AD-A270 610

NAWCWPNS TP 8128

Refinement Of Unit Cell Parameters By Least-Squares: Comments On An Old Technique And The Development Of A New Computer Program

By
C. K. Lowe-Ma
Research Department

SEPTEMBER 1993

DTIC
ELECTE
OCT 12 1993
S B D

NAVAL AIR WARFARE CENTER WEAPONS DVISION
China Lake, California 93555-6001

Approved for public release; distribution is unlimited.

93-24120

Naval Air Warfare Center Weapons Division

FOREWORD

Unit cell parameters obtained from the indexing of powder diffraction data and subsequent minimization fit are widely used in the characterization of optically and electronically important materials. The sensitivity of these parameters to average microscopic/atomic-level variations cause these parameters to be valuable indicators of (intentional or unintentional) doping, average bulk composition as well as of changes in composition, and thermal expansion. For those samples in which an internal standard cannot be incorporated, more precise (and accurate) cell parameters will be obtained from the minimization fit if geometric (optical) aberrations and systematic errors are either eliminated from the diffraction data initially or are explicitly included in the fit. The methodology and program described herein represent the first least-squares (minimization) fit that: (1) explicitly allows refinement of several geometric (optical) aberrations and systematic errors potentially present in Bragg-Bretano powder diffraction data; (2) includes the errors in a general way for all lattice symmetries; and (3) uses singular value decomposition (rather than matrix inversion of the normal equations) to obtain the changes to the parameters at each step of the nonlinear least-squares minimization.

This work was partially supported by the Office of Naval Research and by Independent Research funds from the Naval Air Warfare Center Weapons Division, although a substantial amount of the development was also accomplished on the author's own time. This report was reviewed for technical accuracy by William O. Alltop and Terrell A. Vanderah.

Approved by
R. L. DERR, *Head*
Research Department
22 September 1993

Under authority of
W. E. NEWMAN
RAdm., U.S. Navy
Commander

Released for publication by
S. HAALAND
Deputy Commander for Research and Development

NAWCWPNS Technical Publication 8128

Published by ..... Technical Information Department
Collation ..... Cover, 16 leaves
First printing ..... 50 copies

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	September 1993	Final May 92-April 93

4. TITLE AND SUBTITLE
Refinement of Unit Cell Parameters by Least-Squares: Comments on an Old Technique and the Development of a New Computer Program

5. FUNDING NUMBERS
Cust order 1385052, 1385462, 1130503; Task R2202, R1309, ROONO; Element 61153N & 61152N

6. AUTHORS
C. K. Lowe-Ma

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Naval Air Warfare Center Weapons Division
China Lake, CA 93555-6001

8. PERFORMING ORGANIZATION REPORT NUMBER
NAWCWPNS TP 8128

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION /AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

(U) The determination of unit cell parameters from (X-ray) diffraction data is integral to studies of new crystalline materials. The sensitivity of unit cell parameters to microscopic compositional variations leads to their wide use in the characterization of materials with potentially useful optical and/or electronic properties. Consequently, precise (and accurate) cell parameters are needed even for samples in which incorporation of an internal standard is not possible. To eliminate the requirement of an internal standard, a computer program has been developed that explicitly includes refinement of possible systematic errors and geometric aberrations along with the refinement of the unit cell parameters.

14. SUBJECT TERMS
Systematic errors; Unit cell parameter refinement by least-squares; X-Ray powder diffraction

15. NUMBER OF PAGES
30

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	**UNCLASSIFIED**	**UNCLASSIFIED**	**UL**

CONTENTS

ACKNOWLEDGMENT

Thanks are due to Stephen B. Robie for obtaining the high-temperature powder diffraction data and to Scintag, Inc., Sunnyvale, Calif., for the use of their high-temperature diffraction equipment.

Preliminary results of this work were presented at the Fourth International School and Workshop of Crystallography-Computational Methods in X-Ray Powder Diffraction Analysis, held in Aswan, Egypt, 16-25 January 1993.

QUALITY INSPECTED 3

Accession For
NTIS GRA&I ☑
DTIC TAB ☐
Unannounced ☐
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A-1

INTRODUCTION

The sensitivity of unit cell parameters to composition and temperature cause their precise determination to be an important aspect in the characterization of materials. For example, the value of the c-axis unit cell parameter in $YBa_2Cu_3O_x$ and related materials has been used as an indication of oxygen content (Reference 1). Also, analysis of the variation of unit cell parameters with temperature is one of the methods used to determine the thermal expansion of technologically important materials. The validity of the cell parameters obtained from X-ray diffraction data have been the subject of many studies (see, for example, Reference 2). However, the accurate/precise determination of unit cell parameters continues to be a topic of discussion and study (References 3 through 7).

The most precise lattice parameters will be those obtained by a fit to all of the observed angular data (and from which systematic aberrations and systematic errors have been eliminated). Before easy access to computers, graphical extrapolation methods were used to eliminate systematic aberrations and errors before fitting the observed data. With the advent of (early) computers, more calculationally intensive methods of error correction and fitting became possible with a number of authors suggesting analytical functions for systematic errors (References 8 through 11). However, these functions were mostly designed for the expected aberrations and errors found in film data obtained with camera methods. With the development of modern powder diffractometers came the development of angular (d-spacing) standards. For samples with which a known standard can be mixed, accurate line positions are obtained (at room temperature) by correcting the positions of the sample lines with a "correction curve" determined from the standard (Reference 12). With the current availability of internal standards and the ease of correction of diffractometer data using "external calibration curves," less impetus has existed to calculationally correct for errors with analytical functions appropriate for diffractometers.

In the course of diffraction studies to obtain the oxygen content of high-temperature (T_c) superconducting single crystals as well as to obtain high-temperature thermal expansion data on novel sulfides and ceramic materials, precise and, if possible, accurate unit cell parameters over (possibly) a range of temperatures were needed. In some cases, an internal standard could not be (easily) incorporated in the samples. In addition, an internal standard for high-temperature diffraction studies is not available. To obviate the need for an internal standard and still to obtain precise (and reasonably accurate) unit cell parameters, the capability to explicitly refine systematic errors and geometric aberrations simultaneously with refinement of unit cell parameters has been incorporated into a least-squares unit-cell refinement (computer) program.

MATHEMATICAL FRAMEWORK

In principle, the number of observations (angular measurements) usually exceeds the number of aberration and unit cell parameters that would need to be fit by a minimization procedure. This suggests that parameters for aberrations affecting the observed 2θ values could be explicitly included in the fit, although large correlations might occur.

For each hkL (i^{th}) reflection, the observed angular 2θ position is related to the reciprocal lattice parameters by Equation 1.

$$\sin^2(\theta_i) = (\lambda^2/4)\{Q\} \tag{1}$$

where $\{Q\} = \{h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hka^*b^*\cos\gamma^* + 2hla^*c^*\cos\beta^* + 2klb^*c^*\cos\alpha^*\}$.

