

Indexing of Powder Diffraction Patterns for Low-Symmetry Lattices by the Successive Dichotomy Method

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(Received 8 April 1991; accepted 30 May 1991)

Abstract

The dichotomy method for indexing powder diffraction patterns for low-symmetry lattices is studied in terms of an optimization of bound relations used in the comparison of observed data with the calculated patterns generated at each level of the analysis. A rigorous mathematical treatment is presented for monoclinic and triclinic cases. A new program, *DICVOL91*, has been written, working from the cubic end of the symmetry sequence to triclinic lattices. The search of unit cells is exhaustive within input parameter limits, although a few restrictions for the hkl indices of the first two diffraction lines have been introduced in the study of triclinic symmetry. The efficiency of the method has been checked by means of a large number of accurate powder data, with a very high success rate. Calculation times appeared to be quite reasonable for the majority of examples, down to monoclinic symmetry, but were less predictable for triclinic cases. Applications to all symmetries, including cases with a dominant zone, are discussed.

Introduction

The dichotomy method for the automatic indexing of powder diffraction patterns was introduced in 1972 (Louër & Louër). It is based on the variation, in direct space, of the lengths of cell edges and interaxial angles by finite ranges, which are progressively reduced by means of a dichotomy procedure if they contain a possible solution. With this strategy, solutions are searched exhaustively in an n -dimensional space, n being the number of unknown unit-cell parameters. The method was first applied to orthorhombic ($n = 3$) and higher symmetries ($n = 1$ and 2) with a high success rate. It was described by Shirley (1980) as 'probably the optimal exhaustive strategy in parameter-space'. Later, an optimization of the program (*DICVOL*) and an extension to

monoclinic systems ($n = 4$) were reported (Louër & Vargas, 1982). In particular, a partition of volume space for finding the smallest and most probable solutions was first used, with a subsequent reduction of calculation times. The computing times were short for high symmetries, but could be long (from a few minutes to several hours) for monoclinic cases. The reasons were not totally understood at the time, but were attributed to overestimated intervals generated by the calculated bounds $[Q_-, Q_+]$ for diffraction lines having a product $hl < 0$. This problem needed to be investigated, together with an extension of the method to triclinic symmetry. The present paper deals with new developments concerning the search for monoclinic solutions and the application of the successive dichotomy method to triclinic symmetry; more efficient algorithms introduced in the associated program, without loss of exhaustivity, are also described.

The monoclinic case ($n = 4$)

The problem of finding the direct parameters (a, b, c, β) of the monoclinic unit cell from powder diffraction data can be formulated by means of

$$Q(hkl) = f(A, C, \beta) + g(B) \quad (1)$$

with

$$f(A, C, \beta) = h^2/A^2 + l^2/C^2 - 2hl \cos \beta / AC$$

and

$$g(B) = k^2/B^2,$$

where

$$A = a \sin \beta, B = b \text{ and } C = c \sin \beta.$$

This relation appears to be more convenient in the application of the dichotomy procedure than the usual form, as used in previous versions of the computer program. The four-dimensional domain is defined by the intervals $[A_-, A_+]$, $[B_-, B_+]$, $[C_-, C_+]$ and $[\beta_-, \beta_+]$. The complete space is then covered by incrementing the integers n, m, t and v in

