R. Van Dreele

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THE RIETVELD COMPUTER PROGRAM FOR THE PROFILE REFINEMENT OF NEUTRON DIFFRACTION POWDER PATTERNS MODIFIED FOR ANISOTROPIC THERMAL VIBRATIONS

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 at Harwell. Examples are given of recent work at Harwell in which the technique has been used to study structural transitions in ferroelectrics and hydrogen bonded materials, anisotropic and anharmonic atomic vibrations, and defect and magnetic structures, as well as for standard crystal structure determination.

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CONTENTS

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 some cases in fact, 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 sixy 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). Nevertheless a large amount of information is retained in a powder 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.

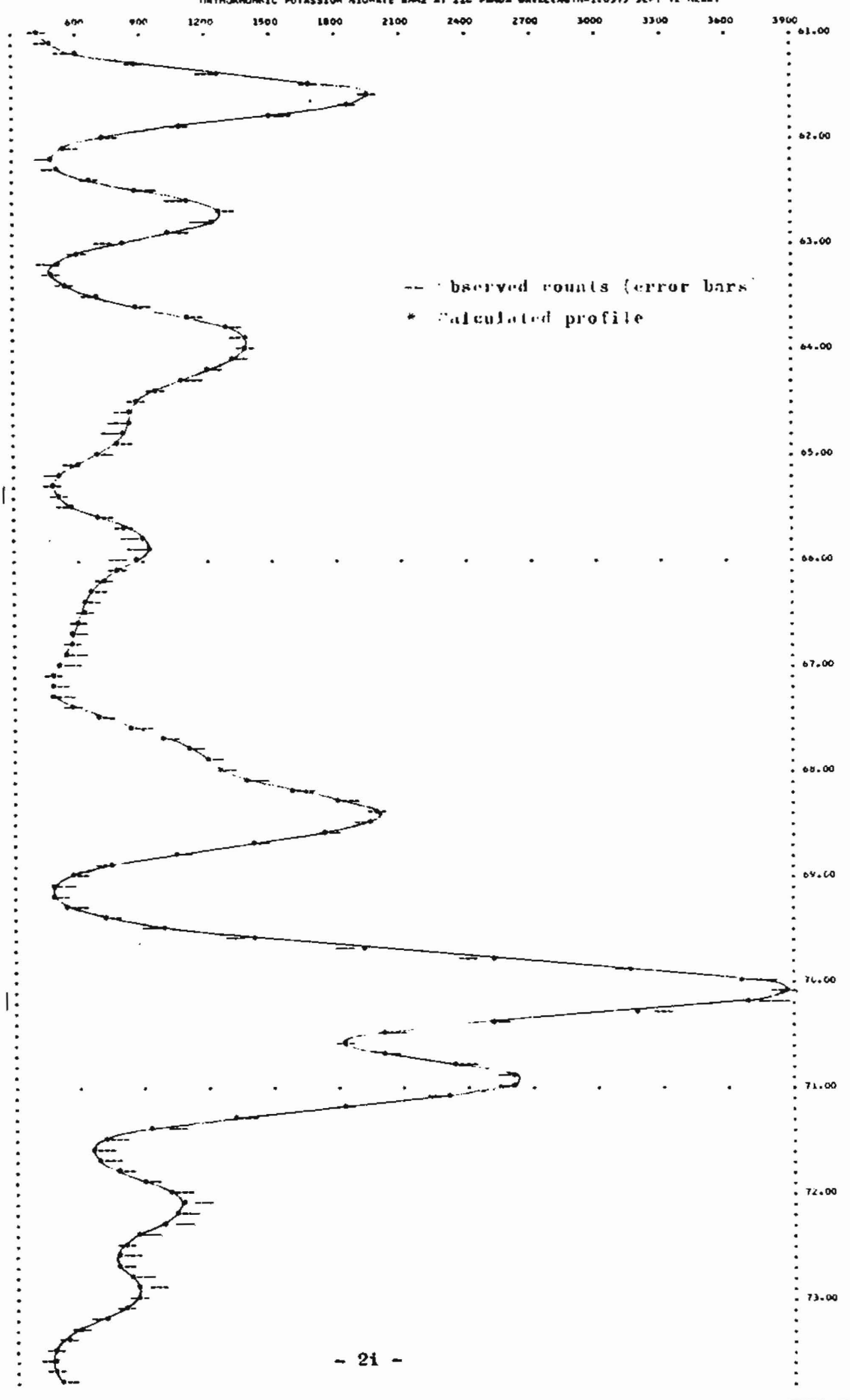
Extinction, or the breakdown of the usual kinematic diffraction theory for the large single crystals needed for neutron structural work, introduces systematic errors into single crystal data and limits the precision with which the crystal structure can be obtained from such data. Other systematic errors 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 error bars indicate the statistical uncertainties in the count obtained at each point, and the stars correspond to the calculated pattern 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 116° in less than twenty-four hours.

Figure 1 Observed and calculated profile section for $KNbO_3$



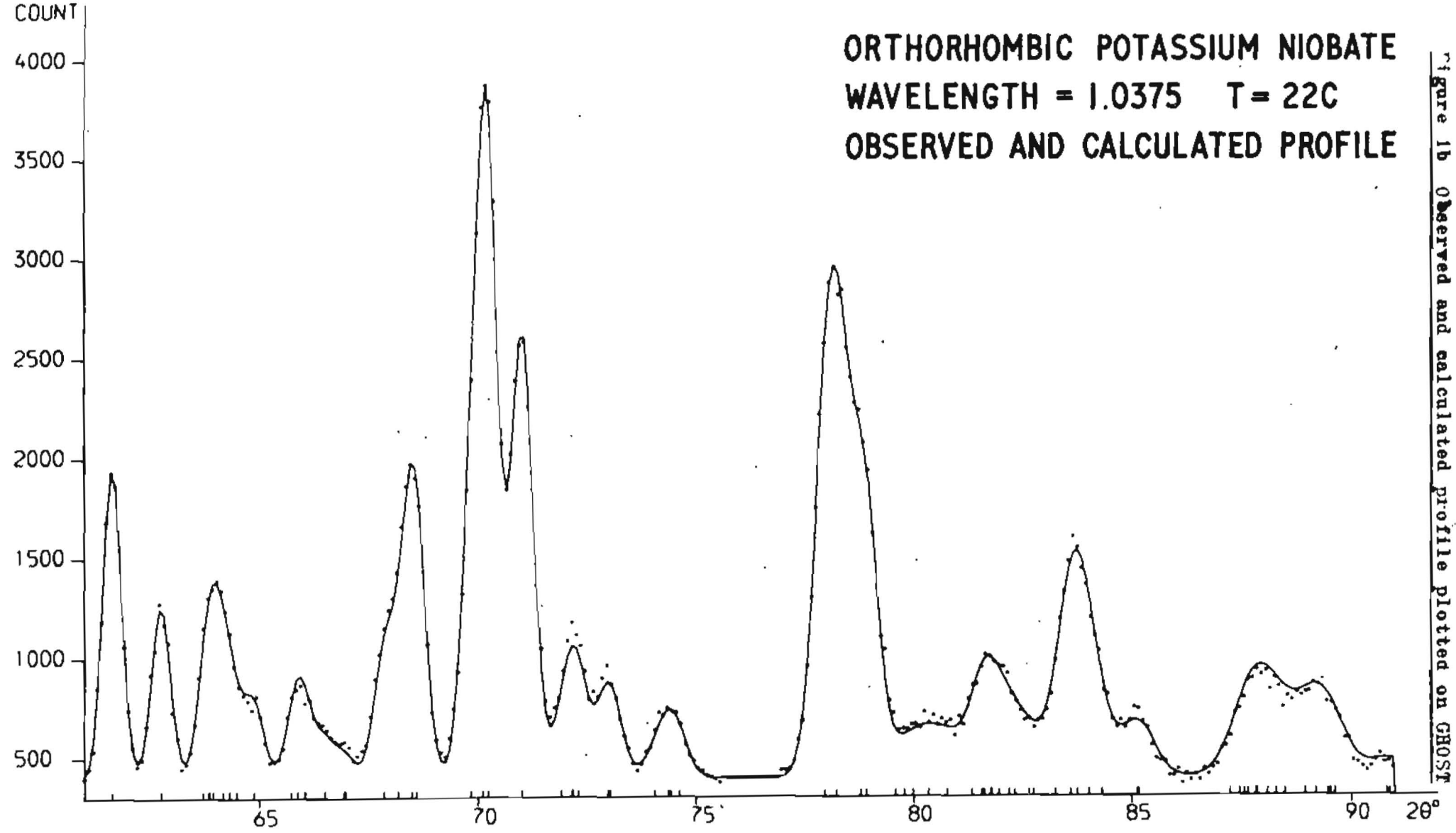


Figure 1b Observed and calculated profile plotted on GHOST

For each 2θ point in this pattern, the profile refinement 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

$$\chi^2 = \sum_i w_i \left[y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc}) \right]^2$$

The summation is over all the 2θ points i, and $w_i \propto 1/\sigma_i^2 \simeq 1/y_i(\text{obs})$ is the weight allotted to the count $y_i(\text{obs})$. 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 $\frac{1}{c} y_i(\text{calc})$ 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 $\frac{1}{c} y_i(\text{calc})$ is given by

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

since each sample count comes from a normal distribution centred on $\frac{1}{c} y_i(\text{calc})$, with standard deviation $\sigma_i = \sqrt{\frac{1}{c} y_i(\text{calc})}$. The probability P that all of the counts are samples of the population $\frac{1}{c} y(\text{calc})$ is the product $\Pi_i p_i$ of the individual probabilities

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

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

Rietveld shows 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

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

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, ($I_k = tF_k^2 j_k L_k 2\sqrt{\ln 2}/(H_k\sqrt{\pi})$ where t is the counter step width, F_k the structure factor, j_k the multiplicity and L_k the Lorentz factor).

