

## Technique and Performance of Powder Diffraction in Crystal Structure Studies\*

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### *Abstract*

A common use of powder diffraction data is for crystal structure studies. Since the pioneering papers of Rietveld (1967, 1969), powder diffraction has been improved in many ways. Some advances in powder diffraction techniques since an earlier review (Cheetham and Taylor 1977) are described, and an indication is given of how the Rietveld method is performing with X-ray and neutron diffraction. This method has been more popular with crystallographers than the integrated-intensity method since it attacks the superposition problem directly and allows more complex structures to be refined. It has been asserted (Sakata and Cooper 1969) that calculated e.s.d. values in the Rietveld method are low by a factor of about two, although the derived positional parameters have never been faulted. This does not negate the value of the method as corrections to the e.s.d. values can be computed (Cooper *et al.* 1981; Scott 1983). The problem of precision versus accuracy is universal; in fact most e.s.d. values published in single-crystal studies are probably low by a similar amount because of the widespread practice of omitting large amounts of 'weak' data in order to artificially lower the residuals and e.s.d. values. It is shown that powder methods, especially the Rietveld, have performed well in a variety of applications.

### 1. Introduction

X-ray and neutron diffraction are basic techniques for studying the structures of solids. In addition to the many single-crystal studies, there is a smaller, but growing, list of studies using powders, as it becomes more difficult with time to find materials which grow as large crystals, and more materials of technological interest are synthesized which only grow as small crystallites. Powder diffraction is an active area of research and it is therefore of some interest to indicate how both the techniques and applications of powder methods as applied to crystal structure studies have progressed since an earlier review on the subject (Cheetham and Taylor 1977).

### 2. Recent Reviews

The principles of the neutron and X-ray fixed-wavelength and fixed-angle powder diffractometers, and the theory of the Rietveld and integrated-intensity refinement methods have been reviewed by Albinati and Willis (1982) and Santoro (1983), so this information will not be repeated in detail here. In the Proceedings of a Symposium

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on Accuracy in Powder Diffraction (NBS 1980) various authors devoted some 560 pages to an in-depth treatment of the state of powder diffraction at the end of the last decade. Other reviews, on various aspects, are mentioned below in connection with their relevant techniques or applications.

### 3. Techniques

#### (a) *Rietveld Method*

Powder diffraction is not as good as single-crystal diffraction since the three dimensional information of the reciprocal lattice is superposed into one dimension. Rietveld's contribution was to recognize that the powder pattern profile is the sum of all the individual ( $hkl$ ) peaks and every point in the step scan is an observation. The chemical structure was 'fitted' to the overall profile by the least-squares method, it being necessary to refine non-structural parameters such as halfwidth, two-theta zero, unit cell and other correction factors as well. The technique was largely ignored for several years until Hewat (1973*a*) built the high-resolution neutron diffractometer D1A at Grenoble, and demonstrated the power of the HRD-Rietveld combination in solving the phase-transition mechanisms in  $\text{KNbO}_3$ . He showed that the method was rapid and simple to use with different sample temperatures. Indeed, in this case, the neutron powder profile analysis (NPPA) results were more accurate than parallel single-crystal neutron studies, because the structure was relatively small, and systematic errors, such as extinction, were much less with the powder. Hewat's pioneering work alerted crystallographers to the possibilities of the NPPA method.

#### (b) *High Resolution Neutron Powder Diffractometry*

The Grenoble fixed-wavelength high-resolution diffractometer D1A (Hewat and Bailey 1976) is presently still a state-of-the-art machine and produces a good quality data set in about ten hours. Its success is one reason why NPPA is currently more popular than the analogous X-ray technique XPPA. The other reason is that lineshapes, which are crucial in the profile method, are more difficult to describe, and sample conditions harder to control with X-ray diffraction. D1A has a minimum linewidth of  $0.3^\circ$  FWHM, which approaches that of X-ray diffractometers and which allows refinement of structures of moderate size (50–100 structural variables). Hewat (1984) has now constructed D2B, which has twice the resolution of D1A, and a bank of 64 counters instead of the 11 on D1A to compensate for the intensity loss on gaining resolution. The D2B probably has the ultimate resolution for fixed-wavelength neutron diffractometers, down to the limits determined by particle-size effects. It should allow refinement of structures in the 200–300 parameter range, and greatly increase the horizons of those wishing to use NPPA on larger structures. Lineshapes and sample effects (strain and particle size) will be more critical on D2B than D1A.

The Lucas Heights Research Establishment has a high-resolution neutron fixed-wavelength powder diffractometer, which has operated for several years (Howard *et al.* 1983). It has the same resolution as D1A, but its intensity is lower by a factor of about 30. It may be possible to upgrade the intensity by installing a different monochromator or increasing the number of counters from the eight already in place.

Variable-wavelength fixed-angle diffractometers have been built on spallation neutron sources at the Argonne and Rutherford-Appleton Laboratories (Jorgensen and Rotella 1982; Von Dreele *et al.* 1982; David 1984). The former, the IPNS-1 facility,

has been operating for several years with Rietveld analysis of the data, and the results compare favourably with the fixed-wavelength machines. These also have good resolution and the advantage of exploring the low  $d$ -space region (by comparison the fixed-wavelength machines run into the  $\sin \theta$  limit). Intensity correction factors such as incident intensity, peak shape and extinction are still under study for these diffractometers (Poyri and Tilli 1983).

### (c) *Moderate Resolution Neutron Powder Diffractometry*

Typical moderate resolution powder diffractometers have a minimum resolution of about  $0.5^\circ$  FWHM at  $2\theta = 30\text{--}40^\circ$  (the take-off angle of the monochromator), and this increases sharply after about  $2\theta = 60\text{--}70^\circ$  to several degrees FWHM and the superposition becomes too great. Despite this, such machines are capable of clearly defining the chemical structure of crystals having less than 30 positional parameters with Rietveld refinement. On the 6HB moderate-resolution powder diffractometer at Lucas Heights (now dismantled), operating in the elastic diffraction mode (Caglioti 1970), a series of 35 halides and oxides of uranium, tungsten, molybdenum, nickel, copper and sulfur were studied by the Rietveld method, beginning in 1971. The work led to the discovery of some new structure types (Taylor 1976; Cheetham and Taylor 1977). A Rietveld program was written incorporating harmonic functions for the plastic cubic phases (Taylor 1980). These studies illustrated the power of the Rietveld method and the scope available with moderate resolution. Tellgren (1984) has described medium-resolution work on the Swedish R2 reactor.

### (d) *X-ray Powder Profile Analysis (XPPA)*

XPPA did not start to develop until the mid 1970s for the reasons given above. Malmros and Thomas (1977) applied XPPA to Guinier–Hagg film data, while Khattak and Cox (1977) demonstrated its feasibility with a conventional X-ray focussing diffractometer. Young *et al.* (1977), Young (1980), Young and Wiles (1981, 1982) and Nord and Stefanidis (1983) have reviewed the progress of XPPA. Thompson and Wood (1983) applied XPPA to the Debye–Scherrer X-ray camera.

In XPPA, systematic errors such as those arising from use of non-optimal peak shape functions, absorption and camera or diffractometer aberrations, have proved to be far more troublesome than with NPPA. In particular, the Guinier–Hagg refinements, although they have been useful in some *ab initio* structure determinations, often give thermal  $B$  factors which are negative and thus physically implausible.

