D2B, A NEW HIGH RESOLUTION NEUTRON POWDER DIFFRACTOMETER AT ILL GRENOBLE

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ABSTRACT

   Applications of high resolution neutron powder diffraction to materials
science have grown rapidly in the past 10 years, with the developement of
Rietveld methods of profile refinement, and new high resolution diffractometers
and multidetectors. Materials studied range from catalysts to zeolites, and from
battery electrodes to prestressed superconducting wires. Although the
techniques have now been adapted for X-ray and synchrotron radiation, neutron
powder diffraction retains unique advantages. In this paper we describe the
design and first test measurements on the latest high resolution neutron powder
diffractometer D2B at ILL Grenoble. A review of the applications is published
in Chemica Scripta (1986).

INTRODUCTION

   High resolution can of course always be obtained at the expense of intensity.
In principle then, neutron sources are at a fundamental disadvantage compared to
synchrotron sources or even ordinary X-ray generators, where intensities are
orders of magnitude greater, permitting extremely high resolution. This is only
partly compensated by the greater penetrating power of the neutron, permitting
larger samples, the absence of a form factor for neutron scattering, and the
high scattering power of light atoms for neutrons. Despite these intensity and
resolution disadvantages, neutron high resolution powder diffraction (HRPD) is
superior for many purposes, mainly because the line shape is simple and well
defined, and the systematic errors are smaller. Errors in HRPD structural
parameters are typically an order of magnitude larger for X-rays than for
neutrons. For most purposes of chemical interpretation, this difference is
critical.

   Figure 1 shows the rapid growth of publications using profile refinement and
HRPD, following the key papers of Rietveld [1,2] in 1967, and the resulting
developement from 1974 of special high resolution neutron diffractometers [3-7].
The Rietveld method allows the crystal structure to be refined directly from the
powder diffraction pattern without the usual crystallographic procedure of
extracting the intensity of the individual peaks, which usually requires a
single crystal. Clearly single crystals are not available for many real materials.

Figure 1.
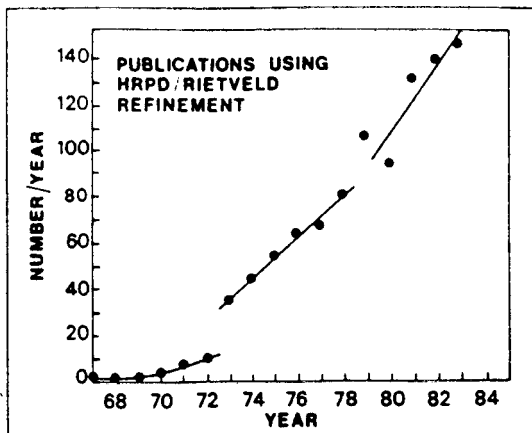
Number of publications using high resolution powder diffraction or Rietveld refinement showing rapid increases with the dissemination of the techniques and the construction of new diffractometers.

Table 1 summarises then the different applications of HRPD, showing the number of publications in the 10-year period 1974-84 with the number in the single year 1984 in parentheses. Several reviews of these applications are available, and further details are given by Hewat [8].

TABLE 1

Classification of Research Using High Resolution Powder Diffraction 10 Year Publication Total 1974/85 (1984 Total)

POWDERS	NEUTRONS	OTHER
87 (7) Structural T./Ns	150 (20) Magnetic structures	23 (7) Minerals
14 (5) Solid liquids. gases	59 (5) Heavy metal compounds	8 (1) Polymers & biological
40 (16) Zeolites	52 (8) Hydrides & H_2 storage	materials
6 (0) Intercalates	32 (1) Hydrogen bonding	47 (6) Other structures
11 (4) Catalysts	3 (1) Other bonding	19 (4) High pressure
81 (15) Solid electrolytes	7 (1) Mixed valence	18 (2) Thermal expansion
73 (10) Order-disorder/defects		20 (1) Texture. stress
7 (1) Superconductors		
33 (4) Ceramics		~ 150 Techniques
36 (2) Other X-ray work		21 (2) Synchrotron papers

10 Year Total (1984 total).

   As well as Rietveld refinement of crystal structures, high resolution powder diffraction has also found practical applications for non-destructive testing of materials. Since neutrons are much more penetrating than normal X-rays, the stress and texture in the interior, rather than the surface, of objects such as pressure vessels, metal plates, welds, composite prestressed wires etc can be examined without cutting the material. Again details are given in reference [8].