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 can 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 $\pm$ 0.001Å and $\pm$ 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)

$$A_k = \sum_\kappa n_\kappa b_\kappa \, e^{-B_\kappa \sin^2\theta_k/\lambda^2} \sum_r \exp_{\kappa r} \cos_{\kappa r}$$

$$B_k = \sum_\kappa n_\kappa b_\kappa \, e^{-B_\kappa \sin^2\theta_k/\lambda^2} \sum_r \exp_{\kappa r} \sin_{\kappa r}$$

where

$$\left.\begin{matrix}\cos_{\kappa r}\\ \sin_{\kappa r}\end{matrix}\right\} = \left.\begin{matrix}\cos\\ \sin\end{matrix}\right\} 2\pi[h_r x_\kappa + k_r y_\kappa + l_i z_\kappa + t_r]$$

$$\exp_{\kappa r} = \exp\{-[(h^2)_r \beta_{11}(\kappa) + (k^2)_r \beta_{22}(\kappa) + (l^2)_r \beta_{33}(\kappa) + (2hk)_r \beta_{12}(\kappa) + (2hl)_r \beta_{13}(\kappa) + (2kl)_r \beta_{23}(\kappa)]\}$$

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 a factor $\exp_{\kappa r}$ multiplies Rietveld's original $\cos_{\kappa r}$ and $\sin_{\kappa r}$ factors, and in the case of the derivatives with respect to $\beta_{ij}(\kappa)$, additional factors of $(hk)_r = h_r k_r$ also appear inside the r summation over equivalent positions.

Apart from the magnetic parameters (Rietveld, 1969), the structural 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 printout of the results.

4. Examples of powder patterns analysed at Harwell

The five diffractometers used for powder work at Harwell have been described by Wedgwood (1968). We will only mention here some recent work on the PANDA machine, for which the monochromator angle can be varied between 30° and 90° giving a range of neutron wavelengths from 0.7Å to 2.4Å. 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 approaching $\pm$ 0.01 degrees over the range -10° to 117° by means of a Moire fringe system.

The neutron flux (about 7×10^5 counts/cm^2/sec at the specimen) is such that a run can often be completed in 24 hours. Any temperature between 4.2K 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 transitions in perovskites

At high temperatures the perovskite ABO_3 structure is cubic, with A atoms on the corners, B atoms on the centres and O atoms on the centres of the faces of the cubic cell. When the temperature is lowered, certain soft vibrational modes become unstable, and the resulting atomic displacements (~ 0.1Å) lower the symmetry of the lattice, with changes of the order