An important development has occurred in the last few years with the setting up of X-ray diffractometers on synchrotron sources such as CHESS (Cornell), DESY (Hamburg), Daresbury (UK), SPEAR (Stanford), Tsukuba (Japan) and NSLS (Brookhaven). These have resolutions as low as  $0.03^\circ$  FWHM, or  $\Delta d/d = 5 \times 10^{-4}$ , several times better than conventional X-ray diffractometers. Their intensities are several thousand times better than ordinary diffraction tubes (Cox *et al.* 1983). As this work is still in the development stage, few Rietveld refinements have been published (see e.g. Hastings *et al.* 1984). This technique promises much for the indexing, solution and refinement of large structures because of the high intensity and resolution, but problems will be encountered in Rietveld refinements since the peak shapes are critical. New integrated-intensity methods may be developed to overcome this problem. Synchrotron data have already been widely used to study the behaviour

of simple structures under extreme conditions of temperature and pressure; a whole session of the Thirteenth International Congress of Crystallography (Hamburg 1984) was devoted to this topic.

(e) *Intensity Improvement*

Although neutron beams are generally weaker than X-ray beams, adequate intensity for structural refinement can be achieved with banks of detectors or, more recently, position-sensitive detectors (PSDs). This allows more of the diffracted intensity to be intercepted at a given time. The 400-cell PSD on D1B at Grenoble cuts data collection time for a powder pattern to minutes, making it very useful for studies where the sample is rapidly changing as in phase transitions, chemical reactions, crystallization from an amorphous phase, etc. High-efficiency neutron PSDs based on a scintillator glass have been recently developed at Jülich for powder diffractometers (Schelten *et al.* 1983; Schafer *et al.* 1984). Flat or curved PSDs are also commercially available on X-ray diffractometers, reducing data collection times to a few seconds with X-ray diffractometers on synchrotron sources.

(f) *Precision and Accuracy of Refinements*

The precision of a refinement is given by the errors computed; these are only accurate if they are correct. Systematic errors in the data or model can result in incorrect e.s.d. values. Sakata and Cooper (1969) criticized Rietveld refinement on the ground that, in contrast to the individual step-scan measurements, the residuals  $y_o - y_c$  are correlated because adjacent measurements over a peak are measuring the same quantity, namely the integrated intensity modified at each step by a widening function. They asserted that this makes the error calculation statistically unsound, a point that Cooper amplified in further papers (Albinati *et al.* 1980; Cooper *et al.* 1981; Cooper 1982, 1983). Cooper *et al.* (1981) also analysed various patterns by Rietveld, SCRAP and integrated-intensity refinement. In SCRAP refinement, the pattern was decomposed analytically by assuming a peak shape function to give intensities for conventional refinement of the integrated intensities (Cooper and Rouse 1981). In their integrated-intensity refinements, Rouse and Cooper (1980) fitted the model to the integrated intensities, with overlapped peaks being treated as a single observation. They found that, except for one case where the peak shapes were hard to define, the Rietveld e.s.d. values were lower than those for the integrated intensity or SCRAP by factors of typically 2 or 3. The goodness-of-fit indices showed the SCRAP method to have the most reliable e.s.d. values, while those for the integrated intensity tended to be too high. No systematic errors could be detected in the Rietveld positional parameters.

Prince (1981) and Hewat and Sabine (1981) showed that the Rietveld and the integrated-intensity methods should give the same result when the errors are statistical. Scott (1983) suggested that the structural parameters in Rietveld refinements were unbiased, but the error matrix reflected precision rather than accuracy, and he also pointed out that the Rietveld e.s.d. values could be made to approach zero as the counting time and number of steps increased; thus, Rietveld refinements place emphasis on the statistics. Scott also considered that the uncertainty in the e.s.d. values did not detract seriously from the value of the method and, along with Cooper *et al.* (1981), gave formulae to correct the Rietveld e.s.d. to more realistic values.

Hill and Madsen (1984) have considered the effect of counting time on Rietveld parameters and errors from X-ray diffractometer data for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\beta$ -PbO<sub>2</sub> and

(Mg, Fe)<sub>2</sub>SiO<sub>4</sub>. When the count times were increased, they found that the goodness-of-fit index increased markedly at a certain stage, while the residuals continued to fall. This was an argument against weighting schemes based on statistics alone for X-ray diffractometer data, which ignore the effects of errors in the model, profile parameters or machine aberrations. They found that the thermal parameters were the first to be affected by systematic errors. Neutron refinements were considered to be less affected, as the intensities are weaker, and systematic errors smaller.

In view of the above, it would seem prudent to mentally revise the Rietveld e.s.d. values upward by a factor of two, unless the corrections of Scott or Cooper have been applied. Thermal parameters should not be given physical significance unless supported by reasonable goodness-of-fit indices.

It is relevant to note here that most published single-crystal e.s.d. values should also be revised upward by a similar amount, because of the widespread practice of leaving out large amounts of data on the grounds that they are 'weak'. This has a cosmetic effect on the *R* factors and e.s.d. values, but the data set becomes biased (Hirshfeld and Rabinovich 1973; Seiler *et al.* 1984). Then the e.s.d. values are not accurate and structural parameters may be affected. Crystallographers were rebuked for this practice (Schomaker 1982). Omission of weak data can also lead to wrong space-group determinations (Marsh 1981).

The problem of precision versus accuracy is a universal one. The Rietveld method gives chemically sensible results for structural crystallographers, providing it is not misused. The e.s.d. values should be regarded with caution, but the Rietveld method remains the best way of treating the superposition and extracting the maximum of structural information. Integrated-intensity methods, as demonstrated by Cooper, are very useful for the better-resolved patterns of moderate-sized structures, but the Rietveld method lends itself to the refinement of larger structures.

#### (g) Peak Shape Functions

*Neutron shape functions (fixed-wavelength case).* Rietveld (1967, 1969) assumed that neutron powder peaks were nearly perfect gaussians, and incorporated this function into his program. The gaussian has proved adequate for most structures on D1A, except in more extreme cases where the crystallite size is small; here the Voigtian function works well. Suortti *et al.* (1979) found that the D1A pattern of Ni was not gaussian, but Voigtian, and Ahtee *et al.* (1984) reached similar conclusions with D1A data for NaTaO<sub>3</sub>. Use of a gaussian instead of a Voigtian for these patterns caused the temperature factors to refine to excessively high values [20%, 300%, 44% and 48% too high for Na, Ta, O(1) and O(2) respectively in NaTaO<sub>3</sub>]. The peaks were so wide that a range of 20 FWHM was necessary; the usual range for a gaussian is 3 FWHM. In the gaussian refinements, some of the peak intensity was lost in the (too high) background. These samples, with their large particle-size broadening, may not be typical. However, if thermal parameters are of interest, the peak shapes should be carefully examined for deviations from the ideal gaussian shape. In studies of oxides on a powder diffractometer at the NBS reactor (Washington), Cava *et al.* (1984a) have also found departures from the gaussian profile, and have used Pearson VII functions.

