

PROFILE REFINEMENT OF NEUTRON POWDER DIFFRACTION PATTERNS

CRYSTAL AND MAGNETIC STRUCTURES

by

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ABSTRACT

The Rietveld technique of profile refinement of powder diffraction patterns makes the powder method much more competitive with the standard single crystal technique for the precise determination of moderately complex crystal structures. This report describes modifications to Rietveld's original computer program to allow the refinement of anisotropic thermal vibrations, and is intended as a guide for the use of the program. It is essentially a revised edition of an unpublished Harwell report *, and examples are given of published Harwell results in which the profile refinement technique has been used to study structural transitions in ferroelectrics, antiferroelectrics and hydrogen bonded materials. No attempt has been made to review the earlier work of Rietveld et al. on magnetic structures nor recent work on defect structures, Debye-Waller factors and standard crystal structure determination.

* Hewat, A.W. Harwell Report 73/239 unpublished, January 1973

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1. INTRODUCTION. ADVANTAGES OF THE NEUTRON POWDER METHOD FOR CRYSTAL STRUCTURE DETERMINATION

It is much easier to obtain a powder specimen than a single crystal of the size required for neutron diffraction : in fact, in some cases it is impossible to grow a suitable single crystal (§ 4.2). Even when single crystals are available, a strong argument can often be made for using the powder method instead.

At first sight, the powder method appears to be at a great disadvantage for work on any but the most simple structures. The usual technique of integrating under the Bragg peak to obtain the intensity or magnitude of the structure factor for each reflexion is impossible for more complex structures because of the overlap of adjacent Bragg peaks. This immediately rules out all of the standard methods of structure refinement developed over the past sixty years. It does not however, mean that the structural information is lost, merely that a new technique is needed to retrieve it (Rietveld, 1967). The very complexity of overlapping powder patterns means that they contain much information about the crystal structure. Rietveld's idea was to forget about separating the individual Bragg reflexions, and to concentrate instead on using the detailed shape of the powder pattern to decide between various structural models. The parameters for these models can be refined to give the best possible fit to the powder pattern profile.

Of course, information is irretrievably lost in a powder pattern if there is exact coincidence of two or more diffraction peaks. For example, in the cubic perovskite structure ABO_3 , differences between the intensities of the (710), (550) and (543) reflexions, all of which appear at the same Bragg angle, contain information about the anisotropy in the vibrations of the oxygen atoms (Hewat 1972a). Never-the-less, a large amount of information is retained in a powder diffraction pattern, including information about the anisotropy of the vibrational amplitudes.

By making use of all of this information it is often possible to learn as much about a crystal structure from a one day powder scan as from a much longer period on a single crystal instrument : the powder patterns mentioned in this report required less than twenty-four hours of instrument time each. In a single crystal experiment, diffractometer time is spent in aligning the crystal and checking for twinning, extinction etc. Sometimes a number of crystals must be tried to find the best one. Even with on-line computer control, a single crystal instrument is often inefficient in operation. If integrated Bragg intensities are required, most of the time is spent off the centre of the peak, measuring the base and the background regions, and more time is spent re-orientating the crystal for each Bragg peak Much less time is spent on aligning and testing a powder-specimen, and for complicated patterns, a greater proportion of the operation time is spent on counting near the centre of a Bragg peak. A simple counter scan is sufficient for a powder run, so that an expensive computer is not required to control the experiment.

Apart from the obvious cost-benefit advantages of high rates of data collection, the study of the effect on the structure of changes in temperature, pressure, etc. becomes very attractive when the run time is short. Such changes in the environment of a sample are very much easier to arrange on a powder diffractometer than on a single crystal machine where the sensitive crystal orientating mechanism is in the way.

Extinction, or the breakdown of the usual kinematic diffraction theory for the large single crystals needed for neutron structural work, introduces systematic errors into single crystal data, and limits the precision with which crystal structures can be obtained from such data. Other systematic errors occur because of the difficulty of correcting for thermal diffuse scattering. The extinction effect is very small for the powder method and the contribution from thermal diffuse scattering appears to be less important, so that in some cases more precise structures can be obtained with the powder method.