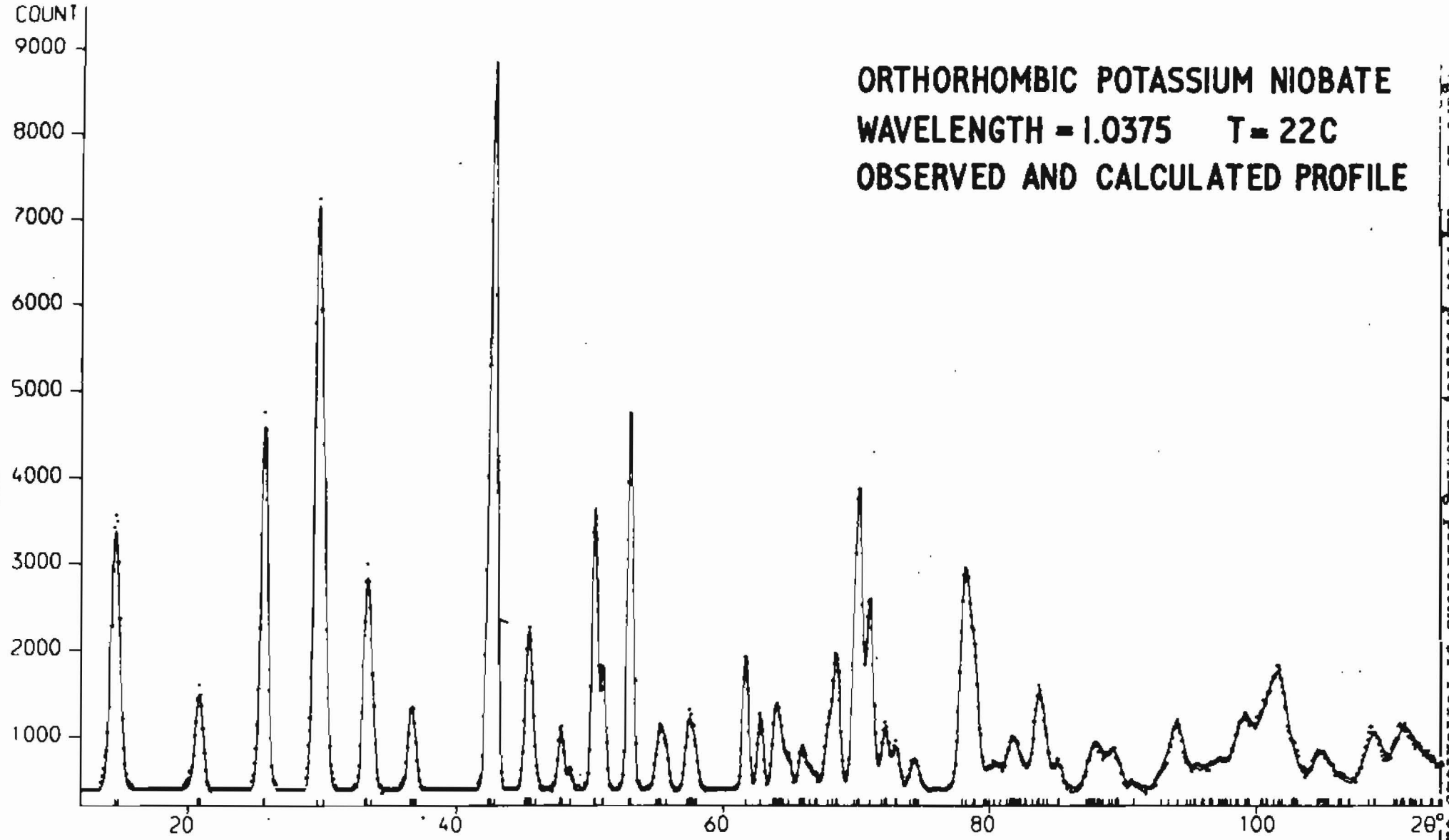


Figure 2a Complete profile, showing positions of reflexions on 2θ axis

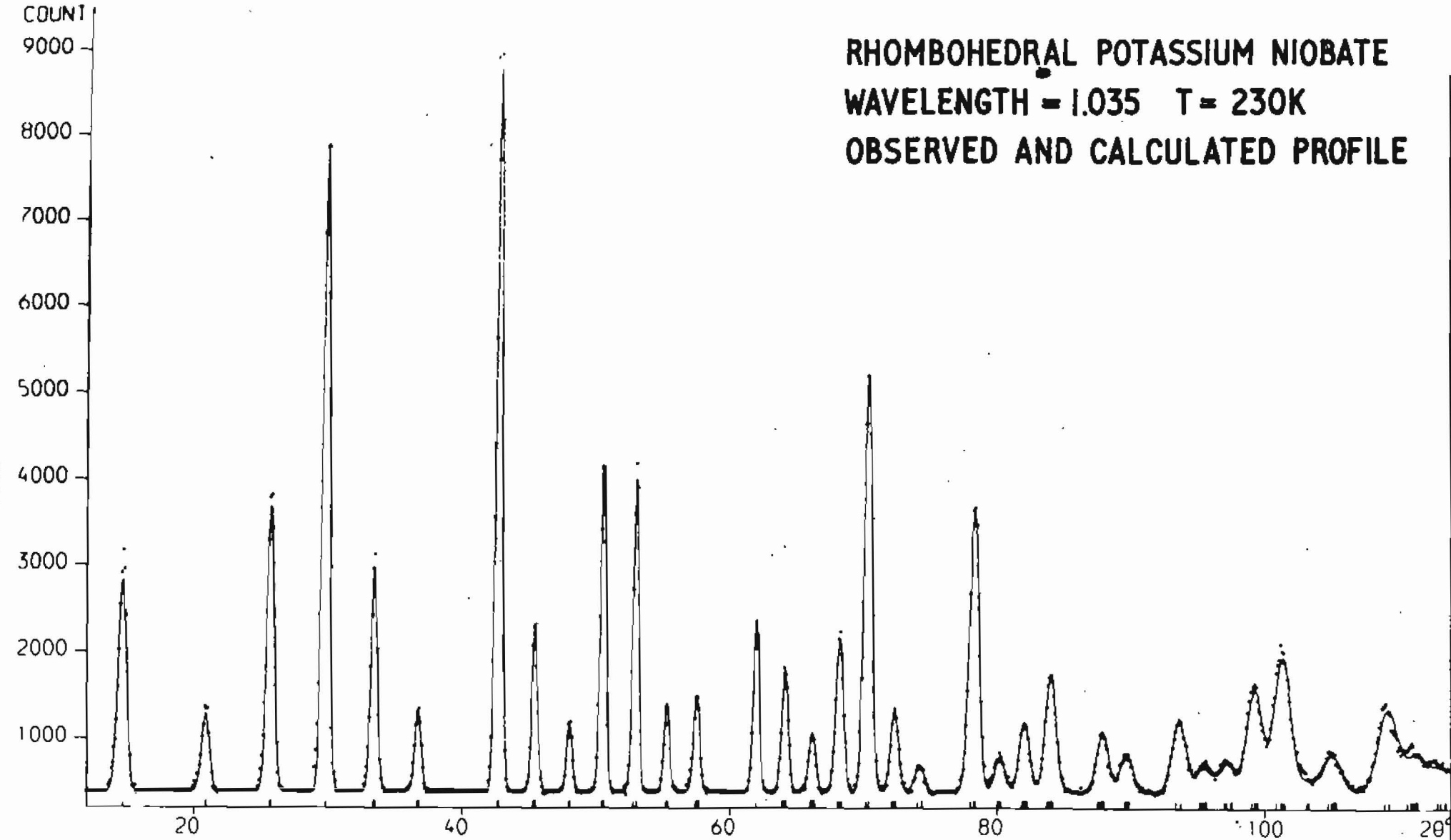


Figure 2b Effect of orthorhombic-rhombohedral phase change on profile

of 1% in the lattice constants (e.g. Cochran and Zia, 1968). These small changes cause splitting of the cubic perovskite diffraction lines, which cannot then be fully resolved; quite complicated powder patterns result (figure 2). As well, in 'antiferroelectric' materials, the unit cell becomes a multiple of the original cell, and superlattice lines appear in the powder pattern. It would be impossible to analyse such complex patterns on the usual basis of integrated intensities. For example, more than 200 distinct reflexions contribute to the pattern for orthorhombic $KNbO_3$ (figure 2a).

We have been able to analyse such patterns though, using the profile refinement program with anisotropic temperature parameters. Figure 1 is typical of the fit obtained: the agreement between calculated and observed points over the entire pattern approaches the limit imposed by purely statistical fluctuations in the number of counts observed. The atomic positions are determined by this fit to at least $\pm$ 0.01Å, the cell dimensions to $\pm$ 0.001Å and the cell angles to $\pm$ 0.02°. To allow comparison of the results of the profile refinement with those of single crystal work, we can calculate the quantity

$$R_{Nuclear} = 100 \sum_k [F_k^2(obs) - \frac{1}{c} F_k^2(calc)] / \sum_k F_k^2(obs)$$

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 $KNbO_3$. This compares favourably with careful single crystal measurements for similar problems (Hewat, Rouse and Zaccai, 1972; Hewat, 1973b). The uncertainties in the values of the structural parameters are no larger for the powder results than for the single crystal work.

Other perovskites studied using the powder method include $BaTiO_3$, $NaNbO_3$, $KTaO_3$, $SrTiO_3$, $PbHfO_3$, $NaTaO_3$, $AgNbO_3$ and $AgTaO_3$.

4.2 Hydrogen bonded antiferroelectrics and ferroelectrics

Single crystals of hydrogen bonded $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ 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 $NH_4H_2PO_4$ when the antiferroelectric transitron occurs (Hewat, 1973c). The lattice symmetry is lowered when the hydrogen atoms order on one or the other of the alternative sites available to them at higher temperatures, as postulated by Nagamiya (see Känzig, 1957). The strong superlattice reflexions appear in the low temperature phase because $NH_4H_2PO_4$ is an antiferroelectric, rather than a ferroelectric like KH_2PO_4. Similar results have been obtained for deuterated $NH_4H_2AsO_4$.

Other hydrogen bonded materials studied using the powder method include deuterated ferroelectric $NaH_3(SeO_3)_2$ and deuterated $SnCl_2.2H_2O$.

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 45K which we are attempting to study using the powder method. Figure 4 shows the pattern obtained at room temperature for Nb_3Sn. A profile analysis of this pattern shows that the chains of Nb atoms vibrate with considerably larger amplitudes in directions perpendicular to these chains than along them. The question of the so-called low temperature anharmonicity of the vibrations of the Sn atoms (Hewat, 1972b) 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 having the rocksalt and zincblende structures.

4.4 Other powder work at Harwell using the profile refinement program

Structural work connected with defect studies has been completed by Cheetham and Norman (1973) on YF_3 and BiF_3. Structural studies of magnetic materials have been started by B. Haywood, and on alloy systems by A. Self. It is expected that the profile refinement program will become increasingly important for the analysis of neutron powder patterns at Harwell.

5. Input and output format for the Fortran program

The program is in two parts which can be run separately.

1) preparation of profile data program.
2) structure refinement program.