*X-ray peak shape functions (fixed-wavelength case).* X-ray peak shapes are difficult to describe with shape functions; for example, Khattak and Cox (1977) found simple gaussians or Lorentzians did not fit the X-ray profile of La<sub>0.75</sub>Sr<sub>0.25</sub>CrO<sub>3</sub>, whereas

intermediate or modified Lorentzians did. Their X-ray profile  $R$  factor was 14.4%, whereas the neutron pattern of the same material refined to 7.8%. Young (1980) remarked on the fact that X-ray profile  $R$  factors are generally twice the neutron values; this is largely due to peak shape fitting. Young and Wiles (1982) reviewed the performance of X-ray profile shape functions for fixed-wavelength X-ray diffractometers and concluded that most X-ray patterns were fitted best by mixtures of gaussians and Lorentzians [although Young *et al.* (1977) obtained a good fit for fluorapatite with a gaussian]. The pseudo-Voigt function was generally the best. With some data, several functions performed equally well, and Young and Wiles concluded better functions might need to be found. As the functions tail differently, it was considered important to carefully consider the peak range, and refine the background as well.

Pyrros and Hubbard (1983) showed that rational functions (the ratio of two polynomials) gave a good fit to a Si X-ray diffractometer pattern. The Pearson VII function was approximated by  $(1 + A_1 x^2 + A_2 x^4)^{-1}$ , where  $x$  is the distance from the centre. Asymmetry was modelled with different  $A_1$  and  $A_2$  values either side of the maximum. Other shapes could be modelled with more complex rational functions, which could be readily programmed.

Baerlocher (1984) used a peak shape function of the form

$$H^{-1} g_s(\Delta 2\theta/H)(1 - A g_a \Delta 2\theta/H),$$

where  $H$  and  $A$  are adjustable halfwidth and asymmetry parameters. The non-analytical functions  $g_s$  and  $g_a$  were 'learned' from a single resolved peak in the profile. This eliminated the need for a shape function, and was a good practical solution to the refinement problem where the study of particle size or strain effects was not an end in itself.

Hastings *et al.* (1984) studied peak shapes on a diffractometer with a Si(111) analyser at the CHESS synchrotron. Patterns with FWHM values as low as  $0.02\text{--}0.03^\circ 2\theta$  were collected in the wavelength range  $1.07\text{--}1.54 \text{ \AA}$ . The analyser removed the well-known flat sample and transparency aberrations (Klug and Alexander 1974). The peak shapes for  $\text{CeO}_2$  were represented by pseudo-Voigt functions, with gaussian predominance, and their peak shape parameters gave a reasonable estimate of crystallite size. The advantage of the very high resolution was lost when the crystallite size fell below  $2 \mu\text{m}$ . The pseudo-Voigt function was also successful in the Rietveld refinement of  $\text{Bi}_2\text{O}_3$  (Cox *et al.* 1983) with CHESS data. These data consisted of 49 ( $hkl$ ) and 15 positional parameters, and Cox *et al.* envisaged future synchrotron refinements with up to 2000 ( $hkl$ ) parameters. As with D2B, peak shape fitting may prove to be a problem with this very high resolution data.

**Peak asymmetry.** On a fixed-wavelength diffractometer, the peaks tail towards  $2\theta = 0$  (or  $2\theta = 180^\circ$ ) because of the misfit of the curved diffraction cone and the rectangular counter aperture. The effect is important in high-resolution diffractometers where high samples, detectors and focussing monochromators are used to maximize the intensity. It is more severe as  $2\theta$  approaches 0 or  $180^\circ$ . In X-ray diffractometers, asymmetry can also be caused by the sample being tangential to the focussing circle ('flat') and being transparent to the beam (Klug and Alexander 1974).

Rietveld recognized asymmetry in his 1969 paper and gave an empirical correction of the form  $1 - A(\Delta 2\theta)^2 S \cot \theta$ , where  $A$  is an asymmetry parameter and  $S$  is the sign of the difference  $\Delta 2\theta = 2\theta_i - 2\theta_{\text{Bragg}}$ . However, this function does not conserve

intensity, has an incorrect  $\theta$  dependence and it does not allow shift of the maximum (Howard 1982). Howard corrected for asymmetry with a sum of gaussians and a single parameter, and incorporated it in the Wiles-Young (1981) program. This function gave better goodness-of-fit indices than the Rietveld function.

Prince (1983) used an Edgeworth series with a single parameter for neutron data. Van Laar and Yelon (1984) calculated peak profiles for various combinations of sample height, detector height and sample-detector distance and, after folding with a gaussian instrument function, incorporated it in the Rietveld program. The peak shift found in their instrument was still significant at  $2\theta = 40^\circ$ , and they calculated corrections to the Lorentz factor due to the curved cone which agreed with earlier calculations by Cooper and Glasspool (1976). Howard (1984) pointed out the good agreement between the various studies of asymmetry and that the Van Laar analysis did not include vertical divergence before the sample, which occurs in the focussing monochromator systems in D1A and D2B. When the analytical functions of Prince or Howard are used, it is still necessary to use the corrected Lorentz factor (C. J. Howard, personal communication).

In X-ray refinements, some authors corrected for asymmetry by using different profile functions for each side of the peak (Young and Wiles 1982). Hastings *et al.* (1984) still had asymmetry in their synchrotron data even though the analyser eliminated the flat sample and transparency aberrations; these authors corrected for asymmetry with a numerical integration method. Thompson and Wood (1983) calculated asymmetry for their Debye-Scherrer geometry. Asymmetry corrections will be important when large structures with low-angle peaks begin to be studied with D2B and synchrotron diffractometers.

*Sample effects on peak shapes and intensities.* A formidable unsolved problem is preferred orientation of the crystallites which can drastically affect the intensities, and even more so with X-ray data. Rietveld (1969) gave a crude but fairly effective formula for plate morphology. Some workers have removed the effect experimentally by mixing with a resin such as Technovit 4030-B (see e.g. Immirzi and Porzio 1982) and regrinding; however, the resin may react with some samples or the hydrogen atoms may give unwanted background in the case of neutron diffraction. Pawley *et al.* (1977) diluted their samples with powdered quartz wool when studying frozen organic materials with the Rietveld method. Some attempts have been made to calculate preferred orientation effects using harmonic functions related to the Laue group for polar axis distributions (Jarvinen *et al.* 1970; Pesonen 1979).

Peak profiles are sensitive to stress and crystallite size. Attempts have been made to calculate profiles for different crystallite shapes. Yucel *et al.* (1980, 1981) calculated profiles for needle-shaped crystals, which had domains so small that the variation in  $F_{hkl}$  over them had to be considered. Langford and Louer (1982) calculated profiles for cylindrical crystallites. De Keijser *et al.* (1983) considered that the profile-refinement method was sufficiently well developed to allow simultaneous determination of size and strain parameters. However, some investigators (see e.g. Suortti *et al.* 1979) have had trouble relating profile parameters with measured crystallite sizes. Cox *et al.* (1983) were able to relate their parameters to the crystallite sizes.

*Peak shape fitting and (hkl) intensity extraction.* This is feasible for simpler structures with 'exact' profile functions. If complex structures can be decomposed successfully in this way, then the way will be open for *ab initio* structure solutions for powder

data with single-crystal direct methods. The results are also of value in search-match powder identification procedures.

