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COMPUTATIONAL METHOD FOR THE INDEXING OF UNKNOWN POWDER PATTERNS AND UNKNOWN ROTATING-CRYSTAL PATTERNS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

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BY

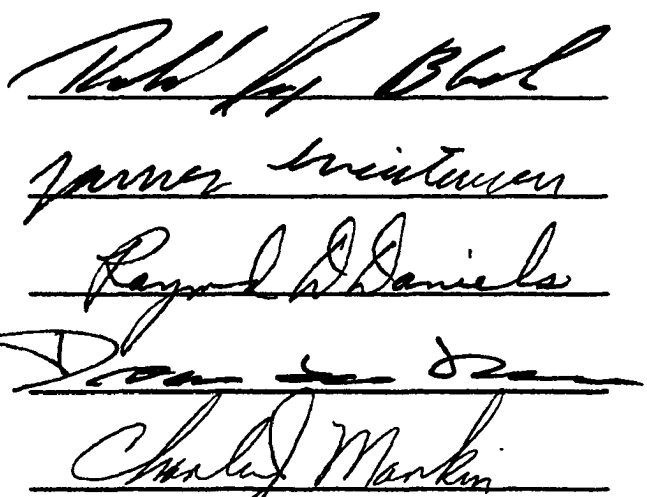
WOODROW SUN

Norman, Oklahoma

1972

COMPUTATIONAL METHOD FOR THE INDEXING OF UNKNOWN POWDER PATTERNS AND UNKNOWN ROTATING-CRYSTAL PATTERNS

APPROVED BY



DISSERTATION COMMITTEE

ABSTRACT

A computational method has been developed for the indexing of both unknown powder patterns and unknown rotating-crystal patterns, based on the choices of possible parameters from the difference analysis of the diffraction data (auxiliary computer programs are used for reducing the number of the possible parameters for orthorhombic, monoclinic and triclinic systems), the techniques of indexing search (branch-and-bound), the refinement of the parameters by the use of least-square method (multiple least-square method are used for monoclinic and triclinic systems) and then selecting the unique solution by using standard deviation determination. The method is also efficient for indexing those patterns in which some reflections are either missing by accident or because of translational symmetry. The programs can be used for all the lattice structures including those of low symmetries, such as monoclinic and triclinic crystals. Several experimental patterns are used for illustrating the method. It should be possible to adapt the method to any digital computer. The present computer programs are written in FORTRAN IV for IBM/360 (WATFIV).

Dedicated to

My Parents

Professor and Mrs. Pan-cheng Sun

and

My Wife, Aurora L. Sun

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COMPUTATIONAL METHOD FOR THE INDEXING OF UNKNOWN POWDER PATTERNS AND UNKNOWN ROTATING-CRYSTAL PATTERNS

CHAPTER I

INTRODUCTION

Introduction

The characteristic X-ray diffraction effect from a fine-grained crystalline aggregate was first discovered by Debye and Scherrer[1] in 1916 and almost simultaneously by Hull.[2,3] This method of investigating crystals has proved to be extraordinarily useful in those cases where one wishes to examine a crystalline material that is not in the form of discrete single crystals. Because the sample is an aggregate of fine crystalline material, this way of examining materials is often called the powder method as well as Debye-Scherrer method.

There are many applications of the powder method, but two of these are of primary importance: (1) The powder method provides a way of investigating the crystallography as mentioned above, and (2) since the powder diffraction photograph produced by a crystalline substance is a characteristic of that substance, the powder method can be used as a means of identification of crystals.

However, it commonly falls to the lot of a chemist, physicist, metallurgist, or even someone without much scientific or technical background, to take powder photographs and interpret them. The initial step is, of course, to index the powder pattern photographs. This requires a knowledge of X-ray diffraction theory, considerable experience, and time-consuming trial and error before a complicated powder pattern photograph can be solved.

During last several decades, many techniques for the indexing of unknown powder patterns were developed using graphic, analytic, and even computer methods. This makes indexing quite difficult because the indexers must learn so many techniques for their purpose. Also, it is inconvenient and time-consuming to index a powder pattern by trying several techniques. Furthermore, the costs for wages and computer time for the indexing of unknown powder patterns are often not economical.

Previous Work

The Cubic System

The first step in indexing any unknown powder photograph is to find whether the symmetry is cubic. A graphic method for indexing powder photograph of isometric crystals was described as early as 1918 by Scherrer.[4] Schiebold[5] suggested a logarithmic chart for the isometric system. Different isometric nomograms

were described by Eulitz[6] in 1930. White[7] described a graphic method for the powder patterns of cubic crystals by using polar coordinates. Later, Straumanis[8] described a graphic method for indexing the powder patterns of cubic substances, based on the application of three dimensional reciprocal lattices. However, the graphic method described by Azroff and Buerger[9] makes a detailed description of these other method superfluous.

In 1941, Thomas[10] suggested a method for indexing powder patterns of isometric symmetry by using a slide rule. If the reflections for which 2θ or $(h^2+k^2+l^2)$ are large are indexed by the graphic methods, a self-indexing method for isometric symmetry was suggested by Bloss[11] in which one calculates the quotients d_1^2/d_1^2, d_1^2/d_2^2, ..., d_1^2/d_n^2 where d_1 is the largest interplanar spacing observed and d_2, ..., d_n are successively smaller ones. A computer algorithm for rapid solution of indexing cubic crystal powder photographs was suggested by the author.[12] The algorithm was based on the comparison between the permissible integers for different Bravais lattice types of cubic materials and the ratios $\mathrm{Sin}^2\theta_{i+1}/\mathrm{Sin}^2\theta_i$ $(i=1,2,\ldots,K-1)$ of the reflections, where K is the total number of the reflections.

The Tetragonal and Hexagonal Systems

Indexing powder patterns becomes much more difficult as the number of unknown lattice parameters increases. For example,

there is only one unknown parameter for the cubic system, the lattice parameter, a, but there are two or more unknowns for noncubic crystals. The tetragonal system is usually considered next to the cubic system since the plane-spacing equation for tetragonal system involves only two unknown lattice parameters, a and c. The hexagonal system is considered next to the tetragonal system althrough the plane-spacing equation of this system also involves the same two unknown lattice parameters.

As early as 1917 and 1918, some numerical methods for solving the powder patterns of tetragonal and hexagonal systems were developed by Runge[13] and Johnson and Toeplitz[14] which were primarily of theoretical interest. Hull and Davey[15] were the first to describe a graphic method, based on the equation:

$$2 \log d_{hkl} = -\log (s+l^2/c^2), \qquad (1)$$

where $s=h^2+k^2$ for the tetragonal system and $s=h^2+hk+k^2$ for the hexagonal system, that allowed construction of chart by plotting $\log d_{hkl}$ vs. c on semilogarithmic paper for each possible combination of the Miller indices (hkl). The Hull-Davey graphic method was modified by Ebert[16] and Schneider,[17] who replaced the curves in the Hull-Davey chart with straight lines.

Bjurstrom[18] prepared a chart by plotting $1/d^2$ vs $1/a^2$ on an arbitrary scale. The indexing of a set of lines on a powder

photograph using the Bjurstrom chart requires, simply, the plotting of measured $1/d^2$ values on a strip of paper and a search for a match on the chart, similar to the procedure used in the Hull-Davey method. A similar chart prepared by Bond (unpublished) plots log (h^2+k^2) and log l^2 against c/a directly. This variation has the advantage that such charts are easier to prepare. Unfortunately, at very large or very small values of c/a the curves are nearly vertical, making them more difficult to use in these ranges.

A graphic method, using nomograms for indexing tetragonal and hexagonal powder photographs, was suggested by Schwarz and Summa.[19] This method permits a more open scale than that of Hull and Davey.[15] Harrington[20] described a graphic method by plotting the axial ratio on a logarithmic scale. When this is done, it turns out that all (hk0) curves have a slope of -2 and all (001) curves a slope of +2. Since the curves of all pyramid planes have the same shape, Harrington's chart can be constructed very easily with the aid of a single template.

Another graphic method of indexing tetragonal and hexagonal powder patterns has been devised by Bunn.[21] Like the Hull-Davey chart, a Bunn chart consists of a network of curves, one for each value of hkl, but the curves are based on somewhat different functions of hkl and c/a than those used by Hull and Davey with

the result that the curves are less crowded in certain regions of the chart. However, Ferro[22] suggested logarithm charts which were a slight variation of the plot of interplanar spacing against c/a described by the previous graphic methods. These graphic method can be used equally well if the crystal is based on a rhombohedral lattice.

A special chart for hexagonal close-packed lattices was also prepared by Bunn[21] by omitting all curves with Miller indices $(h_i k_i l_i)$ for which (h_i+2k_i) is an integral multiple of 3 and l_i is odd. A new chart was constructed by Schnerr[23] for hexagonal and rhombohedral spacing covering c/a from 3 to 18, corresponding to unit cell heights in close-packed structures of 4 to 21 layers. A procedure was described by Ebert[24] for indexing rhombohedral powder patterns. In contrast to the method of Hull and Davey,[15] it uses only systems of straight lines which cross each other and connect equidistant points on two parallel lines.

In 1948, Hesse[25] gave the first complete account of a numerical method for indexing powder patterns of tetragonal, hexagonal, and orthorhombic symmetries without the use of single-crystal data. A method proposed by Lipson[26] for the three systems mentioned is probably easier to understand than Hesse's more mathematical approach, although basically both are the same. An extension in scope and directness of the Hesse's method for index-

ing powder photographs of the three systems can be made by direct solution of the linear Diophantine equation suggested by Stosick.[27]

The numerical method suggested by Hesse[25] has been modified to permit computation on digital computers by Tannenbaum, Lemke, and Kramer.[28] Werner[29] suggested a trial-and-error computer method to index the tetragonal and hexagonal powder patterns based on solving the cell constants by assigning the Miller indices to the selected lower angle reflections. A computer program for the indexing of the powder patterns of tetragonal and hexagonal crystals based on the simultaneous use of reflections with low indices was described by Jamard, Taupin, and Guinier.[30] Hoff and Kitchingman[31] mentioned that a computer program could be done by selecting the cell constants from the difference between the observed values of $Sin^2\theta$ and all combinations of possible cell constants used in trial indexing of the tetragonal powder diffraction data.

The Orthorhombic System

For orthorhombic symmetry, the problem is more difficult because three unknown lattice parameters, a, b and c, have to be found. Moreover, the difficulty increases further if the problem involves large unit-cell dimensions, large numbers of extinguished reflections, or both.

As early as 1927, an extension of the graphic method was

described by Wilhelm[32] for determining crystal structures of the orthorhombic system. Another graphic method was suggested by Jocob and Warren[33] for finding the unit cell of uranium successfully. However, graphic methods of indexing noncubic powder patterns not only have the disadvantage of being time consuming but they also hold the definite risk of a wrong solution, especially when a large number of reflections are extinguished.

Some numerical methods suggested by Hesse,[25] Lipson,[26] and Stosick[27] have been proved rather straightforward when applied to tetragonal and hexagonal powder patterns but more cumbersome and somewhat less systematic when applied to orthorhombic powder patterns. Some organic substances, such as certain forms of soaps, fats, and fatty acids, have unit cells for which one dimension is much larger than the other two. Vand[34] proposed a method to distinguish such cases from the more general ones of long-chain compounds whose three unit-cell edges have more nearly equal lengths.

Ito[35] described a general analytical procedure to index the powder patterns of orthorhombic system that involves a good deal of trial and error and is based on the reciprocal lattice theorem. In 1964, Werner[29] suggested a trial-and-error computer method to index the orthorhombic powder patterns based on solving the cell constants by assigning the Miller indices to the

selected lower angle reflections and selecting one possible cell constant from the difference analysis of the observed $Sin^2\theta$ values. A computer method was described by Hoff and Kitchingman[31] for indexing the orthorhombic powder patterns by selecting the possible unit-cell constants from differences between the observed $Sin^2\theta$ values and then using a trial-and-error method for indexing the data. Jamard, Taupin, and Guinier[30] also suggested a computer program for indexing the powder patterns of orthorhombic materials based on the simultaneous use of reflections with low indices permitting the calculation of the cell volume and eliminating incorrect solutions.

Recently, Visser[35] suggested a computer program by finding the constants of the reciprocal lattice from powder data. Planes through the origin of the reciprocal lattice (zones) are found first. After evaluating these, the program selects pairs of zones with a common row to find reciprocal lattices which are then reduced in a simple way.

The Monoclinic System

Monoclinic substances yield powder patterns of great complexity because the number of unknown parameters involved in now four, a, b, c and β. No generally successful method, either analytical, graphic, or even computer, of indexing such patterns has yet been devised.

A general approach for indexing powder photographs regardless of symmetry was presented by Runge,[13] rediscovered by Ito,[36] and refined by de Wolff.[37] Another method developed by Thewlis and Hutchinson[38] is a variation on that of Ito[36] and is not so rigorous in its demands. The method is correspondingly less powerful than Ito's. An analytical method suggested by Zachariasen[39] for indexing the powder patterns of unknown monoclinic crystals is the most simple and direct. It involves no novel principles and requires no computational aids.

The systematic trial-and-error method of Werner[29] is based on the use of a computer. However, the computing time becomes prohibitive for lower symmetrical lattices. According to Ito's and de Wolff's approach, some computer programmings have been described by Liedl and Vorres[40] and Viswanathan[41] for indexing the powder photographs of lower symmetries.

The Triclinic System

It would appear from the previous literature that the indexing of a unknown triclinic powder pattern is very unlikely to succeed in practice since six lattice parameters, a, b, c, α, β, and γ, are involved.

The general approach for indexing the powder patterns presented by Runge,[13] Ito,[36] and de Wolff[37] attacked the problem from the low symmetries rather than from the higher symmetries

aspect and has to be followed by a cell-reduction procedure. Such procedures are also discussed by Buerger[42] and Azroff and Buerger.[9] Another method was developed by Thewlis and Hutchinson[38] which is a variation on that of Ito and which is not so rigorous in its demands. According to Ito's and de Wolff's approach, some computer programmings have been described by Liedl and Vorres[40] and Viswanathan[41] for indexing the powder patterns of lower symmetries.

In 1968, Vand and Johnson[43] described the theory and method of indexing the powder patterns for the triclinic case that most closely approaches the theory described by de Wolff.[37,44] However, the method seems unlikely to be written into computer programs with a reasonable amount of computer running time.

Scope and Objective

The objective in conducting this extensive study is to develop an improved computational method capable of assigning Miller indices of the reflections of unknown powder patterns of all the six crystal structures.

The computer algorithm may be described briefly as follows:

(1) Calculation of the experimental angles. This is for the purpose of changing the measurements from the powder film reader into the $Sin^2\theta$ values.

(2) Difference analysis for deciding the crystal structure and finding the possible parameters. The method of Lipson[26] is used to select the possible parameters from the differences between the observed values of $Sin^2\theta$. Auxiliary computer programs are designed to reduce the possibilities of the parameters for orthorhombic, monoclinic, and triclinic systems.

(3) Search for Miller indices. Using the Branch-and-Bound method, various indexing techniques are designed for searching the Miller indices of the observed reflections of the powder patterns of six different structures.

(4) Refinement of the parameters by the use of least-square method. The possible parameters are selected from only a subset of the reflections; therefore, the refinement of the parameters is necessary.

(5) Determination of a unique solution by using standard deviation. This ensures a unique and acceptable solution for the unknown patterns. It is believed that the solution determined by minimum standard deviation can certainly satisfy the criteria described by de Wolff[45] and Lester and Lipson.[46]

Generally speaking, the computer running time for this method is quite fast compared to the other computer methods. An attempt has also been made to apply this computer algorithm for the indexing of unknown rotating-crystal patterns. The indexing

procedures are described under the assumption that only one photograph is needed in which the sample rotates around any of the three axes, a, b, and c.

Some examples are used for illustrating the computer technique. The computer programs have been written in FORTRAN IV for IBM/360 (WATFIV).

CHAPTER II

RELATION OF BRAGG ANGLE θ TO CELL GEOMETRY

Introduction

The powder pattern is obtained in the usual way. A powder photograph shows a set of lines, for each of which a measurement can be made that provides the Bragg angle θ for that line. Each θ can be readily transformed into the interplanar spacing d_{hkl} and $Sin^2\theta_{hkl}$ for the plane responsible for the reflection to that line. Primary, then, a powder photograph yields a set of numerical values for the various $Sin^2\theta$ of the crystal sample, one $Sin^2\theta$ for each line of the powder pattern.

Calculation of Bragg Angle θ and $Sin^2\theta$

Let R be the radius of the powder camera and A be the arc length of two corresponding lines on the pattern which is measured by the use of a film reader. The relationship of the diffraction angle, θ, to the measured arc length, A, is shown in Figure 1.

From this it may be seen that

$$4\theta = \frac{A}{R} \quad \text{(radians)},$$

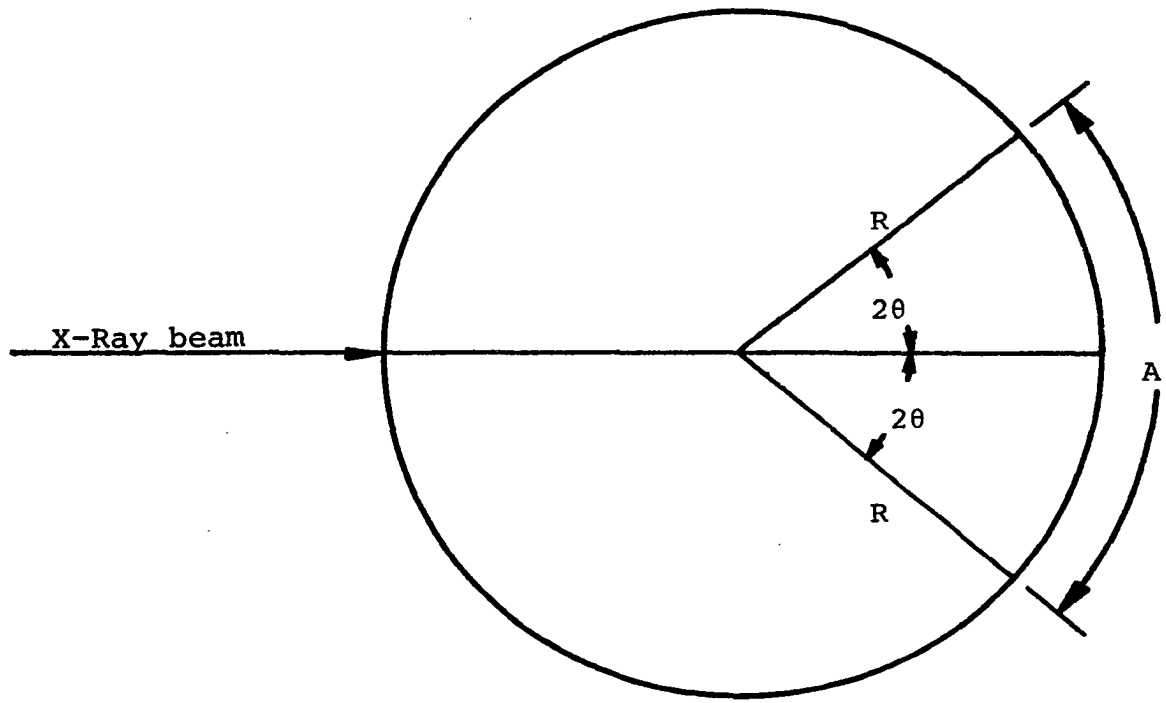

Figure 1 Diagram Showing the Relationship of the Diffraction Angle, θ, to the Arc Length, A.

$$\theta = \frac{A}{4R}, \qquad (2)$$

Therefore, if the distance, A, between corresponding lines on either side of the X-ray beams is measured on the film, the appropriate θ value for the set of reflection planes in question and the corresponding $\mathrm{Sin}^2\theta$ value are then calculated according to the equation (2).

A computer program, CEA, listed in Table 1, is then written for converting the arc lengths of the powder patterns into the $\mathrm{Sin}^2\theta$ values.

Bragg's Law

Consider Bragg's Law:

$$n\lambda = 2d'\mathrm{Sin}\theta,$$

where n=1 is assigned to first order reflections, n=2 is second order, etc. Each successive order exhibits a wider angle. For diffraction, the smallest value of n is 1 (n=0 corresponds to a beam diffracted in the same direction as the transmitted beam), and thus Bragg's Law may be written in the form:

$$\lambda = 2\,\frac{d'}{n}\mathrm{Sin}\theta.$$

Since the coefficient of λ is now unity, we can consider a reflection of any order as a first-order reflection from planes,

TABLE 1

Computer Program (CEA) for Calculating Experimental Angles

```
C COMPUTER PROGRAM FOR CALCULATING EXPERIMENTAL ANGLES
      DIMENSION A(70),T(70)
      IN=5
      IM=6
      READ (IN,1) M
    1 FORMAT (I3)
      DO 20 L=1,M
      READ (IN,2) K,R
    2 FORMAT (I5,F6.0)
      READ (IN,3) (A(I),I=1,K)
    3 FORMAT (5F10.0)
      DO 5 N=1,K
      THETA=A(N)/(4.0*R)
      T(N)=SIN(THETA)*SIN(THETA)
    5 CONTINUE
      WRITE (IM,51)
   51 FORMAT (1H1,' DIFFRACTION LINE',4X,'ARC LENGTH',6X,'DIFFRACTION LI
     INE',4X,'ARC LENGTH')
      WRITE (IM,52)
   52 FORMAT (2X,16('-'),4X,10('-'),6X,16('-'),4X,10('-'))
      LL=K/2
      DO 58 N=1,LL
      IF (K/2*2-K) 54,53,54
   53 LLL=N+LL
      GO TO 55
   54 LLL=N+LL+1
   55 WRITE (IM,56) N,A(N),LLL,A(LLL)
   56 FORMAT (7X,I3,12X,F7.3,14X,I3,13X,F7.3)
   58 CONTINUE
      IF (K/2*2-K) 59,60,59
   59 NL=(K+1)/2
      WRITE (IM,56) NL,A(NL)
   60 WRITE (IM,6)
    6 FORMAT (1H1,' DIFFRACTION',4X,'SIN(SQUARE)',6X,'DIFFRACTION',4X,'S
     1IN(SQUARE)')
      WRITE (IM,7)
    7 FORMAT (5X,'LINE',10X,'(OBSV.)',11X,'LINE',10X,'(OBSV.)')
      WRITE (IM,8)
    8 FORMAT (2X,11('-'),4X,11('-'),6X,11('-'),4X,11('-'))
      KK=K/2
      DO 14 N=1,KK
      IF (K/2*2-K) 10,9,10
    9 KKK=N+KK
      GO TO 11
```

TABLE 1 (CONTINUED)

```
10 KKK=N+KK+1
11 WRITE (IM,12) N,T(N),KKK,T(KKK)
12 FORMAT (5X,I3,10X,F8.5,11X,I3,10X,F8.5)
14 CONTINUE
   IF (K/2*2-K) 16,20,16
16 NL=(K+1)/2
   WRITE (IM,12) NL,T(NL)
20 CONTINUE
   STOP
   END
```

real or fictitious, spaced at a distance 1/n of the previous spacing. This turns out to be a real convenience. Now let d=d'/n and write Bragg's Law in the form:

$$\lambda = 2d \sin\theta, \tag{3}$$

and thus the $\sin^2\theta$ can be expressed by d by using Bragg's Law:

$$\sin^2\theta = \frac{\lambda^2}{4d^2} \tag{4}$$

Relation of $\sin^2\theta$ to Cell Geometry

The Cubic System

The plane-spacing equation for cubic system can be written as:

$$\frac{1}{d^2_{hkl}} = \frac{h^2 + k^2 + l^2}{a^2}, \tag{5}$$

where a is the lattice parameter of the unit cell.

Inserting equation (5) into (4), we have:

$$\mathrm{Sin}^2\theta_{hkl} = \frac{\lambda^2}{4a^2}\,(h^2+k^2+l^2). \qquad (6)$$

For our convenience, equation (6) may be re-written in the form:

$$\mathrm{Sin}^2\theta_i = (h_i^2+k_i^2+l_i^2)\;P, \qquad (7)$$

where i=number of the reflection with Miller indices $(h_i k_i l_i)$ and P=parameter=$\lambda^2/4a^2$. Here, the square of the sines of the angles of reflection are directly proportional to the sums of the squares of the Miller indices h, k, and l of the reflecting planes. Setting $s_i=h_i^2+k_i^2+l_i^2$ we recognize that s_i must be an integer because h_i, k_i, and l_i are integers. It can be verified that s_i can have all the values except $4^p(8q+7)$, where p=0,1,2,... and q=0,1,2,... The permissible integers for the three common Bravais lattice types of the cubic crystals and a Diamond cubic type are partially listed in Table 2.

The Tetragonal System

The plane-spacing equation for tetragonal system can be written as:

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \qquad (8)$$

where a and c are the two lattice parameters of the unit cell.

TABLE 2

Characteristic Sequences of the Three Common Bravais Lattices and Diamond Type of Cubic Crystals

Simple Cubic	1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16, 17, 18, 19, 20, 21, 22, 24, 25, 26, 27, 29, 30, 32, 33, 34, 35, 36, 37, 38, 40, 41, 42, 43, 44, 45, 46, 48, 49, 50, 51, 52, 53, 54, 56, 57, 58, 59, ...
Body-Centered Cubic	2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 58, ...
Face-Centered Cubic	3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32, 35, 36, 40, 43, 44, 48, 51, 52, 56, 59, ...
Diamond Cubic	3, 8, 11, 16, 19, 24, 27, 32, 35, 40, 43, 48, 51, 56, 59, ...

We then obtain a relation between $Sin^2\theta$ and Miller indices $(h_i k_i l_i)$ by inserting equation (8) into (4); thus, we have:

$$Sin^2\theta_i = (h_i^2+k_i^2)P + l_i^2 Q, \quad i=1,2,\ldots,K. \tag{9}$$

where i=number of the reflection with Miller indices $(h_i k_i l_i)$ and $P=\lambda^2/4a^2$ and $Q=\lambda^2/4c^2$. The summation, $h_i^2+k_i^2$, is best carried out in a systematic manner. The quadratic forms of Miller indices for this system are listed in Table 3.

However, the permissible integers of the summation of $h_i^2+k_i^2+l_i^2$ for two common Bravais lattice types, simple and body-centered, of the tetragonal crystals are different. The characteristic sequences of these two Bravais lattice types are shown in Table 4.

The Hexagonal System

The plane-spacing equation for hexagonal system can be written as:

$$\frac{1}{d_{hkl}^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}, \tag{10}$$

where a and c are the two lattice parameters of the unit cell. We then obtain a relation between $Sin^2\theta_i$ and Miller indices $(h_i k_i l_i)$ by inserting equation (10) into (4); thus,

$$Sin^2\theta_i = (h_i^2+h_i k_i+k_i^2)\ P + l_i^2\ Q, \quad i=1,2,\ldots,K, \tag{11}$$

TABLE 3

Quadratic Forms of Miller Indices for Tetragonal Crystals

h^2+k^2	1, 2, 4, 5, 8, 9, 10, 13, 16, 17, 18, 20, 25, 26, 29, 32, 34, 36, 37, 40, 41, 45, 49, 50, 52, 53, 58, ...
l^2	1, 4, 9, 16, 25, 36, 49, ...

TABLE 4

Characteristic Sequences of the Two Common Bravais Lattices of the Tetragonal System

Simple Tetragonal	1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16, 17, 18, 19, 20, 21, 22, 24, 25, 26, 27, 29, 30, 32, 33, 34, 35, 36, 37, 38, 40, 41, 42, 43, 44, 45, 46, 48, 49, 50, 51, 52, 53, 54, 56, 57, 58, 59, ...
Body-Centered Tetragonal	2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 58, ...

where i=number of the reflection with Miller indices $(h_i k_i l_i)$ and $P=\lambda^2/3a^2$ and $Q=\lambda^2/4c^2$. The summation, $h_i^2+h_i k_i+k_i^2$, is most conveniently carried out by arranging the terms in tabular form similar to that of the tetragonal system. The quadratic forms of Miller indices for this system are listed in Table 5.

TABLE 5

Quadratic Forms of Miller Indices for Hexagonal Crystals

h^2+hk+k^2	1, 3, 4, 7, 9, 12, 13, 16, 19, 21, 25, 27, 28, 31, 36, 37, 39, 43, 48, 49, 52, 57, ...
l^2	1, 4, 9, 16, 25, 36, 49, ...

The Orthorhombic System

The plane-spacing equation for orthorhombic system can be written as:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad (12)$$

where a, b, and c are the three lattice parameters of the unit cell. We may obtain a relation between $\mathrm{Sin}^2\theta_i$ and Miller indices $(h_i k_i l_i)$ by inserting equation (12) into (4); thus, we have:

$$\mathrm{Sin}^2\theta_i = h_i^2 P + k_i^2 Q + l_i^2 S, \quad i=1,2,\ldots,K, \tag{13}$$

where i=number of the reflection with Miller indices $(h_i k_i l_i)$ and $P=\lambda^2/4a^2$, $Q=\lambda^2/4b^2$, and $S=\lambda^2/4c^2$.

The Monoclinic System

The plane-spacing equation for the monoclinic system can be written as:

$$\frac{1}{d_{hkl}^2} = \frac{1}{\mathrm{Sin}^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\mathrm{Sin}^2\beta}{b^2} + \frac{l^2}{c^2} + \frac{2hl\mathrm{Cos}\beta}{ac}\right), \tag{14}$$

where a, b, c, and β are the four lattice parameters of the unit cell. We may then obtain a relation between $\mathrm{Sin}^2\theta$ and Miller indices $(h_i k_i l_i)$ by inserting equation (14) into (4); thus, we have:

$$\mathrm{Sin}^2\theta_i = h_i^2 P + k_i^2 Q + l_i^2 S - h_i l_i V, \quad i=1,2,\ldots,K, \tag{15}$$

where i=number of the reflection with Miller indices $(h_i k_i l_i)$ and $P=\lambda^2/4a^2\mathrm{Sin}^2\beta$, $Q=\lambda^2/4b^2$, $S=\lambda^2/4c^2\mathrm{Sin}^2\beta$, and $V=\lambda^2\mathrm{Csc}\beta\mathrm{Cot}\beta/2ac$.

The Triclinic System

The plane-spacing equation for the triclinic system can be written as:

$$\frac{1}{d_{hkl}^2} = \frac{1}{\bar{V}^2}(S_{11}h^2+S_{22}k^2+S_{33}l^2+2S_{12}hk+2S_{23}kl+2S_{13}hl), \tag{16}$$

where the volume of the unit cell,

$$\bar{V} = abc\,(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma)^{\frac{1}{2}}$$

$$S_{11} = b^2c^2\sin^2\alpha$$

$$S_{22} = a^2c^2\sin^2\beta$$

$$S_{33} = a^2b^2\sin^2\gamma$$

$$S_{12} = abc^2(\cos\alpha\cos\beta-\cos\gamma)$$

$$S_{23} = a^2bc(\cos\beta\cos\gamma-\cos\alpha)$$

$$S_{13} = ab^2c(\cos\gamma\cos\alpha-\cos\beta)$$

where a, b, c, α, β, and γ are the six lattice parameters of the unit cell. We may then obtain a relation between $\sin^2\theta_i$ and Miller indices $(h_ik_il_i)$ by inserting equation (16) into (4); thus, we have

$$\sin^2\theta_i=h_i^2P+k_i^2Q+l_i^2S+h_ik_iU+h_il_iV+k_il_iW,\ i=1,2,\ldots,K, \qquad (17)$$

where i=number of the reflection with Miller indices $(h_ik_il_i)$ and $P=S_{11}\lambda^2/4\bar{V}^2$, $Q=S_{22}\lambda^2/4\bar{V}^2$, $S=S_{33}\lambda^2/4\bar{V}^2$, $U=S_{12}\lambda^2/2\bar{V}^2$, $V=S_{13}\lambda^2/2\bar{V}^2$, and $W=S_{23}\lambda^2/2\bar{V}^2$.

CHAPTER III

DIFFERENCE ANALYSIS

Introduction

Lipson's difference method[26] was previously used only for selecting the possible parameters of the more highly symmetrical Bravais lattice types, such as cubic, tetragonal, hexagonal, and orthorhombic systems. As a matter of fact, it sometimes fails to cover all the possibilities. Some additional criteria are described in this chapter to complete the whole list of possible parameters. The selection procedures are also summarized.

Due to the characteristic of the differences of the $Sin^2\theta$ values for various systems, the difference analysis can be also used as a means of determining the possible Bravais lattice type to which the unknown powder pattern belongs. By doing so, we can save quite a lot of effort for indexing a powder pattern as compared to the classical method.

A computer program, DA, listed in Table 6, is so written that the differences of the observed $Sin^2\theta$ values are listed in ascending order

TABLE 6

Computer Program (DA) for the

Difference Analysis of the Diffraction Data

```
C COMPUTER PROGRAM FOR DIFFERENCE ANALYSIS OF THE DIFFRACTION DATA
      DIMENSION T(70),TDIFF(2000),TD(2000)
      IN=5
      IM=6
      READ (IN,1) M
    1 FORMAT (I3)
      DO 300 I=1,M
      READ (IN,1) K
      READ (IN,2) (T(J),J=1,K)
    2 FORMAT (10F7.0)
      WRITE (IM,40)
   40 FORMAT (1H1,' DIFFRACTION',4X,'SIN(SQUARE)',7X,'DIFFRACTION',4X,'S
     1IN(SQUARE)')
      WRITE (IM,50)
   50 FORMAT (5X,'LINE',10X,'(OBSV.)',12X,'LINE',10X,'(OBSV.)')
      WRITE (IM,60)
   60 FORMAT (2X,11('-'),4X,11('-'),7X,11('-'),4X,11('-'))
      KK=K/2
      DO 72 N=1,KK
      IF (K/2*2-K) 64,62,64
   62 KKK=N+KK
      GO TO 68
   64 KKK=N+KK+1
   68 WRITE (IM,70) N,T(N),KKK,T(KKK)
   70 FORMAT (5X,I3,10X,F8.5,12X,I3,10X,F8.5)
   72 CONTINUE
      IF (K/2*2-K) 74,100,74
   74 NL=(K+1)/2
      WRITE (IM,70) NL,T(NL)
  100 WRITE (IM,102)
  102 FORMAT (1H1,11X,'DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DAT
     1A')
      KT=0
      N=0
      IF (K-15) 110,110,112
  110 KO=K
      GO TO 118
  112 KO=15
  118 DO 120 LO=2,KO
      KT=KT+1
      TD(KT)=T(LO)-T(1)
  120 CONTINUE
      TDMAX=TD(KT)
      K1=K-1
```

TABLE 6 (CONTINUED)

```
      DO 130 L1=2,K1
      L2=L1+1
      DO 125 L3=L2,K
      TDF=T(L3)-T(L1)
      IF (TDF-TDMAX) 124,130,130
  124 N=N+1
      TDIFF(N)=TDF
  125 CONTINUE
  130 CONTINUE
      LK=0
      DO 200 J1=1,N
      LK=LK+1
      DO 150 J2=1,KT
      IF (TD(J2)-TDIFF(LK)) 150,140,140
  140 KT2=KT+J2+1
      DO 145 J3=J2,KT
      KT3=KT2-J3
      TD(KT3)=TD(KT3-1)
  145 CONTINUE
      TD(J2)=TDIFF(LK)
      GO TO 160
  150 CONTINUE
  160 KT=KT+1
  200 CONTINUE
      NO=N+KO-1
      IF (NO-712) 230,230,220
  220 NO=712
  230 WRITE (IM,250) (TD(J),J=1,NO)
  250 FORMAT (8F9.5)
  300 CONTINUE
      STOP
      END
```

Difference Analysis

The most probable differences occurring in Lipson's difference method for indexing powder photographs was described

by Zsoldos.[47] In the following, the permissible integers determined by various Bravais lattice types are summarized.

The Cubic System

According to equation (7), the difference between any two $Sin^2\theta$ values can be written in the general form:

$$Sin^2\theta_{hkl} - Sin^2\theta_{h'k'l'} = (h^2+k^2+l^2)P - (h'^2+k'^2+l'^2)P$$

$$= (s - s')P = N\,P, \qquad (18)$$

where N=1,2,3,4,5,6,7,8,9,10,... for simple cubic Bravais type; N=2,4,6,8,10,12,14,16,... for body-centered cubic Bravais type; and N=1,3,4,5,7,8,9,11,... for face-centered cubic Bravais type.

The Tetragonal System

According to equation (9), the difference between any two $Sin^2\theta$ values can be written as:

$$Sin^2\theta_{hkl} - Sin^2\theta_{h'k'l} = \left[(h^2+k^2) - (h'^2+k'^2)\right]P = nP, \qquad (19)$$

$$Sin^2\theta_{hkl} - Sin^2\theta_{h'k'l'} = (l^2 - l'^2)Q = mQ, \qquad (20)$$

where n=1,2,3,4,5,6,7,8,9,10,... for simple tetragonal Bravais type; n=2,4,6,8,10,12,14,16,... for body-centered tetragonal Bravais type; and m=1,3,4,5,7,8,9,11,12,13,... for both Bravais lattice types.

The Hexagonal System

According to equation (11), the difference between any two $Sin^2\theta$ values can be written as:

$$Sin^2\theta_{hkl}-Sin^2\theta_{h'k'l}=\left[(h^2+hk+k^2)-(h'^2+h'k'+k'^2)\right]P=nP, \quad (21)$$

$$Sin^2\theta_{hkl}-Sin^2\theta_{hkl'}=(l^2-l'^2)Q=mQ, \quad (22)$$

where n=1,2,3,4,5,6,7,8,9,10,... and m=1,3,4,5,7,8,9,11,12,13,...

The Orthorhombic System

According to equation (13), the difference between any two $Sin^2\theta$ values can be written as:

$$Sin^2\theta_{hkl}-Sin^2\theta_{h'kl}=(h^2-h'^2)P=mP, \quad (23)$$

$$Sin^2\theta_{hkl}-Sin^2\theta_{hk'l}=(k^2-k'^2)Q=mQ, \quad (24)$$

$$Sin^2\theta_{hkl}-Sin^2\theta_{hkl'}=(l^2-l'^2)S=mS, \quad (25)$$

where m=1,3,4,5,7,8,9,11,12,13,...

The Monoclinic System

According to equation (15), the difference between any two $Sin^2\theta$ values can be written as:

$$Sin^2\theta_{hkl}-Sin^2\theta_{hk'l}=(k^2-k'^2)Q=mQ, \quad (26)$$

where m=1,3,4,5,7,8,9,11,12,13,...

The Triclinic System

According to equation (17), the difference analysis provides no information except that the powder pattern could be triclinic.

Selection of Possible Parameters

From the output of the computer program DA, several recurrent value groups may be selected. Combined the information from equations (18) to (26) and the ratios between the selected recurrent value groups, the possible Bravais lattice type and the possible parameters can be determined. The procedures for various lattice types together with some criteria are described as follows.

The Cubic System

(1) Let P be the medium or average of the smallest recurrent value group. Suppose that there exists a $\sin^2\theta_i \simeq 7P$ (for some i); the parameter P is therefore not the one we are seeking.

(2) Suppose that some values appeared in the difference table which are less than P; the parameter we are seeking may be a fraction of P. Of course, we would try P/2 first, then P/3, then P/4, etc.

(3) Suppose that we have found some recurrent value groups represented by the values P, 2P, 3P, ... and no integral ratio between others; then the unknown powder pattern belongs to

the isometric structure, and P is the possible parameter we are seeking.

The Tetragonal and Hexagonal Systems

(1) From the selected recurrent value groups, if two categories are found, the first consists of those groups having integral ratios of P, 2P, 3P, ..., where P is the value representing the smallest selected recurrent value group; the second consists of those groups having integral ratios Q, 3Q, 4Q, 5Q, ..., where Q is the value representing the smallest recurrent value group in this category. The unknown powder pattern could have tetragonal or hexagonal symmetry. The values P and Q are the possible parameters.

(2) If the parameter P is ascertainable, we may assume that the first or second observed $Sin^2\theta$ value, which is not the integral multiple of P, has low Miller indices such as (001), (002), (101), etc. We may therefore find a set of possible Q values. Comparing with step (1), if more information is available, a possible Q is approved.

(3) If the parameter Q is ascertainable, we may assume that the first or second observed $Sin^2\theta$, which is not the integral multiple of Q, has low Miller indices such as (100), (200), (101), etc. Thus, we may find a set of possible P values. Comparing with step (1), if more information is available, a possible para-

meter P is approved. However, if the difference table could not supply further information of P or Q, the whole set of possible parameters P or Q can be used as the input of the computer program for indexing the unknown powder patterns.

(4) Finally, if the difference table could not provide any information for selecting both possible parameters P and Q, an inspection method can be done by finding two observed $Sin^2\theta$ values having a ratio of two or three (two is for tetragonal; three is for hexagonal) between each other to find the possible parameter P. Then, step (2) is followed.

The Orthorhombic System

(1) From the selected recurrent value group, the only group chosen as possible parameters are those with a 3 : 1 or 4 : 1 ratio to an existing group.

(2) Besides the parameters chosen by step (1), some more possible parameters are chosen from the observed $Sin^2\theta$ values. These low $Sin^2\theta$ values are selected on the basis of a 4 : 1 ratio to an existing $Sin^2\theta$ value, if its group has not been already chosen by step (1).

(3) However, the trial-and-error method of indexing the unknown orthorhombic powder patterns is too time consuming when the possible parameters are numerous. The number of trials for indexing is C_3^n, where n is the total number of possible parameters

chosen from steps (1) and (2), and 3 is due to the parameter P, Q, and S being symmetrical. Therefore, an auxiliary computer program, AOR, listed in Table 7, is designed for the purpose of reducing the possibilities of triplets (P,Q,S) and shortening the computer running time for indexing the patterns.

The logic is as follows. (a) The inputs of the computer program AOR are a set of low angle observed $Sin^2\theta$ values (one usually selects the first four or five $Sin^2\theta$ values from the diffraction data) and a set of possible parameters chosen from steps (1) and (2). Both these sets are arranged in an ascending order. (b) Assume that the low Miller indices, such as (001) up to (222), are assigned to the low angle $Sin^2\theta$ values. (c) Then, the logical loop is devised to select the third possible parameter if the other two are given. From the output of the computer program AOR, a set of triplets (P,Q,S) are chosen as the possible triplets to trial indexing the diffraction data by the main computer program.

The Monoclinic System

(1) From the difference table, the parameter Q can be determined by choosing the lowest recurrent value group with a 1 : 3, 1 : 4, 1 : 3 : 4, etc. ratio to at least one other recurrent value group.

(2) The other three parameters, P, S, and V, cannot be

TABLE 7

Auxiliary Computer Program (AOR) for the

Indexing of Unknown Orthorhombic Crystal Powder Patterns

```
C AUXILIARY COMPUTER PROGRAM FOR THE INDEXING OF ORTHORHOMBIC CRYSTAL
C POWDER PATTERNS
      DIMENSION TT(20),PQ(50),S(300)
      IN=5
      IM=6
      READ (IN,2) M
    2 FORMAT (2I3)
      DO 50 I=1,M
      WRITE (IM,4) I
    4 FORMAT (1H1,' THIS IS THE NUMBER',I3,'  SET OF ORTHORHOMBIC CRYSTA
     1L POWDER PATTERN')
      READ (IN,2) K,L
      READ (IN,6) (TT(J),J=1,K)
      READ (IN,6) (PQ(J),J=1,L)
    6 FORMAT (10F7.0)
      L1=L-2
      DO 50 I1=1,L1
      P=PQ(I1)
      L2=I1+1
      L3=L-1
      DO 50 I2=L2,L3
      L4=I2+1
      Q=PQ(I2)
      N=0
      NN=0
      DO 41 I3=1,K
      DO 41 N1=1,3
      AN1=N1-1
      DO 41 N2=1,3
      AN2=N2-1
      DIFF=TT(I3)-AN1*AN1*P-AN2*AN2*Q
      IF (DIFF) 41,41,10
   10 DO 40 N3=1,2
      SSS=DIFF/(N3*N3)
      DO 40 N4=L4,L
      IF (ABS(SSS-PQ(N4))-0.0005) 20,40,40
   20 N=N+1
      S(N)=SSS
   40 CONTINUE
   41 CONTINUE
      IF (N-1) 50,50,42
   42 WRITE (IM,44) P,Q
   44 FORMAT (/,1X,' IF P=',F8.5,5X,'Q=',F8.5)
      WRITE (IM,45)
```

TABLE 7 (CONTINUED)

```
45 FORMAT (1X,' POSSIBLE S ARE  ')
   N5=N-1
   DO 47 N6=1,N5
   N7=N6+1
   DO 47 N8=N7,N
   IF (S(N6)-S(N8)) 47,47,46
46 SLARG=S(N6)
   S(N6)=S(N8)
   S(N8)=SLARG
47 CONTINUE
   WRITE (IM,48) (S(J),J=1,N)
48 FORMAT (8F9.5)
50 CONTINUE
   STOP
   END
```

found from the difference analysis. Hence, an auxiliary computer program, AMO, listed in Table 8, is designed for the purpose of not only obtaining possible parameter triplets (P,S,V) but also for reducing the possibilities for the trial-and-error method to shorten the computing time.

The logic here is as follows. (a) Assume that several possible parameters (but at least one), P (or S), are found from the observed $Sin^2\theta$ values by inspection. The parameters of P (or S) are possible if there exists two or more observed $Sin^2\theta$ values such that the ratios among them are 1 : 4 : 9, 1 : 4, 4 : 9, etc. This is because such ratios can happen for the observed $Sin^2\theta$ values corresponding to the (100), (010), (001), (101), (110),

TABLE 8

Auxiliary Computer Program (AMO) for the

Indexing of Unknown Monoclinic Crystal Powder Patterns

```
C AUXILIARY COMPUTER PROGRAM FOR THE INDEXING OF MONOCLINIC CRYSTAL
C POWDER PATTERNS
      DIMENSION AH(3),AL(7),TT(10),PS(10),P(700),S(700),V(700),AP(700),S
     1S(700),VV(700),MODE(100),NO(100)
      IN=5
      IM=6
      READ (IN,1) M
    1 FORMAT (2I3)
      DO 2 J0=1,3
      AH(J0)=J0-1
    2 CONTINUE
      DO 3 J1=1,7
      AL(J1)=J1-4
    3 CONTINUE
      DO 50 I=1,M
      WRITE (IM,4) I
    4 FORMAT (1H1,14X,'THIS IS THE NUMBER',I3,'  SET OF')
      WRITE (IM,5)
    5 FORMAT (13X,'MONOCLINIC CRYSTAL POWDER PATTERN')
      READ (IN,1) K,L
      READ (IN,6) (TT(J),J=1,K)
      READ (IN,6) (PS(J),J=1,L)
    6 FORMAT (10F7.0)
      DO 50 L1=1,L
      N=0
      PP=PS(L1)
      WRITE (IM,8) PP
    8 FORMAT (/,18X,'POSSIBLE P OR S=',F8.5)
      DO 25 L2=1,2
      K1=L2+1
      DO 25 L3=K1,K
      DO 25 J2=1,2
      C1=AH(J2)*AH(J2)
      TP1=TT(L2)-C1*PP
      DO 25 J3=1,3
      C2=AH(J3)*AH(J3)
      TP2=TT(L3)-C2*PP
      DO 25 N2=2,6
      C3=AL(N2)*AL(N2)
      TS1=TT(L2)-C3*PP
      DO 25 N3=1,7
      C4=AL(N3)*AL(N3)
      TS2=TT(L3)-C4*PP
      C5=-AH(J2)*AL(N2)
      C6=-AH(J3)*AL(N3)
```

TABLE 8 (CONTINUED)

```
      DEL1=C3*C6-C5*C4
      IF (DEL1) 11,15,11
   11 DELS=TP1*C6-TP2*C5
      S1=DELS/DEL1
      IF (S1) 15,15,12
   12 DELV1=TP2*C3-TP1*C4
      V1=ABS(DELV1/DEL1)
      VMAX1=0.8*SQRT(S1*PP)
      IF (V1-VMAX1) 14,14,15
   14 IF (N) 146,146,147
  146 N=N+1
      MODE(N)=1
      P(N)=PP
      S(N)=S1
      V(N)=V1
      GO TO 15
  147 DO 152 N4=1,N
      IF (ABS(V1-V(N4))-0.0002) 148,148,152
  148 IF (ABS(S1-S(N4))-0.0002) 149,149,152
  149 IF (ABS(PP-P(N4))-0.0002) 150,150,152
  150 MODE(N4)=MODE(N4)+1
      GO TO 15
  152 CONTINUE
      GO TO 146
   15 DEL2=C1*C6-C2*C5
      IF (DEL2) 16,25,16
   16 DELP=TS1*C6-TS2*C5
      P2=DELP/DEL2
      IF (P2) 25,25,17
   17 DELV2=TS2*C1-TS1*C2
      V2=ABS(DELV2/DEL2)
      VMAX2=0.8*SQRT(P2*PP)
      IF (V2-VMAX2) 20,20,25
   20 IF (N) 21,21,22
   21 N=N+1
      MODE(N)=1
      P(N)=P2
      S(N)=PP
      V(N)=V2
      GO TO 25
   22 DO 24 N5=1,N
      IF (ABS(V2-V(N5))-0.0002) 23,23,24
   23 IF (ABS(PP-S(N5))-0.0002) 235,235,24
  235 IF (ABS(P2-P(N5))-0.0002) 236,236,24
  236 MODE(N5)=MODE(N5)+1
      GO TO 25
```

TABLE 8 (CONTINUED)

```
 24 CONTINUE
    GO TO 21
 25 CONTINUE
    NN=0
    DO 30 N6=1,N
    IF (MODE(N6)-2) 30,26,26
 26 NN=NN+1
    AP(NN)=P(N6)
    SS(NN)=S(N6)
    VV(NN)=V(N6)
    NO(NN)=MODE(N6)
 30 CONTINUE
    N7=NN-1
    DO 40 N8=1,N7
    N9=N8+1
    DO 40 N10=N9,NN
    IF (VV(N8)-VV(N10)) 40,40,32
 32 VLARG=VV(N8)
    VV(N8)=VV(N10)
    VV(N10)=VLARG
    BP=AP(N8)
    AP(N8)=AP(N10)
    AP(N10)=BP
    BS=SS(N8)
    SS(N8)=SS(N10)
    SS(N10)=BS
    MNO=NO(N8)
    NO(N8)=NO(N10)
    NO(N10)=MNO
 40 CONTINUE
    DO 44 N11=1,NN
 44 WRITE (IM,46) AP(N11),SS(N11),VV(N11),NO(N11)
 46 FORMAT (10X,'P=',F8.5,2X,'S=',F8.5,2X,'V=',F8.5,2X,'(',I2,')')
 50 CONTINUE
    STOP
    END
```

etc. planes. Here we assume that the values of Q and also the other structures, such as isometric, tetragonal, hexagonal, and orthorhombic, have previously considered. (b) The inputs of the computer program AMO are a set of possible parameters of P (or S) and a set of values in which are either the lower observed $Sin^2\theta$ values or the values of $Sin^2\theta - Q$ (if $Sin^2\theta > Q$). Both sets are arranged in ascending order. (c) The logical loop is devised to choose the suitable possible triplets (P,S,V) for a certain Q. (d) The criterion used in the loop for selecting the possible values of S (or P) and V for all possible values of P (or S) is described as follows.

From equation (15), we have the following relations:

$$P=\frac{\lambda^2}{4a^2Sin^2\beta},\quad S=\frac{\lambda^2}{4c^2Sin^2\beta},\quad \text{and}\quad V=\frac{\lambda^2 Csc\beta Cot\beta}{2ac}. \tag{27}$$

Another form of V is

$$V = \frac{\lambda^2 Cos\beta}{2acSin^2\beta}. \tag{28}$$

From equations (27) and (28), we have

$$PS=\frac{\lambda^4}{16a^2c^2Sin^4\beta} \quad \text{and} \quad V^2=\frac{\lambda^4 Cos^2\beta}{4a^2c^2Sin^4\beta}. \tag{29}$$

Thus, $$V^2= 4PS\ Cos^2\beta$$

and $$|V| = 2\ (PS)^{\frac{1}{2}}|\cos\beta| \qquad (30)$$

Consider

$$0 \leqslant |\cos\beta| \leqslant 0.4 \text{ if } 66^{\circ}25' \leqslant \beta \leqslant 113^{\circ}35' \text{ in general.}$$

The maximum values of V can be obtained as

$$V_{max} = 0.8\ (PS)^{\frac{1}{2}} \qquad (31)$$

(e) From the output of the computer program AMO, one may easily select the recurrent values of triplets (P,S,V) from the V column since the V column is arranged in ascending order. This set of triplets (P,S,V), together with the Q value, are then used for trial indexing the diffraction data by the main computer program.

The Triclinic System

(1) The difference analysis cannot aid in finding any possible parameters because there are hardly any recurrent value groups in the difference table. The only information provided by the difference table is that the powder pattern could possibly belong to the triclinic lattice type.

(2) An auxiliary computer program, ATR, listed in Table 9, is then designed for the purpose of not only finding the possible parameter sets (P,Q,S,U,V,W) but reducing the possibilities for the trial-and-error method so as to shorten the computing time.

The logic is as follows: (a) Assume that a possible

TABLE 9

Auxiliary Computer Program (ATR) for the

Indexing of Unknown Triclinic Crystal Powder Patterns

```
C AUXILIARY COMPUTER PROGRAM FOR THE INDEXING OF UNKNOWN TRICLINIC
C CRYSTAL POWDER PATTERNS
      DIMENSION AH(3),TT(15),AQS(300),AUVW(300),NN(300),AK(4),PPQ(10),PQ
     1S(10),BQS(300),BUVW(300),NO(300)
      IN=5
      IM=6
      AH(1)=0.0
      AH(2)=1.0
      AH(3)=2.0
      AK(1)=1.0
      AK(2)=-1.0
      AK(3)=2.0
      AK(4)=-2.0
      READ (IN,1) M
    1 FORMAT (3I3)
      DO 40 I=1,M
      WRITE (IM,2) I
    2 FORMAT (1H1,5X,'THIS IS THE NUMBER',I3,'  SET OF TRICLINIC CRYSTAL
     1 POWDER PATTERN')
      READ (IN,1) K,L1,L2
      READ (IN,4) (PPQ(J),J=1,L1)
      READ (IN,4) (PQS(J),J=1,L2)
      READ (IN,4) (TT(J),J=1,K)
    4 FORMAT (10F7.0)
      DO 40 I1=1,L1
      P=PPQ(I1)
      DO 40 I2=1,L2
      Q=PQS(I2)
      N1=0
      DO 30 I3=1,K
      T=TT(I3)
      DO 30 I4=1,2
      C1=AH(I4)*AH(I4)
      C2=AK(I4)*AK(I4)
      C3=AH(I4)*AK(I4)
      DO 30 I5=2,3
      C4=AH(I5)*AH(I5)
      DO 30 I6=1,4
      C5=AK(I6)*AK(I6)
      C6=AH(I5)*AK(I6)
      DEL=C2*C6-C3*C5
      IF (DEL) 6,30,6
    6 DELQS=C6*Q-C3*T+P*(C3*C4-C1*C6)
      QS=DELQS/DEL
      IF (QS) 30,30,8
    8 DELUV=C2*T-C5*Q+P*(C1*C5-C2*C4)
      UVW=ABS(DELUV/DEL)
      IF (UVW) 10,30,10
```

TABLE 9 (CONTINUED)

```
 10 UMX=1.36*SQRT(P*QS)
    IF (UMX-UVW) 30,30,12
 12 IF (N1) 14,14,16
 14 N1=N1+1
    NN(N1)=1
    AQS(N1)=QS
    AUVW(N1)=UVW
    GO TO 30
 16 DO 24 I7=1,N1
    IF (ABS(QS-AQS(I7))-0.0002) 17,17,24
 17 IF (ABS(UVW-AUVW(I7))-0.0002) 18,18,24
 18 NN(I7)=NN(I7)+1
    GO TO 30
 24 CONTINUE
    GO TO 14
 30 CONTINUE
    N2=0
    DO 32 I8=1,N1
    IF (NN(I8)-2) 32,31,31
 31 N2=N2+1
    NO(N2)=NN(I8)
    BQS(N2)=AQS(I8)
    BUVW(N2)=AUVW(I8)
 32 CONTINUE
    N3=N2-1
    DO 36 I9=1,N3
    I10=I9+1
    DO 36 I11=I10,N2
    IF (BUVW(I9)-BUVW(I11)) 36,36,34
 34 ULARG=BUVW(I9)
    BQ=BQS(I9)
    BNO=NO(I9)
    BQS(I9)=BQS(I11)
    BUVW(I9)=BUVW(I11)
    NO(I9)=NO(I11)
    BQS(I11)=BQ
    BUVW(I11)=ULARG
    NO(I11)=BNO
 36 CONTINUE
    WRITE (IM,37) P
 37 FORMAT (1H1,4X,'P OR Q=',F8.5,/)
    WRITE (IM,38)
 38 FORMAT (6X,'QS',10X,'UVW',6X,'NO.',4X,'H=-1',6X,'H=1',7X,'H=-2',6X
   1,'H=2')
    WRITE (IM,385)
385 FORMAT (2X,68('-'))
    DO 40 I12=1,N2
    FT1=P+BQS(I12)
    SIN1=FT1-BUVW(I12)
```

TABLE 9 (CONTINUED)

```
      SIN2=FT1+BUVW(I12)
      FT2=4.0*P+BQS(I12)
      SIN3=FT2-2.0*BUVW(I12)
      SIN4=FT2+2.0*BUVW(I12)
      WRITE (IM,39) BQS(I12),BUVW(I12),NO(I12),SIN1,SIN2,SIN3,SIN4
   39 FORMAT (2X,F8.5,5X,F8.5,4X,I2,2X,F8.5,2X,F8.5,3X,F8.5,2X,F8.5)
   40 CONTINUE
      STOP
      END
```

parameter P is found from the observed $Sin^2\theta$ values by inspection. The parameter P is possible if there exists two or more observed $Sin^2\theta$ values such that the ratios among them are 1 : 4 : 9, 1 : 4, 4 : 9, etc. (b) The smallest $Sin^2\theta$ value which is not an integral multiple of P is then chosen as the $Sin^2\theta$ value corresponding to either (010) or (110) plane. A logical loop is devised to find the possible parameters Q and U. (c) The criterion used in the loop for selecting the possible values of Q and U for the possible parameter P is described as follows.

From equation (17), we have:

$$P = \frac{S_{11}\lambda^2}{4\bar{V}^2},\quad Q = \frac{S_{22}\lambda^2}{4\bar{V}^2},\quad \text{and } U = \frac{S_{12}\lambda^2}{2\bar{V}^2}. \tag{32}$$

where $S_{11}=b^2c^2Sin^2\alpha$, $S_{22}=a^2c^2Sin^2\beta$,

and $$S_{12}=abc^2(\cos\alpha\cos\beta-\cos\gamma),$$

From equation (32), we have:

$$PQ = \lambda^4 S_{11}S_{22}/16\bar{V}^4 = \lambda^4 a^2b^2c^4\sin^2\alpha\sin^2\beta/16\bar{V}^2$$

$$= \lambda^4 S_{12}\sin^2\alpha\sin^2\beta/16\bar{V}^4(\cos\alpha\cos\beta-\cos\gamma)$$

$$= \frac{U^2}{4}\left(\frac{\sin\alpha\sin\beta}{\cos\alpha\cos\beta-\cos\gamma}\right)^2.$$

But then,

$$U^2 = 4PQ\left(\frac{\cos\alpha\cos\beta-\cos\gamma}{\sin\alpha\sin\beta}\right)^2.$$

Therefore,

$$|U| = 2(PQ)^{\frac{1}{2}}\left|\frac{\cos\alpha\cos\beta-\cos\gamma}{\sin\alpha\sin\beta}\right| . \qquad (33)$$

Consider

$$66^{\circ}25' \leqslant \alpha, \beta, \gamma \leqslant 113^{\circ}35' \text{ in general;}$$

that is,

$$0 \leqslant |\cos\alpha, \cos\beta, \cos\gamma| \leqslant 0.4, \qquad (34)$$

and

$$|\sin\alpha, \sin\beta| \leqslant 0.916. \qquad (35)$$

Substituting inequalities (34) and (35) into equation (33), we obtain

$$|U| \leqslant 2(PQ)^{\frac{1}{2}}\left|\frac{0.56}{0.839}\right| \leqslant 1.36(PQ)^{\frac{1}{2}}. \qquad (36)$$

Inequality (36) is then used to reduce the number of possible parameter triplets (P,Q,U). Similar relations hold for parameters P, S, and V and for Q, S, and W. (d) From the output of the computer program ATR, the possible parameter triplets (P,Q,U) can be selected by considering the more highly recurrent values which most often match the observed $Sin^2\theta$ values from the H=-1, H=1, H=-2, and H=2 columns, especially the H=-1 column because H=-1 means that the calculated value of $Sin^2\theta$ corresponds to the $(\bar{1}10)$ plane with respect to possible parameters P and Q. (H=1 corresponds to the (110) plane; H=-2 corresponds to the $(\bar{2}10)$ plane; and H=2 corresponds to the (210) plane). (e) After obtaining the possible values of P and Q by inspection, the same procedures are used again to find the other two sets of possible parameter triplets (P,S,V) and (Q,S,W). That is, the computer program ATR is used twice to obtain three sets of possible parameter triplets (P,Q,U), (P,S,V), and (Q,S,W). Comparing the values of these three triplets, a set of possible parameters (P,Q,S,U,V,W) may be determined. This set of possible parameters is then used for trial indexing the diffraction data by the main computer program.

CHAPTER IV

INDEXING SEARCH TECHNIQUE

Introduction

Consider the general relationship between the observed $Sin^2\theta$ and the parameters P, Q, S, U, V, and W that were defined in Chapter II:

$$Sin^2\theta_{hkl} = h^2P + k^2Q + l^2S + hkU + hlV + klW, \qquad (37)$$

where h, k, and l are integers.

For various lattice structures, the criteria may be described as follows:

(1) The cubic system: $P=Q=S\neq 0$, $U=V=W=0$, $h,k,l\geq 0$.

(2) The tetragonal system: $P=Q\neq S\neq 0$, $U=V=W=0$, $h,k,l\geq 0$.

(3) The hexagonal system: $P=Q=U\neq S\neq 0$, $V=W=0$, $h,k,l\geq 0$.

(4) The orthorhombic system: $P\neq Q\neq S\neq 0$, $U=V=W=0$, $h,k,l\geq 0$.

(5) The monoclinic system: $P\neq Q\neq S\neq V\neq 0$, $U=W=0$, $h,k\geq 0$, and l can be any integer.

(6) The triclinic system: $P\neq Q\neq S\neq U\neq V\neq W\neq 0$, $k\geq 0$ and h,l can be any integer.

For each observed $Sin^2\theta_i$, i=1,2,...,K, there exists at

least one Miller index $(h_i k_i l_i)$ such that:

$$\mathrm{Sin}^2\theta_i+\Delta \geq h_i^2P+k_i^2Q+l_i^2S+h_ik_iU+h_il_iV+k_il_iW \geq \mathrm{Sin}^2\theta_i-\Delta, \qquad (38)$$

where Δ is a small fraction of $\mathrm{Sin}^2\theta_i$ and $(h_i k_i l_i)$ is the Miller index for the ith reflection.

In other words, the indexing search problem for the ith reflection can be written mathematically as follows:

minimize $|f(h_i,k_i,l_i)|$, where $f(h_i,k_i,l_i) = \mathrm{Sin}^2\theta_i - (h_i^2P+k_i^2Q+l_i^2S+h_ik_iU+h_il_iV+k_il_iW)$,

subject to $|f(h_i,k_i,l_i)| \leq \Delta$, h_i, k_i, and l_i are integers,

where i=1,2,...,K.

The branch-and-bound method is recommended to solve this indexing search problem because it is efficient and occupies minimal storage in the computer.

Branch-and-Bound Techniques

Branch-and-bound techniques have been developed by Eastman,[48] Little, et al,[49] and Shapiro.[50] Additionally, Hatfield and Pierce[51] used this technique to solve a job sequencing problem but were constrained from further use by the job deadline. The work of Little, et al, is a tour-building algorithm, while Eastman

and Shapiro's studies are examples of subtour elimination algorithms. A rather complete survey of branch-and-bound methods has been given by Lawler and Wood.[52]

Formal Definition of Branch-and-Bound Techniques

Let $G = \{g_j\}$ be the set of possible solutions to a problem P* in which we are interested. Let $|G|$, the cardinality of G, be a finite number. Let f be a function defined on the elements g_j of subset of G. We would like to find the solution $g^* \varepsilon G$ that minimizes the function f and is feasible; i.e., it satisfies a set of conditions {C}.

Suppose we have a property, depending on the nature of the problem, which allows us to make a partition $\mathcal{P}$ of a subset $G^{(n-1)}_{0m_1m_2\ldots m_{r_{n-1}}}$ of G.

$$\mathcal{P} = \{G^{(n)}_{0m_1m_2\ldots m_{r_n}1}, G^{(n)}_{0m_1m_2\ldots m_{r_n}2}, \ldots, G^{(n)}_{0m_1m_2\ldots m_{r_n}m}\}, \quad m>1, \tag{39}$$

where the subsets are defined recursively by

$$G^{(n)}_{0m_1m_2\ldots m_{r_n}m'} \neq \phi, \quad m'=1,2,\ldots,m. \tag{40}$$

$$\bigcup_{m'=1}^{m} G^{(n)}_{0m_1m_2\ldots m_{r_n}m'} = G^{(n-1)}_{0m_1m_2\ldots m_{r_{n-1}}}, \tag{41}$$

$$G^{(n)}_{0m_1m_2\ldots m_{r_n}m'} \cap G^{(n)}_{0m_1m_2\ldots m_{r_n}m''} = \phi, \tag{42}$$

where ϕ is the empty set, for $1 \leq m', m'' \leq m$, and $m' \nsim m''$, with the initial condition

$$G_0^{(1)} = G,$$

A graphic representation of this set of relationships is shown on Figure 2; there we build a tree usually called the search-tree. Each node bears the name of a subset $G^{(n)}_{0m_1m_2\ldots m_{r_n}m'}$ of solution of P*. It is convenient to call the superscript n the level. The set of n indices $0m_1m_2\ldots m_{r_n}m'$ indicates a path from the indices' node to the root of the tree.

On Figure 2 for example, node $G^{(4)}_{011r_4}$ is at level 4, and the path to the root of the tree is $G^{(4)}_{011r_4}$, $G^{(4)}_{011}$, $G^{(4)}_{01}$, $G^{(4)}_{0}$. Sometimes this information is very useful.

A closed node of the search-tree is a node that can no longer be partitioned. A pending node is one that is not closed.

For example, on Figure 2

$G_0^{(1)}$, $G_{01}^{(2)}$ are closed; $G^{(4)}_{011r_4}$ is pending.

Since each subset corresponding to each node is partitioned into two or more non-empty subsets, the cardinality of the subsets decreases monotonically along a branch of the search-tree; i.e.,

$$|G^{(4)}_{011r_4}| < |G^{(3)}_{011}| < |G^{(2)}_{01}| < |G^{(1)}_{0}| = |G|.$$

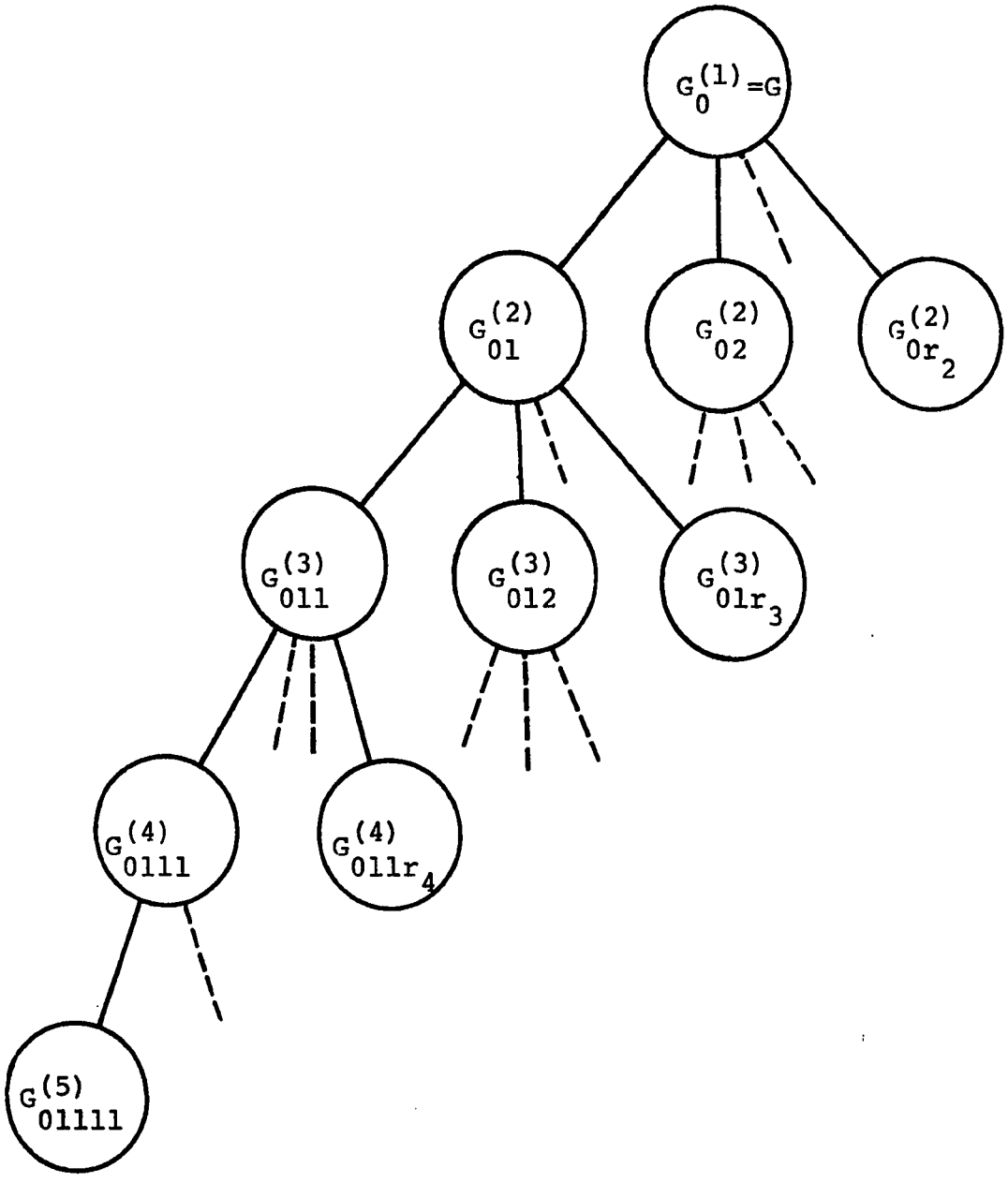

Figure 2 Search Tree for Problem P* (Here each partition contains r_n subsets).

Since |G| is finite, we will eventually reach a level at which one of the pending nodes, $G^{(n)}_{0m\ m\ \ldots m_{r_n} m}$, contains only one element of G; i.e., contains one solution to P*. This is a terminal node.

The goal of the method is to get a minimal solution, g*, by enumerating as few nodes as possible. To do so at each node we must be able to compute, over the subset assigned to the node, an upper and lower bound for the function f. Usually this is an easy task.

The strategy consists of branching from the pending node having the least lower bound. In other words, one uses the property attached to the nature of the problem to make a partition of the most promising pending node. For a terminal node the upper and lower bounds collapse to the value of f for the solution assigned to this node. The search is ended when a node contains a feasible solution, the value of which is less than or equal to the least lower bound of the pending vertices.

Indexing Search Techniques

Using the branch-and-bound method, the indexing search techniques for the six lattice structures are devised as follows.

The Cubic System

Let $T_i = \mathrm{Sin}^2\theta_i$ (observed) for our convenience. Let $\{P_j \mid j=1,2,\ldots,L\}$ be a set of possible parameters, where L is the

total number of possible parameters P. The index-searching technique for the ith reflection of some P_j is to find a unique solution s_i^* from a set of solutions $G_i = \{s_i=h_i^2+k_i^2+l_i^2 \mid h_i, k_i, l_i \geq 0\}$.

