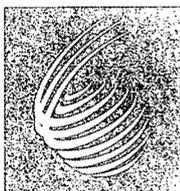


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The Present and Future Potential for Time Resolved Powder Diffraction Studies at ISIS

R I Smith

May 1995

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**THE PRESENT AND FUTURE POTENTIAL
FOR TIME RESOLVED POWDER DIFFRACTION
STUDIES AT ISIS**

R.I. Smith

May 1995

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1. INTRODUCTION

The present generation of high resolution powder diffractometers permit crystal structure analyses to high accuracy and precision using neutron or X-ray diffraction data collected from powder samples; refinement of structural models using the Rietveld method or 'integrated intensity' methods is now routine. More recently, however, the development of very high resolution diffractometers, especially those situated at synchrotron X-ray sources, has opened up the prospect of true 'ab initio' structure determination from powder diffraction data.

The latest generation of high flux radiation sources and fast detector systems have also made it possible to collect complete diffraction patterns in very short periods of time. This is especially the case for diffractometers built on synchrotron X-ray sources, due to the combination of a very high incident flux, which is much greater than that available from present neutron sources, and the greater efficiency with which atoms scatter X-rays compared to neutrons. This opens up the possibility of carrying out time resolved studies, where the evolution of a diffraction pattern as a function of time can be followed. Structural changes occurring in a material during a chemical or physical process can be observed and investigated. The information obtained can be very important in studies of chemical reactions, crystallisations and phase transformations. Of particular interest is the ability to detect transient species which may remain unobserved during static measurements.

Both variable wavelength (time-of-flight or energy dispersive) and fixed wavelength (angle dispersive) powder diffraction experiments can be exploited to yield kinetic information in this area. An important feature of time-of-flight and energy dispersive techniques is the ability to measure an entire diffraction pattern with a single detector configuration. With time-of-flight techniques count rates normally are increased by constructing position sensitive detectors (PSD's) covering large solid angles, however at pulsed spallation neutron sources the angular range of a PSD will be constrained by the resolution function characteristic of time-of-flight diffraction. On fixed wavelength instruments, the use of curved PSD's in place of a single scanning detector makes for much quicker data collection and also enables a high degree of comparison between successive data sets because there is no movement of the detector.

Paradoxically, the lower efficiency of neutron scattering offers some significant complementary advantages over X-ray experiments in that neutron beams are able to penetrate into non-ambient sample environment apparatus, e.g. furnaces, reaction vessels and pressure cells. Careful design of collimation for the incident and scattered neutron beams can ensure that the diffraction patterns measured are not contaminated by signals from the sample environment equipment. Furthermore, the neutron beams will also penetrate several centimetres into the sample, ensuring that the processes recorded are representative of the bulk of the sample and not just restricted to surface effects, as is the case with X-rays. However, the lower scattering efficiency also means that larger quantities of sample are required, which will take longer to reach equilibrium on change of temperature, pressure, etc., reducing the time resolution attainable.

Nevertheless, the best present time resolution for powder neutron diffraction experiments, ranging from 0.5 to 10 minutes, is well suited to the study of many solid

state processes which often have characteristic times of a few hours. In addition, neutrons also allow the study of magnetic transitions, the location of 'light' atoms and water molecules, contrast variation experiments and studies of X-ray sensitive processes.

1.1 Time Resolved Experiments

The ability to perform time resolved experiments successfully requires that the time needed to collect a complete diffraction pattern with adequate counting statistics is much shorter than the relaxation time of the process being studied. The diffraction pattern itself must be simple enough that most of the reflections in the time-of-flight or angular range collected are resolved by the diffractometer and show sufficient change during the transformation under investigation.

Both reversible (i.e. where the change can be induced cyclically) and non-reversible (one-off) processes may be studied. In the non-reversible case, once the process is initiated the data are recorded sequentially. Time resolution in these experiments is thus limited by the time taken to record a diffraction pattern with sufficient statistical accuracy, which must be shorter than the characteristic time of the process being studied. With the best existing neutron PSD diffractometers this time limit is currently about 1 second. Although this is long compared to the nanosecond time limit currently attainable from synchrotron X-ray diffractometers, it is a convenient time scale for the study of many solid state processes such as first order transformations and chemical reactions.

Reversible processes, on the other hand, may be repeated cyclically if the characteristic time is shorter than that needed for collection of a diffraction pattern. By repeating and accumulating from successive cycles, data with sufficient statistical accuracy may be collected. The time resolution in such cases is not limited by the beam flux or sample scattering power but by the data acquisition electronics and the pulsing frequency (and pulse width) of the source.

1.2 Applications Of Time Resolved Diffraction

There are two main areas where time resolved neutron diffraction experiments presently can provide an ideal method of studying chemical and physical processes. These are in kinetic studies (usually isothermal) and neutron thermodiffraction. Although kinetic studies should be isothermal for each 'run' and several 'runs' carried out to cover a range of temperatures to extract the maximum kinetic information, some parameters, such as reaction rate constants and activation energies can still be extracted from thermodiffraction experiments provided that the reaction order is already known.

1.2.1 Kinetic Studies

In kinetic studies, the aim is normally to obtain both qualitative and quantitative information. Quantitative experiments can be performed by measuring the intensities of a few strong reflections from each phase present, allowing their volume fractions to be calculated. From these quantitative studies reaction orders, rate constants and

activation energies can be determined. Transient phases also can often be revealed, provided that their life-time is of the order of the time taken to collect each diffraction pattern.

Studies undertaken to date include phase transformations, normally brought about by a sudden change in pressure, hydration and dehydration reactions and the study of chemical reactions between solids, liquids and gases. Phase transitions involving changes in temperature are less amenable to study due to the high thermal capacity of powdered samples making it difficult to achieve an instantaneous, isotropic temperature change.

Solid-gas reactions, such as intercalation processes, and solid-liquid reactions, such as hydrations, dehydrations and electrochemical reactions at electrode materials, are particularly suitable to this kind of investigation. Neutron diffraction has a very important role in these studies due to its ability to determine 'light' atoms and to allow experiments to be performed in complex sample environments with, given suitable collimation, the minimum of contamination of the measured diffraction pattern with signals from the sample environment equipment.

Although there are no fundamental difficulties preventing the study of solid-solid reactions, problems may arise due to the need to take the reactants from an initial temperature at which no reaction takes place to the temperature at which the kinetics are to be measured. The whole of the sample should be brought to this temperature simultaneously, a process made difficult by the occurrence of temperature gradients.

1.2.2 Neutron Thermodiffractometry

Neutron thermodiffractometry is an important technique available in the study of thermally activated processes, at both elevated and lowered temperatures. Diffraction patterns are recorded over constant time intervals as the temperature is raised or lowered at a constant rate, providing an average picture of the sample during each temperature interval. Temperature resolution is determined in advance by consideration of temperature ramp rates and data collection times, but ultimately is limited by temperature gradients in the sample.

Neutron thermodiffractometry can be particularly useful in studies of phase transitions (reconstructive, structural, polymorphic, order-disorder) where the appearance and disappearance of phases as the temperature changes can be followed. Thermal decomposition reactions, chemical reactions in the solid state - e.g. solid state syntheses - and crystallisation processes of amorphous materials are all amenable to study by thermodiffractometry.