Taupin (1973*a*) and Huang and Parrish (1975) used sum-of-Lorentzian functions, while Hecq (1981) programmed a similar procedure with pseudo-Voigt functions with fewer parameters. Ayers *et al.* (1978) obtained  $2\theta$  and  $I(hkl)$  data for mixtures of simple compounds. Naidu and Houska (1982) fitted profiles with Pearson VII functions, but the test example TiC was a simple structure. These authors showed the second and third derivatives to be useful in estimating the number of reflexions in an overlapped composite. Mortier and Costenoble (1973) decomposed peaks of hydrated K-Y and Ca-Y zeolites describing the profile as a Fourier series, and allowing for the  $(\alpha_1, \alpha_2)$  doublet.

An ingenious method for  $I(hkl)$  extraction was given by Pawley (1981) in which each  $(hkl)$  in the pattern was allotted an  $I$  value which was allowed to vary until the profile was fitted. The output provided a list of  $hkl$ ,  $2\theta$ ,  $I$  and  $\sigma(I)$ , and the refined unit cell and zero. When two reflexions completely overlapped, however, the least-squares procedure became unstable and slack constraints were introduced. For exact superposition, the intensity could only be divided equally between the contending reflexions, which may be a serious drawback to the use of direct methods in complex structures as these are sensitive to errors in the intensity. Overlap is common in structures which deviate slightly from a higher symmetry. This method is perhaps barely feasible on D1A but holds more promise with very high resolution data.

#### (h) Background Intensity

Suortti (1980) summarized the factors contributing to the background intensity. Visually estimated background in regions between Bragg peaks tends to be over-estimated, and it is preferable to refine the background. The Wiles-Young (1981), EDINP (Pawley 1980) and NBS Rietveld programs (Trevino *et al.* 1980) have refinable backgrounds.

Ideally, the sample background should be calculated and subtracted with the instrumental background from the pattern. Sabine and Clarke (1977) did this for the neutron pattern of the mineral cosmochlorite, neglecting thermal diffuse scattering (TDS). In practice, this approach is difficult, because the TDS intensity distribution is difficult to compute, and there also may be background modulations due to dynamic (Boysen and Hewat 1978) or static disorder, or humps due to the presence of amorphous material. Powell *et al.* (1982) lowered their  $R$  factors for the neutron powder data of CS<sub>2</sub> at 150 K by assuming a background of the form  $B + CQ^2 \exp(-C^1 Q^2)$ , where  $B$ ,  $C$  and  $C^1$  are background parameters; this shape was characteristic of TDS. Immirzi (1980) gave background humps in a polypropylene X-ray pattern their own Pearson VII parameter.

#### (i) Constrained Refinement of Powder Diffraction Data

The powder method has the disadvantage of compressing the data into one dimension, with a low ratio of observations to variables, which precludes a full refinement of complicated structures. One way of reducing the number of variables is to fix a known molecular geometry to within certain limits. Little is lost as the dimensions of benzene rings, silicate tetrahedra, etc. are known from single-crystal studies. The powder investigator is more interested in the arrangement of the molecules.

X-ray single-crystal refinement programs such as SHELX have elaborate systems

of constraints. The powder program of Rietveld (Hewat 1973*b*) has only simple constraints, with which octahedra in oxides, for example, can be kept rigid (Hewat 1980). To extend these constraints, Pawley (1980) wrote the program EDINP which is suitable for organic molecular crystals and specifies molecular orientations by three Euler angles. This program has now been applied many times in organic powder refinements; for example, Pawley (1978) showed that disorder in tetraiodoethylene could be detected by constrained neutron powder refinement, which previous workers with the same data had overlooked. Bacon *et al.* (1979) found constrained neutron powder refinement (31 variables) of  $\alpha$ -resorcinol agreed well with single-crystal neutron refinement (125 parameters) although some fine details were lost. The structures of  $p\text{-C}_6\text{F}_4\text{Br}_2$  and  $p\text{-C}_6\text{F}_4\text{I}_2$  were solved from neutron powder data and refined by EDINP (Pawley *et al.* 1977). False minima due to the scattering lengths of F, Br and I being nearly equal were recognized in the constrained refinements.

The fluorine density was constrained in the neutron powder studies of the plastic cubic phases of  $\text{MoF}_6$ ,  $\text{WF}_6$  and  $\text{SF}_6$  (Levy *et al.* 1975, 1976; Taylor and Waugh 1976) to be on the surface of a sphere with a radius equal to the M–F distance. There were only four variables in the refinements in  $I\bar{m}3m$ , the scale, an overall  $B$  factor, a harmonic coefficient and the M–F distance.

With silicates, the  $\text{SiO}_4$  tetrahedra can be regarded as regular in powder refinements. Baerlocher (1984) refined the TPA-ZSM5 structure with  $\text{Cu K}\alpha_1$  X-ray diffractometer data using a modified X-RAY system, originally written for single-crystal refinements, and imposed soft constraints on the tetrahedra and the TPA molecule. There were 165 geometrical constraints and 181 structural parameters, although overall  $B(\text{Si})$  and  $B(\text{O})$  parameters would have been preferable to giving each atom its own isotropic  $B$  factor. The final e.s.d. value in the coordinates was about  $0.02 \text{ \AA}$  for Si and O. This is the largest structure so far refined with powder data. Cartlidge *et al.* (1984) and McCusker (1984) refined other zeolite structures with this program and similar constraints, one structure, gobbinsite, having 64 structural parameters.

Immirzi (1980) has written a program with constraints for powder refinement of helix structures, and it has been applied to X-ray powder studies of polypropylene, which has a  $3_1$  helix, and polymeric  $\text{NaPO}_3$  (Kurrol salt,  $4_1$  helix). Constrained refinements greatly increase the range of powder diffraction because the structures are seen to be built up from larger units instead of individual atoms. They should be used wherever possible.

#### 4. Performance of Powder Methods in Structure Studies

##### (a) Structure Solution from Powder Data

Before such an analysis can commence the unit cell must be found with indexing programs, such as those by Taupin (1973*b*), Visser (1969) and Kohlbeck and Horl (1978). The  $2\theta$  values must be accurate ( $\pm 0.02^\circ$ ) for low symmetry patterns, otherwise the programs generate many possible cells. Werner has had success in indexing low-symmetry patterns with his program TREOR (see e.g. Berg and Werner 1977; Westman *et al.* 1981), as has the Petten school (see e.g. Cordfunke *et al.* 1977).

In single-crystal analysis, structure solution is now semi-automatic with powerful direct method programs such as MULTAN or SHELX. This is not the case for the overlapped data in powder patterns, where structures have in the past been solved (a) by looking for isostructural compounds in tabulations such as that by Wyckoff

(1965) or BIDICS (Brown *et al.* 1969–81), (b) by trial-and-error testing of chemically plausible models, or (c) by deducing the most likely packing configurations for molecules of known geometry. With patterns showing reasonable resolution, the overlapped intensities can sometimes be decomposed into the component (*hkl*) intensities by the intensity-extraction programs mentioned above, and then single-crystal techniques applied.

A search through Wyckoff (1965) showed that the room-temperature form of  $\text{Na}_2\text{UBr}_6$  was of the  $\text{Na}_2\text{SiF}_6$  type (Hewat *et al.* 1980, 1984). The high-temperature form of  $\text{Na}_2\text{UBr}_6$  was solved by noting a resemblance with the patterns of the plastic cubic hexafluorides studied earlier; the sodium atoms were invisible to neutrons because of their high mobility in the fast-ion conductor form (Hewat *et al.* 1980, 1984). Optimal packing configurations were used by Baharie and Pawley (1979) and Pawley *et al.* (1977) in solving the organic structures  $\text{C}_6\text{Br}_6$ ,  $\text{p-C}_6\text{F}_4\text{Br}_2$  and  $\text{p-C}_6\text{F}_4\text{I}_2$  from neutron powder data.