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the intervals

$$[A_- = A_0 + np, A_+ = A_- + p],$$

$$[B_- = B_0 + mp, B_+ = B_- + p],$$

$$[C_- = C_0 + tp, C_+ = C_- + p],$$

$$[\beta_- = 90 + v\theta, \beta_+ = \beta_- + \theta],$$

where the scanning steps p and θ have been chosen as 0.40 Å and 5° respectively and A_0 , B_0 and C_0 are the lowest values for the A , B and C parameters. Some constraints can be used to avoid redundant calculations; if it is assumed that $A \geq C$, minimum limits are $A_0 = d_1 - \Delta d_1$ in the case of $A > B$ and $B_0 = d_1 - \Delta d_1$ if $A < B$, d_1 being the largest d spacing observed. From the intervals of the A , B , C and β parameters defining one domain, a calculated powder pattern is generated, each line being represented in Q space by an interval $[Q_-(hkl), Q_+(hkl)]$. The domain is then retained if the observed lines Q_i lie within $[Q_-(hkl) - \Delta Q_i, Q_+(hkl) + \Delta Q_i]$, ΔQ_i being the absolute error of observed lines, otherwise it is discarded. At this stage the true solution can be included in the domain, which will subsequently be analysed in detail. Consequently, the hkl indices of the exact solution for each observed line constitute a subset of the set of hkl values which have been found possible for this line. This is an important point, since the introduction of a strategy using a simulated recursive procedure for the storage of hkl constitutes a significant reduction in calculation time. If all observed lines are located within the first calculated limits, each domain is divided into 2^4 subdomains by halving the intervals $[A_-, A_+]$, $[B_-, B_+]$, $[C_-, C_+]$ and $[\beta_-, \beta_+]$. Again, calculated lines $[Q_-(hkl), Q_+(hkl)]$ are generated and compared with the observed data, within the limits of experimental error. If a solution exists, the dichotomy approach is applied successively, up to a maximum of seven times. At the last step, the unit-cell parameters are refined by a least-squares treatment and figures of merit M_N (de Wolff, 1968) and F_N (Smith & Snyder, 1979) are displayed for the N lines used in the calculation. Optimization of this arborescent type of analysis requires an exact calculation of the limits $[Q_-(hkl), Q_+(hkl)]$. As indicated above, overestimated bounds were previously used for lines with $hl < 0$ and these were responsible for some of the excessive computation times. A mathematical analysis of the bounds for this case is as follows. There is no change for the case $hl \geq 0$, for which the bounds are written as

$$Q_-(hkl) = f(A_+, C_+, \beta_-) + g(B_+)$$

and

$$Q_+(hkl) = f(A_-, C_-, \beta_+) + g(B_-).$$

In the calculated limits Q_- , Q_+ given previously for lines with $hl < 0$ (Louër & Vargas, 1982), the relations that exist between the parameters h , k , l , A_- , A_+ , ..., β_+ were not taken into account. In fact, a detailed analysis shows that the limits Q_- , Q_+ depend on relations between these different parameters. The calculation is complicated and somewhat tedious. The calculation of Q_- and Q_+ relations is based on the search for the smallest and greatest Q values in the four-dimensional space

$$\mathbb{E} = [A_-, A_+] \times [B_-, B_+] \times [C_-, C_+] \times [\beta_-, \beta_+].$$

By equating partial derivatives of the function Q to zero, for an hkl set, it can be shown that there are two sets of minima:

$$\begin{aligned} Q_{\min 1} &= \{(l^2 \sin^2 \beta_+)/C_+^2 + g(B_+), \\ &\quad (l^2 \sin^2 \beta_+)/C_-^2 + g(B_+)\}, \\ Q_{\min 2} &= \{(h^2 \sin^2 \beta_+)/A_+^2 + g(B_+), \\ &\quad (h^2 \sin^2 \beta_+)/A_-^2 + g(B_+)\}. \end{aligned}$$

Each set consists of two minima, depending on the combination of the sign of C and A , respectively. The smaller Q value (Q_-) is selected from three sets, $Q_{\min 1}$, $Q_{\min 2}$ and $Q_{\min 3}$ given by

$$\begin{aligned} Q_{\min 3} &= \{f(A_+, C_+, \beta_+) + g(B_+), f(A_-, C_+, \beta_+) \\ &\quad + g(B_+), f(A_+, C_-, \beta_+) + g(B_+), \\ &\quad f(A_-, C_-, \beta_+) + g(B_+)\}, \end{aligned}$$

which corresponds to the limits of space \mathbb{E} .

The derivation of the relations Q_+ shows that they are necessarily values of the Q function in the limits of space \mathbb{E} :

$$\begin{aligned} Q_+ \in \{f(A_+, C_+, \beta_-) + g(B_-), f(A_-, C_+, \beta_-) \\ + g(B_-), f(A_+, C_-, \beta_-) + g(B_-), \\ f(A_-, C_-, \beta_-) + g(B_-)\}. \end{aligned}$$

An Appendix containing the mathematical details has been deposited.* Table 1 displays the values of bounds Q_- , Q_+ for all possible cases. These relationships have been used in the program discussed below.

