

## Solving Crystal Structures from Powder Diffraction Data\*

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### *Abstract*

High resolution powder data from both neutron and X-ray (synchrotron) sources have been used to estimate the possibility of direct structure determination from powder data. Two known structures were resolved by direct methods with neutron and X-ray data. With synchrotron X-ray data, the measured range of data was insufficient for a structure analysis, but the *R*-factor calculations showed the intensities extracted from the profile data to be of acceptable quality. The results were used to estimate the largest structure that might be solved using routine techniques. It was found that the limit would be near twenty atoms in the asymmetric part of a centro-symmetric structure.

### **1. Introduction**

It is well known that more detailed and precise information on a crystal structure is obtained from a three-dimensional single crystal diffraction experiment than from a powder diffraction analysis. If, however, single crystals of the compound to be studied are difficult to make, or if only a moderately accurate determination of the crystal structure is aimed at, a powder diffraction experiment may be an interesting approach to the structure investigation.

It is probably also true, that the time and effort required to carry out a powder measurement is similar and perhaps in some cases shorter than the similar single crystal data collection. With the use of conventional X-ray tubes and Guinier cameras with photographic films, or synchrotron X-ray radiation combined with position sensitive detectors, a powder pattern can be measured in a few hours. For neutron powder diffraction, the combination of a high neutron flux and a spectrometer with an array of detectors sets the recording time of a complete powder diffraction pattern to less than 24 hours.

It is therefore clearly of interest to study in some detail how direct structure determination may be done from powder data and to try to estimate the limit for a routine structure analysis in terms of the size of the structural problem.

\* Dedicated to Dr A. McL. Mathieson on the occasion of his 65th birthday.

## 2. Methods

The profile refinement technique is adequate for refinements of structural parameters, but the difficult task, as in all structure determinations, is to solve the phase problem from a powder diffraction pattern. A rather limited number of complex crystal structures has been solved from powder diffraction data alone. Examples are the structures of  $\text{CaCl}_2(\text{NH}_3)_8$  and  $\text{CaCl}_2(\text{NH}_3)_2$  (Westman *et al.* 1981) and of  $(\text{NH}_4)_4[(\text{MoO}_2)_4\text{O}_3](\text{C}_4\text{H}_3\text{O}_5)_2 \cdot \text{H}_2\text{O}$  (Berg and Werner 1977), solved from Guinier photographs by Patterson methods, and the structure of  $\beta$ -oxalic acid solved from a neutron diffraction powder pattern by direct methods (A. W. Hewat, personal communication).

The procedure for a crystal structure determination from powder data involves the following steps:

- (i) Collection of a highly resolved powder pattern.
- (ii) Indexing of the powder pattern and determination of the space group of the unit cell. Several computer programs for this task are available (Shirley 1978).
- (iii) Integration of reflections to make a list of  $hkl$  and  $I$  (Miller indices and intensities). A computer program (Pawley 1981) fits the diffraction pattern to gaussian curves and requires information on the unit cell dimension and space group symmetry only.
- (iv) Structure solution using Patterson methods or direct methods.
- (v) Structure refinement. For diffraction diagrams with a great number of overlapping reflections, the profile refinement method is adequate. For diffraction patterns from X-ray (synchrotron) radiation experiments, where a high resolution of the diffraction peaks is obtained, a realistic approach might be a structure refinement using structure factors determined from the resolved diffraction intensities.

In the following discussion we shall give examples of structure solutions obtained using both neutrons and X rays.

## 3. Neutron Powder Data

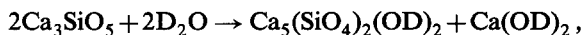
The last decade has shown a strong development of structure analysis based on neutron data. This arises from the combination of computer techniques, whereby the structural variables and the instrument parameters are adjusted to fit the total recorded profile (Rietveld 1969), and new developments in powder diffractometers with a large take-off angle for the monochromator, and a detector bank with high-collimation Soller slits in front of the detectors (Hewat 1973).