The problem can be written mathematically as:

$$\text{minimize} \quad |f(s_i)|, \text{ where } f(s_i)=T_i-s_iP_j, \tag{43}$$

$$\text{subject to} \quad |f(s_i)| \leq \Delta; \tag{44}$$

where s_i is a non-negative integer for each i, i=1,2,...,K and for some j, j=1,2,...,L, and we select $\Delta=0.1T_i$ as our initial least lower bound. This value is empirically designated for the tolerance of various experimental errors. The least lower bound, Δ, is made sufficiently small that there exists a subset of G_i in which only one assignment, s_i^*, satisfies condition (44).

Thus, we may find s_i^* by

$$s_i^* = \left[\frac{T_i}{P_j} + 0.5\right]; \; i=1,2,...,K \text{ and for some } j, \; j=1,2,...,L. \tag{45}$$

where the least lower bound $\Delta = T_i-s_i^*P_j$ and $\left[(T_i/P_j)+0.5\right]$ is the greatest integer which is less than $(T_i/P_j)+0.5$. If s_i^* can not be expressed as the summation of the squares of three non-negative integers, h_i, k_i, and l_i, then the possible P_j is unacceptable. The possible P_j (for some j) will also be automatically withdrawn if $s_i^* = s^*_{i-1}$ $(i\geq 2)$. This makes the search faster if the possible P_j is not the right parameter or the powder pattern does not belong

to cubic crystal structure.

After obtaining such s_i^* values for a certain parameter P_j, the Miller indices h_i, k_i, and l_i can be found by solving the quadratic Diophantine equation $h_i^2 + k_i^2 + l_i^2 = s_i^*$. The parameter P_j is selected from $\{P_j | j=1,2,\ldots,L\}$ if there exists a set of feasible solutions $\{s_i^* | i=1,2,\ldots,K\}$.

The Tetragonal and Hexagonal Systems

Let $T_i=\text{Sin}^2\theta_i$ (observed) as usual. Let $\{P_j | j=1,2,\ldots,L1\}$ and $\{Q_m | m=1,2,\ldots,L2\}$ be two sets of possible parameters, where L1 is the total number of possible parameters P and L2 is the total number of possible parameters Q. The index-searching technique for the ith reflection of some P_j and Q_m is to find a unique solution g_i^* from the set of solutions $G_i = \{g_i=(s_i,l_i) | s_i=h_i^2+k_i^2$ for the tetragonal system; $s_i=h_i^2+h_ik_i+k_i^2$ for the hexagonal system; h_i, k_i, and l_i are non-negative integers$\}$.

The problem can be written mathematically as:

$$\text{minimize} \quad |f(s_i,l_i)|, \text{ where } f(s_i,l_i)=T_i-s_iP_j-l_iQ_m, \tag{46}$$

$$\text{subject to} \quad |f(s_i,l_i)| \leq \Delta; \tag{47}$$

where h_i, k_i, and l_i are non-negative integers for each i, i=1,2, ...,K; for some j and m, j=1,2,...,L1 and m=1,2,...,L2, and we again select $\Delta=0.1T_i$ as our initial least lower bound. The least lower bound Δ is chosen such that there exists a subset of G_i in which only one element, $g_i^*=(s_i^*,l_i^*)$, satisfies condition (47).

Thus, we may find s_i^* and l_i^* from a set of $G_i = \{(s_i, l_i)\}$ such that the maximum value of l_i is obtained by

$$l_{imax} = \left[\sqrt{T_i/Q_m + 0.5}\right] + 1.0, \tag{48}$$

where i=1,2,...,K and for some m, m=1,2,...,L2, and $\left[\sqrt{(T_i/Q_m)+0.5}\right]$ is the greatest integer which is less than $\sqrt{(T_i/Q_m)+0.5}$.

For each $l_i \varepsilon \{0,1,2,\ldots,l_{imax}\}$, there is a corresponding value of s_i such that

$$s_i^* = \left[(T_i - l_i^2 Q_m)/P_j + 0.5\right], \tag{49}$$

where i=1,2,...,K and for some j, j=1,2,...,L1, and $\left[(T_i - l_i^2 Q_m)/P_j + 0.5\right]$ is the greatest integer which is less than $(T_i - l_i^2 Q_m)/P_j + 0.5$.

After obtaining such an s_i^* for a certain parameter pair (P_j, Q_m), the Miller indices h_i, k_i can be calculated by solving the quadratic Diophantine equation $h_i^2 + k_i^2 = s_i^*$ for the tetragonal system and $h_i^2 + h_i k_i + k_i^2 = s_i^*$ for the hexagonal system. The parameter pair P_j^*, Q_m^* is selected from the sets P_j and Q_m if there exists a feasible solution set, $\{(s_i^*, l_i^*) \mid i=1,2,\ldots,K\}$.

The Orthorhombic System

Let $T_i = \mathrm{Sin}^2\theta_i$ (observed) as usual. Let $\{(P_j, Q_j, S_j) \mid j=1,2,\ldots,L\}$ be a set of possible parameters, where L is the total number of possible parameter triplets (P_j, Q_j, S_j). The index-searching technique for the ith reflection of some triplets

(P_j, Q_j, S_j) is to find a unique solution g_i^* from a set of solutions $G_i = \{g_i=(h_i,k_i,l_i) | h_i,\ k_i \text{ and } l_i \geq 0\}$.

The problem can be written mathematically as:

$$\text{minimize} \quad |f(h_i,k_i,l_i)|, \text{ where } f(h_i,k_i,l_i)=T_i-(h_i^2P_j+k_i^2Q_j+l_i^2S_j), \tag{50}$$

$$\text{subject to} \quad |f(h_i,k_i,l_i)| \leq \Delta, \tag{51}$$

where h_i, k_i, and l_i are non-negative integers for each i, i=1,2, ...,K and for some j, j=1,2,...,L, and again we select $\Delta=0.1T_i$ as our initial least lower bound. This least lower bound, Δ, is made smaller until there exists a subset of G_i in which only one element, $g_i^*=(h_i^*,k_i^*,l_i^*)$, satisfies condition (51).

Thus, we may find h_i^*, k_i^*, and l_i^* from the set G_i such that the maximum value of h_i is obtained by

$$h_{imax} = \left[\sqrt{(T_i/P_j) + 0.5}\right] + 1.0, \tag{52}$$

where i=1,2,...,K and for some j, j=1,2,...,L, and $\left[\sqrt{(T_i/P_j)+0.5}\right]$ is the greatest integer that is less than $\sqrt{(T_i/P_j)+0.5}$.

For each $h_i \in \{0,1,2,\ldots,h_{imax}\}$, there exists a set of non-negative integer k_i in which the maximum value is obtained by

$$k_{imax} = \left[\sqrt{(T_i-h_i^2P_j)/Q_j + 0.5}\right] + 1.0, \tag{53}$$

where $\left[\sqrt{(T_i-h_i^2P_j)/Q_j+0.5}\right]$ is the greatest integer that is less than $\sqrt{(T_i-h_i^2P_j)/Q_j+0.5}$.

Again, for each $h_i \varepsilon \{0,1,2,\ldots,h_{imax}\}$ and $k_i \varepsilon \{0,1,2,\ldots, k_{imax}\}$, there exists a unique non-negative integer l_i such that

$$l_i = \left[\sqrt{(T_i - h_i^2 P_j - k_i^2 Q_j)/S_j + 0.5}\right] \tag{54}$$

where $\left[\sqrt{(T_i - h_i^2 P_j - k_i^2 Q_j)/S_j + 0.5}\right]$ is the greatest integer that is less than $\sqrt{(T_i - h_i^2 P_j - k_i^2 Q_j)/S_j + 0.5}$.

The parameter triplet P_j^*, Q_j^*, S_j^* is selected if there exists a set of feasible solutions $\{g_i^* | i=1,2,\ldots,K\}$.

The Monoclinic System

Let $T_i = \text{Sin}^2\theta_i$ (observed) as usual. Let $\{(P_j,Q_j,S_j,V_j) | j=1,2,\ldots,L\}$ be the possible parameters, where L is the total number of possible parameter sets (P_j,Q_j,S_j,V_j). The index-searching technique for the ith reflection for some parameter set (P_j,Q_j,S_j,V_j) is to find a unique solution g_i^* from a set of solutions $G_i = \{g_i=(h_i,k_i,l_i) | h_i,\ k_i \geq 0$ and l_i can be any integer$\}$.

The problem can be written mathematically as:

$$\text{minimize} \quad |f(h_i,k_i,l_i)|, \text{ where } f(h_i,k_i,l_i) = T_i - (h_i^2 P_j + k_i^2 Q_j + l_i^2 S_j - h_i l_i V_j), \tag{55}$$

$$\text{subject to} \quad |f(h_i,k_i,l_i)| < \Delta, \tag{56}$$

where h_i and k_i are non-negative integers, l_i can be any integer, for each i, $i=1,2,\ldots,K$ and for some j, $j=1,2,\ldots,L$.

Thus, we may find h_i^*, k_i^*, and l_i^* from the set of G_i such that the maximum value of k_i is obtained by

$$K_{i1} = \sqrt{T_i/Q_j + 0.5},$$

$$k_{imax} = \lfloor K_{i1} \rfloor + 1.0, \tag{57}$$

where $\lfloor K_{i1} \rfloor$ is the greatest integer that is less than K_{i1}.

For each $k_i \varepsilon \{0,1,2,\ldots,k_{imax}\}$, there exists a set of non-negative integers for h_i in which the maximum value is obtained by

$$K_{i2} = \sqrt{(T_i - k_i^2 Q_j)/P_j + 0.5},$$

$$h_{imax} = \lfloor K_{i2} \rfloor + 1.0, \tag{58}$$

where $\lfloor K_{i2} \rfloor$ is the greatest integer which is less than K_{i2}.

And, for each $h_i \varepsilon \{0,1,2,\ldots,h_{imax}\}$ and $k_i \varepsilon \{0,1,2,\ldots, k_{imax}\}$, there exists two values of l_i such that

$$K_{i3} = \frac{h_i V_j \pm \sqrt{h_i^2 V_j^2 + 4S_j(T_i - h_i^2 P_j - k_i^2 Q_j)}}{2S_j} \pm S_j,$$

$$l_i = \lfloor K_{i3} \rfloor, \tag{59}$$

where $\lfloor K_{i3} \rfloor$ is the greatest integer which is less than K_{i3}.

The parameter set $(P_j^*, Q_j^*, S_j^*, V_j^*)$ is selected if there exists a set of feasible solutions, $\{g_i^* | i=1,2,\ldots,K\}$.

The Triclinic System

Let $T_i = \sin^2\theta_i$ (observed) as usual. Let $\{(P_j, Q_j, S_j, U_j, V_j,$

$W_j)|j=1,2,\ldots,L\}$ be the possible parameters, where L is the total number of possible parameter sets $(P_j,Q_j,S_j,U_j,V_j,W_j)$. The index-searching technique for the ith reflection for some parameter set $(P_j,Q_j,S_j,U_j,V_j,W_j)$ is to find a unique solution g_i^* from a set of solutions, $G_i = \{g_i=(h_i,k_i,l_i)|k_i\geq 0,\ h_i \text{ and } l_i \text{ are any integers}\}$.

The problem can be written mathematically as:

$$\text{minimize} \quad |f(h_i,k_i,l_i)|, \text{ where } f(h_i,k_i,l_i)=T_i-(h_i^2P_j+k_i^2Q_j+l_i^2S_j+h_ik_iU_j+h_il_iV_j+k_il_iW_j), \tag{60}$$

$$\text{subject to} \quad |f(h_i,k_i,l_i)| \leq \Delta,$$

where h_i and l_i are any integers, k_i is a non-negative integer for each i, i=1,2,...,K and for some j, j=1,2,...,L.

Thus, we may find h_i^*, k_i^*, and l_i^* from the set of G_i such that the extreme values of l_i are obtained by

$$K_{il} = \sqrt{T_i/S_j + 0.5},$$

$$l_{imax} = \lfloor K_{il} \rfloor + 1.0 \text{ and } l_{imin} = -\lfloor K_{il} \rfloor - 1.0, \tag{62}$$

where $\lfloor K_{il} \rfloor$ is the greatest integer which is less than K_{il}.

For each $l_i \varepsilon \{l_{imin},\ldots,-1,0,1,\ldots,l_{imax}\}$, there exists a set of non-negative integers of k_i in which the maximum value is obtained by

$$K_{i2} = \sqrt{(T_i-l_i^2S_j)/Q_j + 0.5},$$

$$k_{imax} = [K_{i2}] + 1.0, \tag{63}$$

where $[K_{i2}]$ is the greatest integer that is less than K_{i2}.

Again, for each $k_i \varepsilon \{0,1,2,\ldots,k_{imax}\}$ and $l_i \varepsilon \{l_{imin},\ldots,-1,0,1,\ldots,l_{imax}\}$, there exists two values of h_i such that

$$K_{i3} = \frac{-(k_i U_j + l_i V_j) \pm \sqrt{(k_i U_j + l_i V_j)^2 + 4P_j (T_i - k_i^2 Q_j - l_i^2 S_j)}}{2P_j} + P_j,$$

$$h_i = [K_{i3}], \tag{64}$$

where $[K_{i3}]$ is the greatest integer which is less than K_{i3}.

The parameter set $(P_j^*, Q_j^*, S_j^*, U_j^*, V_j^*, W_j^*)$ is selected if there exists a set of feasible solutions, $\{g_i^* | i=1,2,\ldots,K\}$.

Example

A well-known example, selected from Hesse,[25] is used to illustrate how the branch-and-bound method is applied to index the reflection lines on the powder patterns.

There are eleven reflection lines found on the powder pattern of MoB which belongs to the tetragonal system. Their corresponding $Sin^2\theta$ values are shown in Table 37. The parameters P_j and Q_m are selected from the difference analysis. For P_3 =

0.1352 and $Q_1 = 0.00439$, the index-searching for the eighth reflection line, for example, may be described as follows:

(1) The problem is to find $g_8^* = (s_8^*, l_8^*)$ to minimize

$$|f(s_8,l_8)|, \text{ where } f(s_8,l_8)=0.5050 - 0.1352s_8 - 0.004391l_8^2, \tag{65}$$

subject to $$|f(s_8,l_8)| \leqslant 0.0505, \tag{66}$$

where $s_8=h_8^2+l_8^2$; the initial least lower bound is $0.1T_8=0.0505$ (where $T_8=0.5050$); h_8, k_8, and l_8 are non-negative integers.

(2) Now, the maximum value of l_8 is obtained by using equation (48),

$$l_{8max} = \lfloor\sqrt{0.505/0.00439+0.5}\rfloor+1.0=\lfloor 10.75\rfloor+1.0=11.$$

For each $l_8 \varepsilon \{0,1,2,\ldots,11\}$, there is a corresponding value of s_8:

$$s_8 = \lfloor(0.505-0.004391_8)/0.1352 + 0.5\rfloor, \tag{67}$$

where equation (67) is obtained by using equation (49).

(3) The set of (s_8,l_8) may be then obtained by equation (68). They are (4,0), (4,1), (4,2), (3,3), (3,4), (3,5), (3,6), (2,7), (2,8), (1,9), (0,10), and (0,11).

(4) For convenience, the values of $f(s_8,l_8)$ for each pair of (s_8,l_8) listed in step (3) are calculated and recorded in Table 10.

TABLE 10

Computation of $f(s_8,l_8)$ Values of the Powder Pattern of MoB (For P_3=0.1352 and Q_1=0.00439)

s_8	l_8	$f(s_8,l_8)$
4	0	0.5050 - 0.5408 = -0.0358
4	1	0.5050 - 0.5408 - 0.00439 = -0.04019
4	2	0.5050 - 0.5408 - 0.01756 = -0.05336
3	3	0.5050 - 0.4056 - 0.03951 = 0.05989
3	4	0.5050 - 0.4056 - 0.07024 = 0.02916
3	5	0.5050 - 0.4056 - 0.10975 = -0.01035
3	6	0.5050 - 0.4056 - 0.15804 = -0.05864
2	7	0.5050 - 0.2704 - 0.21511 = 0.01949
2	8	0.5050 - 0.2704 - 0.28096 = -0.04636
1	9	0.5050 - 0.1352 - 0.35559 = 0.00421
0	10	0.5050 - 0.4390 = 0.0660
0	11	0.5050 - 0.53119 = -0.02619

(5) Comparing with all the twelve values of $f(s_8,l_8)$, the solution set g_8^*=(1,9) is then obtained becaues (1,9) is the only element in the set G_8 whose least lower bound is less than or equal to 0.00421. The indexing search procedures may also be

described in the search tree as shown in Figure 3.

(6) The Miller index (h_8^*,k_8^*,l_8^*) of the eighth reflection line is calculated by solving the Diophantine equation $(h_8^*)^2+(l_8^*)^2 = s_8^* = 1$. That is, $h_8^* = 1$, $k_8^* = 0$, and $l_8^* = 9$. The result is agreeable to that in Table 39. This example is described in more detail in Chapter VI.

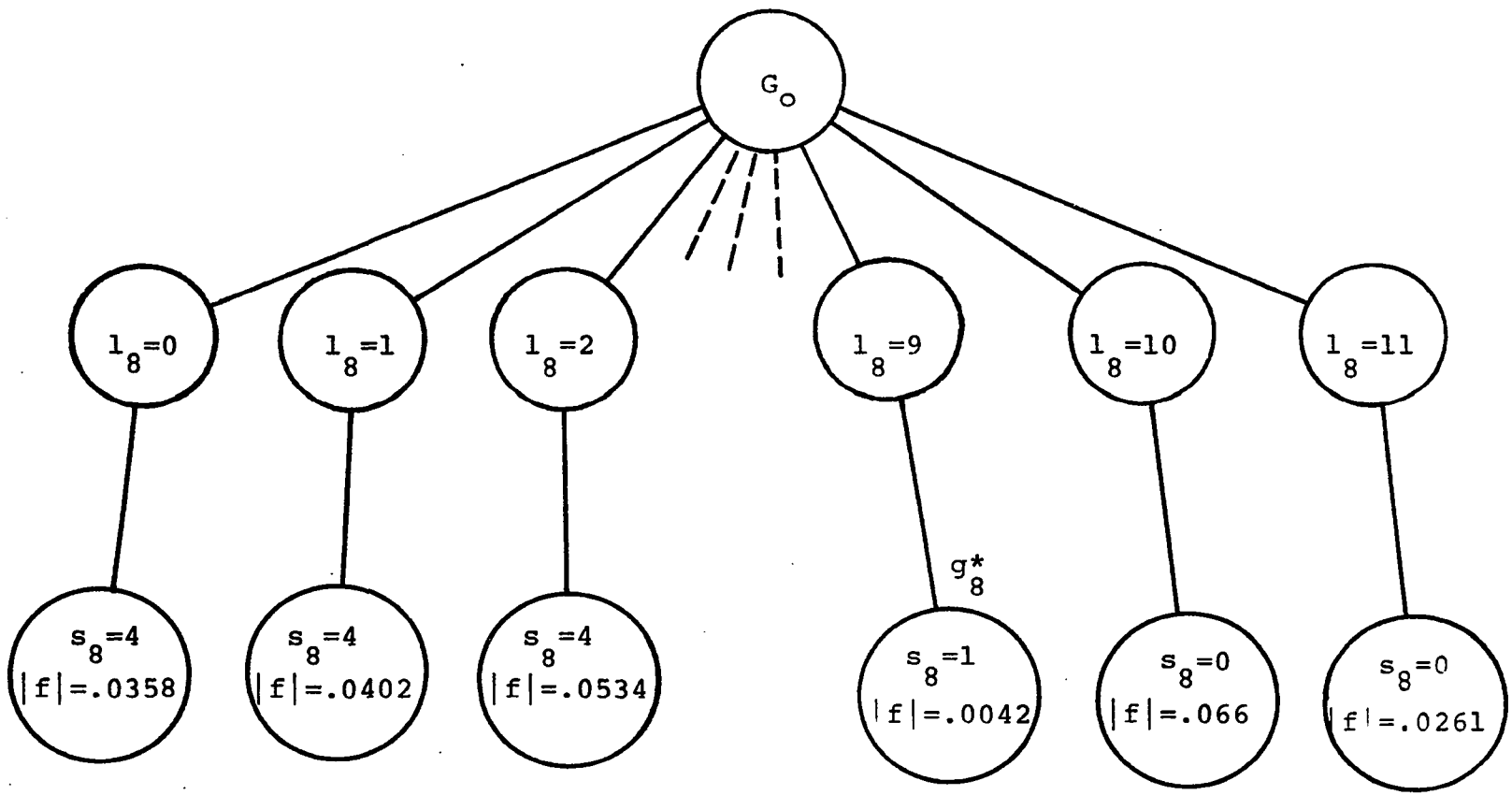

Figure 3 Search Tree for Indexing the Eighth Reflection Line of the Powder Pattern of MoB.

CHAPTER V

REFINEMENT OF PARAMETERS AND SELECTION OF A UNIQUE SOLUTION

Introduction

Because the possible parameters are either selected from some of the lower indexed reflections or from the arithmetic average of the differences of the observed $Sin^2\theta$ values, refinement is necessary. The least-square method is used for refinement of the possible parameters for the cubic, tetragonal, hexagonal, and orthorhombic systems. For monoclinic and triclinic systems however, the multiple least-square method is applied since more precise possible parameters are needed for indexing the reflections. That is, first we apply the least-square method for refinning the possible parameters and then we index the reflections and refine the parameters again. This ensures better solutions than using the least-square method once for these two structures.

As to choosing a unique solution, the branch-and-bound method is applied to select the one with the minimum standard deviation.

Both procedures and formulas used for the refinement of the parameters and the selection of a unique solution are described in detail in the following sections.

Refinement of the Parameters

Let all the summation signs be the summations from i = 1 up to N and $T_i = \mathrm{Sin}^2\theta_i$ (observed), where $1<N\leq K$; K is the total number of the observed reflections to be indexed.

The Cubic System

Even if the possible parameters $\{P_j | j=1,2,\ldots,L\}$ are obtained by taking either the arithmetic average or medium from the smallest recurrent value group of the difference table, the selected possible parameter may still not fit all the observed T_i (i=1,2,...,K) values well enough. The refinement of P_j can be done by setting the error function $Z(P_j)$ such that

$$Z(P_j) = \Sigma(T_i - s_i P_j)^2, \tag{68}$$

where i=1,2,...,K and for some j, j=1,2,...,L.

Differentiating equation (68) with respect to P_j and setting it to zero, we have:

$$\frac{d\ Z(P_j)}{dP_j} = -2\ \Sigma(T_i - s_i P_j)\ s_i = 0. \tag{69}$$

At $P_j=\hat{P}_{jN}$ (where $\hat{P}_{jN}$ varies depending on N), equation (69) can be rewritten as:

$$\Sigma T_i s_i - \Sigma s_i^2 \hat{P}_{jN} = 0. \tag{70}$$

Thus

$$\hat{P}_{jN} = \Sigma T_i s_i / \Sigma s_i^2. \tag{71}$$

$\hat{P}_{jK}$ is the parameter that may best fit all the reflections. Usually, the precised lattice parameter a of the cubic system may be calculated by using equation (7) where $P_j = \hat{P}_{jK}$.

The Tetragonal and Hexagonal Systems

Refinement of the possible parameters $\{P_j | j=1,2,\ldots,L1\}$ and $\{Q_m | m=1,2,\ldots,L2\}$ can be done by setting the error function $Z(P_j,Q_m)$ such that

$$Z(P_j,Q_m) = \Sigma(T_i - s_i P_j - l_i^2 Q_m)^2, \tag{72}$$

where i=1,2,...,K and for some j and m, j=1,2,...,L1 and m=1,2,..., L2. Also we assume that $s=h_i^2+k_i^2$ for the tetragonal system and $s_i=h_i^2+h_i k_i+k_i^2$ for the hexagonal system.

We then differentiate equation (72) with respect to P_j and Q_m; setting them equal to zero, we have:

$$\frac{\partial Z}{\partial P_j} = -2\ \Sigma(T_i - s_i P_j - l_i^2 Q_m) s_i = 0 \tag{73}$$

and

$$\frac{\partial Z}{\partial Q_m} = -2 \Sigma(T_i - s_i P_j - l_i^2 Q_m) l_i^2 = 0. \qquad (74)$$

At $P_j = \hat{P}_{jN}$ and $Q_m = \hat{Q}_{mN}$ (where $\hat{P}_{jN}$ and $\hat{Q}_{mN}$ vary depending on N), equations (73) and (74) may be rewritten as:

$$\hat{P}_{jN} \Sigma s_i^2 + \hat{Q}_{mN} \Sigma s_i l_i^2 = \Sigma T_i s_i \qquad (75)$$

and

$$\hat{P}_{jN} \Sigma s_i l_i^2 + \hat{Q}_{mN} \Sigma l_i^4 = \Sigma T_i l_i^2. \qquad (76)$$

Solving equations (75) and (76) for $\hat{P}_{jN}$ and $\hat{Q}_{mN}$ by using Creamer's rule, we have:

$$\hat{P}_{jN} = \frac{\Sigma T_i s_i \Sigma l_i^2 - \Sigma T_i l_i^2 \Sigma s_i l_i^2}{\Sigma s_i^2 \Sigma l_i^4 - (\Sigma s_i l_i^2)^2}$$

and

$$\hat{Q}_{mN} = \frac{\Sigma T_i l_i^2 \Sigma s_i^2 - \Sigma s_i l_i^2 \Sigma T_i s_i}{\Sigma s_i^2 \Sigma l_i^4 - (\Sigma s_i l_i^2)^2}. \qquad (78)$$

$\hat{P}_{jK}$ and $\hat{Q}_{mK}$ are the two parameters that may best fit all the reflections. Usually, the precised lattice parameters a and c of both the tetragonal and hexagonal systems may be calculated by using equations (9) and (11), where $P_j = \hat{P}_{jK}$ and $Q_m = \hat{Q}_{mK}$.

The Orthorhombic System

Refinement of the possible parameter triplets $\{(P_j, Q_j, S_j) | j=1,2,\ldots,L\}$ can be done by setting the error function $Z(P_j, Q_j, S_j)$

such that

$$Z(P_j,Q_j,S_j) = \Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j)^2, \tag{79}$$

where i=1,2,...,K and for some j, j=1,2,...,L.

We then differentiate equation (79) with respect to P_j, Q_j, and S_j; setting them equal to zero, we have:

$$\frac{\partial Z}{\partial P_j} = -2\ \Sigma(T_i - h_i^2P_j - k_i^2Q_j - l_i^2S_j)h_i^2 = 0, \tag{80}$$

$$\frac{\partial Z}{\partial Q_j} = -2\ \Sigma(T_i - h_i^2P_j - k_i^2Q_j - l_i^2S_j)k_i^2 = 0, \tag{81}$$

and

$$\frac{\partial Z}{\partial S_j} = -2\ \Sigma(T_i - h_i^2P_j - k_i^2Q_j - l_i^2S_j)l_i^2 = 0. \tag{82}$$

At $P_j=\hat{P}_{jN}$, $Q_j=\hat{Q}_{jN}$, and $S_j=\hat{S}_{jN}$ (where $\hat{P}_{jN}$, $\hat{Q}_{jN}$, and $\hat{S}_{jN}$ vary depending on N), equations (80), (81), and (82) may be rewritten as:

$$\hat{P}_{jN}\ \Sigma h_i^4 + \hat{Q}_{jN}\ \Sigma h_i^2k_i^2 + \hat{S}_{jN}\ \Sigma h_i^2l_i^2 = \Sigma T_ih_i^2, \tag{83}$$

$$\hat{P}_{jN}\ \Sigma h_i^2k_i^2 + \hat{Q}_{jN}\ \Sigma k_i^4 + \hat{S}_{jN}\ \Sigma k_i^2l_i^2 = \Sigma T_ik_i^2, \tag{84}$$

and

$$\hat{P}_{jN}\ \Sigma h_i^2l_i^2 + \hat{Q}_{jN}\ \Sigma k_i^2l_i^2 + \hat{S}_{jN}\ \Sigma l_i^4 = \Sigma T_il_i^2. \tag{85}$$

Solving the simultaneous equations (83), (84), and (85) for $\hat{P}_{jN}$, $\hat{Q}_{jN}$, and $\hat{S}_{jN}$ by using Creamer's rule, we obtain:

$$\nabla = \begin{vmatrix} \Sigma h_i^4 & \Sigma h_i^2 k_i^2 & \Sigma h_i^2 l_i^2 \\ \Sigma h_i^2 k_i^2 & \Sigma k_i^4 & \Sigma k_i^2 l_i^2 \\ \Sigma h_i^2 l_i^2 & \Sigma k_i^2 l_i^2 & \Sigma l_i^4 \end{vmatrix},$$

$$\nabla_{\hat{P_{jN}}} = \begin{vmatrix} \Sigma T_i h_i^2 & \Sigma h_i^2 k_i^2 & \Sigma h_i^2 l_i^2 \\ \Sigma T_i k_i^2 & \Sigma k_i^4 & \Sigma k_i^2 l_i^2 \\ \Sigma T_i l_i^2 & \Sigma k_i^2 l_i^2 & \Sigma l_i^4 \end{vmatrix},$$

$$\nabla_{\hat{Q_{jN}}} = \begin{vmatrix} \Sigma h_i^4 & \Sigma T_i h_i^2 & \Sigma h_i^2 l_i^2 \\ \Sigma h_i^2 k_i^2 & \Sigma T_i k_i^2 & \Sigma k_i^2 l_i^2 \\ \Sigma h_i^2 l_i^2 & \Sigma T_i l_i^2 & \Sigma l_i^4 \end{vmatrix},$$

and

$$\nabla_{\hat{S_{jN}}} = \begin{vmatrix} \Sigma h_i^4 & \Sigma h_i^2 k_i^2 & \Sigma T_i h_i^2 \\ \Sigma h_i^2 k_i^2 & \Sigma k_i^4 & \Sigma T_i k_i^2 \\ \Sigma h_i^2 l_i^2 & \Sigma k_i^2 l_i^2 & \Sigma T_i l_i^2 \end{vmatrix}.$$

Thus,

$$\hat{P_{jN}} = \frac{\nabla \hat{P_{jN}}}{\nabla}, \quad \hat{Q_{jN}} = \frac{\nabla \hat{Q_{jN}}}{\nabla}, \text{ and } \hat{S_{jN}} = \frac{\nabla \hat{S_{jN}}}{\nabla}. \tag{86}$$

$\hat{P_{jK}}$, $\hat{Q_{jK}}$, and $\hat{S_{jK}}$ are the parameters that may best fit all

the reflections. The precised lattice parameters a, b, and c of the orthorhombic system may be calculated by using equation (13), where $P_j=\hat{P}_{jK}$, $Q_j=\hat{Q}_{jK}$, and $S_j=\hat{S}_{jK}$.

The Monoclinic System

Refinement of the possible parameters $\{(P_j,Q_j,S_j,V_j)\,|\,j=1,2,\ldots,L\}$ can be done by setting the error function $Z(P_j,Q_j,S_j,V_j)$ such that

$$Z(P_j,Q_j,S_j,V_j)= (T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_il_iV_j)^2, \tag{87}$$

where $i=1,2,\ldots,K$ and for some j, $j=1,2,\ldots,L$.

We then minimize the error function by differentiating equation (87) with respect to P_j, Q_j, S_j, and V_j; setting them equal to zero, we have:

$$\frac{\partial Z}{\partial P_j} = -2\ \Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_il_iV_j)h_i^2 = 0, \tag{88}$$

$$\frac{\partial Z}{\partial Q_j} = -2\ \Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_il_iV_j)k_i^2 = 0, \tag{89}$$

$$\frac{\partial Z}{\partial S_j} = -2\ \Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_il_iV_j)l_i^2 = 0, \tag{90}$$

an

$$\frac{\partial Z}{\partial V_j} = -2\ \Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_il_iV_j)h_il_i=0. \tag{91}$$

At $P_j=\hat{P}_{jN}$, $Q_j=\hat{Q}_{jN}$, $S_j=\hat{S}_{jN}$, and $V_j=\hat{V}_{jN}$ (where $\hat{P}_{jN}$, $\hat{Q}_{jN}$, $\hat{S}_{jN}$, and $\hat{V}_{jN}$ vary depending on N), equation (88), (89), (90), and (91) may

be rewritten as:

$$P_{jN}\Sigma h_i^4 + Q_{jN}\Sigma h_i^2k_i^2 + S_{jN}\Sigma h_i^2l_i^2 - V_{jN}\Sigma h_i^3l_i = \Sigma T_ih_i^2, \quad (92)$$

$$P_{jN}\Sigma h_i^2k_i^2 + Q_{jN}\Sigma k_i^4 + S_{jN}\Sigma k_i^2l_i^2 - V_{jN}\Sigma h_ik_i^2l_i=\Sigma T_ik_i^2, \quad (93)$$

$$P_{jN}\Sigma h_i^2l_i^2 + Q_{jN}\Sigma k_i^2l_i^2 + S_{jN}\Sigma l_i^4 - V_{jN}\Sigma h_il_i^3 = \Sigma T_il_i^2, \quad (94)$$

and $$P_{jN}\Sigma h_i^3l_i + Q_{jN}\Sigma h_ik_i^2l_i + S_{jN}\Sigma h_il_i^3 - V_{jN}\Sigma h_i^2l_i^2=\Sigma T_ih_il_i. \quad (95)$$

Solving the simultaneous equations (92), (93), (94), and (95) for $\hat{P_{jN}}$, $\hat{Q_{jN}}$, $\hat{S_{jN}}$, and $\hat{V_{jN}}$ by using the standard scientific subroutine, SIMQ, which is listed in Table 11, refinement of the parameters, P_j, Q_j, S_j, and V_j can be achieved.

$\hat{P_{jK}}$, $\hat{Q_{jK}}$, $\hat{S_{jK}}$, and $\hat{V_{jK}}$ are the parameters that may best fit all the reflections. The determination of the precised lattice parameters a, b, c, and β may be calculated by using equation (15), where $P_j=\hat{P_{jK}}$, $Q_j=\hat{Q_{jK}}$, $S_j=\hat{S_{jK}}$, and $V_j=\hat{V_{jK}}$.

The Triclinic System

Refinement of the possible parameters $\{(P_j,Q_j,S_j,U_j,V_j,W_j) | j=1,2,\ldots,L\}$ can be done by minimizing the error function $Z(P_j, Q_j,S_j,U_j,V_j,W_j)$ defined by

$$Z = \Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_ik_iU_j-h_il_iV_j-k_il_iW_j)^2, \quad (96)$$

where i=1,2,...,K and for some j, j=1,2,...,L.

TABLE 11

The Standard Scientific Computer Subroutine SIMQ

```
      SUBROUTINE SIMQ(A,B,N,KS)
      DIMENSION A(36),B(6)
      TOL=0.0
      KS=0
      JJ=-N
      DO 65 J=1,N
      JY=J+1
      JJ=JJ+N+1
      BIGA=0
      IT=JJ-J
      DO 30 I=J,N
      IJ=IT+I
      IF(ABS(BIGA)-ABS(A(IJ))) 20,30,30
   20 BIGA=A(IJ)
      IMAX=I
   30 CONTINUE
      IF(ABS(BIGA)-TOL) 35,35,40
   35 KS=1
      RETURN
   40 I1=J+N*(J-2)
      IT=IMAX-J
      DO 50 K=J,N
      I1=I1+N
      I2=I1+IT
      SAVE=A(I1)
      A(I1)=A(I2)
      A(I2)=SAVE
   50 A(I1)=A(I1)/BIGA
      SAVE=B(IMAX)
      B(IMAX)=B(J)
      B(J)=SAVE/BIGA
      IF(J-N) 55,70,55
   55 IQS=N*(J-1)
      DO 65 IX=JY,N
      IXJ=IQS+IX
      IT=J-IX
      DO 60 JX=JY,N
      IXJX=N*(JX-1)+IX
      JJX=IXJX+IT
   60 A(IXJX)=A(IXJX)-(A(IXJ)*A(JJX))
   65 B(IX)=B(IX)-(B(J)*A(IXJ))
   70 NY=N-1
      IT=N*N
      DO 80 J=1,NY
      IA=IT-J
      IB=N-J
      IC=N
```

TABLE 11 (CONTINUED)

```
      DO 80 K=1,J
      B(IB)=B(IB)-A(IA)*B(IC)
      IA=IA-N
   80 IC=IC-1
      RETURN
      END
```

We then differentiate equation (96) with respect to P_j, Q_j, S_j, U_j, V_j, and W_j; setting them equal to zero, we have:

$$\frac{\partial Z}{\partial P_j}=-2\Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_ik_iU_j-h_il_iV_j-k_il_iW_j)h_i^2=0, \quad (97)$$

$$\frac{\partial Z}{\partial Q_j}=-2\Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_ik_iU_j-h_il_iV_j-k_il_iW_j)k_i^2=0, \quad (98)$$

$$\frac{\partial Z}{\partial S_j}=-2\Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_ik_iU_j-h_il_iV_j-k_il_iW_j)l_i^2=0, \quad (99)$$

$$\frac{\partial Z}{\partial U_j}=-2\Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_ik_iU_j-h_il_iV_j-k_il_iW_j)h_ik_i=0, \quad (100)$$

$$\frac{\partial Z}{\partial V_j}=-2\Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_ik_iU_j-h_il_iV_j-k_il_iW_j)h_il_i=0, \quad (101)$$

and

$$\frac{\partial Z}{\partial W_j}=-2\Sigma(T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_ik_iU_j-h_il_iV_j-k_il_iW_j)k_il_i=0. \quad (102)$$

At $P_j=\hat{P}_{jN}$, $Q_j=\hat{Q}_{jN}$, $S_j=\hat{S}_{jN}$, $U_j=\hat{U}_{jN}$, $V_j=\hat{V}_{jN}$, and $W_j=\hat{W}_{jN}$ (where $\hat{P}_{jN}$, $\hat{Q}_{jN}$, $\hat{S}_{jN}$, $\hat{U}_{jN}$, $\hat{V}_{jN}$, and $\hat{W}_{jN}$ vary depending on N), equations (97), (98), (99), (100), (101), and (102) may be rewritten as:

$$\hat{P}_{jN}\Sigma h_i^4+\hat{Q}_{jN}\Sigma h_i^2k_i^2+\hat{S}_{jN}\Sigma h_i^2l_i^2+\hat{U}_{jN}\Sigma h_i^3k_i+\hat{V}_{jN}\Sigma h_i^3l_i+\hat{W}_{jN}\Sigma h_i^2k_il_i$$

$$=\Sigma T_ih_i^2, \tag{103}$$

$$\hat{P}_{jN}\Sigma h_i^2k_i^2+\hat{Q}_{jN}\Sigma k_i^4+\hat{S}_{jN}\Sigma k_i^2l_i^2+\hat{U}_{jN}\Sigma h_ik_i^3+\hat{V}_{jN}\Sigma h_ik_i^2l_i+\hat{W}_{jN}\Sigma k_i^3l_i$$

$$=\Sigma T_ik_i^2, \tag{104}$$

$$\hat{P}_{jN}\Sigma h_i^2l_i^2+\hat{Q}_{jN}\Sigma k_i^2l_i^2+\hat{S}_{jN}\Sigma l_i^4+\hat{U}_{jN}\Sigma h_ik_il_i^2+\hat{V}_{jN}\Sigma h_il_i^3+\hat{W}_{jN}\Sigma k_il_i^3$$

$$=\Sigma T_il_i^2, \tag{105}$$

$$\hat{P}_{jN}\Sigma h_i^3k_i+\hat{Q}_{jN}\Sigma h_ik_i^3+\hat{S}_{jN}\Sigma h_ik_il_i^2+\hat{U}_{jN}\Sigma h_i^2k_i^2+\hat{V}_{jN}\Sigma h_i^2k_il_i+\hat{W}_{jN}\Sigma h_ik_i^2l_i$$

$$=\Sigma T_ih_ik_i, \tag{106}$$

$$\hat{P}_{jN}\Sigma h_i^3l_i+\hat{Q}_{jN}\Sigma h_ik_i^2l_i+\hat{S}_{jN}\Sigma h_il_i^3+\hat{U}_{jN}\Sigma h_i^2k_il_i+\hat{V}_{jN}\Sigma h_i^2l_i^2+\hat{W}_{jN}\Sigma h_ik_il_i^2$$

$$=\Sigma T_ih_il_i, \tag{107}$$

and $$\hat{P}_{jN}\Sigma h_i^2k_il_i+\hat{Q}_{jN}\Sigma k_i^3l_i+\hat{S}_{jN}\Sigma k_il_i^3+\hat{U}_{jN}\Sigma h_ik_i^2l_i+\hat{V}_{jN}\Sigma h_ik_il_i^2+\hat{W}_{jN}\Sigma k_i^2l_i^2$$

$$=T_ik_il_i. \tag{108}$$

Thus, we may solve the simultaneous equations (103), (104), (105),

(106), (107), and (108) for $P_j=\hat{P}_{jN}$, $Q_j=\hat{Q}_{jN}$, $S_j=\hat{S}_{jN}$, $U_j=\hat{U}_{jN}$, $V_j=\hat{V}_{jN}$, and $W_j=\hat{W}_{jN}$ by using the standard scientific subroutine SIMQ. $\hat{P}_{jN}$, $\hat{Q}_{jN}$, $\hat{S}_{jN}$, $\hat{U}_{jN}$, $\hat{V}_{jN}$, and $\hat{W}_{jN}$ are the parameters that may best fit all the reflections. The precised lattice parameters a, b, c, α, β, and γ may be calculated by using equation (17), where $P_j=\hat{P}_{jK}$, $Q_j=\hat{Q}_{jK}$, $S_j=\hat{S}_{jK}$, $U_j=\hat{U}_{jK}$, $V_j=\hat{V}_{jK}$, and $W_j=\hat{W}_{jK}$.

Selection of a Unique Solution

The problem in selecting a unique solution is to choose a feasible solution g_j^* from a set of possible solutions G_j such that $G_j = \{g_j=(P_j,Q_j,S_j,U_j,V_j,W_j) \mid j=1,2,\ldots,L\}$. The criteria in Chapter IV for P_j, Q_j, S_j, U_j, V_j, and W_j for the six different systems hold in this section.

The problem may be written mathematically as:

$$\text{minimize} \quad f(P_j,Q_j,S_j,U_j,V_j,W_j), \text{ where } f(P_j,Q_j,S_j,U_j,V_j,W_j)= \sum_{i=1}^{K} (T_i-h_i^2P_j-k_i^2Q_j-l_i^2S_j-h_ik_iU_j-h_il_iV_j-k_il_iW_j)^2, \quad (109)$$

$$\text{subject to} \quad f(P_j,Q_j,S_j,U_j,V_j,W_j) \leq \Delta, \quad (110)$$

where h_i, k_i, and l_i are integers, i=1,2,...,K, and for some j, j=1,2,...,L.

The initial lower bound 1.0 is selected. Here, the lower bound represents the standard deviation between the calculated $\text{Sin}^2\theta_i$ values and observed $\text{Sin}^2\theta_i$ values for every i, i=1,2,...,K.

A unique solution is selected if such a small standard deviation exists as the least lowder bound that a subset of G_j contains only one element, $g_j^*=(P_j^*,Q_j^*,S_j^*,U_j^*,V_j^*,W_j^*)$; that is, the solution indexed by a pair of possible parameters g_j^* with minimum standard deviation where the standard deviation is defined by

$$\sigma = \left(\sum_{i=1}^{K} (\mathrm{Sin}^2\theta_i(\mathrm{obs.}) - \mathrm{Sin}^2\theta_i(\mathrm{cal.}))^2/K \right)^{\frac{1}{2}}. \qquad (111)$$

If the least lower bound is still equal to one, or a unique solution with an unusually large standard deviation, the powder pattern may happen to be another type of crystals.

CHAPTER VI

EXAMPLES

Introduction

Many examples are used to illustrate the indexing of powder patterns. The use of the six main computer programs for various structures are also described. Some examples have only brief explanations because of their similarity to the indexing procedures of the others. Comparisons with the original published diffraction data are also discussed.

As mentioned in Chapter I, the first step toward indexing procedures is to convert the set of measured arc lengths into $Sin^2\theta$ values. However, in most of our selected examples, observed $Sin^2\theta$ values are given directly from the various sources.

The Cubic System

The Use of the Main Computer Program CUB

The main computer program CUB for indexing the unknown powder patterns of cubic crystals and the flow chart are given in the Appendix A.

For the input of the computer program CUB, M stands for

the total number of the powder patterns to be indexed as cubic structure, K stands for the total number of the reflection lines in each powder pattern, L stands for the total number of possible parameters, T(J) stands for all the observed $Sin^2\theta$ values, and P(J) stands for all the possible parameter of P_j.

The output of the computer program contains the observed $Sin^2\theta$ values, calculated $Sin^2\theta$ values, $s=h^2+k^2+l^2$ integral numbers, and Miller indices of the reflections.

Example A

This example, chosen from Phillips,[53] illustrate the indexing of Sodium Chlorate powder pattern. The powder pattern photograph was taken at a camera radius of 5.0 cm. with radiation $\lambda=0.709\text{Å}$. The indexing procedures may be described as follows. (1) A set of measured arc lengths, listed in Table 12, was inputted to the computer program CEA to be converted into corresponding $Sin^2\theta$ values. The output is listed in Table 13. (2) This set of observed $Sin^2\theta$ values became the input to the computer program DA which calculated their differences. That output is listed in Table 14. (3) In Table 14, there are ten values in the δ-neighborhood of 0.00294. They are 0.00284, 0.00287, 0.00290, 0.00293, 0.00296, 0.00296, 0.00300, 0.00300, 0.00300, and 0.00310 (where δ is a function of the value of $Sin^2\theta_i$; e.g., consider δ is small if $Sin^2\theta_i$ value is small). (4) There are nine values in the δ-

TABLE 12

The Arc Lengths Measured
from the Powder Pattern of Sodium Chlorate

DIFFRACTION LINE	ARC LENGTH	DIFFRACTION LINE	ARC LENGTH
1	1.530	11	3.900
2	1.870	12	4.060
3	2.160	13	4.360
4	2.410	14	4.500
5	2.650	15	4.610
6	3.070	16	4.740
7	3.260	17	4.870
8	3.440	18	5.010
9	3.600	19	5.120
10	3.780		

TABLE 13

$Sin^2\theta$ Values Calculated
from the Powder Pattern of Sodium Chlorate

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.00584	11	0.03755
2	0.00872	12	0.04065
3	0.01162	13	0.04678
4	0.01445	14	0.04978
5	0.01745	15	0.05220
6	0.02338	16	0.05513
7	0.02633	17	0.05813
8	0.02929	18	0.06145
9	0.03205	19	0.06412
10	0.03530		

TABLE 14

Difference Table of the
Powder Diffraction Data of Sodium Chlorate

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00225	0.00242	0.00267	0.00276	0.00284	0.00287	0.00290	0.00293
0.00296	0.00296	0.00300	0.00300	0.00300	0.00310	0.00324	0.00332
0.00535	0.00535	0.00542	0.00549	0.00572	0.00574	0.00577	0.00584
0.00592	0.00592	0.00593	0.00599	0.00600	0.00613	0.00632	0.00825
0.00835	0.00835	0.00859	0.00861	0.00868	0.00874	0.00888	0.00892
0.00896	0.00899	0.00913	0.00923	0.00925	0.01121	0.01135	0.01135
0.01148	0.01155	0.01161	0.01167	0.01176	0.01184	0.01188	0.01192
0.01192	0.01223	0.01417	0.01431	0.01434	0.01448	0.01448	0.01460
0.01465	0.01466	0.01467	0.01472	0.01472	0.01484	0.01690	0.01727
0.01734	0.01748	0.01748	0.01753	0.01758	0.01760	0.01762	0.01768
0.01772	0.01784	0.01983	0.02009	0.02014	0.02044	0.02044	0.02048
0.02049	0.02058	0.02058	0.02080	0.02084	0.02283	0.02290	0.02307
0.02309	0.02319	0.02334	0.02340	0.02344	0.02345	0.02347	0.02368
0.02390	0.02583	0.02586	0.02593	0.02607	0.02615	0.02619	0.02621
0.02640	0.02657	0.02658	0.02879	0.02882	0.02882	0.02883	0.02883
0.02903	0.02932	0.02939	0.02945	0.03170	0.03175	0.03179	0.03193
0.03206	0.03215	0.03232	0.03232	0.03474	0.03475	0.03480	0.03482
0.03511	0.03516	0.03532	0.03767	0.03774	0.03778	0.03806	0.03807
0.03816	0.04058	0.04067	0.04067	0.04074	0.04093	0.04106	0.04348
0.04351	0.04367	0.04393	0.04399	0.04635			

neighborhood of 0.00587 (0.00572, 0.00574, 0.00577, 0.00584, 0.00592, 0.00592, 0.00593, 0.00599, and 0.00600); eight in that of 0.00882 (0.00859, 0.00861, 0.00868, 0.00874, 0.00888, 0.00892, 0.00896, and 0.00899); nine in that of 0.01173 (0.01148, 0.01155, 0.01161, 0.01167, 0.01176, 0.01184, 0.01188, 0.01192, and 0.01192); etc. Hence, if we let P=0.00294, the other recurrent value groups can be represented by 2P, 3P, 4P,... . (5) Now, the value 0.02058 (=7×0.00294) does not appear in Table 13. This ensures that the

possible parameter is 0.00294. (6) Using 0.00294 as the only possible parameter, Table 15 is the output of the computer program CUB.

Comparing the "Number" column of Table 15 with the permissible integers listed in Table 2, Sodium Chlorate has a somple cubic structure. The standard deviation of the observed $Sin^2\theta$ values from the calculated $Sin^2\theta$ values, 0.000176, shows that the experimental data agrees with the calculated value.

Example B

This example, also chosen from Phillips,[53] describes the indexing of the Chromium powder pattern. The powder photograph was taken at a camera radius of 5.0 cm. with radiation λ=0.709Å. The first two steps of the indexing procedures are similar to that of the example A. A set of arc lengths taken from Phillips[53] is listed in Table 16. A set of corresponding $Sin^2\theta$ values is listed in Table 17. The difference table of observed $Sin^2\theta$ values is listed in Table 18. In Table 18, the smallest recurrent value group is 0.02933 (0.02890, 0.02927, and 0.02982). However, 0.02933 is greater than 0.02335 in the table. Next, consider 0.01467 (½×0.02933) as the possible parameter. The value 0.10269 (=7×0.01467) does not appear in Table 18. (here the observed $Sin^2\theta$ does not need to equal 0.10269 exactly). Therefore, 0.01467 is an acceptable possible parameter. The indexed diffraction data

TABLE 15

Indexed Diffraction Data of Sodium Chlorate

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.00584	0.00583	2	1	1	0
0.00871	0.00874	3	1	1	1
0.01161	0.01165	4	2	0	0
0.01445	0.01457	5	2	1	0
0.01745	0.01748	6	2	1	1
0.02337	0.02331	8	2	2	0
0.02633	0.02622	9	3	0	0
0.02929	0.02913	10	3	1	0
0.03205	0.03205	11	3	1	1
0.03529	0.03496	12	2	2	2
0.03754	0.03787	13	3	2	0
0.04064	0.04079	14	3	2	1
0.04677	0.04661	16	4	0	0
0.04977	0.04953	17	4	1	0
0.05219	0.05244	18	4	1	1
0.05512	0.05535	19	3	3	1
0.05812	0.05827	20	4	2	0
0.06144	0.06118	21	4	2	1
0.06411	0.06410	22	3	3	2

PARAMETER= 0.00291 STANDARD DEVIATION=0.000176
THIS IS A CUBIC CRYSTAL POWDER PATTERN

is recorded in Table 19. The standard deviation, 0.001817, indicates that the experimental data is not very close to the calculated value. The "Number" column of Table 19 shows that Chromium has body-centered cubic structure.

Example C

This example, again chosen from Phillips,[53] is concerned

TABLE 16

The Arc Lengths Measured
from the Powder Pattern of Chromium

DIFFRACTION LINE	ARC LENGTH	DIFFRACTION LINE	ARC LENGTH
1	3.490	7	9.570
2	4.970	8	10.300
3	6.160	9	10.970
4	7.170	10	11.740
5	8.010	11	12.400
6	8.820	12	12.890

TABLE 17

$Sin^2\theta$ Values Calculated
from the Powder Pattern of Chromium

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.03014	7	0.21201
2	0.06049	8	0.24259
3	0.09190	9	0.27187
4	0.12311	10	0.30677
5	0.15201	11	0.33760
6	0.18220	12	0.36096

with indexing the powder pattern of periclase. The powder photograph was taken at a camera radius of 5.0 cm. woth radiation $\lambda=0.709\text{Å}$. A set of arc lengths is listed in Table 20, and the corresponding $Sin^2\theta$ values are listed in Table 21. The difference

TABLE 18

Difference Table of the
Powder Diffraction Data of Chromium

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.02335	0.02890	0.02927	0.02982	0.03019	0.03035	0.03058	0.03084
0.03120	0.03141	0.03490	0.05419	0.05909	0.05985	0.06001	0.06010
0.06040	0.06176	0.06261	0.06417	0.06574	0.08891	0.08909	0.08967
0.09029	0.09059	0.09151	0.09296	0.09475	0.09501	0.11836	0.11949
0.11986	0.12011	0.12170	0.12186	0.12457	0.12559	0.14876	0.14894
0.15069	0.15152	0.15205	0.15476	0.15541	0.17876	0.17996	0.18187
0.18210	0.18366	0.18560	0.20895	0.21137	0.21245	0.21450	0.21486
0.23785	0.24172	0.24570	0.24627	0.26905	0.27662	0.27711	0.30046
0.30746	0.33081						

TABLE 19

Indexed Diffraction Data of Chromium

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.03014	0.03039	2	1	1	0
0.06049	0.06079	4	2	0	0
0.09190	0.09118	6	2	1	1
0.12310	0.12158	8	2	2	0
0.15200	0.15197	10	3	1	0
0.18219	0.18237	12	2	2	2
0.21201	0.21276	14	3	2	1
0.24259	0.24316	16	4	0	0
0.27186	0.27355	18	4	1	1
0.30676	0.30395	20	4	2	0
0.33760	0.33434	22	3	3	2
0.36095	0.36473	24	4	2	2

PARAMETER= 0.01520 STANDARD DEVIATION=0.001817
THIS IS A CUBIC CRYSTAL POWDER PATTERN

table of the observed $\sin^2\theta$ values is listed in Table 22. In Table 22, there are three recurrent values in the δ-neighborhood of 0.02826 (0.02813, 0.02828, and 0.02838). However, 0.01826 is greater than several values in the difference table, such as 0.02124, 0.00795, etc. Next, consider 0.01413 (½×0.01826) and 0.00942 (=1/3×0.02826). But both are still larger than 0.00623, 0.00700, and 0.00795. Last, consider 0.00707 (=¼×0.02826) as the possible parameter. We may imagine that 0.00707 is the arithmetic average value of 0.00623, 0.00700, and 0.00795 even they are somewhat separated. The value 0.04949 and its δ-neighborhood do not appear in Table 21; this ensures that 0.00707 is the value we are seeking. The indexed powder pattern is recorded in Table 23.

The "Number" column in Table 23 shows that periclase has a face-centered cubic structure. The standard deviation, 0.000478, shows that the experimental data is reasonably close to the calculated value.

Example D

This example, chosen from Zachariasen,[54] illustrates the indexing of the Pu_2C_3 powder pattern. There were twenty-six reflection lines to be indexed. The indexing procedures are similar to the previous examples. The indexed powder diffraction data is recorded in Table 24. The standard deviation, 0.001662,

TABLE 20

The Arc Lengths Measured
from the Powder Pattern of Periclase

DIFFRACTION LINE	ARC LENGTH	DIFFRACTION LINE	ARC LENGTH
1	2.940	6	6.890
2	3.390	7	7.560
3	4.810	8	7.740
4	5.660	9	8.500
5	5.950		

TABLE 21

$Sin^2\theta$ Values Calculated
from the Powder Pattern of Periclase

DIFFRACTION LINE	SIN(SQUARE) (CRSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.02145	6	0.11406
2	0.02846	7	0.13621
3	0.05673	8	0.14244
4	0.07797	9	0.17001
5	0.08593		

TABLE 22

Difference Table of the
Powder Diffraction Data of Periclase

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00623	0.00700	0.00795	0.02124	0.02215	0.02757	0.02813	0.02828
0.02838	0.02919	0.03380	0.03528	0.03608	0.04952	0.05028	0.05595
0.05651	0.05652	0.05732	0.05747	0.05823	0.06446	0.06447	0.07947
0.08408	0.08560	0.08570	0.09203	0.09260	0.10775	0.11327	0.11398
0.11475	0.12098	0.14155	0.14855				

TABLE 23

Indexed Diffraction Data of Periclase

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.02145	0.02136	3	1	1	1
0.02845	0.02848	4	2	0	0
0.05673	0.05696	8	2	2	0
0.07797	0.07832	11	3	1	1
0.08592	0.08544	12	2	2	2
0.11405	0.11391	16	4	0	0
0.13620	0.13527	19	3	3	1
0.14243	0.14239	20	4	2	0
0.17000	0.17087	24	4	2	2

PARAMETER= 0.00712 STANDARD DEVIATION=0.000478
THIS IS A CUBIC CRYSTAL POWDER PATTERN

shows that the experimental data is not very close to the calculated value. The maximum discrepancy is about ±0.00401. The "Number" column shows that Pu_2C_3 has a body-centered cubic structure.

Example E

This example, chosen from Cullity,[55] describes the indexing of the Cu powder pattern. Only the first eight reflection lines were indexed. The indexed powder diffraction data is recorded in Table 25. The standard deviation, 0.003401, shows that the experimental data is poor. The maximum discrepancy is about ±0.00549. The "Number" column shows that Cu has a face-centered cubic structure.

TABLE 24

Indexed Diffraction Data of Pu_2C_3

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.05390	0.05412	6	2	1	1
0.07260	0.07215	8	2	2	0
0.09130	0.09019	10	3	1	0
0.12850	0.12627	14	3	2	1
0.14610	0.14431	16	4	0	0
0.20120	0.19843	22	3	3	2
0.21950	0.21646	24	4	2	2
0.23620	0.23450	26	5	1	0
0.27240	0.27058	30	5	2	1
0.30850	0.30666	34	5	3	0
0.34420	0.34273	38	6	1	1
0.36200	0.36077	40	6	2	0
0.37970	0.37881	42	5	4	1
0.41540	0.41489	46	6	3	1
0.43350	0.43293	48	4	4	4
0.45280	0.45097	50	7	1	0
0.48770	0.48704	54	7	2	1
0.50510	0.50508	56	6	4	2
0.52290	0.52312	58	7	3	0
0.55870	0.55920	62	7	3	2
0.57660	0.57724	64	8	0	0
0.79450	0.79370	88	6	6	4
0.63030	0.63135	70	6	5	3
0.64800	0.64939	72	8	2	2
0.66490	0.66743	74	8	3	1
0.69950	0.70351	78	7	5	2

PARAMETER= 0.00902 STANDARD DEVIATION=0.001662
THIS IS A CUBIC CRYSTAL POWDER PATTERN

Example F

This example, also chosen from Cullity,[55] illustrates the indexing of the CdTe powder pattern. There were sixteen reflection

TABLE 25

Indexed Diffraction Data of Cu

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.14000	0.13631	3	1	1	1
0.18500	0.18175	4	2	0	0
0.36900	0.36351	8	2	2	0
0.50300	0.49982	11	3	1	1
0.54800	0.54526	12	2	2	2
0.72600	0.72701	16	4	0	0
0.86100	0.86333	19	3	3	1
0.90500	0.90877	20	4	2	0

PARAMETER= 0.04544 STANDARD DEVIATION=0.003401
THIS IS A CUBIC CRYSTAL POWDER PATTERN

lines to be indexed. The indexed powder diffraction data is recorded in Table 26. The standard deviation, 0.003644, shows that the experimental data is far from the calculated value. The maximum discrepancy is about ±0.00574. The "Number" column shows that CdTe has a diamond cubic structure.

Example G

This example, chosen from D'Eye and Wait,[56] illustrates the indexing of the Cs_2TeBr_6 powder pattern. Fourteen low angle reflection lines were indexed. The indexed powder diffraction data is recorded in Table 27. The standard deviation, 0.000124, shows that the experimental data is very close to the calculated value. The "Number" column shows that Cs_2TeBr_6 has a face-centered cubic structure.

TABLE 26

Indexed Diffraction Data of CdTe

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.04620	0.04300	3	1	1	1
0.11980	0.11468	8	2	2	0
0.16150	0.15768	11	3	1	1
0.17900	0.17202	12	2	2	2
0.23400	0.22935	16	4	0	0
0.27500	0.27236	19	3	3	1
0.34600	0.34403	24	4	2	2
0.39100	0.38703	27	5	1	1
0.46100	0.45871	32	4	4	0
0.50400	0.50171	35	5	3	1
0.57500	0.57338	40	6	2	0
0.61600	0.61639	43	5	3	3
0.68800	0.68806	48	4	4	4
0.72900	0.73107	51	7	1	1
0.79900	0.80274	56	6	4	2
0.84000	0.84574	59	7	3	1

PARAMETER= 0.01433 STANDARD DEVIATION=0.003644
THIS IS A CUBIC CRYSTAL POWDER PATTERN

Example H

This example, chosen from Azaroff and Donahue,[57] illustrates the indexing of the NiO powder pattern. The powder photograph was taken in a cylindrical camera having a diameter of 57.3 mm. with CuKα radiation. Nine reflection lines were found from the powder photograph. The measurements of arc lengths from the powder film reader are listed in Table 28. The indexed powder diffraction data is recorded in Table 29. The standard deviation,

TABLE 27

Indexed Diffraction Data of Cs_2TeBr_6

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.01490	0.01498	3	1	1	1
0.01990	0.01997	4	2	0	0
0.03990	0.03994	8	2	2	0
0.05470	0.05491	11	3	1	1
0.05970	0.05990	12	2	2	2
0.07990	0.07987	16	4	0	0
0.09470	0.09485	19	3	3	1
0.11970	0.11981	24	4	2	2
0.13470	0.13478	27	5	1	1
0.15980	0.15974	32	4	4	0
0.17460	0.17472	35	5	3	1
0.19990	0.19968	40	6	2	0
0.21970	0.21965	44	6	2	2
0.23970	0.23962	48	4	4	4

PARAMETER= 0.00499 STANDARD DEVIATION=0.000124
THIS IS A CUBIC CRYSTAL POWDER PATTERN

TABLE 28

The Arc Lengths Measured
from the Powder Pattern of NiO

DIFFRACTION LINE	ARC LENGTH	DIFFRACTION LINE	ARC LENGTH
1	3.740	6	10.700
2	4.345	7	11.115
3	6.310	8	12.935
4	7.560	9	14.700
5	7.970		

0.000988, shows that the experimental data is close to the calculated value. The "Number" column shows that NiO has a face-centered cubic structure.

Example I

This example, chosen from Klug and Alexander,[58] illustrates the indexing of the Tantalum powder pattern. There were nine reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 30. The standard deviation, 0.002841, shows that the experimental data is not very close to the calculated value. The maximum discrepancy is about ±0.00389. The "Number" column shows that tantalum has a body-centered cubic structure.

The Tetragonal System

The Use of the Main Computer Program TET

The main computer program TET for indexing the unknown powder patterns of tetragonal crystals and the flow chart are given in Appendix B.

For the input of the computer program TET, M stands for the total number of the powder patterns to be indexed as tetragonal structure, K stands for the total number of the reflection lines in each powder pattern, L1 stands for the total number of the possible parameters of P_j, L2 stands for the total number of

TABLE 29

Indexed Diffraction Data of NiO

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.10277	0.10217	3	1	1	1
0.13699	0.13622	4	2	0	0
0.27374	0.27245	8	2	2	0
0.37560	0.37461	11	3	1	1
0.41054	0.40867	12	2	2	2
0.64612	0.64706	19	3	3	1
0.68033	0.68111	20	4	2	0
0.81696	0.81734	24	4	2	2
0.91928	0.91950	27	5	1	1

PARAMETER= 0.03406 STANDARD DEVIATION=0.000988
THIS IS A CUBIC CRYSTAL POWDER PATTERN

TABLE 30

Indexed Diffraction Data of Tantalum

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.11265	0.10906	2	1	1	0
0.22200	0.21811	4	2	0	0
0.33099	0.32717	6	2	1	1
0.43944	0.43622	8	2	2	0
0.54732	0.54528	10	3	1	0
0.65538	0.65434	12	2	2	2
0.76183	0.76339	14	3	2	1
0.87054	0.87245	16	4	0	0
0.97862	0.98150	18	4	1	1

PARAMETER= 0.05453 STANDARD DEVIATION=0.002841
THIS IS A CUBIC CRYSTAL POWDER PATTERN

the possible parameters of Q_m, T(J) stands for all the observed $Sin^2\theta$ values, P1(J) stands for all the possible parameters of P_j, and P2(J) stands for all the possible parameters of Q_m.

The output of the computer program contains the observed $Sin^2\theta$ values, calculated $Sin^2\theta$ values, $s=h^2+k^2+l^2$ integral numbers, and the Miller indices of the reflections.

Example A

This example, chosen from D'Eye and Wait,[56] indexes the TiO_2 powder pattern. Observed $Sin^2\theta$ values are listed in Table 31. The indexing procedures may be described as follows. (1) The set of observed $Sin^2\theta$ values is the input of the computer program DA. The output, listed in Table 32, is a difference table. (2) One can easily select the recurrent values and form seven groups: 0.0166 (0.0164, 0.0166, 0.0167), 0.02835 (0.0283, 0.0284), 0.0563 (0.0563, 0.0563), 0.0680 (0.0680, 0.0680), 0.0864 (0.0844, 0.0847, 0.0847), 0.1129 (0.1128, 0.1130), and 0.1691 (0.1691, 0.1691). However, we may find that the ratios 0.02835 : 0.0563 : 0.0846 : 0.1129 : 0.1691 = 1 : 2 : 3 : 4 : 6. This assures us that the possible parameter P=0.02835. (3) It seems that the ratio 0.0116 : 0.0680 = 1 : 4, but 4×0.0116=0.0664. The value 0.0664 is not too close to 0.0680 for such a small value; therefore, Q does not necessarily have to be 0.0166. (4) Since P=0.02835, the $Sin^2\theta$ value of the first reflection line is 0.0565

TABLE 31

$Sin^2\theta$ Values Calculated from the Powder Pattern of TiO_2

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.05650	6	0.20920
2	0.09620	7	0.22560
3	0.11280	8	0.27200
4	0.12450	9	0.28190
5	0.14120		

TABLE 32

Difference Table of the Powder Diffraction Data of TiO_2

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00990	0.01170	0.01640	0.01660	0.01670	0.02830	0.02840	0.03970
0.04500	0.04640	0.05630	0.05630	0.06280	0.06800	0.06800	0.07270
0.08440	0.08470	0.08470	0.09640	0.10110	0.11280	0.11300	0.12940
0.13080	0.14070	0.14750	0.15270	0.15740	0.15920	0.16910	0.16910
0.17580	0.18570	0.21550	0.22540				

(=2×0.02835). Consider 0.0962, the observed $Sin^2\theta$ value of the second reflection line. If its Miller index is (101), then the possible Q is 0.06785; if it is (001), then Q is 0.0962; if it is (002), then Q is 0.0241; if it is (003), then Q is 0.0107, etc.

(5) Actually, comparing the difference analysis with the consideration in step (4), we may select the possible Q as 0.0680.

However, several possible values of Q may be inputted into the computer program TET. The indexed powder pattern is then recorded in Table 33.

Comparing the "Number" column in Table 33 with the permissible integral number listed in Table 4, we may conclude that TiO_2 has a simple tetragonal structure. The standard deviation, 0.000105, shows that the experimental data and the calculated value are quite agreeable.

Example B

This example, chosen from Henry, Lipson and Wooster,[59] indexes the $CuAl_2$ powder pattern. Observed $Sin^2\theta$ values are listed in Table 34. The indexing procedures may be described as follows. (1) The set of $Sin^2\theta$ values is the input of the computer program DA. The output, listed in Table 35, is a difference table. (2) In Table 35, only five recurrent value groups can be found. They are 0.0436 (0.0434, 0.0437, 0.0437), 0.0876 (0.0872, 0.0879), 0.1310 (0.1306, 0.1309, 0.1316), 0.1352 (0.1350, 0.1350, 0.1357), and 0.2669 (0.2666, 0.2672). (3) The ratios 0.0436 : 0.0876 : 0.1310 : 0.1767 : 0.2669 = 1 : 2 : 3 : 4 : 6 (where 0.1767 is the $Sin^2\theta$ value of the 4-th reflection line); thus, the possible P is either 0.0436 or 0.0218. (4) If the possible P= 0.0436, consider $Sin^2\theta_3$=0.1449 (since the $Sin^2\theta$ values of the first two reflection lines are the multiple of P). If 0.1449

TABLE 33

Indexed Diffraction Data of TiO_2

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.05650	0.05641	2	1	1	0
0.09620	0.09622	2	1	0	1
0.11280	0.11282	4	2	0	0
0.12450	0.12442	3	1	1	1
0.14120	0.14103	5	2	1	0
0.20920	0.20904	6	2	1	1
0.22560	0.22564	8	2	2	0
0.27200	0.27205	4	0	0	2
0.28190	0.28205	10	3	1	0

P= 0.02821 Q= 0.06801

STANDARD DEVIATION=0.000105

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TABLE 34

$Sin^2\theta$ Values Calculated
from the Powder Pattern of $CuAl_2$

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.04450	6	0.22040
2	0.08880	7	0.22450
3	0.14490	8	0.31170
4	0.17670	9	0.35540
5	0.18110		

TABLE 35

Difference Table of the Powder Diffraction Data of $CuAl_2$

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00410	0.00440	0.03180	0.03620	0.03930	0.04340	0.04370	0.04370
0.04430	0.04780	0.05610	0.07550	0.07960	0.08720	0.08790	0.09130
0.09230	0.10040	0.13060	0.13090	0.13160	0.13220	0.13500	0.13500
0.13570	0.13660	0.16680	0.17430	0.17590	0.17870	0.18000	0.21050
0.22290	0.26660	0.26720	0.31090				

belongs to the (002) plane, then Q is 0.0362; if it belongs to (003), then Q is 0.0161; if it belongs to (102), then Q is 0.0253; if it belongs to (111), then Q is 0.0613; if it belongs to (112), then Q is 0.0153, etc. However, the only recurrent value group left, 0.1352, that could give some hint for the possible values of Q such as 0.0451 (=1/3×0.1352) or 0.0338 (=¼×0.1352) does not correlate with the values mentioned above. (5) Next, let the possible P=0.0218. Again, 0.1449 is considered. If 0.1449 belongs to (102), then Q is 0.0308; if it belongs to (211), then Q is 0.0359; the rest are identical to those mentioned in step (4). (6) Now, let the possible P=0.0436 and 0.0218 and the possible Q=0.0362, 0.0161, 0.0253, 0.0613, 0.0308, 0.0359, 0.0451, and 0.0338 be the input of the computer program TET; the indexed powder diffraction data is then recorded in Table 36.

The "Number" column in Table 36 shows that $CuAl_2$ has a

TABLE 36

Indexed Diffraction Data of $CuAl_2$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.04450	0.04407	2	1	1	0
0.08880	0.08814	4	2	0	0
0.14490	0.14418	6	2	1	1
0.17670	0.17628	8	2	2	0
0.18110	0.18008	6	1	1	2
0.22040	0.22035	10	3	1	0
0.22450	0.22415	8	2	0	2
0.31170	0.31229	12	2	2	2
0.35540	0.35636	14	3	1	2

P= 0.02204 Q= 0.03400

STANDARD DEVIATION=0.000646

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body-centered tetragonal structure. The standard deviation, 0.000646, shows that the experimental data is not quite as good as that in Example A. The maximum discrepancy between the experimental data and the calculated value is ±0.00102.