The triclinic case ($n = 6$)

The general relation giving $Q(hkl)$ as a function of direct parameters is too complicated to be used in the dichotomy method. It is more convenient to apply the successive dichotomy procedure in Q

* A mathematical Appendix has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54279 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Expressions of limits Q_- and Q_+ for $hl < 0$ in monoclinic symmetry

$\frac{h C_+}{l \cos \beta_+} \in [A_-, A_+]$	$\frac{h C_+}{l \cos \beta_+} \in [A_-, A_+]$							
	$\frac{h C_-}{l \cos \beta_-} \in [A_-, A_+]$	$\frac{h C_-}{l \cos \beta_-} \in [A_-, A_+]$						
		$\frac{l A_+}{h \cos \beta_+} \in [C_-, C_+]$	$\frac{l A_+}{h \cos \beta_+} \in [C_-, C_+]$					
			$\frac{l A_-}{h \cos \beta_-} \in [C_-, C_+]$	$\frac{l A_-}{h \cos \beta_-} \in [C_-, C_+]$				
				$\cos \beta_- < \frac{l A_+}{h C_-}$	$\cos \beta_- \geq \frac{l A_+}{h C_-}$			
					$\cos \beta_- \leq \frac{l A_-}{h C_+}$	$\cos \beta_- > \frac{l A_-}{h C_+}$		
						$\cos \beta_+ < \frac{h C_+}{l A_-}$	$\cos \beta_+ \geq \frac{h C_+}{l A_-}$	
							$\cos \beta_+ < \frac{l A_+}{h C_-}$	$\cos \beta_+ \geq \frac{l A_+}{h C_-}$
$Q_- = \frac{l^2}{C_+^2} \sin^2 \beta_+ + g(B_-)$	$Q_- = Q_1^{(1)}$	$Q_- = \frac{h^2}{A_+^2} \sin^2 \beta_+ + g(B_-)$	$Q_- = Q_1^{(1)}$	$Q_- = Q_2^{(1)}$	$Q_- = Q_2^{(1)}$	$Q_- = Q_3^{(1)}$	$Q_- = Q_2^{(1)}$	$Q_- = Q_1^{(1)}$
$Q_+ : \text{see } (**)$		$Q_+ : \text{see } (***)$		$Q_+ = Q_4^{(1)}$	$Q_+ = Q_4^{(1)}$	$Q_+ : \text{see } (**)$		

(**)

$\frac{1}{A_-} + \frac{1}{A_+} \geq \frac{2l \cos \beta_-}{h C_-}$	$\frac{1}{A_-} + \frac{1}{A_+} < \frac{2l \cos \beta_-}{h C_-}$
$Q_+ = f(A_-, C_-, \beta_-) + g(B_-)$	$Q_+ = f(A_+, C_-, \beta_-) + g(B_-)$

(***)

$\frac{1}{C_-} + \frac{1}{C_+} \geq \frac{2h \cos \beta_-}{l A_-}$	$\frac{1}{C_-} + \frac{1}{C_+} < \frac{2h \cos \beta_-}{l A_-}$
$Q_+ = f(A_-, C_-, \beta_-) + g(B_-)$	$Q_+ = f(A_+, C_-, \beta_-) + g(B_-)$

(1) $Q_1 = f(A_+, C_+, \beta_+) + g(B_+)$; $Q_2 = f(A_+, C_-, \beta_-) + g(B_-)$;
 $Q_3 = f(A_-, C_+, \beta_+) + g(B_+)$; $Q_4 = f(A_-, C_-, \beta_-) + g(B_-)$;
 with $f(x, y, z) = \frac{h^2}{x^2} + \frac{l^2}{y^2} - \frac{2hl \cos z}{xy}$ and $g(x) = \frac{k^2}{x^2}$.