An example of such a diffraction instrument is the D1A powder diffractometer (Hewat and Bailey 1976) of the Institut Laue-Langevin. The instrument is located at a neutron guide, and the monochromator take-off angle is  $122^\circ$ . By using the 115 reflection from a vertically focused Ge monochromator, a resolution of 0.002 in  $\Delta d/d$  is obtained at  $2\theta = 120^\circ$  and the wavelength is 1.909 Å. The powder profile is recorded using a bank of 10 detectors, placed at intervals of  $6^\circ$ . In front of each detector a Soller collimator with  $10'$  divergence (Hey *et al.* 1975) ensures the high resolution of the instrument. At focus ( $2\theta = 122^\circ$ ), the full width at half height is  $0.23^\circ$ . The spectrum is recorded from  $6^\circ$  to  $160^\circ$  in  $2\theta$  in steps of  $0.05^\circ$ . A diffractometer similar to D1A has been constructed at Lucas Heights (Howard *et al.*

1983), and an instrument, D2B, with a resolution twice as good is under construction at the Institut Laue-Langevin (Hewat 1981).

The compound studied was a deuterated synthetic analogue of calcium chondrodite. Its structure is known, except for the atomic positions of the deuterium atoms, from a single crystal X-ray investigation (Kuznecova *et al.* 1980); the crystallographic data are space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 8.925 \text{ \AA}$ ,  $b = 5.072 \text{ \AA}$ ,  $c = 11.463 \text{ \AA}$ ,  $\beta = 108.54^\circ$ .

The deuterated powder sample used in this investigation was made in a hydrothermal preparation at  $270^\circ\text{C}$  from  $\text{Ca}_3\text{SiO}_5$  and  $\text{D}_2\text{O}$ . The chemical reaction is



and thus the sample of calcium chondrodite contained a small impurity of  $\text{Ca}(\text{OD})_2$ .

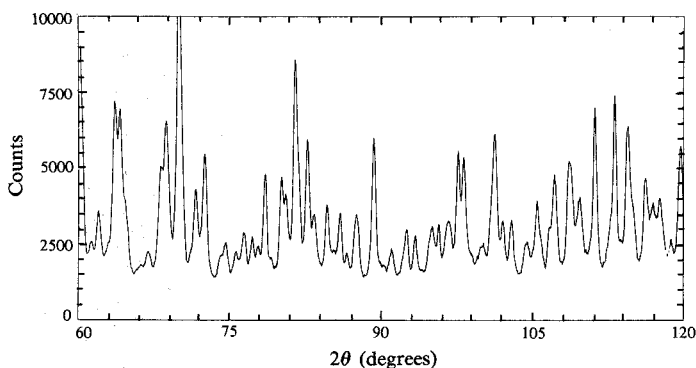


Fig. 1. Neutron powder spectrum of  $\text{Ca}_5(\text{SiO}_4)_2(\text{OD})_2$  for  $2\theta$  in the range  $60\text{--}120^\circ$ .

The pattern was recorded at  $4.2 \text{ K}$  with the D1A diffractometer, and some of the data are shown in Fig. 1. From this pattern the unit cell was confirmed. Individual intensities were extracted using the program of Pawley (1981), which fits the Bragg intensities to the observed profile. The individual powder line is assumed to be gaussian and its full width at half height is assumed to vary as