However, the effect of geometric aberrations on the observed line positions are usually expressed as $[(2\theta)_{obs} = (2\theta)_{true} + \langle\delta(2\theta_i)\rangle]$ (References 2 and 13), where $\langle\delta(2\theta)\rangle$ represents the shift in peak centroid position caused by aberrations or systematic errors. Therefore,

$$\sin[(\theta_i)_{obs}] = \sin[(\theta_i)_{true} + \langle\delta(2\theta_i)\rangle/2] \tag{2}$$

where $(\theta_i)_{true} = \sin^{-1}[(\lambda/2)(\sqrt{Q})]$.

Expanding Equation 2 as a sum of angles results in Equation 3.

$$\sin[(\theta_i)_{obs}] = \sin[(\theta_i)_{true}]\cos[\langle\delta(2\theta_i)\rangle/2] + \cos[(\theta_i)_{true}]\sin[\langle\delta(2\theta_i)\rangle/2] \tag{3}$$

Realistically, a powder diffractometer should be aligned reasonably well and the optical aberrations are relatively small. For example, if $[\langle\delta(2\theta)\rangle/2]$ is ~1° (an enormous error), setting the $\cos[\langle\delta(2\theta)\rangle/2]$ term in Equation 3 equal to 1.0 results in an error of less than 0.1%. Similarly, the sine of a small angle, $\sin[\langle\delta(2\theta)\rangle/2]$ can be approximated by the angle itself (in radians). Therefore, $[\langle\delta(2\theta)\rangle/2]$ should be small and Equation 3 can be approximated by Equation 4, which is good to first-order in δ.

$$\sin[(\theta_i)_{obs}] \approx \sin[(\theta_i)_{true}] + [\langle\delta(2\theta_i)_{true}\rangle/2]\cos[(\theta_i)_{true}] \tag{4}$$

Although $[\langle\delta(2\theta)\rangle/2]$ can be expressed, for common errors and aberrations, as a linear sum of terms (Reference 13), i.e.,

$$[\langle\delta(2\theta)\rangle/2] = \theta_{zero} - HR\cos\theta - G\cot\theta - T\sin(2\theta) \tag{5}$$

Equation 4 remains nonlinear overall.

Nevertheless, the desired unit cell parameters and error/aberration coefficients are those which will best fit Equation 4 for every observation $(\theta_i)_{obs}$. Three (computerized) methods that are employed to determine estimates of the parameters in a nonlinear system (such as Equation 4) are linearization, steepest descent, or Marquardt's compromise (Reference 14). If the error distribution is Gaussian and the observations have been weighted appropriately, then the method of least-squares will give the maximum likelihood estimate of the parameters (Reference 15). Therefore, linearization using the standard method of Taylor series expansion about initial starting values (and neglecting higher-order terms) is used to transform Equation 4 into Equation 6, which can then be treated as a linear least-squares problem by solving for the changes in the parameters (i.e., δa^*, etc.). Using $F(a^*,...T)$ to represent the entire right side of Equation 4,

$$F(a^*,... T) = \sin[(\theta_i)_{true}] + \{\theta_{zero} - HR\cos\theta - G\cot\theta - T\sin(2\theta)\}\cos[(\theta_i)_{true}]$$

then at initial values $F(a^*,...T)_o$ for each observation i $(1 \rightarrow M)$

$$\sum_{1}^{M}\left\{(\delta a^*)\left[\frac{\partial F}{\partial a^*}\right]_o + \ldots(\delta T)\left[\frac{\partial F}{\partial T}\right]_o\right\} = \sin[(\theta_i)_{obs}] - F(a,^*\ldots T)_o \qquad (6)$$

For data points (observations) $1 \rightarrow M$, Equation 6 can be expressed in the matrix form,

$$\mathbf{A} \cdot \mathbf{x} = \mathbf{b}$$

where **A** is the design matrix with dimensions (M x *p*) containing M rows corresponding to each observation for *p* columns of partial derivatives of the *p* parameters a*... T, **x** is the column vector containing the desired changes (δa^*... δT) for the *p* parameters, and **b** is the column vector of length M containing the residuals for each observation (the right side of Equation 6).

The solution for **x** that minimizes the sum of the squares of the residuals is found by solving (in matrix notation)

$$(\mathbf{A}^T \cdot \mathbf{A}) \cdot \mathbf{x} = \mathbf{A}^T \cdot \mathbf{b}$$

or

$$\mathbf{x} = (\mathbf{A}^T \cdot \mathbf{A})^{-1} \cdot \mathbf{A}^T \cdot \mathbf{b} \qquad (7)$$

where $(\mathbf{A}^T \cdot \mathbf{A})$ is called the Hessian or *normal equations* matrix. If the number of observations exceeds the number of parameters (i.e., sufficient *hk*L can be assigned to the observed line positions) and no near degeneracies in the parameters exist, the matrix inversion required in Equation 7 is usually well-behaved. However, one might imagine that inclusion of the systematic error functions which would tend to introduce small corrections (with coefficients that may tend to zero) could cause problems during the normal matrix inversion. Therefore, instead of using normal equations and matrix inversion, the solution, vector **x** in the matrix form of Equation 6, is obtained using

singular value decomposition. This more "resistant" procedure diminishes the problems caused by near singularities in the matrix (or "delicately canceling infinities") (See Reference 16 and references therein, as well as Reference 17). The singular value decomposition will still produce a best solution in the least-squares sense (Reference 16). The matrix **A** can be decomposed as follows:

$$\mathbf{A} = \mathbf{U} \cdot [\mathrm{diag}(s_j)] \cdot \mathbf{V}^T$$

from which it can be shown that the **x** that minimizes $|\mathbf{A} \cdot \mathbf{x} - \mathbf{b}|$ is given by

$$\mathbf{x} = \mathbf{V} \cdot [\mathrm{diag}(1/s_j)] \cdot (\mathbf{U}^T \cdot \mathbf{b})$$

where **U** (MxM) and **V**(p xp) are orthogonal matrices.

For those s_j that are zero or are so small as to approach the floating point precision of the computer, their values of $(1/s_j)$ are set to zero (rather than allowing them to approach infinity) before **x** is determined.

From the decomposition, the covariance matrix is also obtained (Reference 16). The estimated variances for the reciprocal lattice and aberration parameters are obtained in the usual way by multiplying the elements of the covariance matrix by the estimate of the population variance (SGEST), which for M observations and p parameters, SGEST = $[\Sigma(\text{residuals})^2]/(M-p)$ (Reference 15). The estimated variances for the (direct) unit cell parameters are then obtained by (Reference 18)

$$\mathbf{c} = \mathbf{D} \cdot \mathbf{r} \cdot \mathbf{D}^T$$

where **c** is the vector to be calculated containing the (direct) unit cell variances, **D** is a matrix of the derivatives of the unit cell parameters with respect to the reciprocal lattice parameters, **r** is the vector with the estimated variances of the reciprocal lattice parameters obtained from the covariance matrix, and $\mathbf{D}^T$ is the transpose of **D**.

THE PROGRAM

The program, CELLSVD, is an iterative least-squares program for refining unit cell and systematic error parameters by solving the matrix form of Equation 6 using singular value decomposition. The development of CELLSVD is an outgrowth of efforts to adapt an old program "PODEX" for current use.

