where $y_i(obs)$ is the measured intensity at a $2\theta$ point $i$, $c$ is a scale factor, $w_i$ is a least squares weight and $y_i(calc)$ is formed by summing the contributions from all the Bragg reflections which overlap at point $i$, the contribution falling to zero when $|2\theta_i - 2\theta(Bragg)|$ is greater than $1.5\ H_k$. $H_k$ is the full-width at half-height of the Bragg reflection $k$ being considered. Rietveld assumed that the variation of $H_k$ with angle can be represented by a three-term power series in $\tan\theta$:

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

where $U$, $V$, $W$ are half-width parameters.

The contribution $y_i$ of a Bragg peak, assuming a Gaussian shape, to the measured intensity at position $2\theta_i$ is

$$y_i = t \cdot S_k^2 \cdot j_k \cdot L_k \cdot \frac{2(\ln 2)^{1/2}}{H\,\pi^{1/2}}$$

$$\times \exp\left[\left(\frac{-4\ln 2}{H_k^2}\right)(2\theta_i - 2\theta_k)^2\right]$$

where $t$=the step-width of the $BF_3$ counter,

$S_k^2 - F_k^2 + J_k^2$ the sum of the nuclear and magnetic contributions respectively,

$j_k$ = the multiplicity of the reflection,

$L_k$ = the Lorentz factor and

$2\theta_k$ = the calculated position of the Bragg peak corrected for the zero-point shift of the counter.

This can be rewritten simply as

$$y_i = W_{i,k}S_k^2$$

where $W_{i,k}$ is a measure of the contribution of the Bragg reflection at position $2\theta_k$ to the profile intensity at position $2\theta_i$. Where more than one reflection contributes to the profile intensity at point $i$, we have

$$y_i(calc) = \sum_k W_{i,k}S_{k_i}^2$$

The profiles of the peaks obtained from a neutron powder diffractometer are accurately described by a Gaussian function. Apart from the structural parameters, profile parameters such as half-width parameters, asymmetry parameter, preferred orientation parameter and unit cell dimensions are included as variables in the least-squares refinement. Rietveld[1] carried out integrated intensity refinement as well as profile refinement on the same set of neutron powder data for $WO_3$, and showed that the profile method leads to a higher accuracy of the results. In the first major application of the method Loopstra and Rietveld[3] successfully refined 51 parameters and obtained

$$R = \sum_i |\ y_i(obs)$$

$$- \left(\frac{1}{c}\right)y_i(calc)\ |\bigg/\sum_i y_i(obs) = 0.108$$

for $Ca_3UO_6$. Many modifications of the original Rietveld programme, with provision for the refinement of anisotropic temperature factors, introduction of flexible molecular constraints, etc. are now available. Over 200 structures have since been refined by this technique which has now become well-established in neutron diffraction and solid state chemistry[4,5]. It must be pointed out here that this is only a refinement technique, where a starting model is necessary. However, this is not a serious limitation since neutron diffraction is normally used to answer specific questions about known structures rather than for *ab initio* structure solution.

## APPLICATION OF THE RIETVELD TECHNIQUE TO X-RAY POWDER DATA

The success of neutron profile analysis naturally stimulated interest in the possibility of applying this technique to x-ray powder data, especially in view of the fact that x-ray facilities are less expensive and more widely used than neutron sources. The main difficulty has been in the description of the peak shape, which is not normally Gaussian as in the case of neutrons. The method was adapted by groups in Sweden[6] and U.S.A.[7,8] to x-ray powder data collected using a film camera together with a microdensitometer, and diffractometer respectively. The focussing film camera

technique employed has many advantages over the diffractometer, *viz.*, better resolution, complete elimination of $K\alpha_2$ in addition to $K\beta$ contribution, and the reduction of preferred orientation through transmission geometry and sample rotation. As a test case the refinement of the structure of $\alpha$-$Bi_2O_3$ was carried out by Malmros and Thomas[6] using the original Rietveld programme adapted suitably for the x-ray study. Different expressions were tried for the peak profile and Malmros and Thomas found that a modified asymmetrized Lorentz function gave the best fit with the experimental data. Four different Reliability indices defined in the following way were calculated

$$R_p = \sum_i |y_i(\text{obs}) - y_i(\text{calc})| \Big/ \sum_i y_i(\text{obs})$$

$$R_{pw} = \left\{ \sum_i w_i [y_i(\text{obs}) - y_i(\text{calc})]^2 \Big/ \sum_i w_i y_i^2(\text{obs}) \right\}^{1/2}$$

$$R_I = \sum_k |I_k(\text{obs}) - I_k(\text{calc})| \Big/ \sum_k I_k(\text{obs})$$

$$R_F = \sum_k |\sqrt{I_k}(\text{obs}) - \sqrt{I_k}(\text{calc}) \sum_k \sqrt{I_k}(\text{obs})$$

where $I_k$(obs), the integrated intensity for reflection $k$, is not really observed, but is calculated from the observed profile by separating the contributing peaks according to the calculated integrated intensities. $R_F$ corresponds roughly to the conventional R-value for single crystal data. The results obtained have been compared[3] with an earlier single crystal study using visual intensity data and with a powder neutron refinement. While the agreement between the refined parameters was highly satisfactory, it was found that the standard deviations from the x-ray powder study were 2 to 3 times larger than those from the single crystal work. The neutron refinement was inferior to the latter with respect to the bismuth positions but superior in the location of oxygens.