The use of fixed detectors with no moving parts, either in time-of-flight experiments or as PSD's, means that cell parameters can be determined with very high relative accuracy and minute changes measured, allowing very accurate values for, e.g., thermal expansion coefficients to be extracted. Low temperature studies can also reveal many complex magnetic transitions, which remain unobserved during fixed temperature experiments. Thermodiffractometry is also invaluable in detecting transient phases, as mentioned above.

1.3 Present Limitations

The latest time-of-flight diffractometers built at pulsed spallation neutron sources are now competitive with the best constant wavelength instruments at reactor sources, in terms of both resolution and count rate. However, because of the time structure of pulsed neutron beams they may offer new opportunities for time resolved experiments.

With non-reversible processes the only limitation to time resolution is the ratio of the time taken to record a diffraction pattern and the characteristic time for the process. As long as the characteristic time is longer than the repetition time of the pulsed source the two techniques are essentially the same. The only differences occur in the way the time interval is sampled and the diffraction pattern collected.

For reversible processes, provided that the cyclical perturbation can be phased along with the pulsing frequency of the source and the data acquisition electronics, it may be possible to perform experiments with time resolutions down to 10^{-5} seconds.

In neutron diffraction experiments, however, the time resolution is limited ultimately by the velocity of neutrons, which take a finite time to travel through the sample. Time-of-flight experiments also need care because neutrons in the pulsed 'white' incident beam having different wavelengths will reach the sample at different instants and will take different periods of time to travel through the sample.

2. THE POLARIS DIFFRACTOMETER AT ISIS

Over the past three years, from mid 1991 to mid 1994, the Polaris diffractometer at ISIS, figure 1, has undergone significant improvement, with the detector complement in all three main detector banks (measured in terms of solid angle coverage) increasing by a factor of at least 5. This means that Polaris now offers the ability to collect complete diffraction patterns in a matter of minutes, opening up new areas in the field of time resolved studies at ISIS.

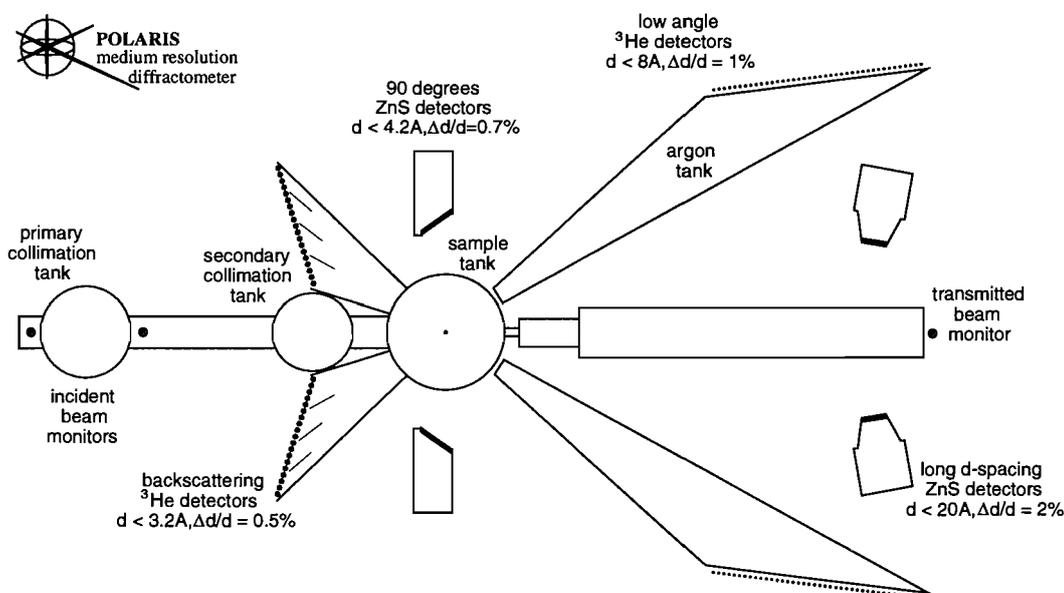


Figure 1. Schematic diagram of the Polaris powder diffractometer at ISIS.

The highest resolution, back scattering detectors are used for the majority of structural, time resolved and kinetic studies on Polaris. The 38 ^3He detectors in this bank are resolution focused and, due to the rich epithermal component to the incident neutron flux on Polaris, provide diffraction data to d-spacings as small as $\sim 0.3\text{\AA}$, with good resolution. Data in this range can be invaluable during structure refinement, particularly of disordered materials. Time-of-flight diffractometers built at pulsed spallation neutron sources have a unique advantage in this respect because they can measure very short d-spacings without the restriction of the $\sin\theta$ limit encountered by fixed wavelength instruments.

The Polaris $2\theta=90^\circ$ detectors provide a count rate and resolution only marginally poorer than the back scattering detectors. These detectors use ZnS scintillator and again are resolution focused. For experiments where count rate is more important than resolution or line shape, the diffraction data from the 90° detectors can be added to that from the back-scattering detectors, further reducing the data collection times required. As mentioned previously, with the provision of appropriate collimation these detectors become extremely important during studies of samples in complex environments, such as measurements at high pressure.

Although they have the lowest resolution and count rate, the Polaris low angle ZnS detector banks are able to measure much longer d-spacings, up to $\sim 20\text{\AA}$. This ability is particularly useful in detecting superlattice reflections resulting from, e.g., ordering of guest molecules during intercalation reactions and in providing low order reflections for indexing purposes and/or identifying transient species.

The resolution focused geometry of the detectors on Polaris not only ensures a well defined peak shape, which in turn can be well modelled during subsequent data analysis, but also avoids the possibility of saturating the detector electronics as bursts of scattered neutrons from Bragg reflections reach all the detectors in a bank simultaneously. This could otherwise be a real possibility with a time focused detector geometry given the very high count rates achieved on Polaris. More significantly, perhaps, this alternative arrangement of time focused detectors would result in a decrease in the solid angle covered due to the larger "canting" angle between the detector bank and the scattered neutron beam required to maintain a time focused geometry.

This design for the Polaris diffractometer contrasts with that of constant wavelength instruments, on both neutron and synchrotron X-ray sources, where either a single detector or a small multi-detector scans, radially, a given 2θ range at a constant sample to detector distance, or a large curved position sensitive detector, with a fixed radius of curvature and covering a wide 2θ range, is located in a single, fixed position around the sample. The resolution function of the constant wavelength diffractometer is determined by the collimation present between source, monochromator, sample and detector and by the band pass of the monochromator. It is well represented by the equation of Caglioti, Paoletti and Ricci (1958) and improves as the take off angle from the monochromator increases.

With energy dispersive, white beam diffractometers built at synchrotron X-ray sources the resolution is determined by the collimation defining the incident and scattered beams and the intrinsic energy resolution of the detector, and is poor compared to that which can be achieved with other X-ray and neutron techniques (Albinati and Willis, 1982). For example, the single crystal germanium detector on the energy dispersive powder diffraction station 9.7 at the Daresbury SRS has an intrinsic energy resolution of $\Delta E/E=0.0253$ (Clark *et al*, 1994).

3. RECENT POLARIS HIGHLIGHTS

As a consequence of the improved performance of Polaris, a healthy programme of time resolved and kinetic experiments has developed. These have spanned several of the areas discussed above, including ageing kinetics, kinetics of solid-gas reactions, dehydration reactions and solid state reactions.