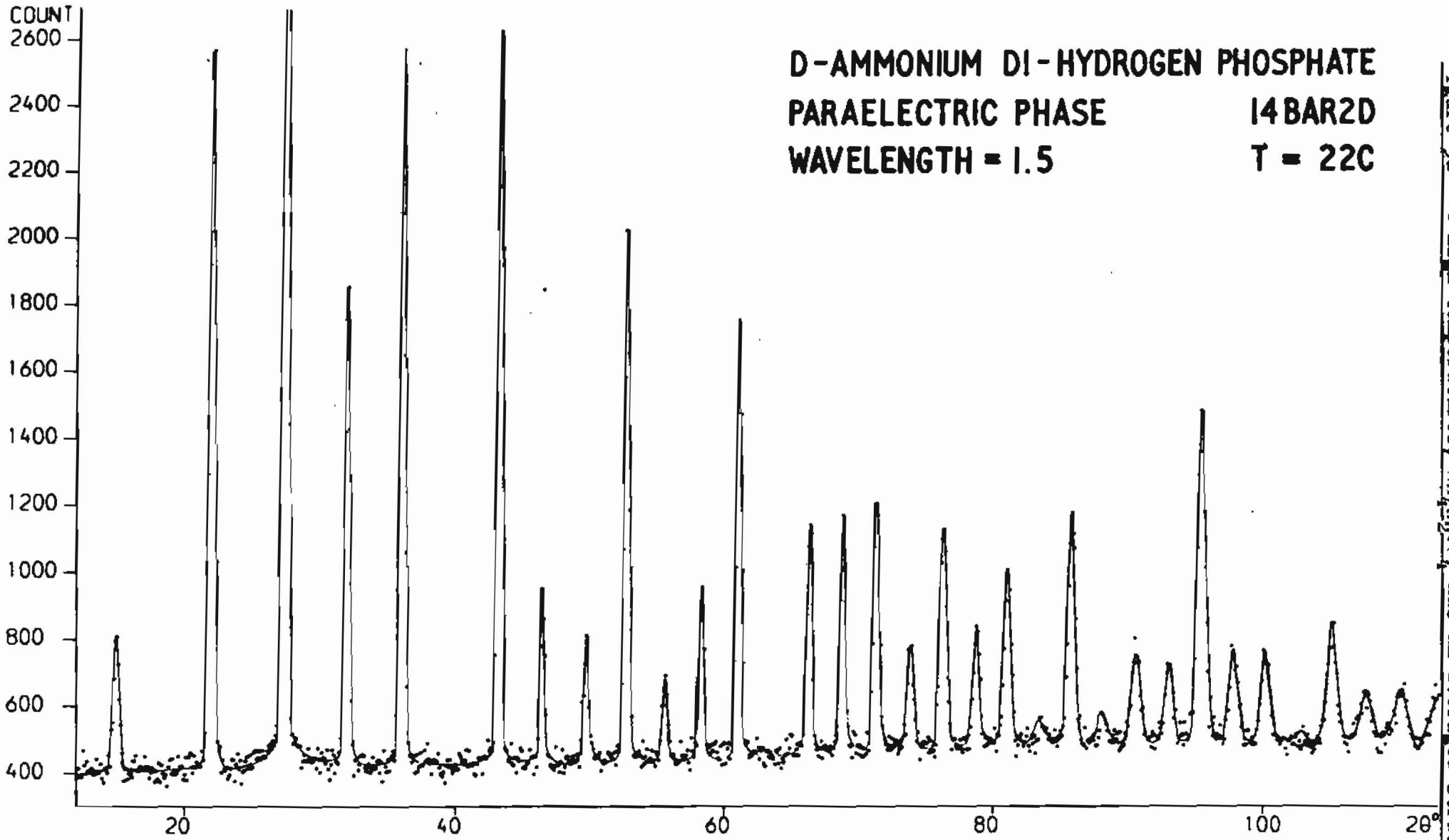


Figure 3a At high temperatures, $NH_4H_2PO_4$ has an averaged structure

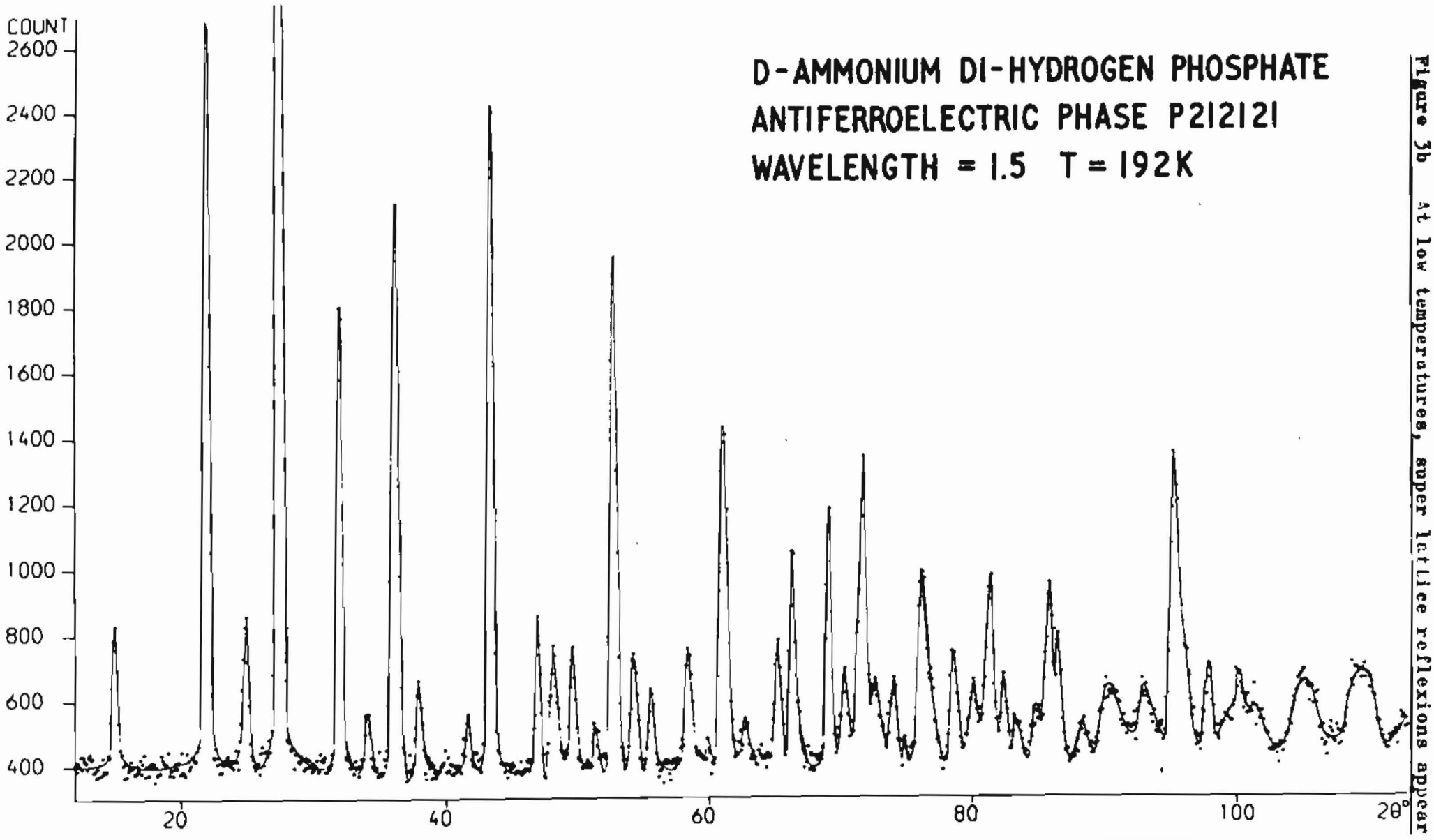


Figure 3b At low temperatures, super lattice reflexions appear

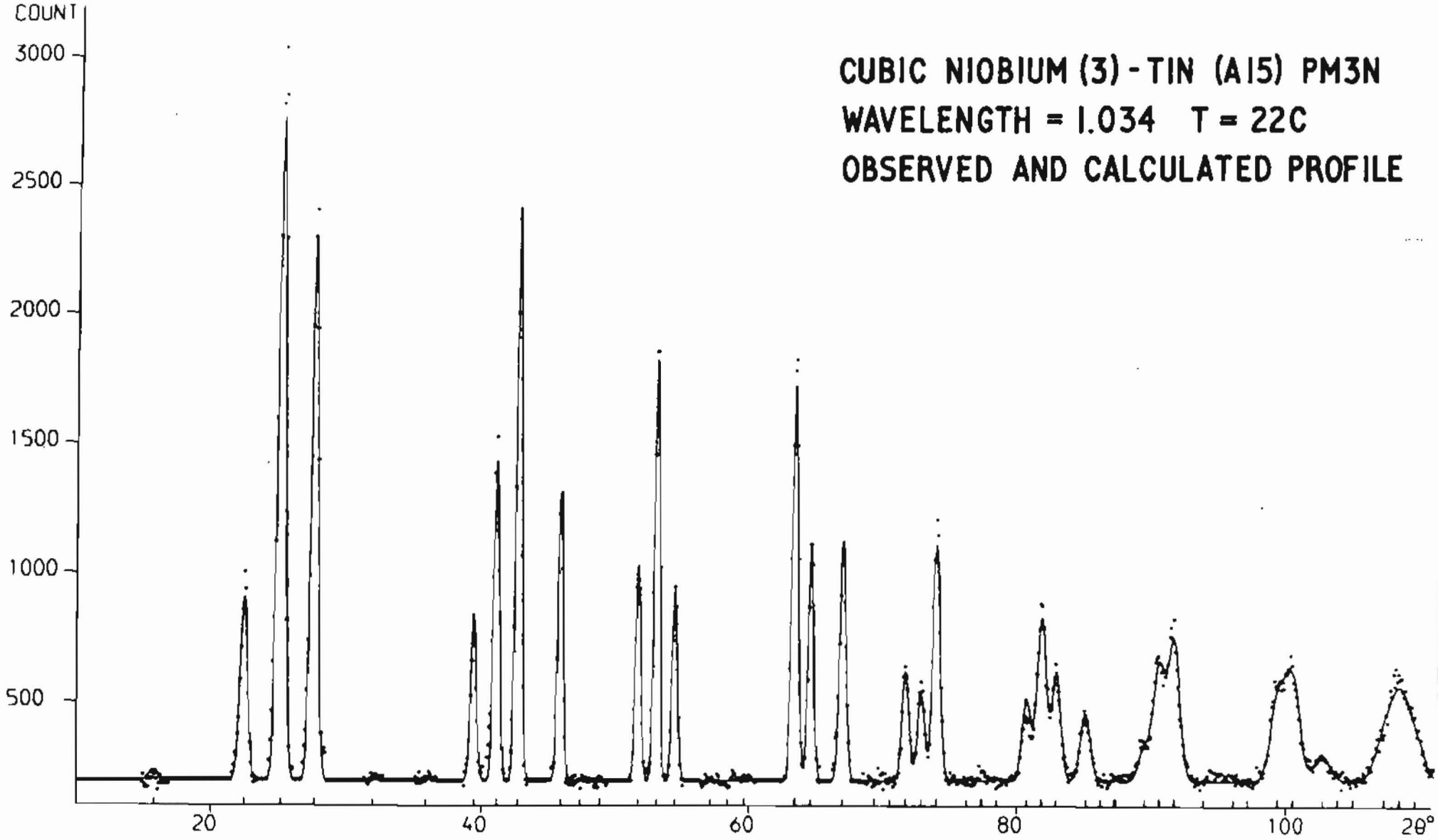


Figure 4. Nb-Sn is a high temperature superconductor

5.1 Preparation of profile data

This program corrects the measured profile intensities Y_i for background. It also determines those reflexions which can theoretically contribute to the intensity Y_i i.e. those which are located within $1\frac{1}{2}$ times their halfwidth of the position $2\theta_i$.

The output, originally saved on magnetic tape, is now stored in a private or scratch disk area, to be used as the input for the refinement program.

5.1.1 Format of the data cards

Data cards for both programs are punched wherever possible in fields of 8.

1. FORMAT (20A4)

   TITLE. - consisting of any Holerith information. This will be used as a heading for the printer output.

2. FORMAT (A4)

   ID. - problem identification, any four characters including blanks.

3. FORMAT (6F8)

   a,b,c,α,β,γ. - lattice constants of the real space cell a,b,c in Å; α,β,γ in degrees.

4. FORMAT (9F8.4,I4)

   λ(1), λ(2) - neutron wavelength in Å; or $K\alpha_1$, $K\alpha_2$ x-rays

   Z, - approximate zeropoint reading of counter in 0.01 degrees 2θ.

   U,V,W. - approximate halfwidth parameters $H^2 = U \tan^2\theta + V \tan\theta + W$ where H is the full width of a single reflexion at half height, in 0.01 degrees 2θ.

continued on back of page 8

5. n_B cards FORMAT (2I8)

   (i) pos(1), B/G(1).
   (ii) pos(2), B/G(2).
   ⋮

   - a number ($n_B \leq 50$) of cards, each containing a 2θ angle pos(i) in 0.01 degrees 2θ, and the background count B/G(i) at this angle. These cards

Card 4 (continued)

SB - standard deviation in background

WDT - width of base of peak = 2 * HW * WDT
Default = 1.5

CTHM - Polarization correction for mono chrometer for x-rays

TMU - Absorption Factor for x-rays

IPCH - 1 for no print of reflections or profile 0 print all.