   Everyone can now have access to HRPD facilities at either reactor or accelerator laboratories such as ILL Grenoble and ISIS near Oxford. Assistance is available so that the techniques can be used like any other by non-specialists. Normally these facilities are provided free of charge for proposals of high scientific merit, but alternatively instrument time and expertise may be purchased without disclosure of either the application or the results obtained for eventual industrial application.

DESIGN PRINCIPLES FOR A CLASSICAL NEUTRON HRPD

- The reactor based machines resemble classical diffractometers, with a monochromator crystal to select a particular wavelength, and a multidetector to register the diffraction pattern as a function of angle (fig. 2). Similar results are obtained by scattering all wavelengths into a particular angle: this alternative energy dispersive or time-of-flight (TOF) technique is particularly suited to accelerator based neutron sources, and is described at this meeting by David et al. In both cases, high resolution is the objective, to increase the mount of information in the pattern, but resolution is obtained at the expense of intensity.

Paradoxically, high resolution implies more complex crystal structures needing higher not lower intensity. Although the total scattering power of the sample depends on the number of atoms, not on the crystal structure, the number of peaks depends on the reciprocal unit cell volume. If all the dimensions of the unit cell were doubled, say from 7A to 14A, the average peak intensity would decrease by a factor of x8 !

Resolution, Intensity and Focussing.

For both the monochromatic and energy-dispersive machines, the resolution is given by

$$\Delta d/d = \Delta\theta \cot\theta \tag{1}$$

where d is the spacing between planes of atoms, and 2θ is the scattering angle, which clearly must be large for high resolution (small $\Delta d/d$). This equation is obtained by differentiation of the Bragg condition for reflexion $\lambda = 2d \sin\theta$. The intensity depends on the waveband

$$\Delta\lambda/\lambda = \Delta\theta_M \cot\theta_M \tag{2}$$

where $\Delta\theta_M$ is the angular mosaic spread of the monochromating crystal reflecting at an angle of $2\theta_M$. The design parameters then result from a compromise between resolution and intensity.

Fortunately the resolution can be much smaller than the waveband $\Delta\lambda/\lambda$ even if $\theta \simeq \theta_M$!

Figure 2.
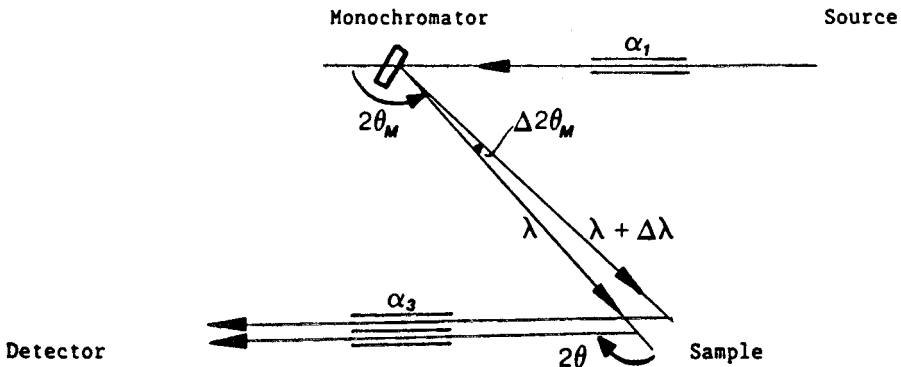
In this wavelength focussing geometry, the incident and detected beams are
-highly collimated by Soller slits α_1 and α_3; the peak width $\Delta 2\theta$ is then the
convolution of these triangular functions

$$\Delta 2\theta \simeq \sqrt{\alpha_1^2 + \alpha_3^2}$$

$\Delta\theta_M$, the mosaic spread of the monochromator crystal, does not affect the
focussed peak width.

