

PROFILE REFINEMENT OF NEUTRON POWDER DIFFRACTION PATTERNS

A. W. Hewat

Institut Max von Laue - Paul Langevin

156X Centre de Tri, 38042 Grenoble

France

The refinement of crystal structures directly from neutron powder diffraction patterns, without first extracting the structure factors, has become an important crystallographic technique in the ten years since Rietveld first introduced it. This profile refinement technique is related to, but different from, the line profile analysis techniques developed even earlier for x-ray powder diffraction. In this paper we first follow the contributions made by Rietveld and others by reviewing the applications of profile refinement to specific types of problems in solid state physics. Starting with magnetic structures, profile refinement was quickly adopted for studies of uranium halides, phase transitions, hydrogen bonding and disordered structures, especially ionic conductors. It has removed many of the limits imposed on classical crystallography by the availability of suitable crystals, extinction, twinning and different sample environments. In fact, it is equally easy to study the solid structure of materials which are normally gases or liquids. With this historical and applications background, we then examine the technique itself in more detail. The correct choice of weights, the use of molecular constraints and Fourier synthesis, the best description of thermal motion for individual atoms and rigid molecules, are all subjects still being debated, although a working consensus does exist. Improvements are also being worked out for the description of the line shape, the background contribution and the effect of absorption. We then turn to the existing experimental techniques, emphasizing the need for high resolution diffractometers, efficient multidetectors and focussing monochromators to give a wide choice of neutron wavelengths. The sample preparation and environment are seen to be simpler than for x-ray powder diffraction, large cryostats, furnaces, and pressure cells can be accommodated in a routine way and since the sample itself is much

larger, preferred orientation is a very much less serious problem. Finally, we mention some of the new experimental techniques being developed, especially the use of high efficiency multidetectors, and intense pulsed neutron sources for time-of-flight diffractometers. We do not believe that these new developments will produce the same kind of revolution that profile refinement did. Rather, we expect the continued improvement in resolution, intensity, and computing techniques to extend the application of neutron powder diffraction to even more fields in solid state chemistry and physics. Such work will be increasingly concentrated at a few large national or international centers open to a wide community of users.

1. Line Profile Analysis and Rietveld Refinement

Interest in powder diffraction profiles is not new. Long before neutron powder diffraction became important, x-ray line profiles were being studied in detail [1]¹. Similar techniques of line profile analysis, though less widely known, have been described for single crystal data [2]. When computers became available, they were applied to x-ray line profile analysis, and this technique can now be used automatically for on-line experiments with a cycle time of the order of seconds [3]. Indeed, cycle times of the order of milliseconds may soon be expected for the study of the chemical kinetics of catalytic surfaces, the electrolysis of battery electrodes etc. [4].

What then is different about the Rietveld Type of profile refinement? With profile line analysis, the emphasis is still on treating single lines or groups of lines to extract the positions and intensities of their components. With the Rietveld technique, the crystal structure itself is refined to fit directly the complete diffraction pattern. There is no intermediate step of extracting intensities or structure factors. This does not mean that the standard crystallographic techniques, such as Fourier synthesis of the crystal structure, are not available [5]. However, it does mean that a starting model for the structure is necessary, and the Rietveld technique is of no use for direct methods of structure solution. An intermediate type of profile refinement is needed if such a starting model is not known.

To understand the differences between profile line analysis and Rietveld profile refinement, it is first necessary to understand some of the difficulties with the former. The Rietveld technique is an effort to circumvent these difficulties. Both techniques are of most value when the powder diffraction lines are not all completely resolved; otherwise integrated intensities can be used for the structure analysis, and profile refinement is really only useful for improving the precision of the measurements of peak positions and hence of the crystal cell dimensions.

¹Figures in brackets indicate the literature references at the end of this paper.

With profile line analysis, one attempts to fit a group of overlapping lines with a function which is the sum of a number of individual lines. Obvious parameters are the positions and intensities of each of the individual lines, but one might also need additional parameters describing the background level and line shape as a function of the scattering angle. With x-ray powder diffractometers, the line shape in particular, may be a very complicated function (e.g., see [1]). Then, we need 2-4 parameters for each line in the diffraction pattern, which might contain up to 10^3 lines for the complete scan. If we are not to have an impossibly large number of parameters, we must identify distinct parts of the scan separated by regions where no lines contribute: these parts can then be treated independently, at least for a given cycle of refinement. The problem of finding such independent groups of lines is less serious for high resolution x-ray studies of inorganic compounds, but becomes virtually impossible for more complex organic structures, especially with relatively low resolution neutron diffractometers.

Apart from the number of parameters, and the need for regions where no lines contribute, the line profile analysis technique suffers from the problem of correlation between parameters. For example, for two closely spaced lines, there will be a strong correlation between the widths and positions (separation) of the lines: there are similar problems if one attempts to refine the background for a complex pattern containing only small regions where no lines contribute. For these reasons, the background levels are usually fixed at "reasonable" values, and an attempt is made to find a function which will also fix the shape of all the lines. This is not easy, because both background and line shape are both sample dependent, and cannot be measured once and for all for a given diffractometer. Even if this were possible, there would remain twice as many parameters as there are diffraction lines, and correlation would still exist between the different line positions and intensities.

The Rietveld technique drastically reduces the number of parameters, and new parameters are directly related to physical quantities. All of the line positions are determined by the unit cell dimensions (at most six parameters) and the line intensities are no longer independent, but are determined by the crystal structure itself. There is no longer any need to break the pattern into groups of lines and groups of parameters; indeed, the best results are obtained when all of the structural parameters are simultaneously refined to fit the complete diffraction pattern (profile). There are then only about 10^2 parameters for the 10^3 lines of the complete scan.

2. Applications of Neutron Powder Profile Refinement

2.1. Magnetic structures

Neutron profile refinement, in the Rietveld [6,7] sense, predated its application to x-rays by a decade. For some years, most other laboratories neglected the work at Petten, which was concerned largely with a rather special field of study, magnetic structures, which have little interest for x-ray crystallographers. Even neutron diffractionists

tended to discredit the use of powder diffraction for magnetic structures, since it was well known [8] that for high symmetry structures, as most commonly studied, some information about the nuclear spin orientation is irretrievably lost when the crystal is powdered. As well, powerful single crystal techniques for magnetic structures depend on applying magnetic fields in a specific crystallographic direction, and in using beams of polarized neutrons and measuring the difference in scattering for different relative orientations of polarization and crystal axes [9].

Such techniques lose much of their force with the random orientation of crystal axes in a powder. Powder diffraction, though most important in the early days of neutron crystallography, had come to be regarded as a poor man's alternative to these new single crystal techniques which had been made possible with the advent of high flux reactors.

However, much valuable work was accomplished in these early years at Petten on materials for which single crystal work was difficult for various reasons [7].

Similar early studies were taken up at Kjeller (Norway) with work by Andresen and van Laar [10] on the magnetic structure of Fe_3Se_4 , and by Holseth, Kjekshus, and Andresen [11], on FeSb_2 and the magnetic transition in CrSb_2 . In the following years, Andresen and his colleagues remained an important group of users of the Rietveld technique for mainly magnetic structures.

2.2. Uranium halides

It was not, however, until 1973 that most other neutron diffraction laboratories took an interest in profile refinement. Taylor and Wilson [12,13] using their own profile refinement program, adapted from the ORFLS single crystal program, extended the work of Loopstra and Rietveld [14] on uranium oxides to halides such UCl_4 and UCl_6 . The interest in uranium compounds was of course mainly due to their importance in the nuclear research projects at Petten (The Netherlands) and Lucas Heights (Australia). Such halides are often volatile, corrosive, hygroscopic and unstable, and thus very difficult to study using normal crystallographic techniques. The early achievements of Zachariasen [15], who succeeded in obtaining the correct structure for UCl_6 and many other such halides with milligram samples, must be regarded as an uncommon "tour de force." With powder profile refinement, Taylor and Wilson not only achieved more precise structures for many of these materials at low temperature, but demonstrated the transformation of some, such as MoF_6 and WF_6 to plastically crystalline phases, with rotations of the halide octahedra before the crystal actually melts.

2.3. Phase transitions in perovskites

Phase transitions were also being studied at Harwell at this time, using neutron profile refinement. Perovskite ferroelectrics, such as KNbO_3 and BaTiO_3 undergo a series of phase transitions to lower symmetry structures as the temperature is lowered. It is

very difficult to obtain single crystals of such materials, since the crystal usually shatters or becomes multiply twinned on passing into the lower symmetry phase. Even though such transitions involve very small displacements of the atoms ($\sim 0.05 \text{ \AA}$), the neutron powder diffraction patterns look quite different for the different phases (fig. 1) and the structures can be readily obtained from profile refinement [16a]. In this case, there were stringent checks on the correctness of the results. Not only could the higher symmetry phases be compared with careful single crystal measurements, but the low symmetry structures could be used to calculate the spontaneous electrical polarization of these ferroelectric materials; these calculations compared exceptionally well with macroscopic measurements. Many such ferroelectric and antiferroelectric phase transitions have been studied since [16b]. With the ILL high flux reactor, complete data sets can be obtained for many different temperatures in a short time. The temperature dependence of the order parameter in the antiferrodistortive material KCaF_3 has thus been studied [17]. The results are in excellent agreement with NMR measurements in the tetragonal phase, and a quantitative relation has been found between the temperature dependence of the order parameter, the lattice dimensions and the anisotropic Debye-Waller factors.

2.4. Phase transitions in inorganic materials

Structural phase transitions are really quite common in many "ordinary" materials. The "crystal structure" usually reported at standard temperature and pressure may not then represent the true equilibrium structure, but only an approximation. The real crystal structure must be determined near absolute zero temperature and although this presents difficulties for conventional techniques, there is no special problem with neutron powder methods. Temperatures of millikelvins are even possible, but the boiling point of liquid helium is usually sufficiently low for most structural studies.