"PODEX" is an iterative least-squares program that minimizes the differences between observed and calculated $\sin^2\theta$, i.e., minimizes the differences between Q_{obs} and Q_{calc}, by refining an initial crystallographic unit cell against observed angular diffraction

data using standard Taylor-series expansion with matrix inversion of the normal equations. "PODEX" has the same capabilities as the various versions of the "Appleman-Evans" least-squares program, but also includes some coding for error functions. The FORTRAN coding of "PODEX" which came to the author via B. Chamberland (University of Connecticut) (hereafter, OPODEX) is that of a very old (approximately 30-year-old) version from DuPont.* A. W. Sleight, while at DuPont, obtained an early version of C. W. Burnham's LCLSQ (Reference 19) from C. T. Prewitt. Sleight modified LCLSQ and renamed this modified program PODEX.**

The coding of OPODEX was subsequently modified by this author to allow different values for the standard wavelengths, the input was modified, the use of input hkL's was changed, the calculation of the Smith-Snyder (F_N) figure-of-merit (Reference 20) was included, and some of the unnecessary output was eliminated. Due to the archaic FORTRAN syntax, additional changes were required in the FORTRAN coding to satisfy the compiler. This modified OPODEX was recompiled under Lahey FORTRAN77 to yield two executable versions; one was optimized for 80286 instructions and requires an 80x87 coprocessor (286PODEX.EXE) and one was compiled with no optimization and with emulation for 80x87 code (NEWPODEX.EXE). The error functions of OPODEX were retained (with some modifications) but the validity of their use and the validity of the programming remains in question. The form of these error functions clearly date back to the methodologies discussed in References 8 through 11 and are not easily related to current diffractometer hardware. 286PODEX has been used locally for a few years, but the systematic errors expected from our experiments were not adequately handled by this program. Consequently, the mathematical treatment described in the previous section was derived and CELLSVD was written.

The overall flow of program logic in CELLSVD, the symmetry constraints and symmetry subroutine for systematic absences, the indexing subroutine (with modifications), and much of the input/output are essentially those of 286PODEX. However, after removal of the undesired, unnecessary, questionable, and out-of-date coding of 286PODEX (and OPODEX), coding for the following were added: (a) coding to include systematic error parameters in a form related to modern diffractometer hardware as expressed by Equation 5; (b) coding to build the design matrix **A** with appropriate derivatives, including the crossterms involving $(\theta_i)_{true}$ in the error functions; (c) coding for singular value decomposition along with associated coding to recover the solution vector **x** and covariance matrix; (d) coding for additional choices of weighting schemes including true unit weights (equally weighted observations) and weighting by the inverse of the variance in $\sin\theta$; (e) the capability to hold indices of some (or all) reflections fixed while allowing other reflections to be automatically indexed; (f) coding to check for convergence; (g) coding to allow the changes to the systematic errors to be damped (or fixed); and (h) miscellaneous coding changes including improved character handling that enabled the

* E. I. DuPont de Nemours & Co., Experimental Station, Wimington, DE 19898.

** A. W. Sleight, Department of Chemistry, Oregon State University, Corvallis, OR 97331-4003, pesonal communication, June 1993.

program to run under modern FORTRAN77. Consequently, although the input and output look similar to OPODEX and Burnham's LCLSQ, the internal mathematics of the program have been drastically altered. The calculational validity of the program (without systematic errors) has been checked using published tests; results are given in Appendix A. Two executable versions of CELLSVD (NEWCELL.EXE and CELLSVD.EXE) were compiled using a Lahey FORTRAN77 compiler; NEWCELL.EXE requires no 80x87 coprocessor and should run on any IBM-type personal computer. CELLSVD.EXE was compiled with an optimized 80286 instruction set and requires the presence of an 80x87 coprocessor.

CELLSVD has been found to be stable, even if rather large systematic errors are refined. However, convergence generally requires many more cycles than the previous FORTRAN77 version of 286PODEX (NEWPODEX). Requesting eleven or twelve cycles has been found to be adequate for most problems; the program will stop if convergence is reached sooner. The speed of execution of CELLSVD on a personal computer with a 386 processor and 387 coprocessor is not significantly slower than observed with 286PODEX. Instructions for input to CELLSVD are given in Appendix B.

EXAMPLES OF THE USE OF CELLSVD

EXAMPLE I

Powdered LaB_6 is available as a certified angular (d-spacing) standard from the National Institute of Standards and Technology (NIST) as SRM 660. The sharp line profiles that this material exhibits makes it valuable as an external (profile) standard as well as for an internal d-spacing (angular) standard. The certified value for the unit cell parameter is 4.15695(6) Å. If systematic errors or inherent optical aberrations in LaB_6 experimental data are included during refinement of its unit cell parameter, the resulting cell parameter should be very close to the expected certified value (within an error due to temperature differences). (However, see Reference 21 for comments regarding the correct absolute values of the unit cell parameters for the NIST SRMs!)

A substantial amount of certified SRM 660 (LaB_6) was mixed with transparent fast-setting epoxy; a thin layer of this mixture was smeared on an "off-axis," AT-cut quartz substrate. After several weeks of curing and aging, the sample was then ground and polished in an optical shop to a flatness of better than 1 μm. This sample was run on a Scintag PAD V diffractometer which (at that time) was known to have a systematic error which increased with increasing 2θ. The diffractometer was equipped with a (liquid-nitrogen-cooled) solid-state germanium detector and the radius was set at 220 mm; a divergence angle of 1.43° and acceptance (receiving) angle of 0.143° were used. Data were acquired using a slow step scan. Peak positions were obtained using Scintag-supplied background correction and peak-picking software. Each of the possible systematic error corrections were tested using the same software-selected peak positions. (The input data, which was used for all of the tests is shown below.) Parameters controlling the refinement

were the same for all of the tests and the observations were weighted equally (unit weights). Only the choice of the systematic error function was varied.

Input Data for the Tests of the Systematic Error Corrections

```
06/15/93    10:31:16.50    CELLSVD by Lowe-Ma
LaB6(in epoxy, grnd flat on AT qtz, .2-.5<4-2) *TEST*

CRYSTAL IS:  CUBIC                  INPUT IS:  2-THETA
INITIAL DIRECT UNIT CELL PARAMETERS
        A =   4.15660              ALPHA =  90.00000
        B =   4.15660               BETA =  90.00000
        C =   4.15660              GAMMA =  90.00000
 THE RADIATION IS:  CU    with WAVELENGTHS:
                     1    1.540598                      2    0.000000
                     3    0.000000                      4    0.000000
```