Monochromator crystals (Ge in this case) are hot pressed to increase their
mosaic spread to some $\Delta\theta_M \simeq 20'$, to obtain sufficient intensity at large $2\theta_M$
(equation 2, while Soller collimators define the beam directions to $\alpha_1 = \alpha_3$
= 5'. These collimators consist of 40 to 50 blades 100mm to 300mm high x 350mm
long, each separated by 0.5mm to make a collimator 20-25mm wide. The individual
blades are 25 micron thick stretched mylar foil painted with neutron absorbing
gadolinium oxide paint. Such collimators [9] are manufactured by CIDIC Ltd.,
Cheltenham, England.

Although the peak neutron flux from a reactor may be an order of magnitude
smaller than from a pulsed source, these considerations mean that the time
averaged flux on the sample can be up to an order of magnitude larger for the
reactor. The moral is that larger gains can be had by improved diffractometer
design than by improved neutron sources.

Multidetectors

The diffractometer efficiency can also be increased by increasing the solid
angle of the detector (using multidetectors). However, this is possible to only
a limited extent on a machine needing collimators of 5' horizontal divergence.
The vertical detector divergence can however be several degrees to match the
vertical divergence from the monochromator: but even with as many as 64
detectors, the horizontal acceptance angle is still only 64x5'.

Instead of using Soller collimators, one can simply make the sample and
detector diameters very small compared to the distance beween them. This
solution, using a position sensitive detector, is in fact used for medium
resolution/high efficiency diffractometers such as D1B and D20 at ILL. Of
course the sample volume and scattered intensity then decreases with the square
of the sample diameter, which limits the efficiency gain.

High resolution can be obtained with low resolution detectors and large
samples (large $\Delta\theta$) provided 2θ is very large (equation 1). This is the basis
of the high resolution backscattering diffractometers used on accelerator driven
neutron sources. Although the incident flight path is long for high resolution,
so that the incident solid angle and average flux on the sample is perhaps an
order of magnitude smaller, the detector solid angle can be an order of
magnitude larger !

Table 2 from a more detailed comparison of existing and future diffractometers shows how the overall efficiency of the reactor and accelerator driven machines may then be very similar.

Comparison of Reactor and TOF Powder Diffractometers

	Existing		New		
	DIA/ILL	GPPD/Argonne	D2B/ILL	HRPD/SNS	
Wavelength λ	1.2 – 6	0.5 – 6	1 – 6	1 – 12	Å
Flux (sample) φ,	2 × 10⁶	~ 10⁵	~ 10⁷	~ 10⁶	n.cm⁻¹.sec⁻¹
Volume (sample) V,	3	5	5	2	cm³
Solid angle (detector) Ω_D	0.004	0.1	0.008	0.1	sterad
Resolution Δd/d	2	2.5	0.5	0.5	x 10⁻³
Speed φ,V,Ω_D	2.4 × 10⁴	5 × 10⁴	4 × 10⁵	2 × 10⁵	

Resolution limits and requirements

Of course the resolution of any powder diffractometer is ultimately limited by the size and perfection of the individual grains of the sample [3]. For a few simple inorganic materials which form more perfect crystals, very high resolution ($\Delta d/d \simeq 10^{-4}$) can in priciple be obtained, but for materials for which single crystals cannot be grown (the most interesting materials for powder diffraction !) the resolution is limited to $\Delta d/d \simeq 10^{-3}$ by particle sizes of 10 microns or less. Although the diffraction lines may appear very sharp for lower scattering angles with synchrotron radiation, the $\Delta d/d$ resolution, which increases with $\cot\theta$, has of course the same sample limitations as for neutrons. In any case, the best resolution is required at higher scattering angles (small d) where the number of peaks is greatest.