For example, Pb_3O_4 undergoes a subtle phase transition at 170 K in which the splitting of the diffraction lines is only visible on a high resolution diffractometer. Gavarri, Weigel and Hewat [18] have shown, by profile refinement of neutron powder data, that the transition occurs because of the opposition between Pb^{2+} ions, the Pb^{4+} and O^{2-} ions playing no part. The structure simply contracts when the temperature is lowered, and at 170 K, the Pb^{2+} ions come into contact: there is then a shearing of the structure to avoid a too close contact.

Such phase transitions represent very small changes of the structure: atomic displacements are a fraction of an angstrom unit. However, relatively large changes result in the diffraction pattern, which is clearly very sensitive to any splitting of the lines. With a line resolution of $\Delta d/d \sim 10^{-3}$, even changes ten times smaller have a noticeable effect.

BiVO_4 is an example of a large group of so called "ferroelastic" materials, where the direction of polarization can be changed by some (often small) external stress.

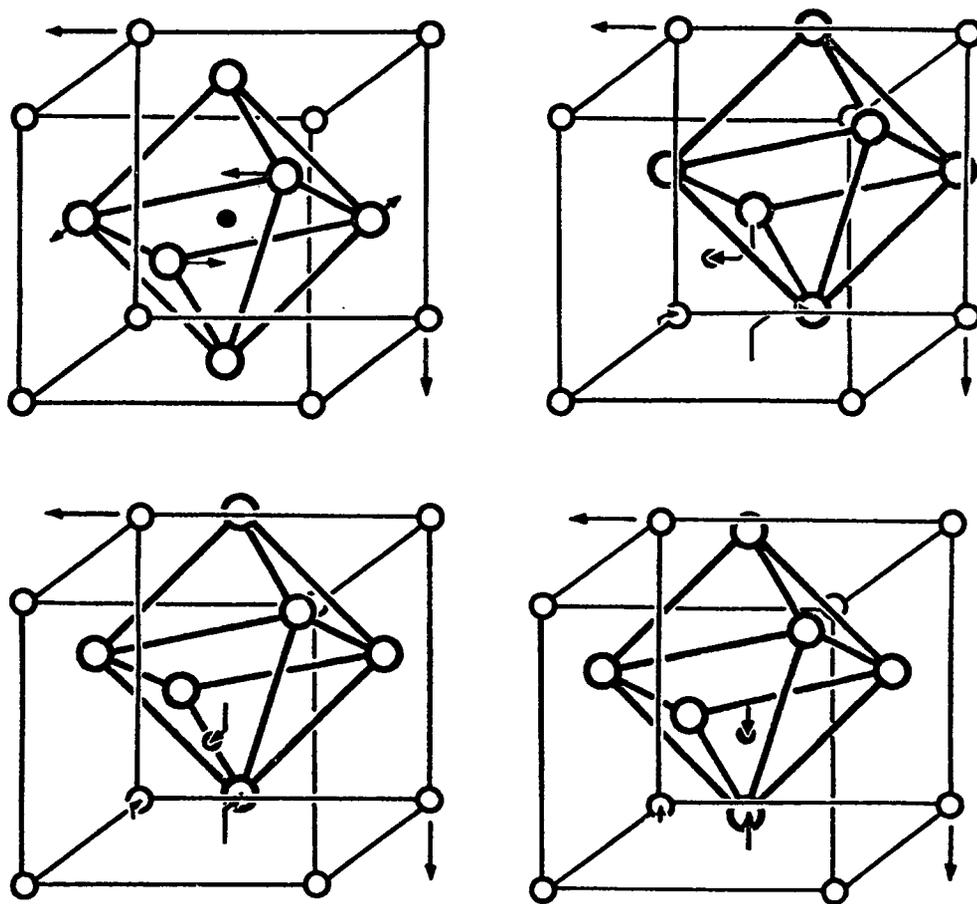


Figure 1. Successive phase transitions occur in most perovskite ferroelectrics. Neutron powder profile refinement has been used to study many such materials.

David, Glazer and Hewat [19] have shown how the bismuth atoms and the rigid VO_4 tetrahedra move along the c-axis to produce this polarization; as the temperature is lowered, the crystal enters the ferroelastic phase at 255 °C. The data is sufficient to resolve even the position of the vanadium atom, which has an unusually weak scattering length for neutrons.

A number of other ferroelastic materials have been studied by Glazer, and also by Hidaka using profile refinement (e.g., see [20]).

2.5. Hydrogen bonds and phase transitions

Phase transitions in hydrogen bonded materials have also been studied for some time using neutron powder diffraction. For example, in $\text{NH}_4\text{H}_2\text{PO}_4$ [21] single crystals are

destroyed on passing into the low temperature phase, which is antiferroelectric in contrast to the ferroelectric structure of the potassium isomorph KH_2PO_4 [22]. This difference was shown to arise because the new hydrogen bonds between the NH_4 and PO_4 groups in $\text{NH}_4\text{H}_2\text{PO}_4$ force the H_2 atoms to take up an alternative hydrogen bonding arrangement, which is apparently less favorable in KH_2PO_4 . More recent measurements on $\text{NH}_4\text{H}_2\text{PO}_4$ [23] are sufficiently precise to allow a detailed interpretation of the anisotropic temperature factors obtained from profile refinement (fig. 2). We notice immediately that above the phase transition both the NH_4 and PO_4 groups are librating strongly. It is remarkable that the major axes of the thermal ellipsoids, although not constrained to lie in any particular direction, refine to be perpendicular to the bonds, as required for rigid body librations. The disordered 0..D..0 bonds appear to be significantly nonlinear, with the two half deuterium positions displaced from the line joining the oxygen atoms. This is not the correct interpretation; the two PO_4 groups are no doubt librating 180° out of phase, synchronized with the motion of the D atom in its double well. The O-D..0 or 0..D-0 bond can be linear at any given instant: the 1/2 D positions do lie on the line joining the opposite extremities of the O ellipsoids. The ND_4 ellipsoids show strong libration plus vibration along y, so as to make and break the N-D..0 hydrogen bonds: this motion must also be synchronized with that of the PO_4 and D groups. Then, instead of the simplified picture of hydrogen bonds tunneling between two minima of a double well potential, which is the classical picture of H-bonded ferroelectrics, we can see that the true "soft-mode" involves all of the atoms, coupled in a more complex collective oscillation. The transition mechanism can be more easily visualized by viewing the 5 K structure on top of that at 300 K.

This example illustrates the utility of using a complete description of the thermal motion, and indicates the potential of profile refinement for studying structures as a function of temperature.

2.6. Disordered structures

After 1973, an explosion of papers on neutron profile refinement occurred, as summarized by Cheetham and Taylor [24]. In one of the first, Cheetham and Norman [25] refined the structures of YF_3 and BiF_3 from data collected at Harwell. The group of Fender in Oxford applied the technique to many of the problems in chemical crystallography that they had already pioneered using classical neutron powder techniques [26,27,28].

In particular, the technique was applied to disorder configurations in non-stoichiometric oxides and hydrides. For example, Titcombe, Cheetham and Fender [29] repeated and extended their earlier conventional powder diffraction work on hydrogen ordering in $\text{CeD}_2 + x$ [30].

Also at Oxford, Von Dreele and others applied profile refinement to large disordered structures made from simple blocks of titanium, niobium and germanium oxides [31]. These block structures are best known from the x-ray work of Wadsley [32] and especially the

PHASE TRANSITION IN $\text{ND}_4\text{D}_2\text{PO}_4$

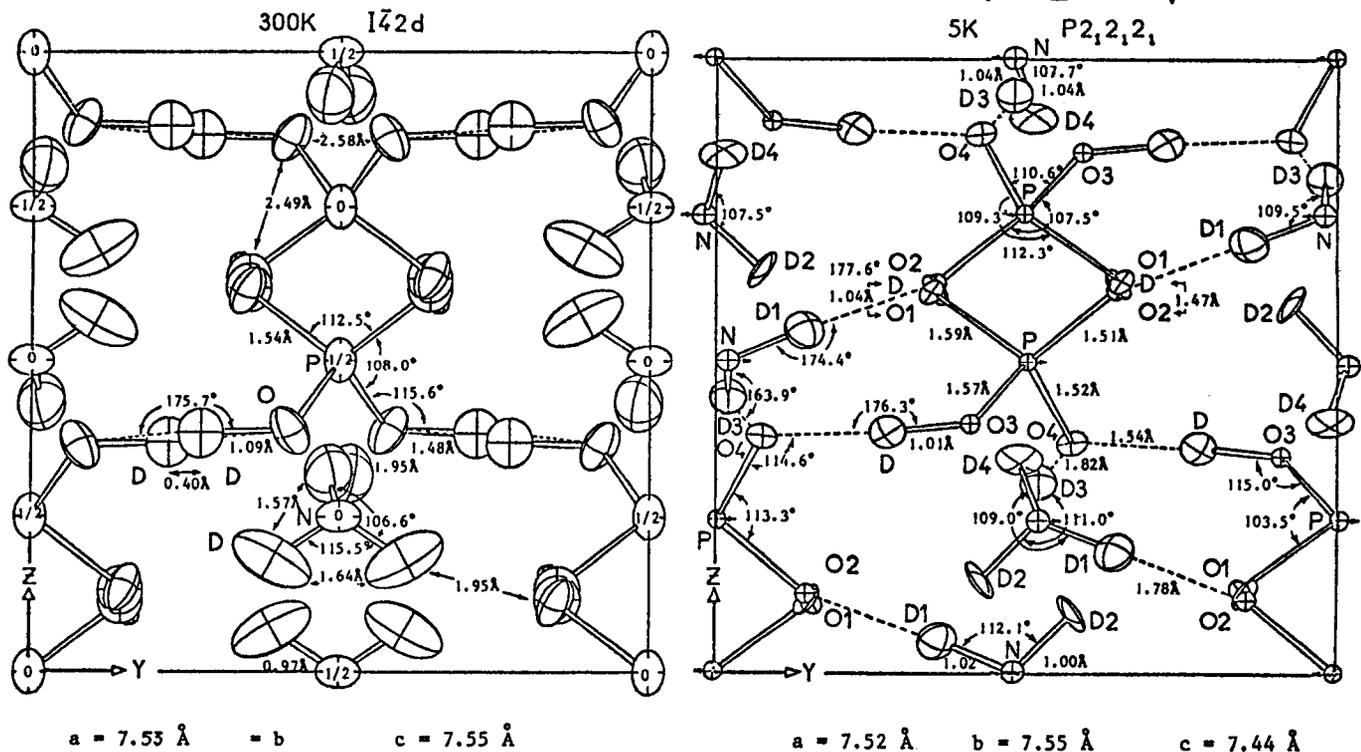


Figure 2. Ammonium dihydrogen phosphate is an example of a more complex type of phase transition studied by profile refinement.