3.1 Neutron Thermodiffractometry

3.1.1 Calcination of Zirconium Hydroxide

Zirconium hydroxide is an important precursor in the formation of the tetragonal and monoclinic polymorphs of zirconia, ZrO_2 , used in high performance ceramics. It can be considered to be intermediate between a hydroxide and a hydrated oxide, with one current model depicting the structure of zirconium hydroxide as an open polymer in which individual units are linked by double hydroxy bridges, figure 2. The calcination of zirconium hydroxide to form zirconia involves an initial conversion of the hydroxide to the oxide followed by the transformation of tetragonal to monoclinic zirconia and has been found to take place in three discrete stages, each stage occurring over a separate temperature range. The kinetics of the conversion and crystallisation processes are sensitive to the sample preparative conditions, especially the pH of the solution from which the hydroxide was precipitated.

Neutron thermodiffractometry experiments have particular advantages in studying dehydration and dehydroxylation reactions because a characteristic background, caused by incoherent neutron scattering from hydrogen atoms, can be used to determine the relative amounts of hydrogenous species present in the sample throughout the course of the reaction. Earlier results from EXAFS measurements had enabled a model for zirconium hydroxide to be developed which predicted that an exchange with methoxy species should involve the outer hydroxyl groups only. Hence, a comparison of the diffraction data from deuterated and hydrogenated methoxy exchanged samples should allow the identification of the calcination stages which involve the outer hydroxyls. Similarly, H_2O/D_2O exchanges during sample preparation would allow the processes involving internal hydroxyls to be identified.

In a series of experiments on Polaris the calcination of zirconium hydroxide was investigated using several samples prepared using specific protonated or deuterated hydroxy and methoxy species. Neutron diffraction patterns were collected every 5 minutes from each sample as it was calcined in a RAL furnace in the neutron beam, during which time the temperature was ramped up from $100^\circ C$ at $2^\circ C$ per minute. Examination of the differences in the incoherent background signals between the various samples allowed the processes occurring at the different sites in zirconium hydroxide to be distinguished and associated with particular stages in the calcination process (Turrillas *et al*, 1995).

Unfortunately, the temperature ramp achieved during calcination was not as accurate as desired, with some runs deviating by as much as $20^\circ C$ from the required temperature, which meant that it was not possible to extract the desired kinetic rate constant information from these experiments. However, the experiments were still able to clarify the nature of the processes occurring during calcination.

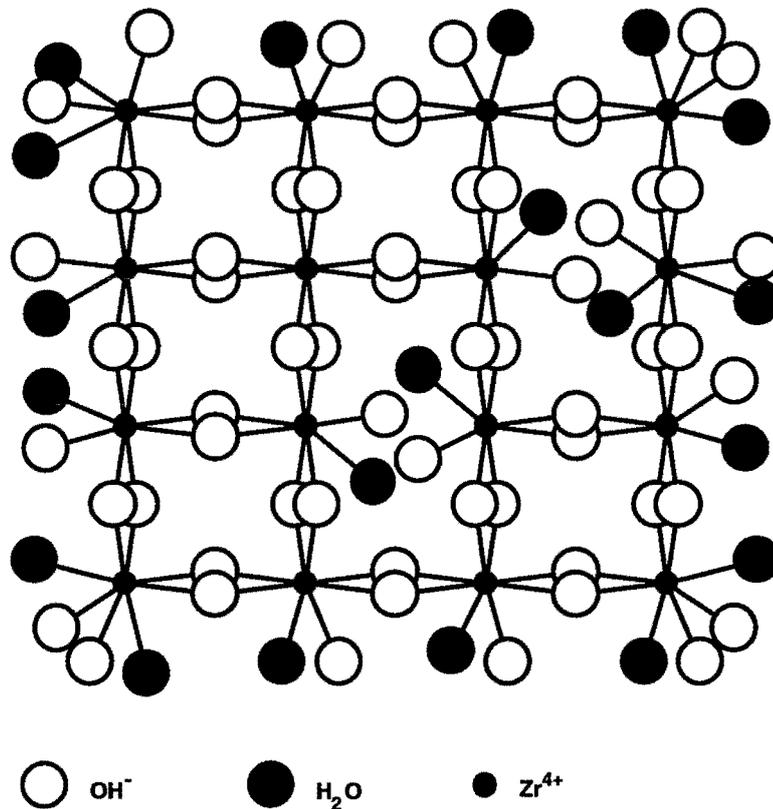


Figure 2. Schematic diagram illustrating the intermediate nature of the so-called amorphous zirconium hydroxide. Basic tetrameric units, partially polymerised, are clearly seen with juxtapositioning of hydroxo bridges, OH^- and water molecules (taken from Turrillas *et al*, 1993).

Analysis of the data collected showed that the first stage of the calcination process involves primarily the loss of loosely bound water molecules and the liberation of terminal water and hydroxyl groups, but with some limited oxolation of the internal hydroxy bonds. The processes occurring in the second stage of calcination are less certain, but by elimination it was concluded that this stage is connected with the liberation of inner water molecules. The third stage involves the final oxolation of hydroxy bonds to oxy bonds, removal of any residual water/hydroxyl groups and crystallisation of the tetragonal zirconia phase. In samples prepared at high pH this third stage becomes co-operative, as shown by the sudden drop in the incoherent background observed in the neutron diffraction patterns.

Finally, an anomalous new "pseudo tetragonal" intermediate phase, which appears along with the expected tetragonal zirconia, was identified in samples prepared using a modified procedure designed to produce purer, sulphate free zirconium hydroxides. The precise structure of this pseudo tetragonal phase and its role in the overall zirconia transformation process are, as yet, still unknown but the presence of this new phase as the first crystallisation product has been confirmed in synchrotron X-ray energy dispersive powder diffraction experiments.

3.2 Kinetics

3.2.1 Ageing Kinetics of Magnesia-Partially Stabilised Zirconia

Magnesia partially stabilised zirconia (Mg-PSZ) is an important transformation toughened ceramic which has several commercial applications, and is one member of a range of zirconia toughened ceramics (ZTC's). Transformation toughened ceramics combine the desirable properties of ceramics, such as extreme hardness and good durability, with a high toughness not normally associated with ceramics. They find applications in many industrially important areas such as metals processing (wire extrusion dies, can seaming rollers), mining and minerals processing (wear resistant bearings), the oil industry (ball valves for corrosive environments), food processing (homogenising tools) and in medicine (replacement joints).

In Mg-PSZ, an important contribution to the high toughness is played by a stress induced martensitic phase transition from tetragonal to monoclinic zirconia, which has an accompanying volume increase of ~5% and a shear of 9°. This transition inhibits crack propagation in the component and means that the material can 'give' via a phase transformation, rather than break, on the application of a tensile stress. The mechanical properties of ZTC's depend sensitively on the microstructure and phase composition of the ceramic, in particular on the amount of tetragonal zirconia present, which in turn is controlled by the processing conditions during manufacture. The aim of the processing is to produce stressed metastable tetragonal zirconia precipitates in a matrix consisting of cubic zirconia and δ phase ($\text{Mg}_2\text{Zr}_5\text{O}_{12}$) by careful cooling from the firing temperature and subsequent sub-eutectoid ageing. In this way the fracture toughness of these materials can be increased by a factor of 10.