$$A_1 + A_2 \tan \theta + A_3 \tan^2 \theta,$$

where  $A_1$ ,  $A_2$  and  $A_3$  are variables in the fit. Additional parameters were the unit cell and the scale factor. In order to reduce computing time, the  $2\theta$  range was divided into the four sections  $25\text{--}81^\circ$ ,  $80\text{--}100^\circ$ ,  $100\text{--}120^\circ$  and  $118\text{--}150^\circ$ , and contributions from  $\text{Ca}(\text{OD})_2$  to the pattern were excluded. The lower limit for  $2\theta$  was set  $1^\circ$  below the lowest observable peak. For the highest  $2\theta$  there was considerable peak overlap leading to high correlation between neighbouring peaks, so only intensities of the reflections with  $2\theta$  less than  $121^\circ$  were used in the structure determination ( $\sin \theta/\lambda \leq 0.46 \text{ \AA}^{-1}$ ). In 28 cases, where two powder peaks were completely overlapping, the intensity was arbitrarily given to one of the pair. The intensities with  $I > 0.5\sigma(I)$  were regarded as observed, and the remaining as unobserved, giving 177 observed and

159 unobserved reflections, and these were used in the structure determination by the MULTAN programs.\* Only one solution was found with a combined figure of merit of 3.0. The total number of phase relationships determined was 225. The structure solution arrived at is listed in Table 1, and all atomic positions including those of the deuterium atoms were found. Nine of these were identified between the thirteen highest peaks as listed by MULTAN, while the last atom was determined directly from the Fourier map as a smaller peak. The positions of the atoms correspond to those known from the X-ray investigation (Kuznecova *et al.* 1980) after a new choice of the unit cell with  $x, y, z \rightarrow \bar{x} + \frac{1}{2}, \bar{z}, y$ . In Table 1 the atomic coordinates from Kuznecova *et al.* (1980) are listed in parentheses, except for deuterium where values come from the refinement.

**Table 1.** Atomic coordinates of  $\text{Ca}_5(\text{SiO}_4)_2(\text{OD})_2$  and peak heights obtained from MULTAN  
Values in parentheses are atomic coordinates from Kuznecova *et al.* (1980)

Atom	$x$	$y$	$z$	Peak height <sup>A</sup>
Ca 1	0.5 (0.5)	0 (0)	0 (0)	1760
Ca 2	0.65 (0.6875)	0.95 (0.9996)	0.33 (0.3301)	1780
Ca 3	0.85 (0.9185)	0.00 (0.0100)	0.14 (0.1195)	1780
Si	0.77 (0.7006)	0.58 (0.5741)	0.18 (0.1452)	1760
O 1	0.74 (0.7065)	0.73 (0.7054)	0.03 (0.0156)	2830
O 2	0.48 (0.5442)	0.73 (0.7099)	0.19 (0.1699)	3020
O 3	0.90 (0.8534)	0.73 (0.7016)	0.31 (0.2524)	2860
O 4	0.65 (0.6996)	0.26 (0.2550)	0.14 (0.1464)	2850
O 5	0.80 (0.9006)	0.27 (0.2552)	0.36 (0.4422)	3100
D	0.96 0.966(2) <sup>B</sup>	0.13 0.083(1) <sup>B</sup>	0.47 0.488(1) <sup>B</sup>	3100

<sup>A</sup> Relative scale. <sup>B</sup> Final atomic coordinates from powder refinement.

The structure of calcium chondrodite was refined using the profile refinement method, first with the Hewat (1973) version of the Rietveld program, and finally with the Wiles and Young (1981) version of the same method. This version permits refinement of two structures simultaneously, in this case  $\text{Ca}_5(\text{SiO}_4)_2(\text{OD})_2$  and  $\text{Ca}(\text{OD})_2$ .

As the crystal structure of  $\text{Ca}(\text{OD})_2$  is well known (Petsch 1961), this structure was not refined and, as the atomic coordinates of the non-hydrogen atoms of calcium chondrodite are known from a single crystal X-ray investigation, only the atomic positions of the deuterium atoms, the scale factors and the necessary profile parameters were refined. The  $R$  factors arrived at,

$$R = \frac{\sum |I_{\text{obs}} - I_{\text{calc}}|}{\sum I_{\text{obs}}}$$

were 10.0% for calcium chondrodite and 5.6% for calcium hydroxide. It was thus possible to confirm the X-ray structure and to determine the position of the deuterium atoms in  $\text{Ca}_5(\text{SiO}_4)_2(\text{OD})_2$  from a neutron diffraction powder pattern using direct methods in the structure determination.