21. FORMAT (F8.4, 2I8)

CONA, LCONI, LCONJ - coefficients and indicies of first linear constraint function. The last term ~~the constant~~ should be preceeded by -100.

22. FORMAT (F8.4, 4I8)

CONA, LCONI, LCONJ, ICON, JCON - coefficients and indicies of first quadratic constraint function. The last term should be preceeded by -100.

23. FORMAT (12A6)

- If IOUT=2 then TITLE to appear on profile plot.
- also need card #24

24. FORMAT (I8, 4F8.0, I8)

ISCALE - Number of counts per print character (120 available)

CMIN - lower limit on counts plotted, set less than CBACK

TMIN - beginning angle in degrees.

TSTEP - interval between observations in degrees.

CBACK - Typical background count

IDIF - number of counts per print character for difference plot.

The program punches on Unit 1 and requires scratch files on Units 4, 8, and 9. The intermediate file is Unit 2 for both programs.

⋮

(n_B) pos(n_B), B/G(n_B).

⋮

- 100

must be in order of increasing 2θ, and are terminated by a card containing -100 in the first field.

The background count at any other angle is obtained from these values by linear interpolation.

6. OPTIONAL ≤ 10 cards

FORMAT (2I8)

-low(i), -high(i).

⋮

- 100

These cards specify up to ten regions of the powder pattern, between 2θ = low(i) and 2θ = high(i) in 0.01 degrees 2θ, which are to be excluded from the refinement. N.B. low(i) and high(i) are preceded by negative signs for reasons of program control.

This set of cards, if included, is terminated by a card containing -100 in the first field.

7.

FORMAT (I8)

N. - number of reflexions in the reflexion list to follow.

8.

FORMAT (3I8)

NH, NK, NL. - denominators of the Miller indices h,k,l. These are included to eliminate the need to write non-integral Miller indices in case of cell enlargement. The program interprets the given indices in the reflexion list as h/NH, k/NK, l/NL.

9. N cards

FORMAT (5I8)

ICODE,

= 1 intensity (h,k,l) due solely to nuclear scattering

= 2 intensity (h,k,l) due solely to magnetic scattering

= 3 intensity (h,k,l) due to both nuclear and magnetic scattering

= 4 intensity from first x-ray wavelength

= 5 " " second " "

h,k,l, – the Miller indices (see card 7). They can be generated on cards for a given Laue group using a program written by J. B. Forsyth of the Rutherford Laboratory, Harwell. All reflexions which contribute to the pattern must be included.

MULT. – the multiplicity of reflexion h,k,l.

10. FORMAT ~~(3I8)~~ I8, F8.2, I8

α, – counter starting angle in 0.01 degrees 2θ. If less than 10 intensities are given with angle of observation on per card

Δ, – counter step size in 0.01 degrees 2θ. - floating point

ω, – counter finishing angle in 0.01 degrees 2θ.

11. $(\omega-\alpha)/10$ cards FORMAT (10I8) or (I8, F8.0)

$I(\alpha), I(\alpha+\Delta) \ldots I(\alpha+10\Delta)$. – the powder pattern counts including background, at angles $\alpha+n\Delta$. There are 10 counts per card. - if $\alpha \leq 10$ then Angle*10, Count

5.1.2 Printout for profile preparation program

The reflexion list is printed with the heading

NO. CODE H K L MULT HW POSN

an ordinal number NO. having been allocated to each reflexion h,k,l. The halfwidth HW and position POSN are in 0.01 degree 2θ units.

The profile intensity list is printed with the heading

POSN I+B B I W NO. NO. ..... NO.

and contains the interpolated background B and count intensity I corrected for background at each step position POSN. $W = 250/I+B+SB^2$ is the weight allotted to each of these counts. The ordinal numbers of all of the reflexions which contribute to this count are listed under the headings NO. If there are more than 40 overlapping reflections at any point this list is truncated.

This data is saved on a private or scratch disk area for use later in the refinement program; it appears on Unit 2

5.2 Structure refinement

The profile and structure parameters are stored in array $X_{i,j}$. With N atoms the array elements are

x_κ	y_κ	z_κ	B_κ	N_κ	Kx_κ	Ky_κ	Kz_κ	β_{11}^κ	β_{22}^κ	β_{33}^κ	β_{12}^κ	β_{13}^κ	β_{23}^κ
.....	i =	1,N											
G	P	1/(c(i)	1/(c(i) Q	Q 1/C									
U	V	W	Z	A	B	C	D	E	F				

Symbols not previously mentioned are defined in Rietveld's paper (1969).

For each of these $X_{i,j}$ a codeword $CX_{i,j}$ is needed. If this codeword is zero, the corresponding $X_{i,j}$ is held fixed throughout the refinement, but otherwise the codeword specifies the ordinal number p of the parameter $X_{i,j}$. p runs from 1 to size, where size is the dimension of the least squares matrix of parameters; every number p in this interval must be allocated to some $X_{i,j}$, but the order of allocation is unimportant.

These codewords may also be used to specify simple linear relations, such as y = ax, between the X_{ij}, since the codeword for $X_{i,j}$ is defined as

$$CX_{i,j} = \text{sign}(a) \times [10p + |a|].$$

If x is regarded as the 8th parameter for the refinement (p = 8) and z the 9th, the codewords for the atom co-ordinates (x, $-\frac{1}{4}$x, z) would be (81., -80.25, 91.). For each increment Δx in x, an increment $-0.25\,\Delta x$ would be added to y.

Since these codewords specify relations between increments, the same codewords would be used if the atom position was actually (x, $-\frac{1}{4}x+\frac{1}{2}$, z): the constant y displacement of $\frac{1}{2}$ is specified by the initial values given for the atom co-ordinates, and is preserved whatever increment is added to x.

A facility for the introduction of more complex relations between the variables is also available. For example, any linear relation such as

$$aX_{i,j} + bX_{k,l} + cX_{m,n} + \ldots = d \qquad (1)$$

can be introduced by specifying a,i,j; b,k,l; c,m,n; etc. and d on the appropriate constraint cards. The variables $X_{i,j}$, $X_{k,l}$, $X_{m,n}$ etc. should all have different least squares parameters assigned to them i.e.

$0 \neq CX_{i,j} \neq CX_{k,l} \neq C_{m,n}$ etc.

For a quadratic relation such as

$$aX^2_{i,j} + bX_{k,l}X_{K,L} + cX_{m,n}X_{M,N} = d \qquad (2)$$

the left hand side should first be differentiated, giving

$$2aX_{i,j}\partial X_{i,j} + bX_{k,l}\partial X_{K,L} + bX_{K,L}\partial X_{k,l} + cX_{m,n}\partial X_{M,N} + cX_{M,N}\partial X_{m,n}$$

In this expression, all the terms for which $\partial X_{i,j} = 0$ i.e. for which the codeword $CX_{i,j} = 0$, are to be cancelled. Assuming $CX_{K,L} = 0$, the expression reduces to

$$2aX_{i,j}\partial X_{i,j} + bX_{K,L}\partial X_{k,l} + cX_{m,n}\partial X_{M,N} + cX_{M,N}\partial X_{m,n} \qquad (3)$$

The quadratic relation(2) is then introduced by specifying 2a,i,j,i,j; b,K,L,k,l; c,m,n,M,N; c,M,N,m,n; and d on the constraint cards.

No mixed relations of linear and quadratic terms are allowed. The maximum number of terms in (1) and (3) is 9 and the total number of linear and quadratic relations must not exceed 4 unless the dimension statements in the Fortran program are adjusted appropriately.

5.2.1 Format of data cards

1. FORMAT (20A4)

TITLE - as for first program

2. FORMAT (A4,4X,F8,I8,3F8,I8)

ID, - the same problem identifier used in programe 1. (Immaterial)

ε, - forced termination of refinement if for all parameters, calculated shift < ε_x estimated error.

CALC, = 0 when only nuclear intensities are to be calculated, i.e. if CODE = 1 for all reflexions.

= 1 when the magnetic intensities are to be calculated according to the formula of Halpern and Johnson (1939).

= 2 when the average magnetic intensities are to be calculated in a uniaxial configurational spin symmetry.

= 3 when the average magnetic intensities are to be calculated in a cubic configurational spin symmetry.

= 4 Gaussian x-ray = 5 Cauchy x-ray

PH,PK,PL, - Miller indices of the normal to the surface of plate like crystals. When no preferred orientation correction is required, the value of these indices is irrelevant.

LIM. - the limiting angle in 0.01 degrees 2θ below which the diffraction peaks are to be corrected for the asymmetrical vertical divergence effect.

2a. HL(J), J=1,3 - If CALC=2 The unique magnetic axis, frequently (001) FORMAT (3F8.4)

3. FORMAT (6I8,F8)

CENTRE, = 1 for non centrosymmetric space groups

= 2 for centrosymmetric space groups

A magnetic structure is centrosymmetric when the atoms in the centre of symmetry related positions have equal magnetic vectors pointing in the same direction.

EQUIV, - number of equivalent positions. These should not be related by a centre of symmetry. The description of the untransformed position (x,y,z) is not included, but is generated by the program.