Example C

This example, chosen from Hesse[25] (originated from Kiessling[60]), indexes the MoB powder pattern. Observed $\sin^2\theta$ values are listed in Table 37. The difference table, calculated by the computer program DA, is recorded in Table 38. From the difference table, several recurrent value groups can be selected. They are 0.0394 (0.0391, 0.0396), 0.0687 (0.0685, 0.0689), 0.1095

TABLE 37

$Sin^2\theta$ Values Calculated
from the Powder Pattern of MoB

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.07320	7	0.43610
2	0.14060	8	0.50500
3	0.17710	9	0.54410
4	0.25020	10	0.61650
5	0.29100	11	0.65610
6	0.35950		

TABLE 38

Difference Table of the Powder Diffraction Data of MoB

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.03650	0.03910	0.03960	0.04080	0.06740	0.06850	0.06890	0.07240
0.07310	0.07660	0.10390	0.10800	0.10930	0.10960	0.11150	0.11200
0.11390	0.14510	0.14550	0.15040	0.15110	0.17700	0.18040	0.18240
0.18460	0.18590	0.21400	0.21780	0.21890	0.22000	0.25310	0.25480
0.25700	0.25900	0.28630	0.29390	0.29550	0.29660	0.32550	0.32790
0.36290	0.36440	0.36510	0.36630	0.36700	0.40350	0.40590	0.43180
0.43940	0.47090	0.47590	0.47900	0.51550	0.54330	0.58290	

(0.1093, 0.1096), 0.1118 (0.1115, 0.1120), 0.1453 (0.1451, 0.1455), 0.1508 (0.1504, 0.1511), and 0.2190 (0.2178, 0.2189, 0.2200). However, the only information provided by the recurrent value group is that 0.0394 : 0.0732 : 0.1118 = 9 : 16 : 25 (where 0.0732 is the $Sin^2\theta$ value of the first reflection line). This implies

that a possible Q is 0.00439. Next, consider the $Sin^2\theta$ value of the second reflection line, 0.1406, which is not a multiple of Q. If 0.1406 belongs to the (100) plane, then the possible P is 0.1406; if it belongs to (200), then P is 0.0352; if it belongs to (101), then P is 0.13521; if it belongs to (201), then P is 0.0338; if it belongs to (102), then P is 0.1230; if it belongs to (103), then P is 0.1008; if it belongs to (202), then P is 0.0308; if it belongs to (203), then P is 0.0252, etc. This almost covers all possibilities for the possible parameter P. Hence, let P = 0.1406, 0.0352, 0.1352, 0.0338, 0.1230, 0.1008, 0.0308, 0.0252 and the possible Q = 0.00439 be the input of the computer program TET; the indexed powder diffraction data is then recorded in Table 39.

The "Number" column in Table 39 shows that MoB has a body-centered structure. The standard deviation, 0.0003, shows that the experimental data and the calculated value are quite agreeable. The final calculated parameters, P=0.13602 and Q=0.00456, shows that the ratio c/a is approximately equal to 5.42.

Example D

This example, chosen from Halteman,[61] indexes the U_2Mo powder pattern. There were twenty-three reflection lines to be indexed. The indexing procedures are similar to the previous

TABLE 39

Indexed Diffraction Data of MoB

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.07320	0.07291	16	0	0	4
0.14060	0.14058	2	1	0	1
0.17710	0.17703	10	1	0	3
0.25020	0.24994	26	1	0	5
0.29100	0.29027	6	1	1	2
0.35950	0.35930	50	1	0	7
0.43610	0.43608	38	1	1	6
0.50500	0.50511	82	1	0	9
0.54410	0.54409	4	2	0	0
0.61650	0.61699	20	2	0	4
0.65610	0.65616	144	0	0	12

A= 0.13602 C= 0.00456

STANDARD DEVIATION=0.000300

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examples. The indexed powder diffraction data is recorded in Table 40. The standard deviation, 0.000533, shows that the experimental data is not very close to the calculated value. The maximum discrepancy is about ±0.00149. The "Number" column shows that U_2Mo has a body-centered tetragonal structure. Consider the 21st reflection line, however. Its $h^2+k^2+l^2=21$, which is the only odd integer among the numbers in the "Number" column. This implies that a revision is needed. To accomplish this, one should either re-measure the 21st reflection line from the powder photograph or find the appropriate Miller index (hkl) which its $Sin^2\theta$

TABLE 40

Indexed Diffraction Data of U_2Mo

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.02460	0.02450	4	0	0	2
0.05670	0.05661	2	1	0	1
0.10130	0.10097	2	1	1	0
0.10560	0.10561	10	1	0	3
0.12570	0.12547	6	1	1	2
0.20220	0.20194	4	2	0	0
0.22060	0.22048	36	0	0	6
0.25850	0.25855	6	2	1	1
0.30780	0.30755	14	2	1	3
0.32160	0.32145	38	1	1	6
0.39300	0.39196	64	0	0	8
0.40460	0.40389	8	2	2	0
0.42260	0.42242	40	2	0	6
0.50600	0.50486	10	3	1	0
0.50800	0.50949	18	3	0	3
0.54630	0.54656	82	1	0	9
0.71140	0.71143	22	3	2	3
0.72470	0.72533	46	3	1	6
0.74820	0.74850	86	2	1	9
0.80820	0.80777	16	4	0	0
0.88250	0.88276	21	4	1	2
0.90900	0.90874	18	3	3	0
0.91300	0.91338	26	4	1	3

P= 0.05049 Q= 0.00612

STANDARD DEVIATION=0.000533

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value is next to (412) and the $h^2+k^2+l^2$ is even. According to the original published paper, the 21st reflection line is belonged to the (00,12) plane. But then, $Sin^2\theta_{00,12}$ is 0.88128.

Example E

This example, chosen from Zachariasen,[62] indexes the YOF powder pattern. There were twenty-seven reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 41. The standard deviation, 0.000896, shows that the experimental data is not very close to the calculated value. The maximum discrepancy is about ±0.00178. However, the solution agrees with the published paper. The "Number" column shows that YOF has a simple tetragonal structure.

Example F

This example, also chosen from Zachariasen,[62] indexes the LaOF powder pattern. There were thirty-three reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 42. The standard deviation, 0.000254, shows that the experimental data is fairly close to the calculated value. The maximum discrepancy is about ±0.00071. The "Number" column shows that LaOF has a simple tetragonal structure.

Example G

This example, chosen from Bartlett and Maitland,[63] indexes the PdF_2 powder pattern. There were twenty-six reflection lines to be indexed. The indexed diffraction data is recorded in Table 43. The standard deviation, 0.000854, shows that the experimental data is not very close to the calculated value. The maximum

TABLE 41

Indexed Diffraction Data of YOF

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.02030	0.02014	1	0	0	1
0.05990	0.05901	2	1	0	1
0.07850	0.07774	2	1	1	0
0.08120	0.08054	4	0	0	2
0.11980	0.11941	5	1	0	2
0.15680	0.15548	4	2	0	0
0.15870	0.15828	6	1	1	2
0.17580	0.17562	5	2	0	1
0.18300	0.18122	9	0	0	3
0.21540	0.21449	6	2	1	1
0.22100	0.22009	10	1	0	3
0.23680	0.23603	8	2	0	2
0.25930	0.25897	11	1	1	3
0.27550	0.27490	9	2	1	2
0.31190	0.31096	8	2	2	0
0.32380	0.32218	16	0	0	4
0.33690	0.33671	13	2	0	3
0.35950	0.36105	17	1	0	4
0.36980	0.36997	10	3	0	1
0.37500	0.37558	14	2	1	3
0.38960	0.38870	10	3	1	0
0.42890	0.43038	13	3	0	2
0.46860	0.46925	14	3	1	2
0.47650	0.47766	20	2	0	4
0.50350	0.50340	25	0	0	5
0.51570	0.51653	21	2	1	4
0.52510	0.52545	14	3	2	1

P= 0.03887 Q= 0.02014

STANDARD DEVIATION=0.000896

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discrepancy is about ±0.00139. The "Number" column shows that PdF_2 has a simple tetragonal structure.

TABLE 42

Indexed Diffraction Data of LaOF

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.01730	0.01738	1	0	0	1
0.05270	0.05279	2	1	0	1
0.06940	0.06951	4	0	0	2
0.07060	0.07083	2	1	1	0
0.08800	0.08820	3	1	1	1
0.10490	0.10492	5	1	0	2
0.14030	0.14034	6	1	1	2
0.14180	0.14165	4	2	0	0
0.15650	0.15640	9	0	0	3
0.15890	0.15903	5	2	0	1
0.19220	0.19181	10	1	0	3
0.19440	0.19444	6	2	1	1
0.21120	0.21116	8	2	0	2
0.22710	0.22722	11	1	1	3
0.24700	0.24657	9	2	1	2
0.27800	0.27804	16	0	0	4
0.28350	0.28330	8	2	2	0
0.29820	0.29805	13	2	0	3
0.31370	0.31346	17	1	0	4
0.33330	0.33346	14	2	1	3
0.33520	0.33609	10	3	0	1
0.34880	0.34887	18	1	1	4
0.35380	0.35413	10	3	1	0
0.37190	0.37150	11	3	1	1
0.38840	0.38822	13	3	0	2
0.41990	0.41969	20	2	0	4
0.42350	0.42364	14	3	1	2
0.43420	0.43444	25	0	0	5
0.44010	0.43970	17	2	2	3
0.45490	0.45511	21	2	1	4
0.46970	0.46985	26	1	0	5
0.47520	0.47511	18	3	0	3
0.47780	0.47774	14	3	2	1

P= 0.03541 Q= 0.01738

STANDARD DEVIATION=0.000254

THIS IS A TETRAGONAL CRYSTAL POWDER PATTERN

TABLE 43

Indexed Diffraction Data of PdF_2

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.07730	0.07643	2	1	1	0
0.12110	0.12000	2	1	0	1
0.15400	0.15287	4	2	0	0
0.15910	0.15821	3	1	1	1
0.19150	0.19109	5	2	1	0
0.27410	0.27287	6	2	1	1
0.30660	0.30574	8	2	2	0
0.32830	0.32711	4	0	0	2
0.38300	0.38217	10	3	1	0
0.40450	0.40355	6	1	1	2
0.42680	0.42573	10	3	0	1
0.48070	0.47998	8	2	0	2
0.51880	0.51820	9	2	1	2
0.57900	0.57860	14	3	2	1
0.61200	0.61148	16	4	0	0
0.63310	0.63285	12	2	2	2
0.65070	0.64970	17	4	1	0
0.68730	0.68791	18	3	3	0
0.70880	0.70929	14	3	1	2
0.73100	0.73147	18	4	1	1
0.76390	0.76435	20	4	2	0
0.77430	0.77422	10	1	0	3
0.81260	0.81244	11	1	1	3
0.84510	0.84613	21	4	2	1
0.92570	0.92709	14	2	1	3
0.93720	0.93859	20	4	0	2

P= 0.03822 Q= 0.08178

STANDARD DEVIATION=0.000854

THIS IS A TETRAGONAL CRYSTAL POWDER PATTERN

Example H

This example, chosen from Parthe and Norton,[64] indexes the Cr_5Ge_3 powder pattern. There were thirty-one reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 44. The standard deviation, 0.000874, shows that the experimental data is not close to the calculated value. The maximum discrepancy is about ±0.00286. The "Number" column shows that Cr_5Ge_3 has a body-centered tetragonal structure. Consider the 9th reflection line, however. Its $h^2+k^2+l^2=17$, which is the only odd integer among the numbers in the "Number" column. The remedy has been mentioned in Example D. According to the published paper, (420) was assigned. As to the 17th and 23rd reflection lines, (600) and (413) were assigned originally. However, better solutions, (103) and (640), are suggested.

Example I

This example, chosen from Mooney,[65] indexes the $ScPO_4$ powder pattern. There were thirty-seven reflection lines to be indexed. The indexed diffraction data is recorded in Table 45. The standard deviation, 0.000240, shows that the experimental data is fairly close to the calculated value. The "Number" column shows that $ScPO_4$ has a body-centered tetragonal structure.

TABLE 44

Indexed Diffraction Data of Cr_5Ge_3

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.11920	0.11827	8	2	2	0
0.13080	0.13144	6	2	1	1
0.14770	0.14783	10	3	1	0
0.23060	0.23011	4	0	0	2
0.23650	0.23653	16	4	0	0
0.25000	0.24971	14	3	2	1
0.26680	0.26610	18	3	3	0
0.28870	0.28924	8	2	0	2
0.29500	0.29406	17	4	0	1
0.30890	0.30884	18	4	1	1
0.34880	0.34837	12	2	2	2
0.46690	0.46664	20	4	0	2
0.47380	0.47307	32	4	4	0
0.48600	0.48624	30	5	2	1
0.49650	0.49621	22	3	3	2
0.50170	0.50263	34	5	3	0
0.53310	0.53252	10	1	0	3
0.59130	0.59133	40	6	2	0
0.70500	0.70317	36	4	4	2
0.72230	0.72277	46	6	3	1
0.73630	0.73916	50	7	1	0
0.76200	0.76230	40	6	0	2
0.76740	0.76873	52	6	4	0
0.82170	0.82144	44	6	2	2
0.84160	0.84104	54	7	2	1
0.85830	0.85743	58	7	3	0
0.91880	0.92043	16	0	0	4
0.94710	0.94646	38	5	2	3
0.95990	0.95931	62	6	5	1
0.96950	0.96927	54	7	1	2
0.97970	0.97956	20	2	0	4

P= 0.01478 Q= 0.05753

STANDARD DEVIATION=0.000874

THIS IS A TETRAGONAL CRYSTAL POWDER PATTERN

TABLE 45

Indexed Diffraction Data of $ScPO_4$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.03130	0.03136	2	1	0	1
0.05480	0.05482	4	2	0	0
0.08610	0.08618	6	2	1	1
0.09800	0.09803	6	1	1	2
0.10960	0.10963	8	2	2	0
0.12540	0.12544	8	2	0	2
0.14090	0.14099	10	3	0	1
0.17250	0.17261	10	1	0	3
0.19570	0.19581	14	3	2	1
0.20760	0.20767	14	3	1	2
0.21920	0.21926	16	4	0	0
0.22730	0.22743	14	2	1	3
0.25050	0.25063	18	4	1	1
0.27400	0.27408	20	4	2	0
0.28220	0.28225	18	3	0	3
0.28980	0.28989	20	4	0	2
0.31720	0.31730	22	3	3	2
0.33700	0.33706	22	3	2	3
0.34460	0.34471	24	4	2	2
0.36010	0.36026	26	5	0	1
0.39230	0.39214	24	2	2	4
0.41490	0.41507	30	5	2	1
0.41920	0.41955	26	3	1	4
0.42680	0.42693	30	5	1	2
0.43860	0.43853	32	4	4	0
0.45470	0.45512	26	1	0	5
0.46490	0.46594	34	5	3	0
0.49360	0.49335	36	6	0	0
0.50200	0.50177	32	4	0	4
0.51010	0.50993	30	2	1	5
0.52490	0.52471	38	6	1	1
0.53680	0.53656	38	5	3	2
0.54840	0.54816	40	6	2	0
0.55680	0.55659	36	4	2	4
0.56420	0.56397	40	6	0	2
0.56500	0.56475	34	3	0	5
0.57980	0.57952	42	5	4	1

P= 0.01370 Q= 0.01766

STANDARD DEVIATION=0.000240

THIS IS A TETRAGONAL CRYSTAL POWDER PATTERN

The Hexagonal System

The Use of the Main Computer Program HEX

The main computer program HEX for indexing the unknown powder patterns of hexagonal crystals and the flow chart are given in Appendix C.

For the input of the computer program HEX, M stands for the total number of the powder patterns to be indexed as hexagonal structure, K stands for the total number of the reflection lines in each powder pattern, L1 stands for the total number of the possible parameter of P_j, L2 stands for the total number of the possible parameters of Q_m, T(J) stands for all the observed $Sin^2\theta$ values, P1(J) stands for all the possible parameters of P_j, and P2(J) stands for all the possible parameters of Q_m.

The output of the computer program contains the observed $Sin^2\theta$ values, calculated $Sin^2\theta$ values, and the Miller indices of the reflections.

Example A

This example, chosen from Azaroff,[66] indexes the GeO_2 powder pattern. Observed $Sin^2\theta$ values are listed in Table 46. The indexing procedures may be described as follows. (1) The set of $Sin^2\theta$ values is the input of the computer program DA. The output, listed in Table 47, is a difference table. (2) One can easily select the recurrent values and the first twelve

TABLE 46

$Sin^2\theta$ Values Calculated
from the Powder Pattern of GeO_2

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.05360	16	0.50020
2	0.08500	17	0.51390
3	0.16060	18	0.55440
4	0.17860	19	0.60750
5	0.19190	20	0.64310
6	0.21450	21	0.65670
7	0.24560	22	0.65990
8	0.28170	23	0.67290
9	0.28600	24	0.69680
10	0.33570	25	0.72810
11	0.33960	26	0.76680
12	0.37500	27	0.78170
13	0.40670	28	0.82200
14	0.44400	29	0.83560
15	0.49590	30	0.87610

recurrent value groups can be listed as: 0.0134 (0.0130, 0.0133, 0.0136, 0.0136, 0.0137), 0.0314 (0.0311, 0.0313, 0.0313, 0.0314, 0.0317), 0.0403 (0.0401, 0.0403, 0.0404, 0.0405, 0.0405), 0.0538 (0.0536, 0.0536, 0.0537, 0.0537, 0.0539, 0.0539, 0.0540, 0.0541, 0.0542), 0.0938 (0.0933, 0.0935, 0.0936, 0.0936, 0.0939, 0.0939, 0.0940, 0.0941, 0.0944), 0.1072 (0.1069, 0.1069, 0.1070, 0.1072, 0.1073, 0.1074, 0.1075), 0.1209 (0.1206, 0.1207, 0.1209, 0.1211, 0.1212), 0.1251 (0.1250, 0.1250, 0.1250, 0.1251, 0.1252, 0.1252, 0.1254), 0.1608 (0.1605, 0.1606, 0.1606, 0.1608, 0.1609, 0.1610,

TABLE 47

Difference Table of the Powder Diffraction Data of GeO_2

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00320	0.00390	0.00430	0.00430	0.01300	0.01330	0.01360	0.01360
0.01370	0.01490	0.01620	0.01680	0.01800	0.01800	0.02260	0.02390
0.02980	0.03110	0.03130	0.03130	0.03140	0.03170	0.03540	0.03560
0.03590	0.03610	0.03690	0.03730	0.03870	0.03930	0.04010	0.04030
0.04040	0.04050	0.04050	0.04920	0.04970	0.05190	0.05240	0.05310
0.05360	0.05360	0.05370	0.05370	0.05390	0.05390	0.05400	0.05410
0.05420	0.05520	0.05520	0.05620	0.05790	0.05850	0.06540	0.06700
0.06710	0.06720	0.06820	0.06880	0.06900	0.06990	0.07000	0.07100
0.07140	0.07150	0.07560	0.08490	0.08500	0.08500	0.08870	0.08900
0.08920	0.08930	0.08980	0.09010	0.09330	0.09350	0.09360	0.09360
0.09390	0.09390	0.09400	0.09410	0.09440	0.10230	0.10310	0.10440
0.10550	0.10690	0.10690	0.10700	0.10720	0.10730	0.10740	0.10750
0.10830	0.10880	0.10930	0.11010	0.11040	0.11160	0.11850	0.12060
0.12070	0.12090	0.12110	0.12120	0.12180	0.12370	0.12500	0.12500
0.12500	0.12510	0.12520	0.12520	0.12540	0.12920	0.12940	0.12950
0.13830	0.13860	0.13880	0.13890	0.14240	0.14280	0.14290	0.14380
0.14600	0.14720	0.14770	0.14770	0.14800	0.14910	0.15630	0.15650
0.15710	0.15800	0.15900	0.15930	0.15970	0.16020	0.16050	0.16060
0.16060	0.16080	0.16090	0.16100	0.16110	0.16210	0.16230	0.16270
0.16350	0.16400	0.16450	0.16530	0.17270	0.17370	0.17420	0.17430
0.17510	0.17570	0.17700	0.17820	0.17890	0.17890	0.17900	0.17930
0.17940	0.18290	0.18310	0.19200	0.19220	0.19250	0.19640	0.19660
0.19670	0.19840	0.19910	0.20080	0.20090	0.20100	0.20320	0.20990
0.21240	0.21270	0.21420	0.21420	0.21420	0.21440	0.21450	0.21480
0.21480	0.21590	0.21620	0.21850	0.21870	0.21940	0.22730	0.22790
0.22790	0.22810	0.22810	0.22810	0.22890	0.22950	0.23220	0.23220
0.23240	0.23250	0.23300	0.23640	0.24610	0.25000	0.25030	0.25070
0.25210	0.25280	0.25290	0.25320	0.25460	0.25460	0.26540	0.26620
0.26660	0.26760	0.26780	0.26790	0.26810	0.26830	0.26840	0.26860
0.27090	0.27180	0.27270	0.28120	0.28140	0.28150	0.28170	0.28210
0.28340	0.28410	0.28490	0.28570	0.28580	0.28600	0.29000	0.29010
0.29790	0.29940	0.30350	0.30400	0.30740	0.30810	0.30830	0.30880
0.31710	0.31730	0.32030	0.32100	0.32140	0.32140	0.32150	0.32160
0.32170	0.32170	0.32170	0.32180	0.32180	0.32200	0.32280	0.32420
0.32580	0.32610	0.33330	0.33530	0.33530	0.33540	0.33720	0.33770
0.33960	0.33970	0.33990	0.35310	0.35310	0.35330	0.35710	0.35720
0.35900	0.36010	0.36110	0.36140	0.36190	0.36220	0.36250	0.37070
0.37390	0.37500	0.37500	0.37580	0.37590	0.37800	0.37820	0.38020
0.38690	0.38850	0.39040	0.39120	0.39160	0.39180	0.39240	0.39300
0.39380	0.39750	0.40670	0.41080	0.41090	0.41110	0.41430	0.41510
0.41520	0.41530	0.41560	0.42720	0.42730	0.42860	0.42890	0.42890
0.42890	0.43110	0.43210	0.44210	0.44210	0.44220	0.44230	

0.1611), 0.1791 (0.1789, 0.1789, 0.1790, 0.1793, 0.1794), 0.2144 (0.2142, 0.2142, 0.2142, 0.2144, 0.2145, 0.2148, 0.2148), 0.2280 (0.2279, 0.2279, 0.2281, 0.2281, 0.2281), and 0.2324 (0.2322, 0.2322, 0.2324, 0.2325, 0.2330). However, we may find that the ratios 0.0538 : 0.1072 : 0.1608 : 0.2144 = 1 : 2 : 3 : 4 and the ratios 0.0314 : 0.0938 : 0.1251 = 1 : 3 : 4. This assures us that the possible parameter P=0.0538 and the parameter Q=0.0314. (3) Consider the $Sin^2\theta$ value of the second reflection line, 0.085; it seems to belong to the (101) plane. (4) Let the possible P= 0.0538 and Q=0.0314 be the input of the computer program HEX; the indexed powder diffraction data is then recorded in Table 48.

The standard deviation, 0.000573, shows that the discrepancy between the experimental data and the calculated value is reasonable. The maximum discrepancy is about ±0.0005.

Example B

This example, chosen from Runnalls and Boucher,[67] indexes the β-$PuSi_2$ powder pattern. Observed $Sin^2\theta$ values are listed in Table 49. The indexing procedures may be described as follows. (1) The set of $Sin^2\theta$ values is the input of the computer program DA. The output, listed in Table 50, is a difference table. (2) One can easily select the recurrent value group are 0.0156 (0.0152, 0.0152, 0.0159, 0.0159), 0.0355 (0.0352, 0.0352, 0.0357, 0.0359), 0.0526 (0.0523, 0.0525, 0.0525, 0.0526, 0.0526, 0.0527, 0.0527,

TABLE 48

Indexed Diffraction Data of GeO_2

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.05360	0.05358	1	0	0
0.08500	0.08486	1	0	1
0.16060	0.16073	1	1	0
0.17860	0.17871	1	0	2
0.19190	0.19201	1	1	1
0.21450	0.21431	2	0	0
0.24560	0.24559	2	0	1
0.28170	0.28156	0	0	3
0.28600	0.28587	1	1	2
0.33570	0.33513	1	0	3
0.33960	0.33944	2	0	2
0.37500	0.37504	2	1	0
0.40670	0.40632	2	1	1
0.44400	0.44228	1	1	3
0.49590	0.49586	2	0	3
0.50020	0.50017	2	1	2
0.51390	0.51347	3	0	1
0.55440	0.55412	1	0	4
0.60750	0.60732	3	0	2
0.64310	0.64292	2	2	0
0.65670	0.65659	2	1	3
0.65990	0.66127	1	1	4
0.67290	0.67420	2	2	1
0.69680	0.69649	3	1	0
0.72810	0.72778	3	1	1
0.76680	0.76805	2	2	2
0.78170	0.78210	0	0	5
0.82200	0.82163	3	1	2
0.83560	0.83567	1	0	5
0.87610	0.87558	2	1	4

P= 0.05358 Q= 0.03128

STANDARD DEVIATION=0.000573

THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN

TABLE 49

$Sin^2\theta$ Values Calculated
from the Powder Pattern of β-$PuSi_2$

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.03640	19	0.57200
2	0.05330	20	0.61580
3	0.08900	21	0.62470
4	0.14380	22	0.63100
5	0.15850	23	0.66770
6	0.19440	24	0.68360
7	0.19650	25	0.68890
8	0.21170	26	0.71880
9	0.24690	27	0.72970
10	0.30140	28	0.77200
11	0.35420	29	0.78220
12	0.36770	30	0.79290
13	0.37440	31	0.82480
14	0.40420	32	0.84070
15	0.47400	33	0.87430
16	0.47970	34	0.93660
17	0.51110	35	0.94260
18	0.53200	36	0.94970

0.0528, 0.0528), 0.1050 (0.1043, 0.1047, 0.1049, 0.1050, 0.1052, 0.1053, 0.1054), 0.1072 (0.1069, 0.1070, 0.1073, 0.1074, 0.1075), 0.1431 (0.1425, 0.1429, 0.1432, 0.1434, 0.1437), 0.1513 (0.1507, 0.1513, 0.1516, 0.1518), 0.1577 (0.1575, 0.1576, 0.1576, 0.1577, 0.1577, 0.1579, 0.1580), 0.1779 (0.1777, 0.1778, 0.1778, 0.1779, 0.1783), and 0.2100 (0.2096, 0.2097, 0.2097, 0.2098, 0.2102, 0.2104, 0.2105). (3) The ratios 0.0526 : 0.1050 : 0.1577 : 0.2100 = 1 : 2 : 3 : 4 and the ratios 0.0355 : 0.1072 : 0.1431 : 0.1779

TABLE 50

Difference Table of the Powder Diffraction Data of β-$PuSi_2$

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00210	0.00530	0.00570	0.00600	0.00630	0.00670	0.00710	0.00890
0.01020	0.01070	0.01090	0.01310	0.01350	0.01470	0.01520	0.01520
0.01590	0.01590	0.01690	0.01730	0.02020	0.02090	0.02090	0.02120
0.02980	0.02990	0.03140	0.03190	0.03360	0.03520	0.03520	0.03570
0.03590	0.03650	0.03670	0.03710	0.03800	0.04000	0.04080	0.04230
0.04260	0.04300	0.04380	0.04610	0.04780	0.04950	0.05000	0.05040
0.05060	0.05110	0.05190	0.05230	0.05250	0.05250	0.05260	0.05260
0.05270	0.05270	0.05280	0.05280	0.05320	0.05320	0.05450	0.05480
0.05790	0.05800	0.05850	0.05890	0.05900	0.06090	0.06200	0.06230
0.06320	0.06340	0.06420	0.06630	0.06780	0.06790	0.06830	0.06870
0.06950	0.06980	0.07300	0.07310	0.07410	0.07540	0.07550	0.08140
0.08310	0.08380	0.08780	0.08840	0.08840	0.08970	0.09050	0.09210
0.09230	0.09270	0.09330	0.09410	0.09510	0.09570	0.09590	0.09800
0.09860	0.09870	0.09900	0.09960	0.10190	0.10230	0.10280	0.10300
0.10310	0.10400	0.10430	0.10470	0.10490	0.10500	0.10520	0.10530
0.10540	0.10600	0.10630	0.10690	0.10700	0.10730	0.10740	0.10750
0.10900	0.10930	0.11100	0.11160	0.11180	0.11200	0.11360	0.11390
0.11450	0.11690	0.11780	0.11980	0.11990	0.12080	0.12190	0.12210
0.12270	0.12490	0.12520	0.12550	0.12750	0.12780	0.13570	0.13590
0.13610	0.13670	0.14100	0.14110	0.14120	0.14180	0.14250	0.14290
0.14320	0.14340	0.14370	0.14460	0.14500	0.14680	0.14730	0.14970
0.15070	0.15120	0.15130	0.15160	0.15180	0.15440	0.15550	0.15600
0.15620	0.15660	0.15680	0.15690	0.15690	0.15700	0.15710	0.15710
0.15730	0.15750	0.15760	0.15760	0.15770	0.15770	0.15790	0.15800
0.15840	0.15980	0.16010	0.16040	0.16190	0.16270	0.16430	0.16460
0.16640	0.16750	0.16780	0.16820	0.17060	0.17120	0.17250	0.17260
0.17300	0.17330	0.17530	0.17710	0.17770	0.17780	0.17780	0.17790
0.17830	0.18000	0.18540	0.18680	0.18800	0.19070	0.19250	0.19360
0.19370	0.19380	0.19570	0.19760	0.19770	0.20000	0.20010	0.20390
0.20430	0.20660	0.20690	0.20770	0.20770	0.20900	0.20920	0.20920
0.20960	0.20970	0.20970	0.20980	0.21020	0.21040	0.21050	0.21160
0.21240	0.21290	0.21490	0.21590	0.21600	0.21780	0.21780	0.21860
0.22000	0.22050	0.22090	0.22380	0.22390	0.22490	0.22680	0.22710
0.23060	0.23060	0.23090	0.23280	0.23910	0.24000	0.24140	0.24330
0.24480	0.24570	0.24770	0.24810	0.24810	0.24960	0.25000	0.25020
0.25030	0.25280	0.25300	0.25370	0.25570	0.25660	0.25700	0.25850
0.25900	0.26040	0.26080	0.26090	0.26090	0.26160	0.26230	0.26330
0.26350	0.26420	0.26500	0.26520	0.26610	0.26800	0.26870	0.26890
0.27050	0.27060	0.27110	0.27490	0.27680	0.27750	0.27870	0.27940
0.27960	0.28180	0.28200	0.28320	0.28470	0.28510	0.28530	0.28540
0.29230	0.29280	0.29330	0.29800	0.29940	0.30000	0.30090	0.30230
0.30250	0.30560	0.30820	0.30870	0.30920	0.31160	0.31190	0.31320
0.31350	0.31370	0.31440	0.31440	0.31450	0.31460	0.31460	0.31520
0.31550	0.31590	0.31670	0.31780	0.31790	0.31870	0.31890	0.32030

TABLE 50 (CONTINUED)

0.32080	0.32110	0.32120	0.32120	0.32330	0.32500	0.32510	0.32550
0.32680	0.32940	0.32960	0.32960	0.33020	0.33130	0.33390	0.33470
0.33650	0.33590	0.33760	0.33800	0.34230	0.34440	0.34510	0.35080
0.35090	0.35110	0.35260	0.35530	0.36030	0.36100	0.36200	0.36320
0.36460	0.36460	0.36630	0.36670	0.36730	0.36780	0.36780	0.36890
0.37060	0.37350	0.37550	0.37550	0.37760	0.37770	0.37780	0.37800
0.38220	0.38410	0.38500	0.38750	0.38820	0.38870	0.39070	0.39460
0.39760	0.40030	0.40410	0.40430	0.40460	0.40780	0.41060	0.41300
0.41350	0.41450	0.41740	0.41770	0.41780	0.41850	0.41930	0.41930
0.42060	0.42070	0.42080	0.42140	0.42210	0.42520	0.42550	0.42640
0.42800	0.42820	0.42820	0.42830	0.43030	0.43150	0.43450	0.43650
0.43660	0.43670	0.43760					

= 1 : 3 : 4 : 5. This assures us that the possible P is 0.0526 and Q is 0.0355. (4) Let P=0.0526 and O=0.0355 be inputs to the computer program HEX; the indexed powder diffraction data is then recorded in Table 51.

The standard deviation, 0.001115, shows that the experimental data is not very close to the calculated value. The maximum discrepancy is about ±0.00209. The calculated $Sin^2\theta$ values in the original published paper were not as accurate as the one calculated by computer method. However, the Miller indices of the reflections for this powder pattern are agreeable.

Example C

This example, chosen from Barabash and Davydov[68] (originated from N. B. S. Circular No. 539[84]), indexes the Zn powder pattern. Observed $Sin^2\theta$ values are listed in Table 52. The

TABLE 51

Indexed Diffraction Data of β-$PuSi_2$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.03640	0.03568	0	0	1
0.05330	0.05253	1	0	0
0.08900	0.08822	1	0	1
0.14380	0.14274	0	0	2
0.15850	0.15760	1	1	0
0.19440	0.19329	1	1	1
0.19650	0.19527	1	0	2
0.21170	0.21014	2	0	0
0.24690	0.24582	2	0	1
0.30140	0.30034	1	1	2
0.35420	0.35288	2	0	2
0.36770	0.36774	2	1	0
0.37440	0.37370	1	0	3
0.40420	0.40342	2	1	1
0.47400	0.47281	3	0	0
0.47970	0.47877	1	1	3
0.51110	0.51048	2	1	2
0.53200	0.53130	2	0	3
0.57200	0.57096	0	0	4
0.61580	0.61555	3	0	2
0.62470	0.62349	1	0	4
0.63100	0.63041	2	2	0
0.66770	0.66610	2	2	1
0.68360	0.68295	3	1	0
0.68890	0.68890	2	1	3
0.71880	0.71863	3	1	1
0.72970	0.72856	1	1	4
0.77200	0.77315	2	2	2
0.78220	0.78109	2	0	4
0.79290	0.79397	3	0	3
0.82480	0.82568	3	1	2
0.84070	0.84055	4	0	0
0.87430	0.87623	4	0	1
0.93660	0.93869	2	1	4
0.94260	0.94465	1	0	5
0.94970	0.95157	2	2	3

P= 0.05253 Q= 0.03568

STANDARD DEVIATION=0.001115

THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN

TABLE 52

$Sin^2\theta$ Values Calculated
from the Powder Pattern of Zn

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.16350	6	0.56360
2	0.18770	7	0.65350
3	0.22870	8	0.72690
4	0.35140	9	0.75120
5	0.55530	10	0.79210

indexing procedures may be described as follows. (1) The set of $Sin^2\theta$ values is the input of the computer program DA. The output, listed in Table 53, is a difference table. (2) One can easily select the recurrent values and form several groups. They are 0.02425 (0.0242, 0.0243), 0.04095 (0.0409, 0.0410), 0.0652 (0.0652, 0.0652), 0.09795 (0.0977, 0.0982), 0.1635 (0.1633, 0.1637), 0.18775 (0.1876, 0.1879), 0.3757 (0.3755, 0.3759), 0.4000 (0.3998, 0.4001), and 0.5634 (0.5634, 0.5634, 0.5635). (3) The ratios 0.04095 : 0.1635 = 1 : 4. The possible parameter Q is assumed to be 0.04095. (4) Since the ratios 0.18775 : 0.3757 : 0.5634 = 1 : 2 : 3. the possible parameter P is 0.18775. (5) Because the $Sin^2\theta$ values of the first two reflections are the multiple of either P or Q, the $Sin^2\theta$ value of the third reflection line, 0.2287, is considered. Since 0.2287≈0.18775 +

TABLE 53

Difference Table of the Powder Diffraction Data of Zn

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00830	0.02420	0.02430	0.04090	0.04100	0.06520	0.06520	0.07340
0.08990	0.09770	0.09820	0.12270	0.13860	0.16330	0.16370	0.17160
0.18760	0.18790	0.19590	0.20390	0.21220	0.22850	0.23680	0.30210
0.32660	0.33490	0.36760	0.37550	0.37590	0.39180	0.39980	0.40010
0.42480	0.44070	0.46580	0.49000	0.49820	0.52250	0.53920	0.56340
0.56340	0.56350	0.58770	0.60440	0.62860			

0.04095, the third reflection may belong to the (101) plane. (6) Let the possible P=0.18775 and Q=0.04095 be the inputs to the computer program HEX; the indexed powder diffraction data is then recorded in Table 54. (7) From Table 54, the final parameter P= 0.18782 and Q=0.04084 show that Zn has a hexagonal close-packed structure. The c/a ratio for a hexagonal close-packed structure is approximately from 1.58 to 1.89; that is, the corresponding P/Q ratio is from 3.3285 to 4.7628. Hence, the parameters P and Q which are recorded in the indexed powder diffraction data may tell whether or not the powder pattern belongs to hexagonal close-packed structure.

The standard deviation, 0.000108, shows that the discrepancy between the experimental data and the calculated value is small. The maximum discrepancy is only about ±0.0002.

TABLE 54

Indexed Diffraction Data of Zn

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.16350	0.16338	0	0	2
0.18770	0.18782	1	0	0
0.22870	0.22867	1	0	1
0.35140	0.35120	1	0	2
0.55530	0.55543	1	0	3
0.56360	0.56347	1	1	0
0.65350	0.65352	0	0	4
0.72690	0.72685	1	1	2
0.75120	0.75129	2	0	0
0.79210	0.79214	2	0	1

P= 0.18782 Q= 0.04084

STANDARD DEVIATION=0.000108

THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN

Example D

This example, chosen from Mooney,[69] indexes the $CePO_4$ powder pattern. Nineteen low angle reflection lines were indexed. The indexing procedures are similar to the previous examples. The indexed diffraction data is recorded in Table 55. The standard deviation, 0.000516, shows that the experimental data is fairly close to the calculated value. The maximum discrepancy is about ±0.00134.

Example E

This example, also chosen from Mooney,[69] indexes the $NdPO_4$

TABLE 55

Indexed Diffraction Data of $CePO_4$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.01600	0.01596	1	0	0
0.03060	0.03026	1	0	1
0.04780	0.04787	1	1	0
0.06410	0.06383	2	0	0
0.07330	0.07317	1	0	2
0.07770	0.07814	2	0	1
0.10510	0.10509	1	1	2
0.11220	0.11171	2	1	0
0.12090	0.12105	2	0	2
0.12600	0.12601	2	1	1
0.12870	0.12873	0	0	3
0.14450	0.14469	1	0	3
0.15810	0.15793	3	0	1
0.16900	0.16892	2	1	2
0.17710	0.17661	1	1	3
0.19040	0.19150	2	2	0
0.19980	0.20084	3	0	2
0.20740	0.20746	3	1	0
0.22310	0.22176	3	1	1

P= 0.01596 Q= 0.01430

STANDARD DEVIATION=0.000516

THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN

powder pattern. Fifteen low angle reflection lines were indexed. The indexed diffraction data is recorded in Table 56. The standard deviation, 0.000318, shows that the experimental data is quite close to the calculated value. The maximum discrepancy is about ±0.00072.

TABLE 56

Indexed Diffraction Data of $NdPO_4$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.01630	0.01632	1	0	0
0.03110	0.03110	1	0	1
0.04890	0.04895	1	1	0
0.06530	0.06527	2	0	0
0.07550	0.07546	1	0	2
0.10790	0.10809	1	1	2
0.11450	0.11423	2	1	0
0.12940	0.12901	2	1	1
0.16170	0.16165	3	0	1
0.17370	0.17337	2	1	2
0.18210	0.18202	1	1	3
0.19650	0.19582	2	2	0
0.20570	0.20600	3	0	2
0.21190	0.21214	3	1	0
0.22620	0.22692	3	1	1

P= 0.01632 Q= 0.01478
STANDARD DEVIATION=0.000318
THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN

Example F

This example, again chosen from Mooney,[69] indexes the $LaPO_4$ powder pattern. Fourteen low angle reflection lines were indexed. The indexed powder diffraction data is recorded in Table 57. The standard deviation, 0.000349, shows that the experimental data is quite close to the calculated value. The maximum discrepancy is about ±0.00076.

TABLE 57

Indexed Diffraction Data of $LaPO_4$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.01600	0.01584	1	0	0
0.03040	0.03006	1	0	1
0.04770	0.04751	1	1	0
0.06410	0.06334	2	0	0
0.07300	0.07272	1	0	2
0.10450	0.10439	1	1	2
0.11130	0.11085	2	1	0
0.12530	0.12507	2	1	1
0.15670	0.15674	3	0	1
0.16760	0.16774	2	1	2
0.19030	0.19002	2	2	0
0.19920	0.19941	3	0	2
0.20580	0.20586	3	1	0
0.21940	0.22008	3	1	1

P= 0.01584 Q= 0.01422

STANDARD DEVIATION=0.000349

THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN

Example G

This example, chosen from Cullity,[55] indexes the Zn powder pattern again. There were thirteen reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 58. The standard deviation, 0.000798, shows that the experimental data is not close to the calculated value. The maximum discrepancy is about ±0.00178. Consider the last reflection line, however. It was assigned to the (212) plane by the original published paper. A better solution for this reflection line is the (006) plane.

TABLE 58

Indexed Diffraction Data of Zn

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.09700	0.09766	0	0	2
0.11200	0.11189	1	0	0
0.13600	0.13630	1	0	1
0.20900	0.20955	1	0	2
0.33200	0.33162	1	0	3
0.39000	0.39063	0	0	4
0.43400	0.43333	1	1	2
0.47200	0.47197	2	0	1
0.54700	0.54522	2	0	2
0.66800	0.66729	2	0	3
0.72200	0.72224	1	0	5
0.80600	0.80764	2	1	1
0.87900	0.87891	0	0	6

P= 0.11189 Q= 0.02441

STANDARD DEVIATION=0.000798

THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN

From the parameters, P=0.11189 and Q=0.02441, Zn has a hexagonal close-packed structure.

Example H

This example, chosen from Schob and Parthe,[70] indexes the Sc_5Ga_3 powder pattern (with $D8_6$ structure). There were thirty-two reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 59. The standard deviation, 0.000448, shows that the experimental data is reasonably close to the calculated value. The maximum discrepancy is about ±0.00087.

TABLE 59

Indexed Diffraction Data of Sc_5Ga_3

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.02720	0.02680	1	0	0
0.08070	0.08039	1	1	0
0.11810	0.11737	1	1	1
0.14770	0.14792	0	0	2
0.17460	0.17472	1	0	2
0.18810	0.18757	2	1	0
0.22480	0.22455	2	1	1
0.22910	0.22831	1	1	2
0.24100	0.24116	3	0	0
0.25450	0.25510	2	0	2
0.34880	0.34834	3	1	0
0.35880	0.35852	2	2	1
0.38580	0.38532	3	1	1
0.38920	0.38908	3	0	2
0.46860	0.46947	2	2	2
0.52090	0.52040	2	1	3
0.54620	0.54609	3	2	1
0.57650	0.57665	4	0	2
0.59200	0.59170	0	0	4
0.65780	0.65703	3	2	2
0.66940	0.66988	5	0	0
0.68080	0.68117	3	1	3
0.71050	0.71062	4	1	2
0.75000	0.75026	4	2	0
0.76050	0.76045	3	3	1
0.77960	0.77926	2	1	4
0.78680	0.78724	4	2	1
0.81740	0.81780	5	0	2
0.83200	0.83285	3	0	4
0.84230	0.84194	3	2	3
0.86800	0.86763	5	1	1
0.89830	0.89819	4	2	2

P= 0.02680 Q= 0.03698

STANDARD DEVIATION=0.000448

THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN

Example I

This example, chosen from Wilson and Sams,[71] indexes the Zr_2Al powder pattern. There were twenty-four reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 60. The standard deviation, 0.000645, shows that the experimental data is not close to the calculated value. The maximum discrepancy is about ±0.00154.

Example J

This example, chosen from Wilson, Thomas and Spooner,[72] indexes the Zr_4Al_3 powder pattern. There were thirtv reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 61. The standard deviation, 0.000133, shows that the experimental data is fairly good. The maximum discrepancy is only about ±0.00037.

The Orthorhombic System

The Use of the Main Computer Program ORT

The main computer program ORT for indexing the unknown powder patterns of orthorhombic crystals and the flow chart are given in Appendix D.

For the input of the computer program ORT, M stands for the total number of the powder patterns to be indexed as orthorhombic structure, K stands for the total number of the reflection

TABLE 60

Indexed Diffraction Data of Zr_2Al

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.03350	0.03312	1	0	0
0.05060	0.05001	1	0	1
0.09990	0.09935	1	1	0
0.10160	0.10069	1	0	2
0.15020	0.14936	2	0	1
0.18580	0.18515	1	0	3
0.20050	0.20004	2	0	2
0.24930	0.24871	2	1	1
0.27110	0.27027	0	0	4
0.29960	0.29806	3	0	0
0.37050	0.36962	1	1	4
0.39780	0.39741	2	2	0
0.44800	0.44742	3	1	1
0.49830	0.49809	3	1	2
0.56840	0.56833	3	0	4
0.58250	0.58255	3	1	3
0.59730	0.59745	4	0	2
0.64150	0.64123	1	0	6
0.66740	0.66768	2	2	4
0.69570	0.69546	4	1	0
0.74040	0.74058	2	0	6
0.83930	0.83993	2	1	6
0.89360	0.89417	3	3	0
0.96460	0.96574	4	1	4

P= 0.03312 Q= 0.01689

STANDARD DEVIATION=0.000645

THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN

lines in each powder pattern, L stands for the total number of possible parameter triplets (P_j,Q_j,S_j), P1(J) stands for all the possible parameters of P_j, P2(J) stands for all the possible parameters of Q_j, P3(J) stands for all the possible parameters

TABLE 61

Indexed Diffraction Data of Zr_4Al_3

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.02040	0.02042	0	0	1
0.02680	0.02680	1	0	0
0.04720	0.04721	1	0	1
0.08050	0.08039	1	1	0
0.08170	0.08167	0	0	2
0.10090	0.10081	1	1	1
0.10730	0.10719	2	0	0
0.10860	0.10847	1	0	2
0.12770	0.12760	2	0	1
0.18870	0.18886	2	0	2
0.20790	0.20799	2	1	1
0.21040	0.21056	1	0	3
0.24120	0.24117	3	0	0
0.26150	0.26159	3	0	1
0.26400	0.26415	1	1	3
0.26920	0.26925	2	1	2
0.29090	0.29095	2	0	3
0.32160	0.32156	2	2	0
0.32670	0.32669	0	0	4
0.34220	0.34198	2	2	1
0.36840	0.36877	3	1	1
0.37110	0.37134	2	1	3
0.40340	0.40323	2	2	2
0.40710	0.40708	1	1	4
0.42500	0.42493	3	0	3
0.43020	0.43003	3	1	2
0.43390	0.43387	2	0	4
0.44900	0.44916	4	0	1
0.51050	0.51045	0	0	5
0.53230	0.53212	3	1	3

P= 0.02680 Q= 0.02042

STANDARD DEVIATION=0.000133

THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN

of S_j.

The output of the computer program contains the observed $Sin^2\theta$ values, calculated $Sin^2\theta$ values, and the Miller indices of the reflections.

Example A

This well-known example, chosen from Hesse,[25] indexes the KNO_3 powder pattern. The first forty reflection lines were indexed. Observed $Sin^2\theta$ values are listed in Table 62. The indexing procedures may be described as follows. (1) The set of $Sin^2\theta$ values is the input to the computer program DA. The output, listed in Table 63, is a partial listing of difference table. (2) One may easily select the lower recurrent values and form several groups. They are 0.0063 (0.0062, 0.0063, 0.0064, 0.0064), 0.0158 (0.0156, 0.0157, 0.0157, 0.0163), 0.0321 (0.0320, 0.0321, 0.0322, 0.0323), 0.0447 (0.0444, 0.0445, 0.0449, 0.0449, 0.0450), 0.0463 (0.0461, 0.0462, 0.0463, 0.0464), 0.0485 (0.0484, 0.0485, 0.0486, 0.0486), 0.0505 (0.0503, 0.0504, 0.0506, 0.0509), 0.0626 (0.0622, 0.0626, 0.0627, 0.0629), 0.0642 (0.0639, 0.0643, 0.0644, 0.0644), 0.0709 (0.0706, 0.0707, 0.0710, 0.0711), 0.0783 (0.0780, 0.0782, 0.0783, 0.0784, 0.0785, 0.0786), 0.0835 (0.0833, 0.0834, 0.0835, 0.0837), 0.0912 (0.0910, 0.0911, 0.0912, 0.0912, 0.0914), 0.0952 (0.0951, 0.0951, 0.0952, 0.0954), 0.0960 (0.0958, 0.0958, 0.0960, 0.0961), 0.1018 (0.1016, 0.1017, 0.1019, 0.1019), 0.1250 (0.1248, 0.1249,

TABLE 62

$Sin^2\theta$ Values Calculated
from the Powder Pattern of KNO_3

DIFFRACTION LINE	SIN(SQUARE) (CPSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.09230	21	0.34620
2	0.09430	22	0.34810
3	0.12710	23	0.35130
4	0.13920	24	0.36890
5	0.14270	25	0.37660
6	0.17200	26	0.41770
7	0.17890	27	0.42230
8	0.18530	28	0.42870
9	0.18770	29	0.45000
10	0.18980	30	0.46000
11	0.22640	31	0.46630
12	0.23390	32	0.49630
13	0.24110	33	0.52390
14	0.24960	34	0.54270
15	0.26780	35	0.55510
16	0.27310	36	0.56240
17	0.28180	37	0.56930
18	0.30600	38	0.57480
19	0.31220	39	0.61510
20	0.32630	40	0.66990

0.1250, 0.1251), 0.1339 (0.1337, 0.1337, 0.1339, 0.1340, 0.1341), etc. However, as we re-examine those groups, some of them may be eliminated if there exists no such group or observed $Sin^2\theta$ value which is three or four times bigger than the value of that group. Therefore, the qualified groups are 0.0158, 0.0321, 0.0447, 0.0463, 0.0709, and 0.0783. (3) We should also consider the observed $Sin^2\theta$

TABLE 63

Difference Table of the Powder Diffraction Data of KNO_3

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00190	0.00200	0.00210	0.00240	0.00320	0.00350	0.00450	0.00460
0.00510	0.00530	0.00550	0.00620	0.00630	0.00640	0.00640	0.00690
0.00690	0.00720	0.00730	0.00750	0.00770	0.00850	0.00870	0.00880
0.01000	0.01090	0.01100	0.01210	0.01240	0.01240	0.01330	0.01400
0.01410	0.01420	0.01470	0.01560	0.01570	0.01570	0.01630	0.01760
0.01780	0.01820	0.01880	0.01970	0.01970	0.01990	0.02030	0.02080
0.02130	0.02180	0.02270	0.02320	0.02350	0.02420	0.02500	0.02530
0.02660	0.02670	0.02760	0.02770	0.02850	0.02930	0.03000	0.03040
0.03040	0.03120	0.03130	0.03200	0.03210	0.03220	0.03230	0.03280
0.03280	0.03290	0.03390	0.03400	0.03480	0.03590	0.03620	0.03630
0.03660	0.03760	0.03770	0.03820	0.03850	0.03870	0.03910	0.03910
0.03920	0.03970	0.04020	0.04030	0.04070	0.04110	0.04110	0.04140
0.04210	0.04230	0.04260	0.04260	0.04400	0.04410	0.04440	0.04450
0.04490	0.04490	0.04500	0.04530	0.04540	0.04570	0.04580	0.04610
0.04620	0.04630	0.04640	0.04670	0.04690	0.04710	0.04750	0.04790
0.04840	0.04850	0.04860	0.04860	0.04880	0.05030	0.05040	0.05060
0.05090	0.05130	0.05180	0.05210	0.05270	0.05320	0.05340	0.05340
0.05440	0.05480	0.05500	0.05540	0.05580	0.05640	0.05670	0.05760
0.05820	0.05850	0.05880	0.05980	0.05980	0.06000	0.06060	0.06190
0.06190	0.06220	0.06260	0.06270	0.06290	0.06390	0.06430	0.06440
0.06440	0.06490	0.06610	0.06630	0.06640	0.06760	0.06910	0.06950
0.06960	0.07060	0.07070	0.07100	0.07110	0.07150	0.07210	0.07240
0.07300	0.07310	0.07340	0.07390	0.07400	0.07420	0.07500	0.07610
0.07640	0.07670	0.07740	0.07760	0.07770	0.07800	0.07820	0.07830
0.07840	0.07850	0.07860	0.07960	0.07970	0.08010	0.08030	0.08060
0.08110	0.08250	0.08250	0.08270	0.08330	0.08340	0.08350	0.08370
0.08460	0.08520	0.08540	0.08580	0.08660	0.08710	0.08720	0.08780
0.08880	0.08890	0.08970	0.09100	0.09110	0.09120	0.09120	0.09140
0.09200	0.09240	0.09270	0.09300	0.09340	0.09410	0.09420	0.09470
0.09480	0.09510	0.09510	0.09520	0.09540	0.09550	0.09580	0.09580
0.09600	0.09610	0.09650	0.09660	0.09740	0.09750	0.09840	0.09850
0.09870	0.09930	0.09990	0.10060	0.10110	0.10110	0.10160	0.10170
0.10190	0.10190	0.10240	0.10240	0.10290	0.10300	0.10350	0.10380
0.10510	0.10510	0.10550	0.10620	0.10680	0.10690	0.10700	0.10750
0.10850	0.10870	0.10880	0.10930	0.10980	0.11010	0.11020	0.11040
0.11170	0.11190	0.11230	0.11240	0.11380	0.11400	0.11400	0.11420
0.11480	0.11480	0.11500	0.11620	0.11630	0.11650	0.11740	0.11820
0.11830	0.11880	0.11930	0.11930	0.11970	0.11980	0.12010	0.12040
0.12070	0.12170	0.12240	0.12250	0.12270	0.12370	0.12450	0.12480
0.12490	0.12500	0.12510	0.12640	0.12690	0.12700	0.12710	0.12720
0.12740	0.12780	0.12860	0.13040	0.13210	0.13280	0.13330	0.13370
0.13370	0.13390	0.13400	0.13410	0.13500	0.13550	0.13590	0.13650
0.13740	0.13780	0.13860	0.13910	0.13960	0.14000	0.14010	0.14020
0.14050	0.14060	0.14070	0.14100	0.14160	0.14250	0.14260	0.14270

TABLE 63 (CONTINUED)

0.14400	0.14460	0.14470	0.14500	0.14600	0.14600	0.14610	0.14680
0.14690	0.14700	0.14730	0.14740	0.14780	0.14820	0.14880	0.14880
0.14920	0.14990	0.15010	0.15020	0.15160	0.15250	0.15400	0.15410
0.15430	0.15450	0.15470	0.15500	0.15510	0.15530	0.15560	0.15640
0.15710	0.15730	0.15830	0.15850	0.16030	0.16040	0.16090	0.16090
0.16150	0.16280	0.16330	0.16360	0.16510	0.16600	0.16610	0.16680
0.16730	0.16810	0.16820	0.16920	0.16950	0.17000	0.17240	0.17260
0.17270	0.17300	0.17350	0.17360	0.17380	0.17420	0.17550	

values if there exists two reflection lines whose $Sin^2\theta$ values have a ratio of four. For example, the $Sin^2\theta$ values of the first and 24th reflections have a ratio of four; i.e., 0.0923 : 0.3689 = 1 : 4. This implies that 0.0231 (=¼×0.0923; we did not choose 0.0923 as one of the possible parameters because it is too big) is one of the possible parameters. Another is 0.0236 (=¼×0.0943). (4) Let the first five observed $Sin^2\theta$ values (0.0923, 0.0943, 0.1272, 0.1392, and 0.1427) and the possible parameters (0.0158, 0.0231, 0.0236, 0.0321, 0.0447, 0.0463, 0.0709, and 0.0783 (in ascending order)) be the inputs to the computer program AOR; the output is recorded in Table 64. The possible combinations of parameter triplets (P,O,S) are (0.0158, 0.0231, 0.03175), (0.0158, 0.0236, 0.03175), (0.0158, 0.0321, 0.0454), (0.0158, 0.0447, 0.0786), (0.0231, 0.0236, 0.0710), (0.0231, 0.0447, 0.0713), (0.0236, 0.0321, 0.0711), and (0.0236, 0.0447, 0.0708). (5) Without using the computer program AOR, the total possibilities of

TABLE 64

Output Data of the Auxiliary Computer Program (AOR) for the Powder Pattern of KNO_3

```
IF P= 0.01580      Q= 0.02310
POSSIBLE S ARE
0.02357  0.03173  0.03177  0.07120  0.07850

IF P= 0.01580      Q= 0.02360
POSSIBLE S ARE
0.03173  0.03177  0.03250  0.04480  0.07070  0.07850

IF P= 0.01580      Q= 0.03210
POSSIBLE S ARE
0.04440  0.04640  0.07850

IF P= 0.01580      Q= 0.04470
POSSIBLE S ARE
0.07850  0.07870

IF P= 0.02310      Q= 0.02360
POSSIBLE S ARE
0.03177  0.04480  0.07070  0.07120

IF P= 0.02310      Q= 0.04470
POSSIBLE S ARE
0.07120  0.07140

IF P= 0.02360      Q= 0.03210
POSSIBLE S ARE
0.04480  0.07070  0.07140

IF P= 0.02360      Q= 0.04470
POSSIBLE S ARE
0.07070  0.07090
```

trial-and-error for indexing the powder pattern may be calculated as $C_3^8 = 56$ times. (C_3^8 is a combination of eight choosing three at a time.) That is, fifty-six attempts are necessary to index

this powder pattern. However, after applying the computer program AOR, we need only to try eight combinations. This will reduce computer running time if there are many possible parameters presented. (6) The inputs of the computer program ORT are a set of observed $Sin^2\theta$ values and a set of possible parameter triplets. The output is recorded in Table 65. (7) The standard deviation, 0.000249, shows that the maximum discrepancy between the experimental data and the calculated value is only about ±0.00058.

Example B

This example, chosen from Mirkin,[73] indexes the $NiAl_3$ powder pattern. The first twenty lower angle reflection lines were indexed. Observed $Sin^2\theta$ values are listed in Table 66. The indexing procedures may be described as follows. (1) The set of $Sin^2\theta$ values is the input to the computer program DA. The output, listed in Table 67, is a difference table. (2) One may easily select the lower recurrent values and form several groups. They are 0.0063 (0.0061, 0.0063, 0.0064), 0.0095 (0.0093, 0.0095, 0.0097), 0.0181 (0.0176, 0.0179, 0.0182, 0.0186), 0.0155 (0.0151, 0.0156, 0.0157), 0.0203 (0.0200, 0.0203, 0.0204, 0.0205), 0.0286 (0.0283, 0.0286, 0.0286, 0.0289), 0.0305 (0.0303, 0.0304, 0.0308), 0.0347 (0.0347, 0.0347, 0.0348), 0.0388 (0.0386, 0.0386, 0.0391, 0.0391), 0.0442 (0.0440, 0.0442, 0.0443), 0.0485 (0.0483, 0.0484, 0.0486, 0.0489), etc. But the qualified groups are 0.0095,

TABLE 65

Indexed Diffraction Data of KNO_3

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.09230	0.09208	1	1	1
0.09430	0.09421	0	1	2
0.12710	0.12706	0	2	0
0.13920	0.13891	1	1	2
0.14270	0.14267	0	2	1
0.17200	0.17176	1	2	0
0.17890	0.17882	2	0	0
0.18530	0.18521	1	0	3
0.18770	0.18737	1	2	1
0.18980	0.18950	0	2	2
0.22640	0.22620	2	1	1
0.23390	0.23421	1	2	2
0.24110	0.24127	2	0	2
0.24960	0.24978	0	0	4
0.26780	0.26756	0	2	3
0.27310	0.27303	2	1	2
0.28180	0.28154	0	1	4
0.30600	0.30588	2	2	0
0.31220	0.31226	1	2	3
0.32630	0.32625	1	1	4
0.34620	0.34619	1	3	1
0.34810	0.34832	0	3	2
0.35130	0.35109	2	1	3
0.36890	0.36832	2	2	2
0.37660	0.37683	0	2	4
0.41770	0.41797	3	0	1
0.42230	0.42204	0	1	5
0.42870	0.42860	2	0	4
0.45000	0.44973	3	1	1
0.46000	0.46037	2	1	4
0.46630	0.46675	1	1	5
0.49630	0.49656	3	1	2
0.52390	0.52383	0	4	1
0.54270	0.54286	3	0	3
0.55510	0.55566	2	2	4
0.56240	0.56204	1	2	5
0.56930	0.56910	2	0	5
0.57480	0.57462	3	1	3
0.61510	0.61537	1	4	2
0.66990	0.66991	3	2	3

P= 0.04471 Q= 0.03176 S= 0.01561

STANDARD DEVIATION=0.000249

THIS IS AN ORTHORHOMBIC CRYSTAL POWDER PATTERN

TABLE 66

$Sin^2\theta$ Values Calculated
from the Powder Pattern of $NiAl_3$

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.04960	11	0.16720
2	0.05300	12	0.17160
3	0.05930	13	0.18580
4	0.06780	14	0.19800
5	0.08820	15	0.19990
6	0.10820	16	0.20630
7	0.12300	17	0.21560
8	0.13250	18	0.22660
9	0.13860	19	0.23660
10	0.15650	20	0.25870

0.0181, 0.0305, 0.0347, and 0.0388. (3) As we consider the observed $Sin^2\theta$ values, 0.0124 (=½×0.0496) and 0.0148 (=⅓×0.0593) are found. (4) Let the first five observed $Sin^2\theta$ values (0.0496, 0.0530, 0.0593, 0.0678, and 0.0882) and the possible parameters (0.0095, 0.0124, 0.0148, 0.0181, 0.0305, 0.0347, and 0.0388) be the inputs to the computer program AOR; the output is then recorded in Table 68. The possible combinations of parameter triplets are (0.0095, 0.0124, 0.0148), (0.0095, 0.0148, 0.0349), (0.0124, 0.0148, 0.0183), and (0.0148, 0.0181, 0.0349). (5) Without using the computer program AOR, the total possibilities of trial-and-error for indexing this powder pattern may be calculated as C_3^7 = 35 times. However, we need only to try four times to index this

TABLE 67

Difference Table of the Powder Diffraction Data of $NiAl_3$

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00190	0.00340	0.00440	0.00610	0.00630	0.00640	0.00830	0.00850
0.00930	0.00950	0.00970	0.01000	0.01070	0.01100	0.01220	0.01410
0.01420	0.01480	0.01480	0.01510	0.01560	0.01570	0.01760	0.01790
0.01820	0.01860	0.02000	0.02030	0.02040	0.02050	0.02100	0.02210
0.02400	0.02430	0.02640	0.02670	0.02830	0.02860	0.02860	0.02890
0.02930	0.02980	0.03030	0.03040	0.03080	0.03210	0.03270	0.03300
0.03350	0.03470	0.03470	0.03480	0.03520	0.03670	0.03860	0.03860
0.03910	0.03910	0.04040	0.04080	0.04150	0.04310	0.04340	0.04400
0.04420	0.04430	0.04720	0.04830	0.04840	0.04860	0.04890	0.04980
0.05040	0.05080	0.05240	0.05330	0.05500	0.05520	0.05520	0.05860
0.05880	0.05900	0.05910	0.05940	0.05940	0.06070	0.06130	0.06280
0.06340	0.06370	0.06470	0.06500	0.06550	0.06740	0.06770	0.06830
0.06940	0.07000	0.07010	0.07080	0.07290	0.07320	0.07340	0.07380
0.07500	0.07690	0.07700	0.07760	0.07900	0.07930	0.07950	0.08010
0.08290	0.08310	0.08330	0.08340	0.08560	0.08710	0.08800	0.08870
0.08900	0.08980	0.09150	0.09170	0.09260	0.09410	0.09720	0.09760
0.09800	0.09810	0.09940	0.10220	0.10350	0.10360	0.10380	0.10410
0.10690	0.10740	0.10790	0.10980	0.11170	0.11230	0.11360	0.11420
0.11760	0.11800	0.11810	0.11840	0.11860	0.12010	0.12200	0.12620
0.12650	0.12740	0.12840	0.13020	0.13210	0.13280	0.13570	0.13620
0.13840	0.13850	0.13870	0.14060	0.14500	0.14690	0.14700	0.14780
0.14840	0.14840	0.15030					

powder pattern now. (6) The inputs of the computer program ORT are a set of observed $Sin^2\theta$ values and a set of possible parameter triplets. The indexed diffraction data is recorded in Table 69. (7) The standard deviation, 0.000184, shows that the maximum discrepancy between the experimental data and the calculated one is about ±0.00042.

TABLE 68

Output Data of the Auxiliary Computer Program (AOR) for the Powder Pattern of $NiAl_3$

```
IF P= 0.00950      Q= 0.01240
POSSIBLE S ARE
0.01457  0.01482  0.01500  0.01820  0.03860

IF P= 0.00950      Q= 0.01480
POSSIBLE S ARE
0.01835  0.03480  0.03500

IF P= 0.01240      Q= 0.01480
POSSIBLE S ARE
0.01820  0.01835  0.03480  0.03860

IF P= 0.01240      Q= 0.01810
POSSIBLE S ARE
0.03490  0.03860

IF P= 0.01480      Q= 0.01810
POSSIBLE S ARE
0.03480  0.03490  0.03490
```

Example C

This example, chosen from D'Eye and Wait,[56] indexes the $ThSe_2$ powder pattern. The first twenty-three low angle reflection lines were indexed. Observed $Sin^2\theta$ values are listed in Table 70. The indexing procedures may be described as follows. (1) The set of observed $Sin^2\theta$ values is the input of the computer program DA. The output, listed in Table 71, is a difference table. (2) One may easily select the lower recurrent values and form several

TABLE 69

Indexed Diffraction Data of $NiAl_3$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.04960	0.04940	1	0	1
0.05300	0.05297	1	1	0
0.05930	0.05912	0	0	2
0.06780	0.06775	1	1	1
0.08820	0.08818	0	2	1
0.10820	0.10801	1	2	0
0.12300	0.12279	1	2	1
0.13250	0.13252	0	2	2
0.13860	0.13846	2	0	0
0.15650	0.15681	2	1	0
0.16720	0.16714	1	2	2
0.17160	0.17159	2	1	1
0.18580	0.18599	1	1	3
0.19800	0.19758	2	0	2
0.19990	0.19976	1	3	0
0.20630	0.20642	0	2	3
0.21560	0.21593	2	1	2
0.22660	0.22664	2	2	1
0.23660	0.23648	0	0	4
0.25870	0.25888	1	3	2

P= 0.03462 Q= 0.01835 S= 0.01478

STANDARD DEVIATION=0.000184

THIS IS AN ORTHORHOMBIC CRYSTAL POWDER PATTERN

groups. They are 0.0071 (0.0069, 0.0069, 0.0070, 0.0073, 0.0073), 0.0210 (0.0206, 0.0208, 0.0209, 0.0214, 0.0215), 0.0266 (0.0261, 0.0262, 0.0263, 0.0265, 0.0266, 0.0269, 0.0270, 0.0272), 0.0305 (0.0301, 0.0302, 0.0304, 0.0306, 0.0307, 0.0308, 0.0309), 0.0337 (0.0336, 0.0336, 0.0337, 0.0338, 0.0339), 0.0372 (0.0369, 0.0370, 0.0372, 0.0377), 0.0514 (0.0511, 0.0512, 0.0514, 0.0515, 0.0516),

TABLE 70

$Sin^2\theta$ Values Calculated
from the Powder Pattern of $ThSe_2$

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.03770	13	0.12090
2	0.03920	14	0.12170
3	0.04100	15	0.13010
4	0.04790	16	0.13650
5	0.06940	17	0.15670
6	0.07140	18	0.16120
7	0.07490	19	0.16370
8	0.07870	20	0.18770
9	0.09550	21	0.19500
10	0.09950	22	0.20190
11	0.10560	23	0.22130
12	0.11560		

0.0576 (0.0572, 0.0576, 0.0576, 0.0577, 0.0578, 0.0578), etc. However, the qualified groups are 0.0071, 0.0210, 0.0266, 0.0305, and 0.0337. (4) As we consider the observed $Sin^2\theta$ values, 0.0098 (=¼×0.0392) and 0.0102 (=¼×0.0410) are found. (5) Let the first four observed $Sin^2\theta$ values (0.0377, 0.0392, 0.0410, and 0.0479) and the possible parameters (0.0071, 0.0098, 0.0102, 0.0210, 0.0266, 0.0305, and 0.0377) be the inputs to the computer program AOR; the output is recorded in Table 72. The possible combination of parameter triplets are (0.0071, 0.0098, 0.0102), (0.0071, 0.0098, 0.0379), (0.0071, 0.0102, 0.0377), (0.0071, 0.0102, 0.0307), (0.0098, 0.0102, 0.0378), (0.0098, 0.0210, 0.0379), (0.0098, 0.0266,

TABLE 71

Difference Table of the Powder Diffraction Data of $ThSe_2$

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00080	0.00150	0.00180	0.00200	0.00250	0.00330	0.00350	0.00380
0.00400	0.00450	0.00530	0.00550	0.00610	0.00610	0.00640	0.00690
0.00690	0.00700	0.00730	0.00730	0.00840	0.00870	0.00920	0.00930
0.01000	0.01010	0.01020	0.01420	0.01450	0.01480	0.01530	0.01560
0.01610	0.01610	0.01680	0.01940	0.02010	0.02020	0.02060	0.02080
0.02090	0.02140	0.02150	0.02220	0.02350	0.02400	0.02410	0.02450
0.02460	0.02470	0.02540	0.02610	0.02620	0.02630	0.02650	0.02660
0.02690	0.02700	0.02720	0.02810	0.02840	0.03010	0.03020	0.03040
0.03060	0.03070	0.03080	0.03090	0.03100	0.03110	0.03130	0.03170
0.03220	0.03360	0.03360	0.03370	0.03380	0.03390	0.03420	0.03460
0.03500	0.03570	0.03580	0.03620	0.03690	0.03700	0.03720	0.03770
0.03820	0.03830	0.03950	0.03950	0.04030	0.04070	0.04070	0.04100
0.04100	0.04110	0.04200	0.04220	0.04280	0.04300	0.04420	0.04520
0.04560	0.04600	0.04620	0.04680	0.04760	0.04810	0.04950	0.05030
0.05110	0.05120	0.05140	0.05150	0.05160	0.05230	0.05450	0.05520
0.05560	0.05630	0.05720	0.05760	0.05760	0.05770	0.05780	0.05780
0.05810	0.05850	0.05850	0.05870	0.06010	0.06030	0.06070	0.06120
0.06160	0.06170	0.06180	0.06420	0.06460	0.06460	0.06490	0.06510
0.06540	0.06570	0.06600	0.06640	0.06680	0.06710	0.06770	0.06790
0.06820	0.07180	0.07210	0.07300	0.07330	0.07380	0.07410	0.07460
0.07640	0.07790	0.07800	0.07940	0.07990	0.08020	0.08070	0.08100
0.08170	0.08180	0.08210	0.08220	0.08250	0.08250	0.08320	0.08400
0.08480	0.08500	0.08530	0.08630	0.08630	0.08730	0.08820	0.08860
0.08880	0.08910	0.08940	0.08980	0.09090	0.09120	0.09180	0.09220
0.09230	0.09240						

0.0379), (0.0098, 0.0305, 0.0379), (0.0102, 0.0210, 0.0377), (0.0102, 0.0266, 0.0377), and (0.0102, 0.0305, 0.0377). (6) The inputs to the computer program ORT are a set of observed $Sin^2\theta$ values and a set of possible parameter triplets. The indexed powder diffraction data is then recorded in Table 73. (7) The

TABLE 72

Output Data of the Auxiliary Computer Program (AOR) for the Powder Pattern of $ThSe_2$

```
IF P= 0.00710      Q= 0.00980
POSSIBLE S ARE
0.00980  0.01020  0.01025  0.02080  0.03060  0.03770  0.03810

IF P= 0.00710      Q= 0.01020
POSSIBLE S ARE
0.03060  0.03060  0.03080  0.03770  0.03770

IF P= 0.00710      Q= 0.02100
POSSIBLE S ARE
0.02690  0.03060  0.03770

IF P= 0.00710      Q= 0.02660
POSSIBLE S ARE
0.03060  0.03770

IF P= 0.00980      Q= 0.01020
POSSIBLE S ARE
0.02100  0.03080  0.03770  0.03770  0.03810

IF P= 0.00980      Q= 0.02100
POSSIBLE S ARE
0.02690  0.03770  0.03810

IF P= 0.00980      Q= 0.02660
POSSIBLE S ARE
0.03770  0.03810

IF P= 0.00980      Q= 0.03050
POSSIBLE S ARE
0.03770  0.03810

IF P= 0.01020      Q= 0.02100
POSSIBLE S ARE
0.02690  0.03080  0.03770  0.03770

IF P= 0.01020      Q= 0.02660
POSSIBLE S ARE
0.03080  0.03770  0.03770

IF P= 0.01020      Q= 0.03050
POSSIBLE S ARE
0.03770  0.03770
```

TABLE 73

Indexed Diffraction Data of $ThSe_2$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.03770	0.03770	1	0	1
0.03920	0.03914	0	1	2
0.04100	0.04102	0	2	0
0.04790	0.04795	1	1	1
0.06940	0.06961	1	1	2
0.07140	0.07150	1	2	0
0.07490	0.07524	0	1	3
0.07870	0.07872	1	2	1
0.09550	0.09546	1	0	3
0.09950	0.09952	0	3	1
0.10560	0.10572	1	1	3
0.11560	0.11553	0	0	4
0.12090	0.12118	0	3	2
0.12170	0.12191	2	0	0
0.13010	0.13000	1	3	1
0.13650	0.13648	1	2	3
0.15670	0.15655	0	2	4
0.16120	0.16104	2	1	2
0.16370	0.16409	0	4	0
0.18770	0.18776	1	3	3
0.19500	0.19456	1	4	0
0.20190	0.20178	1	4	1
0.22130	0.22124	1	1	5

P= 0.03048 Q= 0.01026 S= 0.00722

STANDARD DEVIATION=0.000179

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standard deviation, 0.000179, shows that the maximum discrepancy between the experimental data and the calculated one is about ±0.00044.