electron diffraction lattice imaging technique developed by Allpress [33] and others (see Cowley and Iijima [34] for references). The characteristic feature of such structures is usually the regular array of defects joining large blocks of perfect order. Anderson, Bevan, Cheetham, Von Dreele, Hutchison, and Strähle [35] therefore had recourse to these latter techniques to interpret their profile refinement results for germanium niobium oxide.

In all of these non-stoichiometric problems, one attempts to refine the occupancy of the various sites, and the danger is the correlation to be expected with the Debye-Waller factor. One needs very good data, and even then a knowledge of the average occupation may be difficult to interpret in terms of the detailed crystal structure.

2.7. Fast ion conductors

Structures showing partial occupancy are, however, of increasing importance for the study of ionic conductors, and powder diffraction can make an important contribution here, provided the proper precautions are taken. Wright and Fender [36] studied the phase transition in which AgI becomes a conductor for Ag^+ ions. England, Jacobsen and Tofield [37] showed that the hydrogen atoms in deuterated β -alumina, which are bonded to the oxygen atoms at 4.5 K, become available for ionic conduction at 823 K. A more detailed

account, in which Fourier techniques are used to examine the hydrogen distribution at high temperatures, is given by Tofield, Jacobsen, England, Clarke, and Thomas [5].

Bogacz, Bros, Gaune-Escard, Hewat, and Taylor [38] showed that in the ionic conductor Na_2UBr_6 , the sodium ions are freed at two successive phase transitions. Hewat [39] has measured the complete structure of Bi_2O_3 at six temperatures from 300 K through the "super-ionic" phase transition at 1000 K, where the oxygen ions become distributed over incompletely occupied holes. The intermediate phase previously reported on lowering the temperature, was not found when the sample was prevented from taking up additional atmospheric oxygen.

2.8. Location of hydrogen atoms

Just as neutron diffraction is of value for studying heavy atom structures, such as those of uranium, it is invaluable for the location of very light atoms such as hydrogen. The scattering power for neutrons is of the same order for most elements, and not proportional to the atomic number, as it is for x-rays. In addition to those quoted under earlier headings, the following example may be noted.

Some materials absorb so much hydrogen that they are known as "hydrogen sponges", and since this has possible applications for energy storage, work is currently under way to study the mechanism of such absorption using neutron powder diffraction. Earlier studies of hydrogen in metals using neutron profile refinement include the work of Kuijpers and Loopstra [40].

Sodium per carbonate ($\text{Na}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}_2$) is a well known industrial bleach, which is an unusually stable vehicle for hydrogen peroxide, or active oxygen. Adams, Pritchard, and Hewat [41] have determined the precise hydroxide configuration in this material, which is disordered at room temperature but transforms to an ordered structure at low temperatures. Other perhydrates, such as those of the oxalates of potassium and rubidium (Adams, Ramdas and Hewat, [42] have also been studied in the same way. In such materials, where much of the structure is already known from x-ray methods, the difference Fourier technique applied to neutron powder data immediately reveals the hydrogen atom positions.

2.9. Solid liquids and gases

The crystal structure of materials which are normally liquids or gases can most easily be studied using powder diffraction. Sandor has studied the phase transitions in simple molecular solids in this way, (e.g. see ref. [43]). Solid ammonia is another example which is ideal for studying the dynamics of such materials, and one may ask if the

ammonia molecules in the solid undergo hindered rotation as they do in many salts such as NH_4NO_3 [44].

As an aid to the study of the molecular dynamics of ammonia, the solid was examined by neutron profile refinement as a function of temperature between 2 K and 180 K [45]. No phase transition was found, but even near absolute zero temperature, the ammonia molecule is librating strongly. The amplitude of libration does not increase with temperature as quickly as required for a purely harmonic model, and this suggests a possible quantum mechanical tunneling between the hydrogen sites.

Solid oxalic acid [46] and acetic acid [39] are being studied by profile refinement at low temperature to investigate the possibility of "resonance" structures in which the C-O and C=O bonds become equivalent above a certain transition temperature, with disordering of the hydrogen bonds.

3. Profile Refinement Theory

3.1. Basic principals

All types of profile refinement can be justified by the following simple arguments [47]. Suppose that the count $y_i(\text{obs})$ at the point i in the diffraction pattern is a sample of some model function $y_i(\text{calc})$. In the case of line profile analysis, this model function is the sum of the profiles of all of the individual lines; with the Rietveld method, these individual line profiles are calculated directly from the crystal structure model. Then the probability p_i that a given sample count $y_i(\text{obs})$ will differ from $y_i(\text{calc})$ is given by

$$p_i \propto \frac{1}{\sigma_i} \exp \left\{ - \frac{\frac{1}{2} [y_i(\text{obs}) - y_i(\text{calc})]^2}{\sigma_i^2} \right\}$$

since each sample count comes from a normal (exponential) distribution centered on $y_i(\text{calc})$, with standard deviation $\sigma_i = \sqrt{y_i(\text{calc})}$. The probability P that all of the counts are samples of the population $y(\text{calc})$ is the product $\rho_i p_i$ of the individual probabilities. Then

$$P = \prod_i p_i \propto \left\{ \exp - \frac{1}{2} \sum_i \frac{[y_i(\text{obs}) - y_i(\text{calc})]^2}{\sigma_i^2} \prod_i \left(\frac{1}{\sigma_i} \right) \right\}$$

since the product of exponentials p_i is the exponential of the sum of the separate exponents. The probability P is maximized if the exponent factor

$$\chi^2 = \sum_i \omega_i [y_i(\text{obs}) - y_i(\text{calc})]^2$$

is minimized using the weighting scheme $\omega_i = \frac{1}{\sigma_i^2} \approx \frac{1}{y_i(\text{calc})} \approx \frac{1}{y_i(\text{obs})}$.

It should be noted that the statistical weight is of course calculated from the raw data before subtracting the background. Since the background is a smooth function obtained from the average of many points, the statistical error introduced by the background subtraction is usually neglected, as in single crystal measurements. However, 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 for the crystal structure.

The "R-factor" χ^2 is well known in statistics. 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. Given χ^2 , the number of observations i , and the number of parameters used to minimize χ^2 , then one can consult a table to determine the probability that the model is correct. In practice, we calculate the χ^2 expected if the model were exact, and if the fluctuations in $y_i(\text{obs})$ were purely statistical. The χ^2 obtained by refinement will always be larger than this, but will approach the ideal value as systematic errors in the data or the model are eliminated. The R-factor for integrated intensities is also calculated at the end of the refinement, after dividing each $y_i(\text{obs})$ between the contributing lines according to the calculated intensities. This R-factor is twice the R-factor for structure factors usually quoted by crystallographers.

3.2. The weighting scheme

The weighting scheme used for profile refinement, derived 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 such systematic errors, a purely statistical scheme can also be used for single crystal measurements. Sakata and Cooper [48] propose that the weight for an integrated Bragg reflection should then be inversely proportional to the integrated intensity, just as it is inversely proportional to the intensity for profile refinement. With this assumption, they then go on to show that the calculated standard errors are different for the same data treated by profile

refinement or by refinement on 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 assumption and conclusion are not.

In fact, each count $y_i(\text{obs})$ is an independent estimate of the integrated Bragg intensity; simply adding together these counts does not give the best possible estimate of the integrated intensity, but only an approximation which is not even very good for weak peaks on a high background. The idea of making the weight inversely proportional to this integrated intensity is again an approximation which takes no account of the fact that a number of independent, but not equally good, estimates (a step scan) was made of a function which we know to be a peak. Nor is it possible to argue that the observations are not independent estimates, because they all come from the same Bragg peak, nor to argue even that the Bragg peaks are not independent because they come from the same structure. Here we are concerned only with the notion of statistical independence.

Sakata and Cooper have then correctly demonstrated that, given these approximations, the calculated errors are not the same for the integrated intensity refinement as for profile refinement. They correctly attribute this to the different weighting scheme used, especially for weak reflections. However, the correct conclusion should be that profile refinement must be used for single crystal data, as was shown long ago by Diamond [2].

3.3. Constrained profile refinement

The principals developed above apply to all types of profile refinement: only the parameters are different with different methods. With line profile analysis, we assume nothing at all about the structure; in fact this technique is especially useful for a preliminary analysis of unknown structures or even mixtures of unknown materials.

The positions and strengths of the strong lines can be obtained automatically and compared with a computer file to identify the components. However, if a model structure is 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 and improving the result of the structure refinement. Intermediate types of refinement can also be envisaged. For example, the positions of the first few lines might be obtained by line profile analysis, these lines indexed using one of the computer programs now available [49], and then a new profile refinement attempted in which the parameters were just the lattice constants and the line intensities. This should have some of the advantages of the Rietveld technique in removing parameter correlation without the need to know the details of the structure, which could then be obtained from standard crystallographic techniques and perhaps even direct methods.