Zirconia forms several polymorphs which differ mainly in the positions of the oxygen atoms. Because the scattering power of oxygen relative to zirconium is larger with neutrons than with other probes, especially X-rays and electrons, neutrons are better able to distinguish between these polymorphs. Also, during fabrication of ZTC components, transformations will occur on the surfaces, especially during any kind of surface preparation, hence the composition of the near surface regions is notoriously unrepresentative of the bulk composition. Thus neutron diffraction is the ideal technique for the study of zirconia toughened ceramics.

Early neutron diffraction studies involved collecting data at room temperature from samples processed for various periods of time at different firing and ageing temperatures, and aimed to determine the amounts of monoclinic, tetragonal and cubic polymorphs in Mg-PSZ. These experiments showed also the formation of a new orthorhombic polymorph, allowing its structure to be determined, and confirmed suggestions from TEM experiments that high toughness Mg-PSZ contains substantial amounts of the δ phase, $\text{Mg}_2\text{Zr}_5\text{O}_{12}$. It was found that the inert strength of Mg-PSZ had a marked dependence on the amount of tetragonal zirconia present. However, interpretation of the processes occurring at elevated temperatures was complicated by the presence at room temperature of monoclinic and orthorhombic polymorphs, which were believed to be formed as a result of transformation from tetragonal zirconia on cooling.

The advantages of neutron scattering, discussed above, combined with the high count rate achieved on the Polaris diffractometer, meant that the ageing process could be investigated 'in situ' at temperature in a furnace, to give information on the processes occurring in Mg-PSZ during component fabrication, and in particular on the sample composition, such as had never before been so directly available.

The experiments carried out followed the changes occurring in bars of "as fired" 9.7mol% MgO-ZrO₂ as they were aged in a RAL furnace in the neutron beam. Diffraction patterns were collected every 15 minutes as the furnace temperature was ramped up at 100°C per hour from room temperature to a sub-eutectoid ageing temperature of either 1100°C or 1240°C, held at this temperature for 10 hours, then cooled back down to room temperature at 100°C per hour. The diffraction patterns were analysed by the Rietveld method to determine the phase composition of the sample and the unit cell parameters for each phase throughout the course of the ageing process. This experiment was able not only to confirm some of the conclusions drawn from the earlier room temperature measurements, but also provided important new information (Argyriou, Howard and Smith, 1994).

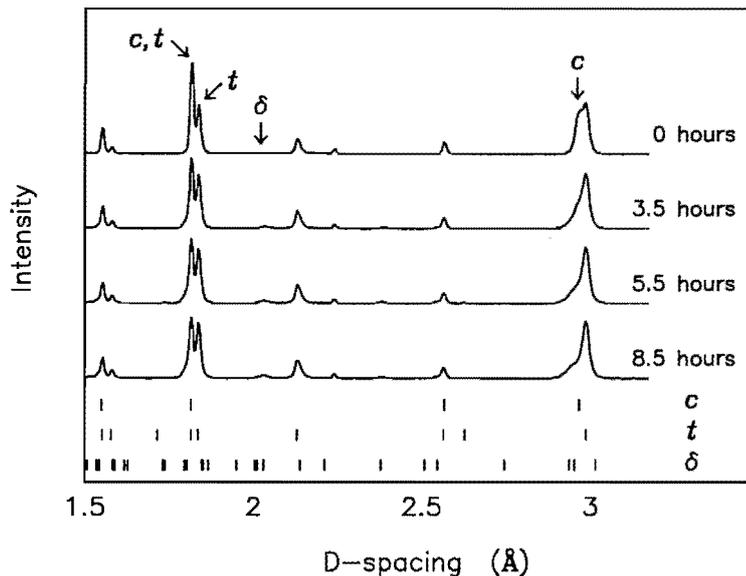


Figure 3. Powder neutron diffraction patterns collected at 1100°C on Polaris showing the progress of the ageing process in Mg-PSZ at ~3 hour intervals. Peaks indicative of cubic and tetragonal zirconia and the δ phase are indicated (taken from Argyriou *et al*, 1994).

During ageing at 1100°C, the diffraction patterns show the development of tetragonal zirconia and the δ phase, both at the expense of cubic zirconia, figure 3. The Rietveld refinement scale factors allowed the volume fraction of each phase to be calculated as a function of ageing time from which it was seen that the ageing process followed first order kinetics and enabled a rate constant to be determined, figure 4.

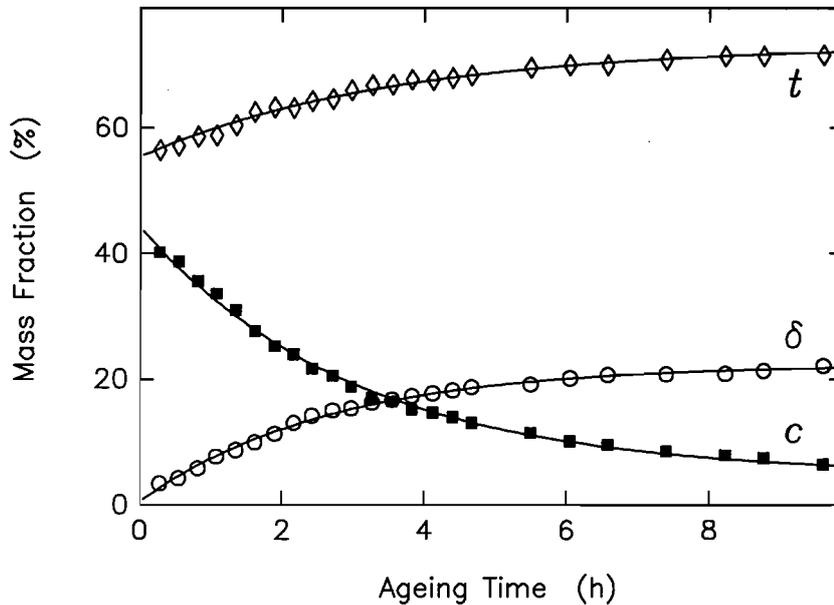


Figure 4. Variation in the amounts of cubic, tetragonal and δ phase in Mg-PSZ with ageing time at 1100°C. The lines through the data points represent the fit of simple exponentials with a common rate constant to the observed phase amounts (taken from Argyriou *et al*, 1994).

Analysis of the unit cell parameters, which give a measure of how much MgO stabiliser is contained in cubic and tetragonal zirconia, showed both the cubic a_c and tetragonal c_t parameters to increase with ageing time, figure 5. This indicates that during ageing both the cubic and tetragonal phases lose MgO stabiliser to the δ phase. Some Bragg reflections also showed some broadening, especially those of tetragonal zirconia, indicating a considerable strain component parallel to the c axis of the tetragonal precipitates.

Finally, on cooling back to room temperature, tetragonal zirconia was seen to transform to the monoclinic and orthorhombic polymorphs at approximately 180°C producing the composition typically seen at room temperature and confirming the results from the early experiments at room temperature.

The occurrence of the δ phase, however, remains a matter of interest. This phase does not appear on the equilibrium phase diagram, from which it is expected that at 1100°C Mg-PSZ decomposes into monoclinic zirconia and MgO. Although it has been reported in previous works that the δ phase is a metastable precursor to this decomposition, there seems to be no evidence at all for decomposition on the time scales (10 hours) of the Polaris experiment. Over these time scales, and prior to eventual decomposition, the processes occurring in Mg-PSZ at 1100°C may be understood most easily as the segregation of the material into relatively lower MgO content zirconia (in both tetragonal and cubic form) and the δ phase itself.