Finally it should be remembered that the profile program is a technique for structure refinement : it was not intended to compete with methods such as those based on Fourier techniques for the solution of structures about which very little is known. However with neutron diffraction we are almost always trying to refine the details of a structure which has already been solved approximately by X-ray or other techniques - finding more precise positions for the atoms, especially those of hydrogen, and the lighter elements, measuring magnetic moments, nuclear and magnetic disorder, defect structures, atomic vibrational amplitudes etc. For these structure refinement problems the Rietveld method of profile analysis of neutron powder patterns often has many advantages over the single crystal technique.

2. SUMMARY OF THE RIETVELD REFINEMENT PROCEDURE

Figure 1 shows a section of the powder pattern obtained at Harwell for the orthorhombic phase of perovskite KNbO_3 (Hewat, 1973a). The points represent the actual counts obtained for each scattering angle 2θ , and the solid line the pattern calculated for the structure obtained from the profile refinement program. In the 2θ range 61° to 75.5° there are 35 Bragg reflexions, the centres of which are marked along the base of the scan. Over 200 independent reflexions contribute to the complete pattern, measured between 2θ limits of 10° and 11° in less than twenty-four hours.

Rietveld showed that each Bragg reflexion can be described by a gaussian peak $y_{i,k}$ whose full width at half height H_k depends on three parameters U, V and W.

$$H_k^2 = U \tan^2 \theta_k + V \tan \theta_k + W$$

This gaussian

$$y_{i,k} = I_k \cdot \exp -b_k(2\theta_i - 2\theta_k)^2$$

with $b_k = 4 \ln 2 / H_k^2$ is arbitrarily cut off at a distance $1.5 H_k$ on either side of its centre $2\theta = 2\theta_k$ i.e. when its contribution becomes very small. The positions $2\theta_k$ and intensities I_k of these reflexions are determined by the structural parameters, ($I_k = t F_k^2 j_k L_k^2 \sqrt{\ln 2} / (H_k \sqrt{\pi})$ where t is the counter step width, F_k the structure factor, j_k the multiplicity and L_k the Lorentz factor).

For each 2θ point in the diffraction pattern, the profile refiner program calculates the contributions from all of the Bragg reflexions in the vicinity, and compares the total $y_i(\text{calc})$ with the observed count $y_i(\text{obs})$ (Rietveld, 1969). The structure parameters, which determine $y_i(\text{calc})$, are then adjusted to minimize the quantity:

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

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

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

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

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

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

This probability is maximized if the exponent factor χ^2 is minimized using the weighting scheme $w_i \propto 1/\sigma_i^2 = 1/y_i(\text{calc}) \approx 1/y_i(\text{obs})$.

At low angles, allowance is made for peak asymmetry, and another parameter P is introduced (Rietveld, 1969). A fifth parameter Z is needed to specify the counter zero-point. In principle these parameters U , V , W , P and Z be determined once and for all for a given diffractometer geometry, but in practice it is necessary to refine at least Z for every pattern since any small change in the counter zero-point would otherwise have a large effect on the correspondence obtained between the observed and calculated patterns.

For the same reason, it is necessary to refine the lattice parameters a , b , c , α , β , γ even if both they and the wavelength are known. On the other hand, the fact that small changes in these parameters have a large effect on χ^2 means that they can be determined very precisely. For example, it is possible to obtain values, reproducible between independent runs on the PANDA diffractometer, to at least $1/4000$ and 0.02° for the cell edges and angles respectively.