Trial-and-error methods using models derived from experience have revealed structures from powder data. The structures of  $\text{UBr}_4$ ,  $\text{UBr}_5$ ,  $\text{UI}_4$ ,  $\text{MoOCl}_4$  and the intermediate phase of  $\text{Na}_2\text{UBr}_6$  were solved in this way with neutron data (sometimes with additional information) (Taylor and Wilson 1974; Levy *et al.* 1978; Levy *et al.* 1980; Taylor and Waugh 1980; Hewat *et al.* 1984). Bevan *et al.* (1982) used their considerable knowledge of structure types in solving and refining the structures of the fluorite-related phases  $\text{Er}_{10}\text{W}_2\text{O}_{21}$  and  $\text{Y}_{10}\text{W}_2\text{O}_{21}$  with X-ray diffractometer data (both had 48 positional parameters). References are given in their paper to seven earlier powder *ab initio* determinations. A further determination in this series was that of Rossell (1982) in the solution of calzirtite (17 positional parameters). Cadee and Ijdo (1981) solved the structure of  $\text{BaSn}_{0.9}\text{Fe}_{5.47}\text{O}_{11}$  by deducing that there were two  $\text{BaO}_3$  and four  $\text{O}_4$  layers by comparison with  $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ , and one of three possible models refined with NPPA. Jacobson and Hutchinson (1980) found the structure of the perovskite-related  $12\text{HBaCoO}_{2.6}$  by a combination of high-resolution electron microscopy (to determine layer sequences) and NPPA. Groult *et al.* (1984) solved the structure of  $\text{KCuNb}_3\text{O}_9$  from X-ray powder data by guessing a model from other oxide structures and refining with integrated intensities.

The Zurich school have used the program CUFIT to decompose their X-ray patterns along with the model-generating program DLS to provide trial structures for zeolites. In this way Baerlocher and Barrer (1974) and Meier and Groner (1981) solved the structures of the zeolites F and EAB. Barri *et al.* (1984) found the 28 positional parameters in the new medium-pore high-silica zeolite THETA-1 by trial-and-error methods.

Scandinavian coworkers have solved some complex structures from Guinier–Hagg data using Patterson methods to locate the heavier atoms and the Rietveld (1969) decomposition formula to locate the other atoms in Fourier syntheses. Examples are the analyses of a molybdenum complex (55 coordinates) by Berg and Werner (1977), some ammines of calcium chloride (Westman *et al.* 1981) and copper paraperiodate hydrate (32 coordinates) by Adelskold *et al.* (1981).

The first application of direct methods to powder data appears to be the analysis of  $\text{MnP}_4$  (15 coordinates) by Nolang and Tergenius (1980) with Guinier data. Christensen (1984) reported progress with direct methods and the Pawley extraction program on  $\alpha\text{-ScOOH}$  and  $\text{Ca}_5(\text{SiO}_4)_2(\text{OD})_2$  and  $\alpha\text{-Zr}(\text{NaPO}_4)(\text{DPO}_4)\text{D}_2\text{O}$ , some data being collected on the DESY synchrotron facility. More *ab initio* determinations such as

these should appear when D2B and synchrotron diffractometers become available for users.

Toraya *et al.* (1984) used the Rietveld (1969) intensity decomposition formula to solve the structure of a metal complex with 113 positional variables. The 'crystals' were actually bundles of fibres and by collecting several layers about the fibre axis on a Weissenberg camera, Toraya *et al.* were able to obtain well-resolved sets of powder data. The heavy atoms were located in a Patterson synthesis of the resolved reflexions. The intensities of the overlapped reflexions could then be extracted by dividing up in the ratios of the calculated intensities by the Rietveld procedure, and the total data (944 reflexions) used in difference syntheses to locate the missing atoms. This decomposition was performed at each refinement stage to convergence. It was possible to arrive at the structure in this way, whereas analysis of the fibre bundles was not possible with single-crystal programs.

### *(b) Survey of Structures Refined by Powder Methods*

A survey of likely journals and authors yielded 141 papers over the last eight years covering 218 structures for neutron powder diffraction and 26 papers (31 structures) for X-ray powder diffraction. This list may be incomplete as some papers may be in (obscure) specialist journals, but it does give some ground for a rough statistical analysis. First, Rietveld refinements are preferred to integrated-intensity refinements by a factor of about 8. The neutron refinements could be apportioned as follows: phase transitions 23 papers (64 structures); oxides 31 (50); hydrides 28 (36); organics 13 (14); zeolites 6 (6); halides 5 (5); uranium compounds 5 (5); and miscellaneous 21 (29). In the field of phase transitions, Hewat and coworkers have contributed 13 papers covering 37 refinements of different phases, Pawley published 7 constrained refinements of organics, and Cava, Roth, Santoro and coworkers 9 papers on oxides at NBS, mainly on Li insertion into host oxide lattices. Fixed-wavelength and TOF work has been done on lead dioxides in battery plates (see also Hill 1982). The Li-insertion compounds, phase transitions and hydrides probably could not have been done by any other technique because the reactions with H, D or Li and the transitions cause the powders to decrease in crystallite size. Zeolite structures are being refined by XPPA at Zurich (Baerlocher, Meier, McCusker) and neutrons at Grenoble (Adams, Hewat). More zeolite structures will appear when workers master the art of locating the thermally mobile occluded molecules in the sometimes large aluminosilicate frameworks. Low-temperature work here is necessary.

It would be tedious here to list each structure solved, and its chemical or physical significance. It is pointed out simply that a large number of meaningful results have been achieved. D1A at Grenoble has contributed more results than any other neutron powder diffractometer.

### *(c) How Well are Powder Methods Performing?*

From the neutron powder refinements mentioned above, we have selected the metal oxide structures (excluding phase transition studies) as being typical. Some details of these refinements are given in Table 1. As there were fewer powder studies by X rays, all the X-ray refinements found, which contain a good proportion of oxides, are given in Table 2. The criteria of accuracy are taken as follows:

(a) The *R* factors: Not all workers quote the same *R* factor so in Table 2 we have tabulated  $R_F$ , the equivalent to the single-crystal *R* factor on *F*, or  $R_I$ , the *R* factor