\* MULTAN was developed in 1977 by P. Main, L. Lessinger, M. M. Woolfson, G. Germain and J.-P. Declercq at the Universities of York and Louvain.

#### 4. X-ray Powder Data

Crystal identification using X-ray powder data is almost as old as the applications of X rays in structure analysis and, as a part of the identification, the intensities of the powder lines are normally estimated. It is therefore quite possible to carry out a structure analysis and, as an example, we have chosen  $\alpha$ -ScOOH. This compound has the diaspore structure and the crystallographic data are space group  $Pbnm$ ,  $Z = 4$ ,  $a = 4.755 \text{ \AA}$ ,  $b = 10.301 \text{ \AA}$  and  $c = 3.209 \text{ \AA}$ .

An indexed powder pattern is available (Christensen 1967), taken with a Guinier-de Wolff camera and Cu  $K\alpha$  radiation and with intensities measured on a double beam micro-densitometer. From this powder pattern, 32 observed structure factors ( $\sin \theta / \lambda \leq 0.403 \text{ \AA}^{-1}$ ) were calculated, where polarization factors for the Guinier photograph and multiplicity of the reflections were taken into consideration. In addition, 20 unobserved, but space group allowed, reflections with small nonzero intensities were added to the list of structure factors. These data were used in a structure determination by the MULTAN programs. The programs determined 22 phase relations and gave one solution, listed in Table 2, corresponding to the three highest peaks listed by MULTAN. For comparison, the refined atomic coordinates (Christensen 1967) are listed in parentheses. [The origin used is shifted to  $(0, \frac{1}{2}, 0)$  and the symmetry operation  $x, y, z \rightarrow -x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$  has been used for the coordinates of O 1.] As seen, the agreement between coordinates from a structure refinement and from the MULTAN programs is good.

**Table 2. Atomic coordinates of  $\alpha$ -ScOOH and peak heights obtained from MULTAN**  
Values in parentheses are refined atomic coordinates from Christensen (1967)

Atom	$x$	$y$	$z$	Peak height <sup>A</sup>
Sc	0.065 (0.065)	0.353 (0.352)	0.244 (0.250)	3865
O 1	0.787 (0.811)	0.207 (0.201)	0.251 (0.250)	1451
O 2	0.165 (0.211)	0.546 (0.553)	0.238 (0.250)	1580

<sup>A</sup> Relative scale.

For a structure analysis using powder data it would be advantageous to use counter data as in the case of neutrons. Unfortunately, with conventional X-ray sources and only a few detectors, the counting time would be long if high resolution is required. The best possibility would therefore be to employ a synchrotron X-ray source, where the inherent collimation is good, and the flux is high. Preliminary tests of the feasibility of such an approach were carried out on the triple-axis spectrometer at HASYLAB in Hamburg. For practical reasons the measurements were done in the horizontal plane, and data were only recorded to a  $2\theta$  value of  $43^\circ$ . The powder sample was held in a 0.2 mm vertical Lindemann glass tube that was rotated about its axis with a frequency of 1 Hz. A linear detector of length 4.25 cm (M. Braun, PSD counter) was located on a  $2\theta$  arm at a distance of 64 cm from the sample, and the other distances were 84 cm for sample-monochromator and 20 m for monochromator-source. The beam was 5 mm high, the flight paths were evacuated in order to reduce intensity loss and the effects of air scattering, and the region around the sample was enclosed in a cylindrical container with mylar windows filled