Example D

This example, chosen from Mooney,[74] indexes the $AlPO_4$ (low-cristobalite type) powder pattern. The first fifty-two reflection lines were indexed. The indexing procedures are similar to the previous examples. The indexed powder diffraction data is recorded in Table 74. Three parameters, P=0.01177, Q= 0.0118, and S=0.01207 are very close to each other. Therefore, careful examination of the difference table is needed when choosing the possible parameters. The Miller indices are in agreement with the original paper except for the 20th reflection line, 0.2125. The Miller index (330) was assigned to this reflection line. A better solution, (141), is suggested. The standard deviation, 0.000262, shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.00076.

Example E

This example, chosen from Mooney,[74] indexes the $GaPO_4$ (low-cristobalite type) powder pattern. The first forty reflection lines were indexed. The indexed powder diffraction data is recorded in Table 75. The parameters P=0.01254, Q=0.01225, and S=0.01203 are found to be very close to one another. Three reflection lines, 18th, 38th, and 40th, have Miller indices assigned differently than in the original published paper. Better

TABLE 74

Indexed Diffraction Data of $AlPO_4$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.02360	0.02358	1	1	0
0.03570	0.03565	1	1	1
0.04720	0.04722	0	2	0
0.04850	0.04828	0	0	2
0.05920	0.05916	2	0	1
0.07210	0.07186	1	1	2
0.09420	0.09431	2	2	0
0.09530	0.09537	2	0	2
0.10650	0.10638	2	2	1
0.11700	0.11776	3	1	0
0.13010	0.13008	1	3	1
0.13270	0.13220	1	1	3
0.14250	0.14259	2	2	2
0.15620	0.15572	2	0	3
0.16650	0.16629	1	3	2
0.18850	0.18887	0	4	0
0.19330	0.19312	0	0	4
0.20020	0.20064	1	4	0
0.20300	0.20293	2	2	3
0.21250	0.21271	1	4	1
0.21680	0.21669	1	1	4
0.22460	0.22426	3	3	1
0.22640	0.22638	3	1	3
0.23650	0.23664	4	0	2
0.24010	0.24021	2	0	4
0.24800	0.24803	2	4	1
0.26060	0.26047	3	3	2
0.28430	0.28424	2	4	2
0.28770	0.28742	2	2	4
0.29780	0.29749	0	4	3
0.30660	0.30667	4	3	1
0.31160	0.31113	1	3	4
0.31900	0.31895	1	5	1
0.32520	0.32532	1	1	5
0.34470	0.34458	2	4	3
0.34850	0.34883	2	0	5
0.35500	0.35516	1	5	2
0.37720	0.37723	4	4	0
0.38190	0.38198	0	4	4
0.38970	0.38981	5	2	2
0.39600	0.39605	2	2	5
0.40120	0.40106	3	5	0
0.40550	0.40531	3	3	4
0.41280	0.41262	5	3	1

TABLE 74 (CONTINUED)

0.41520	0.41550	1	5	3
0.41940	0.41950	3	1	5
0.42440	0.42495	0	6	0
0.42540	0.42551	4	4	2
0.42870	0.42869	4	2	4
0.43410	0.43451	0	0	6
0.43770	0.43702	0	6	1
0.44890	0.44883	5	3	2

P= 0.01177 Q= 0.01180 S= 0.01207
STANDARD DEVIATION=0.000262
THIS IS AN ORTHORHOMBIC CRYSTAL POWDER PATTERN

solutions, (232), (252), and (343), are suggested respectively. The standard deviation, 0.000433, shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.00091.

Example F

This example, chosen from Parthe, Hohnke and Hulliger,[75] indexes the Rh_2S_3 powder pattern. There were forty-four reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 76. All the indexing assignments are agreeable except the 15th reflection line whose Miller index, (411), was assigned. However, a better solution, (310), is suggested. The standard deviation, 0.000431, shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.0009.

Table 75

Indexed Diffraction Data of $GaPO_4$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.02450	0.02457	1	0	1
0.03690	0.03680	1	1	1
0.04870	0.04893	0	2	0
0.05020	0.05017	2	0	0
0.06150	0.06147	1	2	0
0.07460	0.07443	2	1	1
0.09790	0.09829	2	0	2
0.09900	0.09910	2	2	0
0.11030	0.11052	2	1	2
0.12240	0.12263	1	3	0
0.13470	0.13466	1	3	1
0.13710	0.13714	3	1	1
0.14810	0.14722	2	2	2
0.16210	0.16181	3	2	0
0.17280	0.17229	2	3	1
0.19520	0.19572	0	4	0
0.20090	0.20068	4	0	0
0.20840	0.20838	2	3	2
0.21080	0.20993	3	2	2
0.22010	0.22029	1	4	1
0.22450	0.22494	4	1	1
0.23270	0.23338	3	1	3
0.23500	0.23500	3	3	1
0.24580	0.24589	2	4	0
0.24990	0.24961	4	2	0
0.25710	0.25792	2	4	1
0.27020	0.27008	3	2	3
0.29440	0.29401	2	4	2
0.29860	0.29773	4	2	2
0.30900	0.30895	4	0	3
0.31840	0.31835	1	5	0
0.32310	0.32280	4	3	1
0.33110	0.33124	3	3	3
0.33820	0.33782	5	1	1
0.35680	0.35672	3	4	2
0.36840	0.36801	2	5	1
0.39550	0.39639	4	4	0
0.40470	0.40410	2	5	2
0.40970	0.41061	5	2	2
0.41650	0.41687	3	4	3

P= 0.01254 Q= 0.01223 S= 0.01203

STANDARD DEVIATION=0.000433

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TABLE 76

Indexed Diffraction Data of Rh_2S_3

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.07320	0.07320	0	0	2
0.08970	0.08973	1	1	1
0.13910	0.13922	0	2	0
0.14460	0.14463	1	1	2
0.14660	0.14649	2	0	0
0.18150	0.18130	2	1	0
0.19400	0.19414	1	2	1
0.20070	0.20132	1	0	3
0.23590	0.23612	1	1	3
0.24960	0.24904	1	2	2
0.28600	0.28571	2	2	0
0.29290	0.29279	0	0	4
0.30460	0.30401	2	2	1
0.35910	0.35891	2	2	2
0.36490	0.36441	3	1	0
0.36850	0.36817	1	3	1
0.42270	0.42307	1	3	2
0.43280	0.43201	0	2	4
0.43820	0.43761	3	1	2
0.45070	0.45041	2	2	3
0.51450	0.51456	1	3	3
0.52860	0.52891	1	1	5
0.55760	0.55688	0	4	0
0.57940	0.57850	2	2	4
0.58560	0.58597	4	0	0
0.64300	0.64266	1	3	4
0.65980	0.65917	4	0	2
0.70350	0.70337	2	4	0
0.71620	0.71605	3	3	2
0.72250	0.72167	2	4	1
0.72440	0.72519	4	2	0
0.73080	0.73020	1	1	6
0.74330	0.74319	2	2	5
0.75210	0.75253	2	3	4
0.79790	0.79799	0	2	6
0.80660	0.80735	1	3	5
0.86790	0.86807	2	4	3
0.87850	0.87876	4	0	4
0.88950	0.88988	4	2	3
0.92480	0.92505	1	5	1
0.93560	0.93564	3	3	4
0.94430	0.94448	2	2	6
0.97940	0.97995	1	5	2
0.99580	0.99616	2	4	4

P= 0.03662 Q= 0.03481 S= 0.01830

STANDARD DEVIATION=0.000431

THIS IS AN ORTHORHOMBIC CRYSTAL POWDER PATTERN

Example G

This example, chosen from Mumme and Wadsley,[76] indexes the $NaTi_2Al_5O_{12}$ powder pattern. The first fifteen reflection lines were indexed. The indexed powder diffraction data is recorded in Table 77. The first six reflection lines have $Sin^2\theta$ values generated by two of the parameters, Q and S. Thus, it is very difficult and overly time-consuming to index this pattern by the computer method suggested by Werner.[29] Besides, the value of P (=0.06959) is much larger than the other two values (Q= 0.00723 and S=0.00246). Four reflection lines, 6th, 7th, 12th, and 15th, are assigned differently than in the original paper. However, better solutions of Miller indices assignments, (031), (112), (007), and (053), are suggested respectively. The standard deviation, 0.000218, shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.00069.

Example H

This example, chosen from Mumme and Reid,[77] indexes the $Na_{0.90}Fe_{0.90}Ti_{1.10}O_4$ powder pattern. The first twenty-eight reflection lines were indexed. The indexed powder diffraction data is recorded in Table 78. The $Sin^2\theta$ values of the first seven reflection lines are generated by two of the parameters, Q and S. Thus, it is very difficult and overly time-consuming to

TABLE 77

Indexed Diffraction Data of $NaTi_2Al_5O_{12}$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.00964	0.00969	0	1	1
0.00984	0.00985	0	0	2
0.01703	0.01708	0	1	2
0.02938	0.02938	0	1	3
0.03937	0.03938	0	0	4
0.06823	0.06754	0	3	1
0.08699	0.08666	1	1	2
0.09842	0.09851	1	2	0
0.09898	0.09897	1	1	3
0.10832	0.10836	1	2	2
0.10906	0.10897	1	0	4
0.12068	0.12061	0	0	7
0.14952	0.14953	0	2	7
0.17375	0.17405	1	3	4
0.20281	0.20294	0	5	3

P= 0.06959 Q= 0.00723 S= 0.00246
STANDARD DEVIATION=0.000218
THIS IS AN ORTHORHOMBIC CRYSTAL POWDER PATTERN

index this pattern by the computer method suggested by Werner.[29] Also, the value of P (=0.06718) is much larger than that of the other two values (Q=0.00694 and S=0.00461). Three reflection lines, 17th, 19th, and 26th, are assigned differently than in the original paper. Better solutions of Miller indices assignments, (114), (051), and (062), are suggested respectively. The standard deviation, 0.000099, shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.00032.

TABLE 78

Indexed Diffraction Data of $Na_{0.90}Fe_{0.90}Ti_{1.10}O_4$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.01153	0.01154	0	1	1
0.01844	0.01844	0	0	2
0.02536	0.02537	0	1	2
0.04618	0.04618	0	2	2
0.04848	0.04842	0	1	3
0.06697	0.06703	0	3	1
0.07374	0.07375	0	0	4
0.07863	0.07873	1	1	1
0.08081	0.08085	0	3	2
0.09249	0.09256	1	1	2
0.09524	0.09492	1	2	0
0.09948	0.09953	1	2	1
0.10391	0.10390	0	3	3
0.11330	0.11336	1	2	2
0.13623	0.13617	0	3	4
0.14295	0.14298	0	2	5
0.14787	0.14787	1	1	4
0.17098	0.17108	1	3	3
0.17781	0.17799	0	5	1
0.18466	0.18471	0	4	4
0.19382	0.19368	0	2	6
0.21008	0.21016	1	2	5
0.24009	0.24006	1	1	6
0.24706	0.24713	0	5	4
0.25912	0.25900	1	5	2
0.26828	0.26810	0	6	2
0.28853	0.28861	0	5	5

P= 0.06718 Q= 0.00694 S= 0.00461

STANDARD DEVIATION=0.000099

THIS IS AN ORTHORHOMBIC CRYSTAL POWDER PATTERN

Example I

This example, chosen from Zachariasen,[78] indexes the (α-Np) Neptunium metal powder pattern. The first forty-three reflection lines were indexed. The indexed powder diffraction data is recorded in Table 79. The Miller indices of five reflection lines, 8th, 13th, 18th, 23rd, and 27th, are assigned differently than in the original paper. However, better solutions of Miller indices assignments, (211), (300), (032), (214), and (140), are suggested respectively. The standard deviation, 0.000698, shows that the experimental data and the calculated value are not close. The maximum discrepancy is about ±0.00153.

The Monoclinic System

The Use of the Main Computer Program MON

The main computer program MON for indexing the unknown powder patterns of monoclinic crystals and the flow chart are given in Appendix E.

For the input of the computer program MON, M stands for the total number of the powder patterns to be indexed as monoclinic structure, K stands for the total number of the reflection lines in each powder pattern, L stands for the total number of possible parameter pairs (P_j, Q_j, S_j, V_j), P1(J) stands for all the possible parameters of P_j, P2(J) stands for all the possible

TABLE 79

Indexed Diffraction Data of (α-Np) Neptunium

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.06540	0.06507	1	1	1
0.07920	0.07840	0	1	2
0.10040	0.09990	0	2	0
0.10580	0.10514	1	1	2
0.10770	0.10696	2	0	0
0.11390	0.11326	0	2	1
0.14060	0.14000	1	2	1
0.14530	0.14529	2	1	1
0.15260	0.15333	0	2	2
0.18590	0.18536	2	1	2
0.20770	0.20686	2	2	0
0.22080	0.22022	2	2	1
0.24200	0.24065	3	0	0
0.24820	0.24685	1	2	3
0.25230	0.25152	1	3	0
0.26110	0.26028	2	2	2
0.26530	0.26488	1	3	1
0.27890	0.27821	0	3	2
0.30510	0.30495	1	3	2
0.31950	0.31905	3	1	2
0.32690	0.32706	2	2	3
0.34020	0.34034	1	2	4
0.34570	0.34563	2	1	4
0.35320	0.35391	3	2	1
0.41180	0.41298	0	4	1
0.42040	0.42055	2	2	4
0.42710	0.42636	1	4	0
0.43910	0.43848	0	3	4
0.45120	0.45194	2	3	3
0.45450	0.45435	3	0	4
0.46180	0.46076	3	2	3
0.46430	0.46522	1	3	4
0.47890	0.47879	3	3	1
0.50660	0.50658	2	4	0
0.51880	0.51886	3	3	2
0.52620	0.52773	4	2	0
0.54120	0.54109	4	2	1
0.54430	0.54544	2	3	4
0.55330	0.55425	3	2	4
0.55830	0.55868	0	3	5
0.57290	0.57301	4	1	3
0.58070	0.58071	0	2	6
0.58840	0.58777	2	0	6

P= 0.02674 Q= 0.02498 S= 0.01336

TABLE 79 (CONTINUED)

STANDARD DEVIATION=0.000698
THIS IS AN ORTHORHOMBIC CRYSTAL POWDER PATTERN

parameters of Q_j, P3(J) stands for all the possible parameters of S_j, and P4(J) stands for all the possible parameters of V_j.

The output of the computer program contains the observed $Sin^2\theta$ values, calculated $Sin^2\theta$ values, and the Miller indices of the reflections.

Example A

This example, chosen from Andersson,[79] indexes the powder pattern of $Na_2Ti_3O_7$. The first twenty-seven low-angle reflection lines were indexed. Observed $Sin^2\theta$ values are listed in Table 80. The indexing procedures may be described as follows. (1) The set of observed $Sin^2\theta$ values is the input to the computer program DA. The output, listed in Table 81, is a difference table. (2) One may easily select the recurrent values. In this system, the recurrent values can only form several groups among which the ratios are 1 : 3 : 4 etc. (See Chapter III.) However, there may exist only a unique recurrent value group since the value of Q is sometimes so big that the partial listing of the differences of the observed $Sin^2\theta$ values could not cover all the

TABLE 80

$Sin^2\theta$ Values Calculated
from the Powder Pattern of $Na_2Ti_3O_7$

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.00746	15	0.07570
2	0.00847	16	0.08139
3	0.01270	17	0.08464
4	0.01908	18	0.08541
5	0.02972	19	0.08639
6	0.03478	20	0.08833
7	0.04941	21	0.09170
8	0.05055	22	0.09268
9	0.05995	23	0.10654
10	0.06551	24	0.10751
11	0.06660	25	0.13897
12	0.07068	26	0.13971
13	0.07268	27	0.16399
14	0.07471		

other recurrent values. For this example, the only recurrent value group is 0.04095 (0.04087, 0.04091, 0.04092, 0.04094, 0.04096, 0.04103). To verify that the possible value of O is 0.04095, find where 0.16399 (≃4×0.04095) appears among the observed $Sin^2\theta$ values. (3) Now, select a smallest observed $Sin^2\theta$ value, say T_i, where there exists some other observed $Sin^2\theta$ value, T_j, such that $T_i : T_j = 1 : 4$ or $1 : 9$ or $4 : 9$, etc. Thus, we let the possible value of P or S be T_i. For this example, the possible value of P or S is 0.00746 (since 0.00746 :

TABLE 81

Difference Table of the Powder Diffraction Data of $Na_2Ti_3O_7$

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00074	0.00077	0.00097	0.00098	0.00098	0.00099	0.00101	0.00109
0.00114	0.00175	0.00194	0.00200	0.00203	0.00292	0.00302	0.00325
0.00337	0.00369	0.00402	0.00403	0.00408	0.00423	0.00435	0.00500
0.00502	0.00506	0.00517	0.00524	0.00531	0.00556	0.00569	0.00608
0.00629	0.00629	0.00638	0.00665	0.00668	0.00694	0.00706	0.00717
0.00727	0.00804	0.00811	0.00871	0.00894	0.00910	0.00920	0.00940
0.00971	0.00993	0.01019	0.01031	0.01054	0.01061	0.01064	0.01069
0.01070	0.01071	0.01073	0.01129	0.01162	0.01168	0.01196	0.01263
0.01273	0.01273	0.01362	0.01371	0.01386	0.01396	0.01463	0.01473
0.01476	0.01479	0.01483	0.01484	0.01496	0.01565	0.01570	0.01571
0.01575	0.01577	0.01581	0.01588	0.01600	0.01605	0.01610	0.01698
0.01699	0.01702	0.01719	0.01765	0.01797	0.01804	0.01821	0.01881
0.01902	0.01913	0.01918	0.01969	0.01979	0.01990	0.02000	0.02013
0.02015	0.02083	0.02088	0.02102	0.02112	0.02113	0.02125	0.02127
0.02144	0.02173	0.02190	0.02200	0.02208	0.02210	0.02213	0.02226
0.02282	0.02287	0.02327	0.02416	0.02428	0.02469	0.02502	0.02510
0.02515	0.02515	0.02517	0.02530	0.02546	0.02608	0.02612	0.02619
0.02629	0.02631	0.02644	0.02717	0.02732	0.02838	0.03023	0.03033
0.03073	0.03084	0.03084	0.03146	0.03147	0.03175	0.03181	0.03182
0.03183	0.03198	0.03220	0.03243	0.03273	0.03280	0.03317	0.03386
0.03409	0.03483	0.03486	0.03523	0.03579	0.03584	0.03586	0.03590
0.03600	0.03671	0.03683	0.03688	0.03698	0.03778	0.03785	0.03790
0.03992	0.03993	0.03994	0.04087	0.04091	0.04092	0.04094	0.04096
0.04103	0.04115	0.04195	0.04200	0.04208	0.04213	0.04229	0.04296
0.04309	0.04327	0.04499	0.04598	0.04629	0.04643	0.04659	0.04661
0.04703	0.04725	0.04727	0.04752	0.04756	0.04801	0.04986	0.05063
0.05064	0.05138	0.05148	0.05160	0.05161	0.05167	0.05249	0.05258
0.05281	0.05332	0.05355	0.05356	0.05360	0.05390	0.05430	0.05433
0.05492	0.05507	0.05563	0.05569	0.05599	0.05648	0.05662	0.05667
0.05692	0.05696	0.05704	0.05713	0.05745	0.05758	0.05790	0.05798
0.05805	0.05810	0.05813	0.05832	0.05861	0.05914	0.05998	0.06198
0.06201	0.06221	0.06231	0.06296	0.06300	0.06322	0.06327	0.06401
0.06421	0.06426	0.06500	0.06522	0.06556	0.06624	0.06629	0.06633
0.06703	0.06723	0.06725	0.06731	0.06824			

0.02972 = 1 : 4). Another possible value is 0.01270 (since 0.01270 : 0.05055 = 1 : 4). However, we only select the smallest one. (4) To select the possible combination of parameter pairs (P_j,Q_j,S_j,V_j), the auxiliary computer program AMO is applied. Let some of the smaller observed $Sin^2\theta$ values or $Sin^2\theta$ - 0 values together with the possible P or S, 0.00746, be the inputs to the computer program AMO. For this example, the first three observed $Sin^2\theta$ values (0.00847, 0.01270, and 0.01908) next to 0.00746 are selected. The output of the computer program AMO is listed in Table 82. (5) In Table 82, the recurrences are shown in parentheses. We are selecting the most recurrent values of V for the possible value of P or S = 0.00746. For the possible P or S = 0.00746 and 0.00847, V is 0.00323. (It appears sixteen times.) Hence, the possible parameter pairs (P_j,Q_j,S_j,V_j) are (0.00746, 0.04095, 0.00847, 0.00323), (0.00746, 0.04095, 0.00847, -0.00323), (0.00847, 0.04095, 0.00746, 0.00323), and (0.00847, 0.04095, 0.00746, -0.00323). The reason for these kinds of combinations of possible parameter pairs is that the values of P and S are skew-symmetric for the monoclinic system. (6) The inputs to the computer program MON are the set of observed $Sin^2\theta$ values and a set of possible parameter pairs. The output is recorded in Table 83. (7) The standard deviation, 0.000060, shows that the maximum discrepancy between the experi-

TABLE 82

Output Data of the Auxiliary Computer Program (AMO) for the Powder Pattern of $Na_2Ti_3O_7$

POSSIBLE P OR S= 0.00746

P=	0.00746	S=	0.00121	V=	0.00020	(6)
P=	0.00121	S=	0.00746	V=	0.00020	(2)
P=	0.00746	S=	0.00069	V=	0.00032	(2)
P=	0.00746	S=	0.00045	V=	0.00040	(2)
P=	0.00746	S=	0.00141	V=	0.00040	(10)
P=	0.00746	S=	0.00477	V=	0.00047	(4)
P=	0.00477	S=	0.00746	V=	0.00047	(2)
P=	0.00746	S=	0.00317	V=	0.00054	(4)
P=	0.00161	S=	0.00746	V=	0.00060	(2)
P=	0.00746	S=	0.00037	V=	0.00064	(2)
P=	0.00746	S=	0.00078	V=	0.00106	(4)
P=	0.01270	S=	0.00746	V=	0.00108	(2)
P=	0.00746	S=	0.01270	V=	0.00108	(4)
P=	0.00746	S=	0.00212	V=	0.00111	(6)
P=	0.00227	S=	0.00746	V=	0.00126	(2)
P=	0.00746	S=	0.00368	V=	0.00156	(2)
P=	0.00368	S=	0.00746	V=	0.00156	(2)
P=	0.00746	S=	0.00212	V=	0.00162	(14)
P=	0.00746	S=	0.00124	V=	0.00198	(2)
P=	0.00312	S=	0.00746	V=	0.00212	(4)
P=	0.00746	S=	0.00317	V=	0.00217	(6)
P=	0.00746	S=	0.00141	V=	0.00232	(4)
P=	0.00746	S=	0.00212	V=	0.00248	(4)
P=	0.00746	S=	0.00158	V=	0.00265	(2)
P=	0.00746	S=	0.00212	V=	0.00312	(10)
P=	0.00847	S=	0.00746	V=	0.00323	(6)
P=	0.00746	S=	0.00847	V=	0.00323	(10)
P=	0.00746	S=	0.00477	V=	0.00376	(6)
P=	0.00480	S=	0.00746	V=	0.00379	(4)
P=	0.00631	S=	0.00746	V=	0.00530	(2)
P=	0.00746	S=	0.00631	V=	0.00530	(2)

mental data and the calculated value is about ±0.00015. (8) The suggested Miller indices for this powder pattern and the original paper are quite agreeable.

TABLE 83

Indexed Diffraction Data of $Na_2Ti_3O_7$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.00746	0.00741	0	0	1
0.00847	0.00842	1	0	0
0.01270	0.01266	1	0	-1
0.01908	0.01900	1	0	1
0.02972	0.02963	0	0	2
0.03478	0.03474	2	0	-1
0.04941	0.04941	1	1	0
0.05055	0.05062	2	0	-2
0.05995	0.05999	1	1	1
0.06551	0.06557	1	0	-3
0.06660	0.06667	0	0	3
0.07068	0.07062	0	1	2
0.07268	0.07270	1	1	-2
0.07471	0.07467	2	1	0
0.07570	0.07573	2	1	-1
0.08139	0.08132	2	0	-3
0.08464	0.08461	1	0	3
0.08541	0.08539	1	1	2
0.08639	0.08638	3	0	-2
0.08833	0.08842	2	1	1
0.09170	0.09161	2	1	-2
0.09268	0.09271	3	0	1
0.10654	0.10656	1	1	-3
0.10751	0.10766	0	1	3
0.13897	0.13898	4	0	-2
0.13971	0.13964	1	0	4
0.16394	0.16395	0	2	0

P= 0.00842 Q= 0.04099 S= 0.00741 V=-0.00317

STANDARD DEVIATION=0.000060

THIS IS A MONOCLINIC CRYSTAL POWDER PATTERN

Example B

This example, chosen from Kadijk, Huisman and Jellinek,[80] indexes the Ta_2Se_3 powder pattern. The first twenty-nine low-angle reflection lines were indexed. Observed $Sin^2\theta$ values are listed in Table 84. The indexing procedures may be described as follows. (1) The set of observed $Sin^2\theta$ values is the input to the computer program DA. The output, listed in Table 85, is a difference table. (2) One may easily select the recurrent values. The group containing the most recurrent values is 0.05105 (0.05074, 0.05076, 0.05082, 0.05083, 0.05093, 0.05096, 0.05108, 0.05115, 0.05118, 0.05136, 0.05148). Hence, the possible Q is 0.05105. (3) Let us select 0.00754 as the possible P or S (since 0.00754 : 0.02968 = 1 : 4). (4) Let 0.01502, 0.01758, and 0.02741 together with 0.00754 be the inputs to the computer program AMO. The output of the computer program is listed in Table 86. (5) From Table 86, the most recurrent value of V is 0.00498 (it appears sixteen times) for the possible P and S = 0.00754 and 0.01502. (6) The inputs to the computer program MON are the set of observed $Sin^2\theta$ values and the possible parameter pairs (P_j,Q_j,S_j,V_j), which are (0.00754, 0.05105, 0.01502, 0.00498), (0.00754, 0.05105, 0.01502, -0.00498), (0.01502, 0.05105, 0.00754, 0.00498), and (0.01502, 0.05105, 0.00754, -0.00498). The output is recorded in Table 87. (7) The standard

TABLE 84

$Sin^2\theta$ Values Calculated
from the Powder Pattern of Ta_2Se_3

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.00754	16	0.10546
2	0.01502	17	0.10804
3	0.01758	18	0.10870
4	0.02741	19	0.11374
5	0.02968	20	0.11777
6	0.05450	21	0.12048
7	0.05722	22	0.12784
8	0.05869	23	0.13409
9	0.06595	24	0.13876
10	0.06972	25	0.14756
11	0.07718	26	0.15342
12	0.07849	27	0.15620
13	0.08104	28	0.16492
14	0.08607	29	0.17740
15	0.09673		

deviation, 0.000159, shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.00034. (8) There is only one reflection line assigned differently than in the original paper. A better Miller index, (310), is assigned to the reflection line associated with the $Sin^2\theta$ values 0.11777 ((31$\bar{1}$) was original assigned). Another example, similar to this one, was also studied (see Example C below). Both examples agree on the Miller index (310) as a better assignment.

TABLE 85

Difference Table of the Powder Diffraction Data of Ta_2Se_3

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00066	0.00131	0.00147	0.00227	0.00255	0.00256	0.00258	0.00271
0.00272	0.00278	0.00324	0.00377	0.00386	0.00403	0.00419	0.00467
0.00503	0.00504	0.00570	0.00586	0.00625	0.00674	0.00726	0.00736
0.00746	0.00748	0.00758	0.00828	0.00864	0.00872	0.00873	0.00873
0.00877	0.00880	0.00889	0.00907	0.00973	0.00983	0.01004	0.01007
0.01066	0.01092	0.01103	0.01123	0.01131	0.01132	0.01145	0.01150
0.01178	0.01197	0.01210	0.01231	0.01239	0.01244	0.01248	0.01250
0.01254	0.01347	0.01361	0.01410	0.01466	0.01466	0.01502	0.01509
0.01522	0.01569	0.01632	0.01635	0.01701	0.01736	0.01744	0.01824
0.01828	0.01849	0.01914	0.01933	0.01939	0.01955	0.01972	0.01980
0.01980	0.01987	0.01996	0.02012	0.02035	0.02099	0.02104	0.02120
0.02127	0.02197	0.02211	0.02214	0.02235	0.02238	0.02263	0.02268
0.02375	0.02382	0.02398	0.02399	0.02442	0.02482	0.02502	0.02539
0.02558	0.02605	0.02616	0.02654	0.02697	0.02700	0.02701	0.02708
0.02709	0.02738	0.02754	0.02766	0.02767	0.02828	0.02836	0.02863
0.02885	0.02901	0.02955	0.02979	0.02981	0.02984	0.03006	0.03021
0.03072	0.03078	0.03083	0.03086	0.03111	0.03128	0.03152	0.03157
0.03170	0.03270	0.03294	0.03330	0.03382	0.03441	0.03525	0.03565
0.03572	0.03574	0.03627	0.03656	0.03673	0.03692	0.03708	0.03736
0.03804	0.03832	0.03843	0.03854	0.03864	0.03886	0.03898	0.03928
0.03944	0.03948	0.03951	0.03951	0.03952	0.03964	0.03968	0.04004
0.04059	0.04111	0.04177	0.04199	0.04203	0.04209	0.04210	0.04220
0.04223	0.04231	0.04246	0.04275	0.04330	0.04331	0.04367	0.04402
0.04444	0.04472	0.04538	0.04677	0.04680	0.04696	0.04715	0.04750
0.04750	0.04779	0.04796	0.04802	0.04805	0.04816	0.04824	0.04837
0.04881	0.04935	0.04935	0.04956	0.04968	0.04977	0.05001	0.05066
0.05074	0.05076	0.05082	0.05083	0.05093	0.05096	0.05108	0.05115
0.05118	0.05136	0.05148	0.05182	0.05214	0.05269	0.05305	0.05354
0.05363	0.05420	0.05453	0.05470	0.05505	0.05560	0.05622	0.05639
0.05652	0.05669	0.05688	0.05691	0.05692	0.05772	0.05812	0.05841
0.05866	0.05908	0.05924	0.05946	0.05947	0.05960	0.05963	0.06027
0.06055	0.06091	0.06149	0.06158	0.06179	0.06189	0.06216	0.06218
0.06326	0.06327	0.06346	0.06347	0.06366	0.06437	0.06598	0.06602
0.06652	0.06705	0.06735	0.06814	0.06819	0.06849	0.06870	0.06904
0.06907	0.06915	0.06932	0.06936	0.06964	0.07013	0.07038	0.07062
0.07095	0.07105	0.07194	0.07238	0.07281	0.07334	0.07350	0.07493
0.07516	0.07540	0.07578	0.07624	0.07687	0.07771	0.07784	0.07805
0.07836	0.07853	0.07885	0.07902	0.07902	0.07915	0.07959	0.08007
0.08063	0.08067	0.08129	0.08154	0.08161	0.08171	0.08370	0.08388
0.08406	0.08426	0.08633	0.08643	0.08648	0.08747	0.08774	0.08788
0.08809	0.08887	0.08919					

TABLE 86

Output Data of the Auxiliary Computer Program (AMO) for the Powder Pattern of Ta_2Se_3

POSSIBLE P OR S= 0.00754

P= 0.00754	S= 0.00195	V= 0.00017	(4)
P= 0.00754	S= 0.00233	V= 0.00036	(2)
P= 0.00754	S= 0.00207	V= 0.00041	(2)
P= 0.00685	S= 0.00754	V= 0.00063	(2)
P= 0.00754	S= 0.00685	V= 0.00063	(4)
P= 0.00754	S= 0.00219	V= 0.00064	(2)
P= 0.00754	S= 0.00142	V= 0.00091	(2)
P= 0.00754	S= 0.00305	V= 0.00107	(4)
P= 0.00754	S= 0.00439	V= 0.00115	(4)
P= 0.00754	S= 0.00876	V= 0.00128	(2)
P= 0.00876	S= 0.00754	V= 0.00128	(2)
P= 0.00581	S= 0.00754	V= 0.00168	(2)
P= 0.00754	S= 0.00581	V= 0.00168	(2)
P= 0.00754	S= 0.00160	V= 0.00181	(2)
P= 0.00754	S= 0.00095	V= 0.00185	(6)
P= 0.00754	S= 0.00288	V= 0.00203	(2)
P= 0.00754	S= 0.00146	V= 0.00210	(4)
P= 0.01758	S= 0.00754	V= 0.00229	(2)
P= 0.00754	S= 0.01758	V= 0.00229	(4)
P= 0.00754	S= 0.00305	V= 0.00235	(4)
P= 0.00754	S= 0.00130	V= 0.00241	(2)
P= 0.00754	S= 0.00376	V= 0.00249	(10)
P= 0.00754	S= 0.00439	V= 0.00309	(4)
P= 0.00439	S= 0.00754	V= 0.00309	(2)
P= 0.00754	S= 0.00342	V= 0.00310	(4)
P= 0.00754	S= 0.00685	V= 0.00319	(6)
P= 0.00685	S= 0.00754	V= 0.00319	(4)
P= 0.00754	S= 0.00376	V= 0.00325	(4)
P= 0.00754	S= 0.00417	V= 0.00331	(6)
P= 0.00417	S= 0.00754	V= 0.00331	(4)
P= 0.00754	S= 0.00439	V= 0.00357	(4)
P= 0.00754	S= 0.00353	V= 0.00395	(2)
P= 0.00578	S= 0.00754	V= 0.00426	(2)
P= 0.00754	S= 0.00578	V= 0.00426	(2)
P= 0.00754	S= 0.01502	V= 0.00498	(10)
P= 0.01502	S= 0.00754	V= 0.00498	(6)
P= 0.00754	S= 0.01368	V= 0.00619	(2)
P= 0.01368	S= 0.00754	V= 0.00619	(2)

TABLE 87

Indexed Diffraction Data of Ta_2Se_3

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.00754	0.00742	1	0	0
0.01502	0.01488	0	0	1
0.01758	0.01737	1	0	-1
0.02741	0.02724	1	0	1
0.02968	0.02969	2	0	0
0.05450	0.05445	2	0	1
0.05722	0.05708	1	0	-2
0.05869	0.05851	1	1	0
0.06595	0.06598	0	1	1
0.06972	0.06947	2	0	-2
0.07718	0.07684	1	0	2
0.07849	0.07834	1	1	1
0.08104	0.08078	2	1	0
0.08607	0.08579	2	1	-1
0.09673	0.09670	3	0	-2
0.10546	0.10554	2	1	1
0.10804	0.10818	1	1	-2
0.10870	0.10898	2	0	2
0.11374	0.11387	4	0	-1
0.11777	0.11789	3	1	0
0.12048	0.12056	2	1	-2
0.12784	0.12793	1	1	2
0.13409	0.13402	2	0	-3
0.13876	0.13877	4	0	-2
0.14756	0.14758	3	1	1
0.15342	0.15338	4	0	1
0.15620	0.15620	1	0	3
0.16492	0.16497	4	1	-1
0.17740	0.17766	1	1	-3

P= 0.00742 Q= 0.05109 S= 0.01488 V=-0.00494

STANDARD DEVIATION=0.000159

THIS IS A MONOCLINIC CRYSTAL POWDER PATTERN

Example C

This example, also chosen from Kadijk, Huisman and Jellinek,[80] indexes the Nb_2Se_3 powder pattern. The first thirty-six low-angle reflection lines were indexed. The indexing procedures are similar to the previous examples. The indexed powder diffraction data is recorded in Table 88. The suggested Miller indices are agreeable with the original paper except at the 23rd reflection line, 0.11698. Miller index $(31\bar{1})$ was originally assigned to this reflection line. A better solution, (310), is suggested. The standard deviation, 0.000082, shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.00018.

Example D

This example, chosen from Wadsley,[81] indexes the $Ti_2Nb_{10}O_{29}$ powder pattern. The first twenty-five low-angle reflection lines were indexed. The indexed powder diffraction data is listed in Table 89. There are eight reflection lines assigned differently than in the original paper. They are 7th, 11th, 12th, 18th, 20th, 22nd, 24th, and 25th. However, better solutions are obtained by this method than hand calculations. The standard deviation, 0.000063, shows that the experimental data and the calculated value are quite close. The maximum discrepancy is only about ±0.00013.

TABLE 88

Indexed Diffraction Data of Nb_2Se_3

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.00739	0.00739	1	0	0
0.01477	0.01482	0	0	1
0.01736	0.01736	1	0	-1
0.02701	0.02706	1	0	1
0.02956	0.02955	2	0	0
0.03479	0.03467	2	0	-1
0.05418	0.05406	2	0	1
0.05714	0.05698	1	0	-2
0.05787	0.05771	1	1	0
0.05943	0.05929	0	0	2
0.06508	0.06515	0	1	1
0.06655	0.06648	3	0	0
0.06769	0.06768	1	1	-1
0.06936	0.06945	2	0	-2
0.07635	0.07637	1	0	2
0.07737	0.07738	1	1	1
0.07981	0.07987	2	1	0
0.08490	0.08500	2	1	-1
0.09662	0.09669	3	0	-2
0.10439	0.10439	2	1	1
0.10739	0.10730	1	1	-2
0.10816	0.10823	2	0	2
0.11352	0.11362	4	0	-1
0.11698	0.11680	3	1	0
0.11980	0.11977	2	1	-2
0.12668	0.12669	1	1	2
0.13385	0.13386	2	0	-3
0.13876	0.13870	4	0	-2
0.14620	0.14617	3	1	1
0.14694	0.14701	3	1	-2
0.15230	0.15240	4	0	1
0.15531	0.15533	1	0	3
0.15620	0.15625	3	0	-3
0.16388	0.16395	4	1	-1
0.17541	0.17526	5	0	-1
0.17660	0.17657	1	1	-3

P= 0.00739 Q= 0.05032 S= 0.01482 V=-0.00485

STANDARD DEVIATION=0.000082

THIS IS A MONOCLINIC CRYSTAL POWDER PATTERN

TABLE 89

Indexed Diffraction Data of $Ti_2Nb_{10}O_{29}$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.00294	0.00292	1	0	0
0.00608	0.00608	1	0	-2
0.01166	0.01168	2	0	0
0.02266	0.02266	1	0	-4
0.02631	0.02628	3	0	0
0.04251	0.04243	0	1	1
0.04365	0.04367	1	1	0
0.04662	0.04671	4	0	0
0.04714	0.04712	1	1	1
0.05090	0.05077	2	0	-6
0.05242	0.05243	2	1	0
0.05367	0.05369	1	0	5
0.05751	0.05765	2	1	1
0.07382	0.07391	1	0	6
0.07677	0.07673	1	1	-5
0.08232	0.08236	3	1	-5
0.09332	0.09330	2	0	6
0.10284	0.10273	5	1	-2
0.11128	0.11136	5	1	-5
0.11188	0.11197	3	1	-7
0.14076	0.14077	3	0	-10
0.14270	0.14264	4	1	4
0.16305	0.16301	0	2	0
0.17459	0.17458	7	0	2
0.18641	0.18639	3	1	7

P= 0.00292 Q= 0.04075 S= 0.00168 V=-0.00177
STANDARD DEVIATION=0.000063
THIS IS A MONOCLINIC CRYSTAL POWDER PATTERN

Example E

This example, chosen from Conard, Norrby and Franzen,[82] indexes Nb_2Se powder pattern. There were eighteen reflection

lines to be indexed. The indexed powder diffraction data is listed in Table 90. The standard deviation, 0.000135, shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.00036. There are seven reflection lines assigned differently than in the original paper. The recommended computer method gives a better solution.

Example F

This example, chosen from Zachariasen,[39] indexes the alpha plutonium powder pattern. There were sixty reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 91. The standard deviation, 0.000092, shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.00056.

Example G

This example, chosen from Mukherjee,[83] indexes the monoclinic pyrrhotites powder pattern. There were forty-eight reflection lines to be indexed. The indexed powder diffraction data is recorded in Table 92. In this table, there are as many as thirty-five reflection lines assigned differently than in the original paperl The reason for so many mistakes in the hand calculations may be the small value of V. This emphasizes the necessity of a computer method for indexing the powder patterns of lower symmetric materials. The standard deviation, 0.000175,

TABLE 90

Indexed Diffraction Data of Nb_2Se

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.00678	0.00685	0	0	1
0.01208	0.01221	2	0	0
0.01968	0.01975	2	0	1
0.07802	0.07801	0	1	2
0.08171	0.08175	1	1	2
0.08577	0.08596	3	1	1
0.10338	0.10341	3	1	-2
0.10713	0.10714	5	0	2
0.10957	0.10962	0	0	4
0.11441	0.11428	1	1	-3
0.12639	0.12654	2	1	3
0.13213	0.13202	5	1	-1
0.13684	0.13663	3	1	-3
0.20252	0.20243	0	2	0
0.21716	0.21718	8	0	-2
0.31189	0.31205	0	2	4
0.31699	0.31706	4	2	3
0.38456	0.38419	7	2	2

P= 0.00305 Q= 0.05061 S= 0.00685 V=-0.00034
STANDARD DEVIATION=0.000135
THIS IS A MONOCLINIC CRYSTAL POWDER PATTERN

shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.00059.

The Triclinic System

The Use of the Main Computer Program TRI

The main computer program TRI for indexing the unknown

TABLE 91

Indexed Diffraction Data of Alpha Plutonium

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.04637	0.04634	0	0	3
0.06261	0.06248	2	0	-1
0.06482	0.06479	2	0	0
0.06981	0.06979	1	1	2
0.07043	0.07047	2	0	-2
0.07187	0.07187	0	1	3
0.07377	0.07372	1	0	3
0.07690	0.07688	1	1	-3
0.07737	0.07740	2	0	1
0.08244	0.08238	0	0	4
0.08804	0.08802	2	1	-1
0.08878	0.08876	2	0	-3
0.09032	0.09033	2	1	0
0.09601	0.09601	2	1	-2
0.09922	0.09926	1	1	3
0.10211	0.10214	0	2	0
0.10290	0.10293	2	1	1
0.10794	0.10792	0	1	4
0.10924	0.10920	1	1	-4
0.11352	0.11350	1	0	4
0.11425	0.11429	2	1	-3
0.11737	0.11734	2	0	-4
0.12582	0.12584	2	1	2
0.12628	0.12627	1	0	-5
0.13900	0.13903	1	1	4
0.14399	0.14400	3	0	-2
0.14583	0.14578	3	0	0
0.15431	0.15425	0	1	5
0.15633	0.15622	2	0	-5
0.15869	0.15856	3	0	-3
0.16208	0.16212	3	0	1
0.16362	0.16356	1	0	5
0.16518	0.16462	2	2	-1
0.16954	0.16954	3	1	-2
0.17125	0.17132	3	1	0
0.17257	0.17261	2	2	-2
0.17594	0.17587	1	2	3
0.17701	0.17701	2	0	4
0.17948	0.17954	2	2	1
0.18169	0.18176	2	1	-5
0.18446	0.18452	0	2	4
0.18758	0.18765	3	1	1
0.18923	0.18910	1	1	5

TABLE 91 (CONTINUED)

0.19079	0.19090	2	2	-3
0.20259	0.20254	2	1	4
0.20547	0.20540	2	0	-6
0.21086	0.21089	0	1	6
0.21558	0.21564	1	2	4
0.21932	0.21948	2	2	-4
0.22563	0.22568	3	0	3
0.22842	0.22841	1	2	-5
0.23091	0.23093	2	1	-6
0.24233	0.24238	1	0	-7
0.24405	0.24410	3	1	-5
0.24601	0.24602	1	3	0
0.24940	0.24940	4	0	-1
0.25226	0.25229	0	0	7
0.25630	0.25634	2	1	5
0.25829	0.25836	2	2	-5

P= 0.01620 Q= 0.02554 S= 0.00515 V=-0.00373

STANDARD DEVIATION=0.000092

THIS IS A MONOCLINIC CRYSTAL POWDER PATTERN

powder pattern of triclinic crystals and the flow chart are given in Appendix F.

For the input of the computer program TRI, M stands for the total number of the powder patterns to be indexed as triclinic structure, K stands for the total number of the reflection lines in each powder pattern, L stands for the total number of possible parameter pairs (P_j,Q_j,S_j,U_j,V_j,W_j), P1(J) stands for all the possible parameters of P_j, P2(J) stands for all the possible parameters of Q_j, P3(J) stands for all the possible parameters of S_j, P4(J) stands for all the possible

TABLE 92

Indexed Diffraction Data of Monoclinic Pyrrhotites

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.02660	0.02660	2	0	0
0.02860	0.02869	0	0	4
0.03380	0.03388	2	0	2
0.05550	0.05549	2	0	4
0.07960	0.07970	3	1	0
0.09150	0.09152	2	1	5
0.10590	0.10595	2	2	0
0.11410	0.11410	2	0	-7
0.13500	0.13484	2	2	4
0.14280	0.14270	4	1	3
0.17120	0.17137	2	0	-9
0.18510	0.18519	1	3	0
0.19320	0.19314	4	2	2
0.22160	0.22143	2	3	3
0.23850	0.23840	3	3	0
0.25820	0.25822	3	1	-10
0.30160	0.30140	4	3	3
0.31780	0.31773	3	2	-10
0.35130	0.35128	2	4	2
0.36580	0.36581	4	0	12
0.42350	0.42364	5	2	-10
0.43120	0.43119	4	4	2
0.45360	0.45355	8	0	-4
0.45820	0.45807	2	2	14
0.46010	0.46058	5	3	8
0.53360	0.53385	7	3	4
0.53690	0.53695	1	3	14
0.54080	0.54076	0	5	5
0.56140	0.56150	2	4	11
0.56480	0.56464	7	1	11
0.56910	0.56907	8	0	-9
0.67640	0.67581	1	4	14
0.68290	0.68321	4	4	12
0.68730	0.68724	7	4	-5
0.69150	0.69141	5	5	4
0.74180	0.74225	6	5	-2
0.76740	0.76725	6	3	-14
0.77160	0.77155	4	1	-19
0.77690	0.77665	4	4	14
0.78130	0.78133	3	6	2
0.82010	0.82010	11	0	-3
0.82870	0.82866	7	5	-2
0.85110	0.85102	11	0	5

TABLE 92 (CONTINUED)

0.85970	0.85978	3	5	13
0.95280	0.95277	8	3	-14
0.96800	0.96826	0	1	23
0.97900	0.97910	12	1	-1
0.98360	0.98334	11	3	0

P= 0.00665 Q= 0.01984 S= 0.00179 V=-0.00003

STANDARD DEVIATION=0.000175

THIS IS A MONOCLINIC CRYSTAL POWDER PATTERN

parameters of U_j, P5(J) stands for all the possible parameters of V_j, and P6(J) stands for all the possible parameters of W_j.

The output of the computer program contains the observed $Sin^2\theta$ values, calculated $Sin^2\theta$ values, and the Miller indices of the reflections.

Example A

This example, chosen from Bear and Mumme,[85] indexes the β-$Zr(SO_4)_2 5H_2O$ powder pattern. Fifty reflections were indexed. Observed $Sin^2\theta$ values are listed in Table 93. The indexing procedures may be described as follows. (1) The set of observed $Sin^2\theta$ values is the input to the computer program DA. The output, listed in Table 94, is a difference table. (2) Since there are no recurrent values occured in Table 94, one may decide that this is possibly a triclinic powder pattern. (3) Let the smallest observed $Sin^2\theta$ value be the possible parameter

TABLE 93

$Sin^2\theta$ Values Calculated
from the Powder Pattern of β-$Zr(SO_4)_2 5H_2O$

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.00830	26	0.07470
2	0.01060	27	0.08160
3	0.01070	28	0.08270
4	0.01610	29	0.08420
5	0.01710	30	0.08770
6	0.01860	31	0.08840
7	0.01950	32	0.09210
8	0.02180	33	0.09370
9	0.02550	34	0.09610
10	0.02820	35	0.10010
11	0.03050	36	0.10190
12	0.03330	37	0.10380
13	0.03730	38	0.10980
14	0.03820	39	0.11420
15	0.04240	40	0.12610
16	0.04490	41	0.12890
17	0.04790	42	0.13270
18	0.04980	43	0.14560
19	0.05210	44	0.14870
20	0.05450	45	0.15370
21	0.05670	46	0.15710
22	0.05840	47	0.16620
23	0.06140	48	0.16970
24	0.06570	49	0.17260
25	0.06840	50	0.17760

P if other $Sin^2\theta$ values exist such that they have a ratio of four. For this example, we select 0.0083 as P since 0.0083 : 0.0333 = 1 : 4. By doing this, we select the second smallest $Sin^2\theta$ value, which is not a multiple of P, as either belonging

TABLE 94

Difference Table of the
Powder Diffraction Data of β-$Zr(SO_4)_2 5H_2O$

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00010	0.00070	0.00090	0.00090	0.00100	0.00110	0.00150	0.00150
0.00160	0.00170	0.00180	0.00190	0.00190	0.00220	0.00230	0.00230
0.00230	0.00230	0.00240	0.00240	0.00240	0.00240	0.00250	0.00250
0.00260	0.00270	0.00270	0.00280	0.00280	0.00290	0.00300	0.00300
0.00310	0.00320	0.00340	0.00340	0.00350	0.00350	0.00370	0.00370
0.00370	0.00380	0.00390	0.00400	0.00400	0.00400	0.00420	0.00420
0.00420	0.00430	0.00440	0.00440	0.00460	0.00470	0.00470	0.00470
0.00490	0.00490	0.00500	0.00500	0.00500	0.00500	0.00510	0.00510
0.00530	0.00540	0.00550	0.00550	0.00570	0.00570	0.00580	0.00600
0.00600	0.00600	0.00610	0.00630	0.00630	0.00640	0.00640	0.00640
0.00640	0.00650	0.00660	0.00660	0.00670	0.00680	0.00680	0.00690
0.00690	0.00690	0.00690	0.00700	0.00720	0.00730	0.00740	0.00760
0.00770	0.00770	0.00770	0.00780	0.00780	0.00790	0.00790	0.00790
0.00790	0.00800	0.00800	0.00800	0.00810	0.00820	0.00840	0.00840
0.00840	0.00860	0.00870	0.00870	0.00880	0.00880	0.00880	0.00890
0.00900	0.00900	0.00910	0.00910	0.00910	0.00930	0.00940	0.00940
0.00950	0.00950	0.00960	0.00960	0.00970	0.00970	0.00970	0.00980
0.01000	0.01000	0.01010	0.01030	0.01040	0.01050	0.01050	0.01060
0.01100	0.01100	0.01110	0.01110	0.01120	0.01120	0.01120	0.01140
0.01150	0.01150	0.01160	0.01160	0.01160	0.01170	0.01170	0.01170
0.01180	0.01180	0.01190	0.01190	0.01190	0.01190	0.01210	0.01210
0.01210	0.01230	0.01240	0.01250	0.01250	0.01260	0.01270	0.01290
0.01300	0.01320	0.01330	0.01340	0.01340	0.01350	0.01350	0.01350
0.01350	0.01360	0.01370	0.01370	0.01380	0.01390	0.01390	0.01410
0.01420	0.01420	0.01430	0.01430	0.01440	0.01440	0.01450	0.01460
0.01470	0.01470	0.01480	0.01480	0.01490	0.01540	0.01550	0.01550
0.01580	0.01590	0.01590	0.01590	0.01600	0.01600	0.01600	0.01610
0.01610	0.01620	0.01630	0.01630	0.01630	0.01630	0.01640	0.01650
0.01650	0.01670	0.01670	0.01690	0.01700	0.01720	0.01720	0.01720
0.01740	0.01740	0.01740	0.01750	0.01750	0.01760	0.01770	0.01770
0.01780	0.01780	0.01800	0.01810	0.01850	0.01850	0.01850	0.01850
0.01860	0.01870	0.01870	0.01880	0.01890	0.01900	0.01900	0.01910
0.01920	0.01930	0.01930	0.01940	0.01940	0.01950	0.01960	0.01960
0.01970	0.01980	0.01980	0.01990	0.01990	0.02000	0.02020	0.02020
0.02020	0.02020	0.02030	0.02050	0.02050	0.02050	0.02060	0.02060
0.02080	0.02100	0.02100	0.02110	0.02110	0.02110	0.02120	0.02120
0.02130	0.02140	0.02140	0.02160	0.02160	0.02200	0.02210	0.02210
0.02210	0.02220	0.02220	0.02230	0.02240	0.02260	0.02260	0.02260
0.02270	0.02270	0.02280	0.02290	0.02290	0.02310	0.02320	0.02320
0.02330	0.02340	0.02350	0.02370	0.02380	0.02390	0.02390	0.02390
0.02400	0.02410	0.02410	0.02420	0.02430	0.02430	0.02440	0.02480
0.02490	0.02490	0.02500	0.02510	0.02510	0.02530	0.02530	0.02540
0.02540	0.02560	0.02580	0.02580	0.02600	0.02600	0.02600	0.02610
0.02620	0.02630	0.02630	0.02630	0.02630	0.02640	0.02650	0.02660

TABLE 94 (CONTINUED)

0.02660	0.02670	0.02680	0.02700	0.02700	0.02700	0.02710	0.02710
0.02720	0.02750	0.02750	0.02750	0.02760	0.02760	0.02770	0.02780
0.02790	0.02800	0.02800	0.02810	0.02820	0.02820	0.02820	0.02840
0.02840	0.02850	0.02880	0.02880	0.02890	0.02890	0.02900	0.02900
0.02910	0.02930	0.02930	0.02950	0.02970	0.02980	0.02990	0.03000
0.03000	0.03000	0.03020	0.03020	0.03030	0.03030	0.03040	0.03060
0.03070	0.03080	0.03080	0.03090	0.03100	0.03100	0.03110	0.03120
0.03120	0.03140	0.03150	0.03170	0.03170	0.03170	0.03180	0.03180
0.03180	0.03200	0.03210	0.03230	0.03230	0.03240	0.03240	0.03260
0.03260	0.03260	0.03270	0.03270	0.03280	0.03290	0.03290	0.03320
0.03320	0.03350	0.03350	0.03350	0.03370	0.03370	0.03370	0.03390
0.03400	0.03410						

to the (010) plane or the (110) plane. Hence, 0.0106 is the value. Let 0.0083 and 0.0106 together with next fifteen reflection lines (0.0107, 0.0161, 0.0171, 0.0186, 0.0195, 0.0218, 0.0255, 0.0282, 0.0305, 0.0373, 0.0382, 0.0424, 0.0449, 0.0479, and 0.0498) be the inputs to the computer program ATR; the output is recorded in Table 95. (4) In Table 95, we find that if P or Q is 0.0083 and Q or S is 0.0106, the possible U or V or W is then 0.0028 because this value appears eight times. Another important factor in deciding the possible U or V or W is that all four values associated with this value are either equal to or near some of the $Sin^2\theta$ values. Here, we pick up 0.0106 as the possible Q or S because 0.0106 : 0.0424 = 1 : 4. (For the triclinic system, the relation between P and Q to U is identical to P and S to V and Q and S to W. We are using P or Q, Q or S,

TABLE 95

First Output Data of the Auxiliary Computer Program (ATR) for the Powder Pattern of β-$Zr(SO_4)_2 5H_2O$

P OR Q= 0.00830

QS	UVW	NO.	H=-1	H=1	H=-2	H=2
0.00235	0.00005	3	0.01060	0.01070	0.03545	0.03565
0.00207	0.00023	2	0.01013	0.01060	0.03480	0.03573
0.01060	0.00030	4	0.01860	0.01920	0.04320	0.04440
0.00263	0.00033	2	0.01060	0.01127	0.03517	0.03650
0.00285	0.00055	4	0.01060	0.01170	0.03495	0.03715
0.01060	0.00060	6	0.01830	0.01950	0.04260	0.04500
0.00160	0.00070	3	0.00920	0.01060	0.03340	0.03620
0.00330	0.00100	3	0.01060	0.01260	0.03450	0.03850
0.00363	0.00133	2	0.01060	0.01327	0.03417	0.03950
0.01060	0.00140	2	0.01750	0.02030	0.04100	0.04660
0.00052	0.00178	3	0.00705	0.01060	0.03017	0.03727
0.01060	0.00180	2	0.01710	0.02070	0.04020	0.04740
0.01060	0.00205	2	0.01685	0.02095	0.03970	0.04790
0.00445	0.00215	2	0.01060	0.01490	0.03335	0.04195
0.01060	0.00280	8	0.01610	0.02170	0.03820	0.04940
0.01060	0.00300	2	0.01590	0.02190	0.03780	0.04980
0.01060	0.00325	2	0.01565	0.02215	0.03730	0.05030
0.00555	0.00325	4	0.01060	0.01710	0.03225	0.04525
0.00630	0.00400	3	0.01060	0.01860	0.03150	0.04750
0.01060	0.00415	2	0.01475	0.02305	0.03550	0.05210
0.00675	0.00445	2	0.01060	0.01950	0.03105	0.04885
0.00730	0.00500	2	0.01060	0.02060	0.03050	0.05050
0.00765	0.00535	2	0.01060	0.02130	0.03015	0.05155
0.00790	0.00560	3	0.01060	0.02180	0.02990	0.05230
0.01060	0.00587	2	0.01303	0.02477	0.03205	0.05555
0.01060	0.00625	2	0.01265	0.02515	0.03130	0.05630
0.01060	0.00660	8	0.01230	0.02550	0.03060	0.05700
0.01060	0.00692	2	0.01198	0.02582	0.02995	0.05765
0.00975	0.00745	2	0.01060	0.02550	0.02805	0.05785
0.01060	0.00780	4	0.01110	0.02670	0.02820	0.05940
0.01060	0.00820	2	0.01070	0.02710	0.02740	0.06020
0.01060	0.00915	6	0.00975	0.02805	0.02550	0.06210
0.01060	0.00957	2	0.00933	0.02847	0.02465	0.06295
0.01230	0.01000	3	0.01060	0.03060	0.02550	0.06550
0.01060	0.01010	2	0.00880	0.02900	0.02360	0.06400
0.01060	0.01100	2	0.00790	0.02990	0.02180	0.06580
0.01060	0.01125	4	0.00765	0.03015	0.02130	0.06630
0.01060	0.01160	2	0.00730	0.03050	0.02060	0.06700
0.01060	0.01185	2	0.00705	0.03075	0.02010	0.06750
0.01060	0.01215	2	0.00675	0.03105	0.01950	0.06810
0.01060	0.01260	6	0.00630	0.03150	0.01860	0.06900
0.01600	0.01370	3	0.01060	0.03800	0.02180	0.07660
0.01830	0.01600	2	0.01060	0.04260	0.01950	0.08350
0.01945	0.01715	2	0.01060	0.04490	0.01835	0.08695

and U or V or W constantly in this way.) (5) Next, we select another smallest $Sin^2\theta$ value, which is not a linear combination of 0.0083, 0.0106, and 0.0028, as our possible parameter S. For this example, 0.0107 is chosen. Let the possible parameters, 0.0083, 0.0106, and 0.0107 together with another fifteen reflection (0.0171, 0.0186, 0.0195, 0.0218, 0.0255, 0.0282, 0.0305, 0.0373, 0.0382, 0.0449, 0.0479, 0.0498, 0.0521, 0.0545, and 0.0567) be the inputs to the computer program ATR again. The output is recorded in Table 96. (6) From the Table 96, by the same token, we select the possible V as 0.0065 (it appears 10 times) and the possible W as 0.0042 (it appears 8 times) for the same possible S=0.0107. The reason we did not pick either 0.0005 or 0.0018 as the possible W (both appeared 10 times) is that the values associated with them are repeated with those associated with 0.0028 in Table 95, such as 0.0218 and 0.0495. (7) Let the possible parameter pairs (0.0083, 0.0106, 0.0107, 0.0028, 0.0065, 0.0042), (0.0083, 0.0106, 0.0107, 0.0028, -0.0065, 0.0042), and (0.0083, 0.0106, 0.0107, -0.0028, -0.0065, +0.0042) together with all the observed $Sin^2\theta$ values be the inputs to the computer program TRI; the indexed powder diffraction data is then recorded in Table 97. (8) The standard deviation, 0.000163, shows that the maximum discrepancy between the experimental data and the calculated value is about ±0.00048. (9) There are five reflection lines assigned differently than in the original paper.

TABLE 96

Second Output Data of the Auxiliary Computer Program (ATR) for the Powder Pattern of β-$Zr(SO_4)_2 5H_2O$

P OR Q= 0.00830

QS	UVW	NO.	H=-1	H=1	H=-2	H=2
0.00252	0.00012	1	0.01070	0.01093	0.03548	0.03595
0.01070	0.00040	8	0.01860	0.01940	0.04310	0.04470
0.00200	0.00040	2	0.00990	0.01070	0.03440	0.03600
0.01070	0.00065	2	0.01835	0.01965	0.04260	0.04520
0.00320	0.00080	5	0.01070	0.01230	0.03480	0.03800
0.00367	0.00127	3	0.01070	0.01323	0.03433	0.03940
0.01070	0.00160	2	0.01740	0.02060	0.04070	0.04710
0.00412	0.00172	2	0.01070	0.01413	0.03388	0.04075
0.00057	0.00182	3	0.00705	0.01070	0.03012	0.03742
0.01070	0.00190	6	0.01710	0.02090	0.04010	0.04770
0.00435	0.00195	2	0.01070	0.01460	0.03365	0.04145
0.01070	0.00280	8	0.01620	0.02180	0.03830	0.04950
0.00560	0.00320	4	0.01070	0.01710	0.03240	0.04520
0.01070	0.00330	4	0.01570	0.02230	0.03730	0.05050
0.00635	0.00395	3	0.01070	0.01860	0.03165	0.04745
0.01070	0.00410	2	0.01490	0.02310	0.03570	0.05210
0.00680	0.00440	2	0.01070	0.01950	0.03120	0.04880
0.01070	0.00482	2	0.01418	0.02382	0.03425	0.05355
0.00755	0.00515	4	0.01070	0.02100	0.03045	0.05105
0.01070	0.00530	4	0.01370	0.02430	0.03330	0.05450
0.00795	0.00555	3	0.01070	0.02180	0.03005	0.05225
0.01070	0.00597	2	0.01303	0.02497	0.03195	0.05585
0.00870	0.00630	3	0.01070	0.02330	0.02930	0.05450
0.01070	0.00650	10	0.01250	0.02550	0.03090	0.05690
0.01070	0.00690	4	0.01210	0.02590	0.03010	0.05770
0.00980	0.00740	2	0.01070	0.02550	0.02820	0.05780
0.01070	0.00785	4	0.01115	0.02685	0.02820	0.05960
0.01070	0.00920	4	0.00980	0.02820	0.02550	0.06230
0.01070	0.00945	2	0.00955	0.02845	0.02500	0.06280
0.01070	0.00967	2	0.00933	0.02867	0.02455	0.06325
0.01260	0.01010	3	0.01070	0.03090	0.02550	0.06590
0.01070	0.01030	2	0.00870	0.02930	0.02330	0.06450
0.01070	0.01105	2	0.00795	0.03005	0.02180	0.06600
0.01070	0.01145	6	0.00755	0.03045	0.02100	0.06680
0.01070	0.01195	2	0.00705	0.03095	0.02000	0.06780
0.01070	0.01220	2	0.00680	0.03120	0.01950	0.06830
0.01070	0.01265	6	0.00635	0.03165	0.01860	0.06920
0.01570	0.01330	2	0.01070	0.03730	0.02230	0.07550
0.01620	0.01380	2	0.01070	0.03830	0.02180	0.07700
0.01850	0.01610	2	0.01070	0.04290	0.01950	0.08390
0.01940	0.01700	3	0.01070	0.04470	0.01860	0.08660

TABLE 96 (CONTINUED)

P OR Q= 0.01060

OS	UVW	NO.	H=-1	H=1	H=-2	H=2
0.01070	0.00050	10	0.02080	0.02180	0.05210	0.05410
0.00090	0.00080	2	0.01070	0.01230	0.04170	0.04490
0.00112	0.00102	3	0.01070	0.01273	0.04148	0.04555
0.00137	0.00127	3	0.01070	0.01323	0.04123	0.04630
0.01070	0.00180	10	0.01950	0.02310	0.04950	0.05670
0.00190	0.00180	3	0.01070	0.01430	0.04070	0.04790
0.00252	0.00242	2	0.01070	0.01553	0.04008	0.04975
0.01070	0.00270	6	0.01860	0.02400	0.04770	0.05850
0.00330	0.00320	4	0.01070	0.01710	0.03930	0.05210
0.00405	0.00395	3	0.01070	0.01860	0.03855	0.05435
0.01070	0.00420	8	0.01710	0.02550	0.04470	0.06150
0.00450	0.00440	5	0.01070	0.01950	0.03810	0.05570
0.00565	0.00555	3	0.01070	0.02180	0.03695	0.05915
0.01070	0.00690	2	0.01440	0.02820	0.03930	0.06690
0.01070	0.00712	2	0.01418	0.02842	0.03885	0.06735
0.00750	0.00740	3	0.01070	0.02550	0.03510	0.06470
0.01070	0.00760	6	0.01370	0.02890	0.03790	0.06830
0.01070	0.00805	4	0.01325	0.02935	0.03700	0.06920
0.01070	0.00827	2	0.01303	0.02957	0.03655	0.06965
0.00885	0.00875	2	0.01070	0.02820	0.03375	0.06875
0.01070	0.00885	2	0.01245	0.03015	0.03540	0.07080
0.01070	0.00920	4	0.01210	0.03050	0.03470	0.07150
0.01000	0.00990	2	0.01070	0.03050	0.03260	0.07220
0.01070	0.01007	2	0.01123	0.03137	0.03295	0.07325
0.01070	0.01145	4	0.00985	0.03275	0.03020	0.07600
0.01070	0.01175	2	0.00955	0.03305	0.02960	0.07660
0.01070	0.01197	2	0.00933	0.03327	0.02915	0.07705
0.01070	0.01260	4	0.00870	0.03390	0.02790	0.07830
0.01340	0.01330	2	0.01070	0.03730	0.02920	0.08240
0.01070	0.01367	2	0.00763	0.03497	0.02575	0.08045
0.01385	0.01375	2	0.01070	0.03820	0.02875	0.08375
0.01070	0.01395	4	0.00735	0.03525	0.02520	0.08100
0.01070	0.01425	2	0.00705	0.03555	0.02460	0.08160
0.01710	0.01700	3	0.01070	0.04470	0.02550	0.09350
0.01870	0.01860	2	0.01070	0.04790	0.02390	0.09830
0.01965	0.01955	2	0.01070	0.04980	0.02295	0.10115

TABLE 97

Indexed Diffraction Data of β-$Zr(SO_4)_2 5H_2O$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.00830	0.00834	1	0	0
0.01060	0.01062	0	0	1
0.01070	0.01067	0	1	0
0.01610	0.01610	-1	0	1
0.01710	0.01707	0	1	-1
0.01860	0.01846	-1	1	0
0.01950	0.01956	1	1	0
0.02180	0.02182	1	0	1
0.02550	0.02551	0	1	1
0.02820	0.02772	-1	1	-1
0.03050	0.03044	-1	1	1
0.03330	0.03337	2	0	0
0.03730	0.03726	1	1	1
0.03820	0.03827	-2	0	1
0.04240	0.04247	0	0	2
0.04490	0.04486	0	2	-1
0.04790	0.04787	1	1	-2
0.04980	0.04970	2	0	1
0.05210	0.05213	1	2	0
0.05450	0.05496	-1	2	-1
0.05670	0.05653	1	0	2
0.05840	0.05821	-1	1	-2
0.06140	0.06158	0	1	2
0.06570	0.06570	2	1	1
0.06840	0.06827	0	2	-2
0.07470	0.07471	2	2	-1
0.08160	0.08175	-2	2	-1
0.08270	0.08242	-2	1	2
0.08420	0.08411	-3	1	0
0.08770	0.08740	3	1	0
0.08840	0.08840	-2	1	-2
0.09210	0.09240	2	2	-2
0.09370	0.09356	0	1	-3
0.09610	0.09604	0	3	0
0.10010	0.10039	-3	0	2
0.10190	0.10204	0	2	2
0.10380	0.10357	-1	2	2
0.10980	0.10993	-1	1	-3
0.11420	0.11447	-3	2	0
0.12610	0.12612	-2	3	0
0.12890	0.12873	-1	2	-3
0.13270	0.13271	2	3	0
0.14560	0.14535	-4	1	1
0.14870	0.14870	3	2	1

TABLE 97 (CONTINUED)

0.15370	0.15360	0	3	-3
0.15710	0.15721	-3	2	-2
0.16620	0.16618	-3	3	0
0.16970	0.16987	0	0	4
0.17260	0.17262	4	1	1
0.17760	0.17759	-2	2	3
P= 0.00834	Q= 0.01067		S= 0.01062	
V= 0.00286	U= 0.00055		W= 0.00422	

STANDARD DEVIATION=0.000163
THIS IS A TRICLINIC CRYSTAL POWDER PATTERN

This computer method gives better solutions.