For a monochromatic neutron HRPD, we try then to match the resolution as a function of θ (or d-spacing) to the density of lines. Bragg's equation for reflexion (h,k,l) from a cubic lattice of edge a_o is

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

Since (h,k,l) are integers, n is also an integer: successive lines occur at most for $\Delta n = 1$. The spacing between lines is given by differentiation

$$2a_o \cos\theta \cdot \Delta\theta = \frac{1}{2\sqrt{n}} \cdot \Delta n = \frac{\lambda}{4a_o \sin\theta}$$

$$\Delta\theta = \left[\frac{\lambda}{2a_o}\right]^2 \cdot \frac{1}{\sin 2\theta}$$

Peaks are then far apart at small and large scattering angles, and most crowded for $2\theta \simeq 90°$, where resolution should be best.

The instrument line width A also has a minimum, corresponding to the focussing geometry $2\theta \simeq 2\theta_M$

$$A = U \tan^2\theta + V \tan\theta + W$$

with U and W positive, and $V \simeq -2U \tan\theta_M$. This minimum can be made to correspond with the minimum in the seperation of lines if a large monochromator take-off angle $2\theta_M \simeq 90°$ is chosen (fig. 3).

Figure 3.
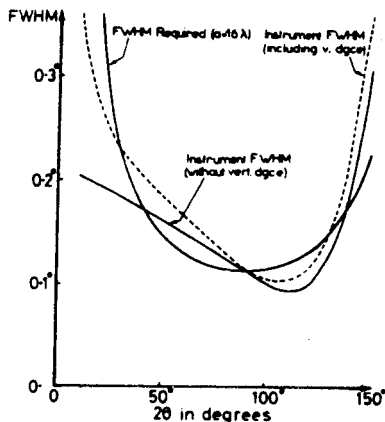
In practice, for lower symmetry structures, the density of peaks reaches a maximum at somewhat higher angles, and because the instrument line width increases more rapidly for $2\theta > 2\theta$, the take-off angle must be larger than 90°. On D1A at the ILL, $2\theta_M = 125°$ while on D2B, $2\theta_M = 135°$.

The backscattering TOF machine at the RAL laboratory uses a fixed scattering angle approaching 180°. High resolution is then maintained for all d-spacings, but for large d-spacings, very long wavelengths $\lambda = 2d$ must be used (eg 20Å !), and not many neutrons are produced with such long wavelengths.
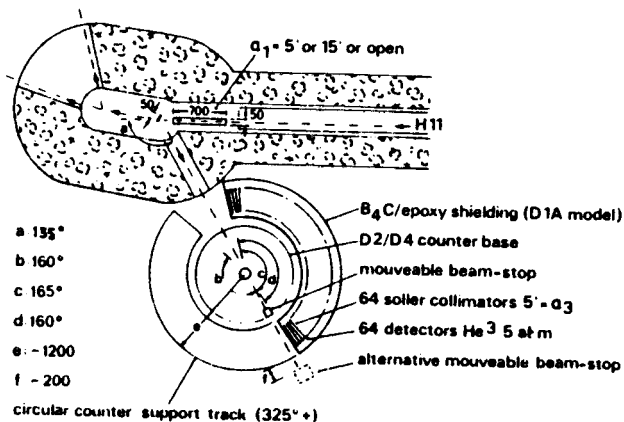
THE NEW D2B MACHINE AT ILL

Figure 4.

Figure 4 is a schematic diagram of the very high resolution neutron diffractometer D2B, recently installed on beam tube H11 of the ILL high flux reactor. The primary horizontal collimation α_1 may be 35' (open) or 5' using a 300mm high x 60mm wide mylar Soller collimator. We intend eventually to fabricate this collimator using stretched aluminium blades, since we do not know how long the 25 micron thick mylar blades will survive under irradiation. This very large beam is produced from a new 200mm diameter beam tube insert, which depletes the reactor flux by only 2 to 3%. The beam is tall to permit intensity gains from vertical focussing from the 300mm composite monochromator, containing thirty 10mm x 10mm thick slices of squashed Ge crystal.