Table 1. Some recent neutron powder refinements of oxides

Compound	Reference	Technique, <sup>A</sup> location	R (%)	$\sigma(O)$ (Å)	$U$ (Å <sup>3</sup> )	Space group	$N_P$	Refinement method <sup>B</sup>
NdAlO <sub>3</sub>	Roult <i>et al.</i> (1983)	TOF, Grenoble	$R_p = 2.2$	0.001	316.5	$R\bar{3}c$	1	R
$\beta$ -PbO <sub>2</sub> :D	Jorgensen <i>et al.</i> (1982)	TOF, ZING-P'	$R_p = 5.5$	0.001	82.9	$P4/mnm$	1	R
$\beta$ -PbO <sub>2</sub> :H			$R_p = 4.3$	0.001	82.7	$P4_2/mnm$	1	R
Mg <sub>2</sub> SiO <sub>4</sub>	Lager <i>et al.</i> (1981 <i>b</i> )		$R_p = 2.1$	0.001	290.0	$Pbnm$	11	R
Al <sub>2</sub> O <sub>3</sub>	Jorgensen & Rotella (1982)		$R_p = 2.7$	0.00026	255.5	$R\bar{3}c$	2	R
Al <sub>2</sub> O <sub>3</sub>	Hewat & Bailey (1976)	FW, D1A	$R_F = 1.0$	0.00036	255.6	$R\bar{3}c$	2	R
Li <sub>0.36</sub> WO <sub>3</sub>	Wiseman & Dickens (1976)	FW, Harwell	$R_I = 1.4$	0.007	412.8	$Im\bar{3}$	2	I
Na <sub>0.73</sub> WO <sub>3</sub>			$R_I = 0.4$	0.0015	454.8	$Im\bar{3}$	2	I
Na <sub>0.54</sub> WO <sub>3</sub>			$R_I = 0.9$	0.0015	448.8	$Im\bar{3}$	2	I
Ca <sub>0.14</sub> WO <sub>3</sub>			$R_I = 0.6$		56.3	$Pm\bar{3}m$	0	I
BaCoO <sub>2.6</sub>	Jacobson & Hutchinson (1980)		$R_p = 15.9$	0.017	820.5	$P6_3/mmc$	14	R
Ba <sub>2</sub> LaRuO <sub>6</sub>	Battle <i>et al.</i> (1983)	FW, D1A	$R_{wp} = 9.5$	0.01	311.9	$P\bar{1}$	12	R
Ca <sub>2</sub> LaRuO <sub>6</sub>			$R_{wp} = 8.0$	0.002	264.5	$P2_1/n$	12	R
Ba <sub>3</sub> SrNb <sub>2</sub> O <sub>9</sub>	Zandbergen & Ijdo (1983)	FW, Petten	$R_p = 4.9$	0.002	490.7	$P6_3/m$	7	R
Ba <sub>3</sub> SrTa <sub>2</sub> O <sub>9</sub>			$R_p = 5.5$	0.002	490.6	$P6_3/m$	7	R
Ba <sub>1.17</sub> Ti <sub>5.04</sub> Al <sub>2.1</sub> O <sub>16</sub>	Sabine & Hewat (1982)	FW, D1A	$R_{nucl.} = 5$	0.003	292.2	$I4/m$	7	R
BaSn <sub>0.9</sub> Fe <sub>5.47</sub> O <sub>11</sub>	Cadee & Ijdo (1981)	FW, Petten	$R_p = 11.7$	0.018	437.6	$P\bar{3}m1$	18	R
CaTiO <sub>3</sub>	Koopmans <i>et al.</i> (1983)		$R_p = 4.5$	0.002	224.1	$Pcmn$	7	R
CaZrO <sub>3</sub>			$R_p = 4.0$	0.002	258.3	$Pcmn$	7	R
CaMnO <sub>2.5</sub>	Poepelman <i>et al.</i> (1982)	FW, Missouri	$R_p = 13.3$	0.008	207.2	$Pbam$	8	R
Ca <sub>2</sub> YRuO <sub>6</sub>	Battle & Macklin (1984)	FW, D1A	$R_{wp} = 8.9$	0.002	254.1	$P2_1/n$	12	R
CeTaO <sub>4</sub>	Santoro <i>et al.</i> (1980)	FW, NBS	$R_p = 8.3$	0.0040	320.6	$P2_1/c$	18	R
CeNbO <sub>4</sub>			$R_p = 7.3$	0.0015	323.9	$I2/a$	8	R
NdTaO <sub>4</sub>			$R_p = 9.4$	0.0022	314.8	$I2/a$	8	R
MnPt <sub>3</sub> O <sub>6</sub>	Schwartz <i>et al.</i> (1983)	FW, BNL	$R_{wp} = 17$	0.01	226.1	$Cmmm$	3	R
CoPt <sub>3</sub> O <sub>6</sub>			$R_I = 2.5$	0.01	221.3	$Cmmm$	3	R
ZnPt <sub>3</sub> O <sub>6</sub>			$R_I = 3.3$	0.01	222.8	$Cmmm$	3	R
MgPt <sub>3</sub> O <sub>6</sub>			$R_I = 5.3$	0.01	222.4	$Cmmm$	3	R
NiPt <sub>3</sub> O <sub>6</sub>			$R_I = 3.5$	0.02	219.3	$Pbam$	8	R

Table 1. [continued]

Compound	Reference	Technique, <sup>A</sup> location	R (%)	$\sigma(\text{O})$ (Å)	$U$ (Å <sup>3</sup> )	Space group	$N_p$	Refinement method <sup>B</sup>
Li <sub>0.64</sub> Pt <sub>3</sub> O <sub>4</sub>	Schwartz <i>et al.</i> (1982 <i>a</i> )		$R_{wp} = 16$	0.002	177.9	$P\bar{4}3n$	1	R
Co <sub>0.37</sub> Na <sub>0.14</sub> Pt <sub>3</sub> O <sub>4</sub>			$R_{wp} = 16$	0.004	178.7	$Pm\bar{3}$	2	R
NaPt <sub>3</sub> O <sub>4</sub>	Schwartz <i>et al.</i> (1982 <i>b</i> )		$R_{wp} = 12$		183.9	$Pm\bar{3}n$	0	R
Na <sub>0.73</sub> Pt <sub>3</sub> O <sub>4</sub>	Ijdo (1982)	FW, Petten	$R_{wp} = 21$		182.8	$Pm\bar{3}n$	0	R
NaCaVO <sub>4</sub> (300 K)			$R_p = 4.6$	0.002	391.0	$Cmcm$	6	R
Ni <sub>2.62</sub> Ti <sub>0.69</sub> O <sub>4</sub>	Lager <i>et al.</i> (1981 <i>a</i> )	TOF, ZING-P'	$R_p = 3.3$	0.001	580.4	$Fd\bar{3}m$	1	R
Ni <sub>2.42</sub> Ti <sub>0.74</sub> Si <sub>0.05</sub> O <sub>4</sub>			$R_p = 3.1$	0.001	576.4	$Fd\bar{3}m$	1	R
9LiTaO <sub>3</sub> ·Ta <sub>2</sub> O <sub>5</sub>	Santoro <i>et al.</i> (1982)	FW, NBS	$R_p = 6.9$	0.003	317.5	$R\bar{3}$	5	R
LiTaO <sub>3</sub>			$R_p = 7.0$	0.003	315.9	$R\bar{3}c$	4	R
Li <sub>2</sub> SnO <sub>3</sub>	Hodeau <i>et al.</i> (1982)		$R_p = 6.7$	0.004	479.2	$C2/c$	15	R
Li <sub>2</sub> ZrO <sub>3</sub>			$R_p = 6.4$	0.003	244.5	$C2/c$	6	R
LiReO <sub>3</sub>	Cava <i>et al.</i> (1982)		$R_p = 5.6$	0.01	300.9	$R\bar{3}c$	4	R
Li <sub>2</sub> ReO <sub>3</sub>			$R_p = 7.6$	0.01	316.5	$R\bar{3}c$	5	R
Li <sub>0.2</sub> ReO <sub>3</sub>			$R_p = 6.9$	0.002	404.9	$Im\bar{3}$	2	R
Li <sub>0.36</sub> ReO <sub>3</sub>	Cava <i>et al.</i> (1983 <i>a</i> )		$R_p = 7.0$	0.002	414.0	$Im\bar{3}$	2	R
LiTi <sub>2</sub> O <sub>4</sub>	Cava <i>et al.</i> (1984 <i>a</i> )		$R_p = 6.6$	0.002	140.5	$Imma$	4	R
LiTi <sub>2</sub> O <sub>4</sub>			$R_p = 6.8$	0.0004	593.4	$Fd\bar{3}m$	1	R
Li <sub>2</sub> Ti <sub>2</sub> O <sub>4</sub>			$R_p = 7.7$	0.002	587.6	$Fd\bar{3}m$	1	R
Li <sub>2</sub> FeV <sub>3</sub> O <sub>8</sub>	Cava <i>et al.</i> (1983 <i>b</i> )		$R_p = 5.8$	0.006	289.3	$C2/m$	14	R
MoO <sub>2</sub>	Cox <i>et al.</i> (1982)	FW, BNL	$R_{wp} = 7.8$	0.004	120.9	$P2_1/c$	9	R
LiMoO <sub>2</sub>			$R_{wp} = 11.6$	0.005	148.9	$P2_1/c$	12	R
Li <sub>3.4</sub> Si <sub>0.7</sub> S <sub>0.3</sub> O <sub>4</sub>	Fitch <i>et al.</i> (1984)	FW, D1A	$R_p = 7.8$	0.002	329.9	$Pmnb$	22	R
Li <sub>3.4</sub> Si <sub>0.7</sub> S <sub>0.3</sub> O <sub>4</sub>			$R_p = 7.8$	0.002	337.0	$Pmnb$	22	R
Li <sub>3.4</sub> Si <sub>0.7</sub> S <sub>0.3</sub> O <sub>4</sub>			$R_p = 8.2$	0.002	345.7	$Pmnb$	22	R
$\beta$ -PbO <sub>2</sub>	D'Antonio & Santoro (1980)	FW, NBS	$R_p = 12.3$	0.001	83.3	$P4_2/mnm$	1	R
LaTaO <sub>4</sub>	Cava & Roth (1981)		$R_p = 6.5$	0.004	327.2	$A2_1am$	12	R
TiO <sub>2</sub>	Sabine & Howard (1982)	FW, Lucas Heights	$R_p = 11.3$	0.001	62.4	$P4_2/mnm$	1	R
Zr <sub>3</sub> V <sub>3</sub> OD <sub>x</sub>	Rotella <i>et al.</i> (1983)	TOF, IPNS-1	$R_p = 2.0$	0.001	1965.4	$Fd\bar{3}m$	9	R