During ageing at 1240°C, however, Mg-PSZ is seen to undergo a different series of transformations (Argyriou, Howard and Hannink, 1994). Firstly, there is no development of the δ phase at this higher ageing temperature, but instead cubic zirconia transforms into a mixture of tetragonal zirconia and MgO, as expected from

the equilibrium phase diagram. This process is relatively slow, and has a time constant of about 45 hours. More interesting is the behaviour of the cubic and tetragonal zirconia cell parameters. a_c is seen to decrease during ageing while c_t increases; these processes having a much shorter time constant, of ~8 hours. This implies that MgO stabiliser is expelled from the tetragonal phase and is incorporated into the cubic phase, rather than forming "free" MgO, in contrast to the behaviour at 1100°C. Further analysis of these results is proceeding in order to understand in greater detail the processes occurring during ageing at 1240°C. Finally, once more the transformation to monoclinic and orthorhombic zirconia is seen as the sample cools to room temperature.

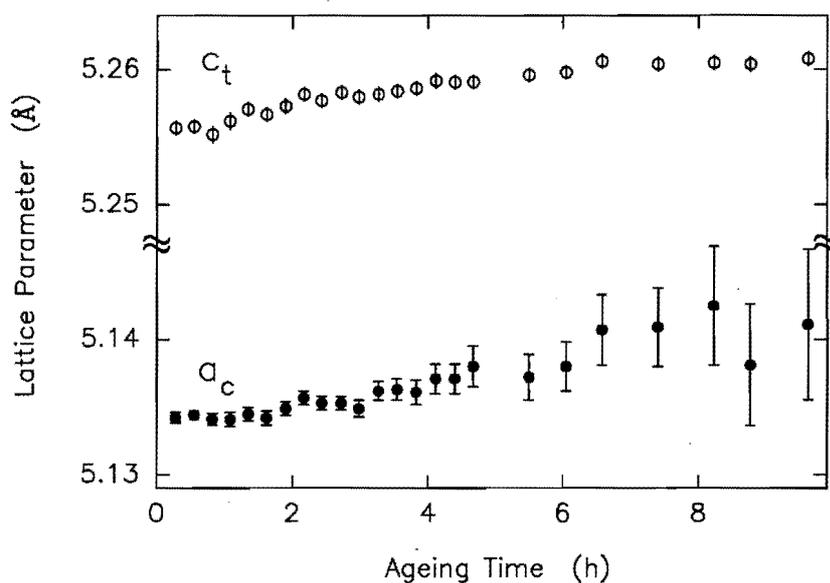


Figure 5. The variation in the cubic a_c and tetragonal c_t lattice parameters in Mg-PSZ, determined during Rietveld refinement, as a function of ageing time at 1100°C (taken from Argyriou *et al*, 1994).

3.2.2 Phase Diagram and Kinetics in The LaNi₅-D System

Intermetallic hydrides with high hydrogen concentrations are good candidates for the replacement of cadmium as the negative electrode in Ni-Cd cells because they are non polluting and durable, and have potentially higher energy densities and charge and discharge rates. LaNi₅ based hydrides have been studied extensively and are found to have many desirable properties, such as a hydrogen capacity of 6 hydrogen atoms per formula unit and a desorption pressure of about 2 atm. at room temperature.

The ability to determine hydrogen (or deuterium) in the presence of heavy atoms, such as lanthanum and nickel, makes neutron diffraction the ideal technique for the study of metal hydride systems. The high count rate achieved on Polaris has allowed time resolved powder neutron diffraction experiments to be performed on the LaNi₅-D system, with the aim of understanding more fully the effects on the

sample of different rates of deuterium absorption and desorption (Kisi and Gray, 1994a,b).

Powdered LaNi_5 was contained in a sample holder constructed from thin walled stainless steel tube, figure 6. Large copper heat sinks attached to the top and bottom of the cell were heated or cooled by Peltier effect heat pumps connected to a temperature controller, with the pumped heat supplied or dumped by an external water circuit. An expansion chamber situated around the upper heat sink kept the top surface of the LaNi_5 powder in contact with the heat sink, thus allowing for the ~24% increase in sample volume between $\alpha\text{-LaNi}_5$ and $\beta\text{-LaNi}_5\text{D}_x$. The D_2 for these experiments was stored as LaNi_5D_x in a separate reservoir and supplied or recovered by adjusting the temperature of the reservoir. Deuterium absorption by the LaNi_5 sample was measured by filling a known reference volume with D_2 to a selected pressure, opening this reference volume to the sample volume and recording the pressure decrease in the total volume so formed.

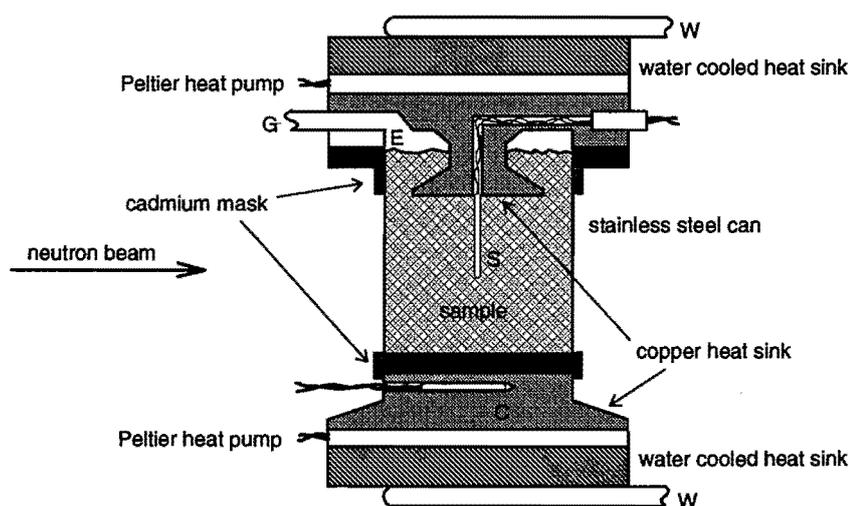


Figure 6. Variable temperature pressurising apparatus used to study $\text{LaNi}_5\text{-D}$ 'in situ' on Polaris. Key: S: Sample thermometer, C: Control thermometer, E: Expansion chamber, G: Gas/vacuum port, W: Water inlet.

In a first set of experiments, the formation of the α and β phases in the $\text{LaNi}_5\text{-D}$ system during deuterium absorption and desorption was investigated to determine the positions of the phase boundaries. During these 'static' measurements, 30 minutes were taken to record each neutron diffraction pattern, with the sample allowed to equilibrate for 30 minutes at each D_2 pressure before data collection commenced. The positions of the phase boundaries were determined by quantitative phase analysis of the diffraction patterns and were found to agree well with those expected from the intersection of extrapolated pressure plateau and pure phase isotherms in the $\text{LaNi}_5\text{-D}$ pressure-composition phase diagram.

Analysis of reflection profiles revealed severe strains in both the α and β phases, providing strong evidence for the presence of microscopic inhomogeneities in partially deuterated LaNi_5 whereby both α and β phases coexist in nanoscale

domains within individual micron sized particles. This disagrees with an alternative model which proposes a mixture containing particles which are wholly α phase and particles which are wholly β phase. Stronger evidence for α and β phase coexistence during deuterium absorption and desorption was found in the behaviour of the unit cell parameters in the two phase region of the phase diagram. Equilibrium thermodynamics predict that unit cell parameters should be constant in a two phase region, in contrast with the variation observed during this study of the $\text{LaNi}_5\text{-D}$ system. The behaviour observed in the two phase region could be explained by a mechanical interaction between the two coexisting phases producing dilatational or compressive stresses, thereby increasing or decreasing the expected cell parameters. A hysteresis effect in the β phase unit cell parameters also implies a fundamental asymmetry in the D absorption and desorption mechanisms.