Example B

This example, chosen from Henry, Lipson and Wooster,[59] indexes the data made from four superimposed single-crystal rotation photographs with the crystal set in four unrelated arbitrary orientations. There were fifteen reflection lines to be indexed. Observed $Sin^2\theta$ values are listed in Table 98. The indexing procedures may be described as follows. (1) The set of $Sin^2\theta$ values is the input of the computer program DA. The output of the computer program, listed in Table 99, is a difference table. (2) Since there are no recurrent values in Table 99, one may decide that this is possibly a triclinic powder pattern. (3) Let 0.0100 be the possible parameter P (0.0100 : 0.0399 = 1 : 4). Also, let 0.0165 be the $Sin^2\theta$ value

TABLE 98

$Sin^2\theta$ Values Calculated
from the Data Chosen from Henry, Lipson and Wooster

DIFFRACTION LINE	SIN(SQUARE) (OBSV.)	DIFFRACTION LINE	SIN(SQUARE) (OBSV.)
1	0.01000	9	0.03990
2	0.01650	10	0.04200
3	0.01950	11	0.04250
4	0.02230	12	0.04370
5	0.02620	13	0.04690
6	0.03100	14	0.05000
7	0.03380	15	0.06060
8	0.03840		

TABLE 99

Difference Table of the Powder Diffraction
Data Selected from Henry, Lipson and Wooster

DIFFERENCE ANALYSIS OF THE POWDER DIFFRACTION DATA

0.00050	0.00120	0.00150	0.00170	0.00210	0.00260	0.00280	0.00280
0.00300	0.00310	0.00320	0.00360	0.00380	0.00390	0.00410	0.00440
0.00460	0.00480	0.00490	0.00530	0.00580	0.00610	0.00630	0.00650
0.00670	0.00700	0.00740	0.00750	0.00760	0.00800	0.00820	0.00850
0.00870	0.00870	0.00890	0.00950	0.00970	0.00990	0.01010	0.01060
0.01100	0.01150	0.01150	0.01150	0.01160	0.01220	0.01230	0.01270
0.01310	0.01370	0.01370	0.01430	0.01450	0.01580	0.01590	0.01610
0.01620	0.01620	0.01630	0.01690	0.01730	0.01750	0.01760	0.01810
0.01860	0.01890	0.01900	0.01970	0.02020	0.02040	0.02070	0.02070
0.02100	0.02140	0.02190	0.02220	0.02250	0.02300	0.02340	0.02380
0.02380	0.02420	0.02460	0.02550	0.02600	0.02680	0.02720	0.02740
0.02770	0.02840	0.02960	0.02990	0.03040	0.03050	0.03200	0.03250
0.03350	0.03370	0.03440	0.03690	0.03830	0.04000	0.04110	0.04410
0.05060							

belonging to either the (010) or (110) plane. Let 0.0100 and 0.0165 together with the other twelve reflection lines be the inputs to the computer program ATR; the output is then recorded in Table 100. (4) In Table 100, the possible U is 0.00715 (average of 0.0070 and 0.0073; it appears eight times) for which the possible P and Q are 0.0100 and 0.0165. The reason is that the values associated with 0.00715, 0.0195, 0.0338, and 0.0419 are equal to or near some of the observed $Sin^2\theta$ values; especially 0.0195 is considered as $(\bar{1}10)$ under the possible parameters 0.0100 and 0.0165. (5) Therefore, we assume that the possible S could be 0.0223. Let the possible parameters 0.0100, 0.0165, and 0.0223 together with the reflection lines, 0.0262, 0.0310, 0.0338, 0.0384, 0.0420, 0.0425, 0.0437, 0.0469, 0.0500, and 0.0606 be the inputs to the computer program ATR again; the output is recorded in Table 101. (6) In Table 101, by the same token, we select the possible V as 0.0061 (it appears six times) and the possible W as 0.00795 (it appears four times) for the possible S=0.0223. (7) Let the possible parameter pairs (0.0100, 0.0165, 0.0223, 0.0071, 0.0061, 0.00795), (0.0100, 0.0165, 0.0223, 0.0071, -0.0061, 0.00795), and (0.0100, 0.0165, 0.0223, -0.0071, -0.0061, 0.00795) together with all the reflections be the inputs to the computer program TRI, the indexed powder diffraction data is then recorded in Table 102. (8) The standard

TABLE 100

First Output Data of the Auxiliary Computer Program (ATR) for the Data chosen from Henry, Lipson and Wooster

P OR Q= 0.01000

QS	UVW	NO.	H=-1	H=1	H=-2	H=2
0.01650	0.00030	2	0.02620	0.02680	0.05590	0.05710
0.00613	0.00037	2	0.01577	0.01650	0.04540	0.04687
0.00567	0.00083	3	0.01483	0.01650	0.04400	0.04733
0.00770	0.00120	4	0.01650	0.01890	0.04530	0.05010
0.00487	0.00163	2	0.01323	0.01650	0.04160	0.04813
0.01650	0.00205	2	0.02445	0.02855	0.05240	0.06060
0.00422	0.00228	2	0.01193	0.01650	0.03965	0.04878
0.00375	0.00275	4	0.01100	0.01650	0.03825	0.04925
0.00940	0.00290	3	0.01650	0.02230	0.04360	0.05520
0.01650	0.00325	2	0.02325	0.02975	0.05000	0.06300
0.00305	0.00345	2	0.00960	0.01650	0.03615	0.04995
0.01050	0.00400	3	0.01650	0.02450	0.04250	0.05850
0.01650	0.00420	2	0.02230	0.03070	0.04810	0.06490
0.00212	0.00437	2	0.00775	0.01650	0.03338	0.05087
0.01650	0.00450	2	0.02200	0.03100	0.04750	0.06550
0.01650	0.00480	2	0.02170	0.03130	0.04690	0.06610
0.01135	0.00485	2	0.01650	0.02620	0.04165	0.06105
0.00160	0.00490	2	0.00670	0.01650	0.03180	0.05140
0.01650	0.00640	2	0.02010	0.03290	0.04370	0.06930
0.01650	0.00700	4	0.01950	0.03350	0.04250	0.07050
0.01650	0.00730	4	0.01920	0.03380	0.04190	0.07110
0.01650	0.00770	2	0.01880	0.03420	0.04110	0.07190
0.01650	0.00905	2	0.01745	0.03555	0.03840	0.07460
0.01650	0.01135	4	0.01515	0.03785	0.03380	0.07920
0.01650	0.01190	2	0.01460	0.03840	0.03270	0.08030
0.01920	0.01270	2	0.01650	0.04190	0.03380	0.08460
0.01650	0.01275	2	0.01375	0.03925	0.03100	0.08200
0.01650	0.01300	2	0.01350	0.03950	0.03050	0.08250
0.01650	0.01400	2	0.01250	0.04050	0.02850	0.08450
0.01650	0.01455	2	0.01195	0.04105	0.02740	0.08560
0.01650	0.01477	2	0.01173	0.04127	0.02695	0.08605
0.01650	0.01515	2	0.01135	0.04165	0.02620	0.08680
0.01650	0.01550	4	0.01100	0.04200	0.02550	0.08750
0.01650	0.01600	8	0.01050	0.04250	0.02450	0.08850
0.01650	0.01690	4	0.00960	0.04340	0.02270	0.09030
0.01650	0.01710	6	0.00940	0.04360	0.02230	0.09070

deviation, 0.000058, shows that the experimental data and the calculated value is very close. The maximum discrepancy is only about ±0.00014. The assigned Miller indices agrees with the original paper.

TABLE 101

Second Output Data of the Auxiliary Computer Program (ATR) for the Data Chosen from Henry, Lipson and Wooster

P OR Q= 0.01000

OS	UVW	NO.	H=-1	H=1	H=-2	H=2
0.02230	0.00085	2	0.03145	0.03315	0.06060	0.06400
0.02230	0.00130	4	0.03100	0.03360	0.05970	0.06490
0.00943	0.00287	3	0.01657	0.02230	0.04370	0.05517
0.00883	0.00347	4	0.01537	0.02230	0.04190	0.05577
0.00760	0.00470	3	0.01290	0.02230	0.03820	0.05700
0.00680	0.00550	2	0.01130	0.02230	0.03580	0.05780
0.00640	0.00590	2	0.01050	0.02230	0.03460	0.05820
0.02230	0.00610	6	0.02620	0.03840	0.05010	0.07450
0.00613	0.00617	3	0.00997	0.02230	0.03380	0.05847
0.00520	0.00710	3	0.00810	0.02230	0.03100	0.05940
0.02230	0.00770	2	0.02460	0.04000	0.04690	0.07770
0.00442	0.00787	2	0.00655	0.02230	0.02868	0.06017
0.00395	0.00835	2	0.00560	0.02230	0.02725	0.06065
0.02230	0.00930	2	0.02300	0.04160	0.04370	0.08090
0.02230	0.00970	4	0.02260	0.04200	0.04290	0.08170
0.02230	0.00990	2	0.02240	0.04220	0.04250	0.08210
0.02230	0.01015	5	0.02215	0.04245	0.04200	0.08260
0.02230	0.01140	2	0.02090	0.04370	0.03950	0.08510
0.02230	0.01195	2	0.02035	0.04425	0.03840	0.08620
0.02620	0.01390	2	0.02230	0.05010	0.03840	0.09400
0.02230	0.01425	2	0.01805	0.04655	0.03380	0.09080
0.02230	0.01460	2	0.01770	0.04690	0.03310	0.09150
0.02230	0.01565	2	0.01665	0.04795	0.03100	0.09360
0.02230	0.01715	2	0.01515	0.04945	0.02800	0.09660
0.02230	0.01770	2	0.01460	0.05000	0.02690	0.09770
0.02230	0.01805	2	0.01425	0.05035	0.02620	0.09840
0.02230	0.01930	2	0.01300	0.05160	0.02370	0.10090
0.02230	0.01980	2	0.01250	0.05210	0.02270	0.10190

TABLE 101 (CONTINUED)

P OR Q= 0.01650

QS	UVW	NO.	H=-1	H=1	H=-2	H=2
0.00618	0.00038	2	0.02230	0.02307	0.07142	0.07295
0.02230	0.00040	2	0.03840	0.03920	0.08750	0.08910
0.00695	0.00115	2	0.02230	0.02460	0.07065	0.07525
0.00775	0.00195	2	0.02230	0.02620	0.06985	0.07765
0.02230	0.00320	2	0.03560	0.04200	0.08190	0.09470
0.00940	0.00360	2	0.02230	0.02950	0.06820	0.08260
0.02230	0.00370	2	0.03510	0.04250	0.08090	0.09570
0.00207	0.00373	2	0.01483	0.02230	0.06060	0.07553
0.02230	0.00500	4	0.03380	0.04380	0.07830	0.09830
0.02230	0.00780	2	0.03100	0.04660	0.07270	0.10390
0.02230	0.00810	2	0.03070	0.04690	0.07210	0.10450
0.02230	0.01120	2	0.02760	0.05000	0.06590	0.11070
0.02230	0.01260	2	0.02620	0.05140	0.06310	0.11350
0.02230	0.01385	2	0.02495	0.05265	0.06060	0.11600
0.02230	0.01915	2	0.01965	0.05795	0.05000	0.12660
0.02230	0.02070	2	0.01810	0.05950	0.04690	0.12970
0.02230	0.02180	2	0.01700	0.06060	0.04470	0.13190
0.02230	0.02230	2	0.01650	0.06110	0.04370	0.13290
0.02230	0.02255	2	0.01625	0.06135	0.04320	0.13340
0.02230	0.02290	2	0.01590	0.06170	0.04250	0.13410
0.02230	0.02315	2	0.01565	0.06195	0.04200	0.13460
0.02230	0.02365	2	0.01515	0.06245	0.04100	0.13560
0.02230	0.02495	2	0.01385	0.06375	0.03840	0.13820

Example C

This example, chosen from Bear and Mumme,[86] indexes the γ-$Zr(SO_4)_2H_2O$ powder pattern. There were forty reflection lines to be indexed. The indexing procedures are similar to the previous examples. The indexed powder diffraction data is recorded

TABLE 102

Indexed Diffraction Data of
the Data Chosen from Henry, Lipson and Wooster

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.01000	0.01000	1	0	0
0.01650	0.01664	0	1	0
0.01950	0.01955	-1	1	0
0.02230	0.02229	0	0	1
0.02620	0.02620	-1	0	1
0.03100	0.03095	0	1	-1
0.03380	0.03374	1	1	0
0.03840	0.03839	1	0	1
0.03990	0.03995	-1	1	-1
0.04200	0.04195	1	1	-1
0.04250	0.04246	-2	1	0
0.04370	0.04372	-1	1	1
0.04690	0.04691	0	1	1
0.05000	0.05011	-2	0	1
0.06060	0.06053	-2	1	1

P= 0.01000 Q= 0.01664 S= 0.02229
V= 0.00610 U= 0.00710 W= 0.00798
STANDARD DEVIATION=0.000058
THIS IS A TRICLINIC CRYSTAL POWDER PATTERN

in Table 103. The standard deviation, 0.00309, shows that the experimental data is not close to the calculated value. The maximum discrepancy is about ±0.0009. There are nine reflection lines assigned differently than in the original paper. This method gives better solutions.

TABLE 103

Indexed Diffraction Data of γ-$Zr(SO_4)_2H_2O$

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	H	K	L
0.00780	0.00784	0	0	1
0.01120	0.01123	1	0	0
0.01500	0.01501	-1	0	1
0.02470	0.02461	-1	1	0
0.03110	0.03137	0	0	2
0.03180	0.03179	-1	1	-1
0.03320	0.03312	-1	1	1
0.03440	0.03448	-1	0	2
0.03740	0.03755	0	1	1
0.04470	0.04463	-2	0	1
0.04640	0.04688	1	1	-1
0.04810	0.04781	1	1	0
0.05080	0.05071	1	0	2
0.05480	0.05465	-1	1	-2
0.05740	0.05731	-1	1	2
0.06030	0.06005	-2	0	2
0.06240	0.06163	1	1	-2
0.06480	0.06443	1	1	1
0.06930	0.06963	-1	0	3
0.07010	0.07058	0	0	3
0.08230	0.08140	0	1	-3
0.08450	0.08484	-2	1	-2
0.08820	0.08809	2	1	-1
0.09100	0.09114	-2	0	3
0.09330	0.09320	-1	1	-3
0.09610	0.09673	1	1	2
0.10100	0.10103	3	0	0
0.10700	0.10709	-2	1	3
0.10810	0.10806	-3	0	2
0.12050	0.12104	3	0	1
0.13500	0.13510	-3	0	3
0.13810	0.13818	1	1	-4
0.14150	0.14195	-3	2	-1
0.15330	0.15292	1	0	4
0.15730	0.15729	-3	2	2
0.17870	0.17853	-4	0	2
0.18530	0.18554	3	1	1
0.19300	0.19272	1	2	2
0.20030	0.20039	-2	0	5
0.20220	0.20216	2	1	3

P= 0.01123 Q= 0.02499 S= 0.00784

V= 0.00406 U= 0.01160 W= 0.00472

STANDARD DEVIATION=0.000309

THIS IS A TRICLINIC CRYSTAL POWDER PATTERN

CHAPTER VII

INDEXING OF UNKNOWN ROTATING-CRYSTAL PATTERNS

Introduction

The rotating-crystal method used to obtain the necessary diffraction data of the crystals was developed in German and England.[87-91] It is superior to any other X-ray method in its ability to determine the dimensions of the true unit of structure of a crystal. In other methods, where diffracted beams are observed from only a limited number of planes, one may mistake diffraction of the second order for first order diffraction from a unit crystal having only half the true dimension. Using this method, such a mistake is much less likely to occur since the rotation about a coordinate axis brings together on a single layer line diffracted beams from planes having a common intercept on the rotation axis but having widely different orientations. With such a wide variety of planes it is quite unlikely that whole layer lines will be missed on the pattern even though they may be quite faint.

In the ordinary rotating-crystal technique, the X-ray

beam is customarily made normal to the axis of rotation (normal beam method), because this brings about a simplicity of interpretation of the films. The interpretation of the rotating-crystal pattern is mostly accomplished in a classical way, such as the graphic method suggested by Bernal.[91]

However, due to the similarity between the powder and rotating-crystal methods, the computational method suggested in the previous chapters is applied for indexing the unknown rotating-crystal patterns under the assumption that only one photograph in which the crystal is rotated about any one of the crystallographic axis is needed.

The Computer Algorithm

The computer algorithm for indexing the rotating-crystal patterns is similar to that for the powder patterns. In the following, some adjustment have been made for rotating-crystal patterns particularly.

Calculating the Experimental Angles

A set of two dimensional measurements of the diffracted spots on the rotating-crystal pattern film is given from the sources. First of all, we are converting them into the $Sin^2\theta$ values. By doing this, a geometrical representation is achieved, as shown in Figure 4. For the equatorial line,

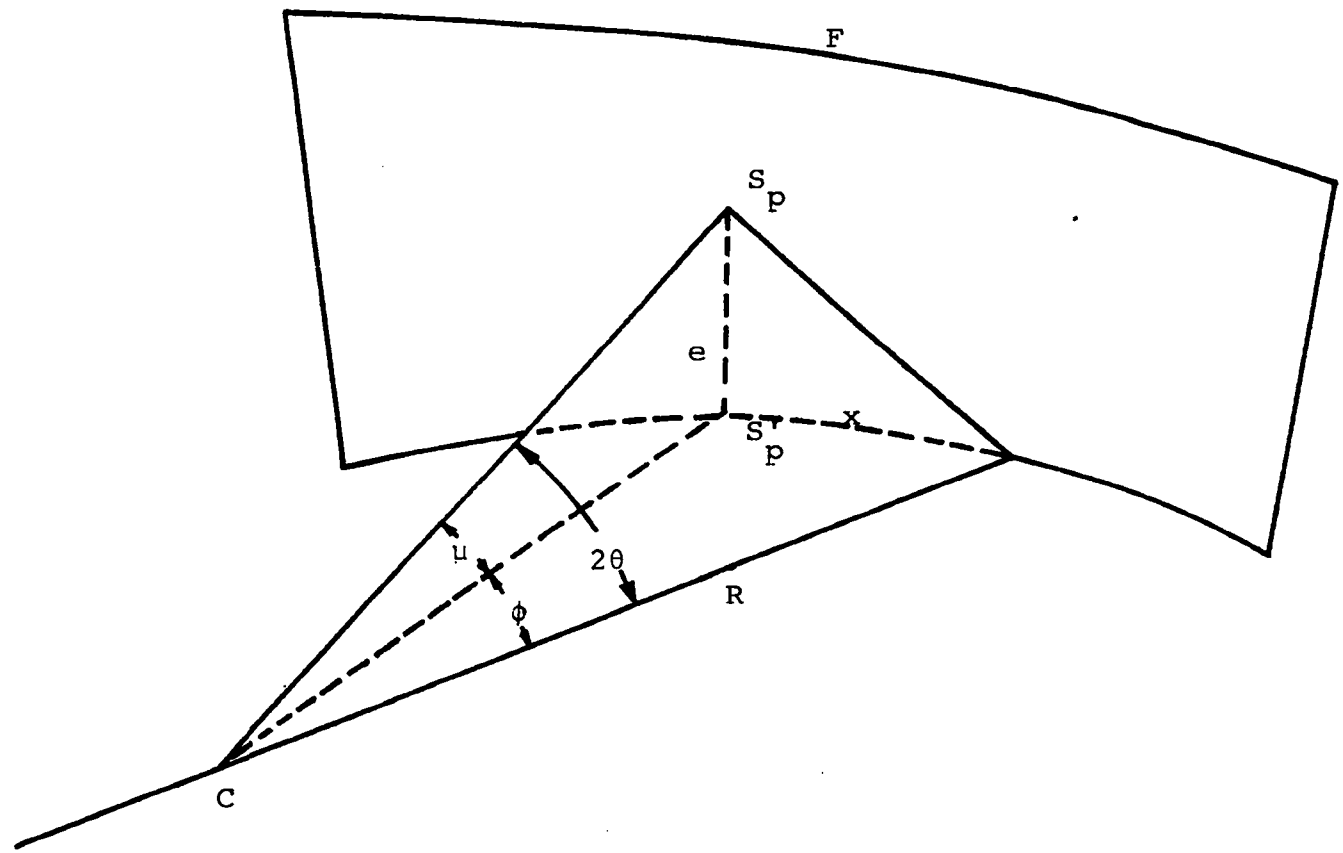

Figure 4 A Geometrical Representation for a Rotating-Crystal Pattern

$$2\theta = x/R, \tag{112}$$

which is the relation for the powder photograph using a cylindrical film.

For the spots not on the equatorial layer, say S_p on the nth layer (where C is the center of the rotating crystal, F a section of the cylindrical film, and R the radius of the camera), the direct X-ray beam passes through the crystal and makes the central spot at O. The angle 2θ between the incident ray CO and the diffracted ray CS_p is given by the relation

$$\text{Cos}2\theta = \text{Cos}\phi\ \text{Cos}\mu, \tag{113}$$

where $\phi = x/R$ and $\text{Cos}\mu = R/(R^2+e^2)^{\frac{1}{2}}$.

From the trigonometrical relationship, we may compute the $\text{Sin}^2\theta$ values from the equation (113) as

$$\text{Sin}^2\theta = \tfrac{1}{2}(1 - \text{Cos}2\theta) = \tfrac{1}{2}(1 - \text{Cos}\phi\ \text{Cos}\mu). \tag{114}$$

A computer program, RCEA, listed in Table 104, was designed for the following purposes. (1) It converts the measurement of the spots into $\text{Sin}^2\theta$ values. (2) It computes the interplanar spacing for both the radiations, CuKα and CuKβ, to select the spots for Kα radiation on the equatorial layer. Since diffraction spots from both the Kα and the Kβ wavelengths

TABLE 104

Computer Program (RCEA) for Calculating
Experimental Angles of the Rotating-Crystal Patterns

```
C COMPUTER PROGRAM FOR CALCULATING SIN(SQUARE) OF THE DIFFRACTION DATA
C OF ROTATING CRYSTAL PATTERNS
      DIMENSION A(6,20),T(6,20),LA(6),D1(6,20),D2(6,20),Y(5)
      IN=5
      IM=6
      READ (IN,10) M
   10 FORMAT (6I3)
      DO 300 I=1,M
      READ (IN,15) KA,R,WAVE1,WAVE2
   15 FORMAT (I3,3F10.0)
      READ (IN,10) (LA(J),J=1,KA)
      DO 20 J=1,KA
      J1=LA(J)
   20 READ (IN,30) (A(J,J2),J2=1,J1)
   30 FORMAT (10F6.0)
      JJ=KA-1
      READ (IN,30) (Y(J),J=1,JJ)
      YY=0.0
      DO 40 J3=1,KA
      JJ1=J3-1
      J4=LA(J3)
      IF (JJ1) 38,38,34
   34 YY=Y(JJ1)/2.0
   38 DO 40 J5=1,J4
      PHI=A(J3,J5)/(2.0*R)
      COSMU=R/SQRT(YY*YY+R*R)
      FTR=SQRT(1.0-SIN(PHI)*SIN(PHI))*COSMU
      SNTA=SQRT((1.0-FTR)/2.0)
      D1(J3,J5)=WAVE1/(2.0*SNTA)
      D2(J3,J5)=WAVE2/(2.0*SNTA)
      T(J3,J5)=SNTA*SNTA
   40 CONTINUE
      DO 80 J6=1,KA
      JJ6=J6-1
      WRITE (IM,45) JJ6
   45 FORMAT (/,'  THE NUMBER',I3,2X,'LAYER LINE')
      WRITE (IM,50)
   50 FORMAT (1X, ' ARC LENGTH',5X,'SPACING(1)',5X,'SPACING(2)',5X,'SIN(
     1SQUARE)')
      WRITE (IM,60)
   60 FORMAT (1X,58('-'))
      J7=LA(J6)
      DO 80 J8=1,J7
      WRITE (IM,70) A(J6,J8),D1(J6,J8),D2(J6,J8),T(J6,J8)
   70 FORMAT (3X,F6.3,9X,F6.3,9X,F6.3,9X,F8.5)
   80 CONTINUE
      J9=KA-1
      PARAM=0.0
      DO 100 J10=1,J9
```

TABLE 104 (CONTINUED)

```
      ALSID=SQRT(R*R+Y(J10)*Y(J10)/4.0)
      SN=Y(J10)/(2.0*ALSID)
      PARAM=PARAM+J10*WAVE1/SN
  100 CONTINUE
      PARA=PARAM/J9
      PA=WAVE1*WAVE1/(4.0*PARA*PARA)
      PAH=WAVE1*WAVE1/(3.0*PARA*PARA)
      WRITE (IM,110) PARA
  110 FORMAT (//,' ONE OF THE LATTICE PARAMETERS=',F8.5,'(A)')
      WRITE (IM,112) PA
  112 FORMAT (/,' PARAMETER P(OR Q OR S)=',F8.5)
      WRITE (IM,114)
  114 FORMAT (3X,'(DIVISOR=4 MAINLY FOR C,I  PARTIALLY FOR H,O,M)')
      WRITE (IM,116) PAH
  116 FORMAT (/,' PARAMETER P=',F8.5,'(DIVISOR=3 FOR HEXAGONAL)')
  300 CONTINUE
      STOP
      END
```

appear on the equatorial layer, care must be taken not to confuse the two sets of spots. This is ordinarily easy because of the relatively lower intensity of the β spots and also because of their positions with regard to the corresponding α spots. (3) It computes the arithmetic average lattice parameter and the possible parameters along the rotation axis. The first possible parameter is obtained from the equation $\lambda^2/4a^2$ ($\lambda^2/4b^2$ or $\lambda^2/4c^2$) for cubic, tetragonal, hexagonal, orthorhombic, and monoclinic systems, and the second possible parameter is obtained from the equation of $\lambda^2/3a^2$ (or $\lambda^2/3b^2$) for the hexagonal system only. The possible parameters are so calculated that we may use them to compare the

recurrent value groups obtained by the difference analysis for helping us decide the possible Bravais lattice type of the rotating-crystal patterns.

Difference Analysis

A computer program, RDA, listed in Table 105, was designed to compute the difference among the $Sin^2\theta$ values on the same layer as well as on the different layers. First of all, the recurrent value groups are selected. Following are the analyses for the six different lattice structures.

(1) The cubic system. Let the smallest recurrent value group be represented by P. In the equatorial layer, if the ratios among all the recurrent value groups are 1:2:3:4, etc. and this P matches the first possible parameter calculated by the computer program RCEA, the cubic pattern is assured.

(2) The tetragonal and hexagonal systems.

A. The rotation is about the crystallographic c-axis. This situation is similar to that of the cubic system except the possible parameter P is not approximately equal to the first possible parameter calculated by the computer program RCEA. However, the first possible parameter (represented by Q) calculated by the computer program RCEA does appear as the lowest recurrent value group obtained from the difference between the different layers.

TABLE 105

Computer Program (RDA) for the Difference Analysis of the Diffraction Data of the Rotating-Crystal Patterns

```
C COMPUTER PROGRAM FOR DIFFERENCE ANALYSIS OF THE DIFFRACTION DATA
C OF ROTATING-CRYSTAL PATTERNS
      DIMENSION T(6,20),TD(250),LA(6)
      IN=5
      IM=6
      READ (IN,10) M
   10 FORMAT (6I3)
      DO 300 I=1,M
      READ (IN,10) KA
      READ (IN,10) (LA(J),J=1,KA)
      DO 20 J=1,KA
      J1=LA(J)
   20 READ (IN,30) (T(J,J2),J2=1,J1)
   30 FORMAT (10F7.0)
      WRITE (IM,115)
  115 FORMAT (1H1,' DIFFERENCE ANALYSIS')
      DO 200 J11=1,KA
      J12=J11-1
      WRITE (IM,120) J12
  120 FORMAT (/,' THE NUMBER',I3,2X,'LAYER LINE')
      N=0
      J13=LA(J11)
      J14=J13-1
      DO 130 J15=1,J14
      J16=J15+1
      DO 130 J17=J16,J13
      N=N+1
      TD(N)=T(J11,J17)-T(J11,J15)
  130 CONTINUE
      N1=N-1
      DO 150 J18=1,N1
      J19=J18+1
      DO 150 J20=J19,N
      IF (TD(J20)-TD(J18)) 140,150,150
  140 TLARG=TD(J18)
      TD(J18)=TD(J20)
      TD(J20)=TLARG
  150 CONTINUE
      WRITE (IM,160) (TD(J),J=1,N)
  160 FORMAT (1X,8F8.5)
  200 CONTINUE
      NN=0
      J21=KA-1
      DO 250 J22=1,J21
```

TABLE 105 (CONTINUED)

```
      J23=J22+1
      J24=LA(J22)
      DO 250 J25=J23,KA
      J26=LA(J25)
      WRITE (IM,205) J25,J22
205 FORMAT (/,' BETWEEN THE NUMBER',I3,'  AND THE NUMBER',I3,'  LAYER
     1LINES')
      DO 222 J27=1,J26
      DO 220 J28=1,J24
      DF=T(J25,J27)-T(J22,J28)
      IF (DF) 222,222,210
210 NN=NN+1
      TD(NN)=DF
220 CONTINUE
222 CONTINUE
      NN1=NN-1
      DO 240 J29=1,NN1
      J30=J29+1
      DO 240 J31=J30,NN
      IF (TD(J31)-TD(J29)) 230,240,240
230 TLARG=TD(J29)
      TD(J29)=TD(J31)
      TD(J31)=TLARG
240 CONTINUE
      WRITE (IM,245) (TD(J),J=1,NN)
245 FORMAT (1X,8F8.5)
250 CONTINUE
300 CONTINUE
      STOP
      END
```

B. The rotation is about the crystallographic a- or b-axis. Two different recurrent value groups (represented by P and Q) appear in the equatorial layer such that the other recurrent value groups in the same layer may be represented as a linear combination of these two. Also, one of the possible

parameters P or Q is approximately equal to the first or second possible parameter obtained from the computer program RCEA. If it is the first possible parameter, the pattern is possibly tetragonal; otherwise, hexagonal. Moreover, the lowest recurrent value group obtained from the differences between the different layers is also approximately equal to one of the possible parameters P or Q.

(3) The orthorhombic system. Because of the symmetric property among all three crystallographic axes, a, b, and c, the indexing of unknown orthorhombic rotating-crystal patterns is much easier than that of the powder patterns. The two recurrent value groups, represented by P and Q, are found in the equatorial layer may be written as a linear combination of these two. However, the possible parameter, say S, obtained from the computer program RCEA is not approximately equal to either P or Q. The recurrent value groups selected among different layers may also identify S as the third possible parameter

(4) The monoclinic system.

A. The rotation is about the crystallographic b-axis. There are no recurrent value groups to be selected from the equatorial layer. However, the only recurrent value group, represented by Q, found from the differences among different layers is approximately equal to the first possible parameter

obtained from the computer program RCEA. The possible parameter triplets (P_j,S_j,V_j) may be obtained by using the auxiliary computer program AMO provided with the $Sin^2\theta$ values on the equatorial layer.

B. The rotation is about the crystallographic a- or c-axis. There are no recurrent value groups to be selected from the differences among the different layers. However, the two lowest recurrent value groups, represented by P and Q, may be selected from the equatorial layer which has no relation to the first possible parameter obtained from the computer program RCEA. The auxiliary computer program AMO is used if we let the possible parameter P and the first three or four smallest positive values of the $Sin^2\theta$ (not on the equatorial layer), subtracting the Q value, be the inputs to the computer program. The possible parameter triplets (P_j,S_j,V_j) may then be obtained.

(5) The triclinic system. If no recurrent value groups appear in the difference table, the rotating-crystal pattern is possibly triclinic. Applying the auxiliary computer program ATR and the $Sin^2\theta$ values of the equatorial layer, the possible parameter triplets (P_j,Q_j,U_j) may be obtained. Let the possible parameters P_j and Q_j together with some selected $Sin^2\theta$ values from the layers other than equatorial be the inputs to the auxiliary computer program ATR to obtain the other two possible

parameter triplets (P_j, S_j, V_j) and (Q_j, S_j, W_j). (This is quite similar to the procedure for triclinic powder patterns.)

Indexing Techniques

The branch-and-bound technique is used to index the rotating-crystal patterns. It is similar to the procedure used for the powder patterns but easier because one of the indices is fixed for each diffracted layer.

Refinement of Possible Parameters and Selection of a Unique Solution

These processes are identical to those of the powder patterns discussed in Chapter IV.

Example

The Use of the Main Computer Program RCTHO

A computer program, RCTHO, listed in Table 106, was designed for indexing the rotating-crystal patterns of cubic, tetragonal, hexagonal, and orthorhombic systems whose rotation is along any of the three crystallographic axes, a, b, or c.

For the input of the computer program RCTHO, M stands for the total number of the patterns to be indexed as cubic, tetragonal, hexagonal, and orthorhombic systems; KA stands for the totaltotal number of the layers in each pattern; L1 stands for the total number of the possible parameter P_j; L2 stands for

TABLE 106

Computer Program (RCTHO) for the
Indexing of Unknown Cubic, Tetragonal,
Hexagonal and Orthorhombic Rotating-Crystal Patterns

```
C COMPUTER PROGRAM FOR INDEXING OF UNKNOWN CUBIC, TETRAGONAL, HEXAGONAL,
C AND ORTHORHOMBIC ROTATING-CRYSTAL PATTERNS
      DIMENSION T(5,18),MH(2,5,18),MK(2,5,18),ML(2,5,18),CAL(2,5,18),PP(
     110),PQ(10),PS(10),SD(2),SI(2,5,18),AP(2),AQ(2),AS(2),LA(6)
      IN=5
      IM=6
      READ (IN,10) M
   10 FORMAT (10I3)
      DO 500 I=1,M
      READ (IN,10) KA,L1,L2,L3,K
      READ (IN,10) (LA(J),J=1,KA)
      DO 20 I1=1,KA
      II=LA(I1)
   20 READ (IN,30) (T(I1,J),J=1,II)
   30 FORMAT (10F7.0)
      READ (IN,30) (PP(J),J=1,L1)
      READ (IN,30) (PQ(J),J=1,L2)
      READ (IN,30) (PS(J),J=1,L3)
      J1=1
      KK=0
      SD(1)=1.0
      SD(2)=1.0
      DO 300 I2=1,L1
      P=PP(I2)
      PT=0.5*P
      DO 298 I3=1,L2
      Q=PQ(I3)
      QT=0.5*Q
      DO 296 L4=1,L3
      S=PS(L4)
      IF (K-1) 40,40,84
C-----INDEXING CUBIC ROTATING-CRYSTAL PATTERNS
   40 SSIN=0.0
      SSUM=0.0
      DO 70 I4=1,KA
      I5=LA(I4)
      KK=KK+I5
      DO 70 I6=1,I5
      TOL=0.1*T(I4,I6)
      IS3=I4-1
      TDF=T(I4,I6)-IS3*IS3*P
      IS=(TDF+PT)/P
      DIFF=ABS(TDF-IS*P)
      IF (TOL-DIFF) 56,56,42
   42 AIS=IS
      IS1=SQRT(AIS)
   44 LT1=IS-IS1*IS1
      ALT1=LT1
      IS2=SQRT(ALT1)
```

TABLE 106 (CONTINUED)

```
      LT2=LT1-IS2*IS2
      IF (LT2) 48,58,58
   48 IF (IS1) 56,56,50
   50 IS1=IS1-1
      GO TO 44
   56 SD(J1)=1.0
      GO TO 74
   58 SI(J1,I4,I6)=IS+IS3*IS3
      MH(J1,I4,I6)=IS1
      MK(J1,I4,I6)=IS2
      ML(J1,I4,I6)=IS3
      KB=I6-1
      IF (KB) 66,66,60
   60 IF (MH(J1,I4,I6)-MH(J1,I4,KB)) 66,62,66
   62 IF (MK(J1,I4,I6)-MK(J1,I4,KB)) 66,64,66
   64 IF (ML(J1,I4,I6)-ML(J1,I4,KB)) 66,56,66
   66 SSIN=SSIN+IS*T(I4,I6)
      SSUM=SSUM+IS*IS
      P=SSIN/SSUM
   70 CONTINUE
      AP(J1)=P
      DTSP=0.0
      AKK=KK
      DO 72 I7=1,KA
      I8=LA(I7)
      DO 72 I9=1,I8
      CAL(J1,I7,I9)=SI(J1,I7,I9)*AP(J1)
      DTSP=DTSP+(CAL(J1,I7,I9)-T(I7,I9))**2
   72 CONTINUE
      SD(J1)=SQRT(DTSP/AKK)
   74 IF (SD(1)-SD(2)) 76,76,80
   76 IF (I2-L1) 78,310,310
   78 J1=2
      GO TO 300
   80 IF (I2-L1) 82,312,312
   82 J1=1
      GO TO 300
C-----INDEXING TETRAGONAL AND HEXAGONAL ROTATING-CRYSTAL PATTERNS
   84 IF (K-5) 86,86,140
   86 TSUM=0.0
      VSUM=0.0
      TVSUM=0.0
      SVSUM=0.0
      SSUM=0.0
      DO 120 I10=1,KA
      I11=LA(I10)
      KK=KK+I11
      DO 120 I12=1,I11
      TOL=0.1*T(I10,I12)
      DF=1.0
```

TABLE 106 (CONTINUED)

```
      IF (K-2) 88,88,98
C-----ABOUT C-AXIS (TETRAGONAL SYSTEM)
   88 IS3=I10-1
      TDF=T(I10,I12)-IS3*IS3*Q
      IS=(TDF+PT)/P
      DIFF=ABS(TDF-IS*P)
      IF (TOL-DIFF) 108,108,90
   90 AIS=IS
      IS1=SQRT(AIS)
   92 LT1=IS-IS1*IS1
      ALT1=LT1
      IS2=SQRT(ALT1)
      LT2=LT1-IS2*IS2
      IF (LT2) 94,97,94
   94 IF (IS1) 108,108,96
   96 IS1=IS1-1
      GO TO 92
   97 DF=DIFF
      SI(J1,I10,I12)=IS+IS3*IS3
      MH(J1,I10,I12)=IS1
      MK(J1,I10,I12)=IS2
      ML(J1,I10,I12)=IS3
      GO TO 106
C-----ABOUT A OR B-AXIS (TETRAGONAL SYSTEM)
   98 IF (K-3) 99,99,105
   99 IS2=I10-1
      TDF=T(I10,I12)-IS2*IS2*P
      KK1=SQRT((TDF+QT)/Q)+1.0
      DO 104 I13=1,KK1
      IS3=I13-1
      KK2=IS3*IS3
      QT1=KK2*Q
      QT2=TDF-QT1
      IS1=SQRT((QT2+PT)/P)
      DIFF=ABS(QT2-IS1*IS1*P)
      IF (DIFF-TOL) 100,104,104
  100 IF (DIFF-DF) 102,104,104
  102 DF=DIFF
      SI(J1,I10,I12)=IS1*IS1+IS2*IS2+KK2
      MH(J1,I10,I12)=IS1
      MK(J1,I10,I12)=IS2
      ML(J1,I10,I12)=IS3
  104 CONTINUE
      GO TO 106
C-----ABOUT C-AXIS (HEXAGONAL SYSTEM)
  105 IF (K-4) 601,601,620
  601 IS3=I10-1
      TDF=T(I10,I12)-IS3*IS3*Q
      IS=(TDF+PT)/P
      DIFF=ABS(TDF-IS*P)
```

TABLE 106 (CONTINUED)

```
      IF (TOL-DIFF) 108,108,605
  605 AIS=IS
      IS1=SQRT(AIS)
      IF (IS-IS1*IS1) 610,608,610
  608 IS2=0
      GO TO 614
  610 IS2=(SQRT(4.0*IS-3.0*IS1*IS1)-IS1)/2.0
      IF (IS-IS1*IS1-IS2*IS2) 612,614,612
  612 IF (IS1) 108,108,613
  613 IS1=IS1-1
      GO TO 610
  614 SI(J1,I10,I12)=IS3*IS3+IS
      MH(J1,I10,I12)=IS1
      MK(J1,I10,I12)=IS2
      ML(J1,I10,I12)=IS3
      GO TO 106
C-----ABOUT A- OR B-AXIS (HEXAGONAL SYSTEM)
  620 IS2=I10-1
      TDF=T(I10,I12)-IS2*IS2*P
      KK1=SQRT((TDF+QT)/Q)+1.0
      DO 630 I17=1,KK1
      IS3=I17-1
      KK2=IS3*IS3
      QT1=KK2*Q
      QT2=TDF-QT1
      IS=(TDF-QT1+PT)/P
      IS1=(SQRT(4.0*IS-3.0*IS2*IS2)-IS2)/2.0
      DIFF=ABS(QT2-IS*P)
      IF (DIFF-TOL) 622,630,630
  622 IF (DIFF-DF) 624,624,630
  624 DF=DIFF
      SI(J1,I10,I12)=IS+KK2+IS2*IS2
      MH(J1,I10,I12)=IS1
      MK(J1,I10,I12)=IS2
      ML(J1,I10,I12)=IS3
  630 CONTINUE
  106 IDF=DF
      IF (IDF-1) 110,108,110
  108 SD(J1)=1.0
      GO TO 127
  110 KB=I12-1
      IF (KB) 115,115,112
  112 IF (MH(J1,I10,I12)-MH(J1,I10,KB)) 115,113,115
  113 IF (MK(J1,I10,I12)-MK(J1,I10,KB)) 115,114,115
  114 IF (ML(J1,I10,I12)-ML(J1,I10,KB)) 115,108,115
  115 F1=IS1*IS1+IS2*IS2
      F2=IS3*IS3
      TSUM=TSUM+T(I10,I12)*F1
      VSUM=VSUM+F2*F2
      TVSUM=TVSUM+T(I10,I12)*F2
```

TABLE 106 (CONTINUED)

```
      SVSUM=SVSUM+F1*F2
      SSUM=SSUM+F1*F1
      DVSR=SSUM*VSUM-SVSUM*SVSUM
      IF (DVSR) 120,120,118
  118 P=(TSUM*VSUM-TVSUM*SVSUM)/DVSR
      Q=(TVSUM*SSUM-SVSUM*TSUM)/DVSR
  120 CONTINUE
      DTSP=0.0
      AKK=KK
      DO 125 I14=1,KA
      I15=LA(I14)
      DO 125 I16=1,I15
      F3=ML(J1,I14,I16)*ML(J1,I14,I16)
      CAL(J1,I14,I16)=P*(SI(J1,I14,I16)-F3)+Q*F3
      DTSP=DTSP+(CAL(J1,I14,I16)-T(I14,I16))**2
  125 CONTINUE
      SD(J1)=SQRT(DTSP/AKK)
      AP(J1)=P
      AQ(J1)=Q
  127 IF (SD(1)-SD(2)) 128,131,131
  128 IF (I3-L2) 130,129,129
  129 IF (I2-L1) 130,340,340
  130 J1=2
      GO TO 298
  131 IF (I3-L2) 133,132,132
  132 IF (I2-L1) 133,342,342
  133 J1=1
      GO TO 298
  140 SHH=0.0
      SHK=0.0
      SHL=0.0
      SKK=0.0
      SLL=0.0
      SKL=0.0
      STH=0.0
      STK=0.0
      STL=0.0
      DO 200 I18=1,KA
      IS3=I18-1
      KK3=IS3*IS3
      I19=LA(I18)
      KK=KK+I19
      DO 200 I20=1,I19
      TOL=0.1*T(I18,I20)
      DF=1.0
      TDF=T(I18,I20)-KK3*S
      KK1=SQRT((TDF+PT)/P)+1.0
      DO 160 I21=1,KK1
      IS1=I21-1
      KKK=IS1*IS1
```

TABLE 106 (CONTINUED)

```
      QT1=KKK*P
      QT2=TDF-QT1
      IF (QT2+QT) 160,142,142
  142 IS2=SQRT((QT2+QT)/Q)
      KK2=IS2*IS2
      QT3=KK2*Q
      DIFF=ABS(QT2-QT3)
      IF (DIFF-TOL) 145,160,160
  145 IF (DIFF-DF) 150,160,160
  150 DF=DIFF
      MH(J1,I18,I20)=IS1
      MK(J1,I18,I20)=IS2
      ML(J1,I18,I20)=IS3
  160 CONTINUE
      IDF=DF
      IF (IDF-1) 164,162,164
  162 SD(J1)=1.0
      GO TO 230
  164 KB=I20-1
      IF (KB) 166,172,166
  166 IF (MH(J1,I18,I20)-MH(J1,I18,KB)) 172,168,172
  168 IF (MK(J1,I18,I20)-MK(J1,I18,KB)) 172,170,172
  170 IF (ML(J1,I18,I20)-ML(J1,I18,KB)) 172,162,172
  172 HH=MH(J1,I18,I20)*MH(J1,I18,I20)
      HK=MK(J1,I18,I20)*MK(J1,I18,I20)
      HL=ML(J1,I18,I20)*ML(J1,I18,I20)
      SHH=SHH+HH*HH
      SKK=SKK+HK*HK
      SLL=SLL+HL*HL
      SHK=SHK+HH*HK
      SHL=SHL+HH*HL
      SKL=SKL+HK*HL
      STH=STH+T(I18,I20)*HH
      STK=STK+T(I18,I20)*HK
      STL=STL+T(I18,I20)*HL
      DEL=SHH*SKK*SLL+2.0*SHK*SKL*SHL-SHH*SKL*SKL-SKK*SHL*SHL
     1-SLL*SHK*SHK
      IF (DEL) 200,200,180
  180 DELP=STH*(SKK*SLL-SKL*SKL)+STK*(SHL*SKL-SHK*SLL)
     1+STL*(SHK*SKL-SKK*SHL)
      DELQ=STH*(SKL*SHL-SLL*SHK)+STK*(SHH*SLL-SHL*SHL)
     1+STL*(SHL*SHK-SHH*SKL)
      DELS=STH*(SHK*SKL-SKK*SHL)+STK*(SHK*SHL-SHH*SKL)
     1+STL*(SHH*SKK-SHK*SHK)
      P=DELP/DEL
      Q=DELQ/DEL
      S=DELS/DEL
  200 CONTINUE
      DTSP=0.0
      AKK=KK
```

TABLE 106 (CONTINUED)

```
      DO 220 I21=1,KA
      I22=LA(I21)
      DO 220 I23=1,I22
      F1=MH(J1,I21,I23)*MH(J1,I21,I23)
      F2=MK(J1,I21,I23)*MK(J1,I21,I23)
      F3=ML(J1,I21,I23)*ML(J1,I21,I23)
      CAL(J1,I21,I23)=F1*P+F2*Q+F3*S
      DTSP=DTSP+(T(I21,I23)-CAL(J1,I21,I23))**2
  220 CONTINUE
      SD(J1)=SQRT(DTSP/AKK)
      AP(J1)=P
      AQ(J1)=Q
      AS(J1)=S
  230 IF (SD(1)-SD(2)) 232,232,240
  232 IF (L4-L3) 238,234,234
  234 IF (I3-L2) 238,236,236
  236 IF (I2-L1) 238,400,400
  238 J1=2
      GO TO 296
  240 IF (L4-L3) 246,242,242
  242 IF (I3-L2) 246,244,244
  244 IF (I2-L1) 246,402,402
  246 J2=1
  296 CONTINUE
  298 CONTINUE
  300 CONTINUE
  310 J1=1
      GO TO 314
  312 J1=2
  314 ISD=SD(J1)
      IF (ISD-1) 320,316,316
  316 WRITE (IM,318) I
  318 FORMAT (1H1,'THE NUMBER',I3,'  SET IS NOT A CUBIC ROTATING-CRYSTAL
     1 PATTERN')
      GO TO 500
  320 WRITE (IM,321)
  321 FORMAT (1H1)
      DO 332 II1=1,KA
      II2=II1-1
      II3=LA(II1)
      WRITE (IM,322) II2
  322 FORMAT (/,' THE NUMBER',I3,'  LAYER LINE')
      WRITE (IM,324)
  324 FORMAT (1X,'SIN(SQUARE)',5X,'SIN(SQUARE)')
      WRITE (IM,326)
  326 FORMAT (2X,'(OBSERVED)',5X,'(CALCULATED)',4X,'NUMBER',3X,'H',3X,'K
     1',3X,'L')
      WRITE (IM,328)
  328 FORMAT (1X,51('-'))
      DO 332 II4=1,II3
```

TABLE 106 (CONTINUED)

```
      II5=SI(J1,III,II4)
      WRITE (IM,330) T(II1,II4),CAL(J1,III,II4),II5,MH(J1,III,II4),MK(J1
     1,III,II4),ML(J1,III,II4)
  330 FORMAT (3X,F8.5,8X,F8.5,7X,I3,4X,I2,2X,I2,2X,I2)
  332 CONTINUE
      WRITE (IM,334) AP(J1),SD(J1)
  334 FORMAT (1X,'PARAMETER=',F8.5,5X,'STANDARD DEVIATION=',F8.6)
      WRITE (IM,336)
  336 FORMAT (1X,'THIS IS A CUBIC ROTATING-CRYSTAL PATTERN')
      GO TO 500
  340 J1=1
      GO TO 344
  342 J1=2
  344 IF (K-3) 345,345,370
  345 ISD=SD(J1)
      IF (ISD-1) 348,346,346
  346 WRITE (IM,347) I
  347 FORMAT (1H1,' THE NUMBER',I3,'  SET IS NOT A TETRAGONAL ROTATING-C
     1RYSTAL PATTERN')
      GO TO 500
  348 WRITE (IM,349)
  349 FORMAT (1H1)
      DO 360 III=1,KA
      II6=III-1
      II7=LA(III)
      WRITE (IM,350) II6
  350 FORMAT (/,' THE NUMBER',I3,'  LAYER LINE')
      WRITE (IM,352)
  352 FORMAT (1X,'SIN(SQUARE)',5X,'SIN(SQUARE)')
      WRITE (IM,354)
  354 FORMAT (2X,'(OBSERVED)',5X,'(CALCULATED)',5X,'NUMBER',3X,'H',3X,'K
     1',3X,'L')
      WRITE (IM,355)
  355 FORMAT (1X,51('-'))
      DO 360 II8=1,II7
      II9=SI(J1,III,II8)
      WRITE (IM,356) T(III,II8),CAL(J1,III,II8),II9,MH(J1,III,II8),MK(J1
     1,III,II8),ML(J1,III,II8)
  356 FORMAT (3X,F8.5,8X,F8.5,7X,I3,5X,I2,2X,I2,2X,I2)
  360 CONTINUE
      WRITE (IM,362) AP(J1),AQ(J1)
  362 FORMAT (/,1X,'P=',F8.5,9X,'Q=',F8.5)
      WRITE (IM,364) SD(J1)
  364 FORMAT (1X,'STANDARD DEVIATION=',F8.6)
      WRITE (IM,366)
  366 FORMAT (1X,'THIS IS A TETRAGONAL ROTATING-CRYSTAL PATTERN')
      GO TO 500
  370 ISD=SD(J1)
      IF (ISD-1) 374,372,372
  372 WRITE (IM,373) I
```

TABLE 106 (CONTINUED)

```
373 FORMAT (1H1,' THE NUMBER',I3,'  SET IS NOT A HEXAGONAL ROTATING-CR
   1YSTAL PATTERN')
    GO TO 500
374 WRITE (IM,375)
375 FORMAT (1H1)
    DO 390 II10=1,KA
    II11=II10-1
    II12=LA(II10)
    WRITE (IM,376) II11
376 FORMAT (/,' THE NUMBER',I3,'  LAYER LINE')
    WRITE (IM,378)
378 FORMAT (1X,'SIN(SQUARE)',8X,'SIN(SQUARE)')
    WRITE (IM,380)
380 FORMAT (2X,'(OBSERVED)',8X,'(CALCULATED)',12X,'H',3X,'K',3X,'L')
    WRITE (IM,382)
382 FORMAT (1X,52('-'))
    DO 390 II13=1,II12
    WRITE (IM,384) T(II10,II13),CAL(J1,II10,II13),MH(J1,II10,II13),MK(
   1J1,II10,II13),ML(J1,II10,II13)
384 FORMAT (3X,F8.5,11X,F8.5,12X,I2,2X,I2,2X,I2)
390 CONTINUE
    WRITE (IM,392) AP(J1),AQ(J1)
392 FORMAT (/,'P=',F8.5,9X,'Q=',F8.5)
    WRITE (IM,394) SD(J1)
394 FORMAT (1X,'STANDARD DEVIATION=',F8.6)
    WRITE (IM,396)
396 FORMAT (1X,' THIS IS A HEXAGONAL ROTATING-CRYSTAL PATTERN')
400 J1=1
    GO TO 410
402 J1=2
410 ISD=SD(J1)
    IF (ISD-1) 415,412,412
412 WRITE (IM,414) I
414 FORMAT (1H1,' THE NUMBER',I3,'  SET IS NOT AN ORTHORHOMBIC ROTATIN
   1G-CRYSTAL PATTERN')
    GO TO 500
415 WRITE (IM,416)
416 FORMAT (1H1)
    DO 460 II14=1,KA
    II15=II14-1
    II16=LA(II14)
    WRITE (IM,417) II15
417 FORMAT (/,' THE NUMBER',I3,'  LAYER LINE')
    WRITE (IM,418)
418 FORMAT (/,1X,'SIN(SQUARE)',7X,'SIN(SQUARE)')
    WRITE (IM,420)
420 FORMAT (2X,'(OBSERVED)',7X,'(CALCULATED)',12X,'H',3X,'K',3X,'L')
    WRITE (IM,430)
430 FORMAT (1X,52('-'))
    DO 460 II17=1,II16
```

TABLE 106 (CONTINUED)

```
    WRITE (IM,440) T(III4,III7),CAL(J1,III4,III7),MH(J1,III4,III7),MK(
   1J1,III4,III7),ML(J1,III4,III7)
440 FORMAT (3X,F8.5,11X,F8.5,12X,I2,2X,I2,2X,I2)
460 CONTINUE
    WRITE (IM,464) AP(J1),AQ(J1),AS(J1)
464 FORMAT (1X'P=',F8.5,5X,'Q=',F8.5,5X,'S=',F8.5)
    WRITE (IM,475) SD(J1)
475 FORMAT (1X,'STANDARD DEVIATION=',F8.6)
    WRITE (IM,490)
490 FORMAT (1X,' THIS IS AN ORTHORHOMBIC ROTATING-CRYSTAL PATTERN')
500 CONTINUE
    STOP
    END
```

the total number of the possible parameter Q_j; L3 stands for the total number of the possible parameter S_j; K represents the structure and the rotating axis (here we set K=1 for the cubic system and the rotation is about any of the a-, b-, or c-axes; K=2 for the tetragonal system and the rotation is about the c-axis; K=3 for the tetragonal system and the rotation is about the a- or b-axis; K=4 for the hexagonal system and the rotation is about the c-axis; K=5 for the hexagonal system and the rotation is about the a- or b-axis; K=6 for the orthorhombic system and the rotation is about any of the a-, b- or c-axes); LA(J) stands for the total number of spots on each layer; T(I,J) stands for the $Sin^2\theta$ value of the Jth spot on the Ith layer; PP(J) stands for all possible parameters of P_j; PQ(J) stands for

all possible parameters of Q_j; and PS(J) stands for all possible parameters of S_j.

The output of the computer program contains the observed $Sin^2\theta$ and the calculated $Sin^2\theta$ values for each spot on the rotating-crystal film together with their Miller indices.

Example

The only example, chosen from Davey,[92] illustrates how a rotating-crystal pattern is indexed. A urea single crystal was the sample. The pattern was taken in a camera of radius 3 cm with Cu radiation, $\lambda(K\alpha)=1.539\text{Å}$ and $\lambda(K\beta)=1.389\text{Å}$. The indexing procedures may be described as follows. (1) The set of two-dimensional measurements of spots together with the length between each layers were the inputs to the computer program RCEA. The output, listed in Table 107, has all the information about the interplanar spacing for both the Kα and the Kβ radiation for the purpose of selecting spots on the equatorial layer, the corresponding $Sin^2\theta$ values for all the diffracted spots, a possible lattice parameter, 4.67407Å, and two possible parameters, 0.02710 and 0.03614. (2) After the α-spots on the equatorial layer are selected, all the $Sin^2\theta$ values of the α-spots in the first quadrant of the film are inputted to the computer program RDA. The output, listed in Table 108, is a difference table. (3) One may easily select several recurrent value groups in each

TABLE 107

Interplanar Spacings and $Sin^2\theta$ Values
Calculated from the Rotating-Crystal Pattern of Urea

THE NUMBER 0 LAYER LINE ARC LENGTH	SPACING(1)	SPACING(2)	SIN(SQUARE)
2.110	4.399	3.970	0.03060
2.340	3.971	3.584	0.03755
2.980	3.131	2.826	0.06041
3.330	2.809	2.535	0.07505
3.730	2.516	2.271	0.09355
4.290	2.199	1.985	0.12245
4.770	1.988	1.794	0.14986
5.370	1.778	1.605	0.18724
6.170	1.565	1.412	0.24188
6.610	1.470	1.327	0.27394
6.980	1.401	1.264	0.30186
7.410	1.329	1.199	0.33524
7.890	1.259	1.136	0.37349
THE NUMBER 1 LAYER LINE ARC LENGTH	SPACING(1)	SPACING(2)	SIN(SQUARE)
1.670	3.579	3.230	0.04623
2.390	3.018	2.724	0.06502
3.400	2.411	2.176	0.10184
3.830	2.212	1.997	0.12100
4.900	1.830	1.651	0.17689
5.220	1.740	1.570	0.19569
5.530	1.661	1.499	0.21472
7.160	1.348	1.216	0.32606
7.410	1.311	1.183	0.34449
7.670	1.276	1.151	0.36394
8.170	1.214	1.095	0.40202
THE NUMBER 2 LAYER LINE ARC LENGTH	SPACING(1)	SPACING(2)	SIN(SQUARE)
0.860	2.162	1.952	0.12665
2.060	2.022	1.825	0.14479
3.420	1.802	1.626	0.18242
3.940	1.715	1.548	0.20123
5.230	1.517	1.369	0.25724
5.630	1.462	1.320	0.27701
5.990	1.415	1.277	0.29566
6.980	1.300	1.173	0.35051
7.930	1.206	1.089	0.40699
8.240	1.179	1.064	0.42600
8.650	1.145	1.034	0.45142

TABLE 107 (CONTINUED)

ONE OF THE LATTICE PARAMETERS= 4.67407(A)

PARAMETER P(OR Q OR S)= 0.02710
(DIVISOR=4 MAINLY FOR C.T PARTIALLY FOR H.O.M)

PARAMETER P= 0.03614(DIVISOR=3 FOR HEXAGONAL)

layer. In the equatorial layer, the groups are 0.03744 (0.03738, 0.03750), 0.05615 (0.05600, 0.05631), 0.09352 (0.09336, 0.09369), etc. In the first layer, the groups are 0.01880 (0.01843, 0.01879, 0.01880, 0.01903, 0.01916, 0.01945), 0.03780 (0.03682, 0.03783, 0.03788, 0.03808), 0.05585 (0.05561, 0.05589, 0.05598), 0.07480 (0.07469, 0.07477, 0.07505), 0.09379 (0.09372, 0.09385), etc. In the second layer, the groups are 0.01875 (0.01824, 0.01865, 0.01881, 0.01901), 0.03800 (0.03763, 0.03842), 0.05600 (0.05485, 0.05587, 0.05601, 0.05644, 0.05648), 0.07475 (0.07468, 0.07482), 0.09400 (0.09327, 0.09443, 0.09459), etc. From the above information, we may let P=0.01880 and the other recurrent value groups may simply be represented as integral multiples of P. (4) The possible P is obviously not equal to both possible parameters suggested in Table 107; thus, the pattern is unlikely to be a cubic rotating-crystal pattern. (5) From the differences between layers, a common recurrent value group is found near the

TABLE 108

Difference Table of the Diffraction Data of Urea

DIFFERENCE ANALYSIS

THE NUMBER 0 LAYER LINE

0.01850 0.03738 0.03750 0.03825 0.05464 0.05600 0.05631 0.07481
0.09202 0.09336 0.09369 0.11219 0.11231 0.13161 0.14800 0.14833
0.14969 0.16683 0.18538 0.18625 0.20433 0.22363 0.24169 0.26019
0.27994 0.29769 0.29844 0.33594

THE NUMBER 1 LAYER LINE

0.01843 0.01879 0.01880 0.01903 0.01916 0.01945 0.03682 0.03783
0.03788 0.03808 0.05561 0.05589 0.05598 0.05753 0.07469 0.07477
0.07505 0.07596 0.09372 0.09385 0.11134 0.11187 0.11288 0.12977
0.13037 0.13066 0.13067 0.14880 0.14917 0.14922 0.14946 0.14970
0.16760 0.16825 0.16849 0.18705 0.18730 0.20506 0.20633 0.22349
0.22422 0.22513 0.24265 0.24294 0.26104 0.26210 0.27947 0.27983
0.28102 0.29826 0.29892 0.30018 0.31771 0.33700 0.35579

THE NUMBER 2 LAYER LINE

0.01824 0.01865 0.01881 0.01901 0.01977 0.02542 0.03763 0.03842
0.04443 0.05485 0.05587 0.05601 0.05644 0.05648 0.07350 0.07468
0.07482 0.07549 0.07578 0.09327 0.09443 0.09459 0.10091 0.11133
0.11245 0.11324 0.12998 0.13034 0.13069 0.13222 0.14899 0.14928
0.14975 0.15046 0.15087 0.15576 0.16809 0.16876 0.16911 0.17441
0.19418 0.20572 0.20576 0.22396 0.22457 0.22477 0.24358 0.25019
0.26220 0.26900 0.28044 0.28121 0.29945 0.30663 0.32487

BETWEEN THE NUMBER 2 AND THE NUMBER 1 LAYER LINES

0.00829 0.00845 0.00868 0.00925 0.02679 0.02703 0.02745 0.02747
0.02748 0.02853 0.02870 0.04583 0.04595 0.06429 0.06486 0.06678
0.08334 0.08345 0.08418 0.10184 0.10214 0.10261 0.12064 0.12117
0.12206 0.13882 0.13934 0.13967 0.15725 0.15814 0.16014 0.17620
0.17670 0.17717 0.19463 0.21408 0.21478 0.23251 0.25094 0.25101
0.25216 0.26944 0.27039 0.28851 0.28889 0.30694 0.30847 0.32639
0.32697 0.36447

BETWEEN THE NUMBER 3 AND THE NUMBER 1 LAYER LINES

0.00829 0.00845 0.00868 0.00925 0.01399 0.01527 0.01536 0.02679
0.02703 0.02745 0.02747 0.02748 0.02853 0.02870 0.03256 0.03300
0.03350 0.03513 0.04583 0.04595 0.05124 0.05137 0.05150 0.05251
0.05378 0.06429 0.06486 0.06678 0.06974 0.07000 0.07175 0.07793
0.08334 0.08345 0.08418 0.08887 0.08900 0.08977 0.09076 0.10184
0.10214 0.10261 0.10724 0.10737 0.10738 0.10768 0.10842 0.10863
0.11618 0.12064 0.12117 0.12206 0.12618 0.12715 0.13882 0.13934
0.13967 0.14487 0.14580 0.15725 0.15814 0.16014 0.16327 0.16368
0.16369 0.16511 0.17620 0.17670 0.17717 0.18219 0.18346 0.18412

TABLE 108 (CONTINUED)

0.19463 0.20065 0.20196 0.20211 0.20954 0.21408 0.21478 0.21969
0.21975 0.22061 0.23251 0.23876 0.23946 0.25094 0.25101 0.25216
0.25696 0.25713 0.25811 0.26418 0.26944 0.27039 0.27546 0.27614
0.28851 0.28889 0.30156 0.30694 0.30847 0.31296 0.31344 0.32639
0.32697 0.33194 0.33245 0.35095 0.35787 0.36447 0.36944 0.37637
0.38845 0.41387

BETWEEN THE NUMBER 3 AND THE NUMBER 2 LAYER LINES
0.00497 0.00553 0.00554 0.00555 0.00602 0.00829 0.00845 0.00868
0.00925 0.01399 0.01527 0.01536 0.02379 0.02398 0.02434 0.02445
0.02471 0.02679 0.02703 0.02745 0.02747 0.02748 0.02853 0.02870
0.03256 0.03300 0.03350 0.03513 0.04252 0.04295 0.04305 0.04583
0.04595 0.04940 0.05124 0.05137 0.05150 0.05251 0.05378 0.06142
0.06153 0.06155 0.06206 0.06229 0.06250 0.06429 0.06486 0.06678
0.06974 0.07000 0.07175 0.07793 0.07977 0.08023 0.08032 0.08035
0.08058 0.08093 0.08094 0.08132 0.08151 0.08334 0.08345 0.08418
0.08748 0.08887 0.08900 0.08977 0.09076 0.09856 0.09939 0.09994
0.09997 0.10012 0.10184 0.10214 0.10261 0.10693 0.10724 0.10737
0.10738 0.10768 0.10842 0.10863 0.11618 0.11740 0.11877 0.12064
0.12117 0.12206 0.12536 0.12618 0.12715 0.13579 0.13619 0.13621
0.13624 0.13882 0.13934 0.13967 0.14487 0.14580 0.15482 0.15500
0.15540 0.15601 0.15725 0.15814 0.16014 0.16327 0.16368 0.16369
0.16511 0.17362 0.17466 0.17517 0.17620 0.17670 0.17717 0.18219
0.18346 0.18412 0.19222 0.19227 0.19382 0.19463 0.20065 0.20196
0.20211 0.20954 0.21101 0.21128 0.21130 0.21199 0.21408 0.21478
0.21969 0.21975 0.22061 0.22951 0.23010 0.23031 0.23064 0.23078
0.23251 0.23670 0.23876 0.23946 0.24867 0.24911 0.24943 0.25094
0.25101 0.25216 0.25573 0.25696 0.25713 0.25811 0.26418 0.26944
0.27039 0.27453 0.27546 0.27614 0.28549 0.28599 0.28851 0.28889
0.30156 0.30428 0.30500 0.30515 0.30694 0.30847 0.31296 0.31344
0.32416 0.32639 0.32697 0.33042 0.33194 0.33245 0.34197 0.34958
0.35095 0.35787 0.36076 0.36098 0.36447 0.36944 0.37637 0.37977
0.38640 0.38845 0.40519 0.41387

value of 0.02710. Comparing with the first possible parameter suggested in Table 107, the pattern could possibly have a tetragonal structure. (6) Let P=0.01880 and Q=0.02710 together with all the $Sin^2\theta$ values of α-spots be the inputs to the computer program RCTHO (here we let K=2); the indexed diffraction data is then recorded in Table 109. (7) The standard deviation, 0.001305, shows that the experimental data and the calculated value are not very close. The maximum discrepancy is about ±0.00615. However, the suggested assignments agree with the original paper.

Discussions

(1) Because of the difficulty of obtaining the experimental data, the computer programs for indexing the monoclinic and triclinic rotating-crystal patterns are not included in this chapter. The mentioned computer programs may be designed similar to those of the powder patterns.

(2) If the orientation of the single crystal is completely random, several (maybe more than three) rotating-crystal patterns are needed for the determination of its lattice structure and necessary diffraction data. This can be treated as a powder pattern if one collects all the α-spots on the equatorial layer.

TABLE 109

Indexed Rotating-Crystal Diffraction Data of Urea

THE NUMBER 0 LAYER LINE

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.03755	0.03743	2	1	1	0
0.07505	0.07485	4	2	0	0
0.09355	0.09357	5	2	1	0
0.14986	0.14971	8	2	2	0
0.18724	0.18714	10	3	1	0
0.24188	0.24328	13	3	2	0
0.33524	0.33685	18	3	3	0
0.37349	0.37427	20	4	2	0

THE NUMBER 1 LAYER LINE

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.04623	0.04582	2	1	0	1
0.06502	0.06453	3	1	1	1
0.10184	0.10196	5	2	0	1
0.12100	0.12067	6	2	1	1
0.17689	0.17681	9	2	2	1
0.19569	0.19553	10	3	0	1
0.21472	0.21424	11	3	1	1
0.32606	0.32652	17	4	0	1
0.34449	0.34524	18	4	1	1
0.36394	0.36395	19	3	3	1
0.40202	0.40138	21	4	2	1

THE NUMBER 2 LAYER LINE

SIN(SQUARE) (OBSERVED)	SIN(SQUARE) (CALCULATED)	NUMBER	H	K	L
0.12655	0.12713	5	1	0	2
0.14479	0.14585	6	1	1	2
0.18242	0.18327	8	2	0	2
0.20123	0.20199	9	2	1	2
0.25724	0.25813	12	2	2	2
0.27701	0.27684	13	3	0	2
0.29566	0.29556	14	3	1	2
0.35051	0.35170	17	3	2	2
0.40699	0.40784	20	4	0	2
0.42600	0.42655	21	4	1	2
0.45142	0.44527	22	3	3	2

P= 0.01871 Q= 0.02711

STANDARD DEVIATION=0.001305

THIS IS A TETRAGONAL ROTATING-CRYSTAL PATTERN

CHAPTER VIII

DISCUSSIONS AND CONCLUSIONS

(1) The suggested computer algorithm was successfully applied for indexing both the unknown powder patterns and the wnknown rotating-crystal patterns. The main computer programs will index the powder patterns if the lattice parameters are already known.

(2) The computer method works well even for those cubic and tetragonal powder patterns in which some of the reflections have very large values of s_i (where $s_i=h_i^2+k_i^2+l_i^2$ for the cubic system, $s_i=h_i^2+k_i^2$ for the tetragonal system).

(3) If the indexed cubic powder diffraction data in the "Number" column appear as integral multiples of those numbers listed in Table 2, the possible parameter P should be changed to that multiple of P for obtaining a solution of the "first-order" reflections.

(4) Some computer programs are based on choosing the cell constants by assigned low Miller indices to the lower reflections of the powder patterns. This may result in a wrong solution if the lower reflection lines were not measured

accurately enough because the relative error is higher for these short distances.

(5) The advantage of selecting the possible parameters by difference analysis is that the possible parameters are chosen from averaging the recurrent values in the difference table, yielding fewer possible parameters than the trial-and-error methods. This will reduce computing time.

(6) Some revisions are needed for indexing of unknown tetragonal powder patterns if the values of h^2+k^2 are even integers for all i, i=1,2,...,K and the crystal does not belong to a body-centered structure. This can be done by doubling the parameter P and re-running the computer program TET.

(7) The rhombohedral powder patterns may be indexed in a method similar to that used for the powder patterns of the tetragonal and hexagonal systems since the plane-spacing equations have two unknown parameters, a and c (or α), for all three systems.

The plane-spacing equation for the rhombohedral system can be written as

$$\frac{1}{d^2_{hkl}} = (h^2+k^2+l^2)P' + (hk+kl+hl)Q', \qquad (115)$$

where

$$P' = \mathrm{Sin}^2\alpha/a^2(1-3\mathrm{Cos}^2\alpha+2\mathrm{Cos}^3\alpha),$$

and

$$Q' = (\mathrm{Cos}^2\alpha-\mathrm{Cos}\ \alpha)/a^2(1-3\mathrm{Cos}^2\alpha+2\mathrm{Cos}^3\alpha),$$

where a and α are the two lattice parameter of the unit cell. We then obtain a relation between $Sin^2\theta$ and Miller indices $(h_i k_i l_i)$ by inserting equation (115) into (4). Thus, we have

$$Sin^2\theta_i = (h_i^2+k_i^2+l_i^2)P + (h_ik_i+k_il_i+h_il_i)Q, \qquad (116)$$

where $P = \lambda^2 P'/4$ and $Q = \lambda^2 Q'/4$ for $i=1,2,\ldots,K$.
The summations $h^2+k^2+l^2$ and $hk+kl+hl$ are carried out in a systematic manner similar to that of the tetragonal and hexagonal systems. Further, equation (116) and equation (9) and (11) are of the same type. Therefore, the rhombohedral system can be treated just like those two systems. Since the plane-spacing equation for this system is too wieldly to be used directly, we will not devote more time to this topic.

(8) The computer method suggested by Werner[29] is generally applicable, but the computing time becomes prohibitive for those cases in which many $Sin^2\theta$ values of the lower reflection lines are generated by two of the three parameters in the orthorhombic system (for example, the powder pattern of $NaTi_2Al_5O_{12}$, selected from Mumme and Wadsley,[76] whose Miller indices of the first seven reflection lines are (110), (020), (120), (130), (040), (240), and (330)) or one of the unit-cell dimensions is much larger than the other two (since its indexing loop only indexes the reflection lines up to (777) in general). At least

500 combinations of the lower Miller indices must be assigned to the three selected reflection lines to complete the trial indexing of a powder pattern of orthorhombic crystals.

(9) The suggested computer method may certainly reduce tremendous working hours on the indexing of the unknown monoclinic and triclinic crystal powder patterns. However, for those powder patterns in which most of the lower reflection lines are accidently missing, the auxiliary computer programs, AMO and ATR, must be revised; that is, more computing time will be needed for selecting the possible parameters.

(10) The computer running time is always our major concern. The computer running times for each of the computer programs are recorded in Table 110.

TABLE 110

Computer Running Time of the Samples for each Computer Program

Computer Program	Number of Examples	Total Computing Time
CEA	4	0.96 sec.
DA	16	148.88 sec.
CUB	9	3.15 sec.
TET	9	22.59 sec.

TABLE 110 (CONTINUED)

Computer Program	Number of Examples	Total Computing Time
HEX	10	11.60 sec.
AOR	3	5.28 sec.
ORT	9	19.15 sec.
AMO	2	6.74 sec.
MON	7	68.60 sec.
ATR	2	17.35 sec.
TRI	3	50.00 sec.
RCEA	1	0.78 sec.
RDA	1	13.28 sec.
RCTHO	1	0.98 sec.