<sup>A</sup> A TOF, time-of-flight technique; FW, fixed-wavelength technique. <sup>B</sup> R, Rietveld method; I, integrated-intensity method.

Table 2. Some recent X-ray powder refinements

Compound	Reference	Technique <sup>A</sup>	R (%)	$\sigma(O)$ (Å)	Space group	$U$ (Å <sup>3</sup> )	$N_p$	Refinement method <sup>B</sup>
KCuTa <sub>3</sub> O <sub>9</sub>	Groult <i>et al.</i> (1984)	XRD, Cu K $\alpha$	$R_I = 6.7$	0.08	<i>Pnc2</i>	689.5	38	I
KCuNb <sub>3</sub> O <sub>9</sub>			$R_I = 6.2$	0.08	<i>Pnc2</i>	687.6	38	I
Ta <sub>5</sub> P <sub>3</sub>	Thomas <i>et al.</i> (1980)	GH, Cr K $\alpha_1$	$R_p = 8.3$	$\sigma(P) = 0.04$	<i>Pnma</i>	987.1	32	R
Ca <sub>2</sub> Zr <sub>5</sub> Ti <sub>2</sub> O <sub>16</sub>	Rossell (1982)	XRD, Cu K $\alpha$	$R_I = 3.1$	0.03	<i>I4<sub>1</sub>/acd</i>	2344.9	17	I
Er <sub>10</sub> W <sub>2</sub> O <sub>21</sub>	Bevan <i>et al.</i> (1982)		$R_I = 3.7$	0.15	<i>Pbcn</i>	1748.0	48	I
Y <sub>10</sub> W <sub>2</sub> O <sub>21</sub>			$R_I = 5.1$	0.15	<i>Pbcn</i>	1767.2	48	I
Mg <sub>2</sub> NiH <sub>x</sub>	Noreus & Werner (1982)		$R_F < 20.0$	$\sigma(Mg) = 0.03$	<i>P6<sub>3</sub>22</i>	317.7	3	R
Cu <sub>2</sub> HfO <sub>6</sub> ·2H <sub>2</sub> O	Adelskold <i>et al.</i> (1981)	GH, Cu K $\alpha_1$	$R_F = 11.5$	0.08	<i>P2<sub>1</sub></i>	310.5	32	R
Sc <sub>3</sub> As <sub>2</sub>	Berger (1980)		$R_p = 21.7$	$\sigma(Sc, As) = 0.01, 0.006$	<i>Pnma</i>	409.7	10	R
CaCl <sub>2</sub> (NH <sub>3</sub> ) <sub>8</sub>	Westman <i>et al.</i> (1981)		$R_F = 21.7$	$\sigma(N) = 0.05$	<i>Pnma</i>	1335.2	18	R
CaCl <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub>			$R_F = 17.4$	$\sigma(N) = 0.10$	<i>Abm2</i>	580.2	7	R
CaClOH			$R_F = 13.8$	0.03	<i>P6<sub>3</sub>mc</i>	147.9	2	R
MnP <sub>4</sub>	Nolang & Tergenius (1980)	GH, Cr K $\alpha_1$	$R_p = 13.7$	$\sigma(Mn, P) = 0.01$	<i>P<math>\bar{1}</math></i>	1163.8	15	R
CuNb <sub>3</sub> O <sub>8</sub>	Marinder <i>et al.</i> (1980)	GH, Cu K $\alpha_1$	$R_p = 21.5$	0.06	<i>P2<sub>1</sub>/a</i>	560.3	36	R
K <sub>0.72</sub> In <sub>0.72</sub> Sn <sub>0.28</sub> O <sub>2</sub>	Delmas & Werner (1978)		$R_F = 12.8$	0 <sup>C</sup>	<i>P6<sub>3</sub>m2</i>	133.9	4	R
Ta <sub>3</sub> P	Willerstrom <i>et al.</i> (1983)		$R_p = 18.0$	$\sigma(Ta) = 0.009$	<i>P4<sub>2</sub>/n</i>	517.0	9	R
(NH <sub>4</sub> )[(MoO <sub>2</sub> ) <sub>4</sub> O <sub>3</sub> ] (C <sub>4</sub> H <sub>3</sub> O <sub>5</sub> ) <sub>2</sub> ·H <sub>2</sub> O	Berg & Werner (1977)		$R_F = 11.0$	$\sigma(Mo-O) = 0.15$	<i>C2</i>	1441.0	55	R

Table 2. [continued]