A second set of experiments on LaNi_5 tested a prediction that temperature gradients brought about by enthalpy released during the hydrogen absorption/desorption process generates macroscopic inhomogeneities in the $\alpha:\beta$ phase composition in LaNi_5 hydrides. During these 'dynamic' measurements, where diffraction patterns were collected every 5 minutes, deuterium absorption and desorption was continuous and the sample did not equilibrate during data collection. Analysis of the neutron diffraction data collected on Polaris combined with laboratory X-ray diffraction data confirmed that a macroscopic compositional inhomogeneity does occur within the bulk of the sample, and which can be so severe that the free surface of the sample remains pure α phase while the bulk of the sample is rich in the β phase.

In both experiments, the volume change at the α to β phase transition resulted in β rich material, formed due to the macroscopic inhomogeneities described above, being pushed up into the sample cell expansion chamber and out of the neutron beam, causing inaccuracies in the $\alpha:\beta$ phase proportions determined by quantitative phase analysis of the neutron diffraction patterns. This effect was confirmed by masking either the edges or the centre of sample cell with Cd and measuring separate diffraction patterns from the two regions. The difference in sample composition between the two regions could be confirmed by inspection and analysis of the diffraction patterns.

It should be noted that in all the experiments described above (except for some of the earliest zirconium hydroxide calcination experiments) the ISIS synchrotron has delivered protons to a tantalum target. An immediate factor of 2 increase in count rate will be achieved when a uranium target is installed. Further small increases in count rate can also be expected when ISIS is able to run routinely with a beam current of $200\mu\text{A}$.

3.3 Experiments At Other Sources

A brief, but by no means exhaustive, search through the literature reveals time resolved powder diffraction programmes at several other neutron and synchrotron X-ray sources.

3.3.1 Neutron Sources

The D1b diffractometer at the ILL in Grenoble has featured in a large number of experiments. Situated at the world's most powerful research reactor and utilising a curved position sensitive detector comprising 400 elements covering 80° in 2θ , the count rate on this instrument provides a temporal resolution of the order of minutes. Several neutron thermodiffractometry studies have been undertaken on D1b, which include decompositions of oxovanadium (IV) pyrophosphate and cobalt (II) acetate tetrahydrate, dehydrations of vermiculites, montmorillonites and $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, and thermal studies of clay minerals and manganese dioxides. The ability of neutron diffraction to determine the presence of hydrogenous species has been fundamental to many of these experiments.

3.3.1.1 Thermodiffractometry

Oxovanadium (IV) pyrophosphate, $(\text{VO})_2\text{P}_2\text{O}_7$, can be prepared by dehydration of any of the oxovanadium (IV) hydrogen phosphate hydrates $\text{VO}(\text{HPO}_4) \cdot y\text{H}_2\text{O}$, $y=0.5, 1, 2, 3, 4$, and is the active phase in the catalytic preparation of maleic anhydride (Amorós *et al*, 1991). The reaction always proceeds via formation of the hemihydrate, $\text{VO}(\text{HPO}_4) \cdot \frac{1}{2}\text{H}_2\text{O}$. However, the mechanism of hemihydrate formation from the hydrates is not known, and a better understanding of the different dehydration processes leading to formation of the pyrophosphate may be relevant from a catalytic point of view. Neutron thermodiffractometry experiments on D1b revealed that regardless of the starting hydrate, the formation of the pyrophosphate from the hemihydrate always follows the same path. More interestingly, this study was able to show that in the final stages of the reaction there is never coexistence of both hemihydrate and pyrophosphate phases, but instead the reaction proceeds through an amorphous precursor.

The thermal decomposition of cobalt (II) acetate tetrahydrate under vacuum or in an inert atmosphere is of interest because it can lead to the formation of three forms of cobalt oxide (Grimes and Fitch, 1991). These have a cubic rock salt structure, a cubic zinc blende structure or a hexagonal wurtzite structure, with the latter two structures being stable only over a limited temperature range, $290\text{--}310^\circ\text{C}$. Selective deuteration of several samples allowed the processes associated with different hydrogenous species in the sample to be distinguished during decomposition. Upon heating, it was found that initially water and/or excess acetate is lost forming a glassy anhydrous acetate phase due to the complete change in co-ordination of the cobalt ion upon dehydration. On further heating, the glassy phase first recrystallises to form the stable crystalline intermediate phase $\text{Co}_4(\text{CH}_3\text{COO})_6\text{O}$ before decomposing to the zinc blende form of CoO . Finally, the cubic rock salt CoO structure forms at 310°C . No evidence was found in this study for the formation of CoO with the hexagonal wurtzite structure.

Preliminary neutron thermodiffractometry studies on the calcination of zirconium hydroxides on D1b revealed the dependence between the temperature at which tetragonal ZrO_2 crystallised and the pH at which the samples were prepared, and indicated the co-operative nature of this process (Turrillas *et al*, 1993). These studies led to the subsequent experiments on Polaris involving many more samples

and utilising isotopic substitution which revealed the structural features associated with each of the of the dehydration stages.

However, these thermodiffraction studies on D1b have not been to the exclusion of investigations of chemical reactions. Electrochemistry experiments have included studies of the behaviour of a $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{D}_x$ electrode during charge-discharge cycles (Latroche *et al*, 1992) and the electrochemical reduction of manganese dioxides (Ripert *et al*, 1991a,b). Solid state chemistry has featured with studies of the formation of superconducting phases in the Bi-Sr-Ca-Cu-O system via the recrystallisation of quenched amorphous precursors (Boardman, Kilcoyne and Cywinski, 1992).

3.3.2 Synchrotron X-Ray Sources

Experiments using energy dispersive techniques with synchrotron X-rays on the 'white' beam station 9.7 at the Daresbury SRS have enabled extremely high count rates to be achieved, with typical data collection times ranging from a few minutes down to 10 seconds from as little as 200mg of sample. Reaction vessels have been designed and constructed to allow time resolved studies of chemical reactions, such as intercalation processes and hydrothermal syntheses, and, in an extension to the experiments on Polaris and D1b described above, the dehydration of zirconium hydroxides. The use of a single fixed detector geometry greatly simplifies the design of the experiment, because only small windows are required in the reaction vessel for the passage of incident and scattered beams, in a manner similar to time-of-flight neutron diffraction studies at high pressure.

The quantity of data collected is strongly dependent on the design of the reaction vessel. The transmission characteristics of both the sample and the vessel can limit severely the X-ray energies which reach the detector, restricting the d-spacing range measured. With the detector at a known scattering angle 2θ , the photon energies can be converted to d-spacings using the relationship $E(\text{keV})=1.699/d(\text{\AA})\sin\theta$. One consequence of white beam experiments is the occasional presence in the measured diffraction pattern of resonance lines from the sample. However, these lines can be used in the subsequent data analysis procedure to determine the amount of sample in the beam.