The 300mm high beam is thus focussed onto only 40mm at the sample positon, 3 metres from the monochromator. An evacuated beam tube will be used to eliminate air scatter over this rather long incident path. With the present monochromator, at 1.6Å the measured flux at the sample position is 7×10^6 n.cm^{-2}.sec^{-1} with 35' primary collimation, and 10^6 n.cm^{-2}.sec^{-1} with 5' primary collimation. This compares with 2×10^6 n.cm^{-2}.sec^{-1} with 19' incident collimation at 1.9A on D1A, and is lower than expected, because the monochromator is too perfect and does not select a sufficiently wide bandwidth of neutrons. The too flat nature of the measured resolution curve confirms that a larger monochromator mosaic spread could be used to boost intensity without compromising too much the resolution.

The Multidetector-Multicollimator

Mylar foil Soller collimators similar to but smaller than the incident collimator are used in front of each of the 64 detectors, providing divergence α_2 = 5' with no alternative. The beam cross-section is 20mm x 100 mm high for 25mm diameter 5 atmosphere He3 detectors, 1 meter from the sample. The vertical divergence from sample to detector (6 degrees) therefore approximately matches that from monochromator to sample. Detectors and collimators are enclosed in B4C loaded resin 150mm thick. Almost all background then comes from the sample itself. Each detector has its own amplifier and scaler, so that the dead times do not depend on the total detector count rate (as for some position sensitive detectors).

The 64 detectors are spaced at 2.5° intervals to cover the complete 160° scattering range, so that a complete can be obtained with 100 detector steps each of 0.025°. Intercalibration of the detectors for efficiency, and more importantly for precise angular seperation, is normally obtained by scanning all detectors through a single peak.

Unfortunately at present the sample axis moves (by about 1.5mm !) when such large scans are performed by the detector bank. This makes it impossible to calibrate by direct measurement the effective detector seperations to the precision required for profile refinement. A mechanical solution to this problem is being manufactured, but in the meantime it is necessary to calibrate each detector against a calculated diffraction profile; an yttrium-iron-garnate (YIG) sample has been used by J. Pannetier to produce the required large number of peaks (fig. 5).

Figure 5.

CALIBRATION YIG
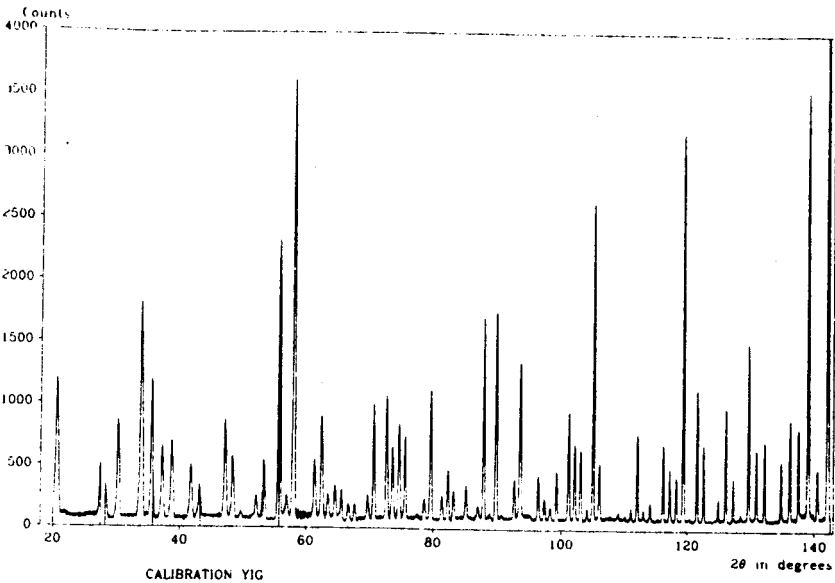
SAMPLE ENVIRONMENT

Sample environment is extremely important for powder work, since the main interest in the speed of data collection over single crystal methods is the possibility of comparing structures at different temperatures and compositions.

