in water content can be measured directly from the decrease in the background, which is accompanied by the transformation of the peaks due to crystalline  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$  into the different set of peaks due to the anhydrous product.

**Fig. 27** The thermal dehydration of  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$  [83].

### 7.3 Chemical Reactions, Crystallisation and Decomposition

Other examples of chemical reactions then can be followed with kinetic neutron diffraction include solid state reactions where the reactants are strongly mixed and pressed, and then heated while observing the changes on the neutron diffraction pattern.

Crystallisation processes can be easily observed with kinetic neutron diffraction. For example when a quasi-crystalline material such as the quenched Al-Mn alloy  $\text{Al}_{85}\text{SiMn}_{14}$  is heated to 630K it transforms into orthorhombic  $\text{Al}_6\text{Mn}$  with the silicon producing an  $\alpha\text{-AlMnSi}$  phase at 710K. Amorphous materials and quasi-crystals have recently excited interests because of their unique electronic and other properties. Kinetic neutron diffraction can help us understand the relations between amorphous and crystalline phases. For example, when  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  is cooled from the melt at 1235K to the solid at 1040K, neutron diffraction showed that the amorphous phase is not produced directly, but rather via intermediate Al-Fe phases which finally dissolve in the remaining Cu-rich liquid. Complex phase diagrams can be mapped out.

### 7.4 Adsorption of Gasses

The study of the adsorption of gasses onto surfaces is interesting as a model for catalysis: the example of hydrocarbons in zeolites has already been mentioned. Much of the pioneering work with neutrons was done by C. Riekel, and is reviewed in two of his papers [84, 85].

Graphite, and graphite compounds such as  $\text{CsC}_{24}$ , have been favoured as model solids, since they present large 2D surfaces and readily accept the intercalation of molecules between the carbon layers [86].

### 7.5 Electrolysis in batteries

The high penetrating power of neutrons, and their strong scattering by light atoms such as hydrogen and oxygen has permitted Ripert et al. [87] to investigate *in situ* the complex chemical reactions that occur at the electrodes of Leclanché batteries during thermal annealing and electrochemical reduction. They showed that the reduction of  $\text{MnO}_2$  (Ramsdellite) to  $\gamma\text{-MnOOH}$  (Groutite) consisted of the up-take of protons by the pyramidal oxygen in the double channels formed by the MnO-octahedrae.

When half these pyramidal channel sites are occupied, half the  $\text{Mn}^{4+}$  are reduced to  $\text{Mn}^{3+}$  and the surrounding octahedrae are strongly distorted by the Jahn-Teller effect. A network of hydrogen bonds distorts the channels, with a transition to a Groutite-type structure. The other half of the pyramidal oxygens are then hydroxylated at a different rate. This first stage electrochemical reduction should be completely reversible (as required for a battery), with no change in the topology of the lattice with the Ramsdellite-Groutite transformation.

However, further hydroxylation attacks the planar oxygen, leaving isolated layers of  $\text{Mn}^{4+}$ , which are immediately and irreversibly further reduced to  $\text{Mn}(\text{OH})_2$  pyrochroite.

Irreversible changes, which are obviously not desirable in a rechargeable battery, are observed at an earlier stage in  $\text{MnO}_2$  samples containing large amounts of rutile defects. In rutile, there are only single channels, and the planar oxygen is apparently attacked at an earlier stage, producing correspondingly large amounts of pyrochroite that can readily be seen in the neutron diffraction patterns.

Such experiments can help us understand the undesirable irreversible processes that occur, and may eventually help in the design of a rechargeable  $\text{MnO}_2$  battery. Similar measurements have been attempted with lead acid batteries, where neutrons are even more interesting for locating the light oxygens in the presence of the very heavy lead atoms.

## 8. Studies of the strength of materials

The mechanical properties of materials are in part determined by internal stresses and 'texture' i.e. the preferred orientation of the constituent crystallites. Neutrons are particularly suited to the study of such problems because they can penetrate large objects, while X-rays are scattered mainly by the surface.

For example, alumina can be strengthened by sintering  $\text{Al}_2\text{O}_3$  powder with SiC fibres at high temperature. When cooled to room temperature, strong internal stresses are induced in the resulting composite because of differences in thermal contraction of the two materials [88]. Clearly, the mechanical properties also depend on the relative orientation of the SiC fibres (texture). It is important to understand the physical

reasons that make this material one of the most successful ceramic-ceramic composites.

A second well known example of the use of internal stress to toughen materials is provided by partially stabilised zirconia. The zirconia in toughened zirconia ceramics can exist as cubic, tetragonal, orthorhombic and monoclinic phases. It can also combine with added 'stabilisers' such as magnesium to form further phases. The martensitic tetragonal-monoclinic transformation is accompanied by a volume increase of almost 5%, and induces strong stresses in the resulting composite material which depend on the relative volume fractions of the different phases. Neutrons can not only probe the internal stress in the bulk material, but also measure with precision the amounts of the different phases [89]. X-rays are also used to measure the relative phase abundance, but only on the surfaces, and phase transformation on surfaces, which can be altered by grinding for example, may not be typical at the bulk material.

Nb<sub>3</sub>Sn-type superconductors undergo structural phase transitions at low temperatures, reducing their current carrying capacity. By pre-stressing the composite wire bundles with steel, this phase transition can be avoided. Neutron diffraction by Pintschovius et al. [90] has been used to measure the resulting uni-axial stress, and how it relaxes at superconducting temperatures.

These different experiments, to measure internal stress, 'texture' and phase abundance can be performed on the same simple neutron diffraction equipment. Figure 5 shows a collimated beam of monochromatic neutrons incident on a large ceramic sample. Simply by measuring the diffraction pattern, the relative abundance of the different phases can be determined from the relative intensities of the peaks characteristic of these phases.

If the sample is heated *in situ*, changes in the relative abundance of the different phases can be monitored. If the orientation of the sample is changed, the intensities of some of the peaks also change when the crystallites are aligned in preferred directions. Such 'texture' can then be investigated by measuring the intensity of a few peaks for a variety of sample orientations.

Finally the changes in internal stress can be monitored by measuring small changes in peak positions, which reflect changes in the crystal lattice dimensions due to stress. The material then acts as its own strain gauge. This method has been applied with great commercial success to look at stresses in oil pipe-line welds, railway lines [10] etc.

## **8. Conclusions**

We have seen that the structure of materials on an atomic scale is fundamental to our understanding of many macroscopic properties, and that neutron powder diffraction offers two main advantages for real materials. Firstly it deals with real materials in ceramic or powdered form. Secondly it is possible to see the light atoms and magnetic atoms as well as the heavy atoms, and to study the material under different chemical and physical conditions.

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