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APPENDIX A

THE COMPUTER PROGRAM AND FLOW CHART FOR CUBIC SYSTEM

TABLE A

Computer Program (CUB) for the
Indexing of Unknown Cubic Crystal Powder Patterns

```
C COMPUTER PROGRAM FOR THE INDEXING OF UNKNOWN CUBIC CRYSTAL POWDER
C PATTERNS
      DIMENSION T(70),P(20),S(2,70),MH(2,70),MK(2,70),ML(2,70),AP(2),CAL
     1(2,70),SD(2)
      IN=5
      IM=6
      READ (IN,1) M
    1 FORMAT (I3)
      DO 40 I1=1,M
      READ (IN,2) K,L
    2 FORMAT (2I3)
      READ (IN,3) (T(J),J=1,K)
      READ (IN,3) (P(J),J=1,L)
    3 FORMAT (10F7.0)
      J1=1
      SD(1)=1.0
      SD(2)=1.0
      DO 26 I2=1,L
      PP=P(I2)
      PT=0.5*PP
      SSIN=0.0
      SSUM=0.0
      DO 15 K1=1,K
      TOL=0.1*T(K1)
      IS=(T(K1)+PT)/PP
      DIFF=ABS(T(K1)-IS*PP)
      IF (DIFF-TOL) 6,13,13
    6 AIS=IS
      IS1=SQRT(AIS)
    8 LT1=IS-IS1*IS1
      ALT1=LT1
      IS2=SQRT(ALT1)
    9 LT2=LT1-IS2*IS2
      ALT2=LT2
      IS3=SQRT(ALT2)
      LT3=LT2-IS3*IS3
      IF (LT3) 10,14,10
   10 IF (IS2) 102,102,101
  101 IS2=IS2-1
      GO TO 9
  102 IF (IS1) 13,13,11
   11 IS1=IS1-1
      GO TO 8
   13 SD(J1)=1.0
```

TABLE A (CONTINUED)

```
      GO TO 20
   14 S(J1,K1)=IS
      MH(J1,K1)=IS1
      MK(J1,K1)=IS2
      ML(J1,K1)=IS3
      KL=K1-1
      IF (KL) 144,144,141
  141 IF (MH(J1,K1)-MH(J1,KL)) 144,142,144
  142 IF (MK(J1,K1)-MK(J1,KL)) 144,143,144
  143 IF (ML(J1,K1)-ML(J1,KL)) 144,13,144
  144 SSIN=SSIN+IS*T(K1)
      SSUM=SSUM+IS*IS
      PP=SSIN/SSUM
   15 CONTINUE
      AP(J1)=PP
      DTSP=0.0
      AKK=K
      DO 18 K2=1,K
      CAL(J1,K2)=S(J1,K2)*AP(J1)
      DTSP=DTSP+(CAL(J1,K2)-T(K2))**2
   18 CONTINUE
      SD(J1)=SQRT(DTSP/AKK)
   20 IF (SD(1)-SD(2)) 21,21,23
   21 IF (I2-L) 22,29,29
   22 J1=2
      GO TO 26
   23 IF (I2-L) 24,30,30
   24 J1=1
   26 CONTINUE
   29 J1=1
      GO TO 130
   30 J1=2
  130 ISD=SD(J1)
      IF (ISD-1) 31,131,131
  131 WRITE (IM,132) I1
  132 FORMAT (1H1,' THE NUMBER',I3,'  SET IS NOT A CUBIC CRYSTAL POWDER
     1PATTERN')
      GO TO 40
   31 WRITE (IM,32)
   32 FORMAT (1H1,' SIN(SQUARE)',5X,'SIN(SQUARE)',4X,'NUMBER',3X,'H',3X,
     1'K',3X,'L')
      WRITE (IM,33)
   33 FORMAT (2X,'(OBSERVED)',5X,'(CALCULATED)')
      WRITE (IM,34)
   34 FORMAT (1X,11('-'),5X,12('-'),4X,6('-'),2X,3('-'),1X,3('-'),1X,3('
```

TABLE A (CONTINUED)

```
  1-'))
   DO 35 K3=1,K
   K4=S(J1,K3)
35 WRITE (IM,36) T(K3),CAL(J1,K3),K4,MH(J1,K3),MK(J1,K3),ML(J1,K3)
36 FORMAT (3X,F8.5,8X,F8.5,7X,I3,4X,I2,2X,I2,2X,I2)
   WRITE (IM,37) AP(J1),SD(J1)
37 FORMAT (' PARAMETER=',F8.5,5X,'STANDARD DEVIATION=',F8.6)
   WRITE (IM,38)
38 FORMAT (' THIS IS A CUBIC CRYSTAL POWDER PATTERN')
40 CONTINUE
   STOP
   END
```

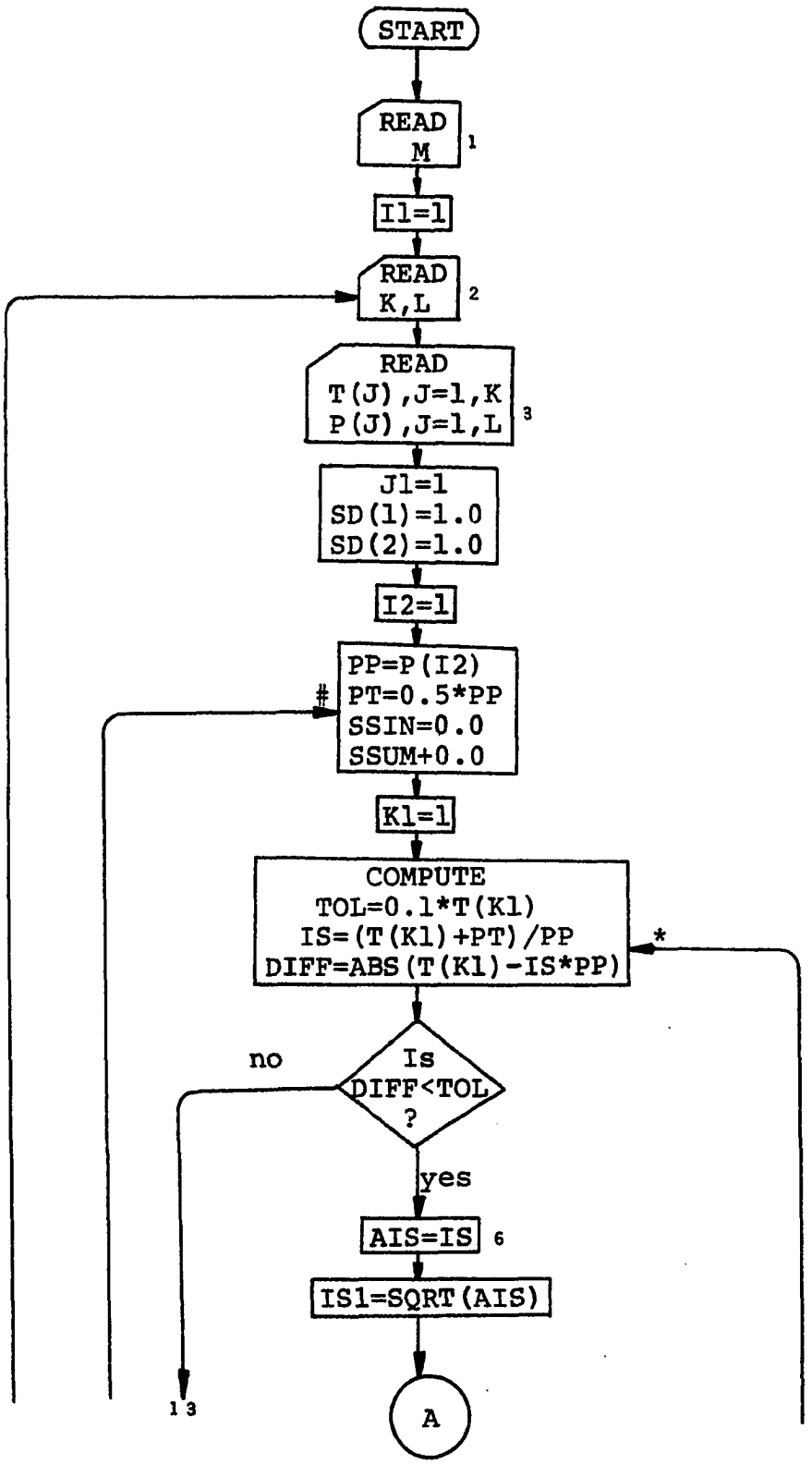
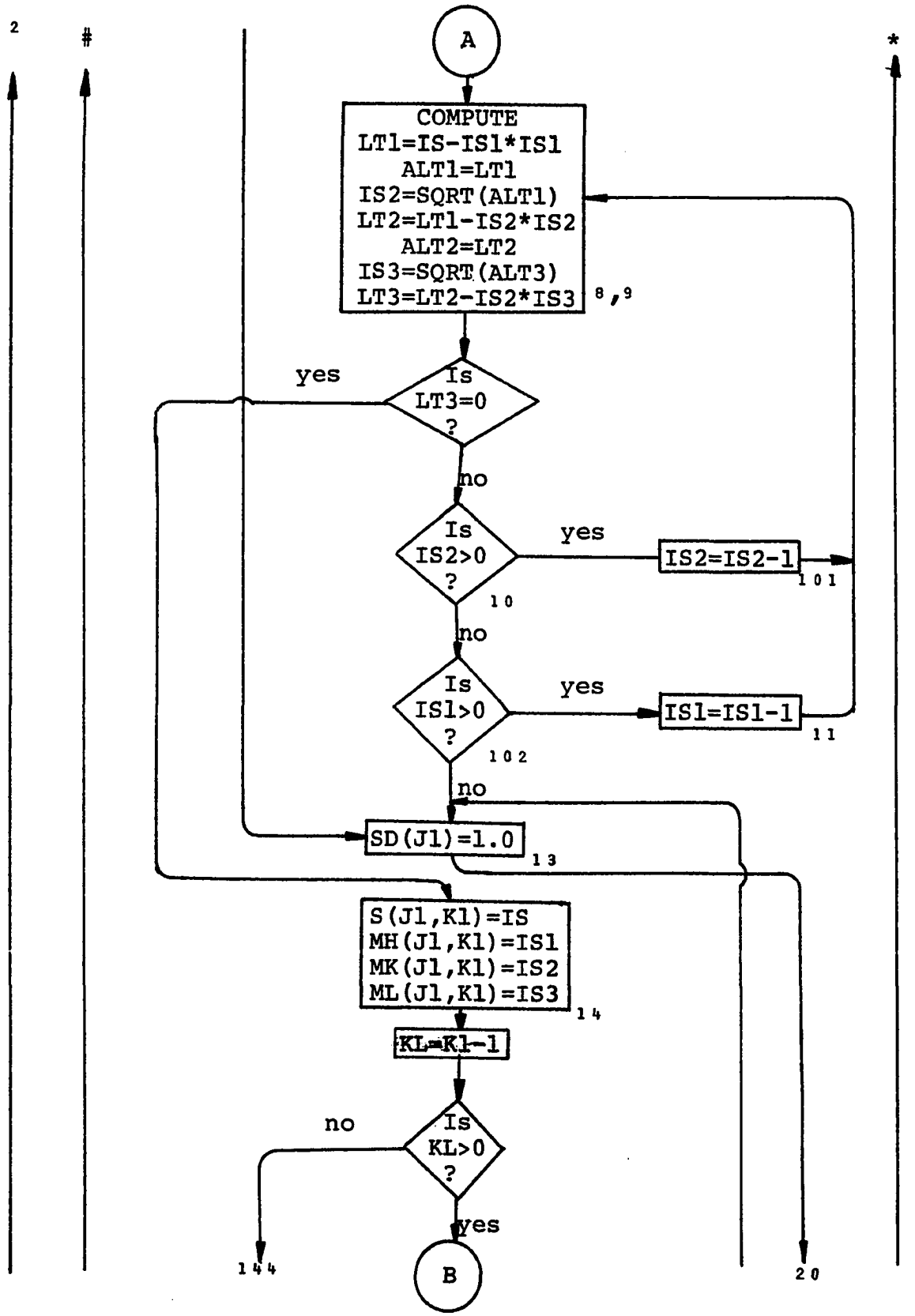
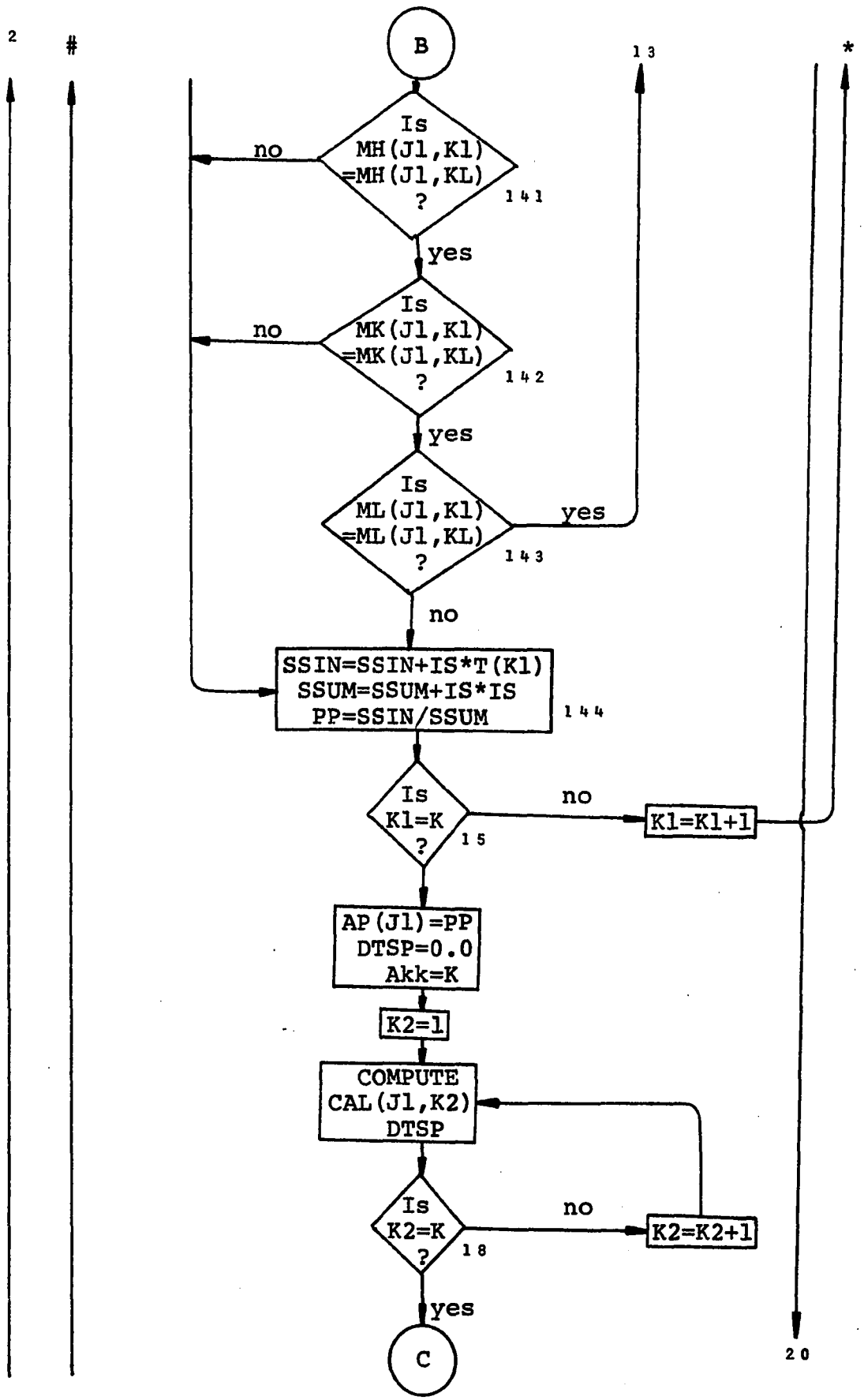
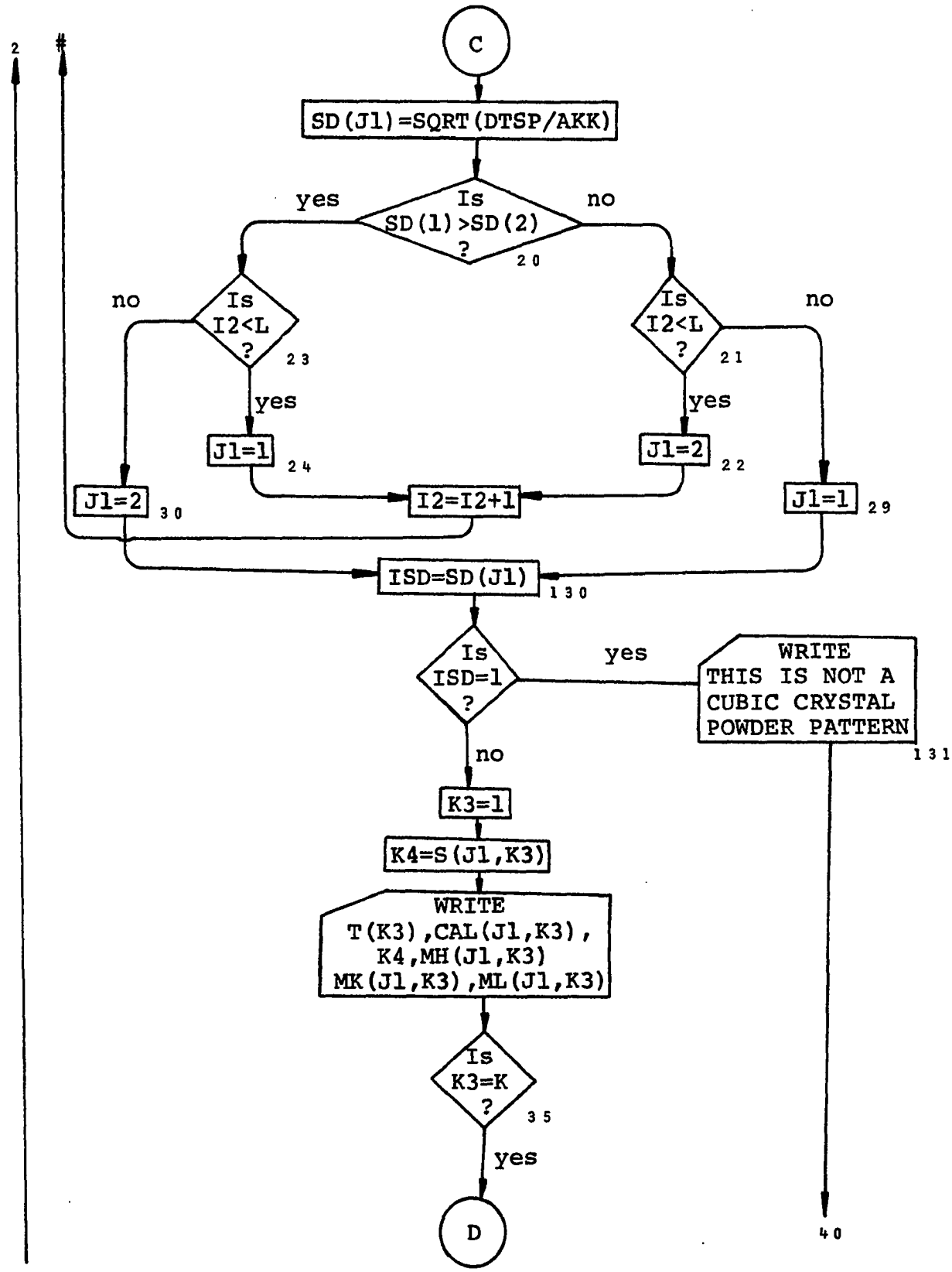
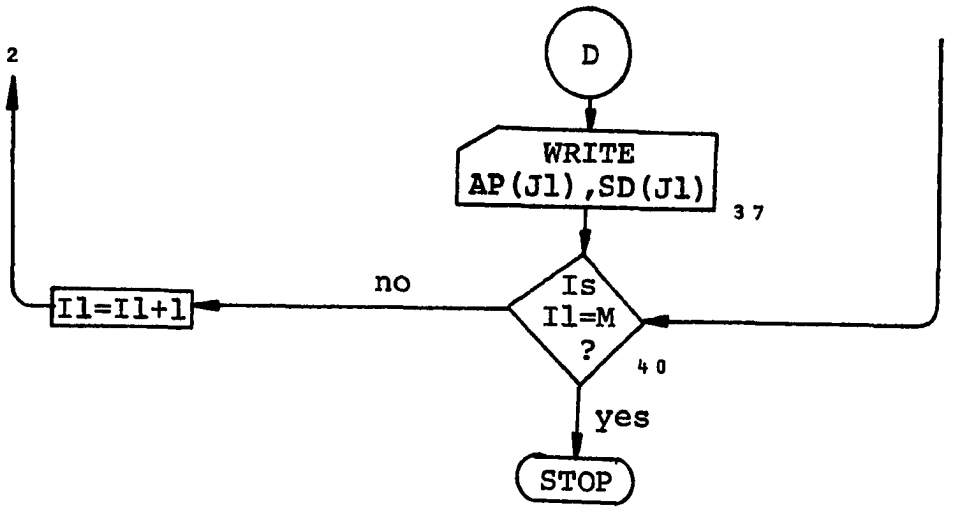


Figure A The Flow Chart of the Computer Program (CUB) for the Indexing of Unknown Cubic Crystal Powder Patterns


2
#
*
A
COMPUTE
LT1=IS-IS1*IS1
ALT1=LT1
IS2=SQRT(ALT1)
LT2=LT1-IS2*IS2
ALT2=LT2
IS3=SQRT(ALT3)
LT3=LT2-IS2*IS3
8,9
Is LT3=0 ?
yes
no
Is IS2>0 ?
10
yes
IS2=IS2-1
101
no
Is IS1>0 ?
102
yes
IS1=IS1-1
11
no
SD(J1)=1.0
13
S(J1,K1)=IS
MH(J1,K1)=IS1
MK(J1,K1)=IS2
ML(J1,K1)=IS3
14
KL=K1-1
Is KL>0 ?
no
yes
144
B
20


2
#
B
13
*
Is MH(J1,K1) =MH(J1,KL) ?
141
no
yes
Is MK(J1,K1) =MK(J1,KL) ?
142
no
yes
Is ML(J1,K1) =ML(J1,KL) ?
143
yes
no
SSIN=SSIN+IS*T(K1)
SSUM=SSUM+IS*IS
PP=SSIN/SSUM
144
Is K1=K ?
15
no
K1=K1+1
AP(J1)=PP
DTSP=0.0
Akk=K
K2=1
COMPUTE CAL(J1,K2) DTSP
Is K2=K ?
18
no
K2=K2+1
yes
C
20


2
#
C
SD(J1)=SQRT(DTSP/AKK)
yes
Is
SD(1)>SD(2)
?
20
no
no
Is
I2<L
?
23
yes
J1=1
24
J1=2
30
Is
I2<L
?
21
yes
J1=2
22
no
J1=1
29
I2=I2+1
ISD=SD(J1)
130
Is
ISD=1
?
yes
WRITE
THIS IS NOT A
CUBIC CRYSTAL
POWDER PATTERN
131
40
no
K3=1
K4=S(J1,K3)
WRITE
T(K3),CAL(J1,K3),
K4,MH(J1,K3)
MK(J1,K3),ML(J1,K3)
Is
K3=K
?
35
yes
D


D
WRITE
AP(J1),SD(J1)
37
Is
I1=M
?
40
no
I1=I1+1
2
yes
STOP

APPENDIX B

THE COMPUTER PROGRAM AND FLOW CHART FOR TETRAGONAL SYSTEM

TABLE B

Computer Program (TET) for the
Indexing of Unknown Tetragonal Crystal Powder Patterns

```
C COMPUTER PROGRAM FOR THE INDEXING OF UNKNOWN TETRAGONAL CRYSTAL
C POWDER PATTERNS
      DIMENSION T(70),P1(20),P2(20),AP1(2),AP2(2),S(2,70),CAL(2,70),
     1MH(2,70),MK(2,70),ML(2,70),SD(2)
      IN=5
      IM=6
      READ (IN,1) M
    1 FORMAT (I3)
      DO 80 I1=1,M
      READ (IN,2) K,L1,L2
    2 FORMAT (3I3)
      READ (IN,3) (T(J),J=1,K)
      READ (IN,3) (P1(J),J=1,L1)
      READ (IN,3) (P2(J),J=1,L2)
    3 FORMAT (10F7.0)
      J1=1
      SD(1)=1.0
      SD(2)=1.0
      DO 50 I2=1,L1
      DO 50 I3=1,L2
      P=P1(I2)
      PT=0.5*P
      Q=P2(I3)
      QT=0.5*Q
      TSUM=0.0
      VSUM=0.0
      TVSUM=0.0
      SVSUM=0.0
      SSUM=0.0
      DO 20 K1=1,K
      TOL=0.1*T(K1)
      DF=1.0
      IF (Q) 50,50,301
  301 KK1=SQRT((T(K1)+QT)/Q)+1.0
      DO 15 K2=1,KK1
      IK2=K2-1
      AK2=IK2*IK2
      QT1=AK2*Q
      IF (P) 50,50,302
  302 KK2=(T(K1)+PT-QT1)/P
      QT2=KK2*P
      FT1=QT1+QT2
      DIFF=ABS(T(K1)-FT1)
      IF (DIFF-TOL) 4,15,15
```

TABLE B (CONTINUED)

```
  4 IF (KK2) 5,5,6
  5 JK2=0
    LK2=0
    GO TO 11
  6 AKK2=KK2
    JK2=SQRT(AKK2)
  7 K11=JK2*JK2
    CK2=K11
    LK2=SQRT(AKK2-CK2)
    K12=LK2*LK2
    IF (KK2-K11-K12) 8,11,8
  8 IF (JK2) 9,15,9
  9 JK2=JK2-1
    GO TO 7
 11 IF (DIFF-DF) 12,12,15
 12 DF=DIFF
    F1=KK2
    F2=AK2
    MH(J1,K1)=JK2
    MK(J1,K1)=LK2
    ML(J1,K1)=IK2
 15 CONTINUE
    IDF=DF
    IF (IDF-1) 17,16,17
 16 SD(J1)=1.0
    GO TO 27
 17 KKK=K1-1
    IF (KKK) 171,174,171
171 IF (MH(J1,K1)-MH(J1,KKK)) 174,172,174
172 IF (MK(J1,K1)-MK(J1,KKK)) 174,173,174
173 IF (ML(J1,K1)-ML(J1,KKK)) 174,16,174
174 S(J1,K1)=F1+F2
    TSUM=TSUM+T(K1)*F1
    VSUM=VSUM+F2*F2
    TVSUM=TVSUM+T(K1)*F2
    SVSUM=SVSUM+F1*F2
    SSUM=SSUM+F1*F1
    DVSR=SSUM*VSUM-SVSUM*SVSUM
    IF (DVSR) 20,20,18
 18 P=(TSUM*VSUM-TVSUM*SVSUM)/DVSR
    Q=(TVSUM*SSUM-SVSUM*TSUM)/DVSR
 20 CONTINUE
    DTSP=0.0
    AKK=K
    DO 25 K3=1,K
```

TABLE B (CONTINUED)

```
      F3=ML(J1,K3)*ML(J1,K3)
      CAL(J1,K3)=P*(S(J1,K3)-F3)+Q*F3
      DTSP=DTSP+(CAL(J1,K3)-T(K3))**2
   25 CONTINUE
      SD(J1)=SQRT(DTSP/AKK)
      AP1(J1)=P
      AP2(J1)=Q
   27 IF (SD(1)-SD(2)) 28,30,30
   28 IF (I3-L2) 29,281,281
  281 IF (I2-L1) 29,54,54
   29 J1=2
      GO TO 50
   30 IF (I3-L2) 32,31,31
   31 IF (I2-L1) 32,56,56
   32 J1=1
   50 CONTINUE
   54 J1=1
      GO TO 57
   56 J1=2
   57 ISD=SD(J1)
      IF (ISD-1) 60,58,58
   58 WRITE (IM,59) I1
   59 FORMAT (1H1,' THE NUMBER',I3,'  SET IS NOT A TETRAGONAL CRYSTAL PO
     1WDER PATTERN')
      GO TO 80
   60 WRITE (IM,62)
   62 FORMAT (1H1,' SIN(SQUARE)',5X,'SIN(SQUARE)',4X,'NUMBER',3X,'H',3X,
     1'K',3X,'L')
      WRITE (IM,64)
   64 FORMAT (2X,'(OBSERVED)',5X,'(CALCULATED)')
      WRITE (IM,66)
   66 FORMAT (1X,11('-'),5X,12('-'),4X,6('-'),2X,3('-'),1X,3('-'),1X,3('
     1-'))
      DO 70 K4=1,K
      IK=S(J1,K4)
   70 WRITE (IM,72) T(K4),CAL(J1,K4),IK,MH(J1,K4),MK(J1,K4),ML(J1,K4)
   72 FORMAT (3X,F8.5,8X,F8.5,7X,I3,4X,I2,2X,I2,2X,I2)
      WRITE (IM,74) AP1(J1),AP2(J1)
   74 FORMAT (' P=',F8.5,9X,'Q=',F8.5)
      WRITE (IM,75) SD(J1)
   75 FORMAT (' STANDARD DEVIATION=',F8.6)
      WRITE (IM,76)
   76 FORMAT (' THIS IS A TETRAGONAL CRYSTAL POWDER PATTERN')
   80 CONTINUE
      STOP
      END
```

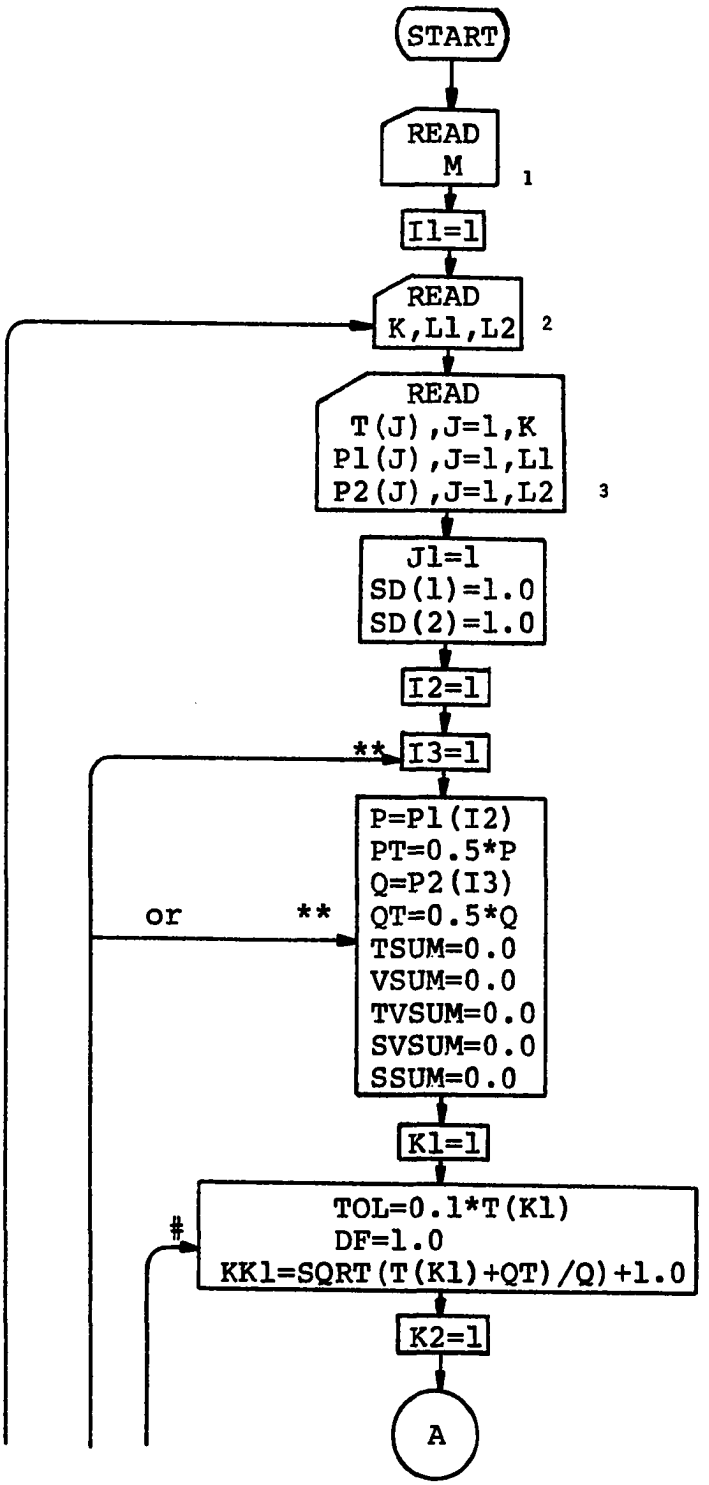
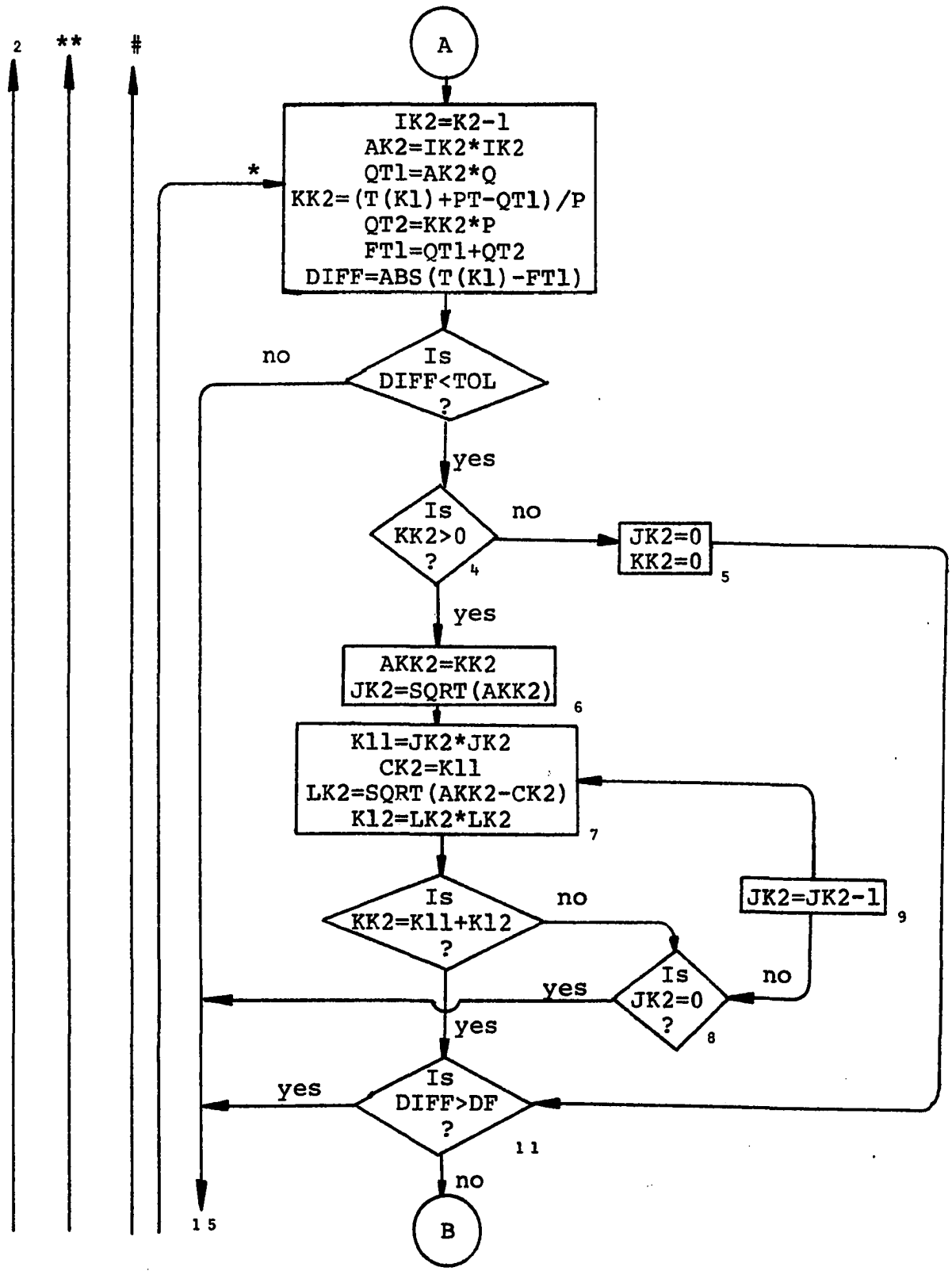
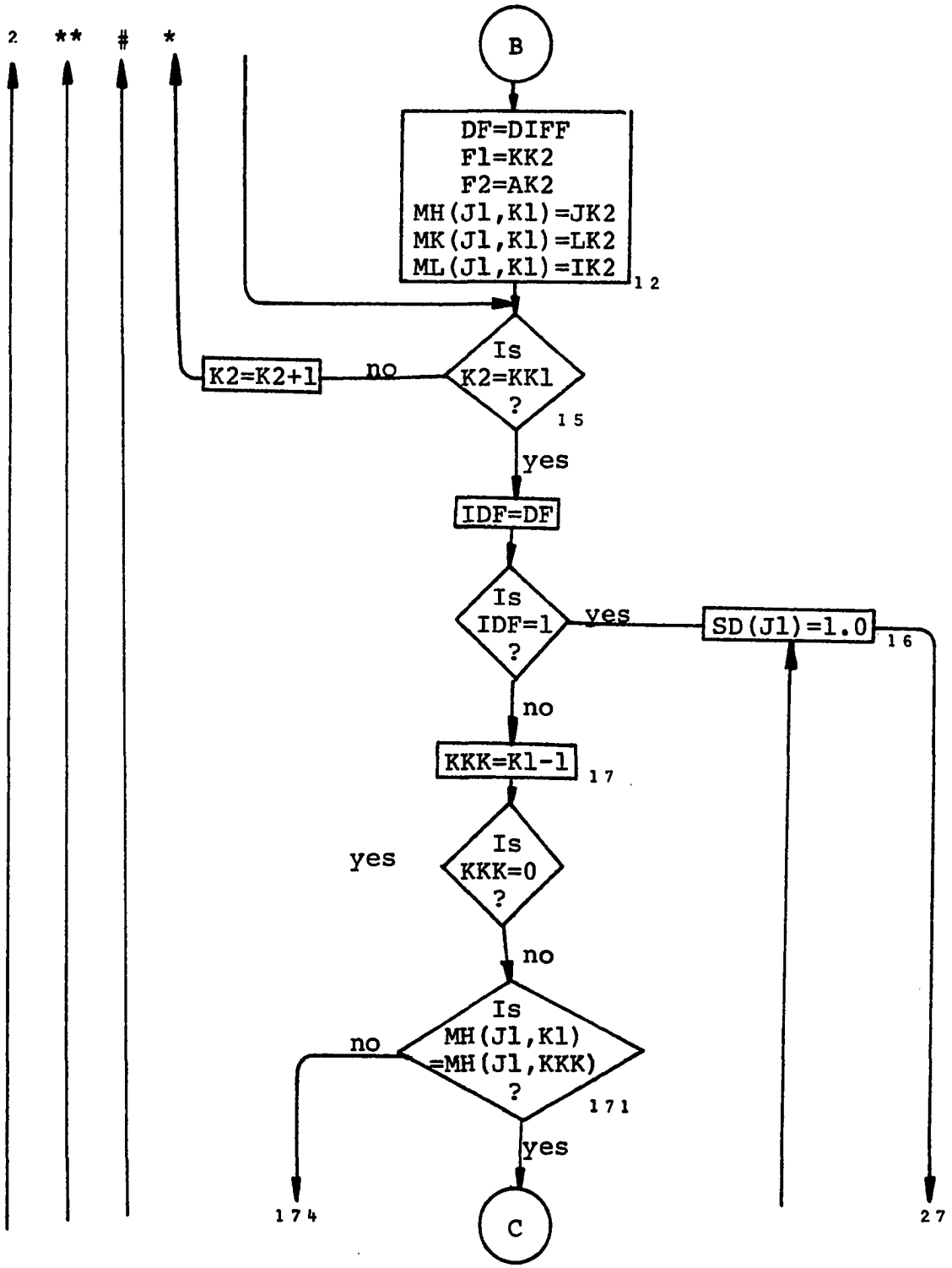
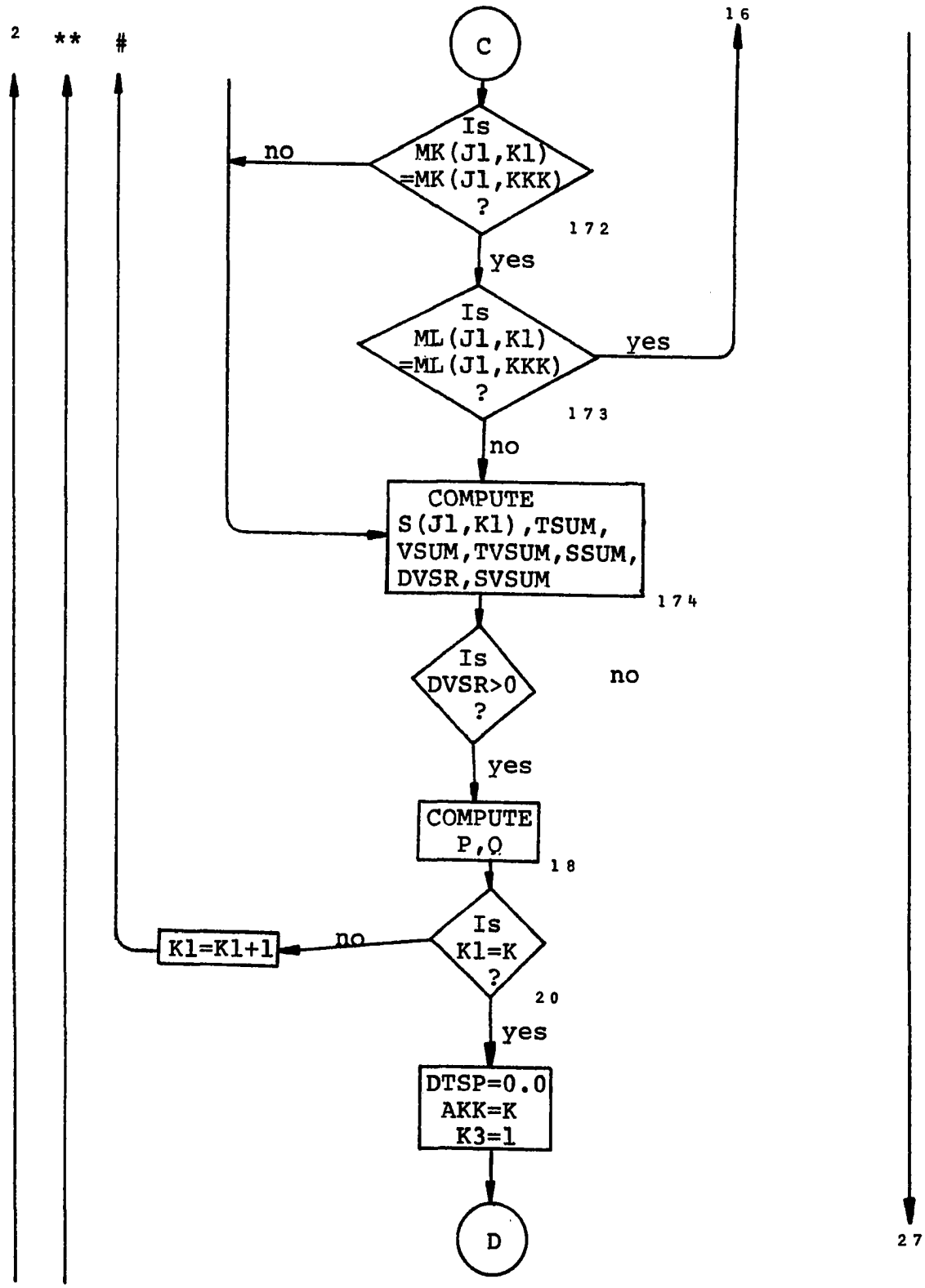
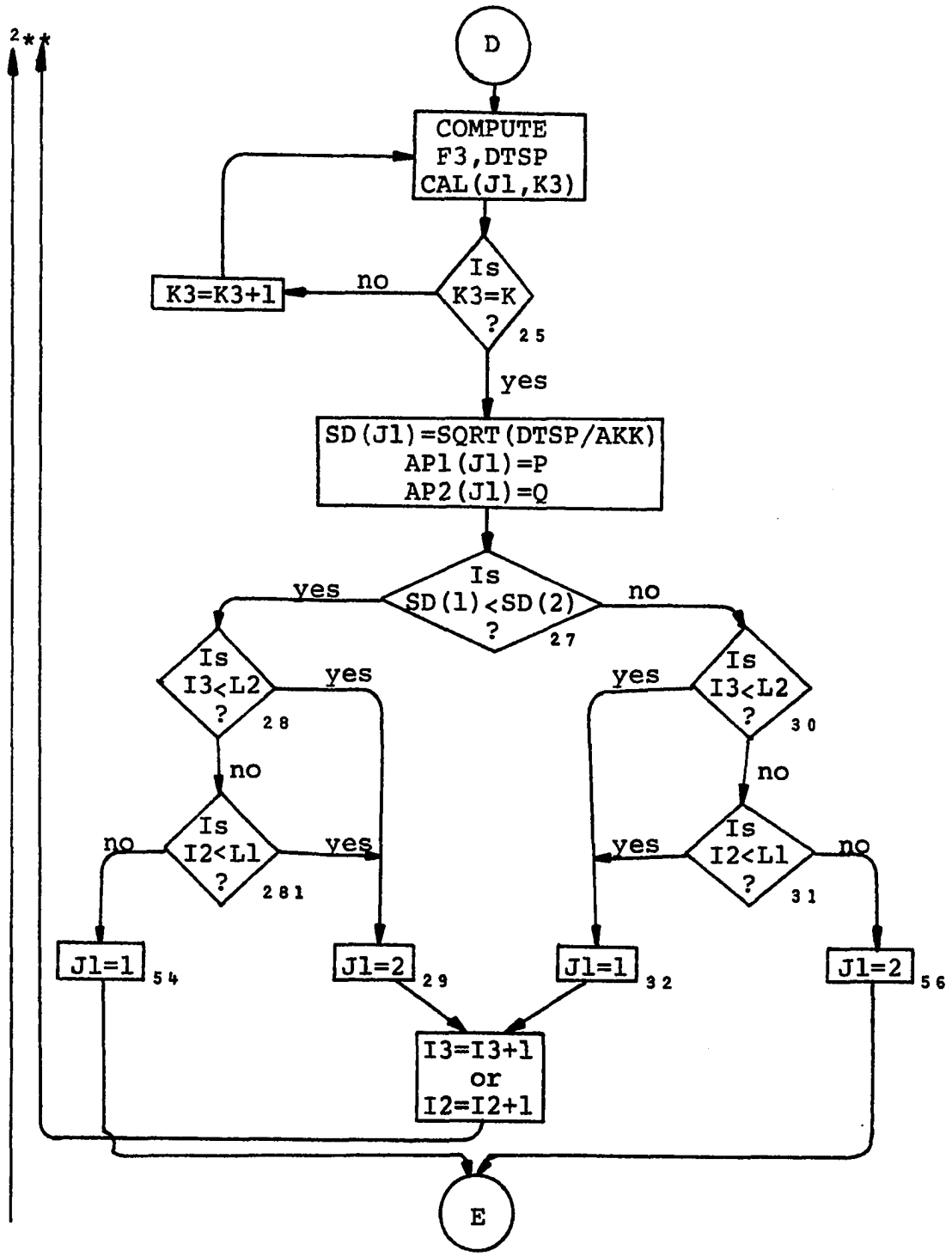


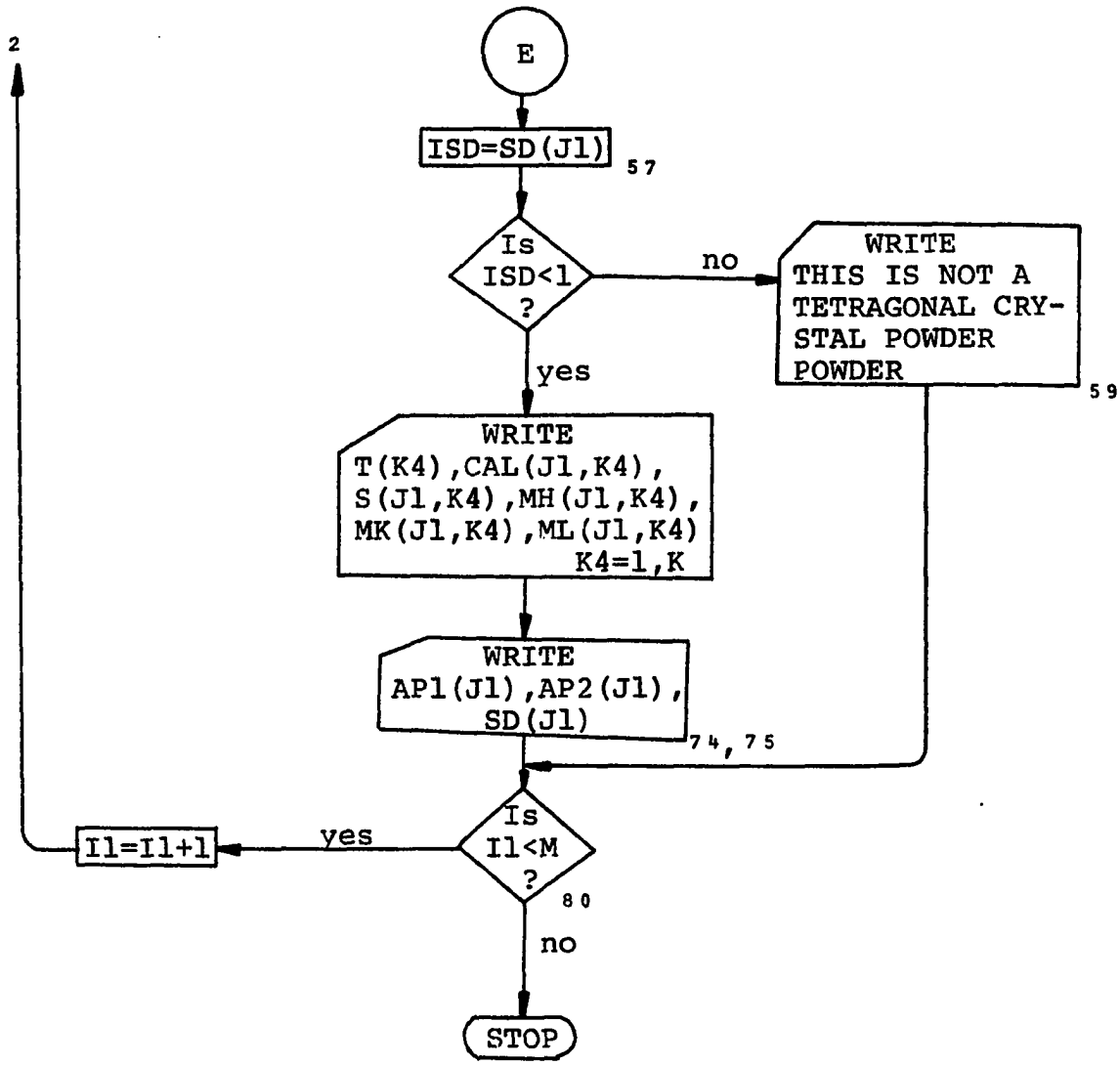
Figure B The Flow Chart of the Computer Program (TET) for the Indexing of Unknown Tetragonal Crystal Powder Patterns


2
**
#
A
IK2=K2-1
AK2=IK2*IK2
QT1=AK2*Q
KK2=(T(K1)+PT-QT1)/P
QT2=KK2*P
FT1=QT1+QT2
DIFF=ABS(T(K1)-FT1)
*
Is DIFF<TOL ?
no
yes
Is KK2>0 ?
4
no
JK2=0
KK2=0
5
yes
AKK2=KK2
JK2=SQRT(AKK2)
6
K11=JK2*JK2
CK2=K11
LK2=SQRT(AKK2-CK2)
K12=LK2*LK2
7
Is KK2=K11+K12 ?
no
JK2=JK2-1
9
Is JK2=0 ?
8
no
yes
yes
Is DIFF>DF ?
11
yes
no
B
15


2
**
#
*
B
DF=DIFF
F1=KK2
F2=AK2
MH(J1,K1)=JK2
MK(J1,K1)=LK2
ML(J1,K1)=IK2
12
Is
K2=KK1
?
15
no
K2=K2+1
yes
IDF=DF
Is
IDF=1
?
yes
SD(J1)=1.0
16
no
KKK=K1-1
17
Is
KKK=0
?
yes
no
Is
MH(J1,K1)
=MH(J1,KKK)
?
171
no
yes
174
C
27


2
**
#
C
16
Is MK(J1,K1) =MK(J1,KKK) ?
172
no
yes
Is ML(J1,K1) =ML(J1,KKK) ?
173
yes
no
COMPUTE S(J1,K1),TSUM, VSUM,TVSUM,SSUM, DVSR,SVSUM
174
Is DVSR>0 ?
no
yes
COMPUTE P,Q
18
Is K1=K ?
20
no
K1=K1+1
yes
DTSP=0.0
AKK=K
K3=1
D
27


2**
D
COMPUTE
F3,DTSP
CAL(J1,K3)
Is
K3=K
?
25
no
K3=K3+1
yes
SD(J1)=SQRT(DTSP/AKK)
AP1(J1)=P
AP2(J1)=Q
Is
SD(1)<SD(2)
?
27
yes
no
Is
I3<L2
?
28
yes
no
Is
I2<L1
?
281
no
yes
J1=1
54
J1=2
29
Is
I3<L2
?
30
yes
no
Is
I2<L1
?
31
yes
no
J1=1
32
J1=2
56
I3=I3+1
or
I2=I2+1
E


E
ISD=SD(J1)
57
Is ISD<1 ?
no
WRITE THIS IS NOT A TETRAGONAL CRYSTAL POWDER POWDER
59
yes
WRITE T(K4),CAL(J1,K4), S(J1,K4),MH(J1,K4), MK(J1,K4),ML(J1,K4) K4=1,K
WRITE AP1(J1),AP2(J1), SD(J1)
74, 75
Is I1<M ?
80
yes
I1=I1+1
2
no
STOP

APPENDIX C

THE COMPUTER PROGRAM AND FLOW CHART FOR HEXAGONAL SYSTEM

TABLE C

Computer Program (HEX) for the
Indexing of Unknown Hexagonal Crystal Powder Patterns

```
C COMPUTER PROGRAM FOR THE INDEXING OF UNKNOWN HEXAGONAL CRYSTAL POWDER
C PATTERNS
      DIMENSION T(70),P1(20),P2(20),AP1(2),AP2(2),CAL(2,70),MH(2,70),MK(
     12,70),ML(2,70),SD(2)
      IN=5
      IM=6
      READ (IN,1) M
    1 FORMAT (I3)
      DO 80 I1=1,M
      READ (IN,2) K,L1,L2
    2 FORMAT (3I3)
      READ (IN,3) (T(J),J=1,K)
      READ (IN,3) (P1(J),J=1,L1)
      READ (IN,3) (P2(J),J=1,L2)
    3 FORMAT (10F7.0)
      J1=1
      SD(1)=1.0
      SD(2)=1.0
      DO 50 I2=1,L1
      DO 50 I3=1,L2
      P=P1(I2)
      PT=0.5*P
      Q=P2(I3)
      QT=0.5*Q
      TSUM=0.0
      VSUM=0.0
      TVSUM=0.0
      SVSUM=0.0
      SSUM=0.0
      DO 20 K1=1,K
      TOL=0.1*T(K1)
      DF=1.0
      IF (Q) 50,50,301
  301 KK1=SQRT((T(K1)+QT)/Q)+1.0
      DO 15 K2=1,KK1
      IK2=K2-1
      AK2=IK2*IK2
      QT1=AK2*Q
      IF (P) 50,50,302
  302 KK2=(T(K1)+PT-QT1)/P
      QT2=KK2*P
      FT1=QT1+QT2
      DIFF=ABS(T(K1)-FT1)
      IF (DIFF-TOL) 501,15,15
```

TABLE C (CONTINUED)

```
501 IF (KK2) 502,502,6
502 JK2=0
    LK2=0
    GO TO 11
  6 AKK2=KK2
    JK2=SQRT(AKK2)
  7 AJK2=JK2
    K11=JK2*JK2
    CK2=K11
    LK2=(SQRT(4.0*AKK2-3.0*CK2)-AJK2)/2.0
    K12=LK2*LK2
    K13=JK2*LK2
    IF (KK2-K11-K12-K13) 8,11,8
  8 IF (JK2) 9,15,9
  9 JK2=JK2-1
    GO TO 7
 11 IF (DIFF-DF) 12,12,15
 12 DF=DIFF
    F1=KK2
    F2=AK2
    MH(J1,K1)=JK2
    MK(J1,K1)=LK2
    ML(J1,K1)=IK2
 15 CONTINUE
    IDF=DF
    IF (IDF-1) 17,16,17
 16 SD(J1)=1.0
    GO TO 27
 17 KKK=K1-1
    IF (KKK) 171,174,171
171 IF (MH(J1,K1)-MH(J1,KKK)) 174,172,174
172 IF (MK(J1,K1)-MK(J1,KKK)) 174,173,174
173 IF (ML(J1,K1)-ML(J1,KKK)) 174,16,174
174 TSUM=TSUM+T(K1)*F1
    VSUM=VSUM+F2*F2
    TVSUM=TVSUM+T(K1)*F2
    SVSUM=SVSUM+F1*F2
    SSUM=SSUM+F1*F1
    DVSR=SSUM*VSUM-SVSUM*SVSUM
    IF (DVSR) 20,20,18
 18 P=(TSUM*VSUM-TVSUM*SVSUM)/DVSR
    Q=(TVSUM*SSUM-SVSUM*TSUM)/DVSR
 20 CONTINUE
    DTSP=0.0
    AKK=K
```

TABLE C (CONTINUED)

```
      DO 25 K3=1,K
      CAL(J1,K3)=P*(MH(J1,K3)*MH(J1,K3)+MH(J1,K3)*MK(J1,K3)+MK(J1,K3)*MK
     1(J1,K3))+Q*ML(J1,K3)*ML(J1,K3)
      DTSP=DTSP+(CAL(J1,K3)-T(K3))**2
   25 CONTINUE
      SD(J1)=SQRT(DTSP/AKK)
      AP1(J1)=P
      AP2(J1)=Q
   27 IF (SD(1)-SD(2)) 28,30,30
   28 IF (I3-L2) 29,281,281
  281 IF (I2-L1) 29,54,54
   29 J1=2
      GO TO 50
   30 IF (I3-L2) 32,31,31
   31 IF (I2-L1) 32,56,56
   32 J1=1
   50 CONTINUE
   54 J1=1
      GO TO 57
   56 J1=2
   57 ISD=SD(J1)
      IF (ISD-1) 60,58,58
   58 WRITE (IM,59) I1
   59 FORMAT (1H1,' THE NUMBER',I3,'  SET IS NOT A HEXAGONAL CRYSTAL POW
     1DER PATTERN')
      GO TO 80
   60 WRITE (IM,62)
   62 FORMAT (1H1,' SIN(SQUARE)',8X,'SIN(SQUARE)',11X,'H',3X,'K',3X,'L')
      WRITE (IM,64)
   64 FORMAT (2X,'(OBSERVED)',8X,'(CALCULATED)')
      WRITE (IM,66)
   66 FORMAT (1X,11('-'),8X,12('-'),10X,3('-'),1X,3('-'),1X,3('-'))
      DO 70 K4=1,K
   70 WRITE (IM,72) T(K4),CAL(J1,K4),MH(J1,K4),MK(JI,K4),ML(J1,K4)
   72 FORMAT (3X,F8.5,11X,F8.5,12X,I2,2X,I2,2X,I2)
      WRITE (IM,74) API(J1),AP2(J1)
   74 FORMAT (' P=',F8.5,9X,'Q=',F8.5)
      WRITE (IM,75) SD(J1)
   75 FORMAT (' STANDARD DEVIATION=',F8.6)
      WRITE (IM,76)
   76 FORMAT (' THIS IS A HEXAGONAL CRYSTAL POWDER PATTERN')
   80 CONTINUE
      STOP
      END
```

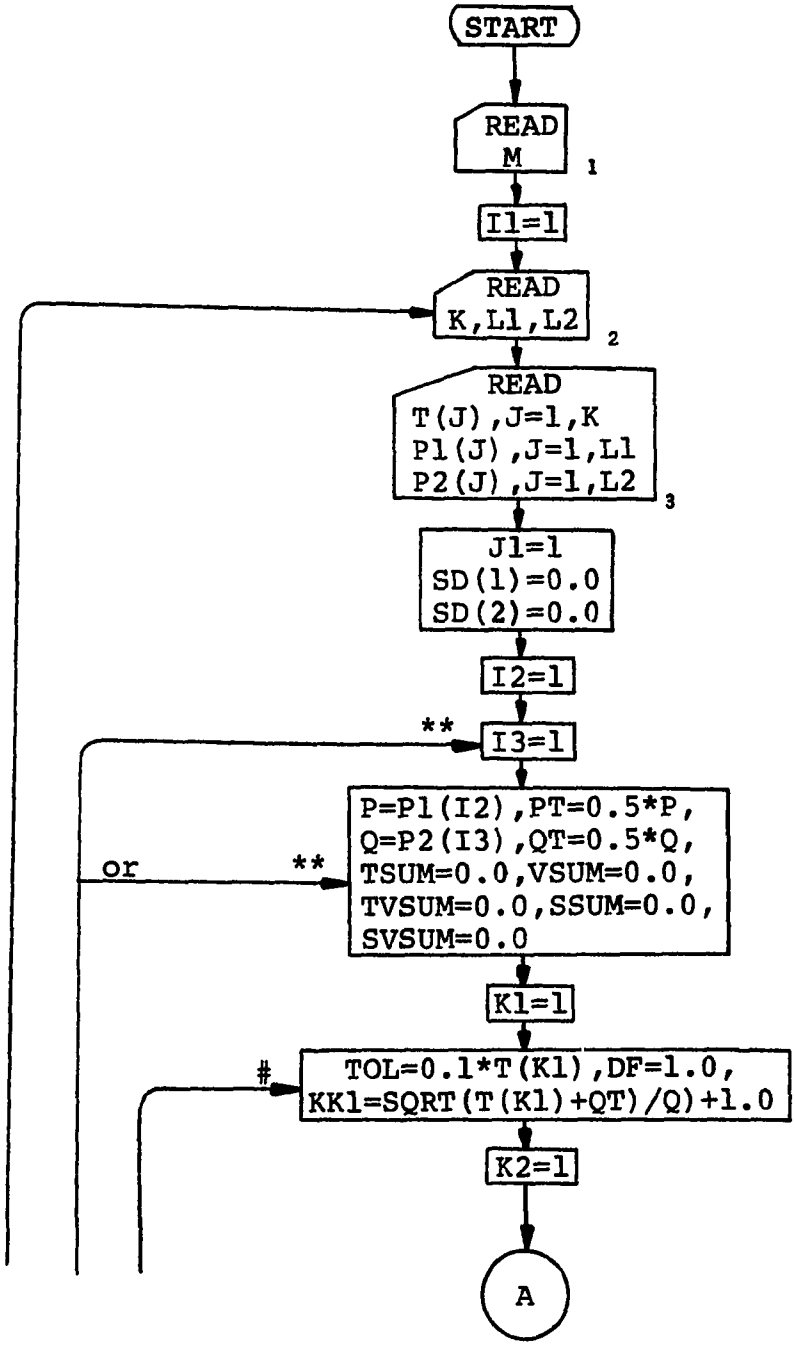
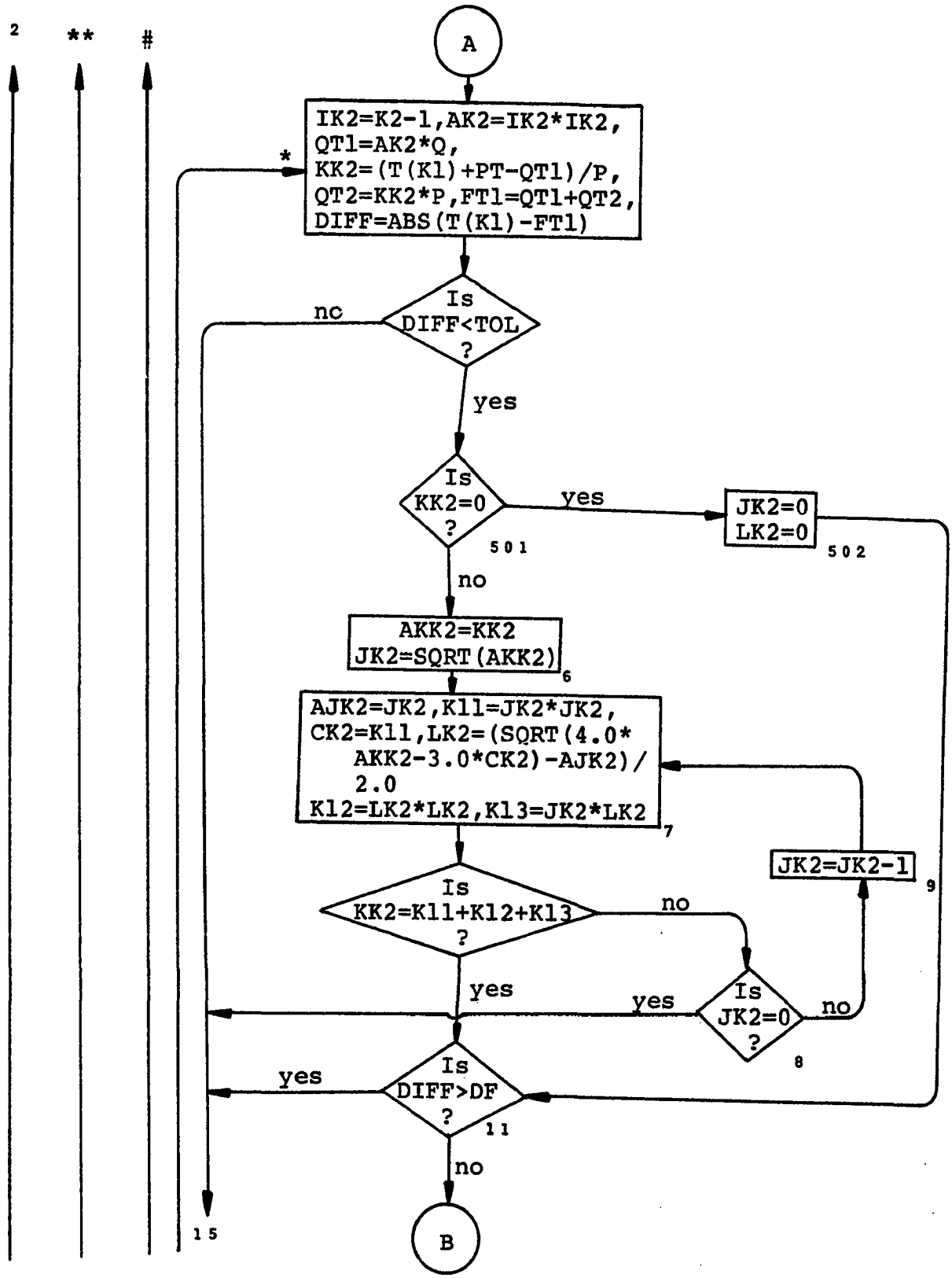
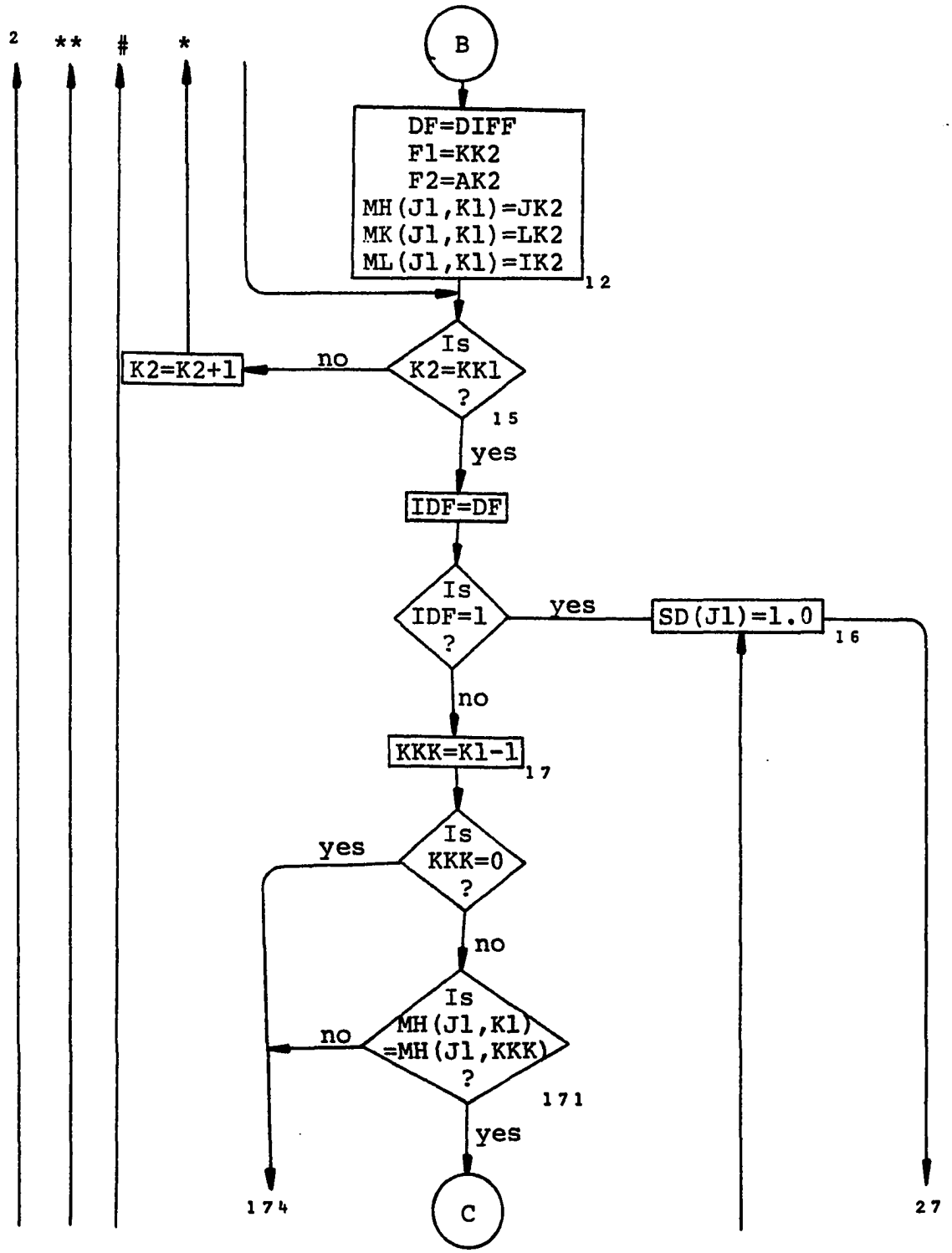
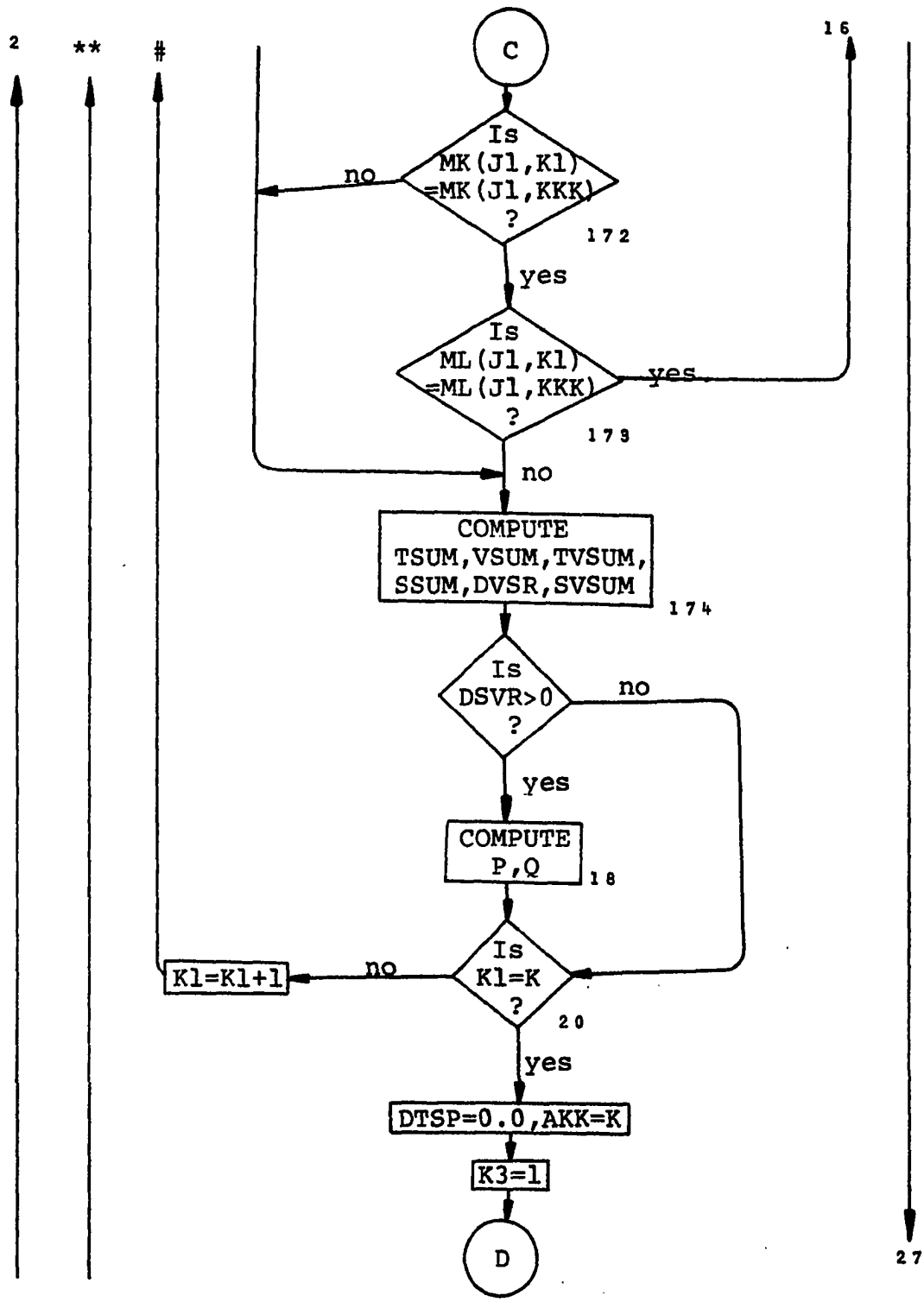
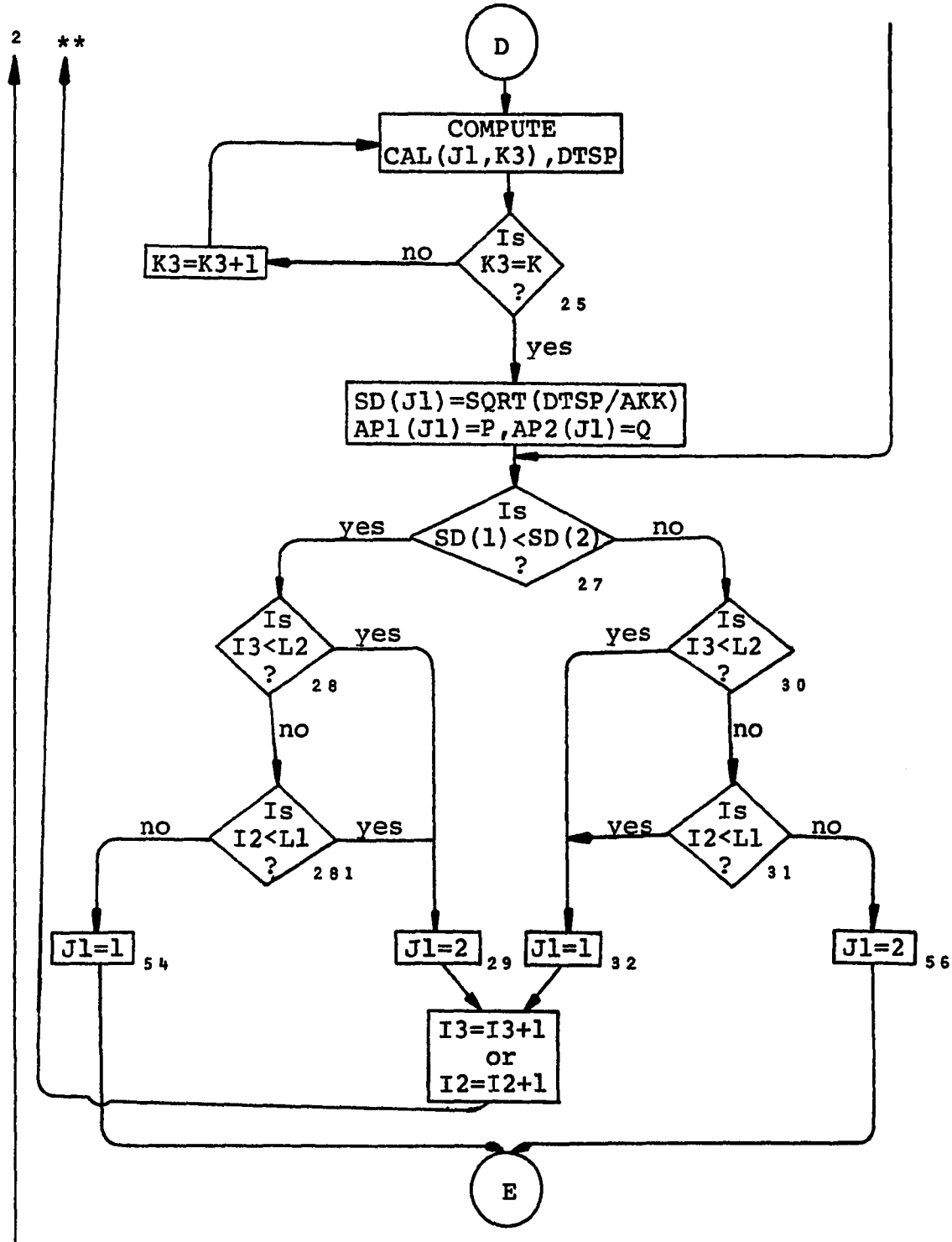