3.3.2.1 Intercalation Reactions

The influence of a layered host on intercalated molecules may produce new materials with interesting and much improved catalytic, optical, etc. properties. Furthermore, the intercalation process can also alter the properties of the host material, e.g. magnetic behaviour. A reaction vessel has been constructed at Daresbury which allows the rapid injection and mixing of precise volumes of air sensitive materials for the 'in situ' study of intercalation reactions, with accurate temperature control between 10 and 150°C (Clark *et al*, 1994a,b). This cell has been used in studies of the kinetics and mechanism of intercalation reactions of potassium, tetramethylammonium and pyridinium cations and cobaltocene into MnPS_3 and SnS_2 hosts (Clark *et al*, 1994a,b; Evans and O'Hare, 1994). The experiments have shown that these intercalation reactions have time constants of

the order of minutes, and proceed very much more quickly than conventional intercalation reactions such as that of lithium into layered transition metal dichalcogenides or graphite.

The intercalation of cobaltocene into SnS_2 was found to have a reaction mechanism of non integral order between Avrami first and second order kinetics, with $n=1.5$. This suggests a deceleratory rate of nucleation, with diffusion into the inter-lamellar space controlling the growth of product. The reactions involving pyridinium and tetramethylammonium intercalation into MnPS_3 were seen to follow first order kinetics whereby the nucleation sites at the crystal edges are saturated, and the overall rate of intercalation is determined by the rate of diffusion of the guest cations into the bulk of the host lattice. However, all these reactions were seen to take place without the formation of intermediate phases or long range ordering processes, such that intercalation appears to occur simultaneously between each of the lattice layers in the host.

3.3.2.2 Thermodiffractometry

The complementarity of neutron and X-ray techniques has been shown with energy dispersive X-ray diffraction studies of the dehydration reactions of zirconium hydroxides on station 9.7 at the Daresbury SRS (Turrillas *et al*, 1993,1995). The X-ray experiments used much smaller samples and a different temperature ramp to the neutron experiments, but confirmed the dramatic difference in behaviour of samples prepared at high pH, with the crystallisation of tetragonal zirconia at 490°C .

Also at Daresbury, a cell has been built which has enabled the 'in situ' investigations of hydrothermal reactions, such as the hydration of cements (Barnes *et al*, 1992; Clark and Barnes, 1994). These experiments were carried out in a manner similar to the intercalation kinetics experiments described above.

Time resolved synchrotron X-ray thermodiffractometry experiments have also been carried out on beamline X7B at the Brookhaven NSLS, in this case using a 120° curved PSD to study the dehydration reactions of the natural zeolites scolecite and mesolite with a time resolution of 5 minutes (Ståhl, 1994). These experiments revealed information on the dehydration temperatures, the order in which water molecules are expelled, phase transitions and also gave some qualitative kinetics information.

4. THE CURRENT PERFORMANCE OF TIME RESOLVED STUDIES AT ISIS

4.1 The Present Capabilities of Polaris

The experience gained thus far at ISIS has not only yielded high quality scientific results, as illustrated in the experiments on Polaris described above, but also has enabled some difficulties and potential problems to be identified. For most of these the solutions are simple, requiring only minor extra thought before commencing the experiment, or the acquisition of appropriate, more specialised equipment.

4.1.1 Sample Environment Performance

During the thermodiffraction experiments, furnace temperature ramps were all achieved via VMS command files running on the Polaris FEM. This meant that the ramp rates produced could vary intermittently, especially if the FEM was being used intensively. Furthermore, some trial and error was required to determine the actual waiting time required between successive increments of the temperature setpoint. Much more convenient would be the provision of temperature controllers which may be programmed with the desired temperature regime (temperature ramps, holds, etc.). Also, some problems were encountered with the setting of PID's for different temperature ranges, causing serious temperature overshooting and oscillating. Provision of so-called "intelligent" temperature controllers, capable of determining PID's automatically, may help to alleviate these problems. However, the PID's can be strongly sample dependent and calibration runs may still be required in order to determine the optimum values.

The RAL furnaces operated satisfactorily at most temperatures of interest during these experiments (up to 1240°C at present) with only minor modifications required, such as the replacement of type K thermocouples with type W5 above for temperatures 1100°C. The poorest performance was observed at temperatures only slightly above ambient, up to ~200-300°C, where the occurrence of temperature gradients in the furnace elements (as indicated by different readings from thermocouples located in different regions of the furnace "hot zone") and problems with temperature overshoot could be severe. With the large thermal mass of the present RAL furnaces, this problem is, perhaps, inevitable for lower temperatures, and some other mechanism for heating samples will be required for work in this temperature regime.

Improvements required for experiments at elevated temperatures, but which would also be of relevance to experiments at ambient temperature, include the construction of a furnace centre stick capable of providing some form of atmosphere control. This would entail a sample can assembly with the facility to pass gasses around the sample. Attention will have to be paid to the choice of metals used in construction of the can because of possible reactions between gas and sample can at elevated temperatures, e.g. H embrittlement of V and Ti. This development is in progress, with a sample stick currently being designed which it is hoped to begin commissioning during 1995.

4.1.2. Instrument Performance

Perhaps the most serious potential instrument problem arose with the time taken by the Polaris instrument computer (FEM) and data acquisition electronics (DAE) to end one run and begin another. This could take as long as 2½ minutes, a very significant period of time when data collection times are of the order of 5 minutes, as in the zirconium hydroxide calcination experiments. The reasons for this length of time are twofold: firstly the data files are large, ~8Mbytes of data for the default Polaris DAE setting of 306 spectra and 6506 time channels, and secondly the Q bus transferring the data from the DAE to the FEM is inherently slow.

There are several ways of tackling this problem. The most convenient method, at present, is to reduce the amount of data to be transferred by reducing either the number of time channels, the number of spectra or both. Where resolution is not a consideration it is perfectly feasible to increase the width of the time channels, thereby decreasing their number; where data are required from only a small number of detectors those not required can be excluded by the instrument software.

A second option is to eliminate the repetitive beginning and ending of runs through the use of periods within the DAE. This involves accumulating several data sets, each of which may have been collected under different sample environment conditions, into consecutive blocks, or periods, within the DAE memory (and, afterwards, in the raw file). During a run the changeover from one period to the next is instantaneous, but beginning and ending it will take much longer because of the need to initialise larger areas of DAE memory before commencing data collection and the larger quantity of data to be written to the raw file at the end of the run. These delays can be minimised by being timed to take place during times when data collection is not required. Although the use of periods is elegant, the maximum number available is limited by the size of the DAE memory and may well be insufficient for many experiments.

A third option is to let the DAE hardware and/or software map all the detectors in a bank into just one spectrum in the raw data file: so-called "electronic time focusing". The characteristic resolution function of time-of-flight diffraction at pulsed spallation neutron sources, where $\Delta d/d(=\Delta t/t)=constant$, combined with the data collection strategy on Polaris, where the time-of-flight limits of the time channel boundaries are defined such that $\Delta T/T=constant$, means that time focusing can be achieved through a simple register shift between individual spectra (David and Jorgensen, 1993). Such a facility is not presently available on Polaris, but will be possible on the replacement for the current DAE, DAE-II. Nevertheless, care may still need to be taken to ensure that the time focused count rate does not overload the electronics.

A final option is to use a faster data bus, with the use of a SCSI interface between the DAE and VAXstation 3200 instrument computer currently being investigated at ISIS. Potentially, this can increase the speed of data transfer from DAE to raw file by a factor of between 2 and 4, although some modification of the SCSI control software may be necessary.