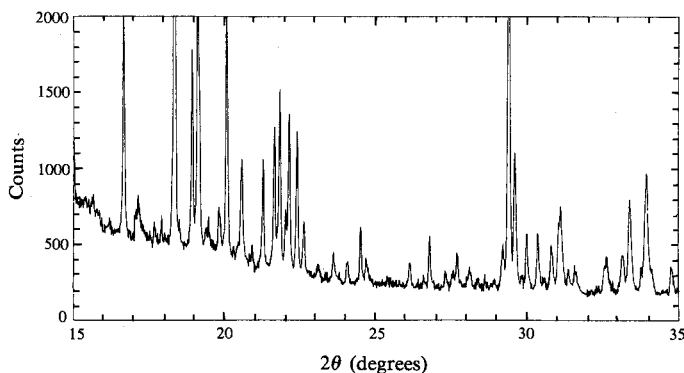


Fig. 2. X-ray powder spectrum of  $\text{Ca}_5(\text{SiO}_4)_2(\text{OD})_2$  for  $2\theta$  from  $15^\circ$  to  $35^\circ$ , recorded with the synchrotron source.

with helium gas. A monochromatic beam with  $\lambda = 0.973 \text{ \AA}$  was produced using the 111 reflection from a perfect Si crystal in reflection position, and higher order contamination was removed by reflecting the beam from a mirror of length 20 cm, located in front of the monochromator. The detector was divided into 260 pixels, giving a pixel length slightly smaller than the resolution of 0.2 mm of the detector. Data were obtained for  $2\theta$  in the range  $8\text{--}43^\circ$  with recordings at  $2.5^\circ$  intervals in  $2\theta$  followed by addition of the individual spectra. Where the spectra overlapped, only one point was retained and the division point between adjacent spectra was taken as being the point of lowest count.

Fig. 2 shows the result of a room temperature measurement of  $\text{Ca}_5(\text{SiO}_4)_2(\text{OD})_2$ . Near focus ( $2\theta = 18^\circ$ ) the full width at half height was found to be  $0.040^\circ$ . The lower limit for the full width at half height would be obtained by neglecting beam divergence, and would only include sample dimension and detector resolution in the calculation. In this case we get  $0.036^\circ$  which is in good agreement with observation.

Intensities were then extracted using Pawley's (1981) program. As before, the lines of  $\text{Ca}(\text{OD})_2$  were removed, and data were kept until  $2\theta$  was  $34^\circ$  ( $\sin \theta/\lambda = 0.30 \text{ \AA}^{-1}$ ) giving 84 reflections for structure solution. These reflections were too few, and both direct and Patterson methods failed to give a solution.

As  $\text{Ca}_5(\text{SiO}_4)_2(\text{OD})_2$  gave very strong and well-defined scattering patterns, it was decided to try a weaker scatterer, and an organic substance was chosen for this test. Similar measurements were therefore performed on glycylglycine (space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 9.421 \text{ \AA}$ ,  $b = 9.558 \text{ \AA}$ ,  $c = 7.828 \text{ \AA}$ ,  $\beta = 124.66^\circ$ ), but again we failed to solve the structure. In this case the  $2\theta$  maximum was fixed at  $33^\circ$  ( $\sin \theta/\lambda = 0.29$ ), and again Pawley's program was used.

Fig. 3 shows a part of the powder profile depicting the observed and calculated profile. For simplicity a gaussian-type shape has been assumed for the individual powder lines, and this is in good agreement with the observed data except for a small additional tail near the edge of the peak. This is undoubtedly not the reason for the failure to solve the structure. Trial calculations using the known structure and structure factors with an increasing number of data showed that with 400 reflections the MULTAN program was successful. This corresponds to  $2\theta 54^\circ$  or  $\sin \theta/\lambda 0.46 \text{ \AA}^{-1}$ .