TYPE, - number of nuclear scattering lengths, or number of x-ray scattering factors

FORM, - number of normalized magnetic scattering curves, must = TYPE for x-rays

ATOM, - number of atoms.

ROT, - number of magnetic vector rotation matrices for each quivalent position. When there are magnetic atoms, ROT should always be larger than zero, even when EQUIV = 0. Also in this latter case, a number of ROT identity matrices are generated by the program for the untransformed (x,y,z).

LABDA1, LAMBDA2 – neutron wavelength in Å, x-ray $K\alpha_1$ and $K\alpha_2$
LABDA(2) = 0.0 for neutrons

4. 'EQUIV x ROT' cards – FORMAT (12F6)

(i)a R_{11}, R_{12}, R_{13}, T_1, – matrix R and vector T describing an
R_{21}, R_{22}, R_{23}, T_2, equivalent position. There is a total
R_{31}, R_{32}, R_{33}, T_3. of EQUIV such cards.

(i)b M_{11}, M_{12}, M_{13}, – matrix M describing the rotation of the
M_{21}, M_{22}, M_{23}, magnetic vector of the first type of
M_{31}, M_{32}, M_{33}. magnetic vector transformations in the
(ii)a ⋮ first equivalent position relative to
position (x,y,z). There is a total of
ROT such cards after each (R,T) card.

5. FORMAT (6F8)

b_1, b_2 ... b_{TYPE}. – total of TYPE scattering lengths. (10^{-12} cm)
or Δf" for all atom types for x-rays/100.

6. 'FORM' sets of cards FORMAT (2F8)

(i)a $\sin\theta_1/\lambda$, f_{11}. – list of $\sin\theta/\lambda$ and f-values describing
(i)b $\sin\theta_2/\lambda$, f_{12}. the normalized magnetic scattering
⋮ curves. Generally, when $\sin\theta/\lambda = 0$,
−100 f = 1. The cards (⩽ 20 for each curve)
⋮ must be arranged in order of increasing
(ii)a $\sin\theta_1/\lambda$, f_{21}. $\sin\theta/\lambda$. Each set, if present, is ter-
⋮ minated by a card with −100 in the first
−100 field. Or list of f+Δf' for x-rays/100.

7. FORMAT (I8,3F8,5I8)

CYCLE, – number of refinement cycles required.

RELAXC, – relaxation factor for co-ordinate shifts.

RELAXB, – relaxation factor for temperature factor and preferred orientation parameter shifts.

RELAXS, – relaxation factor for scale, occupation number, and magnetic vector components. The relaxation factor for shifts in the halfwidth parameters, the zeropoint, the cell parameters, and the asymmetry parameter is permanently set to 0.8.

OUT, = 1 for printed output of observed and calculated profile intensities on last refinement cycle, else = 0. = 2 for printed plot of obs., calc., and diff. profile.

PUNCH, = 1, 2 or 3 for punched output of calculated and separated observed structure factors after last cycle.

= 2 or 3 for punched output of observed and calculated profile intensities on last cycle, else = 0.

MATRIX, = ' for printed output of correlation matrix with all elements multiplied by 100, else = 0.

CORREL, = 1 for punched output of covariance matrix of the co-ordinates of all atoms after last cycle, else = 0.

COORD. = 1 for punched output of coordinates tape with new parameters after last cycle, else = 0.
= 2 Atom cards in standard Fourier format also punched. Either Biso or all Banio = 0

8. FORMAT (3F8)

c(1), c(2) - overall scale factor such that y(calc) = c x y(obs). Scale factors for Kα, and Kα2 for X-rays

Q. - overall isotropic temperature parameter.

9. 2 x ATOM cards FORMAT (A4,3I4,8F8/6F8)

(i)a LABEL, - identification characters for atom.

NTYP, - ordinal number of relevant scattering length, or X-ray scattering factor

MTYP, - ordinal number of magnetic scattering curve; irrelevant for x-rays

MROT, - ordinal number of magnetic vector rotation matrix with each equivalent position. For magnetic atoms MROT > 1.

x,y,z, - fractional atomic coordinates.

B, - isotropic atomic temperature parameter. This is effectively added to the overall temperature parameter Q.

n, - occupation number.

K_x, K_y, K_z. – magnetic vector components in the directions x,y,z. These are only needed when MROT $\geq$ 1.

(i)b

β_{11}, β_{22}, β_{33}, β_{12}, β_{13}, β_{23}. – if DIR = +1 (see card 11) these are the anisotropic β temperature parameters defined in §3.

OR(i)b

B_{11}, B_{22}, B_{33}, B_{12}, B_{13}, B_{23}. – if DIR = −1, anisotropic B_{ij} temperature parameters are given instead. Subroutine CELL then calculates the β_{ij} factors from the reciprocal cell constants a*, b*, c*, α*, β*, γ*.

$$\beta_{11} = \tfrac{1}{4} a^{*2} B_{11}$$
$$\beta_{12} = \tfrac{1}{4} a^{*} b^{*} B_{12} \text{ etc.}$$

These B_{ij} factors are more closely related to the actual vibrational amplitudes than are the β_{ij} factors, and are equivalent to the isotropic B-factor when

$B_{11} = B_{22} = B_{33} = B$ and $B_{12} = B \cos \gamma^*$ etc.

10. FORMAT (4F8)

U,V,W, – halfwidth parameters as in program 1.

Z. – zeropoint position of counter in 0.01 degrees 2θ.

11. FORMAT (I8)

DIR. = +1 when the cell constants on the following card are given as A,B,C,D,E,F,

= −1 when the real cell constants a,b,c,α,β,γ are given.

12. FORMAT (6F8)

A,B,C,D,E,F. – cell constants according to

$$1/d^2 = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk$$

OR 12.

a,b,c. – cell dimensions in Å.

α,β,γ. – cell angles in degrees.

13. FORMAT (2F8)

G, - preferred orientation parameter.

P. - asymmetry parameter.

14. FORMAT (I8)

SIZE. - total number of least squares parameters = size of normal matrix.

15. 2 x ATOM cards FORMAT (8F8/6F8)

(i)a Cx, Cy, Cz, - codewords for the fractional atomic coordinates.

CB, - codeword for the isotropic temperature parameter.

Cn - codeword for the occupation number.

CK_x, CK_y, CK_z. - codewords for the magnetic vector components (if MROT $\geq$ 1)

(i)b $C\beta_{11}$, $C\beta_{22}$, $C\beta_{33}$, $C\beta_{12}$, $C\beta_{13}$, $C\beta_{23}$. - codewords for the anisotropic β_{ij} temperature parameters. This pair of cards is needed for each of the ATOM atoms.

16. FORMAT (3F8)

Cc(1), Ce(2) - codewords for the overall scale factors.

CQ. - codeword for the overall isotropic temperature factor.

17. FORMAT (4F8)

CU,CV,CW, - codeword for the halfwidth parameters

CZ. - codeword for the counter zeropoint.

18. FORMAT (6F8)

CA,CB,CC, CD,CE,CF. - codewords for the cell constants

19. FORMAT (2F8)

CG, - codeword for the preferred orientation parameter

CP. - codeword for the asymmetry parameter

20. FORMAT (2I8)

NLC, - number of linear constraint functions.

NQC. - number of quadratic constraint functions.

21. see back of pg 9 for rest of input.

5.2.2 Printout of structure refinement program

After each cycle, there is printed for each parameter, including the β_{ij} factors

(i) its new value (X),

(ii) the shift (DX) applied to the old value, being the calculated shift multiplied by the relevant relaxation factor,

(iii) its estimated standard deviation (SX) according to the formula:

$$\sigma(X) = |a| \sqrt{M_{pp}^{-1} \cdot \Sigma W\{cy(obs) - y(calc)\}^2/(N-P+C)} ,$$

where M_{pp}^{-1} is the diagonal element of the inverted normal matrix corresponding to the $p^{\underline{th}}$ parameter, "a" the codeword coefficient (§5.2), N the number of statistically independent observations, P the number of least squares parameters, and C the number of constraint functions.

The cell constants are printed in the order: A, B, C, D, E, F. While the refinement is always on the components of the magnetic vector, the magnetic moments (M) and their corresponding standard deviations (SM) are also calculated from these components after each refinement cycle.