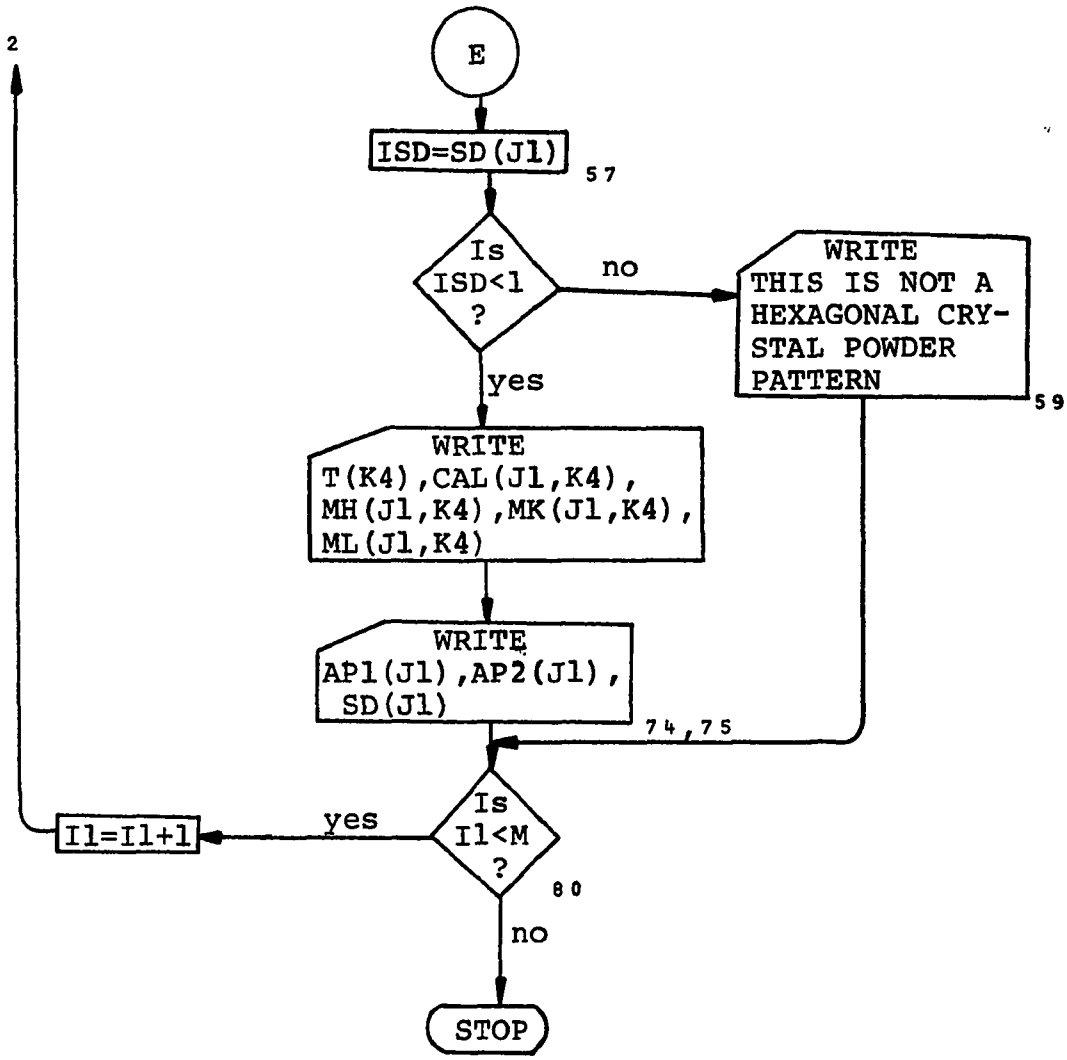
Figure C The Flow Chart of the Computer Program (HEX) for the Indexing of Unknown Hexagonal Crystal Powder Patterns


2
**
#
A
IK2=K2-1,AK2=IK2*IK2,
QT1=AK2*Q,
*
KK2=(T(K1)+PT-QT1)/P,
QT2=KK2*P,FT1=QT1+QT2,
DIFF=ABS(T(K1)-FT1)
Is
DIFF<TOL
?
nc
yes
Is
KK2=0
?
501
yes
JK2=0
LK2=0
502
no
AKK2=KK2
JK2=SQRT(AKK2)
6
AJK2=JK2,K11=JK2*JK2,
CK2=K11,LK2=(SQRT(4.0*
AKK2-3.0*CK2)-AJK2)/
2.0
K12=LK2*LK2,K13=JK2*LK2
7
JK2=JK2-1
9
Is
KK2=K11+K12+K13
?
no
yes
yes
Is
JK2=0
?
8
no
Is
DIFF>DF
?
11
yes
no
15
B


2
**
#
*
B
DF=DIFF
F1=KK2
F2=AK2
MH(J1,K1)=JK2
MK(J1,K1)=LK2
ML(J1,K1)=IK2
12
Is K2=KK1 ?
15
no
K2=K2+1
yes
IDF=DF
Is IDF=1 ?
yes
SD(J1)=1.0
16
no
KKK=K1-1
17
Is KKK=0 ?
yes
no
Is MH(J1,K1) =MH(J1,KKK) ?
171
no
yes
174
C
27


2
**
#
C
16
Is
MK(J1,K1)
=MK(J1,KKK)
?
172
no
yes
Is
ML(J1,K1)
=ML(J1,KKK)
?
179
yes
no
COMPUTE
TSUM,VSUM,TVSUM,
SSUM,DVSR,SVSUM
174
Is
DSVR>0
?
no
yes
COMPUTE
P,Q
18
Is
K1=K
?
20
no
K1=K1+1
yes
DTSP=0.0,AKK=K
K3=1
D
27


2
**
D
COMPUTE
CAL(J1,K3),DTSP
Is
K3=K
?
25
no
K3=K3+1
yes
SD(J1)=SQRT(DTSP/AKK)
AP1(J1)=P,AP2(J1)=Q
Is
SD(1)<SD(2)
?
27
yes
no
Is
I3<L2
?
28
yes
no
Is
I2<L1
?
281
no
yes
J1=1
54
J1=2
29
Is
I3<L2
?
30
yes
no
Is
I2<L1
?
31
yes
no
J1=1
32
J1=2
56
I3=I3+1
or
I2=I2+1
E


2
E
ISD=SD(J1)
57
Is ISD<1 ?
no
WRITE THIS IS NOT A HEXAGONAL CRYSTAL POWDER PATTERN
59
yes
WRITE T(K4),CAL(J1,K4), MH(J1,K4),MK(J1,K4), ML(J1,K4)
WRITE AP1(J1),AP2(J1), SD(J1)
74,75
Is I1<M ?
yes
I1=I1+1
80
no
STOP

APPENDIX D

THE COMPUTER PROGRAM AND FLOW CHART FOR ORTHORHOMBIC SYSTEM

TABLE D

Computer Program (ORT) for the
Indexing of Unknown Orthorhombic Crystal Powder Patterns

```
C COMPUTER PROGRAM FOR THE INDEXING OF UNKNOWN ORTHORHOMBIC CRYSTAL
C POWDER PATTERNS
      DIMENSION T(70),MH(2,70),MK(2,70),ML(2,70),P1(2),P2(2),P3(2),CAL(2
     1,70),SD(2),AP1(50),AP2(50),AP3(50)
      IN=5
      IM=6
      READ (IN,2) M
    2 FORMAT (2I3)
      DO 80 I1=1,M
      READ (IN,2) K,L
      READ (IN,3) (T(J),J=1,K)
      DO 200 J=1,L
  200 READ (IN,3) AP1(J),AP2(J),AP3(J)
    3 FORMAT (10F7.0)
      J1=1
      SD(1)=1.0
      SD(2)=1.0
      DO 55 L1=1,L
      P=AP1(L1)
      PT=0.5*P
      Q=AP2(L1)
      QT=0.5*Q
      S=AP3(L1)
      ST=0.5*S
      SHH=0.0
      SHK=0.0
      SHL=0.0
      SKK=0.0
      SLL=0.0
      SKL=0.0
      STH=0.0
      STK=0.0
      STL=0.0
      DO 40 K1=1,K
      TOL=0.1*T(K1)
      IF (P) 55,55,301
  301 KK1=SQRT((T(K1)+PT)/P)+1.0
      DF=1.0
      DO 21 K2=1,KK1
      AK2=K2-1
      QT1=AK2*AK2*P
      QQT1=T(K1)+QT-QT1
      IF (QQT1) 21,21,4
    4 KK2=SQRT(QQT1/Q)+1.0
      DO 20 K3=1,KK2
      AK3=K3-1
```

TABLE D (CONTINUED)

```
   QT2=AK3*AK3*Q
   QQT2=T(K1)+ST-QT1-QT2
   IF (QQT2) 20,20,5
 5 KK3=SQRT(QQT2/S)
   QT3=KK3*KK3*S
   CALV=QT1+QT2+QT3
   DIFF=ABS(T(K1)-CALV)
   IF (DIFF-TOL) 7,20,20
 7 IF (DIFF-DF) 8,20,20
 8 DF=DIFF
   MH(J1,K1)=AK2
   MK(J1,K1)=AK3
   ML(J1,K1)=KK3
20 CONTINUE
21 CONTINUE
   IDF=DF
   IF (IDF-1) 24,22,24
22 SD(J1)=1.0
   GO TO 46
24 KL=K1-1
   IF (KL) 26,32,26
26 IF (MH(J1,K1)-MH(J1,KL)) 32,28,32
28 IF (MK(J1,K1)-MK(J1,KL)) 32,30,32
30 IF (ML(J1,K1)-ML(J1,KL)) 32,22,32
32 HH=MH(J1,K1)*MH(J1,K1)
   HK=MK(J1,K1)*MK(J1,K1)
   HL=ML(J1,K1)*ML(J1,K1)
   SHH=SHH+HH*HH
   SKK=SKK+HK*HK
   SLL=SLL+HL*HL
   SHK=SHK+HH*HK
   SKL=SKL+HK*HL
   SHL=SHL+HH*HL
   STH=STH+T(K1)*HH
   STK=STK+T(K1)*HK
   STL=STL+T(K1)*HL
   DEL=SHH*SKK*SLL+2.0*SHK*SKL*SHL-SHH*SKL*SKL-SKK*SHL*SHL-SLL*SHK*SH
  1K
   IF (DEL) 40,40,33
33 DELP=STH*(SKK*SLL-SKL*SKL)+STK*(SHL*SKL-SHK*SLL)+STL*(SHK*SKL-SKK*
  1SHL)
   DELQ=STH*(SKL*SHL-SLL*SHK)+STK*(SHH*SLL-SHL*SHL)+STL*(SHL*SHK-SHH*
  1SKL)
   DELS=STH*(SHK*SKL-SKK*SHL)+STK*(SHK*SHL-SHH*SKL)+STL*(SHH*SKK-SHK*
  1SHK)
   P=DELP/DEL
   Q=DELQ/DEL
```

TABLE D (CONTINUED)

```
      S=DELS/DEL
   40 CONTINUE
      DTSP=0.0
      AKK=K
      DO 44 K4=1,K
      CAL(J1,K4)=P*MH(J1,K4)*MH(J1,K4)+Q*MK(J1,K4)*MK(J1,K4)+S*ML(J1,K4)
     1*ML(J1,K4)
      DTSP=DTSP+(T(K4)-CAL(J1,K4))**2
   44 CONTINUE
      SD(J1)=SQRT(DTSP/AKK)
      P1(J1)=P
      P2(J1)=Q
      P3(J1)=S
   46 IF (SD(1)-SD(2)) 48,48,50
   48 IF (L1-L) 49,58,58
   49 J1=2
      GO TO 55
   50 IF (L1-L) 52,59,59
   52 J1=1
   55 CONTINUE
   58 J1=1
      GO TO 60
   59 J1=2
   60 ISD=SD(J1)
      IF (ISD-1) 602,601,601
  601 WRITE (IM,61) I1
   61 FORMAT (1H1,' THE NUMBER',I3,'  SET IS NOT AN ORTHORHOMBIC CRYSTAL
     1 POWDER PATTERN')
      GO TO 80
  602 WRITE (IM,62)
   62 FORMAT (1H1,' SIN(SQUARE)',7X,'SIN(SQUARE)',12X,'H',3X,'K',3X,'L')
      WRITE (IM,64)
   64 FORMAT (2X,'(OBSERVED)',8X,'(CALCULATED)')
      WRITE (IM,66)
   66 FORMAT (1X,11('-'),8X,12('-'),10X,3('-'),1X,3('-'),1X,3('-'))
      DO 70 K5=1,K
   70 WRITE (IM,72) T(K5),CAL(J1,K5),MH(J1,K5),MK(J1,K5),ML(J1,K5)
   72 FORMAT (3X,F8.5,11X,F8.5,12X,I2,2X,I2,2X,I2)
      WRITE (IM,74) P1(J1),P2(J1),P3(J1)
   74 FORMAT (' P=',F8.5,5X,'Q=',F8.5,5X,'S=',F8.5)
      WRITE (IM,75) SD(J1)
   75 FORMAT (' STANDARD DEVIATION=',F8.6)
      WRITE (IM,76)
   76 FORMAT (' THIS IS AN ORTHORHOMBIC CRYSTAL POWDER PATTERN')
   80 CONTINUE
      STOP
      END
```

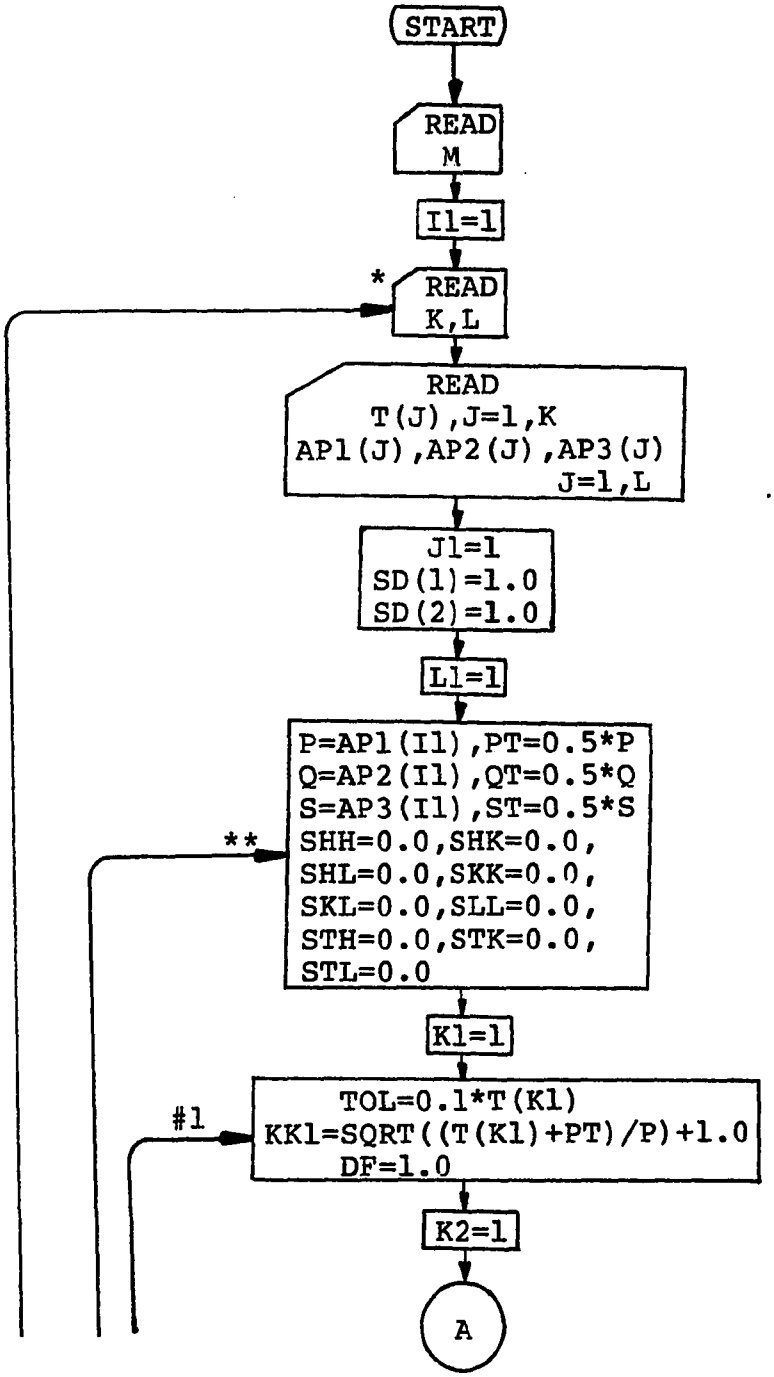
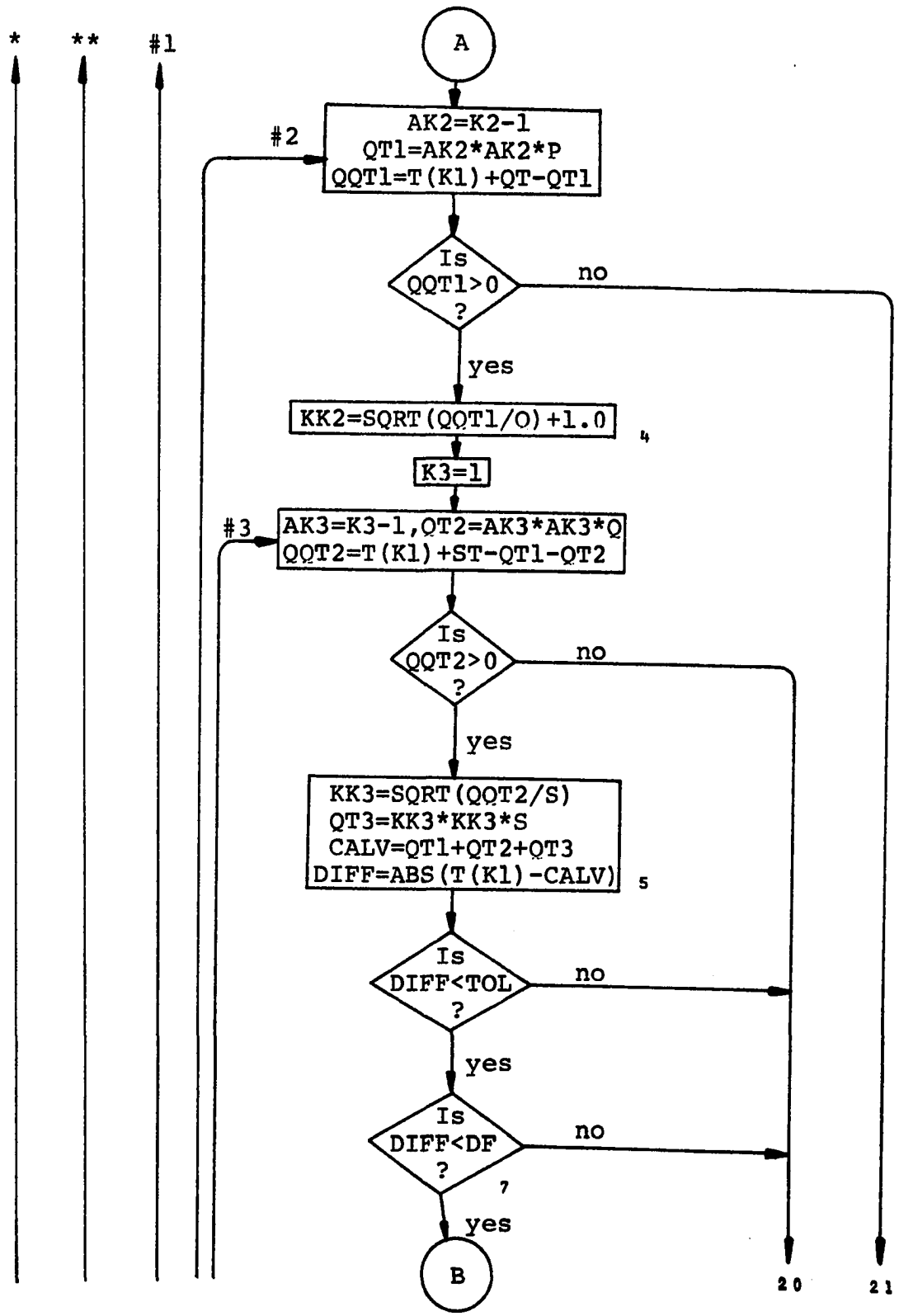
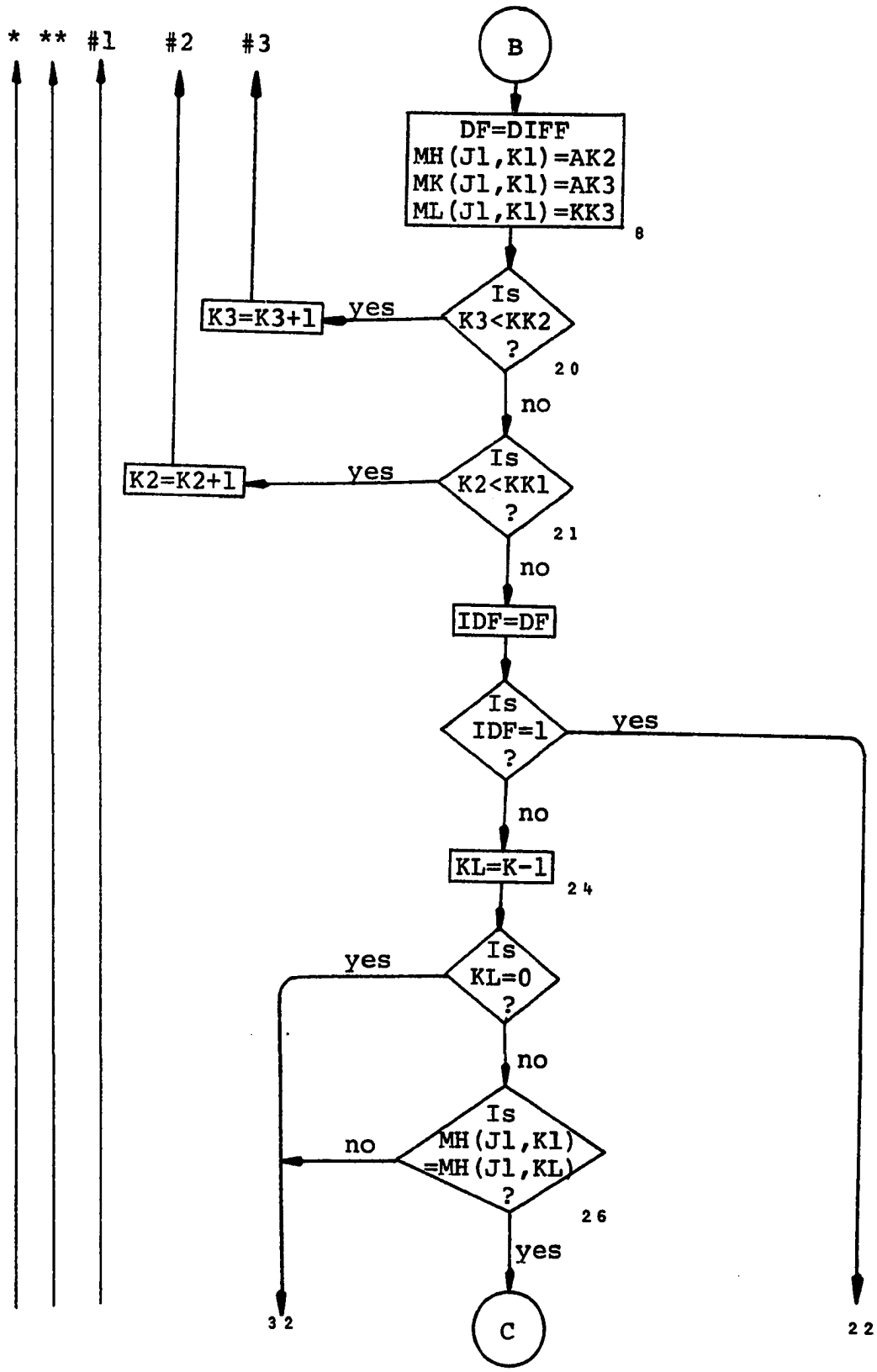
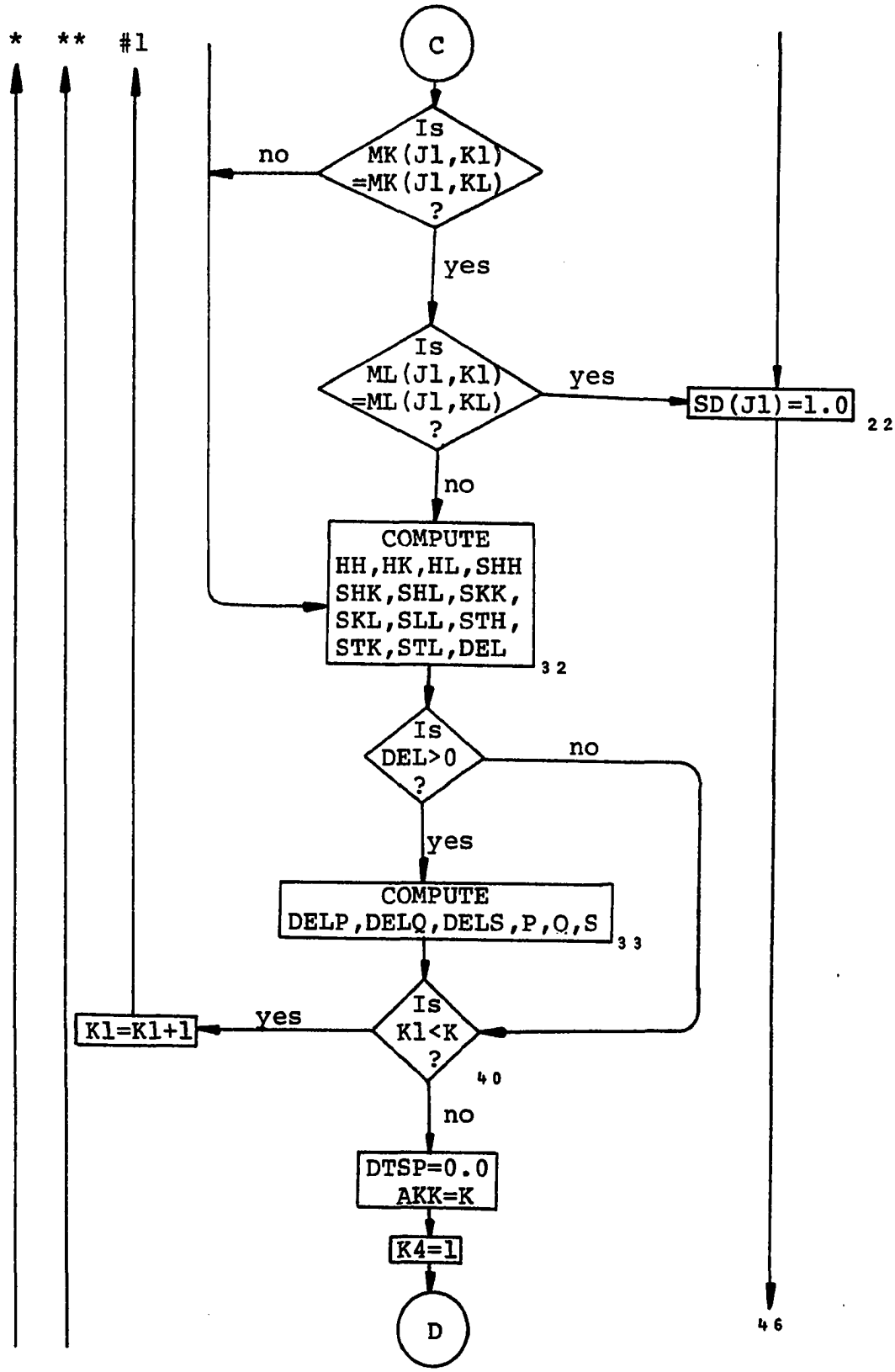
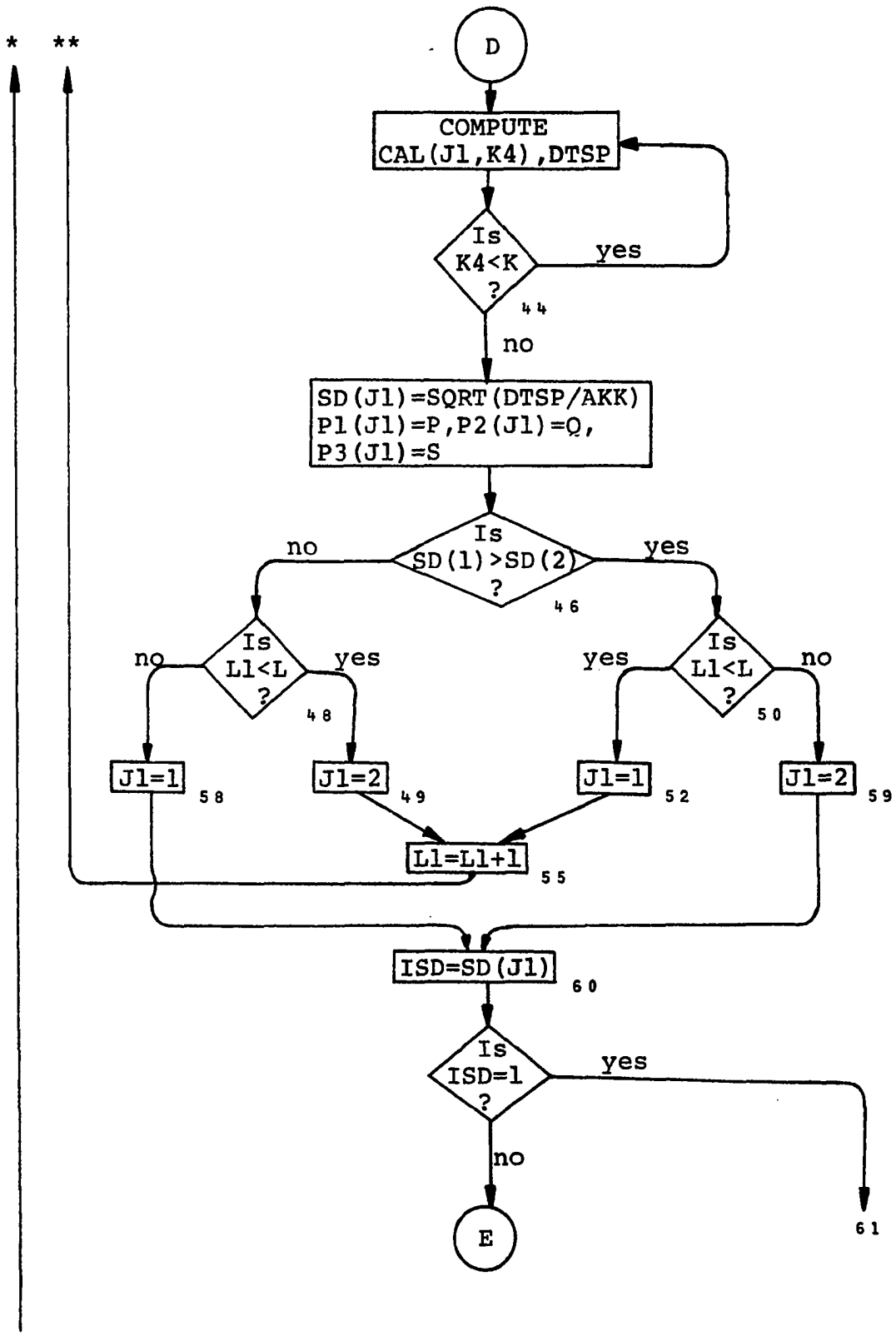


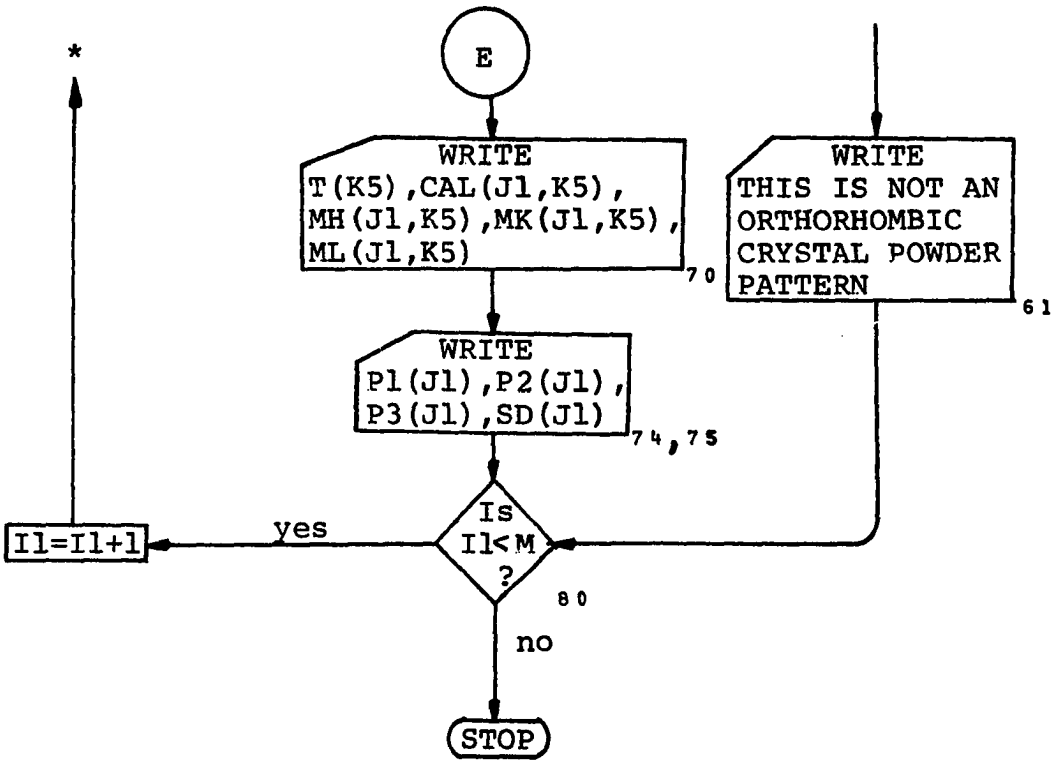
Figure D The Flow Chart of the Computer Program (ORT) for the Indexing of Unknown Orthorhombic Crystal Powder Patterns


*
**
#1
A
#2
AK2=K2-1
QT1=AK2*AK2*P
QQT1=T(K1)+QT-QT1
Is QQT1>0 ?
no
yes
KK2=SQRT(QQT1/O)+1.0
4
K3=1
#3
AK3=K3-1,QT2=AK3*AK3*Q
QQT2=T(K1)+ST-QT1-QT2
Is QQT2>0 ?
no
yes
KK3=SQRT(QQT2/S)
QT3=KK3*KK3*S
CALV=QT1+QT2+QT3
DIFF=ABS(T(K1)-CALV)
5
Is DIFF<TOL ?
no
yes
Is DIFF<DF ?
no
7
yes
B
20
21


* ** #1 #2 #3
B
DF=DIFF
MH(J1,K1)=AK2
MK(J1,K1)=AK3
ML(J1,K1)=KK3
8
Is K3<KK2 ?
20
yes
K3=K3+1
no
Is K2<KK1 ?
21
yes
K2=K2+1
no
IDF=DF
Is IDF=1 ?
yes
no
KL=K-1
24
Is KL=0 ?
yes
no
Is MH(J1,K1) =MH(J1,KL) ?
26
no
yes
C
32
22


*
**
#1
C
Is MK(J1,K1) =MK(J1,KL) ?
no
yes
Is ML(J1,K1) =ML(J1,KL) ?
yes
SD(J1)=1.0
22
no
COMPUTE HH,HK,HL,SHH SHK,SHL,SKK, SKL,SLL,STH, STK,STL,DEL
32
Is DEL>0 ?
no
yes
COMPUTE DELP,DELQ,DELS,P,Q,S
33
Is K1<K ?
yes
K1=K1+1
40
no
DTSP=0.0
AKK=K
K4=1
D
46


*
**
D
COMPUTE
CAL(J1,K4),DTSP
Is
K4<K
?
44
yes
no
SD(J1)=SQRT(DTSP/AKK)
P1(J1)=P,P2(J1)=Q,
P3(J1)=S
Is
SD(1)>SD(2)
?
46
no
yes
Is
L1<L
?
48
no
yes
Is
L1<L
?
50
yes
no
J1=1
58
J1=2
49
J1=1
52
J1=2
59
L1=L1+1
55
ISD=SD(J1)
60
Is
ISD=1
?
yes
no
E
61


*
E
WRITE
T(K5),CAL(J1,K5),
MH(J1,K5),MK(J1,K5),
ML(J1,K5)
70
WRITE
THIS IS NOT AN
ORTHORHOMBIC
CRYSTAL POWDER
PATTERN
61
WRITE
P1(J1),P2(J1),
P3(J1),SD(J1)
74,75
Is
I1<M
?
80
yes
I1=I1+1
no
STOP

APPENDIX E

THE COMPUTER PROGRAM AND FLOW CHART FOR MONOCLINIC SYSTEM

TABLE E

Computer Program (MON) for the
Indexing of Unknown Monoclinic Crystal Powder Patterns

```
C COMPUTER PROGRAM FOR THE INDEXING OF UNKNOWN MONOCLINIC CRYSTAL
C POWDER PATTERNS
      DIMENSION T(70),A(4,4),B(4),P1(10),P2(10),P3(10),P4(10),AP1(2),AP2
     1(2),AP3(2),AP4(2),CAL(2,70),MH(2,70),MK(2,70),ML(2,70),SD(2),
     2C(4,4),CL(70)
      IN=5
      IM=6
      READ (IN,1) M
    1 FORMAT (2I3)
      DO 80 I=1,M
      READ (IN,1) K,L
      READ (IN,3) (T(J),J=1,K)
    3 FORMAT (10F7.0)
      DO 4 J=1,L
    4 READ (IN,400) P1(J),P2(J),P3(J),P4(J)
  400 FORMAT (4F10.0)
      J1=1
      SD(1)=1.0
      SD(2)=1.0
      DO 50 I1=1,L
      P=P1(I1)
      Q=P2(I1)
      S=P3(I1)
      V=P4(I1)
      DO 5 I3=1,4
      DO 5 I4=1,4
      C(I3,I4)=0.0
    5 CONTINUE
      STH=0.0
      STK=0.0
      STL=0.0
      STHL=0.0
      DO 31 II=1,2
      DO 30 K1=1,K
      PT=0.5*P
      QT=0.5*Q
      DF=1.0
      IF (Q) 50,50,495
  495 KK1=SQRT((T(K1)+QT)/Q)+1.0
      DO 150 K2=1,KK1
      AK2=K2-1
      QQT1=AK2*AK2*Q
      QQT11=T(K1)-QQT1
      IF (ABS(QQT11)-0.0002) 496,496,497
  496 DIFF=ABS(QQT11)
```

TABLE E (CONTINUED)

```
      KK2=1
      GO TO 4990
  497 QQT12=QQT11+PT
      IF (P) 150,150,498
  498 IF (QQT12/P) 150,150,499
  499 KK2=SQRT(QQT12/P)+2.0
 4990 DO 15 K3=1,KK2
      AK3=K3-1
      AKK3=AK3*AK3
      QQT2=AKK3*P
      QQT13=QQT11-QQT2
      IF (ABS(QQT13)-0.0002) 4991,4991,4992
 4991 DIFF=ABS(QQT13)
      KK5=0
      GO TO 9
 4992 QQT3=AK3*V
      QQT4=T(K1)-QQT1-QQT2
      QQT5=QQT3*QQT3+4.0*S*QQT4
      IF (QQT5) 15,500,500
  500 QQT6=SQRT(QQT5)
      QQT7=QQT3+QQT6
      IF (QQT7) 501,503,502
  501 KK3=(QQT7-S)/(2.0*S)
      GO TO 505
  502 KK3=(QQT7+S)/(2.0*S)
      GO TO 505
  503 KK3=0
  505 QQT8=QQT3-QQT6
      IF (QQT8) 506,508,507
  506 KK4=(QQT8-S)/(2.0*S)
      GO TO 510
  507 KK4=(QQT8+S)/(2.0*S)
      GO TO 510
  508 KK4=0
  510 QT1=QQT4-KK3*KK3*S+AK3*KK3*V
      QT2=QQT4-KK4*KK4*S+AK3*KK4*V
      DIFF1=ABS(QT1)
      DIFF2=ABS(QT2)
      IF (DIFF1-DIFF2) 6,6,7
    6 DIFF=DIFF1
      KK5=KK3
      GO TO 9
    7 DIFF=DIFF2
      KK5=KK4
    9 TOL=0.1*T(K1)
      NK3=AK3
```

TABLE E (CONTINUED)

```
      NK2=AK2
      IF (DIFF-TOL) 10,15,15
   10 IF (DIFF-DF) 11,15,15
   11 KL=K1-1
      IF (KL) 13,13,12
   12 IF (NK3-MH(J1,KL)) 13,200,13
  200 IF (NK2-MK(J1,KL)) 13,202,13
  202 IF (KK5-ML(J1,KL)) 13,15,13
   13 IF (II-2) 14,203,203
  203 IF (K1-K) 204,14,14
  204 KLL=K1+1
      IF (NK3-MH(J1,KLL)) 14,205,14
  205 IF (NK2-MK(J1,KLL)) 14,206,14
  206 IF (KK5-ML(J1,KLL)) 14,15,14
   14 DF=DIFF
      MH(J1,K1)=NK3
      MK(J1,K1)=NK2
      ML(J1,K1)=KK5
   15 CONTINUE
  150 CONTINUE
      IDF=DF
      IF (IDF-1) 22,16,22
   16 SD(J1)=1.0
      GO TO 37
   22 BK2=MH(J1,K1)*MH(J1,K1)
      BK3=MK(J1,K1)*MK(J1,K1)
      BK4=ML(J1,K1)*ML(J1,K1)
      BK5=MH(J1,K1)*ML(J1,K1)
      IF (II-2) 229,24,24
  229 CL(K1)=P*BK2+Q*BK3+S*BK4-V*BK5
      IF (KL) 24,24,23
   23 IF (CL(K1)-CL(KL)) 230,24,24
  230 DIF=T(K1)-T(KL)
      STH=STH+(MH(J1,KL)*MH(J1,KL)-BK2)*DIF
      STK=STK+(MK(J1,KL)*MK(J1,KL)-BK3)*DIF
      STL=STL+(ML(J1,KL)*ML(J1,KL)-BK4)*DIF
      STHL=STHL+(MH(J1,KL)*ML(J1,KL)-BK5)*DIF
      MH(J1,K1)=MH(J1,KL)
      MK(J1,K1)=MK(J1,KL)
      ML(J1,K1)=ML(J1,KL)
   24 C(1,1)=C(1,1)+BK2*BK2
      C(1,2)=C(1,2)+BK2*BK3
      C(1,3)=C(1,3)+BK2*BK4
      C(1,4)=C(1,4)-BK2*BK5
      C(2,1)=C(1,2)
      C(2,2)=C(2,2)+BK3*BK3
```

TABLE E (CONTINUED)

```
      C(2,3)=C(2,3)+BK3*BK4
      C(2,4)=C(2,4)-BK3*BK5
      C(3,1)=C(1,3)
      C(3,2)=C(2,3)
      C(3,3)=C(3,3)+BK4*BK4
      C(3,4)=C(3,4)-BK4*BK5
      C(4,1)=-C(1,4)
      C(4,2)=-C(2,4)
      C(4,3)=-C(3,4)
      C(4,4)=-C(1,3)
      STH=STH+BK2*T(K1)
      STK=STK+BK3*T(K1)
      STL=STL+BK4*T(K1)
      STHL=STHL+BK5*T(K1)
      IF (C(1,1)) 30,30,123
  123 IF (C(2,2)) 30,30,124
  124 IF (C(3,3)) 30,30,125
  125 IF (C(4,4)) 126,30,126
  126 B(1)=STH
      B(2)=STK
      B(3)=STL
      B(4)=STHL
      DO 130 I5=1,4
      DO 130 I6=1,4
      A(I5,I6)=C(I5,I6)
  130 CONTINUE
      CALL SIMQ(A,B,4,KS)
      IF (KS-1) 25,30,30
   25 P=B(1)
      Q=B(2)
      S=B(3)
      V=B(4)
   30 CONTINUE
   31 CONTINUE
      DTSP=0.0
      AKK=K
      DO 35 K4=1,K
      CAL(J1,K4)=P*MH(J1,K4)*MH(J1,K4)+Q*MK(J1,K4)*MK(J1,K4)+S*ML(J1,K4)
     1*ML(J1,K4)-V*MH(J1,K4)*ML(J1,K4)
      DTSP=DTSP+(CAL(J1,K4)-T(K4))**2
   35 CONTINUE
      SD(J1)=SQRT(DTSP/AKK)
      AP1(J1)=P
      AP2(J1)=Q
      AP3(J1)=S
      AP4(J1)=V
```

TABLE E (CONTINUED)

```
37 IF (SD(1)-SD(2)) 38,38,41
38 IF (I1-L) 40,52,52
40 J1=2
   GO TO 50
41 IF (I1-L) 43,54,54
43 J1=1
50 CONTINUE
52 J1=1
   GO TO 56
54 J1=2
56 ISD=SD(J1)
   IF (ISD-1) 60,58,60
58 WRITE (IM,59) I
59 FORMAT (1H1,' THE NUMBER',I3,'  SET IS NOT A MONOCLINIC CRYSTAL PO
  1WDER PATTERN')
   GO TO 80
60 WRITE (IM,62)
62 FORMAT (1H1,' SIN(SQUARE)',8X,'SIN(SQUARE)',12X,'H',5X,'K',5X,'L')
   WRITE (IM,64)
64 FORMAT (2X,'(OBSERVED)',8X,'(CALCULATED)')
   WRITE (IM,66)
66 FORMAT (2X,10('-'),8X,12('-'),11X,15('-'))
   DO 70 K5=1,K
70 WRITE (IM,72) T(K5),CAL(J1,K5),MH(J1,K5),MK(J1,K5),ML(J1,K5)
72 FORMAT (3X,F8.5,11X,F8.5,12X,I3,3X,I3,3X,I3)
   WRITE (IM,74) AP1(J1),AP2(J1),AP3(J1),AP4(J1)
74 FORMAT (' P=',F8.5,5X,'Q=',F8.5,5X,'S=',F8.5,5X,'V=',F8.5)
   WRITE (IM,75) SD(J1)
75 FORMAT (' STANDARD DEVIATION=',F8.6)
   WRITE (IM,76)
76 FORMAT (' THIS IS A MONOCLINIC CRYSTAL POWDER PATTERN')
80 CONTINUE
   STOP
   END
```

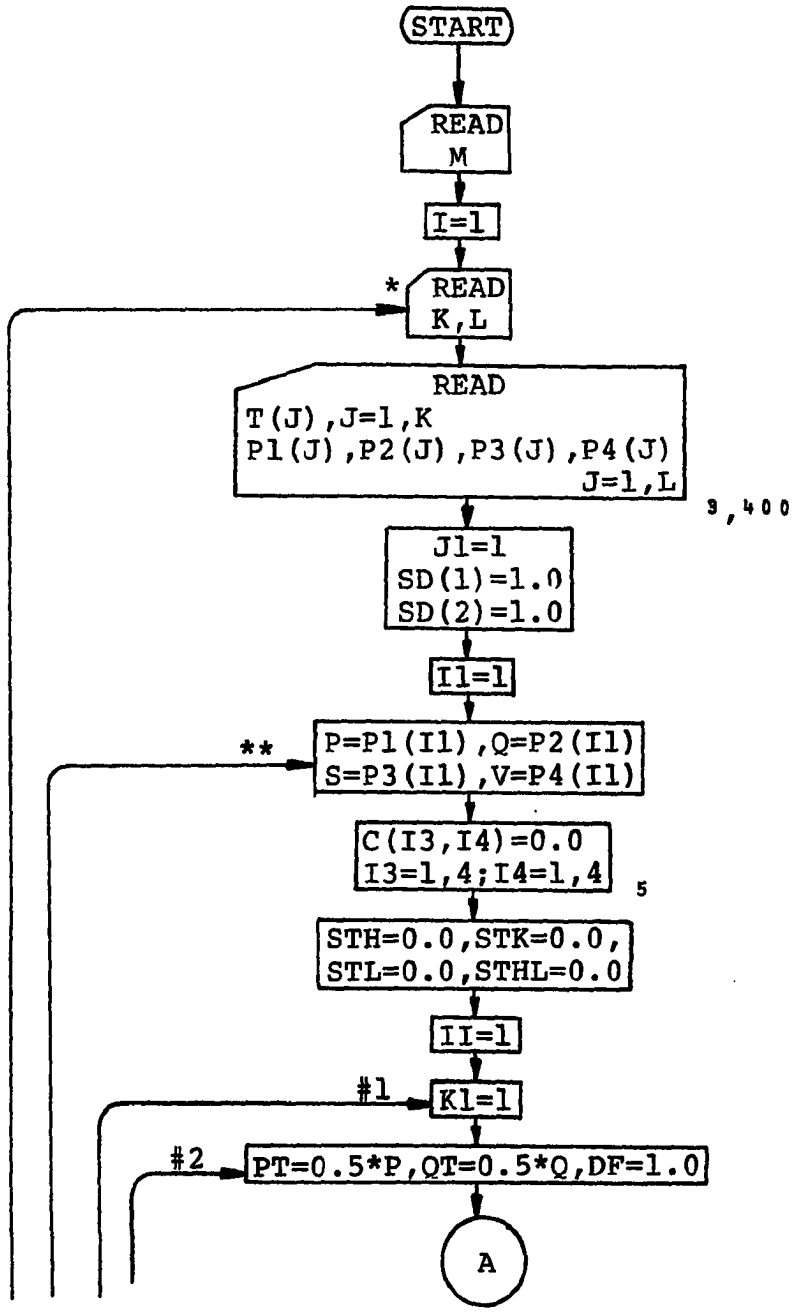
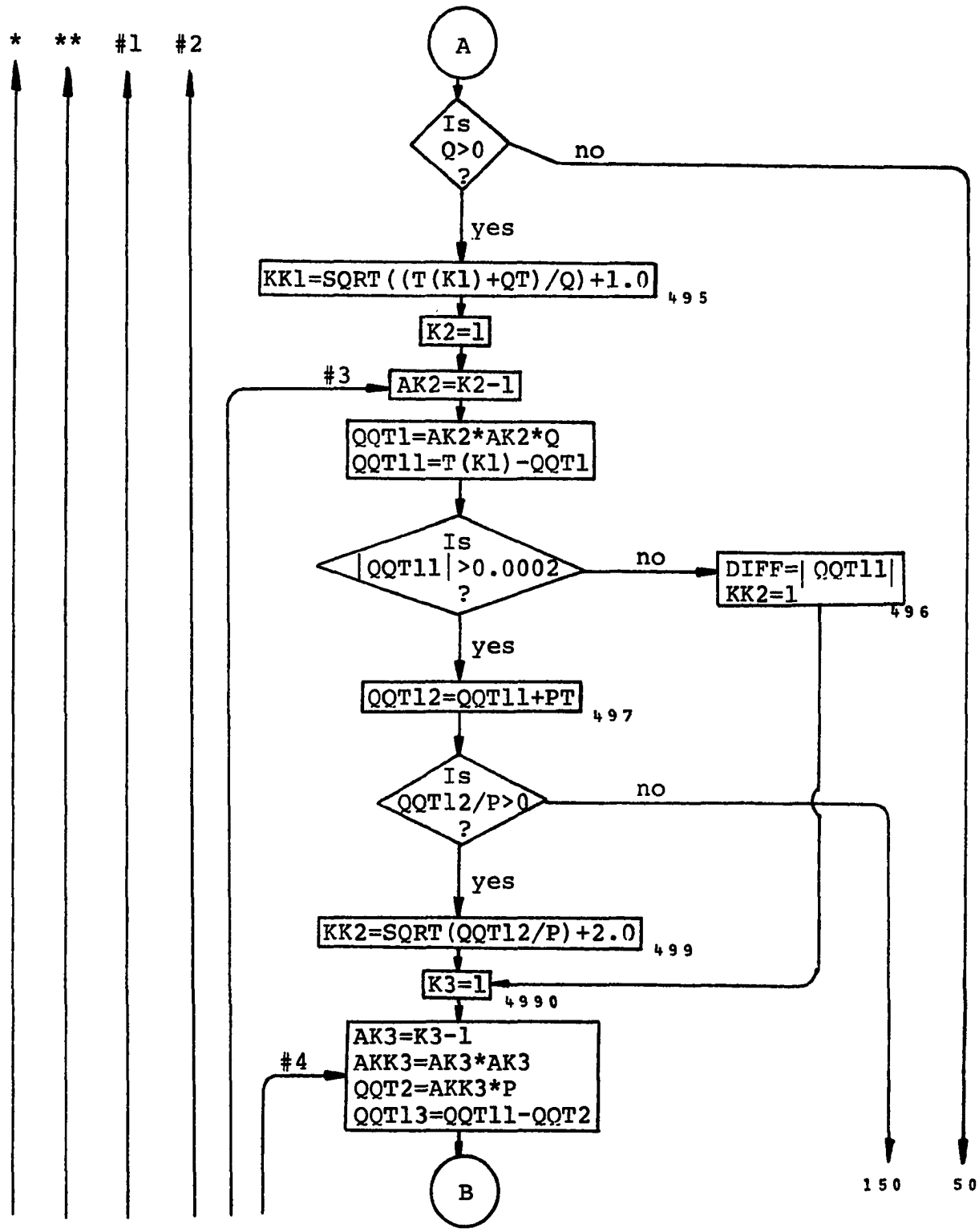
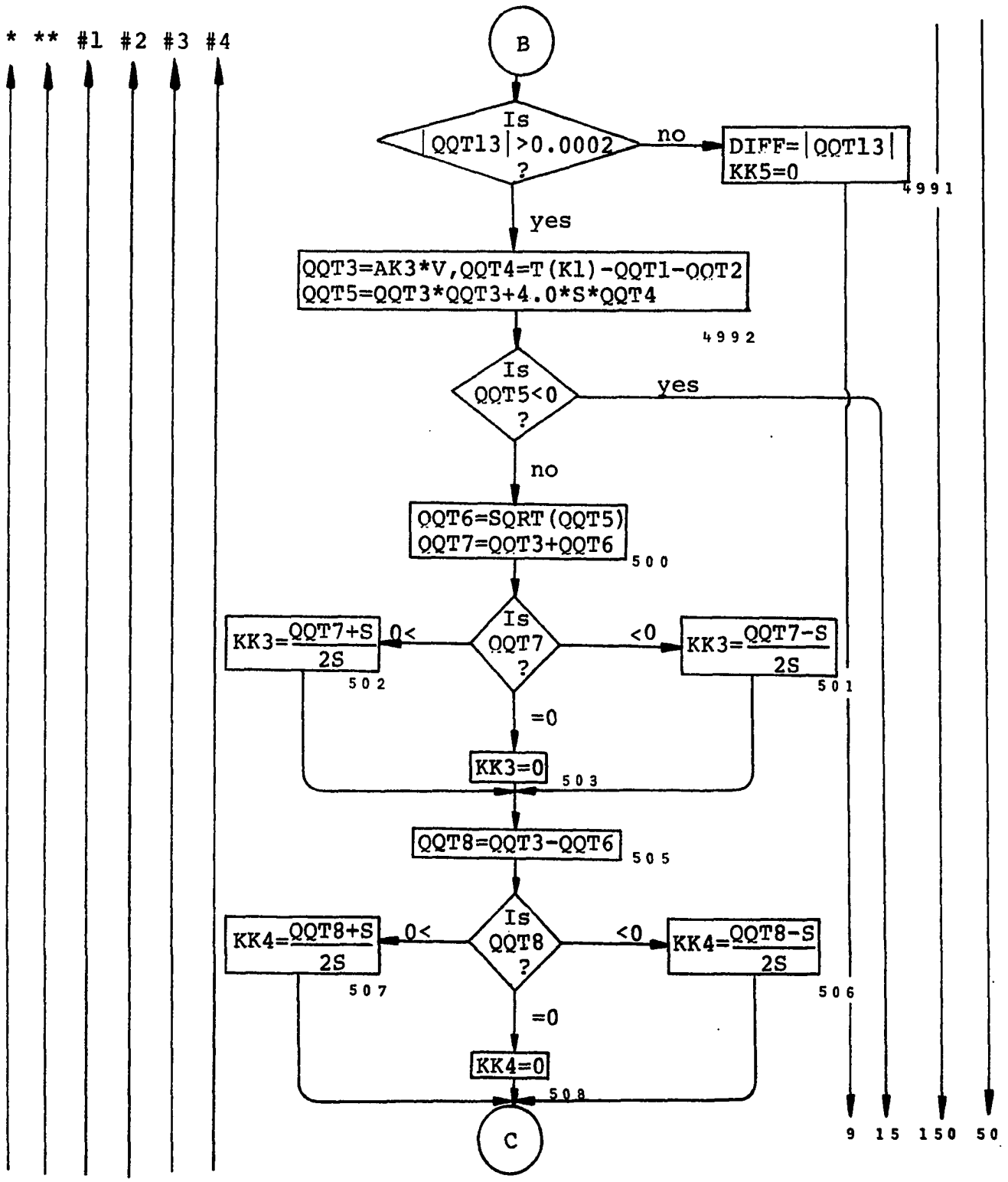
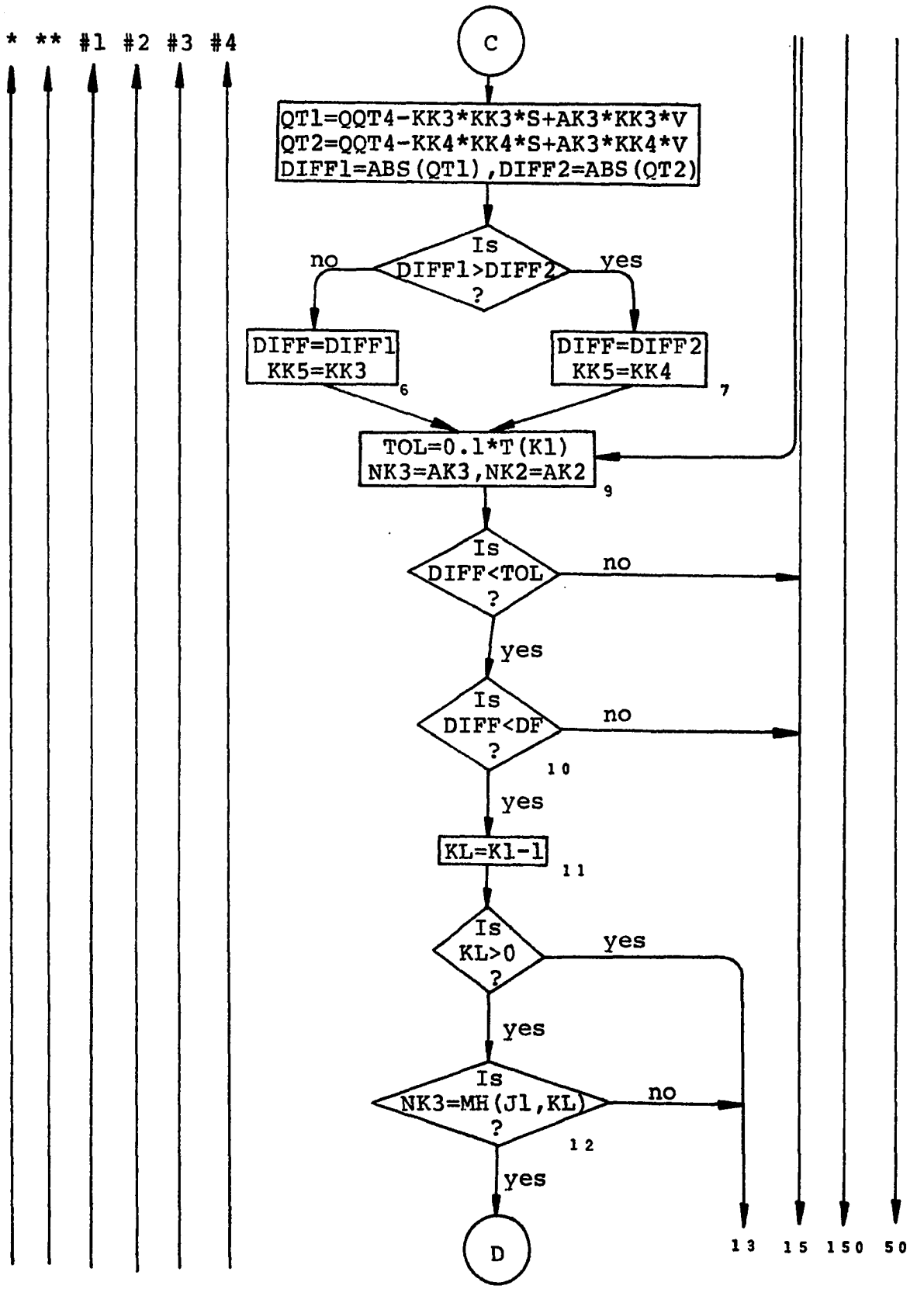
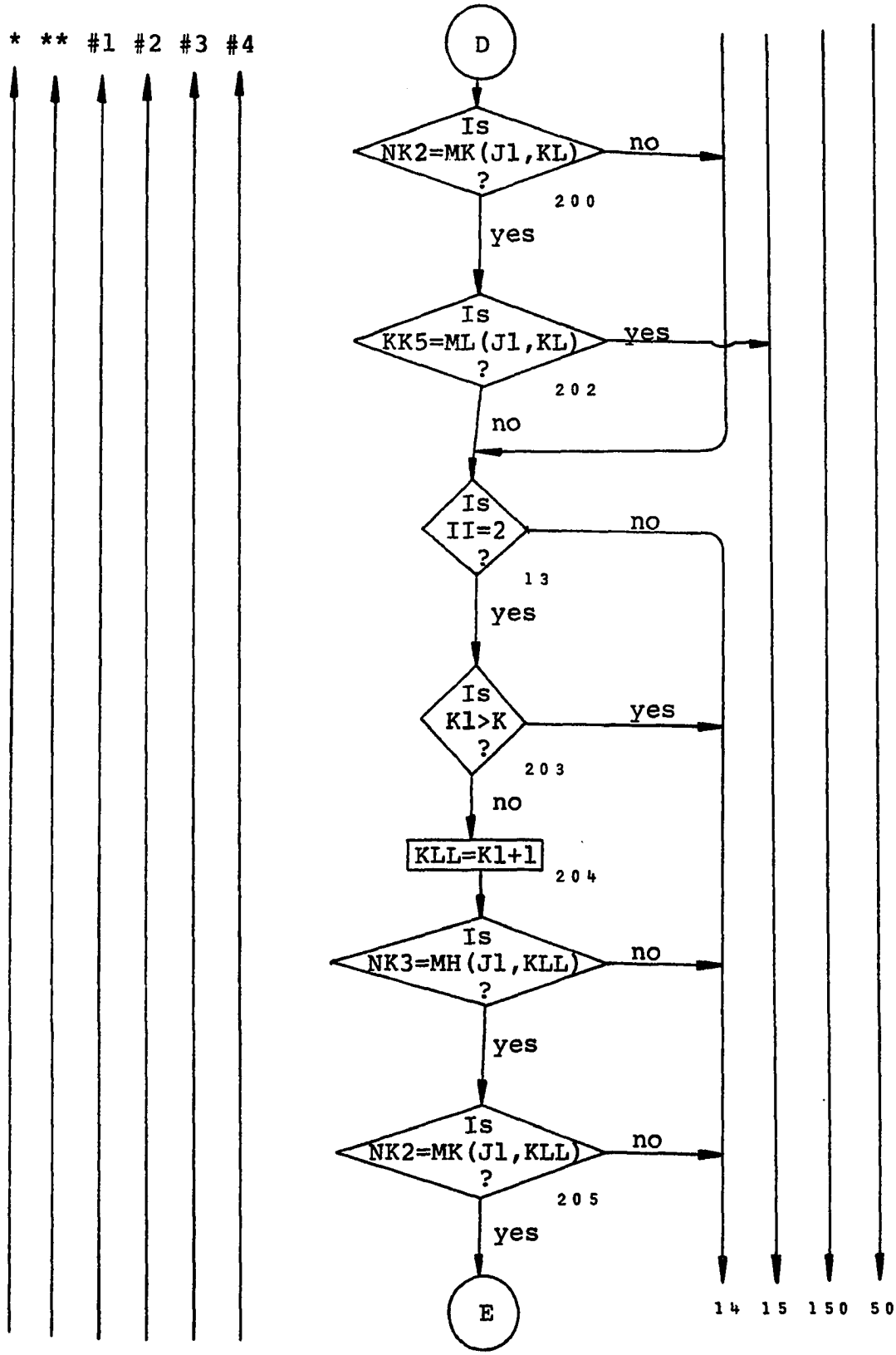