In order to estimate the quality of the data extraction, a least squares refinement of the atomic coordinates and isotropic temperature factors was carried out using

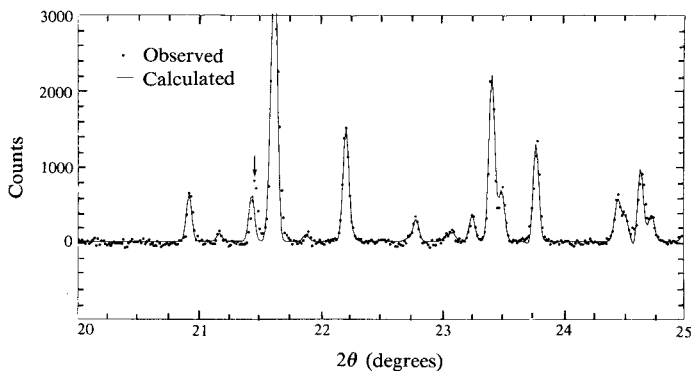


Fig. 3. Observed and calculated intensity profiles of glycylglycine for  $2\theta$  from  $20^\circ$  to  $25^\circ$ . The background has been removed before the calculation. In general, the fit is good except for the peak marked with an arrow. It is quite likely that this peak is due to a small error in setting the detector, as the separation between points is only  $0.015^\circ$ .

Table 3. Refined glycylglycine atomic positions and isotropic temperature factors  $B$  from synchrotron data

Values in parentheses are atomic coordinates from Biswas *et al.* (1968). Standard deviations are  $0.007$  for coordinates and  $1.5 \text{ \AA}^2$  for  $B$

Atom	$x$	$y$	$z$	$B$
N(1)	0.174 (0.177)	0.168 (0.169)	0.100 (0.099)	2.3
C(2)	0.336 (0.344)	0.090 (0.095)	0.241 (0.240)	3.2
C(3)	0.480 (0.486)	0.173 (0.170)	0.231 (0.239)	7.1
O(4)	0.479 (0.479)	0.303 (0.299)	0.224 (0.212)	7.7
N(5)	0.612 (0.617)	0.088 (0.093)	0.279 (0.279)	5.8
C(6)	0.777 (0.768)	0.162 (0.155)	0.312 (0.301)	5.9
C(7)	0.851 (0.862)	0.058 (0.054)	0.253 (0.251)	7.2
O(8)	0.822 (0.821)	$-0.075 (-0.074)$	0.233 (0.232)	8.4
O(9)	0.977 (0.975)	0.107 (0.105)	0.235 (0.236)	10.6

the observed structure factors. It was assumed that the beam was horizontally polarized for all parts of the sample, and the data were corrected accordingly. This is undoubtedly an approximation, but considering that we only use low order data it will be of little consequence for our analysis.

The program SHELX-76 (developed by G. Sheldrick) was used and the scattering factors were from the compilation by Koester and Rauch (1981). The final  $R$  value,

$$R = \frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)}{\sum |F_{\text{obs}}|},$$

for the 95 reflections was  $0.13$ . The coordinates are given in Table 3 for comparison with those from the single crystal analysis of Biswas *et al.* (1968). The ratio of observations to parameters of 3 is obviously not sufficient to allow a solution of the structure, but the  $R$  factor shows that the data would be adequate to allow a solution if sufficient data were available.

## 5. Discussion

Neutron and X-ray (synchrotron) diffractometers are becoming available that can produce powder lines with a full width at half height between  $0.05^\circ$  and  $0.10^\circ$ . Assuming that the areas of two gaussian peaks can be separated by profile fitting techniques, if the positions are fixed and the distance between the two peaks is not much smaller than the half width at half height, we should then in the limiting case be able to extract intensities for peaks which are separated by about  $0.02^\circ$  in  $2\theta$ .

The above structure analyses indicate that if data are available between  $0.4$  and  $0.5 \text{ \AA}^{-1}$  in  $\sin \theta/\lambda$  then structures can be solved by routine techniques. We shall therefore in the following discussion assume a limit in data of  $0.45 \text{ \AA}^{-1}$  in  $\sin \theta/\lambda$ . We must however ensure that a minimum number of peaks overlap at the highest angle, since this eventually limits the applicability of the method.