LaB6(in epoxy, grnd flat on AT qtz, .2-.5<4-2) *TEST*

INPUT DATA

N	H	K	L	D	I	1/DSQ	2-THETA	WV	INPUT	SIGMA
1				4.1500	11	0.05806	21.394	1	21.3940	0.00000
2				2.9352	11	0.11607	30.429	1	30.4290	0.00000
3				2.3970	11	0.17404	37.490	1	37.4900	0.00000
4				2.0759	11	0.23204	43.562	1	43.5620	0.00000
5				1.8567	11	0.29008	49.023	1	49.0230	0.00000
6				1.6950	11	0.34805	54.058	1	54.0580	0.00000
7				1.4681	11	0.46396	63.294	1	63.2940	0.00000
8				1.3842	11	0.52194	67.629	1	67.6290	0.00000
9				1.3132	11	0.57984	71.827	1	71.8270	0.00000
10				1.2522	11	0.63773	75.925	1	75.9250	0.00000
11				1.1520	11	0.75358	83.932	1	83.9320	0.00000
12				1.1101	11	0.81150	87.881	1	87.8810	0.00000

```
   PARAMETERS FOR NEXT CYCLE
Print Controls are:  MPRINT= 0  IALLPR= 1  INDEXW= 1
HKLs are assigned by:  RE-INDEX   Multiples are:  INCLUDED   Type of weighting: IW = 1
Systematic error corrections for:  theta-zero - YES
  cos(th) error - NO    cot(th) error - NO    sin(2th) error - NO
DAMPing multiplier for changes in systematic errors =  1.00
DMIN= 1.09000     DT= 0.15000     TS= 0.05000
 NO SYSTEMATIC ABSENCES
```

Tests of each of the possible systematic errors yielded the results shown below (Table 1) for twelve indexed reflections. The sin(2θ) error function most adequately modeled the diffractometer error and inherent optical aberrations in this particular set of LaB_6 data, yielding the expected unit cell parameter for LaB_6 (within two estimated standard deviations).

TABLE 1. Resulting Unit Cell for LaB_6 Test Data.

	a	F_N	ave.$\lvert\Delta\theta\rvert$
Refine θ_o	4.1543(2)Å	227.7	0.00203°
Refine cosθ error	4.1539(1)	232.2	0.00199
Refine cotθ error	4.1531(1)	158.3	0.00291
Refine sin(2θ) error	4.1566(2)	489.3	0.00094

Note that the differences between the unit cell values in Table 1 are much larger than the estimated standard deviation of the fit! Although each fit yields a reasonably precise value, the differences between values reflect the effect that including systematic errors (or not including them) has on the accuracy of the resultant cell parameter(s).

EXAMPLE II

Sodium-containing β"-alumina is used in high-temperature batteries and is an important component of AMTEC. Therefore, its properties especially at high temperatures are of interest. High-temperature diffraction data were acquired from small ceramic pieces of a commercial Li-stabilized, Na-β"-alumina. Precise unit cell parameters, as functions of temperature, were to be used to determine the thermal expansion of this particular commercial material. In addition, changes in the unit cell parameters were to be used to decide between two proposed models for defects that form in the presence of sodium at high temperatures. CELLSVD was used to successfully refine the high-temperature powder diffraction data which were found, unfortunately, to contain a significant systematic error at a (later) time when recollection of data was not possible.

Room-temperature data for Na-β"-alumina were initially refined against hand-calculated unit cell values. However, the final fit was much poorer than expected. The Smith-Snyder Figure-of-Merit, F_N was very low, the average (absolute) $\Delta\theta$ value was very high, 0.032°, and six lines were not indexed, as shown in the partial output below.

```
   ROGER001: undoped b"-alumina, 27C(before heating) {LINES w/I>5 ONLY}
DIRECT UNIT CELL CONSTANTS AFTER LEAST-SQUARES CYCLE 11
     PARAMETER          OLD          CHANGE          NEW          ERROR
      A (ANG.)        5.64580        0.00000       5.64580       0.00601
      C (ANG.)       34.23462        0.00000      34.23462       0.10288
    UNIT CELL VOLUME
     (CUBIC ANG.)     945.0335         0.0001      945.0336       2.9066

A(RHOMBOHEDRAL) = 11.867950          ALPHA(R) = 27.52044

   PARAMETERS FOR NEXT CYCLE
Print Controls are:  MPRINT= 0     IALLPR= 1        INDEXW= 1
```

HKLs are assigned by: RE-INDEX Multiples are: REJECTED Type of weighting: IW = 6
Systematic error corrections for: theta-zero - NO
cos(th) error - NO cot(th) error - NO sin(2th) error - NO
DAMPing multiplier for changes in systematic errors = 1.00
DMIN= 1.54000 DT= 0.31833 TS= 0.10611
LHKL= 6, LHK0= 0, L0KL= 0, LH0L= 0, LHHL= 0, LHML= 0, LH00= 0, L0K0= 0, L00H= 0

ROGER001: undoped b"-alumina, 27C(before heating) {LINES w/I>5 ONLY}
OBSERVED AND CALCULATED VALUES BASED ON REFINED PARAMETERS AFTER CYCLE 11

N	I	H	K	L	D(OBS)	D CALC(corr)	Q CALC(unc)	2(THo-THccal)	SQRT(Wt)	
1	72	0	0	3	11.55408	11.41154	0.00768	-0.09564	1.5440	
2	61	0	0	6	5.67809	5.70577	0.03072	0.07612	1.5549	
3	6	0	1	2	4.73501	4.70137	0.04524	-0.13521	1.0000	
4	21	1	0	4	4.25798	4.24546	0.05548	-0.06217	1.5664	
5	26	1	1	0	2.82932	2.82290	0.12549	-0.07378	1.6010	M
6	7	1	0	10	2.81114	2.80437	0.12715	-0.07876	1.0000	
9	53	1	1	6	2.52505	2.53017	0.15621	0.07430	1.6177	
10	24	0	2	1	2.43996	2.43849	0.16817	-0.02287	1.6236	
11	5	2	0	2	2.42153	2.42015	0.17073	-0.02193	1.0000	
12	25	0	2	4	2.34861	2.35069	0.18097	0.03514	1.6308	
13	9	2	0	5	2.29886	2.30235	0.18865	0.06171	1.0000	M
14	27	1	1	9	2.25386	2.26687	0.19460	0.23906	1.6393	BD
16	16	0	2	7	2.17894	2.18672	0.20913	0.15403	1.6469	M
19	10	0	3	20	1.61611	1.61559	0.38312	-0.02016	1.0000	M
21	17	1	2	11	1.59120	1.58900	0.39605	-0.08794	1.7606	
22	21	1	1	18	1.57807	1.57732	0.40194	-0.03044	1.7651	
23	8	3	0	6	1.56086	1.56712	0.40719	0.25964	1.0000	BD
24	8	2	0	17	1.55539	1.55435	0.41391	-0.04346	1.0000	

REFLECTIONS NOT USED

N	D(OBS)	Q(OBS)	I
7	2.7781	0.12957	29
8	2.5984	0.14811	49
15	2.2451	0.19840	10
17	2.1574	0.21486	6
18	1.9764	0.25600	83
20	1.5998	0.39070	5

ROGER001: undoped b"-alumina, 27C(before heating) {LINES w/I>5 ONLY}
DISCREPANCY FACTORS BASED ON REFINED PARAMETERS AFTER CYCLE 11
Number of PARAMETERS Varied = 2 Number of OBSERVATIONS = 24
Number of Observations ACCOUNTED FOR = 18
Number of Observations TO BE USED IN NEXT CYCLE = 12
Number of UNUSED INDICES generated = 28 TWO OR MORE INDICES FIT = 4 Observations
AVERAGE OF ABS(DELTA THETA) = 0.03183
Smith-Snyder F(N) = 6.1 for 18 indexed reflections

Careful comparison of the raw 2θ values of the room-temperature data with those from a calculated pattern for Na-β"-alumina in the literature suggested that a constant $\Delta 2\theta_0$ systematic error of ~0.27° was present in the data. With the inclusion of a θ_0 error in the least-squares refinement of the unit cell, the fit was much improved as shown in the partial output below. The F_N dramatically improved and the average (absolute) $\Delta\theta$ was now

much less than 0.008°, as would be expected for good angular data. Note that the refined θ_0 error (x 2) is, indeed, approximately equal to the error expected from comparison to the literature!