This intermediate profile refinement and the Rietveld refinement, can be regarded as constraining the basic line profile refinement to give results consistent with some additional knowledge--first of the unit cell, and then of the structure itself. We can go even further; if we assume that some components of the structure are rigid units, we need

then only refine the positions and orientations of these units as a whole. A simple example, which is already possible with the Rietveld program, is the well known rigidity of the oxygen octahedra in most perovskite oxides [47]. These additional constraints again reduce the number of parameters and the correlations between them.

Pawley, Mackenzie and Dietrich [50] have written a new profile refinement program designed to exploit the full power of such constraints, which Pawley [51] has already developed for single crystal refinements. He has shown that in many molecular crystals, the molecules, or at least parts of them, can be constrained to move as rigid units. This greatly simplifies the refinement, which can then give useful results for quite complex structures, using only the relatively small amount of information contained in a powder pattern. These developments will no doubt increase the upper limit on the size of the structure that can be treated with powder diffraction, now estimated to be a monoclinic cell of volume up to 3500 \AA^3 [52].

Such constrained refinement techniques are also of value in studying the behavior of materials under different conditions of temperature and pressure. Often, it is only certain features of the structure which are changed; for example, one molecule sliding over another, or a rigid unit rotating to accommodate new crystal stresses. Once such features are identified, only the appropriate parameters need to be refined at each temperature or pressure.

3.4. Thermal motion and anisotropic Debye-Waller factors

Rietveld [7] worked with normally stable structures, often at low temperatures to study magnetic ordering. He used rather long wavelength neutrons (2.4 \AA) for reasons of resolution and intensity [53] and therefore obtained data of limited range in $\sin\theta/\lambda$. Under these conditions, isotropic Debye-Waller factors, or even an overall temperature factor, was sufficient. When the profile refinement technique was applied to other problems, especially those involving structural phase transitions, these approximations were no longer sufficient. A phase transition occurs because a structure is basically unstable, and precursor effects are seen as characteristically strong vibrations of groups of atoms. Such effects are described as "soft modes", and are far from isotropic. The Debye-Waller tensor may be four times larger in the soft direction than in the other directions and this makes a big difference to the intensities of high angle lines. Despite this difficulty, powder diffraction may often be the only way of refining such structures where the crystal itself may be destroyed by the phase transition. Anisotropic Debye-Waller factors were therefore soon introduced into profile refinement [47]. Apart from permitting fits to the high angle data which could not be refined with the normal program, they offered physical insight into how soft modes produced phase transitions. With low resolution diffractometers of limited $\sin\theta/\lambda$ range, the absolute values of the Debye-Waller factors may not be well determined because of systematic errors in the background measurement. However, even then, the relative values often showed the

characteristic librations or vibrations of groups of atoms. These effects are most convincing when the results of profile refinement are plotted with the ORTEP program, as in figure 2.

3.5. Cumulant expansion of thermal motion

However, even anisotropic Debye-Waller factors are not adequate for describing certain types of motion found in crystals, especially at high temperatures. These problems do not occur so often for single crystal measurements simply because such measurements are so often limited to standard temperatures and pressures. For example, in MoF_6 at 263 K, the octahedra, which are very rigid units, begin to rotate [54]. Such dissociative phase transitions may be precursors to melting itself, or may for example be associated with the onset of superionic conductivity, as in Na_2UBr_6 [38]. Levy et al. [54] have shown how the cumulant expansion developed by Seymour and Pryor [55] can be used to describe such structures with a few physically meaningful parameters suitable for profile refinement. The dissociation of the structure can then be followed as a function of temperature, since many complete data sets can be collected in a short period.

A similar solution to a related problem has been developed independently by Kurki-Suonio. In NH_4NO_3 [44] this method has been used to find the preferred orientation of the NH_4^+ and NO_3^- groups in the high temperature phase. These groups are rotating, but there is a definite correlation between their orientations. This type of hindered rotation must in fact be quite common, and many more examples will no doubt be discovered now that structures can be precisely measured at many different temperatures with profile refinement.

A related effect occurs in dynamically disordered materials. In CsPbCl_3 [56] the anions occupy holes which are too large for them. At high temperature, they therefore move around these potential wells, but nevertheless, have preferred positions which can be found using the cumulant expansion technique. This effect can be called "anharmonic" thermal motion. At lower temperatures in CsPbCl_3 , the ions no longer have the energy to move around, and become frozen in particular positions after a series of phase transitions. Profile refinement, using powerful on-line computers and interactive programs will be increasingly used to explore such effects, if only because life is not long enough to survey such structures as a function of temperature and chemical composition using traditional single crystal structural studies.

3.6. Fourier techniques

The Rietveld program refines the structure directly to fit the diffraction pattern, without first extracting the structure factors which are needed for Fourier synthesis. Fourier techniques cannot then be immediately applied. 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. The refinement is set up in the usual way, and just the scale factor and cell dimensions are refined using the partial structure. At the end of the refinement, even though the agreement between calculated and observed profiles will not be very good, the experimental structure factors are extracted by dividing up intensities due to overlapping peaks according to the ratio of the calculated structure factors. The phases are also calculated from the model of the partial structure. A difference Fourier is then constructed and searched for features which might be identified with the unknown 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. Such an approximate procedure does not of course produce precise atom coordinates, but only starting positions which can later be refined in the usual way. It works best when no more than about one quarter of the atom positions are unknown, and of course when the structure is centrosymmetric so that the phases are simply 0° or 180° .

Fourier syntheses have often been used to locate hydrogen atoms in structures where the heavy atoms have already been found with x-rays (Sections 2.7 and 2.8). Such techniques should also be of value for disordered structures.

3.7. The line shape

The classical neutron powder diffractometer has an advantage over x-ray powder cameras and diffractometers for profile refinement: the line shape is much simpler. This arises for a number of reasons.

- (i) A monochromated white source of neutrons does not of course contain sharp characteristic lines, such as the α_1 and α_2 compounds of x-rays.
- (ii) The resolution must usually be relaxed for neutrons, since the radiation source is much less bright. Then the effects of particle size and strain are not so important and the line shape is largely determined by the diffractometer, rather than the sample.
- (iii) The sample is much larger ($\sim \text{cm}^3$) for neutrons, so that preferred orientation, surface texture effects etc. are not usually important.
- (iv) The geometry is simpler for neutron diffractometers. The sample is cylindrical and concentrated at the center of the counter bank. Söller collimators or position sensitive detectors are used to define the angular divergence: both have triangular acceptance functions, so that when several are convoluted together, an almost perfect Gaussian results.

Even for high resolution powder diffractometers ($\Delta d/d \sim 10^{-3}$) the line shape is described very well by a simple Gaussian [57]. The only concession made by Rietveld [7] to the diffractometer geometry was to allow the line width to vary in a simple way

with scattering angle, and to correct the small asymmetry observed at low angles due to the finite vertical divergence. These approximations are the only ones used for almost all neutron powder work at present, but a number of authors have shown how they can be improved to describe more rigorously the experimental profiles.

Cooper and Sayer [58] and Thomas [59] have derived more complete corrections for the effect of vertical divergence. They have shown that in addition to a more complex form of asymmetry of the line shape, the centers of the lines are shifted slightly, and the integrated intensities must also be corrected. Of course, these effects are really only important for low (or high) angle lines on high resolution machines with rather large vertical divergences ($\sim 5^\circ$). However, since new diffractometers do aim for fairly high resolution, with the vertical divergence increased to make up for the resulting intensity losses, these more precise corrections should be used more regularly.

Again, with higher resolution neutron diffractometers, the Gaussian line shape approximation which has up to now served so well, needs revision. Suorrti [60] has shown that with high resolution, tails can be seen on each side of the line; these tails cannot of course be described by the Gaussian approximation. He has introduced a Lorentz component to account for these tails and has shown that a very much better fit is obtained when the line shape is described by the convolution of a Gaussian and a Lorentzian, known as a Voigt function.

Since the effect of the tails becomes systematically more important at high scattering angles, the use of the usual Gaussian leads to an overestimation of the overall Debye-Waller factor, although the refined structural parameters are presumably not much affected.

Similar conclusions have been reached for x-ray line profiles. Langford [61] considers a Voigt function represented by the convolution of m Lorentzians and n Gaussians to represent the lattice strain, crystal imperfections and the shape and distribution of the crystallites in addition to the instrumental profile. Both Suorrti and Langford indicate how these more exact line shape functions might be incorporated into profile refinement programs.

3.8. Background subtraction

The existence of long tails on each line emphasizes a rather basic problem with profile refinement: what to do about the background. Profile refinement is needed to resolve overlapping lines for more complex structures, but in that case it becomes difficult to find regions where there are no lines and where the background can be measured. Sabine and Clarke [62] have proposed that just as the structure is refined to fit the peaks, other features such as defect distributions might be refined from the background. They see the background as a valuable source of additional information about the crystal, rather than a problem to be overcome. Windsor [63] has argued that the Debye-Waller factors should be refined to account for the angular dependence of the

thermal diffuse scattering as well as that of the Bragg peaks. Fender [64] has used modulations in the background, in addition to the Bragg peaks, to obtain the defect distribution. Boysen and Hewat [65] have shown that such background modulations in K_2SnCl_6 are due to a dynamic disorder at room temperature which tends to disappear as the crystal undergoes successive phase transitions at lower temperatures. In many such examples, the background can supply new information about the powdered crystal, but to set up a model of the background for profile refinement, which contains only a few physically meaningful parameters, is not something that can yet be done routinely. Some physical insight into each special case is usually needed. At present, the background is measured at positions where no lines appear to contribute, and is thus not part of the profile refinement.