3. MODIFICATIONS FOR ANISOTROPIC TEMPERATURE PARAMETERS

When anisotropic temperature factors β_{ij} are introduced, the real and imaginary parts of the atomic structure factor $F_k = A_k + iB_k$ become (BML-Busing, Martin and Levy, 1962)

XXXXXXXXXX

where

XXXXXXXXXXXXXXXXXX

$$\exp r = \exp \{ -\frac{1}{2} (h^2 k^2 l^2) \frac{1}{K} + (k^2) r^2 \frac{1}{22} + (1) r \frac{1}{333} (K) \}$$

The $(hk)_r$ are index products transformed to the equivalent position r . For atoms in general positions $(hk)_r = h_r k_r$, and this has been taken to be universally true for the purposes of the profile refinement program, as in the OR-FLS program (BML). The usual rules (Levy, 1956) can be used to determine the symmetry properties of the temperature parameter tensors $\beta_{ij}(\kappa)$. Constraint relations between the various β_{ij} can be introduced by means of the parameter codewords and constraint cards (§5.2) so that these symmetry properties are retained throughout the refinement.

New expressions for the derivatives of F_k with respect to the various parameters can easily be obtained from the above expressions : in all cases factor $\exp_{\kappa r}$ multiplies Rietveld's original $\cos_{\kappa r}$ and $\sin_{\kappa r}$ factors, and in case of the derivatives with respect to $\beta_{ij}(\kappa)$, additional factors of $(hk)_r = h_r k_r$ also appear inside the summation over equivalent positions.

Apart from the magnetic parameters (Rietveld, 1969), the structure parameters are now equivalent to those used in the OR-FLS program (BML), except that it is possible to specify either B_{ij} or β_{ij} temperature parameters in the input data. The program converts to β_{ij} for internal calculations, but reconverts to B_{ij} for the detailed print-out of the results.

4. EXAMPLES OF POWDER PATTERNS ANALYSED AT HARWELL

The five diffractometers used for powder work at Harwell have been described by IJedgwood (1968). I'll mention here some recent work on high resolution powder diffraction, for which the monochromator can be used

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} \left(1 - \frac{2\theta}{\lambda_0} \right) \quad \text{for } \lambda_0 = 0.7 \text{ \AA}$$

Characters 1432 73 94.90

from the hkl planes of a squashed germanium monochromator. The full width at half height at the focussing angle 2θ (approximately equal to the monochromator take-off angle) is 0.5 degrees, and 2θ can be set to a precision approach ± 0.01 degrees over the range -10° to 117° by means of a θ - 2θ fringe system. The design of a high resolution powder diffractometer has been discussed elsewhere (Hewat, 1974).

The neutron flux (about 7×10^5 counts/cm²/sec at the specimen) is such that a run can often be completed in 24 hours. Any temperature between 4.2 K and 1200°C is available at the specimen, which usually consists of

5-25 gm of powder in a vanadium or silica glass can.

4.1 Ferroelectric and antiferroelectric structural transition in perovskite

At high temperatures the perovskite AB₃O₃ structure is cubic, with A atoms on the corners, B atoms on the centres and O atoms on the centres of faces of the cubic cell. When the temperature is lowered, certain soft vibrational modes become unstable, and the resulting atomic displacements (~ 0.1 Å) alter the symmetry of the lattice, with changes of the order of 1% in a^2

lattice constants (e.g. Cochran and Zia, 1967). These small changes cause

splitting of the cubic perovskite diffraction lines, which cannot then be resolved; quite complicated powder patterns result (figure 2, from Hewat,

1973 a). As well as in "antiferroelectric" materials, the unit cell becomes a multiple of the original cell, and superlattice lines appear in the powder pattern (Hewat, 1973 c). It would be impossible to analyse such complex patterns on the usual basis of integrated intensities. For example, more than 200 different reflections contribute to the pattern for orthorhombic K₂FeO₃ (figure 2

We have been able to analyse such patterns though, using the present procedure with an isotropic temperature parameter. Figure 2 is typical

of a typical case: the agreement is

quite excellent (see also reference)