On D2B the sample can be up to 20mm diameter x 40mm high, and is usually contained in a sealed vanadium tube to avoid air scatter. The sample table, 500mm below the beam, permits the use of very large cryostats, furnaces, magnets etc. A special cryofurnace, based on a standard ILL orange cryostat, permits a continuous temperature range of 1.5K to 620K. The temperature is set by a microprocessor controlled unit receiving orders from the instrument computer, so that many different temperatures can be programmed for overnight data collection. The cryofurnace will permit, for example, dehydration of zeolites at 350C under vacuum, adsorption of other gases, and the subsequent study of the structure near absolute zero temperature where thermal disorder is minimal.

Three types of high temperature furnace are available for use on D2B. A furnace for the range 100C to 900C permits the use of vanadium sample cans, for non-oxidizing samples under vacuum. Sealed quartz tubes can be used up to 1100C in a second furnace which goes up to about 1500C. Above this temperature, the sample must usually be sealed in electron beam welded tungsten tubes, which can be used in a third very high temperature furnace up to about 2500C. At these temperatures, the vapour pressures of even high melting point materials become appreciable; unless the sample is sealed, it sublimates onto the coldest point in the furnace.

For the cryostats and the 900C furnace, the collimated beam geometry and large sample tail diameter ensures that no extraneous lines are present in the powder pattern. For the higher temperature furnaces, a few tungsten lines are observed.

At the other extreme, dilution refrigerator inserts permit temperatures down to 40mK or lower. In principle, magnetic fields up to 60 Tesla can be applied using a special cryomagnet, but to date only lower field experiments have been performed on our powder instruments.

Various types of pressure cell are available for operation within the cryostats. Up to about 5 kbar, rather large samples (cm³) can be compressed using helium gas (solid at low temperatures and high pressure). The pressure can then be changed in situ. Up to about 10 kbar, slightly smaller samples can be compressed in a clamped aluminium alloy cell: the cell must be warmed and removed from the cryostat to change pressure. This cell produces a few extraneous aluminium lines in the powder pattern; hydrostatic pressure is assured using an inert pressure transmitting fluid. Up to 30 kbar clamped alumina cells are used for samples of about 0.2 cm³ volume, again in a pressure transmitting fluid. Since the alumina contains additives to increase its shear strength (black alumina) the powder pattern contains very many extraneous lines: this cell is then only useful for simple materials, or for compressibility measurements. These pressures are relatively low compared to pressures obtained for X-ray work with diamond anvils, but data suitable for high quality structure refinement is obtained, while X-ray measurements are usually restricted to compressibility and phase diagram studies.

CONTROL COMPUTER AND ELECTRONICS

The PDP11/24 computer runs under the RSX-11 multi-task time sharing system, now also standard on D1A using the same programs. The detector angle, sample angle and monochromator angle (wavelength) are set by individual microprocessor controllers receiving angle commands from the PDP11. Commands for temperature settings are also transmitted to the microprocessor based cryostat or furnace controller. This control computer is linked by DECNET to more powerful DEC-10 and VAX-8600 central computers for dataprocessing. Each block of data is automatically transmitted on completion to the central computer.

FIRST TEST MEASUREMENTS ON D2B

The YIG sample (fig. 5) gives an idea of the potential of D2B for examining relatively large structures with many diffraction lines. The resolution is clearly appropriate to the relatively even density of lines on this scale, and is in fact better than needed for this 12 Å unit cell.

The standard Al2O3 sample is a pressed ceramic cylinder 15mm diameter by 16mm high. This is of course smaller than the 40mm high beam on D2B, but is useful for comparing the intensity and resolution of the new diffractometer with the earlier machines.