ROGER001: undoped b"-alumina, 27C(before heating) {LINES w/I>5 ONLY}
DIRECT UNIT CELL CONSTANTS AFTER LEAST-SQUARES CYCLE 9

PARAMETER	OLD	CHANGE	NEW	ERROR
A (ANG.)	5.60639	0.00000	5.60639	0.00038
C (ANG.)	33.43675	0.00000	33.43675	0.00208
UNIT CELL VOLUME (CUBIC ANG.)	910.1669	0.0000	910.1669	0.1551

A(RHOMBOHEDRAL) = 11.606090 ALPHA(R) = 27.95347

Oldtheta-zero= -0.14791 Change = 0.00000 New theta-zero = -0.14791 Estimated error = 0.2500E-04

PARAMETERS FOR NEXT CYCLE
Print Controls are: MPRINT= 0 IALLPR= 1 INDEXW= 1
HKLs are assigned by: RE-INDEX Multiples are: REJECTED Type of weighting: IW = 6
Systematic error corrections for: theta-zero - YES
cos(th) error - NO cot(th) error - NO sin(2th) error - NO
DAMPing multiplier for changes in systematic errors = 1.00
DMIN= 1.54000 DT= 0.06000 TS= 0.02000
LHKL= 6, LHK0= 0, L0KL= 0, LH0L= 0, LHHL= 0, LHML= 0, LH00= 0, L0K0= 0, L00H= 0

ROGER001: undoped b"-alumina, 27C(before heating) {LINES w/I>5 ONLY}
OBSERVED AND CALCULATED VALUES BASED ON REFINED PARAMETERS AFTER CYCLE 9

N	I	H	K	L	D(OBS)	DCALC(corr)	QCALC(unc)	2(TH-THcal)	SQRT(Wt)
1	72	0	0	3	11.55408	11.57701	0.00805	0.01517	1.5440
2	61	0	0	6	5.67809	5.67783	0.03220	-0.00071	1.5549
3	6	0	1	2	4.73501	4.73563	0.04600	0.00243	1.0000
4	21	1	0	4	4.25798	4.25735	0.05673	-0.00314	1.5664
5	26	1	1	0	2.82932	2.82875	0.12726	-0.00652	1.6010
6	7	0	0	12	2.81114	2.81164	0.12880	0.00580	1.0000
7	29	1	0	10	2.77807	2.77845	0.13186	0.00454	1.6034
8	49	0	1	11	2.59840	2.59785	0.15065	-0.00751	1.6131
9	53	1	1	6	2.52505	2.52439	0.15946	-0.00959	1.6177
10	24	0	2	1	2.43996	2.44004	0.17058	0.00135	1.6236
11	5	2	0	2	2.42153	2.42091	0.17326	-0.00975	1.0000
12	25	0	2	4	2.34861	2.34864	0.18399	0.00053	1.6308
13	9	2	0	5	2.29886	2.29848	0.19204	-0.00668	1.0000
14	27	1	1	9	2.25386	2.25356	0.19971	-0.00545	1.6393
15	10	0	0	15	2.24505	2.24486	0.20125	-0.00357	1.0000
16	16	0	2	7	2.17894	2.17895	0.21351	0.00021	1.6469
17	6	0	1	14	2.15736	2.15756	0.21773	0.00396	1.0000
18	83	0	2	10	1.97643	1.97645	0.25912	0.00047	1.6728
19	10	2	1	10	1.61611	1.61641	0.38639	0.01152	1.0000
20	5	0	0	21	1.59985	1.59970	0.39445	-0.00562	1.0000
21	17	0	2	16	1.59120	1.59118	0.39866	-0.00086	1.7606
22	21	1	2	11	1.57807	1.57827	0.40517	0.00803	1.7651
23	8	3	0	6	1.56086	1.56128	0.41398	0.01730	1.0000
24	8	1	1	18	1.55539	1.55547	0.41706	0.00353	1.0000

ROGER001: undoped b"-alumina, 27C(before heating) {LINES w/I>5 ONLY} DISCREPANCY FACTORS BASED ON REFINED PARAMETERS AFTER CYCLE 9
Number of PARAMETERS Varied = 3 Number of OBSERVATIONS = 24
Number of Observations ACCOUNTED FOR = 24
Number of Observations TO BE USED IN NEXT CYCLE = 24
Number of UNUSED INDICES generated = 26 TWO OR MORE INDICES FIT = 0 Observations
AVERAGE OF ABS(DELTA THETA) = 0.00280
Smith-Snyder F(N) = 85.8 for 24 indexed reflections

For data obtained at higher temperatures on the same sample of Na-β"-alumina, the behavior of each of the unit cell refinements was similar. The $2\theta_o$ error was approximately constant with temperature, as would be expected if most of the error was caused by an initial error in the alignment of the diffractometer hardware.

Cell Refinement Results
Without Inclusion of a Systematic θ_o Error

	a	c	$\lvert\overline{\Delta\theta}\rvert$
27°C	5.6458(60) Å	34.235(103) Å	0.032°[a]
200°C	5.6620(34)	33.381(44)	0.022[b]
400°C	5.6682(28)	33.420(36)	0.022[c]

[a] 6 lines rejected.
[b] 8 lines rejected.
[c] 9 lines rejected.

Cell Refinement Results*
θ_o Error Included

	a	c	$\lvert\overline{\Delta\theta}\rvert$	θ_o
27°C	5.6064(4) Å	33.437(2) Å	0.003°	-0.1479°
200°C	5.6151(5)	33.482(3)	0.004	-0.1369
400°C	5.6206(4)	33.511(2)	0.003	-0.1389
600°C	5.6182(4)	33.501(2)	0.004	-0.1295
800°C	5.6277(4)	33.552(2)	0.003	-0.1157
1000°C	5.6398(5)	33.620(3)	0.005	-0.1360

*For $CuK\alpha_1$ wavelength = 1.540562 Å.

CONCLUDING SUMMARY

A new computer program, CELLSVD, allows explicit refinement of systematic errors and geometric aberrations that can occur in powder diffractometer data. The program uses an approximation for $\sin(\theta_{obs})$ as the observational equation. The nonlinear observational equation is changed to a linear form using standard Taylor series expansion methods. Iterative linear least-squares is accomplished using singular value decomposition techniques. The calculational validity of the program has been verified by comparison with published standard tests. Use of CELLSVD has enabled precise (and accurate) unit cell parameters to be obtained from diffraction data that contained (even substantial) systematic error.

REFERENCES

1. T. A. Vanderah, C. K. Lowe-Ma, D. E. Bliss, M. W. Decker, M. S. Osofsky, E. F. Skelton, and M. M. Miller. "Growth of Near-Free-Standing $YBa_2Cu_3O_7$–Type Crystals Using a Self-Decanting Flux Method," *J. Crystal Growth*, 118 (1992), pp. 385-395.