space, i.e. to the parameters $Q_A, Q_B, Q_C, Q_D, Q_E, Q_F$ with of the linear form

$$Q(hkl) = h^2 Q_A + k^2 Q_B + l^2 Q_C + hk Q_D + kl Q_E + lh Q_F,$$

where

$$Q_A = \mathbf{a}^* \cdot \mathbf{a}^*, Q_B = \mathbf{b}^* \cdot \mathbf{b}^*, Q_C = \mathbf{c}^* \cdot \mathbf{c}^*, Q_D = 2\mathbf{a}^* \cdot \mathbf{b}^*, \\ Q_E = 2\mathbf{b}^* \cdot \mathbf{c}^*, Q_F = 2\mathbf{c}^* \cdot \mathbf{a}^*$$

and $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ are the basis vectors of the reciprocal lattice.

The calculated limits values $[Q_-, Q_+]$ for an hkl set are then given as a function of the limits of Q_A, \dots, Q_F :

$$Q_- = h^2 Q_{A-} + k^2 Q_{B-} + l^2 Q_{C-} + \lambda_{hk} Q_{D-} \\ + (hk - \lambda_{hk}) Q_{D+} + \lambda_{kl} Q_{E-} + (kl - \lambda_{kl}) Q_{E+} \\ + \lambda_{lh} Q_{F-} + (lh - \lambda_{lh}) Q_{F+} \\ Q_+ = h^2 Q_{A+} + k^2 Q_{B+} + l^2 Q_{C+} + \lambda_{hk} Q_{D+} \\ + (hk - \lambda_{hk}) Q_{D-} + \lambda_{kl} Q_{E+} + (kl - \lambda_{kl}) Q_{E-} \\ + \lambda_{lh} Q_{F+} + (lh - \lambda_{lh}) Q_{F-}$$

$$\lambda_{hk} = hk \text{ if } hk \geq 0 \text{ and } \lambda_{hk} = 0 \text{ if } hk < 0,$$

$$\lambda_{kl} = kl \text{ if } kl \geq 0 \text{ and } \lambda_{kl} = 0 \text{ if } kl < 0,$$

$$\lambda_{lh} = lh \text{ if } lh \geq 0 \text{ and } \lambda_{lh} = 0 \text{ if } lh < 0.$$

In order to reduce calculation times, two main restrictions on hkl indices have been imposed:

(a) maximum values h, k and l are limited to 2 for the first five lines.

(b) $h + k + l < 3$ for the first two lines.

Condition (a), coupled with the calculation strategy used in the program, generates 14 possible independent hkl combinations for the first two lines. They are (100,010),* (100,110), (100,011), (100,020),* (110,010), (200,010),* (110,001), (200,110), (110,002), (200,011), (110,020), (110,011), (110,110), (200,020).* These cases are quite representative of the majority of experimental patterns with triclinic symmetry. From an examination of the 29 triclinic cases appearing in the *National Bureau of Standards (US) Monograph No. 25*, 16 belong to the (100,010) case, 7 to (100,110), 1 to (100,011), 1 to (200,010), 1 to

(200,0 $\bar{1}$ 1), 1 to (110,020) and 1 to (110,011). Only one example does not belong to these 14 cases [Nat'l Bur. Stand. (US), 1979b]. This has a large unit-cell volume (1747 Å³), with one long dimension (21.29 Å); this is the (010,120) case. In the algorithm for triclinic symmetry, the 14 cases are analysed successively until a solution has been found. Moreover, a significant decrease of computational times has been obtained by taking into account specific relations in reciprocal space (Runge, 1917; Ito, 1949), which can be applied to the cases marked above with an asterisk. Indeed, for these cases, if pairs of lines $hk0$ and $h\bar{k}0$ can be located, a third 'powder constant' is automatically obtained, giving a problem with only three unknown parameters, which are searched by the successive dichotomy technique.