Figure 6 shows that at 1.6 Å the resolution is better than 10^{-3} for a large scattering range between $2\theta = 120°$ and $160°$, with a minimum of 5.6×10^{-4}. This compares well with the nominal 5×10^{-4} resolution expected for a perfect sample. The insert shows for comparison D1A results at 1.38 Å [4] for the same section. Note that the three lines marked * on D1A are resolved as four lines on D2B, even though D1A is still one of the highest resolution neutron diffractometers. These same lines are resolved almost equally well on the new TOF HRPD on the ISIS pulsed neutron source, though the latter machine has an advantage for such a simple structure in that useful data is produced for very short d-spacings, not normally available on D2B.

0.105	0.095	0.11	0.16	$\Delta\theta$ degree
10.0	7.8	7.1	5.6	$\Delta d/d \times 10^{-4}$

AL2O3 STANDARD ON D2B. TOTAL TIME = 100 MINUTES
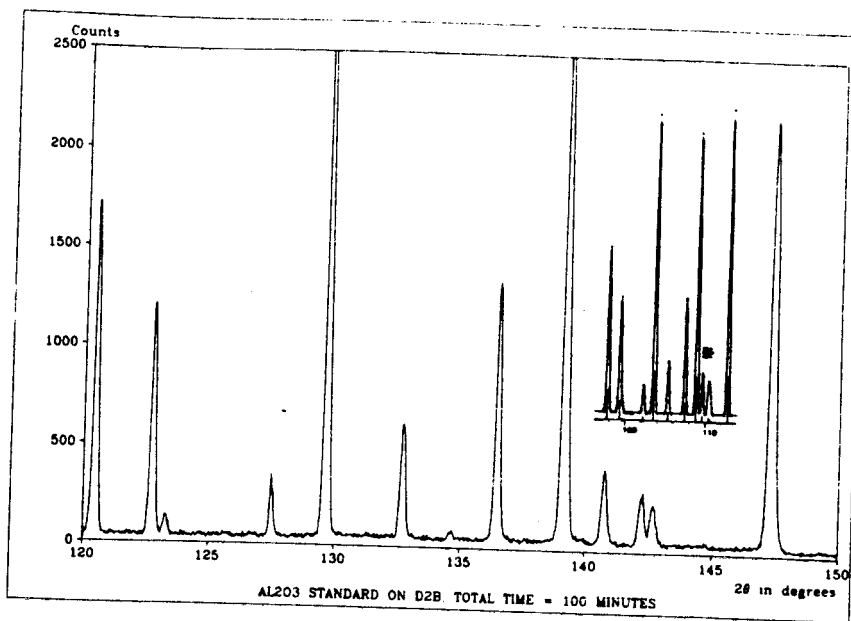
CONCLUSION

The objectives have been to obtain the highest resolution permitted by the nature of the powder samples, to preserve the simple line shape needed for high precision profile refinement, and to deliver the speed of data collection necessary for systematic studies with temperature and composition of even large unit cells. The techniques have been to use a large take-off angle with a composite focussing monochromator and an extended multicollimator/multidetector. The resolution s then tailored to the density of peaks, the time averaged flux and the sample volume is large, and the detector solid angle is maximized.

Preliminary results on the new very high resolution neutron powder diffractometer D2B give an idea of the superiority of this machine over the earlier D1A. Of course D1A remains a powerful diffractometer, responsible for much of the growth in the use of HRPD neutron diffraction in recent years. The new machine will permit this work to be extnded to ever more complex structures. Most importantly we hope that it will open the way for structure solution by direct methods, as well as high precision structure refinement.

We expect the new neutron machines to complement similar new high resolution machines on synchrotron sources. The X-ray machines will be very fast, and in some cases have even higher resolution: but the precision with which chemically interesting structures can be refined will remain inferior to the neutron diffractometers.

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