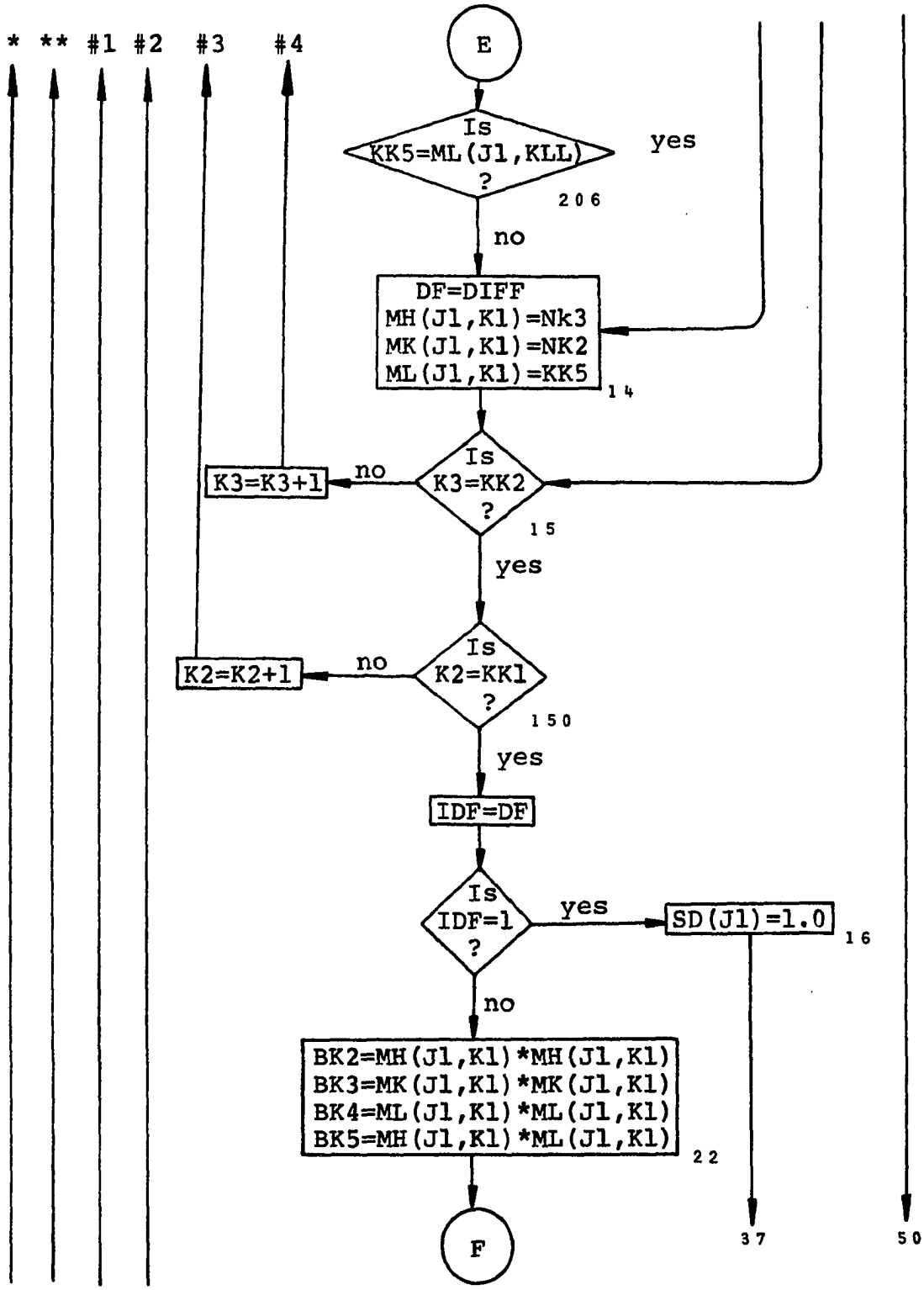
Figure E The Flow Chart of the Computer Program (MON) for the Indexing of Unknown Monoclinic Crystal Powder Patterns

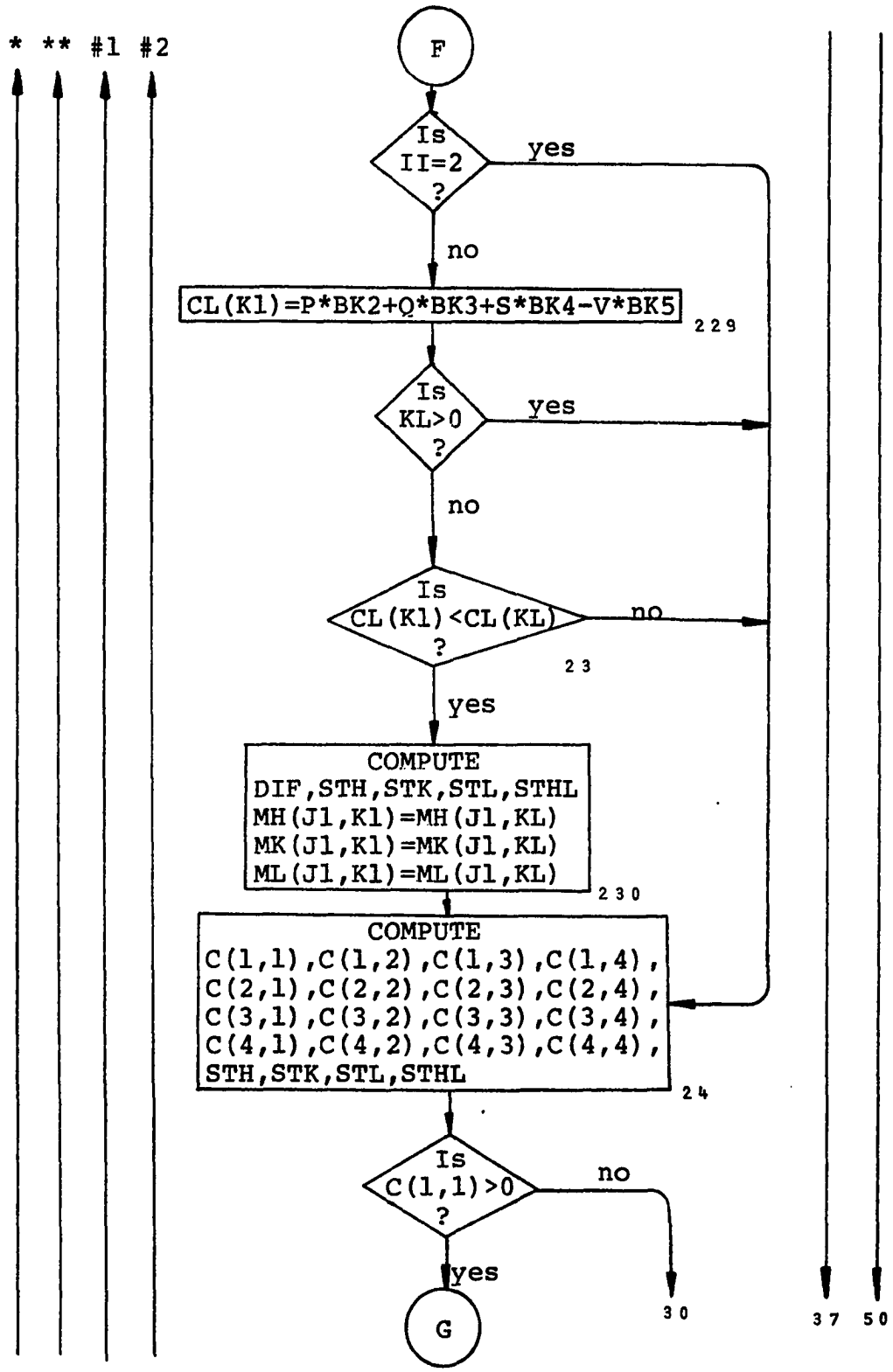

*
**
#1
#2
A
Is Q>0 ?
no
yes
KK1=SQRT((T(K1)+QT)/Q)+1.0
495
K2=1
#3
AK2=K2-1
QQT1=AK2*AK2*Q
QQT11=T(K1)-QQT1
Is |QQT11|>0.0002 ?
no
DIFF=|QQT11|
KK2=1
496
yes
QQT12=QQT11+PT
497
Is QQT12/P>0 ?
no
yes
KK2=SQRT(QQT12/P)+2.0
499
K3=1
4990
#4
AK3=K3-1
AKK3=AK3*AK3
QQT2=AKK3*P
QQT13=QQT11-QQT2
B
150
50

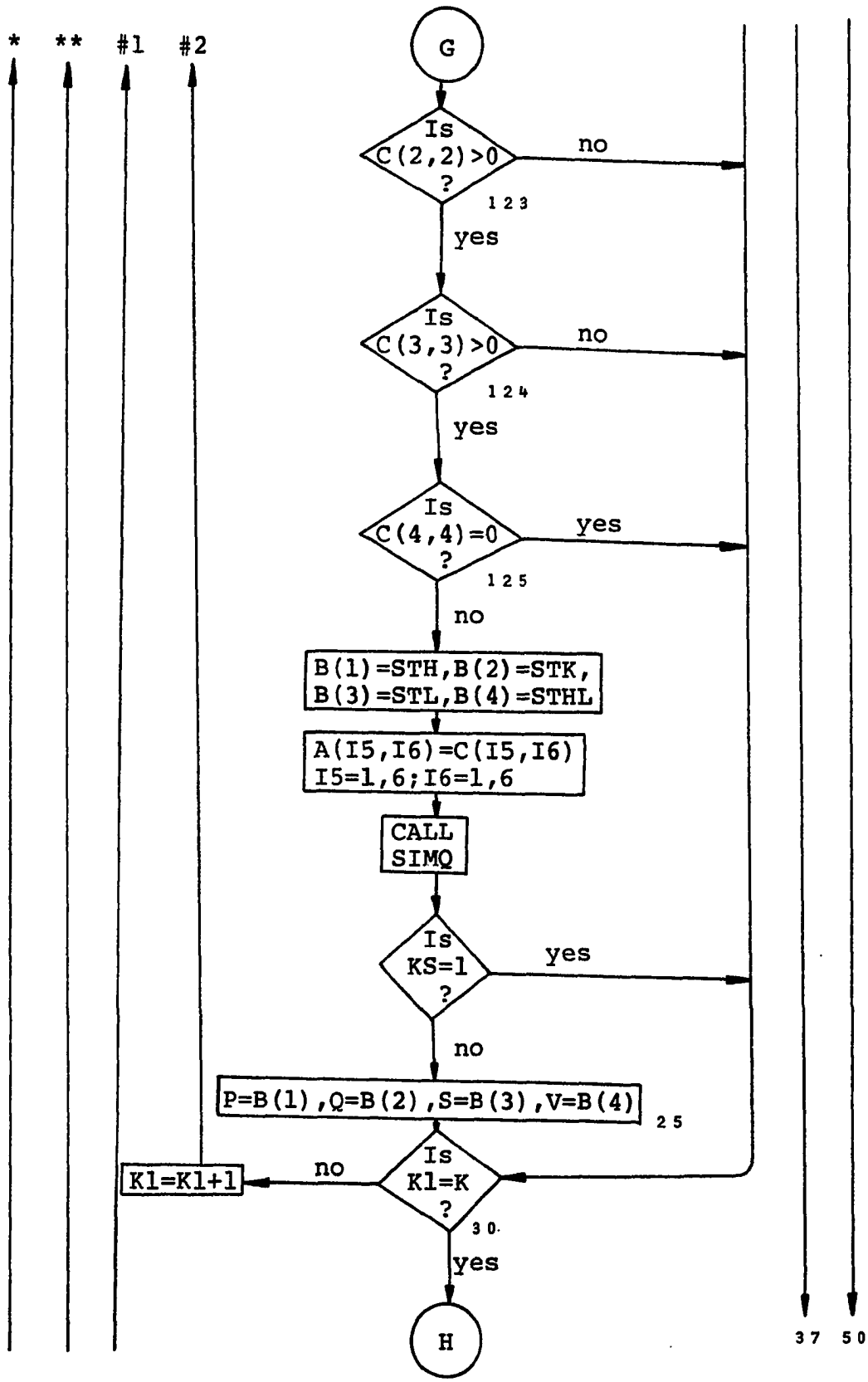

* ** #1 #2 #3 #4
B
Is |QQT13|>0.0002 ?
no
DIFF=|QQT13|
KK5=0
4991
yes
QQT3=AK3*V,QQT4=T(K1)-QQT1-QQT2
QQT5=QQT3*QQT3+4.0*S*QQT4
4992
Is QQT5<0 ?
yes
no
QQT6=SQRT(QQT5)
QQT7=QQT3+QQT6
500
Is QQT7 ?
0<
KK3=(QQT7+S)/2S
502
<0
KK3=(QQT7-S)/2S
501
=0
KK3=0
503
QQT8=QQT3-QQT6
505
Is QQT8 ?
0<
KK4=(QQT8+S)/2S
507
<0
KK4=(QQT8-S)/2S
506
=0
KK4=0
508
C
9
15
150
50

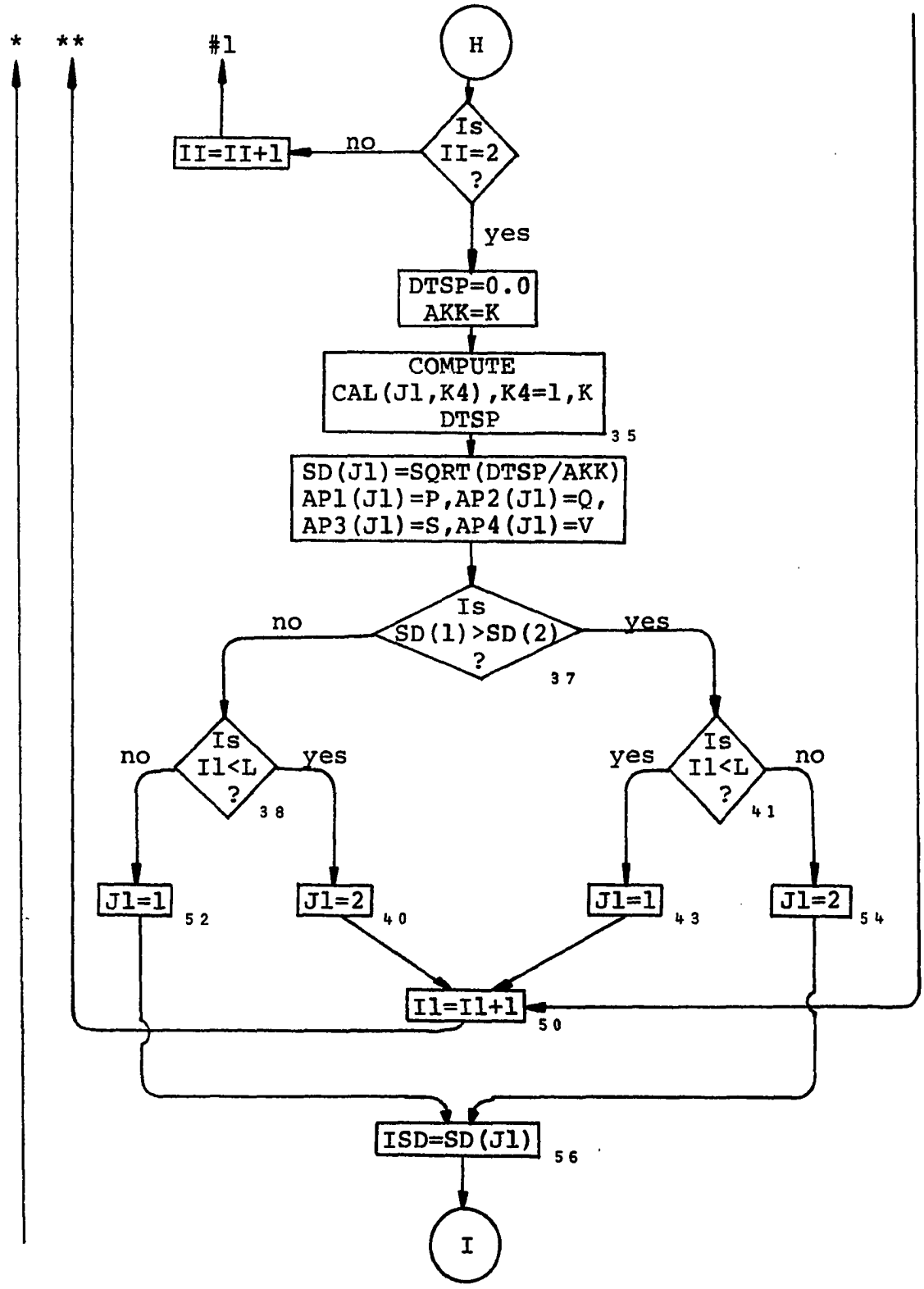

* ** #1 #2 #3 #4
C
QT1=QQT4-KK3*KK3*S+AK3*KK3*V
QT2=QQT4-KK4*KK4*S+AK3*KK4*V
DIFF1=ABS(QT1),DIFF2=ABS(QT2)
Is DIFF1>DIFF2 ?
no
yes
DIFF=DIFF1
KK5=KK3
6
DIFF=DIFF2
KK5=KK4
7
TOL=0.1*T(K1)
NK3=AK3,NK2=AK2
9
Is DIFF<TOL ?
no
yes
Is DIFF<DF ?
no
10
yes
KL=K1-1
11
Is KL>0 ?
yes
yes
Is NK3=MH(J1,KL) ?
no
12
yes
D
13
15
150
50

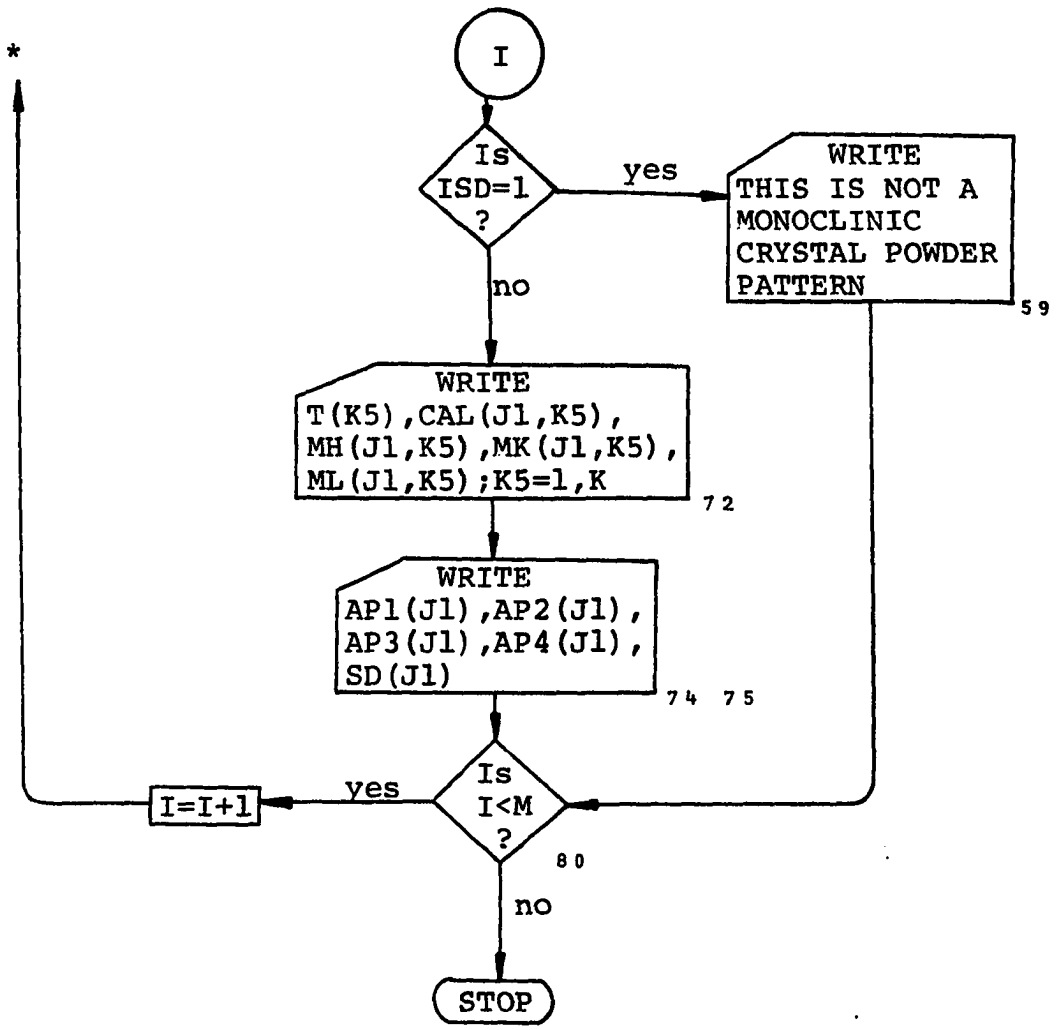

* ** #1 #2 #3 #4
D
Is NK2=MK(J1,KL) ?
no
200
yes
Is KK5=ML(J1,KL) ?
yes
202
no
Is II=2 ?
no
13
yes
Is K1>K ?
yes
203
no
KLL=K1+1
204
Is NK3=MH(J1,KLL) ?
no
yes
Is NK2=MK(J1,KLL) ?
no
205
yes
E
14 15 150 50


* ** #1 #2 #3 #4
E
Is KK5=ML(J1,KLL) ?
206
yes
no
DF=DIFF
MH(J1,K1)=Nk3
MK(J1,K1)=NK2
ML(J1,K1)=KK5
14
Is K3=KK2 ?
15
no
K3=K3+1
yes
Is K2=KK1 ?
150
no
K2=K2+1
yes
IDF=DF
Is IDF=1 ?
yes
SD(J1)=1.0
16
no
BK2=MH(J1,K1)*MH(J1,K1)
BK3=MK(J1,K1)*MK(J1,K1)
BK4=ML(J1,K1)*ML(J1,K1)
BK5=MH(J1,K1)*ML(J1,K1)
22
F
37
50


* ** #1 #2
F
Is II=2 ?
yes
no
CL(K1)=P*BK2+Q*BK3+S*BK4-V*BK5
229
Is KL>0 ?
yes
no
Is CL(K1)<CL(KL) ?
no
23
yes
COMPUTE
DIF,STH,STK,STL,STHL
MH(J1,K1)=MH(J1,KL)
MK(J1,K1)=MK(J1,KL)
ML(J1,K1)=ML(J1,KL)
230
COMPUTE
C(1,1),C(1,2),C(1,3),C(1,4),
C(2,1),C(2,2),C(2,3),C(2,4),
C(3,1),C(3,2),C(3,3),C(3,4),
C(4,1),C(4,2),C(4,3),C(4,4),
STH,STK,STL,STHL
24
Is C(1,1)>0 ?
no
yes
G
30
37
50


*
**
#1
#2
G
Is C(2,2)>0 ?
no
1 2 3
yes
Is C(3,3)>0 ?
no
1 2 4
yes
Is C(4,4)=0 ?
yes
1 2 5
no
B(1)=STH,B(2)=STK,
B(3)=STL,B(4)=STHL
A(I5,I6)=C(I5,I6)
I5=1,6;I6=1,6
CALL SIMQ
Is KS=1 ?
yes
no
P=B(1),Q=B(2),S=B(3),V=B(4)
2 5
Is K1=K ?
no
K1=K1+1
3 0
yes
H
3 7
5 0


*
**
#1
H
Is
II=2
?
no
II=II+1
yes
DTSP=0.0
AKK=K
COMPUTE
CAL(J1,K4),K4=1,K
DTSP
35
SD(J1)=SQRT(DTSP/AKK)
AP1(J1)=P,AP2(J1)=Q,
AP3(J1)=S,AP4(J1)=V
Is
SD(1)>SD(2)
?
37
no
yes
Is
I1<L
?
38
no
yes
Is
I1<L
?
41
yes
no
J1=1
52
J1=2
40
J1=1
43
J1=2
54
I1=I1+1
50
ISD=SD(J1)
56
I


*
I
Is ISD=1 ?
yes
WRITE THIS IS NOT A MONOCLINIC CRYSTAL POWDER PATTERN
59
no
WRITE T(K5),CAL(J1,K5), MH(J1,K5),MK(J1,K5), ML(J1,K5);K5=1,K
72
WRITE AP1(J1),AP2(J1), AP3(J1),AP4(J1), SD(J1)
74 75
Is I<M ?
80
yes
I=I+1
no
STOP

APPENDIX F

THE COMPUTER PROGRAM AND FLOW CHART FOR TRICLINIC SYSTEM

TABLE F

Computer Program (TRI) for the
Indexing of Unknown Triclinic Crystal Powder Patterns

```
C COMPUTER PROGRAM FOR THE INDEXING OF UNKNOWN TRICLINIC CRYSTAL POWDER
C PATTERNS
      DIMENSION T(70),A(6,6),C(6,6),B(6),P1(10),P2(10),P3(10),P4(10),P5(
     110),P6(10),AP1(2),AP2(2),AP3(2),AP4(2),AP5(2),AP6(2),CAL(2,70),SD(
     22),MH(2,70),MK(2,70),ML(2,70),D(6),BK(6),CL(70)
      IN=5
      IM=6
      READ (IN,1) M
    1 FORMAT (2I3)
      DO 80 I=1,M
      READ (IN,1) K,L
      READ (IN,2) (T(J),J=1,K)
    2 FORMAT (10F7.0)
      DO 3 J=1,L
    3 READ (IN,4) P1(J),P2(J),P3(J),P4(J),P5(J),P6(J)
    4 FORMAT (6F10.0)
      J1=1
      SD(1)=1.0
      SD(2)=1.0
      DO 50 I1=1,L
      P=P1(I1)
      Q=P2(I1)
      S=P3(I1)
      V=P4(I1)
      U=P5(I1)
      W=P6(I1)
      DO 5 I2=1,6
      DO 5 I3=1,6
      C(I2,I3)=0.0
    5 CONTINUE
      DO 500 I4=1,6
      D(I4)=0.0
  500 CONTINUE
      DO 31 II=1,2
      DO 30 K1=1,K
      ST=0.5*S
      QT=0.5*Q
      DF=1.0
      IF (S) 50,50,501
  501 KK1=SQRT((T(K1)+ST)/S)+1.0
      KK2=2.0*KK1-1.0
      DO 15 K2=1,KK2
      AK2=K2-1
      IF (K2-KK1-1) 5014,5012,5012
 5012 AK2=K2-2*KK1
 5014 AKK2=AK2*AK2
```

TABLE F (CONTINUED)

```
      QT1=AKK2*S
      QQT=T(K1)-QT1
      AQQT=ABS(QQT)
      IF (AQQT-0.0002) 502,503,503
  502 DIFF=AQQT
      KK3=1
      GO TO 504
  503 IF (Q) 50,50,5035
 5035 IF (QQT+QT) 50,5036,5036
 5036 KK3=SQRT((QQT+QT)/Q)+2.0
  504 DO 15 K3=1,KK3
      AK3=K3-1
      AKK3=AK3*AK3
      QT2=AKK3*Q
      QT3=AK2*AK3*W
      QQT1=QQT-QT2-QT3
      AQQT1=ABS(QQT1)
      IF (AQQT1-0.0002) 505,506,506
  505 DIFF=AQQT1
      KK7=0
      GO TO 9
  506 QQT2=AK2*V+AK3*U
      QQT3=QQT2*QQT2+4.0*P*QQT1
      IF (QQT3) 15,15,6
    6 QQT4=SQRT(QQT3)
      QQT5=QQT4-QQT2
      IF (QQT5) 601,603,602
  601 KK5=(QQT5-P)/(2.0*P)
      GO TO 604
  602 KK5=(QQT5+P)/(2.0*P)
      GO TO 604
  603 KK5=0
  604 QQT6=-QQT2-QQT4
      IF (QQT6) 605,607,606
  605 KK6=(QQT6-P)/(2.0*P)
      GO TO 608
  606 KK6=(QQT6+P)/(2.0*P)
      GO TO 608
  607 KK6=0
  608 VVT=AK2*V
      UUT=AK3*U
      QT4=QQT1-KK5*(KK5*P+VVT+UUT)
      QT5=QQT1-KK6*(KK6*P+VVT+UUT)
      DIFF1=ABS(QT4)
      DIFF2=ABS(QT5)
      IF (DIFF1-DIFF2) 7,7,8
    7 DIFF=DIFF1
```

TABLE F (CONTINUED)

```
      KK7=KK5
      GO TO 9
    8 DIFF=DIFF2
      KK7=KK6
    9 TOL=0.1*T(K1)
      IF (DIFF-TOL) 10,15,15
   10 IF (DIFF-DF) 11,15,15
   11 NK3=AK3
      NK2=AK2
      KL=K1-1
      IF (KL) 12,12,111
  111 IF (KK7-MH(J1,KL)) 12,112,12
  112 IF (NK3-MK(J1,KL)) 12,113,12
  113 IF (NK2-ML(J1,KL)) 12,15,12
   12 IF (II-2) 13,121,121
  121 KLL=K1+1
      IF (KLL-K) 122,122,13
  122 IF (KK7-MH(J1,KLL)) 13,123,13
  123 IF (NK3-MK(J1,KLL)) 13,124,13
  124 IF (NK2-ML(J1,KLL)) 13,125,13
  125 IF (CL(K1)-CL(KLL)) 13,15,15
   13 DF=DIFF
      MH(J1,K1)=KK7
      MK(J1,K1)=NK3
      ML(J1,K1)=NK2
   15 CONTINUE
      IDF=DF
      IF (IDF-1) 22,16,22
   16 SD(J1)=1.0
      GO TO 37
   22 BK(1)=MH(J1,K1)*MH(J1,K1)
      BK(2)=MK(J1,K1)*MK(J1,K1)
      BK(3)=ML(J1,K1)*ML(J1,K1)
      BK(4)=MH(J1,K1)*ML(J1,K1)
      BK(5)=MH(J1,K1)*MK(J1,K1)
      BK(6)=MK(J1,K1)*ML(J1,K1)
      IF (II-2) 211,219,219
  211 CL(K1)=P*BK(1)+Q*BK(2)+S*BK(3)+V*BK(4)+U*BK(5)+W*BK(6)
      IF (KL) 219,219,212
  212 IF (CL(K1)-CL(KL)) 213,219,219
  213 DIF=T(K1)-T(KL)
      D(1)=D(1)+(MH(J1,KL)*MH(J1,KL)-BK(1))*DIF
      D(2)=D(2)+(MK(J1,KL)*MK(J1,KL)-BK(2))*DIF
      D(3)=D(3)+(ML(J1,KL)*ML(J1,KL)-BK(3))*DIF
      D(4)=D(4)+(MH(J1,KL)*ML(J1,KL)-BK(4))*DIF
      D(5)=D(5)+(MH(J1,KL)*MK(J1,KL)-BK(5))*DIF
      D(6)=D(6)+(ML(J1,KL)*MK(J1,KL)-BK(6))*DIF
```

TABLE F (CONTINUED)

```
      MH(J1,K1)=MH(J1,KL)
      MK(J1,K1)=MK(J1,KL)
      ML(J1,K1)=ML(J1,KL)
  219 DO 220 I5=1,6
      C(1,I5)=C(1,I5)+BK(1)*BK(I5)
  220 CONTINUE
      C(2,1)=C(1,2)
      DO 221 I6=2,6
      C(2,I6)=C(2,I6)+BK(2)*BK(I6)
  221 CONTINUE
      C(3,1)=C(1,3)
      C(3,2)=C(2,3)
      DO 222 I7=3,6
      C(3,I7)=C(3,I7)+BK(3)*BK(I7)
  222 CONTINUE
      C(4,1)=C(1,4)
      C(4,2)=C(2,4)
      C(4,3)=C(3,4)
      C(4,4)=C(1,3)
      C(4,5)=C(1,6)
      C(4,6)=C(3,5)
      DO 223 I8=1,4
      C(5,I8)=C(I8,5)
  223 CONTINUE
      C(5,5)=C(1,2)
      C(5,6)=C(2,4)
      DO 224 I9=1,5
      C(6,I9)=C(I9,6)
  224 CONTINUE
      C(6,6)=C(3,2)
      DO 23 I10=1,6
      DO 23 I11=1,6
      A(I10,I11)=C(I10,I11)
   23 CONTINUE
      DO 24 I12=1,6
      D(I12)=D(I12)+T(K1)*BK(I12)
   24 CONTINUE
      IF (A(1,1)) 242,30,242
  242 IF (A(2,2)) 243,30,243
  243 IF (A(3,3)) 244,30,244
  244 IF (A(4,4)) 245,30,245
  245 IF (A(5,5)) 246,30,246
  246 IF (A(6,6)) 247,30,247
  247 DO 25 I13=1,6
      B(I13)=D(I13)
   25 CONTINUE
      CALL SIMQ(A,B,6,KS)
```

TABLE F (CONTINUED)

```
      IF (KS-1) 26,30,30
   26 P=B(1)
      Q=B(2)
      S=B(3)
      V=B(4)
      U=B(5)
      W=B(6)
   30 CONTINUE
   31 CONTINUE
      DTSP=0.0
      AKK=K
      DO 35 K4=1,K
      PT1=P*MH(J1,K4)*MH(J1,K4)
      PT2=Q*MK(J1,K4)*MK(J1,K4)
      PT3=S*ML(J1,K4)*ML(J1,K4)
      PT4=V*MH(J1,K4)*ML(J1,K4)
      PT5=U*MH(J1,K4)*MK(J1,K4)
      PT6=W*ML(J1,K4)*MK(J1,K4)
      CAL(J1,K4)=PT1+PT2+PT3+PT4+PT5+PT6
      DTSP=DTSP+(CAL(J1,K4)-T(K4))**2
   35 CONTINUE
      SD(J1)=SQRT(DTSP/AKK)
      AP1(J1)=P
      AP2(J1)=Q
      AP3(J1)=S
      AP4(J1)=V
      AP5(J1)=U
      AP6(J1)=W
   37 IF (SD(1)-SD(2)) 38,38,41
   38 IF (I1-L) 40,52,52
   40 J1=2
      GO TO 50
   41 IF (I1-L) 43,54,54
   43 J1=1
   50 CONTINUE
   52 J1=1
      GO TO 56
   54 J1=2
   56 ISD=SD(J1)
      IF (ISD-1) 60,58,60
   58 WRITE (IM,59) I
   59 FORMAT (1H1,' THE NUMBER',I3,'  SET IS NOT A TRICLINIC CRYSTAL POW
     1DER PATTERN')
      GO TO 80
   60 WRITE (IM,62)
   62 FORMAT (1H1,' SIN(SQUARE)',8X,'SIN(SQUARE)',12X,'H',5X,'K',5X,'L')
      WRITE (IM,64)
```

TABLE F (CONTINUED)

```
 64 FORMAT (2X,'(OBSERVED)',8X,'(CALCULATED)')
    WRITE (IM,66)
 66 FORMAT (2X,11('-'),7X,12('-'),11X,3('-'),3X,3('-'),3X,3('-'))
    DO 70 K5=1,K
 70 WRITE (IM,72) T(K5),CAL(J1,K5),MH(J1,K5),MK(J1,K5),ML(J1,K5)
 72 FORMAT (3X,F8.5,11X,F8.5,12X,I3,3X,I3,3X,I3)
    WRITE (IM,74) AP1(J1),AP2(J1),AP3(J1)
 74 FORMAT (' P=',F8.5,13X,'Q=',F8.5,13X,'S=',F8.5)
    WRITE (IM,741) AP4(J1),AP5(J1),AP6(J1)
741 FORMAT (' V=',F8.5,13X,'U=',F8.5,13X,'W=',F8.5)
    WRITE (IM,75) SD(J1)
 75 FORMAT (' STANDARD DEVIATION=',F8.6)
    WRITE (IM,76)
 76 FORMAT (' THIS IS A TRICLINIC CRYSTAL POWDER PATTERN')
 80 CONTINUE
    STOP
    END
```

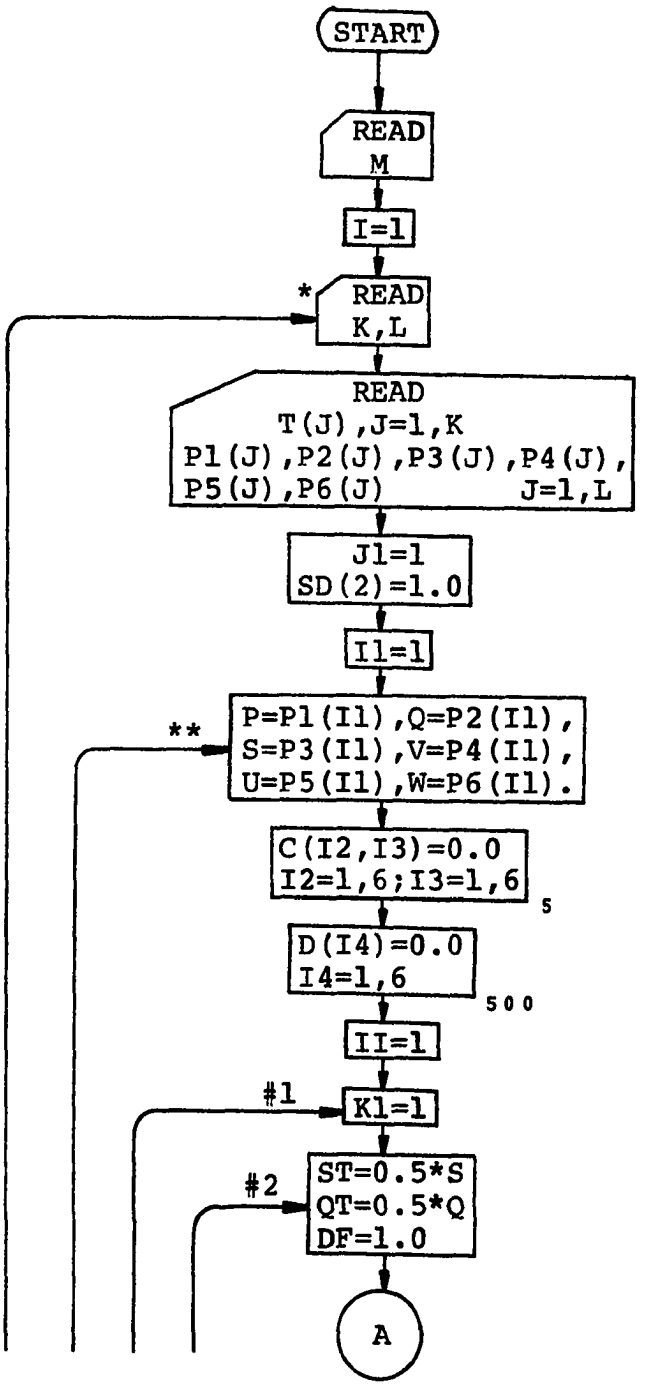
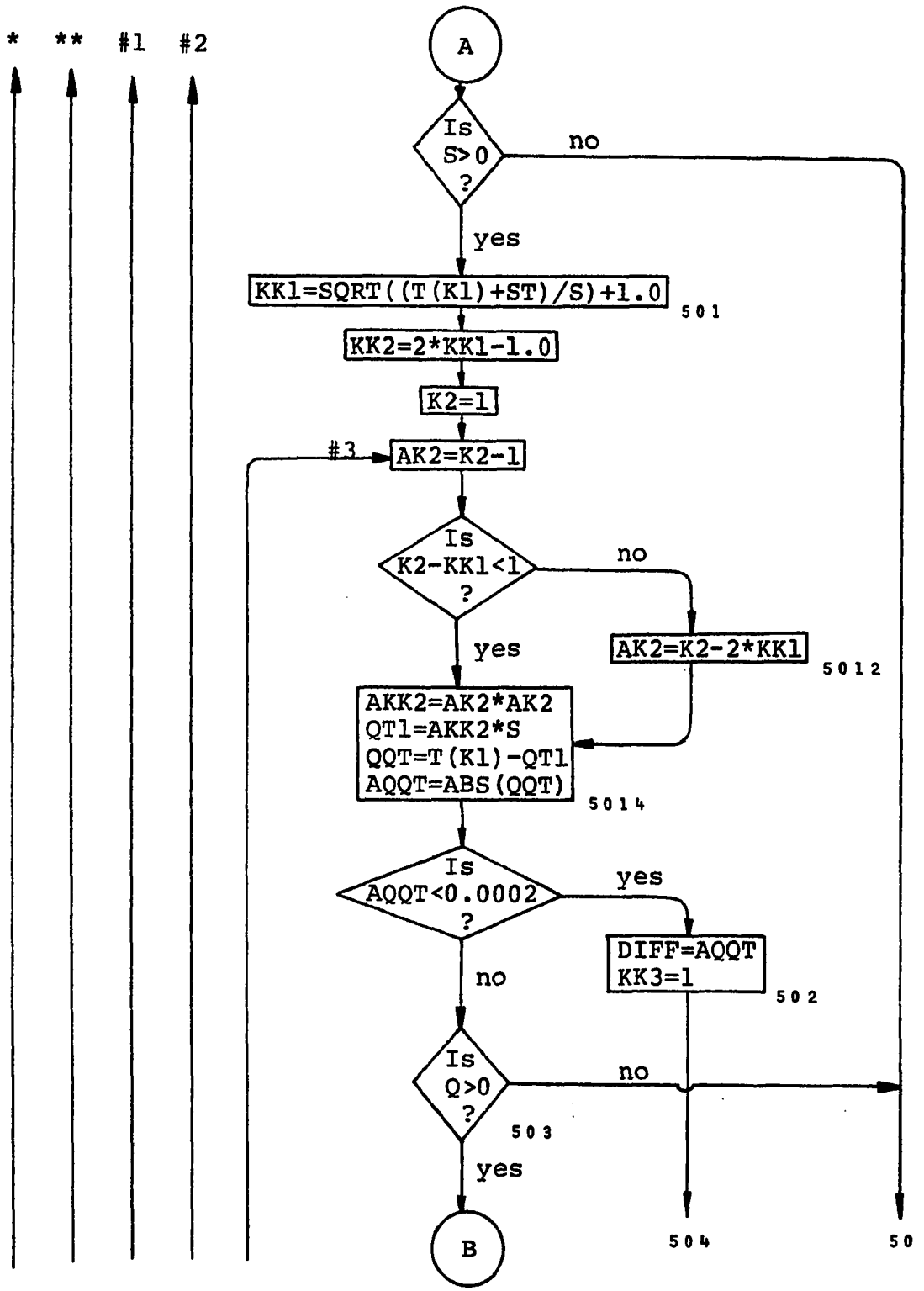
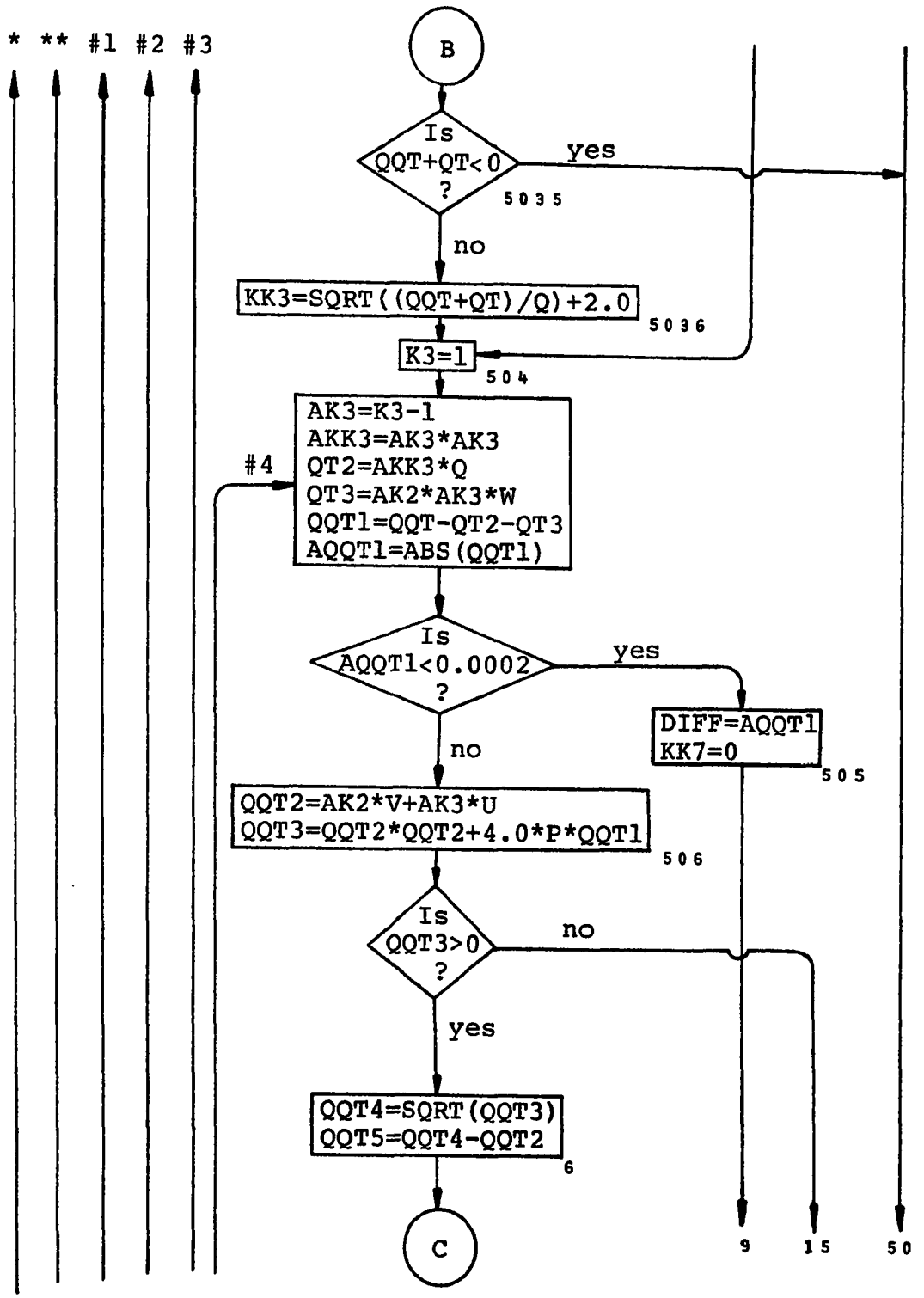
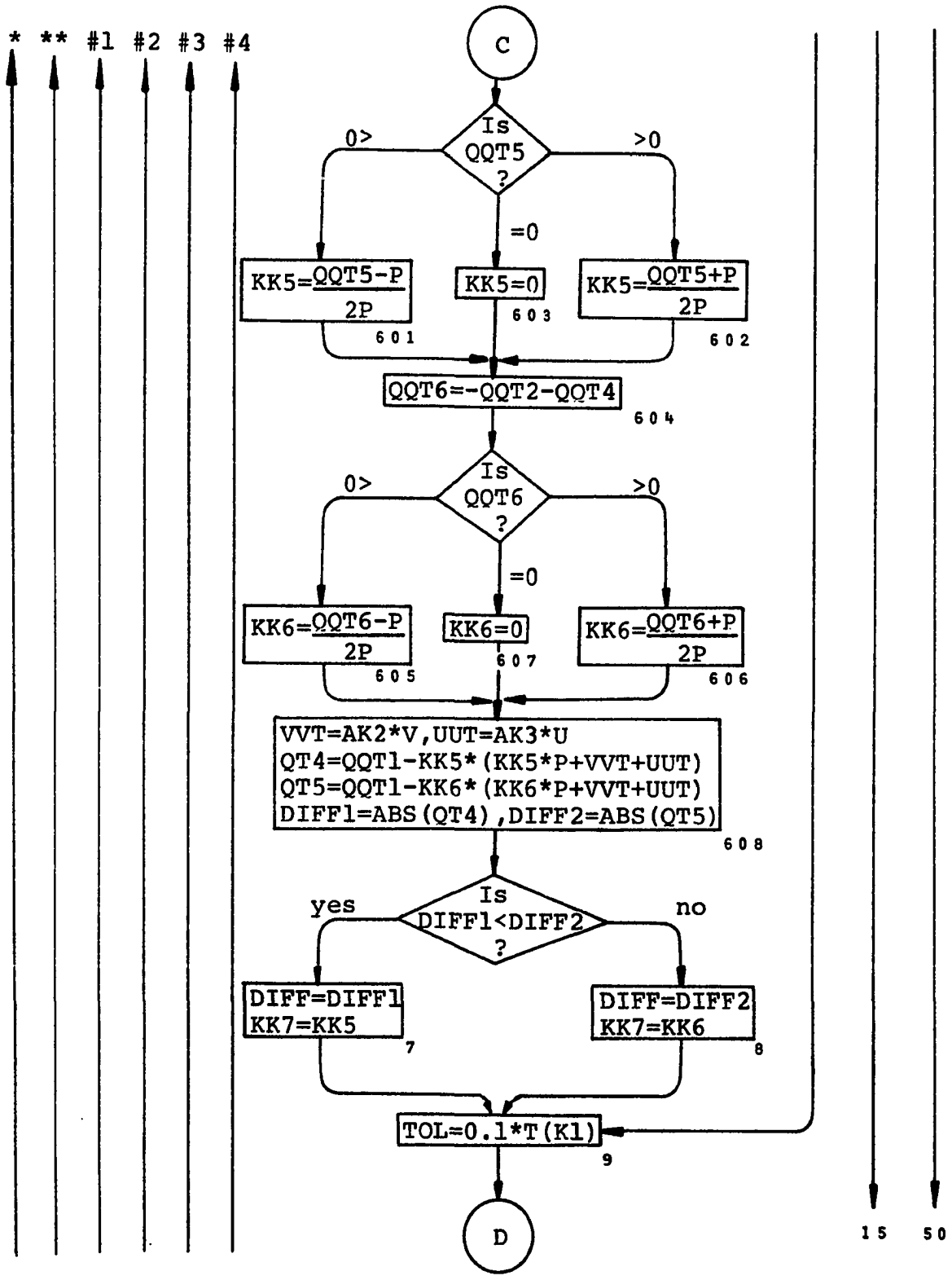
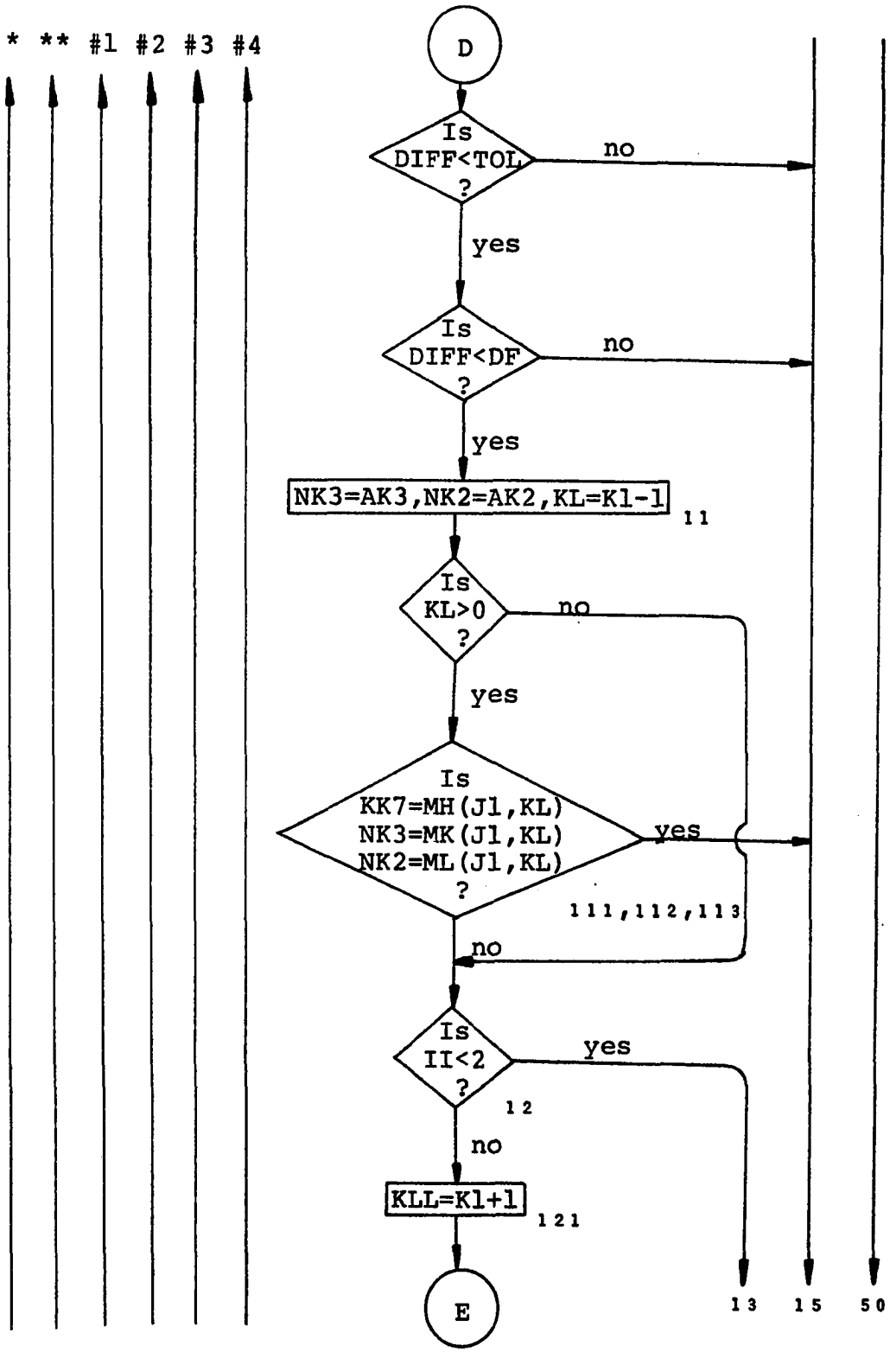


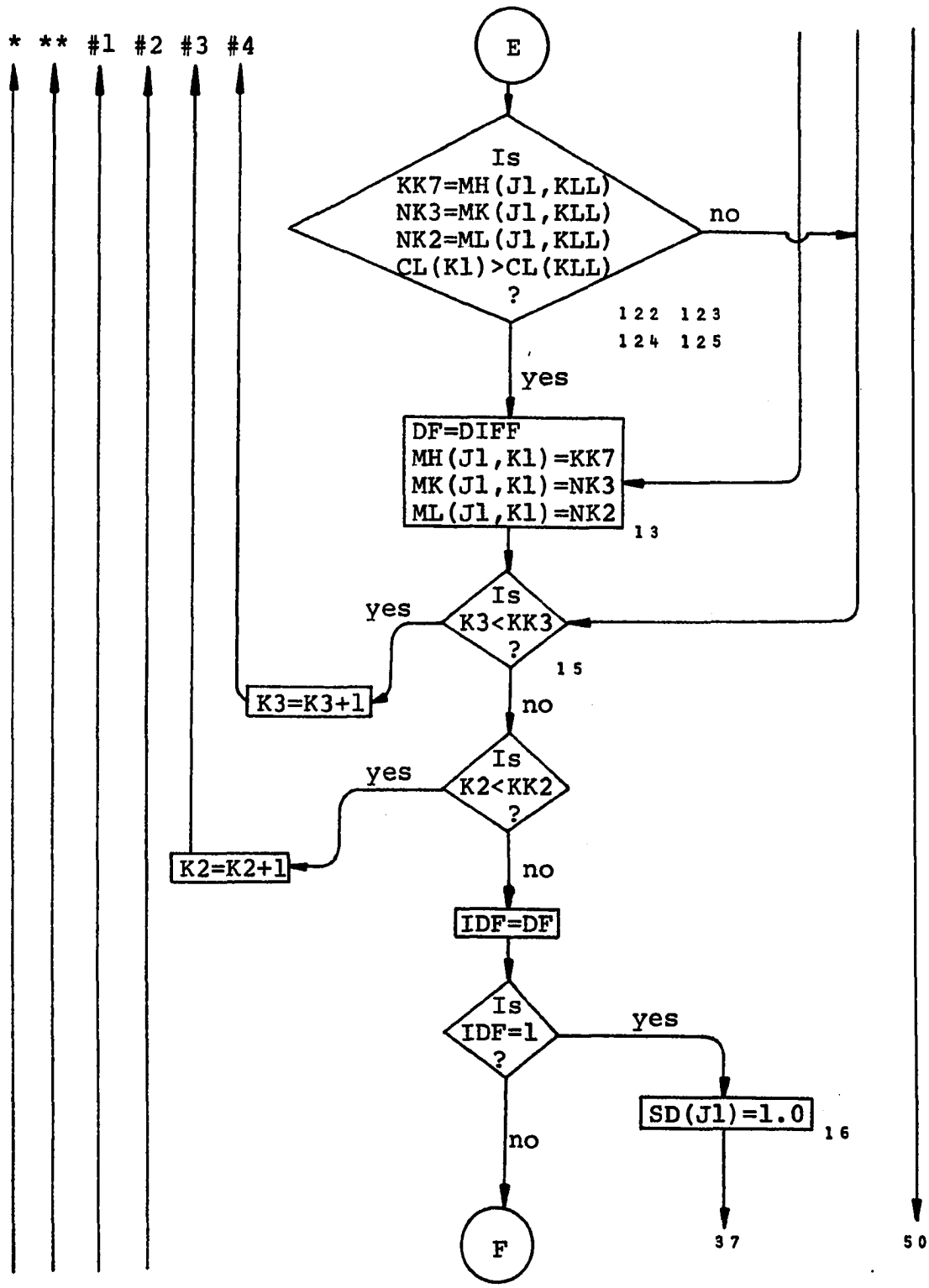
Figure F The Flow Chart of the Computer Program (TRI) for the Indexing of Unknown Triclinic Crystal Powder Patterns

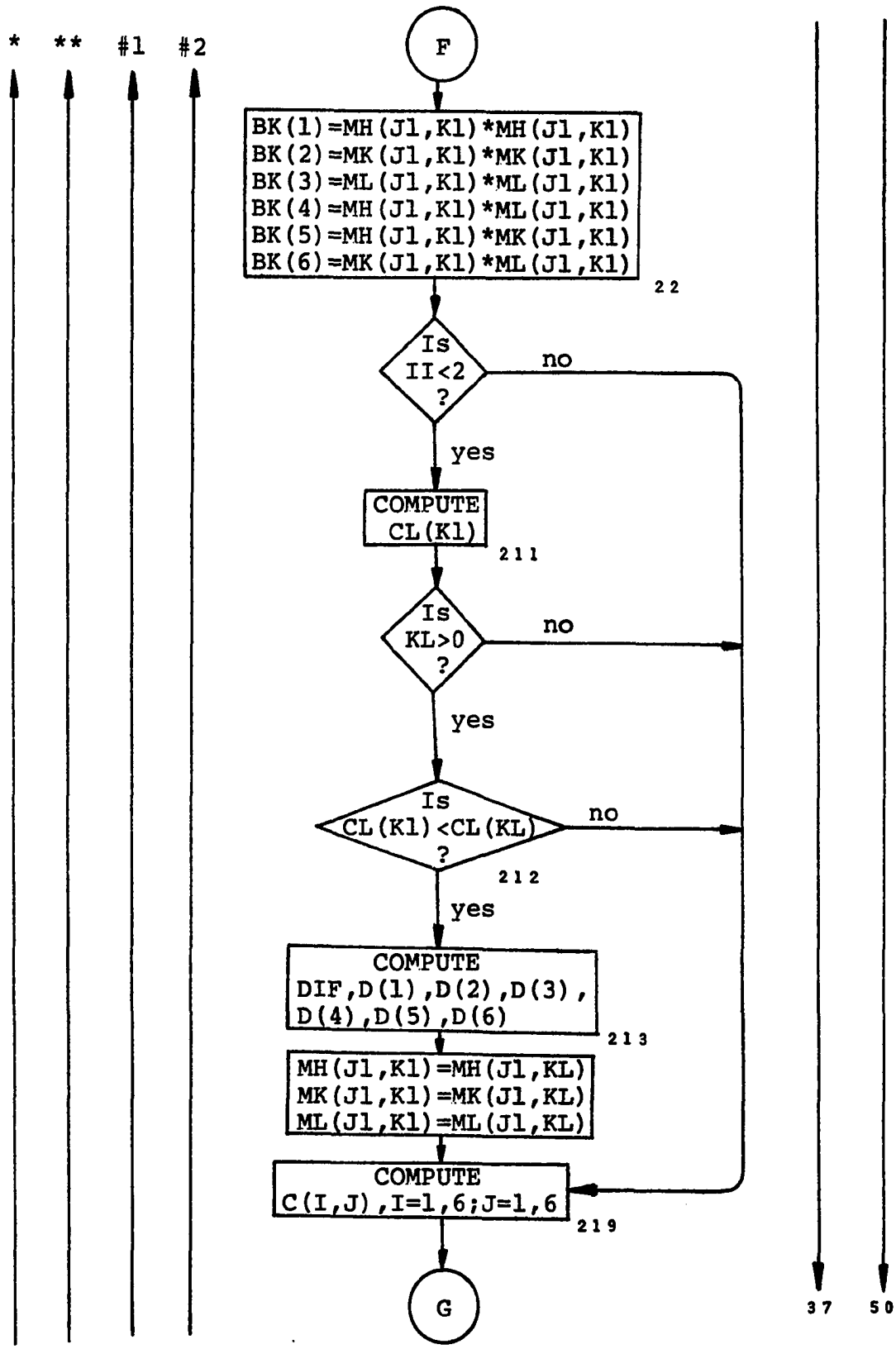

*
**
#1
#2
A
Is S>0 ?
no
yes
KK1=SQRT((T(K1)+ST)/S)+1.0
501
KK2=2*KK1-1.0
K2=1
#3
AK2=K2-1
Is K2-KK1<1 ?
no
yes
AK2=K2-2*KK1
5012
AKK2=AK2*AK2
QT1=AKK2*S
QQT=T(K1)-QT1
AQQT=ABS(QQT)
5014
Is AQQT<0.0002 ?
yes
DIFF=AQQT
KK3=1
502
no
Is Q>0 ?
503
no
yes
B
504
50

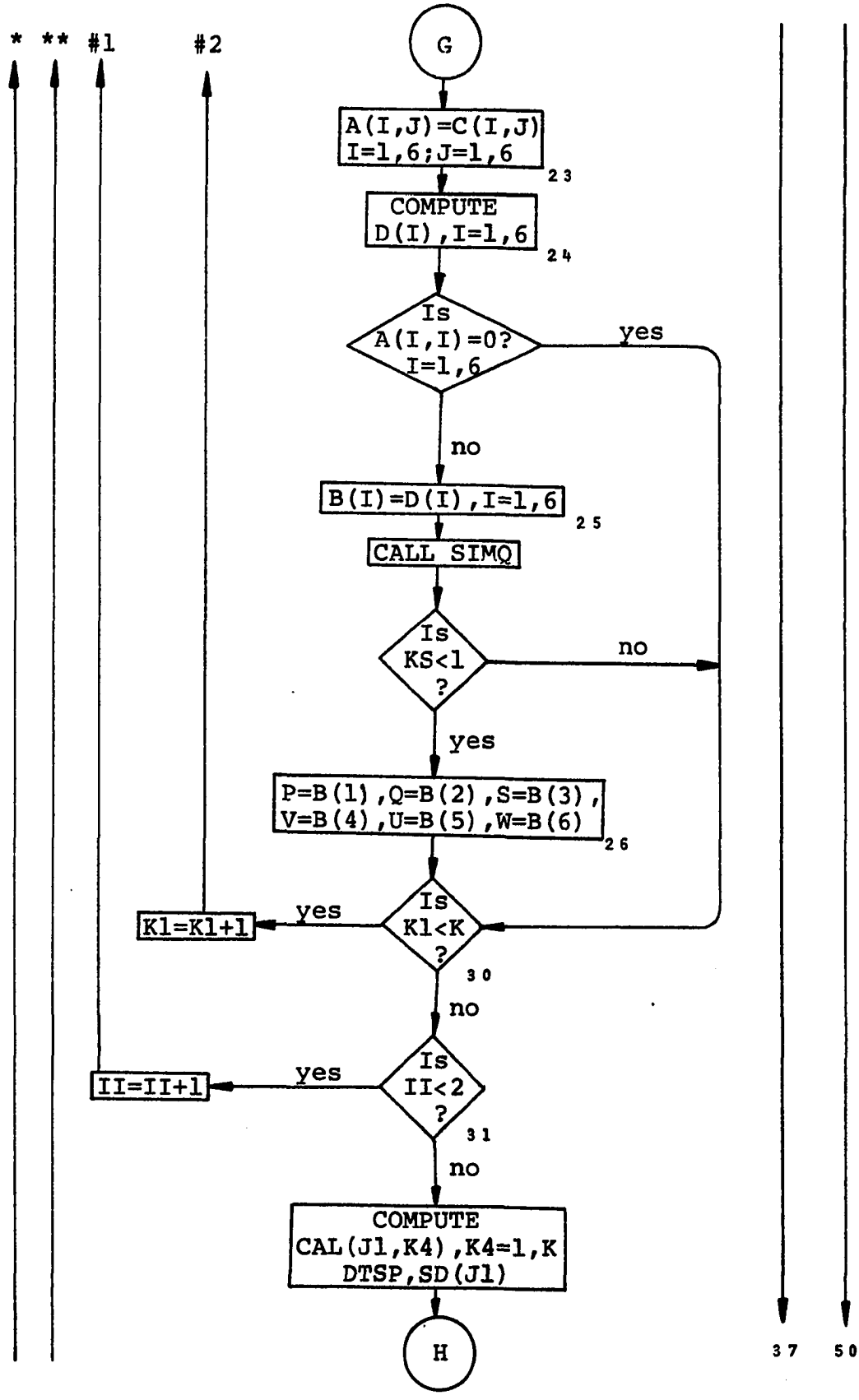

* ** #1 #2 #3
B
Is QQT+QT<0 ?
yes
5035
no
KK3=SQRT((QQT+QT)/Q)+2.0
5036
K3=1
504
#4
AK3=K3-1
AKK3=AK3*AK3
QT2=AKK3*Q
QT3=AK2*AK3*W
QQT1=QQT-QT2-QT3
AQQT1=ABS(QQT1)
Is AQQT1<0.0002 ?
yes
DIFF=AQQT1
KK7=0
505
no
QQT2=AK2*V+AK3*U
QQT3=QQT2*QQT2+4.0*P*QQT1
506
Is QQT3>0 ?
no
yes
QQT4=SQRT(QQT3)
QQT5=QQT4-QQT2
6
C
9
15
50

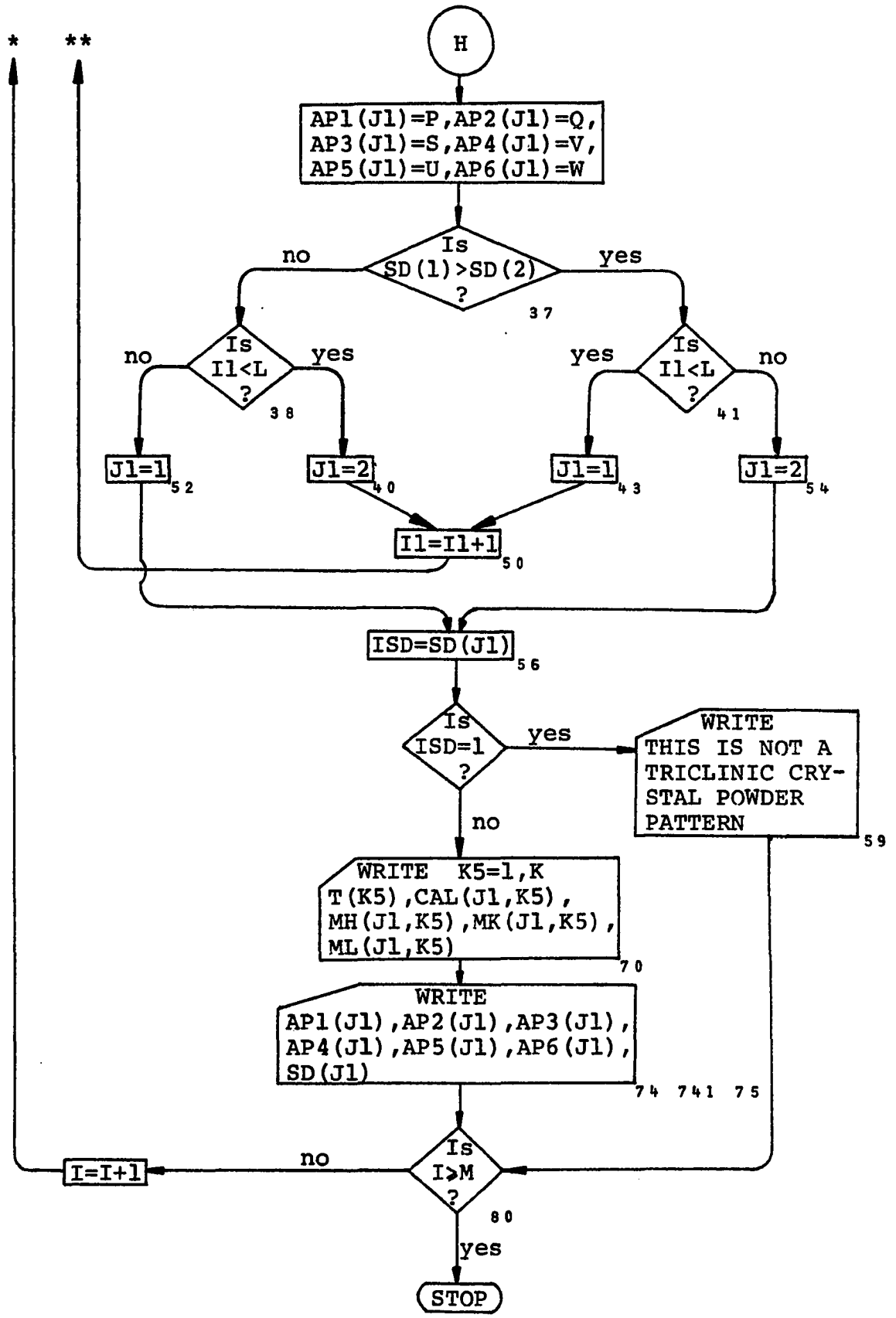

* ** #1 #2 #3 #4
C
Is QQT5 ?
0>
=0
>0
KK5=QQT5-P/2P
601
KK5=0
603
KK5=QQT5+P/2P
602
QQT6=-QQT2-QQT4
604
Is QQT6 ?
0>
=0
>0
KK6=QQT6-P/2P
605
KK6=0
607
KK6=QQT6+P/2P
606
VVT=AK2*V,UUT=AK3*U
QT4=QQT1-KK5*(KK5*P+VVT+UUT)
QT5=QQT1-KK6*(KK6*P+VVT+UUT)
DIFF1=ABS(QT4),DIFF2=ABS(QT5)
608
Is DIFF1<DIFF2 ?
yes
no
DIFF=DIFF1
KK7=KK5
7
DIFF=DIFF2
KK7=KK6
8
TOL=0.1*T(K1)
9
D
15
50


* ** #1 #2 #3 #4
D
Is DIFF<TOL ?
no
yes
Is DIFF<DF ?
no
yes
NK3=AK3,NK2=AK2,KL=K1-1
11
Is KL>0 ?
no
yes
Is KK7=MH(J1,KL) NK3=MK(J1,KL) NK2=ML(J1,KL) ?
yes
111,112,113
no
Is II<2 ?
yes
12
no
KLL=K1+1
121
E
13
15
50


* ** #1 #2 #3 #4
E
Is
KK7=MH(J1,KLL)
NK3=MK(J1,KLL)
NK2=ML(J1,KLL)
CL(K1)>CL(KLL)
?
no
122 123
124 125
yes
DF=DIFF
MH(J1,K1)=KK7
MK(J1,K1)=NK3
ML(J1,K1)=NK2
13
Is
K3<KK3
?
15
yes
K3=K3+1
no
Is
K2<KK2
?
yes
K2=K2+1
no
IDF=DF
Is
IDF=1
?
yes
SD(J1)=1.0
16
no
F
37
50


*
**
#1
#2
F
BK(1)=MH(J1,K1)*MH(J1,K1)
BK(2)=MK(J1,K1)*MK(J1,K1)
BK(3)=ML(J1,K1)*ML(J1,K1)
BK(4)=MH(J1,K1)*ML(J1,K1)
BK(5)=MH(J1,K1)*MK(J1,K1)
BK(6)=MK(J1,K1)*ML(J1,K1)
22
Is II<2 ?
no
yes
COMPUTE CL(K1)
211
Is KL>0 ?
no
yes
Is CL(K1)<CL(KL) ?
no
212
yes
COMPUTE DIF,D(1),D(2),D(3), D(4),D(5),D(6)
213
MH(J1,K1)=MH(J1,KL)
MK(J1,K1)=MK(J1,KL)
ML(J1,K1)=ML(J1,KL)
COMPUTE C(I,J),I=1,6;J=1,6
219
G
37
50


*
**
#1
#2
G
A(I,J)=C(I,J)
I=1,6;J=1,6
23
COMPUTE
D(I),I=1,6
24
Is
A(I,I)=0?
I=1,6
yes
no
B(I)=D(I),I=1,6
25
CALL SIMQ
Is
KS<1
?
no
yes
P=B(1),Q=B(2),S=B(3),
V=B(4),U=B(5),W=B(6)
26
Is
K1<K
?
30
yes
K1=K1+1
no
Is
II<2
?
31
yes
II=II+1
no
COMPUTE
CAL(J1,K4),K4=1,K
DTSP,SD(J1)
H
37
50


*
**
H
AP1(J1)=P,AP2(J1)=Q,
AP3(J1)=S,AP4(J1)=V,
AP5(J1)=U,AP6(J1)=W
Is SD(1)>SD(2) ?
37
no
yes
Is I1<L ?
38
Is I1<L ?
41
J1=1
52
J1=2
40
J1=1
43
J1=2
54
I1=I1+1
50
ISD=SD(J1)
56
Is ISD=1 ?
WRITE THIS IS NOT A TRICLINIC CRYSTAL POWDER PATTERN
59
WRITE K5=1,K
T(K5),CAL(J1,K5),
MH(J1,K5),MK(J1,K5),
ML(J1,K5)
70
WRITE
AP1(J1),AP2(J1),AP3(J1),
AP4(J1),AP5(J1),AP6(J1),
SD(J1)
74 741 75
Is I>M ?
80
I=I+1
STOP