As reported previously, there is great benefit in using a partition of volume space in the strategy of searching for the solution. In the triclinic case, Smith (1977) has shown from the examination of $1/N$ vs d^3 plots for accurate triclinic patterns that a simple approximate relation can be derived for the unit-cell volume as a function of the number of lines N :

$$V_{\text{est}} = 0.60 d^3 / (1/N - 0.0052).$$

In the new version of the program solutions are first sought within a range $\pm 30\%$ of V_{est} . If no solution is found, the search is continued on each side of this range. Moreover, the strategy also benefits from a recursive procedure for the storage of hkl indices at each dichotomy level. The combined effect of the high density of diffraction lines, in the triclinic case, and the progressive reduction of the intervals [$Q_-(hkl)$, $Q_+(hkl)$] can be used for rejecting a solution for which two successive lines would be indexed by an identical hkl set; then the dichotomy route being investigated in the arborescent strategy is immediately stopped.

The indexing program

The new features reported above have been incorporated in the program *DICVOL91*, which is the successor of *DICVOL*. These improvements have resulted in a significant increase in the efficiency of the method for symmetries down to monoclinic and in the introduction of a routine for the indexing of powder patterns for triclinic compounds. In addition to the exhaustive nature of the strategy, the optimization of error limits has led to a considerable decrease in calculation times for monoclinic solutions. The algorithm used for triclinic solutions is based on hkl restrictions for the two first lines, but very few cases, *i.e.* only those for which the hkl indices of the two first lines are excluded from these conditions, cannot be indexed by the new program. This constraint constitutes a deviation from the

exhaustive feature of the dichotomy procedure. The general principles employed in the previous version of the program are still used: a search strategy of solutions from high to low symmetries and the use of a partition of volume space (scanning of successive 400 Å³ shells of volumes, except for triclinic symmetry where the shells are based on V_{est}) in order to find first the smallest and more probable solutions. Indeed, for a given average discrepancy between Q_{obs} and Q_{calc} for the first N lines, it is known that the volume is inversely proportional to the figure of merit M_N ; consequently, the smaller the volume, the greater is the figure of merit. The normal constraints on parameters resulting from the symmetry (Louër & Louër, 1972; Louër & Vargas, 1982) are used to avoid redundant calculations. Being exhaustive, the program can give 'negative (no solution found) as well as positive (solution found) information, within the stated volume and error limits' (Shirley, 1978). With precise data, the number of proposed solutions is generally very small and frequently only one solution is found. The parameters are refined by a least-squares method and figures of merit (M_N and F_N) are displayed. Moreover, in order to help the user, the number of solutions retained at each level of the dichotomy procedure is printed to follow their progress in the arborescent strategy. An examination of these numbers can be useful if too strict an absolute error is applied to the input data relative to the inaccuracy of the data. Clearly, a small increase in the allowed error can facilitate obtaining a solution, but it increases the risk of finding false solutions and of losing the correct one. The possibility of increasing the error window must therefore be used with caution.

The program *DICVOL91* is written in Fortran77 and can be easily adapted to any main-frame computer. The strategy used for indexing begins from the cubic end of the symmetry sequence. The capacity of the program is 270 kbytes. Tests have been carried out on a Control Data Cyber 180/860, a MicroVAX 3100 and a PC AT386 computers. The CPU times given in the following comments have been obtained on the CDC computer. Calculation times on the MicroVAX and PC computers were, on average, 2–4 times and 10–12 times greater, respectively.

Applications

Indexing of a large number of accurate powder diffraction patterns has been carried out by means of *DICVOL91* with a very high success rate. However, for an unbiased test of efficiency of the program, observed data known for their quality, such as those reported in the *National Bureau of Standards (US) Monograph 25*, have been used. Two kinds of tests have been considered; one is based on all powder

diffraction data sets found in §17 of Monograph 25 [Natl Bur. Stand. (US), 1980] and the other is based on all triclinic data sets reported in the complete monograph. In addition, powder data collected from a modern powder diffractometer and indexed by *DICVOL91* are also discussed in terms of accuracy, indexing efficiency and specific examples characterized by a zone dominance.

(i) §17 [Natl Bur. Stand. (US), 1980] reports powder data with all symmetries: cubic (2), tetragonal (5), hexagonal (4), orthorhombic (19), monoclinic (18) and triclinic (6). The standard input data were: the first 20 lines of the pattern, a standard absolute error of $0.03^\circ (2\theta)$ on each diffraction line, a maximum cell edge of 25 \AA , a maximum value of 125° for β in monoclinic symmetry, a maximum unit-cell volume of 1500 \AA^3 and the required M_N figure of merit for printing a solution was set to 5. The results, with ranges of CPU times on the CDC computer, can be summarized as follows. (Unless stated otherwise, the same conditions were applied to all data sets.)