2. A. J. C. Wilson. "Accuracy in Methods of Lattice-Parameter Measurement," in *Proc. Symp. Accuracy in Powder Diffraction, 11-15 June 1979, Gaithersburg, MD,* NBS Special Publication 567 (1980); and references therein.

3. "JCPDS-International Centre for Diffraction Data Task Group on Cell Parameter Refinement," *Powder Diffr.* 1(1) (1986), pp. 66-76.

4. N. A. Razik. "Precise Lattice Constant Determination of Hexagonal, Rhombohedral, and Tetragonal Crystals from X-ray Powder Diffractometric Data," *phys. stat. sol.* (a) 90 (1985), pp. K125-K128.

5. A. Brown. "Lattice Parameter Measurements," *Chemica Scripta,* 26A (1986), pp. 77-83.

6. B. H. Chen and R. A. Jacobson. "A Robust Method for Least-Squares Lattice Parameter Refinement," *Powder Diffr.*, 5(3) (1990), pp. 144-145.

7. Abstracts O2.1, P2.4, and P2.5, in *Accuracy in Powder Diffraction II, 26-29 May 1992, Gaithersburg, MD,* National Institute of Standards & Technology, 1992. Pp. 209-210. Paper UNCLASSIFIED.

8. J. B. Hess. "A Modification of the Cohen Procedure for Computing Precision Lattice Constants from Powder Data," *Acta Cryst.*, 4 (1951), pp. 209-215.

9. L. V. Azaroff and M. J. Buerger. *The Powder Method in X-Ray Crystallography*, New York, McGraw-Hill Book Co., 1958. pp. 238-245.

10. M. H. Mueller, L. Heaton, and K. T. Miller, "Determination of Lattice Parameters With the Aid of a Computer," *Acta Cryst.* 13 (1960), pp. 828-829.

11. R. E. Vogel and C.P. Kempter. "A Mathematical Technique for the Precision Determination of Lattice Parameters," *Acta Cryst.*, 14 (1961), pp. 1130-1134.

12. W. Wong-Ng and C. R. Hubbard. "Standard Reference Materials for X-Ray Diffraction. Part II. Calibration Using d-Spacing Standards," *Powder Diffr.* 2(4) (1987), pp. 242-248; and references therein.

13. A. J. C. Wilson. *Mathematical Theory of X-Ray Powder Diffractometry,* New York, Gordon & Breach Science Publisher, 1963.

14. N. R. Draper and H. Smith. *Applied Regression Analysis*, New York, John Wiley & Sons, 1966, pp. 267-270.

15. E. Prince. *Mathematical Techniques in Crystallography and Materials Science*, New York, Springer-Verlag, 1982, pp.77-85 and 103-104.

16. W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling. *Numerical Recipes —The Art of Scientific Computing*, Cambridge, Cambridge University Press, 1986. pp. 52-64 and 515-519.

17. U. Anselmi-Tamburini and G. Spinolo. "On the Least-Squares Determination of Lattice Dimensions: a Modified Singular Value Decomposition Approach to Ill-Conditioned Cases," *J. Appl. Cryst.*, 26 (1993), pp. 5-8.

18. Y. Bard. *Nonlinear Parameter Estimation*, New York, Academic Press, 1974, pp. 212-215.

19. C. W. Burnham. "Lattice Constant Refinement," *Carnegie Institution of Washington Yearbook*, 61 (1962), pp. 132-135.

20. G. S. Smith and R. L. Snyder. "FN: A Criterion for Rating Powder Diffraction Patterns and Evaluating the Reliability of Powder-Pattern Indexing," *J. Appl. Cryst.*, 12 (1979), 60-65 .

21. D. Yoder-Short. "On a Small Error in SRM640, SRM640a, and SRM640b Lattice Parameters," *J. Appl. Cryst.*, 26 (1993), pp. 272-276.

Appendix A

REFINEMENT TESTS

The least-squares unit cell refinement algorithm of CELLSVD, without the inclusion of any systematic errors, was tested using data given in Reference 3. Results obtained from CELLSVD are compared with the published results for these test data. However, for a thorough comparison, Reference 3 should be consulted. Unit cell refinement programs are not all based on the same observational equations and do not all handle indexing, line rejection, weights, and estimated standard deviations in the same way. Hence, the programs used in the published tests did not yield exactly equivalent results. For example, although the Foris/DuPont results using DuPont's PODEX are given under the tests with unit weights, IW=1 (at least in OPODEX) actually implies the use of "Hess weights," i.e., weights derived from the expected variance of $1/d^2$ (without an additional multiplying factor), NOT equally weighted observations. Note also that the F_N in the published tests is given only for the first 30 lines (or less); CELLSVD gives F_N for all possible data from $2\theta = 0°$ out to the dMIN given on Line/CARD V.

The published data used for these tests also do not necessarily represent the best possible data available for the compounds given. In CELLSVD (and in, i.e., 286PODEX) as a refinement proceeds, and the fit improves, the tolerance factor for assigning indices ("DT") in conjunction with the tolerance factor for inclusion of a reflection in the matrix ("TS") continue to decrease until a minimum of DT = 0.06° (in θ) and TS = 0.02° (in θ) are reached. For a correct unit cell with reasonably good diffractometer data, DT and TS reach the minimum values. However, these minimum tolerance values could not be reached with the test data given for #LS01 and #LS02.

TEST LS#01, Triclinic

	Published results ($ave.\Delta 2\theta = 0.017°$)		CELLSVD results ($2\|\overline{\Delta\theta}\| = 0.014°$)
	Range of values	Range of esd.'s	Values for unit weights
a	7.0305 - 7.0313 Å	.0008 - .0016 Å	7.0312(10) Å
b	10.6092 - 10.6114 Å	.0013 - .0026 Å	10.6107(16) Å
c	6.3660 - 6.3676 Å	.0009 - .0017 Å	6.3670(10) Å
α	101.351 - 101.374°	.007 - .018°	101.363(12)°
β	100.169 - 100.180°	.005 - .016	100.178(11)°
γ	93.811 - 93.820°	.005 - .015°	93.812(11)°

TEST LS#02, Monoclinic

	Published results ($ave.\Delta 2\theta = 0.015°$)		CELLSVD results ($2\|\overline{\Delta\theta}\| = 0.015°$)
	Range of values	Range of esd.'s	Values for unit weights
a	5.14844 - 5.14897 Å	.00026 - .00065 Å	5.14892(33) Å
b	5.20952 - 5.20973 Å	.00021 - .00066 Å	5.20944(32) Å
c	5.31820 - 5.31863 Å	.00025 - .00068 Å	5.31820(33) Å
β	99.232 - 99.245°	.003 - .007°	99.234(5)°

TEST LS#02, Monoclinic

	Published results (variable "Hess" weights) ($ave.\Delta 2\theta = 0.015°$)		CELLSVD results ($2\|\overline{\Delta\theta}\| = 0.015°$)	
	Range of values	Range of esd.'s	Using published "Hess" test weights*	Using weights* for variance in 1/d
a	5.14873 - 5.14885 Å	.00038 - .00052 Å	5.14972(30)Å	5.14886(17) Å
b	5.20956 - 5.20962 Å	.00037 - .00052 Å	5.20950(28) Å	5.20940(17) Å
c	5.31830 - 5.31867 Å	.00035 - .00053 Å	5.31806(30) Å	5.31828(17) Å
β	99.236 - 99.247°	.005 - .006°	99.232(5)°	99.235(3)°

* Note that in the published tests, the variable weights are "Hess" weights, i.e., weights derived from the variance in $1/d^2$ (which assumes a $1/d^2$ or ΔQ fit). These weights are a $1/\sin^2(2\theta)$ [i,e., $(\lambda^2/4\sin(2\theta))^2$] function, varying by approximately a factor of 10 between 17 and 90° (2θ) with the low-angle reflections more heavily weighted. For a fit based on 1/d or $\Delta(\sin\theta)$, the variance in 1/d results in weighting by a $(1/\cos^2\theta)$ [i.e., $(\lambda/\cos\theta)^2$] function which emphasizes the higher-angle reflections.