Following closely on this work, the procedure was applied to x-ray powder diffractometer data independently by Young and coworkers[7] and Khattak and Cox[8]. In Young's refinement procedure, the $\alpha$-doublet of the x-radiation was handled by the explicit use of two wavelengths such that each Bragg reflection gives rise to two profiles. The reflection profiles were represented by either Gaussian or Cauchy functions. Atomic positions and site occupancies were refined for $LaPO_4$, $Ca_5(PO_4)_3F$ and quartz. Khattak and Cox avoided the complications resulting from the overlap of the $\alpha_1\alpha_2$ doublet by using $K\beta$ radiation. They found that the peak shapes could be described reasonably well by Lorentz type functions. The procedure was applied to the profile refinement of data for a rhombohedral perovskite type compound $La_{0.75}Sr_{0.25}CrO_3$. Various features have been introduced into the programme to handle anomalous dispersion, Lorentz and polarisation factors, absorption, site occupancies, choice of profile functions, etc.[7] Some of the advantages of the refinement procedure are: (a) characterisation, at least partially, of substitutions causing non-stoichiometry, (b) quantification of diffraction broadening differences due to size and strain effects, (c) improved characterisation and study of minor phases present in a multiphase mixture. A spin-off benefit is the remarkably precise lattice parameters obtained with accuracy of *ca* 3 in $10^5$. More than 50 structures ranging from inorganic synthetics and an organic through several minerals to human tooth enamel have since been refined[9]. Many versatile refinement programmes have recently been developed[10]

## *AB INITIO* DETERMINATION OF AN UNKNOWN STRUCTURE

Shortly thereafter, Swedish workers showed[11] that this technique, combined with standard Patterson and Fourier methods, could be employed even for the solution of a completely unknown structure. This pioneering work of Berg and Werner will be briefly described.

The compound chosen for the study was tetra-ammonium aa'-$\mu$-oxobis-[[gied $\mu_3$(S)-malato-O(1), O(2),O(4),O(4')]-di-$\mu$-oxobis [dioxomolybdate(VI)]} monohydrate, $(NH_4)_4[(MoO_2)_4O_4](C_4H_3O_5)_2 \cdot H_2O$, for which efforts to prepare stable single crystals were unsuccessful. A powder photograph was

taken in a focussing camera of the Guinier-Hägg type with strictly monochromatised $CuK\alpha_1$, radiation and KCl as internal standard, thus leading to good resolution in the diffraction lines. To avoid simultaneous appearance of front layer and back layer profiles and to diminish the background, a single-coated film was used. Three types of data, *viz.*, peak positions, integrated intensities and step-scan intensities (in steps of $\theta = 0.01586°$) were extracted from the film using an automatic film scanner system. The indexing problem was solved by a trial and error indexing programme, using the $\sin^2\theta$ values of the first 39 lines. A monoclinic solution was derived. The physical significance of the unit cell was checked using the de Wolf figure of merit criterion[11]. From systematic extinctions, the possible space groups were C2, Cm or C2/m. From a knowledge of the cell volume and density, Z was deduced to be 2.

A 3-dimensional Patterson function was calculated from 120 integrated intensities with indices corresponding to the best agreeing calculated $\theta$ values, thus disregarding overlap. From the absence of any Harker peaks at $(0, 2y, 0)$ the space groups Cm and C2/m were excluded. Two four-fold Mo positions were derived in the space group C2. A least squares refinement of the Mo positions refined to an R-value of 0.30. At this stage no model for the oxygen coordination around Mo atoms could be derived from the integrated intensities. Therefore the Rietveld profile analysis refinement programme, modified for Guinier data, was applied using which 505 'observed' structure factors could be derived. Although no more than 2 crystallographically independent reflections contributed to the same intensity for $2\theta < 26°$, a maximum number of 17 overlaps was calculated for $2\theta = 68.14°$! In the first heavy atom phased Fourier synthesis, only 250 reflections below $(\sin\theta)/\lambda = 0.336$ were included. This was to reduce the influence from erroneous assignment of intensities to overlapping reflections caused by an inaccurate model. Therefore, only low angle data were used where smaller number of overlaps occur. Ten four-fold and two two-fold oxygen positions