A SCSI interface will be used to transfer data between DAE-II and the DEC alpha computers, which will replace the current VAXstations as instrument FEM's. DAE-II will offer several advantages over the current DAE in terms of data collection strategy. It will permit electronic time focusing, discussed above, and will be much

more flexible in the generation of time channel boundaries, allowing time channel widths in different detector banks to be matched to the resolution characteristics of that bank. Both these factors will serve to reduce the total number of time channels and, hence, the size of the raw data file.

The count rate on Polaris has proved suitable for the time resolved experiments attempted thus far, but this may be because the experiments carried out to date have been planned around the count rate presently available. Obviously it is easier and cheaper to improve count rates by increasing detector coverage than by increasing the flux from the source (whether a reactor or spallation source). The design of Polaris does allow for additional detectors to be installed with a view to further increasing the count rate. At back scattering angles, it is feasible to place detectors above and below the horizontal plane, in effect completing (partially or fully) the Debye-Scherrer cones. Attention would need to be paid to the contribution of such detectors to the overall detector bank resolution, because the $\Delta\theta$ and ΔL terms in the resolution function will be larger due to the staggered alignment of sample and detector axes.

Some of the most recent experiments on Polaris have made use of the long d-spacing data collected by the very low angle detector banks. In one of these experiments, a time resolved investigation into the sequence of phase formation in the Bi-Sr-Ca-Cu-O system during recrystallisation of melt cast samples, diffraction patterns were collected every 5 minutes while the cylindrical sample, 80mm long by 5mm diameter, was heated by passing a direct current through the rod (Bhakta *et al*, 1995). An important part of data analysis was the identification of several of the recrystallised phases from their $00l$ reflections at characteristic d-spacings of between 10 and 20Å. However, the count rate in the long d-spacing detectors is much lower than in the other three Polaris detector banks, and this reduced the accuracy and precision with which the minor phases could be determined. It is, therefore, vital that the count rate in these detector banks is improved through the installation of two additional ZnS detector modules which are available at ISIS.

Because the count rate is also very much dependent on the sample mass, as much sample as possible should be used, while also considering the resolution and thermal equilibration requirements. The dimensions of the Mg-PSZ samples used in the ageing kinetics experiments could be as large as the Polaris incident neutron beam (and for some samples were) because any degradation in instrumental resolution was insignificant when compared with the reflection broadening caused by particle size and strain effects in these multiphase ceramic samples.

4.2 Immediate Requirements

The discussion above has highlighted several areas where significant improvements in the current performance of time resolved experiments at ISIS can be made with only minor expense. These can be summarised as follows.

1. Programmable, rampable "intelligent" temperature controllers to provide more flexible and accurate sample heating regimes.
2. A furnace is required which can provide reliable thermal stability, without significant overshoot at moderate temperatures (50-250°C).

3. Atmosphere control within furnaces. For example, it may be desirable to control accurately oxygen and/or water partial pressures during experiments on geological systems. This may be easily achieved through the construction of specialised centre sticks for RAL furnaces.
4. Reduce the time taken to begin and end runs. Options include reducing the amount of data, increasing the data transfer rate and the use of periods. DAE-II can offer solutions to all of these options.
5. Improve the count rate by increasing detector complement, completing the Debye-Scherrer cones, especially at back scattering and at very low angles.

5. THE FUTURE POTENTIAL FOR TIME RESOLVED STUDIES

5.1 New Instruments

With the impending move of Polaris to the N7 beamline at ISIS during 1996, the opportunity ought to be taken to improve the performance of the instrument for time resolved experiments. Most importantly in this respect, the new beamline should be designed such that it can accommodate an increase in the back scattering detector complement, should additional detectors become available. These would be more efficiently used to cover a larger portion of the Debye-Scherrer cones rather than extend the angular range of the present bank. Also as part of this move, the existing 90° detector banks are to be replaced with new detectors which will increase the solid angle and improve the count rate, with the current 90° detectors being relocated either side of the new detectors in the horizontal plane to allow studies of texture during high pressure experiments. Finally, as shown in the recent Bi-Sr-Ca-Cu-O recrystallisation experiments, an increase in the long d-spacing ZnS scintillator detector complement would be very beneficial.

Also in the short term, the construction of the new D20 diffractometer at the ILL will provide another weapon in the armoury of instruments available for time resolved powder diffraction experiments. The detector being built for this diffractometer is a 1600 element curved PSD which will cover a much greater angular range (160° in 2θ) than the detector on D1b. Once completed, this detector will improve further the count rates available, while at the same time accessing a wider d-spacing range, thus increasing the amount of information able to be extracted from each diffraction pattern.

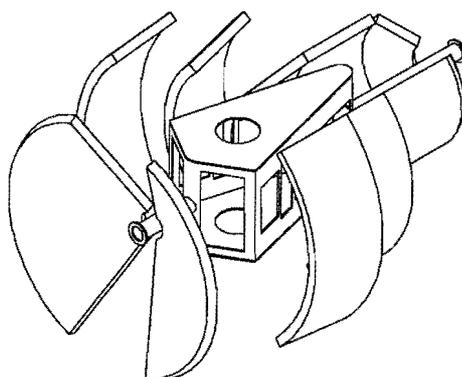


Figure 7. Schematic diagram of the proposed GEM diffractometer showing the multiple detector banks having a total detector area of 10m².

GEM (the GEneral Materials diffractometer) is a new powder diffractometer suitable for powders and liquid/amorphous materials which it is hoped to build at ISIS, and for which funding is currently being sought. GEM, figure 7, will have a 17m incident flight path, a total detector area of 10m² and will view a methane moderator,

resulting in an improved resolution and count rate in all detector banks compared with the current Polaris diffractometer. The count rates in each detector bank on GEM will be more closely matched and the resolution of a bank will be tailored to the d-spacings measured. Obviously with such a large detector area, consideration will have to be given to the efficient collection and storage of the diffraction data, such as will be possible with DAE-II.

Without a doubt, the GEM diffractometer will provide an exciting opportunity for extending the scope of time resolved and kinetic studies, reducing the time scales over which changes can be monitored and allowing more complex systems to be studied.

5.2 New Sources

With the construction of the European Synchrotron Radiation Facility, ESRF, at Grenoble even more intense beams of X-rays are now available for condensed matter research. There are several powder diffraction stations either in operation or in the planning and construction stages at the ESRF, and included in these will be diffractometers optimised for time resolved experiments, using both angle dispersive and energy dispersive detection techniques.

Finally, in the foreseeable future, reactor neutron sources are unlikely to improve on the neutron flux generated at the ILL by much more than a factor of 2-5. Therefore, it would seem that the future for increased neutron fluxes will lie in pulsed spallation sources. Presently under consideration, the European Spallation Source, ESS, is planned to be 30 times brighter than ISIS, with a time averaged neutron flux equal to that of the ILL but with a peak flux 40 times greater (Taylor *et al*, 1992). The design of the ESS will pay particular attention to matching neutron pulse widths, repetition rates and moderator performances to individual instrument requirements.

Optimising the design of instrumentation for kinetic experiments at a dramatically more powerful source such as the ESS will require exploitation of the experience being accumulated both now and in the immediate future. The improvements to Polaris and future assessment of the performance of GEM, while naturally tailored to allow the expansion of the current scientific program in the area of kinetics, will also lead to a better understanding of the imperatives in the design of optimised instrumentation at new sources.

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