TEST LS#03, Orthorhombic

	Published results ($ave.\Delta 2\theta = 0.005°$)		CELLSVD results ($2\|\overline{\Delta\theta}\| = 0.006°$)
	Range of values	Range of esd.'s	Values for unit weights
a	6.71505 - 6.71510 Å	.00010 - .00033 Å	6.71507(17) Å
b	3.64839 - 3.64843 Å	.00005 - .00018 Å	3.64845(9) Å
c	6.19949 - 6.19964 Å	.00010 -.00031 Å	6.19964(16) Å

TEST LS#04, Tetragonal

	Published results ($ave.\Delta 2\theta = 0.008°$)		CELLSVD results* ($2\|\overline{\Delta\theta}\| = 0.008°$)
	Range of values	Range of esd.'s	Values for unit weights
a	5.75847 - 5.75884 Å	.00011 - .00047 Å	5.75895(28) Å
c	9.46724 - 9.46773 Å	.00027 - .00082 Å	9.46722(70) Å
F_N	67.4 (N=21)		64.7 (N=21)
$N_{possible}$	38		39 (to d_{min} = 1.11)

* For variable $[(\lambda/\cos\theta)^2]$ weights, a = 5.75884(15) Å, c = 9.46724(38) Å, F_N = 65.7 (N_{poss} = 39).

TEST LS#05, Trigonal ($R\bar{3}c$)

	Published results ($ave.\Delta 2\theta = 0.003°$)		CELLSVD results* ($2\|\overline{\Delta\theta}\| = 0.003°$)
	Range of values	Range of esd.'s	Values for unit weights
a	4.75922 - 4.75931 A	.00005 - .00017 A	4.75921(7) Å
c	12.99195 - 12.99221 A	.00016 - .00045 A	12.99189(22) Å

* The refined CELLSVD cell gives a calculated rhombohedral cell of a = 5.128778 Å, α = 55.28726°. The CELLSVD refined rhombohedral cell (with unit weights) is a = 5.12878(25) Å, α = 55.287(2)° However, the F_N calculated during the rhombohedral refinement may be incorrect. No attempt was made to modify the systematic absences and symmetry subroutines of OPODEX.

TEST LS#07, Cubic (Pa3)

	Published results ($ave.\Delta 2\theta = 0.005°$)		CELLSVD results ($2|\overline{\Delta\theta}| = 0.005°$)
	Range of values	Range of esd.'s	Values for unit weights
a	7.85556 - 7.85593 Å	.00007 - .00024 Å	7.85556(13) Å
F_N	95 (N=20)		87.3 (N=20)
$N_{possible}$	42		46*

* Pa3 was used as a test because the indices do not permute in this space group. However, in CELLSVD (and 286PODEX) all reflections between $2\theta=0°$ and d_{min} (d_{min} = 1.088 in this case) are considered in counting N_{poss}. Three reflections are allowed below the first observed (111) reflection. No attempt was made to modify the systematic absence and symmetry subroutines of OPODEX.

Appendix B

INPUT INSTRUCTIONS FOR CELLSVD

The original input format of OPODEX and 286PODEX as 80-column card images has been retained due to the ease of rapidly modifying template files with a word-processor or line editor in ASCII mode. The use of template files enables input for multiple calculations involving the same or similar materials to be rapidly prepared, although one obvious improvement would be to have the program directly read a data file containing diffractometer-generated peak list information. Because the input is read in FORTRAN fixed format, it does matter in which column the numbers go. Attempting to refine more than one systematic error in a cycle is NOT recommended.

Line/CARD I

Column	Parameter	Explanation
1-72	TLE	Title

Line/CARD II

Column	Parameter	Explanation
1-2	RADI	Radiation indicator: CU, CO, CR, FE, MO, NI, AG are the only names allowed. If a different radiation is desired, fool the program by using one of these names but include NEWLAM (below).
3	KS	Crystal system: 0, triclinic; 1, monoclinic (γ not 90°); 2, standard monoclinic setting (β not 90°); 3, orthorhombic; 4, rhombohedral; 5, hexagonal; 6, tetragonal; 7, cubic.
4	II	Input type: 0, 2θ values in degrees; 1, d-values; 2, $\sin^2\theta$ values.
5		Not used in CELLSVD
6-9	KT	CELLSVD systematic error functions: col 6, refine θ_o col 7, refine coefficient for $\cos\theta$ (sample displacement or thin speciman error) col 8, refine coefficient for $\cot\theta$ (flat speciman or axial divergence error) col 9, refine coefficient for $\sin(2\theta)$ (thick speciman error)
10-15		not used
16	NPP	Initial correction indicator: 0, θ_o error and error coefficients start at zero; 1, read in initial corrections on CARD IIIA.
17-18		not used
19	NEWLAM	Indicator to change wavelength values for CU, CO, CR, FE, MO, NI, or AG:

		0, no change; 1, change values, different (new) values follow.
20-28	XALPH1	New value for α_1 wavelength. Only α_1 is needed if all data refer to α_2-stripped diffractometer (or Guinier) data.
29-37	XALPH2	New value for α_2 wavelength.
38-46	XBETA	New value for β wavelength.
49-50	LETBEG	Flag to refine systematic errors; -1, apply corrections initially, requires a "CARD IIIA" 0, no refinement of errors N, refine systematic error corrections beginning with cycle N

Line/CARD III

Column	Parameter	Explanation
1-8	P(1)	a (Å). Include only unique (necessary) cell parameters.
9-16	P(2)	b (Å).
17-24	P(3)	c (A).
25-32	P(4)	α (deg).
33-40	P(5)	β (deg).
41-48	P(6)	γ (deg).

Line/CARD IIIA

Column	Parameter	Explanation
1-8	P(7)..P(15)	If NPP=1, read the initial θ_0 correction or values for error coefficients in FORMAT (9F8.0).

Line/CARD IV (Use One Line/Data Card for Each Reflection)

Column	Parameter	Explanation
1-3	IX(1,J)	h
4-6	IX(2,J)	k
7-9	IX(3,J)	L
11-18	YQ	observed 2θ value (or d or $\sin^2\theta$); data "cards" must be input in order of increasing 2θ (or decreasing d).
19-26	SIGMA(J)	σ value; can be blank if weights are assigned below.
28	IV(J)	wavelength indicator: blank or 1 = α_1; 2 = α_2; 3 = weighted mean α; 4 = β
38-40	IN(J)	Relative intensity

Line/CARD V

Column	Parameter	Explanation
		Blank line to end data input.