There are also experimental approaches to the background problem which will be discussed in Section 4.3.

3.9. Absorption corrections

Except for a few isotopes (for example, the most common isotopes of H, B, Cd, Gd, Eu and other transuranics), the effective absorption for neutrons is very much smaller than it is for x-rays. Samples at least 1 cm thick are common. This means that a large cylindrical sample can be used, greatly simplifying the geometry, and providing a true bulk average of the crystal properties. However, even this small absorption ($\mu R \sim 1$) can cause systematic errors in the temperature factors, which will then be underestimated. Rouse et al. [66] and others have published tables of absorption corrections for such samples, but in fact the effect on the Debye-Waller factors can be calculated directly [67,68]. Such corrections are then best left to the end of the refinement.

In the few cases mentioned above where absorption is strong, a nonabsorbing isotope can be used in place of the natural element. Such isotopes are quite inexpensive for the lighter elements due to the advances made with isotope separation in the nuclear industry. For the transuranic elements, the absorption can in some cases be greatly reduced by using a shorter neutron wavelength, below the absorption edge (e.g., 0.5 Å neutrons for Gd).

4. Experimental Techniques

4.1. The classical neutron diffractometer

The classical neutron powder diffractometer, such as that used at Petten or Harwell for many of the early measurements using profile refinement, consists of three main parts (fig. 3): a large monochromating crystal, a counter turning around the sample, and Söller collimators α_1 , α_2 and α_3 . In some cases, such as at Lucas Heights and Brookhaven, an additional analyzing crystal is used in front of the counter to eliminate elastically scattered neutrons contributing to the background [69].

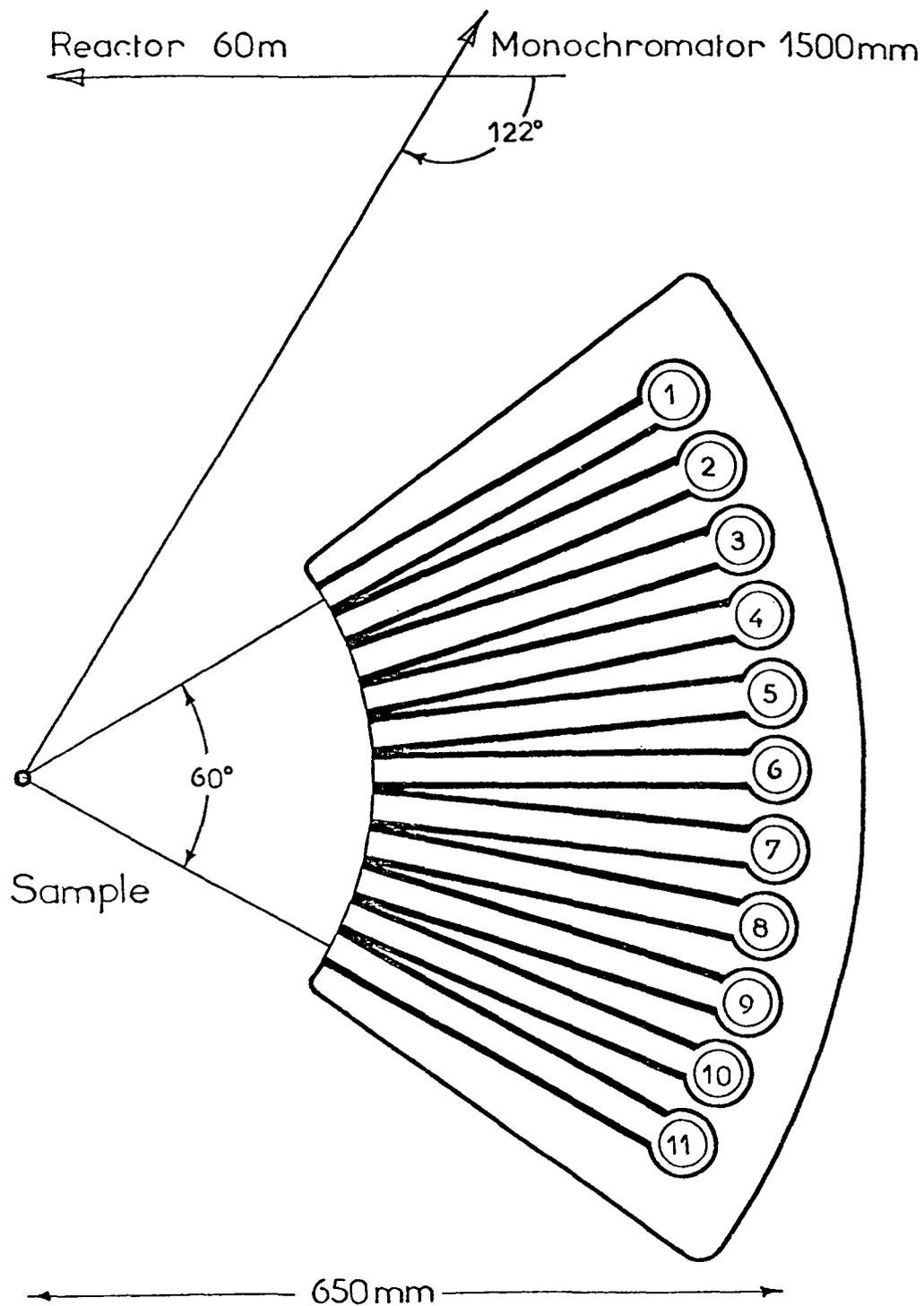


Figure 3. A conventional neutron powder diffractometer with a bank of Söller collimators and counters [57].

The transmission function for a Soller collimator is triangular, and the convolution of two such triangular functions is very nearly a Gaussian [70]. The mosaic spread of the monochromator (β) is also a Gaussian if an average is taken over a volume large compared with the mosaic block size, as is true in this case. The intrinsic line shape from the particle size and strain in the sample does not enter for the typical medium resolution machine, where the instrument itself accounts for most of the line width $A_{1/2}$ at half height (typically 0.5° in 2θ). Caglioti et al. [71] have derived the dependence of $A_{1/2}$ on scattering angle 2θ as

$$\left(A_{1/2}\right)^2 = U \tan^2\theta + V \tan\theta + W$$

where U , V , W are strictly functions of the divergence angles α_1 , α_2 , α_3 and β , but are usually treated as parameters in the refinement.

Together with an elementary correction for line asymmetry at small scattering angles, this simple description of the line shape continues to serve for almost all neutron profile refinements, and is in fact a very good approximation. It is only in the case of high resolution diffractometers that more sophisticated treatments become important (Section 3.7.).

4.2. Requirements for high resolution

The line width can of course be reduced simply by reducing the divergences α_1 , α_2 , α_3 of the collimators. However, since the integrated line intensity is proportional to the product α_1 , α_2 , α_3 , β [71] such a simplistic approach is not usually possible: the integrated intensity would be reduced by a factor of 16 for a reduction of a factor of 2 in each of α_1 , α_2 , α_3 and β . A one day experiment would then take two weeks. In practice, the situation is not quite so bad, since it is the peak intensity and not the integrated intensity that is important for profile refinement: the reduction in peak intensity would be "only" a factor of four. As well, we will see that because of focussing considerations, it is only necessary to reduce α_1 and α_3 : the peak intensity will then be simply proportional to the resolution.

Loopstra [53] has proposed another means of improving the resolution. If a longer wavelength is used, the low angle peaks are spread across the entire angular range, and are therefore better resolved. As well, the same total scattering power is now distributed over fewer reflections, so that the line intensity will actually increase for

longer wavelengths. This is offset somewhat because the peak intensity from the reactor comes at about 1 Å, but nevertheless, there is a net gain up to wavelengths of about 2.5 Å. The diffractometer of Petten is therefore designed to use such a relatively long wavelength, and a special graphite filter is used after the monochromator to remove shorter wavelength harmonics.

This solution is especially interesting for work on magnetic structures, where the magnetic form factors make it impossible in any case to collect data at large values of $\sin\theta/\lambda$. For crystal structures it is interesting to work with shorter wavelengths to better resolve the structure. For example, on the diffractometer D1A at the ILL, the usual wavelength is 1.9 Å, which gives data to $\sin\theta/\lambda = 0.5$ Å, the usual copper limit for x-rays. However, wavelengths as long as 5.7 Å are used to index complex diffraction patterns, where the positions of the first few lines must be determined most precisely [72]. Longer wavelengths are also useful for very large molecular structures, where constrained molecular refinement can be used to limit the number of parameters, and hence reduce the amount of information needed from the diffraction pattern [50].

Fortunately, it is not necessary to have equally good resolution for all values of scattering angle. The density of lines reaches a maximum at $2\theta \sim 90^\circ$, and there are fewer lines at very low or very high angles. The best resolution is obtained when the scattering angle is about equal to the monochromator angle; the different wavelengths $\Delta\lambda$ from the monochromator are then scattered back by the sample along the same direction as the incident beam. The line width is then essentially given by the convolution of α_1 and α_3 ; the collimator α_2 between the monochromator and sample, and the mosaic spread β may have any values. The monochromator angle should then be about 90° to coincide with the region of maximum line density. The objection to using such large monochromator angles θ_M is that the reflectivity is then lower. This is partly due to the Debye-Waller factor for high order reflections from the monochromator, but mainly due to the reduced $\Delta\lambda$ of wavelengths reflected

$$\frac{\Delta\lambda}{\lambda} = \mu \cot \theta_M .$$

The solution is to increase the monochromator mosaic spread β , which does not affect the focussing resolution, and eventually to cool the monochromator to reduce its Debye-Waller factor. With new hot pressing techniques for monochromators [73], the first solution is now easy, and the second is feasible but not usual. In practice, the monochromator angle is made even larger than 90° (on D1A it is 122°), to compensate for the rapid increase in line width at high angles (with $\sin^2\theta$). A more complete account of these considerations is given by Hewat [52].