**Table 4.** Number of reflections  $n$  per degree for  $\sin \theta/\lambda = 0.45 \text{ \AA}^{-1}$  and number of reflections  $m$  with a neighbour within  $\Delta = 0.02^\circ$

Values in parentheses are from the relation  $m = n^2 \Delta$  (see Section 5)

$\lambda$ (Å)	$n$	$m$	$n$	$m$
	Ca <sub>5</sub> (SiO <sub>4</sub> ) <sub>2</sub> (OD) <sub>2</sub>		Glycylglycine	
1.0	20	7.4 (8.0)	23	9.4 (10.6)
1.5	11	3.0 (2.4)	13	2.9 (3.4)
2.0	5	0.8 (0.5)	6	0.8 (0.7)

Table 4 shows several estimates for Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>(OD)<sub>2</sub> and glycylglycine. For the region around  $\sin \theta/\lambda = 0.45 \text{ \AA}^{-1}$  we have calculated the number of reflections per degree and the number that will be rejected because they are less than  $0.02^\circ$  from each other. If there are  $n$  reflections per degree and  $\Delta$  is the minimum allowed angle between reflections, then the probability of rejection for small  $n$  and  $\Delta$  can be approximated by  $p = n\Delta$ . Values of  $n$  and  $m$  for  $\Delta = 0.02$  are given in Table 4. It is clear that at  $\lambda = 1 \text{ \AA}$  the amount of overlap is too large to allow enough data to be extracted. On the other hand, at  $\lambda = 2 \text{ \AA}$ , the situation is satisfactory.

Using the values in Table 4 we can estimate the maximum number of independent atoms where the structure can be solved. The number of reflections per degree may be approximated by

$$n \approx \frac{4}{3} \pi^2 (V/Z) (\sin \theta/\lambda)^2 \cos \theta/\lambda,$$

where  $V$  is the volume of the unit cell and  $Z$  the multiplicity of a general reflection. In the centro-symmetric case  $V/Z$  will thus be the volume of the asymmetric part of the unit cell. If we assume an atom to have an average volume of  $12 \text{ \AA}^3$ , we get  $V/Z = 12N$ , where  $N$  is the number of atoms, and therefore

$$n \approx 10N (\sin \theta/\lambda)^2 \cos \theta/\lambda.$$

We can probably allow that at maximum 20% of the reflections are rejected at the highest angle. For  $\lambda = 2 \text{ \AA}$  we can thus expect to solve structures with up to 20 independent atoms in a centro-symmetric structure.

In the analysis we have entirely neglected the effects of particle broadening on the peak width which, if it occurs, will seriously reduce the capacity of the method. In the examples chosen we saw no indication, in the synchrotron powder data, of any important effect of line broadening. The particle broadening would be  $d/D$ , where  $d$  is the spacing required and  $D$  the diameter of the particle. At the limit of the data range  $d$  is 1 Å so, for a particle size larger than 1  $\mu\text{m}$ ,  $d/D$  would be much less than  $0.01^\circ$ . Many powders are of such quality.

Many technical problems also have to be overcome. Whereas neutron diffractometers with the optimum resolution near  $\sin \theta/\lambda = 0.45 \text{ \AA}^{-1}$  do exist and run in a routine fashion, nothing similar exists in the synchrotron case. This would require monochromators with smaller  $d$  spacings than the Si(111). Moreover, as the resolution will be very high in the synchrotron case, the measurement of the Bragg angle requires an absolute precision of around  $0.001 \text{ \AA}$ . Finally, of course, the measurement should be done in a geometry where the axis of the cylinder holding the powder is coincident with the polarization direction of the beam in order to avoid problems with the polarization correction.

Altogether, however, the present analysis indicates that it is worth while to pursue the further development of methods for routine structure determination from powder data.

### Acknowledgment

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