Line/CARD VI (Refinement control "card" - include one for each cycle.)

Column	Parameter	Explanation
1	KI(1)	1, Vary a; 0, do not vary
2	KI(2)	1, Vary b; 0, do not vary
3	KI(3)	1, Vary c; 0, do not vary
4	KI(4)	1, Vary α; 0, do not vary
5	KI(5)	1, Vary β; 0, do not vary
6	KI(6)	1, Vary γ; 0, do not vary
7	KI(7)	1, Vary θ_o; 0, do not vary
8	KI(8)	1, Vary cosθ coefficient; 0, do not vary
9	KI(9)	1, Vary cotθ coefficient; 0, do not vary
10	KI(10)	1, Vary sin(2θ) coefficient; 0, do not vary
11-15		not used

16	IW	Weighting scheme: the recommended weights to use with CELLSVD are IW=0, 1, 2, or 6. 0: do not change, requires σ's on data cards. *(Due to a programming error the input under option IW=0 in 286PODEX was actually 1/σ. In CELLSVD this has been corrected; input the actual or estimated σ.)* 1: unit weights, in CELLSVD this now means equally weighted observations. *(In OPODEX equally weighted observations did not exist. IW=1 actually meant the use of weights derived for a variance in $1/d^2$, but without any additional multiplication factor! In OPODEX the weights for the variance in $(1/d^2)$ are equivalent to using "Hess" weights, within constant factors of λ. See IW=5 below.)* 2: equally weighted observations scaled down for lines with I<10 3: $[\tan 2\theta/\sin^2(2\theta)]$ weights 4: as for IW=3, scaled down for lines with I<10 5: $[\lambda^2/4\sin(2\theta)]^2$ weights, OPODEX weights based on the variance in $(1/d^2)$. ***NOTE** Weighting options IW=3,4,5 are NOT recommended for use with CELLSVD; they have no mathematical or statistical basis for the Δ(sinθ) fit of CELLSVD.* 6: $[\lambda/\cos\theta]^2$ weights for a variance in (1/d) (except for I≤10, wt=1). *IW=6 is similar to OPODEX weights in that the weights are derived for the variance in the observation equation.* 7: $(1/\sin^2\theta)$ weights, theoretically unjustified, but perhaps useful
17	IDC	Output indicator: 0, usual; 1, suppress direct cell dimensions

18	JPEX	Index indicator: 0, do <u>not</u> change input hkL, but index any unindexed lines; 1, index and ignore all input hkL's. During a run JPEX=0 can be changed to JPEX=1 on subsequent cycle "cards", but <u>NOT</u> the other way!
19	LHKL	Systematic conditions for hkL reflections: 0, no restrictions; 1, C-centered (h+k=2n); 2, A-centered (k+L=2n); 3, B-centered (L+h=2n); 4, F-centered (hkL all odd or even); 5, I-centered (h+k+L=2n); 6, -h+k+L=3n, R(obv.), (hexag.index); 7, +h-k+L=3n; 8, h-k=3n
20	LHK0	Systematic conditions for hk0: 0, no restrictions; 1, h=2n; 2, k=2n; 3, h+k=2n; 4, h+k=4n
21	L0KL	Systematic conditions for 0kL: 0, no restrictions; 1, k=2n; 2, L=2n; 3, k+L=2n; 4, k+L=4n
22	LH0L	Systematic conditions for h0L: 0, no restrictions; 1, L=2n; 2, h=2n; 3, L+h=2n; 4, L+h=4n
23	LHHL	Systematic conditions for hhL: 0, no restrictions; 1, L=2n (tetragonal); 2, 2h+L=4n (tetragonal); 3, L=2n (rhombohedral); 4, L=2n (hexagonal); 5, L=2n (cubic); 6, 2h+L=4n (cubic);
24	LHML	Systematic conditions for hnL: 0, no restrictions; 1, L=2n hhL, hexagonal

25	LH00	Systematic conditions for h00: 0, no restrictions; 1, h=2n; 2, h=4n
26	L0K0	Systematic conditions for 0k0: 0, no restrictions; 1, k=2n; 2, k=4n
27	L00L	Systematic conditions for 00L: 0, no restrictions; 1, L=2n; 2, L=3n; 3, L=4n; 4, L=6n. All systematic conditions should be explicitly indicated!
28	IREJ	Rejection indicator for lines with multiple possible indices: 0, reject lines with multiple indices; 1, do not reject.
29	JRS	Reset systematic error coefficients; 0, do not reset; 1, reset to 0.0
30-36	DMIN	Minimum d-value for current cycle.
37-43	DT	Maximum tolerance in θ (deg.) for an index to be assigned. For good diffractometer data, start with DT $\approx$ 0.2 (or less) to avoid excess multiple fits. The default DT is now 0.15 and, hence, can be left blank if refining diffractometer data. DT should only be given on the first cycle card; DT should be left blank on subsequent cycle cards.
44-50	TS	Maximum allowable delta θ (in deg.) for a reflection to be included in the next least-squares cycle. This can be left blank; TS = DT/3.
52	MPRINT	Print control: 0, suppress matrices & residuals; 1, print matrices & residuals.
53	IALLPR	Print control: 0, print all information; 1, print summary only.

54	INDEXW	Print control: 0, print all generated indices that are not used; 1, suppress printing unused indices.
56-60	DAMP	Multiplier of the change in the systematic error, normally set to 1.0 but could be equal to 0.0 if the value for the error is not to be updated. Note that there is no default value for this parameter; a value must be input or a value of 0.0 will be assumed! FORMAT(F5.2)

Line/CARD VII (Last cycle card)

Column	Parameter	Explanation
1-15		Blank, do not vary any parameters.
16-52		As for previous cycle cards.
53	IALLPR	This should be 0 to print the final table. Flags on data are: "*" for weight of 0.0; "**" for a reflection not rejected but which could be fit by multiple indices; "M" indicates a reflection rejected due multiple possible indices; "BD" indicates bad data, an indexed reflection for which $\Delta\theta$ exceeds TS.
54	INDEXW	This should be 1 to suppress the unused indices list when printing the final table.

INITIAL DISTRIBUTION

1 Naval Research Laboratory (Code 4683, Dr. E. Skelton)
2 Defense Technical Information Center, Alexandria
1 Ain Shams University, Cairo, Egypt (Physics Department, Prof. K. El-Sayed)
1 Alfred University, Alfred, NY (New York State College of Ceramics (Prof. R. L. Snyder)
1 AMOCO Research Corporation, Naperville, IL (AMOCO Research Center, Dr. J. Kaduk)
1 Oregon State Duniversity, Corvallis, OR (Department of Chemistry, Prof. A. W. Sleight)
1 Prof. Giora Kimmel, Israel
2 Scintag, Incorporation, Sunnyvale, CA (Dr. S. B. Robie)
1 University of Connecticut, Storrs, CT (Chemistry Department, Prof. B. Chamberland)