Seen Rejected Percentage

Characters	1637	28	98.29
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the entire pattern approaches the limit imposed by purely statistical fluctuations in the number of counts observed. The atomic positions are determined

this fit to at least $\pm 0.01 \text{ \AA}$, the cell dimensions to $\pm 0.001 \text{ \AA}$ and the cell angles to $\pm 0.02^\circ$. To allow comparison of the results of the profile refinement with those of single crystal work, we can calculate the quantity

$$R_{\text{Nuclear}} = 100 \cdot \frac{\sum |F_k(\text{obs}) - k(\text{calc})|}{\sum F_k(\text{obs})}$$

using the observed Intensities integrated for each reflexion at the end of the refinement. The observed counts can be divided up between overlapping reflexions **according to** the relative contributions of these reflexions computed from the fitted structure (Rietveld, 1969). Typical R_{Nuclear} factors of 2.5 and 2.6 were obtained for the orthorhombic and rhombohedral modifications respectively of KbO_3 . This compares favourably with careful single crystal measurements for similar problems (Hewat, Rouse and Zaccai, 1972; Hewat, 1976b). The uncertainties in the values of the structural parameters are no larger for the powder results than for the single crystal work.

$$G_{\text{rel}} = \frac{\sum |F_k(\text{obs}) - k(\text{calc})|}{\sum F_k(\text{obs})} \cdot C = \frac{\sum |F_k(\text{obs}) - k(\text{calc})|}{\sum F_k(\text{obs})} \cdot \frac{1}{\sum F_k(\text{obs})} \cdot B \cdot I_0$$

(Hewat, 1976b) for NbO_3 (Hewat et al., 1976c), TaO_3 , SrTiO_3 , BiHfO_3 , NaTaO_3 , AgNbO_3 and AgTaO_3 .

4. Hydrogen bonded ferroelectrics and ferroelectrics

Single crystals of hydrogen bonded $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{NH}_4\text{H}_2\text{AsO}_4$ break up when the antiferroelectric structural transition is encountered at lower temperatures. This makes single crystal work almost impossible but has no effect on

powder work. Figure 3 shows the changes observed in the powder pattern of fully deuterated H_2O when the antiferroelectric transition occurs (Hewlett-Packard). The lattice symmetry is C_{2v} and the hydrogen atoms order on one

of the two sites. The C_{2v} symmetry is broken to C_2 when the transition occurs. The lattice parameters are $a = 3.56 \text{ \AA}$, $b = 3.56 \text{ \AA}$, $c = 3.56 \text{ \AA}$. The space group is C_{2v} .

Seen Rejected Percentage

Characters	1553	89	94.27
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as postulated by Nagamiya (see Kanzig, 1957). The strong superlattice reflex appear in the low temperature phase because $\text{NH}_4\text{H}_2\text{P}_2\text{O}_7$ is an antiferroelectric rather than a ferroelectric like $\text{KH}_2\text{P}_2\text{O}_7$. Similar results have been obtained deuterated $\text{NH}_4\text{H}_2\text{AsO}_4$.

Other hydrogen bonded materials studied using the powder method include deuterated ferroelectric $\text{NaH}_3(\text{SeO}_3)_2$ and deuterated $\text{SnC}_2\text{H}_2\text{O}_4$.

4.3 Measurements of anisotropic and anharmonic vibrational amplitudes

Because extinction effects are negligible for the powder method we have used powder patterns to investigate thermal vibrations in several interesting materials.

Vibrational amplitudes, and lattice dynamical measurements in general are of importance for the A15 structure high temperature superconductors, such as Nb_3Sn . This material also has a structural transition at 45 K which we are attempting to study using the powder method. A profile analysis of the powder diffraction pattern shows that the chains of Nb atoms vibrate with considerable amplitude in directions perpendicular to the c chains along the c axis. The question of the so-called low temperature anharmonicity of the vibration of the Sn atoms (Hewat, 1972) has been resolved; further information will become available when the low temperature patterns have been analysed.

Further powder work on anharmonic vibrations has been done on materials including the rocksalt and layered structures.

4.4 Further powder work at Hanford using the profile refinement program

A large amount of work on defect and other structures has been done by Fendler, Jaccard, Cheetham (1973), van Dreele, Collins and others from 1970. Willis, Haywood, Higgins and others at Harwell are also applying the technique of simulation to the study of these fields. The results are

DU"J ~ Jd .

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