were derived from successive profile refinement and Fourier synthesis. The two strongest peaks from a succeeding difference map were attributed to the nitrogen atoms. The carbon atoms did not stand out clearly. They had to be deduced from the carbonyl oxygen positions and knowledge of the shape of the organic molecule. A least-squres profile refinement with 2 Mo, 12 O and 2 N atoms ended with an $R_F$ value of 0.11. The number of structural parameters varied was 51, in addition to 4 profile parameters and a scale factor. The refinement did not completely converge; the structure is not very accurate. Considering the fact that the material is unstable, lines due to the decomposition products may have been introduced into the data. Despite these drawbacks, it is indeed remarkable that a complex, low-symmetry structure could be determined without any assumed model or previous knowledge of symmetry and cell dimensions, using one good Guinier photograph and an accurate measuring system. Todate about 8 structures containing heavy atoms have been solved[13-18] *ab initio* by the Swedish group, which has made maximum contributions in this field. They have shown that, with the use of well-resolved integrated intensities in the initial stages and step-scan intensities for profile refinement in the later stages, moderate size structures (about 50 structures parameters and unit cell volumes $\sim 1500$ Å$^3$) could successfully be tackled. Details of the experimental facilities required have been described[19] Recently the structure of a new triclinic modification of $MnP_4$ has been determined by direct methods from x-ray powder data and refined by profile refinement[20]

## REMARKS

It is obvious from the foregoing that the determination of unknown structures using powder techniques is a much more difficult task compared to single crystal work. The main difficulty is that the observed structure amplitudes, $F_{obs}$'s, which serve as the starting point for the application of Fourier methods cannot be uniquely measured due to overlap.

$F_{obs}|^2$'s have to be extracted, albeit approximately, by dividing the intensities due to overlapping reflections in the ratio of the calculated values, the latter being obtained from the heavy atom contributions or some assumed starting model. Therefore as the structure solution progresses and more atoms are identified. $F_{obs}$'s will converge towards the correct values, exactly as in the case of phases. Furthermore, the presence of impurity lines could sometimes be misleading and result in difficulties even in the first step of indexing the pattern[21] These problems do not arise in single crystal work.

Another difficulty which has been encountered is the occurrence of flat or false minima during refinement[9]. Further, the precision of the structures is inevitably lower than that obtained from single crystal studies. It is also doubtful if any physical significance can be attached to the thermal parameters derived. A major problem to be faced is the description of the peak shapes. Different functions have been tried[9] but no known choice appears to be ideal. It has, however, been shown that while isotropic temperature factors are most strongly affected by the choice of function, background and site occupancy parameters are marginally affected and positional and lattice parameters, fortunately, are not significantly affected[22].

Recently, differing views have been expressed regarding the precision of the results obtained from profile refinement. Cooper and coworkers[23,24], on the basis of a detailed comparison of the method with integrated intensity refinement method, show that when peaks are resolved the values obtained for the structural parameters will not be exactly the same in the two cases. They also conclude that the standard deviations of the structural parameters are incorrectly determined in the profile refinement method, being underestimated by a factor of at least two. This arises from the definition of standard deviation which ignores the correlation between points on the same Bragg peak and the fact that the structural parameters depend only on the Bragg intensity. They also point out that the underestimation of these standard deviations by the profile refinement method is likely to increase as the amount of peak overlap increases. On the other hand, Prince[25] has pointed out that if the powder pattern consists of well-resolved peaks and if it is adequately described by a crystallographic model, as described by statistical tests, the estimates of the parameters and their standard deviations will not be significantly different whether the method of refinement uses peak profiles or integrated intensities. However, if the model does not fit adequately, the standard deviations cannot be calculated by statistical methods, since they depend on the unknown correlations between the estimated parameters and the unknown parameters that are missing from the model. If the peaks overlap, there are correlations between the integrated intensities of the individual Bragg peaks that are handled automatically in the profile method but must be included explicitly in the integrated intensity method. Hewat[5] and Young[9] have also expressed views on this important point.

## EXTENSION TO SYNCHROTRON DATA

Another major advance has been the application of profile refinement to energy dispersive powder data obtained from a synchroton source[26,27]. Due to various favourable features such as the exact Gaussian shapes of the peak profiles, higher intensity of the radiation and possibility of collecting data to much higher angles, as compared to a conventional x-ray source, it has been shown possible to find the structural parameters of a powdered material with a high degree of precision in exceedingly short time intervals, of the order of minutes. It would, therefore, be entirely feasible to monitor semi-continuously the structural changes taking place during a phase transition with changing temperature or pressure.

## CONCLUSION

The far-reaching implications of the above mentioned developments in x-ray

crystallography, particularly in relation to chemistry and materials science, are obvious. There are numerous systems where single crystals cannot be obtained and one is left only with polycrystalline material. Examples are materials prepared at high temperatures or pressures, products of solid state reactions, etc. Structure determination employing x-ray profile analysis is the only solution in such cases. In view of its importance, research activity in this field is bound to show an exponential growth in the coming years.

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