The three entries after R-FACTORS correspond with:

$$R_1 = 100\,\Sigma|I(obs) - \frac{1}{c} I(calc)|/\Sigma I(obs).$$

$$R_2 = 100\,\Sigma|y(obs) - \frac{1}{c} y(calc)|/\Sigma|y(obs)| ,$$

$$R_3 = 100\sqrt{\Sigma W\{y(obs) - \frac{1}{c} y(calc)\}^2/\Sigma W\{y(obs)\}^2} .$$

$$\text{The EXPECTED R-factor} = 100\sqrt{(N-P+C)/\Sigma W\{y(obs)\}^2}.$$

$$R(\text{NUCLEAR}) = 100\,\Sigma|Inuc(obs) - \frac{1}{c} Inuc(calc)|/\Sigma\, Inuc(obs).$$

$$R(\text{MAGNETIC}) = 100\,\Sigma|Imag(obs) - \frac{1}{c} Imag(calc)|/\Sigma\, Imag(obs).$$

N-P+C = the number of degrees of freedom, where N is the number of statistically independent observations y, P the number of least squares parameters, and C the number of constraint functions. The totals at the end of the printout have the following meaning:

SUMYDIF = $\Sigma|y(obs) - \frac{1}{c} y(calc)|$

SUMYOBS = $\Sigma|y(obs)|$

SUMYCALC = $\frac{1}{c}\Sigma y(\text{calc})$

SUMWYOBSSQ = $\Sigma W\{y(\text{obs})\}^2$

SUMIDIF = $\Sigma|I(\text{obs}) - \frac{1}{c} I(\text{calc})|$

SUMIOBS = $\Sigma I(\text{obs})$

SUMNUCDIF = $\Sigma|I\text{nuc}(\text{obs}) - \frac{1}{c} I\text{nuc}(\text{calc})|$

SUMNUCOBS = $\Sigma I\text{nuc}(\text{obs})$

SUMMAGDIF = $\Sigma|I\text{mag}(\text{obs}) - \frac{1}{c} I\text{mag}(\text{calc})|$

SUMMAGOBS = $\Sigma I\text{mag}(\text{obs})$

RESIDUAL = $\Sigma W\{y(\text{obs}) - \frac{1}{c} y(\text{calc})\}^2/(N-P+C)$

SKEWNESS = determinantal value of the normal matrix with normalized column vectors. When all vectors are orthogonal, SKEWNESS = 1.

On the last cycle, a list of y(obs) and $\frac{1}{c}$ (calc) is printed if requested, preceded by the starting and finishing angles and step size in 0.01 degrees 2θ.

Next a list of separated integrated intensities is printed if requested, under the heading

H K L POS INUC IMAG ITOT IOBS DIF ESD

where POS is the position (in 0.01 degrees 2θ) of reflexion (H,K,L)

INUC = $\frac{1}{c} I\text{nuc}(\text{calc})$

IMAG = $\frac{1}{c} I\text{mag}(\text{calc})$

ITOT = $\frac{1}{c} I(\text{calc})$

IOBS = $I(\text{obs})$

DIF = IOBS-ITOT

ESD = σ(IOBS).

The denominators NH, NK, NL of the integers H,K,L are printed immediately below the heading H,K,L.

5.2.3 Punched output of refinement program - This has been changed considerably

The possible output cards, with their formats are:

(1) "OBS + CALC INTENSITIES" (If PUNCH = 2 or 3)

(i) α, Δ, ω. - in units of 0.01 degree 2θ (3I8)

blank card

(ii) $y(obs)_\alpha, \frac{1}{c} y(calc)_\alpha$. - y-values corresponding to $2\theta = \alpha$ to $2\alpha = \omega$, one set per card (2I8). When y(obs) = 0, the value of y(calc) is suppressed.

$\vdots$

$y(obs)_\omega, \frac{1}{c} y(calc)_\omega$.

blank card

(iii) N. - number of reflexions contributing to the intensities in the above scattering range. (I8)

(iv) ICODE, $2\theta_i$. - code and calculated position in 0.01 degrees 2θ for each of these N reflexions, one reflexion per card (I8, F8.1).

3 blank cards

(2) "STRUCTURE FACTORS" (If PUNCH = 1 or 3)

(i) N. - number of reflexions contributing to the pattern in the range (α,ω), as above (I8)

(ii) NH, NK, NL. - denominators of H,K,L (3I8)

(iii) H, K, L, - indices for each reflexion

$cF^2_{Nuc}(calc)$, $F^2_{Nuc}(obs)$, - nuclear contribution to the calculated and observed integrated squared structure factors $S^2(\underline{k})$.

$cJ^2(calc)$, $J^2_{MAG}(obs)$. - magnetic contribution to the calculated and observed integrated squared structure factors $S^2(\underline{k})$. See Rietveld (1969).

2 blank cards

(3) "NEW COORDINATES" (If COORD = 1).

Cards are punched containing the values of the parameters obtained in the last refinement cycle, in the format required for direct input to the next run of the program.

2 blank cards

(4) "COORDINATES COVARIANCES" (If CORREL = 1)

The covariance matrix is punched row by row (8E10.4). The rows (and columns) of this (3 x ATOM, 3 x ATOM) matrix refer to the atom co-ordinates in the order

$$x_1,\ y_1,\ z_1,\ x_2,\ y_2,\ z_2 \cdots\cdots x_{ATOM},\ y_{ATOM},\ z_{ATOM}\ .$$

6. Example of the use of the program

To illustrate all of the features of the modified program, the data for $MnTa_4S_8$ at 4.2K, given by Rietveld (1969b), has been adapted for use as an example. The Mn atom has a magnetic moment, so that in the structure refinement the program has to take account of the magnetic scattering contribution as well as nuclear scattering. At 4.2K these magnetic moments are ferromagnetically ordered in the basal plane, but their direction cannot be determined from the powder data; Rietveld assumed it to be along the x axis.

6.1 General description of the test problem

The space group is hexagonal $P6_3/mmc$ (No.194), with atoms in the special positions

Mn	at	0, 0,0	(2a)
Ta_1	at	0, 0,$\frac{1}{4}$	(2b)
Ta_2	at	x,2x,$\frac{1}{4}$	(6h)
S_1	at	$\frac{1}{3}$,$\frac{2}{3}$, z	(4f)
S_2	at	x,2x,z	(12k)

These positions can be described by the 12 centrosymmetric positions of (12k).

x,y,z; $\bar{y},x-y,z$; $y-x,\bar{x},z$; $\bar{x},\bar{y},\frac{1}{2}+z$; $y,y-x,\frac{1}{2}+z$; $x-y,x,\frac{1}{2}+z$;

$\bar{x},\bar{y},\bar{z}$; $y,y-x,\bar{z}$; $x-y,x,\bar{z}$; $x,y,\frac{1}{2}-z$; $\bar{y},x-y,\frac{1}{2}-z$; $y-x,\bar{x},\frac{1}{2}-z$.

with y = 2x. The lattice dimensions and angles are

$$a = b = 6.60529\text{Å} \qquad c = 12.44817\text{Å}$$
$$\alpha = \beta = 90^\circ \qquad \gamma = 120^\circ$$

Levy (1956) has derived relationships between the β_{ij} factors for these special positions of this space group, using the symmetry transformation (y-x,y,z) which leaves (x,2x,z) unchanged. He obtains $\beta_{12} = \frac{1}{2}\beta_{22}$ and $\beta_{23} = \frac{1}{2}\beta_{13}$. This relation also holds for the B_{ij} factors, since

$$\beta_{ij} = a_i{*}a_i{*}B_{ij}/4. \qquad (1)$$

Since $(y-x,y,\frac{1}{2}-z)$ leaves $(x,2x,\frac{1}{4})$ unchanged, this transformation can be used to show that $\beta_{23}(Ta_2) = 0$. Similarly $(\bar{x},\bar{y},z)$ yields $\beta_{22} = \beta_{11}$ for the Mn, Ta_1 and S_1 atoms. Thus there are four independent β_{ij} factors for S_2, three for Ta_2 and two for each of the Mn, Ta_1 and S_1 atoms. The correct choice of codewords for these parameters will ensure that these symmetry relations are retained throughout any refinement of the temperature factors.

Initial values for the B_{ij} factors can be obtained from the isotropic B factors in terms of the angles α^*, β^*, γ^* of the reciprocal cell;

$$B_{11} = B$$
$$B_{12} = B \cos\gamma^* \text{ etc.} \qquad (2)$$

These starting values automatically satisfy the symmetry relations for the β_{ij} since for example $a^* = b^*$ and $\cos\gamma^* = \cos 60 = \frac{1}{2}$ so that $\beta_{12} = \frac{1}{2}\beta_{22}$ according to (1) and (2).

To limit the amount of output, only a short section of the $MnTa_4S_8$ powder pattern, between $2\theta = 22.69^\circ$ and $2\theta = 75.59^\circ$ has been used, sampling Rietveld's data at intervals of 0.05° 2θ by linear interpolation. This is insufficient data to obtain meaningful results on varying all parameters simultaneously. The full scan is especially needed to determine the B factors, as is indicated by the relatively large standard deviations obtained for $B_{11}(Ta_1)$ and $B_{12}(Ta_2)$, which have been refined merely to illustrate the use of the parameter codewords.

All of the constraint functions consist of simple linear relations between two parameters i.e.

$$y(Ta_2) = 2x(Ta_2)$$
$$y(S_2) = 2x(S_2)$$
$$\beta_{22}(Mn,Ta_1) = \beta_{11}(Mn,Ta_1)$$
$$\beta_{12}(\kappa) = \tfrac{1}{2}\beta_{22}(\kappa) \quad \kappa = \text{all atoms}$$
$$\beta_{13}(Mn,Ta_1,Ta_2) = \beta_{23}(Mn,Ta_1,Ta_2) = 0$$
$$\beta_{23}(S_1,S_2) = \tfrac{1}{2}\beta_{13}(S_1,S_2)$$
$$A = B = F \text{ (hexagonal symmetry)}$$

These relations can therefore be specified by means of the codewords alone. However, to illustrate the use of the constraint functions, the relation A = B = F has been introduced by means of two linear functions A - B = 0 and B - F = 0.

Only two cycles of refinement have been requested, so that the best possible fit has not been achieved although the refinement is converging.

Acknowledgements

We are indebted to Dr. H. M. Rietveld of the Reactor Centrum Nederland (Petten) for supplying a copy of his original Profile Refinement Program, together with a copy of RCN-104 (Rietveld 1969b), on which the latter part of this report is based.