4.3. Background

The experimental determination of the background level is difficult, and this sets limits on the precision with which site occupation numbers and temperature factors can be obtained. We need to have regions throughout the diffraction pattern where the Bragg peak contribution is negligible in order to measure the background level and interpolate to the other points. In particular, it is necessary to find such regions at high scattering angles. On a conventional diffractometer, this is still possible if the take-off angle is greater than 90° , because of the fall off in peak density again in this high angle region. On a time-of-flight machine this is more difficult, because the resolution is constant while the line density continually increases with $\sin\theta/\lambda$.

4.4. Multicounters

The simplest way of improving the statistics for a conventional diffractometer is to replace the single counter by a bank of counters and Söller collimators. However, until recently, it has been very difficult and expensive to make a bank of identical collimators. If the collimators are not identical, the profiles will not be identical either, and it will not be possible to simply add them together. Banks of counters have been used since at least 1966 for integrated intensity measurements (CURRAN at Harwell), but because of intercalibration difficulties the idea was dropped on later machines (PANDA at Harwell), and only taken up with recent advances in collimator design.

The best Söller collimators for neutrons are now made from stretched mylar foil, coated with neutron absorbing paint [74]. Such plastic collimators, first suggested by Meister et al. [70] have efficiencies of the order of 95 percent, but more importantly, collimators of 5' or 10' divergence can be made to be virtually identical at relatively low cost. Such collimators were first used routinely on the D1A diffractometer in Grenoble, where the results of a bank of ten collimators and counters are automatically added together to give a single composite profile for refinement. The computer program makes the remaining small corrections for relative efficiency and alignment, and each point in the profile is weighted according to the number of counters averaged to obtain it [57].

4.5. Position sensitive detectors

The D1B diffractometer at Grenoble also uses a multiple counter, but there are no collimators. Instead the counter consists of 400 independent elements, spaced at 0.2° (5 mm) to cover a total angle of 80° [75]. The angular resolution is determined by the size of the sample, the counting element, and the distance between them (1.5 m). This is then a medium resolution machine operating at rather long wavelengths (2.5 Å), which is of

particular interest for very high rates of data collection. For certain problems, useful diffraction patterns can be collected in times of the order of one second, so that for example, the crystalline products of chemical reactions can be monitored as a function of time. For such "kinetic" reaction experiments, even faster cycle times will be achieved on new instruments at the high flux reactor.

Collimators are still needed however, for high resolution diffractometers, since otherwise the sample would have to be very small.

4.6. Focussing monochromators

Here we are talking about focussing a broad beam of radiation, up to 20 cm high, onto a small sample, 2 cm high for example. This is quite different to focussing a range of wavelengths into the same counter direction, which we have already discussed in Section 4.2. The monochromator is curved about a horizontal axis, so there is little effect on the wavelength composition of the beam.

Large gains in intensity are thus obtained for the usual small samples without much affecting the resolution. The reason is that the beam divergence in the vertical direction may be 5° or more for even a high resolution diffractometer, while the vertical divergence available from the reactor is usually 1° or less because of the extensive radiation shielding. Vertically focussing monochromators can therefore be used to increase this divergence at the expense of beam area, which is normally much larger than available samples. For the same reason, vertically extended counters are used to match the vertical divergences between counter/sample and sample/monochromator. The only disadvantage of divergences of 5° or more is an increased asymmetry of the low and high angle lines, but the corrections for these asymmetry effects [58,59] is a small price to pay for a large increase in intensity. The gains are of particular interest for diffractometers such as D1A and D1B on neutron guide tubes far from the reactor.

The 15 cm high focussing monochromator on D1A is composed of 30 strips of hot-pressed germanium, each 5 x 5 x 40 mm, glued onto a flexible aluminum plate. A relative alignment of the strips to within 3' of arc is assured because they are cut from much larger strips of germanium already glued to a rigid alignment plate. The alignment of the original single crystal is thereby conserved throughout the cutting and transference to the aluminum focussing plate. The orientation of the parent crystal is chosen so that the mosaic spread is large in the horizontal plane, to ensure the selection of a large wavelength band $\Delta\lambda$, and small in the vertical plane to ensure the smallest focal spot size (15 mm). On D1A an order to magnitude is gained in the intensity using this focussing monochromator.

4.7. Wavelengths between 1.1 Å and 5.7 Å

A supplementary advantage of using a large monochromator angle, is that a wide choice of wavelengths is then available simply by selecting different reflection planes. The D1A monochromator was designed to use the [117] plane in germanium to give 1.38 Å, but many other [hh1] planes can be obtained by simple rotation about the vertical axis. Thus focussing is still very good for [115] giving 1.9 Å and [119] giving 1.1 Å. Other useful wavelengths are 1.2 Å, 1.3 Å, 1.5 Å, 2.3 Å, 3.0 Å and 3.7 Å.

Longer wavelength harmonics are in all cases forbidden for such [odd, odd, odd] reflections, and of course $\lambda/2$ is forbidden for the germanium structure. $\lambda/3$ and higher harmonics are filtered out by the guide tube for $\lambda < 2.6$ Å, but a graphite filter should be used for 3 Å, and a cooled beryllium filter for 5.7 Å.

The most common wavelengths used in practice are 1.9 Å for new work, 1.38 Å for refining well determined structures and 3 Å or 5.7 Å for indexing unknown structures. Any wavelength can be obtained within seconds, and under computer control if required.

4.8. Cryostats, furnaces and pressure cells

Closed circuit refrigerators are available down to 10 K, but a helium cryostat is still preferred for most work. Such a cryostat works anywhere between 1.5 K and 310 K, and the ILL design has the advantage that the sample chamber is quite independent of the remainder of the cryostat, so that the sample may be changed within a few minutes.

The standard vacuum furnace works between 300 K and 1300 K with the sample usually sealed in a quartz glass tube. Special furnaces are available for the ranges of 20 °C to 200 °C, 1000 °C to 1600 °C and 1000 °C to 2400 °C. Experiments at the highest temperatures must be completed in the shortest possible time because of possible crystal growth [76]; the sample may be sealed for example in an electron beam welded tungsten can.

Various types of pressure cells for neutron scattering have been developed at the Grenoble CNRS laboratories under the direction of D. Block. The simplest type works with compressed helium gas, up to at least 7 kbar and in a cryostat at lower pressures, depending on the temperature. The sample size is of the order of 0.4 cm³. For pressures up to 10 kbar, 0.1 cm³ samples are contained in a 5 mm hole in a single crystal of sapphire supported by an aluminum alloy cell. The pressure is applied by opposed tungsten carbide pistons acting on a special organic pressure transmitting liquid. Pressures of up to 30 kbar can be obtained by replacing the sapphire crystal by sintered alumina, but then additional lines due to the Al₂O₃ powder are obtained in the diffraction pattern. Such a cell has been used, for example, to study the behavior of the hydrogen bonds in ferroelectric KH₂PO₄ under pressures [77].

Pressures of up to 45 kbar can be obtained by using a special black alumina, which has additives to improve its mechanical properties. Unfortunately, these additives

contribute yet more lines to the diffraction pattern, and this type of cell has so far only been used for studying compressibilities, and the behavior of isolated lines, not profile refinement.

4.9. Sample preparation

Because such a large sample (1-5 cm³) is used, preparation is not so critical as for x-ray powder diffraction. The material is crushed very finely in a pestle and mortar. A dry glove bag is used if the sample is at all sensitive to moisture, because water scatters neutrons strongly, increasing the apparent absorption and background.

Even materials which are normally gases or liquids are best treated this way. In this case, the mortar is immersed in a bath of liquid nitrogen inside the glove bag. The boiling nitrogen readily excludes atmospheric moisture, which would otherwise condense. The pestle, sample can and spatula used to transfer the sample are likewise immersed in the nitrogen bath. The full sample can is left immersed in the liquid nitrogen until it is transferred to the cryostat (a few seconds exposure to the atmosphere), and then any liquid nitrogen which may have leaked into the sample is boiled off by briefly raising the temperature to 80 K. This procedure is surprisingly easy, and has been used even for poisonous gases such as ammonia after alternative methods, such as sublimation or shock freezing produced samples showing preferred orientation [45]. Even materials which have melting points above ambient temperature may be too soft to grind, and may benefit from such treatment.

The sample is pressed into the sample can, never shaken, and provided it has been thoroughly ground, preferred orientation cannot usually be detected. If it is, the preparation should be repeated more carefully. There are, however, three other techniques which may be needed occasionally. Firstly, since the sample is a cylinder, it can be rotated at say 1 revolution per second throughout the measurement: some workers routinely use this technique, which reduces the effect, but does little if the preferred axis is the axis of rotation. Riekel, Convert, Gobert and Lazaro [78], have used a spherical sample container, randomly spun on a jet of gas, so that a "powder pattern" may be obtained even from a single crystal.

The second technique is to dilute the sample with a large amount of some other powder which does not show preferred orientation. Materials with low absorption and simple diffraction patterns are needed, since their effect must later be subtracted. Powdered aluminium has been used, but there is a danger of reaction with finely divided metal powders, especially when used with oxidizing samples in furnaces. Carbon fibre or quartz wool has been used to prevent extensive crystal growth when a liquid is frozen, [50] and powdered quartz wool would seem to be the most generally useful material; it can be removed later by dissolving the sample.

Finally, if all else fails, a preferred orientation correction can be made during the refinement, as introduced by Rietveld [7]. Then something must be known a priori about

the nature of the preferred orientation. None of these three techniques, however, replaces a thorough grinding of the sample, at liquid nitrogen temperatures if necessary followed by annealing at high temperatures, and a careful filling of the sample can.