(a) For solutions with orthorhombic or higher symmetry, all patterns were correctly indexed. If the time of 41 s required for indexing the data for hexagonal chromium iron oxide is omitted, the average time for indexing the other 29 patterns is less than 3 s.

(b) For solutions with monoclinic symmetry, all 18 patterns were indexed; for four of them, discussed below, the input absolute error on observed peak positions was increased slightly for a few lines owing to the inaccuracy of published data. Eight of the patterns were indexed with a CPU time lower than 141 s, seven within 141–298 s and three required a greater time (gypsum: 36 min; potassium hydrogen iodate: 14 min; sodium chlorate hydrate: 280 min). A few comments can be made concerning four patterns. For the data from gypsum, chromium chloride and sodium chlorate hydrate, the standard error on observed Bragg angles was selected to be $0.04^\circ (2\theta)$ owing to the lower quality of data, as shown by the values of the figures of merit [$M_{20} = 24$; $F_{20} = 30(0.010,67)$], [$M_{19} = 16$; $F_{19} = 12(0.018,89)$] and [$M_{20} = 13$; $F_{20} = 17(0.010,118)$]. Another feature of these figures of merit is the rather high value of N_{calc} , which indicates that a large number of lines are missing from the pattern. For chromium chloride the volume of the unit cell was halved, which is probably a consequence of the low quality of data (only 19 lines available). Also, it can be noted that the pattern of the γ phase of potassium hydrogen iodate was indexed after using an absolute error on the 111 line of $0.06^\circ (2\theta)$, according to the reported error; this example took 11 min and the solution is characterized by low figures of merit [$M_{20} = 14$; $F_{20} = 25(0.012,67)$].

(c) For solutions with triclinic symmetry, the six powder patterns were indexed and the CPU times are discussed in (ii).

(ii) The data for all triclinic diffraction patterns reported in the *National Bureau of Standards (US) Monograph No. 25*, except data for $\text{C}_{20}\text{H}_{34}$ ($V = 1747 \text{ \AA}^3$) [Natl Bur. Stand. (US), 1979b], which is a case (010,120) not implemented in the program, were input to *DICVOL91*. Among the 16 examples belonging to case (100,010), ten were indexed in less than 50 s, four required a CPU time between 95 and 255 s and the last two solutions were found in 11 min [Natl Bur. Stand. (US), 1979a] and 10 min [Natl Bur. Stand. (US), 1981]. Calculation times for the seven examples belonging to the case (100,1 $\bar{1}$ 0) were, on average, significantly greater, from 10 to 121 min. For the single case (200,010) the CPU time was 11 min. Among the two cases (1 $\bar{1}$ 0,020) one was indexed in 5 min, while the second one [Natl Bur. Stand. (US), 1978a], as well as the single case (110,01 $\bar{1}$) [Natl Bur. Stand. (US), 1978b], failed. Explanation for the failure was found in the low precision of the reported data, coupled with a large number of missing lines, as revealed by the calculated figures of merit F_{30} , $30(0.014,69)$ and $12(0.013,183)$ respectively. From this analysis, it can be concluded that the majority of the triclinic examples has been indexed, excepted for a few cases with low accuracy. It is difficult to make predictions about CPU times; they can be short (few seconds), but some examples were more time consuming (about 2 h maximum). It should be noted that the number of triclinic cases is rather low when compared with the number of materials with other symmetries. Moreover, if the solution is found for these time-consuming examples, time is probably unimportant, particularly if an *ab initio* structure determination follows this geometrical reconstruction of the reciprocal lattice (Bénard, Louër & Louër, 1991). In general, it can be useful, and sometimes necessary, to transform the solution found into the conventional unit cell. The program *CDF-SRCH* (JCPDS) was used to find the normalized unit-cell parameters, with the further benefit of being able to interrogate the NIST Crystal Data File (1988) database in order to search for an apparently isostructural material.