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Distribution

A.W.Hewat AERE

D.H.C.Harris AERE

6.2 Data cards for profile preparation

```
MAT4SS8-TEST RUN---CARD INPUT ONLY---3 OCTOBER 1972  HEWAT
TRY2
 6.60525 6.60529 12.4482 90.     90.    120.
 2.565 -10.179 8995.   -13214.  5745.
  2268      77
  2628      75
  2988      75
  3348      78
  4068      84
  4428      87
  4788      88
  5508      88
  5868      86
  6948      80
  7308      79
  7574      78
  -100
    18
     1       1       1
     3       0       0       2       2
     3       1       0       0       6
     3       1       0       1      12
     3       1       0       2      12
     3       1       0       3      12
     3       1       1       0       6
     3       0       0       4       2
     3       1       1       2      12
     3       2       0       0       6
     3       2       0       1      12
     3       1       0       4      12
     3       2       0       2      12
     3       1       0       5      12
     3       1       1       4      12
     3       2       1       0      12
     3       2       1       1      24
     3       2       0       4      12
  2269       5    7559
    95      96      99     108     114     118     116     137     161     180
   202     242     298     322     382     464     525     546     558     588
   585     566     532     486     419     331     245     168     108      94
    89      85      73      71      73      79      76      81      95      84
    80      80      83      87      87      81      84      82      75      84
    91      93      96     107     120     131     137     146     159     176
   176     168     178     178     170     151     140     123      92      79
    76      82      65      68      83      87      72      85      91      91
    85      69      71      74      77      65      70      92      77      76
    76      77      74      80      98      90      84      80      79      82
    84      73      74      75      71      71      70      68      69      68
    68      81      78      70      71      74      78      83      88      84
    71      71      66      62      72      78      80      77      86      90
    84      76      76      84      88      84      78      75      71      67
    69      69      71      74      79      82      83      87      88      85
    68      73      78      76      85      84      73      79      80      79
    77      74      74      80      64      58      72      70      75      82
    70      71      79      74      74      78      89      81      77      81
    76      70      67      80      80      76      78      75      68      58
    67      81      97      80      81      87      61      63      72      72
    74      75      75      80      83      83      77      75      74      74
    80      83      75      76      84      97      88      76      63      59
    66      77      77      74      74      80      70      71      84      80
    74      68      81      77      70      74      83      86      78      79
    81      85      85      89      95     106     117     132     153     164
   181     205     208     215     223     219     201     174     139     110
    93      83      80      80      82      78      74      72      76      76
    77      83      80      77      75      78      79      76      82      85
    85      92      78      78      84      77      68      59     191     181
    73      65      79      96      92      93      90      80      83      84
    82      91      91      87      85      90      94      90      95      97
    93      80      80      91      91      90      89      95      91      86
    86      85      87      93      81      74      72      81      88      91
    85      87      89      89      87      82      75      92      87      72
    81      82      82      91      94      89      73      76      81      87
    83      83      87      97      92      82      70      79      82      79
    73      71      72      93      91      81      78      80      83      81
    86      82      68      79      77      81      84      87      87      79
    75      82     106      90      92     111      96      88      86      92
    84      76      80      79      79      82      74      81      87      84
    81      88      90      83      83     104      95      87      84      83
    80      75      73      73      76      88      82      80      90      84
    87      95      73      72      80      75      80      87      93      80
    77      90     100      95      79      82      83      82      75      83
    90      86      87      84      93      92      92      90      83      81
    82      87      98     107     110     123     122     111     120     130
   136     118     103      92      87      81      81      89      81      74
    71     101     106     103     107      98      96     112     110     102
    89      88      90      93      95      96      93      87      95      98
    89      91      91      90      86      81      77      76      72      71
    77      80      85      94      78      77      87      96      98      92
   101      97      97     107     107     107     107     126     116      92
    96      98      99     101      93      89      98      90      92     101
    92      85      80      78      76      76      80      89      90      82
    90      91      87      91      91      88      95      89      90      84
    88      92      97      96     102     110     107      89      74      82
    91      93      81      88      89      86      81      83      90      92
    88      84      87      93      98     100      84      81      86      87
    92     100     115     135     150     152     151     148     144     132
   131     132     114      97      87     100     101      97      89      92
    96     100      91      97     111     124     141     162     189     198
   203     205     183     160     136     106      87      78      90      88
    81      74      89      89      72      86      95      99      92      93
    96      94     109     126     143     159     196     251     303     318
   308     272     227     177     140     118     105     100      89      86
    88      92      88      84      91      91      88      85      98     111
   124     140     150     153     144     144     141     125     114     106
   102      88      80      80      87      82      75      81      85      89
    94      99     102     104      98      94      90      92      90      84
    72     104     118      77      84      89      90      83      82      85
    86      77      71      80      79      79      84      87      83      73
    73      77      82      93      82      84      93      97     109     132
   181     251     355     558     779     958    1160    1199    1132     949
   673     436     251     140     116     104     101      89      79      85
    80      81      94      92      87      90      83      82      78      76
    73      73      78      87      91      89      88      88      91     107
    99      90     110     108     100      92      89      84      75      79
    93      88      91      91      89      85      78      73      70      81
    87      89      79      79      84      86      83      80      81      85
    84      81      83      92     104      91      85      82      83      85
    89      97     103     100      89      82      82      85      84      84
    85      74      83      86      77      88      87      78      86      84
    79      81      83      82      77      85      86      76      90      92
    88      80      80      84      86      83      79      77      66      66
    78      88      82      69      85      83      76      73      78      80
    76      73      76      85      79      83      94     101     109     111
   138     194     239     265     262     246     215     157     122     100
    85      85      88      98      86      81      74      83      88      88
    74      74      78      69      76      78      88      94      98      95
```

```
  85      81      77      87      85      76      56      72      84      68
  82      84      89      91      85      78      79      79      81      85
  81      83      92      75      68      69      82      79      78      99
 103     110     123     127     126     119      98      85      79      85
  88      85      72      85      92      87      77      74      77      80
  79      80      92      85      75      69      80      82      74      78
  80      79      67      71      80      89      79      76      89      80
  76      77      78      85      91      78      77      81      86      68
  63      80      77      73      69      80      87      83      96      94
  90      88      79      69      60      64      74      86      89      81
  73      77      83      86      85      85     101     130     126     120
 113     115      98      84      88      81      75      73      83      85
  81      85      81      76      79      81      81      78      91      97
  94      87      93     103      94     105     116     113      99      97
 101      95      87      77      83      84      85      93     124     180
 273     469     690     927    1090    1102     975     711     460     253
 168     134     114      94      94      93      88      85      69      85
```

6.7 Data cards for structure refinement

```
MNT6458-TEST RUN-FORTRAN IV---3 OCTOBER 1972  HEMAT
TRYZ       0.3          2          0          0          1       2700
         2          5          3          1          5          1 2.5650
   .00 -1.00    .00    .00   1.00 -1.00    .00    .00    .00    .00   1.00    .00
  1.00    .00    .00    .00   1.00    .00    .00    .00   1.00
 -1.00   1.00    .00    .00  -1.00    .00    .00    .00    .00    .00   1.00    .00
  1.00    .00    .00    .00   1.00    .00    .00    .00   1.00
 -1.00    .00    .00    .00    .00  -1.00    .00    .00    .00    .00   1.00    .50
  1.00    .00    .00    .00   1.00    .00    .00    .00   1.00
    .00   1.00    .00    .00  -1.00   1.00    .00    .00    .00    .00   1.00    .50
  1.00    .00    .00    .00   1.00    .00    .00    .00   1.00
  1.00  -1.00    .00    .00   1.00    .00    .00    .00    .00    .00   1.00    .50
  1.00    .00    .00    .00   1.00    .00    .00    .00   1.00
 -0.36     0.70      0.28
   .C       1.0
   .C5       .972
   .10       .894
   .15       .783
   .20       .656
   .25       .530
-100.0
         2    .8        .8        .8             1         3         1         1         1
  0.2987     .0
MN       1    1    1    .0        .0        .0        .4        .167    4.278     .0        .0

TA1      2    0    0    .0        .0        .250      .0        .167
   .4             .4        .4        .2        .0        .0
TA2      2    0    0    .506      .012      .250      .0        .500
   .4             .4        .4        .2        .0        .0
S1       3    0    0    .333      .667      .127      .0        .333
   .4             .4        .4        .2        .0        .0
S2       3    0    0    .828      .656      .123      .0       1.0
   .4             .4        .4        .2        .0        .0
 8995.     -13214.  5745.     -10.179
      -1
 6.60529 6.6052912.44817 90.       90.      120.
  .030     .0
        17
   .C        .0        -0        .0        .0       11.0       .0        .0

   .0        .0        .0        .0        .0
 71.       71.        .0       70.5       .0        .0
 21.C      22.0        .0        .0        .0

   .C        .0       31.0       .0        .0

 41.0      42.0       51.0       .0        .0

 61.         .0
 91.C      91.0      101.0     111.0
121.C     131.0      141.0       .0        .0      151.0
161.C     171.0
         2          0
  1.0               7         5
 -1.0               7         6
-100.0
   .C
  1.C               7         6
 -1.C               7        10
-100.0
    .0
```