The can itself is normally a thin vanadium tube of between 5 and 15 mm diameter. Many such tubes have been manufactured at Harwell from electron beam welded vanadium sheet, with titanium ends made vacuum tight by indium wire seals. Because of the very small coherent scattering length of vanadium, no extra lines are introduced into the diffraction pattern. Such cans (without the indium) are also used in vacuum furnaces up to about 800 °C. For higher temperatures (up to 1100 °C) the sample is sealed under an appropriate atmosphere in a quartz glass tube, which has much lower absorption than ordinary borated glass. The diffuse scattering from the glass then adds to the background, but again there are no Bragg peaks. For still higher temperatures, or for reactive samples, other materials such as electron beam welded tungsten have been used. Neutron absorbing materials, such as cadmium in a cryostat, or boron nitride in a furnace, are used to shield parts which otherwise might scatter neutrons. With Söller collimators the furnace or cryostat dimensions can be chosen so that they are not seen by the counters. Normally then, there are no additional lines in the diffraction pattern, and it is not necessary to make a separate background scan with the sample removed.

4.10. Data collection and treatment

Although the operation of a powder diffractometer is relatively simple, step scanning with one motor and storage of the results of the different counting elements, a small dedicated computer, such as the LSI-II based system used on DIA is of great value. Not only does it permit the storage of the results of a large bank of counters, and the automatic transmission of the data to the central computer, but it allows on-line examination and treatment of the data in the background mode even while controlling the diffractometer in the priority foreground mode (RT-II operating system). As well, with a multiple counter, rapid scans can be programmed at different temperatures and the results compared in a search for phase transitions. More detailed treatment of the data, and in particular, profile refinement, is best done by transmitting the results directly to a central computer, which can be used on-line in a time sharing mode. Eventually, such a system might lead to an automatic structure refinement "machine", which could be used to study the effect of external conditions, such as temperature and pressure, on a given crystal structure. Such a machine could reveal much more about a structure, its stability and the balance of interatomic force than do the present "static" crystallographic techniques.

References

- [1] Wilson, A. J. C., *Mathematical theory of x-ray powder diffraction*, Eindhoven: Centrex (1963).
- [2] Diamond, R., *Profile analysis in single crystal diffractometry*, *Acta Cryst.* A25, 43-55 (1969).
- [3] Ayers, G. L., Huang, T. C., and Parrish, W., *High speed x-ray analysis*, *J. Appl. Cryst.* 11, 229-233 (1978).
- [4] Riekel, C., Convert, P., Jacobé, J., and Klesse, K., *Applications of high intensity neutron powder diffraction*, ILL Internal Report (1979), in preparation.
- [5] Tofield, B. C., Jacobsen, A. J., England, W. A., Clarke, P. J. and Thomas, M. W., *Deuterium beta alumina: atom location and structure refinement by powder neutron diffraction*, *J. Solid State Chem.* (1979), in press.
- [6] Rietveld, H. M., *Line profiles of neutron powder diffraction peaks for structure refinement*, *Acta Cryst.* 22, 151-153 (1967).
- [7] Rietveld, H. M., *A profile refinement method for nuclear and magnetic structures*, *J. Appl. Cryst.* 2, 65-71 (1969).
- [8] Shirane, Gen, *A note on the magnetic intensities of powder neutron diffraction*, *Acta Cryst.* 12, 282-285 (1959).
- [9] Nathans, R., Alperin, H. A., Pickart, S. J., and Brown, P. J., *Measurement of the covalent spin distribution in manganese fluoride using polarized neutrons*, *J. Appl. Phys.* 34, 1182-1186 (1963).
- [10] Andresen, A. F. and van Laar, B., *The magnetic structure of Fe₃Se₄*, *Acta Chem. Scand.* 24, 2435-2439 (1970).
- [11] Holseth, A., Kjekshus, A., and Andresen, A., *Neutron diffraction studies of CrSb₂ and FeSb₂*, *Acta Chem. Scand.* 24, 3309-3316 (1970).
- [12] Taylor, J. C. and Wilson, P. W., *A neutron diffraction study of anhydrous UCl₄*, *Acta Cryst.* B29, 1942-1944 (1973).
- [13] Taylor, J. C. and Wilson, P. W., *Neutron and x-ray powder diffraction studies of the structure of uranium hexachloride*, *Acta Cryst.* B30, 1481-1484 (1974).
- [14] Loopstra, B. O. and Rietveld, H. M., *The structure of some alkaline earth metal uranates*, *Acta Cryst.* B25, 787-791 (1969).
- [15] Zachariasen, W., *Crystal chemical studies of the 5f series of elements V. uranium hexachloride*, *Acta Cryst.* 1, 285-287 (1948).
- [16] (a) Hewat, A. W., *Cubic-tetragonal-orthorhombic-rhombohedral ferroelectric transitions in perovskite potassium niobate*, *J. Phys. C* 6, 2559-2572 (1973a).
(b) Hewat, A. W., *Neutron powder profile refinement of ferroelectric and antiferroelectric crystal structures: sodium niobate at 22 °C*, *Ferroelectrics*, 7, 83-85 (1974).

- [17] Bulou, A., Etude du caractère ordre-désordre de la transition ferroélastique impropre de RbCaF_3 à 198 J, Thèse de 3e cycle, Université Paris 6ème (1979).
- [18] Gavarrri, J. R., Weigel, D., and Hewat, A. W., Oxydes de plomb IV. Evolution structurale de l'oxyde Pb_3O_4 entre 240 K et 5 K et mécanisme de la transition, J. Solid State Chem. 23, 327-339 (1978).
- [19] David, W. F., Glazer, A. M., and Hewat, A. W., The structure and ferroelastic phase transition in BiVO_4 , Acta Cryst. (1979), in press.
- [20] Hidaka, M. and Hewat, A. W., Structural phase transitions in ferroelastic CsVF_4 , Acta Cryst. (1979), to be published.
- [21] Hewat, A. W., Location of hydrogen atoms in ADP by neutron powder profile refinement, Nature 246, 90-91 (1973).
- [22] Bacon, G. E. and Pease, R. S., A neutron diffraction study of potassium hydrogen phosphate by Fourier synthesis, Proc. Roy. Soc. London A220, 397-421 (1953).
- [23] Hewat, A. W., Molecular structure transitions and neutron powder diffraction, Proc. 4th Europ. Cryst. Meet., Oxford, 387-389 (1977).
- [24] Cheetham, A. K. and Taylor, J. C., Profile analysis of neutron diffraction data: its scope, limitations and applications in solid state chemistry, J. Solid State Chem. 21, 253-275 (1977).
- [25] Cheetham, A. K. and Norman, N., The structure of yttrium and bismuth trifluorides by neutron diffraction, Acta Chem. Scand. A28, 55-60 (1974).
- [26] Armytage, D. and Fender, B. E. F., Anion ordering in TaON: A powder neutron diffraction investigation, Acta Cryst. B30, 809-812 (1974).
- [27] Jacobsen, A. J., Collins, B. M., and Fender, B. E. F., A powder neutron diffraction determination of the structure of $\text{Ba}_5\text{W}_3\text{Li}_2\text{O}_{15}$, Acta Cryst. B30, 816-819 (1974).
- [28] Collins, B. M., Jacobsen, A. J., and Fender, B. E. F., A powder neutron diffraction determination of the structure of $\text{Ba}_4\text{Ta}_3\text{LiO}_{12}$, J. Solid State Chem. 10, 29-35 (1974).
- [29] Titcombe, C. G., Cheetham, A. K., and Fender, B. E. F., A neutron diffraction study of the hydrides of the early lanthanide elements at room temperature, J. Phys. C 7, 2409-2416 (1974).
- [30] Cheetham, A. K. and Fender, B. E. F., Neutron diffraction study of non-stoichiometric cerium hydride, J. Phys. C 5, L35-40 (1972).
- [31] Von Dreele, R. B. and Cheetham, A. K., The structures of some titanium-niobium oxides b powder neutron diffraction, Proc. Roy. Soc. London A338, 311-326 (1974).
- [32] Wadlsey, A. D., Mixed oxides of titanium and niobium, Acta Cryst. 14, 660-664 and 664-570 (1961).
- [33] Allpress, J. G., Mixed oxides of titanium and niobium: intergrowth structures and defects, J. Solid State Chem. 1, 66-81 (1969).
- [34] Cowley, J. M. and Iijima, S., Electron microscopy of atoms in crystals, Physics Today, p. 33 (March 1977).