Compound	Reference	Technique <sup>A</sup>	R (%)	$\sigma(\text{O})$ (Å)	Space group	$U$ (Å <sup>3</sup> )	$N_p$	Refinement method <sup>B</sup>
Hf <sub>3</sub> As	Willerstrom <i>et al.</i> (1980)	GH, Cr K $\alpha_1$	$R_p = 12.8$	$\sigma(\text{As}) = 0.019$	$C2/c$	1269.4	24	R
ZrB <sub>51</sub>	Callmer <i>et al.</i> (1978)		$R_F = 6.3$	$\sigma(\text{Zr}) = 0.003$	$R\bar{3}m$	2497.1	7	R
NaPO <sub>3</sub>	Immirzi & Porzio (1982)	XRD, Cu K $\alpha$	$R_p = 5.5$	$\approx 0.10$	$I4_1/a$	1031.4	15	R
[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ] <sub>4</sub> Mo <sub>6</sub> O <sub>20</sub> ·2H <sub>2</sub> O	Toraya <i>et al.</i> (1984)	WPD, Cu K $\alpha$	$R_F = 15.2$	0.08 <sup>D</sup>	$P2_1$	1549.9	113	RD
Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Nord & Stefanidis (1983)	GH, Cr K $\alpha_1$	$R_F = 9.0$	0.015	$P2_1/n$	319.5	15	R
La <sub>0.75</sub> Si <sub>0.25</sub> CrO <sub>3</sub>	Khattak & Cox (1977)	XRD, Cu K $\beta$	$R_p = 13.7$	0.016	$R\bar{3}c$	336.3	1	R
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	Young <i>et al.</i> (1977)	XRD, Cu K $\alpha$	$R_p = 12.0$	0.01	$P6_3/m$	522.7	10	R
SiO <sub>2</sub>			$R_p = 14.2$	0.005	$P3_221$	112.8	4	R
LaPO <sub>4</sub>			$R_p = 18.6$	$\approx 0.07$	$P2_1/n$	307.4	18	R
Bi <sub>2</sub> O <sub>3</sub>	Cox <i>et al.</i> (1983)	SYNCH		0.08	$P2_1/c$	330.3	15	R
SiO <sub>2</sub>	Thompson & Wood (1983)	DS, Cu K $\beta$	$R_p = 14.0$	0.004	$P3_221$	112.8	4	R
Al <sub>2</sub> O <sub>3</sub>			$R_p = 11.8$	0.002	$R\bar{3}c$	255.0	2	R
AlPO <sub>4</sub>			$R_p = 13.7$	0.01	$P3_221$	231.5	8	R
LiTaO <sub>3</sub>			$R_p = 18.7$	0.04	$R\bar{3}c$	317.1	4	R
SiO <sub>2</sub>	Young & Wiles (1982)	XRD, Cu K $\alpha$	$R_{wp} = 12.6$	0.001	$P3_221$	112.8	4	R
Al <sub>2</sub> O <sub>3</sub>			$R_{wp} = 27.5$	0.001	$R\bar{3}c$	254.9	2	R

<sup>A</sup> XRD, X-ray diffractometer; GH, Guinier-Hagg; WPD, Weissenberg powder mode; SYNCH, synchrotron; DS, Debye-Scherrer.

<sup>B</sup> I, integrated-intensity method; R, Rietveld method; RD, Rietveld decomposition.

<sup>C</sup> Not refinable. <sup>D</sup> Value is 0.15 along the needle axis.

on the integrated intensities, or  $R_p$ , the  $R$  factor on the scanpoints, usually quoted with background removed. A small 'w' indicates a weighted  $R$  factor. Goodness-of-fit indicators, unfortunately, are seldom given. The  $R$  factors have been defined by Hewat (1973 *b*).

(*b*) The largest e.s.d. value in an oxygen coordinate in the structure,  $\sigma(\text{O})$ , is taken as a further precision index. Cell volumes, space groups, and  $N_p$ , the number of positional parameters, are also given.

The refinements have gone very well with neutron powder data;  $\sigma(\text{O})$  was 0.00026–0.018 Å, with a mean value of 0.004 Å in Table 1. The profile  $R$  factors varied from 2.1 to 21%, with a mean of 8.2%. The structures were fairly small,  $N_p$  varying from 0–22 with an average of 6. The TOF neutron technique appears to be as precise as the fixed-wavelength high-resolution neutron powder method. Nearly all investigators used the Rietveld method.

By comparison, with modern single-crystal X-ray techniques, a recent issue of *Inorganic Chemistry* was consulted and for six structures containing oxygen  $\sigma(\text{O})$  was 0.005–0.018, with a mean of 0.011 Å ( $N_p$  varied from 59 to 123). On this basis, we may expect to do nearly as well with high-resolution neutron powder refinement as with X-ray single-crystal analysis, providing the structure is not too large. Considering the experimental simplicity and convenience in controlling sample conditions on the neutron diffractometer, it is no wonder that NPPA is so popular. We have not considered the Cooper effect here, as the single-crystal e.s.d. values are probably underestimated as well as the neutron e.s.d. values.

According to Table 2, the X-ray powder refinements have not done as well. With  $\sigma(\text{O})$  values up to 0.15, and an average of 0.05, the X-ray precision is lower by an average factor of 10. The profile  $R$  factors of 5.5–27.5% with a mean of 15.2% are twice as large as for neutrons. Some  $R$  factors on F, in the range 15–20%, occur with the Guinier–Hagg data; these are higher by factors of 3 or 4 than acceptable single-crystal  $R_F$  values. There is a noticeable trend in the Guinier–Hagg work not to publish difference profiles. On the credit side, the X-ray workers are looking at structures which are larger than the neutron structures ( $N_p = 3$ –113 with an average of 20). There have been excellent *ab initio* structure determination and refinements with  $N_p = 38, 48, 32, 36, 55$  and 113 (Table 2), and this trend promises to continue or even improve with the new synchrotron machines. Rietveld refinements also appear to be preferred over integrated-intensity refinements with X-ray data.

We have not considered TOF neutron profile refinements in great detail mainly because there are not many published. However, we can make a direct comparison of fixed-wavelength neutron Rietveld refinements of sulfur-containing Chevrel phases on the NBS reactor (Cava *et al.* 1984), and on the TOF instrument IPNS-1 at Argonne (Jorgensen *et al.* 1983). In the former,  $\sigma(\text{S})$  was 0.005 Å with  $R_p = 6.8\%$ , and the latter  $\sigma(\text{S})$  was 0.004 Å with  $R_{wp} = 4\%$ . This is a strong indication that high-resolution neutron TOF diffractometers perform as well as fixed-wavelength neutron diffractometers. Recently, Rotella *et al.* (1983) located a deuterium atom in  $\text{Zr}_3\text{V}_3\text{OD}_x$  to a precision of  $\sigma(\text{D}) = 0.001$  Å and  $R_p = 2\%$  (see Table 1).

Neutron powder refinements thus continue to improve and approach in precision conventional single-crystal X-ray refinements. However, there is room for improvement in X-ray powder refinements. These may however never reach the precision of neutron refinements because the scattering factors are less favourable, absorption corrections are much more severe, and instrumental aberrations are more troublesome. It

is likely that, in the immediate future, the number of neutron powder studies will still continue to be greater than the number of X-ray studies, despite the limited number of neutron sources. The NPPA, and to a lesser extent XPPA, are thus very useful for studying those structures that are difficult to crystallize or manipulate in single-crystal work. These techniques are obviously here to stay.

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