(iii) It is of interest to comment on specific examples in which one cell dimension is significantly longer or shorter than the others. In the examples described above in (i) and (ii) some powder data correspond to a longer parameter. These examples were indexed by *DICVOL91*; however, the observed trend in the indexing procedure was an increase in the CPU times. Among the powder data having this feature are those for monoclinic phenylhydrazine hydrochloride with $b = 30.641 \text{ \AA}$ [Natl Bur. Stand.

(US), 1980], monoclinic potassium hydrogen iodate with $a = 21.853 \text{ \AA}$ [Natl Bur. Stand. (US), 1980], triclinic clopenthixol hydrate with $b = 21.939 \text{ \AA}$ [Natl. Bur. Stand. (US), 1980] and triclinic calcium hydrogen hydrate with $b = 18.994 \text{ \AA}$ [Natl Bur. Stand. (US), 1976].

Examples with a short axis are probably worth discussing since they are characterized by the presence of one common zero index for all the first lines of the pattern. This situation frequently occurs in materials having a layer-type structure. As examples, powder data of some metal hydroxide nitrates collected by means of a powder diffractometer with strict monochromatic radiation can briefly be commented on. In the powder pattern of lanthanum hydroxide nitrate (Louër, Louër, Lopez Delgado & Garcia Martinez, 1989), the first six lines have a zero k index; in the powder pattern of neodymium hydroxide nitrate (Louër, Deneuve, Herviou & Gourlaouen, 1986) the first seven lines have a zero k index; in the powder pattern of cadmium hydroxide nitrate (Auffrédic, Plévert & Louër, 1990), the first eight consecutive lines are $0kl$. Because in the successive dichotomy method the possible mathematical solutions are not deduced from a limited number of base lines, the presence of a common zero index for the first lines of the pattern does not impede finding the correct solution; consequently, all these examples were indexed by DICVOL91. Evidently, an exceptionally short axis with a large number of initial diffraction lines with a common zero index with respect to the number of input data will introduce difficulties in the search of the solution, with the risk of obtaining pseudo solutions. This can be illustrated by the indexing of the powder diffraction pattern of a zinc hydroxide nitrate, since 14 of the initial lines have a zero k index (Eriksson, Louër & Werner, 1989). From the first 20 lines, DICVOL91 proposed four solutions, with the following unit-cell volumes and M_{20} values: 679 \AA^3 , 18; 748 \AA^3 , 14; 797 \AA^3 , 15 and 757 \AA^3 , 19. From these solutions, the 50 lines of the complete pattern were reviewed by means of the program of data evaluation NBS*AIDS83 (Mighell, Hubbard & Stalik, 1981). The three pseudo solutions did not resist the analysis. Finally, only the correct solution [$a = 17.951(7)$, $b = 3.258(2)$, $c = 14.275(3) \text{ \AA}$, $\beta = 114.95(2)^\circ$, $V = 757.08 \text{ \AA}^3$, $M_{20} = 19$, $F_{20} = 37(0.0095, 57)$] explains the complete data set.

It is of interest to mention here the indexing of the powder pattern for barium titanyl oxalate, a material used for the synthesis of high-purity barium titanate; although this precursor was described a long time ago, its powder diffraction pattern was described as complicated. Accurate data were collected, by means of a powder diffractometer equipped with an incident-beam monochromator, and were indexed by

means of DICVOL91 in 291 s (Louër, Boulitif, Gotor & Criado, 1990). The large volume of the unit cell, 2595 \AA^3 , explained the density of observed lines and furthermore demonstrated that this important precursor of pure stoichiometric barium titanate was a single phase.

To conclude, the mathematical analysis of the dichotomy procedure for indexing monoclinic and triclinic powder diffraction patterns has resulted in a significant improvement of the computer program, DICVOL91; its efficiency in indexing accurate powder diffraction data has been demonstrated by a very high success rate.

The authors acknowledge Dr L. Gatineau, of the CRSOCI at Orléans, for helpful discussions concerning the calculated Q ranges for monoclinic symmetry in the previous version of the program.

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