- [35] Anderson, J. S., Bevan, D. J. M., Cheetham, A. K., von Dreele, R. B., Hutchison, J. L., and Strähle, J., The structure of germanium niobium oxide, an inherently non-stoichiometric block structure, Proc. Roy. Soc. London A346, 139-156 (1975).
- [36] Wright, A. and Fender, B. E. F., The structure of superionic compounds by powder neutron diffraction I Cation distributions in α -AgI, J. Phys. Chem. 10, 2261 (1977).
- [37] England, W. A., Jacobsen, A. J., and Tofield, B. C., Neutron diffraction determination of the structures of deuterium β -alumina at 4.5 K and 823 K, J. Chem. Soc., Chem. Coll., 895 (1976).
- [38] Bogacz, A., Bros, J., Gaune-Escard, M., Hewat, A. W., and Taylor, J. C., Constructing new fast ion conductors from uranium halides - the $UCl_6/NaUCl_6$ structures, J. Phys. C. (1979), submitted.
- [39] Hewat, A. W. and Lehmann, M., The resonance structure of solid formic acid, ILL experimental proposal 5-22-137 (1979).
- [40] Kuijpers, F. A. and Loopstra, B. O., A neutron diffraction study of the structural relationships of RCO_5 hydrides, J. Phys. Chem. Solids, 35, 301-306 (1974).
- [41] Adams, J. M., Pritchard, R. G., and Hewat, A. W., Neutron profile refinement and deuterium positions in $Na_2CO_3 \cdot 1.5 D_2O_2$, Acta Cryst. (1979), in press.
- [42] Adams, Ramdas, and Hewat, (1979).
- [43] Johnson, M. W., Sandor, E., and Arzi, E., The crystal structure of deuterium fluoride, Acta Cryst. B31, 1998-2003 (1975).
- [44] Ahtee, M., Kurki-Suonio, K., Lucas, B. W., and Hewat, A. W., Determination of molecular orientations in cubic ND_4NO_3 by multipole analysis, Acta Cryst. (1979), in press.
- [45] Hewat, A. W. and Riekel, C., The structure of deuterio-ammonia between 2 K and 180 K by neutron powder profile refinement, Acta Cryst. A (1979), in press.
- [46] Lehmann, M. and Speakman, J. C., private communication (1979).
- [47] Hewat, A. W., The Rietveld computer program for the profile refinement of neutron diffraction powder patterns modified for anisotropic thermal vibrations, UKAERE Harwell, Report RRL 73/897 (1973).
- [48] Sakata, M. and Cooper, M. J., An analysis of the Rietveld profile refinement method, J. Appl. Cryst. (1979), in press.
- [49] Shirley, R., Data accuracy for powder indexing, this conference (1979).
- [50] Pawley, G. S., Mackenzie, G. A., and Dietrich, O. W., Neutron powder diffraction and constrained refinement, Acta Cryst. A33, 142-145 (1977).
- [51] Pawley, G. S., Constrained refinement in crystallography, in Advances in Structure Research by Diffraction Methods, W. Hoppe and R. Mason, eds., Vol. 4, 1-64 (Pergamon, Oxford, 1972).
- [52] Hewat, A. W., Design for a conventional high resolution neutron powder diffraction, Nucl. Inst. Methods 127, 361-370 (1975).

- [53] Loopstra, B. O., Neutron powder diffractometry using a wavelength of 2.6 \AA , Nucl. Inst. Methods 44, 181-187 (1966).
- [54] Levy, J. H., Sanger, P. L., Taylor, J. C., and Wilson, P. W., The structures of fluorides. XI kubic harmonic analysis of the neutron diffraction pattern of MoF_6 , Acta Cryst. B31, 1065-1067 (1974).
- [55] Seymour, R. S. and Pryor, A. W., Neutron diffraction study of NH_4Br and NH_4I , Acta Cryst. B26, 1487-1491 (1970).
- [56] Ahtee, M., Kurki-Suonio, K., Valivaselk  and Hewat, A. W., Disordering in cubic CsPbCl_3 by multipole analysis, Acta Cryst. (1979), to be published.
- [57] Hewat, A. W. and Bailey, I., DIA, a high resolution neutron powder diffractometer with a bank of mylar collimators, Nucl. Inst. Methods 137, 463-471 (1976).
- [58] Cooper, M. J. and Sayer, J. P., The asymmetry of neutron powder diffraction peaks, J. Appl. Cryst. 8, 615-619 (1975).
- [59] Thomas, M. W., Peakshifts and peak broadening in powder neutron diffraction patterns due to finite aperture counters, J. Appl. Cryst. 10, 12-13 (1977).
- [60] Suorrti, P., Components of total x-ray scattering, this conference (1979).
- [61] Langford, J. I., A rapid method for analysing the breadths of diffraction and spectral lines using the Voigt function, J. Appl. Cryst. 11, 10-14 (1978).
- [62] Sabine, T. M. and Clarke, P. J., Powder neutron diffraction - refinement of the total pattern, J. Appl. Cryst. 10, 277-280 (1977).
- [63] Windsor, C. J. and Sinclair, R. N., The Debye-Waller factor of nickel measured at high scattering vectors by pulsed neutron powder diffraction, Acta Cryst. A32, 395-409 (1976).
- [64] Fender, B. E. F., Diffuse scattering and the study of defect solids in Chemical Applications of Thermal Neutron Scattering, B. T. M. Willis, ed. (OUP London, 1973).
- [65] Boysen, H. and Hewat, A. W., A neutron powder investigation of the structural changes in K_2SuCl_6 , Acta Cryst. B34, 1412-1418 (1978).
- [66] Rouse, K. D., Cooper, M. J., York, E. J., and Chakera, A., Absorption corrections for neutron diffraction, Acta Cryst. A26, 682-691 (1970).
- [67] Hewat, A. W., Absorption corrections for neutron diffraction, Acta Cryst. A35, 248 (1979).
- [68] Hewat, A. W., Temperature evolution of the structure and ionic conductivity in Bi_2O_3 , J. Phys. Chem. (1979), to be published.
- [69] Caglioti, G., Conventional and three-axis neutron powder diffraction in Thermal Neutron Diffraction, B. T. M. Willis, ed., 14-33 (OUP, London, 1970).
- [70] Meister, H. and Weckermann, B., Neutron collimators with plates of self-contracting foils, Nucl. Inst. Methods 108, 107-111 (1973).
- [71] Paoletti, A., Caglioti, G., and Ricci, F. P., Choice of collimators for a crystal spectrometer for neutron diffraction, Nucl. Inst. Methods, 3 223-228 (1958).

- [72] Hewat, A. W., Shirley, R., and Pawley, G. S., Automatic indexing of neutron powder diffraction patterns, *J. Appl. Cryst.* (1979), to be published.
- [73] Freund, A., Proceedings of the conference on neutron scattering, R. M. Moon, ed. ORNC Report CONF-760601-02, pp. 1143-1150, Oak Ridge (1976); see also, Freund, A. and Forsyth, J. B., A treatise on materials and technology, H. Herman, ed., 15, chap. 10 (Academic Press, NY, 1979).
- [74] Carlile, C. J., Hey, P. D., and Mack, B., High efficiency Söller slit collimators for thermal neutrons, *J. Phys. E* 10, 543-546 (1977).
- [75] Allemant, R., Bourdel, J., Roudaut, E., Convert, P., Ibel, K. Jacobe, J., Cotton, J. P., and Farnoux, B., Position sensitive detectors for neutron diffraction, *Nucl. Inst. Methods* 126, 29-42 (1975).
- [76] Aldebert, P. and Traverse, J. P., Etude par diffraction neutronique des structures de haute température de La_2O_3 and Nd_2O_3 , *Mat. Res. Bull.* 14, 303-323 (1979).
- [77] Nelmes, R. J., Meyer, G. M., Baharie, E., Hutton, J., and Hewat, A. W., The pressure and temperature dependence of the structure of para-electric (tetragonal) KH_2PO_4 and KD_2PO_4 , XI Int. Conf. Cryst. Warsaw (August, 1978).
- [78] Riekel, C., Convert, P., Gobert, G., and Lazaro, C., A spherical sample container for neutron powder diffractometry, *Nucl. Inst. Methods* 151, 201-203 (1978).

Discussion

Comment (Ladell): The difference between Parrish et al. line profile analysis approach and the Rietveld method is that the former isolates the instrumental, spectral and aberrational line broadening factors from the crystal structure factors. By using the Rietveld approach, the least squares refinement may account for the instrumental effects at the expense of the crystallographic parameters since the minimization of errors to determine position and thermal parameters are clearly influenced by the approximation used to define the profile shape. If the models used on the Parrish procedure are correct, and his work seems to confirm that these models are correct at least for the x-ray case; the correct procedure should be to use these models to isolate the variables before using a Rietveld procedure.

Response (Hewat): There are only four "instrument parameters", U, V, W, and F used by Rietveld, and these are not at all strongly correlated with the crystal structure parameters. However, there are small errors in Rietveld's description of the line shape which should be corrected in the manner advocated by Parrish and others.

Comment (Edmonds): (Directed to question of difference between Parrish's profile fitting method and Rietveld analysis, and added after Ted Prince's (NBS) comment:)

Rietveld's technique applies crystal structure determining and data reduction parameters in a least squares fit to the raw data (entire pattern) while Parrish's suggestion would first apply data reduction techniques then least square crystal structure parameters to the derived data (discrete hkl and I). If the same data reduction parameter were available to both formalisms, and the entirety of the powder pattern were used, there would be no differences in the results. However, using discrete data poses the problem of what to do with the weak or below threshold data when multiple hkl 's may be present, where the Rietveld technique will deal with the intensity sums on a dynamic basis. In any case, we are able to fit structural models only by comparing calculated data to observed data, be the latter derived or raw in nature. Forgetting this point will only magnify artificial or superficial differences between techniques and limitations.

Response (Hewat): The techniques would not be equivalent when applied to a complete diffraction pattern, because there would be many more parameters to determine with Parrish's technique. The Rietveld technique greatly reduces the correlation problems that one would have in this case. However, the Parrish technique is valuable for improving the description of single lines.

Comment (Prince): In the discussion of these papers, there seems to be a general misconception that there is a conflict between the profile fitting of Parrish and the total pattern analysis of Rietveld. The Rietveld technique takes a diffraction pattern and an assumed peak shape and determines crystallographic parameters. The Parrish work is a good representation of x-ray peak shape. What is needed now is the marriage of these techniques for x-ray refinement.

Response (Parrish): No comment made or necessary.

Question (Rush): I have several questions related to your high resolution diffraction procedures at Grenoble. How do you determine and subtract background? Do you change collimation or resolution conditions depending on the complexity of the structure? Do you have to worry about subtle changes in line shape when you vary the incident wavelength?

Response (Hewat): The background is measured in regions where no peaks are thought to contribute, using the cursor on a Tektronix screen. The wavelength is chosen according to the complexity expected for the pattern: usual choices are 1.91 Å and 1.38 Å, but wavelengths as long as 3 Å or 5.7 Å are used for indexing unknown patterns. No changes are possible in the collimation. The peak widths change with changes in the wavelength; three parameters are refined to describe the angular dependence of peak width.